$\varepsilon_1 d_{xz} + (1-\varepsilon_1)\pi_L^* \quad \varepsilon_2 d_{xz} + (1-\varepsilon_2)\pi_L^*$

$\varepsilon_1 < \varepsilon_2$

$\nu_1 > \nu_2$

19a   19b

π system and, consequently, larger ring-current effect.

Although ^{13}C NMR data are scarcer due to the low solubility of the studied compounds, some trends similar to those found for ^1H appear. Both types of equatorial carbon atoms are shifted to lower fields than in the free ligand, in agreement with the results of Kohler et al.[28] Also, for the α-carbon atoms of the axial ligand the upfield shifts follow the order 2,6-Me$_2$pz > 4-NCpy > Me$_2$pzol, coincident with eq 2. Substituting CN$^-$ for Cl$^-$ produces variations on the signals of both equatorial and axial methylic carbon atoms (for L = 2,6-Me$_2$pz, compounds **15** and **3**) in the same direction as for the corresponding protons (eq 3) but a change in the chemical shift of C_α opposite to that observed for H_α. This

fact is probably not attributable to a failure of the proposed model but due to the fact that C_α lies close to the nodal surface between shielding and deshielding regions, and significative changes in the trans ligand might result in a change of the direction of the effect experienced by those nuclei.

The idea of linking cis and trans influences through conjugation of the π-electron systems of axial and equatorial ligands might be very useful for the understanding of structural and spectral information of a family of related compounds. Thus, the ligand sequences of eq 2 and 3 could be regarded as the order of increasing π-acceptor ability or decreasing π-donor ability of the axial ligands. However, any extrapolation of the relationships presented here must be taken cautiously unless a careful study of other families of coordination compounds with analogous characteristics is undertaken.

Registry No. 1, 102920-09-2; 2, 102920-10-5; 3, 102920-11-6; 4, 102920-12-7; 5, 102920-13-8; 6, 102920-14-9; 7, 102920-15-0; 8, 102920-16-1; 9, 102920-17-2; 10, 102920-18-3; 11, 102920-19-4; 12, 102920-20-7; 13, 102920-21-8; 14, 102940-11-4; 15, 102920-22-9; 16, 102920-23-0; Co(dmgH)$_2$Cl(H$_2$O), 33896-76-3; Co(dpgH)$_2$Cl(H$_2$O), 36795-68-3; Co(dmgH)$_2$Br(PPh$_3$), 33988-32-8.

Supplementary Material Available: A table of analytical data for the compounds studied in this paper and listings of isotropic thermal parameters, atomic coordinates of hydrogen atoms, anisotropic thermal parameters, and bond lengths and angles for **1, 3, 5,** and **13** (23 pages). Ordering information is given on any current masthead page.

Contribution from Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853

Stereochemistry and Metal-Centered Rearrangements of Eight-Coordinate Niobium(V) and Tantalum(V) Dithiocarbamates and Monothiocarbamates[1]

John R. Weir and Robert C. Fay*

Eight-coordinate niobium(V) and tantalum(V) N,N-disubstituted dithiocarbamato and monothiocarbamato complexes of the type [Nb(Me$_2$dtc)$_4$]Cl, [Ta(R^1,R^{2}dtc)$_4$][TaCl$_6$] (R^1,R^2 = Me,Me; *i*-Bu,*i*-Bu; Me,*i*-Pr; Me,Ch; Me,Ph), [Ta(Me,Bzdtc)$_4$][TaBr$_6$], [Nb(Me$_2$mtc)$_4$][NbCl$_6$], and [Ta(Me$_2$mtc)$_4$][TaCl$_6$] have been prepared by reaction of the metal pentahalides with anhydrous sodium salts of the ligands in dichloromethane. The complexes were characterized by elemental analysis, conductance measurements, and IR and ^1H NMR spectroscopy. Low-temperature ^1H NMR spectra of [Nb(Me$_2$dtc)$_4$]Cl and [Ta(Me$_2$dtc)$_4$][TaCl$_6$] are consistent with a dodecahedral *mmmm-D$_{2d}$* cation, while spectra of the unsymmetrical dithiocarbamato complexes suggest the presence of an equilibrium mixture of *mmmm* stereoisomers that differ in the distribution of methyl groups between the dodecahedral A and B sites. The low-temperature spectra of [Ta(Me$_2$mtc)$_4$][TaCl$_6$] are consistent with the dodecahedral *mmmm-C$_{2v}$* isomer, in which the four sulfur atoms are clustered in all-cis positions, but the predominant cationic solution species in the case of [Nb(Me$_2$mtc)$_4$][NbCl$_6$] appears to be a *mmmm-C$_s$* isomer. The kinetics of metal-centered rearrangement have been studied by total line-shape analysis; barriers ΔG^* are 10–12 kcal/mol for the dtc complexes and 14–15 kcal/mol for the mtc complexes. The higher rearrangement barriers for the mtc complexes point to a polytopal rearrangement mechanism.

Introduction

Niobium and tantalum form a variety of complexes with bidentate *N,N*-dialkyldithiocarbamate ligands, R$_2$dtc$^-$ (**1**; R = Me, Et, CH$_2$Ph, $^1/_2$(CH$_2$)$_4$).[2] Most of these complexes may be as-

I
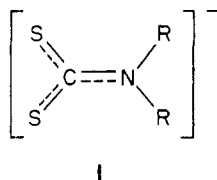
signed to one of the following classes: (i) homoleptic niobium(IV) and tantalum(V) dithiocarbamates of composition Nb(R$_2$dtc)$_4$ and Ta(R$_2$dtc)$_5$;[3–6] (ii) pentagonal-bipyramidal oxo, sulfido, and nitrene complexes of the type MY(R$_2$dtc)$_3$ (M = Nb or Ta; Y = O, S, or NR', where R' is alkyl or aryl);[7–13] (iii) pentagonal-

(1) Presented in part at the Twenty-third International Conference on Coordination Chemistry, Boulder, CO, July 29–Aug 3, 1984; see *Abstracts of Papers*, p 268.

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Table I. Color, Analytical, and Conductance Data

| | | anal.,[a] % | | | | | conductance data[b] | |
| | | C | H | N | halide | Nb (Ta) | concn × 10³, M | molar conductance, Ω^{-1} cm² mol⁻¹ |
compd	color							
[Nb(Me₂dtc)₄]Cl·CH₂Cl₂	dark brown	22.35	3.67	8.06		13.46	1.0	39
		(22.49)	(3.78)	(8.07)		(13.38)		
[Ta(i-Bu₂dtc)₄][TaCl₆]	orange	31.03	5.28	3.95	15.08	26.07	1.0	55
		(31.06)	(5.21)	(4.02)	(15.28)	(26.00)		
[Ta(Me,i-Prdtc)₄][TaCl₆]	orange	20.47	3.50	4.51	17.96	31.21	1.2	51
		(20.57)	(3.45)	(4.80)	(18.22)	(30.99)		
[Ta(Me,Chdtc)₄][TaCl₆]	orange	28.81	4.30	4.27	16.24	27.06	1.0	58
		(28.94)	(4.25)	(4.22)	(16.02)	(27.25)		
[Ta(Me,Phdtc)₄][TaCl₆]	orange	29.45	2.52	4.20	15.62	27.70	1.0	45
		(29.48)	(2.47)	(4.30)	(16.32)	(27.76)		
[Ta(Me,Bzdtc)₄][TaBr₆]	orange	26.79	2.55	3.49	29.04	22.05	1.0	27
		(26.58)	(2.48)	(3.44)	(29.48)	(22.25)		
[Nb(Me₂mtc)₄][NbCl₆]	red	16.74	3.03	6.57	25.61	20.21	1.1	30
		17.23	2.90	6.50	31.16	23.83		
		(17.68)	(2.97)	(6.87)	(26.10)	(22.80)		
[Ta(Me₂mtc)₄][TaCl₆]	yellow	14.65	2.53	5.63	24.62	38.35	1.5	47
		14.12	2.53	5.48	23.51	36.65		
		(14.54)	(2.44)	(5.65)	(21.46)	(36.51)		

[a] Calculated values in parentheses. [b] In dichloromethane at 25.00 ± 0.05 °C.

bipyramidal mixed-ligand complexes of the type MX(OMe)₂-(R₂dtc)₂ (M = Nb, Ta; X = Cl, Br, NCS);[14,15] (iv) 1:1 electrolytes of composition M(R₂dtc)₄X and M(R₂dtc)₂X₃ (M = Nb, Ta; X = Cl, Br).[9,16,17] Compounds in the latter class have been formulated as [M(R₂dtc)₄]X and [M(R₂dtc)₄][MX₆] salts,[9] and this has been confirmed for crystalline [Ta(Me₂dtc)₄]Cl·CH₂Cl₂,[16,17] [Ta(Me₂dtc)₄][TaCl₆]·0.5CH₂Cl₂,[16,17] and [Nb(Et₂dtc)₄]Br[12] by X-ray diffraction. All three compounds contain an eight-coordinate D₂d dodecahedral cation, represented schematically in **2**; the bidentate dithiocarbamate ligands span the m polyhedral edges, which connect dodecahedral A and B sites.

