temperature of $[C_3H_{12}N_2](CuCl_4)$ (13.5 K) with that observed for $[CH_3NH]_2(CuCl_4)$ (8.91 K), a 5.5-K increase in transition temperature accompanying a 0.85-Å decrease in interlayer separation. Besides this, there is also a change in the sign of the coupling between the layers. In $[CH_3NH_3]_2(CuCl_4)$ the Cu atoms sit at face-centered positions in the unit cell while in $[C_3H_{12}N_2](CuCl_4)$ the Cu atoms stack one above the other, and, consequently, from symmetry considerations, there is no cancelation of dipolar effects between the layers (vide supra).

Experiments to clarify some of the pecularities observed in $[C_3H_{12}N_2](CuCl_4)$, with particular attention to the anisotropy in this material, are currently under way in this laboratory on x-ray size single crystals using a highly sensitive susceptometer.

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Registry No. $[NH_3C_3H_6NH_3](CuCl_4)$, 60553-51-7.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Synthesis, Properties, and X-Ray Structural Characterization of a Novel Seven-Coordinate Halogenotris(dithiocarbamato) Complex of Ruthenium(IV)

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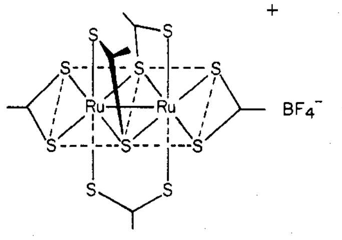
The synthesis of several new oxidation products of tris(*N,N'*-disubstituted dithiocarbamato)ruthenium(III), $Ru(R_2dtc)_3$, where R = C_2H_5 and CH_3 is described. Photolysis of $Ru(Et_2dtc)_3$ in $CHCl_3$ or CH_2Cl_2 or reaction with gaseous HCl in benzene yields two new chlorine-containing compounds. One of the compounds is green and is formulated as $Ru(Et_2dtc)_3Cl$. The crystal structure of this compound has been determined by three-dimensional single-crystal x-ray analysis. The space group is $P2_1/c$ with lattice constants $a = 9.077$ (3) Å, $b = 10.244$ (3) Å, $c = 27.805$ (13) Å, and $\beta = 93.06$ (3)°. The structure was solved by conventional heavy-atom techniques and refined by least-squares methods to a conventional R of 0.055 for 1061 independent reflections. The density of 1.50 g/cm^3 computed from the unit cell volume of 2582 Å^3 on the basis of four $Ru[S_2CN(C_2H_5)_2]_3Cl$ molecules per unit cell agrees well with the 1.53 g/cm^3 determined by flotation methods. The structure consists of well-separated monomeric molecules, each composed of three bidentate Et_2dtc ligands and a chlorine atom with the donor atoms arranged in a distorted pentagonal-bipyramidal configuration around the ruthenium(IV) ion. Two Et_2dtc ligands span equatorial positions while one spans an equatorial and an axial position. The chlorine atom occupies the other axial position. The average Ru–S distance is 2.40 Å and the distances between adjacent sulfur atoms in the equatorial plane are very similar and range from 2.75 to 3.02 Å, all of which are much shorter than the van der Waals contact distance of 3.4 Å. The reaction chemistry of $Ru(Et_2dtc)_3Cl$ is discussed, the most notable reaction being with $AgBF_4$ in acetone solution which yields $[Ru_2(Et_2dtc)_5]BF_4$, thiuram disulfide, and $Ru(BF_4)_3$. The general nature of the oxidation reaction of $Ru(R_2dtc)_3$ is discussed and related oxidation reactions with iodine are described. ^1H NMR properties of $Ru(Et_2dtc)_3Cl$ are also discussed in detail.

Introduction

Recently there have been several reports[1-3] of interesting dimeric cationic metal dithiocarbamato complexes with the stoichiometry $M_2(R_2dtc)_5^+$ where M = ruthenium(III),[1] cobalt(III),[2] and rhodium(III)[3] and R_2dtc = *N,N'*-disubstituted dithiocarbamate. In the case of ruthenium when R = Et (Et = ethyl), a novel triply bridged metal–metal bonded complex I[1,4] is found, whereas the cobalt and rhodium analogues where R = Et and Me (Me = methyl), respectively, have structure II.[2,3] These diamagnetic complexes are syn-



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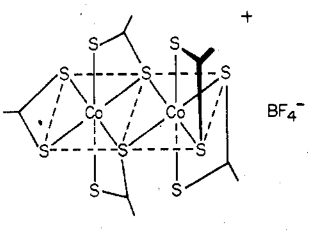

