Synthesis, Crystal Structure, and Characterization of Copper(II) Acetate Complex

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Metal-carboxylate chemistry has received a great deal of attention in several different fields ranging from catalysis[1] to bioinorganic[2] and materials chemistry.[3] Metal-carboxylate clusters have often the aesthetically pleasing structures and exhibit highly unusual magnetic properties.[4] As part of a continuing interest in the structural properties of metal-carboxylate clusters, we have been seeking to develop synthetic routes to an uncommon type of trinuclear copper-carboxylates, $[M_3(O_2CR)_6L_2]^{2+}$ with a linear structure. This type of Mn(II) and Fe(II) complexes as structural models for the active sites in the dioxygen-binding protein hemocyanine and various multimetal oxidases were prepared previously.[5] Recently, we have obtained binuclear complex,[6] $[Cu_2(\mu\text{-}H_2O)(O_2CMe)_4(Phen)_2]$, where the complex have the additional stabilization of coordinated ligands by the second-coordination sphere binding interactions – phen-phen π-stacking, hydrogen-bonding between water bridged to Cu(II) and terminal acetates, and dangling to Cu(II) by oxo group of acetates *et al*. However, the parallel study of $Cu(O_2CMe)_2 \cdot H_2O$ reactions with 2,2'-bipyridine in this work led to a simple mononuclear complex, $[Cu(O_2CMe)_2(bpy)]$, instead of such a binuclear or trinuclear complex. Although many papers for Cu(II) complexes have been reported,[7] the complex is the first example, to our knowledge, of a square planar complex that contain two terminal acatates as monodentate. Thus, this paper reports the synthesis and structural characterization of the mononuclear Cu(II) complex. Some spectroscopic and electrochemical properties of the complex are also discussed.

Experimental Section

Materials. Solvents and reagents were obtained from commercial sources and used as received, unless noted otherwise. The ligand 2,2'-bipyridine was purchased from Fluka Chemical Corp., Ronkonkoma, NY. and $Cu(O_2CMe)_2 \cdot H_2O$ was obtained from Junsei Chemical Co., Ltd. All other chemicals and solvents were reagent grade.

Preparation of $[Cu(O_2CMe)_2(bpy)]$. A solution of 2,2'-bipyridine (0.43 g, 2.72 mmol) in 10 mL of dimethylformamide (DMF) was added to a stirred solution of $Cu(O_2CMe)_2 \cdot H_2O$ (0.81 g, 4.08 mmol) in 20 mL of DMF. The mixture was allowed to stir for 5 h and then filtered, yielding a fine blue solid that was washed with diethyl ether. The solid was dried in vacuo to yield a pale blue powder (0.51 g, 54%): m.p. 238 °C. Λ_M (Mho cm^2 mol^{-1}), 7.5. Anal. Calcd for $C_{14}H_{14}N_2O_4Cu$: C, 48.48; H, 4.36; N, 8.08. Found: C, 48.85; H, 4.33; N, 8.20. UV/vis, λmax/nm (ε/M^{-1}cm^{-1}) 691 (72.8), 310 (23480.0). FT-IR (KBr, cm^{-1}) 2923, 1580 ($\nu_{asym}CO_2$), 1400 ($\nu_{sym}CO_2$), 1375, 1317, 1248, 1027, 923, 771, 676.

Pale blue crystal of the complex suitable for an X-ray diffraction study was obtained within several days by allowing low concentration DMF solutions of $Cu(O_2CMe)_2 \cdot H_2O$ to react with 2,2'-bipyridine and letting the resulting clear, blue solution stand open to the air.

Measurements. Carbon, Hydrogen, and Nitrogen analyses were carried out using a Carlo Reba Model EA-1106 CHNS/O Analyser. IR, ^{1}H NMR, and UV/vis spectra were obtained by using a Mattson Polaris FT-IR Model spectrophotometer (KBr disk), a Varian Model Gemini-200 spectrometer in DMSO-d_6 solution, and a Shimadzu Model UV-0160A spectrophotometer in DMSO, respectively. Chemical shifts are in ppm relative to internal Me_4Si. Melting points and Molar conductances were measured with a Haake Buchler Model apparatus and a YSI Model 31 conductivity bridge in DMSO at 25 °C, respectively. Electrochemical measurements were carried out with a EG&G Model M270 electrochemical system. A three-electrode cell comprising a glassy carbon working, a platinum-wire counter, and a Ag/Ag$^+$ reference electrode was used. The concentration of complex was 2×10^{-3} M with 0.1 M tetraethylammonium perchlorate (supporting electrolyte) in distilled dimethyl sulfoxide (10 mL).

