DALTON
FULL PAPER

Synthesis, crystal structure and magnetic properties of the triangulo-tricopper(II) complex $[Cu_3(cpse)_3(H_2O)_3]·8.5H_2O$

Horacio López-Sandoval,[a] Rosalinda Contreras,[b] Albert Escuer,[c] Ramon Vicente,[c] Sylvain Bernès,[d] Heinrich Nöth,[e] G. Jeffery Leigh[f] and Noráh Barba-Behrens *[a]

[a] *Departamento de Química Inorgánica, Facultad de Química, Universidad Nacional Autónoma de México, C.U., 04510, México D.F., México*
[b] *Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, Apdo. Postal 14740, 07000, México D.F., México*
[c] *Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[d] *Centro de Química del IC-UAP, AP1613, Puebla, 72000, Pue., México*
[e] *Institute of Inorganic Chemistry, University of Munich, Butenandstraße 5-13 (Haus D), D-81377 Munich, Germany*
[f] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ*

Received 28th November 2001, Accepted 16th April 2002
First published as an Advance Article on the web 24th May 2002

The trinuclear copper(II) complex $[Cu_3(cpse)_3(H_2O)_3]·8.5H_2O$ has been obtained from mononuclear $[Cu(Hcpse)_2]·H_2O$ {H_2cpse = *N*-[2-hydroxy-1(*S*)-methyl-2(*S*)-phenylethyl]-*N*-methylglycine, *threo* isomer} and crystallographically characterised. The structure of the compound consists of three Cu^{II} atoms, each having distorted square-pyramidal geometry, linked by oxo-bridges to form an equilateral triangular array. The magnetic behaviour corresponds to an antiferromagnetically coupled triangular system, with $J = -114.2\ cm^{-1}$. The EPR spectra at different temperatures have been determined. The analogue $[Cu(Hceph)_2]·H_2O$ (H_2ceph = *N*-[2-hydroxy-1(*S*)-methyl-2(*R*)-phenylethyl]-*N*-methylglycine), prepared from the *erythro* isomer, was obtained and characterised by X-ray crystallography.

Introduction

The discovery of multicopper centres in copper oxidases known as "blue oxidases" (ascorbate oxidase, laccase and ceruloplasmin)[1–6] has generated interest in the synthesis of angular non-linear tricopper clusters and their physical and chemical properties. As has been clearly shown in these copper oxidases, type-2 (normal single copper) and type-3 (EPR-silent coupled copper atoms) centres together form a unique trimetal active site for the binding and multi-electron reduction of dioxygen. The fully oxidised active site of ascorbate oxidase has a triangular arrangement of copper(II) atoms with Cu–Cu separations in the range 3.6–3.9 Å, with an hydroxide or oxo group acting as a bridge between the two type-3 copper atoms. There are three histidine residues bonded to each copper, while the type-2 copper atom is bonded to two histidine molecules and one water molecule or hydroxide group.[1,2] It is of importance to synthesise low molecular weight trinuclear copper(II) complexes having a triangular arrangement of metal atoms. The first generation of triangular models for the active site of the blue oxidases has been reported,[7–11] and for these triangular copper compounds, the magnetic, structural and redox characteristics[12–21] have been studied in order to contribute to the understanding of the biological centre. The study of triangular trinuclear systems without a central μ_3-OH is also of relevance because such bridging is absent from some biological oxidases, ascorbate oxidase for example. In this paper, we describe a new copper(II) trinuclear compound with *N*-[2-hydroxy-1(*S*)-methyl-2(*S*)-phenylethyl]-*N*-methylglycine (H_2cpse).[22] The H_2cpse is a versatile proligand, due to its flexibility and to the presence of three potential co-ordination sites: the nitrogen atom, the carboxylic acid group and the OH group. In previous work, we reported boron[23] and mononuclear Cu^{II}, Co^{II}, Cd^{II} and Hg^{II} compounds.[24] In these mononuclear compounds, the ligand (Hcpse) is tricoordinated to the metal ions through the nitrogen, the OH group and the deprotonated carboxylic acid in either a *fac* or *mer* arrangement. In the trinuclear copper(II) compound $[Cu_3(cpse)_3(H_2O)_3]·8.5H_2O$, a second deprotonation of the OH group has occurred, giving rise to an oxo bridge between the metal ions. In order to discover whether the configuration of the ligand is a determining factor for the formation of the trinuclear compound, the analogous mononuclear copper(II) compound with the *erythro* isomer *N*-[2-hydroxy-1(*S*)-methyl-2(*R*)-phenylethyl]-*N*-methylglycine (H_2ceph), $[Cu(Hceph)_2]·H_2O$, was synthesised. The spectroscopic and X-ray structures of the mononuclear and trinuclear Cu^{II} complexes are reported here, along with the magnetic properties of the latter.

Experimental

Syntheses

***N*-[2-Hydroxy-1(*S*)-methyl-2(*R*)-phenylethyl]-*N*-methylglycine, (H_2ceph).** The proligand was prepared as described in the literature,[22] as was the compound $[Cu(Hcpse)_2]·H_2O$.[24]

$[Cu_3(cpse)_3(H_2O)_3]·8.5H_2O$. *Method (i).* To a blue solution of $[Cu(Hcpse)_2]·H_2O$ (0.78 g, 1.5 mmol) in EtOH (40 cm^3) 2 equivalents of an aqueous NaOH solution (0.1 N; 0.8 cm^3) were added. Blue crystals suitable for X-ray studies were obtained over a period of two weeks. Yield 30% (Found: C, 40.4; H, 6.5; N, 3.9. $C_{36}H_{54}Cu_3N_3O_{21}$ requires C, 40.7; H, 6.4; N, 3.9%); ν_{max}/cm^{-1} 1631 (ν_{as} COO^-) and 1383 (ν_s COO^-);

DOI: 10.1039/b110915b

UV–Vis data: (reflectance) ν/cm^{-1} 14 042, (ethanol), 14 060 (ε 195 dm^3 mol^{-1} cm^{-1}).

