

H2N(1) on the cation at $x, 1/2 - y, 1/2 + z$ and 2.28 Å between O(7) and H1N(2) on the cation at $x - 1, y, z$.

Discussion

The Cu-S bonds observed in this analysis are rather long in comparison to those determined for other types of S donor ligands. It has been suggested¹⁷ that thioethers do not have a high affinity for Cu(II), and the bond lengths determined here support this contention. It is probable that the perchlorate ion will be lost from the Cu atom coordination sphere in solution, to be replaced by a solvent molecule. The resultant species would be expected to adopt a similar configuration to that found in the solid state. The similarity between the absorption spectrum of the title complex in solution⁷ and that of galactose oxidase in the region of the d-d transitions⁴ is indicative of a similar environment for the metal atom in each system.

Acknowledgment. It is a pleasure to acknowledge our continuing collaboration with Professor Bosnich and to thank the National Research Council of Canada for financial support of this work.

Registry No. [Cu(EEE)(1-MeIm)](ClO₄)₂, 64692-43-9.

Supplementary Material Available: Table IV listing structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

References and Notes

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Stereochemistry of Eight-Coordinate Dodecahedral Complexes of the Type MX₄Y₄. 1. Preparation and Characterization of Some Titanium(IV) and Zirconium(IV) N,N-Dialkylmonothiocarbamates¹

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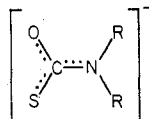
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Eight-coordinate titanium(IV) and zirconium(IV) *N,N*-dialkylmonothiocarbamate complexes of the type [M(R₂mtc)₄] (M = Ti, Zr; R = Me, Et, *i*-Pr) have been prepared by reaction of the metal tetrachlorides with alkali metal *N,N*-dialkylmonothiocarbamates in dichloromethane, benzene, or acetonitrile. Low-temperature proton NMR spectra of the [M(Me₂mtc)₄] complexes exhibit four methyl resonances of approximately equal intensity, consistent with the dodecahedral *mmmm*-C_{2v} stereoisomer that has been found in the solid state for the [M(Et₂mtc)₄] complexes by X-ray diffraction. This isomer has an all-cis structure with the four sulfur atoms on one side of the coordination group and the four oxygen atoms on the other side. Dipole moments in benzene solution (4.49 ± 0.11 D for [Ti(Et₂mtc)₄] and 3.61 ± 0.16 D for [Zr(Et₂mtc)₄]) are also in accord with the highly polar *mmmm*-C_{2v} stereoisomer being the principal species in solution. Variable-temperature NMR spectra of the [M(Me₂mtc)₄] complexes afford evidence for two distinct kinetic processes: (1) a low-temperature process that involves metal-centered rearrangement and (2) a high-temperature process that involves hindered rotation about the C-N bond in the ligand. Thus, these complexes are of interest as unusual examples of tetrakis chelates that are stereochemically rigid on the NMR time scale. Infrared spectra of the [M(R₂mtc)₄] complexes are consistent with bidentate attachment of the monothiocarbamate ligands. M-O and M-S stretching frequencies have been identified by comparison of infrared spectra of the complexes and the alkali metal salts.

Introduction

The preparation, properties, and structural chemistry of metal *N,N*-dialkyldithiocarbamate complexes have been studied extensively.² Less well-known are metal complexes containing the corresponding *N,N*-dialkylmonothiocarbamate

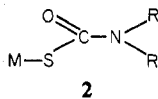
(R₂mtc) ligand **1**. Most of the known monothiocarbamate complexes have been prepared in the last 7 years, and attention has centered primarily on the later transition metals. Complexes of the following metals have been reported: Mn(I),^{3,4} Fe(II),^{5a,6} Fe(III),⁵⁻⁷ Co(II),^{8a} Co(III),^{8b} Rh(I),^{9,10}



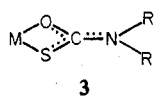
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Ni(II),¹¹⁻¹⁶ Pd(II),^{6,15,17} Pt(II),^{6,15} Cu(I),^{18,19} Ag(I),^{20,21} Au(I),¹⁰ Zn(II),^{22,23} Cd(II),²² Hg(II),²² and Tl(I).²⁴ The chemistry of early transition-metal monothiocarbamate complexes is less well developed. However, a few complexes have been reported for the following metals: Ti(IV),^{1,25} Zr(IV),²⁵ Th(IV),²⁶ U(IV),²⁶ V(IV),²⁷ Ta(V),²⁵ and Mo(II).⁶

X-ray structure determinations have been carried out for monothiocarbamate complexes of Fe(III),⁷ Co(II),^{8a} Ni(II),¹⁶ Cu(I),¹⁸ Ag(I),²⁰ and Zn(II).²³ These studies indicate that the monothiocarbamate ligand adopts a variety of bonding modes including monodentate attachment through sulfur,²³ 2, bidentate attachment,^{7,8a} 3, and two different arrangements

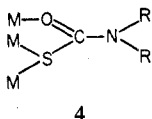


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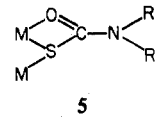


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in which the sulfur atom bridges between two metal atoms,^{16,18,20} 4 and 5. Some important differences between the



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structures of monothiocarbamate complexes and the corresponding dithiocarbamates are evident. Thus, bis(*N,N*-di-*n*-butylmonothiocarbamato)nickel(II) exists as a hexameric metal cluster $[\text{Ni}(\textit{n}\text{-Bu}_2\text{mtc})_2]_6$,¹⁶ while analogous dithiocarbamate complexes $[\text{Ni}(\text{R}_2\text{dtc})_2]$ are square-planar monomers.^{28,29}

We have prepared a series of eight-coordinate dodecahedral titanium(IV) and zirconium(IV) monothiocarbamates of the type $[\text{M}(\text{R}_2\text{mtc})_4]$ (R = Me, Et, *i*-Pr) in order to investigate possible sorting of sulfur and oxygen donor atoms between the inequivalent dodecahedral A and B sites.³⁰ Such sorting is predicted on the basis of Orgel's rule.³¹ The present paper reports the preparation and characterization of the $[\text{M}(\text{R}_2\text{mtc})_4]$ complexes and the unexpected discovery that these tetrakis chelates are stereochemically rigid on the NMR time scale. The following paper³² describes an X-ray crystallographic study of two representative complexes, $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ and $[\text{Zr}(\text{Et}_2\text{mtc})_4]$.

Experimental Section

Reagents and General Techniques. Titanium(IV) chloride (Matheson Coleman and Bell), zirconium(IV) chloride (Alfa Inorganics), and carbonyl sulfide and dimethylamine (Matheson Gas Products) were used as purchased without further purification. Diethylamine and diisopropylamine were refluxed over sodium for 24 h and were distilled immediately before use. Solvents (dichloromethane, benzene, acetonitrile, and hexane) were dried by refluxing over calcium hydride for at least 24 h. All syntheses and subsequent handling of the compounds were conducted under anhydrous conditions in a dry nitrogen atmosphere.

