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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), $[Ti(Et_2mtc)_4]$, and tetrakis(*N*,*N*-diethylmonothiocarbamato)zirconium(IV), $[Zr(Et_2mtc)_4]$, 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 $[Ti(Et_2mtc)_4]$ 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 $[Zr(Et_2mtc)_4]$ 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 $[Ti(Et_2mtc)_4]$ 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 $2\theta \leq 65.00°$ and $|F_o| > 2.00\sigma_F$ (Mo K$\bar{\alpha}$ 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 $2\theta_{\text{Mo K}\bar{\alpha}} \geq 65.13°$ and $|F_o| > 1.58\sigma_F$. The eight-coordinate molecules of $[Ti(Et_2mtc)_4]$ and $[Zr(Et_2mtc)_4]$ 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 $Ti-S_A = 2.609$ (1), $Ti-S_B = 2.533$ (1), $Ti-O_A = 2.117$ (3), and $Ti-O_B = 2.061$ (3) Å for $[Ti(Et_2mtc)_4]$ and $Zr-S_A = 2.689$ (1), $Zr-S_B = 2.669$ (1), $Zr-O_A = 2.200$ (2), and $Zr-O_B = 2.180$ (2) Å for $[Zr(Et_2mtc)_4]$. 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 $CH_3 \cdots CH_3$ 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), $[M(R_2mtc)_4]$;[9] we report herein the crystal and molecular structures of two representative examples, $[Ti(Et_2mtc)_4]$ and $[Zr(Et_2mtc)_4]$. 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 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.

Table I. Crystal Data

	$[Ti(Et_2mtc)_4]$	$[Zr(Et_2mtc)_4]$
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 × 0.25 × 0.20	0.50 × 0.19 × 0.19
μ, cm^{-1}	5.9	6.4
no. of unique reflections	5893	4542
no. of obsd reflections	3899	3741

Experimental Section

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

$[Ti(Et_2mtc)_4]$. Several air-sensitive, red crystals of tetrakis(*N*,*N*-diethylmonothiocarbamato)titanium(IV), $[Ti(Et_2mtc)_4]$, were sealed in 0.3-mm diameter Lindemann glass capillaries under an atmosphere of dry nitrogen. The compound had been prepared by reaction of

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carbonyl sulfide with tetrakis(N,N-diethylamido)titanium(IV) in benzene and had been recrystallized from dichloromethane–hexane (~1:1 v/v).[9] The lattice symmetry and pattern of systematically absent reflections (hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$) as determined from precession and Weissenberg photographs indicated the crystals to be monoclinic with the probable space group $C2/c$ (C_{2h}^6, No. 15).[10] The choice of the centric space group was confirmed by the successful structure solution in that group. The lattice constants were determined by a least-squares refinement of the 2θ, ω, and χ values for 12 reflections ($2\theta > 28°$) measured with a Picker FACS-I automatic diffractometer using Zr-filtered Mo K$\bar{\alpha}$ radiation (λ 0.710 69 Å). The observed density was measured by the flotation method using a solution of hexane and carbon tetrachloride.

The intensity data were measured on the Picker diffractometer using the θ–2θ scan technique with Zr-filtered Mo K$\bar{\alpha}$ radiation at a take-off angle of ~2°. A total of 5893 unique reflections having $2\theta \leq 65.00°$ (1.6 times the number of data in the limiting Cu K$\bar{\alpha}$ sphere) was scanned. The range of each scan, taken at 1°/min, consisted of the estimated base width of 2.0° at $2\theta = 0°$ and an increment of $\Delta(2\theta) = (0.692 \tan \theta)°$ to allow for spectral dispersion; background counts of 40-s duration were taken at both limits of the scan. Reflections with counting rates greater than 20 000 counts/s were automatically attenuated by the insertion of copper foil into the path of the diffracted beam until the intensity was reduced to less than that value. The intensities of three standard reflections, measured at 50-reflection intervals to monitor the stability of the system, displayed no trend with time.

