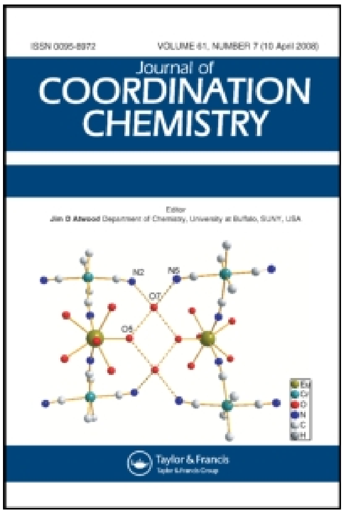

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SYNTHESIS AND CRYSTAL STRUCTURE OF A FUMARATOCOPPER(II) COMPLEX WITH BIPYRIDINE

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The title complex $[Cu_2(C_4H_2O_4)_2\ (bipy)_2\ (H_2O)_3] \cdot 3H_2O$ (bipy = 2,2′-bipyridine) was prepared and its crystal structure determined by X-ray diffraction methods. Both Cu(II) atoms of the binuclear complex assume square pyramidal coordination. The fumarate groups display different coordination modes. One fumarate group bridges two Cu(II) ions to form a binuclear complex while another fumarate group terminally coordinates to a Cu(II) atom with one carboxyl group free from coordination. The terminally coordinated fumarate showed unusual disorder, which may be due to an intermolecular H-bonding interaction. Close stacking of bipy rings is observed as verified by the distance of 3.46 Å between parallel ring planes. IR spectra were assigned based on the molecular structure.

Keywords: Copper(II); Crystal structure; Fumarate; Bipyridine; Aromatic stacking

INTRODUCTION

Because of their potentially useful electronic or magnetic properties, multinuclear metal complexes containing various types of bridging ligands have attracted much interest [1,2]. A series of transition metal complexes bridged by a dicarboxylate has been synthesized in our laboratory. Their crystal structures show versatile coordination modes of the carboxyl group, either bridging or terminal with uni- or bidentate chelation [3–5]. In the present work we used fumaric acid to synthesize a new Cu(II) complex; X-ray analysis shows two different coordination modes in the binuclear complex.

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EXPERIMENTAL

Synthesis

An ethanol solution (10 cm^3) containing 2,2′-bipyridine (0.156 g, 1 mmol) was slowly added to an aqueous solution (10 cm^3) containing $CuCl_2 \cdot 2H_2O$ (0.171 g, 1 mmol) with continuous stirring and refluxing. A great deal of precipitate was produced. An aqueous solution (10 cm^3) containing fumaric acid (0.116 g, 1 mmol) and NaoH (0.0809, 2 mmol) was slowly added to the above reaction mixture with continuous stirring and refluxing until the precipitate was dissolved. After the colour of the solution changed to blue–green, the reaction mixture was cooled to room temperature and filtered. Blue–green single crystals were obtained from the solution by slow evaporation of the solvent.

Elemental analyses for C, N and H were carried out using a Carlo-Erba 1160 instrument. *Anal.* Calc. for $C_{28}H_{32}N_4O_{14}Cu_2$ (%): C, 43.4; N, 7.2; H, 4.1; Found: C, 43.5; N, 7.5; H, 4.0. IR spectra were measured with KBr discs using a Nicolet 5DX FT-IR spectrophotometer.

Crystal Structure Determination

A single crystal of the title complex with approximate dimensions 0.41 × 0.40 × 0.30 mm was mounted on a glass fibre. X-ray diffraction intensity data were collected at 293 K on a Rigaku AFC7S diffractometer up to a 2θ value of 50° with graphite-monochromatized MoKα radiation ($\lambda = 0.7107$ Å) using the $\omega/2\theta$ scan technique. A total of 5821 independent reflections was collected, of which 3639 reflections were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. Usual Lp and empirical adsorption corrections were applied.

The structure was solved by direct methods followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the SHELX-93 program package [6]. After all of the non-H atoms were reasonably located, the terminal fumarate group on Cu(2) atom was found to be disordered. The two different configurations were each given a site occupancy factor of 0.5 in the following cycles of least-squares refinement. H atoms bound to the ordered non-H atoms were located in a difference Fourier map and were set riding on the non-H atoms during structure refinement. Anisotropic refinement including all the non-H atoms converged to $R = 0.047$ for observed reflections. Atomic scattering factors were taken *International Tables for X-ray*

Crystallography [7]. Final fractional atomic coordinates and equivalent isotropic thermal parameters for all the non-H atoms are listed in Table I.

