Bifunctional ligands in uranyl chemistry: Metalloligands and zwitterions

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Abstract

Structural studies of uranyl ion complexes of metalloligands and zwitterions, ligand classes with some degree of overlap, constitute a major contribution to more recent developments in uranium chemistry. To some extent, they have been focussed on basic product characterization but more generally on gaining an understanding of how particular features of ligand structure may influence the complete crystal structure and thus the potential for any applications. Metalloligands provide an obvious means of generating heterometallic complexes but since it is not always necessary to preform a metalloligand prior to its interaction with uranyl ion, they can be identified by somewhat arbitrary excision of appropriate components from a very large number of complete crystal structures, so that only selected examples are considered here. Zwitterion (and oligozwitterion) complex structures are treated more comprehensively, two subclasses here being those where the positive site is aprotic and those where it is protic, differing in the weak interactions involved. Association of zwitterionic ligands with classical, anionic polycarboxylates and with cucurbiturils are recent developments covered extensively.

Keywords: Coordination polymers / Metal–organic networks / Metalloligands / Zwitterionic ligands / Uranyl cation

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Abbreviations: AC, anionic carboxylate; Hahb, 3-amino-5-hydroxybenzoic acid; Hamb, 4-(aminomethyl)benzoic acid; H_4azaC4, *N*-methyl-*p*-*tert*-butyldihomoammoniocalix[4]arene; bcbp, 4,4′-bis(2-carboxylatoethyl)-4,4′-bipyridinium; bcpbp, 1,1′-bis(4-carboxylatophenyl)-4,4′-bipyridinium; bcmim, 1,3-bis(carboxylatomethyl)imidazolium; bdc, 4,4′-biphenyldicarboxylate; bet, betaine; bipyO_2, bipyridine-di-*N*-oxide; bipy, bipyridine; H_2bmta, bis[(3,5-di-*tert*-butyl-2-hydroxyphenyl)methyl]-(trimethylammonioethyl)amine; H_2bpdc, 2,2′-bipyridinedicarboxylic acid; bpdo, 4,4′-bipyridine-1,1′-dioxide; H_4bptc, 2,2′-bipyridinetetracarboxylic acid; CB, cucurbituril; H_2cbbda, *N,N*′-bis(3-carboxylatobenzyl)butane-1,4-diammonium; H_2cbcp, *N*-(4-carboxybenzyl)-4-carboxypyridinium; H_2chdc, cyclohexanedicarboxylic acid; cmim, 1-carboxylatomethyl-3-methylimidazolium; CP, coordination polymer; CSD, Cambridge Structural Database; dabco, 1,4-diazabicyclo[2.2.2]octane; H_4dcpbp, 1,1′-bis(3,5-dicarboxylatophenyl)-4,4′-bipyridinium; H_2dcpp, 4-(3,5-di{hydroxycarbonyl}phenylpyridinium)-pyridine; H_4dcta, *trans*-1,2-diaminocyclohexane-*N,N,N′,N*′-tetraacetic acid; H_4diazaC4, *N*-benzyl-*p*-methyltetrahomodiazacalix[4]arene; dmf, *N,N*-dimethylformamide; dmso, dimethylsulfoxide; H_4dota, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid; H_4dpmta, 2,2′,2″,2‴-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene)bis(azanetriyl))tetraacetic acid; H_2edda, ethylenediamine-*N*,*N*′-diacetic acid; H_4edta, ethylenediaminetetraacetic acid; gaba, γ-aminobutanoic acid; gly, glycine; H_3hbhp, *N*-(4-hydroxycarbonylbenzyl)-3,5-di(hydroxycarbonyl)pyridinium; H_2hbmch, *N,N*-bis(2-hydroxy-5-*tert*-butyl-3-methylbenzyl)-cyclohexylamine; H_3hdbae, *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)-2-aminoethanol; HS, Hirshfeld surface; H_2ida, iminodiacetic acid; Hint, isonicotinic acid; H_2ipht, isophthalic acid; ML, metalloligand, MOF, metal–organic framework; Hnic, nicotinic acid; H_3nta, nitrilotriacetic acid; H_3ntpa, nitrilotri-3-propanoic acid; pbcp, 1,1′-(pentane-1,5-diyl)bis(4-carboxylatopyridin-1-ium; oppm, bis[5-*tert*-butyl-2-oxido-3-(1-pyridiniomethyl)phenyl]methane; H_2pda, phenylenediacetic acid; H_2pdda, 1,2-phenylenedioxydiacetic acid; H_2pht, phthalic acid; Hpic, picolinic acid; pip, piperazine; PLQY, photoluminescence quantum yield; H_2pydc, pyridinedicarboxylic acid; H_2pyzpdc, 2,3-pyrazino[1,10]phenanthroline-2,3-dicarboxylic acid; Hquin, quinaldic acid; salen, *N,N*′-bis(salicylidene)ethylenediamine dianion; SBU, secondary building unit; H_3tca, tricarballylic acid; H_3tcenm, tris(2-carboxyethyl)nitromethane; H_2tdc, 2,5-thiophenedicarboxylic acid; teda, *N,N,N′,N*′-tetramethylethane-1,2-diammonioacetate; H_4teta, 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid; Tf_2N, bis[(trifluoromethyl)sulfonyl]imide; H_4thbdh, *N,N,N′,N*′-tetrakis(2-hydroxy-3-methyl-5-tert-butylbenzyl)diaminoheptane; tmbpc, 1,1′-[(2,3,5,6-tetramethylbenzene-1,4-diyl)bis(methylene)]bis(pyridin-1-ium-3-carboxylate); tmtpc, 1,1′,1″-(2,4,6-trimethylbenzene-1,3,5-triyl)-tris(methylene)-tris(pyridine-4-carboxylate); tpda, *N,N,N′,N*′-tetramethylpropane-1,3-diammonioacetate; H_4tpmta, 2,2′,2″,2‴-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene)bis(azanetriyl))tetraacetic acid; Htpyc, 4′-carboxy-2,2′;6′,2″-terpyridine; H_4trpmta, 2,2′,2″,2‴-(2,4,6-trimethyl-1,3-phenylene)bis(methylene)-bis(azanetriyl)tetraacetic acid; Htpypc, 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine; UOF, uranyl–organic framework; XPS, X-ray photoelectron spectroscopy; ZI, zwitterion.

1. Introduction

Metalloligands and zwitterions can be regarded as particular members of a large family of multifunctional metal ion ligands where donor groups are accompanied by various substituents that, although not donors themselves, can influence both the stability and properties of complexes of those ligands [1–5]. A subset of the family of metalloligands (MLs) is that where the overall charge is zero and it can also be regarded as a subset of the zwitterion (ZI) family, though in most instances a metal cation is not the positively charged site of a ZI [6]. While the term "metalloligand" is of relatively recent coinage, its use largely associated with the rise in importance of heterometallic coordination polymers (CPs) and metal-organic frameworks (MOFs) [5], it is possible to discern such entities in many long-known and simple species. Werner's "hexol", $[Co\{Co(NH_3)_4(OH)_2\}_3]Br_6$ [7], for example, can be regarded as involving coordination of three *cis*-$[Co(NH_3)_4(OH)_2]^+$ chelating MLs to one Co^{III} cation, while his second "hexol", originally misidentified, formally involves bi- and tridentate O-coordination by *cis*-$[Co(NH_3)_4(OH)_2]^+$ and *fac*-$[Co(NH_3)_3(OH)_3]$ [8]. Similarly, crystalline $Na[UO_2(O_2CCH_3)_3]$ can be considered to involve octahedral, tris(bidentate) coordination of Na^I by chelating $[UO_2(O_2CCH_3)_3]^-$ MLs [9]. This last example raises an issue common to all systems involving a supposed ML incorporating a labile metal ion in that while it is possible to make an appropriate dissection of a crystal structure, this does not necessarily identify the dominant species present in the solution giving rise to the crystal. Where the objective of ML use is the formation in particular of CPs or MOFs, this can mean that a multicomponent reaction mixture of a supposedly appropriate composition does not provide crystals with the anticipated components. An example of this is provided in the attempt to obtain a mixed-ligand uranyl ion complex incorporating the metallo-zwitterion $[Ni(tpyc)_2]$ ($tpyc^-$ = 4′-carboxylato-2,2′;6′,2″-terpyridine) where the ZI, although indeed present, was accompanied by a Ni^{II}–co-ligand complex unit in the crystal obtained [10]. The Ru^{II} analogue

of this tpyc$^-$ complex, [Ru(tpyc)$_2$] [11], is, however, a kinetically inert species at the metal ion centre, a property which means that its core structure is retained under a variety of reaction conditions, making it and various related species useful for the synthesis of numerous ML species, not necessarily with a ZI form [12]. This family of ligands was initially described simply as one of "expanded ligands" [11,12], since the interposition of metal ion/aza-aromatic groups between attached donor groups rendered the spatial separation of these donor groups much greater than in simple organic analogues and it may be noted that, in one review [12], the term "metalloligand" does not occur at all. MLs based on truly inert metal ion cores remain relatively rare, other examples including Co^{III} complexes of cage amine ligands [13–15], and polycyano complexes of various metals, where "Prussian Blue" provides a truly ancient example of the (inadvertent) application of their use [16]. Thus, the synthesis of MLs [5] generally demands careful consideration of numerous factors such as the stereochemistry and donor atom preferences of both the core and externally bound metal ions, and the denticity of inner and outer coordination units along with metal ion substitution kinetics and even the choice of solvent for the syntheses. The use of MLs in the formation of actinide-based CPs and MOFs has been relatively limited [17], but what is known in the case of uranyl ion derivatives provides a useful basis for an analysis of the prospects for real applications of such materials.

Organic ZI ligands are a very diverse family and many cases of structurally characterized complexes formed with UO_2^{2+} have been described over the years, with more than 200 crystal structures documented in the Cambridge Structural Database (CSD, Version 5.44) [18,19]. The vast majority of these ligands involve nitrogen-centered positive charges, with only very rare examples of phosphorus-centered ones, in phosphorus ylides [20] and a carboxyl-functionalized ionic liquid [21]. The ammonium-containing ZIs can be separated into different classes according to the nature, aliphatic or aromatic, of the ammonium group,

the degree of substitution at the nitrogen site in the aliphatic case, and the nature of the anionic part. The first two subdivisions have strong implications for the solid state structures of the complexes formed, these being dependent on the weak interactions involved, and particularly on hydrogen bonding (H-bonding) in the case of primary, secondary or tertiary ammonium groups. Concerning the anionic part of the ligand, it is a carboxylate group in most instances (several groups for polyzwitterions). The only notable exceptions are some examples with phenoxides in Schiff bases, homoazacalixarenes and other aminopolyphenols, and more than 50 cases involving pyridine-*N*-oxide derivatives reported in the CSD, with only some of them being dizwitterionic and having thus chelating or bridging abilities. A major section of this review will cover, in a non-exhaustive way and with a particular emphasis on the structural viewpoint, the UO_2^{2+} complexes involving mainly ZI phenoxide and carboxylate ligands, which have been much investigated in recent years, either alone or in association with other ligands, anionic carboxylates (ACs) and cucurbiturils (CBs) in particular. Although strictly speaking a zwitterion has no overall charge, so that the number of amino sites in any aminocarboxylic acid, for example, should equal that of carboxylic acid sites if ZI formation providing carboxylate donors is to occur, several uranyl polymers have been characterized for multidentate ligands where the ratio is not 1:1 but where at least one arm of the bound ligand can be considered to have a ZI form. These “partial ZIs” or “pseudo-ZIs” are anionic, but the term “anionic carboxylate” is reserved here to ligands having no ZI part. It is also to be noted that “bifunctional” is here used in a sense which does not describe only the presence of two different groups suitable for metal ion coordination, but also the association of a coordinating group to another which, although not metal-bound, is a specific assembler through weak interactions and has thus an effect on structure formation, as is particularly the case with protonated ammonium groups, for example.

In view of possible applications of complexes within our selection, as well as of all uranyl ion complexes generally, a disadvantage is the weakly radioactive nature of ^{238}U, the principal isotope of natural uranium, which is an α emitter with a half-life of 4.468×10^9 years. However, the low content in the fissile ^{235}U isotope (~0.71%) of natural uranium, depleted further in some commercially available materials, means that only relatively straightforward precautions in the use of uranyl ion salts and complexes in the laboratory are required. Uranium is a quite common element in Nature, in fact as abundant as or even more abundant than many familiar elements, making its distinctive redox, luminescence and catalytic properties of particular interest [22–24]. Complexes of the linear uranyl ion are also unique in commonly adopting pentagonal- and hexagonal-bipyramidal forms of coordination geometry, a feature of importance both in the design of uranium(VI)-specific, "uranophile"[25] ligands and in determining the solid state crystal structures of its complexes and thus possible selectivity in regard to guest inclusion.

A description of the crystal structures and some physical properties of chosen examples of uranyl ion complexes with metalloligands and organic zwitterionic ligands is given in the next two sections, before a more general discussion of their specificities and possible applications in the last section.

2. Uranyl ion complexes with metalloligands

2.1. Polycyanido complexes as metalloligands

Cyanide ion is a potent bridging ligand and as such has the capacity to bring two metal ions into close proximity favouring electronic and magnetic interactions. Polycyanido-metallate complexes, mostly kinetically inert, thus constitute an interesting group of MLs for the formation of heterometallic CPs [5,17]. While the conventional use of the term "metalloligand" implies that such species are based on an organic framework and cyanide ion

is not usually considered as such, uranyl ion CPs derived from polycyanidometallates do provide some of the more spectacular examples of the consequences of forming heterometallic species. $[Pt(CN)_4]^{2-}$, of interest in its own right because of its tendency to self-associate, is one species which has been of particular interest in actinide coordination chemistry [26,27], though but little of this has concerned UO_2^{2+} [28,29]. Crystalline complexes of UO_2^{2+} formed by kinetically inert, hexacoordinate $[Co(CN)_6]^{3-}$, $[Rh(CN)_6]^{3-}$, $[Ir(CN)_6]^{3-}$, and $[Pt(CN)_6]^{2-}$, with dizwitterionic 4,4′-bipyridine-1,1′-dioxide (bpdo) as co-ligand, have been found to show emission which depends strongly on the metal ion linked to U^{VI} [30]. Only in the case of the complex incorporating $[Pt(CN)_6]^{2-}$ was the typical [23] vibronically structured green emission of uranyl ion observed, whereas the three other cases display broad emissions of different colours which, on the basis of their long excited state lifetimes, were assigned still to uranyl ion emission but from energy levels modified by interactions with both the cyanido-metallate and bpdo ligands. The fact that $[Co(CN)_6]^{3-}$, $[Rh(CN)_6]^{3-}$ and $[Ir(CN)_6]^{3-}$ form isomorphous crystals involving triperiodic CPs of composition $[(UO_2)_2(OH)\{M(CN)_6\}(bpdo)_2]$ in which the bpdo ligands are planar while $[Pt(CN)_6]^{2-}$ gives a diperiodic CP of composition $[(UO_2)_2(OH)_2\{Pt(CN)_6\}(bpdo)_2]$ in which the two rings of bpdo are near orthogonal indicate that various subtle factors may influence the spectroscopy of these complexes. That bpdo may be a specially effective ligand for uranyl ion excitation by energy transfer is also indicated by the fact that in the complex $[UO_2(H_2O)_4(dmf)_2][UO_2\{Co(CN)_6\}(dmf)_2]_2$ (dmf = *N,N*-dimethylformamide), where bpdo is absent, only the structured green emission of uranyl ion is seen [30].

Polycyanidometallates, because of the linearity (or close to it) of M–CN–M′ bonding, are expected to be divergent, *i.e.* non-chelating, donor ligands and in their UO_2^{2+} complexes they display a range of denticity, often below their maximum bonding capacity. Thus, another factor which may influence the electronic structure of the hexacyanido–bpdo complexes

referred to above is that $[Co(CN)_6]^{3-}$, $[Rh(CN)_6]^{3-}$ and $[Ir(CN)_6]^{3-}$ act as square-planar donors through four coplanar CN groups, as in $[(UO_2)_2(OH)\{Rh(CN)_6\}(bdpo)_2]$ (complex **1**, Figure 1a) while $[Pt(CN)_6]^{2-}$ is a linear divergent bidentate donor involving just two *trans* cyanido

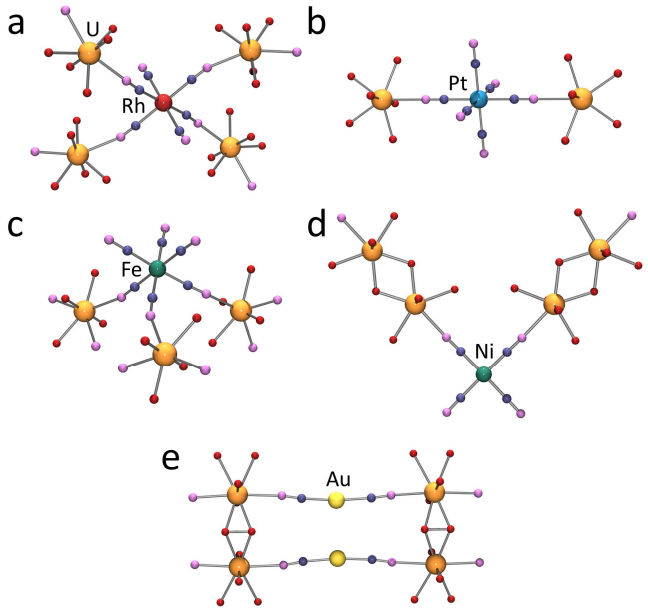


Figure 1. Portions of the crystal structure in CPs of uranyl ion with polycyanidometallate ligands, showing the bonding interactions of each ligand: (a) $[Rh(CN)_6]^{3-}$ in **1** [30]; (b) $[Pt(CN)_6]^{2-}$ in **2** [30]; (c) $[Fe(CN)_6]^{3-}$ in **3** [31]; (d) $[Ni(CN)_4]^{2-}$ in **4** [29]; (e) $[Au(CN)_2]^{-}$ in **5** [32]. As in all other figures, the color code is: U, orange-yellow; O, red; N, purple; C, blue.

ligands in $[(UO_2)_2(OH)_2\{Pt(CN)_6\}(bdpo)_2]$ (**2**, Figure 1b). Yet another factor (apart from different numbers of hydroxido ligands) is that although the isolated anions are presumed to involve C-coordination of cyanide, bridging could result in linkage isomerism from M–CN–M′ to M–NC–M′. Other forms of interaction between polycyanidometallates and UO_2^{2+} have been described in the structures of $[UO_2(H_2O)_4(dmf)_2][UO_2\{Fe(CN)_6\}(dmf)_2]_2$ (**3**, Figure 1c) and its Co analogue [31], where a facial trio of cyanido groups is involved in bridging, in $K_3[(UO_2)_2(OH)\{Pt(CN)_4\}_2]_2(NO_3)\cdot 1.5H_2O$ [28], where the $[Pt(CN)_4]^{2-}$ unit acts as a square-planar quadridentate ligand, and in $[(UO_2)_2(dmso)_4\{Ni(CN)_4\}(OH)_2]$ (**4**, dmso = dimethylsulfoxide) [29], where two *cis* cyanido groups bridge UO_2^{2+} units (Figure 1d). A

thorough investigation [32] of uranyl ion complexation by dicyanidoaurate(I), $[Au(CN)_2]^-$, has shown that although its action as a linear bidentate ligand can give rise to monoperiodic CPs as in $[n\text{-}Bu_4N]_2[(UO_2)_2(O_2)(NO_3)_2\{Au(CN)_2\}_2]$ (**5**, Figure 1e), it can also act as a simple unidentate ligand in molecular species or even be present as an uncoordinated counteranion.

Uranyl ion luminescence is of course a prime factor relating to potential applications of UO_2^{2+} complexes in general [22,23], and it has been suggested, for example, that the properties of the hexacyanidometallate complexes described above could be exploited in new, tunable light-emitting devices [29]. However, the properties seen there are not universal and there is considerable variability within the full family of polycyanidometallate complexes such that a need for a more profound understanding of their electronic structure has been identified [30,32]. Complexes such as $K_3[(UO_2)_2(OH)\{Pt(CN)_4\}_2]_2(NO_3)\cdot 1.5H_2O$ [28] and **4**, are in fact non-emissive, while **5** shows emission due to aurophilic interactions within the solid superimposed upon uranyl emission [32].

