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Synthesis, molecular structure and magnetic properties of tetranuclear copper(II) complexes with pendant-arm macrocyclic ligands

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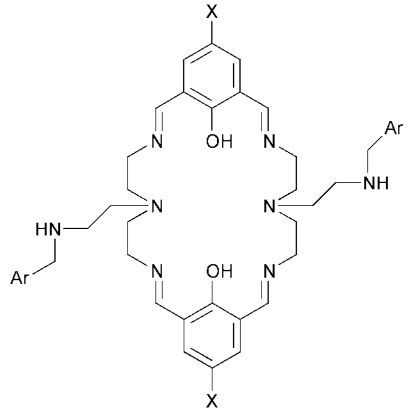
The condensation of sodium 2,6-diformyl-4-X-phenolate (X = Cl, CH_3) with the reduced 1 : 1 Schiff base of 2,2′,2″-tris(aminoethyl)amine (tren) and 2-formylfuran (or benzaldehyde) followed by *in situ* transmetallation with copper(II) perchlorate results in the production of four novel tetranuclear copper(II) complexes of 2 : 2 macrocyclic Schiff bases with functional pendant-arms (H_2L^{1-4}), which have been spectroscopically characterized. A typical complex $[Cu_4L^1Cl_2(OH)_2](ClO_4)_2$ (**1**) has been structurally studied by X-ray diffraction. In the cation of complex **1**, $[Cu_4L^1Cl_2(OH)_2]^{2+}$, a chair-shaped Cu_4O_4 core with two μ_3-hydroxide groups inside is composed of two kinds of crystallographically independent Cu(II) atoms, each of which possesses a distorted square pyramidal configuration. The four metal atoms are in an approximate parallelogram. Two pendant-arms, bonding in a monodentate fashion to their adjacent metal atoms, lie in the '*trans*' position to the macrocycle. The variable temperature magnetic susceptibility of **1** has been measured over the temperature range 4–300 K. The best fitting with a quasi-butterfly magnetostructural model shows antiferromagnetic exchanges within this compound, with $J_{bb} = -270.8$ cm^{-1}, $J_{wb1} = -40.3$ cm^{-1} and $J_{wb2} = -37.5$ cm^{-1}.

Polynuclear copper chemistry plays a significant role in modeling metal biosites,[1] *e.g.* the catalytic oxidation of organic compounds[2] and the transport of dioxygen in biological systems.[3] Since macrocyclic ligands with polynucleating moieties have the advantage of being able to hold more than one metal in a predetermined arrangement within the ring framework, they have also been applied in the modeling of copper biosites. A few dinuclear copper macrocyclic complexes have been used to mimic the haemocyanin[4] and deoxyhaemocyanin sites.[5] A trinuclear copper(II) macrocyclic complex with pendant-arms has been utilized by Fenton *et al.*[6] for modeling the trinuclear site in ascorbate oxidase.[7] In addition, polynuclear copper cluster chemistry has also attracted much attention.[8]

In our continual studies on macrocyclic complexes,[9] we have succeeded in preparing a number of dinuclear macrocyclic complexes with differing pendant-arms *via* a 24-membered macrocyclic skeleton.[10] In an attempt to hold a third metal atom above the macrocyclic ligand to form a trinuclear complex which mimics the structure of the trinuclear copper site in ascorbate oxidase, more than one ligating group in the pendant-arms has been introduced in our studies. However, our recent results indicate that if two donor atoms in the pendant-arm are strong, the arm will chelate the metal ion in a ring framework.[11] To avoid this scenario, weak ligating groups have been used to decrease the coordination ability of the pendant-arm, in an attempt to 'fix' an extra metal above the ring. But, contrary to our expectation, tetranuclear complexes have been yielded. Reported here are the preparation and characterization of four novel tetranuclear copper complexes of the pendant-arm macrocyclic ligands, H_2L^1–H_2L^4, together with the crystal structure and magneto-chemical behavior of a typical complex.



H_2L^1: X = Cl, Ar = furanyl H_2L^2: X = CH_3, Ar = furanyl
H_2L^3: X = Cl, Ar = phenyl H_2L^4: X = CH_3, Ar = phenyl

Experimental

Materials and general methods

Sodium 2,6-diformyl-4-chlorophenolate (sdcp) and sodium 2,6-diformyl-4-methylphenolate (sdmp) were prepared in the same manner as reported previously.[8] All other solvents and chemicals were of analytical grade and used without further purification.

