Synthesis, Structure and Magnetic Properties of a μ-Carboxylato-Bridged Ferromagnetic Trinuclear Copper(II) Complex with Lariat Tetraazacrown Ether as Ligand

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Keywords: Copper / Macrocyclic ligands / X-ray diffraction / Magnetic properties

Four *o*-toluic acid pendant groups have been attached to a tetraaza crown ether to prepare the novel tetraazamacrocyclic ligand H_4L, 4,7,13,16-tetrakis(2-carboxybenzyl)-1,10-dioxa-4,7,13,16-tetraazacyclooctadecane. The trinuclear copper(II) complex of the ligand, $[Cu_3L\cdot 2H_2O]^{2+}\cdot 2NO_3^{-}\cdot 2H_2O$, has been newly synthesized, and its subsequent structural characterization has revealed that it consists of three Cu^{II} cores with a isosceles triangular array and that there is a twofold rotation axis that passes through the Cu2 center. The complex contains two symmetry-related CuN_2O_3 cores in a distorted square-pyramidal geometry and one CuO_4 core in a distorted square-plane geometry. The two μ-bidentate *syn*-*anti* carboxylate groups bridge Cu1 with Cu2, and Cu1A with Cu2. The trinuclear copper(II) complex units are connected in a one-dimensional zigzag chain via μ-H_2O–NO_3^{-}-bridged hydrogen bonds. Variable-temperature susceptibility measurements (2–300 K) reveal a ferromagnetic coupling, $J_a = 8.08\ cm^{-1}$, between the μ-carboxylato-bridged Cu1 and Cu2, or Cu1A and Cu2, and a weak antiferromagnetic interaction, $J_b = -0.40\ cm^{-1}$, between Cu1 and Cu1A.

Introduction

Multimetallic complexes are of great interest due to the special chemical and physical properties that result from the mutual interaction of two or more metal centers.[1] Trinuclear transition metal complexes have received increasing attention recently, partly because of the lack of metallobiomolecules for which the trinuclear core can act as a synthetic analogue. Polynuclear copper(II) complexes possess potential applications as, for example, molecular magnets and as models of metal enzymes.[2] The recent discovery of a ferromagnetically coupled Cu^{II} triad in a subunit of methane mono-oxygenase,[3] and an X-ray structure analysis of ascorbate oxidase from zucchini, which revealed an angled trimeric Cu^{II} unit,[4] have all stimulated an increasing interest in trinuclear copper systems. To date, the magnetic properties of many trinuclear copper(II) compounds have been reported, most of which exhibit antiferromagnetic interactions,[5–12] except for a few examples with ferromagnetic exchange.[13–16]

The acetate ion can provide a strong superexchange path in copper compounds. This is illustrated by an early study on hydrated copper acetate.[17] The carboxylate groups can bridge the metal cores through monodentate, and *syn*-*syn*, *syn*-*anti* and *anti*-*anti* bidentate coordination modes. Both *syn*-*syn*[17–20] and *anti*-*anti* modes[21,22] may promote an antiferromagnetic interaction, but the *syn*-*anti* bridging mode may cause either ferromagnetic[18,22–25] or antiferromagnetic interaction.[26,27] Complexes with s*yn*-*syn*-bridged carboxylate groups are very common, but those with *syn*-*anti* modes are very few.

Many reported polyazamacrocyclic copper(II) complexes are mononuclear and the carboxylate groups nearly all have a monodentate coordination mode,[28–31] with only a few showing bidentate modes.[32] The synthesis of polynuclear complexes of polyazamacrocycles is more difficult and challenging primarily due to a lack of suitably characterized ligands. For $[Cu_2(OAc)_2L]_n(ClO_4)_{2n}$, where L is a hexaazamacrocyclic ligand, *syn*-*anti* acetate bridges result in a pseudodinuclear structure,[26] but the acetate ions are not attached to the macrocyclic crown ether. Surprisingly, we succeeded in preparing a tetraazamacrocyclic ligand, 4,7,13,16-tetrakis(2-carboxybenzyl)-1,10-dioxa-4,7,13,16-tetraazacyclooctadecane), and prepared its novel trinuclear complex, $[Cu_3L(H_2O)_2]^{2+}\cdot 2NO_3^{-}\cdot 2H_2O$. Here we report the crystal structure and magnetic property of the complex, which involves both *syn*-*anti* μ_2-*O*,*O′* bidentate and monodentate carboxylate groups and exhibits a ferromagnetic exchange interaction.

