

Note

THERMAL BEHAVIOUR OF COPPER(II), IRON(II) AND IRON(III) COMPLEXES OF 1-(2'-HYDROXYBENZYL)-(2'-HYDROXYPHENYL)-BENZIMIDAZOLE

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A series of square planar complexes of copper(II) with hydroxy bridges and octahedral complexes of iron(II) and iron(III) have been synthesized and their thermal and differential thermal behaviour studied. From the thermal and differential thermal analyses, the order of their thermal stability is proposed.

INTRODUCTION

Complex compounds of transition metal ions with imidazole, benzimidazole and their substituted derivatives as ligands have been extensively studied [1–5]. Current interest in the study of complexes of copper(II) with imidazole ligands has emphasized the importance of the bonding between copper and the imidazole from histidine residues of blue copper proteins and non-blue proteins [6–8].

The X-ray structural studies of popular plastocyanine [9] and *pseudomonas aeruginosa* azurin [10] have revealed that imidazoles from the histidine residues of these proteins are involved in the bonding of copper(II) at the active site. It is also known that the imidazole acts as a bridging ligand at the active site of bovine erythrocyte superoxide dismutase which catalyses the conversion of superoxide to peroxide [11,12]. The study of a series of model copper(II) complexes has suggested a distorted square pyramidal configuration at the copper site in galactose oxidase in oxyhaemocyanine with magnetically coupled ion pairs behind to constitute type III copper [13]. Recently many low molecular weight complexes of copper(II) containing imidazole ligand(s) have been proposed as models of the active site of copper proteins [14–16]. There is strong evidence that in proteins containing haem as a prosthetic group e.g. in haemoglobin and cytochrome C, the imidazole nitrogen atom, probably in the histidine residues of proteins, is coordinated to the iron atom. Earlier, Wendlandt et al. [17–20] studied the thermal stability order in Schiff's base complexes. As a continuation of our earlier work with 1-(2'-hydroxybenzyl)-(2'-hydroxyphenyl)-benzimidazole

(HBHPB) [21], we report our investigations on the thermal behaviour of complexes of copper(II), iron(II), iron(III) with HBHPB.

APPARATUS

TG and DTA experiments were carried out on an Ulvac Sinku Rikuta 1500 thermal analyser at the Indian Institute of Sciences, Bangalore, India.

EXPERIMENTAL

Synthesis and characteristics of the ligand

HBHPB was prepared using the procedure described earlier [21] by refluxing 1,2-phenylene diamine with salicylaldehyde (1 : 3) in glacial acetic acid. The presence in the IR spectrum of a peak at 3300 cm^{-1} and the disappearance of the band at $3500\text{--}3700\text{ cm}^{-1}$ due to the free phenolic OH indicate intramolecular hydrogen bonding [22–24].

Preparation of solid complexes

Copper(II) complexes. Copper(II) complexes with various anion combinations (acetate, chloride, nitrate, sulphate) were prepared by refluxing the respective metal salts (0.003 mol) with a hot methanolic solution containing the ligand (0.002 mol). After refluxing for 3 h the contents were concentrated under vacuum and cooled until the solid separates out. The separated solid was collected by filtration and washed with aqueous methanol and water to remove excess ligand and excess metal respectively. The product was dried under vacuum for 24 h.

Iron(II) complexes. These complexes were prepared by treating 0.003 mol of the metal solution (in methanol) with 0.002 mol of ligand solution. Refluxing was continued for 6 h. The solid that separated was washed with aqueous methanol and water and dried under vacuum for 24 h.

Iron(III) complexes. These complexes also were prepared as described above by taking iron(III) salts.

RESULTS AND DISCUSSION

Physical properties

All complexes are crystalline coloured substances except iron(III) chloride and iron(II) chloride complexes which are colourless. The copper(II) acetate

