

A high-spin iodo-arsine ruthenium(III) complex

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Abstract. A metathetical reaction conducted between $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ and a large excess of NH_4I afforded a high-spin pentacoordinate complex, $\text{RuI}_3(\text{AsPh}_3)_2$ (high-spin/paramagnetic/triphenylarsine/iodide/ruthenium(III) complex).

Keywords.

1. Introduction

The synthesis of several ruthenium(II) and (III) complexes involving monoteriary phosphines and arsines under a variety of reaction conditions were reported from our laboratory over the last few years (Taqui Khan and Veera Reddy 1981, 1982, 1983). As part of a general synthetic programme and in an attempt to prepare the iodo analogue of Wilkinson's complex, $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ (Stephenson and Wilkinson 1966), we report here the synthesis and characterisation of a new high-spin complex of the composition $\text{RuI}_3(\text{AsPh}_3)_2$.

2. Experimental

Preparation of the complex: The complex $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ (0.20 gm, 0.23 mM) was dissolved in benzene and refluxed with a methanolic solution of NH_4I (0.34 gm, 2.3 mM) for three hours in an atmosphere of nitrogen. The solution was cooled to room temperature. The dark green powder obtained was filtered and washed with 1:1 methanol-water till it gave no test for Cl^- or I^- and finally washed with methanol. The product was recrystallised from dichloromethane-*n*-hexane solvent system and dried *in vacuo*. Yield: 0.20 gm (80%). Analysis (%), Found: C 38.6; H 2.8; I 33.3. Calcd: C 39.5; H 2.7; I 34.8. The complex decomposes above 182°C.

The molecular weight of the complex was measured in chloroform as reported earlier (Taqui Khan and Veera Reddy 1983) and was found to be 960 as against the calculated value of 1094. Magnetic susceptibility of the complex was measured with the solid sample on a Faraday balance at room temperature and the μ_{eff} was found to be 5.12 B.M. The conductivity of the complex in Dimethylacetamide (DMA) indicates that it is a non-electrolyte ($\lambda_{\infty} = 21.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$).

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3. Discussion

The elemental analysis, in conjunction with the conductivity value of the complex, confirms the presence of three iodides in the coordination sphere of the metal ion. Molecular weight measurements on this complex suggest that it is a monomeric pentacoordinate complex. The far-infrared spectrum tentatively supports the formulation of this complex as axially symmetric with three iodides in the trigonal base and the two arsines in the axial positions. Thus a single intense band at 476 cm^{-1} due to ν (Ru-As) and two weak bands at 188 and 208 cm^{-1} due to ν (Ru-I) are in conformity with the proposed structure for the complex. This is also in accord with the observations made earlier on similar complexes, RuCl_3L_2 ($\text{L} = \text{AsPh}_3$, Manoharan *et al* 1973, $\text{AsTol}_3^{\text{para}}$ Taqui Khan and Veera Reddy 1983). The assignment of trigonal bipyramidal geometry is rare for a d^5 configuration, since such geometries occur mostly in d^0 , d^8 and d^{10} configurations. However, some five coordinate metal complexes having trigonal bipyramidal structure with d^5 configuration have been reported in the last decade (Manoharan *et al* 1973; Ruiz-Ramfrez *et al* 1973).

The complex shows paramagnetism corresponding to a spin-free d^5 configuration ($\mu_{\text{eff}} = 5.12$ B.M.). The magnetic moment observed is slightly less than that expected for five unpaired electrons ($\mu_{\text{eff}} = 5.92$ B.M.) and this lowering may be expected due to the strong-field interaction caused by the coordination of triphenylarsine ligands. Iodide is a weak-field ligand lying to the extreme left of the spectrochemical series and thus favouring the formation of high-spin complexes. Despite the strong-field nature of triphenylarsine, which is a good π -acid, the larger size of iodide makes it difficult for the arsine groups to come close enough to the metal ion, and probably forces the arsine ligands to lie at much longer axial distances than expected from the covalent radii. This is a unique observation because $4d$ and $5d$ transition elements form spin-paired complexes even with weak-field ligands. Since iodo complexes are very unstable, not much is known about the behaviour of $4d$ or $5d$ metal ions in the presence of iodide groups.

On the basis of the magnetic moment of the complex and assuming the complex to be in trigonal bipyramidal (D_{3h}) geometry with spin-free d^5 configuration, the ordering of one-electron levels may be written as: $e''(xz, yz) < a'_1(z^2) < e'(x^2 - y^2, xy)$. The ground state configuration, $(e'')^2 (a'_1)^1 (e')^2$ leads to the ground state energy level A'_1 (Muetterties and Schunn 1966). The electronic transitions based on excited state configurations (quartets and doublets) will be all spin-forbidden. The electronic transitions observed at 800 nm ($\epsilon = 510$), 660 nm ($\epsilon = 864$), 380 nm ($\epsilon = 3014$) and 330 nm ($\epsilon = 4360$) may be, therefore, all charge-transfer bands or the low-intensity $d-d$ bands overlapped with charge-transfer bands.

References

- Manoharan P T, Mehrotra P K, Taqui Khan M M and Andar R K 1973 *Inorg. Chem.* **12** 2753
Muetterties E L and Schunn R A 1966 *Quart. Rev.* **20** 245
Ruiz-Ramfrez L, Stephenson T A and Switkes E S 1973 *J. Chem. Soc. Dalton Trans* 1770 (and references therein)
Stephenson T A and Wilkinson G 1966 *J. Inorg. Nucl. Chem.* **28** 945
Taqi Khan M M and Veera Reddy K 1981 *J. Coord. Chem.* **11** 199
Taqi Khan M M and Veera Reddy K 1982 *J. Coord. Chem.* **12** 71
Taqi Khan M M and Veera Reddy K 1983 *Inorg. Chim. Acta* **73** 269