

C_3 symmetric tris(phosphonate)-1,3,5-triazine ligand: homopolymetallic complexes and its radical anion^{†‡}

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The ligand 2,4,6-tris(dimethoxyphosphonate)-1,3,5-triazine **L** has been synthesized and its single crystal X-ray structure determined. The occurrence of $P=O \cdots \pi$ intermolecular interactions, suggested by the short $P=O \cdots$ triazine distances of 3.16–3.35 Å, is observed. The electrochemical reduction of the ligand shows its electron acceptor character by the formation of a stable radical anion. The hyperfine structure observed in the EPR spectra, combined with a theoretical DFT study, evidences the full delocalization of the unpaired electron mainly on the triazine core, with some participation of the phosphonate groups. Theoretical calculations are in agreement with the experimental values of the hyperfine coupling constants of 11.81 G for A_{iso}^{31P} and 1.85 G for A_{iso}^{14N} . Homopolymetallic complexes, formulated as $\{L[Cu(hfac)_2]_3\}$ (**1**), $\{L_2[Co(hfac)_2]_3\}$ (**2**) and $\{L_2[Mn(hfac)_2]_3\}$ (**3**) ($hfac$ = hexafluoroacetylacetonate), have been synthesized and structurally characterized.

Introduction

The synthesis and use of polytopical ligands appropriately designed to provide, upon coordination of diverse metal-containing fragments, discrete polymetallic complexes or coordination networks have known a tremendous and continuously increasing development in the last two decades,¹ especially within the more general frame of the crystal engineering.² One of the main objectives of this approach is the preparation of hybrid metal–organic solids with various properties, such as magnetism, conductivity, luminescence, spin-crossover, *etc.*, afforded by the coordinated metal, the ligand, or both.³ Therefore, the design and use of new functional multi-coordination site ligands is crucial for the continuous development of this field. In this respect, 1,3,5-triazine ligands with ligating groups appended in relative *meta* positions are very attractive in view of their three-fold symmetry, potentially leading to trimetallic building blocks, a favorable situation for the occurrence of ferromagnetic interactions through

spin-polarization mechanism.⁴ Moreover, the triazine moiety, as evidenced by its relatively accessible one-electron reduction potential,⁵ possesses electron-acceptor properties, which can be tuned by the substituents,⁶ and also luminescence properties in some derivatives.⁷ The large majority of the coordinating units attached to the 2,4,6 positions of the 1,3,5-triazine ring consists of N-donor sites, with the triazine nitrogen atoms being involved in only few cases in the coordination of the metallic center. Accordingly, C_3 symmetric tritopical ligands such as 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt),⁸ or 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine (dipytriz)⁹ have been widely used in diverse metallic complexes with various architectures, while among other related ligands, less employed, one can cite 2,4,6-tris(2-pyridyl)-1,3,5-triazine,^{4c,10} 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpymt),^{10,11} 2,4,6-tris(*p*-tetrazolyl-phenyl)-1,3,5-triazine,¹² or 2,4,6-tris(4-((pyridine-4-ylthio)methyl)-phenyl)-1,3,5-triazine.¹³ Comparatively, 1,3,5-triazines containing coordinating groups other than azaheterocycles have been only scarcely explored, for example some interesting coordination complexes being provided by the triphosphine 2,4,6-tris(diphenylphosphino)-1,3,5-triazine.¹⁴ Besides the phosphino groups, which coordinate metals through the λ^3 -phosphorus lone pair, another type of phosphorus-based ligands consists of the family of the neutral mono or polytopical phosphonate esters $(RO)_2P(=O)R$ ¹⁵ and phosphine oxides $R_3P=O$.¹⁶ Within these two classes of compounds the phosphoryl groups play the role of the ligand through the oxygen atom, the large majority of the complexes synthesized so far being based on lanthanides,^{15,16} as a consequence of their well-known oxophilicity. In this respect, a peculiar series of ligands combining the 1,3,5-triazine platform and phosphonate esters substituents is represented by the 2,4,6-tris(phosphonate)-1,3,5-triazines family (Scheme 1), reported in 1957.¹⁷ Nevertheless, since their synthesis,¹⁸ no further studies dealing with either structural or coordination chemistry investigations have been reported, despite their

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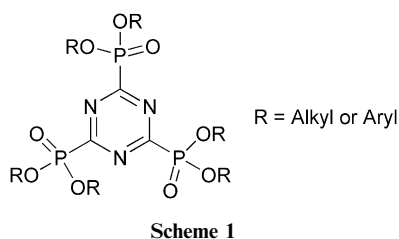
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[†] To the memory of Pascal Le Floch (1958–2010).

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potential interest as three-fold symmetric tritopical ligands, which could also present interesting electron acceptor properties thanks to the triazine platform.

We have therefore undertaken a systematic study on these still unexplored ligands and we describe herein the single crystal X-ray structure of the 2,4,6-tris(dimethoxyphosphonate)-1,3,5-triazine **L** ($R = \text{Me}$ in Scheme 1). The reduced species of **L** is investigated through EPR measurements and theoretical DFT calculations, in order to assess on its stability and electron delocalization. **L** is shown to form homopolymetallic complexes with the paramagnetic centers Cu(II) , Mn(II) and Co(II) as M(hfac)_2 ($\text{hfac} = \text{hexafluoroacetylacetonate}$) fragments; information about the coordination stereochemistry in these complexes is obtained from their crystal structure.