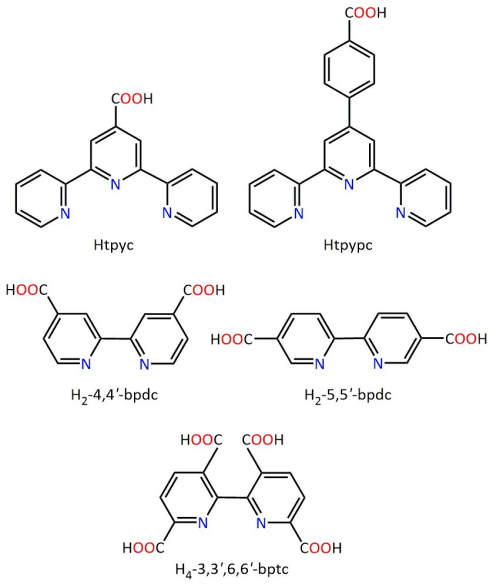
If cyanide ion can be considered for present purposes as an "honorary" organic unit, this is certainly not possible for oxide ion, so that simple anions such as chromate, permanganate, perrhenate or pertechnetate are not considered to be "metalloligands", even though their coordination chemistry is important. Such a restriction seems somewhat more arbitrary in the case of the very long-known polytungstate and polymolybdate anions [33] but their burgeoning recent chemistry, including that concerning UO_2^{2+} complexes [34], has already been the subject of several reviews [35–37].

2.2. Aza-aromatic carboxylate complexes as metalloligands

Structurally characterized complexes of UO_2^{2+} with carboxylate ligands are extremely numerous [38], reflecting their high solution stability due to the marked oxophilicity of uranium(VI) [39] and their ease of crystallization. Other metal ions may not share the same

donor atom preferences, so that in the design of mixed-metal CPs and MOFs, the use of ligands incorporating varied donors, ideally in distinct sites, is an important ploy [40]. Where such ligands can be induced to form a complex with one metal ion, leaving some donor sites unoccupied, the complex can be considered a ML suited to use for reaction with a second metal to form a mixed metal species and, ultimately, new materials including CPs and MOFs [5,41–43]. If only labile metal ions are involved, it is not necessary to preform one complex but, as mentioned in the Introduction, this can lead to complications if the ligand selectivity is imperfect and it is worthy of note that the technique of "post-synthetic modification" can result in different heterometallic complexes to those obtained from complete single reaction mixtures [44]. While it is somewhat artificial to define a ML simply by an appropriate excision from a complete crystal structure, this has been nonetheless a very fruitful approach to the synthesis of heterometallic complexes [5,41,42]. The polycyanidometallate ligands discussed in section 2.1. are "true" ligands in the sense that the N-donor atoms are the only sites open to reaction in these kinetically inert species, so that there is a direct parallel with simple ligands such as, for example, 1,2-ethylenediamine. One way to guarantee formation of a ML is to use a precursor ligand with not only different donor atoms but also sites of different denticity. An illustration of this is found in the formation of the "expanded ligand" $[Ru(tpyc)_2]$ [11,12], a ML which is also a dizwitterion, where the azophilic Ru^{II} centre binds very strongly to the N_3-tridentate terpyridine unit (Scheme 1), leaving the carboxylate group free for binding a more oxophilic metal ion. This explains why, when the moderately labile Ni^{II} is added to a reaction mixture containing the ligand Htpyc and uranyl nitrate, the isolated CP contains $[Ni(tpyc)_2]$ units which link U centres through carboxylate coordination (see ahead) [10], an explanation which also applies to the preceding demonstration of the same behaviour with Fe^{II}, Co^{II} and Ni^{II} and a further expanded terpyridine carboxylate, although in the syntheses here an initial period of reaction between the ligand and the transition metal

ions was used to first form the dizwitterions [45]. Though not considered at the time in terms of ML formation, the same approach was pursued earlier in the formation of mixed uranyl–transition metal ion complexes from carboxylate-substituted bipyridines where the transition metal ions were bound to the chelating N-sites of the ligand [46]. A subsequent publication [47] interpreted related additional structures in terms of ML units, however. The examples of the complexes $[UO_2CuCl(4,4'\text{-bpdc})(H\text{-}4,4'\text{-bpdc})(H_2O)_2]\cdot H_2O$ (**6**, H_2-4,4′-bpdc = 2,2′-bipyridine-4,4′-dicarboxylic acid, Scheme 1), a monoperiodic CP [47], and $[UO_2Cu(5,5'\text{-bpdc})_2]$ (**7**, H_2-5,5′-bpdc = 2,2′-bipyridine-5,5′-dicarboxylic acid, Scheme 1), a triperiodic uranyl–organic framework (UOF) based on inclined 2D + 2D → 3D polycatenated subunits [46], are shown in Figures 2a and b. An even more sophisticated approach to selective metal ion location in luminescent heterometallic uranyl-containing CPs [48] involves the tetracarboxylic-functionalized 2,2′-bipyridine-3,3′,6,6′-tetracarboxylic acid (H_4-3,3′,6,6′-bptc, Scheme 1) which enforces uranyl N-chelation as a result of adjacent carboxylate-O coordination and leaves two carboxylate units free for transition metal ion binding, as in $[UO_2Mn(3,3',6,6'\text{-bptc})(H_2O)_3]$, also a triperiodic UOF (**8**, Figure 2c).



Scheme 1. Aza-aromatic carboxylic acids used for the synthesis of metalloligands.

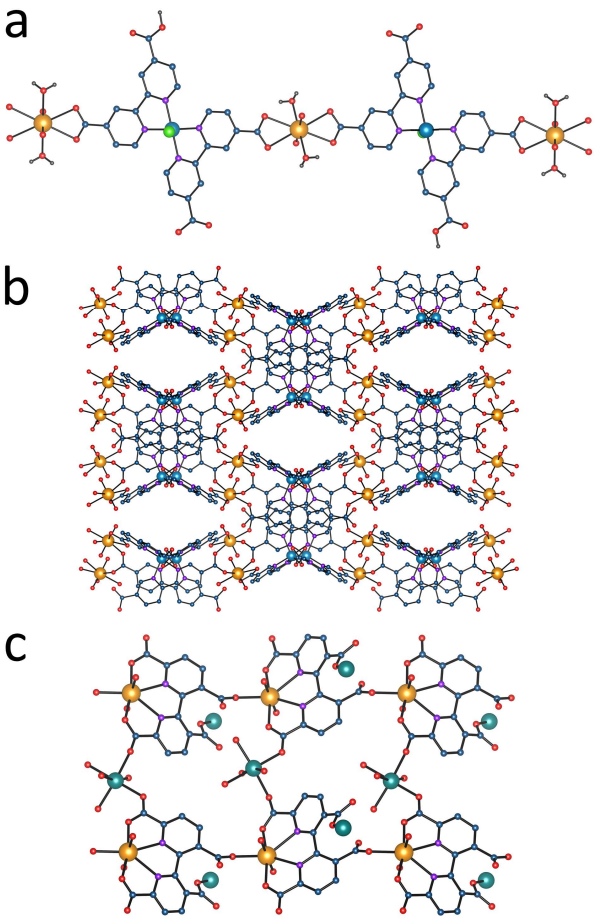


Figure 2. (a) The monoperiodic uranyl–copper(II) complex **6** [47]. (b) The uranyl-copper(II) framework **7** [46]. (c) The connectivity in the uranyl–manganese(II) framework **8** [48]. Color code: same as above, with Cu, blue; Mn, blue-green; Cl, green.

A series of UO_2^{2+} complexes has been reported which is based on the ZI, "expanded ligand" [Ni(tpyc)$_2$] and involves other anionic donors, either small species such as fluoro, oxido or hydroxido anions, or anionic polycarboxylate or polysulfonate ligands, resulting in a great diversity of structures [10,49–51]. Of particular notice is the formation of discrete U_4Ni_2 dinickelatetrauranacycles in the cases in which the additional ligand is either *cis*-1,2-cyclohexanedicarboxylate (*c*-1,2-chdc^{2-}) or 2,5-thiophenedicarboxylate (tdc^{2-}), two curved anions of limited flexibility [10]. The latter complex, $[(UO_2)_2Ni(tpyc)_2(tdc)(NO_3)_2]_2$ (**9**), shown in Figure 3a, involves too large a ring for endocyclic "terpyridine embrace" π-stacking interactions [52,53] to occur, but exocyclic ones are present, and these interactions play a

prominent role throughout the series of structures reported. Similar or even larger (U_5Ni_2, U_6Ni_4, $U_{10}Ni_4$) metallacyclic rings are a recurrent motif in several of the CPs formed in this family. With a distance of ~16 Å between the uranium atoms linked by the [Ni(tpyc)$_2$] ligand, the rings in the diperiodic network formed by $[(UO_2)_2Ni_2(tpyc)_4(O)(H_2O)_4](NO_3)_2{\cdot}6H_2O$ (**10**, Figure 3b) are sufficiently large to allow for twofold parallel interpenetration [49]. The complex in which nitrilotriacetate (nta^{3-}) is introduced as an additional ligand, $[(UO_2)_2(nta)_2Ni_2(tpyc)_2]$ (**11**, Figure 3c), is peculiar in that, while one nickel(II) centre is involved in the formation of the [Ni(tpyc)$_2$] ML, another is bound to the O_2N site of two nta^{3-} ligands (which do not adopt a ZI form as a consequence), resulting in the formation of a triperiodic MOF [10]. The larger "expanded ligand" [Ni(tpypc)$_2$], involving 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (Htpypc, Scheme 1), has been associated with 4,4′-biphenyldicarboxylate (bdc^{2-}) to generate the complex $[UO_2(bdc)_2Ni(tpypc)_2]$, which crystallizes as a honeycomb network with very large hexagonal cells (~42 Å × 27 Å); double layers are built through H-bonding and π-stacking interactions, which still have a pore opening sufficiently large (~28 Å × 20 Å) for inclined 2D + 2D → 3D polycatenation [45]. Although the azophilicity of Ni^{II} makes it particularly well adapted to complexation by $tpyc^-$, a complex in which it is replaced by Pb^{II} has been reported, $[UO_2Pb(tpyc)(HCOO)_2(OH)(H_2O)_2]$ (**12**, Figure 3d), in which however Pb^{II} is only bound to one $tpyc^-$ ligand, further bridging by formate ligands resulting in formation of a diperiodic network [49]. It is notable that, throughout this series of compounds, the carboxylate group of $tpyc^-$ is generally either monodentate or κ^2O,O'-chelating, and bridging modes, such as μ_2-$\kappa^1O{:}\kappa^1O'$ found in **11**, are very unusual, which limits the ability of the "expanded ligand" to generate triperiodic assemblies.

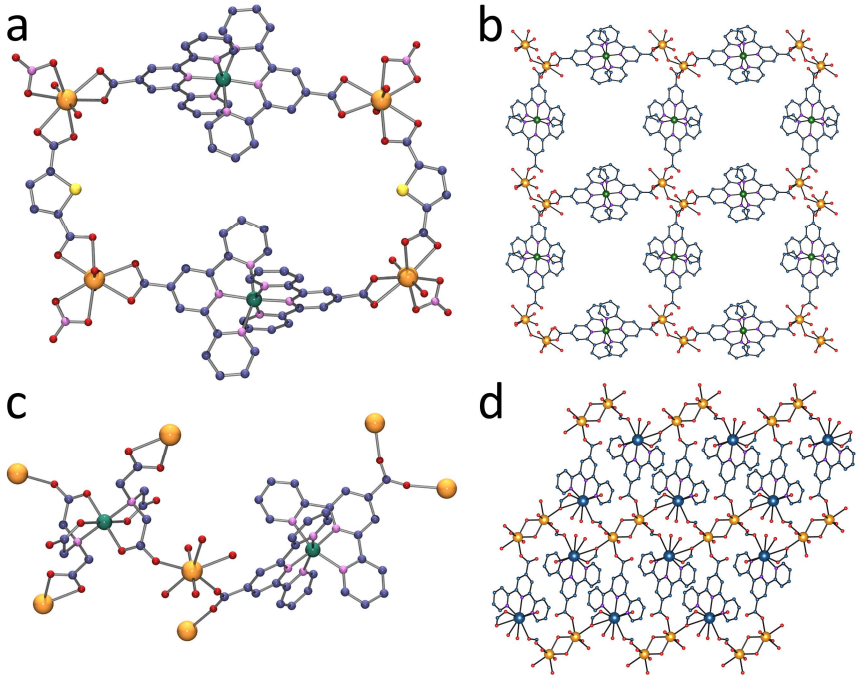


Figure 3. (a) The neutral dinickelatetrauranacycle in **9** [10]. (b) The diperiodic network formed in **10** [49]. (c) Dual role of nickel(II) in **11** [10]. (d) The uranyl–lead(II) complex **12** [49]. Color code: same as above, with Ni, green; Pb, blue; S, yellow.

2.3. Neutral Schiff base complexes as metalloligands

Complexes of *N,N′*-bis(salicylidene)ethylenediamine dianion (salen) and its very numerous analogues have long been known to act as bidentate chelates through their coordinated phenoxide-O atoms for a wide variety of metal ions [54]. Other modes of coordination are known [55,56] but this common mode means that in most instances heterometallic species of low nuclearity are formed. This in turn means that many such species are soluble, a property not seen in CPs such as discussed above, so that it is possible to conduct detailed equilibrium studies that, in the case of UO_2^{2+} binding to Cu^{II} salen-type complexes, have been used to show that the close U^{VI}–Cu^{II} contact leads to efficient quenching of uranyl ion luminescence and that U–O–Cu interaction energies correlate well with uranyl ion vibrational frequencies [56,57].

2.4. Ferrocenecarboxylate as metalloligand

Although very rarely employed in UO_2^{2+} chemistry, ferrocenecarboxylic acid has been shown to give discrete or monoperiodic complexes in which the carboxylate group is either chelating or μ_2-κ^1O:κ^1O'-bridging [58]. A recent report gives an interesting comment about previous dubious chemical and structural descriptions of this system [59]. Ferrocenecarboxylate would possibly be worth further investigation as a ligand for UO_2^{2+} as the known structures show a tendency for the ferrocenyl units to form a redox-active lipophilic covering to uranyl species. It is another example of the small family of kinetically inert metalloligands which could be augmented by other metallocene derivatives.

3. Uranyl ion complexes with organic zwitterionic ligands

3.1. N-oxide ligands

The valence bond representation of an N-oxide unit as N^+–O^- offers an explanation of the enhanced basicity and electrophilicity of such species relative to the parent amines [60] and justifies their description as “vicinal zwitterions” [61]. While aliphatic amine oxides, in particular trimethylamine N-oxide, have been shown to be good ligands for many metal ions [62,63], their principal use in coordination chemistry has been as oxidants for the removal of CO ligands from carbonyl complexes [64], and their binding to UO_2^{2+} has not been explored. The coordination chemistry of aza-aromatic N-oxides has been much more widely investigated [65] and, as noted in section 2.1, 4,4′-bipyridine-1,1′-dioxide has been found to endow some of its UO_2^{2+} complexes with unusual spectroscopic properties [30]. Studies of the basic coordination chemistry of the parent pyridine-N-oxide ligand with UO_2^{2+} are long known [66,67] and established its strong interaction (on the basis of spectroscopic measurements). Structure determinations are available for uranyl ion complexes of 2,2′-bipyridine mono- and di-N-oxides, ligands which act as N,O or O,O chelates [68–71], as in

$[UO_2(2,2'\text{-bipyO}_2)(H_2O)](ClO_4)_2$ (**13**, Figure 4a) [70]. More recent work has been focussed on 4,4′-bipyridine-1,1′-dioxide (4,4′-bipyO$_2$), not just because of its influence upon uranyl ion emission [30] but also because of its capacity to act as a bridging ligand to form coordination polymers [72–77], as well as on the cationic dioxide 1,2-bis(4,4′-bipyridinium-1-oxide)ethane, again found to act as a bridging ligand [78]. The complex $[UO_2(4,4'\text{-bipyO}_2)_2(HPW_{12}O_{40})]$ (**14**, Figure 4b) provides a nice illustration of the bridging ability of 4,4′-bipyO$_2$, with formation of a cationic square grid through uranyl bonding, with a side length of ~13 Å, and further inclusion of an anionic Keggin-type polyoxometalate [74]. The capacity of cavity-containing molecules such as cucurbiturils and crown ethers to accommodate linear ligands of these types has led to the characterization in these works of several polyrotaxane UO_2^{2+}-based CPs [77,78] (see section 3.5.5 for other examples of polyrotaxanes). Ligands which can give rise to cationic coordination polymers are of interest for the capture of small anions which may be environmental pollutants [79], but this prospect is yet to be examined in these cases.

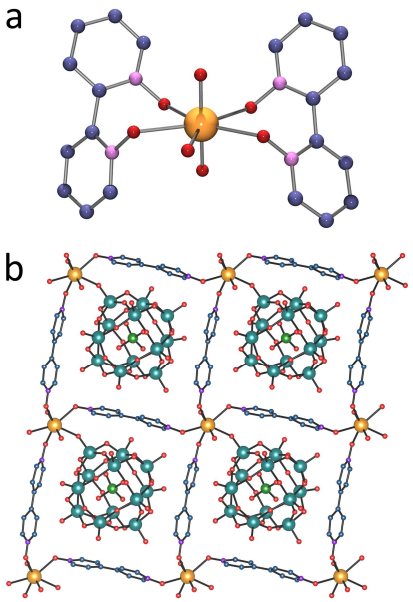


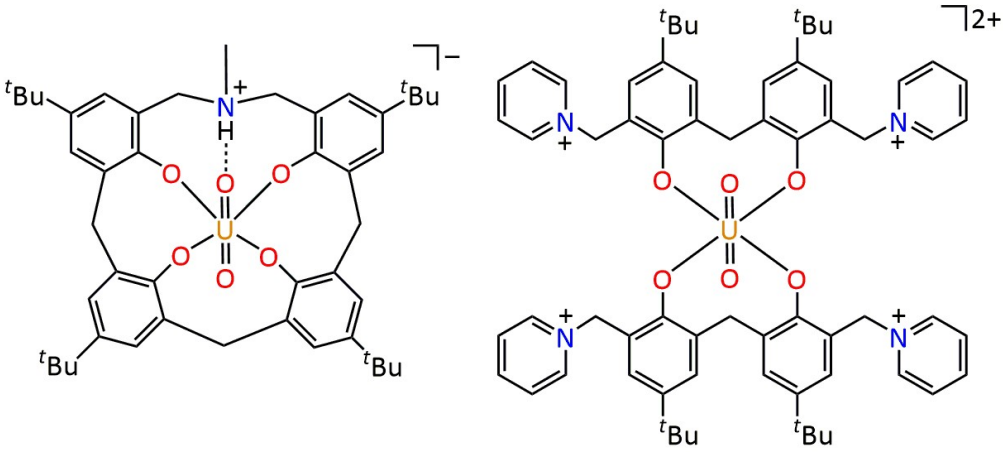
Figure 4. (a) Uranyl chelation by 2,2′-bipyO$_2$ in **13** [70]. (b) Inclusion of a polyoxometalate in the square grid formed by uranyl with 4,4′-bipyO2 in **14** [74]. Color code: same as above, with W, blue-green; P, green.

3.2. Homoazacalixarenes and aminopolyphenols

Homoazacalixarenes are a subclass of calixarenes in which nitrogen atoms are inserted within one or several of the methylene bridges which link the phenolic rings [80]. While intramolecular OH···N H-bonds link the phenolic and amine groups in the uncomplexed species, UO_2^{2+} complexation is accompanied by partial or total phenolic deprotonation and protonation of the amine groups [81–83] (various other instances of the influence of coordination on tautomeric equilibria are discussed ahead). The uranyl cation is located either within the calixarene lower rim and bound to all phenoxide groups, or outside the cavity and bound to only some of the phenoxides. With the mono-ZI *N*-methyl-*p*-*tert*-butyldihomoammoniocalix[4]arene (H_4azaC4), the uranyl cation is inside the cavity and the ammonium group forms an intramolecular NH···O(oxo) H-bond involving UO_2^{2+} (Scheme 2) [83], thus giving an example of "stereognostic" uranyl complexation [84], although the effect of this bond on a possible selectivity for UO_2^{2+} is unknown. An interesting case is that of *N*-benzyl-*p*-methyltetrahomodiazacalix[4]arene (H_4diazaC4) [81,82], for which the location of uranyl varies depending upon the addition of a base during the synthesis. In $[UO_2(H_4diazaC4)(NO_3)_2]\cdot 0.5MeOH\cdot H_2O$ (**15**), obtained in the absence of a base, only two phenolic groups are deprotonated (protonation of the amine groups giving a neutral, truly ZI ligand), and UO_2^{2+} is bound to these only, with two chelating nitrate anions completing the coordination sphere. In contrast, in $[UO_2(H_2diazaC4)]\cdot 2CHCl_3\cdot CH_3CN$ (**16**), synthesized in the presence of NEt_3, internal bonding to all four phenoxide groups occur, accompanied by NH···O(phenoxide) H-bonds, the ligand being dianionic (Figure 5).