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DOI: 10.1002/ejic.200300273

Results and Discussion

IR Spectrum

The band at 1121 cm^{-1}, assigned to ν_{C-O-C} for the free ligand, is shifted to 1086 cm^{-1} in the complex, indicating the complexation of the ether oxygen atoms to the Cu^{2+} ion. The complex exhibits strong bands corresponding to ν_{as}(COO) at 1595 and 1567cm^{-1}, and ν_s(COO) at 1426 and 1366 cm^{-1}. Since the carboxylate group can coordinate to the metal ion in either bidentate or monodentate fashion, the "$\Delta\nu$ criterion" [$\Delta\nu = \nu_{asymm}(COO) - \nu_{symm}(COO)$] was employed to determine the coordination mode of the carboxylate group. The $\Delta\nu$ value of 168 and 201 cm^{-1} in our complex are very similar to that reported for the copper(II) complexes with both bidentate μ_2-*O,O′* and monodentate carboxylate groups,[33] thus indicating the carboxylate groups behave both as bridging bidentate ligands between Cu^{II} atoms,[14,15] and as monodentate ligands. In addition, the band at 1384 cm^{-1} reveals the free nitrate in the complex. A broad band centered at 3426 cm^{-1} for the complex can be assigned to the ν_{O-H} stretch of coordinated or uncoordinated water molecules.

Description of the Structure

The complex consists of a discrete $[Cu_3L(H_2O)_2]^{2+}$ cation, two lattice water molecules and two uncoordinated nitrate anions. The cation of the complex with the atomic labeling scheme (Figure 1) and selected bond lengths and bond angles (Table 1) are given here. The molecule has a twofold symmetry, and the twofold rotation axis passes through the Cu2 center. The complex contains two symmetry-related CuN_2O_3 cores in a distorted square-pyramidal geometry and one CuO_4 core in a distorted square-planar geometry. The two μ-bidentate *syn-anti* carboxylate groups, O4−C22−O5 and O4A−C22A−O5A, bridge Cu2 with the crystallographically equivalent Cu1 and Cu1A cores at 4.554 Å, forming an isosceles triangle. The Cu1 and Cu1A ions are placed on the triangle base, with a longer distance of 4.852 Å connected by the $N-(CH_2)_2-O$ spacer. The overall result is a 16-membered ring Cu3 cluster (Figure 2).

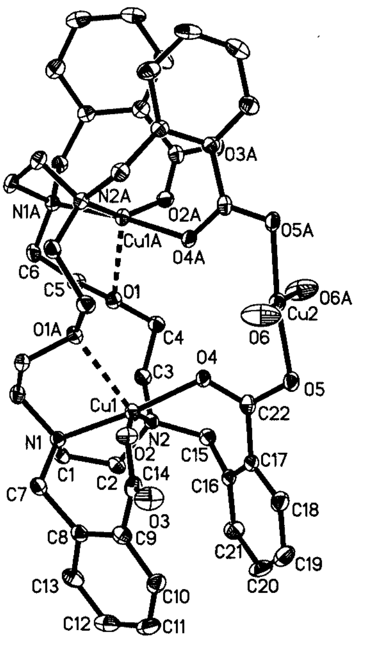


Figure 1. Thermal ellipsoids plot of the cation of $[Cu_3L{\cdot}2H_2O]^{2+}$ with labeling of selected atoms; ellipsoids shown at the 30% probability level