Sodium *N,N*-Dimethylmonothiocarbamate, Na(Me₂mtc). The dimethylammonium salt, $(\text{Me}_2\text{NH}_2)^+(\text{Me}_2\text{mtc})^-$, was first prepared, and then this salt was converted to the sodium salt by reaction with sodium hydride. Approximately 25 mL of dimethylamine was condensed at -78 °C, and carbonyl sulfide was bubbled through the liquid at a moderate rate. The reaction is quite exothermic. The resulting white solid, $(\text{Me}_2\text{NH}_2)^+(\text{Me}_2\text{mtc})^-$, was freed of excess amine by pumping in vacuo. This salt is extremely sensitive to moisture, and it must be handled in an inert atmosphere.

The $(\text{Me}_2\text{NH}_2)^+(\text{Me}_2\text{mtc})^-$ salt (25.86 g, 172 mmol) was dissolved in benzene (~80 mL), and sodium hydride (3.99 g, 166 mmol) was

added slowly with stirring. The reaction proceeds, at first very vigorously, with evolution of hydrogen and dimethylamine. Stirring was continued for 16.5 h. The resulting white solid (18.39 g, 87% theoretical) was collected by filtration and was recrystallized from a mixture of acetonitrile, dichloromethane, and hexane (1:1:2 by volume) at -15 °C; mp 246-250 °C dec. Anal. Calcd for Na(C₃H₆NOS): C, 28.34; H, 4.76; N, 11.02; Na, 18.08. Found: C, 28.35; H, 4.76; N, 10.90; Na, 17.94.

Sodium *N,N*-Diethylmonothiocarbamate, Na(Et₂mtc). The diethylammonium salt, $(\text{Et}_2\text{NH}_2)^+(\text{Et}_2\text{mtc})^-$, was prepared by bubbling carbonyl sulfide through ~50 mL of diethylamine that was cooled in a dry ice-acetone bath. Excess amine was removed by pumping in vacuo for ~30 min. Longer pumping times should be avoided because $(\text{Et}_2\text{NH}_2)^+(\text{Et}_2\text{mtc})^-$ will sublime at room temperature and 10⁻³ Torr. The $(\text{Et}_2\text{NH}_2)^+(\text{Et}_2\text{mtc})^-$ salt (50.64 g, 245 mmol) was dissolved in benzene (~50 mL), and the solution was cooled to 0 °C. Sodium hydride (5.39 g, 225 mmol) was added slowly with stirring, and stirring was continued for 1 day under a dry nitrogen atmosphere. Filtration afforded a white solid which was washed with benzene (~100 mL) and dried in vacuo for 5 h. The yield was 29.11 g (83%); mp 174-177 °C. Anal. Calcd for Na(C₅H₁₀NOS): C, 38.70; H, 6.49; N, 9.03; Na, 14.81; S, 20.66. Found: C, 38.60; H, 6.60; N, 9.16; Na, 14.73; S, 20.57.

Lithium *N,N*-Diisopropylmonothiocarbamate, Li(*i*-Pr₂mtc). With rapid stirring at 0 °C, 34 mL (240 mmol) of diisopropylamine was added dropwise over a period of 10 min to 145 mL of 1.6 M *n*-butyllithium (232 mmol) in hexane. Butane was evolved slowly and the solution became quite viscous. After addition of hexane (90 mL) to decrease the viscosity, carbonyl sulfide was bubbled through the solution for 15 min. The resulting white solid (37.54 g, 97%) was filtered, washed with two 100-mL portions of hexane, and dried in vacuo for 18 h; mp 206-209 °C dec. Anal. Calcd for Li(C₇H₁₄NOS): C, 50.29; H, 8.44; Li, 4.15; N, 8.38. Found: C, 50.18; H, 8.59; Li, 4.07; N, 8.16.

Tetrakis(*N,N*-dimethylmonothiocarbamato)titanium(IV), [Ti(Me₂mtc)₄]. Titanium(IV) chloride (1.30 mL, 11.8 mmol) was added with rapid stirring to a suspension of Na(Me₂mtc) (6.00 g, 47.2 mmol) in 150 mL of dichloromethane. The mixture was refluxed for 18 h and then filtered, and the precipitate was washed with two 40-mL portions of dichloromethane. Reduction of the volume of the combined filtrate and washings to 100 mL followed by addition of 150 mL of hexane afforded red crystals which were dried in vacuo at 90 °C for 16.5 h to remove dichloromethane of crystallization. The yield was 4.82 g (88%); mp 206-207 °C dec. We have also prepared this complex in approximately 55% yield by reaction of tetrakis(dimethylamido)titanium(IV)³³ with carbonyl sulfide in benzene solution.²⁵ Anal. Calcd for Ti(C₃H₆NOS)₄: C, 31.03; H, 5.21; N, 12.06; S, 27.61; Ti, 10.31. Found: C, 30.80; H, 5.36; N, 12.05; S, 27.28; Ti, 10.19.

Tetrakis(*N,N*-diethylmonothiocarbamato)titanium(IV), [Ti(Et₂mtc)₄]. This compound was prepared in 91% yield by reaction of titanium(IV) chloride (1.40 mL, 12.7 mmol) with Na(Et₂mtc) (8.63 g, 55.6 mmol) in benzene (150 mL) using a procedure similar to that employed for preparation of [Ti(Me₂mtc)₄]; mp 182-190 °C dec.

[Ti(Et₂mtc)₄] was also prepared by insertion of carbonyl sulfide into the titanium-nitrogen bonds of tetrakis(diethylamido)titanium(IV).²⁵ Carbonyl sulfide was bubbled vigorously for ~5 min through a solution of Ti(NEt₂)₄³³ (9.09 g, 27.0 mmol) in 30 mL of benzene. The resulting red precipitate was recrystallized from dichloromethane-hexane (~1:1 v/v); yield 10.72 g (69%); mp 182-186 °C dec. Anal. Calcd for Ti(C₅H₁₀NOS)₄: C, 41.65; H, 6.99; N, 9.71; Ti, 8.31. Found: C, 41.20; H, 7.15; N, 9.62; Ti, 7.84.