TABLE I

Thermal analysis

Complex	Metal oxide (wt.%)		Water (wt.%)		Anions (wt.%)		Ligand (wt.%)		Initial decomposition temp. (°C)	T_{max} (°C)
	Found (Temp. (°C))	Calc. (Temp. (°C))	Found (Temp. (°C))	Calc. (Temp. (°C))	Found (Temp. (°C))	Calc. (Temp. (°C))	Found (Temp. (°C))	Calc. (Temp. (°C))		
[Cu(OH)(LH ₂ O) ₂ SO ₄ ·H ₂ O	9.00 (Above 540)	16.83	6.00 (0-230)	5.70	19.00 (230-410)	10.20	68.00 (410-540)	67.16	230	440
[CuOHClCl] ₂ ·2H ₂ O	14.00 (Above 340)	17.66	4.00 (0-100)	4.00	12.00 (240-270)	11.66	69.00 (270-340)	70.20	100	320
[Cu(OH)LOAc] ₂ ·2H ₂ O	13.00 (Above 570)	16.00	4.00 (0-210)	3.80	20.00 (210-410)	16.00	64.00 (410-570)	66.70	210	450
[(Cu(OH) ₂ NO ₃] ₂ NO ₃ ·4H ₂ O	5.00 (Above 360)	16.00	7.00 (0-70)	7.28	15.00 (70-340)	15.90	77.00 (340-360)	63.90	200	340
[FeOHL ₃ SO ₄] ₂ ·6H ₂ O	10.00 (Above 470)	13.66	4.00 (0-100)	4.60	9.00 (100-280)	9.60	77.00 (280-470)	81.00	100	430
[FeSO ₄ (H ₂ O) ₂] ₂	10.00 (Above 380)	9.07	4.00 (0-70)	4.30	9.00 (70-330)	11.72	77.00 (330-380)	77.00	70	330
[FeOHL ₂ NO ₃] ₂ ·4H ₂ O	9.00 (Above 390)	9.23	4.00 (0-160)	4.10	11.00 (160-310)	16.31	76.00 (310-390)	73.10	160	550
[FeL ₄ Cl ₂]Cl	6.00 (Above 490)	5.38			6.00 (110-200)	7.48	88.00 (200-490)	88.00	40	450
[FeOHL ₂ (OAc)] ₂ ·4H ₂ O	9.00 (Above 570)	9.26	4.00 (0-180)	4.19	14.00 (180-300)	13.74	73.00 (300-570)	73.61	180	310
[FeL ₄ (OAc) ₂]·2H ₂ O	5.00 (Above 460)	5.39	3.00 (0-200)	2.44	9.00 (200-310)	8.01	86.00 (310-460)	85.81	200	340
[FeL ₄ Cl ₂]·2H ₂ O	6.00 (Above 520)	5.57	3.00 (0-140)	2.52	5.00 (140-340)	4.97	87.00 (340-520)	88.63	140	490
[FeL ₄ (NO ₃) ₂] ₂ ·2H ₂ O	6.00 (Above 490)	5.37	3.00 (0-160)	2.43	8.00 (160-310)	8.38	84.00 (310-490)	85.46	160	510

and nitrate complexes are green, while the sulphate and chloride complexes are red- and black-coloured solids respectively. The remaining iron(II) and iron(III) complexes are brown-coloured compounds. All complexes are insoluble in water but soluble in organic solvents.

Thermal analysis

The thermal behaviour of the complexes is presented in Table 1. The table also shows the temperature regions in which the water of hydration, the anions and the ligands leave the complexes, the initial decomposition temperature and the decomposition peak maximum temperature T_{\max} . All complexes lose their water of hydration below 200°C showing that water molecules in the complexes are absorbed or coordinated. The anhydrous compounds are stable up to 200°C . Afterwards, the anion components and ligands decompose. The anion loss takes place in a single step in all complexes except in the copper nitrate complex where two steps are observed. The first step may be due to the loss of the ionic nitrate group whereas the second step corresponds to the loss of the coordinated group. The decompositions are complete below 600°C and a plateau region is obtained as a result of the conversion of metal into metal oxide. Extrapolation of the fairly linear portions of the pyrolysis curve at high and low temperatures, taking the intersecting point as the decomposition temperature, leads to the following order of thermal stability: chloride > nitrate > sulphate > acetate. In the case of iron complexes the order is acetate > nitrate > chloride > sulphate.

The residues from thermogravimetric runs of the compounds were weighed and compared with the weight that would be obtained if the residue were a metal oxide. In all cases the percentage of metal found experimentally is less than the theoretical value except in the copper(II) chloride complex. The sum of the percentages of metal and ligand from the thermograms agrees with the theoretical value. Thus, it may be concluded that some of the metal oxide escapes together with the ligand during the process of decomposition.

Differential thermal analysis

All exothermic peaks obtained below 200°C may be associated with the loss of water of hydration as borne out by TG curves. Since no sharp peak (exothermic) is observed below 540°C , it can be concluded that the reduction of metal does not take place.

The structures of all the complexes given in Table 1 have been confirmed by spectral, magnetic and conductance studies and by elemental analysis, and correspond to the molecular formulas represented on the basis of thermal analysis.

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