Changes in magnetic properties from solid state to solution in a trinuclear linear copper(II) complex

Iryna A. Koval,[a] Hilda Akhideno,[a] Stefania Tanase,[a] Catherine Belle,*[b] Carole Duboc,[c] Eric Saint-Aman,[b] Patrick Gamez,[a] Duncan M. Tooke,[d] Anthony L. Spek,[d] Jean-Louis Pierre[b] and Jan Reedijk*[a]

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A linear trinuclear copper(II) complex containing phenoxido- and alkoxido-bridges between the metal centers has been isolated and structurally characterized. The complex cation consists of a linear array of three copper ions, assembled by means of two doubly deprotonated ligands. The octahedral coordination sphere of the two peripheral copper(II) ions is completed by weakly bound methanol molecules, and the square-planar central metal ion is located on an exact, crystallographic inversion center. Temperature-dependent magnetic susceptibility studies reveal the presence of antiferromagnetic exchange coupling between the copper(II) ions in the trinuclear unit along with small intermolecular antiferromagnetic interactions in the low temperature range. The results were fitted in two different ways, (i) taking into account solely the exchange interaction between the adjacent metal centers or, (ii) regarding exchange interactions between both adjacent and non-adjacent copper(II) ions. Solid-state temperature-dependent X-band EPR studies in the range 4.2–250 K indicate a doublet ground spin state $|\frac{1}{2}, 1\rangle$. In solution, the ground spin state of the complex is found to be a quartet ($S = \frac{3}{2}$), suggesting a modification of the exchange coupling interactions between the copper(II) ions. The simulation of the 4.2 K solution spectrum gives rise to the best parameters $D > 0.8$ cm^{-1}, $g_\perp = 2.04$ and $g_\parallel = 2.21$.

Introduction

The design and architecture of polynuclear copper complexes have received significant attention from the scientific community in the past decades, in particular in the fields of magnetochemistry and material science.[1–3] One of the important aims regarding the design and preparation of such compounds, is to gain a better understanding of the molecular features determining the nature of exchange coupling between neighboring metal centers, through multi-atom bridging ligands.[4] Furthermore, these compounds are of interest because of their relevance to the active sites of some metalloproteins.[5–7] Polynuclear copper complexes have also attracted much attention due to their ability to perform DNA strand scission.[8–10]

Previously, some of us have reported on the synthesis and magnetic properties of several linear trinuclear copper(II) compounds with the metal ions bridged by either pyrazolato[11] or imidazolato rings.[12] In this paper, we present the synthesis, and structural and magnetic properties of a novel trinuclear linear copper(II) complex $[Cu_3(py2O)_2(CH_3OH)_2](BF_4)_2\cdot 0.75CH_3OH$ (Hpy2OH = 2-(*N*,*N*-bis(2-pyridinylmethyl)aminomethyl)-6-(hydroxymethyl)-4-methylphenol), in which two neighboring copper ions are doubly bridged by the oxygen atoms of deprotonated phenol and benzylic alcohol functions of the ligands. All trinuclear polymetallic units can be classified as (i) closed triangular, (ii) open triangular and (iii) linear, according to the spatial arrangements of the metal centers. Currently, complexes of the latter type have been described in the literature, but rarely characterized by EPR and magnetic susceptibility.[9,11–14] In the present case, solid-state magnetic susceptibility studies and EPR spectroscopy have been carried out to explore the mechanism of the exchange coupling experienced by the linear trinuclear complex. The combination of these two techniques has proved to be highly valuable for the investigation of the spin-state of the trinuclear unit, both in the crystal lattice and in solution.

Results and discussion

Synthesis

The phenol-based ligand Hpy2OH (Fig. 1) was synthesized by a reduction of the earlier reported ligand Hpy2ald,[15,16] with sodium borohydride in methanol. The trinuclear complex $[Cu_3(py2O)_2(CH_3OH)_2](BF_4)_2\cdot 0.75CH_3OH$ was prepared by mixing three equivalents of copper(II) tetrafluoridoborate hexahydrate, two equivalents of the ligand, and four equivalents of base (NBu_4OH) in methanol, followed by slow diethyl ether diffusion. The product was obtained as dark-green/brownish single crystals, suitable for the X-ray analysis.

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[a] *Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands. E-mail: reedijk@chem.leidenuniv.nl*
[b] *Département de Chimie Moléculaire, UMR-5250, ICMG FR-2607, CNRS, Université J. Fourier, BP-53, 38041 Grenoble Cedex 9, France. E-mail: catherine.belle@ujf-grenoble.fr*
[c] *High Magnetic Field Laboratory, UPR CNRS 5021, 25 Avenue des Martyrs, 38042 Grenoble Cedex 9, France*
[d] *Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

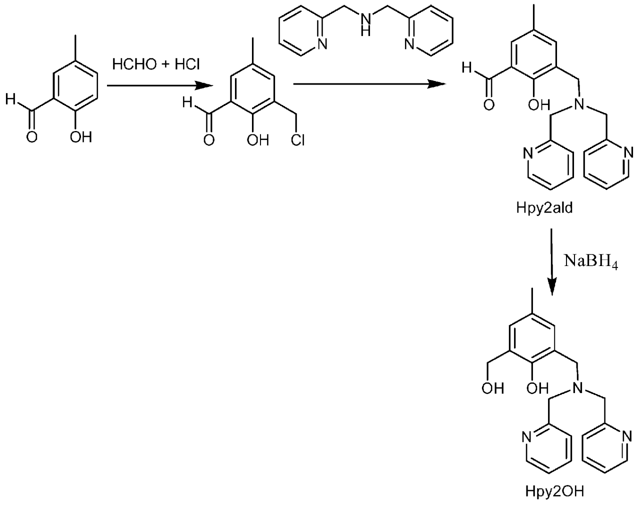

Fig. 1 The reaction scheme of the synthesis of the ligand Hpy2OH.

