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Studies on A Novel Mixed-Valence Complex of Copper (I, II) α-Methacrylate with Imidazole and Aqua

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Abstract: A novel mixed-valence copper (I, II) complex $Cu_3[CH_2=C(CH_3)COO]_5(imH)_3(H_2O)$ has been synthesized and characterised by XPS spectra and single crystal X-ray structural analysis. The title complex crystallized in monoclinic space group $P2_1/c$, with a=11.225 (3), b=13.9023 (12), c=24.559 (2)Å, β=92.372 (10)° and Z=4. Final R=0.0495 for 5546 reflections [$I>2\sigma(I)$].

Keywords: Mixed-valence copper (I, II) complex; synthesis; crystal structure.

Mixed-valence copper (I, II) complexes play an important role in a vast range of chemical and biochemical catalytic systems[1]. The crystal structures of mixed-valence copper (I, II) complexes have been received considerable attention for what they may reveal about structural changes accompanying oxidation and reduction of copper in metalloenzymes[2]. Here we report a novel structure of mixed-valence copper (I, II) complex containing bridging carboxylate group, obviously different in structure with the mixed-valence complexes reported previously[3-6].

Synthesis

Methanol solution of copper (II) α-methacrylate (synthesized according to the literature method[7]) (1 mmol) and thiourea (0.5 mmol) were mixed, stirred 8 h and filtered. Imida-zole (1 mmol) was added to the filtrate, stirred and refluxed for 4 h and then filtered under anhydrous condition. The solution was left to stand at room temperature, and bule-green crystals were obtained. Anal. Calc. for $C_{29}H_{39}Cu_3N_6O_{11}$ (%): C, 41.55; H, 4.69; N, 10.03; Cu, 22.74. Found (%): C, 41.73; H, 4.51; N, 9.95; Cu, 22.56.

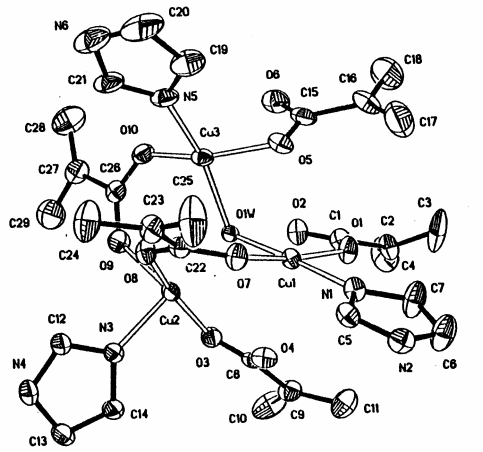
Results and discussion

The title complex is monoclinic with space group $P2_1/c$; a=11.225 (3), b=13.9023 (12), c= 24.559 (2) Å, β = 92.372 (10)°, V = 3829.2 (10) Å^3, Dc = 1.454 g·cm^{-3}, F(000) = 974, μ(Mo$K\alpha$) = 17.10 cm^{-1}, Z=4, and final R = 0.0495 for 5546 reflections [$I>2\sigma(I)$].

Figure 1 shows the molecular structure of the title trinuclear mixed-valence complex, in which the oxidation number of the Cu (1) and Cu (3) is +2, and that of Cu (2) is +1. The

coordination sphere of the Cu (1) and Cu (3) atoms is a square planar geometry, while the Cu (2) atom has a distorted tetrahedral configuration. The molecular unit contains two coordinating mode carboxylate ligands (μ_2-carboxylate-O, O' bridging group and monodentate group) and a μ_2-aqua bridging ligand.

Figure 1. Perspective view of title complex



The calculation of bond-valence theory[8] shows $S_{Cu\,(1)}$=1.9326, $S_{Cu\,(3)}$=1.9741 and $S_{Cu\,(2)}$=0.9979 (S is the calculated bond valence) , indicating that the oxidation number of the Cu (1) and Cu (3) atoms is +2, as that of the Cu (2) atom is +1. $Cu2p_{3/2}$ XPS spectra of the title complex gave the binding energes (eV) for Cu (II) and Cu (I) are 934.5 and 932.4 respectively. The peak area ratio of Cu (II) and Cu (I) is 2:1, consistent with the complex composition.

Acknowledgments

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