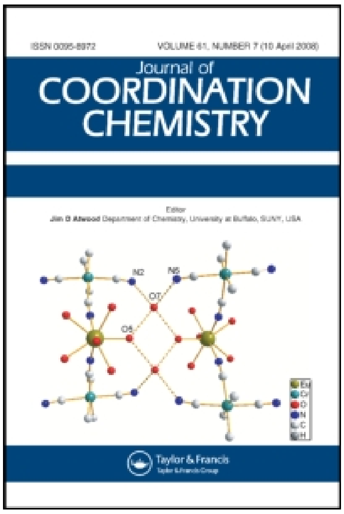

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Synthesis, Crystal Structure and Magnetic Properties of Diaqua(1,10-Phenanthroline-*N,N'*)-Hydrogenmaleatocopper(Ii) Hydrogenmaleate Monohydrate

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF DIAQUA(1,10-PHENANTHROLINE-*N*,*N*′)-HYDROGENMALEATOCOPPER(II) HYDROGENMALEATE MONOHYDRATE

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(Received 17 September 2001)

Reaction of freshly-prepared $CuCO_3$, phenanthroline monohydrate and maleic acid in CH_3OH/H_2O (1 : 1 v/v) at pH = 2.13 yielded diaqua(1,10-phenanthroline-*N,N*′)hydrogenmaleatocopper(II) hydrogenmaleate monohydrate, $[Cu(phen)(H_2O)_2(C_4H_3O_4)](C_4H_3O_4)(H_2O)$, which consists of $[Cu(phen)(H_2O)_2(C_4H_3O_4)]^+$ complex cations, hydrogenmaleate anions and lattice H_2O molecules. Within the complex cations, the Cu atoms are each square-pyramidally coordinated by two N atoms of one chelating phen ligand and three O atoms of two H_2O molecules and one hydrogenmaleato ligand with one H_2O molecule at the apical position (d(Cu–N) = 2.001, 2.009 Å, equatorial d(Cu–O) = 1.966 Å and axial d(Cu–O) = 2.235 Å). Through hydrogen bonding, the complex cations, hydrogenmaleate anions and lattice H_2O molecules are assembled into 1D chains, which are held together by weak Cu···O interactions (3.139 Å) to form corrugated 2D layers. Significant π–π stacking interactions between neighboring phen ligands leads to supramolecular assembly of the 2D layers. Over the temperature range 5–300 K, the complex obeys the Currie–Weiss law with an effective magnetic moment of 1.78 BM at room temperature.

Keywords: Copper(II); Hydrogenmaleato; Phenanthroline; Crystal structure; Magnetics

INTRODUCTION

It is well-known that weak interactions such as π–π stacking and hydrogen bonding are fundamental to supramolecular chemistry [1]. Especially, π–π stacking interactions between aromatic rings are recognized to be very important in proteins and protein–DNA systems for protein stabilization and various regulatory processes [2–4]. On the other hand, hydrogen bonds play vital roles in highly efficient and specific biological reactions and are essential for molecular recognition and self-organization of molecules in supramolecular systems. Furthermore, hydrogen-bond assembled molecular materials are of considerable interest since the incorporation of a transition metal

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ion is important in the crystal engineering of promising functional materials with specific properties for industrial and technological applications [5].

The seemingly simple hydrogenmaleate anion is an ideal candidate to study the nature of strong asymmetric hydrogen bonds [6,7]. Owing to significant, strong intramolecular hydrogen bonds, the hydrogenmaleate anion may be used as a rigid organic bridging ligand. Hitherto, however, work on hydrogenmaleato complexes has been sketchy [8] in comparison with maleato complexes [9–11]. In this article, we report a new mixed ligand Cu(II) complex with both hydrogenmaleato ligand and hydrogenmaleate anion.

EXPERIMENTAL

Physical Measurements

Microanalyses were performed with a Heraeus Rapid-CHNO instrument, FT-IR spectra were recorded using KBr pellets in the range 4000–400 cm^{-1} on a Protege 460 spectrometer. Magnetic susceptibilities were measured using a powdered sample (67 mg) with a SQUID magnetometer (Quantum Design Model MPMS-7) in the temperature range $5 \leq T(K) \leq 300$ with an applied field of 1 T. The susceptibilities were corrected for diamagnetic contributions using Pascal constants ($\chi_{dia} = -230 \times 10^{-6}\,cm^3\,mol^{-1}$) [12].