Collection and Reduction of X-Ray Data. The crystal of the complex, approximately $0.08 \times 0.16 \times 0.08$ mm, was obtained as described above and mounted in glass capillary. Measurement was made on a Enraf-Nonius CAD4 TURBO diffractometer with graphite-monochromatized Mo-K$_\alpha$ radiation (λ = 0.71069 Å) at 20(1) °C. Preliminary experiments for the cell parameters and orientation matrix for crystal were carried out by least-squares refinement, using the setting angles of 25 carefully centred reflections in the range $20^o < 2\theta < 35^o$. Diffraction intensity was collected using the ω-2θ scan technique with variable scan speeds. Omega scans of several intense reflections were made prior to the data collection to optimize the proper scan width for crystal. Details of the crystal data and intensity collections are summarized in Table 1.

The intensities of three representative reflections were monitored every 150 reflections and no significant decay was observed. Of the reflections collected, those with I >

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Table 1. Experimental Details of the X-ray Diffraction Studies for the Complex, $[Cu(O_2CMe)_2(bpy)]$

Parameter	$[Cu(O_2CMe)_2(bpy)]$
Empirical formula	$C_{14}H_{14}N_2O_4Cu$
Mw (g mol^{-1})	337.82
Crystal system	triclinic
Space group	$P\bar{1}(P-1)(\#2)$
Z	1
A (Å)	7.599(1)
B (Å)	9.541(1)
C (Å)	9.736(3)
α (°)	87.62(1)
β (°)	79.46(1)
γ (°)	84.82(1)
V(Å^3)	691.0(2)
ρ calc(g/cm^3)	1.359
μ (cm^{-1} with Mo-K$_\alpha$)	15.9
Transmission factor	94.6735-99.9375
Scan type	ω-2θ
Scan width(ω) (deg)	1.34+0.55tan(θ)
2θ max(deg)	52.64
No. of reflections measured	2976
No. of reflections observed (I > 3σ(I))	1924
No. of variables	190
Discrepancy indices, R^a(R_w^b) (%)	0.048(0.058)
Goodness of fit indicator^c	1.58
Maximum shift in final cycles	less than 0.01

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bR_w = [(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where w = $[\sigma(F^2)]^{-1}$. ^{c}Estimated standard deviation of an observation of unit weight: $[(\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$, where N_o = Number of observations and N_v = Number of variables.

3σ(I) were used for structure determination. The structure was solved by direct method (MULTAN[8]) and refined by full matrix least-squares on F^2 (program MolEN[9]). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were not refined, but included in the structure factor calculations at idealized positions.

Results and Discussion

Synthesis. The initial goal of this work was to synthesise the trinuclear copper-acetate complexes, $Cu_3(O_2CMe)_6$-(L-L)$_2$, similar to the Fe(II) and Mn(II) analogues[5] by reaction of $Cu(O_2CMe)_2 \cdot H_2O$ with neutral bidentate ligands. However, unfortunately the treatment of $Cu(O_2CMe)_2 \cdot H_2O$ with 0.67 equivalent of 2,2'-bipyridine in DMF led to the mononuclear complex, $[Cu(O_2CMe)_2(bpy)]$.

The conductivity data in DMSO showed that the complex is nonelectrolyte.

Structural Description of Complexes. The crystal structure of complex is shown in Figure 1. The selected bond lengths and angles are given in Table 2. The coordination geometry of complex is well described as monomeric square planar with a bipyridine as bidentate and two acetates ligands. The coordinated bipyridine fragment is a very mediocre plane, having torsion angles of 2.76° and 4.86° at their