The distorted square-pyramidal Cu1 core consists of N1, N2, O2, O4, and O1A, in which N1, N2, O2 and O4 form the basal plane, and the apical positions are occupied by O1A. The distorted square-pyramidal Cu1A core consists of N1A, N2A, O2A, O4A and O1. The N1, N2, N1A, N2A, O1 and O1A atoms are all from the crown ether ring. O2 and O2A are from two carboxylate groups with a monodentate coordination mode, while O4 and O4A are from two other carboxylate groups with bidentate mode. Unlike Cu1 or Cu1A, the Cu2 ion is tetracoordinated to O5 and O5A, from the other oxygen atom of two μ_2-bidentate carboxylate groups, and O6 and O6A, from two water molecules. The deviations from the mean square-plane defined by Cu2, O5, O5A, O6 and O6A are −0.0951, 0.0225, 0.0225, 0.0251 and 0.0251 Å, respectively. Thus, the Cu2 ion is slightly above the basal square plane.

The complex obviously has a different structure from that of other reported macrocyclic polyazapolycarboxylato copper(II) complexes.[28−31] The nearly equal bond lengths of C22−O4 [1.263(4) Å] and C22−O5 [1.258(4) Å] show the bidentate coordination mode, while the significantly different lengths of C14−O2 [1.280(5) Å] and C14−O3 [1.241(5) Å] confirm its monodentate mode. The Cu−O bond lengths of the carboxylate group that bridges Cu1 and Cu2, 1.953(3) and 1.955(3) Å for Cu1−O4 and Cu2−O5, respectively, are nearly equal, but the Cu−O−C−O−Cu superexchange path is not symmetric. The crown ether ring is severely twisted to meet the requirement of the coordination geometry. The six donor atoms of crown ring, N 1, N2, N1A, N2A, O1 and O1A, are not coplanar and roughly adopt a boat conformation, which is in contrast with the chair conformation of the tetrakis(2-cyanobenzyl)-substituted tetraazacrown ether **2** in the solid state.[34] This may be due to steric hindrance from the four bulk pendant arms and the coordination requirement of the trinuclear complex.

Because of the limited cavity size of the parent macrocyclic free base (1,10-dioxa-4,7,13,16-tetraazacyclooctadecane) there are only two dinuclear complexes with its derivative ligand containing four (2-pyridyl)methyl pendant arms, from which the pyridyl nitrogen atoms are coordinated with the central metal atoms.[35,36] To our knowledge, the present complex is the first trinuclear complex of this tetraazamacrocyclic ligand.

There are intermolecular hydrogen bonds in the crystal of the complex. Oxygen atoms from the water molecule (O10) and the disordered nitrate anion (O7 and O9′) act as hydrogen-bond acceptors for the coordinated water mol-

Table 1. Selected bond lengths [Å] and bond angles [°] for the complex

Cu(1)−O(2)[a]	1.964(3)	Cu(1)−O(4)	1.953(3)
Cu(1)−N(1)	2.021(3)	Cu(1)−N(2)	2.061(3)
Cu(1)−O(1)#1	2.503(3)	Cu(1)#1−O(1)	2.503(3)
Cu(2)−O(5)	1.955(3)	Cu(2)−O(5)#1	1.955(3)
Cu(2)−O(6)	1.896(3)	Cu(2)−O(6)#1	1.896(3)
C(14)−O(2)	1.280(5)	C(14)−O(3)	1.241(5)
C(22)−O(4)	1.263(4)	C(22)−O(5)	1.258(4)
O(2)−Cu(1)−O(4)	90.00(11)	O(2)−Cu(1)−N(1)	94.36(12)
O(4)−Cu(1)−N(1)	173.78(12)	O(2)−Cu(1)−N(2)	154.98(12)
O(4)−Cu(1)−N(2)	91.09(11)	O(5)−Cu(2)−O(5)#1	173.10(15)
O(5)−Cu(2)−O(6)	89.40(13)	O(5)−Cu(2)−O(6)#1	90.16(13)
O(5)#1−Cu(2)−O(6)	90.16(13)	O(5)#1−Cu(2)−O(6)#1	89.40(13)
O(6)−Cu(2)−O(6)#1	172.7(3)	C(14)−O(2)−Cu(1)	127.6(2)
C(22)−O(4)−Cu(1)	124.4(3)	C(22)−O(5)−Cu(2)	110.0(2)
O(2)−C(14)−O(3)	122.9(4)	O(4)−C(22)−O(5)	120.9(4)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, y, $-z + {}^1/_2$.