2
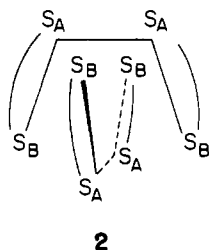
A preliminary communication from this laboratory[16] reported variable-temperature ¹H NMR spectra of the [Ta(Me₂dtc)₄]⁺ cation. The presence of two equally intense methyl resonances below the coalescence temperature of −62 °C suggested that the same mmmm-D₂d stereoisomer (**2**) is present in solution. [Ta(Me₂dtc)₄]⁺ was the first reported example of an eight-coordinate tetrakis chelate that becomes stereochemically rigid on the NMR time scale.

The purpose of the present work was to explore further the stereochemistry and metal-centered rearrangements of Nb(V) and Ta(V) tetrakis chelates, especially complexes that contain unsymmetrical bidentate ligands. Reported herein are syntheses and ¹H NMR studies of [Nb(Me₂dtc)₄]Cl, [Ta(R¹,R²dtc)₄][TaCl₆] (R¹,R² = Me,Me; i-Bu,i-Bu; Me,i-Pr; Me,Ch (Ch = cyclohexyl); Me,Ph), [Ta(Me,Bzdtc)₄][TaBr₆] (Bz = benzyl), [Nb-

(Me₂mtc)₄][NbCl₆], and [Ta(Me₂mtc)₄][TaCl₆] (Me₂mtc = N,N-dimethylmonothiocarbamate). To our knowledge, monothiocarbamato complexes of niobium and tantalum have not been reported previously.

Experimental Section

Reagents and General Techniques. Sodium salts of the N,N-dialkyldithiocarbamate ligands Na(R¹,R²dtc), were prepared by reaction in aqueous solution (10–15 °C) of equimolar amounts of the appropriate secondary amine, carbon disulfide, and sodium hydroxide.[18] Secondary amines were obtained from commercial sources except for N-methylisopropylamine [bp 48–51 °C (745 Torr) (lit.[19] bp 50 °C (760 Torr))], which was synthesized by reduction of N-formylisopropylamine with LiAlH₄.[20] The Na(R¹,R²dtc) salts were dried in vacuo over phosphorus pentoxide, first at room temperature and then at 110 °C for at least 2 weeks. Anhydrous sodium N,N-dimethylmonothiocarbamate was prepared as described by Hawthorne et al.[21]

Niobium(V) chloride, tantalum(V) chloride, and tantalum(V) bromide (all from Alfa-Ventron) were used as received without further purification. Solvents were dried by refluxing over calcium hydride for at least 24 h and distilling immediately prior to use.

Because the niobium and tantalum complexes are susceptible to hydrolysis, they were prepared and handled under anhydrous conditions in a dry-nitrogen atmosphere.

Tetrakis(N,N-dimethyldithiocarbamato)niobium(V) Chloride–Dichloromethane ([Nb(Me₂dtc)₄]Cl·CH₂Cl₂). Na(Me₂dtc) (3.49 g, 24.4 mmol) was added to a slurry of niobium(V) chloride (1.22 g, 4.52 mmol) in 50 mL of dichloromethane. The slurry was stirred at room temperature for 24 h during which time the color turned from dark red to dark brown. After filtration, addition of hexane (10 mL) to the filtrate afforded a small amount (~0.1 g) of a light brown powder. A further filtration and addition of hexane (20 mL) yielded dark brown crystals of [Nb(Me₂dtc)₄]Cl·CH₂Cl₂: yield 0.485 g (15.5%); mp 260–262 °C dec. Analytical data are included in Table I.

Tetrakis(N,N-dimethyldithiocarbamato)tantalum(V) Hexachlorotantalate(V)–Dichloromethane ([Ta(Me₂dtc)₄][TaCl₆]·CH₂Cl₂). This complex was prepared by reaction for 24 h of Na(Me₂dtc) (3.70 g, 25.8 mmol) with tantalum(V) chloride (1.82 g, 5.08 mmol) in refluxing dichloromethane (150 mL). Filtration of the reaction mixture and addition of hexane (50 mL) to the dark orange-yellow filtrate gave a mixture of yellow and orange crystals (~1 g), presumably [Ta(Me₂dtc)₄]Cl·CH₂Cl₂ and [Ta(Me₂dtc)₄][TaCl₆]·CH₂Cl₂, respectively.[17] A further filtration and addition of hexane (50 mL) afforded orange crystals of pure [Ta(Me₂dtc)₄][TaCl₆]·CH₂Cl₂ (0.683 g, 24% yield), which was identified by infrared and ¹H NMR spectra.[17]

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Tetrakis(*N*,*N*-diisobutyldithiocarbamato)tantalum(V) Hexachloro-tantalate(V) ([Ta(*i*-Bu₂dtc)₄][TaCl₆]). This compound was prepared by reaction for 24 h of Na(*i*-Bu₂dtc) (5.86 g, 25.8 mmol) and tantalum(V) chloride (1.88 g, 5.25 mmol) in refluxing dichloromethane (60 mL). Addition of benzene (60 mL) to the dark orange filtrate from the reaction mixture gave orange crystals of [Ta(i-Bu₂dtc)₄][TaCl₆]. A second crop of slightly impure product was obtained by addition of more benzene (30 mL). Both crops contained a small amount of benzene, which was removed by pumping (0.01 Torr) for 48 h at room temperature. Yield: first crop, 1.36 g (37%); second crop, 0.93 g (25%). The compound develops a wet appearance at 215 °C and decomposes to a red mass with bubble formation at 221.5–224 °C.

Tetrakis(*N*-methyl-*N*-isopropyldithiocarbamato)tantalum(V) Hexa-chlorotantalate(V) ([Ta(Me,*i*-Prdtc)₄][TaCl₆]). This complex was synthesized by reaction for 17 h at room temperature of Na(Me,*i*-Prdtc) (4.52 g, 26.4 mmol) with tantalum(V) chloride (1.93 g, 5.39 mmol) in 50 mL of dichloromethane. The product separated as a brown-orange oil upon addition of hexane (∼10 mL) to the filtrate from the reaction mixture. This oil, when cooled to −15 °C for 2 weeks, solidified to an orange-yellow powder, yield 0.780 g (25%). The powder decomposes to an orange oil at 233.5–236 °C and chars above 260 °C.

Tetrakis(*N*-methyl-*N*-cyclohexyldithiocarbamato)tantalum(V) Hex-achlorotantalate(V) ([Ta(Me,Chdtc)₄][TaCl₆]). Na(Me,Chdtc) (3.07 g, 14.5 mmol) was added over 30 min to a slurry of tantalum(V) chloride (1.97 g, 5.50 mmol) in 50 mL of dichloromethane that had been cooled to 0–5 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. After filtration, addition of hexane (50 mL) to the filtrate precipitated the product as an orange powder, yield 1.95 g (53%). The powder decomposes to a red mass at 249.5–253 °C, with rapid bubble formation above 255 °C.

Tetrakis(*N*-methyl-*N*-phenyldithiocarbamato)tantalum(V) Hexa-chlorotantalate(V) ([Ta(Me,Phdtc)₄][TaCl₆]). This complex was prepared by reaction for 14 h at 0–5 °C of Na(Me,Phdtc) (2.90 g 14.1 mmol) and tantalum(V) chloride (2.22 g, 6.20 mmol) in dichloromethane (50 mL). Addition of hexane (∼10 mL) to the filtrate from the reaction mixture gave a red-orange oil, which was redissolved in a minimum amount of dichloromethane. Subsequent addition of an equal volume of benzene precipitated an orange solid, [Ta(Me,Phdtc)₄][TaCl₆]·xC₆H₆, where $x \simeq 1$ on the basis of ¹H NMR spectra. The benzene was removed by heating the solid in vacuo at 80 °C for 24 h: yield 0.895 g (22%); mp 234–238 °C dec. A second crop of slightly impure product (0.41 g, 10%) was isolated.