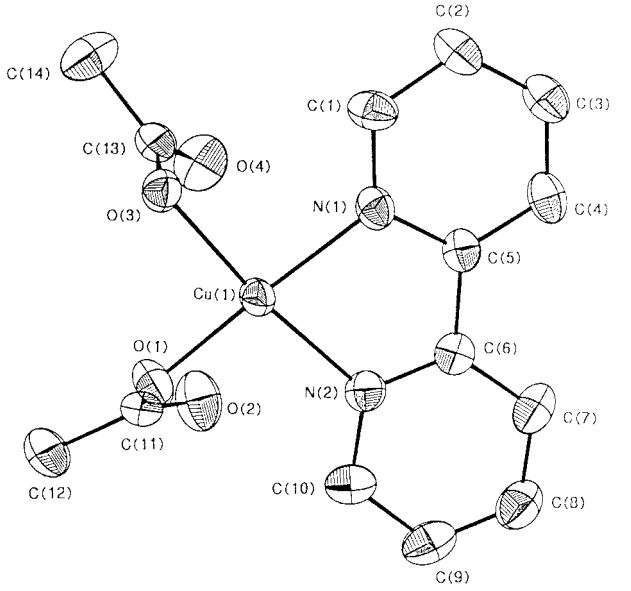

Figure 1. ORTEP drawing showing 50% probability ellipsoids and labeling scheme for the complex, $[Cu(O_2CMe)_2(bpy)]$.

intersections – CuN(1)C(5)C(6)N(2) and N(2)C(6)C(7)C(8) C(9)C(10) plane, and CuN(1)C(5)C(6)N(2) and N(1)C(2) C(3)C(4)C(5) plane. Each of two acetates is also very excellent trigonal planes and dihedral angle between O(3)O(4) C(14) and O(1)O(2)(C12) planes is 83.11°. The mean values of Cu-N and Cu-O (acetate) separations [2.018(5) and 1.940(4) Å, respectively] are similar to those observed for complexes[6,10,11] reported previously. The CuN_2O_2 coordination sphere is subject to slightly distortion from the ideal square planar geometry. This distortion is confirmed by the dihedral angle (1.47°) between two adjacent CuN(1)O(3) and CuN(1)N(2) planes, and the mean deviation (0.035 Å) of the N(1)N(2)O(1)O(3) plane. Also, the angles at the metal center show somewhat deviations from the ideal values of 90° and 180° (Table 2). The Cu···O(2) and Cu···O(4) distances [6.719(5) and 5.356(5) Å, respectively] are considerably longer than typical interactive separations (below 3.0

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex, $[Cu(O_2CMe)_2(bpy)]$

Cu(1)--O(1)	1.927(4)	O(2)--C(11)	1.226(7)
Cu(1) (((O(3)	1.952(4)	O(3)--C(13)	1.289(6)
Cu(1)--N(1)	2.020(5)	O(4)--C(13)	1.221(7)
Cu(1)--N(2)	2.015(5)	C(11)--C(12)	1.53(1)
O(1)--C(11)	1.265(7)	C(13)--C(14)	1.516(9)
O(1)--Cu(1)--O(3)	90.5(2)	Cu(1)--N(2)--C(6)	115.5(3)
O(1)--Cu(1)--N(1)	173.0(2)	N(1)--C(5)--C(6)	114.2(5)
O(1)--Cu(1)--N(2)	96.3(2)	N(2)--C(6)--C(5)	114.9(5)
O(3)--Cu(1)--N(1)	93.2(2)	O(1)--C(11)--O(2)	125.3(6)
O(3)--Cu(1)--N(2)	172.9(2)	O(1)--C(11)--C(12)	114.9(5)
N(1)--Cu(1)--N(2)	79.8(2)	O(2)--C(11)--C(12)	119.8(5)
Cu(1)--O(1)--C(11)	123.7(4)	O(3)--C(13)--O(4)	122.8(5)
Cu(1)--O(3)--C(13)	113.4(3)	O(3)--C(13)--C(14)	116.1(5)
Cu(1)--N(1)--C(5)	115.0(3)	O(4)--C(13)--C(14)	121.1(5)

Å[12,13]). So, the stabilization by additional metal to acetate interactions in the complex is not expected.

Oxidation state for the copper ion in the complex is +2, which was assigned on the basis of overall charge consideration, and confirmed by the bond lengths and by the ^{1}H NMR silence due to the paramagnetism of Cu(II) (d^9).