Results and discussion

Synthesis, single crystal X-ray structure and electrochemistry of **L**

The tritopical ligand **L** has been synthesized following an Arbusov-type rearrangement between the 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) and trimethyl phosphate with no addition of solvent, as previously described.¹⁷ The quantitative formation of the compound is ascertained by the unique resonance observed in ^{31}P -NMR at 3.3 ppm. The infrared spectrum shows in particular the vibration of the $\text{P}=\text{O}$ bond at 1263 cm^{-1} , value which should shift upon coordination to a metal centre. Colourless crystals, suitable for X-ray diffraction analysis, were obtained by recrystallization from an acetone–diethyl ether mixture. The compound crystallizes in the monoclinic system, space group $P2_1/a$, with one independent molecule in the asymmetric unit. Although the molecule could in principle present a C_3 symmetry axis, its conformation in the solid state possesses no symmetry element (Fig. 1).

Moreover, the oxygen atoms of one phosphonate group are disordered over two positions, with a ratio $\text{O(A)}:\text{O(B)}$ refined at 0.83:0.17. Selected bond lengths and angles are listed in Table T1 (ESI†). The $\text{P}=\text{O}$ distances are shorter by about 0.1–0.12 Å than the $\text{P}-\text{O}$ bonds, while the CN bonds of the triazine ring range all around 1.33–1.34 Å. The three phosphoryl groups form dihedral angles with the triazine cycle of 59.9° for $\text{P(1)}=\text{O(4)}$, 65.9° for $\text{P(2)}=\text{O(6)}$, and 15.5° (on average) for $\text{P(3)}=\text{O(8)}$. Interestingly, the molecules form chains upon interaction between the $\text{P(1)}=\text{O(4)}$ and $\text{P(2)}=\text{O(6)}$ groups and the neighboring triazine rings, as ascertained by the short distances between O(4) or O(6) and the triazine atoms, respectively (Fig. 2), with distances of

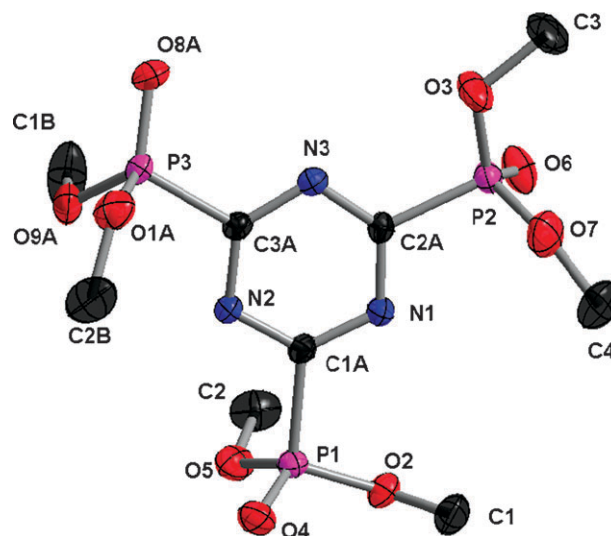


Fig. 1 Molecular structure of **L** in the solid state with thermal ellipsoids drawn at the 40% probability level (H atoms omitted). Only the major form (80%) of the phosphonate group at P(3) is shown.

3.16–3.35 Å. To the best of our knowledge, this is the first crystal structure where this type of $\text{P}=\text{O} \cdots \pi$ intermolecular interaction is evidenced.

Generally, triazine derivatives show rather good electron acceptor character, which depends on the substituents attached to the ring.^{5,6c} Since the three dimethoxy-phosphoryl substituents should in principle exert an electron withdrawing effect on the ring, one can reasonably expect good electron acceptor properties for the ligand **L**. In order to check this assumption, cyclic voltammetry measurements have been performed with a solution of **L** in THF. Interestingly, the compound shows a reversible reduction wave at $E_{1/2} = -1.05\text{ V vs. Ag/AgCl}$ (Fig. 3). Moreover, the values of i_a and i_c are hardly sensitive to the number of scans, thus suggesting that the radical anion $\text{L}^{\bullet-}$ is stable.

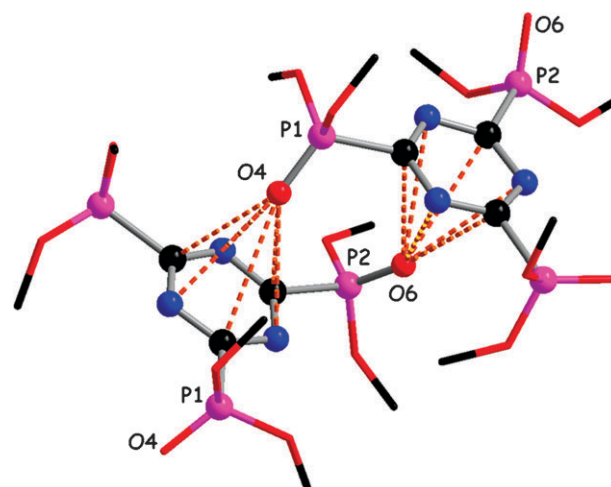


Fig. 2 Formation of chains of **L** through short $\text{P}=\text{O} \cdots \text{triazine}$ contacts highlighted in dotted lines.

