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Synthesis of *trans*-Dichlorobis(ethylenediamine)-osmium(III) Chloride

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While investigating the properties of an unusual H_2O-stable osmium hydride,[2] *cis*-$[Os(en)_2H_2]^{2+}$, the authors have synthesized *trans*-$[Os(en)_2Cl_2]\cdot H_2O$ and the analogous bromide complex. The methods of preparation and characterization are the subject of this communication.

Preparative procedure

The complex ion $[Os(en)_2Cl_2]^+$ was prepared by air oxidation of the species $[Os(en)_2H_2]^{2+}$ in 3*M* aqueous hydrochloric acid according to the following procedure. A 0.49 g sample of the salt $[Os(en)_2O_2]Cl_2$[2] was reduced with amalgamated mossy zinc in 20 ml 1*M* HCl while bubbling with purified N_2. After one hour the resulting solution of dihydrido complex was introduced by syringe transfer into a fritted 20 mm column containing *ca.* 20 ml of deoxygenated Dowex 50-X2 cation exchange resin, under N_2. The column was charged with the hydrido ion and subsequently washed with 100 ml deaerated 0.75 *M* HCl to remove zinc ion. The yellow osmium complex was then eluted with *ca.* 50 ml 3*M* deoxygenated HCl. After exposure of the solution to the air for twelve hours with stirring, it was stored for two days at 5 °C and then evaporated *in vacuo* at 35 °C to approximately 5 ml volume. At this point a yellow, microcrystalline precipitate appeared. On cooling to ice-bath temperature and treatment with ethanol–ether 0.31 g (58% yield) of the crude product was isolated. This material was recrystallized by dissolution in a minimum amount (*ca.* 0.5 ml) of hot (80 °C) 1*M* HCl and cooling slowly to 0 °C. *Anal.* Calc'd. for $[Os(en)_2Cl_2]Cl\cdot H_2O$: C, 11.05; N, 12.89; H, 4.14; Cl, 24.46. Found: C, 10.95; N, 13.15; H, 3.95; Cl, 24.47.[3]

A similar procedure starting with 0.46 g $[Os(en)_2O_2]Cl_2$ but subsequently washing and eluting the hydrido complex with 100 ml 0.75 *M* HBr and 100 ml 1.5 *M* HBr yielded 0.36 g of the orange salt $[Os(en)_2Br_2]Br\cdot H_2O$. *Anal.* Calc'd: C, 8.46; N, 9.86; H, 3.19; Br, 42.2. Found: C, 8.36; N, 10.11; H, 3.09; Br, 41.9.

Magnetic susceptibilities of the complexes were measured in aqueous solution by the nmr method.[4] The chloride and the bromide complex were found to be paramagnetic, with $\mu = 1.91$ and 1.95 ± 0.15 B.M., respectively, at *ca.* 40 °C. Small corrections for ligand diamagnetism were applied in obtaining these values.

Conductivity Measurements

The specific molar conductances found for the species $[Os(en)_2Cl_2]Cl\cdot H_2O$ and $[Os(en)_2Br_2]Br\cdot H_2O$ (10^{-3} *M*) in aqueous solution were 103 and 106 ohm^{-1} cm^2 mol^{-1}, respectively. This indication that the osmium(III) salts are 1:1 electrolytes was confirmed by conductometric titrations with silver nitrate showing that 0.97 ± 0.03 and 0.98 mol respectively, of free, titrable halide ion per mol of osmium are generated immediately upon dissolution of the chloride and bromide salts.

