Complexes of Ru(II), Pd(IV), Rh(III) & Pt(II) with Substituted Thiosemicarbazide & Thiosemicarbazones

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Complexes of Ru(II), Pd(IV), Rh(III) and Pt(II) with 4-nicotinamidothiosemicarbazide (NTSC), 1-(o-methoxyphenyl)-4-benzamidothiosemicarbazide (o-MBTS), 1-(p-methoxyphenyl)-4-benzamidothiosemicarbazide (p-MBTS), 1-(α-furyl)-4-benzamidothiosemicarbazone (FBTS) and 1-phenyl-4-nicotinamidothiosemicarbazone (PNTS) have been prepared. The complexes have been characterised on the basis of analytical, infrared and electronic spectral and magnetic susceptibility data. The Ru(II), Pd(IV), Rh(III) complexes have pseudoctahedral stereochemistry while Pt(II) complexes are square-planar. Various ligand field parameters of classical and Normalised Spherical Harmonic Hamiltonian have been calculated which support the assigned stereochemistries.

IN recent years a large number of transition metal complexes of thiosemicarbazides, thiosemicarbazones and other sulphur-nitrogen containing ligands have been studied. A few platinum metal complexes of such ligands have also been reported. These studies appear to be useful in view of the reported anti-cancer activity of platinum metal salts used were procured from M/s Johnson-Matthey, London. The ligands were synthesised by the methods described earlier.

Preparation of the complexes: [Ru(MBTS)2Cl2] and [Ru(FBTS)2Cl2] — [RuCl4]2− was prepared by a method suggested by Rose and Wilkinson. The deep-blue ethanolic solution of [RuCl4]2− was treated with the appropriate ligand also dissolved in ethanol. The deep-green mixture so obtained was refluxed in a water-bath for 2 hr and left overnight. Dark-green crystals obtained were recrystallised from ethanol.

[Rh(MBTS)2Cl2] Cl2, [Rh(FBTS)2Cl2]Cl and [Rh(NTSC)2Cl2]Cl — Rhodium chloride (5 mmole) dissolved in ethanol was mixed with ethanolic solution of the ligand (10 mmole). The mixture was refluxed for 3 hr and subsequently concentrated when an orange mass separated. The complexes were dried in vacuo. The corresponding bromo compounds, [Rh(MBTS)2 Br2] Br and [Rh(FBTS)2 Br2] Br, were prepared in a similar manner.

Materials and Methods

All the chemicals used were of analytical grade. The platinum metal salts used were procured from M/s Johnson-Matthey, London. The ligands were synthesised by the methods described earlier.

Preparation of the complexes: [Ru(MBTS)2Cl2] and [Ru(FBTS)2Cl2] — [RuCl4]2− was prepared by a method suggested by Rose and Wilkinson. The deep-blue ethanolic solution of [RuCl4]2− was treated with the appropriate ligand also dissolved in ethanol. The deep-green mixture so obtained was refluxed on a water-bath for 2 hr and left overnight. Dark-green crystals obtained were recrystallised from ethanol.

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Results and Discussion

The elemental analyses (Table 1) reveal 1:2 (metal-ligand) stoichiometry for Ru(II), Rh(III) and Pd(IV) complexes and 1:1 for Pt(II) complexes. The complexes do not melt up to 250° and are sparingly soluble in common organic solvents. The molar conductance measurements in nitrobenzene and dimethylformamide indicate that Pt(II) and Ru(II) complexes are non-electrolytes, while Rh(III) and Pd(IV) complexes behave as 1:1 and 1:2 electrolytes, respectively.

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Accordingly, the complexes may be formulated as PtLX₂, RuL₂X₂, RhL₂X₂ X and PdL₂X₂ X₂, where L = any of the ligands and X = Cl or Br.

**Infrared spectra** — The assignments of infrared spectral bands are based on earlier studies²⁻¹₉⁻¹₃. The bands in the regions 3000–3300 and 1620–1625 cm⁻¹ in the spectra of the ligands are assigned to vNH and vC= N vibrations, respectively. The vNH and vC= N bands are lowered by c. 100 and c. 15 cm⁻¹ in the spectra of complexes thereby indicating the coordination of the terminal hydrazinic and azomethine nitrogen atoms⁴,⁵, respectively. In the far IR region, the bands appearing around 290–375 cm⁻¹. The bands observed in the ligands around 1455, 1290, 1025 and 730 cm⁻¹ are assigned to the transition ³A₁→³T₂, which is expected to the transition ³A₁→³T₂ in octahedral complexes of Ru(II). This may be due to the lowering of symmetry from Od to D₆h which is expected with the donor set N₅SₓXₜ. Accordingly, the first two bands can be assigned to the transitions ³A₁→³T₂, which like that in the related cobalt (III) complexes (d⁶ system), remains unsplit. The splitting (~ 6000 cm⁻¹) of ³A₁→³T₂ band suggests that these complexes have cis configuration¹⁸.