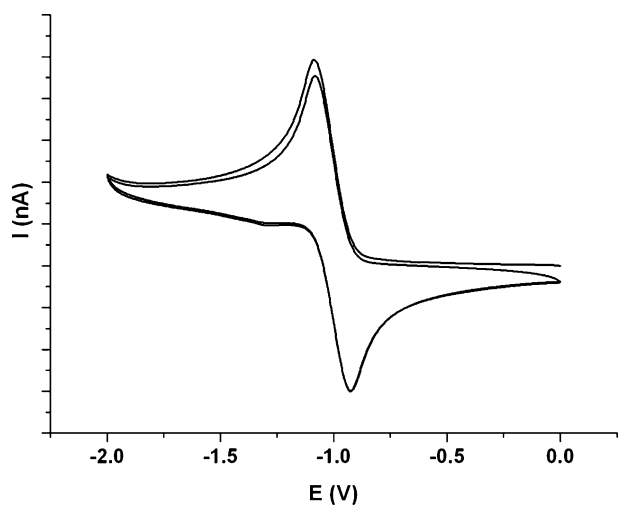


Fig. 3 Cyclic voltammetry of **L** (0.1 mol L⁻¹ solution of [(*n*-Bu)₄N]PF₆ in THF, 0.1 V s⁻¹, ref. Ag/AgCl).

EPR spectroscopy and theoretical study on the radical anion L^{•-}

The expected stability of the radical anion of **L** prompted us to undertake an EPR study to investigate on the electron delocalization. The electrochemical reduction of **L** (5×10^{-3} M) in a CH₂Cl₂ solution with 0.1 M [(*n*-Bu)₄N]PF₆ at 213 K leads to the spectrum presented in Fig. 4. No colour change is observed upon reduction. Switching off the voltage causes a decrease in the intensity of the signal, which disappears within minutes.

Simulation of the spectrum by taking into account the coupling of the unpaired electron with three equivalent ³¹P and three equivalent ¹⁴N nuclei, with isotropic hyperfine coupling constants of $A_{\text{iso}} = 11.81$ G and $A_{\text{iso}} = 1.85$ G, respectively, perfectly reproduces the experimental spectrum. The line-width is rather large (close to 1 G), thus suggesting that some dynamic effects occur. The hyperfine pattern is, *a priori*, consistent with a full delocalization of the electron on the triazine ring. In order to determine the most stable

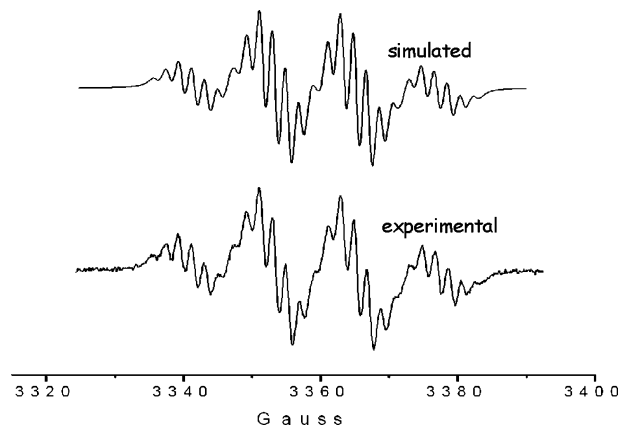


Fig. 4 Simulated and experimental EPR spectra of the radical anion L^{•-} generated by the electrochemical reduction of **L** (CH₂Cl₂ sol., [(*n*-Bu)₄N]PF₆ 0.1 M, $T = 213$ K, $\nu = 9426$ MHz, $g_{\text{iso}} = 2.0047$).

conformations of the radical anion species L^{•-} and to estimate the coupling constants and the spin distribution, theoretical calculations at the DFT level have been undertaken. The geometry optimization of the radical anion was performed with the Turbomole package¹⁹ (B-P86 functional and SV(P) standard basis set). Four energy minima have been identified (Fig. 5), the small differences in between being essentially due to the rotation of the phosphonate groups around the C(triazine)–P bonds.

The dihedral angles between the triazine (TZ) ring and the P=O groups, which mainly characterize the differences between the four energy minima are listed in Table 1.

They show the same trend as the experimental values (*vide supra*), since there are always two rather close values which are largely superior to the third one.

Min **4** is found to correspond to the most stable isomer; the energy differences between the four minima are, however, particularly small (ΔE (kcal mol⁻¹) = 2.35 for Min **1**, 0.35 for Min **2**, 0.46 for Min **3**, 0 for Min **4**). It is clear that in solution at least the four stable rotamers provided by the gas phase calculations can coexist and that exchange between these conformations will likely induce some line-width broadening. The isotropic hyperfine coupling constants, calculated at the DFT level (UB3LYP/6-31G*) with the Gaussian03 package,²⁰ are shown in Table 2.

Taking into account a rapid exchange in solution between the four stable conformations together with the indiscernability between the three P and the three N atoms, averaged coupling constants ¹⁴N- A_{iso} of 2.47 G and ³¹P- A_{iso} of -10.19 G are calculated. They very well agree with the experimental values.

The single occupied molecular orbitals (SOMOs) of each optimized conformation (Fig. 6) clearly show a full delocalization of the electronic density on the triazine core, with some contribution of the (O)P(OMe)₂ groups.

The electronic spin distribution for each of the four energy minima strongly supports this analysis; for each rotamer the unpaired electron is found at 90% on the triazine ring and at 10% on the phosphonate groups (ESI†).

These combined experimental and theoretical investigations clearly evidence the propensity of the ligand **L** to generate a rather persistent, fully delocalized, radical anion, which could be also considered as potential ligand.