Tetrakis(*N*-methyl-*N*-benzyldithiocarbamato)tantalum(V) Hexa-bromotantalate(V) ([Ta(Me,Bzdtc)₄][TaBr₆]). This compound was prepared from Na(Me,Bzdtc) (2.14 g, 9.76 mmol) and tantalum(V) bromide (2.41 g, 4.15 mmol) by a procedure similar to that employed for the synthesis of [Ta(Me,Phdtc)₄][TaCl₆]. Benzene was removed from the product, [Ta(Me,Bzdtc)₄][TaBr₆]·xC₆H₆ ($x \simeq 1$), by slurrying the orange solid in refluxing diethyl ether for 8 h and then evaporating the mixture to dryness in vacuo; yield 0.676 g (20%). A second crop (1.05 g, 31%) was isolated but could not be purified. The compound develops a wet appearance at 142–145 °C and decomposes to a viscous, red mass with rapid bubble formation at 160 °C.

Tetrakis(*N*,*N*-dimethylmonothiocarbamato)niobium(V) Hexachloro-niobate(V) ([Nb(Me₂mtc)₄][NbCl₆]). Na(Me₂mtc) (1.24 g, 9.75 mmol) was added to a slurry of niobium(V) chloride (0.942 g, 3.49 mmol) in 100 mL of dichloromethane that had been cooled to −78 °C. The reaction mixture was stirred for 18 h at −78 °C and then filtered at −78 °C. Addition of two 10-mL portions of hexane to the filtrate followed by storage for 48 h at −25 °C after each addition precipitated an impure light orange powder. A further filtration and addition of hexane (10 mL) afforded a red, crystalline solid: yield 0.60 g (42%); mp 209–213 °C dec.

Tetrakis(*N*,*N*-dimethylmonothiocarbamato)tantalum(V) Hexa-chlorotantalate(V) ([Ta(Me₂mtc)₄][TaCl₆]). This compound was synthesized from Na(Me₂mtc) (1.47 g, 11.6 mmol) and tantalum(V) chloride (1.83 g, 5.11 mmol) by a procedure similar to that used for preparation of [Nb(Me₂mtc)₄][NbCl₆]. The filtrate from the reaction mixture was warmed from −78 to −25 °C. Addition of hexane in 10-mL portions gave yellow crystals of [Ta(Me₂mtc)₄][TaCl₆], yield 1.48 g (58%). The solid develops a wet appearance at 190 °C and decomposes to a yellow mass with bubble formation at 202–205 °C.

Analytical Data. Microanalyses (Table I) were determined by Galbraith Laboratories, Knoxville, TN, on samples submitted under a dry-nitrogen atmosphere. Duplicate analyses on the same sample of the monothiocarbamato complexes exhibited discrepancies for Cl and Nb (Ta), evidently due to problems in handling. However, analyses for C, H, and N are satisfactory, and ¹H NMR spectra suggest that the mo-nothiocarbamato complexes are pure.

Physical Measurements. Conductance measurements were made with an Industrial Instruments Model RC 16B2 conductivity bridge; the

bridge frequency was 1000 Hz. Infrared spectra were recorded in the region 4000–250 cm⁻¹ with a Perkin-Elmer 521 grating spectrophotometer; the estimated uncertainty in reported frequencies is ±4 cm⁻¹. ¹H NMR chemical shifts and coupling constants were determined at 37 °C with a Varian A60-A spectrometer.

Variable-Temperature ¹H NMR Spectra. Spectra of sealed, degassed solutions of [Ta(Me,Rdtc)₄][TaCl₆] (R = *i*-Pr, Ch, Ph), [Ta(Me,-Bzdtc)₄][TaBr₆], and [M(Me₂mtc)₄][MCl₆] (M = Nb, Ta) were recorded with a Bruker HX-90 spectrometer, while spectra of [Nb-(Me₂dtc)₄]Cl and [Ta(R₂dtc)₄][TaCl₆] (R = Me, *i*-Bu) were obtained with a Varian A60-A spectrometer. Experimental procedures have been described in a previous paper.[22] Probe temperatures, estimated to be accurate to ±0.5 °C, were measured by using a copper–constantan thermocouple (Bruker HX-90) or were determined from the temperature-dependent chemical shift between the inequivalent protons of methanol[23] (Varian A60-A).

Rate constants for exchange of dithiocarbamate and monothiocarbamate methyl groups were determined by comparison of experimental spectra with theoretical spectra calculated with use of total line shape programs. The multisite program PZDMFX[24] was used for studies of [M(Me₂mtc)₄][MCl₆] and [Ta(Me,*i*-Prdtc)₄], and a two-site program based on the Gutowsky–Holm equation[25] was employed for [Nb-(Me₂dtc)₄]Cl, [Ta(Me₂dtc)₄][TaCl₆], and [Ta(Me,Chdtc)₄][TaCl₆]. Observed and calculated spectra were compared with respect to the following line-shape parameters: frequency separations ($\delta\nu$) and line widths at three-fourths ($w_{3/4}$), one-half ($w_{1/2}$), and one-fourth ($w_{1/4}$) maximum amplitude and, in the case of [Nb(Me₂dtc)₄][NbCl₆], three-sixteenths ($w_{3/16}$), one-eighth ($w_{1/8}$), and one-sixteenth ($w_{1/16}$) maximum amplitude. Amplitude ratios (maximum amplitude to amplitude at the central minimum) were also compared in the case of the two-site exchanges. For all of the complexes, transverse relaxation times [$T_2 = (\pi w_{1/2})^{-1}$] were temperature-dependent. T_2 values at temperatures in the coalescence region were estimated by plotting log $w_{1/2}$ vs. $1/T$ over a wide temperature range and then extrapolating these plots linearly from the fast- and slow-exchange regions into the coalescence region. Chemical shifts in the absence of exchange were temperature-independent for the dithiocarbamate complexes but slightly temperature-dependent for the monothiocarbamate complexes. Chemical shifts in the coalescence region were determined by extrapolating linear plots of $\delta\nu$ vs. $1/T$ from the slow-exchange region into the coalescence region. The chemical shifts and T_2 values used in calculating the theoretical line shapes are given in the footnotes to Table V.

Results and Discussion

Synthesis and Characterization of Compounds. Tetrakis(*N*,*N*-dialkyldithiocarbamato)tantalum(V) complexes of the type [Ta(*i*-Bu₂dtc)₄][TaCl₆], [Ta(Me,Rdtc)₄][TaCl₆] (R = *i*-Pr, Ch, Ph; Ch = cyclohexyl), and [Ta(Me,Bzdtc)₄][TaBr₆] (Bz = benzyl) have been synthesized by reaction of TaX₅ (X = Cl, Br) with the anhydrous sodium salt of the appropriate *N*,*N*-dialkyldithio-carbamate in dichloromethane solution (eq 1). Although the

$$2TaX_5 + 4Na(R_2dtc) \rightarrow [Ta(R_2dtc)_4][TaX_6] + 4NaX \quad (1)$$

TaX₅:Na(R₂dtc) mole ratios employed in these reactions varied from 1:2.3 to 1:5, only hexahalotantalate, and no halide, salts were isolated. The reaction of TaCl₅ with Na(Me₂dtc) (1:5 mole ratio), however, yielded a mixture of [Ta(Me₂dtc)₄]Cl (eq 2) and [Ta-

$$TaCl_5 + 4Na(Me_2dtc) \rightarrow [Ta(Me_2dtc)_4]Cl + 4NaCl \quad (2)$$
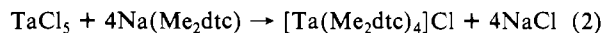
(Me₂dtc)₄][TaCl₆]; the relatively low solubility of [Ta(Me₂dtc)₄]Cl may be a factor favoring its isolation.