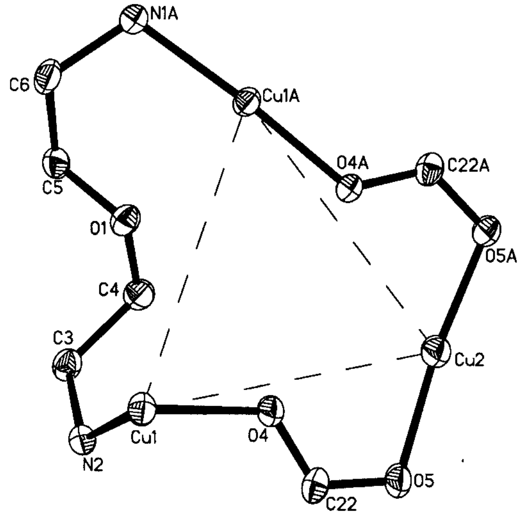


Figure 2. The 16-membered ring, showing the triangular Cu_3 skeleton and bridges

ecule involving O6. The water molecule involving O10, also as a hydrogen donor, is hydrogen-bonded to the uncoordinated oxygen atom (O3) of the carboxylate group, as well as to O8 and O8′ of its adjacent nitrate anion. Moreover, the nitrate anion is also hydrogen-bonded to the coordinated water molecule of the adjacent $[Cu_3L(H_2O)_2]^{2+}$ unit. Interatomic distances and bond angles are listed in Table 2. These hydrogen bonds form a μ-$H_2O-NO_3^-$ "band" consisting of four water molecules and two nitrate ions to tie the molecules together, forming a one-dimensional zigzag chain in the unit cell (Figure 3). In addition, the adjacent chains are linked by a π-π stacking interaction between the phenyl rings C8−C13 and C8B−C13B (related by $-x + 1/2$, $-y + 1/2$, $-z + 1$). The interacting rings are strictly coplanar by symmetry and are separated by 3.356 Å, with their centroids being offset by 1.85 Å. The complex may thus be stabilized by both the hydrogen bonding and π-π stacking interaction.

Table 2. Hydrogen-bonding parameters

D−H···A[a]	H···A [Å]	D···A [Å]	D−H···A [°]
O6−H6C···O7$^{(i)}$	1.768	2.582	172.5
O6−H6C···O9′$^{(i)}$	2.171	2.738	126.5
O6−H6D···O10	1.817	2.615	163.7
O10−H10A···O8$^{(i,i)}$	2.206	2.967	153.4
O10−H10A···O8′$^{(i,i)}$	1.963	2.776	168.6
O10−H10B···O3	2.015	2.808	161.6

[a] Symmetry code: (i): $-x$, y, $-z + {}^1/_2$; (ii): x, $-y + 2$, $z + {}^1/_2$.

Magnetic Properties

The variable-temperature magnetic susceptibility χ_m per trinuclear Cu^{II} unit has been measured. At room temperature χ_mT is 1.27 $cm^3\ mol^{-1}$ K, which is slightly higher than the expected 1.12 $cm^3\ mol^{-1}$ K for three uncoupled spin-only Cu^{II} ions ($S = 1/2$, $g = 2$). χ_mT increases upon cooling, reaching 1.88 $cm^3\ mol^{-1}$ K at 2.14 K (Figure 4). A plot of χ_m^{-1} versus T is essentially linear, and least-squares fitting of the data to the Curie−Weiss law gave $C = 1.24$ $cm^3\ mol^{-1}$ K and $\theta = +1.16$ K. The increase of χ_mT upon cooling, and the small positive Weiss constant suggest a ferromagnetic interaction between Cu^{II} ions in the trimer.

