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Thermal, IR and X-Ray Diffraction Studies on Dimetavanadate BIS (8-Hydroxyquinoline) Copper(II) Monohydrate Complex

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Mixed ligand Cu(II) complex with metavanadate ion and 8-hydroxyquinoline has been prepared and some physical properties have been studied. Magnetic and electronic studied suggesting that the square planar configuration of this complex. Thermal data suggests the presence of one water molecule in the crystal lattice, its confirm in the IR spectra, IR spectra also suggests the 8-hydroxyquinoline is N and O donor bidentate ligand. The X-ray powder diffraction pattern reveals the presence of orthorhombic unit cell, the lattice constants for which have been reported.

INTRODUCTION

In continuation to our earlier studies[1] we have reported the structural behaviour of some copper (II) complexes having VO_3^- as anion and amines as secondary ligands. In this paper we report the 8-hydroxyquinoline as a N and O donor bidentate secondary ligand with copper (II) metavanadate. The literature reveals that this type of complex has not yet been widely investigated. The aim of our investigation is to study the structural change in the presence of new anion.

EXPERIMENTAL

All chemicals used were of AnalaR grade. Copper(II) metavanadate $\{Cu(VO_3)_2\}$ was prepared by the method reported in the literature[2,3] and its chemical composition has been checked by estimation of copper and vanadium separately gravimetrically by the recommended procedure[4]. The complex was isolated by refluxing a mixture of copper metavanadate (1 mol.) with the required 8-hydroxyquinoline (2 mol.) in 100 ml. ethanol for about 24 hours. The product was filtered, washed[3–4] times with ethanol recrystallised from double distilled water, again washed with ethanol and dried under reduced pressure over P_4O_{10} before analysis.

RESULTS AND DISCUSSION

The complex is coloured, solid and quite stable in air. Based on elemental analyses the stoichiometry of the complex has been computed to be $Cu(HQ)_2(VO_3)_2H_2O$ where HQ = 8−hydroxyquinoline. The complex is insoluble in water and in common organic solvents, indicating that the non-ionic (non-electrolytic) nature of the complex[5]. The μ_{eff} value 2.01 B. M. indicates the complex is paramagnetic at room temperature, which is in good agreement with the Cu(II) complexes lie in the usual range of one unpaired electron, this value indicate the square planar geometry[6]. The electronic reflection spectra of the complex shows only a single broad band centered around at 648 nm or 154321 cm^{-1}. This absorption may be assigned to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$. The spec-data also suggest a square planar configuration for this complex[7-10].

The assignments for principal bands have been made with the help of reported data[11,12]. A broad band at 3610–3300 cm^{-1} and a weak band at 1620 cm^{-1} in the spectra of complex indicate the presence of lattice water molecule and may be assigned to ν_{O-H} (stretching) and δ_{H-O-H} (bending) respectively[13]. The absence of a weak broad band in region at 3050 cm^{-1} due to OH group of ligand in the complex indicate the deprotonation of the replaceable hydrogen atom and leading to the involvement of the phenolic oxygen atom in the coordination[14]. This is supported by the appearance of a band at 430 cm^{-1} due to ν_{M-O} . The oxime complex give two absorption bands at 1550 and 1595 cm^{-1} due to $\nu_{C=C}$ and $\nu_{C=N}$ vibration respectively[15]. The absorption bands[16] for metavanadate VO_3^- ion lie between 720–1000 cm^{-1}. The change observed in the spectra of metavanadate complex shows new bands at *ca* 890(v_5), *ca* 810(v_3) and *ca* 760 em^{-1}(v_1) which are consistent with the monodentate nature of metavanadate group[17].

The thermal data of the copper(II) complex are given in (Table 1) These complex dissociate thermally in two steps. In first step the weight loss due to elimination of water molecule at 110°C, 3.56% (3.16% calcd) confirms the presence of one water molecule in the crystal lattice. In second step the major weight loss occurs at 210–558°C due to elimination of ligand (HQ) molecules. This major weight loss is found to be 51.70% (calcd 50·95%). The exothermic peak at 461°C is due

TABLE 1

THERMOGRAVIMETRIC ANALYSIS OF $Cu(HQ)_2(VO_3)_2.H_2O$ CODPLEX

Total weight loss (%)	Weight loss steps with temperature range			Thermochemical process
	Temperature (°C)	Weight loss (%)		
		Observed	Calculated	
	110	3.56	3.16	Elimination of lattice water molecule.
55.26	210-558	51.70	50.95	Elimination/oxidation of ligand molecules.

to oxidation of ligand molecules. The decomposition pattern may be summed up as under :

$$Cu(HQ)_2(VO_3)_2 \cdot H_2O \xrightarrow[-H_2O]{110°C} Cu(HQ)_2(VO_3)_2 \xrightarrow{210\text{–}558°C} Cu(VO_3)_3 \text{ or } CuO \cdot V_2O_5$$

The X-ray powder diffraction pattern of the complex records fifty two reflections (Table 2) between 5–70°(2θ). Most of the reflections have been indexed for h, k, l value using method reported in the literature[18]. The unit cell of the complex has been found to be orthorhombic type with lattice constant a = 20.9178, b = 15.0983 and c = 11.0817 A°. The values of $\sin^2 \theta$ for each peak have been calculated with the help of the cell parameters and corresponding h k l in all cases which are in good agreement with observed $\sin^2 \theta$ values, these are listed in Table 2. The volume of a unit cell is $V = 3499.8581$ A^3 and calculated number of molecules per unit cell is n = 4. Calculated density of the complex is in good agreement with that of experimental value. The density of complex has been calculated by using the formula $\rho = n\frac{M}{NV}$, where ρ = density, n = number of molecules per unit cell, M = molecular weight, V = unit cell volume and N = Avogadro's number.

