[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, NORTHWESTERN UNIVERSITY AND UNIVERSITY OF SYDNEY]

Osmium Complexes with Ethylenediamine

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Ammonium hexabromoösmate(IV) reacted exothermally with anhydrous ethylenediamine with the formation of a 6-covalent Os(IV) complex containing three molecules of ethylenediamine, from which two protons had been lost. This substance behaved as a weak monoacid base, could be reduced to the trisethylenediamine–Os(III) salt, and added a fourth molecule of ethylenediamine to yield an 8-covalent Os(IV) complex. In the latter substance with d^4sp^3 bonds, there should be two promoted electrons, and this is supported by the ease of oxidation to the corresponding 8-covalent Os(V) and Os(VI) compounds.[1]

When anhydrous ethylenediamine was added to solid ammonium hexabromoösmate(IV), a very violent reaction occurred and a green vitreous residue of uncertain composition remained. The same substance was formed when ethylenediamine vapor and ammonium bromoösmate were heated at 250° or when hexammine–osmium(III) bromide and the base were heated at 90°. However, finely powdered dry bromoösmate added slowly to anhydrous ethylenediamine at 10° reacted smoothly and a pink crystalline substance I separated.

Although elementary analysis and the electrical conductivity indicated that I contained three molecules of ethylenediamine and two ionized atoms of bromine for each atom of osmium and thus could be formulated as $[\mathrm{Os\ en_3}]\mathrm{Br_2}$ the lack of reducing properties was inconsistent with an osmium(II) complex. Hexammine–osmium(III) salts,[2] for instance, rapidly reduced silver salts to the metal and the Os(II) ammines can be expected to be very powerful reducing agents. The substance I behaved as a weak monoacid base, $pK = 8.2$, accepting one proton, and only one, in strongly acid solution. The color changed from pink to green and a green substance II could be isolated. This substance, for which the analysis indicated an additional bromine atom, was also devoid of reducing properties and hence could not be trisethylenediamine–osmium(III) bromide. This latter substance III was prepared by the reduction of either I or II in aqueous solution with sodium hydrosulfite and isolated as the yellow iodides $[\mathrm{Os\ en_3}]\mathrm{I_3}$. It reduced silver nitrate to the metal and its paramagnetism (1.6–1.7 B.M.) is consistent with tervalent osmium.

It was concluded that the pink and green compounds I and II are Os(IV) complexes, the quadrivalency of the metal being maintained by the loss of protons from the nitrogen atoms. If (en-H) is taken to represent an ethylenediamine molecule which has lost one proton we may represent I as $[\mathrm{Os(en\text{-}H)_2en}]\mathrm{Br_2}$ and II as $[\mathrm{Os(en\text{-}H)en_2}]\mathrm{Br_3}$. A similar situation was noted by Block and Bailar[3] with the ethylenediamine complex of gold(III).

The electronegativity of osmium is quite large for a metal[4] and it may be supposed that with the hypothetical parent substance $[\mathrm{Os\ en_3}]^{4+}$ such a large fractional positive charge is carried by hydrogen atoms attached to the nitrogen atoms that it acts as a strong acid with respect to the loss of one proton and a weak acid with respect to the loss of the second.

$$[\mathrm{Os(en)_3}]^{4+} \longrightarrow \underset{\text{Green II}}{[\mathrm{Os(en\text{-}H)en_2}]^{3+}} \rightleftarrows \underset{\text{Pink I}}{[\mathrm{Os(en\text{-}H)_2en}]^{2+}}$$

In 2 N acid there was no evidence for the transformation of either I or II into $[\mathrm{Os\ en_3}]^{4+}$ nor in caustic soda solution for the existence of the ion $[\mathrm{Os(en\text{-}H)_3en}]^{+}$ or the non-electrolyte $[\mathrm{Os(en\text{-}H)_4}]^{\circ}$.

The pink and green compounds are both only slightly paramagnetic (0.4 B.M.), though octahedral osmium(IV) complexes should have a moment of 2.83 B.M. corresponding to two unpaired electrons. This is not unique, however, since the moment of the magnetically dilute ammonium bromoosmate was found[5] to be 1.49 B.M., a value confirmed[6] by recent work on its temperature independent susceptibility.