Homooxacalixarene cleavage during a complexation attempt involving the U^{IV} cation resulted in isolation of a UO_2^{2+} complex with two acyclic bis[5-*tert*-butyl-2-oxido-3-(1-pyridiniomethyl)phenyl]methane (oppm) molecules displaying a diphenoxide part with two

pyridinium appendages, the latter playing some part in the packing through π-stacking interactions with other complexes and with solvent pyridine molecules (Scheme 2) [85].



Scheme 2. Uranyl ion complexation by HazaC4^{3-} (left) [83] and oppm (right) [85]. The H-bond is shown as a dotted line.

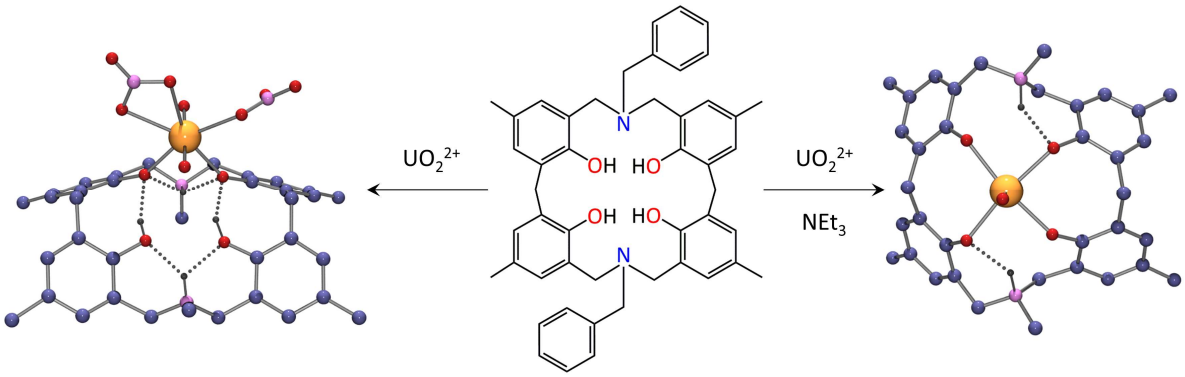


Figure 5. Uranyl complexation by H$_4$diazaC4 in the absence (**15**) or presence of a base (**16**) [81,82]. Phenyl groups of the N-benzyl units are omitted for clarity. As in all other figures, H-bonds are shown as dotted lines.

Uranyl ion complexes of acyclic analogs of homoazacalixarenes have been thoroughly investigated by the Sillanpää group, as possible extractants for uranium [86–91]. The aminodiphenol ligands generally give 1:2 (metal/ligand) complexes with UO_2^{2+}, the metal centre being bound to four phenoxide donors and the protonated amine groups being engaged in intramolecular H-bonding, as in [UO_2(Hhbmch)$_2$], shown in Figure 6a, (**17**, H_2hbmch =

(*N,N*-bis(2-hydroxy-5-*tert*-butyl-3-methylbenzyl)-cyclohexylamine) [88]. Exceptions occur when the alkyl chain bears an additional alcohol coordinating group, with 1:2 or dimeric 2:2 complexes being formed upon variation of the reaction conditions, for example in $[(UO_2)_2(H_2hdbae)_2(NO_3)_2]$ (**18**, H_3hdbae = *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)-2-aminoethanol, Figure 6b) [86]. The case of diaminotetraphenols, in which two aminodiphenol units are linked through an alkyl chain bridging the amine groups leads to linear 2:1 or cyclic 1:1 (metal/ligand) complexes, the latter being particularly remarkable as examples of neutral, dinuclear metallacycles, illustrated by $[(UO_2)_2(H_2thbdh)_2]\cdot 6MeCN$ in Figure 6c (**19**, H_4thbdh = *N,N,N′,N′*-tetrakis(2-hydroxy-3-methyl-5-tert-butylbenzyl)diaminoheptane) [91]. These ligands were tested for uranyl extraction from water to dichloromethane solutions, one of the diaminotetraphenols for example achieving 70% extraction in 4 h and 90% selectivity over Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} [91]. Another group studied an aminodiphenol ligand with an alkyl chain bearing a terminal quaternary ammonium group, which results in the formation of the 1:1 complex $[UO_2(bmta)(OAc)][H_2bmta]I\cdot 4MeOH$ (**20**, H_2bmta^+ = bis[(3,5-di-*tert*-butyl-2-hydroxyphenyl)methyl]-(trimethylammonioethyl)amine, Figure 6d) with the tertiary amine bridge coordinated and the charged substituent extending outwards [92]. The quaternary ammonium group here was intended to form an ion pair with iodide in view of using the complex as a catalyst for the coupling of CO_2 with epoxides. In all of these examples, the bound ligands have an overall charge and thus are not true ZIs but their appended positively charged groups have similar supramolecular functions to those of ZIs.

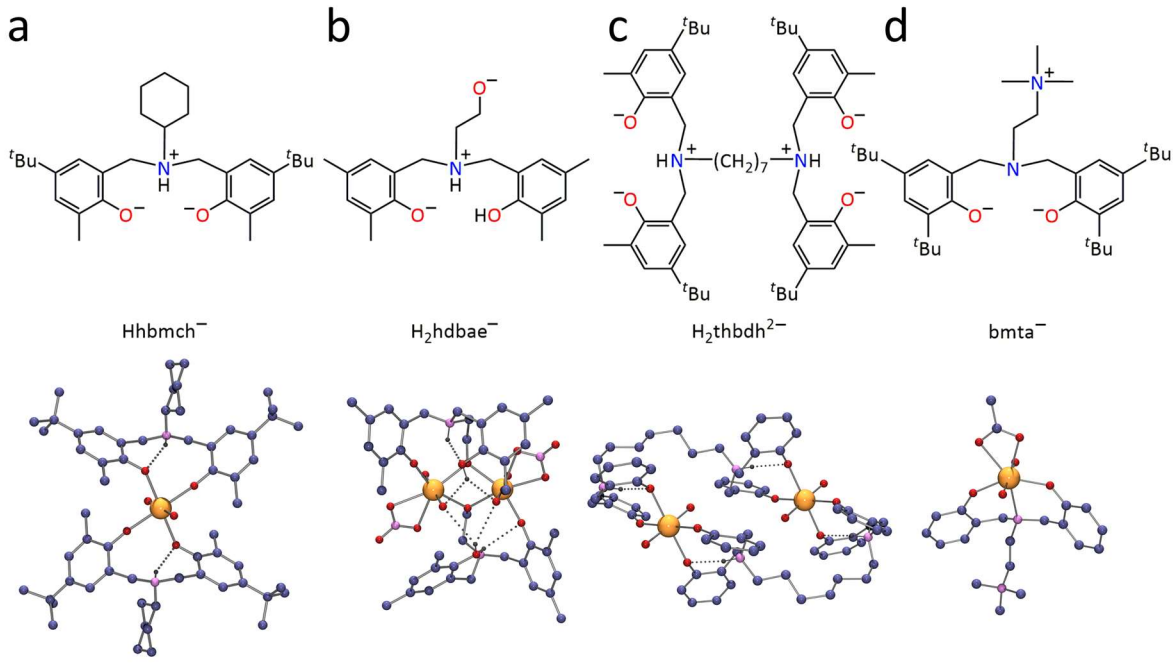
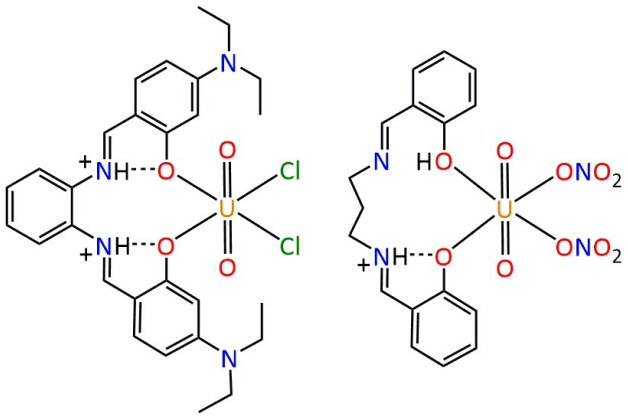


Figure 6. Examples of aminodi- and tetraphenols in their pseudo-ZI form and their uranyl ion complexes. (a) The most common case of a 1:2 complex involving $Hhbmch^-$ (**17**) [88]. (b) 2:2 complex **18** with H_2hdbae^- [86]. (c) The dinuclear metallacycle **19** formed with H_2thbdh^{2-} (methyl and *tert*-butyl substituents omitted for clarity in the lower view) [91]. (d) Complex **20** of $bmta^-$ with tertiary amine coordinated and terminal quaternary ammonium group (*tert*-butyl substituents omitted for clarity in the lower view) [92].

3.3. Schiff bases zwitterions

Functionalized Schiff bases, in particular those of the very numerous family derived from polyamines by their reaction with salicylaldehyde and its analogues, can in principle exist in several tautomeric forms [93]. The crystal structure of the parent species of this family, *N,N′*-bis(salicylidene)ethylenediamine (H_2salen) shows the aromatic hydroxyl groups to retain their protons, though they are involved in H-bonding to the imine-N atoms [94]. In solution, however, there is evidence for the presence of forms where the proton has been transferred from O to N [93], and given that this concerns centres which are both Lewis bases, metal ion binding might be expected to perturb such equilibria. Indeed, in the crystalline UO_2^{2+} complex of neutral *N,N′*-bis[(4,4′-diethylamino)salicylidene]-1,2-phenylenediamine the ligand

has a dizwitterionic form where uranium is bound to phenoxide-O atoms also involved in H-bonding to protonated imine-N atoms (**21**, Scheme 3) [95]. This complex was isolated from the same reaction medium as that where the complex of a far more familiar form involving the doubly-deprotonated Schiff base was also present (note that expressions such as "salen complex" are commonly applied without specification that "salen" is the dianion derived from the neutral Schiff base). Another variation on proton transfer within a uranyl-bound neutral Schiff base has been described in the case of *N,N′*-propylenebis(salicylideneimine), in which one nitrogen is protonated while one phenolic oxygen atom retains its proton [96], so that the ligand is a monozwitterion (**22,** Scheme 3). In general, displacement of ligand tautomeric equilibria by metal ion coordination is not an uncommon situation [97] and with UO_2^{2+} it does have particular importance concerning the use of amidoxime ligands, as discussed in the following section.



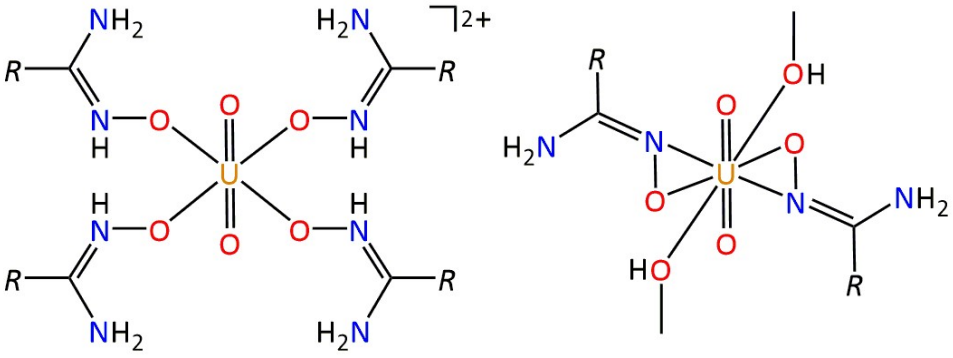
Scheme 3. Uranyl ion complexes with zwitterionic Schiff bases in **21** [95] and **22** [96].

3.4. Amidoximes

Amidoximes, ligands formally containing the group $C(NR_2)$=NOH but having several possible forms [98], have gained particular attention in UO_2^{2+} coordination chemistry for their potential use in the extraction of uranium from sea water [99–103]. Early application of amidoximes as colorimetric reagents for uranium analysis eventually led to crystal structure

determinations on acetamidoxime and benzamidoxime complexes [104] which showed that four such ligands were bound to octahedral U^{VI} as unidentate ZIs through oximate-O, with proton transfer to the oxime-N producing vicinal charges as in N-oxides (Scheme 4). This form of coordination may reflect the high oxophilicity of U^{VI}, since transition metal complexes of both neutral and deprotonated amidoximes appear to prefer oxime-N coordination, though this may be influenced by the fact that structurally characterized complexes involve functionalized or poly-amidoximes which coordinate by chelate ring formation [105–108]. A uranyl ion complex of benzylamidoxime has been shown to have a structure in which the ZI form of the ligand acts as a bridging oximato-O donor between pentagonal-bipyramidal U^{VI} centres having additional chelating nitrate ligands [109]. Deprotonation of acetamidoxime and benzamidoxime results in UO_2^{2+} complexes with novel structures where the N–O unit acts as an η^2-donor [110] (Scheme 4) and where the U^{VI} coordination sphere could be said to be octahedral if the N–O units were considered to occupy a single coordination site or hexagonal-bipyramidal if not. This coordination mode for the anion, known also for the Mo^{II} complex of acetamidoximate [111], was shown computationally to be the most stable form, a conclusion supported by later solution XPS (X-ray photoelectron spectroscopy) and further computational studies [112]. The structural data for ZI forms indicate that they are ligands which bind at least as strongly as acetate to U^{VI} and the novel nature of the anion coordination may in part explain the observed selectivity [101] of polymeric amidoximes in abstracting uranium from sea water. While polymeric amidoximes derived from poly(acrylonitrile) are obvious materials for use in UO_2^{2+} extraction from sea water, insoluble coordination polymers derived from simpler oligoamidoximes present a prospect for selective isolation of uranium from nuclear waste and it has been shown that 1,4-di(amidoximyl)benzene can indeed be used to form a highly insoluble, triperiodic CP in which both dizwitterionic and dianionic ligand units are present, both acting simply as

unidentate O-donors, unexpected for the dianions but rationalized in terms of electronic effects within the aromatic system [113].



Scheme 4. Different coordination modes of amidoximes to uranyl, illustrated by acetamidoxime (*R* = CH_3) and benzamidoxime (*R* = Ph), either in their unidentate ZI form (left) [104] or in their η^2-bonded deprotonated form (right) [110].

3.5. Ammonium-containing zwitterionic carboxylates

3.5.1. Aliphatic ammonium-containing zwitterionic carboxylates

Perhaps the most obvious members of this family of ligands are the natural amino-acids but there is surprisingly little structural information on their complexes with uranyl ion. The interaction of UO_2^{2+} with biomolecules such as proteins is of fundamental importance in regard to understanding the toxicity of the metal [114–116] and a considerable number of protein structures do involve uranium atoms, in most instances because of the use of uranyl ions as heavy atom labels, and these provide confirmation of the expected interaction of uranyl ion with carboxylate side chains such as those of aspartate and glutamate residues but with low precision on bond lengths and angles [115,117]. Few structures of complexes with natural amino-acids are known, and all involve ZI forms with carboxylate binding to U^{VI}. As these amino acids are zwitterionic in their crystals, these structures are not examples of coordination-induced proton transfer.

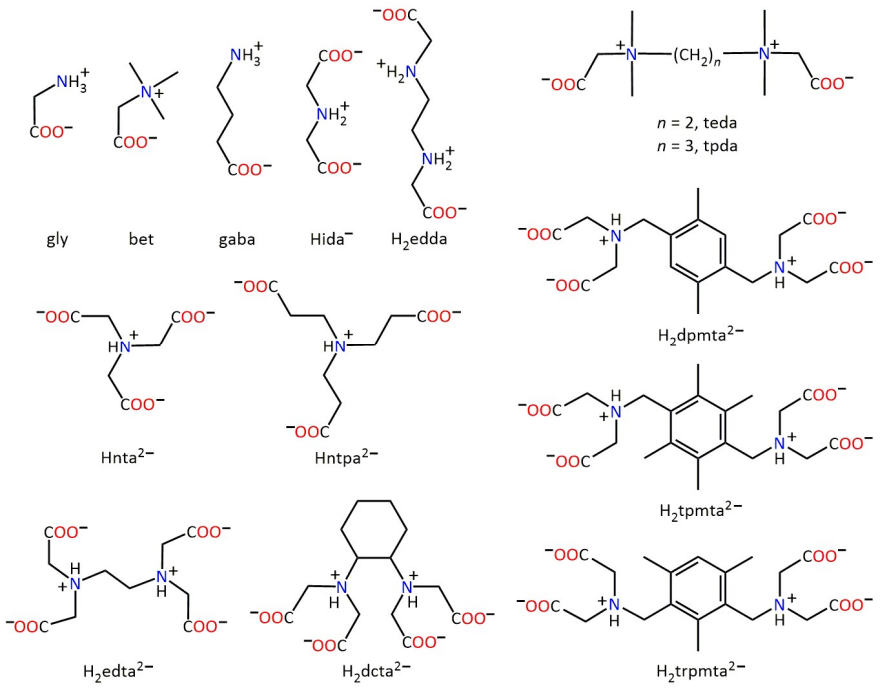
The simplest ligand in this category is glycine (gly, Scheme 5), whose complexing properties toward UO_2^{2+} have been investigated by several groups [118–122]. This work was first motivated by its environmental relevance, both to improve the understanding of uranyl ion behaviour in living systems, and to help in the development of decontaminating molecules [119], but was later expanded to using "charge-assisted H-bonding" in supramolecular organization [120]. In the discrete complex $[UO_2(gly)_4](NO_3)_2$, which was the first to be characterized by its crystal structure, four ligands are bound to the uranium atom, two of them κ^2O,O'-chelating and the other two monodentate, with a *trans* arrangement, and NH···O(carboxylate) H-bonds assemble the cations into chains [118]. Forbes *et al.* used glycine (and also L-alanine in one case) to crystallize a series of complexes under mild acidic aqueous conditions, with uranyl hydrolysis generating oxo and hydroxo anions and resulting in the formation of monoperiodic chains with slightly variable connectivities but in which all ZI ligands are μ_2-κ^1O:κ^1O'-bridging [120,121]. Of particular interest is the complex $[(UO_2)_3(gly)_2(O)_2(OH)_2]\cdot 6H_2O$, in which wide channels are created by the packing of chains held by interchain, multifurcated H-bonding of amino groups to three uranyl oxo groups and the central μ_3-oxo bridge. This H-bonding network is sufficiently strong for the crystal structure to be unaffected by the removal of the water molecules occupying the channels. H-bonding of amines to uranyl oxo groups is well known (see section 3.2) and it often plays an important role in the supramolecular arrangement of uranyl-containing species; the in-built ability of amino acids to join a complexing site to a H-bond donor within the same molecule is an asset for this purpose since, in contrast to azacalixarenes or aminopolyphenols, the H-bonds formed here are not intramolecular, but between separate complex units. This work also suggested that the NH···O(uranyl) H-bonds have an effect on the U=O bond, as indicated by a linear relationship between the donor···acceptor distance and the average U=O bond valence [121]. The related γ-aminobutanoic acid (gaba, Scheme 5) in its ZI form, with a

longer carbon chain, gives mononuclear UO_2^{2+} complexes in which the metal is tris(κ^2*O,O′*-chelated) and the ammonium groups are H-bonded to carboxylate and nitrate or perchlorate oxygen atoms [123,124]. The crystal structure of a complex involving monodentate L-proline has also been described [125].

A large volume of structural information is available for complexes of amino-acid derivatives where alkylation of the amino group prevents deprotonation causing loss of their ZI character. Extensive and thorough investigations largely due to the group of Mak and concerning trimethylammonio-glycine, "betaine" (bet, Scheme 5) [126] and analogues in their complexes with a wide variety of metal ions established the important fact that the donor capacity of a carboxylate group showed negligible sensitivity to a nearby positive charge. Thus, although of identical complexing ability to glycine, the quaternized ZI betaine offers a completely different prospect for supramolecular organization, albeit only a few examples of UO_2^{2+} complexation with betaine have been reported. The first study was part of an investigation of functionalized or task-specific ionic liquids aiming at better solubilization of metal salts or oxides, the counterion being bis[(trifluoromethyl)sulfonyl]imide (Tf_2N^-) [127]. The betaine complex formed in this work, from reaction with $UO_3 \cdot 2H_2O$ (while uranyl nitrate or acetate salts are most often used in the synthesis of UO_2^{2+} complexes generally, this has the advantage of introducing but a single anion into the reaction mixture), $[(UO_2)_2(bet)_6(H_2O)_2](Tf_2N)_4$, is a dimeric species in which two bet ligands are μ_2-κ^1*O*:κ^1*O′*-bridging and the other four are monodentate, a structure different from the monoperiodic CP formed under the same conditions with a carboxylate-functionalized pyrrolidinium ZI or the mononuclear complex with a carboxylate-functionalized imidazolium (see ahead). A very similar dimeric structure was also obtained with the phosphonium analogue of betaine, although two of the ligands are chelating and no water molecule is coordinated in this case [21]. Betaine has been used as an additional, monodentate, structure-directing ligand with

uranyl arsenate or sulfate [128,129], (as well as, after protonation, as a counter cation) and as a chelating ligand in decorative substituents on a uranyl ion polymer formed with 1,3-phenylenediacetate [130]. Chelating, chelating-bridging and μ_2-κ^1O:κ^1O'-bridging modes of coordination have been characterized by Burns *et al.* in a series of six complexes including mono- and diperiodic CPs, one being a homoleptic, cationic U–Li polymer of bet alone [131].

