

Metal complexes of isonicotinic acid hydrazide

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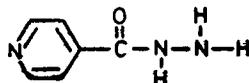
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Abstract. Complexes of platinum(IV), ruthenium(III), rhodium(III), iridium(III), gold(III), dioxouranium(II), zinc(II), cadmium(II), mercury(II) and manganese(II) with isonicotinic acid hydrazide were prepared and characterized on the basis of analytical, conductometric, magnetic susceptibility and spectral data. Platinum(IV) ruthenium(III), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) form six-coordinate complexes while gold(III), zinc(II), cadmium(II) and mercury(II) form four coordinate complexes.

Keywords. Metal complexes ; isonicotinic acid hydrazide ; characterization.

1. Introduction

Metal complexes of isonicotinic acid hydrazide (INH) are of great importance because of their antituberculous properties. The limited information available on the structural aspects of metal-INH complexes prompted the authors to study and report on the complexes of Pt(IV), Ru(III), Rh(III), Ir(III), Au(III), UO_2 (II), Mn(II), Zn(II), Cd(II) and Hg(II) with INH, which has the following structure.



2. Experimental

2.1. Materials

Chlorides of platinum(IV), ruthenium(III), rhodium(III), iridium(III) and gold(III) were obtained from Arora Mathew Limited, Calcutta. Chlorides of zinc(II), cadmium(II), mercury(II) and manganese(II) and uranyl nitrate and INH (Analar BDH) were used as such. Acetone and ethanol were purified by standard methods.

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2.2 Preparation of the complexes

Acetone solution (50 ml of 0.01 M) of the chloride of M [$M = \text{Pt(IV)}$, Ru(III) , Rh(III) , Ir(III) or Au(III)] or 50 ml of 0.01 M ethanolic solution of uranyl nitrate or the chloride of M^1 [$M^1 = \text{Zn(II)}$, Cd(II) , Hg(II) or Mn(II)] was treated with 50 ml of 0.02 M solution of INH in the respective solvent. The complexes of Pt(IV) , Ru(III) , Rh(III) , Ir(III) and Au(III) are precipitated immediately while the complexes of $\text{UO}_2(\text{II})$, Zn(II) , Cd(II) , Hg(II) and Mn(II) get precipitated after heating on a boiling water bath for one hour. The solid complexes were filtered, washed several times with the respective solvent and dried over anhydrous calcium chloride in a desiccator.

2.3. Analytical and physical measurements

Elemental analysis of the complexes was carried out by conventional methods. The Gouy method was used to measure the magnetic susceptibilities at room temperature 27°C . Visible spectra and conductance measurements were recorded on 10^{-4}M solutions of the complexes in dimethylformamide (DMF). Infrared spectra were recorded on KBr discs containing INH and its complexes.

2.4. Results and discussion

All the complexes are stable up to 250°C . Platinum(IV), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) complexes are yellow, gold(III) complex is black, ruthenium(III) complex is brown and zinc(II), cadmium(II) and mercury(II) complexes are white in colour. The complexes are practically insoluble in water. Platinum(IV), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) complexes are slightly soluble in DMF and dimethyl sulfoxide (DMSO), ruthenium(III) and gold(III) complexes are soluble and zinc(II), cadmium(II) and mercury(II) complexes are insoluble in common organic solvents.

Analytical data for the complexes show that the composition of the complexes is $[(\text{INH})_2\text{PtCl}] \text{Cl}_2$; $[(\text{INH})_2\text{MCl}_2] \text{Cl}$ [where $\text{M} = \text{Ru(III)}$, Rh(III) or Ir(III)]; $[(\text{INH})_2\text{UO}_2](\text{NO}_3)_2$; $[(\text{INH})_2\text{MnCl}_2]$; $[(\text{INH})\text{AuCl}_2] \text{Cl}$; and $[(\text{INH})\text{MCl}_2]$ [(where $\text{M} = \text{Zn(II)}$, Cd(II) or Hg(II)].

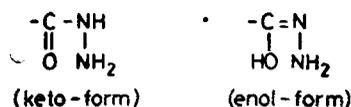
The molar conductance values of platinum(IV), ruthenium(III), rhodium(III), iridium(III), dioxouranium(II) and gold(III) complexes indicate that they are electrolytes in DMF. The electrolytic behaviour of the other complexes could not be studied due to their insolubility in DMF.

The diamagnetism of platinum(IV), rhodium(III), iridium(III) and dioxouranium(II) complexes reflect the favourable octahedral geometry of these complexes. The diamagnetic behaviours of zinc(II), cadmium(II) and mercury(II) complexes point out their preferred tetrahedral geometry. The diamagnetism of gold(III) complex suggests a square planar geometry. The magnetic moment value of 2.2 B.M. observed for the ruthenium(III) complex, though rather high for one unpaired electron, is nevertheless in the right range for octahedral ruthenium(III) complexes for which a considerable orbital contribution is expected (Ruiz-Ramirez and Stephenson 1975). Further, the presence of non-equivalent stoichiometric sites in the complex molecule suggests a slight distortion in the regular octahedral geometry of this complex. Manganese complex forms a high spin complex having

a magnetic moment value of about 5.94 B.M. which suggests an octahedral arrangement of the ligand molecules around the central metal ion.

The visible spectra of platinum(IV), ruthenium(III), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) complexes show charge transfer bands at 380, 385, 360, 375, 365 and 400 nm, respectively. The $d-d$ bands were not observed probably due to their masking by the intense charge-transfer bands. The visible spectra of zinc(II), cadmium(II) and mercury(II) complexes could not be recorded due to their insolubility. Gold(III) complex showed three bands at 600, 520 and 445 nm and these bands have been assigned to $^1A_{1g} \rightarrow ^3A_{2g}$, $^1A_{1g} \rightarrow ^3E_g$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions respectively which are characteristic of square planar gold(III) complexes (Gajendragad and Agarwala 1975).

A shift in the bands at 3430 and 1715 cm^{-1} due to $\nu(\text{NH}_2)$ and $\nu(\text{C}=\text{O})$ respectively in the infrared spectrum of INH by about 90 cm^{-1} in the spectra of its complexes indicates the involvement of the nitrogen atom of the NH_2 group and the oxygen atom of the $\text{C}=\text{O}$ group in coordination (Sahni *et al* 1977). Further, a shift in the $\nu(\text{C}-\text{N})$ band observed at 1490 cm^{-1} in the INH spectrum by about 50 cm^{-1} in the spectra of its complexes indicates the preference of the keto form to the enol form of the ligand for coordination.



Coordination through the oxygen atom of the $\text{C}=\text{O}$ group resulted in a decrease in its double bond character and new bands observed around $1,100\text{ cm}^{-1}$ in the spectra of the complexes are assigned to the $\text{C}=\text{O}$ stretching vibrations. Low frequency bands in the $420\text{--}500\text{ cm}^{-1}$ and $520\text{--}610\text{ cm}^{-1}$ regions in the spectra of the complexes are assigned to the $M-\text{N}$ and $M-\text{O}$ modes respectively (Olliff and Odell 1967, 1967; Olliff and Odell 1968).

A strong band at 920 cm^{-1} and a weak band at 870 cm^{-1} in the UO_2 (II) complex are assigned to the ν_3 asymmetric and ν_1 symmetric stretching frequencies which are characteristic of the uranyl ion (Selbin and Angew 1966). Further, the appearance of ν_1 symmetric stretching frequency indicates that the uranyl ion is almost linear (Sacconi *et al* 1958).

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