Dissolution of I preferably as the iodide in hot anhydrous ethylenediamine in the absence of oxygen gave a deep green solution from which a green solid IV could be isolated. Although never obtained pure, IV contained apparently four molecules of ethylenediamine and could be formulated as $[\mathrm{Os(en\text{-}H)_2en_2}]\mathrm{Br_2}$. If we assume that a d orbital can be made available for further bonding in I, by pairing all of the eight d electrons, the addition of the fourth molecule of ethylenediamine as a monodentate ligand is easily understood, but I did not react with ammonia gas under seven atmospheres pressure at temperatures from 25–150°. At higher temperatures (200–250°), ethylenediamine was partly displaced and a dark colored mixture of products resulted. The Os:N ratio, however, was not greater than 1:6. It must be concluded that the ethylenediamine in IV is attached as a bidentate ligand to account for the stability and hence that the substance is an 8-covalent Os(IV) complex, with probably d^4sp^3 bonds. In order to accommodate the sixteen bonding electrons it is necessary to promote two to an upper s or d orbital. The promotional energy necessary is readily available in structures involving the higher covalencies of an element where the "normal" bonds are strong, since it can be distributed over a large number of bonds. It can be inferred that the "normal" Os–N bond is weakened as a result but not so seriously as to make the structure unstable. The promoted electrons are probably in the 7s orbital, where they would be

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(1) F. P. Dwyer and J. W. Hogarth, THIS JOURNAL, **75**, 1008 (1953).

(2) F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. N. S. W.*, **85**, 113 (1951).

(3) B. P. Block and J. C. Bailar, THIS JOURNAL, **73**, 4722 (1951).

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945.

(5) D. P. Mellor, *J. Proc. Roy. Soc. N. S. W.*, **17**, 143 (1943).

(6) R. B. Johannesen and A. R. Lindberg, THIS JOURNAL, **76**, 5349 (1954).

paired, rather than in the 6d, since IV is diamagnetic.

As anticipated, the promoted electrons are easily removed, and IV oxidized spontaneously in the air, the color changing to brown. Two substances, V and VI, were obtained by fractional precipitation of the methanol solution with ether. The least soluble substance V was paramagnetic (1.6–1.8 B.M.), and hence still had one promoted electron. The analysis was consistent with the formulation $[Os(en\text{-}H)_3en]I_2$ indicating a pentavalent osmium complex—the first described.

The substance VI, which could also be obtained by the oxidation of V, was diamagnetic, as required for an 8-covalent osmium(VI) complex. The analysis indicated the formula $[Os(en\text{-}H)_4]I_2$. Direct analysis for C and H in osmium compounds does not seem possible owing to the volatility and ease of reduction of osmium tetroxide, hence the loss of protons can only be inferred from the valence requirement of the metal. Although the colors of dilute solutions of V and VI darkened on the addition of strong acids, *p*H titration studies in the range of *p*H 1–6 did not reveal the acceptance of protons necessary for the formation of substances $[Os(en\text{-}H)_2en_2]I_3$ or $[Os(en\text{-}H)_2en_2]I_3$. At various times, substances were obtained from methanolic solutions of V and VI after treatment with hydriodic acid, containing much enhanced proportions of iodide ion. Presumably V and VI are such weak bases that the salts are very easily hydrolyzed.

The potentials of the Os(IV)/Os(V) and Os(V)/Os(VI) couples have not been determined in acid or alkaline solution, but the behavior of osmium tetroxide with hydrobromic acid, which carries the reduction from Os(VIII) to Os(IV), would indicate values of about one volt negative. Qualitative experiments suggest that the $[Os(en\text{-}H)_3en]^{++}/[Os(en\text{-}H)_4]^{++}$ couple is close to the Fe^{++}/Fe^{+++} couple, *i.e.*, about −0.7 v. The Os(V) and Os(VI) complexes are excellent examples of valence stabilization. The latter complex, with $d^4\ sp^3$ bonding has the s, p and d orbitals completely filled. It is not attacked by concentrated hydrochloric acid or caustic alkali and sodium hydrosulfite carries the reduction to Os(V) but no further. With 2,2′-bipyridine and 1,10-phenanthroline similar stabilization of the bivalent state occurs,[7] the d, s and p orbitals being completely filled again.