The simplest example of an ammoniodicarboxylate anion is that derived from iminodiacetic acid (H_2ida), and the first crystallographically characterized UO_2^{2+} complex of $Hida^-$ (Scheme 5), a monoperiodic CP with interchain H-bonding of ammonium to carboxylate groups, was reported as long ago as 1974 [132]. The geometry of H_2ida is however conducive to the formation of complexes with ONO-chelation of the dianionic (non-zwitterionic) ida^{2-} form [133–135]. Of particular originality is the work of Forbes *et al.*, who have found a synthetic path, under ambient conditions, allowing the isolation of $(H_2pip)_{0.5}[UO_2(ida)(Hida)]\cdot 2H_2O$ (**23**, pip= piperazine), a complex in which both the dianionic and the monoanionic (pseudo-zwitterionic) forms coexist, the former bound in the ONO-chelating mode and the latter in the bridging, bis(monodentate) mode [136,137]. This complex forms hexanuclear rings with a shape extremely heavily puckered, these rings being stacked one upon the other so as to form nanotubes with a diameter of ~12 Å (Figure 7), this arrangement being assisted by inter-ring ammonium–carboxylate H-bonding. The authors were specially interested in the ordering of the water molecules located inside the nanotubes, which are involved in an “ice channel” arrangement through H-bonding. The crystalline order of the nanotubes is retained under water removal, and the reuptake of water is selective over that of other solvents. In the course of this work, a dimeric species, $(H_2pip)[(UO_2)_2(ida)_2(Hida)_2]\cdot 8H_2O$, was also characterized as a ring fragmentation product [137].



Scheme 5. Aminocarboxylic acids and their derivatives shown in forms where at least one arm can be regarded as having a zwitterionic nature.

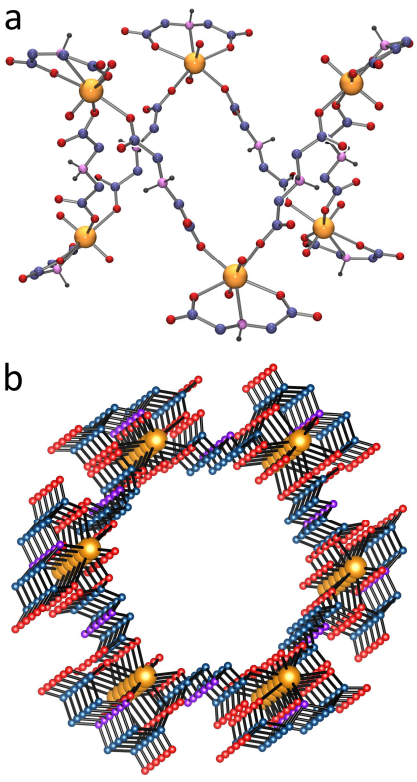


Figure 7. (a) The $\{[UO_2(ida)(Hida)]_6\}^{6-}$ ring and (b) the nanotubular stacking of rings in complex **23** [136].

Incorporation of a second ammonium group in a dicarboxylate ligand is provided in the true (potential) ZI ethylenediamine-*N*,*N*′-diacetic acid (H_2edda, Scheme 5), but only one crystal structure of a uranyl ion complex, [$(UO_2)_2$(edda)$_2$(H_2edda)], has been reported, with here also a mixture of dianionic and neutral, dizwitterionic forms [138]. The uranium atom is chelated by the two nitrogen atoms and two oxygen atoms from one curved, dianionic ligand, and the extended, bis-monodentate ZI bridges two uranium atoms to form the dimer, a connectivity akin to that found in complex **23**. Further instances of ZI arm formation result with ligands placing three carboxylic acid groups around a tertiary amine, as in nitrilotriacetic acid (H_3nta) and nitrilotri-3-propanoic acid (H_3ntpa). The tricarboxylate, pseudo-ZI form of these two molecules is dianionic (Scheme 5), and the 1:1 complex that $Hnta^{2-}$ forms with UO_2^{2+}, [UO_2(Hnta)(H_2O)$_2$]·3H_2O (**24**), is thus neutral [139,140]. This complex crystallizes as a monoperiodic CP built from fused diuranacyclic units. The protonated nitrogen atom forms a trifurcated H-bond with the three uncomplexed carboxylate oxygen atoms (Figure 8a), thus having an effect on the conformation adopted by the ligand, but not a direct role in supramolecular organization. With longer carbon chains, $Hntpa^{2-}$ gives mono- or diperiodic CPs, and in the latter the ammonium–carboxylate H-bonds link adjacent layers [141]. As in the case of ida^{2-}, nta^{3-}, formed in the presence of dabco (1,4-diazabicyclo[2.2.2]octane) as a base, simply behaves as a ONO-chelate toward uranyl, the third carboxylate arm being diverted away to generate a diperiodic CP [142].

No UO_2^{2+} complex contains deprotonated ethylenediaminetetraacetic acid (H_4edta, Scheme 5) in a pseudo-ZI form as a carboxylate donor, the only crystal structures known being of ONO-chelated species [142–144]. However, the related and slightly more constrained *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (H_4dcta, Scheme 5), when reacted with uranyl nitrate under hydrothermal conditions in the presence of either imidazole, NaOH or CsOH, is found with one or two ZI arms, the complexes being mono- or

diperiodic [145]. The H-bonds in which the ammonium groups are engaged are intramolecular only, as shown in Figure 8b in the case of $[UO_2(H_2dcta)(H_2O)_2]\cdot 3H_2O$ (**25**).

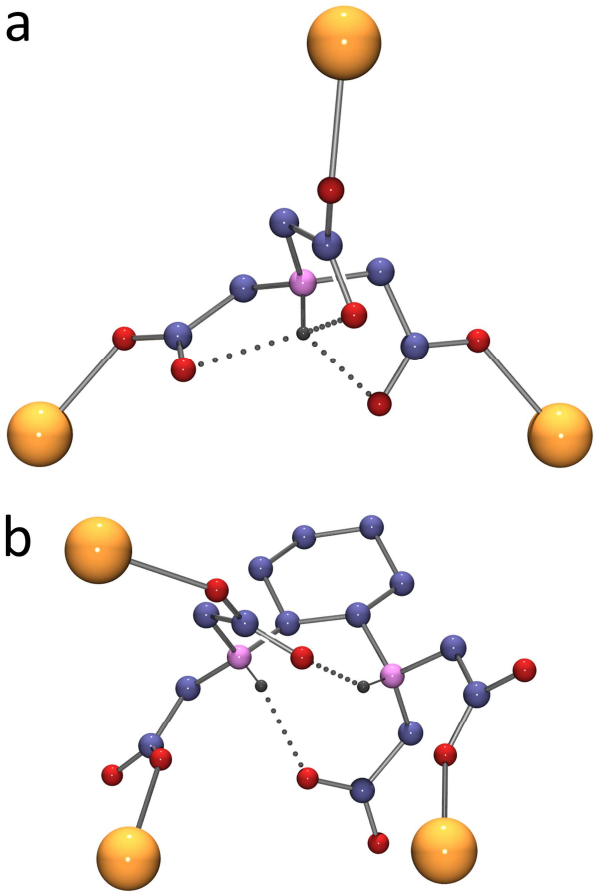


Figure 8. (a) Intramolecular trifurcated H-bonding in the $Hnta^{2-}$ complex **24** [140]. (b) Intramolecular H-bonding in the H_2dcta^{2-} complex **25** [145].

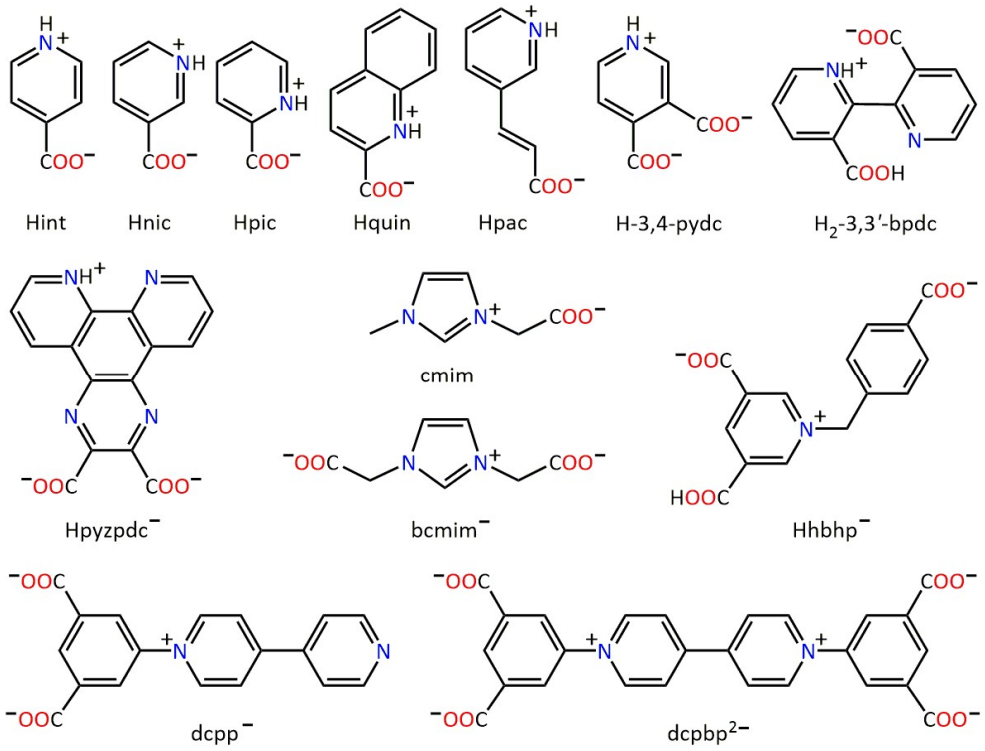
The two elongated dizwitterions *N,N,N′,N′*-tetramethylethane-1,2-diammonioacetate (teda) and *N,N,N′,N′*-tetramethylpropane-1,3-diammonioacetate (tpda), shown in Scheme 5, gave uranyl ion complexes with additional chloride and/or oxo and hydroxo anions [146]. $[(UO_2)_2Cl_2(teda)_3][(UO_2Cl_3)_2(teda)]$ is an ionic compound in which discrete, binuclear anions cross the cells of the cationic honeycomb network, and $[(UO_2)_7(O)_3(OH)_{4.3}Cl_{2.7}(tpda)_2]Cl\cdot 7H_2O$ crystallizes as a twofold interpenetrated, triperiodic UOF in which the ZI ligands connect chlorouranate monoperiodic subunits.

Although they are not strictly aliphatic, three ligands possessing two aminodiacetic acid groups attached to an aromatic ring are included here for their relatedness to H_4dcta [147,148]. The three semi-rigid tetraacids 2,2′,2″,2‴-(2,5-dimethyl-1,4-phenylene)bis(methylene)-bis(azanetriyl)tetraacetic acid (H_4dpmta), 2,2′,2″,2‴-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene)bis(azanetriyl))tetraacetic acid (H_4tpmta), and 2,2′,2″,2‴-(2,4,6-trimethyl-1,3-phenylene)bis(methylene)-bis(azanetriyl)tetraacetic acid (H_4trpmta), shown in Scheme 5, complex uranyl under their dianionic, pseudo-dizwitterionic form. The CPs thus generated are diperiodic, and the ammonium groups are involved in intramolecular H-bonding to carboxylate groups.

3.5.2. Aza-aromatic ammonium-containing zwitterionic carboxylates

Isonicotinic (pyridine-4-carboxylic) acid (Hint, Scheme 6) was used early on to generate a series of mono- and diperiodic CPs in which the ammonium protons form H-bonds providing additional connectivity [149]. In another work with Hint, the interesting and rare coordination of two pertechnetate (TcO_4^-) or perrhenate (ReO_4^-) anions to UO_2^{2+} was observed, favoured by the neutrality of the Hint ligand in its ZI form and the resulting dicationic nature of $UO_2(Hint)_3^{2+}$; H-bonding of the ammonium groups assembles the discrete, neutral complexes into a layered structure [150]. Uranyl halides have been shown to form asymmetric dinuclear complexes $[(UO_2)_2Br_4(C_5H_5NCO_2)_2(H_2O)]$ with ZI picolinic (Hpic, pyridine-2-carboxylic) and nicotinic (Hnic, pyridine-3-carboxylic) acids (Scheme 6), the different position of the ammonium protons resulting in intra- or intermolecular NH···Br H-bonding, respectively, this difference having an effect on the geometry (planar or bent) of the complex; in contrast, Hint forms only a mononuclear species with uranyl chloride, which contains however a mixture of cationic $[UO_2Cl(Hint)_3]^+$ and anionic $[UO_2Cl_3(Hint)]^-$ units [151]. In another study, isonicotinic acid was shown to adopt either a ZI form in $[(UO_2)(NO_3)_2(Hint)_2]$ or a form in

which the nitrogen atom is unprotonated and bound to uranium in [$(UO_2)(OH)(int)$], depending on the solution pH, with KOH being added in the last case, and temperature [152]. Picolinic acid adopts both zwitterionic and anionic forms in $[UO_2(pic)_2(Hpic)]$ [153]. Nicotinic acid has also been used in the synthesis of a mixed-ligand complex involving also phthalic acid (H_2pht), $[(UO_2)_2(pht)_2(Hnic)_2(H_2O)_2]$, in which discrete dinuclear units are assembled into triperiodic assemblies by H-bonding involving the ammonium groups, among others [154].



Scheme 6. Aza-aromatic zwitterionic carboxylates and closely related species.

Perrhenate complexation to UO_2^{2+} is also found in the case of quinaldic acid (quinoline-2-carboxylic acid, Hquin, Scheme 6), a ligand which results from an extension of the aromatic system of picolinic acid, and an example of a mixed-ligand complex involving Hquin and 2,6-pyridinedicarboxylate has also been described, in which the ammonium groups of two ZI ligands are H-bonded to carboxylate oxygen atoms of the dianion [155]. Another type of extension consists in increasing the distance of the carboxylate group to the aromatic ring, as

in *trans*-3-(3-pyridyl)acrylic acid (Hpac, Scheme 6) which is involved as both an anionic and a ZI ligand in $[(UO_2)_3(pac)(Hpac)(O)(OH)_3]\cdot 2.5H_2O\cdot CH_3CN$ (**26**, Figure 9a), a monoperiodic CP assembled into a triperiodic network through H-bonding; a hydroxido ligand is here a mediator between the protonated and unprotonated nitrogen atoms through formation of N–H···O–H···N H-bonds [156]. Yet another variation on these pyridinecarboxylate ligands is provided by 2,2′-bipyridine-3,3′-dicarboxylic acid (H_2-3,3′-bpdc, Scheme 6), but there seems to be only one example of its coordination to UO_2^{2+} under a partial ZI form, in $[UO_2(3,3'\text{-bpdc})(H_2\text{-}3,3'\text{-bpdc})]\cdot H_2O$, a monoperiodic complex in which the ammonium group is only involved in intrachain H-bonding [157].

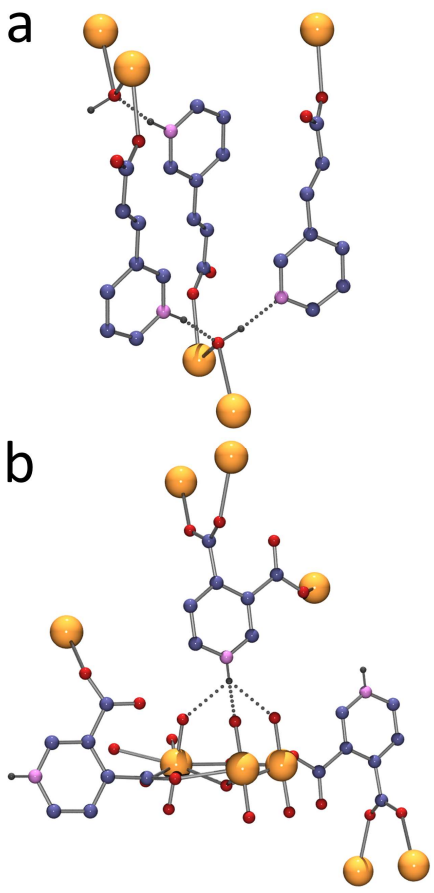
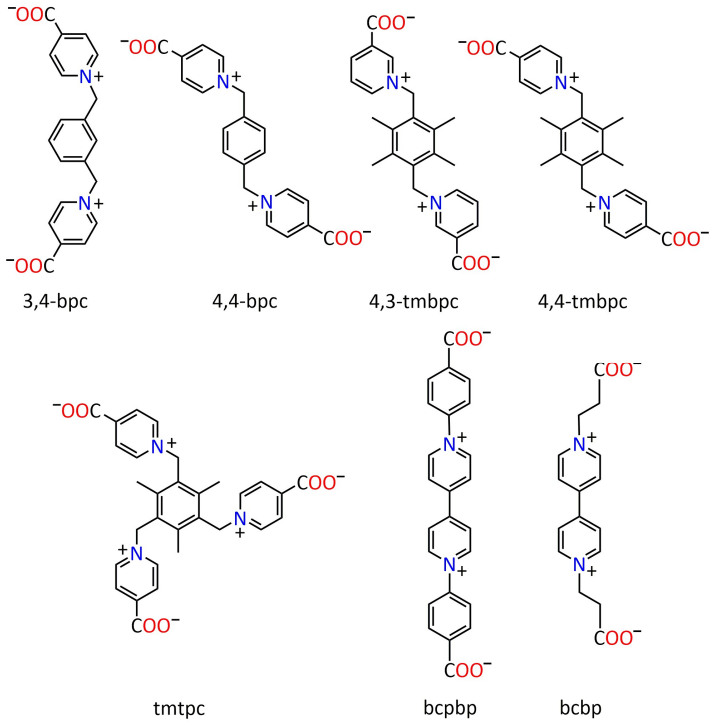


Figure 9. (a) Hydroxo-mediated H-bonding in complex **26** [156]. (b) Trifurcated H-bonding of the ammonium group to three uranyl oxo groups in complex **27** [158]. Oxo groups and other coordinated atoms are omitted for most U atoms.

Complexes formed with 2,3-, 2,4- and 3,4-pyridinedicarboxylates (H_2pydc, Scheme 6) in their monoanionic, ZI form crystallize as diperiodic CPs [158,159], with in the latter case a remarkable interlayer trifurcated H-bonding interaction between the ammonium group and three uranyl oxo atoms in the complex $[(UO_2)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_2(H\text{-}3,4\text{-}pydc)(3,4\text{-}pydc)_{0.5}]$ (**27**, Figure 9b) [158]. In contrast, 2,6-pyridinedicarboxylate is always bound to UO_2^{2+} in its dianionic form, formation of two adjacent five-membered chelate rings involving nitrogen as a donor being a particularly common motif. Unlike H-2,3-pydc, the 2,6 isomer does not adopt a ZI form in its crystal. Pyrazine-based carboxylates are much less common than pyridine-based ones, and in the only case of formation of a ZI ligand, with 2,3-pyrazino[1,10]phenanthroline-2,3-dicarboxylic acid (H_2pyzpdc, Scheme 6), the protonated nitrogen atom pertains in fact to a phenanthroline unit [160].

