*Notes*

# Synthesis, Characterization and Crystal Structure of (2, 2'-Bipyridine)(μ-maleato)copper(II) Dihydrate

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The title polymeric complex $[Cu(C_4H_2O_4)(C_{10}H_8N_2)]_n \cdot 2nH_2O$ was prepared and its crystal structure was determined by X-ray diffraction methods. The crystal belongs to space group $P2_1/c$ with cell dimensions of $a = 1.0104(1)$, $b = 1.9952(2)$, $c = 0.7357(2)$ nm, $\beta = 98.38(2)°$ and $Z = 4$. The complex forms zig-zag chains along crystallographic axis $c$ via Cu—O (carboxyl) bond in the apical direction. Each repeated unit consists of a square pyramidal Cu(II) centre with one maleate dianion and one 2,2'-bipyridine forming a basal plane. Adjacent chains link to each other by H-bonding between carboxyl groups and crystalline water. The distance of 0.3482 nm between parallel bipyridine rings shows a π-π stacking interaction. The title complex was also characterized by IR, UV and ESR spectra.

**Keywords**  copper(II), polymeric complex, crystal structure, maleate, bipyridine, π-π stacking

## Introduction

In the past decade, a lot of interest has been concentrated on preparing and characterizing bridging metal complexes for investigating their potentially useful electronic or magnetic properties.[1,2] Recently, several metal complexes bridged by dicarboxylate have been synthesized in our laboratory. Their crystal structures showed different coordination modes of the carboxyl group.[3,4] Searching of the Cambridge Structure Database showed versatile coordination of maleate,[5-8] in order to investigate versatility of coordination mode of maleate in metal complexes, we prepared the title maleate complex of Cu(II) and determined its crystal structure. The molecular structure of the maleate-bridging complex displays the existence of a significant π-π stacking interaction between 2,2-bipyridine (bipy) ligands.

## Experimental

### Synthesis

An ethanol solution (10 mL) containing 2,2'-bipyridine (bipy) (0.156 g, 1 mmol) was slowly added to an aqueous solution (10 mL) containing $CuCl_2 \cdot 2H_2O$ (0.171 g, 1 mmol) with stirring. After refluxing, a great deal of precipitate was produced. An aqueous solution (10 mL) containing maleic acid (0.116 g, 1 mmol) and NaOH (0.080 g, 2 mmol) was slowly added to the above reaction mixture with continuous stirring. The mixture was refluxed until the precipitate was dissolved. The solution was cooled to room temperature and filtered. Dark-blue single crystals, which are stable in the air, were obtained after a week.

### Elemental analysis

C, N and H contents were analyzed using a Carlo-Erba 1160 elemental analytic instrument. Anal. calcd for $C_{14}H_{14}N_2O_6Cu$: C 45.47, N 7.58, H 3.82; found C 45.44, N 7.60, H 3.65.

### Physical measurements

IR spectrum of the title complex was measured on

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KBr disc using a Nicolet 5DX FT-IR spectrophotometer $(4000$—$400$ cm$^{-1})$.

UV spectrum of the title complex was recorded on a Beckmann DU-50 spectrophotometer.

ESR spectra of the title complex both in ethanol solution and powder crystalline state were recorded on a JES-FEIXG spectrometer with X-band, field modulation frequency 100 kHz and amplitude modulation $5 \times 10^{-4}$ T, microwave power 4 mW, the sweep width $1000 \times 10^{-4}$ T and measurement temperature 298 K. The concentration of the solution is approximately $5 \times 10^{-3}$ mol/L.

*Crystal structure determination*

A prism single crystal of the title complex with approximate dimensions $0.35 \times 0.30 \times 0.25$ mm$^3$ was mounted on a glass fiber. X-ray diffraction intensity data were collected at 293 K on a Rigaku AFC-7S diffractometer up to a $2\theta$ value of $50°$ with graphite monochromatized Mo $K_\alpha$ radiation ($\lambda = 0.07107$ nm) using $\omega/2\theta$ scan technique. A total of 2587 independent reflections were collected, among which 2130 reflections were considered as observed $[I > 2\sigma(I)]$ and used for the structure determination. Usual $Lp$ and empirical absorption corrections were applied. The structure was solved by direct method followed by Fourier synthesis. Structure refinements were carried out by full-matrix least-squares procedure using the SHELX-93 program package.[9] H atoms were located on a difference Fourier map. Anisotropic refinement including all non-H atoms converged to $R = 0.029$ and $wR = 0.076$ for observed reflections, where $w = [\sigma^2(F_o^2) + (0.0391\ P)^2 + 1.4820\ P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$.

