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Cyanomethylene-bis(phosphonate) as ditopical ligand: stepwise formation of a 2–D heterometallic Fe(III)-Ag(I) coordination network

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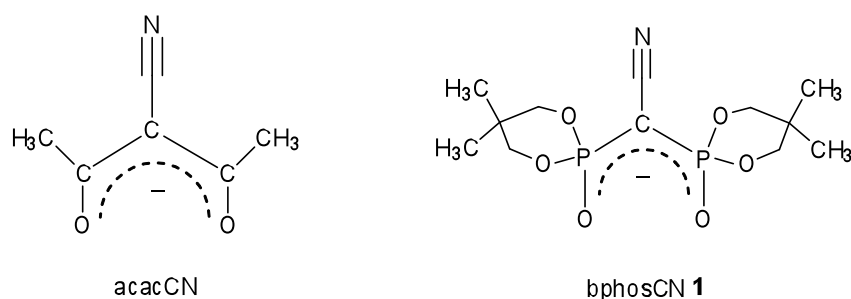
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Abstract:

A new heteroditopic ligand, cyanomethylene-bis(5,5-dimethyl-2-oxo-1,3,2 λ^5 -dioxaphosphorinane) **1** (bphosCN), has been reacted with Fe(ClO₄)₃ to afford the mononuclear complex Fe(bphosCN)₃ **2** which crystallized in the cubic system, space group *Pa-3*. The iron center, chelated by the oxygen atoms of the ligand, shows an almost perfect octahedral geometry, with the CN groups disposed at 120° each other. Further reaction with AgClO₄ provided the heterometallic coordination polymer $2^{\infty}\{[(\text{Fe}(\text{bphosCN})_3)_3\text{Ag}_3(\text{H}_2\text{O})_2]\cdot 3\text{ClO}_4\}\cdot 0.5\text{H}_2\text{O}$ **3** as unique crystalline polymorph, in the monoclinic space group *P2₁/a*. The targeted 2D honeycomb type structure has been achieved through an interplay between coordinative CN-Ag bonds and CN \cdots H₂O bonds. The magnetic measurements demonstrate the existence of isolated paramagnetic Fe(III) centers in both complexes.

Introduction

The use of polytopical ligands in the field of coordination chemistry with the aim of synthesizing homo- or hetero-polymetallic coordination networks represents a most valuable strategy to reach these complex architectures by design,¹ all the more since the ultimate goal of this approach is to address the crystalline solids with specific properties such as magnetism, luminescence, spin-crossover behavior, etc.² Therefore, the conception of new ligands possessing at least two different coordinating units is of great importance, especially for the construction of hetero-metallic systems which are more challenging than the homo-metallic ones. Indeed, the controlled synthesis of the former requires a sequential strategy, involving the preparation in a first step of a metal complex bearing additional coordinating groups available for the interaction with a second metal ion.³ In this respect, functionalized acetylacetonate (acac) derivatives,⁴ such as 3-(4-pyridyl)-acetylacetonate,⁵ have been successfully used as ditopic ligands in polymetallic coordination networks, in spite of the tendency of the latter to decompose.⁶ A much more stable derivative is the 3-cyanoacetylacetonate (acacCN) (Scheme 1),⁷ for which several monometallic complexes of Cu(II),^{7,8} Co(II),⁹ or Zn(II)¹⁰ have been described. Moreover, Burrows reported the sequential formation of Cu(II)-Ag(I) and Fe(III)-Ag(I) coordination networks starting from the corresponding Cu(II) and Fe(III) monometallic complexes,¹¹ while Englert described the synthesis of Cr(III)-Ag(I) coordination polymers through a similar procedure.¹² More recently, Baudron and Hosseini synthesized and structurally characterized heteroleptic coordination networks involving the Cu(II)-Ag(I) and Co(III)-Ag(I) couples, acacCN and functionalized dipyrin (dpm) ligands.¹³ It is thus clear that once the chelating *O,O* unit of the acacCN ligand is involved in coordination, the remaining CN group still possesses a good propensity towards the ligation of a second metallic centre, especially silver.

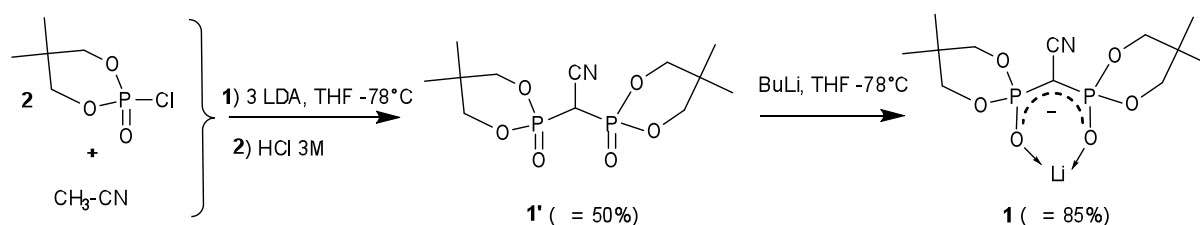


Scheme 1 Schematic representation of the **acacCN** and **bphosCN 1** ligands.

A similar behaviour could be expected from cyanomethylene-bis(phosphonate) (bphosCN) ligands, which are endowed with a chelating *O,O* moiety and a CN group. Yet these ligands, described by Savignac,¹⁴ have never been used in coordination chemistry studies, although the presence of phosphonate groups allows for the characterization of the compounds by ³¹P NMR and provides additional modularity to the system. We have therefore undertaken a systematic study on these so far unexplored ligands, and we describe herein a first report dealing with the synthesis, structural and spectroscopic characterizations, and magnetic properties of the first transition metal complex, i.e. Fe(III), based on a cyanomethylene-bis(phosphonate), namely the cyanomethylene-bis(5,5-dimethyl-2-oxo-1,3,2λ⁵-dioxaphosphorinane) anion **1** (Scheme 1), together with a Fe(III)-Ag(I) coordination network prepared through a sequential strategy.

Results and Discussion

The anionic bphosCN ligand **1** has been synthesized according to the protocol described by Savignac,¹⁴ which first involves the isolation of the neutral precursor **1'** after a carbanionic reaction between MeCN, LDA (lithium diisopropylamide) and the corresponding chlorophosphate in a ratio 1:3:2 followed by acidic treatment, and then deprotonation (Scheme 2).



Scheme 2 Synthesis of the bphosCN ligand **1**.

The deprotonation reaction is easily monitored by ³¹P NMR due to the large difference in chemical shifts between the neutral (-2.8 ppm) and the anionic species (30.1 ppm).