Crystal structure description

The compound $[Cu_3(py2O)_2(CH_3OH)_2](BF_4)_2 \cdot 0.75CH_3OH$ (**1**) crystallizes in the space group $P\bar{1}$ with one formula unit per unit cell, consisting of one cationic molecular entity $[Cu_3(py2O)_2(CH_3OH)_2]^{2+}$, two non-coordinated counter-anions BF_4^- and 0.75 molecules of methanol in the crystal lattice as non-coordinated solvent. The molecular structure of the complex cation $[Cu_3(py2O)_2(CH_3OH)_2]^{2+}$ is shown in Fig. 2.

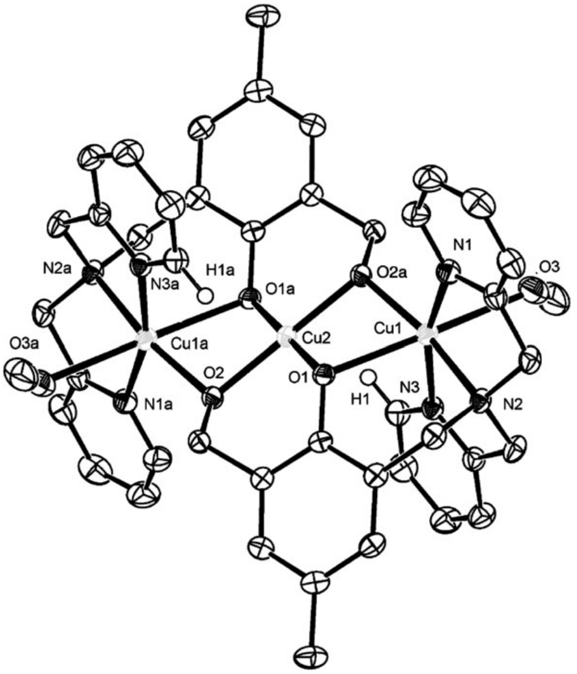

Fig. 2 ORTEP projection (50% probability level) of the complex cation $[Cu_3(py2O)_2(CH_3OH)_2]^{2+}$. Hydrogen atoms are omitted for clarity, except H1 and H1a.†

Table 1 Selected bond lengths and bond angles for the complex $[Cu_3(py2O)_2(CH_3OH)_2](BF_4)_2 \cdot 0.75CH_3OH$ (**1**)

Bond lengths/Å			
Cu1–O1	2.3021(14)	Cu1···Cu2	2.9122(5)
Cu1–O3	2.5057(19)	Cu2–O1	1.9360(14)
Cu1–N1	2.0378(19)	Cu2–O2	1.9027(15)
Cu1–N2	2.0209(17)	Cu1···Cu1a	5.8244(9)
Cu1–N3	2.001(2)		
Cu1–O2a	1.9290(15)		
Bond angles/°			
O1–Cu1–O3	172.75(6)	O1–Cu2–O2	94.85(6)
O1–Cu1–N1	90.70(6)	O1–Cu2–O1a	180
O1–Cu1–N2	93.51(6)	O1–Cu2–O2a	85.15(6)
O1–Cu1–N3	99.41(6)	Cu1–O2a–Cu2	98.93(6)
O1–Cu1–O2a	75.16(6)	Cu1–O1–Cu2	86.35(6)
O3–Cu1–N1	84.87(7)		
O3–Cu1–N2	91.66(7)		
O3–Cu1–N3	86.24(7)		
O3–Cu1–O2a	99.95(6)		
N1–Cu1–N2	83.31(7)		
N1–Cu1–N3	163.55(7)		
N1–Cu1–O2a	100.21(7)		
N2–Cu1–N3	83.15(7)		
N2–Cu1–O2a	168.10(7)		
N3–Cu1–O2a	94.94(7)		

Symmetry operation: $a = 1 - x, 1 - y, 1 - z$.

Selected bond lengths and angles are given in Table 1. The complex cation consists of a linear chain of three copper ions, two doubly deprotonated ligands and two methanol molecules, weakly bound to the two peripheral metal ions. The central metal ion Cu2 is located on an exact, crystallographic inversion center. The neighboring copper ions, located at a very short distance of 2.9122(5) Å, are doubly bridged by two oxygen atoms of the deprotonated phenol and benzylic alcohol groups of the two different ligands. The double positive charge of the cation is compensated by two tetrafluoridoborate counter-anions. In addition, 0.75 molecules of methanol per one formula unit are present in the crystal lattice.

