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Physico-Chemical Studies On Some Coordination Compound Of Metals With Sulphadiazine

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ABSTRACT

Co(II) and Cu(II) complex with sulphadiazine have been synthesized and characterized. On the basis of elemental analysis and molar conductance, general formulas $Co(C_{10}H_{10}N_4O_2S)_2VO_3\cdot H_2O$ and $Cu(C_{10}H_{10}N_4O_2S)_2VO_3\cdot H_2O$ have been suggested for the complexes under study. The geometries of the complexes have been proposed on the basis of magnetic moment, electronic and infrared spectral data. Thermo gravimetric analyses(TGA) have been carried out to determine the pattern of their decomposition. The crystal system, lattice parameters, unit cell volume and number of molecules in it have been determined by X-ray diffraction data (XRD).

KEYWORDS

Thermo-gravimetric analysis;
Infrared spectroscopy;
X-ray diffraction;
Electronic spectroscopy;
Vanadate.

INTRODUCTION

In continuation of the work being carried out in our laboratory on the metal vanadate with some organic ligand, the present note describes two new complexes of cobalt(II) and copper(II) with sulphadiazine ($C_{10}H_{10}N_4O_2S$) having vanadate(VO_3) anion. The complexes have been synthesized and characterized using analytical and spectral methods.

EXPERIMENTAL

The starting material $MVO_3\cdot H_2O$[where M=Co(II) and Cu(II)] was synthesized by reported methods[1-6]. Complexes were isolated by shaking MVO_3(10mmol, 0.25g) with a required amount of ligand(30mmol, 0.75g) in water(~100mL). The products were filtered, washed 3-4 times with diethyl ether and dried. The metal was determined by various

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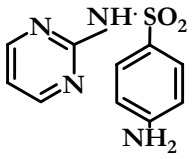

Figure 1: Structure of ligand (Sulphadiazine)

methods[7]. Elemental analyses of the prepared complexes were carried out by lab india and ASCHO lab mumbai; X-ray diffraction(XRD) of the prepared complex was carried out by the inter university consortium(IUC), indore, India. The electronic spectra of solution of the complexes in the water were (Taken at approximate concentration M/500) recorded on chemito-2500 UV/visible spectrophotometer. Electronic spectra were carried out at forensic science laboratory(FSL) sagar, India in the range of 300-900 nm. Thermogravimetric and infrared spectral analyses(FTIR) of synthesized complexes were performed at centre for advanced technology(CAT) indore(M.P.) India, KBr pellets were used in the FTIR spectral analyses. The weight loss was measured from room temperature up to 950^0C at a heating rate of 15^0C per minute.

RESULTS AND DISCUSSION

The analytical and physical data of the prepared complexes are given in TABLE 1. The cobalt(II) and copper(II) complexes found brown and light brown in color respectively molecular formula of the complexes has been worked out on the basis of the above data, to $M(C_{10}H_{10}N_4O_2S)_2VO_3{\cdot}H_2O$[where M=Co(II)/ Cu(II)] Synthesized complexes are insoluble in water

TABLE 1: Analytical and physical data of the complexes

Mol. formula	Observed/calculated %							
	Colour	M.W.	Metal*	VO_3	C	H	N	S
$Co(L)_2VO_3{\cdot}H_2O$	Brown	676.47	8.617 (8.711)	14.852 (14.626)	36.421 (35.478)	3.387 (3.252)	17.012 (16.556)	9.370 (9.460)
$Cu(L)_2VO_3{\cdot}H_2O$	Light brown	681.08	9.681 (9.329)	15.103 (14.526)	32.965 (35.238)	3.850 (3.230)	17.124 (16.444)	9.654 (9.396)

Metal* = Co/Cu, L = $C_{10}H_{10}N_4O_2S$

TABLE 2: Principle IR frequency(in cm^{-1}) and their assignment for its complexes

Drug/Ligand	Co $(C_{10}H_{10}N_{42}S)_2$ $VO_3{\cdot}H_2O$	$Cu(C_{10}H_{10}N_4O_2S)_2$ $VO_3{\cdot}H_2O$	Assignment
3445 sh	3445 br	3444 br	NH_2
3380 s	3356 br	3355 mbr	
2950 s	2937 s	2936 sp	ν C–H of CH_3
2872 s	2873 vs	2872 s	
1670 m	1653 w	1651 sh	C=O
1622 ms	1620 sp	1621 sp	NH_2
1600 s	1594 sp	1594 w	Benzene ring
1472 w	1493 s	1493 w	C–CH_3(asym)
1380 s	1408 sp	1403 w	C–CH_3(sym)
1342 sh	1332 sp	1338 sp	C_6H_4-NH_2
1330 s	1326 s	1326 s	SO_2 N(asym)
1140 s	1157 w	1157 sp	SO_2 N(sym)
1080 s	1093 sp	1092 s	Para substituted benzene ring
1030 s	1020 s	1020 vs	
835 ms	824 s	823 sp	
-	484 vs	483 sp	M–N
-	501 s	503 vs	M–O
-	940 w	943 sh	M–S

br=broad, mbr=medium broad, s=sharp, ms=medium sharp, w=weak, sh=shoulder, vs=very short

