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Mixed ligand chelates of copper(II) with substituted diamines

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Abstract

The copper complexes, oxalato(*N*,*N*,*N*′*N*′-tetramethylethylenediamine)copper(II) tetrahydrate (**1**), oxalato(*N*,*N*,*N*′-trimethyl-1,3-propanediamine)copper(II) (**2**), and oxalato(*N*,*N*,*N*′-trimethylethylenediamine)copper(II) (**3**), have been synthesized and structurally characterised. Compounds **1** and **2** share a common zig-zag polymeric structure in which the oxalates are bridging as well as chelating. The copper is in a distorted octahedral position in both compounds. Compound **3** is monomeric and the oxalate is chelating only. The copper is in a distorted square planar position. Diffuse reflectance spectroscopy and ESR spectroscopy showed a clear difference between the two types of structures.

Keywords: Copper; Oxalato; Tetramethylenediamine; Synthesis; Structure; Mixed ligand; ESR; Substituted diamines; X-ray

1. Introduction

The mixed ligand systems based on copper(II) salts form stable complexes of approximately square planar geometry and such complexes have been extensively studied [1]. Copper(II) ion forms stable ternary complexes with π-acceptor ligands such as 2,2′-bipyridyl (bipy) ligands and oxalate ($C_2O_4^{2-}$) ions [2,3]. It has been shown that this complex is subject to polymorphism indicated by colour changes as well as changes in the electronic and ESR spectra.

Stone et al. [2] have prepared $[Cu(bipy)(O_4C_2)]\cdot 2H_2O$ which turned green and then finally dehydrated to give an anhydrous compound; $[Cu(bipy)_2]$ $[Cu(O_4C_2)_2]$. Sigel et al. [1] and Hathaway and co-workers [3] have prepared a blue-green anhydrous mixed ligand complex by a different method but no solid-state reactivity was observed. There have also been several studies of mixed ligand Cu(II) bipy complexes with carboxylic or amino-acids [4–7].

The copper chelates with diamines have proven to be active catalysts for the hydrolysis of phosphate esters [8]. The stability of 1:1 copper(II) chelate complexes is controlled by the tendency to disproportionate to 2:1 chelate and copper hydroxide. Since the copper(II) chelate complexes are square planar, the substitution of alkyl groups in place of the amino groups should help the disproportionation reaction by steric repulsion. It has been reported that the soluble 1:1 copper(II) chelate complexes of TMEDA and *N*,*N*′-dimethylethylenediamine (DMEDA) did not disproportionate in aqueous solutions at pH 7 and above, but 1:1 copper(II) chelate complex of ethylenediamine was not stable, and did convert to 2:1 chelate complex and copper hydroxide [9].

However, Marjit and Sharma [10] have reported that 1:1 complexes are not only difficult to isolate but if

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isolated, their stability was low in the reaction medium. The copper(II) nitrate–TMEDA 1:1 complex became turbid in aqueous solution due to disproportionation reaction and form a more stable 1:2 complex. Previously, it has been shown that dimers of the chelate complexes tend to show negligible catalytic activity [11]. In order to better define the coordination chemistry of substituted diamines with copper(II), mixed ligand complexes of oxalate and diamines have been synthesized and discussed.

2. Experimental

$CuSO_4$, $K_2(C_2O_4)$ and diamines were used as purchased from Aldrich company Limited. $Cu(C_2O_4)\cdot 1/2H_2O$ was prepared according to the reported method [12].

2.1. Preparation of Cu(TMEDA)oxalate·4H$_2$O (1)

To a stirred solution of TMEDA (0.48 ml, 3.2 mmol) in water (2 ml), finely powdered $Cu(C_2O_4)\cdot 1/2H_2O$ (0.25 g, 1.6 mmol) was added. Unreacted copper oxalate was removed by filtration. Ethanol (2 ml) was added to the filtrate and the solution was allowed to stand. After several days, a mixture of colourless and blue crystals formed. The blue crystals of **1** were separated for analysis; m.p. 232 °C; yield, 79%. *Microanal*. Calc. for $CuC_8H_{22}O_8N_2$: C, 28.3, H, 7.1, N, 8.2. Found: C, 28.3, H, 7.3, N, 8.1%. IR bands: 3407 (s), 2926 (m), 1673 (s), 1046 (m), 520 (m). UV/Vis bands: $\lambda_{max} = 15.0 \times 10^3$ cm^{-1} with a shoulder at 9.8×10^3 cm^{-1}.