II

thesized in good yield by air oxidation of $M(R_2dtc)_3$ using boron trifluoride gas in benzene solution.[5] Under identical reaction conditions,[6] $Fe(R_2dtc)_3$ and $Mn(R_2dtc)_3$ are completely converted into monomeric cationic tris-chelate complexes of Fe(IV) and Mn(IV).[7,8] The iron(IV) complex with $R_2 = (CH_2)_4$ has a trigonally twisted tris-chelate geometry ($\sim D_3$)[7] and is paramagnetic ($S = 1$, $\mu_{eff} = 3.22\ \mu_B$).[6]

In order to elucidate the mechanism of the oxidation reaction of $Ru(R_2dtc)_3$ and to understand the conditions which govern whether ligand or metal is oxidized, we have carried out several new reactions employing chemical and photochemical methods. We wish to report here several new oxidation products of $Ru(R_2dtc)_3$ which result from photochemical reaction with $CHCl_3$ or CH_2Cl_2 and chemical reaction with HCl and iodine. The structure of one of these products which has the formula $Ru(Et_2dtc)_3Cl$ has been determined by x-ray diffraction. The reaction chemistry and NMR properties of this and related compounds will also be discussed.

Experimental Section

Synthesis and Characterization Data. Photolysis of an ca. 0.01 M solution of $Ru(Et_2dtc)_3$ in freshly purified and degassed $CHCl_3$ or CH_2Cl_2 with unfiltered radiation from a mercury vapor lamp changes the color of the solution from red-brown to light orange in ca. 1 h. The residue remaining after solvent evaporation was chromatographed on a silica gel column and eluted with benzene, acetone, and methanol solvents, respectively. The first two solvent fractions yielded only unreacted $Ru(Et_2dtc)_3$ while the methanol fraction contained a brown compound, III, in good yield. Compound III is insoluble in benzene but quite soluble in acetone, chloroform, and dichloromethane and slowly decomposes after prolonged storage (several months) in solid or solution phases. One of the decomposition products is a green compound, IV, which is soluble in benzene and can be isolated by column chromatography on silica gel using acetone as eluent.[36] Compounds III and IV can be simultaneously synthesized in high yield by reaction of $Ru(Et_2dtc)_3$ with gaseous HCl in benzene solution. Column chromatography as outlined above yielded compounds IV and III in the acetone and methanol fractions, respectively.

Pure IV is stable and was recrystallized from CH_2Cl_2–heptane to yield green rectangular needles. The compound is diamagnetic in solid and solution phases. Elemental analysis of compound IV is consistent with its formulation as $Ru(Et_2dtc)_3Cl$. Anal. Calcd for $RuC_{15}H_{30}ClN_3S_6$: C, 31.00; H, 5.20; Cl, 6.10. Found: C, 31.50; H, 5.17; Cl, 6.34. The ^1H NMR spectrum of compound IV dissolved in $CDCl_3$ shows one ethyl group at τ 8.66 (triplet, CH_3; $J = 7.1$ Hz) and 6.25 (quartet, CH_2; $J = 7.1$ Hz). The ir spectrum (KBr disk) shows two ($C\overset{...}{-}N$) absorptions at 1513 and 1500 cm^{-1} compared with one at 1490 cm^{-1} for $Ru(Et_2dtc)_3$. Other features of the ir spectrum are very similar to $Ru(Et_2dtc)_3$ in the region 4000–700 cm^{-1}. The uv–vis spectrum recorded in CH_2Cl_2 shows the following bands (λ_{max}, ϵ): 271 nm, 50 100 $M^{-1}\ cm^{-1}$; 352 (sh) nm, 9700 $M^{-1}\ cm^{-1}$; 429 (sh) nm, 830 $M^{-1}\ cm^{-1}$; 536 (sh) nm, 220 $M^{-1}\ cm^{-1}$. Conductivity in nitromethane at 25 °C yielded an equivalent conductance, Λ_M, of 22 $\Omega^{-1}\ cm^2\ mol^{-1}$ compared with 87 and 90 $\Omega^{-1}\ cm^2\ mol^{-1}$ for $[Fe(Et_2dtc)_3]BF_4$ and $[Ru_2(Et_2dtc)_5]BF_4$, respectively.[1]

Compound III is also diamagnetic in solid and solution and has an ir spectrum (KBr disk) which is identical with that of IV. Its ^1H NMR spectrum recorded in $CDCl_3$ reveals at least two nonequivalent ethyl groups neither of which exactly match the chemical shifts of the ethyl resonances of IV. The uv–vis spectrum recorded in CH_2Cl_2 shows the following bands (λ_{max}): 262, 288, 329 (sh), 436 (sh), 555 (sh), 950 (broad) nm. Work is in progress on the determination of the formula and structure of compound III.