Crystal Data

$C_{28}H_{32}N_4O_{14}Cu_2$, FW = 775.66, monoclinic, space group $P2_1/c$, $a = 14.091(3)$, $b = 13.407(3)$, $c = 18.595(4)$ Å, $\beta = 109.48(3)^\circ$, $V = 3311.9(11)$ Å^3, $Z = 4$, $F(000) = 1592$, $D_c = 1.556\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{MoK}\alpha) = 1.357\,\mathrm{mm^{-1}}$, $S = 1.05$, $\rho_{\max} = 1.19$, $\rho_{\min} = -0.56$ e Å^{-3}.

RESULTS AND DISCUSSION

Crystal Structure

Selected atomic separations and angles are listed in Table II. The molecular structure of the binuclear complex is illustrated in Fig. 1. Both Cu atoms are square-pyramidally coordinated with a water molecule at the apex. Cu(II) atoms deviate from the equatorial coordination planes towards the apical ligand by about 0.2 Å. The equatorial coordination planes of both Cu atoms are almost perpendicular to the plane of the bridging fumarate ligand. Uncoordinated oxygen atoms on both ends of the bridging fumarate are very close to the *trans* position with respect to the apical water molecules. This makes the coordination geometry of the Cu atoms almost octahedral with one very long (2.78 Å) apical Cu–O distance and another apical Cu–O distance slightly longer than those in the equatorial plane. This is consistent with Jahn-Teller distortion in the complexes. Different coordination environments are observed for Cu(1) and Cu(2) atoms, a fumarate group terminally coordinates the Cu(2) atom but not the Cu(1) atom.

The fumarate groups display different coordination modes in the present complex. A bridging fumarate links two Cu(II) atoms to form a binuclear complex. A terminal fumarate coordinates to the Cu(2) atom with one carboxyl group free from coordination. Except for the uncoordinated carboxyl group, the terminal fumarate is disordered as shown in Fig. 1 (solid ellipsoids for fumarate A and dashed ellipsoids for fumarate B). The nearest distances between the terminal fumarate and the non-H atoms of the neighbouring complex are listed in Table II. Nearest contacts of 3.621 Å for fumarate A and 3.755 Å for fumarate B indicate the presence of some space around the terminal fumarate in the crystal. H-bonds between the disordered fumarate groups and water molecules are observed

TABLE I Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$]