Method (ii). In order to increase the yield of the trinuclear compound, an alternative synthesis was carried out. The mononuclear complex [Cu(Hcpse)$_2$]·H$_2$O (0.78 g, 1.5 mmol) was dissolved in ethanol (40 cm^3) and Cu(O$_2$CMe)$_2$·H$_2$O (0.29 g, 1.5 mmol) was added, followed by 2 equivalents of NaOH (0.1 N, 0.80 cm^3). Very thin blue needles separated over one week. These only gave an adequate set of data in the X-ray structure analysis when a diffractometer equipped with a rotating anode was used. Yield 91.6% (Found: C, 40.7; H, 6.4; N, 4.0. $C_{36}H_{54}Cu_3N_3O_{21}$ requires C, 40.7; H, 6.4; N, 3.9%).

[Cu(Hceph)$_2$]·H$_2$O. H$_2$ceph (0.34 g, 1.5 mmol) was dissolved in ethanol (10 cm^3) and added to a solution of Cu(O$_2$CMe)$_2$·H$_2$O (0.15 g, 0.75 mmol) in ethanol (10 cm^3). The mixture was stirred for 5 min and then set aside at room temperature until a precipitate formed. The resulting precipitate was filtered off, washed and dried *in vacuo*. Pale blue crystals were obtained from a solution of this precipitate dissolved in methanol after one week. Yield 86.3% (Found: C, 55.76; H, 6.46; N, 5.41. $C_{24}H_{33}CuN_2O_{6.5}$requires C, 55.71; H, 6.43; N, 5.42%); ν_{max}/cm^{-1} 1626 (ν_{as} COO$^-$) and 1389 (ν_s COO$^-$); UV–Vis (reflectance): ν/cm^{-1} 16 363.

Spectroscopic studies

The conversion in solution of the monomeric octahedral [Cu(Hcpse)$_2$]·H$_2$O to the cyclic trinuclear [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O was followed spectrophotometrically on a Cary 5E UV–Vis–NIR spectrophotometer over the range 250–1000 nm (40 000–10 000 cm^{-1}). To an ethanolic solution (4 cm^3) of Cu(O$_2$CMe)$_2$·H$_2$O (3.6×10^{-3}g, 1.83×10^{-2} mM) was added a solution of H$_2$cpse (4.1×10^{-3} g, 1.83×10^{-2} mM) in ethanol (0.5 cm^3) and the monomeric light blue species [Cu(Hcpse)$_2$]·H$_2$O was formed, displaying a band at $\lambda_{max} \geq 723$ nm (13,830 cm^{-1}), $\varepsilon = 195$ M^{-1} cm^{-1}. Stepwise 10 µL additions of NaOH (0.1 N) to this solution resulted in the formation of the cyclic trinuclear complex, after 2.0 equivalents of NaOH were added (deep blue solution), $\lambda_{max} = 711$ nm, $\varepsilon = 330$ M^{-1} cm^{-1}. The formation of an intermediate showing an absorption band at $\lambda_{max} = 683$ nm (14 640 cm^{-1}), $\varepsilon = 195$ M^{-1} cm^{-1} is also observed after addition of 1.5 equivalents NaOH. Addition of two equivalents of HCl (0.1 N) regenerates the spectrum of the mononuclear [Cu(Hcpse)$_2$]·H$_2$O.

Physical measurements

IR spectra in the range 4000–400 cm^{-1} were recorded on a Nicolet FT-IR 740 spectrophotometer using KBr pellets. Electronic spectra, solution and diffuse reflectance, were measured on a Cary 5E UV–Vis–NIR spectrophotometer over the range 250–2500 nm (10000–4000 cm^{-1}). Elemental analyses were performed on a Fisons EA 1108 elemental analyser. Magnetic susceptibility measurements were carried out with a pendulum-type magnetometer (MANICS DSM8) equipped with an Oxford CF 1200 S helium continuous-flow cryostat working in the temperature range 300–4 K in a magnetic field of 1.5 T. Diamagnetic corrections were estimated using Pascal constants. EPR spectra were recorded with a Bruker ES200 spectrometer at X-band frequency.

Crystallography

Crystal data and information about the data collection and structure refinement details are given in Table 1. Diffraction data for [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O were collected at 183 K and at 200 K for [Cu(Hceph)$_2$]·H$_2$O with Mo-Kα radiation (λ = 0.71073 Å) on an Enraf Nonius IPD diffractometer, equipped with a rotating anode using 10 s exposure per frame in a hemisphere-scan mode. 14 234 reflections were measured in the range 2θ = 3–58° for [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O and 62119 reflections in the range 2θ = 2–55 for [Cu(Hceph)$_2$]·H$_2$O, corrected for absorption effects using SADABS. The structures were solved and refined using standard methods,[25] without restraints or constraints, applying an adequate weighting scheme and an extinction correction during the least-square cycles. H atoms were placed on idealised positions, except for the water molecules (O5 to O9) in [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O, for which H atoms were found on a difference map. In the case of [Cu(Hceph)$_2$]·H$_2$O, the H atoms for the hydroxy group and the water molecule (O4 and O10) were omitted in the refinement. Non-H atoms were refined anisotropically, while H atoms were refined using a riding model and fixed isotropic thermal parameters. No significant residuals were observed in the final difference map. The chiral character of the space group was confirmed on the basis of Wilson's statistics and successful refinement. The absolute configurations were determined from the refinement of a Flack parameter,[26] [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O yielding x = 0.010(13) and the expected configuration for the cpse moiety and for [Cu(Hceph)$_2$]·H$_2$O yielding $x = -0.010(19)$. The expected value for H is $x = 0.010(13)$.