Synthesis, spectroscopic characterization and structural investigations of the metal complexes 1–3

As outlined in the Introduction, the compound **L** is *a priori* a tris(monodentate) ligand, appropriately designed for the preparation of trimetallic metal complexes. Since the ligand is neutral, in order to avoid any charge balance issues, we have focused during this work on the use of the neutral paramagnetic transition metal fragments M^{II}(hfac)₂ (hfac = hexafluoro-acetylacetonate). Although the metallic centers Cu(II), Co(II) and Mn(II) are not particularly oxophilic, the coordination by the electron withdrawing groups hfac⁻ exalts their coordination propensity towards weaker ligating groups such as P=O, when non-coordinating solvent are used. Accordingly, the complexes **1–3** have been conventionally synthesized by the direct reaction of the ligand **L** with the

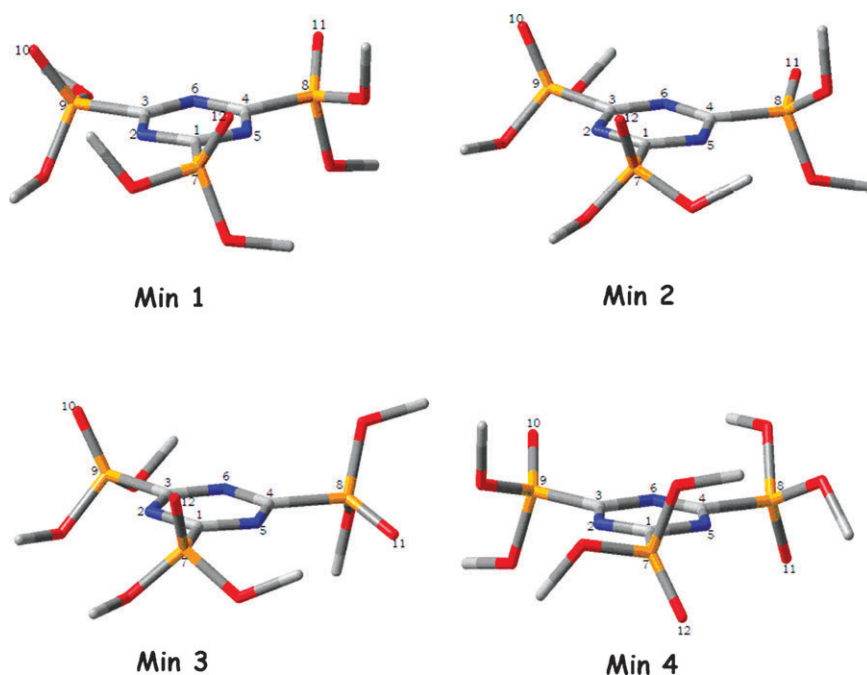


Fig. 5 Optimized minima for the radical anion $L^{\bullet-}$ (DFT/B-P86/SV(P)).

Table 1 Dihedral angles TZ...P=O in the optimized structures of $L^{\bullet-}$

Dihedral angles ($^{\circ}$)	Min 1	Min 2	Min 3	Min 4
$N_5C_1P_7O_{12}$	60.06	100	94.2	-59.03
$N_2C_3P_9O_{10}$	64.93	76.52	76.14	141.95
$N_6C_4P_8O_{11}$	39.39	17.35	-158.18	-74.66

$M(hfac)_2$ precursors in a 1:1 mixture of CH_2Cl_2 -hexane. Suitable single crystals for the three compounds have been grown upon slow evaporation of the solvent mixture. Their infrared analysis shows the stretching frequency for the P=O bond at 1211 cm^{-1} (**1**), 1198 cm^{-1} (**2**), and 1206 cm^{-1} (**3**), to be compared with 1263 cm^{-1} for the free ligand. Other vibrations such as the stretching of the C=N and P-O bonds do not practically vary, while in the complexes the characteristic vibrations of the hfac ligand, such as the stretching of the C-O (1640 – 1650 cm^{-1}) and C-F (1148 cm^{-1}) bonds, are clearly identified. The electronic absorption spectra in diffuse

reflectance mode in the solid state for the complexes and for the ligand are presented in Fig. 7. They show some common and also specific features. For example, the bands observed at $\lambda = 310$ – 330 nm obviously arise from ligand based π – π^* transitions. Then, in the complexes, the less intense bands at λ_{max} 432 nm (**1**), 423 nm (**2**), and 406 nm (**3**) can be attributed to some LMCT transitions. In the complex **1**, the relatively intense band at $\lambda_{\text{max}} = 716\text{ nm}$, with an asymmetric shape, is very likely generated by d – $d_{x^2-y^2}$ transitions, typical for a d^9 ion in a square pyramid environment.²¹ For the Co(II) complex, **2**, one out of the three expected d – d bands for a (pseudo)octahedral Co(II) chromophore, namely the one due to the $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transition, appears at $\lambda_{\text{max}} = 539\text{ nm}$.²² The spectrum of the Mn(II) complex, **3**, does not contain any crystal field bands since the d – d transitions are spin forbidden, and the intensity of the corresponding bands, if any, is very low. Consequently, the manganese complex has a light yellow color.