The crystal structure of $[\text{Fe}(\text{bphosCN})_3]\cdot\text{H}_2\text{O}$ (**2**)

The ligand **1** is very stable in its anionic form and can be kept indefinitely in normal conditions and further used in coordination chemistry studies without any precautions. Its reaction with $\text{Fe}(\text{ClO}_4)_3$ in a ratio 3:1 proceeds very smoothly in methanol at room temperature and affords orange cubic shaped crystals in quantitative yield upon slow

evaporation of the solvent and filtration to remove the soluble lithium salts. The complex **2**, formulated as $[\text{Fe}(\text{bphosCN})_3]\cdot\text{H}_2\text{O}$, crystallizes in the cubic system, centrosymmetric space group $Pa-3$, with one ligand in general position, and one Fe(III) ion and the oxygen atom of the crystallization water molecule in special positions, with s.o.f. = 0.333, corresponding to a C_3 axis. The iron center is chelated by three crystallographically equivalent bphosCN ligands **1** through the oxygen atoms and lies in an almost perfect octahedral environment (Fig. 1), as suggested by the Fe–O distances of 1.972(4) and 1.987(4) Å respectively, and the bite angle of the bphos ligand (O1–Fe1–O4) amounting to $87.66(15)^\circ$ (Table 1).

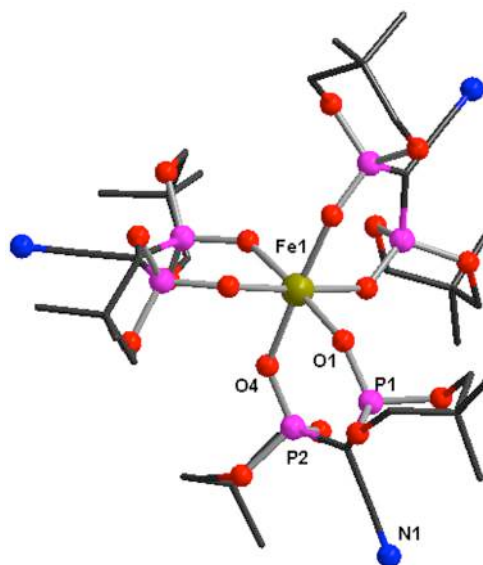


Fig. 1 Crystalline structure of the Fe(III) complex **2**. Hydrogen atoms and the crystallization H_2O molecule have been omitted.

The P–C bonds are much shorter (~ 1.70 Å), as already noticed in the crystal structure of the lithium salt **1**,¹⁴ when compared to those in the neutral bis(phosphonate) **1'** (1.84 Å),¹⁴ while the P=O bonds are a little bit longer (1.485 Å in average compared to 1.45 Å in **1'**), thus indicating a significant charge delocalization within the chelating unit. The shortening of the C–C bond from 1.47 Å in **1'** to 1.41 Å in **2**, together with the slight elongation of the C≡N from 1.13 Å in **1'** to 1.142 Å in **2**, suggests that the CN unit also takes part to this delocalization. The five member ring metallacycles are not planar, as indicated by the dihedral angle of 21.38° between the planes defined, respectively, by the Fe and O atoms, and the O, P and C atoms of the chelating unit. Since the metal ion lies on a C_3 axis, the angles between the cyano groups are exactly 120° , like in 1,3,5-tricyano-benzene, which represents a favorable situation for the establishment of honeycomb type networks. Nevertheless, no short weak intermolecular interactions are observed in the structure of **2**, while the packing diagram (Fig.

2) shows quite large separations between the iron centers, with the shortest distance amounting to 11.46 Å.

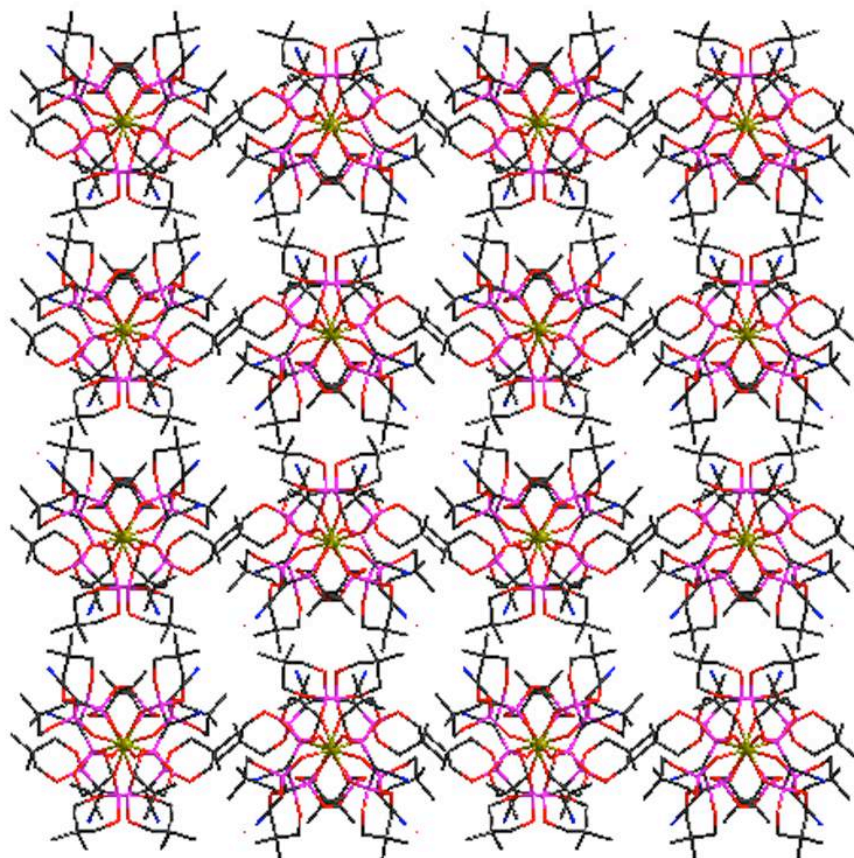


Fig. 2 Packing diagram of **2**.

Table 1. Selected bond lengths (Å) and angles (°) for compounds **2** and **3**

2			
Fe1-O1	1.972(4)	O1-Fe1-O1	90.54(17)
Fe1-O4	1.987(4)	O1-Fe1-O4	87.66(15)
P1-O1	1.478(4)	O1-Fe1-O4	176.96(16)
P1-O3	1.561(4)	O1-P1-O3	110.1(3)
P1-O2	1.563(4)	O1-P1-O2	111.0(2)
P2-O4	1.490(4)	O3-P1-O2	103.6(2)
P2-O6	1.557(4)	O4-P2-O6	110.1(2)
P2-O5	1.571(4)	O4-P2-O5	111.0(2)
C2-N1	1.142(9)	O6-P2-O5	104.9(2)
C1-C2	1.414(9)	N1-C2-C1	178.5(9)
C1-P1	1.698(6)	O1-Fe1-O1	90.54(17)
C1-P2	1.706(6)	O1-Fe1-O4	87.66(15)
		O1-Fe1-O4	176.96(16)
		O1-P1-O3	110.1(3)
		O1-P1-O2	111.0(2)
		O3-P1-O2	103.6(2)