The coordination sphere around the Cu1 ion is a distorted octahedron, with the equatorial positions occupied by the three nitrogen atoms N1, N2 and N3 from the bis(pyridylmethyl)amino arm of the ligand, at an average distance of 2.0 Å and the oxygen atom O2a from the deprotonated benzylic alcohol moiety at a distance of 1.9290(15) Å. The atoms O1 from the deprotonated phenol group, and O3 from a methanol molecule at the distances of 2.3021(14) and 2.5057(19) Å, respectively, occupy the axial positions, with the O1–Cu1–O3 angle of 172.75(6)°.

The coordination sphere around the Cu2 ion is square planar, constituted of the two *trans*-located phenolic oxygen atoms O1 and O1a, at a distance of 1.9360(14) Å, and the two *trans*-located oxygen atoms O2 and O2a of the deprotonated benzylic alcohol moieties at a distance of 1.9027(15) Å. The Cu2 ion is in the plane defined by the atoms O1, O2, O1a and O2a *i.e.* in a planar environment. The deviation from a perfect planar geometry is specified by the angles around Cu2 (O1–Cu2–O2 = 94.85(6)° and O1–Cu2–O2a = 85.15(6)°). Thus, the angles are 4.85° outside the ideal 90° value. Interestingly, the α-hydrogen atoms H1 and H1a of the pyridine

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† "a" letters in the atom labels indicate that these atoms are at an equivalent position by a symmetry operation $(1 - x, 1 - y, 1 - z)$.

rings are located in close proximity to the central copper ion (the Cu2–H1 distance is 2.621 Å), with an angle between the H1–Cu2–H1a axis and the $Cu2O_4$ plane of 88.85°. Recently, an interesting discussion about the nature of hydrogen–metal interactions (*e.g.* agostic *versus* a hydrogen bond) has emerged in the literature.[17,18] In the present case, the nature of the interaction can apparently be best described as a very weak intramolecular multicenter hetero-acceptor hydrogen bond (IMH), which involves, besides the copper ion, the oxygen atoms O1 and O2 (the corresponding H1–O1 and H1–O2 distances are 2.850 Å and 3.644 Å, respectively). Indeed, the following geometric criteria of IMH have been identified by Braga *et al.*:[19] (i) a metal–hydrogen distance $d_{M\cdots H}$ is shorter than a metal–carbon distance $d_{M\cdots C}$; (ii) the angle M···H–C is larger than 100°. On the other hand, in the case of agostic bonds, the M···H and M···C distances are comparable, whereas the C–H bond is usually elongated. In the present example, the Cu2···H1 distance is indeed shorter than the copper–carbon distance (2.621 Å *versus* 3.136 Å), with the Cu2···H1–C1 angle of 114.5°, while the C1–H1 distance is 0.95 Å.

Physicochemical properties and solution stability

The electrospray mass spectrum of **1** recorded in methanol is characterized by two peaks at $m/z = 972$ and 443. The first one corresponds to the monocharged species $[Cu_3(py2O)_2(BF_4)]^+$, whereas the second one originates from the doubly charged cation $[Cu_3(py2O)_2]^{2+}$. These data suggest that the trinuclear core remains stable in solution. The solid-state UV-Vis spectrum (diffuse reflectance) of the complex is characterized by two bands at 425 nm and 746 nm, whereas in methanol solution, two absorption bands at 400 nm (ε = 1500 M^{-1} cm^{-1}) and 743 nm (ε = 276 M^{-1} cm^{-1}) are observed. The first absorption is likely to correspond to the charge transfer band from the deprotonated phenol and/or benzylic alcohol groups of the ligand to the Cu^{II} ions, whereas the second one is attributed to the d–d transitions of the Cu^{II} ions.

The electrochemical properties of **1** have been studied by cyclic voltammetry (CV) in methanol–acetone (85 : 15 v/v), using tetra-*n*-butylammonium tetrafluoridoborate as a supporting electrolyte (the solubility of the complex in pure methanol in the presence of an excess of tetrafluoridoborate ions is very poor). The potentials have been referred to the standard Ag/AgCl + 3 M KCl reference electrode. While scanning towards the negative range of potentials, the CV curve (Fig. 3) recorded in 0.5 mM solution of **1**, is characterized by one signal at $E_{\frac{1}{2}} = -0.45$ V ($E_{pc} = -0.57$ V, $E_{pa1} = -0.32$ V at 0.1 V s^{-1}). This one-electron signal appears to be not fully reversible. Accordingly, on the reverse scan, two additional anodic waves, at $E_{pa} = +0.03$ V and +0.45 V, respectively, are observed. Not surprisingly, the mixed-valence compound obtained upon metal-centered electrochemical reduction of **1**, is unstable at the time scale of the CV, and decomposes, resulting in the formation of a mixture of species, the oxidation of which is then observed on the reverse scan. At higher potential, a fully irreversible signal at $E_{pa} = +1.04$ V is attributed to the oxygen-centered oxidation of the phenol-based ligand.