Synthesis

All chemicals of p.a. grade were purchased from the Shanghai Chemical Company and used without further purification. For successful synthesis, fresh $CuCO_3$ was necessary. Firstly, addition of 3.0 cm^3 of (1M) Na_2CO_3 to an aqueous solution of 0.43 g (2.50 mmol) $CuCl_2 \cdot 2H_2O$ in 6.0 cm^3 of H_2O produced blue precipitate, which was washed with double-distilled water until no Cl^- ions were detected. The $CuCO_3$ was added to a solution containing 0.50 g (2.50 mmol) of phenanthroline monohydrate and 0.29 g (2.50 mmol) of maleic acid dissolved in 50 cm^3 of CH_3OH/H_2O (1 : 1 v/v) with continuous stirring to give a blue solution (pH = 3.45), to which powdered maleic acid was further added to pH = 2.13. The resulting solution was allowed to stand at room temperature. After four days, blue crystals had grown. Yield: *ca.* 75% on the basis of initial $CuCl_2 \cdot 2H_2O$. *Anal.* Calc. for $C_{20}H_{20}CuN_7O_{11}$ (%): C, 45.50; H, 3.82; N, 5.31. Found: C, 45.75; H, 3.83; N, 5.23; IR (cm^{-1}): 3446s, 3042m, 1959w, 1828w, 1575vs, 1507vs, 1424s, 1364vs, 1195s, 1149s, 1109s, 998vs, 905m, 878s, 868s, 856s, 770m, 723vs, 647m, 555s, 428w.

X-ray Crystallography

A suitable fragment was cleaved from a bulky crystal and glued to a fine glass fiber with epoxy cement. Unit cell parameters and the orientation matrix were determined by least-squares refinement using the setting angles of 25 centred reflections ($10 \leq 2\vartheta \leq 25°$) measured on a Bruker P4 diffractometer with graphite-monochromatized Mo*Kα* radiation ($\lambda = 0.71073$ Å). Intensity data were collected at 293 K using a ϑ–2ϑ scan technique up to a maximum 2ϑ value of 55°. Three standard reflections were monitored for crystal and instruments stabilities after every 97 data measurements. No significant variation was observed. Of 6308 measured reflections ($h \rightarrow -10$ to 1, $k \rightarrow -1$ to 28, $l \rightarrow -16$ to 16), 4938 reflections were independent ($R_{\mathrm{int}} = 0.0335$) and 3998 reflections with $I \geq 2\sigma$ (I) were considered as observed and used for the structure determination. Intensity data were corrected for Lorentz and polarization effects and empirical absorption. The structure was solved using direct methods [13]. Subsequent difference Fourier syntheses enabled all heavier atoms to be located. After several cycles of refinement, all hydrogen atoms were located from successive difference Fourier syntheses. Hydrogen and nonhydrogen atoms were refined with isotropic and anisotropic displacement parameters, respectively. Final refinement based on full-matrix least-squares techniques [14] converged very smoothly to agreement factors $R1 = 0.0457$ and $wR2 = 0.1057$. Atomic scattering factors were supplied by the SHELX programs [13,14]. Crystal data, intensity collection and structure refinement details are summarized in Table I; final positional parameters, selected interatomic distances and bond angles are given in Tables II and III, respectively. Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 169823 ($[Cu(phen)(H_2O)_2(C_4H_3O_4)](C_4H_3O_4)(H_2O)$). Copies of the data can be obtained, free of charge, on application to CCDC,

TABLE I Crystal data and structure refinement details for the complex

Compound	$[Cu(phen)(H_2O)_2(C_4H_3O_4)]$ $(C_4H_3O_4)H_2O$
Empirical formula	$C_{20}H_{20}CuN_7O_{11}$
Color shape	Blue prismatic
Size (mm)	$0.467 \times 0.356 \times 0.289$
Formula weight	527.92
Temperature	293 K
Crystal system, Space group	Monoclinic, $P2_1/n$
a (Å)	7.862(1)
b (Å)	22.123(2)
c (Å)	12.440(1)
β (Å)	94.30(1)
Volume (Å^3), Z	2157.6(4), 4
$D_{\mathrm{calcd.}}$ (g cm^{-3})	1.625
μ (Mo $K\alpha$) (cm^{-1})	10.79
$F(000)$	1084
Diffractometer	Bruker P4
Radiation	Graphite monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å)
Scan type	ϑ–2ϑ
No. of measured reflections	Total: 6308; unique: 4936 ($R_{\mathrm{int}} = 0.0335$)
Correction	Semi-empirical based on psi-scan
Structure solution	Direct methods (SHELXS-97)
Refinement	Full-matrix least-squares (SHELXL-97)
Refinement method	Full-matrix least-squares on F^2
Treatment of H atoms	Diff. Map and refined isotropically
No. of observed reflections [$I \geq 2\sigma(I)$]	3998
No. of variables	388
Goodness-of-fit on F^2	1.099
Final R indices [$I \geq 2\sigma(I)$]^a	$R1 = 0.0457$, $wR2 = 0.1057$
R indices (all data)^a	$R1 = 0.0594$, $wR2 = 0.1143$
A, B values in weighting scheme^b	0.0689, 0.0987
Extinction coefficient	0.014(1)
Max. and min. peak in final diff. map	0.764 and -0.659 e$^-$/Å^3