X-Ray Analysis. The compound crystallizes as green rectangular needles which usually grow together in fan-shaped clusters. After numerous attempts to find a satisfactory single crystal failed, a small crystal of dimensions 0.28 × 0.10 × 0.16 mm^3, elongated parallel to c, was selected for data collection. The compound crystallizes in the monoclinic space group $P2_1/c$ as determined by systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) using Weissenberg film data (Cu Kα radiation). The unit cell dimensions are $a = 9.077$ (3) Å, $b = 10.244$ (3) Å, $c = 27.805$ (13) Å, $\beta = 93.06$ (3)°, and $V = 2582$ Å^3 and were determined by least-squares refinement using θ angle values for 13 Mo Kα (λ 0.7107 Å) peaks which were carefully centered with a diffractometer. The range of θ values used was 9.3–17.3°. The measured density is 1.53 (3) g/cm^3 from flotation which is in good agreement with the calculated value of 1.50 g/cm^3, with four molecules per unit cell.

Intensity data were collected on a four-circle Hilger and Watts automatic diffractometer using Zr-filtered Mo Kα radiation out to θ of 21°. A total of 2539 independent reflections were collected over one quadrant and 1061 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in solution and refinement of the structure. Three standard reflection intensities were checked at intervals of 25 sequential reflections. No changes greater than 3% from the average value and no trends with time in the check reflections were noted.

The data were processed in the manner described by Corfield, Doedens, and Ibers;[9] the value of 0.03 was used for p in the $\sigma(I)$ equation. The intensity data were corrected for Lorentz and polarization effects but not for absorption due to the small size of the crystal ($\mu = 11.6\ cm^{-1}$). Conventional heavy-atom techniques were used to solve the structure, and refinement[10] with the ruthenium, six sulfur, and chlorine atoms thermally anisotropic and all other nonhydrogen atoms thermally isotropic (145 variables) by full-matrix least-squares methods has converged to values of 0.055 and 0.017 for the conventional R and r indices, respectively.[11] A final Fourier map did not show any unusual electron density.

The final atomic coordinates with their standard deviations and the final anisotropic and isotropic thermal parameters with their standard deviations are given in Table I. A table of observed and calculated structure factors is available (supplementary material).

Infrared spectra were recorded on a Perkin-Elmer Model 237 grating instrument. Electronic absorption spectra were obtained at 25 °C using a Cary Model 14 spectrophotometer and NMR spectra were recorded on a Varian XL-100 instrument. Photolysis was carried out on degassed solutions under purified nitrogen at ca. 30 °C contained in quartz reaction vessels using unfiltered radiation from a 450-W Hanovia medium-pressure mercury vapor lamp. Conductivity experiments were carried out using a Yellow Springs Instrument Co. Model 31 conductivity bridge. The reagent grade nitromethane and spectrograde 1,2-dichloroethane solvents were used without purification.

Results and Discussion

X-Ray Analysis. An x-ray diffraction study of compound IV was undertaken because the stereochemistry of the compound could not be determined by conventional spectroscopy. The NMR spectrum shows all ethyl groups to have identical magnetic environments on the NMR time scale even at −90 °C in CD_2Cl_2 and the diamagnetism suggests a coordination number other than 6.[13] The results of the x-ray analysis confirm the formulation of IV as $Ru(Et_2dtc)_3Cl$. The structure consists of well-separated monomeric molecules, each composed of three bidentate Et_2dtc ligands and a chlorine atom with the donor atoms arranged in a distorted pentagonal-bipyramidal (PBP) configuration around the ruthenium atom. Figures 1 and 2 show a labeled and a stereoscopic drawing of the molcule, respectively. Selected bond lengths and angles in the RuS_6Cl core and their estimated standard deviations are listed in Table II. The bond lengths and angles in the ligands are in good agreement with those of other dtc complexes[1,14] and are listed with their estimated standard deviations in Table III.

The structure of the RuS_6Cl core is very similar to that of $Mo((n\text{-}Bu)_2dtc)_3NO$ (n-Bu = n-butyl).[15] In both structures two dtc ligands span equatorial positions while one spans an

Table I. Final Atomic Fractional Coordinates and Thermal Parameters with Standard Deviations for $Ru(Et_2dtc)_3Cl$

