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HYDROTHERMAL PREPARATION OF OSMIUM(III) COMPLEXES WITH ETHYLENEDIAMINETETRAACETIC ACID

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Osmium(III) complexes with ethylenediaminetetraacetic acid have been prepared by the reaction of hexachloroosmate(IV) and ethylenediaminetetraacetic acid suspended in water in a Teflon bucket at 140°C. The complexes have been formulated as $H[OsCl_2H_2edta]\cdot 2.5H_2O$ and $NH_4[OsCl_2H_2edta]$ from elementary analyses, pH titration, ir and magnetic measurements.

Of all the platinum metals, osmium is the only one that has not been characterized as its EDTA complexes. However, we have succeeded in synthesizing the complexes by employing a Teflon bucket$^{1)}$ at temperatures in excess of 100°C.

The starting material, $H_2[OsCl_6]$ was prepared by reduction of OsO_4 with a mixture of 12 M HCl and ethanol. Four mmol of H_4edta (edta: tetraanion of ethylenediaminetetraacetic acid) was added to 15 ml of aqueous solution containing 4 mmol of $H_2[OsCl_6]$ in a Teflon bucket of 20 ml capacity. The mixture was stirred and then the bucket and the sealing disk were set in a stainless vessel. The vessel was placed in an electric oven and heated at 140°C for 16 hr. The black aqueous solution which formed was cooled and evaporated to about 10 ml on a water bath. After addition of 10 ml of 12 M HCl, the solution was evaporated to about 10 ml again. On cooling, yellowish needles separated. The crystals were collected by filtration and washed with a small volume of ethanol and ether. The yield based upon OsO_4 was 70%.

Anal. Found: C,20.03; H,3.37; N,4.63; Cl,11.99; H_2O(by TG),7.26; Os,31.73%.
Calc. for $H[OsCl_2H_2edta]\cdot 2.5H_2O$: C,20.11; H,3.38; N,4.69; Cl,11.87; H_2O,7.54; Os,31.85%.

From Gouy magnetic measurements (solid state), the effective magnetic moment of the osmium ion was found to be 1.79 B.M.(13°C). Thus, we suggest that osmium has t_{2g}^5 configuration, and that an oxidation state is +3.

The equivalent weight of the complex was found to be 199.6 by pH titration. The theoretical value is 199.1. The average pK for three equivalents of strong acid, on the basis of the equivalent weight, is 2.8.

The acid, $H[OsCl_2H_2edta]$ was converted to the ammonium salt, $NH_4[OsCl_2H_2edta]$ by treatment with NH_4Cl.

Anal. Found: Os,33.97; Cl,12.31%. Calc. for $NH_4[OsCl_2H_2edta]$: Os,33.41; Cl,12.45%.

Figure shows the ir spectra of the complexes, $H[OsCl_2H_2edta]\cdot2.5H_2O$ (I) and $NH_4[OsCl_2H_2edta]$ (II), in the region of 1000-2000 cm^{-1}. The bands at 1735 cm^{-1} of I, and 1723, 1705 cm^{-1} of II have been assigned to the free carboxylic acid groups, and the bands at 1590 cm^{-1} of I and II to the coordinated carboxyl groups. In the case of II, an anhydrous compound, the intensities of these two types of bands are comparable; in the case of I, however, the intensity of the band at lower wave number is stronger, probably because of the overlapping of the absorption due to water of crystallization.$^{2)}$

The uv and visible spectra of the aqueous solutions of I and II are essentially the same and show a shoulder at 280 nm ($\log \varepsilon = 3.38$) and a peak at 234 nm ($\log \varepsilon = 3.73$). Both may be charge transfer bands.

The weight loss by heating I at 100°C for 1.5 hr corresponds closely to two and a half molecules of water. In view of the possibility that the weight loss might be due to the release of molecular hydrogen chloride, chloride analysis was run on a sample subjected to heating at 100°C for 1.5 hr. The result corroborates that there was no loss of chloride by heating. Further attempts to remove the HCl in nitrogen atmosphere by raising the temperature caused no loss in weight up to 200°C.

The complexes of Os(III) are usually octahedral.$^{3)}$ Therefore, the Os(III) ion in the EDTA complex, $[OsCl_2H_2edta]^-$ is assumed to have two chloride ions and a single H_2edta^{2-} group acting as a quadridentate ligand. The stereochemistry of this system is currently being pursued.

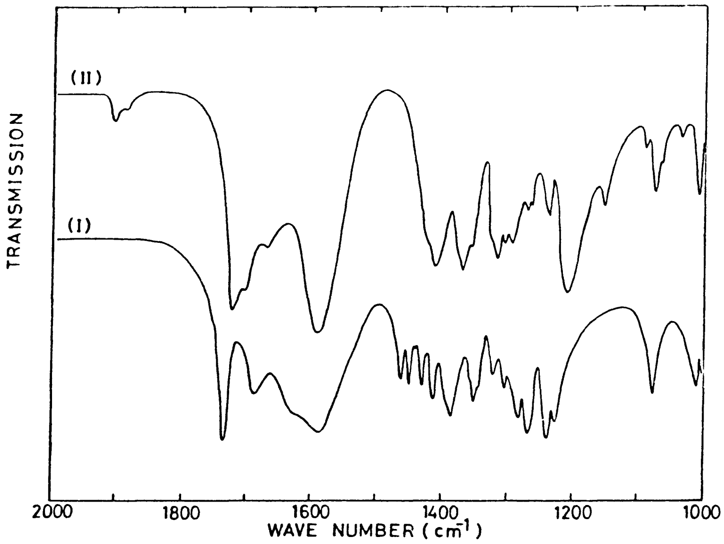

Figure. The ir spectra of Os(III) complexes with EDTA.
(I): $H[OsCl_2H_2edta]\cdot2.5H_2O$
(II): $NH_4[OsCl_2H_2edta]$

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