Table 2 Calculated isotropic hyperfine coupling (in Gauss) for the four minima of $L^{\bullet-}$ together with the averaged values

	$^{14}\text{N-A}_{\text{iso}}$	$^{31}\text{P-A}_{\text{iso}}$	Average $^{14}\text{N-A}_{\text{iso}}$	Average $^{31}\text{P-A}_{\text{iso}}$
Min 1	5.85 2.20 -0.88	-3.70 -19.50 -9.35	2.39	-10.85
Min 2	6.22 0.34 1.05	-5.73 -18.01 -5.14	2.53	-9.63
Min 3	6.01 -0.47 1.98	-8.22 -18.07 -3.62	2.51	-9.97
Min 4	-0.41 5.97 1.79	-7.38 -4.13 -19.42	2.45	-10.31
Average of the four minima			2.47	-10.19

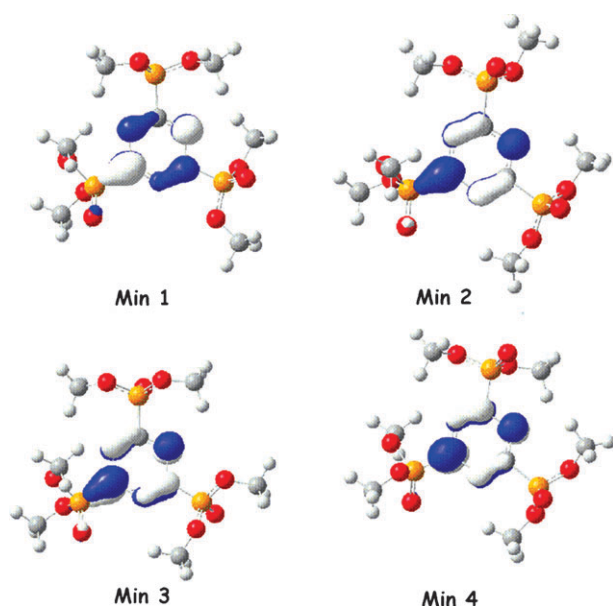


Fig. 6 SOMOs of the optimized conformations of L^{2-} .

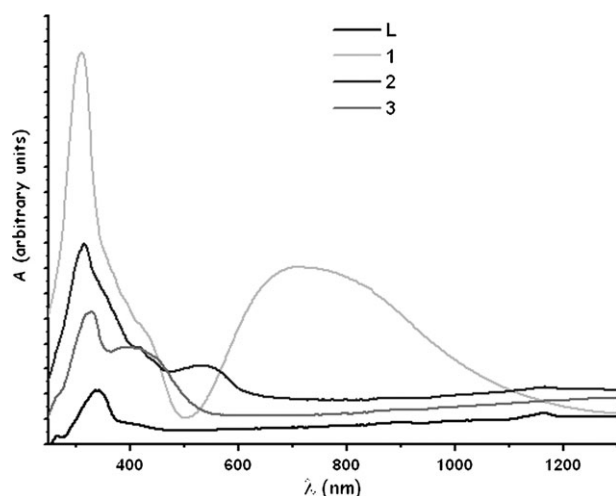
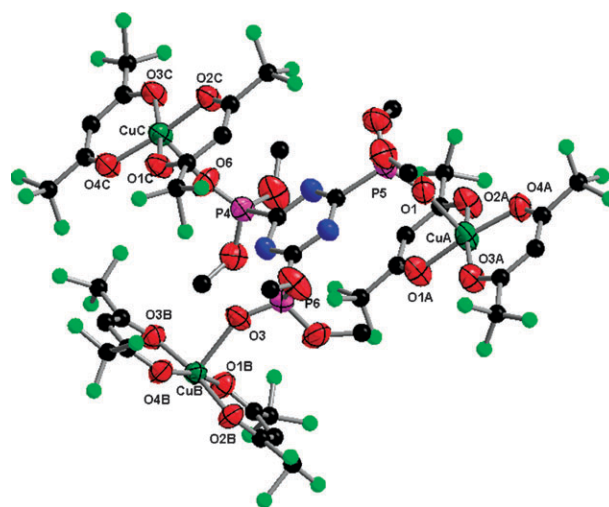


Fig. 7 Solid state absorption spectra on **L** and **1–3**.

The complex **1** has been isolated as light green crystals. The compound, formulated as $\{L[Cu(hfac)_2]_3\}$, crystallizes in the monoclinic system, space group $P\bar{1}$, with one independent molecule in the asymmetric unit. Three $Cu(hfac)_2$ fragments, with the metallic centers being pentacoordinated by five oxygen atoms provided by two hfac units and one $P=O$ group, are connected through the tris(phosphonate)–triazine ligand within a triangular geometry (Fig. 8).

The coordination stereochemistry of the metal ion is square pyramidal, with the hfac ligands in equatorial position and the oxygen atom of the phosphoryl group in apical position. The apical Cu–O distances amount to 2.221(6) Å for Cu(A)–O(1), 2.186(4) Å for Cu(B)–O(3), and 2.214(5) Å for Cu(C)–O(6), these distances being about 0.2 Å longer than (P)O–Cu bonds in complexes described in the literature,²³ yet, in these latter, the phosphonate ligands are derived from the corresponding phosphonic acids. The basal plane of the pyramid is formed by the oxygen atoms of the two hfac ligands, with Cu–O bond