Tetrakis(*N,N*-diisopropylmonothiocarbamato)titanium(IV), [Ti(*i*-Pr₂mtc)₄]. This complex was prepared by reaction of titanium(IV) chloride (2.23 mL, 20.3 mmol) with Li(*i*-Pr₂mtc) (13.57 g, 81.2 mmol) in dichloromethane (150 mL). The red product was ground to a fine powder and dried in vacuo for 5 days at 100 °C to remove dichloromethane of crystallization; yield 11.52 g (82%); mp 241-250 °C dec. Anal. Calcd for Ti(C₇H₁₄NOS)₄: C, 48.82; H, 8.19; N, 8.13; Ti, 6.95. Found: C, 48.85; H, 8.09; N, 8.00; Ti, 6.81.

Tetrakis(*N,N*-dimethylmonothiocarbamato)zirconium(IV), [Zr(Me₂mtc)₄]. Na(Me₂mtc) (3.23 g, 25.4 mmol) was added to a slurry of zirconium(IV) chloride (1.72 g, 7.38 mmol) in 40 mL of acetonitrile, and the mixture was allowed to reflux with stirring for 5 h. The acetonitrile was pumped off, and the product was extracted with dichloromethane. Addition of hexane afforded a white solid, which

Table I. Proton Chemical Shift^a and Coupling Constant^b Data

compd	CH	CH ₂	CH ₃	J
Na(Me ₂ - mtc) ^c			-3.06	
[Ti(Me ₂ - mtc) ₄]			-3.09, -3.07	
[Zr(Me ₂ - mtc) ₄]			-3.11, -3.08	
Na(Et ₂ - mtc) ^c	-3.56	-1.08		7.0
[Ti(Et ₂ - mtc) ₄]	-3.53, -3.50	-1.14, -1.12		7.1, 7.1
[Zr(Et ₂ - mtc) ₄]	-3.59, -3.55	-1.20, -1.16		7.0, 7.0
Li(<i>i</i> -Pr ₂ - mtc) ^d	-5.08, -3.70		-1.30, -1.22	7.1, 7.4
[Ti(<i>i</i> -Pr ₂ - mtc) ₄]	-4.58, -3.46		-1.41, -1.11	6.8, 6.7
[Zr(<i>i</i> -Pr ₂ - mtc) ₄]	-4.77, -3.48		-1.42, -1.15	6.7, 6.7

^a In ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume). The solvent is CDCl₃ unless indicated otherwise. Spectra of Li(*i*-Pr₂mtc) and the [Ti(R₂mtc)₄] complexes were recorded at 90 MHz and 34 °C; spectra of the Na(R₂mtc) and [Zr(R₂mtc)₄] compounds were obtained at 60 MHz and 37 °C. ^b In Hz (±0.2). The first coupling constant listed applies to the downfield methyl resonance; the second applies to the upfield methyl resonance. ^c In CD₃CN. ^d In CD₂Cl₂.

was recrystallized from dichloromethane-hexane; yield 3.12 g (97%); mp >280 °C. Anal. Calcd for Zr(C₃H₆NOS)₄: C, 28.38; H, 4.76; N, 11.03; Zr, 17.96. Found: C, 27.99; H, 4.65; N, 10.86; Zr, 18.10.

Tetrakis(*N,N*-diethylmonothiocarbamato)zirconium(IV), [Zr(Et₂mtc)₄]. This complex was prepared by reaction of Na(Et₂mtc) (5.47 g, 35.2 mmol) and zirconium(IV) chloride (2.04 g, 8.75 mmol) in acetonitrile (25 mL) at room temperature. The reaction time was 0.5 h. Recrystallization from dichloromethane-hexane afforded 3.87 g (71%) of a white solid; mp 215–218 °C dec. This complex was also prepared by insertion of carbonyl sulfide into the zirconium-nitrogen bonds of tetrakis(diethylamido)zirconium(IV).³³ Anal. Calcd for Zr(C₃H₁₀NOS)₄: C, 38.74; H, 6.50; N, 9.04; S, 20.69; Zr, 14.71. Found: C, 38.62; H, 6.57; N, 8.98; S, 20.63; Zr, 14.66.

Tetrakis(*N,N*-diisopropylmonothiocarbamato)zirconium(IV), [Zr(*i*-Pr₂mtc)₄]. This compound was prepared by reaction of Li(*i*-Pr₂mtc) (3.19 g, 19.1 mmol) and zirconium(IV) chloride (1.10 g, 4.72 mmol) in acetonitrile (40 mL). The procedure was the same as for preparation of [Zr(Me₂mtc)₄] except that the reaction time was 1 day. Recrystallization from dichloromethane-hexane afforded 3.10 g (90%) of a white solid; mp 250–255.5 °C dec. Anal. Calcd for Zr(C₇H₁₄NOS)₄: C, 45.93; H, 7.71; N, 7.65; Zr, 12.46. Found: C, 46.12; H, 7.45; N, 7.44; Zr, 12.45.

Conductance Measurements. Conductance measurements were made in dry dichloromethane at 25.00 ± 0.05 °C with an Industrial Instruments Model RC 16B2 conductivity bridge and a Freas-type solution cell with bright platinum electrodes. The bridge frequency was 60 Hz, and the cell constant was 0.113 cm⁻¹. The specific conductance of the purified solvent was less than 4.5 × 10⁻⁸ Ω⁻¹ cm⁻¹.

Infrared Spectra. Infrared spectra were recorded in the region 4000–250 cm⁻¹ with a Perkin-Elmer 521 grating spectrophotometer. The complexes were studied as Nujol mulls supported between cesium iodide plates. The estimated uncertainty in reported frequencies is ±4 cm⁻¹.

Nuclear Magnetic Resonance Spectra. Proton chemical shifts and coupling constants were measured at ambient probe temperature with a Varian A-60A or a Varian EM-390 spectrometer. Each spectrum was swept at least three times, and the values reported in Table I are average values; the sweep width was calibrated with a standard sample of chloroform and tetramethylsilane.

Dipole Moment Measurements. Using a method described previously,³⁴ dipole moments were determined for [Ti(Et₂mtc)₄] and [Zr(Et₂mtc)₄] in dilute benzene solution at 25.00 ± 0.05 °C. The slopes, α, β, and γ, respectively, of linear plots of the dielectric constant, ε₁₂, specific volume, v₁₂, and refractive index, n₁₂, of the solution vs. weight fraction of the solute, w₂, were evaluated by least-squares analysis. Total molar polarizations, τP_2 , were obtained from the Halverstadt-Kumler equation,^{35a} and electronic molar polarizations,

Table II. Dipole Moment Data in Benzene Solution at 25.0 °C^a

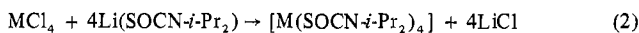
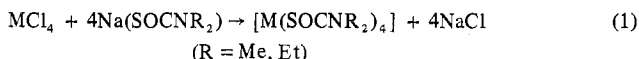
	[Ti(Et ₂ mtc) ₄]	[Zr(Et ₂ mtc) ₄]
α	4.14 ± 0.17	2.45 ± 0.20
β, cm ³ g ⁻¹	-0.37 ± 0.06	-0.40 ± 0.17
γ	0.12 ± 0.02	0.06 ± 0.01
τP_2 , cm ³	582 ± 21	425 ± 39
ϵP_2 , cm ³	171 ± 12	159 ± 31
σP_2 , cm ³	411 ± 20	266 ± 24
μ, D	4.49 ± 0.11	3.61 ± 0.16

^a Errors are estimated at the 95% confidence limit.