2.2. Preparation of Cu(TriMPDA)oxalate (2)

To a stirred solution of *N*,*N*,*N*′-trimethyl-1,3-propanediamine (0.37 ml, 1.6 mmol) in water (4 ml) was added $Cu(C_2O_4)\cdot 1/2H_2O$ (0.25 g, 6.4 mmol). The excess copper oxalate was removed by filtration. The addition of ethanol immediately precipitated a blue solid which was dissolved in water (2 ml) and allowed to stand for crystallization. After several days blue crystals of **2** were formed which were separated by filtration, dried, m.p. 240 °C; yield, 68%. *Microanal*. Calc. for $CuC_8H_{16}O_4N_2$: C, 35.9, H, 6.0, N, 10.5. Found: C, 35.8, H, 5.8, N, 10.6%. IR bands: 3443 (m), 2930 (m), 1619 (s), 1044 (m), 495 (m). UV/Vis bands: $\lambda_{max} = 13.6 \times 10^3$ cm^{-1} with a shoulder at 9.6×10^3 cm^{-1}.

2.3. Preparation of Cu(TriMEDA)oxalate (3)

To a stirred solution of $Cu(C_2O_4)\cdot 1/2H_2O$ (0.5 g, 3.2 mmol) in ethanol (5 ml) and water (5 ml), was added *N*,*N*,*N*′-trimethylethylenediamine (0.81 ml, 6.4 mmol). The resulting solution was allowed to stand. Blue/violet crystals of **3** were grown after a few days; m.p. >240 °C; yield, 77%. *Microanal*. Calc. for $CuC_7H_{14}O_4N_2$: C, 33.1, H, 5.5, N, 11.0. Found: C, 33.2, H, 5.4, N, 11.4%. IR bands: 3424 (m), 2927 (m), 1619 (s), 1055 (m), 790 (s), 490 (m). UV bands: $\lambda_{max} = 18.4 \times 10^3$ cm^{-1}.

Table 1
Crystal data and structural refinement parameters

Compound	$C_8H_{24}N_2CuO_8$ (**1**)	$C_8H_{16}N_2CuO_4$ (**2**)	$C_7H_{14}N_2CuO_4$ (**3**)
F_w	339.83	267.77	253.74
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	*Pbca*	$Pca2_1$
a (Å)	7.362(2)	11.368(3)	10.994(3)
b (Å)	8.891(8)	9.844(6)	8.557(10)
c (Å)	11.841(4)	18.639(7)	10.752(3)
α (°)	101.44(6)	90	90
β (°)	98.08(3)	90	90
γ (°)	92.53(8)	90	90
Volume (Å^3)	750.0(7)	2085(2)	1011.5(4)
Z	2	8	4
d_{calc} (Mg/m^3)	1.505	1.705	1.666
Absorption coefficient (mm^{-1})	1.490	2.091	2.151
Index ranges	$-8 \leqslant h \leqslant 8$ $0 \leqslant k \leqslant 10$ $-14 \leqslant I \leqslant 13$	$-4 \leqslant h \leqslant 13$ $-11 \leqslant k \leqslant 0$ $-7 \leqslant I \leqslant 22$	$-3 \leqslant h \leqslant 13$ $-10 \leqslant k \leqslant 1$ $-6 \leqslant I \leqslant 12$
Collected/unique	2887/2621	1875/1823	969/945
Data/restraints/parameters	2621/0/214	1823/0/144	945/2/134
Goodness-of-fit on F^2	1.078	0.940	1.020
R_1, wR_2 [$I > 2\sigma(I)$]	0.0565, 0.1696	0.0321, 0.0936	0.0231, 0.0656
R_1, wR_2 (all data)	0.0605, 0.1720	0.0407, 0.0969	0.0277, 0.067
Differential peak, hole (e Å^{-3})	1.639, −1.285	0.469, −0.638	0.222, −0.359