CCDC reference numbers 174684 and 174685.

See http://www.rsc.org/suppdata/dt/b1/b110915b/ for crystallographic data in CIF or other electronic format.

Results and discussion

(a) Trinuclear copper(II) complex of cpse

The cyclic trinuclear compound [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O was obtained from mononuclear [Cu(Hcpse)$_2$]·H$_2$O[24] by deprotonation of the OH groups with 2 equivalents of aqueous NaOH (Fig. 1). The compound was characterised by C, H and N analyses, IR, EPR and magnetic measurements, UV–Vis–IR spectroscopy in solution and in the solid state, and by X-ray diffraction.

The IR spectrum of H$_2$cpse shows the ν_{asym} and ν_{sym} modes of the carboxylic acid group at 1638 and 1384 cm^{-1}, shifted in the mononuclear compound to 1633 and 1401 cm^{-1} respectively, and in the trinuclear compound to 1631 and 1383 cm^{-1}.

The reflectance spectrum of the crystalline compound has a band at 712 nm (14 042 cm^{-1}), in the region expected for a pentacoordinate copper(II) compound. In ethanolic solution, this band remains in the same region, 711 nm (14 060 cm^{-1}), indicating that the compound has a similar coordination geometry in solution and in the solid state. This allowed us to follow the synthesis reaction by UV–Vis–IR spectroscopy. The formation of trinuclear [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O by addition of NaOH (0–2 equiv.) to an ethanolic solution of [Cu(Hcpse)$_2$] is traced in Fig. 2. The [Cu(Hcpse)$_2$]·H$_2$O initial absorption band (1) (λ_{max} = 13 803 cm^{-1}) shifts to 13 700 cm^{-1} (2) on addition of 1 equivalent of NaOH (0.1 N), corresponding to the deprotonation of the first OH group. On continuing the addition up to 1.5 equivalents, the absorption band shifts to a λ_{max} at 14 640 cm^{-1} (3), when 50% of the second OH deprotonation would be expected to have occurred. After addition of two equivalents of NaOH, the characteristic absorption of the trinuclear compound at 14 060 cm^{-1} is observed, not moving when an excess of NaOH is added. The reaction is reversible, as shown by the addition of two equivalents of HCl (0.1 N), when the mononuclear [Cu(Hcpse)$_2$]·H$_2$O compound is regenerated.

Crystal structure. The crystal structure of [Cu$_3$(cpse)$_3$(H$_2$O)$_3$]·8.5H$_2$O is shown in Fig. 3 and selected parameters referring to crystallography, data collection and structure refinement are collected in Table 1. Selected bond distances and angles are listed in Table 2. The cyclic trinuclear copper(II) units are chiral and centred on a 3-fold axis, with the three copper atoms connected by oxo bridges and at the corners of an equilateral triangle. The Cu$_3$O$_3$ central core of the complex

Table 1 Crystal data and structure refinement for $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$ and $[Cu(Hceph)_2]\cdot H_2O$

	$[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$	$[Cu(Hceph)_2]\cdot H_2O$
Formula	$[(C_{12}H_{15}NO_3)Cu(H_2O)]_3(H_2O)_{8.5}$	$[(C_{24}H_{32}N_2O_6Cu]H_2O$
M	2123.19	526.07
Crystal system	Trigonal	Tetragonal
Space group	$R32$ (no. 155)	$I4$ (no. 79)
T/K	183	293
a/Å	15.1559(1)	27.5016(4)
c/Å	37.3630(7)	6.72060(10)
U/Å^3	7432.51(14)	5083.05(10)
Z, Z'	6, 1/3	8, 1
D(calc)/g cm^{-3}	1.423	1.367
F(000)	3336	2116
μ(Mo-Kα)/mm^{-1}	1.350	0.900
No. reflections measured	14234	62119
No. unique reflections (R_{int})^a	3010	5832
No. variables	190	308
Final R_1, wR_2 $[I > 2\sigma(I)]^a$ (%)	2.74, 6.29	5.77, 13.44
Final R_1, wR_2 (all data)^a (%)	3.40, 6.61	9.88, 16.68
Goodness of fit on F^2 (S)^a	1.023	1.137

[a] R_{int}, R_1, wR_2 and S are defined as follows: $R_{int} = \Sigma|F_o^2 - \langle F_o^2\rangle|/\Sigma F_o^2$, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $S = [\Sigma w(F_o^2 - F_o^2)^2/(m - n)]^{1/2}$.

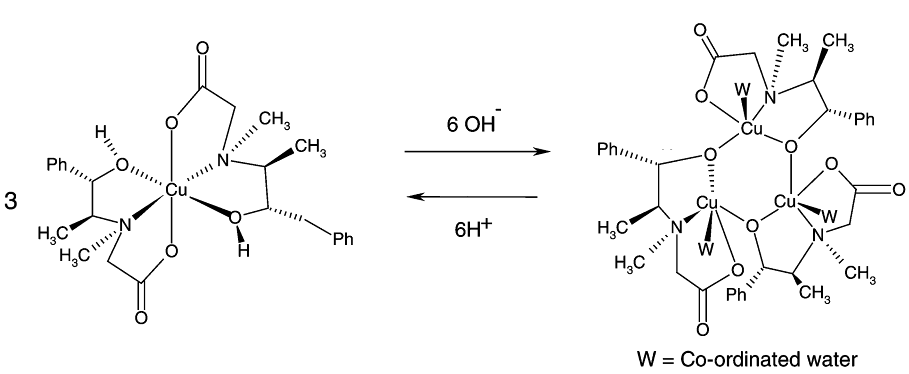

Fig. 1 Reversible formation of $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$ by addition of NaOH (0–2 equiv.). Note the *trans* orientation of the Ph and Me groups in the cpse backbones.

