



X-ray structures of dinuclear copper(I) and polynuclear copper(II) complexes with the 2,4-bis(cyanamido)cyclobutane-1,3-dione dianion

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X-ray structures of dinuclear copper(I) and polynuclear copper(II) complexes with the 2,4-bis(cyanamido)cyclobutane-1,3-dione dianion

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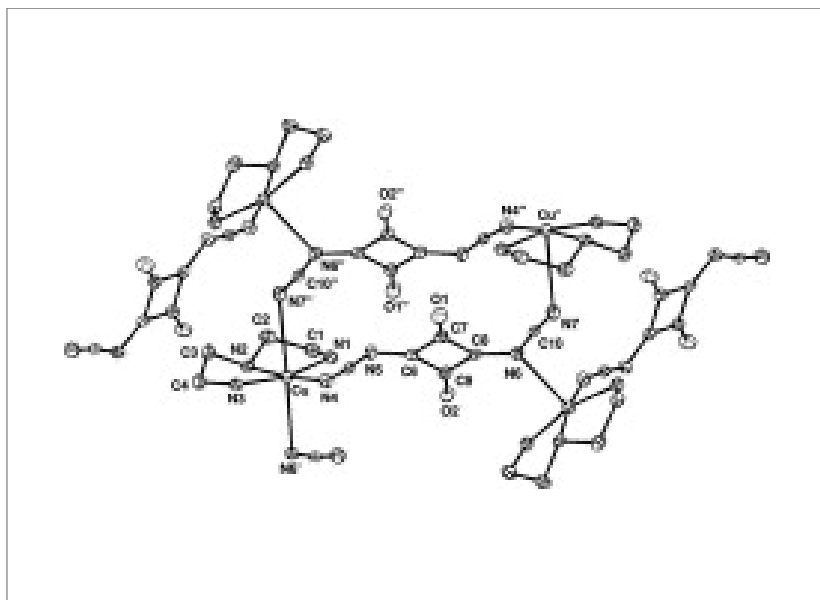
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Abstract

From the 2,4-bis(cyanamido)cyclobutane-1,3-dione dianion ($2,4\text{-NCNsq}^{2-}$), two copper complexes $[\text{Cu}_2(\text{PPh}_3)_4(\text{PhCN})_2(\mu\text{-}2,4\text{-NCNsq})] \cdot \text{PhCN}$ (**1**) and $[\text{Cu}(\text{dien})(\mu\text{-}2,4\text{-NCNsq}) \cdot \text{H}_2\text{O}]_n$ (**2**) have been synthesized and characterized by IR and electronic absorption spectroscopies. Their structures have been determined by X-ray crystallography. Complex **1** is a dinuclear copper(I) compound with a $2,4\text{-NCNsq}^{2-}$ ligand bridging two copper atoms through the nitrile nitrogen atoms. Complex **2** appears as a 3D network constituted of copper(II) atoms bridged by $2,4\text{-NCNsq}^{2-}$ dianions. This complex presents an unexpected coordination mode of the bis(cyanamido) ligands which are both coordinated via the nitrile functions and via the amido nitrogen atoms of the NCN groups.

Graphical abstract



Reactions of copper with $2,4\text{-NCNsq}^{2-}$ yield new complexes presenting a bridging coordination mode. In the copper(I) complex, a bidentate end-on coordination occurs by the two nitrile nitrogen atoms of the NCN groups. For the first time, a tridentate coordination of the $2,4\text{-NCNsq}^{2-}$ ligand is observed in the copper(II) complex.

Keywords: Pseudo-oxocarbons; X-ray diffraction; Copper(I) dimer; Copper(II) chain; Cyanamido complexes

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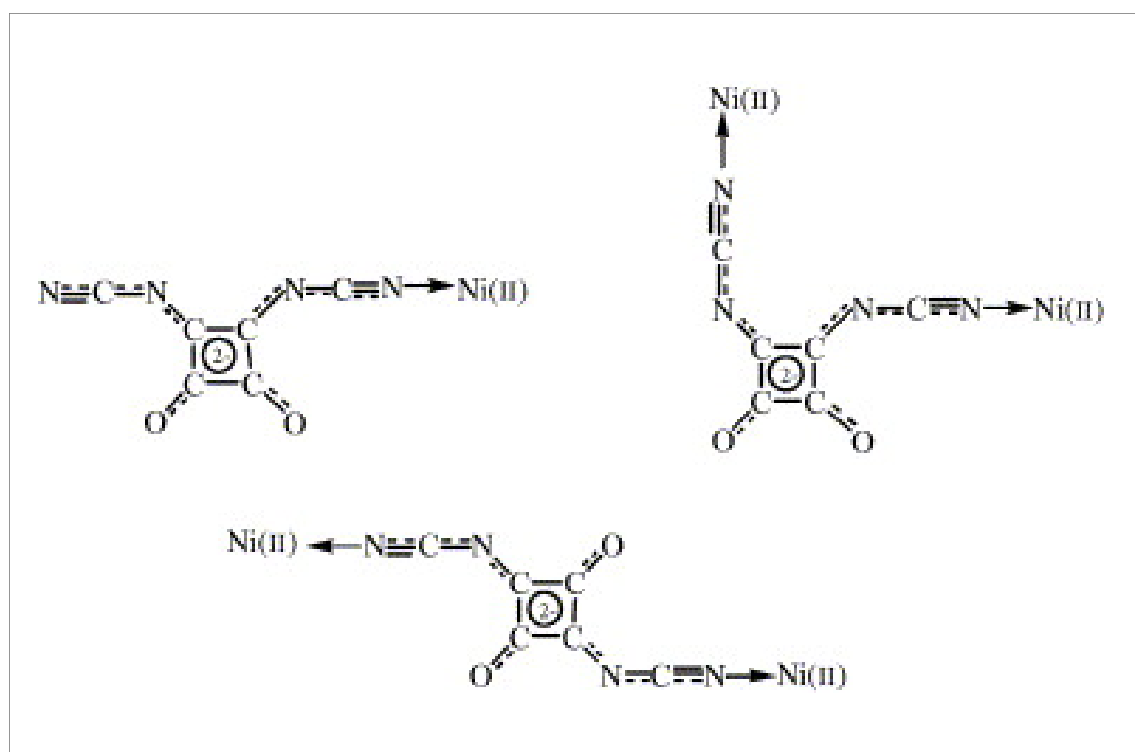
1. Introduction

Cyanamido complexes have received much attention since the discovery of radical copper salts of DCNQI derivatives (*N,N'*-dicyano-*p*-benzo-2,5-dimethylquinone) which present increased conductivities at low temperature and were therefore considered as new organic metal systems [1], [2], [3], [4], [5] and [6]. Crutchley et al. [7] have largely investigated the coordination chemistry of metals, and in particular ruthenium with phenylcyanamide ligands (pcyd), which may be viewed as reduced forms of DCNQIs.

