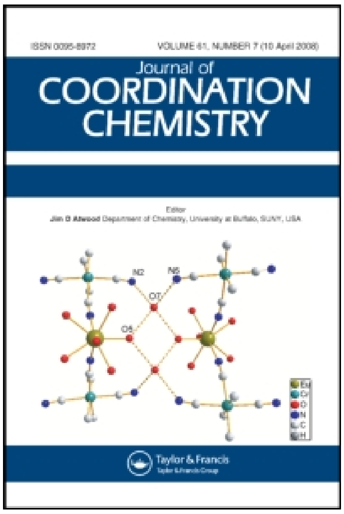

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A NOVEL BINUCLEAR COPPER(II) COMPLEX: BIS[1,10-PHENANTHROLINE-*N,N'*-MALEATO- *O,O'*-COPPER(II)] DIMETHANOL TETRAHYDRATE

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A NOVEL BINUCLEAR COPPER(II) COMPLEX: BIS[1,10-PHENANTHROLINE-*N*,*N'*-MALEATO-*O*,*O'*-COPPER(II)] DIMETHANOL TETRAHYDRATE

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A novel binuclear Cu(II) complex, $[Cu_2(mal)_2(phen)_2]\cdot 4H_2O\cdot 2MeOH$ (phen = 1,10-phenanthroline, mal = maleato dianion), has been synthesized and characterized by elemental analysis, IR spectroscopy, solid-state ESR analysis and X-ray single crystal study. The complex consists of [Cu(mal)(phen)] subunits with two water and one methanol solvate molecules. The subunits show a distorted planar arrangement, existing in centrosymmetrically related pairs in the crystal packing. They have a distorted four-coordinate square-planar arrangement of N and O atoms about the central Cu atom; pairs of these [Cu(mal)(phen)] subunits form dimers by interaction of the fifth position on each Cu center with an O atom of a maleato ligand of the associated subunit with a Cu–Cu distance of 3.3425(9) Å. The coordination around each Cu atom is best described as distorted square-pyramidal. The lattice water and methanol molecules are also confirmed by the TG study and IR spectra. The X-band solid-state ESR spectrum at room temperature exhibits an anisotropic feature with $g_{\parallel} = 2.24$, $g_{\perp} = 2.06$.

Keywords: Binuclear; copper; square planar; crystal structure

INTRODUCTION

Multi-nuclear metal complexes are of great interest not only in elucidating the magnetic coupling between metal ions but also in model compounds of the active sites of multi-metalloenzymes.[1–3] For the synthesis of polynuclear complexes, a polynucleating ligand exhibiting multi-unequivalent

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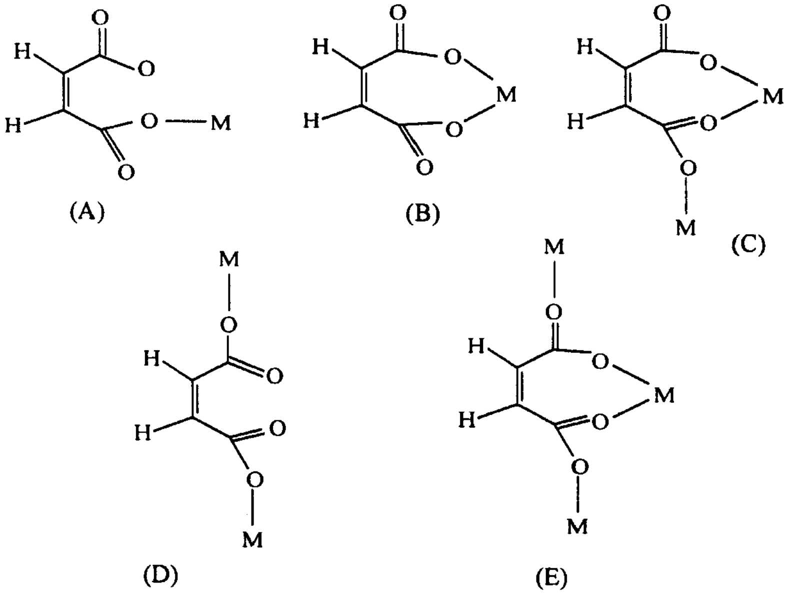
coordination sites is important.[4,5] There have been many publications of transition metal complexes containing monocarboxylate ligands. Recently some dicarboxylate ligands, *e.g.*, oxalate and malonate dianions, have also been reported to coordinate to transition metal ions in a number of ways. It is found that the oxalate ion (ox) with 2,2′-bipyridine coordinates to Cu(II) in two forms [Cu(bipy)(ox)(H_2O)] · $2H_2O$ (A) and [Cu(bipy)(ox)] · $2H_2O$ (B). X-ray structural analyses demonstrate that the former consists of a monomeric Cu(II) ternary complex while the latter contains a bridging oxalate ion.[6] Nevertheless, maleato-containing complexes are limited. Like other di-carboxylate ligands, we have found that it is a versatile ligand which exhibits the ability to coordinate to metal atoms in several ways as shown in Scheme I. A number of maleato-containing complexes have been prepared in our laboratory, *e.g.*, [Zn(imidazole)$_3$(maleato)] (in which it serves as a monodentate ligand[7]), [Co(phen)(maleato)(H_2O)$_2$] (bidentate bridging mode[8]), [Cu(bipy)(maleato)]$_n$ (tridentate bridging and chelate mode[9]) and [Mn(bipy)(maleato)]$_n$ (tetradentate bridging and chelate mode[10,11]). As a continuation of our work, we report herewith the title complex, [Cu_2(mal)$_2$(phen)$_2$] · $4H_2O$ · 2MeOH, in which the maleato ligand serves as a bidentate ligand in a chelate mode.