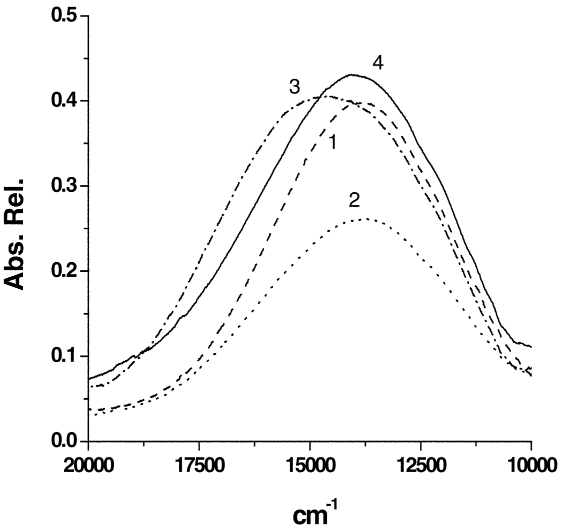

Fig. 2 Formation of $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$ *in situ* from $[Cu(Hcpse)_2]\cdot H_2O$ by addition of NaOH. (0–2 equiv.) in EtOH. (1) $[Cu(cpse)_2]$ without NaOH; (2), (3) and (4) with 1, 1.5 and 2 equivalents of NaOH, respectively.

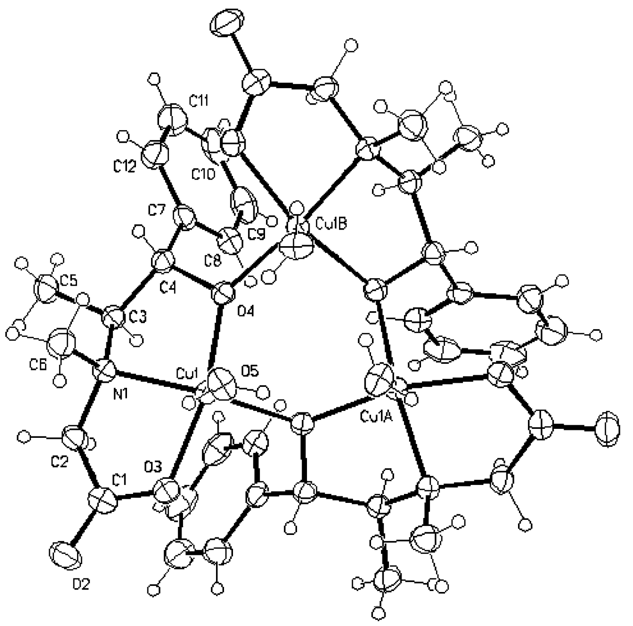

Fig. 3 Crystal structure of $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$, with the numbering scheme for the asymmetric unit. Water of crystallisation was omitted for clarity. Thermal ellipsoids are at the 30% probability level. The projection is normal to the three-fold axis of the $R32$ space group.

displays a chair conformation, common for 6-membered metal-containing rings.[27,28] The Cu ··· Cu distance in the Cu_3 triangle is 3.553(5) Å, similar to the Cu ··· Cu separation in the fully oxidised active site of the ascorbate oxidase.[1,2] The three phenyl groups form the rim of a cage. Each copper(II) atom is square pyramidal and pentacoordinate. The four basal positions are occupied by one tricoordinated cpse, with the nitrogen atom, an oxygen from the carboxylate group and a μ-oxo atom from the deprotonated hydroxo group, which bridges to another copper ion. The fourth position in the basal plane is occupied by an

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$

Cu1–O3	1.995(2)	Cu1–O4	1.950(2)
Cu1–O5	2.337(2)	Cu1–N1	2.017(3)
Cu1–O4a	1.953(2)	O2–C1	1.234(3)
O3–C1	1.288(4)	O4–C4	1.439(4)
O3–Cu1–O4	167.27(9)	Cu1–N1–C2	104.9(2)
O3–Cu1–O5	84.80(7)	O3–Cu1–N1	82.71(9)
O3–Cu1–O4a	96.4(1)	O4–Cu1–O5	97.25(8)
O4–Cu1–N1	84.70(9)	O4–Cu1–O4a	95.9(1)
O5–Cu1–N1	107.36(9)	O4a–Cu1–O5	96.79(9)
O4a–Cu1–N1	155.61(9)	Cu1–O4–Cu1b	131.1(1)

oxo atom derived from another cpse, closing a ring of three copper atoms. The deviation of the metal ion from this basal plane is 0.22 Å. As expected for the basal plane, the bond lengths are short: 1.995(2), 2.017(2) and 1.950(2) Å for Cu(1)–O(3), Cu(1)–N(1) and Cu(1)–O(4), respectively. The two five-membered chelate rings have smaller angles, O(3)–Cu(1)–N(1) 82.72(8) and O(4)–Cu(1)–N(1) 84.70(9)°, than those of the inner chelate six-membered ring O(4)–Cu(1)–O(4a) 95.9(1) and O(3)–Cu(1)–O(4a) 96.4(8)°. The apical position about each copper atom is occupied by the oxygen atom of a coordinated water molecule, Cu(1)–O(5) 2.337(2) Å. The three water molecules are placed on the same face of the Cu_3O_3 central core, while the opposite face is oriented toward the phenyl group of cpse. With this unusual arrangement, the overall molecular complex presents a hydrophilic side and a hydrophobic side, Fig. 4. The distance between the O(5) atoms, 2.769(3) Å, is indicative of the intramolecular hydrogen bonds, O(5)–H(51) ··· O(5)′, between the three apical water molecules, with a H ··· O separation of 2.063 Å, and an OH ··· O angle of 154.11°.