Yields of the [Ta(R₂dtc)₄][TaX₆] complexes were low owing to side reactions between Na(R₂dtc) and dichloromethane, which produce organic products such as (R₂dtc)₂CH₂.[9,26] In order to minimize formation of organic products and subsequent separation problems, reactions are best carried out at room temperature or at 0–5 °C. Reactions of Na(R₂dtc) with NbCl₅ are further complicated by possible reduction yielding [Nb(R₂dtc)₄].[3,9] We prepared [Nb(Me₂dtc)₄]Cl in low yield by reaction of NbCl₅ and Na(Me₂dtc) (1:5.4 mole ratio), but attempts to synthesize [Nb-

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Table II. Proton Chemical Shift[a] and Coupling Constant[b] Data

compd	CH	CH₂	CH₃	J
[Nb(Me₂dtc)₄]Cl			3.49	
[Ta(Me₂dtc)₄]Cl[c]			3.40	
[Ta(Me₂dtc)₄][TaCl₆][c]			3.40	
[Ta(i-Bu₂dtc)₄][TaCl₆]	2.24	3.60	0.94	6.5, 7.3
[Ta(Me,i-Prdtc)₄][TaCl₆]	4.93[d]		3.22 (Me), 1.32 (i-Pr)	6.7
[Ta(Me,Chdtc)₄][TaCl₆]	4.46[d]	1.76[d]	3.23	
[Ta(Me,Phdtc)₄][TaCl₆][e]			3.71	
[Ta(Me,Bzdtc)₄][TaBr₆][f]		5.02	3.32	
[Nb(Me₂mtc)₄][NbCl₆]			3.18, 3.34	
[Ta(Me₂mtc)₄][TaCl₆]			3.17, 3.25	

[a] In ppm (±0.01) downfield from an internal reference of tetramethylsilane (1% by volume) for CD₂Cl₂ solutions at 37 °C. [b] In Hz (±0.1) at 37 °C. For the isobutyl derivative, the first J value listed is J(CH₃–CH); the second is J(CH₂–CH). [c] Reference 17. [d] Center of a multiplet. [e] Phenyl multiplet centered at 7.47 ppm. [f] Phenyl multiplet centered at 7.32 ppm.

(i-Bu₂dtc)₄][NbCl₆] and [Nb(Me,Rdtc)₄][NbCl₆] (R = i-Pr, Ch) at room temperature and at –78 °C gave intractable mixtures of products.

Analogous monothiocarbamato complexes [M(Me₂mtc)₄]-[MCl₆] (M = Nb, Ta) were obtained in respectable yields from reactions of MCl₅ with anhydrous Na(Me₂mtc) (~1:2.5 mole ratio) in dichloromethane at –78 °C. The low temperature seems to be important; syntheses at room temperature gave mixtures of products.

The purity of the complexes was established by satisfactory elemental analyses (Table I) and by ¹H NMR spectra (Table II). All of the complexes behave as 1:1 electrolytes in dichloromethane, exhibiting molar conductances in the range 27–55 Ω⁻¹ cm² mol⁻¹ at concentrations of ~10⁻³ M (Table I). The structurally characterized complexes, [Ta(Me₂dtc)₄]Cl and [Ta(Me₂dtc)₄]-[TaCl₆], show conductances of 98 and 63 Ω⁻¹ cm² mol⁻¹, respectively, at a concentration of 5.5 × 10⁻⁴ M.[17]

Infrared spectra of the dithiocarbamato complexes (cf. Table III) exhibit a strong, broad ν(C⁓N) band at 1488–1557 cm⁻¹, a weak ν(C⁓S) band near 1000 cm⁻¹, and a ν(M–S) band in the region 356–382 cm⁻¹. In addition, complexes that contain [TaCl₆]⁻ show a strong band at 316–327 cm⁻¹ due to the ν₃(t₁ᵤ) Ta–Cl stretching mode of the anion.[27] The data in Table III indicate that the ν(C⁓N) and ν(C⁓S) modes shift to higher frequency on going from the sodium dithiocarbamate salts to the corresponding Nb(V) and Ta(V) complexes. The shifts in ν(C⁓N) are very substantial (34–66 cm⁻¹), indicative of considerable double-bond character in the C⁓N bond and associated with relatively strong metal–sulfur bonding owing to the high oxidation state of the metal and positive charge on the cation. The close similarity of solid-state and solution-state infrared spectra of [Ta(Me₂dtc)₄][TaCl₆] suggests that the *mmmm-D₂d* structure of the cation (**2**)[17] is preserved on going from the solid state to the solution state.

Characteristic infrared frequencies for the monothiocarbamato complexes [Nb(Me₂mtc)₄][NbCl₆] and [Ta(Me₂mtc)₄][TaCl₆] are listed in Table IV along with corresponding frequencies for the electrically neutral Ti(IV) and Zr(IV) analogues and the sodium salt. The intense, broad band envelope near 1600 cm⁻¹ is assigned to bands due to coupled C⁓O and C⁓N stretching vibrations of the bidentate monothiocarbamate ligand.[28] The high frequency of ν(C⁓O) and ν(C⁓N) bands in the Nb(V) and Ta(V) complexes in comparison with corresponding frequencies in the titanium(IV), zirconium(IV), and sodium monothiocarbamates is again indicative of strong metal–ligand bonding.

It is interesting to note that the ν(M–S) band in the monothiocarbamates occurs at lower frequency (~320 cm⁻¹) than in the corresponding dimethyldithiocarbamates (~360 cm⁻¹). The lower frequency of ν(M–S) in the monothiocarbamates could be due to a strengthening of the M–O bonds at the expense of the M–S bonds. Alternatively, the low ν(M–S) frequency might arise from vibrational coupling of M–O and M–S stretching modes of the same symmetry. The latter explanation seems more likely in view of the nearly identical mean Ti–S bond lengths in [Ti(Et₂mtc)₄][29] and [Ti(Et₂dtc)₄].[30] A strong band near 575 cm⁻¹ in the infrared spectra of [Nb(Me₂mtc)₄]⁺ and [Ta(Me₂mtc)₄]⁺ may be assigned to a ν(M–O) stretching mode. The ν₃(t₁ᵤ) stretching mode of [NbCl₆]⁻ is observed at 348 cm⁻¹.[27]

Variable-Temperature ¹H NMR Spectra and Stereochemistry. Proton NMR spectra of [Ta(Me₂dtc)₄][TaCl₆] in CH₂Cl₂–CD₃CN (10–15% CD₃CN by weight) and the less soluble [Nb-(Me₂dtc)₄]Cl in *cis*-1,2-dichloroethylene exhibit a single methyl proton resonance at room temperature, which splits into two lines of equal intensity below the coalescence temperatures of –62 and –76 °C, respectively; spectra of the tantalum complex are shown in Figure 2 of ref 16, and spectra of the niobium compound are similar. These spectra are consistent with the dodecahedral *mmmm-D₂d* stereoisomer (**2**) found in the crystal structures of [Ta(Me₂dtc)₄]Cl·CH₂Cl₂,[17] [Ta(Me₂dtc)₄][TaCl₆]·0.5CH₂Cl₂,[17] and [Nb(Et₂dtc)₄]Br.[12] The two methyl resonances arise from dithiocarbamate methyl groups in the equally populated dodecahedral A and B sites.

The methyl region of ¹H NMR spectra of the unsymmetrical dithiocarbamate complexes [Ta(Me,Chdtc)₄][TaCl₆], [Ta-(Me,i-Prdtc)₄][TaCl₆], and [Ta(Me,Bzdtc)₄][TaBr₆] in CD₂Cl₂ solution (Figures S1–S3, supplementary material) show similar line broadening, with a single methyl resonance at the higher temperatures splitting into two resonances below coalescence temperatures of –51 to –61 °C. Although the two resonances are equally intense in low-temperature spectra of [Ta(Me,-Chdtc)₄][TaCl₆], the higher field resonance is more intense than the lower field resonance (by ~10% and ~30%, respectively) in spectra of [Ta(Me,i-Prdtc)₄][TaCl₆] and [Ta(Me,Bzdtc)₄][TaBr₆].

Assuming that the dodecahedral *mmmm* ligand wrapping pattern (**2**) is maintained in [Ta(Me,Rdtc)₄]⁺ (R = Ch, i-Pr, Bz), these complexes may exist in six isomeric forms that differ in the distribution of methyl groups (and R groups) between the dodecahedral A and B sites. Two of the isomers have two methyl groups in A sites and two in B sites (C₂ᵥ or C₂ symmetry). The other four isomers have zero, one, three, or four methyl groups in A sites (D₂d, Cₛ, Cₛ, or D₂d symmetry, respectively). The six isomers are analogous to the six possible *mmmm* stereoisomers of a tetrakis(monothiocarbamato) complex (vide infra; cf. Figure 2). Observation of just two methyl resonances, in some cases of unequal intensity, suggests the presence of an equilibrium mixture of two or more (probably all six) *mmmm* stereoisomers. However, separate resonances for the various isomers are not resolved; only the local environment of the methyl groups (A or B site) can be distinguished. The relative intensities indicate that the population of methyl groups (and R groups) in the A and B sites is influenced by the nature of R, and the preference of methyl or R for one or the other of the two sites increases as R varies in the order cyclohexyl < isopropyl < benzyl.