Microanalyses were measured with a Perkin-Elmer 1400C analyser. Infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet FTIR 170X spectrophotometer. Electronic spectra were recorded on a Shimadzu UV-3100 spectrophotometer in the region 800–350 nm in CH_3CN solution, reflectance spectra (solid state) on a Shimadzu UV-240 spectrophotometer in the region 900–350 nm. Electrospray ionization (ES) mass spectra were performed in CH_3CN–CH_3OH on a Finnigan MAT SSQ 710 mass spectrometer in the scan range 300–1200 u. The room temperature magnetic moments of all complexes were measured using a CAHN-2000 magnetometer {calibrant: $[Ni(en)_3](S_2O_3)$}.The variable temperature magnetic susceptibilities of complex **1** were measured in a superconducting quantum interference device (SQUID). The sample was first loaded from room temperature directly to the 4 K sample chamber in the SQUID magnetometer, and the measurement

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was scanned in the range 4 K to 300 K using a warming mode. All data have been corrected using Pascal constants.

Preparation of the complexes

Polyamines. A methanol solution (50 cm^3) containing tren [2,2′,2″-tris(aminoethyl)amine] (0.15 g, 1 mmol) and 2-formylfuran (0.10 g, 1 mmol) or benzaldehyde (0.11 g, 1 mmol) was stirred at room temperature for 30 min, then excess $NaBH_4$ (0.20 g, 5.2 mmol) was added in portions. After the solution was stirred for a further 2 h, dilute hydrochloric acid was added. The mixture was refluxed for half an hour to remove the residual $NaBH_4$, and then the solution was adjusted to pH 10 by adding 2 mol dm^{-3} NaOH aqueous solution. The resulting solution was concentrated, and the remainder dissolved in 20 cm^3 water and extracted with CH_2Cl_2 (3 × 20 cm^3). The CH_2Cl_2 solution was dried over Na_2SO_4 and then filtered. Removing the solvent under reduced pressure yielded a yellow oil of *N*-(2-methylenefuranyl)tris(2-aminoethyl)amine or *N*-(2-methylenephenyl)tris(2-aminoethyl)amine.

Copper complexes. The above oil dissolved in methanol (10 cm^3) was added to a suspension of sodium 2,6-diformyl-4-substituted phenolate (sdcp or sdmp) (1 mmol) in methanol (30 cm^3). The solution was stirred in an ice–water bath for 2 h, then $Cu(ClO_4)_2\cdot 6H_2O$ (0.37 g, 1 mmol) and NaCl (0.03 g, 0.5 mmol) were added. The mixture was heated under reflux for a further 0.5 h, a green precipitate was collected, washed with methanol and dried over P_2O_5.

$[Cu_4L^1Cl_2(OH)_2](ClO_4)_2$ (1). Yield 0.47 g (72%) (Found: C, 35.10; H, 3.87; N, 8.67. $C_{38}H_{46}Cl_6N_8O_{14}Cu_4$ requires C, 34.92; H, 3.52; N, 8.58%). ν_{max}/cm^{-1} 3428m, 3264w, 1640s, 1100vs and 625s. ES-MS: *m*/*z* $[Cu_4L^1Cl_2(OH)_2]^{2+}/2$ 553 (100%).

$[Cu_4L^2Cl_2(OH)_2](ClO_4)_2$ (2). Yield 0.44 g (70%) (Found: C, 37.10; H, 3.98; N, 8.73. $C_{40}H_{52}Cl_4N_8O_{14}Cu_4$ requires C, 37.97; H, 4.11; N, 8.86%). ν_{max}/cm^{-1} 3445m, 3258w, 1645s, 1109vs and 624s. ES-MS: *m*/*z* $[Cu_4L^2Cl_2(OH)_2]^{2+}/2$ 533 (100%).

$[Cu_4L^3Cl(OH)_2(ClO_4)](ClO_4)$ (3). Yield 0.47 g (71%) (Found: C, 38.54; H, 4.28; N, 7.95. $C_{42}H_{50}Cl_6N_8O_{16}Cu_4$ requires C, 39.09; H, 4.24; N, 8.48%). ν_{max}/cm^{-1} 3428m, 3260w, 1641s, 1110 vs, 1098vs and 624s. ES-MS: *m*/*z* $[Cu_4L^3(OH)_2Cl(ClO_4)]^{2+}/2$ 595 (100%).