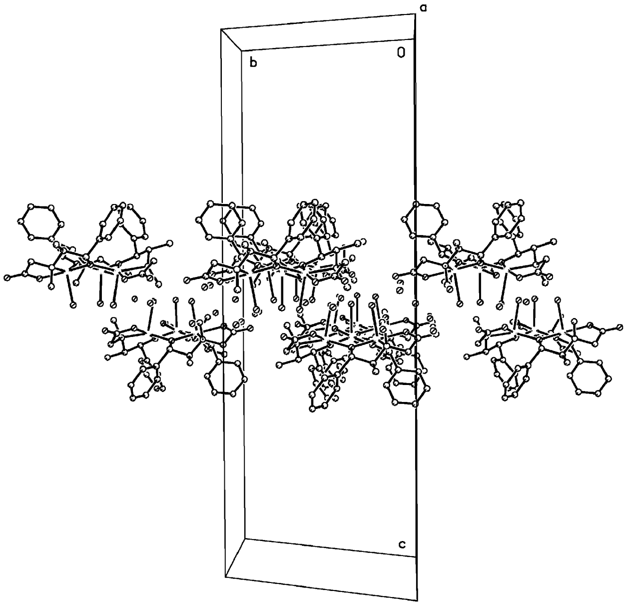

Fig. 4 Packing diagram of $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$. The overall molecular complex presents a hydrophilic side and a hydrophobic side. Intramolecular hydrogen bonds between the three apical water molecules are observed.

A complicated intermolecular hydrogen-bonding network and a two-dimensional arrangement of the trinuclear units stabilises the crystal. One layer of cyclic trinuclear units is connected to another through strong intermolecular hydrogen bonding. This occurs between the three coordinated water molecules from a cyclic trinuclear unit of copper(II), and the O(2) atom from the carboxylate groups of another unit of the neighbouring layer (characteristic O ··· O separation and angle for the H bond: 1.879 Å, 175.33°). Water molecules of crystallisation O6 to O9 are included in the hydrophilic phase of the two layers, contributing to the hydrogen-bonding network, with O ··· H separations in the range 1.880 to 2.133 Å. Finally, a void of *ca.* 181 Å^3 accessible to solvents is observed at the origin of the unit cell.[29] This may accommodate severely disordered water molecules.

Magnetic properties. A plot of $\chi_M T$ *vs.* T in the 300–4 K range for $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$ is shown in Fig. 5. The overall behaviour corresponds to an antiferromagnetically coupled trinuclear system. The value for $\chi_M T$ at room temperature of 0.95 cm^3 K mol^{-1} decreases continuously on cooling, and tends to a value close to 0.4 cm^3 K mol^{-1} at low temperature. Below 25 K, decay down to 0.30 cm^3 K mol^{-1} at 2 K is observed. The low temperature value expected for a trinuclear S = 1/2 antiferromagnetically coupled system is 0.40 cm^3 K mol^{-1} (g = 2.1). The experimental value of $\chi_M T$ at 2 K, 0.30 cm^3 K mol^{-1}, indicates an intermolecular antiferromagnetic interaction. Consistent with the triangular equilateral structure, the magnetic data were analysed by means of the analytical expression derived for the magnetic susceptibility with the Hamiltonian $\boldsymbol{H} = -J[\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_1\boldsymbol{S}_3 + \boldsymbol{S}_2\boldsymbol{S}_3]$ for local spin values $S = 1/2$. With the introduction of an intercluster interaction zJ', χ_M is expressed as shown in eqn. 1.

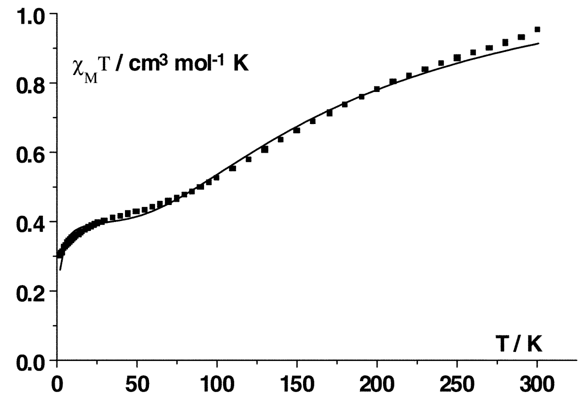

Fig. 5 Temperature dependence of $\chi_M T$ for $[Cu_3(cpse)_3(H_2O)_3]\cdot 8.5H_2O$. The solid line is generated from the best-fit magnetic parameters.

$$\chi_M = \frac{Ng^2\mu_B^2(1+5\exp(3J/2kT))}{4k(T-zJ')(1+\exp(3J/2kT))} \qquad (1)$$

The best fit parameters were $J = -114.2$ cm^{-1}, $g = 2.10$; $zJ' = -1.1$ K. This moderately strong antiferromagnetic coupling is as expected for an interaction promoted through Cu–O–Cu bridges with a bond angle of 131.1°.