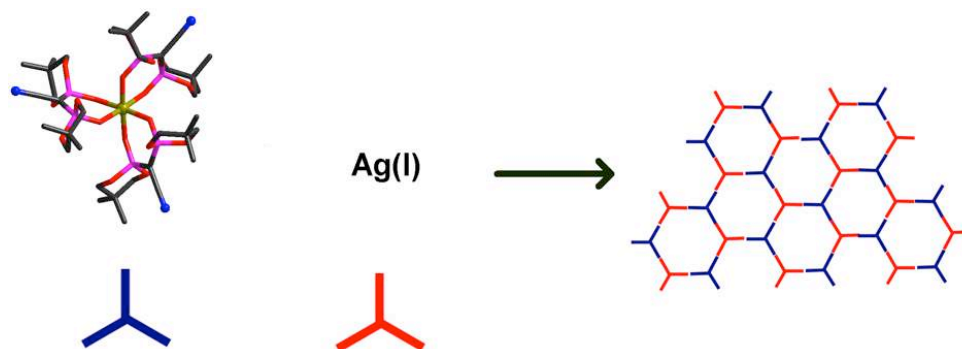
		O4-P2-O6	110.1(2)
		O4-P2-O5	111.0(2)
		O6-P2-O5	104.9(2)
		N1-C2-C1	178.5(9)
		3	
O2w Ag2	2.47(3)	N1B Ag1 N1C	121.9(7)
O3w Ag3	2.34(3)	N1B Ag1 N1A	109.8(7)
N3C Ag3	2.16(2)	N1C Ag1 N1A	128.2(7)
N3A Ag2	2.19(2)	N2B Ag2 N3A	155.9(8)
Ag1 N1B	2.27(3)	N2B Ag2 O2w	101.3(9)
Ag1 N1C	2.24(2)	N3A Ag2 O2w	102.7(9)
Ag1 N1A	2.32(2)	N2C Ag3 N3C	157.1(8)
Ag2 N2B	2.14(2)	N2C Ag3 O3w	87.5(9)
Ag2 N3A	2.19(2)	N3C Ag3 O3w	115.4(9)
Ag3 N2C	2.15(2)	O4C FeC O2C	177.6(5)
Ag3 N3C	2.16(2)	O4C FeC O3C	87.9(5)
FeC O4C	1.987(12)	O2C FeC O3C	90.0(5)
FeC O2C	1.988(14)	O4C FeC O5C	91.2(5)
FeC O3C	1.987(12)	O2C FeC O5C	90.0(5)
FeC O5C	1.988(13)	O3C FeC O5C	89.4(5)
FeC O1C	1.991(13)	O3B FeB O2B	88.9(6)
FeC O6C	2.005(12)	O3B FeB O5B	92.9(6)
FeB O3B	1.961(14)	O2B FeB O5B	177.3(6)
FeB O2B	2.000(17)	O3B FeB O1B	91.4(6)
FeB O5B	1.906(12)	O2B FeB O1B	88.4(6)
FeB O1B	2.006(12)	O5B FeB O1B	89.7(4)
FeB O4B	2.028(13)	O3B FeB O4B	86.4(5)
FeA O3A	1.986(15)	O3A FeA O6A	90.4(6)
FeA O5A	1.988(14)	O5A FeA O6A	88.9(6)
FeA O6A	1.992(14)	O3A FeA O4A	89.8(6)
FeA O4A	1.991(14)	O5A FeA O4A	88.2(5)
FeA O1A	2.012(13)	O6A FeA O4A	94.9(6)

The IR spectra of **1** and **2** are quite similar (see Supp. Inf.), with the vibration of the CN group occurring at 2187 cm⁻¹ and that of the P=O groups at 1210 cm⁻¹ for **2**, while those for **1** appear at 2179 cm⁻¹ (CN) and 1212 cm⁻¹ (P=O). The electronic absorption spectrum in diffuse reflectance mode for **2** (Supp. Inf.) shows a band centered at $\lambda_{\max} = 259$ nm, very likely due to intra-ligand transitions, while the one at $\lambda_{\max} = 400$ nm is certainly generated by LMCT transitions, since the d – d transitions of Fe(III) HS are spin forbidden.

The crystal structure of $2^{\infty} \{[(\text{Fe}(\text{bphosCN})_3)_3\text{Ag}_3(\text{H}_2\text{O})_2] \cdot 3\text{ClO}_4\} \cdot 0.5\text{H}_2\text{O}$ (**3**)

The presence of three cyano groups, disposed at relative angles of 120°, in the structure of the mononuclear species **2** prompted us to attempt the construction of a honeycomb type

coordination polymer by the use of Ag(I) as assembling ion, as exemplified in Scheme 3, knowing its preference for trigonal coordination stereochemistry.



Scheme 3 Schematic view of the targeted coordination network Fe-Ag.

The preparation of the hetero-bimetallic complex Fe-Ag **3** proceeds smoothly upon mixing ethanolic solutions of **2** and $\text{AgClO}_4 \cdot x\text{H}_2\text{O}$ in equimolar amounts. Yellow crystals formulated as $2^\infty \{[(\text{Fe}(\text{bphosCN})_3)_3\text{Ag}_3(\text{H}_2\text{O})_2] \cdot 3\text{ClO}_4\} \cdot 0.5\text{H}_2\text{O}$ were formed within a few days. The complex crystallizes in the monoclinic system, space group $P2_1/a$, with three neutral units $[\text{Fe}(\text{bphosCN})_3]$ (named as FeA, FeB and FeC), three Ag(I) (Ag1, Ag2 and Ag3) ions, three perchlorate ions and two coordinated water molecules, each disordered on two positions, in general positions in the asymmetric unit, together with a crystallization water molecule on a C_2 axis. The coordination geometries of the iron centers are slightly distorted octahedra (Fig. 3), with Fe–O distances ranging between 1.958 and 2.028 Å and bite angles of the bphosCN ligands slightly below 90° (Table 1).

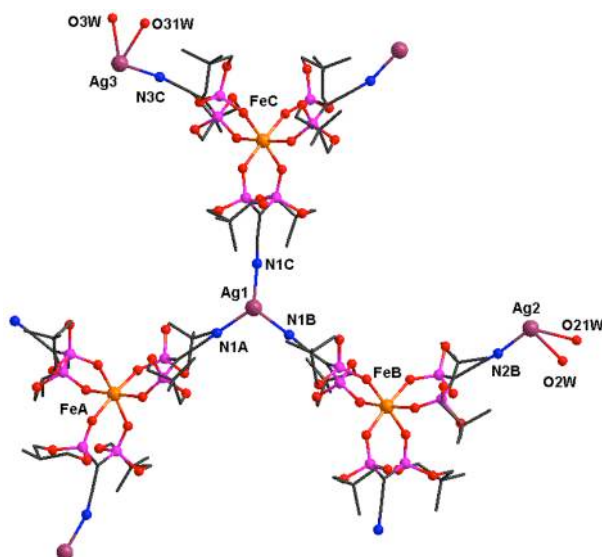


Fig. 3 Asymmetric unit in the crystalline structure of the Fe-Ag complex **3**, with an emphasis on the trigonal coordination of the Ag1 center. Hydrogen atoms, crystallization water molecule and perchlorate ions have been omitted.

