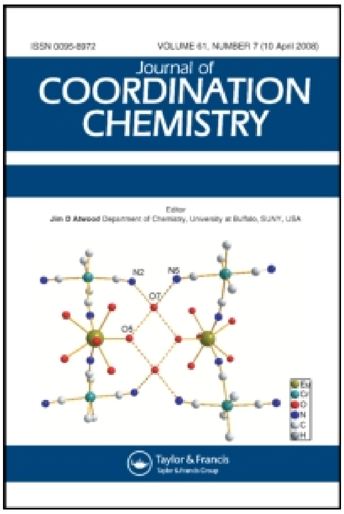

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Note: Synthesis And Crystal Structure Of A Binuclear Fumarate Complexof Copper(II) With 1,10-Phenanthroline

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Note

SYNTHESIS AND CRYSTAL STRUCTURE OF A BINUCLEAR FUMARATE COMPLEX OF COPPER(II) WITH 1,10-PHENANTHROLINE

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As dicarboxylate complexes of transition metal possess potentially useful electronic and magnetic properties, [Mehrotra and Bohra (1983). *Metal Carboxylates*. Academic Press, London], much interest in their synthesis and structure has been apparent recently [Kaneko and Tsuchida (1981). *J. Polymer Sci., Macromolecular Reviews*, **16**, 397; Holton, Lappert, Pearce and Yarrow (1983). *Chem. Reviews*, **83**, 135]. A series of metal complexes bridged by dicarboxylates has been synthesized in our laboratory and crystal structures show versatile coordination modes for the carboxyl group [Cheng, Liu, Xu and Xu (1999). *J. Coord. Chem.*, **48**, 495; Nie, Liu, Luo and Xu (2001). *J. Coord. Chem.*, **53**, 365]. As a part of this investigation, we have synthesized a binuclear fumarate complex of Cu(II). X-ray analysis shows considerable coordination distortion resulting from close stacking interaction of aromatic phen rings.

Keywords: Copper; Phenanthroline; Fumaric acid; X-ray structure

EXPERIMENTAL

An aqueous solution (5 cm^3) containing fumaric acid (0.058 g, 0.5 mmol) and NaOH (0.040 g, 1 mmol) was slowly added to an aqueous solution (5 cm^3) containing $CuCl_2 \cdot 2H_2O$ (0.171 g, 1 mmol) with continuous stirring. After refluxing the above solution for 30 min, a great deal of precipitate was produced. An ethanol solution (10 cm^3) containing 1,10-phenanthroline (0.198 g, 1 mmol) was slowly added to the reaction mixture with stirring and refluxed for about 2 h until the precipitate dissolved. The color of the solution changed to blue–green and the reaction mixture was cooled to room temperature and filtered. Blue–green single crystals were obtained from the filtrate by slow evaporation.

Elemental analyses were carried out using a Carlo-Erba 1160 instrument. *Anal.* Calc. for $C_{28}H_{22}Cl_2N_4O_6Cu_2$ (%): C, 47.47; N, 7.91; H, 3.11; Found: C, 47.58;

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N, 7.73; H, 3.22. IR spectra were measured on KBr discs using a Nicolet 5DX FT-IR spectrophotometer.

X-ray diffraction intensity data were collected on a Rigaku AFC7R diffractometer up to a 2θ value of 50° with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan technique. A total of 2672 independent reflections was collected, of which 1843 reflections were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. Usual Lp and empirical absorption corrections were applied. Structure refinement was carried out by full-matrix least-squares procedures using the SHELX-93 program package [6]. Anisotropic refinement on F^2 including all the nonhydrogen atoms converged to $R = 0.037$.

Crystal Data: $[C_{14}H_{11}ClN_2O_3Cu]_2$, $Mr = 708.48$, monoclinic, space group $p2_1/n$, $a = 10.242(4)$, $b = 10.337(5)$, $c = 13.344(3)$Å, $\beta = 105.29(3)°$, $V = 1362.7(9)$Å^3, $z = 2$, $F(000) = 716$, $D_c = 1.727\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo}K\alpha) = 1.809\,\mathrm{mm^{-1}}$, $S = 1.03$, $\rho_{\max} = 0.759$, $\rho_{\min} = -0.614\,\mathrm{e}$Å^{-3}.

