THERMAL BEHAVIOUR OF TRANSITION METAL COMPLEXES OF 4-METHOXYBENZALDEHYDE-4-PHENYL-3-THIOSEMICARBAZONE

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ABSTRACT

Some new transition metal complexes of 4-methoxybenzaldehyde-4-phenyl-3-thiosemi-carbazone (MBPT) have been synthesized and their thermal behaviours have been studied. All complexes except the mercury complex are hydrated crystalline powders decomposed by mineral acids. Copper(II), cobalt(II), nickel(II), palladium(II), gold(III), silver(I) and mercury(II) were estimated by reported methods.

INTRODUCTION

Very few systems are reported in the literature which show the relationship between the thermal stability of metal chelates and the structure of the chelating agents [1]. Wendlandt, Hill and co-workers [2–7] studied the thermal behaviour of metal chelates with various chelating ligands. The chelating ligands used were mostly from the oxime class of compounds. Renewed interest by the present authors in the phenylthiosemicarbazones [8–14] is due to their high stability, ease of extractability and their effective use in chemical separations.

A thorough survey of the literature reveals that no attempt has been made to study the thermal stability of transition metal complexes of thiosemi-carbazones. Hence we report our investigations on the thermal behaviour of complexes of MBPT.

Synthesis and characterization of the ligand

A solution prepared by dissolving 0.835 g of 4-phenyl-3-thiosemicarbazide in 50 ml methanol and 2 ml of glacial acetic acid was added dropwise to a solution of 4-methoxybenzaldehyde (0.68 g) in 50 ml methanol with stirring. A white product formed and quickly separated. It was recrystallized in methanol (m.p. 182–184°C, yield 75%).

Identification of the synthesized MBPT was carried out using the results of elemental analyses and nuclear magnetic resonance spectra. The IR

spectrum taken in potassium bromide pellets showed absorption bands at 1610 and 1540 cm^{-1} corresponding to the stretching vibrations of the azomethine bond ($>$C=N). The peaks at 1070, 1025, 835 and 740 cm^{-1} can be assigned to ν(C=S), and a band corresponding to νNH is observed at 3320 cm^{-1}. The absence of a band due to the SH stretching mode near 2570 cm^{-1} suggests that the molecule remains in thione form in the solid state. The nuclear magnetic resonance spectrum measured in dimethylsulphoxide also showed a peak at 9.8 p.p.m. which is attributed to the –NH group, indicating that the ligand is in thione form. On the basis of these results the structure of MBPT is represented as (%): Calc.: C, 63.08; H, 5.257; S, 11.25; Found: C, 63.38; H, 5.316; S, 11.36.

Synthesis of metal complexes of MBPT

Au(III)–MBPT complex

30 ml of MBPT (1×10^{-2} M) in methanol was added to 30 ml of Au(III) solution (5×10^{-2} M) in methanol, and the mixture was refluxed for about 1 h. A yellow solid separated out which was filtered, washed with water and dried under reduced pressure over P_4O_{10} for 24 h. Yield: 60%.

Rh(III)–MBPT complex

30 ml of MBPT (2×10^{-1} M) in methanol was added to 60 ml of Rh(III) solution (5×10^{-2} M) in methanol and the mixture was refluxed for about half an hour. A red-coloured solid separated out which was filtered, washed with water and dried over P_4O_{10} for 24 h under vacuum. Yield: 60%.

Cu(II)–MBPT complex

40 ml of reagent solution (2×10^{-2} M) in methanol was added dropwise to a hot solution of cupric acetate (2×10^{-2} M) in 50 ml methanol and the mixture was refluxed for 30 min. The resulting solution was concentrated to half its volume. A green solid separated out which was washed with water and dried under reduced pressure for 24 h over P_4O_{10}. Yield: 50%.

Ni(II)–MBPT complex

50 ml of a hot solution of MBPT (1×10^{-2} M) in methanol was added to 50 ml of (1×10^{-2} M) nickel ammonium sulphate solution in methanol and the mixture was refluxed for 30 min. A grey brown product separated out which was filtered, washed with methanol and dried under vacuum for 20 h over P_4O_{10}. Yield: 80%.

Co(II)–APT complex

A hot solution of MBPT (5×10^{-2} M) in 50 ml methanol was added to 50 ml of cobalt nitrate solution (5×10^{-2} M) and the mixture was refluxed for 1 h. The resulting brown solution was concentrated and the brown solid that

separated was filtered, washed with water and dried under vacuum for 24 h over P_4O_{10}. Yield: 80%.

Pt(IV)–MBPT complex

30 ml of Pt(IV) solution (2.5×10^{-3} M) in methanol was added to MBPT solution (1×10^{-2} M) in methanol and the mixture was refluxed for about 1 h. The resulting yellow solid that separated was filtered, washed with water and dried over P_4O_{10} under reduced pressure. Yield: 50%.

Pd(II)–MBPT complex

30 ml of MBPT (1×10^{-2} M) in methanol was added to 30 ml of Pd(II) solution (5.5×10^{-3} M) in methanol and the mixture was refluxed for about 30 min. The yellow solid that separated was filtered off, washed with water and dried over P_4O_{10} for about 24 h. Yield: 75%.

Os(VIII)–MBPT complex

30 ml of MBPT (3×10^{-1} M) in methanol was added to 30 ml of Os(VIII) solution in 50 ml methanol and the mixture was refluxed for 30 min. The resulting solution was concentrated to half its volume. A black solid separated out which was filtered, washed with water and dried under reduced pressure for 24 h over P_4O_{10}. Yield: 60%.

