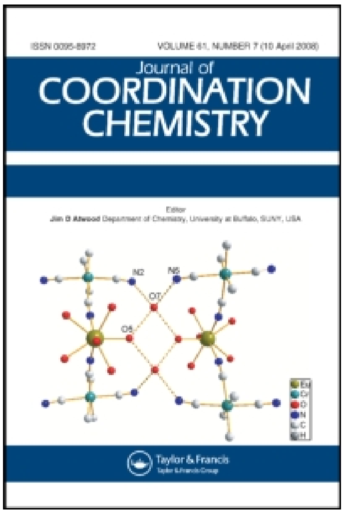

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THE POLYMERIC COPPER COMPLEX 2,2′-BIPYRIDINE-*N*,*N*′-(μ-MALEATO-*O*, *O*′ : *O*″)COPPER(II) DIHYDRATE

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Preparation and isolation of the polynuclear copper(II) complex, $\{[Cu(bipy)(maleato)]\cdot 2H_2O\}_n$, was accomplished by reaction of an aqueous solution containing sodium maleate and an ethanolic solution of $Cu(NO_3)_2\cdot 4H_2O$ and bipy. The crystal structure of the title complex was determined by single-crystal X-ray methods. The structure consists of one-dimensional infinite chains. The copper atom is five-coordinate and presents a square-pyramidal coordination sphere, which consists of the two imine N atoms of bipy and two terminal carboxylate O atoms of a maleate^{2-} ligand in the basal plane with Cu–N bond distances of 2.016(3) and 1.987(3) Å and Cu–O distances of 1.909(2) and 1.947(2) Å, respectively. In the apical site an O atom of the maleate^{2-} ligand from an adjacent complex coordinates to copper (2.264(2) Å). The coordination fashion of the maleato ligand is also confirmed by the IR spectrum.

Keywords: Copper(II); bipyridine; crystal structure

INTRODUCTION

The synthesis of polymetallic coordination complexes, particularly those having two- or three-dimensional and supramolecular structures, is of current interest for inorganic chemists seeking to design new molecular materials with unusual magnetic and electrical properties.[1–3] To prepare polynuclear metal complexes, two strategies have developed, the use of

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polynucleating ligands[4] and the use of 'metal complexes as ligands.[5,6] As for the first method, from a literature survey it appears that the majority of the polynucleating ligands used so far contain two or more equivalent coordination sites, which can be occupied by metal ions to afford di- and tetra-nuclear metal complexes.[7] The second strategy, which relies on the reaction of a metal complex containing potential donor groups with a metal ion or a metal complex with empty coordination sites, is more convenient to prepare more complex systems that may represent new polymetallic magnetic models.[8–12] We introduce here the maleate ligand, which is able to be involved in both strategies.

EXPERIMENTAL

Physical Measurements

Analyses for C, H and N were carried out with a Perkin Elmer Analyzer, Model 240. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer with KBr discs. The X-ray crystal structure study was carried out with a Rigaku AFC7R diffractometer. Thermal analyses were performed using a Perkin Elmer 7 Series System under N_2 ($40\,cm^3\,min^{-1}$) and a heating rate of $20°C\,min^{-1}$.

Preparation of $\{[Cu(bipy)(maleato)]\cdot 2H_2O\}_n$

Some 2.41 g (10 mmol) of $Cu(NO_3)_2\cdot 4H_2O$ was dissolved in $40\,cm^3$ of ethanol followed by the addition of 1.56 g (10 mmol) of 2,2′-bipyridine with stirring. The mixture solution was heated for 1 h at 75°C, then $20\,cm^3$ of an aqueous solution containing 1.16 g (10 mmol) of maleic acid and 0.8 g (20 mmol) of NaOH was slowly added with continuous stirring for 0.5 h at 75°C. The resulting solution was filtered and slowly cooled to room temperature. After several days, well-shaped, dark blue, single crystals were obtained. *Anal.* Calcd. for $C_{14}H_{14}N_2O_6Cu$(%): C, 45.47; H, 3.82; N, 7.58. Found: C, 45.26; H, 3.75; N, 7.40.