While the pyridinium-based ZI carboxylates described above involve protonated nitrogen atoms and as a consequence can take part in H-bonding, there are also many cases of pyridinium- and imidazolium-based carboxylates containing quaternized ammonium groups that do not offer the same prospect for structure extension through weak interactions. The U-shaped ligand 1,1′-[1,3-phenylenebis(methylene)]bis(pyridin-1-ium-4-carboxylate) (3,4-bpc, Scheme 7) was shown by Shi *et al.* to give different UO_2^{2+} complex species depending on the pH of the solutions treated hydrothermally, in particular the dinuclear, double metallamacrocycle $[(UO_2)_2(\mu_2\text{-}OH)_2(3,4\text{-}bpc)_2(H_2O)_2](NO_3)_2$ and the diperiodic CP $[(UO_2)_8O_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(C_2O_4)_2(3,4\text{-}bpc)_2]$, which contains an unusual octanuclear secondary building unit (SBU) [161]. Association with μ_3-bridging sulfate anions to form a diperiodic CP was achieved with the isomer 1,1′-[1,4-phenylenebis(methylene)]bis(pyridin-1-ium-4-carboxylate) (4,4-bpc, Scheme 7) [162]. In the same family of ligands, 1,1′-[(2,3,5,6-tetramethylbenzene-1,4-diyl)bis(methylene)]bis(pyridin-1-ium-3-carboxylate) (4,3-tmbpc, Scheme 7) gave the complex $[(UO_2)_3(4,3\text{-}tmbpc)(O)_2(OH)(H_2O)](NO_3)_{0.8}Cl_{0.2}\cdot 3H_2O$ (**28**,

Figure 10a), in which monoperiodic oxo- and hydroxo-bridged SBUs are assembled into a diperiodic network by the divergent ZI ligands bound in a μ_2-κ^1O:κ^1O'-bridging mode [163]. A tri-zwitterionic tricarboxylate ligand containing three pyridinium units, 1,1′,1″-(2,4,6-trimethylbenzene-1,3,5-triyl)-tris(methylene)-tris(pyridine-4-carboxylate) (tmtpc), complexes UO_2^{2+} to give either a neutral diperiodic CP based on tetranuclear motifs, $[(UO_2)_4(tmtpc)_2Cl_4(\mu_3\text{-}O)_2]\cdot 4H_2O$ (**29**, Figure 10b), or a cationic, triperiodic UOF, $[UO_2(tmtpc)_2](NO_3)_2\cdot H_2O$, depending on the pH and the nature of the uranyl salt [164]. The same ligand tmtpc also gives another, cationic diperiodic network, containing dinuclear SBUs, whose anion exchange properties have been demonstrated with ReO_4^- and $H_2PO_4^-$ [165]. A particular development with these and other large ZI dicarboxylates consists in their association with anionic polycarboxylates so as to generate mixed-ligand complexes, or with cucurbiturils to give supramolecular assemblies, two strategies which will be discussed in sections 3.5.4 and 3.5.5, respectively.



Scheme 7. Pyridinium-based di- and trizwitterionic ligands.

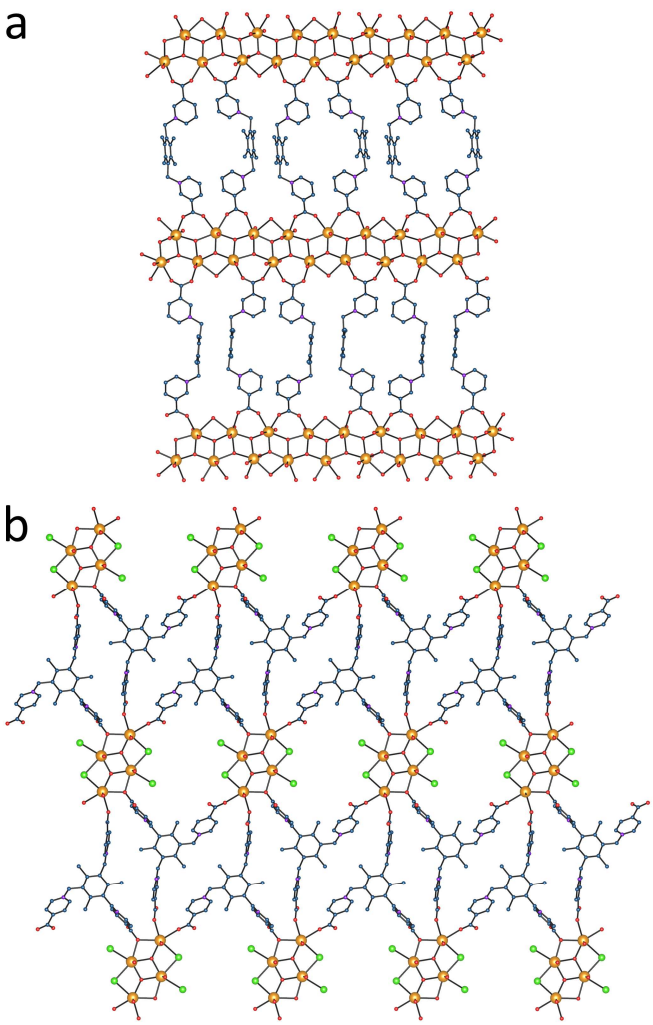


Figure 10. (a) The diperiodic complex **28** with ligand 4,3-tmbpc [163]. (b) The diperiodic complex **29** with ligand tmtpc [164].

Imidazolium-containing ZI ligands were first described in the context of studies of carboxyl-functionalized ionic liquids as solvents for the U^{VI} oxide UO_3, which is of interest for nuclear fuel cycle applications [127]. The UO_2^{2+} complex with 1-carboxylatomethyl-3-methylimidazolium (cmim, Scheme 6) is a discrete species in which acidic imidazolium protons form CH···O bonds with the Tf_2N^- counteranions [127]. The related dicarboxylate 1,3-bis(carboxylatomethyl)imidazolium ($bcmim^-$, Scheme 6) was found to react with uranyl nitrate to give four different mono- or diperiodic species as a function of the solution pH, due to different bridging by oxo and hydroxo anions, or by oxalate formed *in situ* under the most

acidic conditions, the degree of uranyl ion association within secondary building units generally increasing with the pH [166]. The same ligand has also been used in an investigation of the effect of ZI ligands on water ordering within the pores defined by the CP formed; it was found that the well-ordered water molecules interact more strongly with carboxylate than with imidazolium groups, and that one of the compounds synthesized supports an extensive water network [167].

The diacid cation 4-(3,5-di{hydroxycarbonyl}phenylpyridinium)-pyridine (H_2dcpp^+, Scheme 6), with a benzenedicarboxylic acid moiety linked to a bipyridine unit by quaternization of one pyridine-N centre, could, by loss of one proton, adopt a dizwitterionic dicarboxylate form with the remaining proton located on the pyridine-N, and it has yielded a series of UO_2^{2+} complexes with very diverse geometries depending upon pH variations, some of them having photochromic and thermochromic properties [168]. but all containing the fully deprotonated $dcpp^-$ ligand of only partial zwitterionic character, even though the pyridine-N is coordinated in only one case. The complex formulated as $[UO_2(dcpp)_2(H_2O)_2]\cdot 3H_2O$ is described as forming a H-bonded honeycomb diperiodic polymer involved in inclined 2D + 2D $\rightarrow$ 3D polycatenation, while twofold parallel interpenetration of H-bonded diperiodic networks is found in $[UO_2(dcpp)_2(H_2O)_2]\cdot 7H_2O$, which differs from the previous complex by the orientation of the $dcpp^-$ ligands. $[(UO_2)_2(\mu_2\text{-}OH)_2(dcpp)_2]$ (**30**) is an example of a triperiodic UOF, unusual in this family of compounds, containing helical subunits; however, the connectivity here is only due to the dicarboxylic part of the ligand, the bipyridinium being only a pendent group (Figure 11a). This is no longer true in $[(UO_2)_2(\mu_2\text{-}O)(dcpp)_2)]$ (**31**), a diperiodic CP in which the pyridine nitrogen atom of one of the ligands is coordinated (Figure 11b). The corresponding dianionic tetracarboxylate, 1,1′-bis(3,5-dicarboxylatophenyl)-4,4′-bipyridinium (H_4dcpbp, Scheme 6), which again could adopt diprotonated ZI forms, yields a series of CPs through variations in the nature of inorganic acids added during the synthesis,

with diverse mono- to triperiodic arrangements, the most remarkable being a helical chain; only in one case is the true ZI present, simply as an uncomplexed species associated in the crystal with a uranyl sulfate chain [169]. Uranyl luminescence quenching by Fe^{III} cations makes one of these complexes a possible candidate for selective detection of this species.

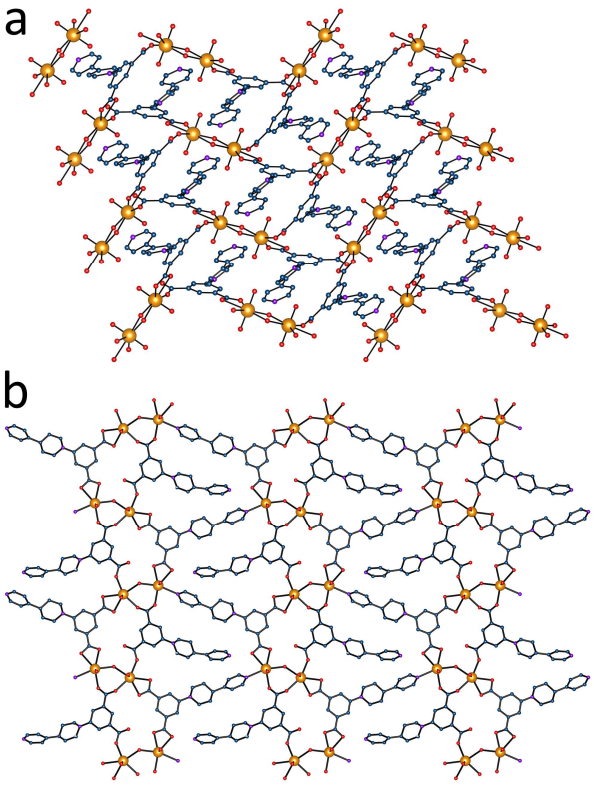


Figure 11. (a) Triperiodic UOF formed by complex **30**. (b) Diperiodic network with partial pyridine group coordination in **31** [168].

The cationic tricarboxylic acid *N*-(4-hydroxycarbonylbenzyl)-3,5-di(hydroxycarbonyl)pyridinium (H_3hbhp^+, Scheme 6), again a species that, by monodeprotonation, could adopt ZI forms, acts nonetheless as an anionic ligand by double deprotonation in forming a monoperiodic CP with UO_2^{2+}, $[UO_2(OH)(H_2hbhp)(Hhbhp)]\cdot 4H_2O$, with further extension of the structure through π-stacking interactions [170]. Under excitation at 365 nm, this compound displays the characteristic emission of uranyl complexes, but uranyl luminescence is quenched after irradiation by X-

rays (4.7 kGy), with a linear relationship between I_0/I and the dose received. This phenomenon, which appears to be due to the formation of ligand-based radical species providing a nonradiative de-excitation pathway, has potential applications for X-ray dosimetry.

3.5.3. Cyclic zwitterionic carboxylates: H_4dota and H_4teta

Both the functionalized macrocycles 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (H_4dota) and 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid (H_4teta), with a 1:1 ratio of carboxylic to amino groups, can adopt true ZI forms. In contrast to many other metal cations, lanthanides in particular, UO_2^{2+} does not fit into the N_4 cavity and binds preferentially to the carboxylate groups, thus leading to the formation of di- or triperiodic CPs, some of them including additional oxalate linkers formed *in situ* under the hydrothermal conditions used. Figure 12 shows two representative examples, both diperiodic assemblies: $[(UO_2)_2(H_2dota)(C_2O_4)(H_2O)_2]\cdot 6H_2O$ (**32**), in which H_2dota^{2-} is dianionic due to the protonation of only two amine groups which form intramolecular H-bonds [171], and $[UO_2(H_4teta)(H_2O)]\cdot NO_3\cdot Cl$ (**33**), in which the neutral H_4teta ligand is a tetrazwitterion forming H-bonds with carboxylate or nitrate anions [172]. It is notable that complex **33** provides the only case of tetrazwitterionic H_4teta in the CSD. The partial ZI character of H_2dota^{2-} in **32** is lost upon introduction of additional lanthanide cations which occupy the N_4O_4 site of the tetraanionic form of the ligand, as in $[(UO_2)_2Ln(dota)(C_2O_4)(OH)(H_2O)]\cdot 3H_2O$ [Ln = Gd or Eu] [173], but no comparable heterometallic complex could be obtained with $teta^{4-}$.

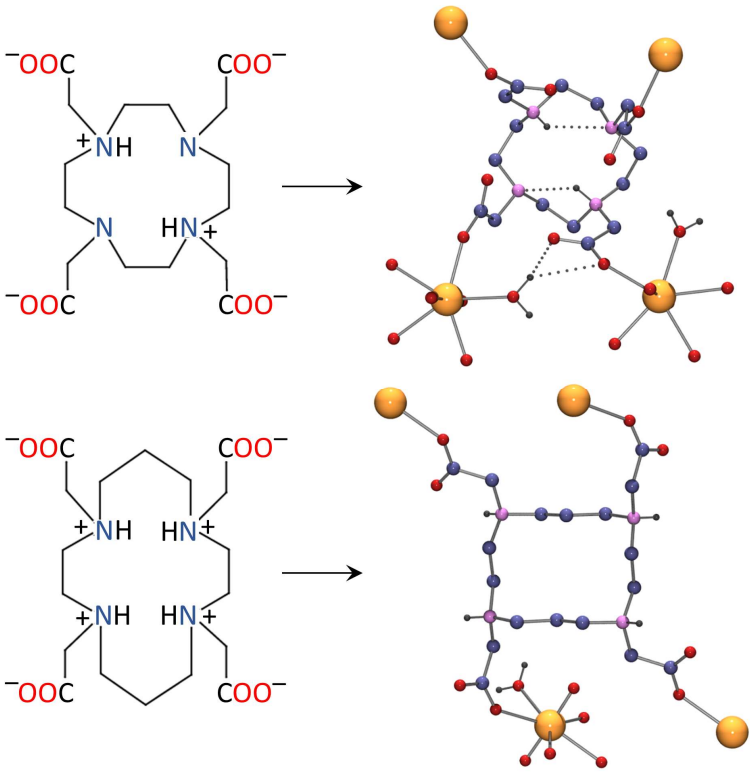


Figure 12. Uranyl ion complexes **32** with dizwitterionic H_2dota^{2-} (top) [171] and **33** with tetrazwitterionic H4teta (bottom) [172]. Oxo groups and other coordinated atoms are omitted for most U atoms.

3.5.4. Anionic/zwitterionic carboxylate mixed-ligand complexes

Structures of complexes containing both ZI polycarboxylates and oxalate ligands are known [161,166,171,174,175], the latter ligand being often found to be generated *in situ* under hydrothermal conditions. However, although examples of triperiodic UOFs and entangled structures have been found in some of these complexes [174], the planar nature, small size, rigidity and bridging, bis-chelating nature of oxalate [176] often restrain polymerization to be mono- or diperiodic. Some examples of mixed-ligand complexes involving other small carboxylates are limited to monoperiodicity, such as in the cases of succinate and Hint in its ZI form [177], or 2,6-pyridinedicarboxylate and iminodiacetate ($Hida^-$) [178], and the present section more particularly concerns the use of large-sized ZIs, an approach extensively developed in recent years (see section 2.2 for other examples involving

ZI metalloligands). In an early report by Shi *et al.*, the elongated, linear dizwitterion 1,1′-bis(4-carboxylatophenyl)-4,4′-bipyridinium (bcpbp, Scheme 7) has been coupled with phthalic, terephthalic and biphenyl-4,4′-dicarboxylic acids, yielding neutral mono- and diperiodic CPs [179].

Using a wider spectrum of anionic polycarboxylates with several different ZI di-and tricarboxylates, a series of complexes displaying a notable diversity of periodicities and topologies has been reported in the last few years [130,146,163,180−182]. The highly flexible aliphatic ZI ligands teda and tpda (see section 3.5.1 and Scheme 5), when associated with eight different anionic di- and tetracarboxylates, gave 10 uranyl ion complexes covering all the periodicity range since they crystallize as zero-, mono-, di- or triperiodic species [146]. As just two examples, $[(UO_2)_2(tpda)(H\text{-}2,4\text{-}pydc)_4]$ is a discrete complex in which the bis(monodentate) ZI ligand bridges two uranyl cations which are bis(ON-chelated) by two 2,4-pyridinedicarboxylate anions, while $[(UO_2)_5(teda)_7(tdc)(H_2O)][(UO_2)_2(tdc)_3]_4 \cdot CH_3CN \cdot 12H_2O$, where tdc^{2-} is 2,5-thiophenedicarboxylate, displays an entanglement involving the cationic, triperiodic framework and the anionic, diperiodic honeycomb network. The latter complex thus exemplifies a case of self-sorting of the two types of ligands, and it is also the first example of hetero-interpenetration in uranyl chemistry, the two subunits differing by both their periodicity and chemical nature.

Both 4,3-tmbpc (see section 3.5.2) and its positional isomer 1,1′-[(2,3,5,6-tetramethylbenzene-1,4-diyl)bis(methylene)]bis(pyridin-1-ium-4-carboxylate) (4,4-tmbpc, Scheme 7), and also the trizwitterion tmtpc, have also been associated with very diverse anionic polycarboxylate coligands, here also producing a series of complexes of remarkable variety [180]. The ligand 4,4-tmbpc adopting a curved shape results in the complex $[(UO_2)_2(4,4\text{-}tmbpc)_2(cbtc)(H_2O)_2] \cdot 10H_2O$ (**34**, $cbtc^{4-}$ = *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylate) being a neutral, discrete dinuclear complex having the shape of

a double ring with a central cbtc^{4-} pillar (Figure 13a). While elongated conformations of 4,4-tmbpc yield simple monoperiodic CPs, the ligand in curved shape, in association with 1,2-phenylenedioxydiacetate (pdda^{2-}) gives [UO_2(4,4-tmbpc)(pdda)]$_3$·10H_2O (**35**), a ribbon-like chain (Figure 13b). Among several diperiodic networks, two, obtained with 4,4-tmbpc and 1,2-phenylenediacetate or with 4,3-tmbpc and *cis/trans*-1,4-cyclohexanedicarboxylate, are three-fold parallel interpenetrated honeycomb networks, an arrangement made possible by the large size of the hexanuclear rings (~9 Å × 25 Å and ~10 Å × 22 Å, respectively). In the latter complex, an intersheet short contact, at 2.85 Å, between one uranyl oxo group and a pyridinium nitrogen atom is probably indicative of a type of interaction which has been found in other cases [85,164,168,183]. As with the teda ligand, tdc^{2-} and 4,3-tmbpc are self-sorted in the complex [(UO_2)$_2$(4,3-tmbpc)$_3$(H_2O)$_2$][(UO_2)$_2$(tdc)$_3$]$_2$·10H_2O, but both independent CPs are here diperiodic [163]. Two complexes involving 4,4-tmbpc and either 3- or 2-sulfobenzoate dianions are also known, the first a monoperiodic CP and the second a diperiodic network displaying the kagome topology [163].

The trizwitterion tmtpc and 1,3-adamantanedicarboxylate (adc^{2-}) associate to build the complex [Htmtpc][(UO_2)$_3$(tmtpc)(adc)$_3$]Br (**36**), which contains a very thick and corrugated honeycomb network with two different kinds of cells; the uncoordinated Htmtpc$^+$ cation associates with the coordinated tmtpc in the anionic CP to form a capsule containing the bromide anion (Figure 13c) [180]. Combined with the same tripodal ZI ligand, *trans*-1,4-cyclohexanedicarboxylate (*t*-1,4-chdc^{2-}) affords [(UO_2)$_2$(tmtpc)$_2$(*t*-1,4-chdc)](NO_3)$_{1.7}$$Br_{0.3}$·6$H_2O$ (**37**), an instance of a cationic triperiodic UOF (Figure 13d) [180].