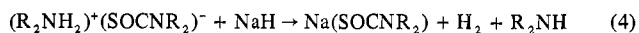
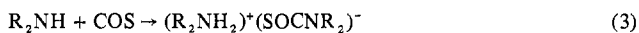
ϵP_2 , from the modified Halverstadt-Kumler equation.^{35b} Atomic polarization was neglected. Dipole moments were calculated from the relation $\mu = \sqrt{3/2} [kT\sigma P_2 / \pi N]^{1/2}$ where the orientation molar polarization is given by $\sigma P_2 = \tau P_2 - \epsilon P_2$, and the symbols *k*, *T*, and *N* have their usual significance. Results are presented in Tables II and III.³⁶

Results and Discussion

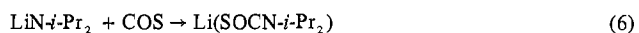
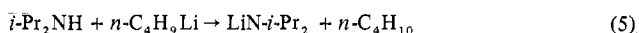
Preparation and Properties. Titanium(IV) and zirconium(IV) *N,N*-dialkylmonothiocarbamates of the type [M(R₂mtc)₄] (R = Me, Et, *i*-Pr) have been prepared in excellent yield by reaction of the metal tetrachlorides with alkali metal *N,N*-dialkylmonothiocarbamates in dichloromethane or benzene (M = Ti) or acetonitrile (M = Zr) (eq 1 and 2). The



intermediate sodium salts were obtained by reaction of carbonyl sulfide with the dialkylamine to give the dialkylammonium salts; the dialkylammonium salts were converted to sodium salts upon reaction with sodium hydride (eq 3 and 4). The intermediate Li(*i*-Pr₂mtc) was synthesized via



LiN-*i*-Pr₂ (eq 5 and 6). The methods used for preparation



and isolation of these compounds (see Experimental Section) give products of good purity as judged by satisfactory elemental analyses and proton NMR spectra (Table I). Three of the [M(R₂mtc)₄] complexes (M = Ti, R = Me or Et; M = Zr, R = Me) have been prepared by Chisholm and Extine²⁵ by insertion of carbonyl sulfide into the metal-nitrogen bonds of the corresponding dialkylamides, M(NR₂)₄. We have also employed the COS insertion method (see Experimental Section), but we find that preparation of these complexes via the alkali metal salts is more convenient. The alkali metal salts are easily prepared in 20–40-g quantities in high yield (85–95%). Though hydrolytically unstable, they are thermally stable and can be stored in an inert atmosphere until needed. Moreover, these intermediates also provide a convenient route to mixed-ligand complexes of the type [Ti(R₂mtc)₂Cl₂] and [Ti(R₂mtc)₃Cl].³⁷

The [M(R₂mtc)₄] complexes are soluble in dichloromethane and chloroform, less soluble in benzene, and essentially insoluble in saturated hydrocarbons. In general, the solubility increases with increasing size of the alkyl group (Me < Et < *i*-Pr), and it appears that these complexes are somewhat more soluble than the corresponding *N,N*-dialkylthiocarbamates.³⁸ All of the [M(R₂mtc)₄] complexes are thermally stable, but they are hydrolyzed rapidly upon exposure to air. The solid complexes exhibit evidence of hydrolysis within minutes; hydrolysis of solutions is immediate. The rate of hydrolysis

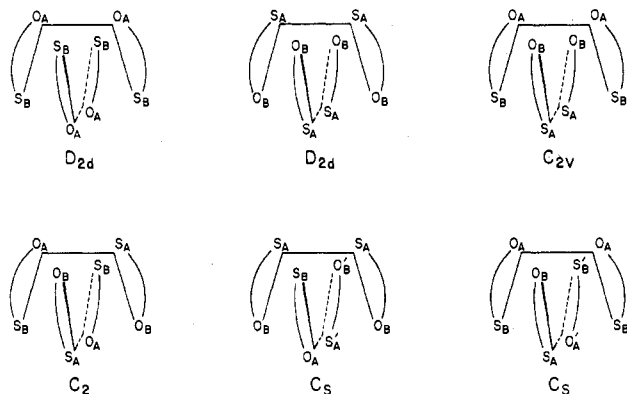


Figure 1. Schematic representation of the six possible *mmmm* dodecahedral stereoisomers of an $[M(R_2mtc)_4]$ complex. The two mutually perpendicular trapezoids of the D_{2d} dodecahedron are outlined, and the A and B site occupancy of the sulfur and oxygen atoms is shown. The isomers are labeled according to their point-group symmetry.

increases with decreasing size of the alkyl substituent ($i\text{-Pr} < \text{Et} < \text{Me}$), and the titanium compounds appear to hydrolyze somewhat faster than the zirconium analogues.

All of the $[M(R_2mtc)_4]$ complexes behave as nonelectrolytes in dichloromethane solution. Molar conductances of $\sim 2 \times 10^{-3}$ M solutions are in the range $0.03\text{--}0.33 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for $[\text{Ti}(R_2mtc)_4]$ and $0.05\text{--}0.09 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for $[\text{Zr}(R_2mtc)_4]$ ($R = \text{Me}, \text{Et}, i\text{-Pr}$).