Attempts to resolve the octahedral compounds, I, II and III, were fruitless. No separation of the enantiomers, for instance, was observed with the trisethylenediamine osmium(III) ion operating with the chloride/*d*-tartrate or the α, nitrocamphor salts. These resolving agents have been used successfully for the Co(III), Cr(III), Rh(III), Ir(III) and Pt(IV) compounds.

The stereochemistry of the stable 8-covalent compounds V and VI and the preparation of the analogous Ru compounds are under investigation.

Experimental

Bis-(β-aminoethylamido)-ethylenediamine-osmium(IV) Bromide, $[Os(en\text{-}H)_2en]Br_2$.—Dry, finely powdered ammonium hexabromoösmate (IV) (2 g.) was added in small portions over five minutes to anhydrous ethylenediamine (5 ml.) at 8–10°. The addition of each portion was attended with a hissing sound and the solid dissolved to a cherry red solution. Between additions, the mixture was shaken, and any lumps broken up with a glass rod. Larger amounts of material were reacted under an atmosphere of nitrogen in a vessel fitted with a rapidly moving stirrer. Finally, the mixture was heated to 40–50° for 3–4 minutes and then cooled to 10°. The pink crystalline precipitate was filtered through a sintered glass filter, washed with a little absolute alcohol, and recrystallized several times by dissolution in a very small amount of water and precipitated by the addition of absolute alcohol containing 20% ether. It was difficult to remove ethylenediamine hydrobromide formed in the reaction. The yield was 40–50%, the loss being due to formation of the green $[Os(en\text{-}H)_2en_2]Br_2$ and its oxidation to the brown Os(V) and Os(VI) compounds, as well as the high solubility of the compound itself.

The substance crystallized in pink micaceous plates and leaflets, easily soluble in water and methanol, sparingly soluble in ethanol. The aqueous solution reacted alkaline to litmus. By titration with 0.1 *N* hydrobromic acid the substance behaved as a weak monoacid base, and from the *p*H of solutions containing equal concentrations of base and salt, $K = 6 \times 10^{-9}$.

Anal. Calcd. for $C_6H_{22}N_6Br_2OS$: Os, 36.01; N, 15.91; Br, 30.3. Found: Os, 35.9; N, 15.9; Br, 30.5.

Bis-(β-aminoethylamido)-ethylenediamine-osmium(IV) Iodide, $[Os(en\text{-}H)_2en]I_2$.—This, the most convenient starting material for other preparations is easily obtainable by double decomposition between aqueous solutions of the *crude* bromide and sodium iodide. After crystallization from hot water it gave pink plates. The molar conductance in 10^{-3} *M* solution was 290 ohms^{-1}.

Anal. Calcd. for $C_6H_{22}N_6I_2Os$: Os, 30.56; N, 13.52; I, 40.87. Found: Os, 30.3; N, 13.5, 13.62; I, 41.0.

β-Aminoethylamido-bis-ethylenediamine-osmium(IV) Bromide Trihydrate, $[Os(en\text{-}H)en_2]Br_3 \cdot 3H_2O$.—A solution of the pink bromide (0.5 g.) in water (15 ml.), was treated with 5 *N* hydrobromic acid (1 ml.). The green precipitate was crystallized from hot water by adding hydrobromic acid and gave green needles. These dissolved in water to a pale green solution which soon became pink. The molar conductivities of 450 and 520 ohms^{-1} in 2×10^{-3} and 10^{-3} *M* solution are much too high for a ter-univalent electrolyte but are consistent with the extensive hydrolysis.

Anal. Calcd. for $C_6H_{29}O_3N_6Br_3Os$: Os, 28.69; N, 12.68; Br, 36.20. Found: Os, 28.9; N, 12.50, 12.68; Br, 36.3.

β-Aminoethylamido-bis-ethylenediamine-osmium(IV) Iodide, $[Os(en\text{-}H)en_2]I_3$.—This compound was prepared by the addition of hydrochloric acid and sodium iodide to a solution of the pink bromide. The brown plates gave a pale green solution in water, subsequently becoming pink.

