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# THERMAL BEHAVIOR OF COBALT(II) AND MANGANESE(II) COMPLEXES OF 1-(2′-HYDROXYBENZYL)-2-(2′-HYDROXYPHENYL)-BENZIMIDAZOLE

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The benzimidazole nucleus and its derivatives are known to play crucial parts in the structure and functioning of a number of biologically important molecules, generally by virtue of their being coordinated to metal ions. Thus dimethyl benzimidazole supplies one of the five nitrogen atoms coordinated to Co(III) in vitamin $B_{12}$ and several of its derivatives. Current evidence indicates that the manganese–oxygen evolving system in green plant photosynthesis contains at least some of the metal not as the porphyrin complex but as manganese bound directly to a protein. In general metal ions bind to proteins through functional groups that are substituents on the macropolypeptide backbone [2]. For example, metal ions can interact with the imidazole nitrogen of histidine, the phenolic oxygen of tyrosine, the carboxylic oxygen of glutamic acid, the amine nitrogen of lysine or the imine nitrogen of arginine. Metal–protein binding also involves multidentate coordination to two, three or more of the coordination positions of the metal ion. Good models for protein bound metals would thus be complexes with multidentate ligands with phenolic oxygen and imine-like nitrogen donors, e.g. tetradentate Schiff's base complexes. Only a small number of rather scattered reports of manganese Schiff's base complexes have appeared [3], and very few systems are reported showing the linear relationship between thermal stability of metal chelates and structure of chelating agents have been reported [4]. The thermal properties of metal chelates with various ligands have been studied earlier [5–9]. The chelating ligands in these cases are mostly oximes. In continuation of our earlier work [10], with this ligand, we report herein our studies on the thermal behavior of complexes of Co(II) and Mn(II) with 1-(2′-hydroxybenzyl)-2-(2′-hydroxyphenyl)-benzimidazole (HBHPB).

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## APPARATUS

TGA and DTA were recorded on a ULVAC SINKU RIKUTA-1500 thermal analyser at the Indian Institute of Sciences (IISc), Bangalore, India.

## RESULTS AND DISCUSSION

### *Synthesis and characteristics of the ligand*

HBHPB was prepared according to the procedure described earlier [10], by refluxing 1,2-propylene-diamine with salicylaldehyde (1 : 3) in glacial acetic acid.

The IR spectrum measured in KBr pellets showed a peak at 1480 $cm^{-1}$ assigned to $\nu$(C=N) stretching. A peak at 3500–3700 $cm^{-1}$ corresponding to the free phenolic OH is not observed; instead a peak at 3300 $cm^{-1}$ confirms the intramolecular hydrogen bonding of the two OH groups [11–13].

### *Preparation of solid complexes*

Methanolic solutions of ligand and corresponding metal salts, were refluxed at 70–80 °C for 3 h. The resulting solution was distilled under vacuum until the solid crystallized. The precipitates were filtered off and washed with aqueous methanol. The product was dried in vacuo for 24 h.

### *Physical properties*

All complexes are crystalline powders, freely soluble in MeOH, DMSO and DMF, decomposed only by strong hot perchloric acid.

### *Chemical analysis*

Cobalt and manganese content was determined volumetrically [14]. The percentage of water, anions and ligands were calculated from thermal analysis.

## THERMAL ANALYSIS

The TG data of the complexes of cobalt(II) and manganese(II) are reported in Table 1. The overall mass-loss in air agrees with elemental analysis. The weight loss in all the complexes over the range 60 to 220 °C indicates their anhydrous nature. The complexes containing water of crystallization show a weight loss below 100 °C and complexes containing