Stereochemistry. Because of the short bite of the monothiocarbamate ligand, it was anticipated that the $[M(R_2mtc)_4]$ complexes would adopt an eight-coordinate dodecahedral structure with bidentate ligands spanning the *m* edges³⁰ of the dodecahedron. This has been confirmed by X-ray diffraction studies of two representative complexes, $[\text{Ti}(\text{Et}_2mtc)_4]$ and $[\text{Zr}(\text{Et}_2mtc)_4]$.³² The X-ray studies have shown, in addition, that the $[M(\text{Et}_2mtc)_4]$ complexes exist in the solid state as the C_{2v} stereoisomer, which has two sulfur atoms in dodecahedral A sites and two in B sites. This isomer is one of six possible stereoisomers that have an *mmmm* ligand wrapping pattern (see Figure 1). A perspective view of the $[\text{Ti}(\text{Et}_2mtc)_4]$ molecule is shown in Figure 1 of the following paper.³²

Several lines of evidence indicate that the C_{2v} stereoisomer is also the principal species in solution. First, proton NMR spectra of the $[M(\text{Me}_2mtc)_4]$ complexes in dichloromethane in the slow-exchange limit can be interpreted in terms of four overlapping methyl resonances of approximately equal intensity. Typical spectra for $[\text{Ti}(\text{Me}_2mtc)_4]$ are presented in Figure 2. The four resonances observed at -104°C are attributed to the four inequivalent methyl groups of the C_{2v} stereoisomer; the methyl groups occupy four equally populated sites adjacent to donor atoms $S_A, S_B, O_A,$ and O_B (see Figure 1). The -104°C spectrum could be attributed to the four inequivalent methyl groups of the C_2 stereoisomer, but this interpretation seems unlikely in view of the solid-state structures of $[M(\text{Et}_2mtc)_4]$ ³² and dipole moment evidence (vide infra). It is difficult to rule out small amounts of the other stereoisomers; however, since the D_{2d} and C_s isomers would give two and six methyl resonances, respectively, these isomers must be present in considerably smaller concentrations than the C_{2v} isomer.

Dipole moment measurements in benzene solution (Tables II and III) have afforded values of 4.49 ± 0.11 D and 3.61 ± 0.16 D for $[\text{Ti}(\text{Et}_2mtc)_4]$ and $[\text{Zr}(\text{Et}_2mtc)_4]$, respectively. These values point to a highly polar structure, consistent with the C_{2v} stereoisomer, which is the most polar of the six possible *mmmm* stereoisomers. The group dipole moment of the $M(\text{SOCNET}_2)$ moiety can be resolved into a radial part, μ_r , oriented along the quasi-twofold axis of the ligand and a

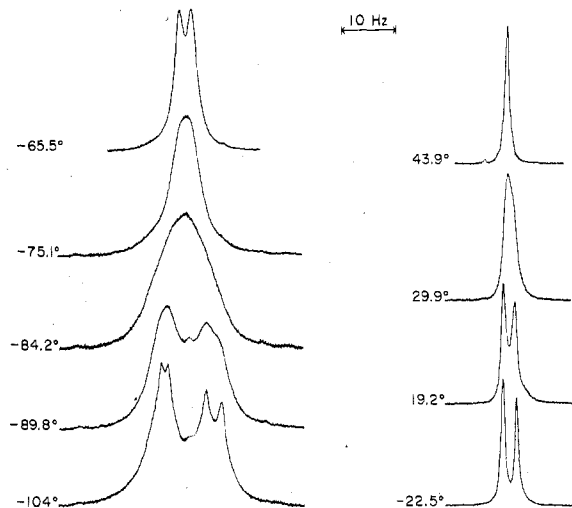


Figure 2. Variable-temperature 90-MHz proton NMR spectra (methyl resonances) of $[\text{Ti}(\text{Me}_2mtc)_4]$ in dichloromethane solution.

tangential part, μ_t , perpendicular to the quasi-twofold axis. A rough estimate of the relative dipole moments of the six *mmmm* isomers can be made by assuming that the four μ_r components in a dodecahedral $[M(\text{SOCNET}_2)_4]$ complex cancel owing to the near (or exact) D_{2d} arrangement of the four μ_r vectors. Employing the observed values of $\theta_A = 37^\circ$ and $\theta_B = 79^\circ$,³² the relative molecular moments can be expressed in terms of the tangential part of the $M(\text{SOCNET}_2)$ group moment. Results are $3.7\mu_t, 1.0\mu_t,$ and $2.0\mu_t$ for the $C_{2v}, C_2,$ and C_s isomers, respectively; the moments of the D_{2d} isomers are zero by symmetry. We do not know the value of μ_t . However, in view of the small dipole moment of COS (0.71 D),³⁹ a value of μ_t in the neighborhood of 1 D seems reasonable. It follows that the dipole moment of the C_{2v} isomer is expected to be in the neighborhood of 3.7 D, but that of the C_2 isomer, in the neighborhood of 1 D. It is on this basis that we prefer to interpret the four-line NMR spectrum (Figure 2) in terms of the C_{2v} stereoisomer found in the solid state.

The fact that the dipole moment of $[\text{Zr}(\text{Et}_2mtc)_4]$ is 0.9 D less than that of $[\text{Ti}(\text{Et}_2mtc)_4]$ suggests that the fraction of the molecules present as the less polar stereoisomers may be slightly higher in the case of the zirconium compound. This is also suggested by the low-temperature NMR spectrum of $[\text{Zr}(\text{Me}_2mtc)_4]$, which is qualitatively similar to that of $[\text{Ti}(\text{Me}_2mtc)_4]$ but less well resolved and which exhibits relative intensities that deviate somewhat from the $1:1:1:1$ ratio expected for the C_{2v} stereoisomer. Nevertheless, the C_{2v} isomer appears to be the major species present in solution. The preferred stability of the C_{2v} stereoisomer is *not* in accord with Orgel's rule,³¹ factors which could influence the donor atom sorting pattern in these complexes are discussed in the following paper.³²

The NMR spectra of $[\text{Ti}(\text{Me}_2mtc)_4]$ (Figure 2) and $[\text{Zr}(\text{Me}_2mtc)_4]$ exhibit evidence of two distinct kinetic processes: (1) a low-temperature process (LTP) in which the four methyl resonances collapse in a pairwise fashion to give two time-averaged resonances in the fast-exchange limit and (2) a high-temperature process (HTP) in which the two time-averaged resonances merge to give a single time-averaged resonance. The coalescence temperatures for the LTP and HTP, respectively, are -84 and $+30^\circ\text{C}$ for $[\text{Ti}(\text{Me}_2mtc)_4]$ and -54 and $+78^\circ\text{C}$ for $[\text{Zr}(\text{Me}_2mtc)_4]$. The presence of four resonance lines in the slow-exchange limit indicates that both metal-centered rearrangement and hindered rotation about the $C\text{--}N$ bond are slow on the NMR time scale. Thus, these complexes may be added to the still small list of eight-coordinate tetrakis chelates that are stereochemically rigid on