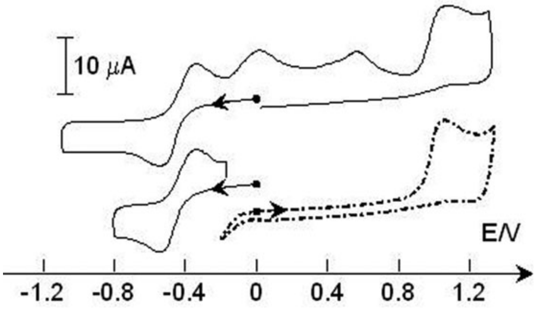

Fig. 3 Cyclovoltammetric curves recorded in 0.5 mM solution of **1** in methanol–acetone (85 : 15 v/v) + 0.1 M NBu_4BF_4 on a vitreous carbon disc (∅ = 3 mm); $V = 0.1$ V s^{-1}. Solid line: cyclovoltammetric curve recorded while scanning towards the negative range of potentials, with the direction of the scan reversed at −1.5 V; dashed line: cyclovoltammetric curve recorded while scanning towards positive range of potentials.

Magnetic susceptibility studies

The variable-temperature (2–300 K) magnetic susceptibility of **1** has been measured on a polycrystalline sample, in a field of 0.1 T. The plots $\chi_M T$ *vs.* T and χ_M *vs.* T are shown in Fig. 4; the $\chi_M T$ value at 300 K is *ca.* 0.99 cm^3 K mol^{-1}, which is somewhat lower than the spin-only value of 1.2 cm^3 K mol^{-1} expected for magnetically uncoupled trinuclear copper(II) complexes ($S_{Cu} = \frac{1}{2}$). The $\chi_M T$ value decreases smoothly by lowering the temperature, reaching a value of 0.40 cm^3 K mol^{-1} at *ca.* 7 K. The $\chi_M T$ value is practically constant from 7 K to 4 K, and there is a slight decrease to 0.38 cm^3 K mol^{-1} at 2 K. This behavior suggests the occurrence of antiferromagnetic exchange coupling between the copper(II) ions in the trinuclear unit, along with small intermolecular antiferromagnetic interactions in the low temperature range. The $\chi_M T$ *vs.* T plot has been analyzed based on the Heisenberg–Dirac–van Vleck (HDVV) spin Hamiltonian for linear trinuclear complexes,[4] $\hat{H} = -J_1(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) - J_2\hat{S}_1\hat{S}_3$, where J_1 describes the interaction between adjacent copper(II) ions whilst J_2 illustrates the interaction between non-adjacent metal centers.

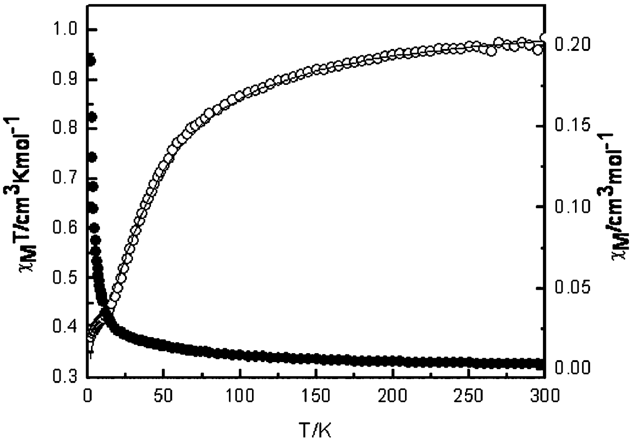

Fig. 4 Plot of χ_M (●) and $\chi_M T$ (○) of **1** *vs.* temperature under a 0.1 T applied field. Solid line represents the best fit obtained based on the HDVV spin Hamiltonian for linear trinuclear complexes.

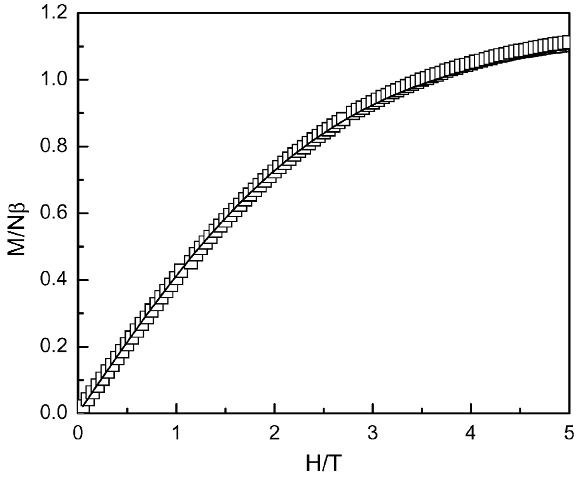

Fig. 5 The field dependence of the magnetization measured at 2 K (the solid line represents the theoretical curve calculated with the Brillouin function).