$^a wR2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$; $^b w = \left[\sigma^2(F_o^2) + (AP)^2 + BP\right]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for nonhydrogen atoms. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Cu	0.93236(3)	0.89601(1)	0.80504(2)	0.0321(1)
N(1)	1.0834(2)	0.86818(9)	0.6914(1)	0.0335(4)
N(2)	0.9923(2)	0.97773(8)	0.7502(2)	0.0342(4)
C(1)	1.1332(3)	0.8127(1)	0.6678(2)	0.0422(5)
C(2)	1.2457(4)	0.8021(1)	0.5871(2)	0.0512(7)
C(3)	1.3039(4)	0.8486(1)	0.5296(2)	0.0491(6)
C(4)	1.2516(3)	0.9076(1)	0.5515(2)	0.0386(5)
C(5)	1.3025(3)	0.9606(2)	0.4948(2)	0.0487(7)
C(6)	1.2538(3)	1.0155(1)	0.5223(2)	0.0494(7)
C(7)	1.1474(3)	1.0248(1)	0.6107(2)	0.0402(5)
C(8)	1.0930(3)	1.0815(1)	0.6455(3)	0.0496(7)
C(9)	0.9921(4)	1.0848(1)	0.7292(3)	0.0509(7)
C(10)	0.9430(3)	1.0318(1)	0.7810(2)	0.0427(6)
C(11)	1.0932(3)	0.9740(1)	0.6657(2)	0.0330(5)
C(12)	1.1442(3)	0.9151(1)	0.6347(2)	0.0326(5)
C(13)	0.7667(3)	0.9129(1)	1.0071(2)	0.0345(5)
C(14)	0.6731(3)	0.9564(1)	1.0731(2)	0.0372(5)
C(15)	0.5765(3)	0.9457(1)	1.1544(2)	0.0386(5)
C(16)	0.5268(4)	0.8884(1)	1.2062(2)	0.0431(6)
C(17)	1.2561(4)	0.7387(1)	1.0095(2)	0.0496(6)
C(18)	1.3764(4)	0.7516(1)	0.9254(3)	0.0537(7)
C(19)	1.4196(4)	0.8029(1)	0.8810(2)	0.0467(6)
C(20)	1.3632(3)	0.8660(1)	0.8958(2)	0.0406(5)
O(1)	0.6860(3)	0.8910(1)	0.7035(2)	0.0489(5)
O(2)	0.9207(3)	0.81380(8)	0.8638(2)	0.0419(4)
O(3)	0.8281(2)	0.93531(7)	0.9257(1)	0.0413(4)
O(4)	0.7821(3)	0.85842(8)	1.0340(2)	0.0546(5)
O(5)	0.4221(3)	0.8896(1)	1.2729(2)	0.0604(6)
O(6)	0.5962(3)	0.83757(9)	1.1815(2)	0.0583(6)
O(7)	1.2351(3)	0.6853(1)	1.0326(2)	0.0737(7)
O(8)	1.1856(3)	0.7826(1)	1.0549(2)	0.0613(5)
O(9)	1.4187(3)	0.90551(8)	0.8393(2)	0.0531(5)
O(10)	1.2545(3)	0.8778(1)	0.9667(2)	0.0604(6)
O(11)	0.7430(3)	0.7228(1)	0.7769(2)	0.0534(5)