The angles between the CN groups are close to 120° , i.e. the value observed in the monometallic precursor (*vide supra*), which is a prerequisite for the construction of the desired honeycomb architecture. In comparison, in the Fe(III)(acacCN)_3 monometallic complex, described by Burrows,¹¹ the angles between the CN groups differed substantially from 120° , and this was probably one of the factors which favoured the formation of coordination chains in the structure of the Fe(III)-Ag(I) polymeric network, instead of honeycomb layers, since the silver ions were coordinated only by two cyano groups. Note that the angles between the cyano groups were also rather different from 120° in the coordination chains, although the differences were smaller than in the monometallic complex. In the crystal structure of our complex **3** (Fig. 3) the silver ion Ag1 connects three different Fe(III) units FeA, FeB and FeC through the coordination of a cyano group of each monometallic complex within a distorted trigonal coordination geometry, as shown by the angles N-Ag1-N ranging between $109.8(7)^\circ$ and $128.2(7)^\circ$, while the bond lengths Ag-N are comprised between 2.24(2) and 2.32(2) Å. The three Fe-Ag1 distances are practically equal and amount to ~ 8.4 Å. The coordination pattern of Ag2 and Ag3 centers, however, is drastically different, since they adopt a T shape stereochemistry and their coordination sphere is formed by two nitrogen atoms from cyano groups and one water molecule (Fig. 4).

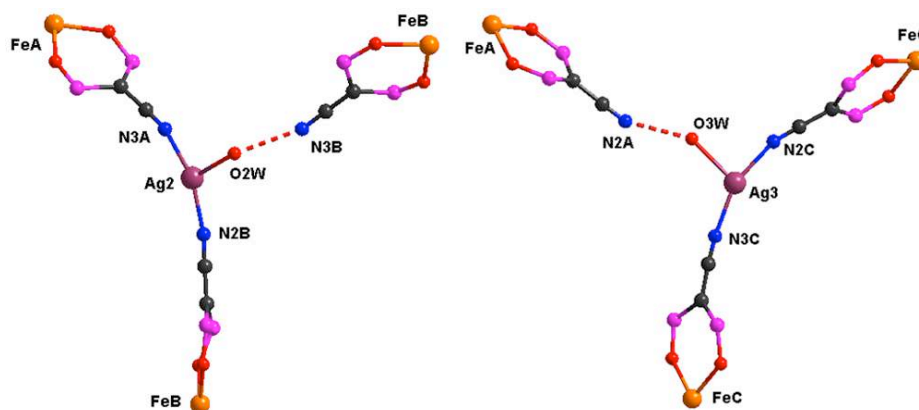


Fig. 4 Coordination of the Ag2 and Ag3 centers in the structure of the Fe-Ag complex **3**. Only the major occupational sites (refined at 0.57 for O2W and O3W) for the water molecules are shown.

Accordingly, the Ag2 ion connects a FeA and a FeB unit through Ag2-N3A and Ag2-N2B bonds of 2.19(2) and 2.14(2) Å, respectively, with an N-Ag2-N angle of $156.0(8)^\circ$, while the Ag3 ion is coordinated by N2C (Ag3-N2C distance of 2.15(2) Å) and N3C (Ag3-N3C distance of 2.16(2) Å) nitrogen atoms of two different FeC units, with an N-Ag3-N angle of $156.9(8)^\circ$. The Ag-O distances are much longer (2.37 - 2.47 Å) and the N-Ag-O angles

range between 88.5° and 114.6° . Thus, the three CN groups of the FeC unit are involved in further coordination with Ag ions (one Ag1 and two Ag3), while in the FeA and FeB units the nitrogen atoms N2A and N3B, respectively, do not coordinate any Ag centers. Nevertheless, these two uncoordinated N atoms engage in hydrogen bonds with coordinated water molecules, as indicated by the intermolecular distances $N2A \cdots O3W$ and $N3B \cdots O2W$ of 2.79 \AA and 2.69 \AA , respectively, leading to the formation of distorted hexagons, and thus to the establishment of a 2-D honeycomb architecture (Fig. 5). Probably, the steric hindrance of the ligands hamper the formation of the network based only on coordinative bonds, while the interplay with hydrogen bonding interactions allows its construction. Unlike the Fe-Ag distances around the Ag1 center, which are all equal, those related to Ag2 and Ag3 show two equivalent values of about 8.3 \AA and a longer one of $\sim 11 \text{ \AA}$, while the shortest Fe \cdots Fe distances within a layer, observed around the Ag1 center, range between 14 and 15 \AA . Smaller values of $10.8 - 11.3 \text{ \AA}$ are observed, however, between Fe centers belonging to neighbouring layers.

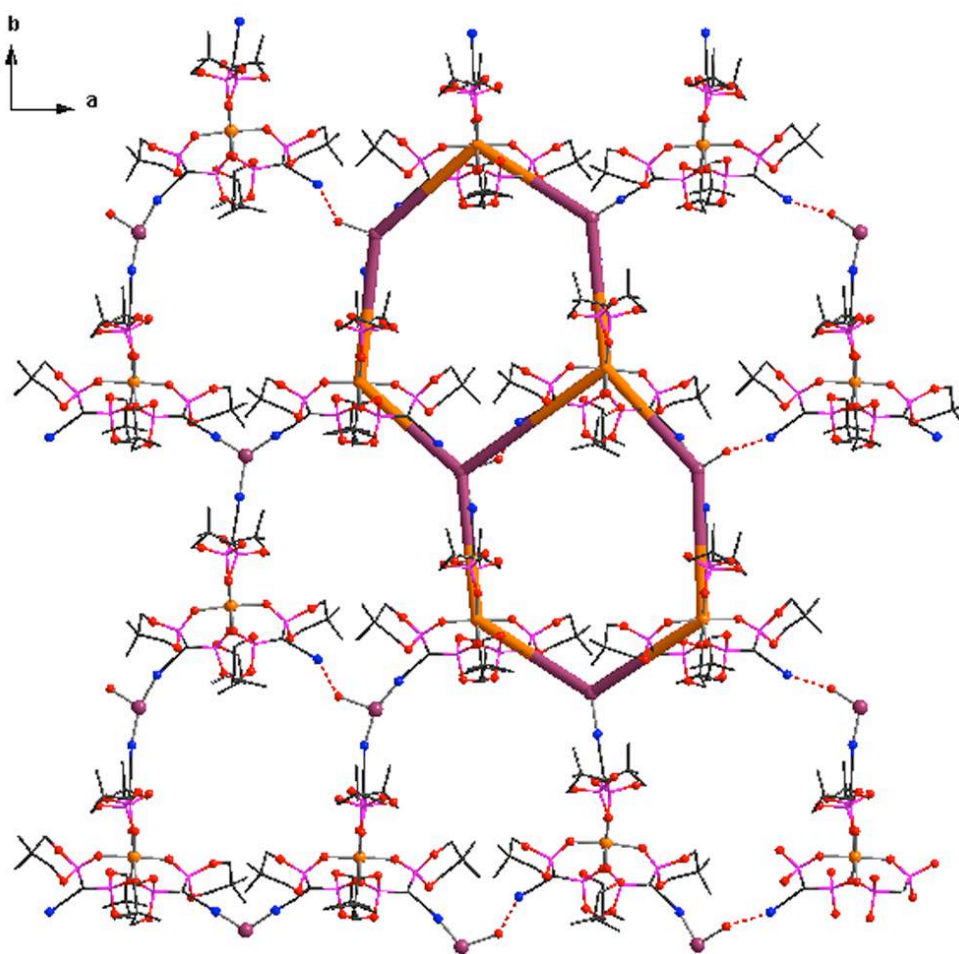


Fig. 5 Honeycomb type network in the structure of 3.