TABLE 2

X-RAY DIFFRACTION DATA OF $Cu^{II}(HQ)_2(VO_3)_2.H_2O$ COMPLEX

Peak No.	d spacing	Relative Intensity	Observed $\sin^2 \theta$	Calculated $\sin^2 \theta$	(h k l)
1.	15.1002	3.424	0.002607	0.002607	(0 1 0)
2.	11.0822	4.348	0.004839	0.004839	(0 0 1)
3.	10.4582	81.196	0.005433	0.005433	(2 0 0)
4.	8.6955	6.386	0.007861	0.007446	(0 1 1)
5.	7.8298	100.00	0.010189	0.010272	(2 0 1)
6.	7.4806	65.924	0.010620	0.010428	(0 2 0)
7.	7.1248	12.772	0.011707	0.011786	(1 2 0)
8.	6.8080	30.924	0.012823	0.012224	(3 0 0)
9.	5.7429	17.554	0.018020	0.017100	(3 0 1)
10.	5.3492	8.967	0.020769	0.020715	(1 0 2)
11.	5.2206	6.033	0.021807	0.021964	(0 1 2)
12.	4.6722	6.630	0.027227	0.027397	(2 1 1)
13.	4.2863	7.935	0.032349	0.032160	(4 2 0)

TABLE (cont.)

Peak No.	d spacing	Relative Intensity	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	(h k l)
14.	4.0338	12.174	0.036526	0.036563	(5 1 0)
15.	3.9058	14.511	0.038957	0.038800	(5 0 1)
16.	3.7858	6.739	0.041263	0.041712	(0 4 0)
17.	3.6756	8.044	0.043990	0.043554	(0 0 3)
18.	3.5506	15.652	0.047141	0.047519	(1 1 3)
19.	3.4735	6.848	0.094260	0.048896	(6 0 0)
20.	3.3418	29.511	0.053216	0.053313	(5 0 2)
21.	3.2856	6.793	0.055053	0.055389	(1 2 3)
22.	3.1595	6.359	0.059534	0.059415	(2 2 3)
23.	3.0616	5.054	0.063407	0.063444	(4 4 0)
24.	3.0368	7.554	0.064445	0.065175	(0 5 0)
25.	2.9172	6.957	0.069838	0.069160	(7 1 0)
26.	2.9016	10.326	0.070663	0.070608	(2 5 0)
27.	2.8701	9.783	0.072151	0.072450	(2 3 3)
28.	2.7708	5.380	0.077411	0.077429	(0 0 4)
29.	2.7468	5.761	0.078769	0.078787	(1 0 4)
30.	2.5913	5.652	0.088511	0.088517	(7 1 2)
31.	2.5633	8.315	0.090449	0.090608	(6 4 0)
32.	2.5206	3.967	0.093541	0.093852	(0 6 0)
33.	2.4933	7.717	0.095600	0.095500	(6 4 1)
34.	2.3399	5.163	0.108549	0.108263	(7 4 0)
35.	2.2339	6.848	0.119095	0.118221	(5 4 3)
36.	2.2118	7.663	0.121480	0.122340	(1 0 5)
37.	2.1069	4.620	0.133889	0.132769	(1 2 5)
38.	2.0480	4.946	0.141697	0.142604	(0 5 4)
39.	2.0245	9.293	0.144999	0.144446	(0 3 5)
40.	1.9675	6.033	0.153278	0.153570	(9 0 3)
41.	1.9548	6.033	0.155525	0.154828	(3 5 4)
42.	1.9106	5.326	0.162810	0.162695	(0 4 5)
43.	1.8222	4.457	0.178981	0.179648	(2 0 6)
44.	1.8004	5.924	0.183357	0.182255	(2 1 6)
45.	1.7615	4.076	0.191544	0.190142	(7 1 5)

TABLE (cont.)

Peak No.	d spacing	Relative Intensity	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	(h k l)
46.	1.6613	3.533	0.215346	0.214835	(0 6 5)
47.	1.6519	4.891	0.217805	0.216600	(2 9 0)
48.	1.5917	5.109	0.234589	0.233399	(7 8 0)
49.	1.5693	4.565	0.241367	0.242559	(2 0 7)
50.	1.5069	5.489	0.261720	0.261947	(1 3 7)
51.	1.4624	5.109	0.277909	0.277720	(7 9 0)
52.	1.4240	5.000	0.293106	0.294659	(9 2 6)

SYSTEM—ORTHORHOMBIC

$$\sin^2\theta = Ah^2 + Bk^2 + CI^2$$

where $A = \frac{\lambda\lambda}{4a^2}$, $B = \frac{\lambda^2}{4b^2}$ and $C = \frac{\lambda^2}{4c^2}$

$A = 0.00135822$; $B = 0.002607$ and $C = 0.0048393$

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