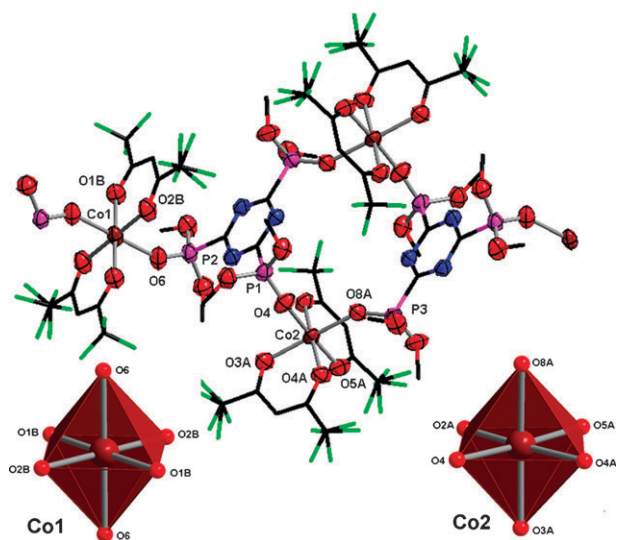


Fig. 10 Crystalline structure of the complex **2** (C and F atoms not shown and H atoms omitted for clarity), with an emphasis on the coordination sphere of the two cobalt ions (thermal ellipsoids drawn at the 40% probability level).

Cu...phosphonate coordination is weak and dissociation occurs in solution.

The complexes **2** and **3**, formulated as $^1_\infty\{\text{L}_2[\text{Co}(\text{hfac})_2]_3\}$ and $^1_\infty\{\text{L}_2[\text{Mn}(\text{hfac})_2]_3\}$, respectively, are isomorphous and crystallize in the triclinic system, space group $P\bar{1}$. Only the structure of the Co(II) complex **2** will be detailed hereafter (see ESI† for **3**). The asymmetric unit consists of a cobalt ion Co(1) on an inversion center, a second cobalt ion Co(2) in general position, and three hfac and one L ligands in general positions (Fig. 10).

Although the coordination stereochemistry of both cobalt ions is octahedral, the arrangement of the two hfac and two P=O ligands is different. Selected bond lengths and angles are listed in Table T1 (ESI†). For Co(1) the equatorial plane is occupied by four oxygen atoms provided by two hfac fragments, with Co–O bond lengths of 2.063(2) Å for Co(1)–O(1B) and 2.040(2) Å for Co(1)–O(2B). At a somewhat longer distance (2.109(3) Å), are situated the oxygen atoms O(6) of two apical P=O ligands. This value is similar to the ones reported in the literature for Co(II)–O=P complexes with phosphonate ligands.²⁴ In the coordination sphere of the Co(2) ions, which form centrosymmetric dyads through a double bridging by the P(1)=O(4) and P(3)=O(8) groups from two ligands L, one hfac ligand is situated in the equatorial plane, while the other coordinates the metal in one equatorial and one apical positions. The remaining equatorial and apical positions are occupied by the O(4) and O(8) oxygen atoms of the phosphoryl groups, at distances which are similar to those with the hfac ligands. On each triazine ligand of the dyad the third phosphoryl group P(2)=O(6) coordinates Co(1) ions, as mentioned above, thus leading to the development of coordination polymeric chains (Fig. 11).

The shortest Co...Co distances within the chains amount to 8.55 Å for Co(1)...Co(2) and 8.00 Å for Co(2)...Co(2). Here again, magnetic couplings between the metallic ions are expected to be negligible.

Magnetic susceptibility measurements of 1–3

Since the three complexes contain paramagnetic ions, variable temperature magnetic susceptibility measurements have been performed. For the trinuclear Cu(II) complex **1**, the room temperature χT product is $1.3 \text{ cm}^3 \text{ K mol}^{-1}$, which is in good agreement with the expected value for the presence of three Cu(II) ions ($S = 1/2$, $C = 0.42 \text{ cm}^3 \text{ K mol}^{-1}$) taking into account a g value of 2.12. When the temperature is lowered, the χT product at 1000 Oe stays constant (Fig. 12) down to 1.8 K indicating a Curie behaviour and confirming that the magnetic interaction between Cu(II) centres through the ligand is extremely weak and not measurable with data above 1.8 K. For the chain polymeric complexes **2** and **3**, the room temperature χT product is 10.2 and $13.5 \text{ cm}^3 \text{ K mol}^{-1}$, respectively, which is in good agreement with the expected values for the presence of three Co(II) ($S = 3/2$, $C \approx 3.4 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.7$) and Mn(II) ions ($S = 5/2$, $C = 4.5 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.03$).²⁵ When the temperature is lowered, the χT product at 1000 Oe for **3** stays roughly constant down to 20 K (Fig. 12). Below this temperature, the χT product decreases slightly and reaches $13.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. This thermal behavior indicates a Curie–Weiss behaviour with a Curie constant of $13.49(3) \text{ cm}^3 \text{ K mol}^{-1}$ and an extremely small Weiss constant of $-0.08(1) \text{ K}$. This result demonstrates the antiferromagnetic nature of the interaction between Mn(II) centres through the ligand but also its very weak amplitude. On the contrary, the χT product at 1000 Oe for **2** continuously decreases down to 1.8 K, to reach $6.6 \text{ cm}^3 \text{ K mol}^{-1}$ (Fig. 12). Expecting however negligible magnetic interactions between Co(II) centres, as already seen for **1** and **3**, this thermal behavior is likely solely due to the presence of spin–orbit coupling well known in Co(II) systems. This effect results in the splitting of the energy levels arising from the $^4\text{T}_{1g}$ ground term which finally stabilises a doublet ground state at low temperatures.^{25a}

It is thus clear, that the ligand L, in spite of its propensity to assemble three metal ions either in discrete or polymeric structures, is not adapted to promote strong magnetic coupling. The communication between the coordinated metallic centres could be possibly enhanced by the use of the radical anion of the ligand, when taking into account the full delocalization of the unpaired electron.