*Crystal data*　　　$C_{14}H_{14}N_2O_6Cu$, $M_r = 369.81$, monoclinic, $P2_1/c$, $a = 1.0104(1)$, $b = 1.9952(2)$, $c = 0.7357(2)$ nm, $\beta = 98.38(2)°$, $V = 1.4672(5)$ nm$^3$, $Z = 4$, $F(000) = 756$, $D_x = 1.674$ g/cm$^3$, $\mu(\text{Mo } K_\alpha) = 1.52$ mm$^{-1}$, $S = 1.08$, $(\Delta\rho)_{max} = 315$ e/nm$^3$, $(\Delta\rho)_{min} = -427$ e/nm$^3$.

## Results and discussion

*Crystal structure*

The final atomic coordinates and thermal parameters for non-H atoms are listed in Table 1. The molecular structure is illustrated in Fig. 1. The repeated unit of the polymeric complex is simply a Cu(II) atom with two dif-

ferent bidentate ligands: bipy ligand and maleate dianion. The linkage between units is achieved by the apical coordination of an O(4) atom on the maleate group of the adjacent unit. Therefore each Cu(II) center is in a square pyramidal coordination. It is notable that the basal coordination plane is poorly planar, O(3) atom deviates from the plane defined by O(1), N(1) and N(2) atoms about 0.063 nm. As presented in Table 2, bond angles involving O(3) atom $[\text{O}(3)\text{-Cu-N}(2) = 154.76(9)]°$ and $\text{O}(3)\text{-Cu-O}(4\alpha) = 110.38(8)°]$ also show significantly deviation of O(3) atom from expected position for a normal square pyramidal geometry. The serious deviation of O(3) atom from the coordination basal plane may be due to the fact that the bridging carboxyl group bearing O(3) and O(4) atoms has to twist a bit in order to form a significant bonding interaction between O(4) and Cu($\beta$) atoms (Fig. 1). The deviation of O(3) atom from the basal plane results in a longer Cu—O(3) distance of 0.1946(2) nm, as compared with Cu—O(1) distance of 0.1907(2) nm.

**Table 1**　Atomic fractional coordinates $[\times 10^4]$ and equivalent isotropic displacement parameters $[\times 10^5\ \text{nm}^2]$

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
| --- | --- | --- | --- | --- |
| Cu | 8607(1) | 1490(1) | 1388(1) | 29(1) |
| O(1) | 6816(2) | 1325(1) | 252(3) | 39(1) |
| O(2) | 4665(2) | 1518(1) | −572(4) | 50(1) |
| O(3) | 8701(2) | 2349(1) | 162(3) | 37(1) |
| O(4) | 8038(2) | 3362(1) | −774(3) | 34(1) |
| Ow(1) | 5178(3) | 259(2) | −2267(4) | 83(1) |
| Ow(2) | 6239(3) | 4387(1) | −420(4) | 58(1) |
| N(1) | 10546(2) | 1523(1) | 2381(3) | 32(1) |
| N(2) | 8957(2) | 501(1) | 1751(3) | 30(1) |
| C(1) | 5769(3) | 1685(2) | 243(4) | 33(1) |
| C(2) | 5849(3) | 2343(1) | 1218(4) | 32(1) |
| C(3) | 6740(3) | 2832(1) | 1162(4) | 30(1) |
| C(4) | 7900(3) | 2840(1) | 111(3) | 27(1) |
| C(5) | 11264(3) | 2083(2) | 26985) | 42(1) |
| C(6) | 12576(3) | 2080(2) | 3541(5) | 48(1) |
| C(7) | 13158(3) | 1476(2) | 4054(6) | 56(1) |
| C(8) | 12421(3) | 892(2) | 3741(5) | 47(1) |
| C(9) | 11111(3) | 933(1) | 2905(4) | 31(1) |
| C(10) | 10215(3) | 345(1) | 2523(4) | 30(1) |
| C(11) | 10595(3) | −310(2) | 2901(5) | 43(1) |
| C(12) | 9664(4) | −816(2) | 2471(5) | 49(1) |
| C(13) | 8388(3) | −658(2) | 1669(5) | 43(1) |
| C(14) | 8063(3) | 2(2) | 1327(4) | 37(1) |