The EPR spectra of trinuclear $S = 1/2$ compounds have been analysed in terms of three active states (one quartet and two doublets), with temperature-dependent populations. In the light of the super-exchange parameter from the magnetic measurements, at low temperatures, only the doublets should be populated, whereas at room temperature, signals due to the transitions inside the quartet may also be observed. Below 90 K, the spectrum consists of a quasi-isotropic broad signal (peak-to-peak linewidth 353 G at 90 K and 174 G at 4 K) centred at $g = 2.11$ (Fig. 6), which may be assigned to the transitions within the doublets. At room temperature, the spectrum becomes more complicated and the signals are weaker, indicating a mixture of 1/2 and 3/2 spin states. Due to long relaxation times, weak signals or even EPR silent behaviour at room temperature is common for strongly coupled trinuclear systems. In our case, the spectrum shows a strong signal centred at $g = 2.10$ and several resonances at g 2.33, 2.45 and 3.02, which arise from mixing of the doublet and quartet spectra. Simulation of the spectra

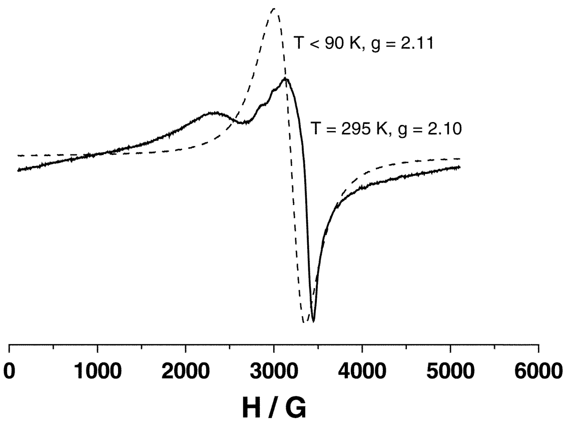

Fig. 6 X-Band EPR spectra of $[Cu_3(cpse)_3(H_2O)_3]·8.5H_2O$.

shows that the signal at $g = 3.02$ may be tentatively assigned to the low field parallel signal of the quartet, taking into account a weak zero-field splitting of 0.04 cm^{-1}. Unfortunately, attempts to unambiguously confirm this assumption by performing single-crystal measurements along the (001) axis of the crystal were unsuccessful, due to the high noise/signal ratio.

(b) Mononuclear copper(II) complex of Hceph

In order to investigate whether the sterochemistry of the H_2cpse is a driving factor for the formation of the trinuclear Cu^{II} complex, the compound $[Cu(Hceph)_2]·H_2O$, from the *erythro* isomer H_2ceph, was synthesised. This isomer was chosen due to the *trans* orientation of the C–Me and phenyl groups.

The IR spectrum of H_2ceph is similar to that of H_2cpse, with bands due to the stretching modes of the carboxylic acid group at 1638 and 1384 cm^{-1} (ν_{asym} and ν_{sym}, respectively), shifted to 1626 and 1389 cm^{-1}, respectively, in $[Cu(Hceph)_2]·H_2O$.

The reflectance spectrum shows a broad band at 16 364 cm^{-1}, indicative of a distorted geometry, and its magnetic moment (2.07 B.M.) is as expected for a copper(II) ion.

In order to obtain the analogous trinuclear compound, NaOH (0–2 equiv.) was added to an ethanolic solution of $[Cu(Hceph)_2]$, but no trinuclear compound was formed.

Crystal structure. A perspective view of $[Cu(Hceph)_2]·H_2O$, with the labelling scheme, is given in Fig. 7. Selected bond distances and angles are listed in Table 3. One Hceph ligand is coordinated to the metal in a tridentate mode, giving a byciclic chelate with two distorted five-membered rings, where the nitrogen and the oxygen atoms from the carboxylate and the OH groups are bonded to the copper(II) ion in a *facial* arrangement, as observed in the $[Cu(Hcpse)_2]·H_2O$ analogue.[24] The second Hceph molecule is bidentate, chelating through the nitrogen and an oxygen from the carboxylate group. The compound is square pyramidal, with two nitrogens and two oxygens from the carboxylic acid groups co-ordinated to the metal atom in the basal plane. The Cu–N(1) and Cu–N(2) bond distances are 2.065(4) and 2.042(4) Å, respectively, and the distances for the carbonyl oxygens, Cu–O(3) and Cu–O(6) are 1.932(4) and 1.929(3) Å. These bond lengths are similar to those observed in the analogous five-membered ring in $[Cu(cpseH)_2]·H_2O$,[24] as are the angles O(3)–Cu(1)–N(1) [85.42(1)] and O(6)–Cu(1)–N(1) [79.20(1)°]. The apical position is occupied by an oxygen atom from the OH group of one Hceph, the Cu–O(4) bond length is 2.357(3) Å. The OH group from the second Hceph is hydrogen bonded to an oxygen from a carboxylate group of a neighbouring molecule, O(6)–H(51) ··· O(2)′, with a H ··· O separation of 2.063 Å, and an OH ··· O angle of 175°.

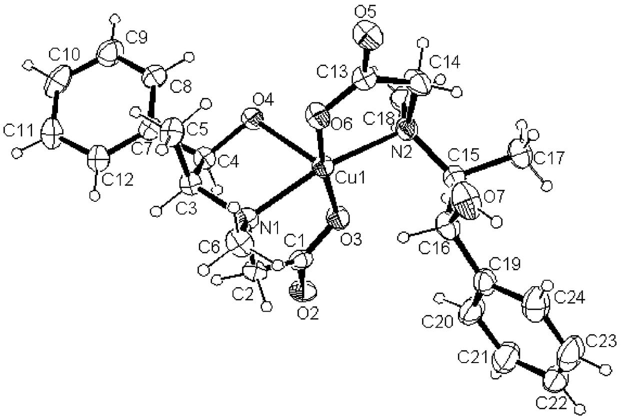

Fig. 7 Geometry and atom numbering for $[Cu(Hceph)_2]·H_2O$.