The methyl region of the low-temperature ¹H NMR spectrum of [Ta(Me,Phdtc)₄][TaCl₆] consists of a very broad peak arising from two or more resonances of unequal intensity. The individual components are not sufficiently well resolved to adequately define the limiting slow-exchange spectrum, but the line shape does lend further support to the notion that the [Ta(Me,Rdtc)₄]⁺ complexes exist in solution as an equilibrium mixture of *mmmm* stereoisomers.

The isobutyl methyl doublet and methylene doublet of [Ta-(i-Bu₂dtc)₄][TaCl₆] exhibit line broadening in the same tem-

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Table III. Characteristic Infrared Frequencies for Metal *N,N*-Dialkyldithiocarbamates (cm^{-1})^a

compd	ν(C$\rightharpoonup$N)	ν(C$\rightharpoonup$S)	ν(M—S)	ν(M—Cl)	compd	ν(C$\rightharpoonup$N)^b	ν(C$\rightharpoonup$S)
[Nb(Me$_2$dtc)$_4$]Cl	1547 s, b	985 w	362 s		Na(Me$_2$dtc)	1491 s, b	976 vs
							961 vs
[Ta(Me$_2$dtc)$_4$]Cl^c	1557 s, b	992 w	358 m				
[Ta(Me$_2$dtc)$_4$][TaCl$_6$]^c	1552 s, b	1000 w	359 m	316 s			
[Ta(Me$_2$dtc)$_4$][TaCl$_6$]^d	1547 s, b	1012 w	356 w	320 m			
[Ta(i-Bu$_2$dtc)$_4$][TaCl$_6$]	1514 s, b	998 w	358 m	323 s	Na(i-Bu$_2$dtc)	1470 s, b	997 vs
[Ta(Me,i-Prdtc)$_4$][TaCl$_6$]	1507 s, b	989 m	377 m	325 s	Na(Me,i-Prdtc)	1468 s, b	967 vs
[Ta(Me,Chdtc)$_4$][TaCl$_6$]	1502 s, b	987 w	376 s	327 vs	Na(Me,Chdtc)	1465 s, b	966 vs
			366 s				
[Ta(Me,Phdtc)$_4$][TaCl$_6$]	1488 s, b	986 w	376 w	324 s	Na(Me,Phdtc)	1454 s, b	964 vs
[Ta(Me,Bzdtc)$_4$][TaBr$_6$]	1512 s, b	958 w	382 m		Na(Me,Bzdtc)	1477 s, b	960 vs

^{a} Unless indicated otherwise, as Nujol mulls between CsI plates. ^{b} As hexachlorobutadiene mulls between CsI plates. ^{c} Reference 17. ^{d} As dichloromethane solution in CsBr cell.

Table IV. Characteristic Infrared Frequencies for Metal *N,N*-Dimethylmonothiocarbamates (cm^{-1})^a

compd	ν(C$\rightharpoonup$O), ν(C$\rightharpoonup$N)	ν(C$\rightharpoonup$S)	ν(M—O)	ν(M—S)	ν(M—Cl)
[Nb(Me$_2$mtc)$_4$][NbCl$_6$]	1600 s, b	933 w	573 s	315 m	348 s
[Ta(Me$_2$mtc)$_4$][TaCl$_6$]	1599 sh	931 w	580 s	320 s	320 s
	1586 s, b				
[Ti(Me$_2$mtc)$_4$]^b	1543 vs, b	936 m	562 s	321 s	
[Zr(Me$_2$mtc)$_4$]^b	1550 vs, b	935 m	556 s		
Na(Me$_2$mtc)	1524 s, b	923 m			

^{a} As Nujol mulls between CsI plates. ^{b} Reference 21.
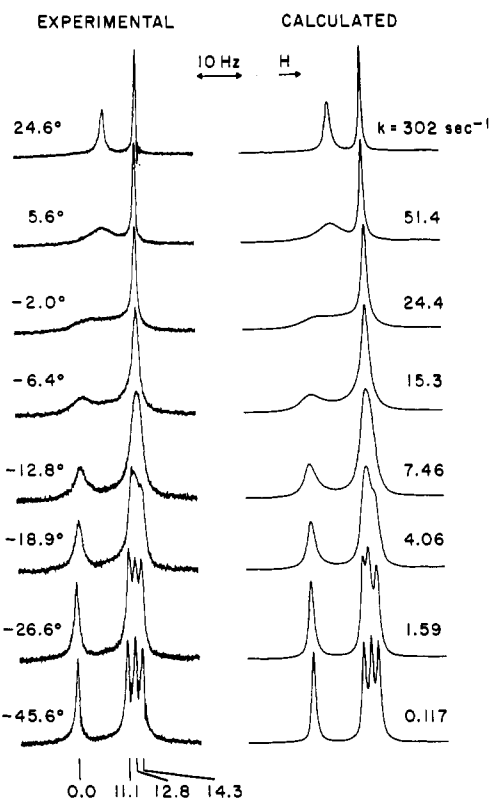

Figure 1. Methyl proton resonances of [Ta(Me$_2$mtc)$_4$][TaCl$_6$], 0.073 M in CH$_2$Cl$_2$, at 90 MHz.

perature region as observed for the other dtc complexes, but the spectra in the slow-exchange region are not well resolved.

Low-temperature ^{1}H NMR spectra of [Ta(Me$_2$mtc)$_4$][TaCl$_6$] (Figure 1) exhibit four methyl resonances of equal intensity, consistent with the dodecahedral *mmmm-C$_{2v}$* stereoisomer found in the solid state for [M(Et$_2$mtc)$_4$] (M = Ti, Zr)^{29} and in solution for [M(Me$_2$mtc)$_4$] (M = Ti, Zr).^{21,31} This isomer, shown schematically in Figure 2, is one of six possible *mmmm* isomers for a tetrakis(monothiocarbamato) complex. In the C_{2v} isomer,
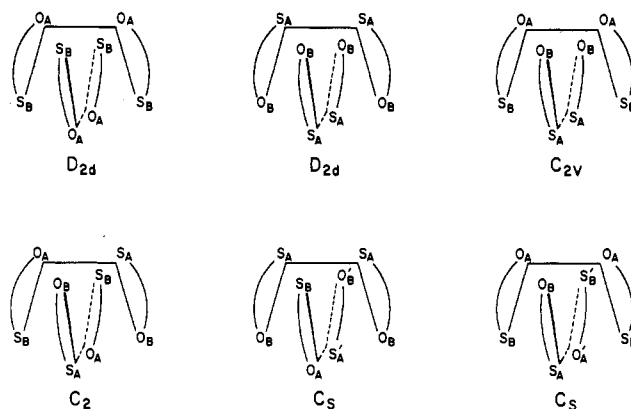

Figure 2. Schematic representation of the six possible *mmmm* dodecahedral stereoisomers of an [M(R$_2$mtc)$_4$] complex. The two mutually perpendicular trapezoids of the D_{2d} dodecahedron are outlined, and the A and B site occupancy of the sulfur and oxygen atoms is shown. The isomers are labeled according to their point-group symmetry. An analogous set of six *mmmm* isomers is possible for tetrakis(unsymmetrical dithiocarbamato) complexes [M(Me,Rdtc)$_4$].

all four sulfur atoms are clustered in all-cis positions on one side of the coordination polyhedron. This isomer may be stabilized by a trans influence of the sulfur atoms.^{29} The four methyl resonances arise from methyl groups adjacent to S$_A$, S$_B$, O$_A$, and O$_B$.