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TABLE 3: Thermogravimetic data of complexes

Complex	Total weight loss(%) steps [obs./cal.] with temperature range		Total weight loss(%) [obs./cal.]
	Lattice water Molecule	Ligand molecule	
$Co(L)_2VO_3 \cdot H_2O$	2.702/2.661 [310K-410K]	75.342/74.001 [430K-780K]	78.044/76.662
$Cu(L)_2VO_3 \cdot H_2O$	2.965/2.642 [300K-375K]	75.699/73.500 [440K-950K]	78.804/76.142

$L = C_{10}H_{10}N_4O_2S$

TABLE 4: Crystal parameters and density of the complex

Complexes	Crystal lattice edge (A°)			Cell volume	n	Density obs. Density calc.	Crystal system
	a	b	c	Å³			
$Co(L)_2VO_3 \cdot H_2O$	17.818	17.818	20.727	6580.699	15	2.710 2.307	Tetragonal
$Cu(L)_2VO_3 \cdot H_2O$	18.823	18.823	18.786	6556.665	21	3.592 3.567	Tetragonal

$L = C_{10}H_{10}N_4O_2S$

TABLE 5: X-ray powder diffraction data of $Co(C_{10}H_{10}N_4O_2S)_2VO_3 \cdot H_2O$ complex

Peak No.	d-Spacing	Relative Intensity $I/I_0 \times 100$	Observed $Sin^2\theta$	Calculated $Sin^2\theta$	(h k l)
1	15.41983	100.0	0.00249	0.00249	(1 0 0)
2	12.39073	39.1	0.00387	0.00387	(1 0 1)
3	9.33510	28.3	0.00636	0.00636	(1 1 1)
4	7.39784	30.6	0.01044	0.01134	(2 0 1)
5	6.82594	70.2	0.01342	0.01242	(0 0 3)
6	6.17988	24.4	0.01448	0.01548	(2 0 2)
7	5.31990	38.0	0.02228	0.02238	(2 0 3)
8	4.62926	50.0	0.02705	0.02706	(1 1 4)
9	4.45143	24.4	0.02792	0.02793	(3 0 2)
10	4.12122	54.7	0.03473	0.03483	(3 0 3)
11	3.84618	66.7	0.03985	0.03984	(4 0 0)
12	3.59555	20.9	0.04444	0.04446	(2 0 5)
13	3.40520	35.7	0.05218	0.05217	(1 0 6)
14	3.22569	29.5	0.05695	0.05691	(3 0 5)
15	3.13855	41.9	0.05965	0.05964	(2 0 6)
16	3.02092	38.8	0.06763	0.06762	(0 0 7)
17	2.47292	98.3	0.09810	0.09828	(2 0 8)
18	2.34592	47.5	0.11080	0.11073	(3 0 8)
19	2.06791	69.5	0.13439	0.13419	(3 0 9)

A=0.00249, C=0.00138, a=17.8181Å, c=20.7277Å, Cell volume[V]=6580.6996 Å³, n =15, Density observed=2.7109gm cm^{-3}, Density Calculated=2.5602gm cm^{-3}

and soluble in common organic solvents, indicative of the non-electrolyte nature of these complexes[8].

The magnetic moment of the Co(II) complex is 4.99B.M. The electronic spectra of the Co(II) complex shows three distinct bands appears at 11121cm^{-1}(ν_1), 18263cm^{-1}(ν_2), 25113cm^{-1}(ν_3) which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3) transition respectively . The ligand field parameters Dq(1112.1), B(981.31) and β(0.94) are in good agreement with those for an octahedral geometry of the cobalt(II) complexes[9,10].

The magnetic moment of the Cu(II) complex is 1.9B.M. indicates the presence of one unpaired electron .The electronic spectra of the complex shows

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TABLE 6: X-ray powder diffraction data of $Cu(C_{10}H_{10}N_4O_2S)_2VO_3 \cdot H_2O$ complex