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RESULTS AND DISCUSSION

Synthesis

Systematic investigations show that reaction of phenanthroline and $CuCl_2 \cdot 2H_2O$ in presence of maleic acid and NaOH in CH_3OH/H_2O at pH = 2.0 yields the green chloro-bridged dinuclear complex $Cu_2(phen)_2Cl_4$ [15] and blue hydrogenmaleato-bridged $Cu(phen)Cl(C_4H_3O_4)$ [16] at 50°C and room temperature, respectively. When the synthetic system is cooled from 50°C to room temperature, initially-formed green crystals of $Cu_2(phen)_2Cl_4$ completely turn to blue $Cu(phen)Cl(C_4H_3O_4)$ after four days [16]. However, change from the blue $Cu(phen)Cl(C_4H_3O_4)$ to green $Cu_2(phen)_2Cl_4$ is not observed when the reaction system containing

TABLE III Selected interatomic distances (Å) and bond angles (°) for the complex

Cu–O(1)	2.235(2)	C(6)–C(7)	1.446(4)	C(14)–C(15)	1.331(4)
Cu–O(2)	1.965(2)	C(7)–C(8)	1.403(4)	C(15)–C(16)	1.487(4)
Cu–O(3)	1.966(2)	C(7)–C(11)	1.399(3)	C(16)–O(5)	1.213(3)
Cu–N(1)	2.009(2)	C(8)–C(9)	1.358(5)	C(16)–O(6)	1.297(3)
Cu–N(2)	2.001(2)	C(9)–C(10)	1.406(4)	C(17)–O(7)	1.230(4)
C(1)–N(1)	1.328(3)	C(10)–N(2)	1.323(3)	C(17)–O(8)	1.271(4)
C(1)–C(2)	1.406(4)	C(11)–N(2)	1.365(3)	C(17)–C(18)	1.490(4)
C(2)–C(3)	1.352(4)	C(11)–C(12)	1.425(3)	C(18)–C(19)	1.318(4)
C(3)–C(4)	1.402(4)	C(12)–N(1)	1.362(3)	C(19)–C(20)	1.479(4)
C(4)–C(5)	1.441(4)	C(13)–O(3)	1.256(3)	C(20)–O(9)	1.223(3)
C(4)–C(12)	1.394(3)	C(13)–O(4)	1.255(3)	C(20)–O(10)	1.300(3)
C(5)–C(6)	1.328(4)	C(13)–C(14)	1.494(3)		
O(1)–Cu–O(2)	95.9(1)	N(1)–Cu–N(2)	82.5(1)	O(7)–C(17)–O(8)	124.0(3)
O(1)–Cu–O(3)	93.5(1)	O(3)–C(13)–O(4)	123.9(2)	O(7)–C(17)–C(18)	116.9(3)
O(1)–Cu–N(1)	96.9(1)	O(3)–C(13)–C(14)	115.1(2)	O(8)–C(17)–C(18)	119.1(3)
O(1)–Cu–N(2)	93.9(1)	O(4)–C(13)–C(14)	121.0(2)	C(17)–C(18)–C(19)	131.1(3)
O(2)–Cu–O(3)	95.2(1)	C(13)–C(14)–C(15)	129.5(2)	C(18)–C(19)–C(20)	132.1(3)
O(2)–Cu–N(1)	91.4(1)	C(14)–C(15)–C(16)	131.6(2)	C(19)–C(20)–O(9)	118.7(2)
O(2)–Cu–N(2)	169.1(1)	C(15)–C(16)–O(5)	119.5(2)	C(19)–C(20)–O(10)	119.6(2)
O(3)–Cu–N(1)	167.1(1)	C(15)–C(16)–O(6)	120.5(2)	O(9)–C(20)–O(10)	121.8(2)
O(3)–Cu–N(2)	89.1(1)	O(5)–C(16)–O(6)	119.9(3)		

Hydrogen bonding contacts

D–H	d(D–H)	d(H···A)	(D–H···A)	d(D–H···A)	A
O(1)–H(20)	0.59(4)	2.21(4)	156	2.764(3)	O7 [*x*–1/2, –*y*+3/2, *z*–1/2]
O(1)–H(21)	0.77(4)	2.06(4)	169	2.812(3)	O9 [*x*–1, *y*, *z*]
O(2)–H(22)	0.88(4)	1.77(4)	166	2.636(3)	O11
O(2)–H(23)	0.73(4)	2.01(4)	146	2.644(3)	O4
O(11)–H(24)	0.73(4)	2.06(4)	164	2.768(3)	O8 [*x*–1/2, –*y*+3/2, *z*–1/2]
O(11)–H(25)	0.81(5)	2.05(4)	172	2.859(3)	O5 [*x*+1/2, –*y*+3/2, *z*–1/2]
O(6)–H(a)	0.78(4)	1.70(4)	176	2.474(3)	O4
O(10)–H(b)	1.14(5)	1.33(4)	168	2.455(3)	O8

