(2) Dobson, G. R.; Smith, L. A. H. *Inorg. Chem.* **1970**, *9*, 1001.
(3) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Clark, H. C. *Isr. J. Chem.* **1977**, *15*, 210.
(4) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.
(5) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.
(6) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.
(7) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286.
(8) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.
(9) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14.
(10) Poilblanc, R.; Bigorgne, M. *Bull. Soc. Chim. Fr.* **1962**, 1301.
(11) For example, $Mo(CO)_5(PPh_3)$ was heated in ^{13}CO-saturated C_2Cl_4 for 24 h at 55 °C with no measurable CO exchange or formation of $Mo(CO)_5(^{13}CO)$.
(12) On the basis of kinetic evidence, i.e., the fairly nondiscriminating ability of $[Mo(CO)_4(PPh_3)]$, these displacement reactions are thought to proceed with essentially complete molybdenum–phosphorus bond breaking.[7]
(13) It is however expected that in cases where L and L′ differ significantly in electronic character this generalization will not necessarily hold true.
(14) Darensbourg, D. J., unpublished results.
(15) The related 16-electron group 6B metal derivatives, $[Cr(CO)_5]$, have an average characteristic inverse lifetime in CO-saturated cyclohexane solution of $\sim 3 \times 10^4\ s^{-1}$.[16,17]
(16) Kelly, J. M.; Hermann, H.; Koerner von Gustorf, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105.
(17) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.
(18) It is nevertheless possible to scramble CO groups via a TBP transition state such that an incoming ^{13}CO ligand leads to a $Mo(CO)_5(PPh_3)$ species where the two ^{13}CO ligands are trans to one another without concomitant formation of a ^{13}CO axially labeled $Mo(CO)_5(PPh_3)$ species.
(19) (a) Darensbourg, D. J.; Salzer, A. *J. Organomet. Chem.* **1976**, *117*, C90. (b) Darensbourg, D. J.; Salzer, A. *J. Am. Chem. Soc.* **1978**, *100*, 4119.
(20) Although the intermediates in Scheme I are represented as nonsolvated species, it is likely in tetrachloroethylene that transient solvated species are present; e.g., unstable $M(CO)_5(TCNE)$ (M = Cr, Mo, W)[21] and $Fe(CO)_4(C_2Cl_4)$[22] derivatives have been reported as well as $(PPh_3)_2Pt(C_2Cl_4)$.[23]
(21) Herberhold, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 305.
(22) Fields, R.; Godwin, G. L.; Hazeldine, R. N. *J. Organomet. Chem.* **1971**, *26*, C70.
(23) (a) Bland, W. J.; Kemmitt, R. D. W. *J. Chem. Soc. A* **1968**, 1278. (b) Francis, J. N.; McAdam, A.; Ibers, J. A. *J. Organomet. Chem.* **1971**, *29*, 131.
(24) Qualitatively similar observations have been reported for this process carried out in toluene in ref 1.
(25) We have previously incorrectly reported a somewhat higher quantity of *trans*-$Mo(CO)_4(^{13}CO)(PPh_3)$ afforded by this reaction based on rather difficult to analyze $\nu(CO)$ infrared data alone.[26,27]
(26) Darensbourg, D. J.; Murphy, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 463.
(27) Darensbourg, D. J.; Murphy, M. A. *Inorg. Chem.* **1978**, *17*, 884.
(28) Black, J. D.; Braterman, P. S. *J. Organomet. Chem.* **1973**, *63*, C19.
(29) Poliakoff, M. *Inorg. Chem.* **1976**, *15*, 2892.
(30) The activation enthalpy for the cis → trans isomerization of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ has been found to be 24.5 kcal.[9] The electronic influences on the metal center of P-*n*-Bu_3 or $PPhCy_2$ in the *cis*-$Mo(CO)_4L_2$ derivatives are quite similar as indicated by their $\nu(CO)$ infrared frequencies.[4] Thus, we would expect the ΔH^* values for Mo–P bond cleavage in these two derivatives to be essentially the same (ΔH^* observed for Mo–P dissociation in *cis*-$Mo(CO)_4(PPhCy_2)_2$ is 30.2 kcal/mol).
(31) Schwenzer, G.; Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* **1972**, *11*, 1967.

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Synthesis, Characterization, and Electrochemical Properties of Dithiocarbamato Complexes of Osmium(III) and -(IV)

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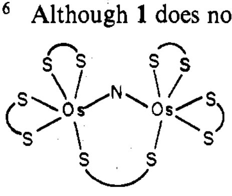
Several new *N,N*-dialkyldithiocarbamato (R_2dtc) complexes of osmium(III) and -(IV) have been synthesized and characterized. An electrochemical study on $Os(Et_2dtc)_3$, $ClOs(Et_2dtc)_3$, and $Os_2N(Et_2dtc)_5$ has been carried out and the results compared with those of analogous ruthenium and iron complexes. In propylene carbonate solution, $Os(dtc)_3$ exhibits a four-membered electron-transfer series $[Os(Et_2dtc)_3^- \rightleftarrows Os(Et_2dtc)_3 \rightleftarrows Os(Et_2dtc)_3^+ \rightleftarrows Os(Et_2dtc)_3^{2+}]$ while in acetonitrile solution the redox chemistry is complex with $Os(Et_2dtc)_3$ showing a one-electron irreversible oxidation to $[(CH_3CN)Os(Et_2dtc)_3]^+$ in a manner similar to $Ru(Et_2dtc)_3$. The ^1H NMR properties of the complexes $XOs(R_2dtc)_3$ (X = Cl, I, and PPh_3), $[Os_2(R_2dtc)_5]Cl$, and $Os(Et_2dtc)_3$ have been determined.

Introduction

Only a few reports have appeared on the synthesis, characterization, and properties of osmium dithiocarbamate complexes. The preparation of tris(*N,N*-diethyldithiocarbamato)osmium(III), $Os(Et_2dtc)_3$, and the tetrakis osmium(IV) complex, $Os(Et_2dtc)_4$, has recently been reported.[1] A number of mixed-ligand dithiocarbamate complexes of Os(II) with carbonyl and phosphine ligands have also recently been prepared.[2,3] Almost no work has been done on the structural, redox, and reactivity properties of osmium dithiocarbamate complexes, and therefore we have undertaken a comprehensive study of osmium R_2dtc (R = Me or Et) chemistry and its relation to the well-developed chemistry of iron[4] and ruthenium.[5] We recently reported the structural characterization of a novel μ-nitrido complex of Os(IV), $Os_2N(Me_2dtc)_5$ (**1**).[6] Although **1** does not have a ruthenium or iron analogue, it is of interest to determine if the reactions of $Os(R_2dtc)_3$ with HCl, I_2, and BF_3 mimic those of iron and ruthenium. The products of these reactions are $ClFe(R_2dtc)_2$,[7] $IFe(R_2dtc)_2$,[8] and $[Fe(R_2dtc)_3]BF_4$,[9] respectively, for iron and $ClRu(R_2dtc)_3$ (**2**),[10] $IRu(R_2dtc)_3$,[8] and β-$[Ru_2(R_2dtc)_5]BF_4$ (**3**),[11] respectively, for ruthenium. α-$[Ru_2(R_2dtc)_5]Cl$ (**4**), an isomeric form of the cation **3**, has also been prepared by photolysis of $Ru(R_2dtc)_3$ in chlorocarbon solvents[12] or by reaction of $RuCl_3{\cdot}xH_2O$ with NaR_2dtc in aqueous solution and separation from $Ru(R_2dtc)_3$ by column chromatography.[13]