Conclusions

During this work we have synthesized and structurally characterized the C_3 symmetric ligand 2,4,6-tris(dimethoxyphosphonate)-1,3,5-triazine L. An interesting feature, consisting in the establishment of P=O... π intermolecular interactions between the phosphoryl groups and the triazine ring, is observed in the crystal structure of L. As shown by cyclic voltammetry, electrochemical reduction of L is reversible. EPR spectroscopy indicates that the resulting radical anion is rather persistent. Measured hyperfine constants, together with theoretical calculations, demonstrate the delocalization of the unpaired electron on the triazine ring. Paramagnetic transition metal complexes based on the tritopic monodentate ligand L have been synthesized and their single crystal X-ray structure described. Because of the relatively long range distance

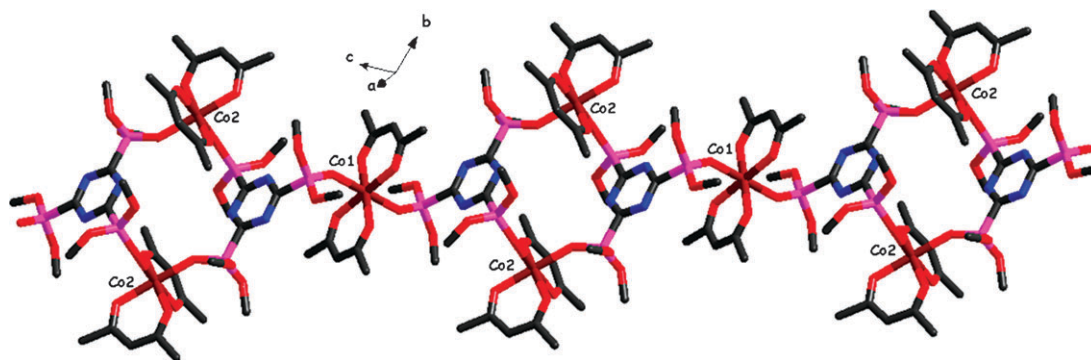


Fig. 11 Coordination polymeric chain in **2** (H and F atoms omitted).

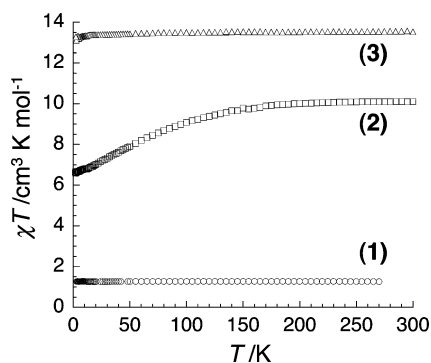


Fig. 12 Temperature dependence of χT product (χ being the molar magnetic susceptibility defined as M/H) for **1** (circles), **2** (squares) and **3** (triangles) under 0.1 T.

between the metal ions, no significant magnetic coupling could be detected. Further work will be devoted to the use of the radical anion of **L** in coordination chemistry, as well as that of the anionic ligands derived from the triphosphonic acid of **L**.

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 . Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet; d, doublet. 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 200–2000 nm range were recorded on a JASCO V-670 spectrometer using MgO as a standard.

Syntheses

The ligand **L** = 2,4,6-tris(dimethoxyphosphonate)-1,3,5-triazine has been synthesized as previously reported.¹⁷ Colourless crystals suitable for X-ray diffraction were obtained by recrystallization from acetone-diethylether mixture. ^1H NMR (CDCl_3): δ 4.06 (d, $^3J_{\text{H-P}}$ = 10.5 Hz, OMe). ^{31}P NMR (CDCl_3): δ 3.3 (s). IR (cm^{-1} , KBr): 2964, 2860, 1509 ($\text{C}=\text{N}$), 1263 ($\text{P}=\text{O}$), 1055 ($\text{P}-\text{O}$), 1020, 861, 754, 578, 524.

Anal. Calcd. for $\text{C}_9\text{H}_{18}\text{N}_3\text{O}_9\text{P}_3$: C, 26.67; H, 4.48; N, 10.37%. Found C, 26.42; H, 4.31; N, 10.48%.