**Magnetic moments and electronic spectra** — All these complexes are diamagnetic. The Ru(II) complexes show bands in the regions 17500–18000, 23600–24700 and 25500–26000 cm⁻¹. The positions of these bands are not consistent with the regular octahedral stereochemistry of the complexes. The bands in the regions 17500-18000 and 23600-24700 cm⁻¹ appear to be split components of one band which occurs around 22000 cm⁻¹ and is assigned to the transition ³A₁→³T₂ in octahedral complexes of Ru(II). This may be due to the lowering of symmetry from Od to D₆h which is expected with the donor set N₅SₓXₜ. Accordingly, the first two bands can be assigned to the transitions ³A₁→³T₂, which like that in the related cobalt (III) complexes (d⁶ system), remains unsplit. The splitting (~ 6000 cm⁻¹) of ³A₁→³T₂ band suggests that these complexes have cis configuration. The electronic spectra can be rationalised further in terms of the ligand field parameters (Dq⁹, Dq* and Dr) which have been evaluated (Table 1). The value of
Ds, another radial ligand field parameter, could not be evaluated due to unsplit nature of $^1A_g \rightarrow ^1T_g$ band. It may be pointed out that the value of Dt does not include the off diagonal fourth order contribution and the classical Dq value, factorised into $D_{qy}$ and $D_{qz}$, measures the in-plane and out-of-plane ligand field strengths only. Lever et al. have recently advanced the theory of Normalised Spherical Harmonic (NSH) Hamiltonian to overcome these drawbacks of the classical ligand field theory.

The values of NSH parameters Dq, and Dt have also been evaluated (Table 2). The ratio $D_t/D_q$, which is a useful measure of the degree of tetragonal distortion is in the range 0.14-0.16. The values obtained are small compared to the limiting value (0.42) of square-planar complex, an extreme case of tetragonal distortion.

Rh(III) and Pd(IV) complexes show bands in the regions 15500-17200 and 20300-23200 cm$^{-1}$. The first two bands appear to be the split components of the transition $^4A_g \rightarrow ^4T_{2g}$ expected in octahedral complexes. Like Ru(II) complexes, the Rh(III) and Pd(IV) complexes also appear to have effective $D_{qy}$ symmetry and hence the first two bands may be assigned to the transitions $^4A_g \rightarrow ^4T_{2g}$ and $^4A_g \rightarrow ^4T_{2g}$ in the increasing order of energy. The third band appearing around 25000 is assigned to the transition $^4A_g \rightarrow ^4T_{2g}$ in both Rh(III) and Pd(IV) complexes. The various ligand field parameters of classical and NSH Hamiltonian theories have been evaluated by assuming $D_{qy}$ symmetry. The degree of distortion ($D_t/D_q$), lying in the range 0.14-0.18, is comparatively small and indicates that the complexes are slightly distorted.

In addition to three $d-d$-bands, the complexes show more bands around 30,000 and 32,000 cm$^{-1}$ which can be assigned to $\pi \rightarrow \pi^*$ ($C-\pi$) and $\pi \rightarrow \pi^*$ ($C = N$) transitions of the ligands.

The electronic spectra of Pt(II) complexes show bands in the regions 18000-18000, 20500-21800, 25500-25700, 28000-28800, 30700-31000 and 32500-33000 cm$^{-1}$. The first three bands are assigned to the transitions $^4A_g \rightarrow ^4A_g$, $^4A_g \rightarrow ^4T_{2g}$ and $^4A_g \rightarrow ^4T_{2g}$ in order of increasing energy. The bands occurring at 30700 and 32500 cm$^{-1}$ are attributable to $\pi \rightarrow \pi^*$ ($C = S$) and $\pi \rightarrow \pi^*$ ($C = N$) transitions of the ligands. The values of various single electron parameters $\Delta_1$, $\Delta_2$ and $\Delta_3$ have been calculated (Table 2) and their values are comparable to these observed for other platinum complexes involving similar donor atoms.

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### References