Crystal Structure Determination

A brown prismatic crystal of the complex having approximate dimensions of 0.20 × 0.20 × 0.30 mm was mounted on a glass fibre. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation and a 12 kW rotating anode generator. Cell

TABLE I Crystal data and structure refinement details

Compound	[Cu(II)(maleato)(bipy)] · $2H_2O$
Colour/shape	Blue/prismatic
Empirical formula	$C_{14}H_{14}O_6N_2Cu$
Formula weight	369.82
Temperature	293 K
Crystal system	Monoclinic
Space group	$P2_1/a$
No. of reflections used for unit cell determination (2θ range)	20 (13.5–21.5°)
a (Å)	7.355(4)
b (Å)	19.957(3)
c (Å)	10.102(5)
β (°)	98.33(5)
V (Å^3)	1467.0(1)
Z	4
D_{calc} (g/cm^3)	1.674
μ (MoKα) (cm^{-1})	15.23
F(000)	756
Diffractometer	Rigaku AFC7R
Radiation	MoKα ($\lambda = 0.71069$ Å) graphite-monochromated
Scan type	ω–2θ
Scan width	$(0.89 + 0.30 \tan\theta)$°
$2\theta_{max}$	50°
No. of reflections measured	Total: 2888; unique: 2676 ($R_{int} = 0.022$)
Correction	Lp
Structure solution	Direct methods (SHELX86)[18]
Refinement	Full-matrix least-squares (DIRDIF92)[19]
No. of observations ($I > 2.5\sigma(I)$)	2079
No. of variables	299
Reflection/parameters ratio	9.95
Residuals: R; R_w	0.031; 0.040
S	1.44
Max. peak in final diff. map	0.29 e Å^{-3}

constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 18 carefully centred reflections in the range $13.5° < 2\theta < 21.5°$. Hydrogen atoms were refined isotropically. A summary of data collection and structure refinement is given in Table I final atomic positional parameters, selected bond lengths and bond angles are given in Tables II and III, respectively.

RESULTS AND DISCUSSION

Crystal Structure

The copper atom has square-pyramidal five-coordination as shown in Figure 1. In the basal plane, two N atoms of a bipy ligand coordinate to the

TABLE II Atomic parameters and equivalent isotropic thermal parameters

Atom	*x/a*	*y/b*	*z/c*	*Beq*(Å^2)
Cu	0.13886(5)	0.64895(2)	0.36066(4)	2.313(9)
O(1)	0.0258(3)	0.6323(1)	0.1814(2)	3.02(5)
O(2)	−0.0569(4)	0.6518(1)	−0.0338(2)	3.89(6)
O(3)	0.0158(3)	0.7348(1)	0.3702(2)	2.92(5)
O(4)	−0.0773(3)	0.8361(1)	0.3037(2)	2.69(5)
O(5)	0.0400(4)	0.0612(1)	0.8760(3)	4.52(7)
O(6)	0.7263(5)	0.0248(1)	0.9792(3)	6.20(9)
N(1)	0.1748(3)	0.5500(1)	0.3952(2)	2.31(5)
N(2)	0.2382(4)	0.6523(1)	0.5543(2)	2.51(6)
C(1)	0.0243(4)	0.6684(2)	0.0767(3)	2.58(7)
C(2)	0.1216(4)	0.7341(2)	0.0843(3)	2.56(6)
C(3)	0.1161(4)	0.7831(1)	0.1744(3)	2.37(6)
C(4)	0.0109(4)	0.7839(1)	0.2902(3)	2.16(6)
C(5)	0.1328(5)	0.5002(2)	0.3064(3)	2.88(7)
C(6)	0.1673(5)	0.4343(2)	0.3390(3)	3.34(8)
C(7)	0.2467(5)	0.4186(2)	0.4657(4)	3.77(8)
C(8)	0.2891(5)	0.4690(2)	0.5595(3)	3.39(8)
C(9)	0.2520(4)	0.5342(1)	0.5211(3)	2.33(6)
C(10)	0.2908(4)	0.5930(1)	0.6116(3)	2.42(6)
C(11)	0.3740(5)	0.5891(2)	0.7426(3)	3.68(8)
C(12)	0.4047(6)	0.6474(2)	0.8147(4)	4.3(1)
C(13)	0.3541(5)	0.7080(2)	0.7570(3)	3.73(8)
C(14)	0.2696(5)	0.7084(2)	0.6270(3)	3.29(8)

TABLE III Selected inter-atomic distances (Å) and bond angles (°)