$[Cu_4L^4Cl_2(OH)_2](ClO_4)_2$ (4). Yield 0.44 g (69%) (Found: C, 41.43; H, 4.21; N, 8.35. $C_{44}H_{56}Cl_4N_8O_{12}Cu_4$ requires C, 41.12; H, 4.36; N, 8.72%). ν_{max}/cm^{-1} 3439m, 3282w, 1643s, 1098vs and 623s. ES-MS: *m*/*z* $[Cu_4HL^4Cl_2(OH)_2(ClO_4)]^{2+}/2$ 593 (100%).

Crystallography

Green crystals of $[Cu_4L^1Cl_2(OH)_2](ClO_4)_2\cdot 2DMF$ suitable for X-ray determination were grown from a DMF solution of complex **1**. $C_{44}H_{60}Cl_6Cu_4N_{10}O_{16}$, M = 1451.88, monoclinic, space group $P2_1/n$, $a = 10.275(3)$, $b = 23.194(3)$, $c = 13.061(2)$ Å, $\beta = 108.11(2)°$, $U = 2958.5(10)$ Å^3, T = 293 K, Z = 2, μ(Mo-Kα) = 1.761 mm^{-1}, 6433 reflections measured, 5185 unique (R_{int} = 0.0333) which were used in all calculations. The final value of $R1 = 0.0511$ and $wR2 = 0.1189$ with $I > 2\sigma(I)$.

X-Ray diffraction data were collected on a Siemens P4 four-circle diffractometer with monochromated Mo-Kα (λ = 0.71073 Å) radiation using a $\theta/2\theta$ scan mode with a variable scan speed 5.0–50.0° min^{-1} in ω. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.[12] The absorption correction was carried out with semi-empirical calculations from psi-scans. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in calculated positions (C–H, 0.96, N–H, 0.90 and O–H, 0.85 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 times for the O–H and methyl groups) and allowed to ride on their respective parent atoms. All computations were done using the SHELXTL-PC program package.[13]

CCDC reference number 169476.

See http://www.rsc.org/suppdata/dt/b1/b102366g/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and spectral characterization

The whole preparation has been completed by (i) condensation of one mole equivalent of tren with the aromatic aldehyde, and then reduction of the resulting Schiff base by excess $NaBH_4$ to generate the polyamine derivatives; (ii) reaction of the polyamine with the sodium salt of the phenolate precursors and then addition of metal salts. The condensation reaction must be rigorously controlled so that formation of the 1 : 1 Schiff base of tren and not 1 : 2 or 1 : 3 Schiff base side products are obtained. The resulting Schiff base must be reduced completely by $NaBH_4$ to form *N*-(2-methylene-furanyl or -phenyl)tris(2-aminoethyl)amine, otherwise side products like cryptates would dominate the subsequent condensation reaction.[14] As described previously, multi-imine macrocyclic sodium compounds are usually liable to be hygroscopic and unstable in air, hence the expected macrocyclic dinuclear metal complexes were produced by *in situ* transmetallation of metal salts. Addition of sodium chloride is to provide exogenous ligands to coordinate the metal completely.

The infrared spectra of the four complexes are similar. The absence of the first amine and carbonyl vibrations and the presence of the imine stretch at 1640–1645 cm^{-1} prove the nature of the macrocyclic complexes. A weak band at 3258–3282 cm^{-1} is attributed to the second amine mode. All of the complexes exhibit a broad medium-intensity band at 3428–3445 cm^{-1} assigned to δ(OH).[15] The spectra of **1**, **2** and **4** also present a very strong band at ≈1100 cm^{-1} and a medium band at ≈625 cm^{-1} due to the ν_3 and ν_4 modes of the uncoordinated ClO_4^-, respectively.[15] In contrast, the same ν_3 vibration of **3** is split, suggesting the presence of a coordinated perchlorate anion in the structure. In the ES-MS spectra, fresh solutions (CH_3CN–CH_3OH) of the four complexes display one double-charged peak attributed to the corresponding tetranuclear copper(II) species. However, a solution of crystalline samples of **1**, stored for two weeks, presents a double-charged peak at 553 (100%) and a mono-charged peak at 976 (70%) assigned to $[Cu_4Cl_2(OH)_2L^1]^{2+}/2$ and $[Cu_2L^1(ClO_4)]^+$, respectively. It seems that the anionic μ_3-hydroxide bridges are unstable in solution, and the macrocyclic framework readily “wraps” to accommodate two copper(II) ions.