SCHEME I Coordination modes for maleato ligand: (A) monodentate, (B) bidentate (chelate mode), (C) tridentate (bridging and chelate mode), (D) bidentate (bridging mode) and (E) tetradentate (bridging and chelate mode).

EXPERIMENTAL

Physical Measurements

The reagents $Cu(NO_3)_2 \cdot 3H_2O$, phen, NaOH and maleate acid were commercially available and were of AR grade.

C, H and N analyses were carried out with a Perkin-Elmer Analyzer Model 240. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer with KBr discs. An X-ray crystal structure determination was carried out on a Rigaku AFC7R diffractometer. A solid-state ESR study was carried out on a Brucker ENDOR Electron Nuclear Double Resonance Spectrophotometer. Thermal studies were made on a Perkin-Elmer 7 Series System with the conditions of N_2 atmosphere (40 mL/min) and the temperature-rising rate of 10°C/min.

Synthesis of $[Cu_2(mal)_2(phen)_2] \cdot 4H_2O \cdot 2MeOH$

$Cu(NO_3)_2 \cdot 3H_2O$ of 2.41 g (10 mmol) was dissolved in 40 mL of methanol, followed by adding 1.98 g (10 mmol) of 1,10-phenanthroline with stirring. The solution was heated for 1 h at 75°C, then 20 mL of an aqueous solution containing 1.16 g (10 mmol) of maleate 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 $C_{14}H_{14}N_2O_6$-Cu (in %): C, 47.94; H, 4.26; N, 6.58. Found (in %): C, 48.26; H, 4.65; N, 6.40.

X-ray Structure Determination

A crystal of $[Cu_2(mal)_2(phen)_2] \cdot 4H_2O \cdot 2MeOH$ was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo$K\alpha$ radiation and a 12 kW rotating anode generator; the intensity data were collected by the $\omega/2\theta$ scan technique. Three standard reflections were monitored after every 97 data measurements. The crystal structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques.[12] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.[†] The crystal data are summarized in Table I. Atomic coordinates are shown in Table II.

[†] Molecular Structure Corporation, *TEXSAN, Single Crystal Structure Analysis Software*, Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1989.

TABLE I Summary of crystallographic data for the complex

Formula	$C_{34}H_{36}N_4O_{14}Cu_2$
Molecular weight	851.77
Crystal system	Monoclinic
Space group	C2/c
a (Å)	18.072(4)
b (Å)	12.515(2)
c (Å)	14.680(3)
β (°)	103.28(2)
V (Å^3)	3231(1)
Z	4
Temperature	293
No. observations $(I) > 2.0\sigma(I)$	2806
No. variables	248
R	0.039
Rw	0.054
Goodness of fit indicator	2.12
Max. shift in final cycle (Δ/σ)	0.00
Largest peak in final diff. map (eÅ^{-3})	0.31

TABLE II Fractional coordinate and equivalent isotropic thermal parameters for non-H atoms