TABLE 1

Thermal analysis data

| Complex | % $H_2O$ |  | % Anions |  | % Ligand |  | % Metal |  | $T_a$ | $T_b$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Calc. (Temp. range (°C)) | Found | Calc. (Temp. range (°C)) | Found | Calc. (Temp. range (°C)) | Found | Calc. (Temp. range (°C)) | Found |  |  |  |
| $CoL(NO_3)_2 \cdot 2H_2O$ | 6.70<br>(0–220) | 7.00 | 23.19<br>(220–430) | 23.00 | 59.12<br>(430–500) | 62.00 | 10.94<br>( > 500) | 7.60 | 220 | 500 | 460 |
| $CoL_2Cl_2 \cdot 2H_2O$ | 7.00<br>(0–200) | 6.50 | 25.45<br>(200–460) | 27.00 | – | – | – | – | 200 | – | 490 |
| $CoL_3(OAc)_2 \cdot 4H_2O$ | 6.50<br>(0–160) | 6.00 | 10.01<br>(160–300) | 10.00 | 79.00<br>(300–380) | 79.09 | 4.80<br>( > 380) | 3.60 | 160 | 380 | 330 |
| $CoL(oxal)_2 \cdot 2H_2O$ | 5.43<br>(0–210) | 6.00 | 38.03<br>(210–330) | 37.00 | 47.69<br>(330–540) | 47.00 | 8.33<br>( > 540) | 5.87 | 210 | 540 | 490 |
| $CoLSO_4 \cdot 3H_2O$ | 10.20<br>(0–210) | 10.00 | 18.30<br>(210–310) | 18.00 | 60.24<br>(310–580) | 61.00 | 11.15<br>( > 580) | 9.35 | 210 | 580 | 570 |
| $MnL_2(OAc)_2 \cdot 3H_2O$ | 6.40<br>(0–280) | 6.00 | 14.20<br>(280–420) | 14.00 | 74.90<br>(420–470) | 74.00 | 6.51<br>( > 470) | 4.35 | 280 | 470 | 440 |
| $MnL_2Cl_2 \cdot 4H_2O$ | 8.60<br>(0–170) | 8.00 | 8.44<br>(280–320) | 8.00 | 76.00<br>(320–560) | 75.00 | 6.62<br>( > 560) | – | 280 | 560 | 530 |
| $MnL_2SO_4 \cdot 3H_2O$ | 6.45<br>(0–190) | 7.00 | 23.00<br>(190–300) | 11.47 | 75.51<br>(300–590) | 62.00 | 6.55<br>( > 590) | 5.29 | 190 | 590 | 540 |
| $MnL_2(NO_3)_2 \cdot 4H_2O$ | 8.15<br>(0–260) | 7.00 | 14.04<br>(260–360) | 14.00 | 71.58<br>(360–500) | 70.00 | 6.22<br>( > 500) | 4.39 | 260 | 500 | 480 |

coordinated water show a weight loss above 100 ° C in accordance with the report of Nikalov et al. [15]. The anions in the complexes decomposed in the range 160–460 ° C with maximum decomposition occurring from 300 to 500 ° C and the process is complete around 590 ° C. (The thermal properties of the complexes are presented in Table 1.) Extrapolation of the approximately linear portions of the pyrolysis curves at high and low temperatures (taking the intersection as the decomposition temperature) gives the following thermal stabilities: Co(II) nitrate > Co(II) sulphate = Co(I) oxalate > Co(II) chloride > Co(II) acetate and Mn(II) acetate = Mn(II) chloride > Mn(II) nitrate > Mn(II) sulphate.

### *Residues*

The residues from the thermogravimetric runs of the compounds were weighed and compared to the weight that would be obtained if the residue were a metal oxide. In all cases, the percentage of metal found (experimental) is less than theoretical, whereas the sum percentage of metal and ligand from the thermogram equals the theoretical values. Hece it can be assumed that during the process of decomposition some of the metal volatilises and escapes with the ligand.

## DIFFERENTIAL THERMAL ANALYSIS

The first endotherm and exotherm obtained in all the hydrated compounds below 220 ° C may be associated with loss of water of hydration as born out by the TGA curves. Since no sharp exothermic peaks are observed in the range 300–590 ° C, it can be concluded that reduction of the metal does not take place. The temperature ($T_{max}$) of the decomposition peak maximum was used in determining the relative thermal stability of chelates. These structures have been further confirmed by spectral, magnetic, elemental analysis, and conductance data.

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