Table IV. Characteristic Infrared Bands for Metal *N,N*-Dialkylmonothiocarbamates (cm⁻¹)^a

compd	$\nu(\text{C}=\text{O}), \nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{S})$	other bands ^b
Na(Me ₂ mtc)	1519 vs, b	924 m			1344 s, 1263 s, 1105 s, 1044 m, 704 m, 685 m, 507 w, 486 m, 412 m
[Ti(Me ₂ mtc) ₄]	1543 vs, b	936 m	562 s	321 s	1393 s, 1364 s, 1316 w, 1242 s, 1124 s, 1047 w, 708 s, 658 m, 481 m, 410 s
[Zr(Me ₂ mtc) ₄]	1550 vs, b	935 m	556 s		1394 s, 1367 s, 1328 w, 1242 s, 1127 s, 1049 w, 799 w, 705 s, 663 m, 477 m, 408 m, 304 w
Na(Et ₂ mtc)	1520 vs, b	944 m			1450 s, 1436 s, 1400 s, 1363 s, 1302 m, 1254 s, 1222 m, 1118 s, 1097 m, 1081 w, 1072 m, 1004 w, 875 s, 784 m, 679 m, 673 m, 503 m, 450 m, 392 m, 326 vw
[Ti(Et ₂ mtc) ₄]	1547 s, 1530 vs	941 m	558 s	320 s	1437 s, 1400 s, 1358 s, 1306 m, 1266 s, 1209 m, 1140 s, 1099 m, 1088 m, 1080 m, 1070 w, 1015 w, 887 s, 785 m, 686 s, 669 m, 514 m, 474 w, 448 m, 424 w, 401 m
[Zr(Et ₂ mtc) ₄]	1533 vs, b	940 m	552 s		1437 s, 1397 s, 1357 s, 1339 m, 1319 w, 1306 m, 1273 s, 1209 m, 1144 s, 1097 m, 1088 m, 1081 m, 1069 m, 1013 vw, 882 s, 782 m, 679 s, 669 m, 512 m, 467 w, 449 m, 424 w, 394 m, 326 vw
Li(<i>i</i> -Pr ₂ mtc)	1549 m, 1536 s 1507 s, 1489 s	918 m			1415 w, 1402 w, 1310 s, 1284 s, 1211 m, 1149 m, 1135 m, 1115 m, 1036 m, 873 m, 830 m, 691 m, 634 w, 570 w, 523 m, 420 w, 355 w
[Ti(<i>i</i> -Pr ₂ mtc) ₄]	1540 m, 1513 s	925 w	571 s	313 s	1412 w, 1347 w, 1318 m, 1304 m, 1209 m, 1165 w, 1149 m, 1131 m, 1037 s, 878 w, 848 w, 840 w, 733 w, 688 m, 642 w, 525 m, 512 w, 386 w
[Zr(<i>i</i> -Pr ₂ mtc) ₄]	1515 vs, b	927 m	569 m		1407 w, 1356 s, 1324 s, 1308 m, 1210 m, 1168 m, 1154 m, 1132 m, 1038 s, 877 w, 841 m, 736 w, 678 w, 636 m, 526 m, 374 vw

^a As Nujol mulls between CsI plates. ^b 2000–250-cm⁻¹ region.

the NMR time scale.^{40–42} A detailed total line-shape analysis of the spectra is in progress, and the results will be published elsewhere. Suffice it to say at this point that we interpret the LTP in terms of metal-centered rearrangement and the HTP in terms of C=N bond rotation. The former process exchanges methyl groups between the dodecahedral A and B sites, and the latter process exchanges methyl groups between sites adjacent to sulfur and sites adjacent to oxygen. Hindered C=N bond rotation in the *O*-methyl ester, MeOC(S)NMe₂, has been studied previously,⁴³ and the coalescence temperature (~75 °C) is in the range of the HTP for the [M(Me₂mtc)₄] complexes.

Chisholm and Extine²⁵ have argued for slow C=N bond rotation in [Ti(Me₂mtc)₄] at 40 °C on the basis of the 60-MHz proton NMR spectrum of [Ti(SO¹³CNMe₂)₄] in dichloromethane. Asymmetry in the methyl doublet was attributed to a ~0.3-Hz chemical shift between the resonances of the methyl groups adjacent to sulfur and oxygen and a ~0.3-Hz difference in the two ¹³C–¹H coupling constants. Our spectra at 90 MHz in the same solvent (Figure 2) exhibit a chemical shift of 2.4 Hz between the two methyl resonances at –22.5 °C. In CDCl₃, C=N bond rotation is slow on the NMR time scale at ambient probe temperature (34–37 °C) for all of the [M(R₂mtc)₄] (M = Ti, Zr; R = Me, Et) complexes as evidenced by observation of two methyl and two methylene proton resonances (see Table I).

Proton NMR spectra of the [M(*i*-Pr₂mtc)₄] complexes also exhibit two sets of resonance lines for the alkyl groups; however, the chemical shifts (~0.3 ppm between the two methyl doublets and ~1.2 ppm between the two CH septets; cf. Table I) are very much larger than the shifts observed for the [M(Me₂mtc)₄] and [M(Et₂mtc)₄] complexes. These chemical shifts are comparable to those observed for the

corresponding dithiocarbamate complexes, [M(*i*-Pr₂dtc)₄],³⁸ which suggests that the chemical shifts arise from “inner” and “outer” sites rather than from adjacency to sulfur or oxygen. Figure 3 shows the probable conformations of the isopropyl groups based on the X-ray structure of crystalline [Ni(*i*-Pr₂dtc)₂].²⁹ The methine protons lie in the plane of the ligand in “inner” sites, near the quasi-twofold axis of the ligand, and in “outer” sites, away from this axis. Similarly, the methyl groups occupy equally populated inner and outer sites. Because the monothiocarbamate ligand is unsymmetrical, there are two possible ligand conformations (I and II in Figure 3) and four inequivalent sites; methine protons and methyl groups may be in inner or outer sites adjacent to sulfur or oxygen. Since only two equally intense and relatively widely separated isopropyl resonances are observed, we assume that (1) the chemical shift arising from adjacency to sulfur or oxygen is too small to be observed or (2) only one ligand conformation is present in solution. Exchange of methyl groups and of methine protons between inner and outer sites can occur by a synchronous gearlike rotation about the two C–N single bonds^{38,44} (Figure 3); if only one ligand conformation is present, the exchange process would require rotation about the C–N single bonds and rotation about the C=N partial double bond. Variable-temperature NMR spectra of [Ti(*i*-Pr₂mtc)₄] in diphenylmethane indicate that the exchange process becomes fast on the NMR time scale at temperatures above 110 °C.