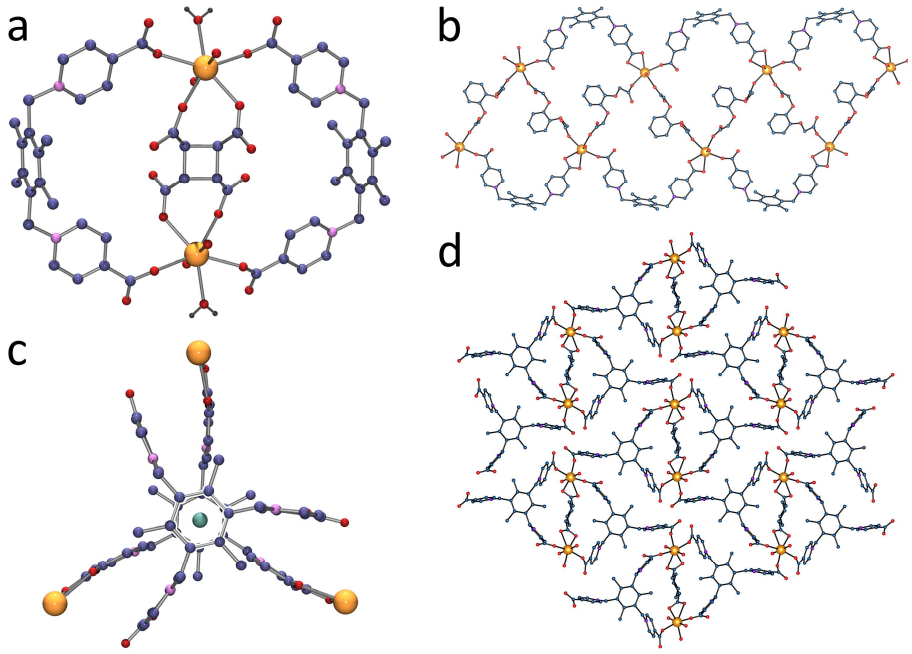


Figure 13. (a) Dinuclear complex **34**. (b) Ribbon-like CP in **35**. (c) Inclusion of Br^- (green sphere) in the capsule formed by complexed tmtpc and uncomplexed $Htmtpc^+$ in **36**.(d) Triperiodic framework in **37** [180].

The ligand 4,4-bpc, analogous to 4,4-tmbpc but devoid of methyl substituents, behaves differently and has given some notable results. In the presence of 4-ketopimelate ($kpim^{2-}$), it yields the complex $[(UO_2)_4(4,4\text{-bpc})(O)_2(kpim)_2]$, a diperiodic CP containing bis(μ_3-oxo)-bridged U_4O_2 SBUs as nodes and displaying rings sufficiently large (~8 Å × 9 Å) to make possible 2D + 2D → 3D inclined polycatenation [130]. This is one of the few cases of entangled networks involving uranate polynuclear nodes [146,184−186]. An interesting feature of this structure is the presence of parallel-displaced π-stacking interactions between ZI ligands pertaining to different sheets, possibly playing some role in the formation of the entangled structure. The same ligand 4,4-bpc affords an even more remarkable compound when coupled with tricarballylate (tca^{3-}), an anion which has previously been shown to give nanotubular uranyl ion complexes, either alone [187,188] or with the $Ni(tpyc)_2$ ML [10]. The complex $[NH_4]_2[UO_2(4,4\text{-bpc})_2][UO_2(tca)]_4\cdot 2H_2O$ (**38**) affords yet another instance of self-sorting of the two types of ligands, each of them generating its own CP [182]. The nature of

these units makes this complex very unusual, since that formed by tca^{3-} is an anionic, NH_4^+-containing nanotubule with a square cross section analogous to that previously found in $[NH_4][(UO_2)_2Pb(tca)_2(NO_3)(bipy)]$ (bipy = 2,2′-bipyridine) [187], while that generated by 4,4-bpc is a sixfold interpenetrated, cationic triperiodic framework (Figure 14a). A twofold templating effect may be at play here, with NH_4^+ cations being necessary for the formation of the nanotubes, and the latter required in their turn for the building of the entangled framework. The emission spectrum of **38** in the solid state, under excitation at 420 nm, can be deconvoluted into two separate sequences of fine-structure peaks corresponding to the two components, a possible indication of the reduced donor strength of 4,4-bpc compared to tca^{3-} (see Section 4.2).

The bipyridinium-based ligand 4,4′-bis(2-carboxylatoethyl)-4,4′-bipyridinium (bcbp, Scheme 7) is more flexible than bcpbp, which has very notable consequences on the structures of the complexes formed. This ligand was combined with four carboxylate anions of varying curvature, isophthalate ($ipht^{2-}$) and 1,2-, 1,3- or 1,4-phenylenediacetate (1,2-, 1,3- and 1,4-pda^{2-}) [181]. Different periodicities and geometries result from the different couplings of conformations of the two ligands. With both of them being divergent linkers, as happens with $ipht^{2-}$, 1,2- and 1,4-pda^{2-}, monoperiodic CPs are formed. While $[(UO_2)_2(bcbp)(ipht)_2]$ and $[(UO_2)_2(bcbp)(1,2\text{-}pda)_2]\cdot 2H_2O$ are ribbon-like chains, $[(UO_2)_2(bcbp)(1,4\text{-}pda)(H\text{-}1,4\text{-}pda)_2]$ contains two families of sinuous threads woven [189] into a diperiodic network, and $[(UO_2)_4(Hbcbp)_2(1,4\text{-}pda)_5]\cdot H_2O\cdot 2CH_3CN$, containing tetranuclear rings, displays H-bond-mediated polycatenation. In contrast, with all ligands in a convergent conformation, $[(UO_2)_2(bcbp)(1,3\text{-}pda)_2]\cdot 0.5CH_3CN$ (**39**) is a heteroleptic dinuclear cage (Figure 14b), the first of this kind in uranyl–carboxylate chemistry. This complex is akin to uranyl-based triple-stranded helicates involving long-chain aliphatic dicarboxylates [190]

and it is chiral like them (but crystallizing as a racemate); its particularity however is to be neutral.

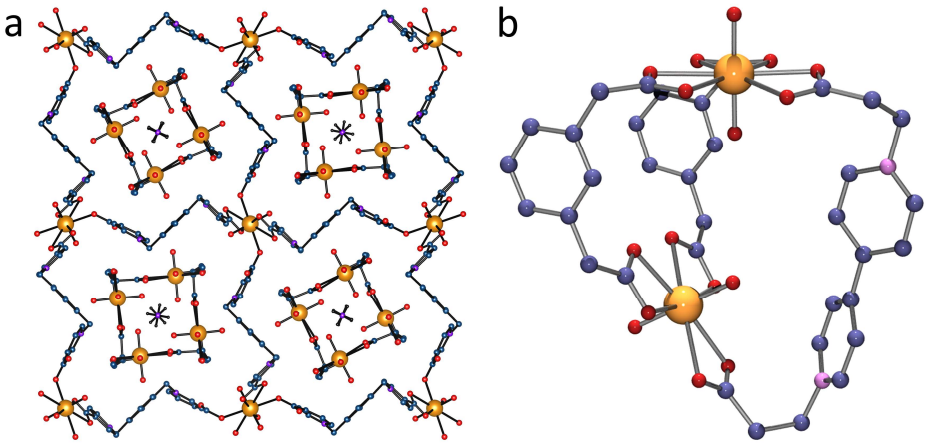


Figure 14. (a) Nanotubule inclusion in complex **38** viewed down the tube axis [182]. (b) Heteroleptic cage in complex **39** [181].

3.5.5. Zwitterionic carboxylates in association with cucurbiturils

An example of the use of ZI carboxylate ligands containing terminal, primary ammonium groups, is provided by a series of complexes involving aminobenzoic acid derivatives, in association with cucurbit[6]uril molecules [191]. Cucurbituril macrocycles display a strong affinity for ammonium groups, with which they form ion-dipole and H-bonding interactions [192−196], meaning that ammoniocarboxylates could enable both UO_2^{2+} complexation and association of the complex formed with cucurbit[6]uril (CB6). This is indeed what is observed in $[UO_2(Hamb)(OH)(HCOO)(H_2O)]_2{\cdot}2CB6{\cdot}2DMF{\cdot}14H_2O$ (**40**, Hamb = 4-(aminomethyl)benzoic acid, Figure 15a), $[(UO_2)_4(Hamb)_2(amb)O_2(OH)_2(H_2O)_4]{\cdot}2CB6{\cdot}0.5CB8{\cdot}Hamb{\cdot}NO_3{\cdot}20H_2O$ (**41**), and $[UO_2(Hahb)(ahb)_2]{\cdot}3CB6{\cdot}16H_2O$ (**42**, Hahb = 3-amino-5-hydroxybenzoic acid, Figure 15b). Only in **40** is the ligand completely in its ZI form, whereas in **41** and **42** a mixture of ZI and anionic forms is found. Although direct attachment of UO_2^{2+} to CB molecules is possible [197−200], even in the presence of carboxylate ligands [201], it does not occur here, and the

CBs interact only with the ammonium and amine groups through H-bond formation (involving also an included *N,N*-dimethylformamide molecule in **40**). Depending on the geometry of the uranyl ion complex, the resulting supramolecular assemblies are either linear and dumbbell-shaped (**40**), monoperiodic linear with appendages (**41**), or trigonal (**42**).

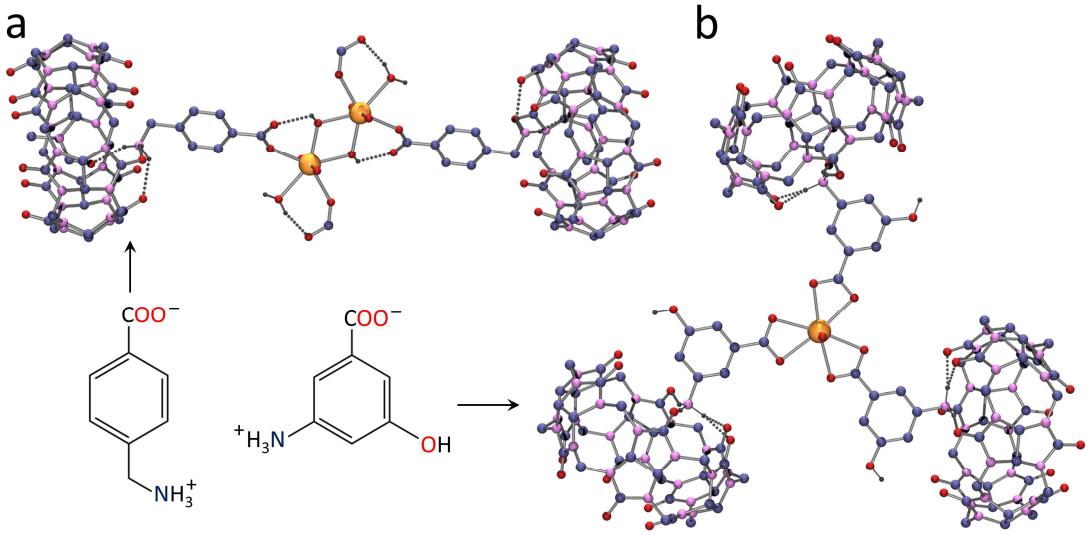


Figure 15. Uranyl ion complexes **40** (a) and **42** (b), involving aminobenzoic acid derivatives and CB6 molecules [191].

A related approach was later adopted by Shi *et al.* to synthesize polyrotaxanes,[202–204] involving uranyl-containing strings and CB6 macrocyclic beads, a strategy first used by Kim *et al.* in the case of copper(II) cations [205]. Although mostly pyridinium-based ZI carboxylates have been used in this substantial work, some cases involve secondary alkanediammonium-containing ligands. For example, *N,N′*-bis(3-carboxylatobenzyl)butane-1,4-diammonium (H_2cbbda, generated *in situ* from hydrolysis of the bis(3-cyanobenzyl) derivative) is threaded through CB6 to form a pseudorotaxane, with hydrophobic effects probably added to the ion-dipole and H-bonding interactions between the ammonium groups and the oxygen atoms of the CB6 portals. Further carboxylate coordination to oxo-bridged, tetranuclear uranyl SBUs yields the triperiodic polyrotaxane assembly **43** (Figure 16), which includes additional, uncomplexed pseudorotaxane units [206]. However, in other compounds,

neutral amino groups are present instead of ammonium groups, and the complexed ligands are thus not in their ZI form [207,208], which may give rise to some doubts about the protonation scheme in **43**. Among the other complexes formed along similar lines are polypseudorotaxanes in which the pseudorotaxane units are only appendages on a polymeric uranyl oxalate network [209], as well as "superpolyrotaxanes", which might possibly be called also "heteropolyrotaxanes" since they are built from the threading of two polyrotaxane subunits of different periodicities (chains and layers), and which have the peculiarity of containing either tri- or hexanuclear uranyl SBUs in one of the polymeric units [210,211].

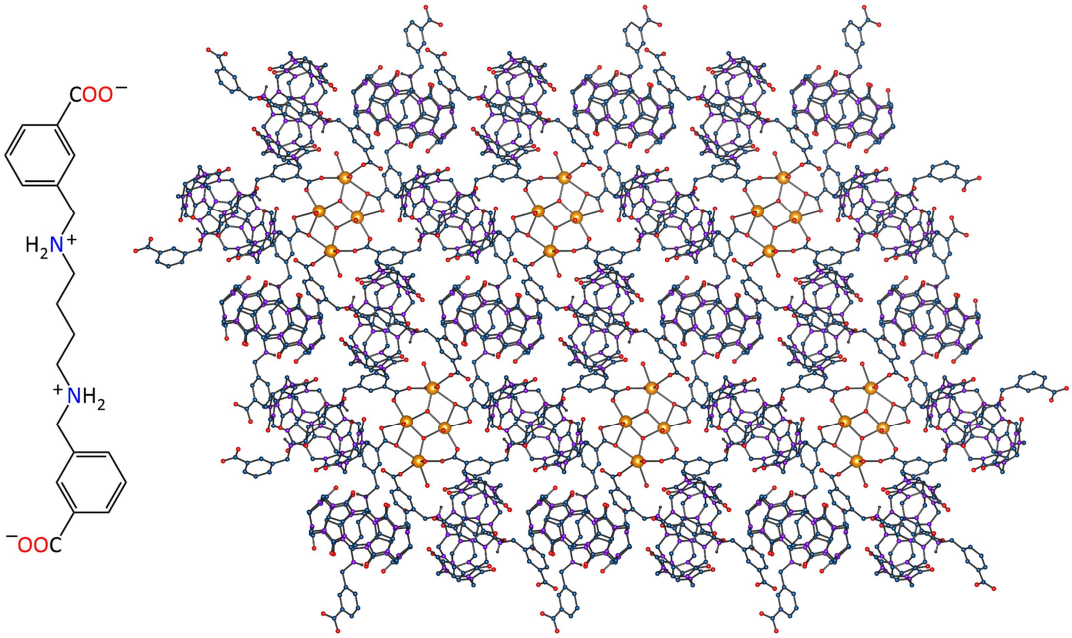


Figure 16. Ligand H_2cbbda and partial view of the polyrotaxane complex **43**, with uncomplexed, included pseudorotaxane units omitted for clarity [206].

In addition to the use of alkyldiammonium carboxylate ligands to generate polyrotaxanes with CB6 beads, Shi's group has produced a wealth of polyrotaxane structures involving pyridinium-based ZI carboxylates and CB*n* beads (*n* = 6 (mainly), 7 and 8). Most of them involve bis(4-carboxylatopyridinio)alkanes, with the number of carbon atoms in the chain varying from 4 to 8 [212−217]. In contrast to the case of alkyldiammonium-based ligands, no

H-bond accompanies the inclusion in the macrocycle here, ion-dipole interactions and hydrophobic effects only being operant. The CB portals are thus more accessible and, in some cases, proper choice of the chain length allows direct coordination of UO_2^{2+} to the macrocycle, producing interwoven polyrotaxane assemblies, as in $[UO_2(pbcp)(CB6)(SO_4)]\cdot 5H_2O$ (**44**, pbcp = 1,1′-(pentane-1,5-diyl)bis(4-carboxylatopyridin-1-ium, Figure 17a) [215]. Some of the polyrotaxanes thus synthesized involve anionic coligands such as sulfate or oxalate and are thus mixed-ligand species [213,215]. Another example of such a complex is $[(UO_2)_4(hbcp)(C_2O_4)_4(H_2O)_2]$ (**45**, hbcp = 1,1′-(hexane-1,6-diyl)bis(4-carboxylatopyridin-1-ium, Figure 17b), which crystallizes as a diperiodic CP containing uranyl oxalate chains. A case of temperature-induced, reversible crystal-to-crystal isomerization was shown to be associated with a transition between monodentate and κ^2*O,O*′-chelating coordination modes for one carboxylate donor [214]. Replacement of the para pyridiniumcarboxylate ligand by the meta isomer 1,1′-(hexane-1,6-diyl)bis(3-carboxylatopyridin-1-ium) brings the carboxylate group closer to the CB6 portal, resulting in different coordination modes, some of them involving CB6 coordination, and novel polyrotaxane geometry [218], a work later extended to ligands with 7-carbon atoms alkyl chains by Liu *et al.* [219]. A comparison of polyrotaxanes involving either uranyl or neptunyl cations was reported, suggesting a greater affinity of CB6 as a ligand for Np^{V} than for U^{VI} [220]. Overall, the influence of multiple factors (alkyl chain length and conformation, position of the carboxylate groups, competing ligands, pH) was investigated at length within this series of quite remarkable compounds, of which only a small sampling is given here.

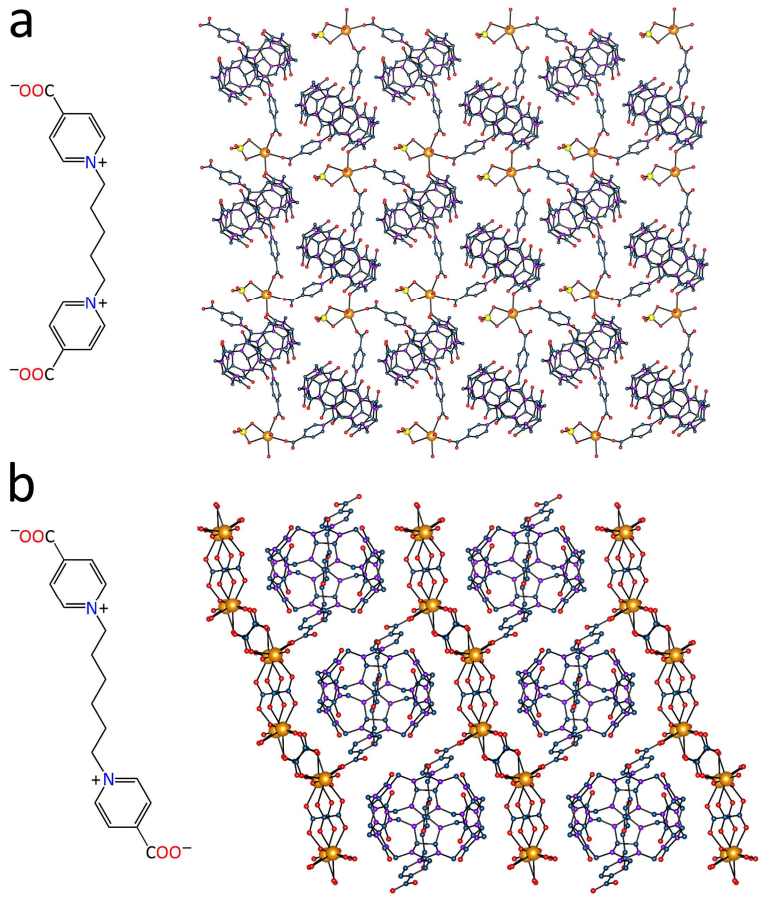


Figure 17. (a) Ligand pbcp and interwoven polyrotaxane assemblies in **44** with direct uranyl bonding to CB6 and additional sulfate ligands [215]. (b) Ligand hbcp and packing in the mixed-ligand polyrotaxane complex **45** [213].

Besides these ZI ligands with long alkyl chains, the U-shaped bis(pyridinium) ligand containing a central aromatic ring, 1,1′-[1,3-phenylenebis(methylene)]bis(pyridin-1-ium-4-carboxylate) (3,4-bpc, see also section 3.5.2), was used in association with CB7 and CB8 to generate either a trinuclear cyclic trirotaxane (**46**) or a supramolecular assembly in which mononuclear, double metallacycles are partially embedded in CB8 molecules (**47**), respectively (Figure 18) [221]. The analogous ligand with 1,4 positioning of the substituents on the central ring was extensively investigated either alone or associated with CB7 (with the additional presence of hydroxide or oxalate ligands in some cases) in order to probe the effect of ligand inclusion in the macrocycle on the nature and geometry of the species formed and

the ligand thermal stability under hydrothermal conditions [174]. Among the complexes reported in this work, a helical polyrotaxane is particularly notable. Concerning the stability of the ligand, the conclusion was reached that inclusion in CB7 protected it from hydrolysis and oxidation through to oxalate anions.