Surprisingly, low-temperature ^{1}H NMR spectra of [Nb-(Me$_2$mtc)$_4$][NbCl$_6$] (Figure 3) display four methyl resonances of approximate relative intensities 3:1:3:1. If a single stereoisomer is present, the spectra point to one of the two *mmmm-C$_s$* isomers (Figure 2). The more likely C_s isomer, the one in which three sulfur atoms are clustered in all-cis positions, has three methyl groups adjacent to S$_A$ or S$_A'$, one adjacent to S$_B$, three adjacent to O$_B$ or O$_B'$, and one adjacent to O$_A$. In the other *mmmm-C$_s$* isomer, the A and B site occupancies are reversed. Both isomers would give four methyl resonances of relative intensities 3:1:3:1 if the resonances due to methyl groups adjacent to the primed and unprimed sulfur (oxygen) atoms are not resolved, i.e. if only the local environment of the methyl groups within a single stereoisomer (A or B site, adjacent to sulfur or oxygen) can be distinguished. If the four local environments of different stereoisomers are indistinguishable, then the solution might contain an equilibrium mixture of two or more of the isomers in Figure

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Table V. Rate Constants for Methyl Group Exchange in Metal Dithiocarbamate and Monothiocarbamate Complexes[a]

[Nb(Me₂dtc)₄]Cl[b]		[Ta(Me₂dtc)₄]-[TaCl₆][c]		[Ta(Me,i-Prdtc)₄][TaCl₆][d]		[Ta(Me,Chdtc)₄]-[TaCl₆][e]		[Nb(Me₂mtc)₄]-[NbCl₆][f]		[Ta(Me₂mtc)₄]-[TaCl₆][g]	
temp, °C	k, s⁻¹	temp, °C	k, s⁻¹	temp, °C	k, s⁻¹	temp, °C	k, s⁻¹	temp, °C	k, s⁻¹	temp, °C	k, s⁻¹
-90.0	5.43	-77.6	1.82	-76.9	1.21	-60.3	7.80	-29.4	0.257	-29.4	0.949
-87.6	5.68	-74.3	2.51	-74.4	1.89	-58.7	9.43	-26.6	0.383	-26.6	1.59
-86.2	7.37	-72.7	3.97	-72.4	2.39	-57.5	10.8	-25.4	0.389	-24.2	2.01
-83.9	8.91	-71.4	4.50	-69.9	3.12	-56.1	12.5	-24.2	0.472	-21.8	3.16
-83.2	9.53	-69.1	6.49	-67.4	4.58	-55.3	13.7	-21.8	0.891	-18.9	4.06
-81.9	11.1	-68.0	7.20	-64.9	5.61	-54.2	14.7	-18.9	1.22	-17.4	4.88
-80.8	13.0	-64.3	10.7	-63.5	6.68	-52.8	17.8	-15.2	1.92	-15.2	5.76
-79.3	13.6	-63.4	11.9	-61.4	9.76	-51.5	21.0	-12.8	1.99	-14.4	6.63
-77.8	17.5	-62.0	16.2	-59.5	14.7	-50.8	24.1	-10.4	2.60	-12.8	7.46
-76.0	22.2	-60.8	17.5	-57.2	16.6	-49.3	27.9	-6.4	5.40	-11.6	9.12
-74.9	22.9	-57.4	22.8	-55.0	22.4	-47.7	31.6			-10.4	10.2
-71.6	29.4	-53.9	36.5	-53.1	32.2	-46.4	34.5			-9.2	10.9
-70.8	31.6	-48.1	62.0	-48.6	47.3	-45.0	41.4			-6.4	15.3
-69.4	34.6	-45.6	96.9	-47.1	62.4	-44.2	47.8			-3.7	19.7
-68.2	40.5	-39.4	200	-45.5	65.5	-42.7	54.4			-2.0	24.4
-66.8	45.2					-41.4	61.4			0.7	31.5
-65.3	49.5					-40.1	69.5			3.4	43.9
-62.4	67.4					-38.9	80.0			5.6	51.4
-61.5	75.5					-37.9	86.6			9.7	73.1
-57.7	107					-33.6	122			13.7	109
						-32.0	179			15.9	147
										19.8	222

[a] The probable uncertainty in the rate constants is ~20%. [b] 2.0×10^{-3} M in *cis*-1,2-dichloroethylene; relative populations $P_1 = P_2 = 0.500$; $\delta\nu =$ 9.75 Hz at 60 MHz; variation in T_2 from low temperature (-90.0 °C) to high temperature (-57.7 °C) is 0.185–0.253 s. [c] 2.8×10^{-3} M in CH_2-Cl_2–CD_3CN (10–15% CD_3CN by weight); $P_1 = P_2 = 0.500$; $\delta\nu = 7.20$ Hz at 60 MHz; $T_2 = 0.173$–0.315 s. [d] 0.096 M in CD_2Cl_2; $P_1 = 0.475$, $P_2 = 0.525$; $\delta\nu = 10.3$ Hz at 90 MHz; $(T_2)_1 = 0.078$–0.136 s, $(T_2)_2 = 0.084$–0.135 s. [e] 0.050 M in CD_2Cl_2; $P_1 = P_2 = 0.500$; $\delta\nu = 10.6$ Hz at 90 MHz; $T_2 = 0.127$–0.181 s. [f] 0.013 M in CH_2Cl_2; $P_1 = P_3 = 0.375$, $P_2 = P_4 = 0.125$. Temperature variation in chemical shifts (Hz at 90 MHz) and T_2 values for peaks 1–4 in order of increasing field: $\nu_1 = 0.00$ Hz, $T_2 = 0.446$–0.501 s; $\nu_2 = 2.70$–2.43 Hz, $T_2 = 0.491$–0.551 s; $\nu_3 = 14.62$–14.70 Hz, $T_2 = 0.446$–0.501 s; $\nu_4 = 16.08$–16.13 Hz, $T_2 = 0.491$–0.551 s. [g] 0.073 M in CH_2Cl_2; $P_1 = P_2 = P_3 = P_4 = 0.250$. $\nu_1 = 0.00$ Hz, $T_2 = 0.363$–0.497 s; $\nu_2 = 11.29$–11.93 Hz, $T_2 = 0.403$–0.552 s; $\nu_3 = 12.77$ Hz, $T_2 = 0.363$–0.497 s; $\nu_4 = 14.42$–15.13 Hz, $T_2 = 0.403$–0.552 s.
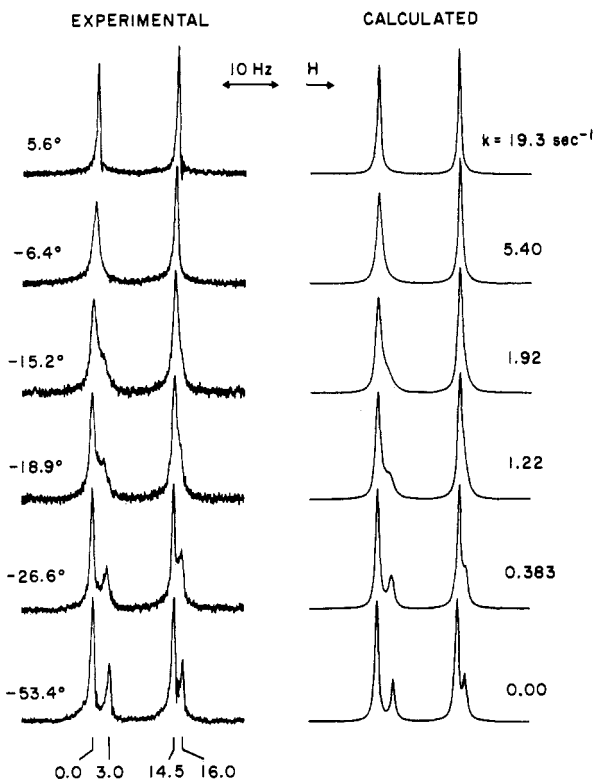

Figure 3. Methyl proton resonances of [Nb(Me₂mtc)₄][NbCl₆], 0.013 M in CH_2Cl_2, at 90 MHz.

2, as in the case of the unsymmetrical dtc complexes [Ta(Me,-Rdtc)₄]⁺. This latter possibility cannot be ruled out, and small concentrations of the C_{2v} isomer might be present. However, the presence of appreciable concentrations of the other stereoisomers seems unlikely in view of the sharpness of the resonances (Figure 3) and the tendency of sulfur atoms to cluster in [M(R₂mtc)₄] (M = Ti, Zr).[21,29,31] In any case, the predominant solution species

for [Nb(Me₂mtc)₄]⁺ is not the C_{2v} stereoisomer found for [Ta-(Me₂mtc)₄]⁺. We do not understand why [Nb(Me₂mtc)₄]⁺ avoids maximum clustering of sulfur atoms. Our attempts to grow single crystals of [Nb(Me₂mtc)₄][NbCl₆] suitable for X-ray diffraction have been unsuccessful.

Kinetics of Metal-Centered Rearrangement. Rate constants (Table V) for exchange of methyl groups between the dodecahedral A and B sites were determined by total line-shape analysis using procedures described in the Experimental Section. For the dithiocarbamate complexes, $k = k_{12} = k_{21}$, except for [Ta-(Me,i-Prdtc)₄][TaCl₆] where the populations of the two sites are unequal; in the latter case, values of k_{12} are listed (Table V) where site 1, of fractional population 0.475, gives rise to the resonance at lower field. For the monothiocarbamate complexes, pairwise exchange results in coalescence of resonance lines so as to give two time-averaged lines in the fast-exchange limit (Figures 1 and 3). Theoretical spectra were calculated as a function of a single rate constant, $k = k_{13} = k_{24} = k_{31} = k_{42}$ for [Ta(Me₂mtc)₄][TaCl₆] and $k = k_{12} = k_{34} = k_{21}/3 = k_{43}/3$ for [Nb(Me₂mtc)₄][NbCl₆], where 1, 2, 3, and 4 label the methyl sites associated with the four resonance lines in Figures 1 and 3, in order of increasing field. Agreement between observed and calculated spectra is illustrated in the figures.