The main absorptions of the solution electronic spectra and the solid reflectance spectra of the four complexes are listed in Table 1. The electronic spectra of freshly prepared complex solutions in CH_3CN are very similar to those of the corresponding reflectance spectra of the solids, inferring that the structure observed in the solid is maintained in solution. The tetra-copper complexes exhibit an intense band at 24813–24271 cm^{-1} (ε = 25510–35541 dm^3 mol^{-1} cm^{-1}) attributed to LMCT transitions. A broad d–d band assigned to the Cu(II) ions in all of the complexes appears in the region 16722–15873 cm^{-1} (ε = 214–365 dm^3 mol^{-1} cm^{-1}). In general, the electronic spectra of the copper(II) complexes with a square pyramidal configuration exhibit two clearly resolved bands in the range 15000 ± 2000 cm^{-1}, and the complexes with a trigonal bipyramidal configuration with $^2A_1{}'$ ground states show one relatively strong absorption at 12500 ± 1500 cm^{-1}.[16] On the basis of the actual crystal structure of complex **1**, a square pyramidal geometry is assigned to the tetranuclear copper(II) centers in complexes **1**–**4**. Nishida and Kida[17] have discussed splitting of the d orbital in

Table 1 Physical properties of the complexes

Compound	$\mu_{eff}{}^{a}/\mu_B$	λ^{b}/nm (ε/dm^3 mol^{-1} cm^{-1})	Reflectance spectrum/nm
$[Cu_4L^1Cl_2(OH)_2](ClO_4)_2$ (**1**)	1.41	412 (31463), 618 (365)	595
$[Cu_4L^2Cl_2(OH)_2](ClO_4)_2$ (**2**)	1.42	409 (31161), 598 (214)	597
$[Cu_4L^3Cl(OH)_2(ClO_4)](ClO_4)$ (**3**)	1.38	411 (35541), 615 (274)	600
$[Cu_4L^4Cl_2(OH)_2](ClO_4)_2$ (**4**)	1.47	403 (25510), 630 (238)	612

[a] At room temperature. [b] In CH_3CN.

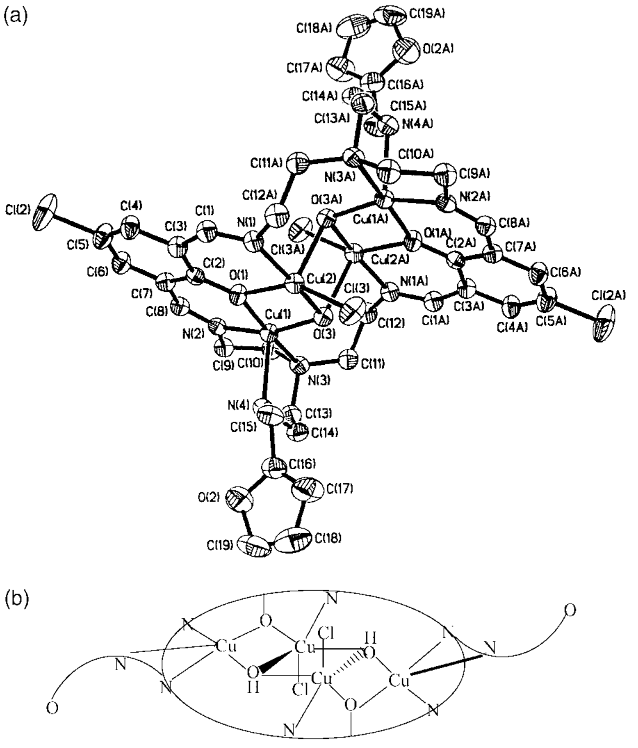


Fig. 1 (a) An ORTEP view of complex **1** with the atom numbering scheme; (b) the Cu_4O_4 core arrangement.

square-planar copper(II) complexes in terms of the effect of π bonding. The present large splitting of the d–d bands can be attributed to the strong π character of the macrocyclic ligands.