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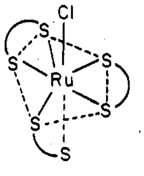

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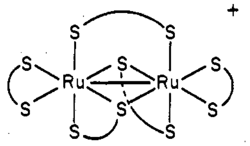

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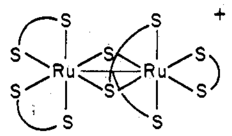

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It is also important to compare the electrochemistry of the various (dithiocarbamato)osmium complexes to that of iron and ruthenium. The oxidative electrolysis of $M(R_2dtc)_3$ in

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Table I. Characterization Data for Dithiocarbamato Complexes of Osmium

	elemental analysis, %						mol wt (37 °C in $CHCl_3$)		equiv conductance (25 °C), Ω^{-1} cm^2 $equiv^{-1}$		^1H NMR, δ (mult, J)[a]	
	found			calcd								
complex	C	H	N	C	H	N	found	calcd	CH_3NO_2	CH_3CN	CH_2	CH_3
$Os(Et_2dtc)_3$	28.22	4.71	6.50	28.37	4.76	6.62	625	635			13.30 (br)	1.22
$ClOs(Et_2dtc)_3$	26.97	4.40	6.27	26.87	4.51	6.27			26.6	64.9	3.69 (4.71)	1.30 (3.71)
$IOs(Et_2dtc)_3$	24.07	4.04	5.12	23.65	3.97	5.52			62.0	123	3.71 (4.71)	1.29 (3.71)
$[Os(Et_2dtc)_3]BF_4$	25.82	4.14	5.66	24.96	4.19	5.82			61.2	114		
$[(PPh_3)Os(Et_2dtc)_3]Cl$	42.81	4.93	4.60	42.49	4.86	4.51			81.5	91.2	3.44 (4.71)	1.16 (3.71)
$[Os_2(Me_2dtc)_5]Cl$	17.72	2.79	6.48	17.72	2.97	6.89	1008	1017	89.7			3.376, 3.324, 3.315, 3.097, 2.825[b]
$Os_2N(Me_2dtc)_5$	18.25	3.04	8.45	18.11	3.00	8.45	987	995	0.35			3.75, 3.32, 3.27, 3.26, 3.21
$Os_2N(Et_2dtc)_5$	26.40	4.78	7.42	26.44	4.44	7.40			0.56		complex	

[a] Chemical shifts in ppm relative to Me_4Si (δ 0) at 30 °C in $CDCl_3$; mult = multiplicity of multiplet; J in Hz. [b] Recorded in CD_3CN; five lines of equal intensity.

CH_3CN solution yields $[Fe(R_2dtc)_3]^+$ [14] and $[(CH_3CN)Ru(R_2dtc)_3]^+$,[5] respectively. Results on the corresponding osmium complexes have been determined here and are important to the understanding of the redox and photoredox chemistry of the iron group dithiocarbamates. Additionally, the magnetic and spectroscopic properties of the various osmium dithiocarbamates have been examined and will be discussed in relation to analogous iron and ruthenium compounds.

Table II. UV-Vis Spectral Data for Dithiocarbamato Complexes of Osmium

complex	solvent	λ_{max}, nm (log ϵ)
$Os(Et_2dtc)_3$	CH_2Cl_2	245 (4.60), 320 (sh, 3.69), 350 (sh, 3.88), 385 (4.03), 490, (sh, 3.43)
$ClOs(Et_2dtc)_3$	$CHCl_3$	260 (4.62), 332 (3.94), 385 (sh, 3.72), 420 (sh, 3.41), 510 (2.62), 595 (sh, 2.40)
$IOs(Et_2dtc)_3$	CH_2Cl_2	258 (4.59), 340 (sh, 3.91), 420 (sh, 3.45), 500 (sh, 2.80), 580 (sh, 2.64)
$[Os(Et_2dtc)_3]BF_4$	CH_2Cl_2	252 (4.64), 345 (4.22), 365 (sh, 4.11), 455, (sh, 3.53), 500 (3.78), 545, (sh, 3.64)
$[(PPh_3)Os(Et_2dtc)_3]Cl$	CH_2Cl_2	265 (4.61), 320 (sh, 4.04), 360 (3.84), 460 (sh, 2.74), 530 (sh, 2.35)
$[(CH_3CN)Os(Et_2dtc)_3]Cl$[a]	CH_3CN	265 (4.61), 300 (sh, 4.02), 355 (3.90), 470 (sh, 2.53), 535 (sh, 2.42)
$[Os_2(Me_2dtc)_5]Cl$	CH_2Cl_2	260 (sh, 4.61), 370 (sh, 3.96), 530 (sh, 3.05), 1005 (2.15)
$Os_2N(Et_2dtc)_5$	CH_2Cl_2	254 (4.82), 331 (4.40), 363 (sh, 4.33), 496 (sh, 2.99)
$Os_2N(Me_2dtc)_5$	CH_2Cl_2	252 (4.88), 330 (4.48), 361 (sh, 4.41), 495 (sh, 3.05)

[a] Obtained by dissolving $ClOs(Et_2dtc)_3$ in CH_3CN solvent and qualitatively the same as the one-electron oxidative electrolysis product of $Os(Et_2dtc)_3$ in CH_3CN (see text).

Experimental Section

Preparation of Compounds. Analytical and spectroscopic data are given for the compounds in Tables I–III. Methyl analogues are prepared in the same manner as ethyl compounds.