The successive parallel sheets are shifted with respect to each other, such as a relatively densely packed structure results, without formation of channels (Fig. 6).

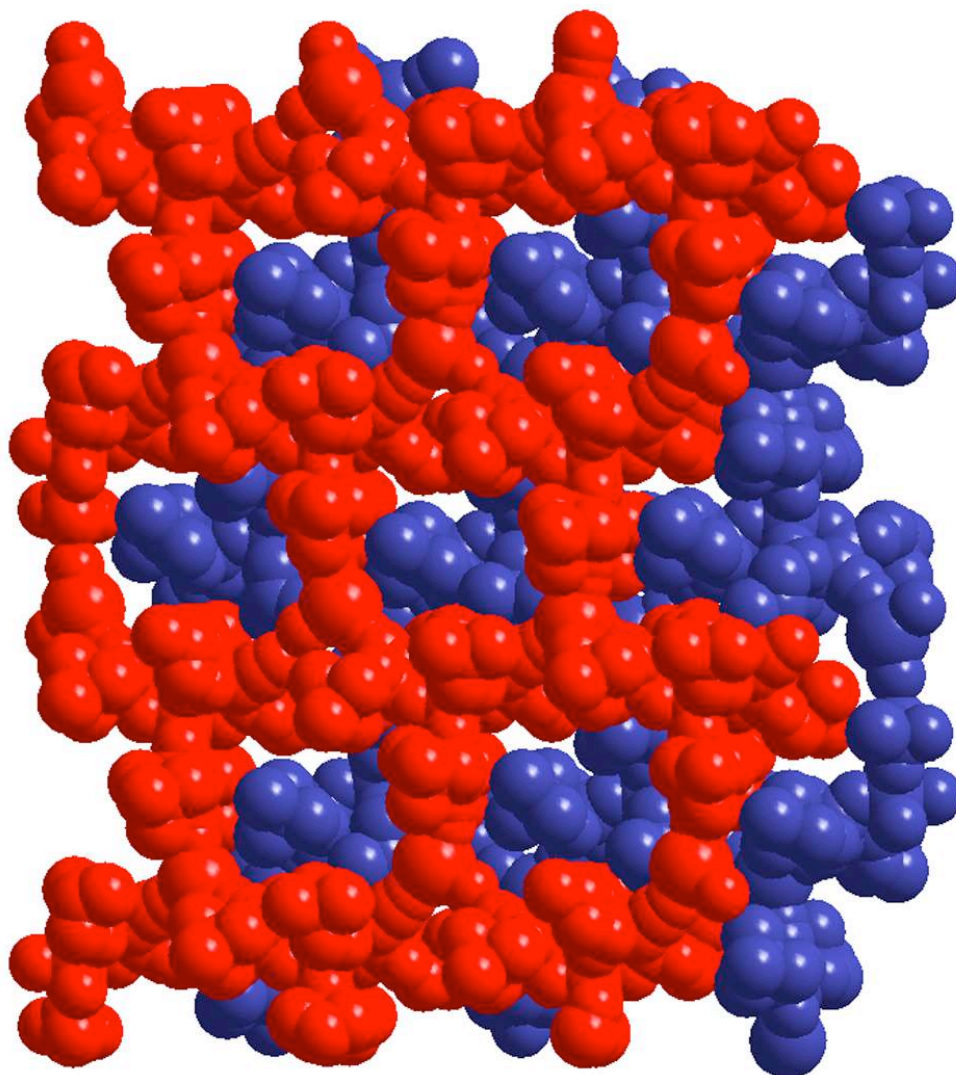


Fig. 6 Successive parallel layers in the structure of **3**.

The experimental PXRD diagram (Supp. Inf.) of **3** is in excellent agreement with the simulated one generated from the single crystal X-ray structure, thus demonstrating that no other crystalline polymorph was formed besides **3**.

The IR spectrum (Supp. Inf.) shows the vibrations of the CN groups at 2196 cm^{-1} and the one of the P=O bonds at 1226 cm^{-1} , to compare with the values of 2187 cm^{-1} and 1210 cm^{-1} , respectively, observed in **2**. These shifts, especially the one associated to the CN group, are indicative of the coordination of the second metal center. Moreover, the typical large band of the ClO_4 anion, centered at 1147 cm^{-1} , is also clearly observed.

Magnetic susceptibility measurements on **2** and **3**.

The magnetic properties of a polycrystalline sample of **2** and **3** have been determined by temperature dependent magnetic susceptibility measurements. At room temperature the χT product is $4.4 \text{ cm}^3 \cdot \text{K/mol}$ for both compounds. This value is in good agreement with the expected values for the presence of a Fe(III) ($S = 5/2$, $C = 4.375 \text{ cm}^3 \text{K/mol}$ with $g = 2$) center. When the temperature is lowered, the χT product at 1000 Oe stays roughly constant down to 1.8 K indicating a Curie behavior and confirming that the magnetic interaction between $S = 5/2$ Fe(III) centers through the bridging groups is extremely weak and not measurable with data above 1.8 K (Fig. 7).

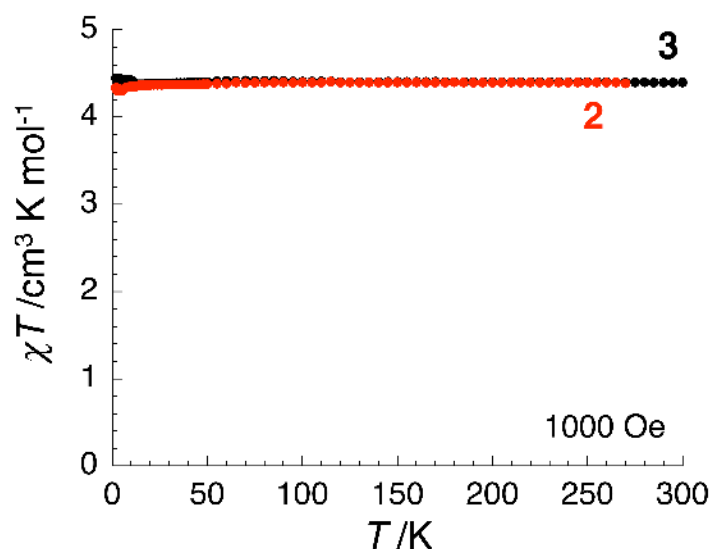


Fig. 7 Temperature dependence of χT product (χ being the molar magnetic susceptibility defined as M/H) for **2** (red dots) and **3** (black dots) under 0.1 T.

This behavior is in agreement with the large Fe \cdots Fe separations observed in the crystalline structures of **2** and **3**.

