Dichloro(diphenylarsino)ruthenium(III) & Its Reactions with Some Nitrogen Donors

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Preparation and characterization of dichloro(diphenylarsino)ruthenium(III), [RuCl₂As(C₆H₅)₂]
and its reactions with various nitrogen donors have been studied. Probable structures have been proposed on the basis of analytical, spectral (IR and visible) and magnetic susceptibility data.

Many binuclear transition metal complexes with carbon, sulphur and halogen bridges are known. However, comparatively less work has been done on the complexes containing phosphorus and arsenic as bridging atoms. Hayter has reported the reactions of a number of diphenylphosphines [R₂P] and diphenylarsines [R₂As] with ruthenium(III) to give R₂M. The M-M bond of the ligand cleaved to give R₂M radical which could act as bridging group in linking two metal atoms. Chatt and Thornton have also reported the reactions of a number of diphosphines [R₂P], tetraphenyldiarsine was prepared as described in literature.

In this paper we report the preparation, properties and characterization of dichloro(diphenylarsino) ruthenium(III), [RuCl₂As(C₆H₅)₂] and its reactions with ligands containing nitrogen donor atoms.

Materials and Methods

The chemicals used were of AR or CP grade. Tetraphenyldiarsine was prepared as described in literature.

(i) Dichloro(diphenylarsino)ruthenium(III), [RuCl₂As(C₆H₅)₂] - To a solution of 0.1 g (0.25 mmole) of [RuCl₂As(C₆H₅)₂] in 10 ml of o-chloroaniline gave a reddish brown compound [Found: C, 55.04; H, 5.02; N, 8.73; Cl, 11.6%.]

(ii) Dichlorodiphenylarsino-ruthenium(II), [Ru₂Cl₂As(C₆H₅)₂(C₁₀H₈N₂)] - To a solution of 0.25 g (1.6 mmole) of 2,2'-bipyridyl in 10 ml of benzene, 0.1 g (0.25 mmole) of [RuCl₂As(C₆H₅)₂] was added. The mixture was refluxed for 4 hr when a dark-brown compound separated out. It was centrifuged, washed successively with benzene and ether and dried in vacuo [Found: C, 46.8; H, 3.1; N, 7.0; Cl, 7.8%;].

(iii) Dichlorotetrakis(2-methoxyaniline)ruthenium(II), [RuCl₂As(C₆H₅NCl)₄] - To a solution of 0.1 g (0.25 mmole) of [RuCl₂As(C₆H₅NCl)] in 10 ml of benzene was added, 0.1 g (0.25 mmole) of [RuCl₂As(C₆H₅NCl)] was added. The mixture was refluxed for 4 hr when a dark-brown compound separated out. It was washed repeatedly with benzene and ether and dried in vacuo [Found: C, 47.5; H, 3.0; N, 3.0; Cl, 7.8%;].

(iv) Dichlorodiphenylarsino(o-phenanthroline)diruthenium(II), [Ru₂Cl₂As(C₆H₅NCl)₂(C₁₀H₈N₂)] - To a solution of 0.1 g (1.6 mmole) of o-phenanthroline in 10 ml of benzene was added, 0.1 g (0.25 mmole) of [Ru₂Cl₂As(C₆H₅N₂)] was added. The mixture was refluxed for 4 hr when a dark-brown compound separated out. It was washed repeatedly with benzene and ether and dried in vacuo [Found: C, 46.8; H, 3.1; N, 3.0; Cl, 8.2; Ru₂Cl₂As(C₆H₅N₂)₂(N₂H₅Cl₄) requires: C, 41.5; H, 3.27; N, 5.47%.]

(v) Dichlorobis(diphenylarsino)(o-phenanthroline)dichlorobis(diphenylarsino)(o-phenanthroline)dichlorobis(diphenylarsino)(o-phenanthroline)dichlorobis(diphenylarsino)(o-phenanthroline)dichlorobis(diphenylarsino)(o-phenanthroline)diruthenium(II), [Ru₂Cl₂As(C₆H₅NCl)₂(C₁₀H₈N₂)] - To a solution of 0.1 g (1.6 mmole) of o-phenanthroline in 10 ml of benzene was added, 0.1 g (0.25 mmole) of [Ru₂Cl₂As(C₆H₅N₂)] was added. The mixture was refluxed for 4 hr when a dark-brown compound separated out. It was washed repeatedly with benzene and ether and dried in vacuo [Found: C, 47.5; H, 3.0; N, 3.0; Cl, 7.8%;].

(vi) Dichloro(diphenylarsino)tetras[(2-chloroaniline)][RuCl₂As(C₆H₅NCl)₄] - To a solution of 0.1 g (1.6 mmole) of 2-chloroaniline gave a blue compound [Found: C, 51.6; H, 5.63; N, 9.36; Cl, 12.9%. RuCl₂As(C₆H₅ON₄) requires: C, 50.6; H, 5.41; N, 8.73; Cl, 11.6%.]

(vii) Heptachlorodiphenylarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)dodeca(1-acetonitrile)tetraphenyldiarsino)
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H, 4-39; N, 12-36; Cl, 18-53. RuCl₂(As(C₆H₅)₂)(CH₂CN)₂ requires: C, 31-2; H, 3-5; N, 12-17; Cl, 18-53%)

Results and Discussion

[Ru₂As(C₆H₅)₂Cl₄] — The magnetic moment of the complex determined by the Gouy method was found to be 1-73 BM which corresponds to one unpaired electron. For octahedral complexes of Ru(III) with 1T₂g ground state, the value of the magnetic moment should be around 1-0 BM. The lower experimental value may be due to the departure from the O₃ symmetry, so that the ground state is either A, B or E instead of T thus quenching the orbital contribution to the magnetic moment leading to the spin-only value. However, the value of the magnetic moment indicates that oxidation state of ruthenium in the complex is +3, and the symmetry of the ligand around ruthenium ion is distorted octahedral.

The ground state of the spin-paired Ru(III) complex is 1T₂g and the first excited doublet levels are 3A₂g and 1T₂g (ref. 9). The energy gap between the ground and the first excited state, 3A₂g, is 10 Dq = -2F₁ = -20F₁ which in the electronic spectrum of the complex (null) a moderately weak band appears at 20000 cm⁻¹ which may be assigned to the transition 1T₂g → 3A₂g (Table I). Assuming F₁ = 10F₁ = 1000 cm⁻¹ one gets the value of Dq to be equal to 2500 cm⁻¹ which agrees with those found for other octahedral Ru(III) complexes.

Except for three new bands at 280, 300 and 350 cm⁻¹ in the IR spectrum (KBri) of the complex rest of the IR bands appear at the similar positions as in the free ligand. The new bands have been assigned to bridging υ Ru-Cl and υ Ru-As modes of vibrations. These may not be due to pure stretching vibration of any one particular bond but may arise from the normal coordinates having contributions from υRu-Cl and υ Ru-As modes of vibrations.

Thus, from the above studies it appears that the symmetry of the ligand around metal ion is distorted octahedral and Ru(III) is linked with Cl and As in agreement with the general tendency of Ru(III) to form low-spin octahedral complexes with π-donor acids and σ-donor ligands. The octahedral symmetry of the ligand around Ru(III) requires both chloride ion and As(C₆H₅)₂ to act as bridging ligands forming three-dimensional polymer. The complete insolubility of the complex in water and most of the non-coordinating organic solvents further suggests its polymeric nature.

Other complexes — In order to get more evidence regarding the polymeric nature of [Ru₂As(C₆H₅)₂Cl₄], its reactions with a number of coordinating organic solvents and with other σ-donor ligands in non-coordinating solvents have been carried out under refluxing conditions, so that the bridges may be completely or partially cleaved to form either a six-coordinated monomer or a partial polymer. As a result of these reactions, Ru(III) gets reduced to Ru(II) but complete demetallization of the complex does not take place in any of the reactions except in the case of reactions with o-methoxyanilines and quinoline. It is also to be noted that both the halide and the arsenic ligands are removed simultaneously and, therefore, in all the new complexes except that formed with o-methoxyaniline and quinoline, both halide ion and arsenic ligand are present.

The reduction of Ru(III) to Ru(II) is not unusual because the Ru(II) complexes may be easily prepared from the reactions of unsaturated amines and Ru(III) without recourse to reducing agents, due to the stabilization of Ru(II) by unsaturated amines.

All the complexes are found to be diamagnetic which corroborates oxidation state +2 for ruthenium and further suggests that the arrangement of the ligand molecules around ruthenium is octahedral.

The ground state of Ru(II) in octahedral geometry is 1A₁g. The other four excited states in order of their increasing energies are 1T₁g, 3T₁g, 3T₂g, 1T₂g and 1A₂g. Accordingly four bands (two spin-allowed and two spin-forbidden) can be expected corresponding to the transitions 1A₁g → 1T₁g, 1A₁g → 3T₁g, 1A₁g → 3T₂g and 1A₁g → 1A₂g. Bands corresponding to charge-transfer from ligand to metal (L → M) do not appear in the visible region in the case low spin d⁶ systems11,12. However, complexes of ruthenium(II) with unsaturated amines exhibit intense charge-transfer (metal to ligand) bands in the visible region14. These intense charge-transfer bands might mask the usual weak d-d bands.

In the electronic spectra of these complexes a few weak to moderately intense bands appear in the visible region (Table I). In the absence of the extinction coefficient values it is very difficult to assign these bands as due to d-d transition. These may arise due to metal-ligand charge-transfer.

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<th>Table 1 — Electronic Spectral Bands with Their Assignments</th>
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<tr>
<td>Compound</td>
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<tr>
<td>RuCl₂(As(C₆H₅)₂)(Py)₂</td>
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<tr>
<td>RuCl₂(As(C₆H₅)₂)(Py)₂</td>
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The assignments are also suggested by the shifts of the position of 20000 cm\(^{-1}\) band towards higher wavenumber side with the increase in the conjugation of the ligand. However, the relative values of the absorption of the different bands in the complex indicate that these bands arise possibly, both due to charge-transfer band as well as due to \(d-d\) transition. The positions of the bands due to \(d-d\) transition shown in Table 1 indicate the octahedral geometry of the complexes\(^2\).

The IR spectra (KBr) of all the complexes show bands due to tetraphenyldiarsine, amines and other ligands with slight shifts in the band positions in the spectra of complexes as compared to their positions in free ligands or the solvents. This indicates the interaction of the metal ion with tetraphenyldiarsine, ligands and/or amines in the complexes.

Thus, it can be concluded from the above studies that the structure of the complex \([\text{RuAs}(_6\text{H}_5)_2\text{Cl}_2]\) is distorted octahedral and it is polymeric in nature.

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References