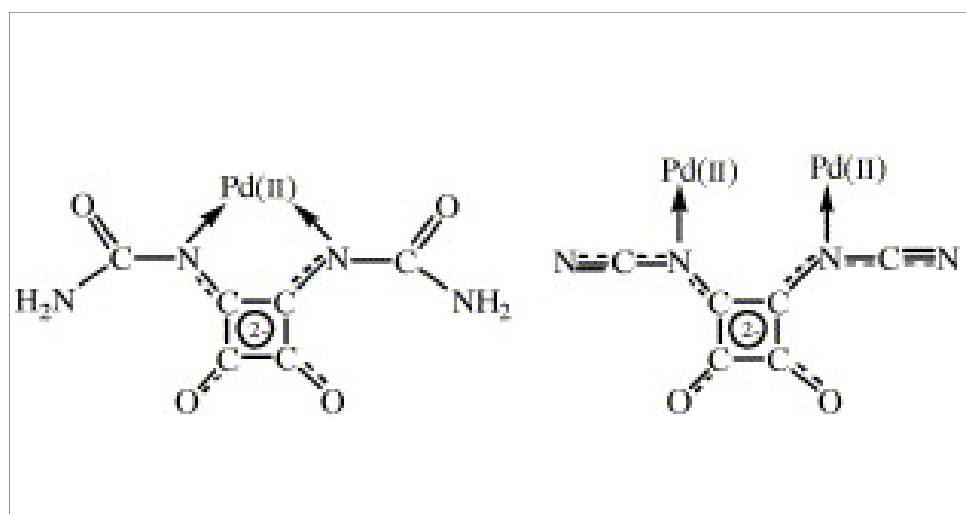
We are interested in pseudo-oxocarbons derived from the squarate dianion, compounds characterized by extensive π electrons delocalization, interesting redox behaviour and, for some of them, strong colours and intrinsic electrical conductivity [8]. Recently, we reported the synthesis and characterization of several transition metal complexes obtained from two cyanamido squarate derivatives: the 3,4-bis(cyanamido)cyclobutane-1,2-dione dianion (3,4-NCNsq²⁻) [9], [10] and [11] and the 2,4-bis(cyanamido)cyclobutane-1,3-dione dianion (2,4-NCNsq²⁻) [12] showing a structure close to that of the DCNQI.

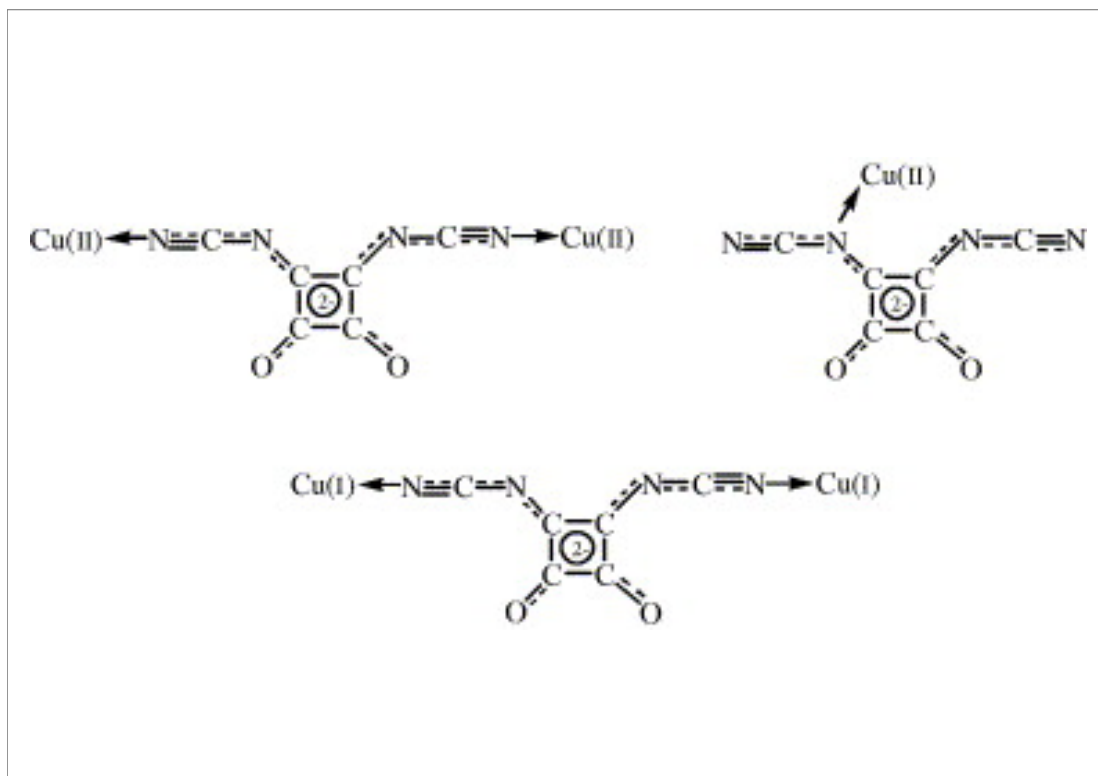
These anions are ambidentate ligands and the complexes obtained in our laboratory show a remarkable structural diversity. The most frequent coordination mode observed is the terminal one, i.e., using the nitrile nitrogen atom of the NCN moiety. The dianion appears to be a monodentate or bis-monodentate ligand and yields monomeric, dimeric or polymeric complexes. In nickel(II) complexes (Scheme 1 and [10] and [12]), all the complexes obtained are of this type, both with the 3,4-NCNsq²⁻ and the 2,4-NCNsq²⁻ dianions. However, palladium(II) complexes obtained with the 3,4-NCNsq²⁻ dianion only present an N(amido) coordination of the NCN group, leading either to chelating (with, in this case, the hydration of the cyanamido function into carboxamide) or to bridging complexes (Scheme 2 and [11]). In copper complexes containing the 3,4-NCNsq²⁻ ligand, the two types of coordination occur: the nitrile (terminal or end-on) coordination has been established in one copper(I) and one copper(II) complex (respectively, dimeric and polymeric complexes) while the amido coordination has been encountered in the case of one monomeric copper(II) complex (Scheme 3 and [9]).