$Os(Et_2dtc)_3$ was synthesized by separately dissolving ~0.125 g (0.284 mmol) of $(NH_4)_2OsCl_6$, which was prepared by published methods,[15] and 0.486 g (2.84 mmol) of $NaEt_2dtc$ in 25 mL of a 1:1 H_2O–CH_3OH solution. The metal-containing solution was slowly added to the ligand solution with stirring and allowed to gently reflux for 1.5 h under a N_2 atmosphere. The red-brown precipitate was filtered, washed with petroleum ether, and air-dried at room temperature. The dried precipitate was dissolved in CH_2Cl_2 and chromatographed on a neutral alumina column, eluting off the orange band of $Os(Et_2dtc)_3$ with CH_2Cl_2. A green band (presumably $Os(Et_2dtc)_4$)[1] remained on the column. This band turned orange after standing in the dark on the column for 24 h and elution with CH_2Cl_2 yielded additional $Os(Et_2dtc)_3$. Dark red crystals of $Os(Et_2dtc)_3$ were obtained in ca. 76% yield by crystallization from CH_2Cl_2–heptane in the dark. $Os(Et_2dtc)_3$ is slowly converted into $ClOs(Et_2dtc)_3$ in chlorocarbon solvents by fluorescent lights. Infrared (KBr disk): $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1495 cm^{-1}. Magnetic data (solid state): $\chi_M = 748 \times 10^{-6}$ cgsu mol^{-1} giving μ_{eff} of 1.61 μ_B at 25 °C with a diamagnetic correction of 320×10^{-6} cgsu mol^{-1}. Mass spectral analysis gave the following major peaks [m/e (relative abundance)]: 636 (18.5%) (P^+), 572 (7.9%), 520 (13.2%), 488 (4.2%), 459 (3.7%), 404 (3.0%), 372 (1.7%), 149 (19.1%), 116 (100%). These fragments are consistent with the formulation $Os(Et_2dtc)_3$.[16]

$ClOs(Et_2dtc)_3$ was prepared from $Os(Et_2dtc)_3$. Anhydrous HCl was bubbled through a 0.01 M toluene solution of $Os(Et_2dtc)_3$ for ca. 5 min and stirred for 1 h. The solvent was removed in vacuo, and the residue was washed with petroleum ether. Dark brown needlelike crystals of $ClOs(Et_2dtc)_3$ were obtained in good yield by slow evaporation from CH_2Cl_2–heptane. Alternatively, $ClOs(Et_2dtc)_3$ can be prepared by UV photolysis of $Os(Et_2dtc)_3$ (0.01 M) in degassed $CHCl_3$ solution in a manner similar to the preparation of $ClRu(Et_2dtc)_3$ from $Ru(Et_2dtc)_3$.[10,12] The quantum yield for the quantitative conversion is 0.61, using 265-nm radiation at 31 °C.[17] Infrared (KBr disk): $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1506 cm^{-1}. The compound is diamagnetic in solid and solution. The mass spectrum is very similar to that of $Os(Et_2dtc)_3$.

$IOs(Et_2dtc)_3$ was prepared by addition of a twofold excess of I_2 in toluene to a 0.01 M toluene solution of $Os(Et_2dtc)_3$. The solvent was removed in vacuo, and the remaining residue was thoroughly washed with heptane. Purification was accomplished by column chromatography on silica gel, eluting with CH_2Cl_2 and then with acetone, respectively. $IOs(Et_2dtc)_3$ was obtained from the acetone eluent in good yield and crystallized as dark red-brown needles from CH_2Cl_2–heptane. Infrared (KBr disk): $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1506 cm^{-1}. The compound is diamagnetic in solid and solution.

$[(PPh_3)Os(Et_2dtc)_3]Cl$ was prepared by addition of a small molar excess of PPh_3 to a CH_2Cl_2 solution of $ClOs(Et_2dtc)_3$. An immediate color change from red-brown to dark yellow occurred, and purification was carried out by column chromatography on silica gel, eluting with CH_2Cl_2, acetone, and methanol, respectively. $[(PPh_3)Os(Et_2dtc)_3]Cl$ was isolated from the methanol eluent in good yield and crystallized by slow evaporation from CH_2Cl_2–heptane. Infrared (KBr disk): $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1520 cm^{-1}; $\nu(PPh_3)$ 1481, 754, 700 cm^{-1}. The compound is diamagnetic in solid and solution.

$[Os(Et_2dtc)_3]BF_4$ was prepared by bubbling BF_3 gas through an aerobic CH_2Cl_2 solution of $Os(Et_2dtc)_3$ (ca. 0.01 M) for 30 s. The resulting purple solution was purged with N_2 and extracted once with an equal volume of water. The solvent was removed in vacuo leaving a brown residue of product. Purification of this complex is difficult, and so far only impure samples have been obtained. The compound can also be prepared by controlled-potential electrolysis of $Os(Et_2dtc)_3$ in propylene carbonate ($C_4H_6O_3$) at 0.30 V vs. SCE. The best evidence for the existence of $[Os(Et_2dtc)_3]^+$ is the reversible redox couple $Os(dtc)_3 \rightleftharpoons Os(dtc)_3^+$ observed in the cyclic voltammetry of both members of the couple. Thus far, the highest purity achieved for $Os(Et_2dtc)_3^+$ via the BF_3 preparation is ca. 85%, determined electrochemically. The ^1H NMR shows peaks which are broadened and shifted considerably from the expected diamagnetic positions suggesting

Table III. Electrochemical Data for *N,N*-Diethyldithiocarbamato Complexes of Osmium[a]

				dc voltammetry		cyclic voltammetry			
complex[b]	solvent	process	product	$E_{1/2}$, V	$E_{1/2} - E_{3/4}$, mV	E_{pc}, V	E_{pa}, V	ΔE_p, mV	i_{pc}/i_{pa}
$Os(dtc)_3$	CH_3CN	redn	$[Os(dtc)_3]^-$	−1.10	56	−1.11	−1.06	52	1.00
	$C_4H_6O_3$	redn	$[Os(dtc)_3]^-$	−1.06	51	−1.11	−1.05	58	1.04
	CH_3CN	oxidn (1)	$[(S)Os(dtc)_3]^+$	0.01	55	−0.93	0.06	*c*	*c*
		oxidn (2)	$[(S)Os(dtc)_3]^{2+}$	1.06	59	1.05	1.01	50	1.03
	$C_4H_6O_3$	oxidn (1)	$[Os(dtc)_3]^+$	0.13	52	0.085	0.146	61	1.04
		oxidn (2)	$[Os(dtc)_3]^{2+}$	1.08	47	1.026	1.100	73	1.05
$[(S)Os(dtc)_3]Cl$	CH_3CN	redn (1)	$Os(dtc)_3$	−0.94[d]	106[d]	−0.92	0.06	*c*	*c*
		redn (2)	$[Os(dtc)_3]^-$	−0.94[d]	106[d]	−1.11	−1.06	52	*d*
		oxidn	$[(S)Os(dtc)_3]^{2+}$	1.04[d]	95[d]	1.05	*e*		
$[Os(dtc)_3]BF_4$	$C_4H_6O_3$	redn (1)	$Os(dtc)_3$	0.13	53	0.09	0.15	59	0.99
		redn (2)	$[Os(dtc)_3]^-$	−1.05	55	−1.09	−1.04	57	1.12
		oxidn	$[Os(dtc)_3]^{2+}$	1.07	64	1.04	1.10	63	0.83
$Os_2N(dtc)_5$[f]	CH_3CN	oxidn (1)	$[Os_2N(dtc)_5]^+$	0.43	49	0.41	0.47	56	0.99
		oxidn (2)	?	0.93	89		0.94		