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu(Hceph)_2]·H_2O$

Cu1–O3	1.932(4)	Cu1–N2	2.042(4)
Cu1–O6	1.929(3)	O2–C1	1.224(6)
Cu1–O4	2.357(3)	O3–C1	1.296(6)
Cu1–N1	2.065(4)	O4–C4	1.424(6)
O6–Cu1–O3	171.95(1)	O3–Cu1–N1	85.42(1)
O6–Cu1–O4	100.43(1)	O3–Cu1–N2	90.10(1)
O6–Cu1–N1	97.69(1)	O4–Cu1–N1	79.20(1)
O6–Cu1–N2	85.54(1)	N2–Cu1–N1	169.24(1)
O3–Cu1–O4	87.43(1)		

Stereochemistry

In previous work, we have reported the synthesis of the octahedral compound $[Cu(Hpse)_2]·H_2O$.[24] The ligand in this compound is a *threo* isomer {H_2cpse = *N*-[2-hydroxy-1(*R*)-methyl-2(*R*)-phenylethyl]-*N*-methylglycine} with the phenyl and the C–Me in *trans* positions. Only one isomer (a) of the two possible all-*trans* isomers (a and b) was isolated and the X-ray structure obtained. A schematic description of the helicoidal structure is shown in Fig. 8. The ligand is coordinated in a tridentate mode to the metal ion, in a *fac* geometry, giving

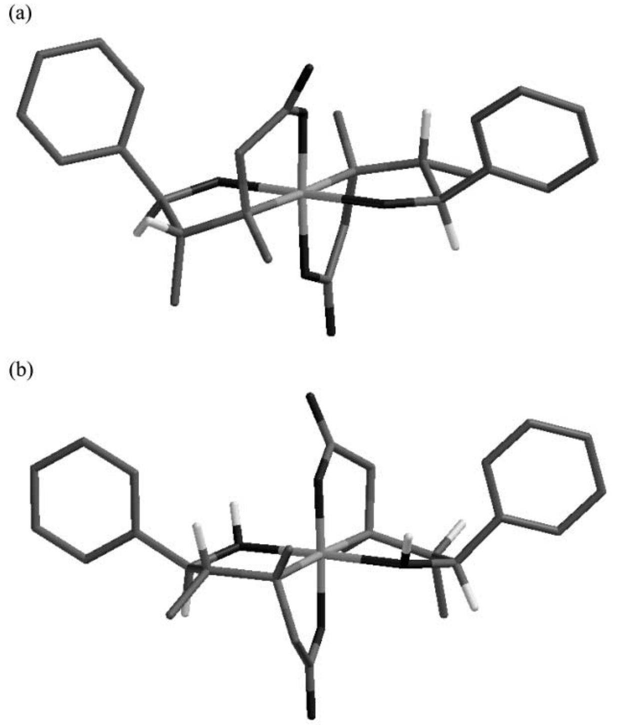

Fig. 8 PM3 schematic representation of the two possible octahedral helicoidal all-*trans* Cu^{II} isomers derived from H_2cpse.

bicyclic five-membered rings, the nitrogen atoms being stereogenic centres. In this molecule, the phenyl and the C–Me groups are in *trans* positions, a stable arrangement. Attempts to prepare the analogous compound [Cu(Hceph)$_2$]·H$_2$O derived from the *erythro* isomer (phenyl and C–Me in *cis* positions) did not give the expected octahedral helicoidal structures (c and d) depicted in Fig. 9. Instead, a pentacoordinate square-pyramidal geometry was observed. A possible explanation for the lack of coordination of the OH group is the sterically hindered positions of the *cis* substitutents. From the X-ray structure of compound [Cu(Hceph)$_2$]·H$_2$O, it is deduced that it corresponds to the opening of the idealised octahedral molecule (c) of Fig. 9.

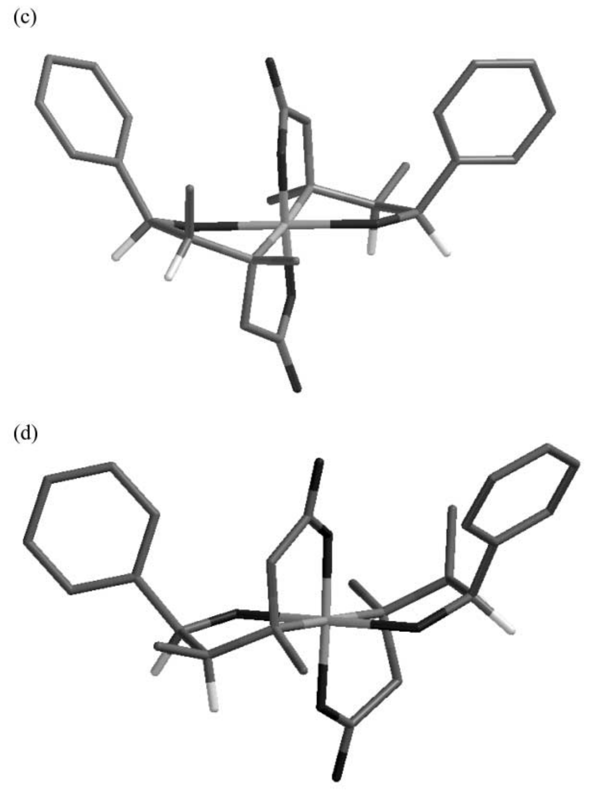

Fig. 9 PM3 schematic representation of the two possible octahedral helicoidal all-*trans* Cu^{II} isomers derived from H$_2$ceph.

Conclusions

The versatility of the ligand cpse allows it to form a stable trinuclear Cu^{II} compound from its mononuclear complex on changing the basicity of the medium, promoting the formation of oxo bridges *via* deprotonation of the OH groups, a reaction that is reversible upon addition of acid. The Cu ··· Cu distance in the triangle is 3.553(5) Å, similar to the Cu ··· Cu distance in the fully oxidised active site of the ascorbate oxidase.

Changing the configuration of the ligand from *threo* to *erythro* prevents the formation of the analogous trinuclear compound. Clearly, the stereochemistry of the ligand is a significant factor in the rearrangement of the initial mononuclear compound on deprotonation.