Spectroscopic and Electrochemical Properties. Apart from X-ray crystallography, infrared spectroscopy might be expected to provide an useful information about complexes containing carboxylates bound in various modes. The crystal IR spectrum of the complex displayed broad bands due to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ at *ca.* 1,580 and *ca.* 1,400 cm^{-1}, respectively. The appearance of broad bands for each of stretching vibrations probably reflects no symmetry between two acetate groups in the crystal structure (Figure 1, Table 2). However, $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ vibrations for acetates of the binuclear Cu(II) complex,[14] [$Cu_2(\mu$- $H_2O)(O_2CMe)_4(phen)_2$], having an additional stabilization by hydrogen bonding and dangling of acetate groups to metal were observed at *ca.* 1,587 cm^{-1} as a broad band with a overlapping feature and at 1,430 and 1,395 cm^{-1} as two distinct bands, respectively. This fact shows that the complex prepared in this work does not have any additional interaction between metal and acetate groups. The crystal IR spectrum of the complex is identical to that of its solid-state, but the solution IR spectrum in DMSO showed one broad $\nu_{asym}(CO_2)$ band at 1,620 cm^{-1}. The solution IR spectrum of binuclear complex,[14] [$Cu_2(\mu$-$H_2O)(O_2CMe)_4(phen)_2$] in DMSO also showed one broad band at 1,623 cm^{-1} as this mononuclear complex, although solid-state spectrum is considerably different.

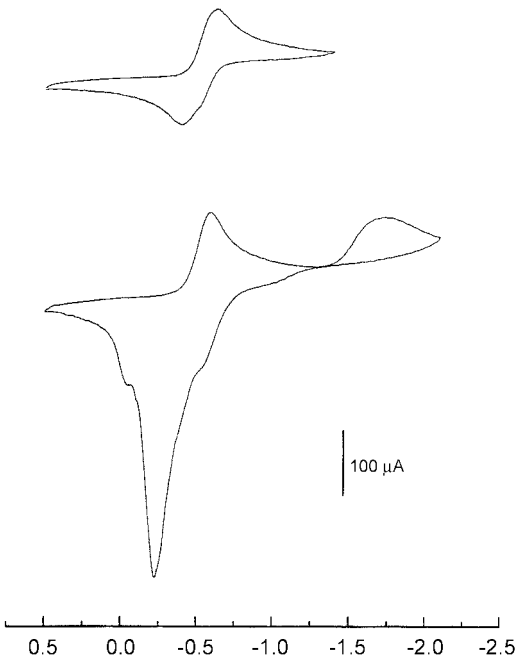

Figure 2. Cyclic voltammograms (200 mV/s) of [$Cu(O_2CMe)_2$(bpy)] complex in DMSO (1.0 mM) in the range +0.50 to -1.40 V (top) and +0.5 to -2.10 V (bottom). The quoted potentials are *vs* ferrocene/ferricinium.

Electronic spectra of the complex in DMSO showed one very broad d-d band at 691 nm (ε = 72.8 M^{-1}cm^{-1}) and a band in the UV region of 310 nm (ε = 23480.0 M^{-1}cm^{-1}) due to acetate-to-copper LMCT transitions[15] comparing to the free ligand bands.

Cyclic voltammetric measurements were also carried out for the complex at a glassy carbon working electrode in DMSO solution and the cyclic voltammogram was showed at Figure 2. A complete scan (bottom) displayed two cathodic processes of comparable peak currents at E_p values of -0.54 and -1.66 V, and a large anodic feature on the reverse scan assignable to oxidation of copper metal deposited on the electrode surface. The reversal of the potential scan at -1.40 V exhibited the first process to be quasi-reversible: $E_{1/2}$ = -0.37 V (ΔE_p = 0.35 V, i_{pc}/i_{pa} = 1.38; both i_{pc}/i_{pa} and $i_p/\nu_{1/2}$ are independent of scan rate (ν) in the range 50-400 mV s^{-1}. The CV processes are summarized in Eq. (1).

$$Cu^{II} \overset{-0.37\ V}{\rightleftharpoons} Cu^{I} \overset{-1.66\ V}{\rightleftharpoons} Cu^{0} \qquad (1)$$

Electronic and electrochemical behaviours of the complex are similar to those of binuclear complex with phenanthroline,[14] presumably supporting that both complexes are similar species in DMSO.

Supplementary Material Available. Details of X-ray data collection parameters, atomic coordinates, and anisotropic thermal parameters are available from the author.

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