Atom	*x/a*	*y/b*	*z/c*	*Beq* (Å^2)
Cu	0.19971(2)	0.15053(3)	0.03206(2)	3.37(1)
O(1)	0.2275(1)	0.2989(2)	0.0703(1)	3.99(5)
O(2)	0.2863(1)	0.0956(2)	0.1226(2)	4.54(5)
O(3)	0.2845(1)	0.4060(2)	0.1838(2)	5.14(6)
O(4)	0.3475(1)	0.0563(2)	0.2666(2)	5.53(6)
O(5)	0.6452(3)	0.0385(3)	0.0409(2)	9.5(1)
O(6)	0.4876(8)	0.0571(8)	0.5708(7)	10.0(4)
O(7)	0.4096(4)	0.0741(5)	0.6506(5)	10.7(2)
N(1)	0.0979(1)	0.1892(2)	−0.0487(2)	3.39(5)
N(2)	0.1598(1)	0.0017(2)	−0.0001(2)	3.30(5)
C(1)	0.0687(2)	0.2860(2)	−0.0710(2)	4.11(7)
C(2)	−0.0050(2)	0.2990(3)	−0.1282(3)	4.92(8)
C(3)	−0.0473(2)	0.2123(3)	−0.1622(2)	4.49(8)
C(4)	−0.0178(2)	0.1096(3)	−0.1396(2)	3.56(6)
C(5)	−0.0578(2)	0.0114(3)	−0.1700(2)	4.22(7)
C(6)	−0.0261(2)	−0.0837(3)	−0.1468(2)	4.23(7)
C(7)	0.0496(2)	−0.0926(2)	−0.0885(2)	3.59(6)
C(8)	0.0862(2)	−0.1894(3)	−0.0599(3)	4.66(8)
C(9)	0.1570(2)	−0.1888(3)	−0.0016(3)	4.93(9)
C(10)	0.1927(2)	−0.0913(2)	0.0274(2)	4.17(7)
C(11)	0.0894(2)	0.0011(2)	−0.0576(2)	3.04(6)
C(12)	0.0556(2)	0.1028(2)	−0.0829(2)	3.10(6)
C(13)	0.2460(2)	0.3277(2)	0.1573(2)	3.53(6)
C(14)	0.2178(2)	0.2616(3)	0.2272(2)	4.37(7)
C(15)	0.2390(2)	0.1622(3)	0.2508(2)	4.60(8)
C(16)	0.2945(2)	0.0999(2)	0.2110(2)	4.17(7)
C(17)	0.4479(5)	0.1109(7)	0.7374(8)	8.3(3)

RESULTS AND DISCUSSIONS

Crystal Structure

The molecular structure of the title complex is shown in Figure 1. Selected bond distances and angles are listed in Table III. The geometry around the Cu(II) ion is five-coordinate distorted square-pyramidal. Both the phenanthroline and maleate ions are symmetrically coordinated (mean Cu–N, 2.010, mean Cu–O, 1.952 Å), with the four atoms in the equatorial plane. The Cu(II) ion is raised above the equatorial plane defined by N1, N2, O1, O2 by 0.132 Å towards the apical O^i atom (symmetry code: (i) $1/2-x$, $1/2-y, -z$) of the neighboring maleato ligand of the associated subunit. The Cu atom to apical O^i bond is remarkably tilted away from the normal to the basal plane [O1–Cu–O1^i 77.28(9)°, N1–Cu–O1^i 97.58(9)°, O2–Cu–O1^i 93.07(9)°, N2–Cu–O1^i 109.21(9)°]. The O1^i atom occupying the fifth coordination position is at 2.301(2) Å. This is comparable to those reported for $[Cu(phen)(malonato)(H_2O)] \cdot 1.5H_2O$[13] and $[Cu(bipy)(ox)(H_2O)] \cdot 2H_2O$.[6] The bite angle N–Cu–N of 81.6° is close to those reported for $[Cu(phen)(malonato)(H_2O)] \cdot 1.5H_2O$ (81°), $[Cu(phen)(Nal)(H_2O)]NO_3 \cdot 3H_2O$ (81.9°)[14] (Nal = nalidixate) and $[Cu(phen)_2Br]ClO_4$ (81.1°).[15]