[a] All potentials were determined at 0 °C vs. SCE with a glassy carbon electrode unless stated otherwise; S in the table refers to the solvent CH_3CN; cyclic voltammetric scan rate was between 50 and 200 mV s^{-1}; dtc = Et_2dtc. [b] Parent complex in solution. [c] The cathodic peak appeared far removed from the anodic peak (see text). [d] Closeness of two waves makes measurement inaccurate. [e] Anodic peak is combination of two peaks at ca. 1.08 and 1.00 V; the latter peak is due to the process $Cl^- \rightarrow {}^1/_2Cl_2 + e^-$. [f] dtc = Me_2dtc; with a platinum electrode.

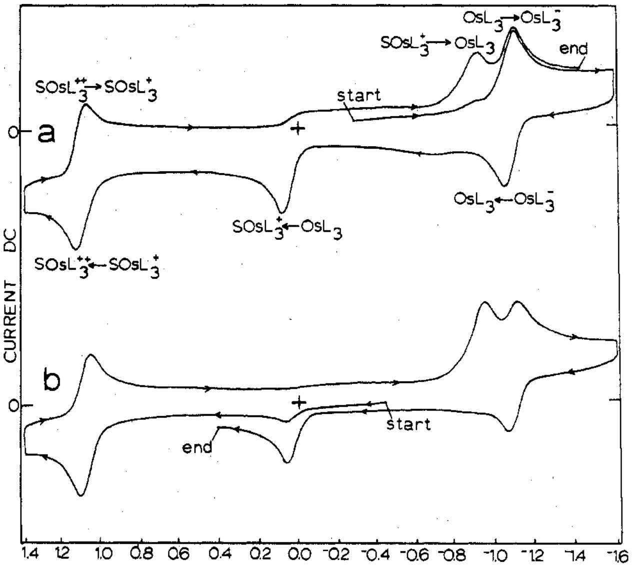

Figure 1. (a) Cyclic voltammogram of $Os(Et_2dtc)_3$ in CH_3CN (~0.1 M $[NEt_4][ClO_4]$). (b) Cyclic voltammogram of the above solution after controlled-potential electrolysis at 0.3 V. The zero current–zero potential position is marked by a cross (scan rate = 100 mV s^{-1}).

that the complex is paramagnetic. The complex does exhibit paramagnetism in the solid. Infrared (KBr disk): ν(C⋯N) 1506 cm^{-1}; ν(B–F) 1060 (br) cm^{-1}.

$[Os_2(Me_2dtc)_5]Cl$ was prepared by refluxing a 4:1 mixture of $NaMe_2dtc$ and $(NH_4)_2OsCl_6$ in a 1:1 methanol–water solution for 24 h under a N_2 atmosphere. The liquid was distilled off, and the remaining brown residue was dissolved in CH_2Cl_2 and run down a column of alumina (Alcoa F-20). The CH_2Cl_2 eluent contained $Os(Me_2dtc)_3$ in ca. 10% yield. (This yield can be increased by use of a larger excess of $NaMe_2dtc$ and shorter reaction times.) The brown band remaining on the column was eluted with acetone and methanol, respectively. The methanol removed a brown compound. Purification of the brown compound was achieved by chromatography on a 2-cm silica gel column with 1:2 acetone–CH_2Cl_2 and methanol eluents, respectively. The use of a longer column results in considerable product loss. $[Os_2(Me_2dtc)_5]Cl$ was isolated as a powder from the methanol eluent in 30% yield (based on Os) and judged pure by elemental analysis and ^1H NMR (Table I and Figure 1). Infrared (KBr disk): ν(C⋯N) 1536 cm^{-1} (1524 cm^{-1} for $Os(Me_2dtc)_3$). The compound is diamagnetic in solid and solution.

$Os_2N(R_2dtc)_5$, R = Me or Et, was prepared by dissolving $Os(R_2dtc)_3$ (0.45 mmol), NaR_2dtc (1.8 mmol), and $K_2(NOsCl_5)$ (0.45 mmol), prepared according to the literature,[15] in 100 mL of methanol. The solution was stirred at 50 °C for 1 h. The black precipitate which formed was filtered and column chromatographed (Alcoa alumina F-20) with CH_2Cl_2 eluent to give a 70% yield of the orange-brown complex. Crystallization can be achieved by slow evaporation from CH_2Cl_2–heptane. The complexes were judged pure by elemental analysis and ^1H NMR (Table I), and the formulation $Os_2N(Me_2dtc)_5$ was confirmed by single-crystal X-ray analysis.[6] Infrared (KBr disk) for R = Me and Et, respectively: ν(C⋯N) 1524, 1493 cm^{-1}; ν(Os–N–Os, asym) 1052, 1060 cm^{-1}. The complexes are diamagnetic in solid and solution. Mass spectrum gave major peaks for R = Et which are consistent with the formulation $Os_2N(Et_2dtc)_5$ [*m*/*e* (relative abundance) assignment]: 636 (0.6%) $Os(Et_2dtc)_3^+$, 604 (13.2%), 572 (2.5%), 540 (0.8%), 520 (1.1%), 502 (16.9%) $NOs(Et_2dtc)_2^+$, 149 (56.4%), 116 (53.6%), base peak 44 (100%).

$Fe(Et_2dtc)_3$ was prepared as previously reported.[4]

Electrochemical Measurements. All measurements were made with a three-electrode Princeton Applied Research Model 170 instrument with a glassy carbon indicator electrode, a saturated calomel reference electrode (SCE), and a platinum auxiliary electrode. A coil of heavy-guage platinum wire was used as the electrode in electrolysis experiments. Several measurements were also done with a small platinum wire indicator electrode. The SCE was separated from the sample compartment by three nonaqueous salt bridges connected by glass frits. Solutions were ca. 0.5–2 mM in complex and tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte. All experiments were done under a nitrogen atmosphere. The cyclic voltammograms were recorded on an X-Y recorder at 50–200 mV s^{-1}. Burdick and Jackson "distilled in glass" acetonitrile and propylene carbonate ($C_4H_6O_3$) solvents were dried over molecular sieves and used without further purification. Eastman reagent grade TEAP was recrystallized six times from water and dried in vacuo. CH_3CN solutions were 0.1 M in TEAP while $C_4H_6O_3$ solutions were 0.2 M in TEAP.