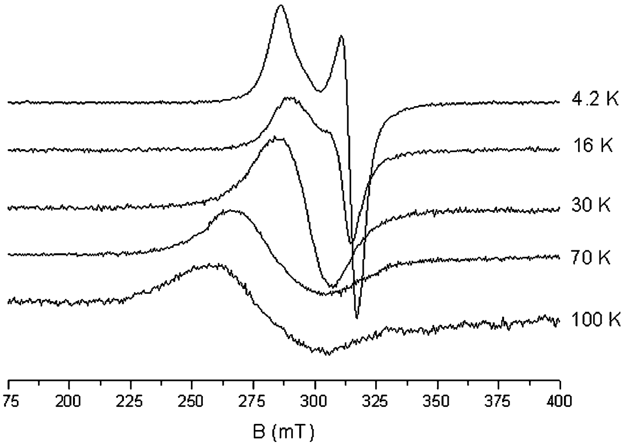

Fig. 6 Powder X-band EPR spectra of complex **1** recorded at different temperatures.

A J' parameter has been used to take into account the interactions between the trinuclear units in the molecular-field approximation, and a temperature independent paramagnetism (TIP) of 60×10^{-6} cm^3 mol^{-1} per copper(II) ion has been considered. In a first approximation, the magnetic susceptibility data have been fitted treating g, J_1 and J' as adjustable parameters and holding $J_2 = 0$. The best fit was obtained with the magnetic parameters $g = 2.15$, $J_1 = -28.73$ cm^{-1}, $J' = -0.22$ cm^{-1} with a final $R = 7 \times 10^{-5}$. These results suggest that the magnetic behavior of the complex rises from weakly antiferromagnetic coupled copper(II) ions. The field dependence of the magnetization measured at 2 K is given in Fig. 5. The magnetization varies linearly with low applied fields and then progressively tends to saturation, reaching a value of 1.12 Nβ at 5 T. The variation of the magnetization with the magnetic field follows that predicted by the Brillouin function for $S = \frac{1}{2}$ with $g = 2.26$. For trinuclear copper(II) complexes, the g tensor of the doublet ground state is related to the individual tensors of the copper(II) ions.[20] Therefore the resulting tensor for the doublet ground state is expected to be weakly anisotropic and of axial symmetry, as also suggested by the powder EPR spectra (see below). Since EPR spectroscopy is generally presented as a molecular probe allowing the determination of both the ground-state symmetry and multiplicity,[21] we have used the g parameters from the EPR spectra below 10 K ($g_\perp = 2.39$ and $g_\parallel = 2.11$) to fit the magnetic susceptibility data when J_2 is allowed to vary. The best fit is achieved with $J_1 = -14.93$ cm^{-1}, $J_2 = 0.45$ cm^{-1}, $J' = -0.06$ cm^{-1} and $R = 1.2 \times 10^{-4}$. It is worth recalling here, as previously reported, that the J_1 and J_2 parameters are strongly correlated in determining the temperature dependence of the magnetic susceptibility.[22,23] The only effect of J_2 is to modify the position of the excited doublet state, the other two states remaining unchanged. In the present case, the energy separation of the two doublets is of 14 cm^{-1}.

The weak intramolecular antiferromagnetic exchange coupling in the present complex is solely assigned to the superexchange mechanism within the central-terminal copper(II) pairs. Magneto-structural correlations for the hydroxido- or alkoxido-bridged copper(II) dinuclear complexes have been extensively studied by analyzing the influence of the Cu–O distance, the effect of the asymmetry at the bridging backbone, and the hinge distortion of the bridge.[24] Thus, an antiferromagnetic exchange coupling is found for complexes with Cu–O–Cu angles larger than 98° while ferromagnetic exchange coupling appears for smaller values of this Cu–O–Cu angle. Two possible mechanisms to account for the exchange interaction in the hydroxido-bridged Cu^{II} dinuclear complexes are the direct interaction between the copper ions and the superexchange interaction through the hydroxido bridge.[24] The decrease in the Cu–O distance causes a shortening of the Cu···Cu distance, which increases the direct interaction and the ferromagnetic contribution. Simultaneously, these changes will produce a better overlap between the orbitals on the copper ions and the donor atoms of the bridge, increasing the antiferromagnetic character of the compound. Structural modeling and magneto-structural correlations for hydroxido-bridged copper(II) dinuclear complexes have shown that the calculated J_1 values seem to indicate that the shortening of the Cu–O distance mainly affects the ferromagnetic term, diminishing the overall antiferromagnetic character of the complex.[25,26] The short Cu1···Cu2 distance (2.9122(8) Å), the high asymmetry of the Cu_2O_2 core (Cu1–O1–Cu2 = 86.35(6)°, Cu1–O2a–Cu2 = 98.93(6)°) and the hinge angle of 141.87(9)° that deviates significantly from the value of 180° (for a perfect planar structure) account for the weak antiferromagnetic interactions observed in the present trinuclear complex.

Temperature-dependent X-band EPR studies

The coupling between three $S = \frac{1}{2}$ Cu^{II} ions leads to several spin states.[4] Their relative energies depend on J_1 and J_2. J_1 indicating antiferromagnetic interactions, the ground spin state is a doublet ($|\frac{1}{2}, 1\rangle$). A second doublet ($|\frac{1}{2}, 0\rangle$) should be populated at around 15.5 K, and a quartet ($|\frac{3}{2}, 1\rangle$) at 22.5 K. Fig. 6 displays the powder EPR spectra issued from a temperature-dependent study performed between 4.2 and 250 K.