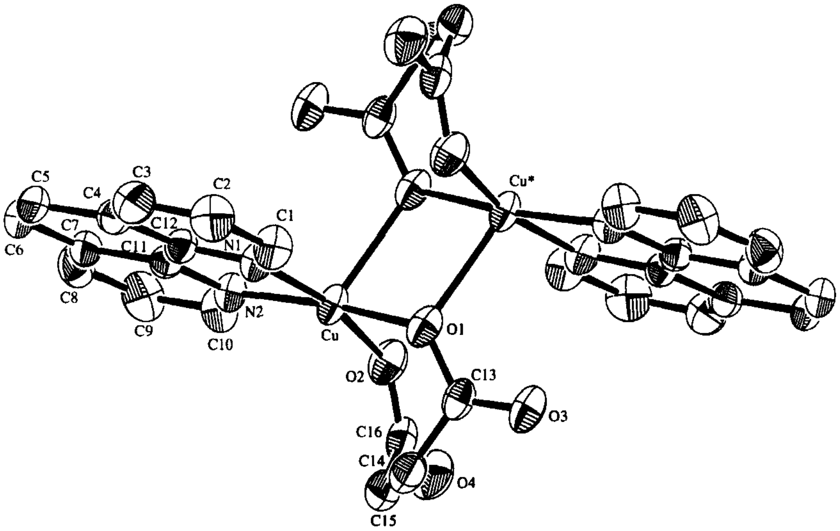


FIGURE 1 Perspective view of $[Cu_2(mal)_2(phen)_2]$ represented by 30% thermal ellipsoids. Hydrogen atoms were not included for clarity (see text footnote † for reference).

TABLE III Bond distances (Å) and bond angles (°) for (2)

Cu–O1	1.971(2)	Cu–N2	2.014(2)
Cu–O1^{i}	2.301(2)	C13–C14	1.497(5)
Cu–O2	1.932(2)	C14–C15	1.325(5)
Cu–N1	2.006(2)	C15–C16	1.491(5)
Cu–Cu^{i}	3.3425(9)		
O1–Cu–O1^{i}	77.28(9)		
O1–Cu–O2	91.50(9)		
O1–Cu–N1	94.60(9)		
O1–Cu–N2	172.80(9)		
O1^{i}–Cu–O2	93.07(9)		
O1^{i}–Cu–N1	97.58(9)		
O1^{i}–Cu–N2	109.21(9)		
O2–Cu–N1	168.7(1)		
O2–Cu–N2	91.24(9)		
N1–Cu–N2	81.6(1)		
Cu–O1–Cu^{i}	102.72(9)		
Cu–O1–C13	122.3(2)		
Cu–O1–C13	120.7(2)		
Cu–O2–C16	125.0(2)		
Cu–N1–C1	128.5(2)		
Cu–N1–C12	112.9(2)		
Cu–N2–C10	129.0(2)		
Cu–N2–C11	112.6(2)		

Symmetry code: (i): $1/2-x$, $1/2-y$, $-z$.

On comparison with other reported structures of complexes containing phen, there are no unusual bond angles or bond lengths.

The maleato ligand chelates the copper ion *via* two terminal carboxylate oxygen atoms forming a seven-membered ring with the O1–Cu–O2 angle of 91.50(9)°. The C14–C15 distance of 1.325(5) Å which is moderately shorter than those for C15–C16 (1.491(5) Å) and C13–C14 (1.497(5) Å) suggests that the π-electrons are partially delocalized. This is also confirmed by the C13–C14–C15–C16 torsion angle of 0.2°. The Cu–Cu^{i} distance is 3.3425(9) Å.

Thermochemistry Study

TG showed that it is possible to obtain the anhydrous, methanol-free complex by heating to about 100°C for a short period (Figure 2). The first step of weight loss was the lattice water and methanol molecules. The resulting solvate-free complex is stable in the range 100–200°C. At 220°C, the maleato ligand began to decompose quickly with a weight loss of 19.2%. Then a second platform is observed between 225°C and 300°C. The weight loss of 41.5% between 380°C and 540°C is in agreement with the weight