Atom	x	y	z	B, Å^2
Ru	0.1561 (3)[a]	0.0611 (2)	−0.1429 (1)	3.3 (1)[b]
S(A1)	0.2963 (8)	0.2276 (7)	−0.1008 (3)	4.1 (3)[b]
S(A2)	0.0909 (8)	0.2613 (7)	−0.1796 (3)	4.3 (3)[b]
S(B1)	−0.0824 (9)	−0.0460 (9)	−0.1494 (3)	4.9 (2)[b]
S(B2)	0.0115 (8)	0.1186 (7)	−0.0750 (3)	4.2 (2)[b]
S(C1)	0.1362 (7)	−0.0416 (7)	−0.2215 (2)	4.0 (2)[b]
S(C2)	0.3959 (7)	0.0349 (7)	−0.1746 (2)	3.8 (2)[b]
Cl	0.2374 (8)	−0.1316 (7)	−0.0967 (3)	4.3 (2)[b]
C(A)	0.1966 (29)	0.3397 (26)	−0.1364 (10)	4.2 (7)
N(A)	0.1979 (27)	0.4689 (25)	−0.1276 (8)	6.1 (6)
C(A1)	0.2942 (37)	0.5229 (30)	−0.0890 (12)	7.1 (9)
C(A2)	0.0915 (33)	0.5614 (36)	−0.1555 (11)	7.0 (8)
C(A3)	0.1991 (39)	0.5351 (37)	−0.0459 (13)	9.4 (10)
C(A4)	0.1742 (42)	0.5986 (36)	−0.2005 (14)	9.5 (11)
C(B)	−0.1217 (28)	0.0126 (23)	−0.0946 (9)	3.4 (6)
N(B)	−0.2370 (24)	−0.0226 (20)	−0.0691 (7)	4.4 (5)
C(B1)	−0.3388 (32)	−0.1253 (29)	−0.0870 (11)	5.8 (8)
C(B2)	−0.2574 (26)	0.0401 (26)	−0.0205 (8)	4.1 (6)
C(B3)	−0.2960 (38)	−0.2600 (35)	−0.0646 (13)	8.7 (10)
C(B4)	−0.3732 (35)	0.1460 (30)	−0.0294 (11)	6.6 (8)
C(C)	0.3243 (25)	−0.0544 (27)	−0.2209 (8)	3.1 (5)
N(C)	0.3970 (23)	−0.1210 (20)	−0.2530 (8)	4.0 (5)
C(C1)	0.3207 (31)	−0.1963 (27)	−0.2917 (10)	4.9 (7)
C(C2)	0.5620 (32)	−0.1342 (27)	−0.2452 (10)	5.5 (7)
C(C3)	0.3302 (38)	−0.1212 (33)	−0.3405 (12)	8.7 (11)
C(C4)	0.5967 (31)	−0.2558 (28)	−0.2137 (11)	5.7 (8)

Atom	$10^4\beta_{11}$[c]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ru	112 (4)	63 (2)	12 (1)	−1 (4)	5 (1)	0 (1)
S(A1)	133 (14)	65 (9)	17 (2)	−6 (10)	−3 (4)	−3 (3)
S(A2)	146 (13)	73 (10)	16 (2)	19 (10)	−7 (4)	2 (3)
S(B1)	147 (13)	138 (10)	14 (1)	−37 (12)	11 (3)	−9 (4)
S(B2)	128 (13)	101 (10)	14 (1)	−4 (9)	13 (3)	−9 (3)
S(C1)	117 (12)	101 (9)	13 (1)	2 (10)	5 (3)	−4 (3)
S(C2)	101 (11)	91 (10)	14 (1)	−9 (9)	5 (3)	0 (3)
Cl	178 (14)	63 (8)	14 (1)	17 (10)	9 (4)	4 (3)

[a] The numbers in parentheses in this and succeeding tables represent the estimated standard deviations of the last significant figure(s). [b] Atoms refined anisotropically: equivalent isotropic B reported. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

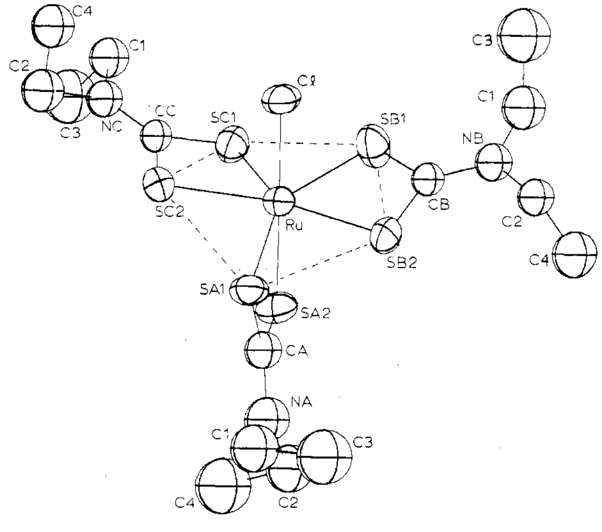

Figure 1. ORTEP drawing of the molecule $Ru(Et_2dtc)_3Cl$ showing the labeling scheme and the approximate pentagonal-bipyramidal geometry. Ellipsoids are 50% probability surfaces.