Structural description of complex 1

The structure of $[Cu_4L^1Cl_2(OH)_2](ClO_4)_2\cdot 2DMF$, obtained from an X-ray single crystal diffraction study, shows several features as shown in Fig. 1. The selected bond lengths and angles are listed in Table 2. The ligand is a 24-membered 2 : 2 Schiff base macrocycle with two functional pendant-arms in a '*trans*' position with respect to the ring. The central Cu_4O_4 core of the cation is composed of two kinds of crystallographically independent Cu(II) atoms [namely, Cu(1) and Cu(2)]. The four copper ions, which lie on a plane, form an approximate parallelogram. The inter-atomic distances between the crystallographically independent Cu(II) atoms, Cu(1) ··· Cu(2) and Cu(1) ··· Cu(2A) composed of the short and the long sides of the parallelogram, are 3.059 Å and 3.326 Å, respectively. The two diagonals of the parallelogram, Cu(1) ··· Cu(1A) and Cu(2) ··· Cu(2A), are 5.593 Å and 3.095 Å in length, respectively. Because the short diagonal is approximately equal to the short side of the parallelogram, this arrangement could be considered as originating from two equilateral triangles sharing a common edge, which is similar to the acyclic complex, $[Cu_4(dpk)(CH_3O)_4(CH_3O)_2](ClO_4)_2$ (dpk = di-2-pyridylketone), where the four copper atoms comprise a rhombus arrangement.[18]

All metal atoms are bound within the macrocyclic framework in **1** possessing the same configuration of a distorted square pyramid, however, there are two sets of coordination environments around the copper atoms. Cu(1) is located in a plane consisting of an imine nitrogen, one phenoxide oxygen, one amine nitrogen and a hydroxide ion, the axial position is occupied by the secondary amine nitrogen on the arm. But for Cu(2), the plane is composed of one hydroxide ion, an imine nitrogen, one phenoxide oxygen and a chloride anion, and the corresponding axial position is taken by the other hydroxide ion. It is of interest to note that the axis of the pyramid of the two copper atoms beside one phenolic moiety is opposite to that of the remaining two copper atoms near the other phenolic ring. Two pendant-arms point in opposite directions away from the macrocycle, in which two furan rings, not bonding to the metal atoms, are parallel to each other. Four metal atoms are connected by two μ-phenol oxygen atoms as expected, and also by two μ_3-hydroxo groups which are situated in the chamber of the macrocycle. No bond lengths between the metal atoms and the bridging oxygen atoms are equal. The Cu_4O_4 core consists of a chair-shaped structure in which three Cu_2O_2 planes have been formed by Cu(1)Cu(2)O(1)O(3) (**I**), Cu(2)Cu(2A)O(3)-O(3A) (**II**) and Cu(1A)Cu(2A)O(1A)O(3A) (**III**), respectively. Planes **I** and **III**, with a maximum deviation of 0.0438 Å from their least-squares planes, are parallel to each other, but both have a dihedral angle of 104.3° with plane **II**. Two phenolic ring moieties, composed of C(1)C(2)C(3)C(4)C(5)C(6)C(7)C(8)-N(1)N(2)O(1)Cl(2) and its counterpart, are also parallel to each other. They have the same dihedral angle of 9.3° with planes **I** and **III**, and an angle of 95.2° with plane **II**. It is noted that the macrocyclic framework has been bent in a stair form with saturated carbon and nitrogen chains so that the chair-shaped structure of Cu_4O_4 can be maintained.

The study of multinuclear metal oxidase has recently been carried out by several groups in an attempt to generate chemical model compounds.[19] Although our original motivation was to model a trinuclear copper oxidase with macrocyclic ligands, our current attempt has failed. Tetranuclear copper(II) complexes have been widely investigated,[20] the most common arrangement for tetranuclear copper(II) compounds is tetrahedral, and there are a number of examples with approximate rectangular planar[21,22] and rhombus[18,20b,23] arrangements. However, there seems to be no report on pendant-arm macrocyclic tetranuclear copper(II) complexes where metal atoms are in a parallelogram arrangement. Among macrocyclic systems, one tetranuclear copper complex of a 2 : 2 macrocyclic Schiff base has been reported by McKee *et al.*,[21] which is prepared from 2,6-diformyl-4-methylphenol and 1,5-diamino-3-hydroxypentane *via* a template reaction. In its structure, the alcohol groups which are directly attached to the saturated side chains of the macrocycle serve as endogenous bridging ligands, and the four copper atoms in close proximity are in a square plane arrangement, where the Cu_4O_4 core is coplanar with a μ_4-hydroxide at the center. In our research of flexible pendant-arm macrocyclic ligands, more than one donor atom in the arm has been designed and prepared in order to study whether the pendant-arm is to provide the additional coordination sphere for the accommodation of extra metals above the ring. Our recent studies indicate that if the flexible pendant-arm contains two strong ligating groups (the secondary amine group and a pyridinyl group) it will bond to the metal atom on the macrocyclic framework to generate a dinuclear complex.[11] The

