

Synthesis and characterization of Ru(III), Rh(III), Pt(IV) and Ir(III) thiosemicarbazone complexes

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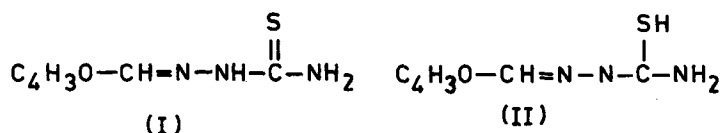
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Abstract. Ru(III), Rh(III), Pt(IV) and Ir(III) complexes of 2-furfural thiosemicarbazone as ligand have been synthesised. These complexes have the composition $[M(\text{ligand})_2X_2]X$ ($M = \text{Ru(III)}$, Rh(III) and Ir(III) , $X = \text{Cl}$ and Br) and $[\text{Pt}(\text{ligand})_2X'_2]X'_2$ ($X' = \text{Cl}$, Br and $1/2\text{SO}_4$). The deprotonated ligand forms the complexes of the formulae $M(\text{ligand-H})_3$ and $\text{Pt}(\text{ligand-H})_3\text{Cl}$. All these complexes have been characterized by elemental analysis, magnetic measurements, electronic and infrared spectral studies. All the complexes are six-coordinate octahedral.

Keywords. 2-Furfural thiosemicarbazone; deprotonated ligand; magnetic moment; reflectance spectra; effective positive charge; infrared spectra.

1. Introduction

Metal complexes of thiosemicarbazones have long been known (Jensen 1934, 1936), but there are very few reports on the platinum metal complexes with such ligands. Platinum metal complexes with thiosemicarbazones show pharmacological activities (Ali and Livingstone 1974). In the present communication, the preparation and characterization of Ru(III), Rh(III), Pt(IV) and Ir(III) complexes of 2-furfural thiosemicarbazone (ligand) are reported. The complexes have been characterized by elemental analysis, magnetic moments, electronic and infrared spectral studies. The ligand acts as a neutral bidentate ligand in its keto form. In solution, the keto and enol forms (I and II) are in equilibrium, the enol form being favoured in alkaline solution (Mukkanti *et al* 1982, 1986; Chandra 1983).



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2. Experimental

Hydrated RuCl_3 , RhCl_3 and IrCl_3 were obtained from Fluka, Switzerland. Hexachloroplatinic acid, H_2PtCl_6 , was used for the preparation of platinum complexes.

2.1 Preparation of the ligand

The ligand was prepared following the method of Sah and Daniels (1950), and recrystallised as a yellow solid from hot ethanol, m.p. 155° (Found: C = 42.57%; H = 4.15%; N = 24.79% and calcd. C = 42.59%; H = 4.17% and N = 24.84%). Yield = 80%.

2.2 Preparation of the chelates

2.2a $[M(\text{ligand})_2X_2]X$ and $[Pt(\text{ligand})_2X'_2]X_2$: (M = Ru(III), Rh(III) & Ir(III); X = Cl or Br and X' = Cl, Br, I or $1/2\text{SO}_4$). These chelates were prepared by mixing ethanolic solutions (0.001 mol in 20–30 ml) of the corresponding metal salt and the ligand in ethanol (0.002 mol in 20–30 ml). The mixtures were refluxed for about an hour in each case. The complex separated out on cooling. The product was filtered, washed with ethanol and dried in vacuum over P_2O_5 .

For the preparation of Ru(III), Rh(III) and Ir(III) chelates, the mixture was acidified with a few drops of the corresponding acid. In the case of platinum chelates, pH was adjusted to nearly 2.0 with the corresponding acid. 0.25 mol of the corresponding potassium salt was also added for preparation of bromide, iodide and sulphate chelates.

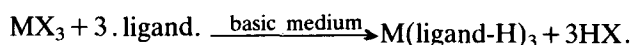
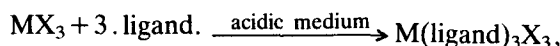
2.2b $M(\text{ligand-H})_3$ and $Pt(\text{ligand-H})_3\text{Cl}$: (M = Ru(III), Rh(III) or Ir(III)): An aqueous solution (20 ml) of metal chloride (0.001 mol) was added to an ethanol solution (30 ml) of ligand (0.003 mol). Aqueous solution of NH_4OH (1.0 M) was added dropwise until the solution was weakly alkaline. The product, which precipitated after refluxing for about an hour, was filtered after cooling. The complex was washed with ethanol and dried in vacuum over P_2O_5 .

2.3 Physical measurements

The room temperature magnetic susceptibility measurements were carried out on a Gouy balance, using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as a calibrant ($X_g = 16.44 \times 10^{-6}$ cgs unit). Infrared spectra of the complexes were recorded on a Perkin-Elmer 621 spectrophotometer in KBr pellets. Electronic spectra (nujol mull) of the complexes were recorded on a DMR-21 automatic recording spectrophotometer. The metal contents in the complexes were determined by methods reported earlier (Mahadevappa *et al* 1976).