Table II. Selected Interatomic Distances and Angles in the RuS_6Cl Core[a]

	Distances, Å		
Ru–S(A1)	2.397 (7)	S(A1)–S(B2)	2.939 (10)
Ru–S(A2)	2.352 (7)	S(A1)–S(C2)	3.021 (10)
Ru–S(B1)	2.425 (8)	S(B1)–S(C1)	2.896 (9)
Ru–S(B2)	2.428 (8)	S(A2)–S(B1)	3.638 (11)
Ru–S(C1)	2.423 (7)	S(A2)–S(B2)	3.366 (11)
Ru–S(C2)	2.407 (7)	S(A2)–S(C1)	3.349 (10)
Ru–Cl	2.448 (7)	S(A2)–S(C2)	3.609 (10)
S(A1)–S(A2)	2.823 (11)	Cl–S(B1)	3.301 (10)
S(B1)–S(B2)	2.766 (10)	Cl–S(B2)	3.356 (10)
S(C1)–S(C2)	2.746 (10)	Cl–S(C1)	3.661 (10)
Cl–S(A1)	3.721 (9)	Cl–S(C2)	3.164 (10)
	Angles, Deg		
S(A1)–Ru–S(A2)	72.9 (3)	S(A2)–Ru–S(B1)	99.2 (3)
S(B1)–Ru–S(B2)	69.5 (3)	S(A2)–Ru–S(B2)	89.5 (3)
S(C1)–Ru–S(C2)	69.3 (2)	S(A2)–Ru–S(C1)	89.0 (3)
S(A1)–Ru–S(B2)	75.1 (3)	S(A2)–Ru–S(C2)	98.6 (3)
S(A1)–Ru–S(C2)	78.0 (3)	Cl–Ru–S(A1)	100.3 (3)
S(B1)–Ru–S(C1)	73.3 (2)	Cl–Ru–S(B1)	85.3 (3)
S(A2)–Ru–Cl	173.0 (3)	Cl–Ru–S(C1)	97.4 (3)
Cl–Ru–S(B2)	87.0 (3)	Cl–Ru–S(C2)	81.4 (3)

[a] For numbering system see Figure 1.

Table III. Interatomic Distances (Å) and Angles (deg) in the Ligands[a]

	Ligand A	Ligand B	Ligand C
	Distances		
S(1)–C	1.74 (3)	1.69 (2)	1.71 (2)
S(2)–C	1.70 (3)	1.69 (2)	1.68 (2)
C–N	1.35 (4)	1.34 (3)	1.33 (3)
N–C(1)	1.46 (4)	1.47 (4)	1.47 (4)
N–C(2)	1.53 (4)	1.52 (3)	1.51 (4)
C(1)–C(3)	1.52 (5)	1.55 (5)	1.56 (4)
C(2)–C(4)	1.54 (5)	1.52 (4)	1.55 (4)
	Angles		
Ru–S(1)–C	86.8 (9)	90.2 (8)	89.9 (7)
Ru–S(2)–C	89.2 (10)	90.1 (9)	91.2 (9)
S(1)–C–S(2)	110 (1)	110 (1)	108 (1)
S(1)–C–N	123 (2)	126 (2)	124 (1)
S(2)–C–N	126 (2)	124 (2)	127 (2)
C–N–C(1)	120 (2)	120 (2)	122 (2)
C–N–C(2)	121 (2)	119 (2)	118 (2)
C(1)–N–C(2)	118 (2)	120 (2)	119 (2)
N–C(1)–C(3)	106 (3)	111 (2)	109 (2)
N–C(2)–C(4)	104 (3)	106 (2)	109 (2)

[a] For numbering system see Figure 1.

equatorial and an axial position. In IV the axial–equatorial ligand differs from the two ligands in the equatorial plane by having an S–S chelate "bite" distance and S–Ru–S "bite" angle which are larger by 0.067 Å and 3.5°, respectively, than the corresponding values of the equatorial dtc ligands. In addition, the Ru–S_{ax} distance is 0.06 Å longer than the average of the five essentially equivalent Ru–S_{eq} distances. The average Ru–S value of 2.40 Å is similar to those of 2.38 and 2.41 Å found in $Ru(Et_2dtc)_3$[14] and $[Ru_2(Et_2dtc)_5]BF_4$, respectively.

The pentagonal base of the RuS_6Cl core is puckered at the S(A1) position due to the geometrical constraints imposed by the small "bite" angle of the A ligand (72.9 (3)° compared to 90° for an ideal PBP). In addition, the Cl–Ru–S(A2) angle of 173.0 (3)° differs somewhat from linearity. The weighted least-squares plane containing S(B1), S(B2), S(C1), and S(C2) has the equation $-0.1281X + 0.5862Y - 0.7913Z - 0.1176 = 0$ and the following distances of atoms from the plane in Å: Ru, 0.17; S(A1), 0.87; S(B1), −0.24; S(B2), 0.15; S(C1), 0.24; S(C2), −0.15; Cl, −2.26. It should be noted that the distortions from planarity in the pentagonal base of $Ru(Et_2dtc)_3Cl$ are much more severe than those found in $Mo((n\text{-}Bu)_2dtc)_3NO$. The S–Ru–S angles in the pentagonal base are all close to the ideal PBP value of 72°, ranging from 69.3 to 79.0° with the intraligand S–Ru–S chelate "bite" angles being slightly smaller than the interligand S–Ru–S angles.