Vibrational Spectra. Infrared frequencies for the [Ti(R₂mtc)₄] and [Zr(R₂mtc)₄] complexes and for alkali metal salts of the ligands are listed in Table IV. All of the complexes exhibit an intense, broad band, sometimes split, in the region 1500–1550 cm⁻¹. This band envelope is believed to contain bands due to the coupled C=O and C=N stretching vibrations of the bidentate monothiocarbamate ligand.¹¹ No bands are

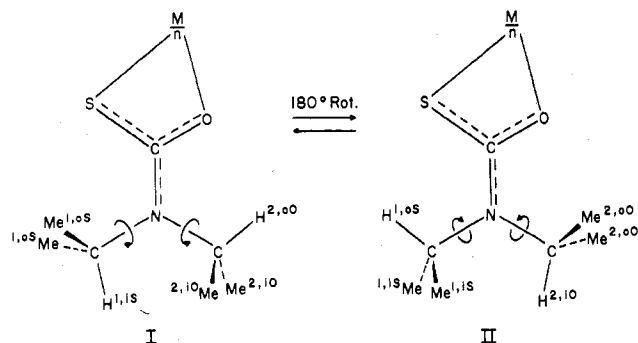


Figure 3. Probable ligand conformations (I and II) in metal *N,N*-diisopropylmonothiocarbamate complexes. Numbers label protons and letters label the four inequivalent environments: inner near sulfur (iS), outer near sulfur (oS), inner near oxygen (iO), and outer near oxygen (oO). Exchange of protons between inner and outer sites can occur by a gearlike rotation (180°) about the C–N single bonds.

observed in the $1560\text{--}1665\text{-cm}^{-1}$ region where a $\nu(\text{C}=\text{O})$ stretching frequency has been found for complexes which are believed to contain S-bonded monodentate monothiocarbamate ligands.^{9,10,15,22}

Metal–oxygen and metal–sulfur stretching frequencies may be identified by comparison of infrared spectra of the complexes and the alkali metal salts. The $[\text{Ti}(\text{R}_2\text{mtc})_4]$ complexes exhibit intense bands, not present in spectra of the alkali metal salts, at $558\text{--}571$ and $313\text{--}321\text{ cm}^{-1}$ (Table IV); these bands may be assigned to $\nu(\text{Ti}\text{--}\text{O})$ and $\nu(\text{Ti}\text{--}\text{S})$, respectively. It is interesting to note that $\nu(\text{Ti}\text{--}\text{S})$ is $30\text{--}40\text{ cm}^{-1}$ lower than $\nu(\text{Ti}\text{--}\text{S})$ in the corresponding dithiocarbamate complexes $[\text{Ti}(\text{R}_2\text{dtc})_4]$ ^{38,45} and $\nu(\text{Ti}\text{--}\text{O})$ is $100\text{--}120\text{ cm}^{-1}$ higher than $\nu(\text{Ti}\text{--}\text{O})$ in the corresponding carbamate complexes $[\text{Ti}(\text{O}_2\text{CNR}_2)_4]$.²⁵ These frequency shifts could be due to a strengthening of the Ti–O bond in $[\text{Ti}(\text{R}_2\text{mtc})_4]$ at the expense of the Ti–S bond; however, this seems unlikely in view of the fact that the mean Ti–S bond lengths in $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ ³² and $[\text{Ti}(\text{Et}_2\text{dtc})_4]$ ⁴⁶ differ by only 0.007 \AA . We suggest that the frequency shifts may arise from a coupling of Ti–O and Ti–S stretching modes of the same symmetry. The $[\text{Zr}(\text{R}_2\text{mtc})_4]$ complexes exhibit a strong band at $552\text{--}569\text{ cm}^{-1}$ (Table IV) that can be assigned to $\nu(\text{Zr}\text{--}\text{O})$. Curiously, however, the $250\text{--}380\text{-cm}^{-1}$ region of spectra of the Zr(IV) complexes contains no strong- or medium-intensity bands that can be attributed to $\nu(\text{Zr}\text{--}\text{S})$. Evidently the $\nu(\text{M}\text{--}\text{S})$ bands are too weak to be observed, as is the case in some Pd(II) monothiocarbamate complexes studied by Krankovits et al.¹⁵

Chisholm and Extine²⁵ have suggested that the band at 409 cm^{-1} in spectra of $[\text{M}(\text{Me}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$) should be attributed to $\nu(\text{M}\text{--}\text{O})$. However, this band appears to be due to a vibration of the Me_2mtc ligand since it is also present in the spectrum of the sodium salt (Table IV).

We tentatively assign $\nu(\text{C}=\text{S})$ to a medium-intensity band in the $918\text{--}944\text{-cm}^{-1}$ region. This assignment is in accord with $\nu(\text{C}=\text{S})$ frequencies in the corresponding dithiocarbamate complexes $[\text{M}(\text{R}_2\text{dtc})_4]$ ($\sim 960\text{--}1000\text{ cm}^{-1}$)^{38,45} and with the close similarity of the C=S distances in $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ ³² and $[\text{Ti}(\text{Et}_2\text{dtc})_4]$.⁴⁶

Infrared spectra of $[\text{M}(\text{Me}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$) in dichloromethane solution were recorded in an attempt to find evidence for more than one stereoisomer in solution. The solution spectra are very similar to spectra of Nujol mulls, and no new bands are observed in the metal–ligand stretching region.

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Registry No. $\text{Na}(\text{Me}_2\text{mtc})$, 18992-87-5; $\text{Na}(\text{Et}_2\text{mtc})$, 21055-93-6; $\text{Li}(i\text{-Pr}_2\text{mtc})$, 66758-52-9; $[\text{Ti}(\text{Me}_2\text{mtc})_4]$, 66791-67-1; $[\text{Ti}(\text{Et}_2\text{mtc})_4]$,

61359-07-7; $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$, 66758-38-1; $[\text{Zr}(\text{Me}_2\text{mtc})_4]$, 66791-68-2; $[\text{Zr}(\text{Et}_2\text{mtc})_4]$, 66758-39-2; $[\text{Zr}(i\text{-Pr}_2\text{mtc})_4]$, 66758-53-0; $[\text{Ti}(\text{Me}_2\text{mtc})_4]$ (salt form), 62242-01-7; $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ (salt form), 61372-28-9; $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$ (salt form), 66750-62-7; $[\text{Zr}(\text{Me}_2\text{mtc})_4]$ (salt form), 62444-65-9; $[\text{Zr}(\text{Et}_2\text{mtc})_4]$ (salt form), 66750-63-8; $[\text{Zr}(i\text{-Pr}_2\text{mtc})_4]$ (salt form), 66750-64-9.

Supplementary Material Available: Table III, dielectric constant, specific volume, and refractive index data for $[\text{M}(\text{Et}_2\text{mtc})_4]$ complexes in benzene solution at 25.0°C . (1 page). Ordering information is given on any current masthead page.