Cu–O(1)	1.909(2)	C(1)–C(2)	1.491(4)
Cu–O(3)	1.947(2)	C(2)–C(3)	1.339(4)
Cu–O(4)	2.264(2)	C(3)–C(4)	1.494(4)
Cu–N(1)	2.016(3)	O(1)–C(1)	1.278(4)
Cu–N(2)	1.988(3)	O(2)–C(1)	1.233(4)
O(3)–C(4)	1.268(4)	O(4)–C(4)	1.244(3)
O(1)–Cu–O(3)	93.3(1)	Cu–N(2)–C(10)	115.7(2)
O(1)–Cu–O(4)	94.19(9)	Cu–O(3)–C(4)	128.3(2)
O(1)–Cu–N(1)	91.3(1)	Cu–N(1)–C(5)	126.6(2)
O(1)–Cu–N(2)	170.7(1)	Cu–N(2)–C(14)	125.3(2)
O(3)–Cu–O(4)	110.40(9)	O(3)–C(4)–O(4)	122.9(3)
O(3)–Cu–N(1)	154.7(1)	C(1)–C(2)–C(3)	128.0(3)
O(3)–Cu–N(2)	91.6(1)	C(2)–C(3)–C(4)	127.6(3)
O(4)–Cu–N(1)	94.06(9)	O(2)–C(1)–C(2)	116.6(3)
O(4)–Cu–N(2)	91.4(1)	O(4)–C(4)–C(3)	115.7(3)
N(1)–Cu–N(2)	80.9(1)	O(1)–C(1)–C(2)	120.5(3)
Cu–O(1)–C(1)	129.6(2)	O(3)–C(4)–C(3)	121.4(3)
Cu–O(4)–C(4)	130.8(2)	O(1)–C(1)–O(2)	122.9(3)
Cu–N(1)–C(9)	114.7(2)		

Cu(II) atom with an average Cu–N distance of 2.00 Å and two O atoms of the maleato ligand chelate the Cu(II) atom forming a seven-membered chelate ring, with the O1–Cu–O3 bond angle being 93.3(1)°. This is significantly larger than that found in [$Mn_4(\mu\text{-maleato})_2(bipy)_8](ClO_4)_4$ (87.52°).[13]

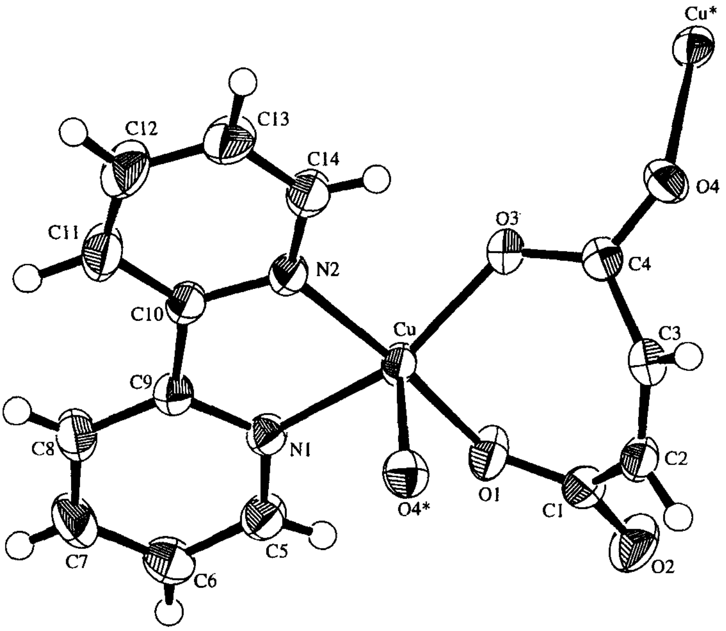

FIGURE 1 Crystal structure of $\{[Cu(bipy)(maleato)] \cdot 2H_2O\}_n$ with thermal ellipsoids drawn at the 50% probability level.