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu_4L^1Cl_2(OH)_2](ClO_4)_2{\cdot}2DMF$ with estimated standard deviations in parentheses

Cu(1)–N(2)	1.933(5)	Cu(1)–O(3)	1.937(4)
Cu(1)–O(1)	1.985(4)	Cu(1)–N(3)	2.099(5)
Cu(1)–N(4)	2.291(6)	Cu(1)–Cu(2)	3.0592(12)
Cu(2)–O(3)	1.950(4)	Cu(2)–N(1)	1.962(5)
Cu(2)–O(1)	2.011(4)	Cu(2)–O(3A)	2.229(4)
Cu(2)–Cl(3)	2.276(2)	O(3)–Cu(2A)	2.229(4)
N(2)–Cu(1)–O(3)	160.9(2)	N(2)–Cu(1)–O(1)	91.2(2)
O(3)–Cu(1)–O(1)	78.3(2)	N(2)–Cu(1)–N(3)	85.4(2)
O(3)–Cu(1)–N(3)	103.6(2)	O(1)–Cu(1)–N(3)	174.2(2)
N(2)–Cu(1)–N(4)	104.2(2)	O(3)–Cu(1)–N(4)	93.7(2)
O(1)–Cu(1)–N(4)	102.4(2)	N(3)–Cu(1)–N(4)	83.0(2)
N(2)–Cu(1)–Cu(2)	130.6(2)	O(3)–Cu(1)–Cu(2)	38.24(13)
O(1)–Cu(1)–Cu(2)	40.35(11)	N(3)–Cu(1)–Cu(2)	141.85(14)
N(4)–Cu(1)–Cu(2)	97.0(2)	O(3)–Cu(2)–N(1)	166.9(2)
O(3)–Cu(2)–O(1)	77.4(2)	N(1)–Cu(2)–O(1)	91.3(2)
O(3)–Cu(2)–O(3A)	84.4(2)	N(1)–Cu(2)–O(3A)	90.9(2)
O(1)–Cu(2)–O(3A)	100.9(2)	O(3)–Cu(2)–Cl(3)	95.61(14)
N(1)–Cu(2)–Cl(3)	97.5(2)	O(1)–Cu(2)–Cl(3)	150.56(14)
O(3A)–Cu(2)–Cl(3)	106.99(13)	O(3)–Cu(2)–Cu(1)	37.93(13)
N(1)–Cu(2)–Cu(1)	131.0(2)	O(1)–Cu(2)–Cu(1)	39.74(11)
O(3A)–Cu(2)–Cu(1)	96.54(11)	Cl(3)–Cu(2)–Cu(1)	125.62(6)
Cu(1)–O(1)–Cu(2)	99.9(2)	Cu(2)–O(3)–Cu(2A)	95.2(2)
Cu(1)–O(3)–Cu(2)	103.8(2)	Cu(1)–O(3)–Cu(2A)	105.8(2)

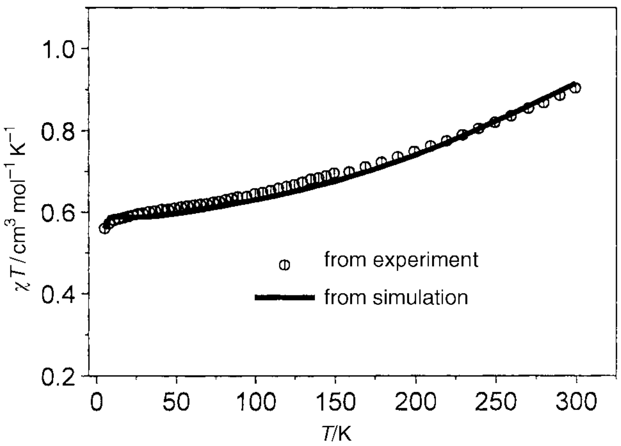


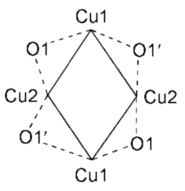
Fig. 2 Plot of χ_mT *vs.* T for a powder sample of **1**: open circle, experimental data; solid line, calculated from simulation.

present compound is, we believe, the first example of a macrocyclic tetranuclear copper complex with pendant-arms, where four metal ions are located in a parallelogram arrangement with a Cu_4O_4 core in a chair-like configuration.