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Stereochemistry of Eight-Coordinate Dodecahedral Complexes of the Type MX_4Y_4 . 2. Crystal and Molecular Structures of Tetrakis(*N,N*-diethylmonothiocarbamato)titanium(IV)¹ and Tetrakis(*N,N*-diethylmonothiocarbamato)zirconium(IV)^{1b}

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The crystal and molecular structures of tetrakis(*N,N*-diethylmonothiocarbamato)titanium(IV), $[\text{Ti}(\text{Et}_2\text{mtc})_4]$, and tetrakis(*N,N*-diethylmonothiocarbamato)zirconium(IV), $[\text{Zr}(\text{Et}_2\text{mtc})_4]$, have been determined by X-ray diffraction techniques. Crystals of the two compounds are isomorphous and crystallize in the monoclinic space group $C2/c$ with four molecules per unit cell; the molecules are therefore required to have twofold symmetry. The unit cell dimensions for $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ are $a = 13.687$ (2) Å, $b = 13.974$ (3) Å, $c = 16.990$ (4) Å, and $\beta = 111.39$ (2)° ($\rho_{\text{measd}} = 1.267$, $\rho_{\text{calcd}} = 1.266$ g cm⁻³) and those for $[\text{Zr}(\text{Et}_2\text{mtc})_4]$ are $a = 13.730$ (1) Å, $b = 14.101$ (1) Å, $c = 17.117$ (2) Å, and $\beta = 110.82$ (1)° ($\rho_{\text{measd}} = 1.33$, $\rho_{\text{calcd}} = 1.329$ g cm⁻³). The structure of $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ was solved by the heavy-atom method and refined anisotropically to final residuals $R_1 = 0.086$ and $R_2 = 0.087$ using 3899 diffractometer-measured reflections having $2\theta \leq 65.00^\circ$ and $|F_o| > 2.00\sigma_F$ (Mo $K\alpha$ radiation). The structure of the isomorphous zirconium compound was refined anisotropically to final residuals $R_1 = 0.064$ and $R_2 = 0.049$ using 3741 diffractometer-measured reflections having $2\theta_{\text{MoK}\alpha} \geq 65.13^\circ$ and $|F_o| > 1.58\sigma_F$. The eight-coordinate molecules of $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ and $[\text{Zr}(\text{Et}_2\text{mtc})_4]$ adopt a slightly distorted dodecahedral structure in which the bidentate monothiocarbamate ligands span the m edges to give the $mmmm$ stereoisomer. The sulfur and oxygen atoms of the ligands do not completely sort into the A and B sites of the dodecahedron, as predicted by Orgel's rule but rather partially sort so that half of the sulfur atoms occupy A sites and the other half, B sites. The four sulfur atoms are thus located on one side of the molecule in an all-cis arrangement. Bond distances in the coordination groups are $\text{Ti}-\text{S}_A = 2.609$ (1), $\text{Ti}-\text{S}_B = 2.533$ (1), $\text{Ti}-\text{O}_A = 2.117$ (3), and $\text{Ti}-\text{O}_B = 2.061$ (3) Å for $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ and $\text{Zr}-\text{S}_A = 2.689$ (1), $\text{Zr}-\text{S}_B = 2.669$ (1), $\text{Zr}-\text{O}_A = 2.200$ (2), and $\text{Zr}-\text{O}_B = 2.180$ (2) Å for $[\text{Zr}(\text{Et}_2\text{mtc})_4]$. Bond distances in the monothiocarbamate ligands are remarkably similar to corresponding distances in bidentate carbamate and dithiocarbamate ligands. One of the ethyl groups of one monothiocarbamate ligand is disordered, apparently due to a rather severe $\text{CH}_3 \cdots \text{CH}_3$ intermolecular contact.

Introduction

The importance of the electronic configuration of the metal ion and the π -bonding capabilities of the ligands in determining the stereochemistry of eight-coordinate, dodecahedral complexes was first recognized by Orgel in 1960.² Orgel suggested that complexes of the type MX_4Y_4 should exhibit sorting of the two different ligands into the two nonequivalent dodecahedral coordination sites, A and B.³ In complexes of d^1 and d^2 metal ions, the better π -acceptor ligands should occupy the B sites so as to take advantage of $d\pi-p\pi$ back-bonding involving the partially or completely filled $d_{x^2-y^2}$ orbital on the metal and a π -acceptor orbital on the ligands. In complexes of d^0 metal ions, the reverse site occupancy would be expected; i.e., the better π donors should occupy the B sites.⁴ Several structures which tend to support Orgel's rule have been reported,⁵⁻⁸ but the number of MX_4Y_4 complexes whose structures have been determined is still quite small. Previous structural studies of metal chelate complexes of the type MX_4Y_4 are limited to compounds in which the ligating atoms are nitrogen and oxygen.^{4,6-8}

In order to explore the generality of Orgel's rule, we thought it of interest to investigate some chelate systems containing donor atoms other than nitrogen and oxygen. Accordingly, we have prepared and characterized a series of tetrakis(monothiocarbamate) complexes of Ti(IV) and Zr(IV), $[\text{M}(\text{R}_2\text{mtc})_4]$;⁹ we report herein the crystal and molecular structures of two representative examples, $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ and $[\text{Zr}(\text{Et}_2\text{mtc})_4]$. It seems likely that both oxygen and sulfur will behave as π donors toward d^0 ions such as Ti(IV) and Zr(IV), though it is not clear which atom will be the better

Table I. Crystal Data

	$[\text{Ti}(\text{Et}_2\text{mtc})_4]$	$[\text{Zr}(\text{Et}_2\text{mtc})_4]$
crystal system	monoclinic	monoclinic
space group	$C2/c$	$C2/c$
a , Å	13.687 (2)	13.730 (1)
b , Å	13.974 (3)	14.101 (1)
c , Å	16.990 (4)	17.117 (2)
β , deg	111.39 (2)	110.82 (1)
vol, Å ³	3025.7	3097.6
mol wt	576.72	620.04
Z	4	4
ρ (calcd), g/cm ³	1.266	1.329
ρ (measd), g/cm ³	1.267	1.33
crystal size, mm ³	$0.45 \times 0.25 \times 0.20$	$0.50 \times 0.19 \times 0.19$
μ , cm ⁻¹	5.9	6.4
no. of unique reflections	5893	4542
no. of obsd reflections	3899	3741

π donor. Nevertheless, there should be a difference in the π -donor ability of oxygen and sulfur toward Ti(IV) and Zr(IV), and on the basis of Orgel's rule one would expect sorting of the better π donor into the dodecahedral B sites. Instead, the sulfur and oxygen atoms cluster on opposite sides of the molecule so as to give an all-cis arrangement of sulfur atoms.

Experimental Section

Crystallography. The relevant crystal data for the two compounds are listed in Table I.

$[\text{Ti}(\text{Et}_2\text{mtc})_4]$. Several air-sensitive, red crystals of tetrakis(*N,N*-diethylmonothiocarbamato)titanium(IV), $[\text{Ti}(\text{Et}_2\text{mtc})_4]$, were sealed in 0.3-mm diameter Lindemann glass capillaries under an atmosphere of dry nitrogen. The compound had been prepared by reaction of