Scheme 1.



Scheme 2.





Scheme 3.

In the present paper, synthesis and spectroscopic data of two copper complexes with 2,4-NCNsq²⁻ dianion are presented along with their single crystal X-ray structures: the dinuclear copper(I) complex $[\text{Cu}_2(\text{PPh}_3)_4(\text{PhCN})_2(\mu\text{-2,4-NCNsq})] \cdot \text{PhCN}$ (**1**) and the polymeric copper(II) complex $[\text{Cu}(\text{dien})(\mu\text{-2,4-NCNsq}) \cdot \text{H}_2\text{O}]_n$ (**2**). In the latter compound, a new coordination mode of the cyanamido squarate ligands is established since the same ligand is both nitrile and amido coordinated to the metal atoms.

2. Experimental

2.1. General

All solvents and chemicals were reagent grade or better and used as received unless otherwise

noted. Squaric acid, cyanamide and dien were purchased from Acros.

Bis(triphenylphosphine)copper(I) nitrate was prepared by the method of Cotton and Goodgame [13]. $\text{Na}_2\text{L} \cdot 2\text{H}_2\text{O}$ and $(\text{Ph}_4\text{P})_2\text{L} \cdot 4\text{H}_2\text{O}$ ($\text{L}^{2-} = 2,4\text{-NCNsq}^{2-}$) [12] were prepared from the 1,3-dimethylaminocyclobutene diolate ($2,4\text{-N}(\text{CH}_3)_2\text{sq}$) obtained according to a method adapted from Neuse et al. [14].

The complexes are isolated as air-stable crystals. UV–Vis spectra have been performed in dmf solution on a Cary 1E spectrophotometer. IR spectra were recorded in the solid state in KBr pellets using a Bruker Vector 22 spectrometer.

2.2. Preparation of $[\text{Cu}_2(\text{PPh}_3)_4(\text{PhCN})_2(\mu\text{-L})] \cdot \text{PhCN}$ (1)

A solution of $(\text{PPh}_3)_2\text{L} \cdot 4\text{H}_2\text{O}$ (0.455 g, 0.5 mmol) in acetonitrile (80 cm^3) was added dropwise to an acetonitrile solution (100 cm^3) of $[\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2]$ (0.650 g, 1 mmol). After 2 h of stirring, a yellow powder was filtered off. By recrystallization in hot benzonitrile, pale yellow crystals of **1** were obtained. Yield: 12%. *Anal.* Calc. for $\text{C}_{49.5}\text{H}_{37.5}\text{N}_{3.5}\text{OP}_2\text{Cu}$: C, 72.25; H, 4.59; N, 5.96.

Found: C, 71.89; H, 4.36; N, 6.26%. IR data (KBr disc) cm^{-1} : 3431m (br), 3056m, 2227m, 2220m, 2153vs, 1598s, 1589m, 1578s, 1569m, 1556w, 1479m, 1433s, 1400vs, 1178w, 1155w, 1121w, 1095m, 1069w, 1025w, 996w, 921w, 848w, 744s, 689s, 617w, 565w, 548w, 526w, 516m, 502m, 441w.

2.3. Preparation of $[\text{Cu}(\text{dien})(\mu\text{-L}) \cdot \text{H}_2\text{O}]_n$ (2)

A solution of dien (0.206 g, 2 mmol) in water (20 cm^3) was added to copper(II) nitrate trihydrate (0.465 g, 2 mmol) in water (20 cm^3). After 2 h of stirring, the light blue colour of the solution turned to strong blue. $\text{Na}_2\text{L} \cdot 2\text{H}_2\text{O}$ (0.484 g, 2 mmol) in water (40 cm^3) was added. At the end of this addition, the solution was dark blue and a blue powder precipitated. The mixture was stirred for 1 h to ensure complete reaction and then filtered. The precipitate was washed with ethanol, diethyl ether and vacuum dried. The product was then recrystallized with water solution to give blue crystals of **2**. Yield: 36%. *Anal.* Calc. for $\text{C}_{10}\text{H}_{15}\text{N}_7\text{O}_3\text{Cu}$: C, 34.79; H, 4.35; N, 28.41. Found: C, 34.48; H, 3.98; N, 28.36%. IR data (KBr disc) cm^{-1} : 3625w, 3320m, 3257m, 3223m, 3144m, 2953w, 2906w, 2326w, 2168vs (deconvoluted in 2185s, 2177s, 2168vs and 2155s), 1613s, 1576s, 1547m, 1451vs, 1438vs, 1417vs, 1148m, 1131m, 1087m, 1067m, 1034m, 983w, 935w, 895w, 867w, 832w, 727w, 629w, 586w, 565w, 541w.

2.4. X-ray structure determination

Measurements were performed at 293(2) K for compound **1** and at 160(2) K for compound **2** on a one circle stoe Imaging Plate Detector X-Ray diffractometer system (Mo radiation, $\lambda = 0.71073 \text{ \AA}$). A phi scan strategy was used for the data collection, frames were integrated using the stoe software package x-red [15].

Absorption corrections were applied for all data using the difabs program [16]. The sir 92 software package [17] and shelxl-97 [18] were used for phase determination and structure refinement, respectively. Direct methods of phase determination, followed by some subsequent difference Fourier map, led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement and Fourier difference synthesis, all of the non-hydrogen atoms were identified. Atomic coordinates and isotropic and anisotropic displacement parameters of all non-hydrogen atoms were refined by means of a full-matrix least-squares procedure on F^2 . H-atoms were included in the refinement in calculated positions, riding on the carbon atoms with an isotropic thermal parameter fixed 20% higher than carbon atoms to which there were attached. All the excepted hydrogen atoms of water molecules and H atoms connected to nitrogen atoms for the compound **2**, were isotropically refined. All calculations were carried out using the wingx 32 software package [19], drawing of molecule was achieved using the soft ortep 32 [20].

A summary of selected crystal data, intensity measurements and structure refinement is given in Table 1.

Table 1.

