

Synthesis and Characterization of Tris(diethyldithiocarbamato)osmium(III) and Tetrakis(diethyldithiocarbamato)osmium(IV).

Electrochemical Behaviour of the Tris Complex

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Despite considerable interest in transition metal dithiocarbamate complexes [1] relatively little has so far been done on the preparation and characterization of the osmium compounds. Bozis [2] reported the preparation of a tris dithiocarbamate complex, Os(pdtc)₃ (p = pentamethylene), and more recently Os(II) mixed ligand dithiocarbamates with phosphines and carbonyl as ligands have been prepared [3, 4]. Furthermore, evidence is given for the existence in solution for Os(IV)- and Os(VI)-dithiocarbamates [5].

Tetrakis(diethyldithiocarbamato)osmium(IV) can be prepared by the reaction of (NH₄)₂OsCl₆ with NaEt₂dtc·3H₂O in a 1:5 molar ratio in aqueous methanol, and was obtained as a dark green crystalline precipitate after a reaction time of about three hours. In several cases, however, due to a prolonged reaction time, impure products were obtained, as these were contaminated with tris(diethyldithiocarbamato)osmium(III). The tetrakis complex is decomposed in organic solvents, which makes its purification impossible.

Tris(diethyldithiocarbamato)osmium(III), Os(Et₂dtc)₃, was prepared by conversion in refluxing tetrahydrofuran of the impure tetrakis products.

Elemental analyses and molecular weight determinations are consistent with the proposed formulas (Table I).

TABLE I. Analytical and Physical Data^a.

| | Os(Et ₂ dtc) ₃ | Os(Et ₂ dtc) ₄ | |
|-------------------------------|--------------------------------------|--------------------------------------|--------------------|
| Analytical Data | %C | 28.13 (28.37) | 30.89 (30.67) |
| | %H | 4.73 (4.76) | 5.07 (5.15) |
| | %N | 6.52 (6.62) | 7.18 (7.15) |
| Melting Points | 218 °C dec. | 155 °C dec. | |
| Colour | Dark Red | Dark Green | |
| Molecular Weight ^b | 606 (635) | 770 (783) | |
| Infrared Data ^c | ν(C–N) | 1493 (s) | 1510 (s) |
| | ν(C–S) | 1005 (m) | 1000 (s, very br.) |
| | ν(Os–S) | 389 (w), 338 (w) | 357 (w) |
| | | 305 (w) | |

^aTheoretical values in parentheses. ^bOsmometric method in chloroform at 37 °C. ^cCsi disc, in cm⁻¹.

The infrared spectra of the complexes show bands usually found for chelate dithiocarbamates and the most important are given in Table I. For the tetrakis complex, Os(Et₂dtc)₄, additional bands are found at 1400, 1260 and 1000 cm⁻¹ which are indicative of the presence of a monodentate bonded diethyldithiocarbamate ligand. These bands also appear in the spectra of Ru(NO)(Et₂dtc)₃ [6], Sn(Et₂dtc)₄ [7], Au(Et₂dtc)₃ [8], and Ir(Et₂dtc)₃(C₈H₁₂) [9] compounds with both mono and bidentate bonded diethyldithiocarbamate ligands.

In the cyclic voltammogram of Os(Et₂dtc)₄ no oxidation wave of the dithiocarbamate ligand is observed, indicating that in the tetrakis complex four ligands are co-ordinated. The electrochemical behaviour of Os(Et₂dtc)₄ is very complex and will be a subject of further study.

The data of the electrochemical oxidation and reduction of Os(Et₂dtc)₃ in acetone are summarized in Table II. Two oxidation waves and one reduction wave were observed. Cyclic voltammetry reveals the various processes to be reversible, because for each

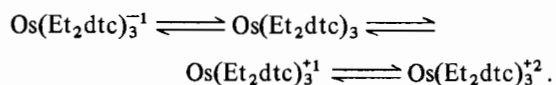
TABLE II. Electrochemical Data for Os(Et₂dtc)₃^a.

| Process | Pulse Polarography ^b | | | AC Voltammetry ^b | | | Cyclic Voltammetry ^c | | | |
|---------|---------------------------------|---|-----------------------------------|-----------------------------|--|-----------------------------------|--|--------------------------------------|--------------------------------------|--|
| | E _{1/2} (V) | E _{3/4} – E _{1/4} (mV) | i _p /conc. (mA/mol) | E _p (V) | ΔE _{1/2} ^d (mV) | i _p /conc. (mA/mol) | E _p ^{cath.} (V) | E _p ^{an.} (V) | ΔE _p ^e (mV) | i _p ^{cath.} i _p ^{an.} |
| 0 → -1 | -0.986 | 85 | 424 | -0.988 | 132 | 30.4 | -0.944 | -1.031 | 87 | 1.0 |
| 0 → +1 | 0.395 | 65 | 393 | 0.388 | 133 | 28.8 | 0.334 | 0.421 | 87 | 1.0 |
| +1 → +2 | 1.363 | 65 | 408 | 1.358 | 128 | 23.3 | 1.290 | 1.392 | 102 | 1.0 |

^aAt a platinum electrode in acetone (0.1 M Bu₄NClO₄) vs. a Ag/AgCl (0.1 M LiCl–acetone) reference electrode. ^bScan rate 5 mVsec⁻¹. Ac frequency 77.5 Hz. Amplitude 10 mV peak to peak. ^cScan rate 200 mVsec⁻¹. ^dWidth at half peak height. ^ePeak separation.

process an anodic as well as a cathodic peak was observed with a unity ratio of anodic to cathodic peak currents. However, with pulse polarographic and AC techniques rather large values for the reversibility criteria are found ($E_{3/4} - E_{1/4}$; $\Delta E_{1/2}$). The coulometric data from controlled potential oxidation of $\text{Os}(\text{Et}_2\text{dtc})_3$ at 0.55 V indicate that this oxidation is a 1-electron process.

Thus these electrochemical data define the following electron transfer series between tris-chelate complexes in four oxidation states, II, III, IV and V:



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