The Ru–Cl distance of 2.45 Å is long compared with 2.39 Å found in the dichloro(2,7-dimethyl-octa-2,6-diene-1,8-diyl)ruthenium(IV) dimer,[16] the only other structurally

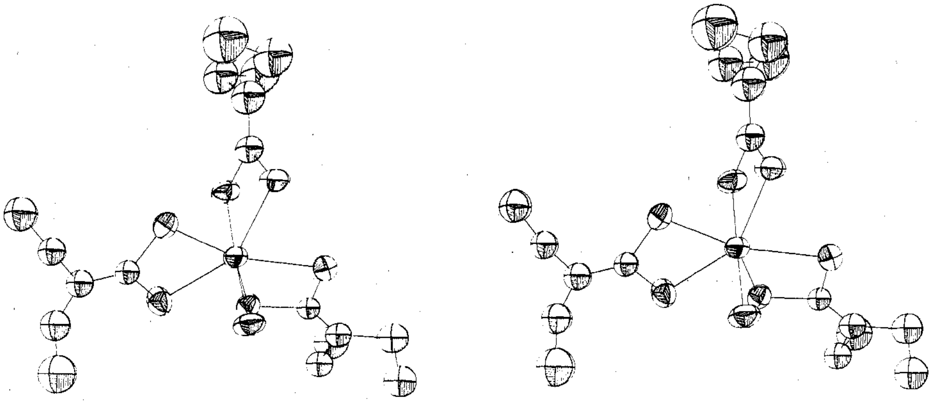

Figure 2. ORTEP stereoview of $Ru(Et_2dtc)_3Cl$ thermal ellipsoids. Ellipsoids are 50% probability surfaces.

characterized compound of Ru(IV) containing a Ru–Cl bond which we have found. Six-coordinate complexes of Ru(II) typically have Ru–Cl distances of 2.35–2.39 Å;[17] however, several compounds with distances in the range 2.43–2.51 Å are known.[18] Since Ru(IV) should have a smaller ionic radius than Ru(II) but seven-coordination should slightly increase the radius, it is difficult to estimate a reasonable Ru–Cl distance in $Ru(Et_2dtc)_3Cl$. However, the observed distance does seem long and this is consistent with the suspected lability of this bond (vide infra). The Cl–S distances range from 3.16 to 3.72 Å with an average value of 3.44 Å. Several of these distances are short compared with the Cl–S van der Waals contact distance of 3.65 Å.[19]

The distances between adjacent sulfur atoms in the equatorial plane are very similar and range from 2.75 to 3.02 Å, all of which are much shorter than the van der Waals contact distance of 3.4 Å.[20,21] The average interligand S–S distance in the equatorial plane is 2.95 Å which indicates that ligand–ligand interactions are operative and that they may help stabilize the equatorial pentagonal plane. Such interactions have been postulated in complexes of other 1,1- and 1,2-dithio ligands.[15,21] The $Ru(Et_2dtc)_3Cl$ molecular units are well separated in the unit cell. There are no abnormally short intermolecular distances.

Several structures have been reported[15,22-28] which have the tris-chelate PBP geometry and all have the same arrangement of the bidentate ligands as is found in $Ru(Et_2dtc)_3Cl$. It is interesting to note that $Ru(Et_2dtc)_3NO$ is six-coordinated with one of the dtc ligands monodentate.[29] This is not surprising since the complex contains a Ru(II) d^6 metal ion which has a marked preference for an octahedral t_{2g}^6 configuration. The bonding scheme for $Ru(Et_2dtc)_3Cl$ is similar to the one published for $Mo((n\text{-}Bu)_2dtc)_3NO$ [15] and details will not be discussed here. The diamagnetism results from a e_1^4 configuration assuming C_{5v} local symmetry.

^1H NMR Measurements. ^1H NMR spectra of IV recorded using $CDCl_3$ and CD_2Cl_2 solvents show resonances which are due to only one ethyl group. The resonances show no sign of exchange broadening down to −90 °C. Since in PBP geometry there are two nonequivalent dtc ligands (two $(dtc)_{eq}$ and one $(dtc)_{eq-ax}$) and in the limit of slow $S_2C–N$ bond rotation four nonequivalent ethyl environments result, the complex is stereochemically nonrigid. Accidental degeneracy of the resonances is not likely because nonequivalent methyl and methylene groups are clearly resolved in similar diamagnetic Et_2dtc and Me_2dtc complexes, for example, in $Mo(Me_2dtc)_3NO$,[30] $Ru(Me_2dtc)_3NO$,[31] and $[Ru_2(Et_2dtc)_5]BF_4$.[1] In addition, $S_2C–N$ bond rotation is most certainly slow on the ^1H NMR time scale at −95 °C.[32] The structure of IV is assumed to be the same in solid and solution since the solid (KBr disk) and solution ($CHCl_3$ solvent) ir spectra are identical and the solid uv–vis spectrum (Nujol) shows the same features as the solution spectrum.