Crystallographic data for $[\text{Cu}_2(\text{PPh}_3)_4(\text{PhCN})_2(\mu\text{-L})] \cdot \text{PhCN}$ (**1**) and $[\text{Cu}(\text{dien})(\mu\text{-L}) \cdot \text{H}_2\text{O}]_n$ (**2**)

	1	2	
Formula	$\text{C}_{49.5}\text{H}_{37.5}\text{N}_{3.5}\text{OP}_2\text{Cu}$	$\text{C}_{10}\text{H}_{15}\text{N}_7\text{O}_3\text{Cu}$	
Formula weight	822.81	344.83	
Crystal system	triclinic	monoclinic	
Space group	$P\bar{1}$	$P2_1/c$	
a (Å)	12.222(4)	7.4052(5)	
b (Å)	12.652(3)	15.1376(12)	
c (Å)	16.954(5)	12.5619(8)	

	1	2	
α (°)	106.14(3)		
β (°)	100.04(4)	104.043(7)	
γ (°)	110.24(3)		
U (Å ³)	2253.9(11)	1366.07(17)	
Z	2	4	
D_c (g cm ⁻³)	1.212	1.677	
$F(0\ 0\ 0)$	852	708	
T (K)	293 ± 2	160 ± 2	
Measured reflections	16 686	8948	
Independent reflections	6110	2234	
R_{int}	0.0602	0.0409	
R^a observed all	0.0549, 0.1009	0.0317, 0.0410	
wR^b observed all	0.1326, 0.1537	0.0772, 0.0808	

$$^a R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|.$$

$$^b wR = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$$

3. Results and discussion

Selected bond lengths and angles from the structural determinations of complexes **1** and **2** are given in Table 2 and Table 3. The structure of the coordinated 2,4-NCNsq²⁻ dianion in the copper complexes will be compared to the free anion structure [12].

Table 2.

Selected bond lengths (Å) and angles (°) for **1** with e.s.d.'s in parentheses

Cu–N1	2.312(7)	Cu–N2	1.967(5)	Cu–P1	2.2673(17)
Cu–P2	2.266(2)	N2–C8	1.168(7)	C8–N3	1.304(7)
N3–C9	1.326(6)	C9–C10	1.457(7)	C9–C10'	1.449(7)
C10–O1	1.240(6)				
<i>PhCN</i>					
N1–C1	1.143(9)	C1–C2	1.430(11)	C2–C3	1.386(9)
C3–C4	1.352(11)	C4–C5	1.358(13)	C5–C6	1.382(13)
C6–C7	1.369(12)				
N1–Cu–P1	108.61(18))	N1–Cu–P2	99.19(17)	N1–Cu–N2	92.5(3)
N2–Cu–P1	106.33(14))	N2–Cu–P2	118.06(15))	P1–Cu–P2	125.85(7)
Cu–N2–C8	173.0(5)	N2–C8–N3	171.4(5)	C8–N3–C9	120.6(4)
N3–C9–C10	136.8(5)	N3–C9–C10'	132.5(5)	C10'–C9–C10	90.8(4)
C9–C10–O1	133.8(5)	O1–C10–C9'	137.0(5)	C9'–C10–C9	89.2(4)
<i>PhCN</i>					
Cu–N1–C1	132.4(6)	N1–C1–C2	176.7(8)	C1–C2–C3	120.8(7)
C1–C2–C7	119.1(6)	C7–C2–C3	120.1(7)	C2–C3–C4	120.7(8)
C3–C4–C5	119.6(8)	C4–C5–C6	120.2(8)	C5–C6–C7	120.8(9)
C6–C7–C2	118.6(8)				

Symmetry operation: $-x + 1, -y + 1, -z$.

Table 3.

Selected bond lengths (Å) and angles (°) for **2** with e.s.d.'s in parentheses

Cu–N1	2.007(2)	Cu–N2	2.005(2)	Cu–N3	1.994(2)
Cu–N4	1.974(3)	Cu–N7''	2.661(3)	Cu–N6'	2.562(3)
C5–N4	1.164(4)	C5–N5	1.300(4)	C6–N5	1.332(3)
C10–N7	1.162(4)	C10–N6'	1.329(4)	C8–N6	1.330(3)
C6–C7	1.460(4)	C7–C8	1.471(4)	C8–C9	1.447(4)
C9–C6	1.457(4)	C7–O1	1.232(3)	C9–O2	1.246(3)
<i>Dien</i>					
C1–N1	1.483(4)	C2–N2	1.480(4)	C3–N2	1.463(4)
C4–N3	1.479(4)	C1–C2	1.509(4)	C3–C4	1.512(4)
N1–Cu–N2	85.02(10)	N1–Cu–N3	166.48(10)	N1–Cu–N4	93.77(10)
N1–Cu–N7''	81.10(10)	N1–Cu–N6'	94.49(9)	N2–Cu–N3	85.45(10)
N2–Cu–N4	174.21(10)	N2–Cu–N7''	84.56(9)	N2–Cu–N6'	88.33(9)
N3–Cu–N4	94.75(10)	N3–Cu–N7''	88.48(10)	N3–Cu–N6'	94.79(9)
N4–Cu–N7''	89.66(9)	N4–Cu–N6'	97.42(9)		
Cu–N4–C5	156.0(2)	N4–C5–N5	172.1(3)	C5–N5–C6	121.0(2)
N5–C6–C7	130.0(3)	N5–C6–C9	138.9(3)	C7–C6–C9	91.0(2)
C6–C7–C8	88.4(2)	C6–C7–O1	135.8(3)	O1–C7–C8	135.8(3)
C7–C8–C9	91.0(2)	C7–C8–N6	135.9(3)	N6–C8–C9	133.0(3)
C8–C9–C6	89.5(2)	C8–C9–O2	134.9(3)	O2–C9–C6	135.7(2)
C8–N6–C10'	115.8(2)	N6'–C10–N7	172.2(3)	Cu–N7–C10''	123.98(20)

Cu–N6''–C8''	129.29(17)	Cu–N6''–C10''	134.86(7)		
<i>Dien</i>					
Cu–N1–C1	110.07(17)	Cu–N2–C2	107.79(17)	Cu–N2–C3	106.55(18)
Cu–N3–C4	108.90(19)	N1–C1–C2	109.0(2)	C1–C2–N2	108.4(2)
C2–N2–C3	116.4(2)	N2–C3–C4	107.2(2)	C3–C4–N3	109.2(2)

