[Complexes of Adenosine Triphosphate with Ru(II), Ru(III), Rh(III) & Ir(III)]

BADAR T. KHAN, M. R. SOMAYAJULU & M. TAQUI KHAN*
Department of Chemistry, Nizam College, Hyderabad 500001

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The preparation of the first series of solid metal complexes of adenosine triphosphate (H₃ATP) having the general molecular formula [M(H₃ATP)(H₂O)₆]Cl₂, where M = Ru(III), Rh(III) and Ir(III) complexes with ATP and their characterization based on elemental analysis, IR, conductivity and TGA data. The site of coordination seems to be N-7 of purine moiety as already reported in literature.

**Materials and Methods**

Chromatographically pure sample of ATP was supplied by Sigma Chemicals Company, USA. Pure samples of metal chlorides were obtained from Alpha-Ventran, USA. Hexammineruthenium(II) chloride and chloropentamminerhodium(III) chloride were prepared by literature methods. IR and NMR spectra were taken on Perkin-Elmer 577, and NMR A-60, respectively. TGA was carried out on Perkin-Elmer thermogravimetric analyser. Spectrophotometric estimation of ionic chloride was carried out on Perkin-Elmer UV spectrophotometer. Elemental analysis was performed at CSIRO, Australia.

**Tetraaquoadenosinetriphosphaterhodium(III) chloride**

[Rh(H₃ATP)(H₂O)₆]Cl₂ (2): ATP (0.5 g) was dissolved in acidified aq. methanol (5 ml) and to this was added a solution of rhodium trichloride (0.263 g) in methanol-water (1:1). The resultant solution was continuously stirred at room temperature for 60 hr. A precipitate was formed gradually during the course of stirring. The contents of the flask were kept in a refrigerator overnight. The crystalline substance formed was filtered and washed with dry ether and stored at 0°C over silica gel. The complex is soluble in water, m.p. > 300°C. The equivalent conductivity of the complex in water at 30°C is 252 mhos cm⁻² (yield 0.250 g) (Found: C: 15.35; H: 2.64; N: 8.92; Cl: 9.83. Calc: C: 15.96; H: 3.06; N: 9.31; Cl: 9.44%). Percentage of weight loss at 150°C = 9.44% corresponds to 3-94 water molecules.

**Tetraaquoadenosinetriphosphatertiranium(III) chloride**

[Tr(H₃ATP)(H₂O)₂]Cl₂ (3): ATP (0.3 g) was dissolved in acidified aq. methanol (2:1) and to this was added a solution of iridium trichloride (0.150 g) in aq. methanol (8 ml). The resultant solution became turbid and was stirred at room temperature for 50 hr and thereafter kept in a refrigerator overnight. The crystalline substance formed was filtered and washed with ice-cold methanol and dry ether successively. The complex is soluble in water, m.p. > 10°C. The equivalent conductivity of the complex in water at 30°C is 242 mhos cm⁻² (yield 0.150 g). (Found: C: 14.50; H: 2.70; N: 8.01; Cl: 8.14. Calc: C: 14.26; H: 2.73; N: 8.32; Cl: 8.44%). Percentage of weight loss at 150°C = 9.02% corresponding to 4-21 water molecules.

**Pentaammoniadinosinetriphosphatodichlororuthenium(II) trihydrate**

[Ru(H₃ATP)(NH₃)₅Cl₂·3H₂O] (4): ATP (0.506 g) was dissolved in acidified aq. methanol (5 ml) and to this was added a solution of ruthenium dichloride (0.265 g) in aq. methanol (5 ml). The resultant dark red solution was stirred at room temperature for 68 hr and was kept in a refrigerator overnight. The crystalline solid obtained was filtered and washed with dry ether and stored at 0°C over silica gel. The complex is soluble in water, m.p. = 240-42°C. The equivalent conductivity of the complex in water at 30°C is 256 mhos cm⁻² (yield ~ 0.300 g) (Found: C: 15.76; H: 3.11; N: 8.98; Cl: 9.64. Calc: C: 16.02; H: 3.06; N: 9.33; Cl: 9.46). Percentage weight loss at 150°C = 10.17 corresponded to 4-23 water moles. The complex is paramagnetic with \( \mu_{eff} = 1.45 \) B.M. indicating one unpaired electron.