Anal. Calcd. for $C_6H_{23}N_6I_3Os$: N, 11.20; I, 50.81. Found: N, 11.3; I, 50.84.

Tris-ethylenediamine-osmium(III) Iodide Trihydrate, $[Os\ en_3]I_3 \cdot 2H_2O$.—The pink iodide above (1 g.) was suspended in warm water (10 ml.) and sodium hydrosulfite (1 g.) added. The solid rapidly dissolved to a pale yellow solution which then became deep green. Addition of solid sodium iodide (3 g.) gave a bright yellow precipitate, which was crystallized from hot water by the addition of sodium iodide. The yellow plates of the substance were washed with alcohol. The filtrate remaining after the removal of the yellow precipitate was usually blue in color, but efforts to isolate the substance responsible were fruitless.

Tris-ethylenediamine-osmium(III) iodide gave a colorless solution in water, reduced silver nitrate solution immediately to the metal, and absorbed oxygen, becoming brown. In alkaline solution, very rapid absorption of oxygen occurred with the separation of the pink Os (IV) compound. The substance was paramagnetic (1.5–1.6 B.M.).

In the presence of chloride or bromide ions, crystals with mixed anions such as $[Os(en)_3]ICl_2$ were very easily obtained.

Anal. Calcd. for $C_6H_{28}O_2N_6I_3Os$: Os, 24.20; N, 10.69; I, 48.46. Found: Os, 24.3; N, 10.8; I, 48.5.

Tris-ethylenediamine-osmium(III) Chloride Trihydrate, $[Os\ en_3]Cl_3 \cdot 3H_2O$.—The iodide above was ground up with wet, freshly prepared silver chloride until the initial brown color changed to yellow. A few milliliters of water were added and, after filtering, the colorless solution was treated

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[7] W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 959 (1954).

with two drops of concentrated hydrochloric acid and twenty volumes of acetone. The fine white needles were very soluble in water.

Anal. Calcd. for $C_6H_{30}O_3N_6Cl_3Os$: N, 15.82; Cl, 20.16; Os, 35.8. Found: N, 16.0; Cl, 20.1; Os, 35.7.

Bis-(β-aminoethylamido)-bisethylenediamine-osmium(IV) Iodide, $[Os(en\text{-}H)_2en_2]I_2$.—The pink iodide $[Os(en\text{-}H)_2en]I_2$ above (1 g.) in a small tube containing anhydrous ethylenediamine (1 ml.), was placed under partial vacuum (5 mm.) until about half the base had boiled away. The tube was then sealed under vacuum and heated in a boiling water-bath for an hour, when the pink solid had dissolved to an intense green solution. This solidified on cooling. The original mixture, before heating, was slightly paramagnetic due to the small moment of the pink substance (0.4–0.5 B.M.) but after heating was diamagnetic. The contents of the tube were washed out with oxygen-free absolute alcohol. With protracted washing a pink tint could be detected in the product. This could be due either to incompleteness of the reaction or subsequent dissociation. The analyses showed an Os–N ratio of between 8.7 and 7.6, and attempts to isolate a pure product were fruitless. The substance dissolved in air-free water to a green solution, which instantly turned brown with oxygen.

Anal. Calcd. for $C_8H_{29}N_8I_2Os$: N, 16.44; Os, 27.92. Found: N, 16.4, 15.4; Os, 26.5, 27.2; whence N:Os = 8.7:1 and 7.6:1.

Tris-(β-aminoethylamido)-ethylenediamine-osmium(V) Iodide Tetrahydrate, $[Os(en\text{-}H)_3en]I_2 \cdot 4H_2O$.—The iodide $[Os(en\text{-}H)_2en]I_2$ above (2 g.), with anhydrous ethylenediamine (5 ml.) was heated at 90–100° while a slow current of dry, CO_2-free air was passed through for 20 hours. At the end of this time most of the ethylenediamine had evaporated leaving a brown resinous material, which was dissolved in 50 ml. of hot methanol and then fractionally precipitated with ether. The least soluble fractions were recrystallized from methanol and ether to yield a black micro-crystalline powder, which was dried at 98°. The substance was very deliquescent, but sparingly soluble in ethanol and acetone. Very dilute aqueous solutions were brownish green changing to light green on the addition of cerium(IV) sulfate. The perchlorate and sulfate were also very soluble in water, but were investigated further. The molar conductivity in 10^{-4} *M* solution of 252 $ohms^{-1}$ is consistent with a bi-univalent electrolyte.