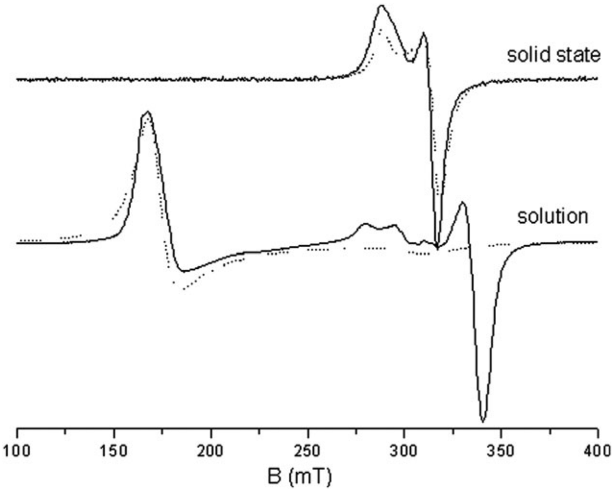

Fig. 7 Experimental (—) and simulated (···) X-band EPR spectra recorded at 7.5 K of **1** in solid state and in a methanolic solution.

Below 10 K, the spectra are characterized by two narrow peaks whose intensity decreases when the temperature is raised. The signal originates from an axial $S = \frac{1}{2}$ spin ($g_{\perp} = 2.39$ and $g_{\parallel} = 2.11$; Fig. 7, solid state) and behaves as a ground spin state. This result agrees with the magnetic experiments concluding that the ground spin state is the doublet $|\frac{1}{2}, 1\rangle$. Between 10 and 100 K, the signal broadens and is converted into a single peak shifting to low field ($g = 2.45$ at 100 K). Between 100 and 250 K, the transition does not shift but becomes broader. No evidence of a characteristic signal attributable to a spin quartet was found (between $g = 4.25$ and 5.5).[27] Assuming the rate of transition from the lowest to the excited multiplets is fast on the EPR time scale, the observed spectrum at a given temperature would be the thermal average of the spectra of the three different multiplets. Consequently, below 10 K the signal should characterize the ground spin state, whereas those at higher temperatures should also bear the contributions of the excited spin states. Furthermore, we found a non-negligible intermolecular exchange interaction J' leading to quasi isotropic or isotropic spectra. Therefore, the anisotropy of the molecular g value is usually not well defined, all the more because the g-anisotropy of the different multiplet is different.[22]

A methanolic solution of the trinuclear Cu^{II} complex has also been analyzed by EPR spectroscopy. Fig. 8 shows the EPR spectra recorded between 4.2 and 60 K. The temperature-dependent EPR measurements reveal completely different spectra compared to those recorded in the solid-state. At low temperature, the spectrum exhibits two intense signals, one centred at around 167 mT, characteristic of a quartet, and a second close to 320 mT corresponding to a mononuclear Cu^{II} species, probably resulting from the dissociation of the trinuclear compound in solution. Below 15 K, the shape of the $g = 4.04$ feature is similar and its intensity diminishes when the temperature increases. Consequently, the spin ground state of this trinuclear compound is $S = \frac{3}{2}$. Similar signals have been observed earlier for complexes characterized by a ferromagnetic J_1 exchange interaction.[13,27,28] The zero field splitting parameter of the quartet is usually large in the trinuclear Cu^{II} complexes ($|D| > 1$ cm^{-1}).[13,27,28] The energy gap between the $\pm\frac{3}{2}$ and $\pm\frac{1}{2}$ Kramers doublets ($2|D|$) is then much greater than the energy provided by the spectrometer ($\sim$0.3 cm^{-1}), leading to the observation of transitions occurring within the Kramers doublets only. The low-field transition originates from the $\pm\frac{1}{2}$ Kramers doublet and is associated to the lowest in energy considering its intensity behavior as a function of the temperature. Accordingly, the sign of D is positive. At 4.2 K, the effective g-values $g'_{\perp} = 4.04$ of this effective $S = \frac{1}{2}$ state can be assigned to the transition between the $\pm\frac{1}{2}$ levels of the quartet, whereas the $g'_{\parallel}$ can be deduced from the shape of the signal corresponding to the mononuclear Cu^{II} species. Indeed, the expected negative absorption shape of this peak is visible at around $g = 2.21$. We performed simulations of the 4.2 K spectrum: $D > 0.8$ cm^{-1}, $g_{\perp} = 2.02$ and $g_{\parallel} = 2.21$ (Fig. 7, methanolic solution). Since the transitions occur only within the $\pm\frac{1}{2}$ Kramers doublet, a precise determination of the D magnitude cannot be obtained. The g-values, however, are in good agreement with the relations established for axial systems, relating the g' values of the effective $S = \frac{1}{2}$ state and the g-values of the quartet: $g_{\perp} = g_{\perp}'/2$ and $g_{\parallel} = g_{\parallel}'$.[29,30]