Symmetry operations:

$$' - x + 2, +y - 1/2, -z + 1/2.$$

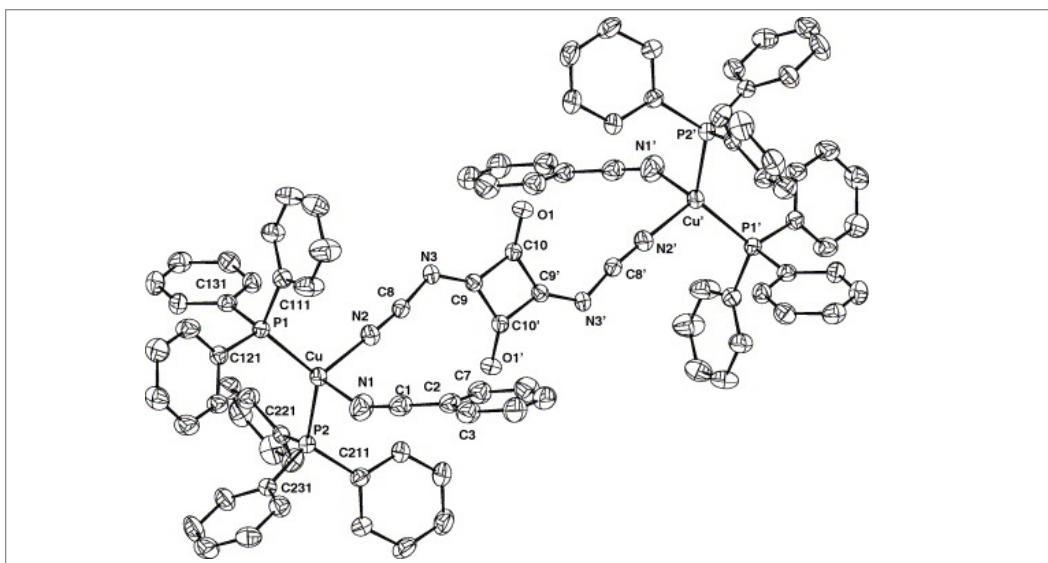
$$'' - x + 2, -y + 1, -z + 1.$$

3.1. Crystal structure of [Cu₂(PPh₃)₄(PhCN)₂(μ-L)] · PhCN (1)

A view of the molecule, along with the numbering scheme, is shown in Fig. 1. The compound consists of discrete centrosymmetric [Cu₂(PPh₃)₄(PhCN)₂(μ-L)] binuclear molecules separated by a short benzonitrile interplanar distance of 4.71(2) Å. The structural pathway is completed by one benzonitrile molecule in the lattice. The two Cu(I) ions are bridged by a bis monodentate L²⁻ ion with a Cu...Cu long distance of 12.342(29) Å. An inversion centre is located at the middle of the squarate ring. So, the *P* $\bar{1}$ space group of the free ligand 2,4-NCNsq²⁻ is not affected by complexation. Each Cu(I) ion is four-coordinated, using two phosphorus atoms of two PPh₃ molecules, one nitrogen atom of a PhCN molecule and the nitrile nitrogen atom from one cyanamido group of the ligand 2,4-NCNsq²⁻. This coordination mode corresponds to that observed in its homologous complex with the 3,4-NCNsq²⁻ dianion: [Cu₂(PPh₃)₄(MeCN)₂(μ-3,4-NCNsq)] · MeCN [9]. In complex **1**, the geometry around the copper(I) atom is distorted tetrahedral with an average angle of 108.42°. The nitrogen atom N1 of the bonded benzonitrile molecule is weakly coordinated with a long Cu–N1 distance of 2.312(7) Å, while the Cu–N2 (nitrile nitrogen atom of L²⁻) distance is 1.967(5) Å. This Cu–N2 bond distance is shorter than the 2.013(3) Å distance observed in [Cu₂(PPh₃)₄(MeCN)₂(μ-3,4-NCNsq)] · MeCN [9] and may be compared to the distances observed in the complexes (2,5-R₁,R₂-DCNQI)₂Cu (R₁, R₂ = CH₃, CH₃O, Cl, Br) which range from 1.968 to 1.986 Å [2] and [5] or to the Cu–N distance of 1.99 Å in [Cu(MeCN)₄](ClO₄)

[21]. The Cu–P bond lengths (2.266(2) and 2.2673(17) Å) are similar to those found in other copper(I) complexes containing two Cu–P bonds [9], [22] and [23]. Deviation from an ideal tetrahedral geometry ($P1-Cu-P2 = 125.85(7)^\circ$) arises from the geometrical constraints imposed by the two bulky PPh_3 entities. The Cu–N2–C8 angle value of $173.0(5)^\circ$ close to the ideal value of 180° corresponds to the linear nitrile (end-on) coordination mode, the most common mode for a cyanamido group. The Cu–N1–C(benzonitrile) angle of $132.4(6)^\circ$, which corresponds to a long Cu–N1 distance of 2.312(7) Å, differs from those observed in other Cu(I)–N(nitrile) complexes as $CuX \cdot C_6H_5CN$ ($175.5(6)^\circ$ for $X = Cl$, $172.3(5)^\circ$ for $X = Br$) [24], $[Cu(MeCN)_4](ClO_4)$ (angles ranging from 169° to 179° with an average value of 174°) [21] or as $[Cu(NCCH_2CH_2CN)_2](ClO_4)$ ($169.7(5)^\circ$) [25].

Fig. 1. Molecular structure and atom numbering scheme of $[Cu_2(PPh_3)_4(PhCN)_2(\mu-L)] \cdot PhCN$ (**1**).



In complex **1**, the ligand 2,4-NCNsq²⁻ is perfectly planar by contrast with the free dianion [12]. As in the free 2,4-NCNsq²⁻ ligand, the C–C distances (1.449(7) and 1.457(7) Å) are indicative of a π delocalized system. The NCN moiety is affected by complexation since the nitrile bond (C8–N2 = 1.168(7) Å) is slightly longer than in the free dianion (1.152(3) Å) corresponding to a weak decrease of the nitrile bond character while the C8–N3 bond becomes shorter (1.304(7) instead of 1.349(3) Å). The C10–O1 distance of 1.240(6) Å is normal for a carbonyl group. Bond distances and angles of the PPh₃ ligands are given as supplementary materials.