Spectral Measurements. Electronic absorption spectra were recorded with a Cary 14 spectrophotometer using 1-cm quartz cells. Infrared spectra were recorded on a Perkin-Elmer Model 237 grating instrument. ^1H NMR spectra were obtained on a Varian CFT 20 instrument. A Yellow Springs Instrument Co. Model 31 conductivity bridge was used for conductivity measurements. Complex concentrations used in the conductivity experiments were ca. 1 × 10^{-3} M. Magnetic measurements were made at 23 °C by use of the Faraday technique, and $Hg[Co(SCN)_4]$ was used as a calibrant. Mass spectra were obtained with an AEI MS-30 mass spectrometer, and samples were introduced with the solid-sample probe. All spectra were measured at an ion-source temperature of 200 °C or less and an ionization energy of 70 eV.

Results and Discussion

Several new R_2dtc complexes of osmium(III) and -(IV) have been prepared and characterized. Since our primary goal was to understand the structural and redox chemistry of osmium dithiocarbamate complexes and their relation to the analogous chemistry of ruthenium and iron, a thorough spectroscopic and electrochemical study has been undertaken. Future work will involve examining the photochemical and reactivity properties of these and related complexes.

Synthesis and Characterization. The complexes listed in Tables I and II have been prepared (see Experimental Section) and thoroughly characterized. In all cases the R = Me or Et analogues have been prepared and have very similar properties. $Os(Et_2dtc)_3$ has previously been reported[1,18] but has not been thoroughly characterized by NMR and UV–vis spectroscopy. This complex is obviously a monomeric six-coordinate tris chelate with magnetic electrochemical and spectroscopic properties very similar to those of the analogous ruthenium compound.[5,12,19] Magnetically it is low-spin d^5 ($S = {}^1/_2$) with $\mu_{eff} = 1.61\ \mu_B$. Its ^1H NMR properties are very similar to those of $Ru(Et_2dtc)_3$[20] and will be discussed in a later section. Reaction of $Os(Et_2dtc)_3$ with HCl, I_2, and aerobic BF_3 has been carried out yielding the osmium(IV) products $ClOs(Et_2dtc)_2$, $IOs(Et_2dtc)_3$, and $[Os(Et_2dtc)_3]BF_4$, respectively. The products of the HCl and I_2 reactions appear to be identical to the seven-coordinate products (**2**) obtained with $Ru(Et_2dtc)_3$, except that with HCl a small amount of α-$Ru_2(Et_2dtc)_5$ (**4**) is also produced.[12] The similarity of the magnetic UV–vis and ^1H NMR properties of the Os and Ru complexes $XM(Et_2dtc)_3$ [X = Cl or I] strongly suggests that they have identical structures (see Experimental Section, Tables I and II, and ref 8 and 10). The reaction of $Os(Et_2dtc)_3$ with BF_3 yields a six-coordinate cationic tris-chelate complex of Os(IV) (Experimental Section and Electrochemistry Section) which is analogous to $[Fe(Et_2dtc)_3]BF_4$ prepared in the same manner[9] but is different from the metal–metal-bonded Ru(III) compound $[\beta$-$Ru_2(Et_2dtc)_5]BF_4$ (**3**) obtained from reaction of BF_3 with $Ru(Et_2dtc)_3$.[11] In the case of the BF_3 reaction, the chemistry of osmium is identical to that of iron. This contrasts with the reaction of $M(Et_2dtc)_3$ complexes with HCl and I_2 where the ruthenium and osmium chemistries are very similar to but quite different from that of iron. Reaction of HCl and I_2 with $Fe(R_2dtc)_3$ (R = Me or Et) yields the five-coordinate compounds $ClFe(R_2dtc)_2$[7] and $IFe(R_2dtc)_2$,[8] respectively. Although it appears that the six-coordinate cation $[M(Et_2dtc)_3]^+$ is favored with osmium and iron, whereas such a compound cannot be synthesized for ruthenium, it is noteworthy that the reaction of $[Os(Et_2dtc)_3]BF_4$ with Cl^- yields the seven-coordinate compound $ClOs(Et_2dtc)_3$. This contrasts with iron where reaction of Cl^- with $[Fe(Et_2dtc)_3]BF_4$ yields the five-coordinate compound $ClFe(Et_2dtc)_2$.[4]

As previously observed with ruthenium,[5] the seven-coordinate complexes of Os(IV) are quite stable. Indeed, the purple complex $[Os(Et_2dtc)_3]BF_4$ is readily converted into yellow-brown diamagnetic seven-coordinate complexes upon addition of Lewis bases such as Cl^-, I^-, CH_3CN, or PPh_3. All of these seven-coordinate compounds are stereochemically nonrigid on the NMR time scale even at −90 °C (Table I) and presumably have distorted pentagonal-bipyramidal structures as found for the analogous ruthenium complexes.[8,10]

The dimeric complex $[Os_2(Me_2dtc)_5]Cl$ has been obtained by long-term reaction of $(NH_4)_2[OsCl_6]$ with $NaMe_2dtc$ (Experimental Section). Its formulation is based on elemental analysis, conductivity, and molecular weight data (Table I) and on the similarity of its ^1H NMR and UV–vis–near-IR spectra (Table II) with those of α- and β-$[Ru_2(Me_2dtc)_5]BF_4$ (**3** and **4**).[5]

The ^1H NMR spectra of the complexes $[Os_2(Me_2dtc)_5]Cl$ and α- and β-$[Ru_2(Me_2dtc)_5]BF_4$ in CD_3CN show five-line patterns in each case, but it is not possible to assign the α or β stereochemistry to the osmium complex on the basis of these spectra. The α and β ruthenium complexes have been shown to possess different high-temperature NMR coalescence patterns as well as different exchange patterns with added $NaMe_2dtc$.[5] In principle, such experiments should allow an assignment of stereochemistry to the osmium complex, if indeed $[Os_2(Me_2dtc)_5]Cl$ possesses one of these two possibilities. Unfortunately, $[Os_2(Me_2dtc)_5]Cl$ decomposes at elevated temperatures in $(CD_3)_2SO$ solvent prior to coalescence to give at least eight new methyl signals, and no sign of exchange broadening is observed upon the addition of excess $NaMe_2dtc$ in CD_3CN solution. Therefore, the stereochemistry of $[Os_2(Me_2dtc)_5]Cl$ cannot be determined by these experiments. Comparison of the near-IR spectrum of $[Os_2(Me_2dtc)_5]Cl$ with those of the α and β ruthenium complexes[5] reveals broad absorption bands in each case with λ_{max} (ϵ) values of 1000 nm (140 $M^{-1}\ cm^{-1}$), 1040 (250), and 950 (151), respectively. Again, it is not possible to assign stereochemistry on the basis of these data, and the final determination must wait for a single-crystal X-ray analysis.