To estimate the magnitude of the magnetic coupling in the trinuclear complex, an isotropic Heisenberg−Dirac−van Vleck (HDVV) Hamiltonian [Equation (1)] was used:

$$H = -2J_{12}(S_1 \cdot S_2) - 2J_{13}(S_1 \cdot S_3) - 2J_{23}(S_2 \cdot S_3) \quad (1)$$

where $J_{12,}$ J_{13} and J_{23} are the exchange coupling constants (negative for an antiferromagnetic AF interaction, positive for a ferromagnetic F interaction) and $S_1 = S_2 = S_3 = {}^1/_2$ for the three Cu^{II} centers. For the geometry of an isosceles triangle with C_{2c} symmetry, two coupling constant are in-

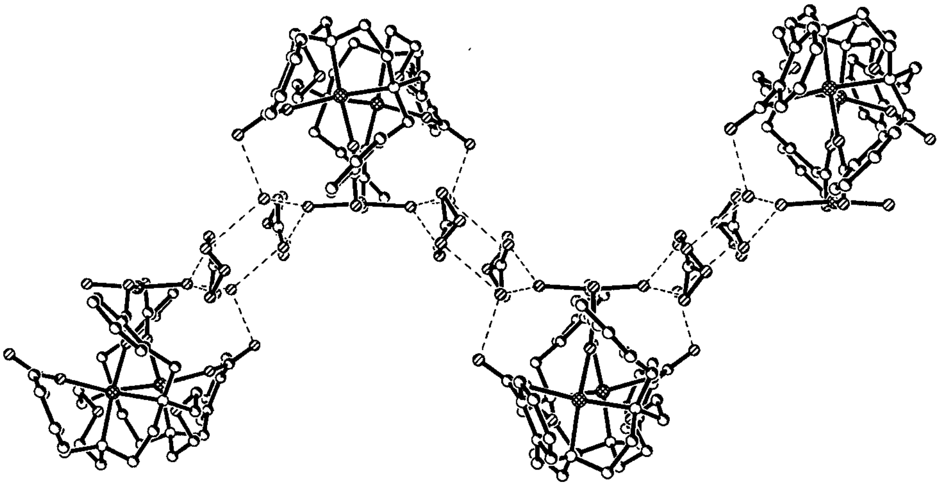


Figure 3. One-dimensional chain structure in the crystal linked by hydrogen bonding (viewed along the *a* axis, hydrogen atoms omitted for clarity)

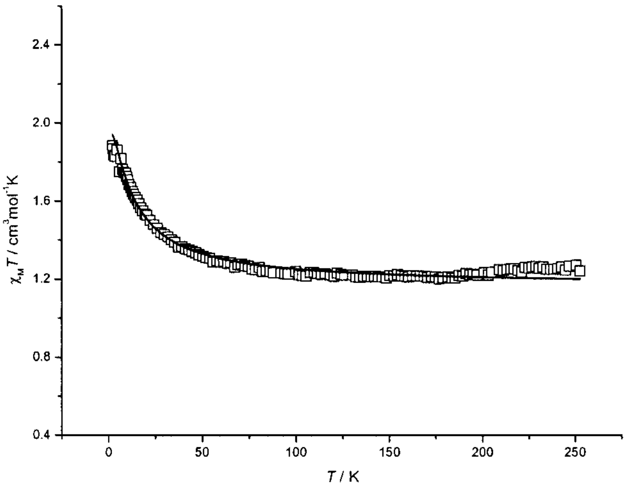


Figure 4. Temperature dependence of $\chi_m T$ of the complex, measured at 10 kOe; solid line corresponds to the best theoretical fitting (see text)

volved.[37] Thus, we employed Equation (2) to describe the low-lying electronic states:

$$H = -2J_a(S_1 \cdot S_2 + S_1 \cdot S_3) - 2J_b(S_2 \cdot S_3) \qquad (2)$$

where $J_a = J_{12} = J_{13}$ is the coupling constant between bidentate carboxylato-bridged Cu2 and Cu1, or Cu2 and Cu1A, while $J_b = J_{23}$ is that between Cu1 and Cu1A, which are connected by the N−(CH$_2$)$_2$−O spacer (Figure 2). Application of van Vleck's susceptibility equation, and adding the Zeeman term to the preceding Hamiltonian (considering equal and isotropic *g* values for the three copper ions), gives Equation (3) for the molar susceptibility:

$$\chi_m = \frac{Ng^2\beta^2}{4kT}\,\frac{10\exp(J_a+2J_b)/kT+\exp(-2J_a+2J_b)/kT+1}{2\exp(J_a+2J_b)/kT+\exp(-2J_a+2J_b)/kT+1} \qquad (3)$$