3.2. Crystal structure of [Cu(dien)(μ -L) · H₂O]_n (**2**)

A view of the structure, along with the numbering scheme, is shown in Fig. 2. The structure of **2** is made of [Cu(dien)(μ -L)] units with one water molecule of crystallisation per unit. The main feature of the structure is that in each L²⁻ ligand, the two cyanamido groups exhibit different coordination modes: one is monodentate, coordinating through the terminal cyano nitrogen, and the other is bidentate, binding two different copper atoms through the cyano and the amido nitrogen atoms. A possible way to describe the structure of the polynuclear complex **2** is to consider a network of [Cu₂(dien)₂(μ -L)₂] “packs”, each one containing two parallel L²⁻ bridging ligands which are end-on coordinated. The least-squares planes of these L²⁻ pairs pile up along both the (1 0 1) and (1 1 0) axes with shortest interplanar distances of 4.42 and 3.90 Å, respectively, values which are comparable to those observed (3.13–3.21 Å) in (2,5-R₁,R₂-DCNQI)₂Cu salts (R₁,R₂ = CH₃, CH₃O, Cl, Br) [26]. A view of the packing is given in Fig. 3. A crystallographic inversion centre is located at the middle of the Cu—Cu distance. These “packs” are bound together by the mean of four Cu–N(amido) long distance bonds. Within the [Cu₂(dien)₂(μ -L)₂] group, the Cu—Cu distance value is 9.457(3) Å when the inter-“pack” value is 6.457(3) Å. Each copper(II) ion is *pseudo*-octahedrally coordinated and the observed angles (81.10(10)–97.42(9)°) do not differ significantly from the ideal value. The copper(II) atom deviates from the square plane by a distance of 0.137(2) Å. The Cu–N bond distance values notably differ from one another: the structure is best described as a (4 + 2) geometry, indicative of an important Jahn-Teller effect. Actually, three nitrogen atoms of the dien molecule and one N(nitrile) atom of one L²⁻ ligand are in an almost square planar configuration in the equatorial plane with normal Cu–N bond lengths (1.974(3)–2.007(2) Å). The coordination sphere is made up by two nitrogen atoms of two different L²⁻ ions (one N(nitrile) and one N(amido)) in the apical positions with long Cu–N bond lengths (2.661(3) and 2.562(3) Å, respectively). This structure may be related to that observed in Cu(H₂O)₄(SO₄) · H₂O [27] which involves a tetrahydrate copper(II) cation (Cu–O = 1.97 Å) and bridging semi-coordinated SO₄²⁻

anion ($\text{Cu}-\text{O} = 2.4 \text{ \AA}$). Another $(4 + 2)$ copper(II) complex has been obtained with $[\text{Cu}(\text{trans-cdcb})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}]_n$. (cdcb^{2-} = dianion 2,4-bis(dicyanomethylene)-cyclobutane-1,3-dione) [28].

Fig. 2. Molecular structure and atom numbering scheme of $[\text{Cu}(\text{dien})(\mu\text{-L}) \cdot \text{H}_2\text{O}]_n$ (2).

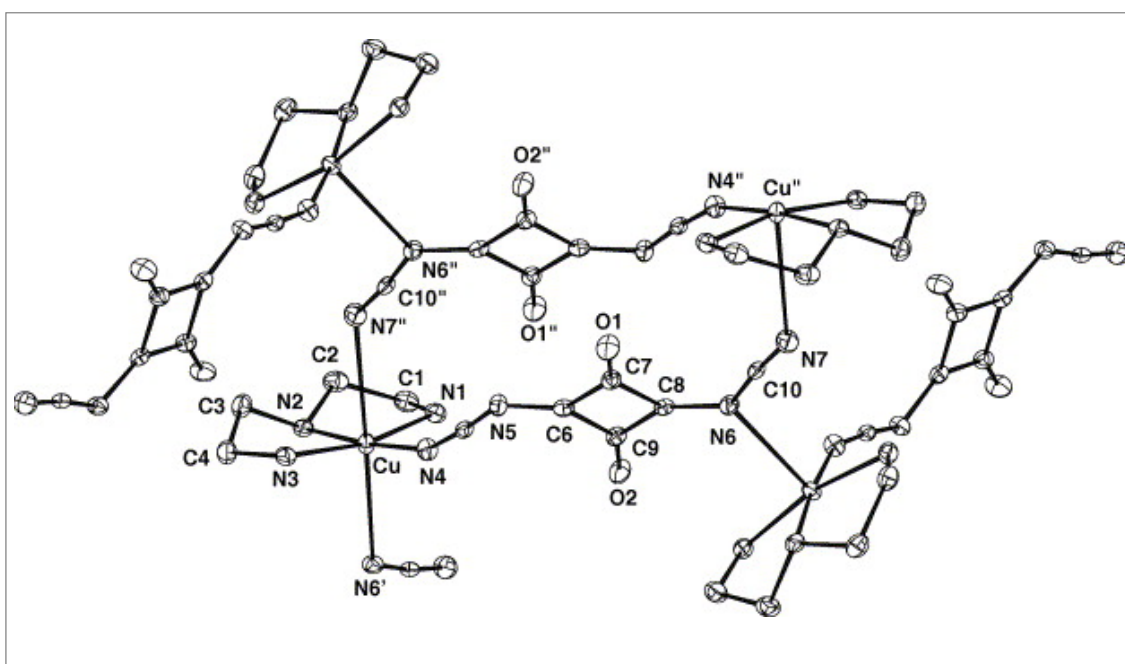
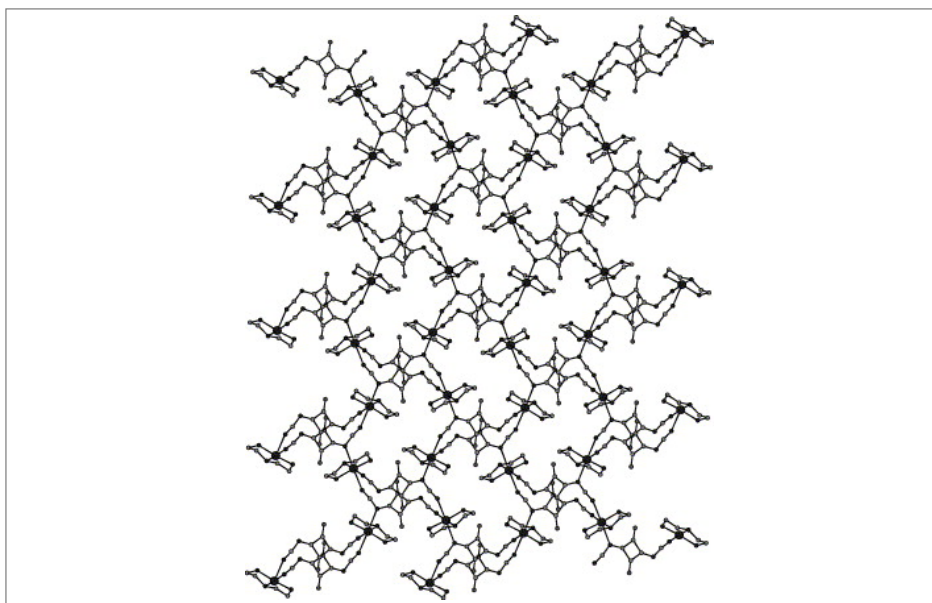
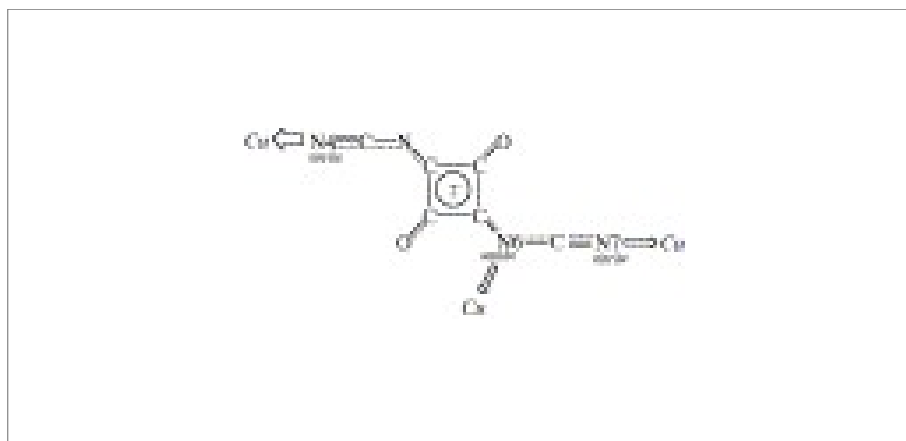


