

Complexes of Cu(II) Monochloroacetate & Dichloroacetate with Some Oxygen Donor Ligands

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New complexes of Cu(II) monochloroacetate and dichloroacetate with some amine oxides, phosphoryl ligands and triphenylarsine oxide have been synthesized. The IR spectra suggest the formation of O → Cu bond which is apparent from the changes in the frequencies of the ligands and that of the carboxylate group. The electronic spectra and magnetic moments of a few of the complexes have been examined and the latter suggest appreciable Cu-Cu interaction in the complexes of Cu(II) monochloroacetate.

ALTHOUGH complexes of the ligands having >P=O , -N-O and >As=O donor groups with a variety of acceptors have been prepared and studied, their complexes with Cu(II) carboxylates have not been reported, except for a 1:1 complex of triphenylphosphine oxide with Cu(II) acetate¹. It has been established that Cu(II) acetate and its monohydrate are dimeric^{2,3}, having a strong Cu-Cu bond^{4,5}. Further, it has been suggested that the strength of this M-M bond may decrease either with electron withdrawing substituents on carboxylates as evidenced by the magnetic moment values of various Cu(II) haloacetates^{6,7} or from the attached ligands in the case of complexes⁸. It is, therefore, of interest to examine the combined effect of the weak donors such as those mentioned above and of the monochloro- and dichloroacetate groups attached to Cu(II) in place of the acetate group. The result of the study of magnetic moment, electronic and infrared spectra of these new complexes are reported in this note.

Materials and Methods

Cu(II) monochloroacetate tetrahydrate⁹ on heating at 100° for several hours yielded anhydrous Cu(II) monochloroacetate (dark green), m.p. 218°. Cu(II) dichloroacetate tetrahydrate was prepared by known method¹ and was dehydrated by heating at 60° *in vacuo*, to pale green anhydrous salt, m.p. 247-48° (d). Both the compounds gave satisfactory elemental analysis.

The complexes of Cu(II) monochloroacetate and dichloroacetate with pyridine-N-oxide, α_1 -, β_1 - and γ -picoline-N-oxides, hexamethyl-phosphoramide, triphenylphosphine oxide, triphenylarsine oxide and 2,2-bipyridyl-N,N-dioxide were prepared by mixing the methanol solution of the carboxylates and the ligand in 1:2 molar proportions. However, changing the proportion of the reactants produced the same complexes. The resulting solutions were warmed ($\sim 60^\circ$) and allowed to stand for some time. The adduct was precipitated by adding

excess of dry ether. It was filtered under anhydrous conditions, washed a number of times with dry ether and dried under vacuum. In the case of Cu(II) dichloroacetate adduct with 2,2'-bipyridyl-N,N'-dioxide, the resulting solution had to be refluxed. The yield of the complexes varied from 60-70%.

The metal and chlorine were estimated by usual methods¹⁰. Magnetic susceptibility measurements were made on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the standard.

Results and Discussion

Cu(II) monochloroacetate and dichloroacetate form 1:1 and 2:1 (ligand-carboxylate) adducts as revealed by the analytical data given in Table 1. However, Cu(II) dichloroacetate forms 1:1 adducts with triphenylphosphine oxide and 2,2'-bipyridyl dioxide. The complexes are slightly hygroscopic and have sharp melting points. The adducts are quite soluble in methanol or ethanol. However, their insolubility or insufficient solubility in solvents like benzene or nitrobenzene precludes their molecular weight determination. The magnetic moment values of the 1:1 complexes of Cu(II) monochloroacetate (Table 1) are quite close to that of pure Cu(II) acetate monohydrate⁶ and some of the complexes of copper (II) monochloroacetate with amides¹¹, indicating an appreciable Cu-Cu interaction in these complexes. On the other hand the magnetic moment values of 1:2 complexes of dichloroacetate are nearly the same as for normal Cu(II) complexes¹² (1.8-2.2 BM). The electronic spectra in the visible and near IR regions of the methanolic solutions of the present complexes show only one broad band with low extinction coefficient appearing around 13.0 kK and this is the region where a six-coordinate tetragonally distorted octahedral Cu(II) complex is expected to absorb¹³⁻¹⁵.