Magnetic properties

Room temperature magnetic moments of the four complexes are listed in Table 1. It is noted that these values are all smaller than those for uncoupled Cu(II) centers, indicative of antiferromagnetic coupling. To explore the magneto-structural correlation between metal ions, variable-temperature magnetic susceptibilities of complex **1** have been investigated. The temperature dependence of the magnetic susceptibility is depicted in Fig. 2 in the χ_mT *vs.* T form. The value of χ_mT, either at room temperature (0.90 cm^3 K mol^{-1}) or at low temperatures (≈0.5 cm^3 K mol^{-1}), is much smaller than that expected for four uncoupled Cu(II) ions (1.5 cm^3 K mol^{-1}), indicative of deviation of the ground spin state from $S = 2$.

As shown by the crystal structure, the copper atoms of the tetranuclear complexes are actually in a parallelogram arrangement, which is similar to the so-called quasi-butterfly $[Mn_4O_2]^{n+}$ complexes reported previously.[24] The obvious distinction from the butterfly $[Mn_4O_2]^{n+}$ structure is that two wing–body connections between Cu1 and Cu2 are not identical due to inequivalent O bridges. The magnetic exchange interactions in this copper system can be fitted by the isotropic spin Hamiltonian given by an improved butterfly exchange mode in eqn. (1),[25] where the magnetic interaction between two Cu1 atoms in the wings is approximately ignored.



$$H = -2J_{bb}(S_1S_{1'}) - 2J_{wb1}(S_1S_{2'} + S_{1'}S_2) - 2J_{wb2}(S_1S_2 + S_{1'}S_{2'}) \quad (1)$$

Here J_{wb1} and J_{wb2} represent those two "wing–body" (Cu1–O1–Cu2, Cu1–O1′–Cu2) exchange interactions about the periphery of the tetranuclear core, and J_{bb} represents the "body–body" or "hinge" (Cu2–OR–Cu2) interaction of the two central Cu(II) ions. $J_{wb} = (J_{wb1} + J_{wb2})/2$ and $\Delta = (J_{wb1} - J_{wb2})/2$ are used for replacing J_{wb1} and J_{wb2} for a better expression, and the new Hamiltonian is given in eqn. (2).

$$H = -2J_{wb}(S_1S_2 + S_2S_{1'} + S_{1'}S_{2'} + S_{2'}S_1) - 2J_{bb}(\vec{S}_1\vec{S}_{1'}) - 2\Delta(\vec{S}_1\vec{S}_2 - \vec{S}_2\vec{S}_{1'} + \vec{S}_{1'}\vec{S}_{2'} - \vec{S}_{2'}\vec{S}_1) \quad (2)$$

Defining $\vec{S}_A = \vec{S}_1 + \vec{S}_{1'}$, $\vec{S}_B = \vec{S}_2 + \vec{S}_{2'}$, $\vec{S}_T = \vec{S}_A + \vec{S}_B$ and $\vec{S}_{A'} = \vec{S}_1 - \vec{S}_{1'}$, $\vec{S}_{B'} = \vec{S}_2 - \vec{S}_{2'}$, $\vec{S}_{T'} = \vec{S}_{A'} + \vec{S}_{B'}$, the resulting eigenvalue of the Hamiltonian is given by eqn. (3).

$$E = -J_{wb}[S_T(S_T + 1) - S_A(S_A + 1) - S_B(S_B + 1)] - J_{bb}[S_B(S_B + 1) - S_1(S_1 + 1) - S_{1'}(S_{1'} + 1)] - \Delta[S_{T'}(S_{T'} + 1) - S_{A'}(S_{A'} + 1) - S_{B'}(S_{B'} + 1)] \quad (3)$$

For a system of four $S = 1/2$ copper ions disposed in such a quasi-butterfly-type arrangement, the overall degeneracy ($2^4 = 16$) is distributed over 8 spin states with S values ranging from 0 to 2. An expression for the molar paramagnetic susceptibility, χ_m, is derived for complex **1** by using the Van Vleck equation.[26]

Consequently, the Van Vleck equation for eqn. (3) is incorporated into a nonlinear, least-squares computer program we designed, which is then used to fit the experimental molar magnetic susceptibilities at each temperature. The temperature independent paramagnetism (TIP) for complex **1** is fixed at 800×10^{-6} cm^3 K mol^{-1}.[25] Complex **1** gives an isotropic EPR