The complex $Os_2N(Me_2dtc)_5$ has recently been synthesized and structured by single-crystal X-ray analysis.[6] This novel compound was synthesized in 70% yield by the reaction of ROC/RIC (Cat. No. OS-14) $OsCl_3 \cdot xH_2O$ with $NaMe_2dtc$ in refluxing CH_3CN under a N_2 atmosphere. The source of the nitrido nitrogen atom was not known when our original paper appeared.[6] Additional experiments with another source of $OsCl_3$ (Alpha, Cat. No. 55100) revealed that the origin of the nitrido nitrogen was a major nitride impurity in the ROC/RIN $OsCl_3$.[21] Subsequently, the complexes $Os_2N(R_2dtc)_5$ where R = Me and Et were prepared in high yield by reaction of $K_2(NOsCl_5)$[15] with $Os(R_2dtc)_3$ in the presence of excess R_2dtc^- in methanol (Experimental Section). The complexes were characterized by elemental analysis, conductivity, MS, molecular weight, ^1H NMR, and IR data (Table I and Experimental Section). A single-crystal X-ray analysis of the R = Me compound revealed its bimetallic nature (**1**) with a slightly bent Os–N–Os linkage and one bridging Me_2dtc ligand. The R = Et complex presumably has the same structure as judged by IR, UV–vis, and ^1H NMR data.

Electrochemical Studies. $Os(Et_2dtc)_3$. The electrochemistry of $Os(Et_2dtc)_3$ in acetone has recently been communicated by van der Linden and co-workers.[1] Their results show the presence of a four-membered electron-transfer series given in eq 1 which involves osmium in the II, III, IV, and V oxidation

$$Os(Et_2dtc)_3^- \rightleftarrows Os(Et_2dtc)_3 \rightleftarrows Os(Et_2dtc)_3^+ \rightleftarrows Os(Et_2dtc)_3^{2+} \quad (1)$$

states. Our results with propylene carbonate ($C_4H_6O_3$) solvent at 0 °C confirm this observation. Dc and cyclic voltammetric data are presented in Table III. All three waves are reversible as judged by the ΔE_p and i_{pc}/i_{pa} values presented in Table III. Controlled-potential electrolysis of $Os(Et_2dtc)_3$ at 0.3 V gives the purple cation $[Os(Et_2dtc)_3]^+$ which has identical UV–vis and electrochemical properties with samples prepared by the reaction of aerobic BF_4 with $Os(Et_2dtc)_3$ (vide supra). The one-electron nature of this oxidation has been verified by coulometry. These electrochemical results strongly suggest that the one-electron oxidation product of $Os(Et_2dtc)_3$ is the six-coordinate tris-chelate $[Os(Et_2dtc)_3]^+$. This contrasts with the analogous ruthenium chemistry where the one-electron oxidation product of $Ru(Et_2dtc)_3$ in $C_4H_6O_3$ is a solvent- or anion-stabilized seven-coordinate complex.[5] Additionally, it is not possible to reach the +5 oxidation state with ruthenium.

The electrochemical results for $Os(Et_2dtc)_3$ in CH_3CN at 0 °C are considerably different than the above results with $C_4H_6O_3$, but they are very similar to the CH_3CN data observed with $Ru(Et_2dtc)_3$.[5] The electrochemical data are presented in Table III and Figure 1a. The overall cyclic voltammetric process in CH_3CN which is illustrated in Figure 1a is best represented by Scheme I. The one-electron re-

Scheme I

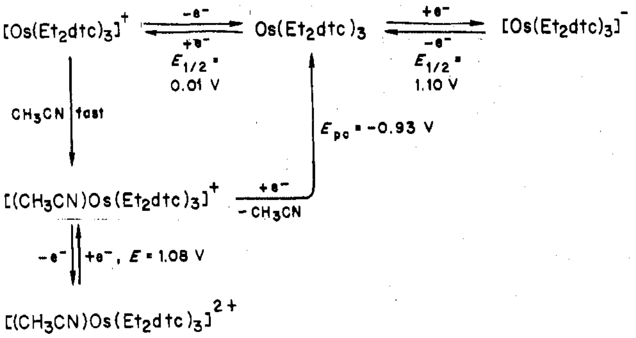

Table IV. Voltammetric Data for $M(Et_2dtc)_3$ Complexes of Iron, Ruthenium, and Osmium[a]

	iron[c,f]		ruthenium[g]		osmium[f]	
process[b]	$E_{1/2}$, V	ΔE_p, mV[d]	$E_{1/2}$, V	ΔE_p, mV	$E_{1/2}$, V	ΔE_p, mV
			$C_4H_6O_3$ Solvent			
$M \rightleftarrows M^-$	−0.48	67	−0.73	67	−1.06	58
$M \rightleftarrows M^+$	+0.30	57	+0.38	*e*	+0.12	60
			CH_3CN Solvent			
$M \rightleftharpoons M^-$	−0.51	64	−0.71	67	−1.10	52
$M \rightleftharpoons M^+$	+0.30	56	+0.33	*e*	+0.07	*e*

[a] All potentials were determined at 0 °C vs. SCE. [b] M = $M(Et_2dtc)_3$. [c] The electrochemistry of $Fe(Et_2dtc)_3$ has not previously been reported under the conditions used here. [d] Cyclic voltammetric scan rates varied between 50 and 200 mV s^{-1}. [e] Irreversible wave corresponding to the process

$$M(Et_2dtc)_3 \xrightarrow[-e^-]{S} [SM(Et_2dtc)_3]^+$$

where S = solvent or anion in which case the product is neutral. [f] This work. [g] Reference 5.

duction at $E_{1/2} = -1.10$ V is reversible while the oxidation at $E_{1/2} = 0.01$ V (or $E_{pa} = 0.06$ V) is irreversible with the cathodic return peak appearing at $E_{pc} = -0.93$ V. This peak appears only after oxidation of $Os(Et_2dtc)_3$ and is initially present after controlled-potential oxidative electrolysis of $Os(Et_2dtc)_3$. The cyclic voltammogram shown in Figure 1b was recorded after exhaustive electrolysis at 0.3 V such that the parent species is $[(CH_3CN)Os(Et_2dtc)_3]^+$. The complex $[(CH_3CN)Os(Et_2dtc)_3]^+$ has identical UV–vis and electrochemical properties with $ClOs(Et_2dtc)_3$ in CH_3CN (Tables II and III). This chemistry is identical with that observed for the analogous ruthenium complexes[5] except for the additional reversible one-electron oxidation of $[(CH_3CN)Os(Et_2dtc)_3]^+$ to $[(CH_3CN)Os(Et_2dtc)_3]^{2+}$ at $E_{1/2} = 1.08$ V, which is not observed for ruthenium. The evidence presented here and the similarity to the analogous ruthenium electrochemistry[5] strongly support the redox reaction of Scheme I.