RESULTS AND DISCUSSION

Final fractional atomic coordinates and equivalent isotropic thermal parameters for all nonhydrogen atoms are listed in Table I. The molecular structure of the binuclear complex is illustrated in Fig. 1. The Cu atom assumes a distorted square pyramidal coordination geometry. A water molecule [O3] occupies the apex with a longer coordination distance of 2.265(4) Å, showing typical Jahn–Teller distortion. The Cu(II) atom deviates 0.329 Å from the basal plane formed by C1, N1 and N2 atoms towards the fifth atom, similar to other Cu(II) complexes with square pyramidal coordination geometry [7]. It is notable that O1 deviates from the above plane by

TABLE I Fractional atomic coordinates [× 10^4] of nonhydrogen atoms and equivalent isotropic thermal parameters [× 10^3]

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
Cu	3117(1)	2033(1)	6155(1)	29(1)
C1	1584(1)	967(1)	6780(1)	54(1)
O1	1941(3)	3523(3)	5784(2)	34(1)
O2	952(3)	2557(4)	4297(3)	55(1)
O3	4351(4)	3253(4)	7477(3)	54(1)
N1	4322(3)	2587(3)	5230(3)	32(1)
N2	4566(3)	656(3)	6562(3)	31(1)
C1	4150(5)	3534(5)	4533(4)	45(1)
C2	5138(6)	3849(6)	4033(4)	57(1)
C3	6313(6)	3203(6)	4245(4)	57(2)
C4	7750(5)	1426(6)	5253(5)	57(2)
C5	7883(5)	450(6)	5939(5)	57(2)
C6	6881(6)	– 875(5)	7130(5)	57(2)
C7	5808(6)	– 1105(5)	7515(4)	57(2)
C8	4641(5)	– 333(5)	7207(4)	45(1)
C9	5505(4)	1922(4)	5447((3)	35(1)
C10	6550(5)	2197(5)	4980(4)	45(1)
C11	6830(5)	140(5)	6423(4)	46(1)
C12	5633(4)	880(4)	6168(3)	35(1)
C13	1015(4)	3428(4)	4940(3)	34(1)
C14	– 22(4)	4472(4)	4720(3)	35(1)

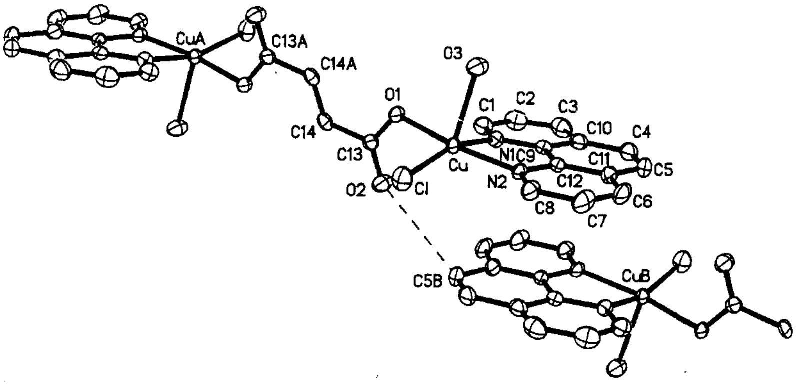

FIGURE 1 An ORTEP drawing of the binuclear molecular structure showing 30% probability displacement ellipsoids; H atoms are omitted for clarity. The dashed line shows a short contact between the coordinated carboxyl group and a phen ligand of an adjacent molecule. The atoms with suffix A and B are generated by the transform $-x$, $1-y$, $1-z$ and $1-x$, $-y$, $1-z$, respectively.

0.804 Å, also towards the fifth atom. Although the appreciable distortion results in less overlap of atomic orbital of Cu(II) and O1, the Cu–O1 distance of 1.937(3) Å is normal. This may imply more electrostatic interaction between the atoms.

The complex is centrosymmetric. A fumarate dianion bridges two Cu atoms by monodentate carboxyl groups to form the binuclear molecule. The carbon skeleton of fumarate possesses good planarity and is almost perpendicular to the basal coordination plane, the dihedral angle being 87.6°. C–C distances of 1.487(6) and 1.316(9) Å showed no electron delocalization in the fumarate moiety.

Close stacking of aromatic rings is observed between adjacent molecules as shown in Fig. 1. Two phen rings related by an inversion center overlap each other with a separation of 3.43 Å, significantly shorter than the van der Waals thickness of aromatic rings [8]. As a result of close stacking of phen rings, C5B of the phen ring lies towards the sixth coordination site of an adjacent Cu(II) atom as shown in Fig. 1, the O3–Cu–C5B angle being 162.4°. Although the Cu–C5B distance of 3.732 Å suggests no bonding interaction between Cu(II) and C5B, the O2···C5B distance of 3.374 Å shows a possible contact between the carboxyl group and the adjacent phen ligand. This indicates possible repulsion between the carboxyl group and the adjacent phen ligand and is considered as a reason for the serious deviation of the O1 atom from the basal coordination plane.

Intermolecular H-bonding interactions exist between C1 and water [C1–O3$(0.5-x, -0.5+y, 1.5-z)=3.204$ Å] and between carboxyl group and water [O2–O3 $(-0.5+x, 0.5-y, -0.5+z)=2.681$ Å].

IR spectra of the complex was assigned based on the solid state structure. Stretches observed at 1377 cm^{-1} [ν_s(COO)] and 1571 cm^{-1} [ν_{as}(COO)], agree with those found in other metal complexes with a carboxyl group as a monodentate ligand [9].

Acknowledgment

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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