IR spectra of the complexes reveal the trend in changes in the characteristic frequencies of the ligands which point out to the site of coordination to Cu(II). The $\nu(\text{N-O})$ of the amine oxides appear

TABLE 1 — COLOUR, MELTING POINTS, ANALYSES AND MAGNETIC MOMENTS OF THE COMPLEXES OF Cu(II) MONOCHLOROACETATE AND DICHLOROACETATE

Complex	Colour	m.p. (°C)	Cu (%)		Cl (%)		μ_{eff} (BM)
			Found	Reqd	Found	Reqd	
*A.Py-O	Green	159	18.1	18.4	20.0	20.5	1.38
A. α -Pic-O	Dark green	146	17.0	17.7	20.1	19.8	1.42
A. β -Pic-O	Green	112	16.9	17.7	19.6	19.8	—
A. γ -Pic-O	Bluish green	119	17.4	17.7	19.0	19.8	—
A.Dipy.O ₂	Green	89(d)	16.1	14.5	17.3	16.2	—
A.HMPA	do	173	14.2	14.7	16.2	16.5	—
A.Ph ₃ P=O	do	191	12.1	12.0	13.2	13.4	1.53
A.Ph ₃ As=O	do	178	11.3	11.1	12.4	12.4	1.56
*B.2Py-O	Bluish green	165	12.4	12.5	27.3	27.8	1.85
B.2 α -Pic-O	Blue	96	11.9	11.8	26.2	26.4	1.72
B.2 β -Pic-O	Green	119-20	11.6	11.8	26.6	26.4	1.85
B.2 γ -Pic-O	do	157	11.5	11.8	26.1	26.4	—
B.Dipy.O ₂	Light green	159	11.9	12.5	28.6	28.0	—
B.Ph ₃ P=O	Green	225	11.1	10.6	23.5	23.8	1.84
B.2Ph ₃ As=O	Sky blue	178-79	6.5	6.6	14.1	14.7	2.00

*A = Cu(ClCH₂CO₂)₂ and B = Cu(Cl₂CHCO₂)₂.

around 1250 cm⁻¹ which shift to lower frequency regions in the complexes. The $\delta(\text{N-O})$ which appears at 850 cm⁻¹ in the amine oxides also shifts to lower frequency region. In the case of phosphoryl ligands there is marked shift of $\nu(\text{P}=\text{O})$ of the pure ligand (1190 cm⁻¹) to the lower frequency region (1120 cm⁻¹) in the spectra of the complexes. Similarly, $\nu(\text{As}=\text{O})$ of pure triphenylarsine oxide at 880 cm⁻¹ shifts to 875 and 863 cm⁻¹ respectively in the spectra of its complexes with Cu(II) monochloroacetate and dichloroacetate. These results indicate coordination of these ligands through their oxygen atom¹⁶⁻¹⁸. In the IR spectra of the complexes in nujol, the asymmetric and symmetric stretching carboxylate frequencies are observed at 1610-1640 and 1355-1380 cm⁻¹ respectively for the complexes of Cu(II) monochloroacetates and at 1610-1650 and 1350-1400 cm⁻¹ respectively for the complexes of Cu(II) dichloroacetate. The position of these vibrations compare well with the complexes of Cu(II) monochloroacetate with amides¹¹ and pyridine complex of Cu(II) dichloroacetate¹⁹. These results indicate that in the Cu(II)-dichloroacetate complexes, the carboxylate group is acting as a bidentate ligand and not bridging since the difference in $\nu_{\text{as}} \text{COO}$ and $\nu_{\text{s}} \text{COO}$ is not expected to exceed by 260 cm⁻¹ for the former and by more than 290 cm⁻¹ for the latter. The present complexes have a difference of the order of 260 ± 10 cm⁻¹. The O-Cu vibrations²⁰ which are present at (385 m, 330 vvw cm⁻¹) and (393 w, 376 sh, 325 w, 303 s cm⁻¹) in Cu(II) monochloroacetate monohydrate and Cu(II) dichloroacetate monohydrate respectively are either present at nearly the same spectral

frequencies or are slightly shifted to the lower spectral region in the spectra of the complexes.

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