Fig. 3. Stacking of **2** with the hydrogen bond network.



So, the 2,4-NCNsq²⁻ dianion bridges three copper atoms, on one side through the nitrile nitrogen atom (N4) (strong nitrile coordination: Cu–N4 = 1.974(3) Å) and on the other side through both the nitrile (N7) and amido (N6) nitrogen atoms (weak nitrile (2.661(3) Å) and amido (2.562(3) Å) coordination).



The bidentate coordination mode of the NCN fragment has already been observed even if the end-on coordination is more usual. In phenylcyanamido dinuclear complexes such as $[\{\text{Cu}(\text{bipy})(\text{pcyd})\}_2(\mu\text{-pcyd})_2]$ [29], $[\{\text{Mn}(2,2'\text{-bpm})(\text{H}_2\text{O})(4\text{-Clpcyd})\}_2(\mu\text{-}4\text{-Clpcyd})_2]$ [30a] and $[\{\text{Mn}(\text{pcyd})(\text{phen})(\text{MeOH})\}_2(\mu\text{-pcyd})_2]$ [30b] (bipy = 2,2'-bipyridine, phen = 1,10-phenantroline, bpm = 2,2'-bipyrimidine) two pcyd[−] derivatives bridge two metal atoms using both the nitrile and the amido nitrogen atoms. It should be noted that in the polymer $[\text{Mn}(\text{pcyd})(\text{MeOH})(\mu\text{-pcyd})(\mu\text{-}2,2'\text{-bpm})_{0.5}]_n$, the same coordination mode of the pcyd[−] ligand is observed and Mn(II) atoms are bridged by double bidentate phenylcyanamido and 2,2'-bipymidine in an alternating arrangement along the chain [30a].

Complex **2** presents a short distance Cu–N4(nitrile) of 1.974(3) Å and a long distance Cu–N7(nitrile) of 2.661(3) Å. In copper(II) complexes of substituted phenylcyanamides, when the ligand is coordinated by the nitrile nitrogen atom, distance values range from 1.928(7) to 1.951(7) Å [31]. Larger distance values have been observed in cyanamido copper(II) complexes, as in $[\text{Cu}(\text{bpy})_2\text{N}(\text{CN})_2]^-$ Cu–N(nitrile) = 2.015(3) Å [32] or in $[\text{Cu}(\text{NO}_2\text{NCN})_2(1\text{-meiz})_4]$ (1-meiz = 1-methylimidazole) Cu–N(nitrile) = 2.600(3) Å [33], corresponding to a terminal mode of coordination.

The Cu–N6(amido) bond of 2.562(3) Å is longer than those observed in other amido complexes as in $[\{\text{Cu}(\text{bipy})(\text{pcyd})_2\}_2]$ (2.355(6) Å) [29] or in $[\text{Cu}(\text{tren})(2,4\text{-NCNsq})]$ (2.027(3) Å) [9].

In complex **2**, the two NCN groups deviate weakly on the same side from the squarate ring mean plane. The N6C10N7 group, the less coordinated, shows a dihedral angle of 11.2(6)°; the more coordinated N4C5N5 deviates by a dihedral angle of 9.1(5)°. Whatever coordination mode may be adopted (nitrile or nitrile/amido), the nitrile groups present similar bond distance values (C5–N4 = 1.164(4) Å and C10–N7 = 1.162(4) Å). The N4–C5–N5 and N6–C10–N7 angle values are 172.1(3)° and 172.2(3)°, respectively. However, the CuN4C5 and CuN7C10 angles of 156.0(2)° and 123.98(20)°, respectively, are greatly different and deviate from the expected value of 180°, the lowest value corresponding to the less coordinated nitrile group. The C–C distance values in the squarate ring range from 1.447(4) to 1.471(4) Å and are indicative of a delocalized π system as observed in the squarate [34] and the 2,4-NCNsq^{2−} ions [12]. The C–O distances are normal for carbonyl groups. So, even if the coordination modes of the two cyanamido groups differ, the high symmetry of the dianion is retained.

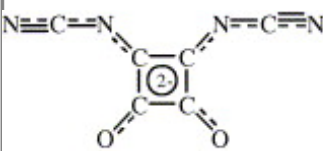
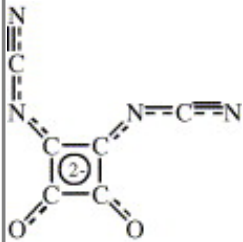
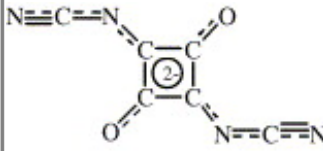
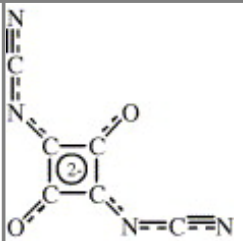
The hydrogen bond network involves as donor groups, the water molecule and the N–H groups of

the dien ligand, and as acceptors, the oxygen atoms of the 2,4-NCNsq²⁻ ligand, the one of the water molecule and the nitrile nitrogen atom N7 of the L²⁻ ligand.

As it is typical for (dien)Cu^{II} complexes, the conformation of the dien ligand is such that the primary amine nitrogen atoms occupy trans positions in the coordination sphere [35], [36] and [37]. The angles of dien are normal for a copper(II) complex [38] and [39].