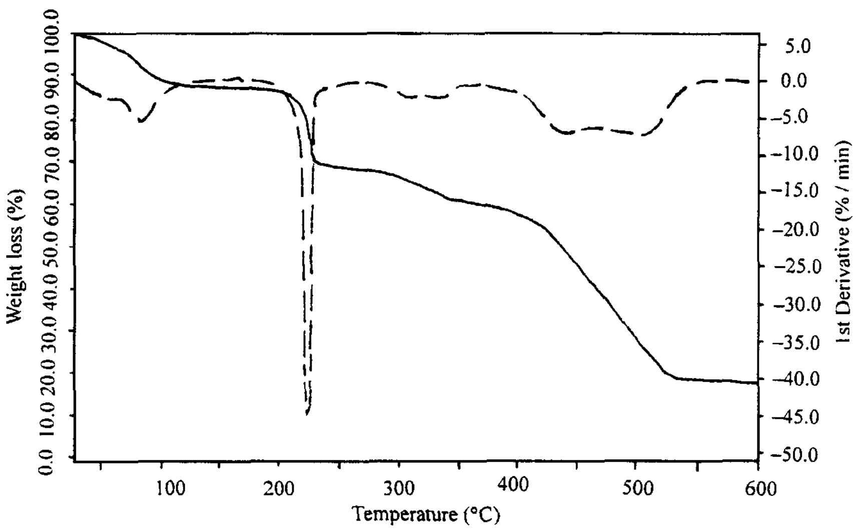


FIGURE 2 Weight loss curve for $[Cu_2(mal)_2(phen)_2]\cdot 4H_2O\cdot 2MeOH$; (—) represents the weight loss; (- - -) represents the rate of weight loss.

required for phen which is comparable to [Cu(phen)(ox)] (460–580°C), $[Cu(phen)(ser\text{-}O)]\cdot 0.5SO_4\cdot H_2O$ (400–500°C), $[Cu(phen)(tyr\text{-}O)]Cl\cdot 2H_2O$ (420–560°C).[14] At 540°C, all organic groups have decomposed and the last black residue of 18.76% is in agreement with that required for CuO.

IR and ESR Spectra

IR spectrum of the complex showed a broad peak centered at about $3401\,cm^{-1}$ which is indicative of the lattice water molecules. A peak at $3060\,cm^{-1}$ is assigned to 6C–H bending vibrations of phen and maleate ion. The C=O absorption peak of free maleaic acid at $1718\,cm^{-1}$ is shifted to $1587\,cm^{-1}$ in the title complex which is comparable to the maleate copper complexes.[16] A peak at $1429\,cm^{-1}$ is attributed to the C–O vibration. The metal–oxygen stretches were found at $779\,cm^{-1}$ comparable to those of other M–O(carboxylate) bonds.[13] A solid-state X-band ESR study of the complex showed two anisotropic peaks (Figure 3) with $g_{\parallel}=2.24$ and $g_{\perp}=2.06$ which is similar to those reported for $[Cu(phen)(malonato)(H_2O)]\cdot 1.5H_2O$ ($g_{\parallel}=2.27$ and $g_{\perp}=2.03$), [Cu(bipy)(malonato)] ($g_{\parallel}=2.26$ and $g_{\perp}=2.04$) and [Cu(phen)(ox)] ($g_{\parallel}=2.35$ and $g_{\perp}=2.08$).[13] No half-field signal is observed at room temperature. This suggests no magnetic interaction between the two copper ions.

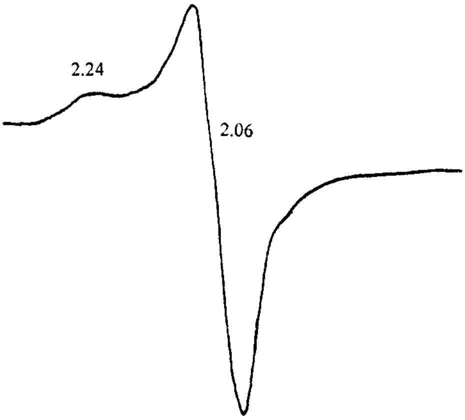


FIGURE 3 Solid-state ESR spectrum of $[Cu_2(mal)_2(phen)_2]$. Conditions: temperature, 21°C; gain, 3.2×10^5; scan time, 4 min; time constant, 0.5 s; modulation frequency, 100 kHz; fieldset, 3000 G; scan range, 3000 G; frequency, 9.783 GHz.

Acknowledgments

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Supplementary Materials

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 117665. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0)1223-336033 or E-mail: deposit@chemcrys.cam.ac.uk).

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