**Table 2**   Selected atomic separations (nm) and angles (°)

| | | | |
|---|---|---|---|
| Cu—O(1) | 0.1907(2) | Cu—O(3) | 0.1946(2) |
| Cu—N(1) | 0.1989(2) | Cu—N(2) | 0.2016(2) |
| Cu—O(4α) | 0.2264(2) | O(1)—C(1) | 0.1279(3) |
| O(2)—C(1) | 0.1233(3) | O(3)—C(4) | 0.1266(3) |
| O(4)—C(4) | 0.1247(3) | C(1)—C(2) | 0.1493(4) |
| C(2)—C(3) | 0.1331(4) | C(3)—C(4) | 0.1495(4) |
| O(2)···Ow(1) | 0.2885(4) | O(4)···Ow(2) | 0.2774(3) |
| Ow(1)···Ow(2β) | 0.2785(4) | Ow(2)···Ow(1γ) | 0.2694(4) |
| O(1)-Cu-O(3) | 93.22(9) | O(1)-Cu-N(1) | 170.67(9) |
| O(3)-Cu-N(1) | 91.66(9) | O(1)-Cu-N(2) | 91.49(9) |
| O(3)-Cu-N(2) | 154.76(9) | N(1)-Cu-N(2) | 80.77(9) |
| O(1)-Cu-O(4α) | 94.26(9) | O(3)-Cu-O(4α) | 110.38(8) |
| N(1)-Cu-O(4α) | 91.48(9) | N(2)-Cu-O(4α) | 93.95(8) |
| C(1)-O(1)-Cu | 129.6(2) | C(4)-O(3)-Cu | 128.3(2) |
| C(4)-O(4)-Cu(β) | 130.8(2) | O(1)-C(1)-O(2) | 122.7(3) |
| O(2)-C(1)-C(2) | 117.0(3) | O(1)-C(1)-C(2) | 120.3(2) |
| C(1)-C(2)-C(3) | 128.2(3) | C(2)-C(3)-C(4) | 127.5(3) |
| O(3)-C(4)-O(4) | 122.8(3) | O(4)-C(4)-C(3) | 115.7(2) |
| O(3)-C(4)-C(3) | 121.5(2) | | |

Symmetry code: α) $x$, $0.5 - y$, $0.5 + z$; β) $x$, $0.5 - y$, $-0.5 + z$; γ) $1 - x$, $0.5 + y$, $-0.5 - z$.
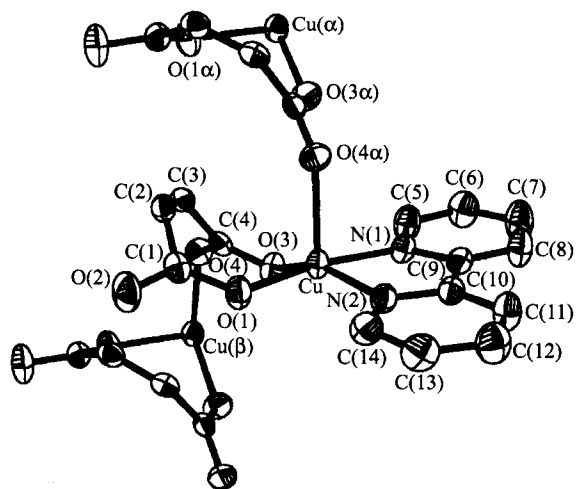


**Fig. 1**   Molecular structure of the title complex showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity and the suffix α and β are defined as in Table 2.

The maleate dianion chelates a Cu center with carboxyl groups of both ends. The seven membered ring formed by a Cu atom and bidentate maleate possesses a boat configuration. One of carboxyl groups uses the remaining O(4) atom to bind the next Cu center [Cu(β) in

Fig. 1] and hence forming the polymeric structure, whereas the remaining O(2) atom of other carboxyl group is free from coordination but links crystalline water by an H-bond. Therefore two carboxyl groups of a maleate dianion exhibit different coordination modes in the structure. This is a new coordination mode differing from those found in maleate-bridging complexes cited above.

Polymer chains link to each other by extensive H-bonding network between crystalline water and carboxyl groups as shown in Fig. 2. The geometric parameters of H-bond network are also outlined in Table 1. As illustrated in Fig. 3, a π-π stacking interaction occurs between bipy rings of adjacent polymeric chains. The distance of 0.3482 nm between adjacent parallel bipy rings is much shorter than the thickness of aromatic ring (0.37 nm).[10] Short contacts of 0.3518(4) nm [C(9)—C(13δ)] and 0.3537(4) nm [C(11)—N(2δ)] are also observed between adjacent bipy rings.
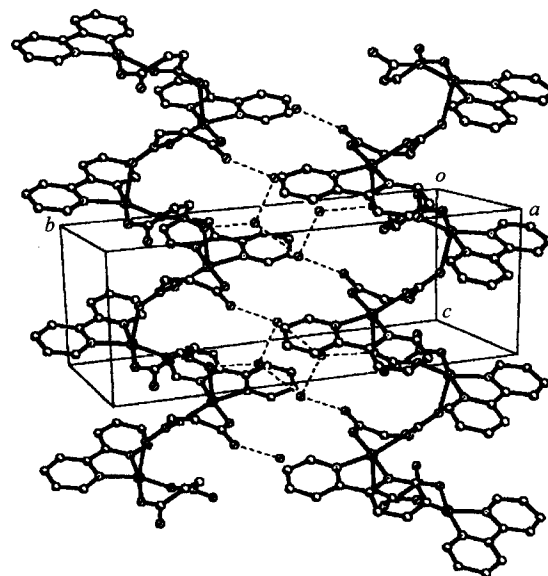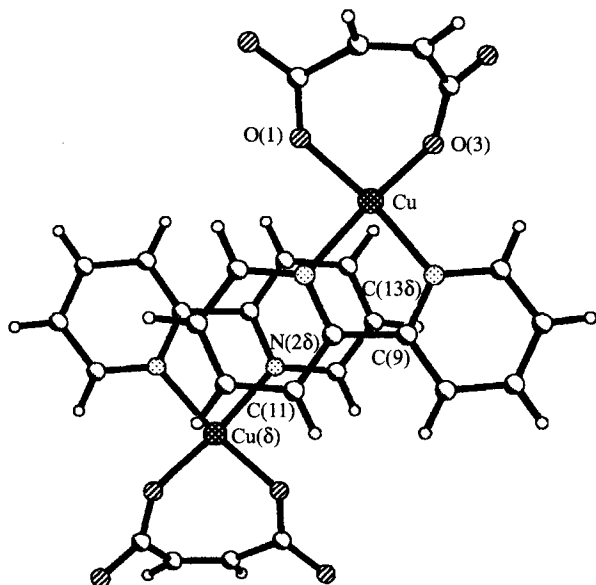