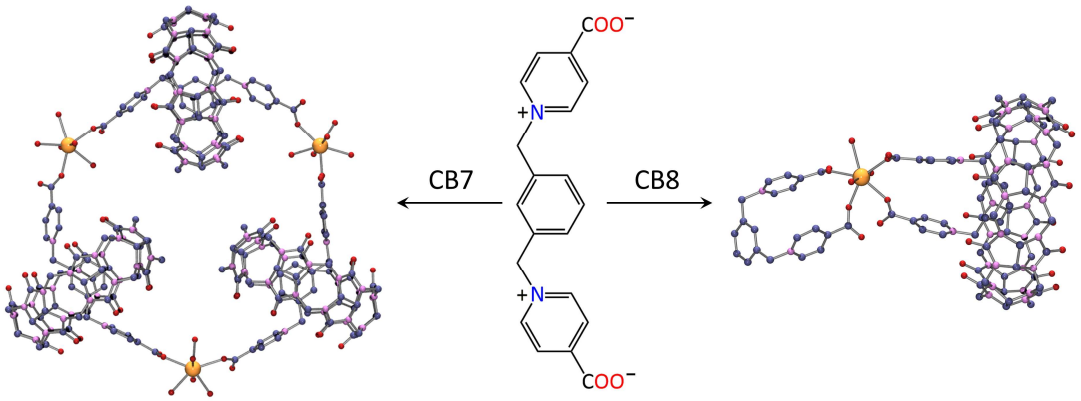


Figure 18. The ligand 3,4-bpc and the complexes **46** and **47** formed in the presence of CB7 or CB8, respectively [221].

4. General overview

4.1. A remark on metalloligands

In restricting the discussion herein to complexes of uranyl ion with metalloligands and zwitterionic ligands, our objectives, apart from providing detailed structural summaries, were to discern any unique features there might be in their solid state structures and to assess any ways in which these features have led or could lead to significant applications. Although the number of structures considered incorporating ZI ligands and closely related partially ZI species considerably exceeds the number incorporating MLs, this, as noted earlier, is partly because dissection of a structure in terms of ML units was not a focus of some early work and partly because the development of syntheses was based on other perspectives. Transition metal complexes of tetra-aza macrocycles, for example, were initially considered simply as large cations which might be involved as countercations in crystalline forms of anionic uranyl

ion coordination polymers but structure determinations showed that in some cases, by axial coordination interactions, they were actually present as part of the CP [222]. Hence, a *post hoc* identification of a ML unit is possible in such cases but this serves only to further illustrate the fundamental aspect of ML use that one metal ion can be used to block a certain number of coordination sites on a ligand, leaving others available for a second.

4.2. Zwitterionic *versus* anionic ligand donor strength

Since the vast majority of the ligand systems surveyed involve O- and in particular carboxylate-O-donors, differences in basic structural features such as bond lengths and bond angles from those known in general for O-donors [38,223] were expected to be subtle and indeed this appears to be so. Taking U–O bond lengths as a measure of bond strength, comparisons for different ligands are complicated by the fact that data are not always available for species where the uranyl ion coordination sphere geometry or the data quality are the same. Thus, the complexes of benzamidoxime and acetamidoxime ZIs involve the relatively rare square-bipyramidal ("octahedral") coordination geometry of U^{VI}, with a mean U–O(oximato) bond length of 2.31(2) Å, a value which may be compared to the average of 2.30(2) Å for analogous but non-zwitterionic carboxylato species found in the CSD, though a particular recent example provides values which range from 2.263(3) to 2.338(2) Å [142]. Hence, it can only be said that zwitterionic amidoximes are ligands of comparable strength to carboxylates and this does not offer an obvious explanation of the selectivity observed with polyamidoximes in the extraction of uranium from sea water unless perhaps this results from a polymer-conformation enforced preference for square-pyramidal coordination, carboxylates being found far more commonly in pentagonal- or hexagonal-bipyramidal arrays. For aza-aromatic N-oxide ZIs, U–O bond lengths range between 2.32 and 2.40 Å for complexes of pentagonal-bipyramidal coordination geometry involving chelating mono- and di-oxides of

2,2′-bipyridine, a range which covers that for the one known hexagonal-bipyramidal complex of the dioxide [68] and also that for the various pentagonal-bipyramidal complexes of 4,4′-bipyridine-1,1′-dioxide, indicating that chelation has no discernible effect on the bond lengths in the former series. U–O(carboxylate) bond lengths in comparable pentagonal-bipyramidal species (which are again relatively rare in involving unidentate coordination of carboxylate but which can be found, for example, in complexes of imino-, oxy- and thio-diacetates [134,136,224], also blanket this range, so once again it can only be concluded that carboxylate and N-oxide ligands provide donor atoms of similar binding capacity. The significant difference of course is that true ZI ligands are uncharged overall and thus must be accompanied by charge-balancing ligands in any complex, while this is not so for ACs or any other anionic ligands (including non-zwitterionic MLs). This is illustrated in the complexes involving 4,4′-bpdo and polycyanidometallates, where the combinations, even if for U^{VI} in the common pentagonal-bipyramidal coordination geometry, can produce unique luminescence properties.

In relation to the use of bond length as a measure of donor capacity of a ligand, a note of caution should be sounded here in that it is known that stability constants measured in water show that acetate binds more strongly than glycine to both lanthanides and actinides in the +III state [225] and the same is true for UO_2^{2+} [226,227], with solvation effects considered to be the cause. As well, in recent work with the dizwitterionic ligands 4,4-bpc and bcbp (Scheme 7) [130,182], it has been pointed out that the sum of bond valence parameters [228] was slightly but consistently less for ZI than for AC donors (Table 1), with for example sum values of 2.532 and 2.694/2.726 for the two types of donors, respectively, in $[NH_4]_2[UO_2(4,4\text{-bpc})_2][UO_2(tca)]_4\cdot 2H_2O$ (**38**, section 3.5.4). If bond valence parameters are considered as a measure of donor strength, such an observation indicates a possible decrease of the latter in ZI ligands. The consequence of this difference in bond valence parameters for equatorial donors

is an opposite variation in the strength of axial, oxo donors, possibly revealed in the splitting of peaks in the emission spectrum of **38** (Figure 19) [182]. However, further clarification of this question of relative donor strength of ZI and AC ligands would need more experimental work ideally completed by DFT calculations. The difference between true ZIs and anionic, pseudo-ZIs would be worth investigating also.

Table 1. Bond valence (BV) parameters in some mixed-ligand complexes [<BV_{AC}>, mean value for anionic carboxylate oxygen donors; <BV_{ZI}>, mean value for zwitterionic carboxylate oxygen donors; <BV_{axial}>, sum of BV parameters for the axial oxo groups in purely anionic (AC), purely zwitterionic (ZI) or mixed-ligand units (mixed)].[a]

Complex	<BV_{AC}>	<BV_{ZI}>	<BV_{axial}> (AC)	<BV_{axial}> (ZI)	<BV_{axial}> (mixed)	Ref.
$[(UO_2)_2(4,4\text{-bpc})(pht)_2]$	0.53(2)	0.517			3.409	130
$[(UO_2)_2(bet)_2(1,3\text{-pda})_2]$	0.45(2)	0.431(10)	3.445(12)		3.55(3)	130
$[(UO_2)_4(4,4\text{-bpc})(O)_2(kpim)_2]$	0.49(7)	0.425(7)	3.355(2)		3.416(10)	130
$[H_2bcbp][UO_2(bcbp)(H_2O)_2][UO_2(tcenm)]_4{\cdot}2H_2O$[b]	0.45(2)	0.424(7)	3.458(5)	3.539		130
$[NH_4]_2[UO_2(4,4\text{-bpc})_2][UO_2(tca)]_4{\cdot}2H_2O$	0.452(11)	0.42(12)	3.400(6)	3.436		182

[a] Esds (estimated standard deviations) measure the dispersion of individual values; no esd is given when a single value is present. [b] $tcenm^{3-}$ = tris(2-carboxylatoethyl)nitromethane

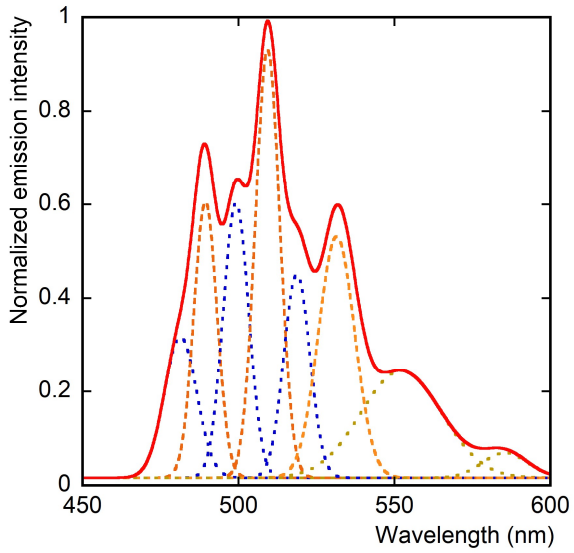


Figure 19. Emission spectrum of complex **38** in the solid state (excitation at 420 nm) showing the components associated with the separate subunits formed by the ZI and AC ligands [182].

4.3. Easy synthesis of mixed-ligand complexes

If the small anions formate and oxalate, often formed *in situ* during hydrothermal processes, are disregarded, the number of uranyl ion complexes involving two different AC ligands is rather limited [229–231], the complexes crystallized from solutions containing mixtures of ligands generally involving only one of those. However, it is most often not so when one of the ligands is an AC and the other pertains to the families of MLs or ZIs which have been thus tested, true heteroleptic complexes being obtained in the large majority of cases. Structure determination is crucial here, however, as there are rare examples where a crystal of mixed ligand composition actually contains independent, "self-sorted" homoleptic, ionic components (which in fact provide some of the most remarkable architectures in the series) [130,146,163,182]. Among MLs, the $[Ni(tpyc)_2]$ neutral dicarboxylate ligand (which is also a ZI) has been successfully coupled with very diverse ACs [10,50], and the complete list of these complexes is given in Table 2 together with their main characteristics. An even more extended AC range has been used with organic ZIs, as seen also in Table 2. With the unique exception of $[(UO_2)_2(tmtpc)_2(t\text{-}1,4\text{-}chdc)](NO_3)_{1.7}Br_{0.3}$ (complex **37**, section 3.5.4), all these mixed-ligand complexes are neutral, some of them including nitrato (in the case of MLs), oxo or hydroxo ligands (in both cases) in addition to ACs. The fact that nitrato ligands are found in 9 out of 13 complexes involving $[Ni(tpyc)_2]$ but in no complex with an organic ZI possibly indicates that its donor strength is higher than that of $[Ni(tpyc)_2]$ but lower than that of any of the ZIs used even though U–O bond length comparisons indicate the opposite.

Table 2. Mixed-ligand complexes involving the metalloligand [Ni(tpyc)$_2$] or organic zwitterions (some "partial") and anionic carboxylates (formate excluded), with the periodicity of the uranyl−ML/ZI complex moiety, and main characteristics.

Complex[a]	AC	Periodicity	Characteristics	Ref.
Heteroleptic complexes				
Complexes with [Ni(tpyc)$_2$]				
[(UO$_2$)$_2$Ni(tpyc)$_2$(*c*-1,2-chdc)(NO$_3$)$_2$]$_2$	*c*-1,2-cyclohexanedicarboxylate	0	U$_4$Ni$_2$ dinickelatetrauranacycle	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(tdc)(NO$_3$)$_2$]	2,5-thiophenedicarboxylate	0	U$_4$Ni$_2$ dinickelatetrauranacycle	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(NO$_3$)$_2$(*t*-1,4-chdc)]·H$_2$chdc	*t*-1,4-cyclohexanedicarboxylate	1	simple chain	50
[(UO$_2$)$_4$Ni$_2$(tpyc)$_4$(bdc)$_3$(NO$_3$)$_2$]	1,4-benzenedicarboxylate	1	daisychain	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(tca)(NO$_3$)]	tricarballylate	1	nanotubular	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(1,2-pda)(H-1,2-pda)(NO$_3$)]	1,2-phenylenediacetate	1	meander-like chain	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(ox)$_2$]	oxalate	1	chain with U$_4$Ni rings	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(Hbtc)(NO$_3$)]	1,2,3,4-butanetetracarboxylate	2	honeycomb network	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(Hcbtc)(NO$_3$)]	1,2,3,4-cyclobutanetetracarboxylate	2	honeycomb network	10
[(UO$_2$)$_4$Ni$_2$(tpyc)$_4$(*t*-*R*-1,2-chdc)$_4$]	*t*-*R,R*-1,2-cyclohexanedicarboxylate	2	network with U$_{10}$Ni$_4$ rings	10
[(UO$_2$)$_2$Ni(tpyc)$_2$(ndc)(OH)(NO$_3$)]	2,6-naphthalenedicarboxylate	2	square network with U$_4$Ni$_2$ rings	10
[(UO$_2$)$_4$Ni$_2$(tpyc)$_4$(1,3-pda)$_4$]	1,3-phenylenediacetate	2	interdigitated networks	10
[(UO$_2$)$_2$Ni$_2$(tpyc)$_2$(nta)$_2$]	nitrilotriacetate	3	triperiodic framework	10
Complexes with organic ZIs				
[(UO$_2$)$_2$(H$_2$dota)(C$_2$O$_4$)(H$_2$O)$_2$]	oxalate	2	corrugated layers	171
[(UO$_2$)$_2$(H$_2$teta)(C$_2$O$_4$)(H$_2$O)$_2$]	oxalate	2	thick layers	172
[(UO$_2$)$_2$(bcmim)$_2$(C$_2$O$_4$)]	oxalate	1	chain with dinuclear rings	166
[(UO$_2$)$_8$O$_4$(OH)$_4$(3,4-bpc)$_2$(C$_2$O$_4$)$_2$]	oxalate	2	network with octanuclear SBUs	161
[(UO$_2$)$_2$(OH)$_2$(4,4-bpc)(C$_2$O$_4$)]	oxalate	3	3-fold interpenetrated framework	174
[UO$_2$(Hcbcp)(C$_2$O$_4$)][b]	oxalate	1	simple chain	175
[(UO$_2$)$_2$(teda)(C$_2$O$_4$)$_2$]	oxalate	2	honeycomb network	146
[(UO$_2$)$_2$(bet)$_2$(1,3-pda)$_2$]	1,3-phenylenediacetate	1	simple chain	130
[UO$_2$(Hint)$_2$(succ)]	succinate	1	simple chain	177
[UO$_2$Li(Hida)(2,6-pydc)(H$_2$O)$_2$]	2,6-pyridinedicarboxylate	1	simple chain	178
[(UO$_2$)$_2$(tpda)(H-2,4-pydc)$_4$]	2,4-pyridinedicarboxylate	0	dinuclear complex	146
[(UO$_2$)$_2$(teda)(ipht)$_2$]	isophthalate	1	double stranded chain	146
[(UO$_2$)$_2$(teda)(1,4-pda)$_2$]	1,4-phenylenediacetate	1	double stranded chain	146
[(UO$_2$)$_2$(tpda)(ipht)$_2$]	isophthalate	2	V_2O_5-type network	146
[(UO$_2$)$_2$(teda)(2,5-pydc)$_2$]	2,5-pyridinedicarboxylate	2	honeycomb network	146
[(UO$_2$)$_2$(teda)(dnhpa)$_2$]	3,5-dinitro-2-hydroxyphenoxyacetate	2	honeycomb network	146
[(UO$_2$)$_3$(teda)(Hthftc)$_2$(H$_2$O)]	tetrahydrofurantetracarboxylate	2	FeS-type network	146
[(UO$_2$)$_2$(bcpbp)(pht)$_2$]	phthatate	1	dimer-containing chain	179
[(UO$_2$)$_2$(bcpbp)(tpht)$_2$]	terephthalate	2	wave-shaped network	179
[(UO$_2$)$_2$(bcbp)(ipht)$_2$]	isophthalate	1	double-stranded chain	181
[(UO$_2$)$_2$(bcbp)(1,2-pda)$_2$]	1,2-phenylenediacetate	1	double-stranded chain	181
[(UO$_2$)$_2$(bcbp)(1,3-pda)$_2$]	1,3-phenylenediacetate	0	heteroleptic dinuclear cage	181
[(UO$_2$)$_2$(bcbp)(1,4-pda)(H-1,4-pda)$_2$]	1,4-phenylenediacetate	1	woven chains	181
[(UO$_2$)$_4$(Hbcbp)$_2$(1,4-pda)$_5$]	1,4-phenylenediacetate	1	1D + 1D polycatenation	181

$[(UO_2)_2(4,4\text{-tmbpc})_2(cbtc)(H_2O)_2]$	1,2,3,4-cyclobutanetetracarboxylate	0	dinuclear double ring	180
$[UO_2(4,4\text{-tmbpc})(H_2pm)(H_2O)_2]$	pyromellitate	1	simple chain	163
$[(UO_2)_2(4,4\text{-tmbpc})_3(3\text{-sb})_2]$	3-sulfobenzoate	1	daisychain	163
$[(UO_2)_2(4,3\text{-tmbpc})(1,3\text{-pda})_2]$	1,3-phenylenediacetate	1	daisychain	180
$[UO_2(4,4\text{-tmbpc})(pdda)]_3$	1,2-phenylenedioxydiacetate	1	double-stranded chain	180
$[UO_2(4,4\text{-tmbpc})(pht)]$	phthatate	2	square network	180
$[(UO_2)_3(4,3\text{-tmbpc})(pht)_2(OH)_2]$	phthatate	2	square network	180
$[(UO_2)_2(4,4\text{-bpc})(pht)_2]$	phthatate	2	V_2O_5-type network	130
$[(UO_2)_2(4,4\text{-tmbpc})(c/t\text{-}1,3\text{-chdc})_2]$	*c*/*t*-1,3-cyclohexanedicarboxylate	2	V_2O_5-type network	180
$[UO_2(4,4\text{-tmbpc})(t\text{-}1,4\text{-chdc})]$	*t*-1,4-cyclohexanedicarboxylate	2	square network	180
$[(UO_2)_2(4,3\text{-tmbpc})(c/t\text{-}1,4\text{-chdc})_2]$	*c*/*t*-1,4-cyclohexanedicarboxylate	2	3-fold interpenetrated honeycomb network	180
$[(UO_2)_2(4,4\text{-tmbpc})(1,2\text{-pda})_2]$	1,2-phenylenediacetate	2	3-fold interpenetrated honeycomb network	180
$[(UO_2)_2(4,4\text{-tmbpc})(2\text{-sb})_2]$	2-sulfobenzoate	2	kagome network	163
$[(UO_2)_4(4,4\text{-bpc})(O)_2(kpim)_2]$	4-ketopimelate	2	2D + 2D inclined polycatenation	130
$[Htmtpc][(UO_2)_3(tmtpc)(adc)_3]Br$	1,3-adamantanedicarboxylate	2	honeycomb network	180
$[(UO_2)_2(4,4\text{-tmbpc})(kpim)_2]$	4-ketopimelate	3	triperiodic framework	180
$[(UO_2)_2(tmtpc)_2(t\text{-}1,4\text{-chdc})](NO_3)_{1.7}Br_{0.3}$	*t*-1,4-cyclohexanedicarboxylate	3	triperiodic framework	180
"Self-sorted" complexes				
Complexes with [Ni(tpyc)$_2$]				
$[Ni(Htpyc)(H_2O)_3][UO_2(1,2,3\text{-btc})]_2$	1,2,3-benzenetricarboxylate	1	dimer-containing chain	10
$[UO_2Ni_2(tpyc)_4][UO_2(Hcit)]_2$	citrate	2	1D + 2D semi-interpenetration	10
Complexes with organic ZIs				
$[H_2teda][UO_2(2,6\text{-pydc})_2]$	2,6-pyridinedicarboxylate	0	H-bonded ion pair	146
$[H_2bcbp][UO_2(bcbp)(H_2O)_2][UO_2(tcenm)]_4$	tris(2-carboxylatoethyl)nitromethane	1	H-bond-mediated polycatenation	130
$[(UO_2)_2(4,3\text{-tmbpc})_3(H_2O)_2][(UO_2)_2(tdc)_3]_2$	2,5-thiophenedicarboxylate	2	honeycomb network	163
$[(UO_2)_5(teda)_7(tdc)(H_2O)][(UO_2)_2(tdc)_3]_4$	2,5-thiophenedicarboxylate	3	2D + 3D heterointerpenetration	146
$[NH_4]_2[UO_2(4,4\text{-bpc})_2][UO_2(tca)]_4$	tricarballylate	3	6-fold interpenetrated framework with included nanotubes	182

[a] Solvent molecules excluded. [b] H_2cbcp^+ = *N*-(4-carboxybenzyl)-4-carboxypyridinium.