The stereochemically nonrigid nature of $Ru(Et_2dtc)_3Cl$ probably results from metal-centered rearrangement rather than from dtc ligand exchange. An approximately equimolar mixture of $Ru(Et_2dtc)_3Cl$ and $Ru(Me_2dtc)_3Cl$ in $CDCl_3$ at 30 °C shows ^1H NMR resonances which are unshifted from their pure unmixed positions. In addition, a mixture of $Ru(Et_2dtc)_3Cl$ and $(Et_2dtc)_2$ in $CDCl_3$ solution also shows separate non-exchange-averaged Et resonances in the ^1H NMR resonances at 30 °C which argues against rapid dtc exchange via an oxidized ligand mechanism. The mechanism of the rearrangement could involve (i) a nondissociative polyhedral rearrangement of the PBP structure of the type discussed by Davis et al.[30] via a capped trigonal-prismatic geometry, (ii) partial dissociation of a dtc ligand followed by rearrangement of the six-coordinate structure followed by recombination, or (iii) dissociation of Cl^- and rearrangement of the $Ru(Et_2dtc)_3^+$ cation followed by recombination. The conductivity of $Ru(Et_2dtc)_3Cl$ in 1,2-dichloroethane indicates no measurable ionic dissociation ($\Lambda_M < 0.13\ \Omega^{-1}\ cm^2\ mol^{-1}$); however significant dissociation is observed in nitromethane but it is possible that this results from slight hydrolysis. $Ru(Et_2dtc)_3Cl$ also rapidly gives an AgCl precipitate upon reaction with Ag^+ in acetone solution (vide infra) which indicates that the Ru–Cl bond can be easily ruptured. All seven-coordinate complexes of the type $M(chelate)_3X$ where X = halide are stereochemically nonrigid [$Ti(R_2dtc)_3Cl$, R = Me and Et,[24] $Zr(acac)_3Cl$,[33] and $Zr(acac)_3Br$[33]] whereas $Mo(Me_2dtc)_3NO$ is rigid up to ~60 °C.[30] The former complexes all show slight ionic dissociation in ionizing solvents.[24,33] In addition, since $Mo(Me_2dtc)_3NO$ is a d^4 metal complex as is $Ru(Et_2dtc)_3Cl$ and since NO cannot dissociate because an irreversible oxidation to NO_2 would occur, mechanism (iii) is perhaps most reasonable. However, mechanisms (i) and (ii) cannot be ruled out. It is interesting to note that the six-coordinate complexes of Ru(II) $Ru(Me_2dtc)_3NO$[31] and $Rh(Me_2dtc)_3PPh_3$[30] are stereochemically rigid at 30 °C. This is not surprising, however, since low-spin d^6 complexes of octahedral geometry are particularly stable with respect to rearrangement or dissociation.

Reactions of $Ru(Et_2dtc)_3Cl$ and Synthesis of Related Compounds. Since one of the primary goals of this research has been to understand the factors which control the oxidation chemistry of $Ru(R_2dtc)_3$, several reactions of $Ru(Et_2dtc)_3Cl$ have been studied. It is surprising that a six-coordinate cationic complex of Ru(IV) has never been synthesized even though oxidation of analogous $Fe(R_2dtc)_3$ complexes via BF_3–air[6] or $FeCl_3$[34] gives the Fe(IV) cation $Fe(R_2dtc)_3^+$. In an attempt to synthesize $Ru(Et_2dtc)_3^+$, $Ru(Et_2dtc)_3Cl$ was reacted with $AgBF_4$ in acetone solution. An immediate precipitate of AgCl resulted and analysis of the other products by ir and ^1H NMR spectra and thin layer chromatography on silica gel, TLC, showed the presence of only $[Ru_2(Et_2dtc)_5]BF_4$ which has structure I, tetraethylthiuram disulfide, $(Et_2dtc)_2$, and $Ru(BF_4)_3$. The overall balanced reaction is

$$10Ru(Et_2dtc)_3Cl + 10AgBF_4 \rightarrow 10AgCl + 4[Ru_2(Et_2dtc)_5]BF_4 + 5(Et_2dtc)_2 + 2Ru(BF_4)_3$$

From this result it is apparent that $Ru(Et_2dtc)_3^+$ in the presence of BF_4^- is unstable with respect to decomposition into the dimeric Ru(III) complex I and oxidized ligand. This is consistent with electrochemical data which show that the wave associated with $Ru(Et_2dtc)_3 \xrightarrow{-e^-} Ru(Et_2dtc)_3^+$ in dimethylformamide with Et_4NClO_4 supporting electrolyte is irreversible.[1] On the other hand, reaction of $Ru(Et_2dtc)_3Cl$ with $NaEt_2dtc$ in acetone solution proceeds immediately giving $Ru(Et_2dtc)_3$, $(Et_2dtc)_2$, and NaCl according to the equation

$$2Ru(Et_2dtc)_3Cl + 2NaEt_2dtc \rightarrow 2Ru(Et_2dtc)_3 + (Et_2dtc)_2 + 2NaCl$$