Conclusions

We have reported here the first coordination chemistry studies involving the ditopical anionic ligand cyanomethylene-bis(5,5-dimethyl-2-oxo-1,3,2 λ^5 -dioxaphosphorinane) **1** (bphosCN), as phosphorous analogue of the more conventional 3-cyano-acetylacetonate (acacCN) ligand. The homoleptic monometallic iron (III) complex $\text{Fe}(\text{bphosCN})_3$ **2** has been structurally characterized and further used in the construction of the crystalline heterometallic polymeric coordination network Fe-Ag **3**, which shows a honeycomb architecture, thanks to the interplay between coordinative CN-Ag bonds and CN \cdots H $_2$ O hydrogen bonds, as unique

crystalline form. These first examples of transition metal complexes demonstrate the versatility of the functional methylene-bis(phosphonate) ligands towards the rational design of homo and heterometallic coordination networks. Moreover, the chelating *O,O* motif, resembling the one encountered in acac type ligands, is well adapted for the coordination of lanthanide ions and this is one of the directions actively investigated in our laboratories.

Experimental

General. Reactions were carried out under normal atmosphere and with solvents of commercial purity. NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for ^1H and 202.39 MHz for ^{31}P . The IR spectra were recorded on KBr pellets with a Bruker TENSOR 37 spectrophotometer in the 4000–400 cm^{-1} range. Solid state (diffuse reflectance) spectra in the 200–900 nm range were recorded on a JASCO V-570 spectrometer using MgO as a standard.

Syntheses.

Except where mentioned, all the chemicals were purchased from commercial sources and were used as received. The perchlorate salts were manipulated with great care, and only small amounts were used. The ligand **bphosCN** = cyano(lithio)methylenebis(5,5-dimethyl-2-oxo-1,3,2 λ^5 -dioxaphosphorinane) (**1**) has been obtained as already reported.¹⁴

[Fe(bphosCN)₃]·H₂O (2).

To a methanolic- CH_2Cl_2 (1:1) solution (10 mL) containing 0.15 mmol of anionic ligand, 5 mL methanolic solution containing 0.05 mmol $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ were added under stirring. Orange crystals of **2** formed within several days, which have been isolated by filtration. Selected IR bands (KBr, cm^{-1}): 3481, 2976(CH), 2891(CH), 2187(CN), 1210(P=O), 1048(P-O), 640, 570, 482. Diffuse reflectance spectrum: 259 nm; 400 nm. Anal. Calcd. for $\text{C}_{36}\text{H}_{60}\text{FeN}_3\text{O}_{19}\text{P}_6$: C, 40.01; H, 5.59; N, 3.88. Found C, 39.67; H, 5.21; N, 3.75.

Synthesis of $2^\infty \{[(\text{Fe}(\text{bphosCN})_3)\text{Ag}_3(\text{H}_2\text{O})_2] \cdot 3\text{ClO}_4\} \cdot 0.5\text{H}_2\text{O}$ 3

To a ethanolic solution (20 mL) containing 0.1 mmol of **[Fe(bphosCN)₃]·H₂O**, 10 mL ethanolic solution containing 0.1 mmol $\text{AgClO}_4 \cdot x\text{H}_2\text{O}$ were added, under stirring. Yellow crystals of **3**, isolated by filtration, formed within several days. Selected IR bands (KBr, cm^{-1}):

3394, 2974(CH), 2895(CH), 2196(CN), 1225(P=O), 1145(Cl-O), 1047(P-O), 630, 574, 486. Diffuse reflectance spectrum: 258 nm; 405 nm. Anal. Calcd. for $C_{216}H_{360}Ag_6Cl_6Fe_6N_{18}O_{137}P_{36}$: C, 33.64; H, 4.70; N, 3.26. Found C, 33.21; H, 4.61; N, 3.11.

X-Ray Structure Determinations. Details about data collection and solution refinement are given in Table 2. X-ray diffraction measurements were performed on a on a STOE IPDS I diffractometer for **2** and Bruker Kappa CCD diffractometer for **3**, both operating with a Mo-K α ($\lambda = 0.71073$ Å) X-ray tube with a graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full-matrix least-square procedures on F^2 . All non-H atoms of the donor molecules were refined anisotropically, and hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined. Crystallographic data for the structures have been deposited in the Cambridge Crystallographic Data Centre, deposition numbers CCDC xxxxx (**2**), CCDC xxxxx (**3**).[2]

Table 2. Crystallographic data, details of data collection and structure refinement parameters.

Compound	2	3
Chemical formula	$C_{36}H_{60}FeN_3O_{19}P_6$	$C_{216}H_{360}Ag_6Cl_6Fe_6N_{18}O_{137}P_{36}$
M (g mol $^{-1}$)	1080.54	7711.16
Crystal system	cubic	Monoclinic
Space group	$Pa-3$	$P2_1/a$
Temperature, (K)	273	273
Wavelength, (Å)	0.71073	0.71073
a (Å)	22.9238(17)	20.464(3)
b (Å)	22.9238(17)	26.576(5)
c (Å)	22.9238(17)	30.784(5)
α ($^\circ$)	90	90
β ($^\circ$)	90	99.474(12)
γ ($^\circ$)	90	90
V (Å 3)	12046.5(15)	16513(5)
Z	8	2
D_c (g cm $^{-3}$)	1.192	1.551
μ (mm $^{-1}$)	0.470	0.919
$F(000)$	4520	7916
Goodness-of-fit on F^2	0.820	1.595
Final $R1$, wR_2 [$I > 2\sigma(I)$]	0.0678, 0.1660	0.1283, 0.3710
$R1$, wR_2 (all data)	0.1708, 0.2085	0.2016, 0.4228
Largest diff. peak and hole (eÅ $^{-3}$)	0.542, -0.264	2.382, -1.733

$$^a R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

Magnetic measurements.

The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL housed at the Centre de Recherche Paul Pascal. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on polycrystalline samples of 16.81 and 7.73 mg for **2** and **3** respectively introduced in sealed polyethylene bags ($3 \times 0.5 \times 0.02$ cm). The magnetic data were corrected for the sample holder and the diamagnetic contributions.

Acknowledgements.

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Supporting Information Available: IR and UV-Vis spectra, PXRD diagram.

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Cyanomethylene-bis(phosphonate) as ditopical ligand: stepwise formation of a 2-D heterometallic Fe(III)-Ag(I) coordination network

