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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 $\text{Co}(\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S})_2\text{VO}_3 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S})_2\text{VO}_3 \cdot \text{H}_2\text{O}$ 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).

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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 ($\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$) having vanadate (VO_3) anion. The complexes have been synthesized and characterized using analytical and spectral methods.

EXPERIMENTAL

The starting material $\text{MVO}_3 \cdot \text{H}_2\text{O}$ [where $\text{M}=\text{Co(II)}$ 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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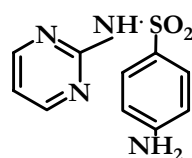


Figure 1: Structure of ligand (Sulphadiazine)

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(F'TIR) 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°C at a heating rate of 15°C 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) ₂ VO ₃ ·H ₂ O | 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) ₂ VO ₃ ·H ₂ O | 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 = C₁₀H₁₀N₄O₂STABLE 2: Principle IR frequency(in cm⁻¹) and their assignment for its complexes

| Drug/Ligand | Co (C ₁₀ H ₁₀ N ₄ S) ₂ VO ₃ ·H ₂ O | Cu(C ₁₀ H ₁₀ N ₄ O ₂ S) ₂ VO ₃ ·H ₂ O | 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 ₆ H 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

TABLE 3: Thermogravimetric 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) ₂ VO ₃ ·H ₂ O | 2.702/2.661 [310K-410K] | 75.342/74.001 [430K-780K] | 78.044/76.662 |
| Cu(L) ₂ VO ₃ ·H ₂ O | 2.965/2.642 [300K-375K] | 75.699/73.500 [440K-950K] | 78.804/76.142 |

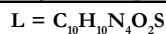
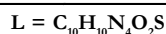


TABLE 4: Crystal parameters and density of the complex

| Complexes | Crystal lattice edge (Å°) | | | Cell volume | n | Density obs. | Crystal system |
|--|---------------------------|--------|--------|----------------|----|----------------|----------------|
| | a | b | c | Å ³ | | Density calc. | |
| Co(L) ₂ VO ₃ ·H ₂ O | 17.818 | 17.818 | 20.727 | 6580.699 | 15 | 2.710 2.307 | Tetragonal |
| Cu(L) ₂ VO ₃ ·H ₂ O | 18.823 | 18.823 | 18.786 | 6556.665 | 21 | 3.592 3.567 | Tetragonal |

TABLE 5: X-ray powder diffraction data of Co(C₁₀H₁₀N₄O₂S)₂VO₃·H₂O complex

| Peak No. | d-Spacing | Relative Intensity I/I ₀ ×100 | Observed Sin ² θ | Calculated Sin ² θ | (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 complexes⁸¹.

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(v₁), 18263cm⁻¹(v₂), 25113cm⁻¹(v₃) which may be assigned to ⁴T_{1g}(F)→⁴T_{2g}(F) (v₁), ⁴T_{1g}(F)→⁴A_{2g}(F) (v₂)

and ⁴T_{1g}(F)→⁴T_{2g}(P) (v₃) 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^{9,101}.

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 $\text{Cu}(\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S})_2\text{VO}_3 \cdot \text{H}_2\text{O}$ complex

| Peak No. | d-Spacing | Relative Intensity $I/I_0 \times 100$ | Observed $\text{Sin}^2\theta$ | Calculated $\text{Sin}^2\theta$ | (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]=6556.6655Å³, n=21, Density Observed=3.592gm cm⁻³, Density calculated=3.5679gm cm⁻³

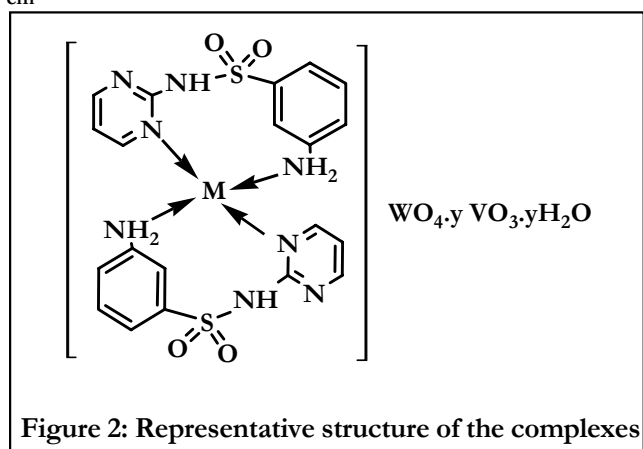


Figure 2: Representative structure of the complexes

one broad band in the region 14688cm^{-1} which may be assigned to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ 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 $1670\text{-}1600\text{cm}^{-1}$ 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 $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{CH}_2)$ (asymmetric) and $\nu(\text{CH}_2)$ (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-

gous compounds have been characterized^[11,12]. The NH₂ 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 NH₂ is confirmed by the IR data of NH₂ 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 $\nu(\text{C}=\text{O})$, C-CH₂ and CH₂ 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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