Peak No.	d-Spacing	Relative Intensity $I/I_0 \times 100$	Observed $Sin^2\theta$	Calculated $Sin^2\theta$	(h k l)
1	16.30820	20.6	0.002231	0.002231	(1 0 0)
2	12.30443	23.7	0.003920	0.003920	(1 0 1)
3	9.29549	14.1	0.006240	0.006140	(1 1 1)
4	7.14954	36.1	0.011140	0.011150	(2 1 0)
5	6.80861	29.4	0.014510	0.014520	(2 1 2)
6	6.18137	34.3	0.015110	0.015120	(0 0 3)
7	5.99785	10.5	0.017330	0.017350	(1 0 3)
8	5.31782	14.2	0.019580	0.019590	(1 1 3)
9	4.63322	16.4	0.026280	0.026270	(2 1 3)
10	4.44013	13.4	0.029120	0.029110	(1 0 4)
11	4.22684	100.0	0.032980	0.032960	(2 2 3)
12	4.12409	48.2	0.035680	0.035690	(4 0 0)
13	3.85299	25.6	0.038040	0.038030	(2 1 4)
14	3.78252	8.9	0.042000	0.042000	(0 0 5)
15	3.59791	18.7	0.046480	0.046470	(1 1 5)
16	3.40321	15.6	0.050830	0.050810	(4 0 3)
17	3.22903	16.9	0.053140	0.053040	(4 1 3)
18	3.01501	35.7	0.066470	0.066480	(4 1 4)
19	2.87130	98.2	0.071620	0.071630	(2 1 6)
20	2.69709	30.9	0.082310	0.082320	(0 0 7)
21	2.56340	44.3	0.096180	0.096170	(4 0 6)
22	2.47323	52.3	0.098400	0.098400	(4 1 6)
23	2.37835	33.2	0.102500	0.102400	(3 0 7)
24	2.27122	29.4	0.118110	0.118010	(4 0 7)
25	2.24676	27.1	0.118660	0.118670	(2 1 8)
26	2.06388	38.5	0.136180	0.136080	(0 0 9)
27	1.94595	22.5	0.158380	0.158390	(3 1 9)
28	1.82678	26.3	0.171670	0.171770	(4 0 9)
29	1.78682	33.6	0.185510	0.185610	(3 5 8)
30	1.76841	30.2	0.191950	0.191850	(3 4 9)
31	1.23737	16.4	0.376550	0.376540	(9 9 3)

A=0.002231, C=0.00168, a=18.8239Å, c=18.7860Å, Cell Volume[V]=6556.6655Å^3, n=21, Density Observed=3.592gm cm^{-3}, Density calculated=3.5679gm cm^{-3}

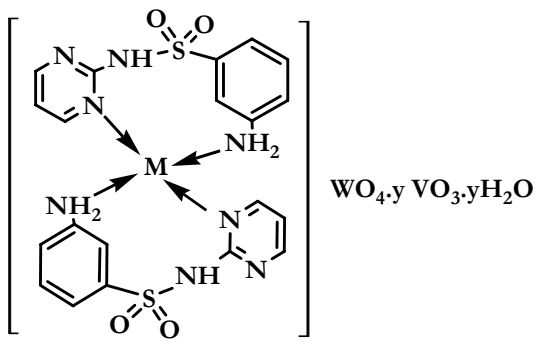

Figure 2: Representative structure of the complexes

one broad band in the region 14688cm^{-1} which may be assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, suggests a square-planar geometry for the complex.

The IR spectra of all complexes under study shows a broad band 3445cm^{-1} and another band between 1670-1600cm^{-1} which may be assigned to asymmetric and symmetric O-H stretching and H-O-H bending modes, respectively, indicating the presence of water of crystallization in the complexes. In the spectra of the complexes of sulphadiazine the bands displayed by the ligand at 1670, 1472 and 1380cm^{-1} assignable to ν(C=O), ν(C-CH_2) (asymmetric) and ν(CH_2) (symmetric) remained unchanged in the complex, ruling out the possibility of involvement of the carboxyl oxygen in the metal binding.

The IR spectrum of sulphadiazine and its analo-

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gous compounds have been characterized[11,12]. The NH_2 group gives two absorption bands in the region 3500-3300cm^{-1}. The first of these bands is due to asymmetric stretching and is usually found near 3500cm^{-1}. In the present case, two bands obtained at 3445cm^{-1} and 3380cm^{-1} for the drug can be assigned to these two vibrations. In the metal complexes, asymmetric and symmetric bands are shifted to lower frequencies by 10-20cm^{-1} and 15-25cm^{-1}, respectively suggesting the involvement of the amino nitrogen in chelation. The involvement of NH_2 is confirmed by the IR data of NH_2 in sulphadiazine observed at 1622cm^{-1}. These are shifted to lower frequencies in the metal complexes due to chelation. An overall range of 3450-3050cm^{-1} has been assigned to the free NH vibration.

The bands displayed by the ligand at 1670, 1472 and 1380cm^{-1} assignable to ν(C=O), C-CH_2 and CH_2 remained almost unchanged in the complexes, ruling out the possibility of involvement of the carbonyl-oxygen in metal binding. In the far-infrared region combined frequencies of two metal nitrogen bands were observed around 480-510cm^{-1}, as shown in TABLE 2.

The thermo gravimetric data shown in TABLE 3 show the decomposition of complexes in two steps. First step weight loss 300-410K that indicates the loss of loosely bound water of crystallization. The second step in the thermogram shows the loss of ligand molecules of the complex. Which occurs between 430-950K. The metal oxides are formed in the both cases.

The X ray diffraction data of the these complexes in TABULATED 4-6 and shows 19 and 31 peaks for Co(II) and Cu(II) respectively clearly indicating the crystalline nature of complexes. The X ray patterns have been indexed by trial and error method[13-15], the unit cell parameters were calculated from indexed data. It is also clear from the data that all prepared complexes possess tetragonal symmetry. The calculated and experimental values of density of the complexes are good agreement within the limits of experimental error. On the basis of above studies figure 2 are suggested for the studied complexes.

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