The best fit of the data through Equation (3) gives $g = 2.04$, $J_a = 8.08$ cm^{-1} and $J_b = -0.40$ cm^{-1}. The reliability factor, defined as $R\ (\chi_m T) = (\chi_m T_{\mathrm{obs}} - \chi_m T_{\mathrm{calcd.}})^2/(\chi_m T_{\mathrm{obs}})^2$, is 4.02×10^{-4}. The calculated data curve (solid line in Figure 4) matches the experimental magnetic data well. The positive J_a and the small negative J_b imply a ferromagnetic exchange interaction between the μ-carboxylato-bridged Cu2 and Cu1, or Cu2 and Cu1A, with a weak antiferromagnetic exchange interaction between Cu1 and Cu1A.

The magnetization measured at 1.84 K increases with the field, and reaches 3.25 Nβ per Cu$_3$ at 70 kOe, which is slightly higher than the expected saturation value of 3 Nβ for three spin-only Cu$^{\mathrm{II}}$ ions with $S = {}^1/_2$, $g = 2.0$ (Figure 5).

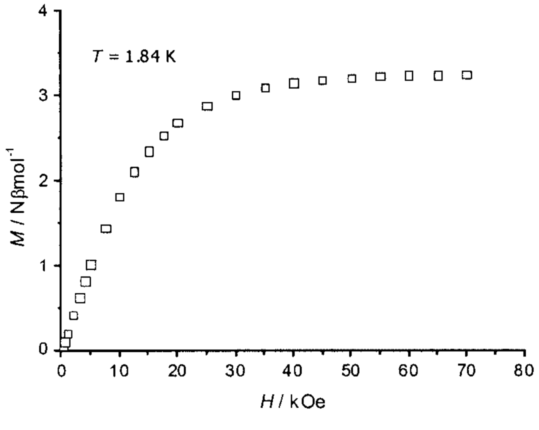


Figure 5. Magnetization versus field up to $H = 70$ kOe (at 1.84 K)

The exchange coupling in acetato- and related carboxylato-bridged complexes is largely determined by the conformation of the bridge and the interaction between the d orbitals of the metal ion and the bridge. In complexes where the metal ions are bridged in a *syn-syn* manner, the Cu−Cu distances are very small (e.g. 2.64 Å[38]) and the exchange coupling constants are very large, and nearly all with antiferromagnetic interaction. The dimeric complex $Cu_2(OAc)_4{\cdot}2H_2O$ ($2J = -286\ cm^{-1}$) is one example of such bridging.[39] As previously noted, the magnitude of the antiferromagnetic interaction depends on the overlap of the magnetic orbitals centered on nearest-neighbor copper ions. In such complexes, the acetato ligands interact directly with the d orbitals of the copper ions. However, in complexes containing *syn-anti* type bridges, the exchange coupling constants ($J \approx 4-7\ cm^{-1}$) are usually smaller and the exchange is ferromagnetic.[22–25] This might be because the *syn-anti* bridging carboxylate groups bind copper ions with a Cu−Cu distance that is too long to form a direct interaction (such as the Cu−Cu distance of 4.554 Å in the present complex). For the *syn-anti* conformation of the Cu−O−C−O′−Cu′ bridges, the 2p orbitals of O and O′ belonging to the magnetic orbitals centered on Cu and Cu′, respectively, are unfavorably oriented to give a strong overlap. This reduces the antiferromagnetic contribution, which would lead ultimately to an overall ferromagnetic behavior.[25]

Rodríguez-Fortea et al. have recently reported a theoretical study of the exchange coupling through *syn-anti* bridging carboxylate groups.[40] Their computational study showed that the calculated coupling constant in the *syn-anti* case is weakly ferromagnetic ($+10.2\ cm^{-1}$). Because of the rareness of the *syn-anti* case, the authors can only compare their results with the one available compound with a *syn-anti* coordination mode. The coupling constant of $+8.08\ cm^{-1}$ in our present compound agrees well with the result above, providing an important *syn-anti* case.