One of the carboxylate O atoms, O4, coordinates to an adjacent copper atom in the apical site with the Cu–O4 bond distance being 2.264(2) Å. In this way, a one-dimensional infinite chain is formed (Figure 2), which is comparable to that in our previous report.[14] The Cu(II) atom is 0.274 Å above the least-squares plane defined by N1, N2, O1 and O3 toward the $O4^{ii}$ atom (ii, symmetry code: $1/2 - x$, $1/2 + y$, z). C1, C2, C3 and C4 atoms are coplanar with the torsion angle C1–C2–C3–C4 being 0.1°. Nevertheless, the C2–C3 bond distance of 1.339(4) Å and the C1–C2 and C3–C4 bond distances of 1.490(4) and 1.494(4) Å, respectively, suggest that the π-electrons of C3 and C4 are not delocalized. Of the two carboxylate groups of maleato ligand, one carboxylate group bridges two Cu(II) atoms in a *syn–anti* conformation, which is different from that of $[Mn(bipy)(maleato)]_n$[15] (in which, one carboxylate group coordinates to two Mn(II) atoms in a *syn–syn* fashion, and the other in a *anti–anti* fashion), $[Mn_4(\mu\text{-maleato})_2(bipy)_8]^{4+}$[13] (in which both the carboxylate groups coordinate to Mn(II) atoms in a *anti–anti* fashion) and $[Mn_2(salpa)_2(PhCOO)_2]$ (H_2salpa = *N*-3-hydroxypropyl-salicylaldeneimine)[16] (in which carboxylate groups coordinate to Mn(III) in a *syn–syn* fashion). The C9–C10 bond distance of 1.49 Å in the

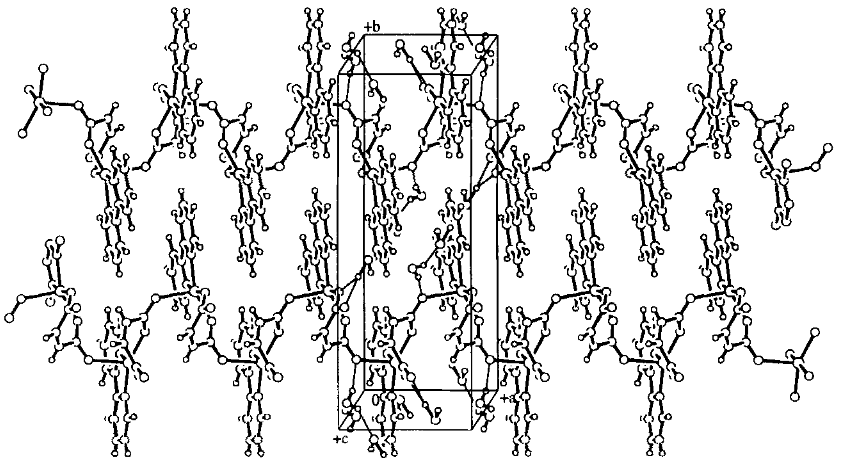

FIGURE 2 Molecular packing down the *a* axis.

bipy ligand and the N1–Cu–N2 angle of 80.9(1)° are consistent with other Cu(II) bipyridine complexes.

The distance between the uncoordinated carboxylate O3 atom and the lattice water O6* atom (*, symmetry code: $-x$, $1-y$, $1-z$) of 2.912(4) Å suggests a hydrogen bond between them. The apical O atom, O4, also forms hydrogen bond with a lattice water molecule with the $O4 \cdots O5^{iii}$ distance of 2.778(3) Å (iii, symmetry code: $-x$, $1-y$, $1-z$).

IR Spectrum

The IR spectrum of the complex shows two strong and broad IR bands centred at 3450 and 3380 cm^{-1} which are assigned to the O–H stretching of the lattice water molecules. Carboxylate groups can coordinate to metal ions in a number of ways and IR spectroscopy is a useful tool in diagnosing the nature of carboxylate coordination. The separation between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ when significantly less than the free carboxylate anion value is considered indicative of a bidentate bridging or chelating carboxylate group, and separation more than the free anion value is indicative of a unidentate ligand.[17] The IR spectrum of the complex displays a $\nu_{as}(COO^-)$ band at 1560 and a $\nu_s(COO^-)$ band at 1402 cm^{-1}; the 158 cm^{-1} separation being significantly smaller than the value of 200 cm^{-1} for the free maleate dianions, indicating that the carboxylate groups coordinate to metal ions in a bidentate bridging or chelating mode. It should be noted that in the complex the uncoordinated O3 atom interacts with a lattice water molecule (as confirmed by the crystal structure analysis). Bands at *ca.* 1600, 766 and 625 cm^{-1} correspond to ν(C=C) and δ(C–H) skeletal bending vibrations of bipy.[13]

Thermogravimetric Study

The complex loses lattice water molecules from about 50°C to about 100°C. This, compared with elemental analysis and the crystal structure, confirms the molecular structure. At about 210°C, organic ligands began to decompose quickly. At about 650°C, the weight of a black solid residual is in agreement with CuO.

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request at zcungen@kali.com.cn.

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