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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 dithiocarbamato 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 dithiocarbamato 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 $(NH_4)_2OsCl_6$ with $NaEt_2dtc\cdot 3H_2O$ 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(Et$_2$dtc)$_3$, was prepared by conversion in refluxing tetrahydrofurane 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$\doteq$N)	1493 (s)	1510 (s)
	ν(C–S)	1005 (m)	1000 (s, very br.)
	ν(Os–S)	389 (w), 338 (w) 305 (w)	357 (w)

[a] Theoretical values in parentheses. [b] Osmometric method in chloroform at 37 °C. [c] CsI 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(Et$_2$dtc)$_4$, 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)(Et$_2$dtc)$_3$ [6], Sn(Et$_2$dtc)$_4$ [7], Au(Et$_2$dtc)$_3$ [8], and Ir(Et$_2$dtc)$_3$(C$_8$H$_{12}$) [9] compounds with both mono and bidentate bonded diethyldithiocarbamato ligands.

In the cyclic voltammogram of Os(Et$_2$dtc)$_4$ 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(Et$_2$dtc)$_4$ is very complex and will be a subject of further study.

The data of the electrochemical oxidation and reduction of Os(Et$_2$dtc)$_3$ 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(Et$_2$dtc)$_3$[a].

Process	Pulse Polarography[b]			AC Voltammetry[b]			Cyclic Voltammetry[c]			
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	i_l/conc. (mA/mol)	E_p (V)	$\Delta E_{1/2}$[d] (mV)	i_p/conc. (mA/mol)	$E_p^{cath.}$ (V)	$E_p^{an.}$ (V)	ΔE_p^e (mV)	$\frac{i_p^{cath.}}{i_p^{an.}}$
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

[a] At a platinum electrode in acetone (0.1 *M* Bu$_4$NClO$_4$) *vs. a* Ag/AgCl (0.1 *M* LiCl–acetone) reference electrode. [b] Scan rate 5 mVsec^{-1}. Ac frequency 77.5 Hz. Amplitude 10 mV peak to peak. [c] Scan rate 200 mVsec^{-1}. [d] Width at half peak height. [e] Peak 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 $Os(Et_2dtc)_3$ 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:

$$Os(Et_2dtc)_3^{-1} \rightleftharpoons Os(Et_2dtc)_3 \rightleftharpoons Os(Et_2dtc)_3^{+1} \rightleftharpoons Os(Et_2dtc)_3^{+2}.$$

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