3.3. IR and electronic spectroscopies

The IR spectra of cyanamides and related diimides have been already discussed [40], [41] and [42]. In particular, solid state infrared studies on 3,4-NCNsq²⁻ [9], [10], [11], [43] and [44] and 2,4-NCNsq²⁻ [12] salts show that, in the 2200–2100 cm⁻¹ area, assigned to –N≡C≡N stretching vibrations domain, the spectra depend on the nature of the counter ion due to the existence of two conformers per dianion (A and B) as shown below. In solution, the two conformers coexist with the predominant form A.

Conformation	A	B
Counter-ion in the salt	<u>PPh₄⁺</u>	Na ⁺
3,4-NCNsq ²⁻	 $\nu_a(\text{NCN}) = 2120 \text{ cm}^{-1}$	 $\nu_a(\text{NCN}) = 2163 \text{ cm}^{-1}$
2,4-NCNsq ²⁻	 $\nu_a(\text{NCN}) = 2127 \text{ cm}^{-1}$	 $\nu_a(\text{NCN}) = 2180 \text{ cm}^{-1}$

A summary of selected infrared data of the 2,4-NCNsq²⁻ salts and of complexes **1** and **2** is given in Table 4. According to the crystal data of complexes **1** and **2**, the 2,4-NCNsq²⁻ ligand is always in the A conformation. So the $\nu_a(\text{NCN})$ value of 2127 cm⁻¹ has been chosen as a reference and

compared with the IR data of the complexes.

Table 4.

IR data for $X_2(2,4\text{-NCNsq})$ salts ($X = \text{Na}, \text{PPh}_4$) and for compounds **1**, **2** (in cm^{-1} , in KBr)

Compound	Conformer of 2,4-NCNsq ²⁻	$\nu_a(\text{NCN})$	$\nu_{\text{CO} + \text{CC}}$	ν_{CC}	$\nu_s(\text{NCN})$
$\text{Na}_2(2,4\text{-NCNsq})$	B	2180	1653–1541	1477–1426	1192; 1132
$(\text{PPh}_4)_2(2,4\text{-NCNsq})$	A	2127	1631–1541	1482–1413	1183; 1163
1	A	2153	1598–1569	1479–1400	1178; 1155
2	A	2168	1613–1547	1487–1411	1148; 1131

In complex **1**, a strong $\nu_a(\text{NCN})$ band is observed at 2153 cm^{-1} with a positive shift of 26 cm^{-1} in comparison with the free ligand. This value is close to that observed in $[\text{Cu}_2(\text{PPh}_3)_4(\text{MeCN})_2(\mu\text{-}3,4\text{-NCNsq})] \cdot \text{MeCN}$ ($\Delta\nu = +29 \text{ cm}^{-1}$) [9]. The positive shift observed in the two complexes is consistent with end-on bonded cyanamido groups which correspond to the σ -donation of the nitrile nitrogen electrons of the cyanamido groups to the metal.

In addition, in the same region, two bands at $2227(\text{m})$ and $2220(\text{w}) \text{ cm}^{-1}$ may be attributed to the CN stretching vibrations of benzonitrile molecules. The $\text{C}\equiv\text{N}$ group can act either as a σ -donor, by donating nitrogen electrons to the metal, or as a π -donor, by donating nitrile π -bond electrons. The wavenumber of the $\text{C}\equiv\text{N}$ stretching vibration is shifted to higher values in the case of σ -donation and to lower values in the case of π -donation [45]. The strong $\text{C}\equiv\text{N}$ stretching absorption band of pure benzonitrile being observed at 2228 cm^{-1} , the band with almost the same position in complex **1** spectrum most probably corresponds to the free benzonitrile molecules and the slightly shifted band observed at 2220 cm^{-1} corresponds to coordinated benzonitrile. The weak difference between these two CN frequencies emphasises the fact that the benzonitrile ligand is here weakly coordinated to copper ($\text{Cu-N1} = 2.312(7) \text{ \AA}$) when shorter Cu(I)-N(nitrile) bond distances close to 1.99 \AA are observed in the literature [21], [24] and [25]. It should be noted that complex **1** has unusually weak π -back-bonding character in agreement with the Cu-N1-C1 angle value of $132.4(6)^\circ$.

In complex **2**, the ligand $2,4\text{-NCNsq}^{2-}$ coordinates the copper atoms via both the nitrile nitrogen atom and the amido nitrogen atom. This unusual complexation yields to a series of $\nu(\text{NCN})$ bands

centred at 2168 cm^{-1} (positive shift of 41 cm^{-1} in comparison with the free ligand).

As expected, $\nu_{\text{CO} + \text{CC}}$ bands centred at 1584 and 1580 cm^{-1} for complexes **1** and **2**, respectively, are not affected by complexation (1586 cm^{-1} in the PPh_4^+ salt).

3.3.1. Study in solution

Molar conductivity measurements using dimethylformamide as solvent indicate that the complexes are non-electrolytes. Therefore, the anionic $2,4\text{-NCNsq}^{2-}$ ligands remain coordinated in solution.

The electronic spectra of $2,4\text{-NCNsq}^{2-}$, performed in methanol by Köhler et al. [46] are characterized by two bands at 273 ($\log \varepsilon = 4.20$) and 352 nm ($\log \varepsilon = 4.80$). The same values of 270 ($\log \varepsilon = 4.44$) and 364 nm ($\log \varepsilon = 4.73$) are observed in dmf solution at $10^{-5}\text{ mol L}^{-1}$. Only the predominant form A is observed as found for the $3,4\text{-NCNsq}^{2-}$ dianion [9] and [47]. These $\pi\text{-}\pi^*$ transitions are not affected by complexation. They are observed at 265 ($\log \varepsilon = 4.43$) and 366 nm ($\log \varepsilon = 4.33$) in complex **1**, 266 ($\log \varepsilon = 4.30$) and 360 nm ($\log \varepsilon = 4.70$) in complex **2**. For complex **2**, the two additional bands at 420 nm ($\log \varepsilon = 3.12$) and 606 nm ($\log \varepsilon = 2.40$) have been assigned to $\text{p}\pi\text{-d}\sigma^*$ LMCT and ligand field d-d transitions, respectively, in analogy to the similar visible spectra of phenylcyanamide copper complexes [30] and [48] and to those of the $3,4\text{-NCNsq}$ copper(II) complexes [9].

4. Supplementary material

Further details on the Crystal Structure Investigation are available on request from the Director of the Cambridge Crystallographic Data centre, 12 Union Road, GB-Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) on quoting the full journal citation. (CCDC 284988-284989).

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