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	99(1)	5166(1)	2000(1)	33(1)
Cu(2)	5009(1)	318(1)	3168(1)	39(1)
N(1)	−411(3)	6290(3)	1248(2)	36(1)
N(2)	−610(3)	4370(3)	1059(3)	36(1)
N(3)	5692(3)	986(3)	4169(3)	42(1)
N(4)	5528(3)	−896(3)	3807(3)	37(1)
O(1)	803(3)	3982(3)	2528(2)	38(1)
O(2)	1868(3)	4373(3)	1921(2)	44(1)
O(3)	4343(3)	1561(3)	2714(2)	44(1)
O(4)	3133(3)	1021(3)	3130(2)	44(1)
O(5)	944(3)	6046(3)	2836(2)	48(1)
O(6)	−1176(3)	5131(4)	2460(2)	58(1)
O(8)	4247(3)	−400(4)	2250(3)	68(1)
O(7)	6373(3)	475(4)	2720(3)	61(1)
O(9A)	4983(6)	42(8)	1551(4)	60(3)
O(9B)	3067(9)	−1233(6)	2573(4)	78(4)
O(10)	1253(4)	−427(4)	−135(2)	62(1)
O(11)	2258(4)	−332(4)	−816(3)	76(2)
C(1)	−299(5)	7266(5)	1398(4)	51(2)
C(2)	−640(5)	7973(5)	844(4)	59(2)
C(3)	−1091(6)	7683(5)	103(5)	66(2)
C(4)	−1213(5)	6672(5)	−67(3)	48(2)
C(5)	−876(4)	5996(4)	518(3)	36(1)
C(6)	−979(4)	4900(4)	417(3)	34(1)
C(7)	−1431(4)	4431(5)	−284(3)	46(2)
C(8)	−1491(5)	3415(5)	−311(4)	59(2)
C(9)	−1132(5)	2874(5)	344(4)	56(2)
C(10)	−698(5)	3373(4)	1016(4)	48(2)
C(11)	5750(5)	1965(5)	4298(4)	54(2)
C(12)	6172(5)	2369(5)	5020(4)	58(2)
C(13)	6541(5)	1736(5)	5624(4)	58(2)
C(14)	6505(4)	710(5)	5503(4)	49(2)
C(15)	6079(4)	359(4)	4769(3)	41(1)
C(16)	5991(4)	−708(4)	4550(3)	39(1)
C(17)	6360(5)	−1479(5)	5075(4)	53(2)
C(18)	6236(5)	−2452(5)	4804(4)	61(2)
C(19)	5776(5)	−2637(5)	4049(4)	55(2)
C(20)	5434(4)	−1839(4)	3568(4)	47(1)
C(21)	1589(4)	3826(4)	2350(3)	36(1)
C(22)	2150(4)	2888(4)	2654(3)	43(1)
C(23)	2925(4)	2580(4)	2504(3)	45(1)
C(24)	3481(4)	1646(4)	2800(3)	38(1)
C (25A)	4250(8)	−296(8)	1704(7)	38(3)
C (25B)	3404(8)	−817(8)	2040(6)	35(2)
C (26A)	3259(11)	−466(9)	1067(9)	39(3)
C (26B)	2679(7)	−803(8)	1258(5)	29(2)
C (27A)	3168(10)	−138(10)	376(7)	38(3)
C (27B)	2828(10)	−359(10)	647(10)	41(3)
C(28)	2092(5)	−338(5)	−198(4)	56(2)
OW1	−679(4)	5443(4)	3958(2)	67(1)
OW2	2254(5)	−3038(5)	2297(4)	102(2)
OW3A	5685(7)	−99(9)	320(5)	73(3)
OW3B	5894(10)	83(17)	1107(6)	154(8)

TABLE II Selected atomic separations [Å] and angles [°]

Cu(1)-O(1)	1.953(4)	Cu(1)-O(5)	1.997(4)
Cu(1)-N(2)	2.009(5)	Cu(1)-N(1)	2.018(4)
Cu(1)-O(6)	2.232(4)	Cu(2)-O(7)	1.942(5)
Cu(2)-O(3)	1.960(4)	Cu(2)-N(3)	1.999(5)
Cu(2)-N(4)	2.004(5)	Cu(2)-O(8)	2.345(4)
O(1)-C(21)	1.275(6)	O(2)-C(21)	1.241(6)
O(3)-C(24)	1.282(6)	O(4)-C(24)	1.233(7)
O(7)-C(25A)	1.027(12)	O(7)-C(25B)	1.252(11)
O(9A)-C(25A)	1.25(2)	O(9B)-C(25B)	1.35(2)
O(10)-C(28)	1.232(9)	O(11)-C(28)	1.248(9)
C(21)-C(22)	1.492(7)	C(22)-C(23)	1.282(8)
C(23)-C(24)	1.482(8)	C(25A)-C(26A)	1.52(2)
C(25B)-C(26B)	1.472(14)	C(26A)-C(27A)	1.32(2)
C(26B)-C(27B)	1.36(2)	C(27A)-C(28)	1.56(2)
C(27B)-C(28)	1.57(2)		
C(25A)-C(19)[a]	3.826	C(26A)-C(12)[b]	3.779
C(27A)-C(12)[b]	3.621	C(25B)-O(6)[c]	3.786
C(26B)-O(6)[c]	3.890	C(27B)-C(12)[b]	3.755
O(1)-Cu(1)-O(5)	91.1(2)	O(1)-Cu(1)-N(2)	91.6(2)
O(5)-Cu(1)-N(2)	170.4(2)	O(1)-Cu(1)-N(1)	163.4(2)
O(5)-Cu(1)-N(1)	94.6(2)	N(2)-Cu(1)-N(1)	80.4(2)
O(1)-Cu(1)-O(6)	97.4(2)	O(5)-Cu(1)-O(6)	93.5(2)
N(2)-Cu(1)-O(6)	95.3(2)	N(1)-Cu(1)-O(6)	97.8(2)
O(8)-Cu(2)-O(3)	89.9(2)	O(8)-Cu(2)-N(3)	173.5(2)
O(3)-Cu(2)-N(3)	91.9(2)	O(8)-Cu(2)-N(4)	96.0(2)
O(3)-Cu(2)-N(4)	166.7(2)	N(3)-Cu(2)-N(4)	81.0(2)
O(8)-Cu(2)-O(7)	90.6(2)	O(3)-Cu(2)-O(7)	95.9(2)
N(3)-Cu(2)-O(7)	95.4(2)	N(4)-Cu(2)-O(7)	95.9(2)
O(10)-C(28)-O(11)	124.6(6)	O(10)-C(28)-C(27A)	134.1(9)
O(11)-C(28)-C(27A)	101.1(8)	O(10)-C(28)-C(27B)	103.8(9)
O(11)-C(28)-C(27B)	131.3(9)		