Anal. Calcd. for $C_8H_{37}N_8O_4I_2Os$: N, 14.87; I, 33.74; Os, 25.25; H_2O, 9.57. Found: N, 14.7; I, 33.6; Os, 25.4; H_2O, 9.6.

Tetrakis-(β-aminoethylamido)-osmium(VI) Iodide Trihydrate.—The most soluble fractions from the methanol/ether fractionation above were crystallized several times from methanol by adding ether, rejecting the least soluble material. The green to brown microcrystalline powder was dried at 98°. It was very deliquescent. Very dilute aqueous solutions were green, unaffected by acid solutions of Ce(IV) salts, but became brown on treatment with sodium hydrosulfite due to the formation of the Os(V) compound. The molar conductance in 10^{-3} *M* solution was 245 $ohms^{-1}$.

Anal. Calcd. for $C_8H_{35}O_3N_8I_2Os$: N, 15.25; I, 34.60; Os, 25.91. Found: N, 15.3; I, 34.2; Os, 25.8.

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Solubility of Isomeric Hexanes in Perfluoroheptane

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Critical solution temperatures are reported for mixtures of four isomeric hexanes with perfluoroheptane. Analysis of the values obtained indicates that the geometry of the molecule does not significantly influence the extent to which the apparent solubility parameter of the hydrocarbon exceeds the theoretical value.

It has been established that for liquid mixtures of alkanes and perfluoroalkanes the entropy of mixing is not ideal, hence that the conditions for the application of the Hildebrand regular solution equations are not met.[1] Nevertheless, it has been shown that for these solutions, the Hildebrand equations correctly represent the properties provided that an empirical solubility parameter be used for the hydrocarbon rather than the theoretical value, $(\Delta E_v/v)^{0.5}$.[1,2]

In the course of investigating the behavior of mixtures of alkanes with various non-polar substances, the critical solution temperature (c.s.t.) values for four of the five isomeric hexanes in mixtures with perfluoroheptane have been determined. These values permit some evaluation of the effect of structure of the hydrocarbon on the extent to which the empirical parameter for the hydrocarbon exceeds the theoretical value, uncomplicated by differences in molecular weight, or significant variation in molecular volume. It is also felt that complications are avoided by using for all the determinations a homogeneous sample of fluorocarbon—a small cut from the distillation of a single fluorocarbon sample. In this Laboratory, no fluorocarbon material has been purified to more than 98 mole % purity as measured by time–temperature cooling curves; therefore, comparisons of results involving different samples of fluorocarbon are subject to some doubt as to whether the impurities of the various samples are the same.

Experimental

Materials.—The alkanes used were Matheson, Coleman and Bell products, best available grades. Each sample was washed with sulfuric acid, water and potassium carbonate solution. The samples were passed through a column 0.5 m. in length packed with activated silica gel, dried over potassium carbonate, and distilled through a ten-plate column packed with stainless steel helices. A middle fraction of 100 ml. was taken for use from the 500 ml. charge. Table I summarizes the distillation data for the alkanes and perfluoroheptane. Exposed stem corrections were made on the calibrated thermometer, and the observed b.p. values corrected to 760 mm. using the data of reference (3).

The perfluoroheptane, furnished by the Minnesota Mining and Manufacturing Co., was washed with sulfuric acid, water and potassium carbonate solution. It was dried over anhydrous potassium carbonate, passed over activated silica gel in a 0.5 m. column, and refluxed four hours over bright sodium. A middle fraction of 30 ml. from a 150-ml. charge was taken for use. The value of the b.p. at 760 mm.

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[1] J. H. Hildebrand, B. B. Fisher and H. A. Benesi, THIS JOURNAL, **72**, 4348 (1950).

[2] J. A. Neff and J. B. Hickman, *J. Phys. Chem.*, **59**, 42 (1955).

[3] F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," (Circular C461) U. S. Govt. Printing Office, Washington, D. C., 1947, pp. 483.