It is interesting to compare the oxidation and reduction half-wave potentials for $M(Et_2dtc)_3$ complexes of Fe, Ru, and Os. The appropriate data are presented in Table IV. The trend is as expected for the half-wave potentials corresponding to the reversible process $M(Et_2dtc)_3 + e^- \rightleftarrows M(Et_2dtc)_3^-$ in that the ease of reduction decreases in the order Fe > Ru > Os. The half-wave potentials for the process $M(Et_2dtc)_3 \rightleftarrows M(Et_2dtc)_3^+ + e^-$ are nearly identical for Fe and Ru but much lower for Os. It is expected that Os should be the easiest to oxidize, but the similarity in potential for Fe and Ru is unexpected. It should be emphasized, however, that the Ru oxidation is irreversible in all solvents used, and therefore less certainty should be attached to the $E_{1/2}$ values in this case.

$ClOs(Et_2dtc)_3$. The cyclic voltammetry of this complex in CH_3CN solution is identical to that of $[(CH_3CN)Os(Et_2dtc)_3]^+$ (vide supra) which was generated by controlled-potential oxidative electrolysis of $Os(Et_2dtc)_3$ in CH_3CN, except that an additional anodic peak is observed with $ClOs(Et_2dtc)_3$ at ~1.0 V corresponding to the process $Cl^- \xrightarrow{-e^-} Cl\cdot$. This observation supports the conclusion that CH_3CN replaces Cl^- from the apical coordination site of the pentagonal-bipyramidal complex, as has been observed in the analogous ruthenium chemistry.[5] UV–vis data also support this conclusion (Table II). The electrochemistry of $ClOs(Et_2dtc)_3$ in propylene carbonate solution is complicated by the presence of an equilibrium between coordinated and uncoordinated chloride. Work is in progress on this system.

$Os_2N(Et_2dtc)_5$. In CH_3CN solution this complex possesses a well-defined reversible one-electron oxidation at $E_{1/2} = 0.43$ V vs. SCE and a second irreversible wave at $E_{1/2} = 0.93$ V. The neutral complex contains the Os(IV)–N–Os(IV) linkage, and therefore the one-electron oxidation product should be mixed-valence Os(IV)–N–Os(V) complex. This compound has not been isolated but should be easily obtainable. The second oxidation presumably forms a bimetallic complex of Os(V); however, the irreversibly formed products have not been examined.

^1H NMR Properties of $Os(Et_2dtc)_3$. This complex is a member of an extensive series of $M(R_2dtc)_3$ complexes which are stereochemically nonrigid on the ^1H NMR time scale.[22] Numerous tris chelate complexes of this type which contain diastereotopic methylene protons have been studied by NMR spectroscopy, and kinetic parameters for optical inversion have been reported.[22] $Os(Et_2dtc)_3$ was therefore examined by ^1H NMR in CD_2Cl_2 solutions as a function of temperature. The methylene signal which is broad at room temperature (δ 13.5) separates into two well-defined narrow peaks as the temperature is lowered to −60 °C (δ 13.5 and 18.6). This behavior is exactly analogous to that observed for $Ru(Et_2dtc)_3$.[20] The coalescence is reversible as the temperature is increased. The chemical shift separation $\Delta\nu$ of the two frozen-out methylene peaks was carefully measured over the temperature range −80 to −45 °C and plotted vs. $1/T$. Extrapolation of the straight line to the coalescence temperature, T_c, of −10 °C gave a $\Delta\nu_c$ of 321 Hz. The rate constant k for the dynamic process was calculated by use of the coalescence equation[23] $k = (\pi\Delta\nu_c)/2^{1/2}$ to be 7.13×10^2 s^{-1}. By analogy to numerous other $M(R_2dtc)_3$ complexes and because ligand exchange is slow on the NMR time scale, this dynamic process is assigned to metal-centered optical inversion of the complex.[22,24] Since a complete line shape analysis has been carried out for the analogous process of $Ru(Et_2dtc)_3$,[20] it is possible to compare the inversion rates of both complexes. The rate constant at −10 °C for $Ru(Et_2dtc)_3$ is only 240 s^{-1} compared with 713 s^{-1} for $Os(Et_2dtc)_3$. Although there is some error associated with the coalescence temperature method of determining rate constants, our experience indicates that the error is not greater than ±10%. Therefore, the rate of inversion is clearly faster for osmium. This result is unexpected since experiments on other tris-chelate complexes of dithiocarbamate, β-diketonate, and tropolonate ligands have shown that complexes of the heavier transition metals within a group are more inert to rearrangement. For example, the following rate trends have been observed: for dithiocarbamate[22] and β-diketonate tris chelates, Fe > Ru, Co > Rh; for α-substituted tropolonates, Co > Rh.[25] Since these trends have never been explained satisfactorily and clearly involve subtle differences in structural and electronic factors,[22] further discussion here is unwarranted.

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Registry No. $Os(Et_2dtc)_3$, 64478-70-2; $ClOs(Et_2dtc)_3$, 69421-31-4; $IOs(Et_2dtc)_3$, 69421-32-5; $[Os(Et_2dtc)_3]BF_4$, 69421-34-7; $[(PPh_3)Os(Et_2dtc)_3]Cl$, 69421-35-8; $[(CH_3CN)Os(Et_2dtc)_3]Cl$, 69421-36-9; $[Os_2(Me_2dtc)_5]Cl$, 69493-68-1; $Os_2N(Et_2dtc)_5$, 63866-81-9; Os_2N-

$(Me_2dtc)_5$, 63866-82-0; $(NH_4)_2OsCl_6$, 12125-08-5; $K_2(NOsCl_5)$, 23209-29-2; $Fe(Et_2dtc)_3$, 13963-59-2.