Conclusion

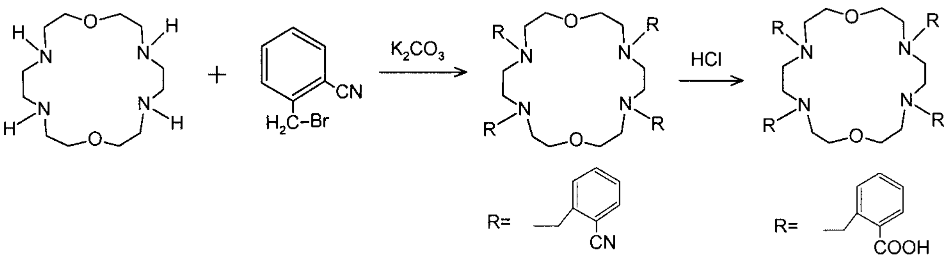
The novel tetraazamacrocyclic ligand containing four pendent *o*-toluic acid groups has been prepared by the hydrolysis of the cyano groups. Because of the strong coordinating ability of the carboxylate groups and the large steric hindrance from the four bulk *o*-toluic acid pendant arms, we obtained its trinuclear copper(II) complex. For the complex, the three Cu^{II} cores are in an isosceles triangular arrangement and adjacent copper ions are connected by μ_2-didentate *syn-anti* carboxylate groups and an $N{-}(CH_2)_2{-}O$ spacer. The trinuclear copper(II) complex units are connected into a one-dimensional zigzag hydrogen-bonding chain. Magnetic property studies revealed a ferromagnetic interaction, which corresponds with the magnetic coupling observed for other *syn-anti*-bridged complexes.

Experimental Section

General Remarks: All commercially available chemicals were of analytical grade and were used as received. C, H and N were determined using an Elementar vario EL elemental analyzer. The IR spectra were recorded with a Nicolet-AVATAR 360 FT-IR spectrometer using KBr pellets in the 4000−400 cm^{-1} regions. Variable-temperature magnetic susceptibility data for a crystalline sample of complex were obtained in an external field of 10.0 kG with an Oxford Maglab 2000 system magnetometer from 300 to 2 K. 1,10-Dioxa-4, 7,13,16-tetraazacyclooctadecane (**1**) was prepared according to a literature procedure.[41]

4,7,13,16-Tetrakis(2-cyanobenzyl)-1,10-dioxa-4,7,13,16-tetraazacyclooctadecane (2): To prepare compound **2** (Scheme 1) a mixture of azacrown ether **1** (0.26 g, 1 mmol) and anhydrous K_2CO_3 (1.10 g, 8 mmol) was heated under reflux in acetonitrile (15 mL) for 4 h, and then an acetonitrile solution (15 mL) of 2-(bromomethyl)benzonitrile (0.78 g, 4 mmol) was added. The resultant mixture was heated under reflux for a further 20 h. The so-obtained precipitate was then filtered off and the mother liquor was cooled slowly to room temperature. After 2 h, colorless plate crystals of **2** formed from the mother liquor. Mp 119−121°C. $C_{44}H_{48}N_8O_2$ (720.9): calcd. C 73.29, H 6.66, N 14.89; found C 73.10, H 6.39, N 14.79. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): = 2.79−2.83 (m, 16 H, NCH_2), 3.56−3.58 (t, $J_{H,H}$ = 5.5 Hz, 8 H, OCH_2), 3.80 (s, 8 H, CH_2), 7.31−7.34 (t, $J_{H,H}$ = 7.7 Hz, 4 H, ArH), 7.49−7.53 (m, 4 H, ArH), 7.59−7.61 (d, $J_{H,H}$ = 7.7 Hz, 8 H, ArH) ppm. IR (KBr pellet): $\tilde{\nu}$ = 2223 s, 1596 m, 1483 m, 1447 s, 1363 m, 1350 m, 1310 m, 1284 m, 1121 s, 1063 s, 1051 s, 937 m, 772 m, 561 w cm^{-1}.