Ru(III)–MBPT complex

25 ml of MBPT (2×10^{-1} M) in methanol was added dropwise to 60 ml of Ru(III) (5×10^{-2} M) solution in methanol and the mixture was refluxed for about 3 h. The resulting brown solution was concentrated to half its volume and filtered. A grey-brown solid separated out which was washed with water and dried over P_4O_{10} under vacuum for 24 h. Yield: 75%.

Ag(I)–MBPT complex

30 ml of MBPT solution (5×10^{-3} M) in methanol was added dropwise to 30 ml of a hot solution of silver nitrate (1×10^{-2} M) in methanol and the mixture was refluxed for 2 h. The resultant solution was concentrated to half its volume. A grey-coloured solid separated out which was filtered, washed with water and dried under reduced pressure over P_4O_{10} for 24 h. Yield: 50%.

Hg(II)–MBPT complex

50 ml of MBPT solution (2×10^{-2} M) in methanol was added dropwise to a hot solution of mercuric chloride (5×10^{-2} M) in methanol and the mixture was refluxed for 30 min. A yellow crystalline solid separated out which was filtered and dried under reduced pressure over P_4O_{10} for 10 h. Yield: 60%.

Apparatus

TG and DTA were recorded on an Ulvac Sinku-Rikuta 1500 thermal analyser at the Indian Institute of Science, Bangalore, India.
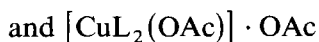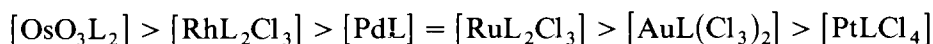
RESULTS AND DISCUSSION

In the present investigations on the thermal behaviour of metal complexes of MBPT it was observed that all complexes except mercury complex are hydrated. The platinum, palladium, cobalt and silver complexes are mono-hydrates and the rhodium, copper and nickel complexes are dihydrated, whereas osmium and ruthenium complexes have four water molecules.

In general, the water of hydration can be considered either as crystal or coordinated water. According to Nikolav et al. [15], water eliminated below 150°C can be considered as crystal water, and that eliminated above 150°C may be due to its coordination to the central metal ion. In the present study the water of hydration was eliminated below 150°C, which suggests that the water of hydration was crystal water. The amount of water found from the weight loss in the thermogram approaches the theoretical value calculated for the mono-, di- and tetrahydrates.

A survey of the literature reveals that the order of decomposition by pyrolysis of the constituents of solid complexes is: water, anion, ligand and final residue, corresponding to either metal oxide or free metal. In the present study rhodium(III), copper(II), silver(I) and mercury(II) follow this order, whereas the order for gold(III), platinum(IV), ruthenium(III), nickel(II) and cobalt(II) is water, ligand, anion and final residue. A plateau in TG corresponding to the decomposition of anions is not observed in the palladium(II) complex, indicating the absence of chloride ions, which is further substantiated by qualitative analyses and the absence of an additional band in the far-IR spectrum that is attributed to the Pd–Cl bond.

Extrapolating the fairly linear portions of the pyrolysis curves at high and low temperatures and taking the intersection as the decomposition temperature leads to the following thermal stability.

$$[OsO_3L_2] > [RhL_2Cl_3] > [PdL] = [RuL_2Cl_3] > [AuL(Cl_3)_2] > [PtLCl_4]$$

and $[CuL_2(OAc)] \cdot OAc$

$$[NiL_2SO_4] > HgL_2Cl_2 > [CoL_2(NO_3)_2] > [AgL(NO_3)]$$

Residues

The ultimate decomposition residues on heating in air were found to correspond to free metal in the case of Au(III), Pd(II), Pt(IV) and Ru(III)

and to MO oxide for Cu(II) and Ni(II). The residue was found to be Rh_2O_3 and Co_3O_4 for Rh(III) and Co(II) complexes, respectively. Osmium volatalizes above 300°C. The residues from the thermogravimetric runs of the compounds were weighed and compared to the theoretical value if the residue was a metal. Good agreement was found.

Metal content

Complexometric titration methods using EDTA [16] were employed for the estimation of copper, cobalt and nickel in the respective solid complexes. Gold and palladium, silver and mercury are determined by volumetric methods [16,17] in the complexes using hydroquinone and dimethylglyoxime [16], respectively. Other metals are determined by pyrolysis of the solid chelate at high temperatures and weighing the residue obtained as free metal.
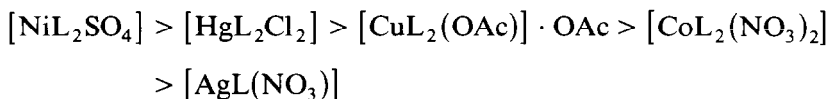
Differential thermal analysis

The first endotherm obtained in all hydrated compounds below 150°C may be associated with the loss of water of hydration as borne out by the TG curve. The broad exothermic peaks observed in the complexes in the range 300–670°C correspond to the loss of ligand and anions. The temperature of the decomposition peak maximum, T_{max}, was used in determining the relative thermal stability of chelates.

The order of thermal stability for the platinum metals is

$$[OsO_3L_2] > [RhL_2Cl_3] > [PdL] > [RuL_2Cl_3] > [AuL(Cl_3)_2] > [PtLCl_4]$$

and that for other normal transition metals is

$$[NiL_2SO_4] > [HgL_2Cl_2] > [CuL_2(OAc)] \cdot OAc > [CoL_2(NO_3)_2]$$
$$> [AgL(NO_3)]$$

A comparison of thermal stabilities from DTA (T_{max}) and TG (procedural decomposition temperature) showed that they are in good agreement with each other.

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