The three complexes $\{\text{L}[\text{Cu}(\text{hfac})_2]_3\}$ (**1**), $1_\infty\{\text{L}_2[\text{Co}(\text{hfac})_2]_3\}$ (**2**), and $1_\infty\{\text{L}_2[\text{Mn}(\text{hfac})_2]_3\}$ (**3**), have been synthesized by the same general procedure: to a solution of **L** (0.05 mmol) in 20 mL 1:1 CH_2Cl_2 –hexane mixture, were added 50 mL solution of $[\text{M}(\text{hfac})_2] \cdot n\text{H}_2\text{O}$ (0.15 mmol in 1:1 CH_2Cl_2 –hexane mixture). The resulting solutions were stirred for about 1.5 h and then filtered. The slow evaporation of the filtrate at room temperature yielded green crystals (**1**), dark-red crystals (**2**) and yellow crystals (**4**). IR data (KBr, cm^{-1}): Complex **1**: 2966, 1640 ($\text{C}-\text{O}$), 1533 ($\text{C}=\text{N}$), 1482, 1257 ($\text{C}-\text{C}$), 1211 ($\text{P}=\text{O}$), 1148 ($\text{C}-\text{F}$), 1054 ($\text{P}-\text{O}$), 858, 803, 747, 681, 597. Anal. Calcd. for $\text{C}_{39}\text{H}_{24}\text{Cu}_3\text{F}_{36}\text{N}_3\text{O}_{21}\text{P}_3$: C, 25.47; H, 1.32; N, 2.29%. Found C, 25.59; H, 1.40; N, 2.38%. Complex **2**: 2965, 1650 ($\text{C}-\text{O}$), 1509 ($\text{C}=\text{N}$), 1466, 1260 ($\text{C}-\text{C}$), 1198 ($\text{P}=\text{O}$), 1150 ($\text{C}-\text{F}$), 1055 ($\text{P}-\text{O}$), 1020, 861, 754, 670, 524. Anal. Calcd. for $\text{C}_{48}\text{H}_{42}\text{Co}_3\text{F}_{36}\text{N}_6\text{O}_{30}\text{P}_6$: C, 25.84; H, 1.90; N, 3.77%. Found C, 25.69; H, 1.81; N, 3.61%. Complex **3**: 2970, 1649 ($\text{C}-\text{O}$), 1556, 1531, 1505 ($\text{C}=\text{N}$), 1256 ($\text{C}-\text{C}$), 1206 ($\text{P}=\text{O}$), 1148 ($\text{C}-\text{F}$), 1052 ($\text{P}-\text{O}$), 866, 798, 759, 655, 583. Anal. Calcd. for $\text{C}_{48}\text{H}_{42}\text{F}_{36}\text{Mn}_3\text{N}_6\text{O}_{30}\text{P}_6$: C, 25.98; H, 1.91; N, 3.79%. Found C, 25.71; H, 1.82; N, 3.62%.

X-Ray structure determinations

Details about data collection and solution refinement are given in Table 3. X-Ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer for **L** and **3** (Mn) and on a STOE IPDS I diffractometer for **1** (Cu) and **2** (Co), both operating with a Mo- $\text{K}\alpha$ (λ = 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 .²⁶ 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 765555 (**L**), CCDC 765556 (**1**), CCDC 765557 (**2**) and CCDC 765558 (**3**).

Electrochemical studies

Cyclic voltammetry measurements were performed using a three-electrode cell equipped with a platinum millielectrode of

Table 3 Crystallographic data, details of data collection and structure refinement parameters

Compound	1	2	3
Chemical formula	C ₉ H ₁₈ N ₃ O ₉ P ₃	C ₃₉ H ₂₄ Cu ₃ F ₃₆ N ₃ O ₂₁ P ₃	C ₄₈ H ₄₂ Co ₃ F ₃₆ N ₆ O ₃₀ P ₆
<i>M</i> /g mol ^{−1}	405.17	1838.14	2229.49
Temperature, (K)	293	293	293
Wavelength, (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 1	<i>P</i> 1
<i>a</i> /Å	10.6958(8)	11.5334(11)	10.7033(11)
<i>b</i> /Å	11.0822(6)	12.8817(17)	14.7008(17)
<i>c</i> /Å	15.5505(14)	23.900(3)	15.6481(17)
α (°)	90	76.767(14)	112.260(13)
β (°)	107.187(7)	77.375(12)	98.811(13)
γ (°)	90	78.485(14)	106.294(13)
<i>V</i> /Å ³	1760.9(2)	3330.9(7)	2091.8(4)
<i>Z</i>	4	2	1
<i>D</i> _c /g cm ^{−3}	1.528	1.833	1.770
μ/mm ^{−1}	0.385	1.191	0.861
<i>F</i> (000)	840	1806	1107
Goodness-of-fit on <i>F</i> ²	1.044	0.724	0.893
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0493, 0.1080	0.0512, 0.0953	0.0468, 0.1187
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0880, 0.1273	0.1803, 0.1244	0.0816, 0.1327
Largest diff. peak and hole/e Å ^{−3}	−0.362, 0.524	−0.327, 0.400	−0.483, 0.993

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

0.126 cm² area, a silver wire pseudo-reference and a platinum wire counter-electrode. The potential values were then re-adjusted with respect to the Ag/AgCl electrode, using the ferrocene as internal reference. The electrolytic media involved a 0.1 mol L^{−1} solution of [(*n*-Bu)₄N]PF₆ in THF. All experiments have been performed at room temperature at 0.1 V s^{−1}. Experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation.

EPR measurements

EPR spectra were recorded on a Bruker ESP 300 spectrometer (X-band) equipped with a variable temperature attachment. Electrochemical reductions at a controlled potential were performed by using a quartz electrolytic cell that was present *in situ* in the EPR cavity. A silver wire electrode was used as pseudoreference. The working electrode and the counter electrode were platinum. Simulation of the spectra was performed using WINEPR SimFonia.²⁷

Computational details

Geometry optimizations of the radical anion were performed with the Turbomole package¹⁹ (B-P86 functional and SV(P) standard basis set), while the hyperfine couplings calculations were performed with the Gaussian03 package²⁰ using the B3LYP functional²⁸ and the 6-31+G* basis sets. Minima were characterized with harmonic frequency calculations (no imaginary frequencies). Molecular orbitals were represented by using the GaussView program.²⁹

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 a polycrystalline sample of 9.5 mg of **1**, 5.58 mg of **2**, and

15.21 mg of **3**. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

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