4,7,13,16-Tetrakis(2-carboxybenzyl)-1,10-dioxa-4,7,13,16-tetraazacyclooctadecane Tetrahydrochloride ($H_4L{\cdot}4HCl$): A solution of azacrown ether **2** (0.72 g, 1.0 mmol) in 4 M aqueous HCl (30 mL) was heated under reflux overnight (see Scheme 1). The solvent was then removed by evaporation on a water bath. The resultant residue was dissolved in aqueous HCl (1:1, 10 mL) and heated at 70−80°C. After cooling, plate crystals were obtained as the tetrahydrochloride salt. $C_{44}H_{56}Cl_4N_4O_{10}$ (942.4): calcd. C 56.05, H 5.94, N 6.79;



1 **2** **H_4L**

Scheme 1

found C 55.87, H 6.13, N 6.41. IR (KBr pellet): $\tilde{\nu}$ = 3390 s, 1704 s, 1600 m, 1579 m, 1449 s, 1399 s, 1300 s, 1230 s, 1119 m, 1081 m, 971 w, 745 m, 650 m cm^{-1}.

$[Cu_3L\cdot 2H_2O]^{2+}\cdot 2NO_3^{-}\cdot 2H_2O$: $Cu(NO_3)_2\cdot 3H_2O$ (0.04 g, 0.15 mmol) was added to a water/methanol (1:4, 10 cm^3) solution of the ligand $H_4L\cdot 4HCl$ (0.047 g, 0.05 mmol). The pH of the reaction solution was adjusted to 5 with triethylamine. Subsequent slow concentration at room temperature afforded blue crystals suitable for X-ray determination. $C_{44}H_{56}Cu_3N_6O_{20}$ (1179.57): calcd. C 44.76, H 4.75, N 7.12; found C 44.51, H 4.41, N 7.35. IR (KBr pellet): $\tilde{\nu}$ = 3429 m, 1608 m, 1594 s, 1567 s, 1457 m, 1426 s, 1384 s, 1365 s, 1336 s, 1285 w, 1086 m, 991 w, 745 m cm^{-1}.

X-ray Crystallographic Study: An X-ray diffraction analysis of a crystal (0.60 × 0.26 × 0.22 mm) was preformed with a Bruker SMART 1000 CCD diffractometer at 293 K with graphite-monochromatized Mo-K_{α} radiation (λ = 0.71073 Å). Semiempirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXS-97 and SHELXL-97 programs.[42] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinements. Disorder of the nitrate anion was found in the crystal. The site occupation factor for each nitrate anion was refined to 70.4 and 29.9%, respectively. Crystallographic data and details of the structure refinements are summarized in Table 3. CCDC-205577 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure refinement details for the complex

Empirical formula	$C_{44}H_{56}Cu_3N_6O_{20}$
Formula mass	1179.57
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *C*2/*c*
Unit cell dimensions	a = 29.454(16) Å b = 9.756(6) Å c = 17.473(10) Å β = 110.157(9)°
Volume	4713(4) Å^3
Z, calculated density	4, 1.662 Mg/m^3
Absorption coefficient	1.430 mm^{-1}
F(000)	2436
Crystal size	0.60 × 0.26 × 0.22 mm
θ range for data collection	2.21−25.00°
Limiting indices	$-34 \leq h \leq 32$, $-11 \leq k \leq 11$, $-10 \leq l \leq 20$
Reflections collected/unique	9907/4119 [R(int) = 0.0464]
Completeness to θ = 25.00°	99.2%
Absorption correction	semiempirical from equivalents
Max. and min. transmission	1.000000 and 0.747142
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	4119/93/371
Goodness of fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0417, $wR2$ = 0.0827
Extinction coefficient	0.00043(7)
Largest diff. peak/hole	0.432/−0.425 e·A^{-3}

Acknowledgments

We are grateful to the Municipal Natural Science Foundation of Beijing (No. 2022011).

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Received May 8, 2003
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