Cu(phen)Cl($C_4H_3O_4$) was kept at 50°C. Above observations suggests that the formation of Cu_2(phen)$_2$$Cl_4$ is kinetically favorable and Cu(phen)Cl($C_4H_3O_4$) is thermodynamically stable. In addition, use of $CuNO_3 \cdot 2H_2O$ in place of $CuCl_2 \cdot 2H_2O$ affords only Cu(phen)(NO_3)($C_4H_3O_4$) [16] in high yield at 50°C as well as at room temperature. When the solution is neutralized, the reaction produces a new Cu(II) maleato complex {[Cu(phen)]$_2$($C_4H_2O_4$)$_2$} · 4.5H_2O [16]. This fact suggests that low pH (e.g., pH = 2) is crucial to the formation of the hydrogenmaleato complex. Furthermore, it is essential to employ freshly-prepared $CuCO_3$ for successful synthesis of the title complex.

Crystal Structure

The title compound is built up of [Cu(phen)(H_2O)$_2$($C_4H_3O_4$)]$^+$ cations, hydrogenmaleate anions and lattice H_2O molecules. As illustrated in Fig. 1, Cu atoms are each surrounded by two N atoms of one phen ligand and three O atoms of two H_2O molecules and one hydrogenmaleato ligand to complete somewhat distorted square-pyramidal coordination with one water O atom at the apical position. The central Cu atom is practically equidistant to both the equatorial water O atom and the carboxylate O atom within experimental error (mean value: 1.966 Å), and the Cu–N bond distances are 2.001, 2.009 Å, while the axial Cu–O bond distance is 2.235(2) Å. Cu is displaced by 0.174(1) Å from the equatorial plane defined by N(1), N(2), O(3)

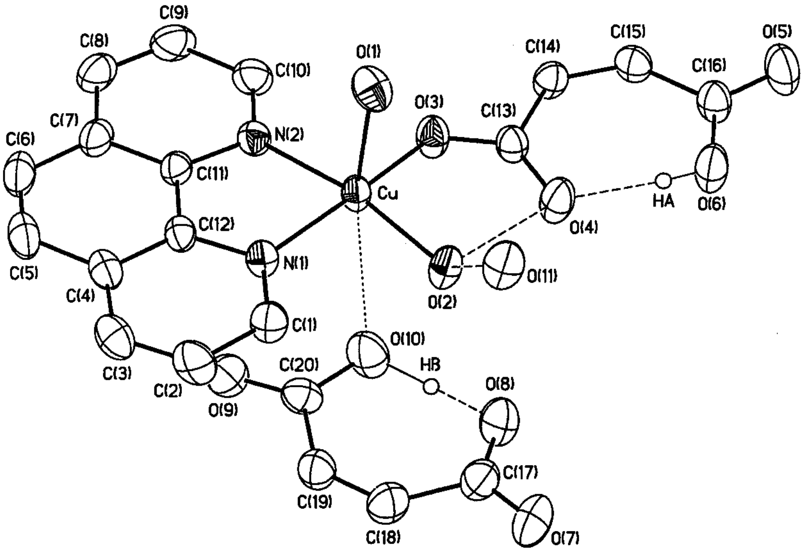

FIGURE 1 Ortep view of the $[Cu(phen)(H_2O)_2(C_4H_3O_4)]^+$ complex cation together with the hydrogen bonded H_2O molecule and the hydrogenmaleate anion with displacement ellipsoids (45% probability) and atom labeling.

and O(2) atoms towards O(1). Complex cations exhibit relatively strong intramolecular hydrogen bonds between the water O(2) and carboxylate O(4) atoms with $d(O(2)\cdots O(4)) = 2.644$ Å and $\angle(O(2){-}H\cdots O(4)) = 146°$. The carboxyl O(10) atom of one hydrogenmaleate anion is 3.139(3) Å away from its closest Cu atom, indicating weak Cu···O interaction and the hydrogenmaleato ligand and the weakly-associated hydrogenmaleate anion are nearly parallel.