References and Notes

(1) A. H. Dix, J. W. Diesveld, and J. G. M. van der Linden, *Inorg. Chim. Acta*, **24**, L51 (1977).
(2) P. B. Critchlow and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1367 (1975).
(3) D. J. Cole-Hamilton and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 2396 (1976).
(4) G. L. Miessler, E. Zoebisch, and L. H. Pignolet, *Inorg. Chem.*, **17**, 3636 (1978), and references cited therein.
(5) S. H. Wheeler, B. M. Mattson, G. L. Miessler, and L. H. Pignolet, *Inorg. Chem.*, **17**, 340 (1978), and references cited therein.
(6) K. W. Given and L. H. Pignolet, *Inorg. Chem.*, **16**, 2982 (1977).
(7) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).
(8) B. M. Mattson and L. H. Pignolet, *Inorg. Chem.*, **16**, 488 (1977).
(9) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972); R. L. Martin, N. M. Rohde, G. B. Robertson, and D. Taylor, *J. Am. Chem. Soc.*, **96**, 3647 (1974).
(10) K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **15**, 3152 (1976).
(11) B. M. Mattson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, **15**, 564 (1976).
(12) K. W. Given, B. M. Mattson, M. F. McGuiggan, G. L. Miessler, and L. H. Pignolet, *J. Am. Chem. Soc.*, **99**, 4855 (1977).
(13) C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2418 (1975).
(14) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **14**, 1894 (1975).
(15) A. F. Clifford and C. S. Kobayashi, *Inorg. Synth.*, **6**, 204 (1960).
(16) K. W. Given, G. M. Mattson, G. L. Miessler, and L. H. Pignolet, *J. Inorg. Nucl. Chem.*, **39**, 1309 (1977).
(17) K. W. Given, L. Maheu, S. H. Wheeler, and L. H. Pignolet, to be submitted for publication.
(18) The preparation of $Os[(CH_2)_4dtc]_3$ has also been reported; however, the compound was not characterized nor isolated in pure form: R. A. Bozis, *Diss. Abstr. Int. B*, **32**, 6268 (1972); cf. *Chem. Abstr.*, **77**, 108887 (1972).
(19) L. H. Pignolet, *Inorg. Chem.*, **13**, 2051 (1974).
(20) D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, **11**, 2843 (1972).
(21) The impure ROC/RIC $OsCl_3$ (hydrated) material can be identified by the presence of an IR absorption at 1139 cm^{-1} (KBr disk). No lot number was given on the sample and ROC/RIC has refused to believe that their product is impure, even when supplied with our data.
(22) L. H. Pignolet, *Top. Curr. Chem.*, **56**, 91 (1975).
(23) J. A. Pople, W. F. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959, p 223.
(24) Optical inversion is the interconversion of Δ and Λ isomers.
(25) S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.*, **95**, 1116 (1973).

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Circular Dichroism and Carbon-13 Nuclear Magnetic Resonance Studies of Some Phenyl-Substituted Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate Analogues

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The cobalt(III) complexes containing the *l*-stilbenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion, $[Co(l\text{-}sdta)]^-$, and the xylylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion, $[Co(xdta)]^-$, have been synthesized and characterized by circular dichroism and carbon-13 nuclear magnetic resonance spectroscopy. Both complexes are analogues of $[Co(edta)]^-$ (edta = ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion). The complex $[Co(l\text{-}sdta)]^-$ contains a benzene ring bonded to each carbon of the ethylenediamine backbone, producing two asymmetric centers. The formation of the complex is stereoselective, yielding only one optical isomer. The complex $[Co(xdta)]^-$ has a benzene ring incorporated into the ethylenediamine backbone, producing a seven-membered ring when coordinated. Although studies indicated that the complex may be somewhat labile, resolution by fractional recrystallization after diastereoisomer formation was successful. The absorption, circular dichroism, ^1H NMR, and ^{13}C NMR spectra are reported and compared to those of other cobalt(III) sexidentate complexes. The phenyl groups appear to be the cause of some unusual behavior.

Introduction

The two model compounds $[Co(l\text{-}sdta)]^-$ and $[Co(xdta)]^-$ (Figure 1) are related to $[Co(edta)]^-$, a complex which has been thoroughly investigated by absorption, circular dichroism (CD), and X-ray studies.[1,2] Van Saun and Douglas[3] reported a series of complexes where the strain in the chelate ring systems was varied, but the type of coordinated atoms was kept the same as for $[Co(edta)]^-$. The series included (1,3-propanediaminetetraacetato)cobaltate(III), $[Co(1,3\text{-}pdta)]^-$, and [*cis*(*N*)-bis(iminodiacetato)]cobaltate(III), *cis*-$[Co(ida)_2]^-$, in which the backbone diamine ring was enlarged and eliminated, respectively. The complex (ethylenediaminetetrapropionato)cobaltate(III), $[Co(edtp)]^-$, in which both the "in-plane" (G) and "out-of-plane" (R) rings were enlarged, was also included. The intensities of the visible absorption bands are less for these model compounds, as would be predicted because of the decrease in ring strain. However, the CD spectra show an increase in net rotational strength for the less-strained model complexes, a result not expected from some theories of optical activity.[4,5]

The complex ions (1,2-propanediaminetetraacetato)cobaltate(III), $[Co(pdta)]^-$, and (*trans*-1,2-cyclohexanediaminetetraacetato)cobaltate(III), $[Co(cdta)]^-$, were prepared by Dwyer and Garvan.[6] These compounds are related to $[Co(edta)]^-$, containing one and two asymmetric centers, respectively, in the backbone. They found that the preparation of both complexes is stereospecific; that is, only one isomer forms when an optically active ligand is used to synthesize the complex. This was due to the fact that the methyl group in the pdta complex prefers an equatorial position and the cyclohexanediamine ring in the edta complex prefers one particular conformation. Brennen et al.[7] reported the CD spectra of $(-)_{546}$-$[Co\text{-}(+)\text{-}pdta]^-$ and $(-)_{546}$-$[Co\text{-}(+)\text{-}cdta]^-$. They found that the spectrum of the pdta complex was very similar to the spectrum of $[Co(edta)]^-$, whereas, the spectrum of the cdta complex, while similar to the other two, showed a high-energy peak in the $^1T_{1g}$ region with greater intensity. The authors concluded that the asymmetric carbon in the pdta complex has little effect on the CD spectra; on the other hand, there was a greater contribution from the cdta ligand on the CD spectra. Soma and Mizukami[8] prepared a cobalt(III) complex which contains *cis*-2-butene-1,4-diamine-*N*,*N*,*N*′,*N*′-tetraacetate. A seven-membered ring is formed upon coordination. The CD and ^1H NMR spectra were similar to those of analogous complexes.

The two model complexes $[Co(l\text{-}sdta)]^-$ and $[Co(xdta)]^-$ were synthesized to study the effects of the benzene rings on the spectra. The polarizability theory of optical activity[9-14] indicates that phenyl groups, which possess a large and anisotropic polarizability, may exert a large influence on CD spectra. Also, it was of interest to investigate the stereospecificity of complex formation of $[Co(l\text{-}sdta)]^-$.

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