The products were identified by ^1H NMR and ir spectra and TLC. Again Ru(IV) is reduced to Ru(III) but I is not produced. This result is surprising since $[Ru_2(Et_2dtc)_5]^+$ does not react with Et_2dtc^- even after several days in CH_3CN solution at 80 °C and implies that the formation of $[Ru_2(Et_2dtc)_5]^+$ depends on the anion. Hence in the presence of Et_2dtc^-, $Ru(Et_2dtc)_3Cl$ does not decompose into I. Further experiments are needed to fully understand the anionic dependence.

The synthesis of $Ru(Et_2dtc)_3Cl$ from HCl and $Ru(Et_2dtc)_3$ most likely involves the oxidative addition of a chlorine radical. Hydrogen gas is the probable by-product. The analogous reaction with $Fe(Et_2dtc)_3$ yields paramagnetic $Fe(Et_2dtc)_2Cl$ and HEt_2dtc. It is interesting that in the case of ruthenium the oxidation reaction products of $Ru(Et_2dtc)_3$ with HCl and BF_3–air are diamagnetic ($Ru(dtc)_3Cl$ and $[Ru_2(dtc)_5]BF_4$,[1] respectively), whereas the analogous iron products are paramagnetic ($Fe(dtc)_2Cl$[35] and $[Fe(dtc)_3]BF_4$,[6] respectively). This supports the well-known trend that the heavier transition metals prefer to have spin-paired electronic configurations. Another reaction which leads to a diamagnetic ruthenium complex results when iodine is added to $Ru(Me_2dtc)_3$ in $CHCl_3$ solution. Tiny gold crystals precipitate out of the reaction mixture immediately upon addition of iodine. Elemental analysis and molecular weight measurement lead to a molecular formula of $Ru(Me_2dtc)_3I_3$. Since this compound is also stereochemically nonrigid at −95 °C in CD_2Cl_2 solution, it is likely to be structurally similar to $Ru(Et_2dtc)_3Cl$. An x-ray analysis is in progress.

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Registry No. $Ru(Et_2dtc)_3Cl$, 60490-51-9; $Ru(Et_2dtc)_3$, 31656-15-2.

Supplementary Material Available: Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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(4) Compounds with the formulas $[Ru_2((i\text{-}Pr)_2dtc)_5]X$ where X = Cl and *i*-Pr = isopropyl and Ru_2Cl_6 were recently characterized by x-ray analysis to be structurally similar to II but with short Ru–Ru bonds (2.79 Å). These compounds were isolated in low yield as by-products in the preparation of $Ru((i\text{-}Pr)_2dtc)_3$ from $RuCl_3$ and $Na(i\text{-}Pr)_2dtc$: see C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2410 (1975).
(5) The other initial product of this reaction is most likely tetraalkylthiuram disulfide, $(R_2dtc)_2$, which undergoes oxidation to 3,5-bis(*N*,*N*-dialkyliminium)-1,2,4-trithiolane bis(tetrafluoroborate) under the reaction conditions. This later product has been confirmed in the case of M = Ru where R = CH_3 and C_2H_5.
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(10) Three local programs by Dr. L. W. Finger were used to solve and refine the structure: UMPREL for statistics and Patterson map; UMLSTSQ for full-matrix least-squares refinement; and BADTEA for bond distances, angles, and errors. All data processing was done with the Control Data 6600 computer at the University of Minnesota Computer Center.
(11) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $r = \sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4$; the numerator or r was the function minimized; the weights were $1/[\sigma(F^2)]^2$ where $\sigma(F_o^2) = \sigma(I)/Lp$. Atomic scattering factors were taken from "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A (S, C, N, and Cl) and Table 3.3.1B (Ru). Anomalous dispersion corrections from the same source (Table 3.3.2C) were used for ruthenium: $\Delta f' = -1.2$, $\Delta f'' = 1.1$.
(12) Purification of $CHCl_3$ and CH_2Cl_2 solvents was carried out by distillation from BaO under nitrogen and column chromatography on activated alumina just prior to use.
(13) Ru(IV), d^4, should be paramagnetic for octahedral or slightly distorted octahedral geometries. The six-coordinate Fe(IV) compound $[Fe(R_2dtc)_3]BF_4$ has $S = 1$.
(14) See, for example, L. H. Pignolet, *Inorg. Chem.*, **13**, 2051 (1974).
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(36) **Note Added in Proof.** Compound IV is not reproducibly prepared from the decomposition of III and the procedure using HCl is more reliable.