Symmetry codes are a: $1-x$, $0.5+y$, $0.5-z$; b: $1-x$, $-0.5+y$, $0.5-z$; c: $-x$, $-0.5+y$, $0.5-z$.

[O(9A) − OW3A = 2.786 Å and O(9B) − OW2 = 2.681 Å]. These are considered to be the reason for the disorder of the terminal fumarate group. An H-bonding distance of 2.744 Å is also observed between the O(11) atom on the uncoordinated carboxyl group and the coordinated water molecule O(5) [$x, 0.5-y, -0.5+z$] of a neighbouring complex. This fixes the uncoordinated carboxyl group and results in distortion of bond angles around the C(28) atom as shown in Table II.

The crystal structure consists of the complex and crystalline water molecules. An extensive H-bonding network exists in the crystal structure. The distance of 3.46 Å between parallel bipy planes shows rather tight aromatic stacking of the bipy rings [8].

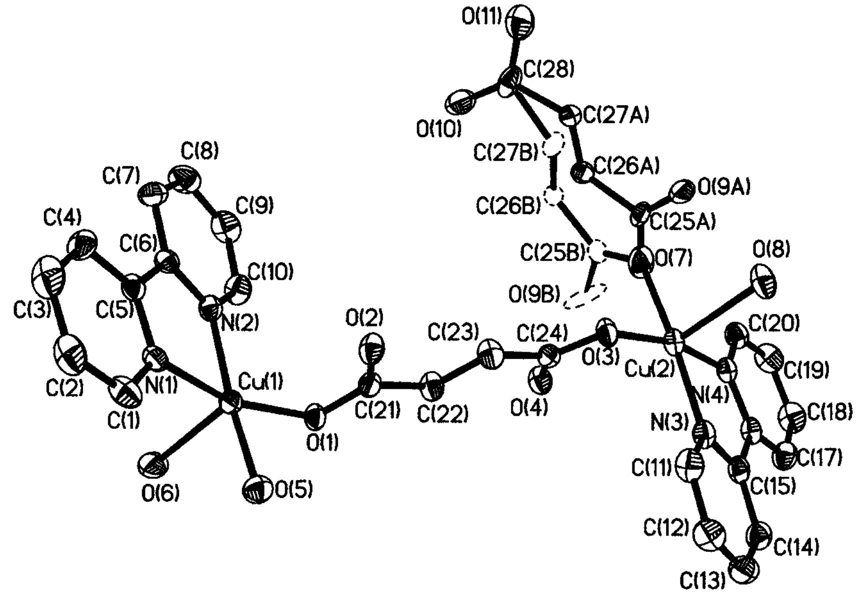

FIGURE 1 ORTEP drawing of the molecular structure showing 30% probability displacement ellipsoids and the disordered structure of the terminal fumarate. H atoms are omitted for clarity.

IR Spectra

IR spectra of the title complex were assigned based on the solid state structure. For the coordinated carboxyl group, stretching was observed at 1387 cm^{-1} [ν_s(COO)] and 1579 cm^{-1} [ν_{as}(COO)]; and for the uncoordinated carboxyl group stretching was observed at 1387 cm^{-1} [ν_s(COO)] and 1560 cm^{-1} [ν_{as}(COO)]. The $\Delta\nu$ values of 192 and 173 cm^{-1} agree with those reported previously [9].

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Supplementary Material

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

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