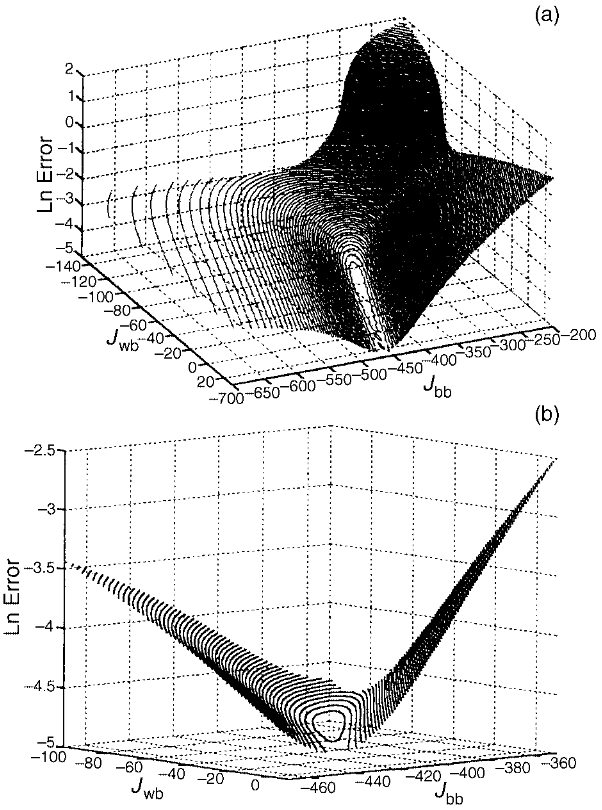


Fig. 3 (a) The scanning of J_{bb} and J_{wb} over a wide range (-140 cm^{-1} < J_{wb} < 20 cm^{-1}, -700 cm^{-1} < J_{bb} < -200 cm^{-1}), the *z* axis is the logarithm of the sum of errors in the least-squares refinement of the experimental and calculated molar magnetic susceptibilities. (b) The thorough scanning of J_{bb} and J_{wb} over a small range (-100 cm^{-1} < J_{wb} < 0 cm^{-1}, -460 cm^{-1} < J_{bb} < -360 cm^{-1}), the minimum in the sum of errors in the least-squares refinement of the experimental and calculated molar magnetic susceptibilities indicates that $J_{bb} = -270.8$ cm^{-1} and $J_{wb} = -38.9$ cm^{-1} when $\Delta = 1.4$ cm^{-1} and $\chi_{TIP} = -800$ cm^3 mol^{-1}.

signal *g* tensor at room temperature with $g = 2.086$. Therefore, three parameters J_{bb}, J_{wb} and Δ are scanned for the minimum sum in the least-squares refinement of the experimental and calculated molar magnetic susceptibilities.

In order to make the calculation unique, a search of all three parameters is begun in a large space with large increments and a more thorough search is performed after the rough scanning. The best fit gives results of $J_{bb} = -270.8$ cm^{-1}, $J_{wb1} = -40.3$ cm^{-1} and $J_{wb2} = -37.5$ cm^{-1} and $\Delta = 1.4$ cm^{-1} and the least-squares are shown in Fig. 3a and b. The calculated $\chi_m T$ curve with the best fit parameters is plotted in Fig. 2 for comparison and shows a good agreement with the measured points, revealing that our theoretical model and program are suitable for the magnetic exchange system of the tetra-copper complex. The small difference Δ between the two "body–wing" coupling constants implies that the system is very similar to the so-called butterfly system.

Conclusion

Reaction of 2,6-diformyl-4-substituted phenolates with the reduced 1 : 1 Schiff base of tren and different aromatic aldehydes followed by addition of a copper(II) salt has produced a number of tetranuclear copper(II) complexes of 2 : 2 Schiff base macrocyclic ligands with functional pendant-arms. The crystal structure of a typical complex **1** indicates that a chair-shaped Cu_4O_4 core with two μ_3-hydroxide groups inside the macrocyclic framework, where the four copper atoms are in an approximate parallelogram arrangement has been obtained. To our knowledge **1** is the first example of a chair-shaped Cu_4O_4 core in a macrocyclic environment. This compound provides an example of a magnetic system in which antiferromagnetic coupling dominates in a tetranuclear Cu(II) system inclusive of an $S = 0$ ground state at low temperatures.

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