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Supporting Information

IR spectra

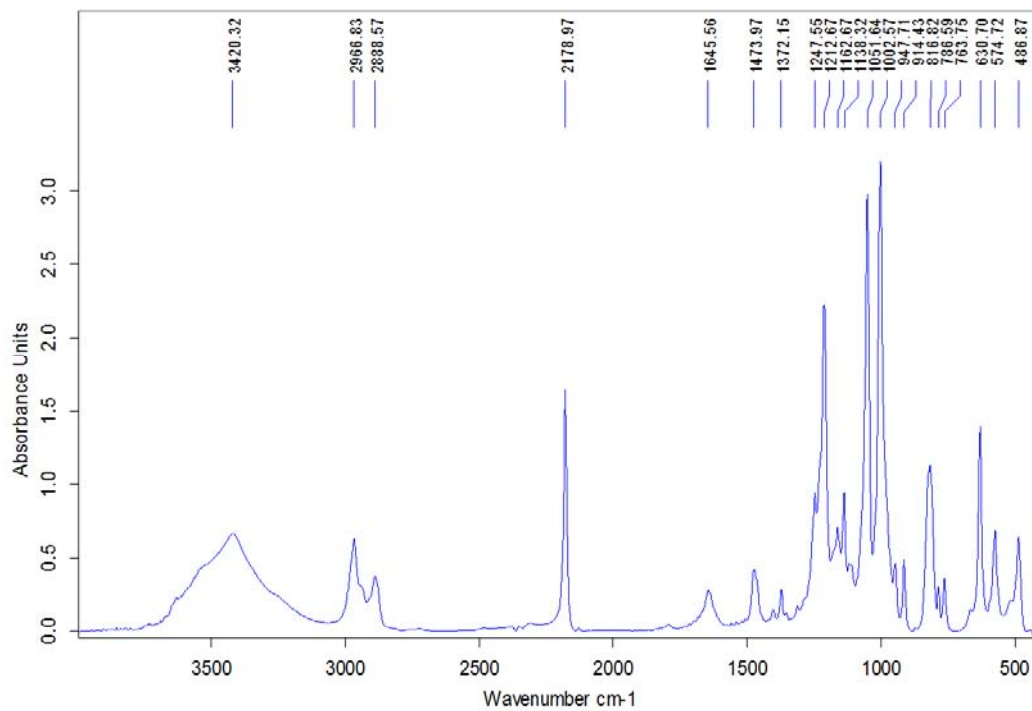


Figure S1. IR spectrum of **1**

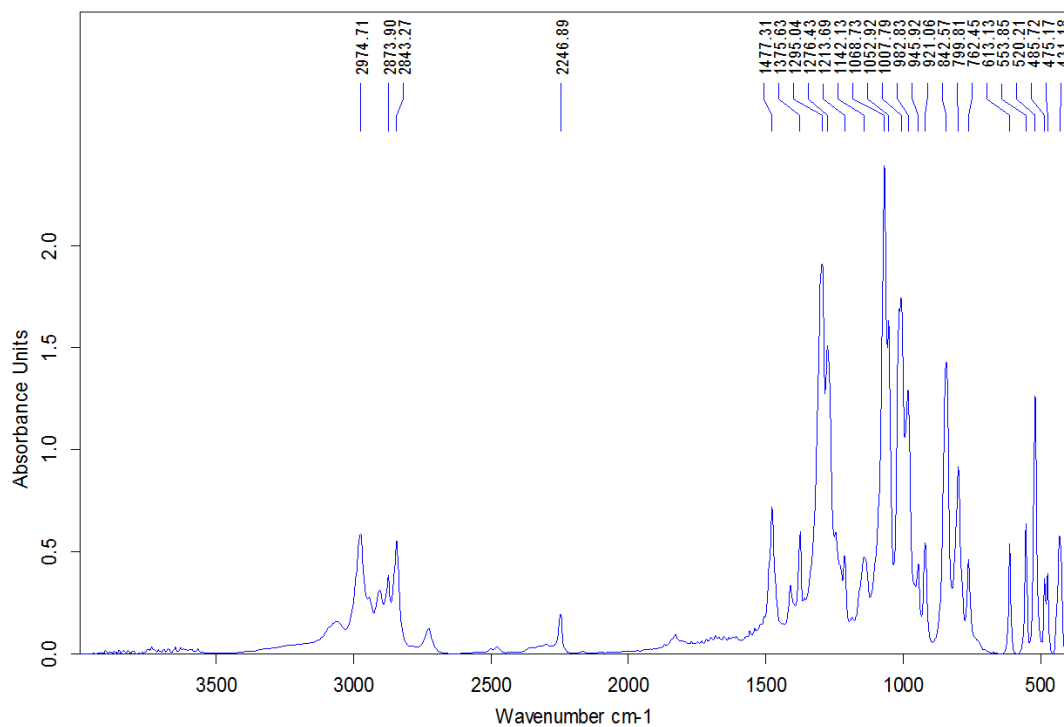


Figure S2. IR spectrum of **1'**

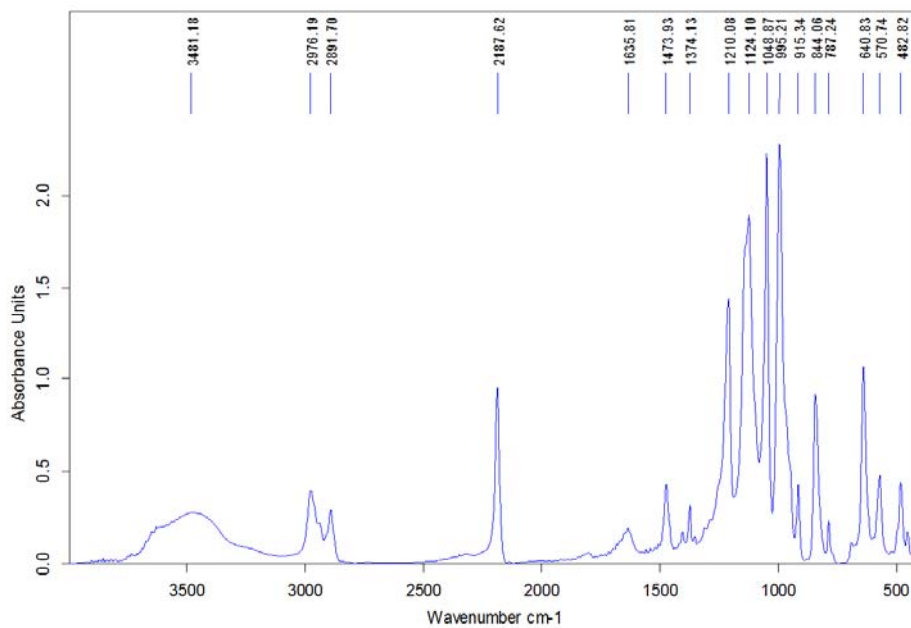


Figure S3. IR spectrum of **2**

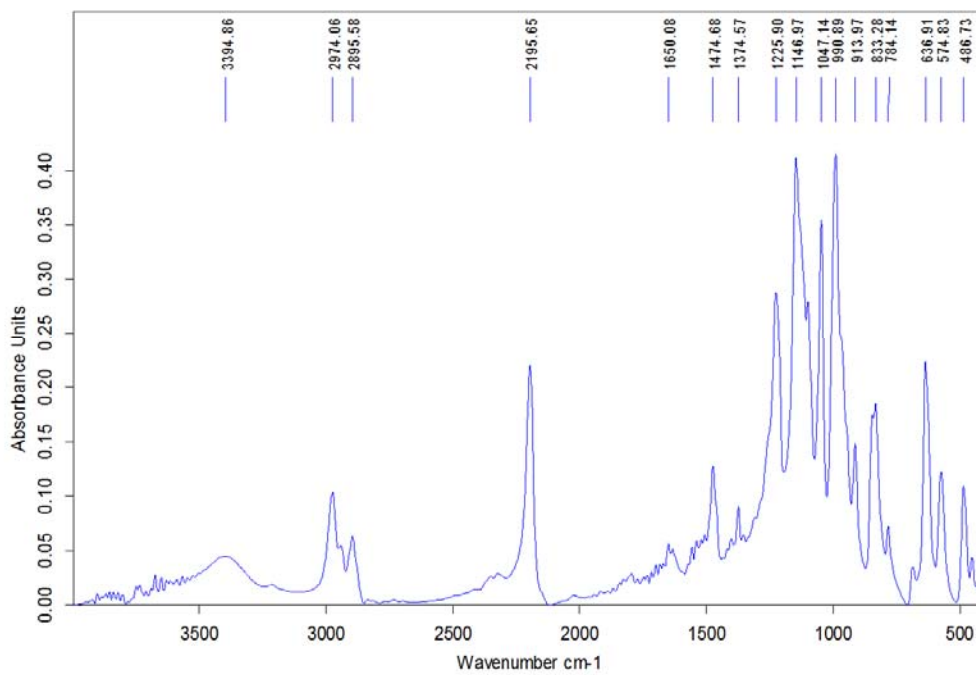


Figure S4. IR spectrum of **3**

The electronic absorption spectra

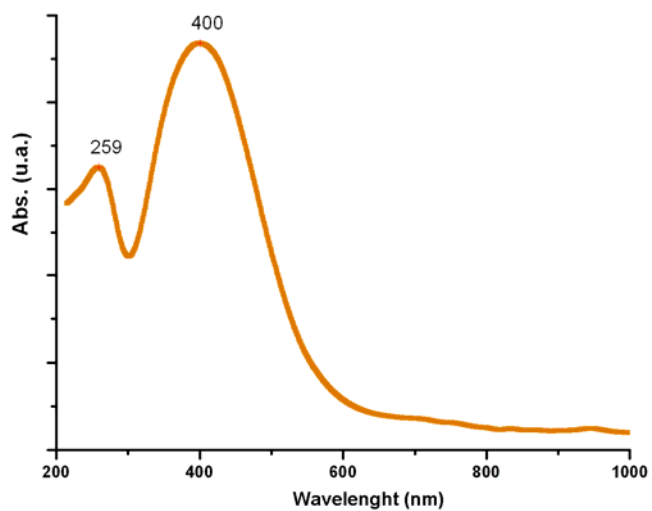