**Fig. 2**   Molecular packing diagram of the title complex, dashed lines indicating the H-bonding interaction between zig-zag chains.

### IR and UV spectra

Two carboxylic groups in the present crystal possess different coordination modes as mentioned above. For the bridging carboxyl group, the stretching vibration was observed at 1424 cm$^{-1}$ [$\nu_s$(COO)] and 1561 cm$^{-1}$ [$\nu_{as}$(COO)]. And for the monodentate carboxyl group, the stretching was observed at 1405 cm$^{-1}$ [$\nu_s$(COO)] and

1592 cm$^{-1}$[$\nu_{as}$(COO)]. The $\Delta\nu$ values [$\nu_{as}$(COO) - $\nu_s$ (COO)] of 137 cm$^{-1}$ and 187 cm$^{-1}$ agree with those found in bridging complexes and monodentate complexes, respectively.[11]

formula of $\kappa_0 = (\bar{A}/p) + (\bar{g} - 2.0023)$ and $p = 0.0354$ cm$^{-1}$, isotropic Fermi contact term $\kappa_0$ of 0.308 was calculated in ethanol solution.



55.6X10$^{-4}$ T

$m_I$ = +3/2          +1/2          -1/2          -3/2

$\bar{g}$

**Fig. 4**  ESR spectrum of the title complex in ethanol solution at room temperature.



**Fig. 3**  A diagram viewed along the normal of bipy mean plane shows a π-π stacking interaction between bipy rings. The atoms with suffix δ are generated using symmetric transform of 2 - x, - y, - z.
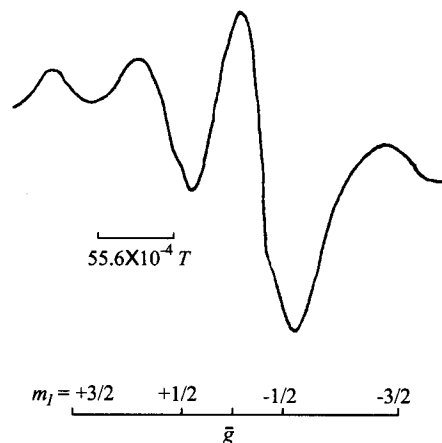
Four bands were observed in UV spectrum of the title Cu(II) complex. Bands at 196 nm and 300 nm agree with 201 nm and 301 nm reported for free bipy and maleic acid, respectively.[12] Bands at 456 nm and 640 nm are assigned to Cu(II)→ligand charge transfer transition and d-d transition in the metal center and agree with that found in the square pyramid geometry in solution.[13-14]

*ESR spectrum*

The ESR spectrum of the powder crystalline sample measured at room temperature exhibits the anisotropic feature. The spectral parameters are $g_{\parallel}$ = 2.237, $g_{\perp}$ = 2.063 and $\bar{g}$ = 2.121. The spectrum of the crystalline sample does not show absorption at the position of half field, which means no magnetic super-exchange interaction occurring in the sample.

The ESR spectrum of the complex in ethanol solution exhibits four isotropic hyperfine lines as shown in Fig. 4. The spectral parameters of $\bar{g}$ = 2.089 and $\bar{A}$ = 78.3 × 10$^{-4}$ cm$^{-1}$ were measured from the spectrum. Using the

The different intensities of splitting peaks in ESR spectrum of the title complex shows that the relaxation effect is significant.[15] The fact that separations between hyperfine splittings peaks increase with increasing of the intensity of magnetic field shows the relaxation effect should be well described by the second approximation.[15]

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