As expected, both hydrogenmaleate anions and the hydrogenmaleato ligands display strong asymmetric intramolecular hydrogen bonds with $d(O\cdots O) = 2.455, 2.474$ Å and $\angle(O{-}H\cdots O) = 168, 176°$ (Table III). Along the asymmetric hydrogen bonds, the hydrogen atom in the hydrogenmaleato ligand is more substantially apart from the central position than in the hydrogenmaleate anion. Accordingly, the hydrogen atoms H(a) and H(b) are covalently bonded to O(6) and O(10), respectively. In this sense, the terminal containing C(16) and C(20) atoms are the carboxylic groups and the others are carboxylates. The present asymmetrically hydrogen bonded O···O distances are slightly longer than the asymmetric ones in sodium hydrogenmaleate trihydrate [6,7], but close to others reported for symmetric hydrogen bonds [17,18]. As seen in Table III, the apical H_2O molecule forms hydrogen bonds to carboxylate O(7) and carboxide O(9) atoms from different hydrogenmaleate anions whereas the equatorial H_2O molecule donates one hydrogen atom to the lattice H_2O molecule that is, in turn, hydrogen bonded to the O(5) atom of a neighboring complex cation and to O(8) atom of the adjacent hydrogenmaleate anion. Through such hydrogen bonds, the complex cations are arranged to form 1D chains along the $[1\,0\,\bar{1}]$ directions and the resulting chains are assembled *via* weak Cu···O interactions into 2D layers parallel to (0 1 0) with all axial Cu–O bonds orientating in the same direction. The 2D layers are corrugated with the chelating phen ligands distributed on both sides (Fig. 2). The layers are closely packed so that the neighboring parallel phen ligands of different layers face

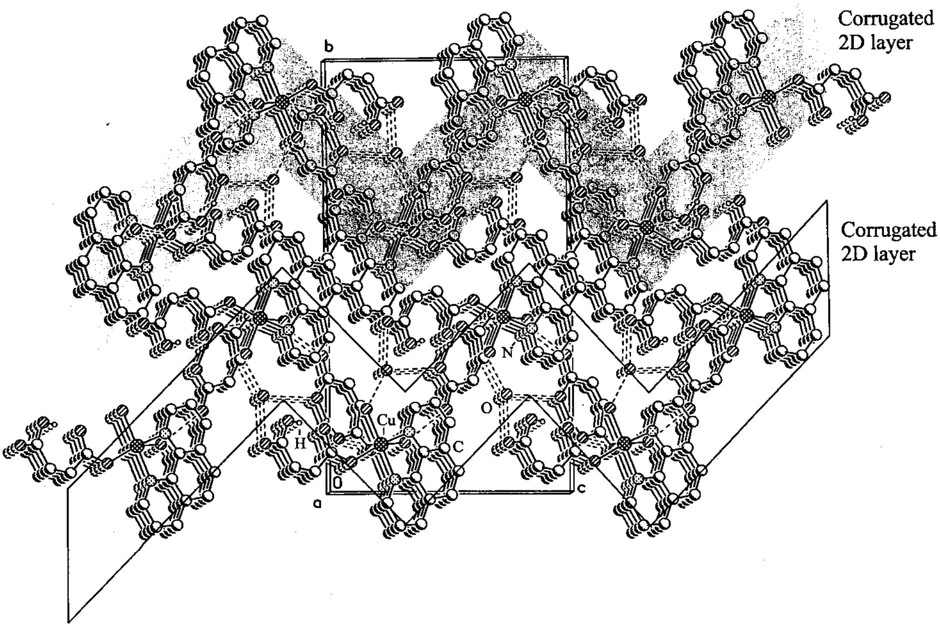

FIGURE 2 Stacking of the corrugated 2D layers along the crystallographic *b* axis. The corrugated layers are shaded for clarity.

opposite directions with the fragments containing N(2) partially overlapped at an interplanar distance of 3.47 Å, indicating significant π–π stacking interaction [19–21]. This implies that π–π stacking interactions are responsible for the supramolecular assembly of the 2D layers.

Magnetic Properties

The title complex is paramagnetic. At room temperature, the effective magnetic moment is 1.78 BM in excellent agreement with the spin-only value expected for one unpaired electron [22]. Molar susceptibilities over the temperature range 5–300 K obey the Curie–Weiss law $\chi_m(T-\theta) = 0.410\,\mathrm{cm^3\,mol^{-1}\,K}$ with a small Weiss constant of $\theta = 2.75$ K.

Acknowledgments

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