Figure S5 The electronic absorption spectrum in diffuse reflectance mode in the solid state for **2**

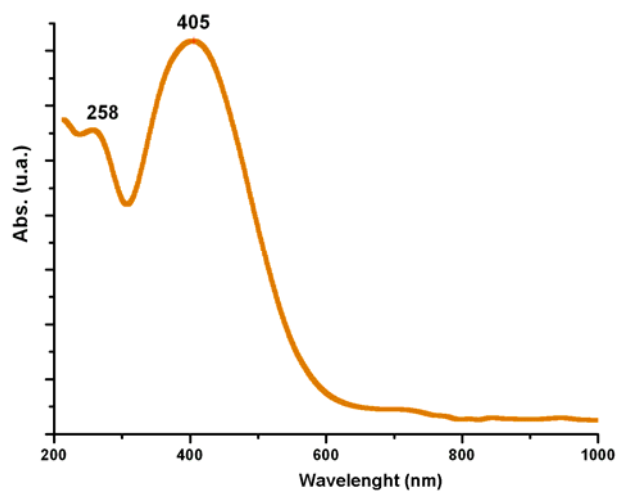


Figure S6 The electronic absorption spectrum in diffuse reflectance mode in the solid state for **3**

PXRD characterization compound 3

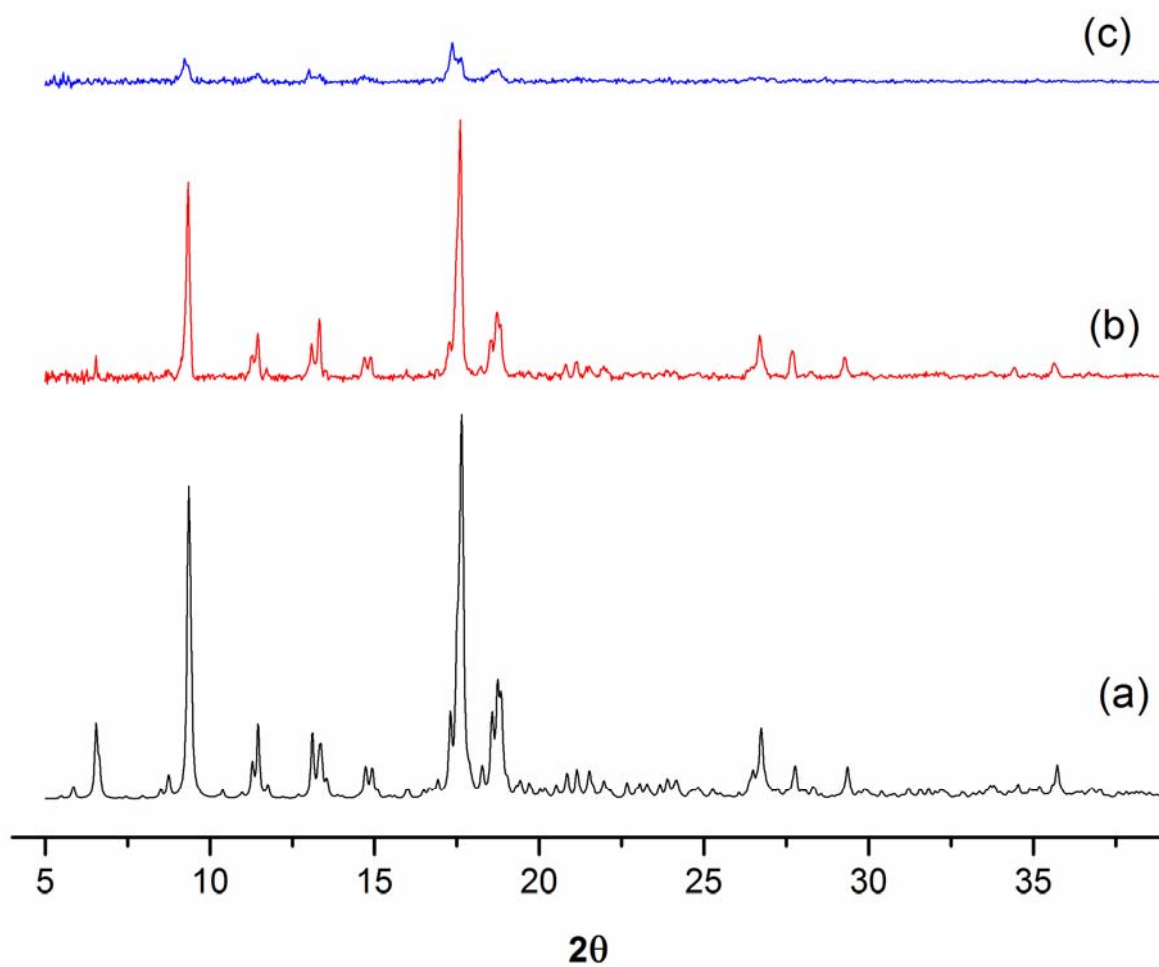


Figure S7 Comparison of the simulated (a), recorded (b) and recorded after deshydration at 373K for 1 hour under vacuum (c) , PXRD pattern for **3**.