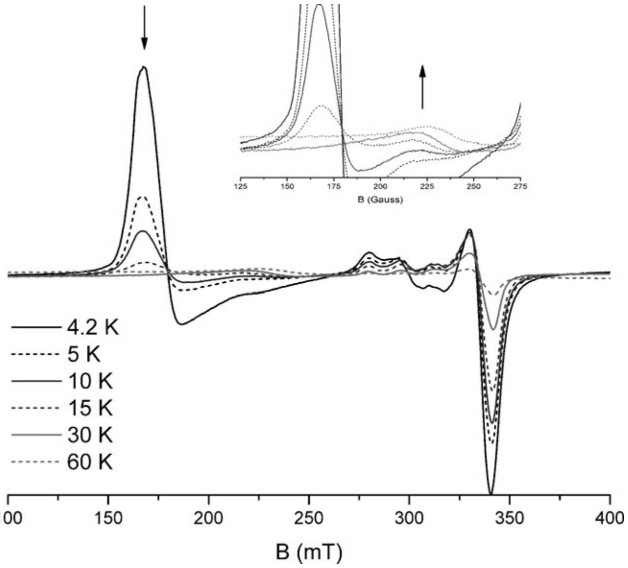

Fig. 8 X-Band EPR spectra of a methanolic solution of complex **1** at different temperatures. Inset: zoom of the spectra between 125 and 275 mT.

Above 15 K, a strong shift of the transition located at 167 mT occurs. At 60 K, it is positioned at 225 mT, leading to a variation of g between 4 and 60 K in the order of $\Delta g = 1.04$. Variations of the thermal populations of the different spin levels were assumed to explain this effect. The same phenomenon has already been detected for other linear trinuclear Cu^{II} complexes ($0.03 < \Delta g < 1.7$). [13,22,28]

In the solid state, compound **1** is characterized by a doublet ground state originating from an antiferromagnetic exchange interaction J_1, whereas in methanolic solution, **1** presents a quartet ground state. This finding reveals that the nature of the exchange interaction between the Cu^{II} ions is modified, and that in solution, the exchange coupling J_1 is ferromagnetic. Such modification of the exchange interaction is the signature of a structural change. The mass-spectroscopic data on **1** are consistent, however, with the solid-state structure of the complex. This suggests that the change in the exchange coupling nature is caused by minor deviations from the solid state geometry in solution, possibly related to the interaction of the metal centers with solvent molecules and/or the loss of methanol molecules weakly bound to the peripheral copper ions. Related studies on O-bridged dicopper complexes have evidenced that the magnetic properties are influenced by such factors as the Cu–O(bridge) distance, the Cu···Cu distance and protonation of the terminal ligand,[31] but the major factor affecting exchange is the Cu–O–Cu bridge angle.[10,13,32] Herein the ferromagnetic interaction observed in solution may thus reflect a modification of the dihedral angle between the equatorial planes of the terminal and central copper(II) ions.

Conclusions

We have prepared and fully characterized a new linear trinuclear copper(II) complex and demonstrated that in the solid state, its magnetic behavior is governed by a weak intramolecular antiferromagnetic exchange coupling within the central–terminal copper(II) pairs. ESI-MS measurements suggest that the trinuclear moiety is mostly preserved in a methanolic solution. X-Band EPR spectroscopic studies, however, clearly show that in solution, the ground spin state of the complex is a quartet, resulting from a ferromagnetic coupling between the metal centers. To the best of our knowledge we thus report the first example of a change in the exchange coupling mechanism from antiferromagnetic to ferromagnetic upon dissolution of a copper complex. Although no definitive explanation of this phenomenon can be offered at the moment, one can speculate that this change can be caused by a structural modification of the coordination surrounding of the metal centers, possibly related to a loss of methanol molecules, which are weakly bound to the peripheral metal centers in the solid state or/and coordination in solution of methanol molecule(s) on the central copper ion.

The reported results also clearly demonstrate that EPR spectroscopy is a very powerful instrument to study the magnetic properties of polynuclear metal complexes in solution. Furthermore, a combination of solid-state magnetic susceptibility studies and EPR studies in solution is highly beneficial to improve our knowledge of the mechanism of magnetic interactions between metal centers in polynuclear complexes, and to understand factors which govern these interactions.

Experimental

Materials and methods

All starting materials were commercially available and used as purchased, unless stated otherwise. The phenol-based ligand Hpy2ald was synthesized by the previously described procedure,[15,16] according to the reaction scheme shown in Fig. 1. The ^{1}H NMR spectra were recorded on a DPX300 Bruker spectrometer. All chemical shifts were reported with respect to the residual solvent peak. The ligand field spectrum in 0.5 mM methanol solution was recorded on a Varian Cary 50 Scan UV-Vis spectrophotometer. The ligand field spectrum of the solid (diffuse reflectance) was taken on a Perkin-Elmer 330 spectrophotometer equipped with a data station. The electrospray mass spectrum (ESI-MS) in methanol solution was recorded on a Thermo Finnigan AQA apparatus. X-Band electron paramagnetic resonance (EPR) measurements were performed on a Bruker ESP 300E spectrometer equipped with a Bruker nitrogen flow cryostat and on Bruker EMX equipped with an Oxford Instrument ESR_900 continuous-flow helium cryostat and an EPR 4116 DM Bruker cavity. The electrochemical behavior of the complex was investigated in a 0.1 M solution of tetra-*n*-butylammonium tetrafluoridoborate in methanol–acetone (85 : 15 v/v), using a CH Instruments 660 B potentiostat. The experiments were performed at room temperature in a three-compartment cell. Potentials are referred to a standard Ag/AgCl, aqueous 3 M KCl reference electrode. The working electrode was a vitreous carbon disk of 3 mm diameter. The working electrode was polished with 1 μm diamond paste prior to each recording. Bulk magnetization measurements were performed on a polycrystalline sample of **1** in the temperature range 2–300 K with a Quantum Design MPMS-5S SQUID magnetometer, in a 0.1 Tesla applied field. The data were corrected for the experimentally determined contribution of the sample holder. Corrections for the diamagnetic response of the complex, as estimated from Pascal's constants, were applied.[33]