4.4. Effect of specific weak interactions of zwitterionic ligands on supramolecular organization

Specific weak interactions involving the positively charged centre of ZIs essentially depend on the presence or absence of hydrogen atoms on this site, since the former case provides H-bonding sites and thus one of the strongest possible forms of weak interaction. Although best endowed in this respect, primary ammonium groups are terminal and thus generally part of quite simple, monocarboxylate ligands which offer moderate prospects for the building of CPs with high periodicity, as in the case of gly (see ahead). However, such

simple molecules have been shown to behave as assemblers of cucurbiturils (section 3.5.5 and Figure 15). Secondary ammonium groups may be part of dicarboxylate ligands such as $Hida^-$ and H_2edda (Scheme 5) and the H-bonding interactions formed by the first of these two ligands play an essential role in the formation of one of the most remarkable arrangements described here (complex **23**, Figure 7) [136]. Tertiary ammonium groups are found in homoazacalixarenes, aminopolyphenols and Schiff bases (sections 3.2 and 3.3), forming usually discrete complexes in which H-bonds are mainly intramolecular. They are also found in several polycarboxylates, in particular those in the aliphatic group (Scheme 5) and also in some aromatic molecules (Scheme 6), and the H-bonds formed can be either intramolecular, as in complexes **24** and **25** (Figure 8) or between different polymeric units as in **26** and **27** (Figure 9), and thus having a possible effect on the conformation of the ligand or the supramolecular arrangement, respectively. Quaternary ammonium groups are only involved in weaker interactions, a notable one in the case of UO_2^{2+} complexes with quaternary pyridinium-containing ZIs being with the uranyl oxo group, as recently discussed in the related case of anionic uranyl ion complexes with the 1,1′-dimethyl-4,4′-bipyridinium counterion [183].

An important question relative to the use of such complexes in catalytic reactions (see next section) is whether UO_2^{2+} can be given an environment, most desirably one where it remains emissive, where its reactions could become selective. In solution, this could occur if the uranyl complex and substrate selectively formed a close aggregate, meaning that both the nature and spatial disposition of interaction sites on the uranyl complex become important considerations. Real prospects exist here with complexes of ZIs where the positive charge of the ligand is due to protonation. Considering for example the structure of $[UO_2(gly)_4](NO_3)_2$ [118], NH···O bonding is intricate and forms a triperiodic network involving both carboxylate- and nitrate-O as acceptors. The same tetrakis(glycine) species can be formed in

solution [118] though exact values of the stepwise formation constants are not known. What is apparent in the crystal structure is that the four ammonio groups on any one cation are all involved in distinct sets of interactions and not in small cyclic arrays which might indicate a tendency to bind a single substrate. That the ligands are neutral and the complex unit thus cationic means that cation···anion interactions should be strong and the NH···O-nitrate bonds are relatively short (< 2.0 Å), being only slightly longer than the bonds to uncoordinated carboxylate-O. Given also that the ligands are flexible due to unrestricted rotation about single bonds, these facts appear to militate against $[UO_2(gly)_4]^{2+}$ being a selective binding agent. As a conformationally restricted ZI, H_4teta might be expected to be of greater interest and indeed in $[UO_2(H_4teta)(H_2O)](NO_3)Cl$, while the NH groups are again involved in bonding to separate nitrate-O and unbound carboxylate-O centres, the macrocyclic ring appears to act as a chloride ion receptor through CH···Cl interactions visible on the Hirshfeld surface (HS) [232]. This complex, however, is a coordination polymer and its nature in solution, assuming it might show appreciable solubility, is unknown. Note that the HS for $[UO_2(gly)_4](NO_3)_2$ also provides evidence of CH interactions and that just these two examples illustrate the complicated nature of analysis of possible complex–substrate interactions. Significantly, the HS for $[(UO_2)_2(bet)_6(H_2O)_2](Tf_2N)_4$ [127], a water-soluble complex, also shows a plethora of CH···O interactions involving both CH_3 and CH_2 groups (particularly strong when these groups are located on the N^+ centre), principally with sulfonyl-O atoms, and the betaine ligands adopt several rotameric forms relative to the diuranyl unit, indicating that interactions of the cation could readily adapt to different substrates. Unfortunately, the picture here is incomplete, since H-atoms were not located on the water ligands and they could have a role in any substrate interactions, although none of the bistriflimide anions approach the O-atoms sufficiently close for any H-bonds to be considered present. These are

only some examples involving particularly simple ZIs, the considerable variety of such ligands and of their effect on structure formation precluding any generalization.

4.5. Potential applications of uranyl ion complexes with zwitterionic ligands

Several possible applications of ZI ligands or their uranyl ion complexes have been examined by various authors and have been briefly mentioned in the preceding sections, such as the use of aminopolyphenols [91] and amidoximes [99–103] for uranyl extraction from sea water (sections 3.2 and 3.4), the use of amidoximes for uranium extraction from nuclear waste [113], or the use of complexes of pyridinium-based ZIs for cation detection [169] or X-ray dosimetry [170], or for their photochromic and thermochromic properties [168] (section 3.5.2). The specific effect of ZI ligands on the properties is a much more complicated issue to assess than that on the structures, partly because of the variety of systems considered and also because the positive centre of ZIs can only have an indirect effect on the properties through its influence on the structure. The present section concerns some broad issues related to the principal classes of applications which can be contemplated, illustrated by some specific examples. It must be emphasized however that, due to the radioactivity and toxicity of uranium, the search for applications of its complexes lags very significantly behind that related to more environment-friendly metal cations, and most of the studies reviewed here are essentially structural in character.

4.5.1. Catalysis

In relation to any application, properties such as solubility, stability, luminescence, redox or catalytic activity are of greater relevance than the structure alone, although they can of course be interpreted in terms of structure, even if this is never simple. For the majority of structurally characterized complexes, however, full definition of their other properties is

relatively infrequent, so assessment of prospects for the majority on the basis of features of the minority is necessarily speculative. In broad terms, however, applications might be based on solution or solid state behaviour and since crystal structures define more precisely the solid state, they are more readily interpreted for the latter.

Regardless of bonding interactions, an important classification of all UO_2^{2+} complexes is that involving distinction of soluble and insoluble species. In solution, it has been very long known that the aqua-uranyl ion can act as a photo-oxidant able to attack oxalate and even aliphatic CH groups [23,233–235], along with a variety of other substrates (*e.g.* substituted aromatics [236], water [237], or organic sulfides [238]. Uranyl salts have also been immobilized on supports such as metal oxides and silica and shown to behave as efficient photo-oxidation catalysts for a variety of materials [239–241], as indeed have MOFs [242]. Efforts to explore detailed theoretical explanations of this capacity continue to this day [243–246] but what is obvious in a practical sense is that these are not selective reactions. This is not necessarily a disadvantage if the objective is, for example, the destruction of a range of environmental pollutants but clearly application of a radioactive and toxic material for such large-scale purposes would involve considerable difficulties, so that it is more reasonable, at least in regard to homogeneous catalysis, to envisage specific small-scale applications for uranyl catalysts. Outside the frequently investigated area of photocatalysis, such has indeed been observed [45,247–249], though the truly diverse prospects for homogeneous catalysis with uranium involve exploitation of its multiple oxidation states [22].

A mechanism whereby protonic ZIs appear to have an influence on selectivity in UO_2^{2+} coordination of substrates can be seen in the structures of isonicotinic acid complexes involving the tetrahedral counter-anions perchlorate, pertechnetate and perrhenate. Unsurprisingly, given their near identical size, TcO_4^- and ReO_4^- give isostructural complexes of composition $[UO_2(Hint)_3(MO_4)_2]$ with the anions directly coordinated to U^{VI}, while ClO_4^-

is uncoordinated in a complex of composition $[UO_2(Hint)_4](ClO_4)_2$ [150]. In the crystal structures, both CH···O and NH···O interactions are numerous in all but of the 8 NH centres in $[UO_2(Hint)_4](ClO_4)_2$, 6 interact with carboxylate-O (NH···O < 2 Å), one appears not to be involved in H-bonding and only one interacts weakly (NH···O 2.35 Å) with perchlorate-O, the 3 inequivalent perchlorate ions being otherwise involved in CH···O bonding. In contrast, the anions of $[UO_2(Hint)_3(MO_4)_2]$ have interactions of both CH···O and O···C(aromatic) types and one of the inequivalent pair on each U centre is also involved in an NH···O interaction. The sum of these interactions means that both anions can be considered to be part of a chelate ring on U^{VI} and thus that the core heterometallic complex, a soluble species, could have a selective pincer action towards particular substrates in solution.

For the solid state alone, one of the motivations for investigating the structural coordination chemistry of carboxylate oligozwitterions was to see if such neutral ligands, by elaborating the structure of anionic polycarboxylate complexes, would serve to introduce cavities suited to the inclusion of specific substrates, subsequently to be subjected to photocatalytic reaction. This notion is supported by the observation that tripodal ligands which could have a protic ZI form do produce tetranuclear uranyl ion cages [250], though only in their anionic form and with any selectivity in inclusion by the cages yet to be demonstrated, as is true in general for previously known uranyl ion cages [251]. While both protic and aprotic monozwitterions such as glycine and betaine can form CPs, aprotic oligozwitterions provide many more examples. Qualitatively, such species usually appear to have negligible solubility in any solvent under ambient conditions and low solubility can be an important advantage in regard to recovery and recycling of catalyst species. However, of the large number of mixed ZI–AC complexes which have been synthesized and structurally characterized (Table 2), only one is a true but small heteroleptic cage species [181] and one other involves a solid where separate homoleptic cationic and anionic polymers define tubular

structures which contain a potentially exchangeable guest (NH_4^+) [182]. In many instances, interpenetration serves to reduce the potential availability of any space within the structures. Thus, any real promise in this approach remains to be demonstrated and it may be noted that there is some evidence [49,252] that coordination polymers based on oligozwitterions alone may offer better prospects. Perhaps significantly, though, while cavity-defining molecules such as cucurbiturils have been found to form UO_2^{2+} complexes alone and in association with long chain dicarboxylates in which the cavity is unoccupied [201], long dizwitterions form polyrotaxanes by occupying the CB cavity (section 3.5.5). Similarly, while crown ethers can be used to form heterometallic UO_2^{2+} complexes with dicarboxylates involving alkali metal ions [253], with dizwitterions the macrocyclic "hole" of crowns is occupied by rotaxane formation [78].

4.5.2. Photophysical properties

Photo-oxidant activity of a uranyl ion complex requires a relatively long excited state lifetime, reflected, in the absence of a substrate, by the observation of the vibronically structured green emission considered typical of UO_2^{2+} [23]. For many of the complexes discussed herein, solid state emission spectra have not been recorded but there is nonetheless a considerable body of data showing that both the form of the emission spectra and photoluminescence quantum yields (PLQYs) vary greatly for reasons which are certainly not fully understood [254]. Initial studies of complexes of the metallazwitterion $[Ni(tpyc)_2]$ showed uranyl ion emission to be completely quenched, presumed to be most probably due to the absorption by the ZI being much stronger than that of the uranyl centre at the excitation wavelength employed [10]. This explanation is refuted by the later observation that the mixed-ligand complex of $[Ni(tpyc)_2]$ and *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate shows the "typical" uranyl emission [51].

Diminution of the emission of uranyl nitrate on titration with Cu^{II} salen-type metalloligands to form heterometallic species has been interpreted in terms of excited state deactivation by energy transfer to the copper centre [56] and indeed apparent quenching of uranyl ion luminescence by Cu^{II} and other open shell transition metal ions in heterometallic coordination polymers has been quite commonly observed [44,47,156,255,256] but the effect is not universal [257]. In uranyl–Cu^{II} CPs derived from 2-carboxyphenylphosphonate, strong emission is observed but with a very different component structure to that considered as typical [258]. Zn^{II}, as a closed shell species, is not usually considered likely to quench uranyl ion emission but in a uranyl–Zn^{II} CP closely related to a Cu^{II} species showing uranyl emission, no luminescence is apparent [257]. Broadly speaking, mixed-ligand complexes of ZI and AC ligands, both aliphatic and aromatic, are emissive and show "typical" vibronic progressions but with considerable variations in PLQY values and there are again instances of undetectable emission or emission of a broad and unique form [146,163,180].

Unusual spectroscopic features detected in UO_2^{2+} complexes of the "hemizwitterion" 1-(3,5-dicarboxylatophenyl)-4,4′-bipyridine [168] were those of photochromism and thermochromism. Although first attributed to the viologen-like character of the ligand, subsequent work showed that the same phenomena could be observed for the coordination polymer obtained with the simpler ligand 3,5-bis(4′-carboxylatophenyl)pyridine, this material being used to construct a UV radiation dosimeter [259].

4.5.3. Anion binding selectivity

While anionic uranyl ion CPs associated in their crystals with simple organic cations (dimethylammonium in particular) are rather commonly encountered and have, in some cases, been shown to undergo cation exchange reactions generating new heterometallic complexes [260–264] with, again in some cases, retention of the crystal structure [265], cationic CPs are

less well characterized and their properties less extensively explored. The first such cationic polymer, based on a carboxylate trizwitterion and with bromide counter ions was described in 2016 and was shown to behave as an anion exchanger, in particular acting as an efficient absorber of perrhenate (used as a surrogate for pertechnetate) [165]. Similar properties were subsequently observed for cationic polymers based on a bipyridinium dizwitterion where the formal charge on the polymer was reduced by partial coordination of chloride counterions [179]. Several polymeric complexes of the metalladizwitterion $[Ni(tpyc)_2]$ have also been found to involve small anion coordination but the counteranion is uncoordinated in $[UO_2\{[Ni(tpyc)_2]\}_2](I_3)_2$ [50]. Anion exchange reactions have not been investigated for these compounds. Recently, the aromatic dizwitterion 4,4-tmbpc has been shown to react with uranyl nitrate in the presence of $KReO_4$ to give a monoperiodic coordination polymer of composition $[UO_2(4,4\text{-tmbpc})(OH)(H_2O)](ReO_4)$, indicating a possible preference for perrhenate over the nitrate and chloride ions also present in the reaction mixture [252].

5. Conclusions

What may be considered a resurgence of uranium chemistry over the past two decades not only covers non-aqueous uranium organometallic chemistry [266], but has also been largely associated with the synthesis and evaluation of uranyl ion coordination polymers and frameworks [17,38,267–269], some of them displaying remarkable structures and/or properties [270–273]. The present review was intended to provide a survey of the diversity of approaches to the synthesis of complexes from bifunctional ligands of two types, metalloligands and zwitterions, principally as characterized through structural studies. It should be noted that there is an extensive field of uranyl ion CP and UOF chemistry based on (poly)phosphonate ligands [274], not covered here, which has many parallels with that based on (poly)carboxylates but in which ZI ligands are of much lesser importance.

A point concerning the design of CP and UOF syntheses that would warrant further investigation relates to the almost universal use of solvothermal conditions, where long periods of heating under pressure at temperatures in the range of 140–180 °C are commonly employed. This is an extraordinarily valuable technique for obtaining crystals of very insoluble materials but in some instances the crystals are obtained on returning the reaction mixture to ambient conditions, in others they are deposited from the hot, pressurised reaction mixture and it is not clear what difference this may make to the nature of the crystallized material. It is also frequently unclear in many reported syntheses as to whether or not light was excluded and this is a particular issue when uranyl ion is concerned. Most importantly, it is clear from the many examples cited of materials which contain constituents such as oxalate, formate and dimethylammonium ions that the extreme reaction conditions often result in major changes of the reaction medium and while their exact origin requires more detailed investigation, these changes could well be put to more logical application.

The obvious objective in the use of metalloligands is the creation of heterometallic products and many such species are known. Some complexes are heterometallic because of the presence of a cation such as $[Ni(bipy)_3]^{2+}$ as the counter cation to an anionic, homoleptic uranyl CP [275] but many others are CPs where the additional metal ion forms part of the polymer chains, if sometimes as a purely decorative unit. In the latter cases, it is possible to discern entities within the structure which are probably best termed “metalloligand motifs” [47], but since the deliberate use of a metalloligand reactant was not, in most cases, part of the strategy of synthesis, we have chosen to illustrate the value of this perspective with but a few examples encompassing both “true”, kinetically inert metalloligands and kinetically labile species which need not necessarily be assembled prior to their incorporation into a polymer. Zwitterionic systems have been dealt with in greater detail, though it may be noted that the dizwitterion $[Ni(tpyc)_2]$, here treated also as a metalloligand, provides an example of a

moderately labile species which need not be assembled prior to its incorporation in a polymer. With the complexes prepared from $tpypc^-$ [45], however, it is likely that at least the Fe^{II} species would be sufficiently kinetically inert to be the actual reacting species.

The metalloligand systems discussed illustrate both the sometimes dramatic effects of another metal ion on the luminescence of uranyl centres and the complicated nature of the analysis of structural features which may influence these effects. Efforts to provide a detailed theoretical understanding of uranyl ion luminescence are a continuing endeavour [245,276–278]. Consideration of aza-aromatic carboxylates as precursors to metalloligand "motifs" illustrate the basic principles of their design based on multitopic molecules with appropriately chosen donor atoms which may even enable alternation of binding site preferences. As noted, it has been found that heterometallic uranyl ion coordination polymers can show catalytic action dependent on the presence of both metal ions [45,249] and an extension of such work that might be pursued would be to use palladium zwitterions [279] to form bimetallic polymers incorporating this especially active metallocatalyst.

True zwitterionic ligands, in addition to being neutral and therefore requiring that they be accompanied in any solid by anionic ligands or counterions for which there is an almost limitless choice, bring a wide variety of sources of weak interactions as influences on solid state structures, H-bonding being prominent with primary, secondary or tertiary ammonium groups. In aprotic ZIs with methylene groups adjacent to the positive charge centre, the CH-donor capacity of these groups is clearly enhanced. Uranyl complexes involving either protic or aprotic ZI dicarboxylates with a large separation between the complexing sites have also been found to be suitable for inclusion in neutral macrocycles, most notably cucurbiturils, to form polyrotaxanes. Aromatic groups of ZI complexes are frequently found in interacting arrays and polymers derived from $[Ni(tpyc)_2]$ and $[M(tpypc)_2]$ ZIs in many cases show forms of the "terpyridine embrace" as a structural influence. Given that the metal ion in $[M(tpypc)_2]$

units has a stable and enveloping shield of tpypc$^-$ ligands which would seem to protect it from any substrate attachment, it is remarkable that the uranyl ion complexes are active catalysts of the reaction of CO_2 with epoxides and it is intriguing to consider what interactions may be responsible for this. In general, the issue of how to engender selectivity in the interactions of any uranyl ion polymer or framework remains open to resolution, one aspect of this being the possibility of asymmetric catalysis, with a full characterization of the coordination chemistry of amino acid ZIs and other chiral organic ligands being a further goal to pursue. Chiral coordination polymers incorporating a luminescent metal ion such as UO_2^{2+} and having high PLQY values are also of spectroscopic interest as sources of circularly polarized light [280].

In relation to the synthesis of the complexes described, a significant and interesting question arises as to the reasons why mixtures of ACs and ZIs so readily yield true mixed-ligand complexes, even if there are some examples showing that there can be a delicate balance. An influence of the neutrality of the complexes formed is not excluded since it may decrease the solubility and promote crystallization of the mixed-ligand species over that of the homoleptic, ionic species which may also be formed in solution. A factor favoring the formation of mixed complexes could be related to a decrease of electrostatic repulsions in the uranium coordination sphere, when compared to those in a complex involving only ACs. Anyway, this strategy appears very promising for the design of original architectures and it opens the way for the synthesis of complexes involving ligands endowed with distinct properties.

Conflict of Interest

The authors declare no conflict of interest.

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Table of Contents Entry

Bifunctional ligands in uranyl chemistry: metalloligands and zwitterions

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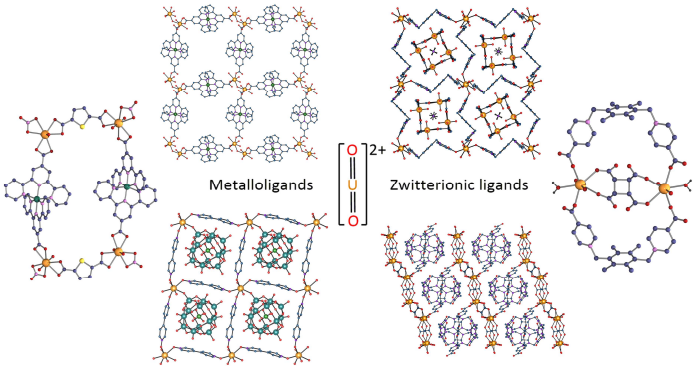

Uranyl ion complexes with metalloligands and zwitterions, which constitute a major contribution to recent developments in uranium chemistry, are reviewed mainly from a structural viewpoint, prospective applications being also presented.