3. Results and discussion

The metal salts interact with the ligand according to the following equations:



Analytical data for the complexes are given in table 1. The complexes of Rh(III) and Pt(IV) are diamagnetic as expected. Ru(III) complexes have a magnetic moment in the range of 1.75–1.80 BM at room temperature. This value is slightly lower than the value for the free Ru(III) ion (2.10 BM) (Figgis and Lewis 1960). This may be due to low symmetry ligand fields or extensive electron delocalisation (Livingstone *et al* 1975).

3.1 Reflectance spectra

Electronic spectra (table 2) for all complexes in this study exhibit three bands which can be assigned as follows: for Ru(III) ${}^2T_{2g} \rightarrow {}^4T_{1g}$ (ν_1), ${}^2T_{2g} \rightarrow {}^4T_{2g}$ (ν_2) and ${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{1g}$ (ν_3); for Rh(III), Pt(IV) and Ir(III) ${}^1A_{1g} \rightarrow {}^3T_{1g}$ (ν_1), ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (ν_2) and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (ν_3) (Jørgenson 1964; Lever 1968). The band

Table 1. Elemental analysis and magnetic moment values of the platinum metal complexes

Complex (colour)	Yield (%)	M.P. ^b (°C)	M% Found (Calcd)	C% Found (Calcd)	H% Found (Calcd)	N% Found (Calcd)	S% Found (Calcd)	μ_{eff}
[Ru(ligand) ₂ Cl ₂]Cl (black)	60	250	18.55 (18.52)	26.18 (26.40)	2.43 (2.41)	13.15 (13.34)	11.85 (11.75)	1.75
[Ru(ligand) ₂ Br ₂]Br (black)	55	260	14.99 (14.88)	21.20 (21.22)	2.08 (2.08)	12.42 (12.37)	9.45 (9.44)	1.80
[Ru(ligand-H) ₃] (black)	60	255	16.58 (16.77)	35.84 (35.65)	3.00 (2.99)	20.92 (20.79)	15.99 (15.87)	1.77
[Rh(ligand) ₂ Cl ₂]Cl (orange yellow)	55	240	18.71 (18.79)	26.52 (26.31)	2.57 (2.57)	15.28 (15.34)	11.85 (11.71)	dia
[Rh(ligand) ₂ Br ₂]Br (light brown)	60	250	15.03 (15.11)	21.36 (21.16)	2.06 (2.07)	12.35 (12.34)	9.44 (9.42)	dia
[Rh(ligand-H) ₃] (light yellow)	60	245	16.99 (16.93)	35.64 (35.68)	2.98 (2.98)	20.77 (20.75)	15.85 (15.83)	dia
[Pt(ligand) ₂ Cl ₂]Cl ₂ (orange yellow)	45	265	28.85 (28.89)	21.32 (21.34)	2.10 (2.09)	12.42 (12.44)	9.59 (9.49)	dia
[Pt(ligand) ₂ Br ₂]Br ₂ (light yellow)	45	285	22.89 (22.87)	17.05 (16.89)	1.77 (1.65)	9.87 (9.85)	7.64 (7.52)	dia
[Pt(ligand) ₂ SO ₄]SO ₄ (Greenish yellow)	50	280	26.89 (26.88)	19.74 (19.86)	1.95 (1.94)	11.59 (11.58)	17.84 (17.67)	dia
[Pt(ligand-H) ₃]Cl (light yellow)	60	250	28.01 (27.88)	31.02 (30.89)	2.58 (2.59)	18.04 (18.02)	13.69 (13.75)	dia
[Ir(ligand) ₂ Cl ₂]Cl (light yellow)	40	280	30.18 (30.17)	22.48 (22.63)	2.21 (2.21)	13.25 (13.19)	10.05 (10.07)	dia
[Ir(ligand) ₂ Br ₂]Br (yellowish green)	50	290	25.01 (24.95)	18.78 (18.71)	1.81 (1.83)	10.99 (10.91)	8.38 (8.38)	dia
[Ir(ligand-H) ₃] (light brown)	55	300	27.39 (27.58)	31.22 (31.02)	2.61 (2.60)	18.18 (18.09)	13.89 (13.80)	dia

^bAll the complexes decompose before melting.