Syntheses

2-(*N*,*N*-Bis(2-pyridinylmethyl)aminomethyl)-6-(hydroxymethyl)-4-methylphenol (Hpy2OH). To a solution of 0.40 g (0.0011 mol) of Hpy2ald in methanol, 0.28 g (0.0072 mol) of sodium borohydride was added. Spontaneous bleaching of the solution and evolution of H_2 gas were observed. After stirring the resulting solution at 50 °C for 2 h, the reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was re-dissolved in a water–dichloromethane mixture, and the organic layer was separated. The water layer was washed a few times with dichloromethane, and the pooled organic phases were dried over Na_2SO_4. After filtration and evaporation of the solvent under reduced pressure, the product was obtained as viscous yellow oil. Yield: 0.29 g, 0.84 mmol (75.5%). δ_H (300 MHz, $CDCl_3$): 2.21 (s, 3H, CH_3); 3.76 (s, 2H, $ArCH_2N$); 3.86 [s, 4H, $N(CH_2py)$]; 4.71 (s, 2H, CH_2OH); 6.81 (s, 1H, 3′Ar); 6.93 (s, 1H, 5′Ar); 7.16 (t, J = 6.2 Hz, 2H, 5′py), 7.30 (d, J = 7.8 Hz, 2H, 3′py); 7.62 (td, J = 7.0, J' = 1.7 Hz, 2H, 4′py); 8.55 (d, J = 0.7 Hz, 2H, 6′py); 10.7 (br s, 1H, Ar-OH) ppm.

$[Cu_3(py2O)_2(CH_3OH)_2](BF_4)_2 \cdot 0.75CH_3OH$. A solution of 29.6 mg (0.088 mmol) of $Cu(BF_4)_2 \cdot 6H_2O$ in a small amount of methanol was added to a methanolic solution of 20 mg (0.058 mmol) of Hpy2OH. 75 μl of a 40% aqueous solution of NBu_4OH (0.114 mmol) was added to the resulting clear green solution, leading to a color change to very dark brown-green. The slow diffusion of diethyl ether into the resulting solution led to the formation of rectangular brownish-green crystals, which were found to be suitable for single-crystal X-ray analysis: $[Cu_3(py2O)_2(CH_3OH)_2](BF_4)_2 \cdot 0.75CH_3OH$ (20 mg, 60.1%). The complex loses non-coordinated methanol, when taken out of the mother liquor. Elemental analysis, found: C, 45.66; H, 4.95; N, 7.74. $C_{44}H_{50}B_2Cu_3F_8N_6O_6$ requires C, 45.73; H, 4.93; N, 7.62%. ESI-MS (methanol): M^+, 972; M^{2+}, 443. UV-Vis: λ_{max}/nm (diffuse reflectance) 425, 746.

X-Ray crystal structure determination

X-Ray data were collected on a NONIUS KappaCCD diffractometer on rotating anode (graphite monochromated MoKα radiation, $\lambda = 0.71073$ Å, $T = 150$ K, $\theta_{max} = 27.5°$). Pertinent data: green-blue crystal ($0.3 \times 0.3 \times 0.3$ mm^3). $C_{44}H_{50}Cu_3N_6O_6 \cdot 2(BF_4) \cdot 0.75(CH_4O)$, triclinic, space group $P\bar{1}$ (#2), $a = 9.3629(13)$, $b = 10.7928(9)$, $c = 12.9505(16)$ Å, $\alpha = 68.589(8)$, $\beta = 83.856(9)$, $\gamma = 85.975(7)°$, $V = 1210.7(3)$ Å^3, $Z = 1$, $D_{calc} = 1.574$ g cm^{-3}, $\mu = 1.392$ mm^{-1}. A total of 29 700 reflections were measured and corrected for absorption (SADABS[34]), averaged into a unique set of 5520 reflections ($R_{int} = 0.0357$) of which 4845 with $I > 2\sigma(I)$. The structure was solved with SHELXS-86[35] and refined on F^2 with SHELXL-97.[36] The structure contains a methanol molecule, disordered over an inversion center. Hydrogen atoms were introduced at calculated positions (for the methanol taken from the difference map) and refined riding on their supporting atoms. Convergence was reached at $R = 0.0312$, w$R2 = 0.0864$, $S = 1.05$, 336 parameters. A final difference map showed no residual density outside the range −0.050–0.85 e Å^{-3}. The ORTEP illustration, geometry calculations and structure validation were done with PLATON.[37] CCDC reference number 630701. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618154f

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