Acknowledgements

R. V. and A. E. thank CICYT (Grant BQU2000/0791) for partial support of this research. N. B.-B. acknowledges DGAPA-UNAM (Grant IN-213800) for financial support. H. L.-S. thanks CONACYT for a scholarship.

References

1 (*a*) A. Messerschmidt, A. Rossi, R. Ladenstein, R. Huber, M. Bolognesi, G. Gatti, A. Marchesini, R. Petruzzelli and A. Finazzi-Agro, *J. Mol. Biol.*, 1989, **206**, 513; (*b*) A. Messerschmidt, R. Ladenstein, R. Huber, M. Bolognesi, L. Avigliano, R. Petruzzelli, A. Rossi and A. Finazzi-Agro, *J. Mol. Biol.*, 1992, **224**, 179; (*c*) A. Messerschmidt, H. Luecke and R. Huber, *J. Mol. Biol.*, 1993, **230**, 997; (*d*) A. Messerschmidt, in *Bioinorganic Chemistry of Copper*, ed. K. D. Karlin, Z. Tyeklar, Chapman and Hall, New York, 1993, 471.

2 (*a*) E. I. Solomon, M. J. Baldwin and M. D. Lowery, *Chem. Rev.*, 1992, **92**, 521; (*b*) E. I. Solomon, U. M. Sundaran and T. E. Machokin, *Chem. Rev.*, 1996, **96**, 2564.

3 D. A. Fenton and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 1993, 1349.

4 H. R. Holm, P. Kennepohl and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239.

5 W. Kaim and J. Rall, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 43.

6 I. Zaitseva, V. Zaitsev, G. Card, K. Moshov, B. Bax, A. Ralph and P. Lindley, *J. Biol. Inorg. Chem.*, 1996, **1**, 15.

7 K. O. Karlin, Q.-F. Gan, A. Farooq, S. Liu and J. Zubieta, *Inorg. Chem.*, 1990, **29**, 2549.

8 P. Chaudhuri, I. Karpenstein, M. Winter, C. Butzlaff, E. Bill, A. X. Trautwein, U. Flörke and H.-J. Haupt, *J. Chem. Soc., Chem. Commun.*, 1992, 321.

9 H. Adams, N. A. Bailey, M. J. S. Dwyer, D. Fenton, P. C. Hellier, P. D. Hempstead and J. M. Latour, *J. Chem. Soc., Dalton Trans.*, 1993, 1207.

10 S. Meenakumari, S. K. Tiwary and A. R. Chakravaraty, *Inorg. Chem.*, 1994, **33**, 2085.

11 J. Padilla, D. Gatteschi and P. Chaudhuri, *Inorg. Chim. Acta*, 1997, **260**, 217.

12 P. Chaudhuri, I. Karpenstein, M. Winter, B. P. C. Della Védova, E. Bill, A. X. Trautwein, S. Gehring, P. Fleischhauer, B. Nuber and J. Ewiss, *Inorg. Chem.*, 1991, **30**, 2148.

13 E. Colacio, J. M. Domínguez-Vera, A. Escuer, M. Klinga, R. Kivekäs and A. Romerosa, *J. Chem. Soc., Dalton Trans.*, 1995, 343.

14 P. Fleischhauer, S. Gehring, C. Saal, W. Haase, Z. Tomkowicz, C. Zachini, D. Gatteschi, D. Davidov and A. L. Barra, *J. Magn. Magn. Mater.*, 1996, **159**, 166.

15 A. Escuer, R. Vicente, E. Peñalba, X. Solans and M. Font-Bardía, *Inorg. Chem.*, 1996, **35**, 248.

16 A. P. Cole, D. E. Root, P. Mukherjee, E. I. Solomon and T. D. P. Stack, *Science*, 1996, **273**, 1848.

17 S. T. Frey, H. H. J. Sun, N. N. Murthy and K. D. Karlin, *Inorg. Chim. Acta*, 1996, **242**, 239.

18 L. Spiccia, B. Graham, M. T. W. Eran, G. Lazarev, B. Moubaraki, K. S. Murria and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1997, 4089.

19 P. L. Jones, J. C. Jeffery, J. P. Maher, J. A. McCleverty, P. H. Rieger and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 3088.

20 E. Monzani, L. Casella, G. Zoppellaro, M. Gullotti, R. Pagliarin, R. P. Bonomo, G. Tabbi, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 1988, **282**, 180.

21 S. Ferrer, J. G. Haasnoot, J. Reedijk, E. Müller, M. Biagini Cingi, M. Lanfranchi, A. M. Manoti Lanfredi and J. Ribas., *Inorg. Chem.*, 2000, **39**, 1859.

22 N. Farfán-García, L. Cuellar, J. M. Aceves and R. Contreras, *Synthesis*, 1987, 927.

23 T. Mancilla and R. Contreras, *J. Organomet. Chem.*, 1987, **321**, 191.

24 H. C. López-Sandoval, N. Barba-Behrens, S. Bernès, N. Farfán-García and H. Höpfl, *J. Chem. Soc., Dalton Trans.*, 1997, 3415.

25 G. M. Sheldrick, SHELX 97-2 Users Manual, University of Göttingen, Germany, 1997.

26 *International Tables for X-Ray Crystallography*; Kynoch Press, Birmingham, 1974, vol. IV, p. 99.

27 S. Bernès, J. C. Aguilar, E. Rodríguez de San Miguel, M. A. Nuñez G. and J. de Gyves, *Acta Crystallogr., Sect. C.*, 1999, **55**, 1627.

28 R.-G. Xiong, J. L. Zuo and X.-Z. You, *Inorg. Chem.*, 1997, **36**, 2472.

29 A. L. Speck, *Acta Crystallogr., Sect. A*, 1990, **46**, 34.