Arrhenius and Eyring activation parameters were obtained in the usual way from the least-squares straight lines of log k vs. $1/T$ plots (Figure 4) and log (k/T) vs. $1/T$ plots, respectively. Activation parameters are listed in Table VI along with coalescence temperatures and extrapolated values of k at 25 °C. Also included in Table VI, for comparison, are kinetic data for metal-centered rearrangement in the corresponding Ti(IV) and Zr(IV) complexes.

Total line-shape analysis could not be carried out for [Ta-(Me,Bzdtc)₄][TaBr₆] because the limiting slow-exchange spectrum was not yet reached at the lowest accessible temperatures (cf. Figure S3). However, an approximate value of $\Delta G^{\ddagger}(T_c) = 11.12$ kcal/mol was estimated[32] for [Ta(Me,Bzdtc)₄][TaBr₆] from the

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Table VI. Kinetic Data for Metal-Centered Rearrangement in Metal Dithiocarbamate and Monothiocarbamate Complexes[a]

compd[b]	T_c, °C	$\Delta G^*(T_c)$, kcal/mol	ΔH^*, kcal/mol	ΔS^*, eu	E_a, kcal/mol	log A	$\Delta G^*(25\ °C)$, kcal/mol	$k(25\ °C)$, s^{-1}
[Nb(Me$_2$dtc)$_4$]Cl[c]	-76.0	10.16 ± 0.05	7.0 ± 0.2	-16.5 ± 1.2	7.4 ± 0.2	9.4 ± 0.3	11.87 ± 0.11	1.2 × 10^4
[Ta(Me$_2$dtc)$_4$][TaCl$_6$][d]	-62.0	11.05 ± 0.08	10.4 ± 0.4	-3.1 ± 2.0	10.9 ± 0.4	12.4 ± 0.4	11.35 ± 0.18	3.0 × 10^4
[Ta(Me,i-Prdtc)$_4$][TaCl$_6$]	-55.0	11.29 ± 0.09	11.1 ± 0.5	-1.0 ± 2.2	11.5 ± 0.5	12.9 ± 0.5	11.36 ± 0.19	2.9 × 10^4
[Ta(Me,Chdtc)$_4$][TaCl$_6$]	-51.5	11.50 ± 0.05	10.7 ± 0.3	-3.7 ± 1.5	11.1 ± 0.3	12.3 ± 0.3	11.78 ± 0.11	1.4 × 10^4
[Tl(Et$_2$dtc)$_4$][e]	<-140							
[Zr(Et$_2$dtc)$_4$][e]	<-140							
[Nb(Me$_2$mtc)$_4$][NbCl$_6$]	-15.2	14.70 ± 0.17	16.1 ± 1.9	5.3 ± 7.4	16.6 ± 1.9	14.3 ± 1.6	14.54 ± 0.33	1.4 × 10^2
[Ta(Me$_2$mtc)$_4$][TaCl$_6$]	-2.0	14.10 ± 0.07	14.6 ± 0.3	1.7 ± 1.1	15.1 ± 0.3	13.6 ± 0.2	14.05 ± 0.08	3.2 × 10^2
[Ti(Me$_2$mtc)$_4$][f]	-84.2	9.88 ± 0.08	10.7 ± 0.3	4.5 ± 1.6	11.1 ± 0.3	14.0 ± 0.3	9.39 ± 0.12	7.6 × 10^5
[Zr(Me$_2$mtc)$_4$][f]	-53.5	11.25 ± 0.05	9.5 ± 0.3	-8.2 ± 1.3	9.9 ± 0.3	11.3 ± 0.3	11.89 ± 0.07	1.1 × 10^4

[a] The uncertainties in the activation parameters are random errors estimated at the 95% confidence level. [b] In CH$_2$Cl$_2$ or CD$_2$Cl$_2$, unless indicated otherwise. [c] In cis-1,2-dichloroethylene. [d] In CH$_2$Cl$_2$–CD$_3$CN (10–15% CD$_3$CN by weight). [e] In CHClF$_2$–CD$_2$Cl$_2$ (Muetterties, E. L. *Inorg. Chem.* **1973**, *12*, 1963). [f] Reference 31.
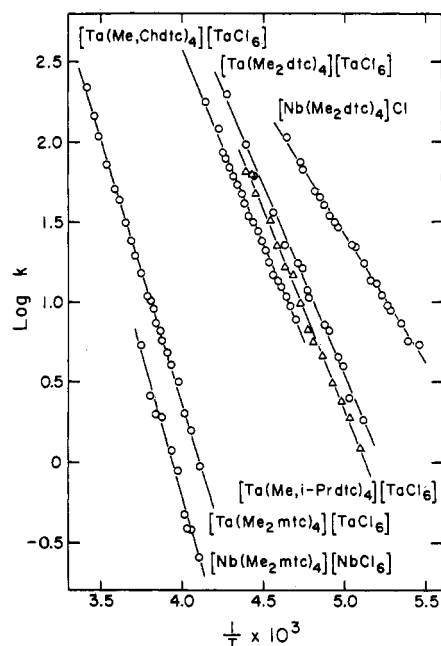

Figure 4. Arrhenius plots for metal-centered rearrangement.

maximum observed chemical shift (6.80 Hz at 90 MHz) and the coalescence temperature (-61.1 °C). This value compares favorably with values of $\Delta G^*(T_c)$ (11.05–11.50 kcal/mol) obtained by total line-shape analysis for the other tantalum dtc complexes.

The observed exchange of methyl groups between the A and B sites of the dtc and mtc complexes is assigned to an intramolecular process. Intermolecular processes can be ruled out on the basis of the following experimental evidence: (i) rate constants for 0.0021 and 0.0028 M [Ta(Me$_2$dtc)$_4$][TaCl$_6$] in CH$_2$Cl$_2$–CD$_3$CN are independent of concentration; (ii) ^{1}H NMR spectra at 37 °C of mixtures of [Ta(Me$_2$dtc)$_4$][TaCl$_6$] and Na(Me$_2$dtc) in 50% w/w CH$_2$Cl$_2$–CD$_3$CN and mixtures of [Ta(Me$_2$mtc)$_4$][TaCl$_6$] and Na(Me$_2$mtc) in 50% w/w CDCl$_3$–CD$_3$CN exhibit separate, unperturbed resonances for the complex and excess ligand. Therefore, intermolecular ligand exchange is slow on the NMR time scale at temperatures where exchange of methyl groups is fast.

Comparison of ν(C⁓N) infrared frequencies (Table III) and kinetic data (Table VI) for the metal dtc complexes with corresponding data for the methyl esters, MeSC(S)NR$_2$,[33] indicates that the exchange process involves metal-centered rearrangement rather than rotation about the C⁓N partial double bond in the ligands. For the mtc complexes [M(Me$_2$mtc)$_4$] (M = Ti, Zr), both low-temperature metal-centered rearrangement (T_c = -84.2 and -53.5 °C, respectively) and high-temperature C⁓N rotation (T_c = 29.9 and 78.2 °C, respectively) processes have been observed.[31] In the case of [M(Me$_2$mtc)$_4$][MCl$_6$] (M = Nb, Ta),

however, only metal-centered rearrangement is detected. At 70 °C, the limit of our measurements, C⁓N rotation is still slow on the NMR time scale; line widths of the two methyl resonances at 70 °C are 0.51 ± 0.04 Hz.

The rates of metal-centered rearrangement (Table VI) are substantially slower for the cationic Nb(V) and Ta(V) complexes than for the electrically neutral Ti(IV) and Zr(IV) analogues. Since the dimensions of the coordination polyhedra are nearly identical for [Ta(Me$_2$dtc)$_4$]$^{+\,17}$ and [Ti(Et$_2$dtc)$_4$],[30] it is evident that the charge on the Nb(V) and Ta(V) complexes plays a dominant role in slowing the rate of rearrangement. The rates differ by less than a factor of 3–4 for [Nb(Me$_2$mtc)$_4$]$^+$ and [Ta(Me$_2$mtc)$_4$]$^+$, and differ by less than a factor of 4–10 for [Nb(Me$_2$dtc)$_4$]$^+$ and [Ta(Me$_2$dtc)$_4$]$^+$. Values of ΔH^* and ΔS^* (Table VI) are rather different for [Nb(Me$_2$dtc)$_4$]Cl and [Ta(Me$_2$dtc)$_4$][TaCl$_6$], but the difference in the anion and solvent should be noted. For [Ta(Me,Rdtc)$_4$][TaCl$_6$] (R = Me, i-Pr, Ch), the rates and activation parameters are relatively independent of the R group.