Table 2. Electronic spectral data of the platinum metal complexes

Complex	Bands observed (cm ⁻¹)			10 Dq cm ⁻¹	B cm ⁻¹	C cm ⁻¹	β	ν_2/ν_1	Z
	ν_1	ν_2	ν_3						
[Ru(ligand) ₂ Cl ₂]Cl	13,790	17,540	25,000	29210	468.7	3267	0.75	1.27	1.04
Ru(ligand-H) ₃	14,080	17,860	25,640	29960	472.5	3380	0.76	1.27	1.06
[Rh(ligand) ₂ Cl ₂]Cl	14,280	17,540	24,390	20880	428.1	3342	0.59	1.23	0.69
[Pt(ligand) ₂ Cl ₂]Cl ₂	13,900	16,950	23,500	20110	409.4	3162	0.57	1.22	0.61
[Ir(ligand) ₂ Cl ₂]Cl	24,690	28,990	37,730	31140	546.3	2150	0.83	1.17	1.36

Similar values were observed for other related complexes.

positions, ν_1/ν_2 ratios, and ligand field parameters, are all consistent with a six coordination about the metal ions (Bertelli *et al* 1975; Marcotrigiano *et al* 1975; Preti and Tosi 1977; Sengupta *et al* 1980; Sahni *et al* 1978, 1979). The decrease in the values of the Racah interelectronic repulsion parameters (B) from those of the free ions suggests that strong covalent bonding occurs between the ligand and metal ions. Effective positive charge (Z), evaluated by the relation (Jørgenson 1962),

$$B(\text{cm}^{-1}) = 472 + 28q + 50(Z + 1) - 500/(Z + 1),$$

are considerably lower than the formal oxidation states of +3 or +4.

3.2 Infrared spectra

The IR spectra of the ligand have not been reported, but studies on similar compounds are available. The present assignments are based on these studies (Burns 1968; Rana *et al* 1976; Mukkanti *et al* 1986).

Upon complexation, the νNH modes of the ligand at 3430 and 3155 cm⁻¹ move to lower regions in the ionic complex, while a shift towards higher wave numbers is noted in the case of deprotonated species. The band at 1643 cm⁻¹ in thiosemicarbazide (bending mode of NH₂) is absent in the thiosemicarbazone (ligand) due to substitution of the furfural group, C₄H₃O HC=, in place of the two hydrogen atoms of the hydrazinic nitrogen. The band around 1600 cm⁻¹ of the free ligand due to C=N modes shifts to lower frequencies ($\Delta\nu=15-20$ cm⁻¹) in metal complexes, suggesting coordination through hydrazinic nitrogen (Wiles and Suprunchuk 1969).

A band around 840 cm⁻¹ is mainly due to the $\nu\text{C}=\text{S}$ stretching frequency (Mashima 1964). In the i.r. spectra of complexes this band is shifted downwards by ~ 90 cm⁻¹. A strong band at 1090 cm⁻¹ in the ligand spectrum has also some contribution from the $\nu\text{C}=\text{S}$ stretching. This band has a contribution from the N-C-N stretching vibration (Yamaguchi *et al* 1958) or N-N stretching and N-C-N deformation vibrations. The band has shifted to higher positions in the complexes, as also observed in the spectra of some thiosemicarbazones (Campbell *et al* 1976). In conclusion, comparative study of the i.r. spectra of the ligand and its metal chelates indicate that the ligand acts as a bidentate ligand, coordinating through the C=S sulphur and the nitrogen of the hydrazine group.

On the basis of the above studies, a six-coordinate octahedral structure may be assigned to all these complexes (figures 1 and 2). However, in the absence of any

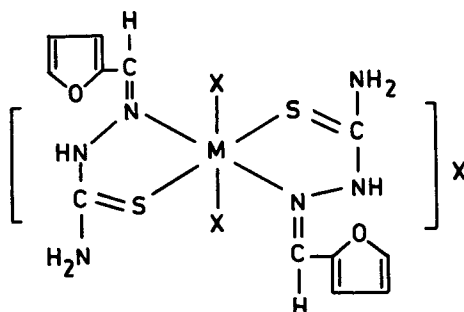


Figure 1. Tentative structure of 1:2 M(III):ligand (keto form).

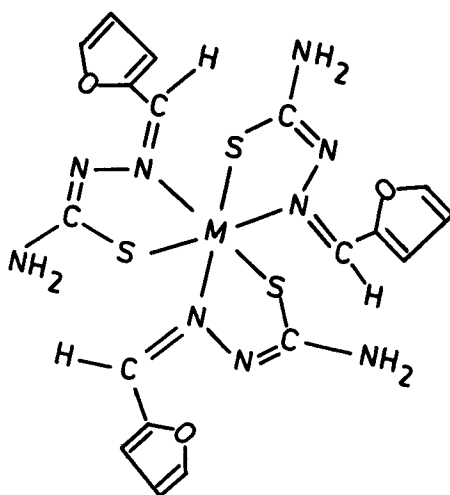


Figure 2. Tentative structure of 1:3 M(III):ligand (enol form).

positive evidence it is not possible to say conclusively whether the complexes have *cis* or *trans* geometry.

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