Infrared and Raman Spectra

The IR spectrum of $[Os(en)_2Cl_2]Cl\cdot H_2O$ in the 400 - 1300 cm^{-1} range appears in Figure 1. Important regions of the spectrum are those between 1120 and 1150 cm^{-1} and between 850 - 900 cm^{-1}. For bis(ethylenediamine)cobalt(III) complexes the existence of two bands in the former region was shown by Chamberlain and Bailar[5,6] to indicate a *cis*-configuration while a single band was correlated with *trans*-geometry. Baldwin[7] found that a single absorption in the 850 - 900 cm^{-1} range is indicative of the *trans*-arrangement. Also, Hughes and McWhinnie[8] observed for a number of bis(ethylenediamine) complexes that no *trans*-isomer had more than three bands in the 455 - 620 cm^{-1} region while all complexes of *cis*-geometry investigated by those authors exhibited at least four bands in the same region. Each of these criteria supports the identification of a *trans*-structure for the complex whose IR spectrum is given in Figure 1.

More evidence for *trans*-geometry was provided by a He–Ne laser Raman spectrum of the salt in the 500 -

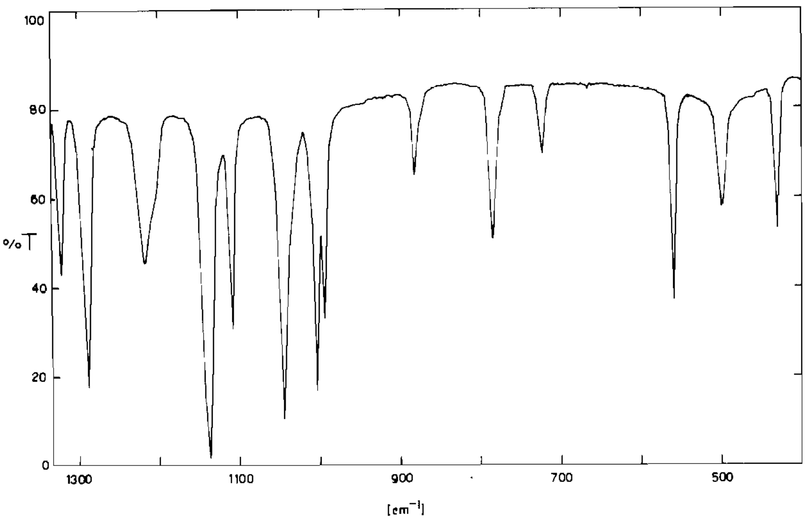

Figure 1. Infrared spectrum of $[Os(en)_2Cl_2]Cl \cdot H_2O$ in the region 400 - 1350 cm^{-1} (KBr Pellet).

800 cm^{-1} range showing absorption bands at 451, 535, 705, 755 cm^{-1}. Since some of the infrared and Raman active modes in this region are expected to involve metal–ligand stretching vibrations, it is significant that no infrared absorption coincided with a Raman band. An inversion center, which would not be present in the *cis*-configuration, is indicated.

In spite of repeated attempts, definitive infrared and Raman spectra of the species $[Os(en)_2Br_2]Br \cdot H_2O$ were not obtained. However, both the method of preparation of this complex and its aqueous ultraviolet spectrum suggest *trans*-geometry. Moreover, a partially resolved crystal structure indicates a Br–Os–Br angle of *ca.* 179°.[9]

Ultraviolet Spectra

In the ultraviolet region, each of the complexes in solution shows an intense absorption band appearing at 283 nm ($\epsilon = 4.53 \times 10^3$ M^{-1} cm^{-1}) for the dichloro species and at 330 nm ($\epsilon = 4.94 \times 10^3$) for the dibromo complex. These ligand-to-metal charge-transfer bands closely resemble the major absorptions seen in *trans*-$[Os(NH_3)_4X_2]^+$ complexes,[10] for which λ_{max} is 271 or 317 nm, respectively, when $X = Cl^-$ or Br^-. Verdonck and Vanquickenborne[11] have given theoretical justification for the occurrence of two intense charge-transfer bands in the *cis*-dihalotetraamines and only one such band in the *trans*-species.

It is interesting that the preparation described herein involves a dihydrido osmium(IV) species which is oxidized by air to give a dihalo complex of osmium (III). Since this requires a transfer of three electrons, a multistep oxidation by O_2 is implicated.

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