The most important result in Table VI and Figure 4 is the greater stereochemical rigidity of the mtc complexes in comparison with the dtc analogues. Coalescence temperatures are -52 to -76 °C for the Nb(V) and Ta(V) dtc complexes (ΔG^* = 10–12 kcal/mol) and -2 to -15 °C for the mtc complexes (ΔG^* = 14–15 kcal/mol). A similarly striking difference in rates was found for analogous Ti(IV) and Zr(IV) dtc and mtc complexes (cf. Table VI); the Ti(IV) and Zr(IV) dtc complexes are still nonrigid on the NMR time scale at -140 °C.

In an earlier paper, it was suggested that the Ti(IV) and Zr(IV) complexes rearrange by a polytopal mechanism involving a cubic or (more probably) a square-antiprismatic *llll* transition state (cf. Figure 7 of ref 31). Because the energy difference between the dodecahedral *mmmm* ground state and a square-antiprismatic *llll* transition state increases with decreasing normalized bite of the ligand,[34] a polytopal rearrangement mechanism predicts greater rigidity for the mtc complexes. On the other hand, a bond rupture mechanism predicts little difference in rearrangement rates for the mtc and dtc complexes since [Ti(Et$_2$mtc)$_4$][29] and [Ti(Et$_2$dtc)$_4$][30] have nearly identical mean Ti–S bond lengths. The greater rigidity of the Nb(V) and Ta(V) mtc complexes in comparison with the dtc analogues lends further support to a polytopal mechanism. The observed values of ΔS^* (Table VI), which are nearly zero or are negative, are also consistent with a polytopal mechanism.

There is, however, one piece of evidence that does not fit rearrangement via a cubic or square-antiprismatic *llll* transition state, viz. the exchange of methyl groups between the A and B sites of the C_s isomer of [Nb(Me$_2$mtc)$_4$]$^+$. Although this mechanism nicely accounts for exchange between the A and B sites of the C_{2v} isomer observed for the Ti(IV), Zr(IV), and Ta(V) complexes, it does not exchange methyl groups within a single C_s isomer. Instead, it interconverts the two C_s isomers. In order to exchange methyl groups within a single C_s isomer, a lower

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symmetry polytopal rearrangment is required, for example, digonal twisting of one ligand about its quasi-twofold axis. A bond rupture mechanism will also effect methyl group exchange within the C_s isomer, but we regard this mechanism as less likely for the reasons mentioned earlier.[31]

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Registry No. [Nb(Me₂dtc)₄]Cl, 102921-79-9; [Ta(Me₂dtc)₄]Cl,

Supplementary Material Available: Figures S1–S3 showing the methyl proton resonances of [Ta(Me,Chdtc)₄][TaCl₆], [Ta(Me,i-Prdtc)₄]-[TaCl₆], and [Ta(Me,Bzdtc)₄][TaBr₆] in CD₂Cl₂ solution (3 pages). Ordering information is given on any current masthead page.


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Photochemical Disproportionation of Mn₂(CO)₁₀. Nineteen-Electron Intermediates and Ligand and Intensity Dependence
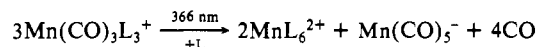
Albert E. Stiegman, Alan S. Goldman, Cecelia E. Philbin, and David R. Tyler*

The photochemical disproportionation of Mn₂(CO)₁₀ proceeds as

$$\text{Mn}_2(\text{CO})_{10} \xrightarrow[\text{+L, -2CO}]{\text{366 nm}} \text{Mn(CO)}_5^- + \text{Mn(CO)}_3\text{L}_3^+$$
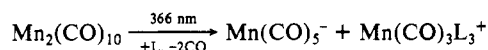
where L is a nitrogen or oxygen donor ligand. With many ligands, but not CH₃CN, a secondary disproportionation of Mn(CO)₃L₃⁺ occurs:
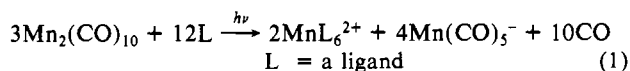
$$3\text{Mn(CO)}_3\text{L}_3^+ \xrightarrow[\text{+L}]{\text{366 nm}} 2\text{MnL}_6^{2+} + \text{Mn(CO)}_5^- + 4\text{CO}$$

The net reaction is thus

$$3\text{Mn}_2(\text{CO})_{10} + 12\text{L} \xrightarrow{h\nu} 2\text{MnL}_6^{2+} + 4\text{Mn(CO)}_5^- + 10\text{CO}$$

The stoichiometry of Mn(CO)₅⁻ formation in CH₃CN solution was measured and found to be as described in the initial equation above. Disproportionation of Mn₂(CO)₁₀ occurs with nitrogen- and oxygen-donor ligands but not with monodentate phosphines and phosphites; disproportionation does result, however, with the multidentate 1,2-bis(dimethylphosphino)ethane (dmpe), bis-(2-(diphenylphosphino)ethyl)phenylphosphine (triphos), and 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos) ligands. These results are interpreted in terms of the previously proposed radical-chain pathway for Mn₂(CO)₁₀ disproportionation involving 19-electron Mn(CO)₃L₃ intermediates. It is proposed that steric bulk and electron-donating ability are the dominant factors in determining whether or not the dimer will photochemically disproportionate with a particular ligand. Disproportionation occurs with the chelating ligands because these ligands effectively increase the concentration of the key 19-electron intermediate. Two experiments provide additional evidence for the 19-electron intermediate: (1) Reaction of PMe₃ with Mn(CO)₃depe (depe = 1,2-bis(diethylphosphino)ethane) in the presence of Mn₂(CO)₁₀ in the dark gives disproportionation products. It is proposed that PMe₃ attacks Mn(CO)₃depe, giving the 19-electron complex Mn(CO)₃(depe)(PMe₃), which then reduces Mn₂(CO)₁₀. (2) The cationic product from the reaction of Mn₂(CO)₁₀ with tetraphos is Mn(CO)₃(tetraphos-P,P',P'')⁺. The formation of this product and not Mn(CO)₂(tetraphos-P,P',P'',P''')⁺ supports the proposal that the chain reaction involves electron transfer from a 19-electron Mn(CO)₃L₃ species rather than from a 17-electron Mn(CO)₂L₃ intermediate; the latter would yield the Mn(CO)₂L₄⁺ cation product. The dependence of the disproportionation quantum yields on the exciting light intensity was investigated. In agreement with the proposed radical-chain mechanism, the quantum yields are linearly proportional to $I^{-1/2}$ (I = the absorbed intensity).

We have been studying the mechanism of the photochemical disproportionation reactions of Mn₂(CO)₁₀ (eq 1).[1,2] Our research

$$3\text{Mn}_2(\text{CO})_{10} + 12\text{L} \xrightarrow{h\nu} 2\text{MnL}_6^{2+} + 4\text{Mn(CO)}_5^- + 10\text{CO}$$
$$\text{L = a ligand} \qquad (1)$$

has two specific objectives: (1) we want to know the mechanism of reaction 1 and (2) we want to know why the dimer will photochemically disproportionate with some ligands but not others. In a recent paper, we discussed and answered questions pertaining to the first of these objectives.[3] In this paper we report results relevant to the second objective and we also report results consistent with our earlier proposal[3] that a 19-electron species is a key intermediate in reaction 1. Because the stoichiometry of eq 1 has never been measured, we also report experimental results

concerning the stoichiometry of this reaction.

Experimental Section

Mn₂(CO)₁₀ was obtained from Strem Chemical Co. and sublimed prior to use. Pyridine (py), triethylamine (NEt₃), cyclohexylamine (NH₂Cy), and diethylenetriamine (dien) were obtained from Aldrich, stirred over sodium metal, and distilled under argon. Diethylenetriamine was vacuum distilled. Ethylenediamine (en, anhydrous) was obtained from Fisher and used as received. 1,2-Bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), 1,2-bis(diphenyl-phosphino)ethane (dppe), bis(2-(diphenylphosphino)ethyl)phenyl-phosphine (triphos), 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphade-cane (tetraphos), di-n-propylphosphine, phenylphosphine, and tri-methylphosphine were obtained from Strem and used as received.

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