*Part of the work presented at the XVII ICCC, Hamburg, W. Germany (1976).*
tance was formed. The gummy substance on scratching for 1-1.5 hr gave a crystalline material which was filtered, washed with dry ether and kept over silica gel at 0°. The complex is hygroscopic and soluble in water, m.p. 63-66°. The equivalent conductivity of the complex in water at 30° is 380 mohs cm² mol⁻¹ (yield 0.350 g). (Found: C, 13.26; H, 4.47; N, 16.71; Cl 8.91. Calc.: C, 14.6; H, 4.50; N, 17.11; Cl, 8.68%). Percentage weight loss at 110° = 7.05 corresponding to 3-20 water molecules. The complex is diamagnetic.

**Pentammineadenosinetriphosphatorhodium(III) chloride** [Rh(H₂ATP)(NH₃)₅][Cl₃] (5) — ATP (0.6 g) was dissolved in water (5 ml) and to this was added a solution of chloropentamminerhodium(III) chloride (0.150 g) dissolved in boiling water (10 ml) after cooling to room temperature. The resultant light yellow solution was stirred for 50 hr at room temperature continuously and kept in a refrigerator overnight. To this solution, methanol-ether (1:1) was added and again kept in a refrigerator for two days when a gummy material separated out. The gummy material was treated with acetone, scratched for 1 to 1.5 hr when a crystalline substance precipitated out. It was kept in a refrigerator for 4 hr, filtered, washed with acetone and dry ether and was kept over silica gel at 0°. The complex is soluble in water, m.p. 59-60°. The equivalent conductivity of the complex in water at 30° is 464 mhos cm⁻² (yield ~0.100 g). (Found: C, 15.88; H, 3.82; N, 16.82; Cl, 12.46. Calc.: C, 15.07; H, 3.89; N, 17.54; Cl, 12.74%).

**Results and Discussion**

Direct estimation of ionic chloride in complexes (1-3) by spectrophotometric technique¹⁰ indicate that all chloride is ionic in nature. Conductivity data indicate that complexes (1-3) are 2:1 electrolytes and complexes (4) and (5) are 2:1 and 3:1 electrolytes, respectively. Estimation of lattice water and coordinated water was carried out by thermogravimetric analysis. In the case of complex (4) all the water is lost at a lower temperature 110° as compared to complexes (1-3) where water is lost at 150°, indicating that water is present in complex (4) as lattice water. Complex (4) is quite stable in solution in regards to the exchange of neutral H₂ATP by H₂O. There was no interaction with N₂ indicating that Ru(II) ATP complex (4) is quite stable.

The IR data of tetraaqo-ATP (1-3) and pentammine-ATP (4,5) complexes indicate the absence of metal halogen frequency in the usual range of 250-400 cm⁻¹. The ligational peak of ATP are present in all these complexes. The binding sites in ATP are N(3), N(7) and 6-NH₂ of the purine moiety and the phosphate chain on the riboside. Quantum mechanical calculations by Pullman and Pullman²¹ and the work on complexes of adenosine³⁴ indicate that N(7) is the most basic site in the purine residue followed by N(3). Infrared data of ATP complexes gives the C=O and C=N stretching modes in the region 1400-1600 cm⁻¹. The shift is about 30-40 cm⁻¹. The N-H mode is not at all affected by complexation. The IR data thus supports coordination by ring nitrogen N(7) or N(3) to the metal ion. The assignment of phosphate modes in IR becomes difficult because of the extensive hydrogen bonding in the range of 3000-3500 cm⁻¹. The P-O stretching modes around 1100 cm⁻¹ in complex (3) is slightly shifted indicating a weak coordination of phosphate group in the complex.

In order to decide the binding site N(7) or N(3) in the purine ring NMR technique was used. Equilibration of the complexes with D₂O for 1 hr, exchange the sugar OH, PO₄ and NH₂ protons with D, leaving the complicated pattern of peaks between 6 and 7.5 ppm for HD or PO₄ protons, the aromatic Hₘ and Hₗ protons appear as singlets at 8.3 and 8.5 ppm, respectively. There is not much change in the peaks due to Hₗ proton on complexation of ATP with metal ion but the peaks due to Hₘ proton is shifted downfield to the extent of 0.6 ppm indicating N(7) as the coordination site in ATP complexes.³⁴ Thus in aquo complexes (1-3) ATP acts as a bidentate ligand coordinating through N(7) and one of the phosphate oxygen, and in the pentammine complexes as a monodentate ligand coordinating through N(7). Though there are many donor oxygen atoms on the phosphate chain, the soft platinum group metal ions are preferentially coordinated to the purine N(7), except for aquo complexes where a weak coordination through phosphate is also possible. This behaviour is different from the 3d transition metal ions which preferentially bind to phosphate groups.

**References**