With the cited crystal dimensions and linear absorption coefficient, absorption corrections were considered to be unnecessary; the maximum error resulting from neglect of absorption corrections was estimated to be <6% in any intensity and <3% in any structure amplitude. The intensity data were reduced to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factors. Those reflections with $|F_o| > 2.00\sigma_F$, where σ_F is defined elsewhere,[11] were retained as "observed" for the structure analysis.

[Zr(Et$_2$mtc)$_4$]. Clear, colorless crystals of [Zr(Et$_2$mtc)$_4$] were air-sensitive and were, therefore, mounted in glass capillaries under a dry nitrogen atmosphere. The compound has been prepared by reaction of carbonyl sulfide with tetrakis(N,N-diethylamido)zirconium(IV) in benzene and had been recrystallized from dichloromethane–hexane (~1:1 v/v).[9] Preliminary precession and Weisenberg photographs indicated the crystals to be isomorphous with those of [Ti(Et$_2$mtc)$_4$]. The lattice constants and intensity data were measured by the method described above for [Ti(Et$_2$mtc)$_4$]. The intensities of the standard reflections remained constant for the first 3000 intensity measurements and then decreased approximately linearly to a final value 10% lower than the original value. The intensity data were corrected for this small amount of crystal decomposition. A total of 4542 unique reflections having $2\theta \leq 65.13°$ (the equivalent of 1.6 limiting Cu K$\bar{\alpha}$ spheres) was collected.

On the basis of the dimensions of the crystal used for data collection and the linear absorption coefficient for Mo K$\bar{\alpha}$ radiation, the maximum error resulting from the neglect of absorption corrections was estimated to be <8% in any intensity and <4% in any structure amplitude. An absorption correction was therefore not made. Those reflections with $|F_o| > 1.58\sigma_F$ were considered reliable and were retained for the structure analysis.

Structure Determination and Refinement. [Ti(Et$_2$mtc)$_4$]. With four molecules per unit cell and the space group $C2/c$, the titanium atom is required to be on the twofold axis or at an inversion center.[10] An analysis of a three-dimensional Patterson synthesis indicated that the titanium atom is positioned on the twofold axis; the remaining nonhydrogen atoms were located in subsequent Fourier syntheses.

The model structure was refined according to the outline given in Table II. Following the first three cycles of refinement using anisotropic thermal parameters, a C–C distance for an ethyl group of one of the monothiocarbamate ligands was abnormally short (1.33 Å). A Fourier synthesis calculated in the region of the ethyl group revealed that the group was disordered. The terminal carbon atom occupied two distinct sites in the ratio 2 to 1 as determined from the relative peak heights. The peak representing the other carbon atom was subject to a pronounced elongation in one direction, an indication that the methylene carbon atom also occupied two different positions but that the positions were sufficiently close so that they could not be resolved by the X-ray diffraction experiment. The disordered ethyl group was treated in the following way in the subsequent refinement. The two positions of the terminal carbon atom were assigned occupancy factors of $^2/_3$ and $^1/_3$; the other carbon atom was treated as an ordered atom occupying a single site. Both atoms were treated anisotropically. However, the atomic coordinates of the disordered ethyl group as determined from the Fourier synthesis were not varied during the least-squares refinement; an attempt at refinement varying these parameters failed.

Table II. Scheme of Refinement[a]

	[Ti(Et$_2$mtc)$_4$]	[Zr(Et$_2$mtc)$_4$]
Fourier synthesis with all nonhydrogen atoms		
R_1, R_2	0.250, 0.231	0.206, 0.218[b]
refinement with isotropic thermal parameters-unit weighting	3 cycles	3 cycles
R_1, R_2	0.162, 0.147	0.150, 0.163[b]
refinement with anisotropic thermal parameters-unit weighting	3 cycles	3 cycles
R_1, R_2	0.100, 0.099	0.102, 0.135[b]
refinement with hydrogen atoms included but not refined	3 cycles	3 cycles
R_1, R_2	0.086, 0.087	0.064, 0.070
refinement with polynomial weighting scheme	3 cycles	2 cycles
R_1, R_2	0.086, 0.095	0.064, 0.049

[a] Full-matrix, least-squares calculations were used throughout the refinement. [b] The carbon atoms of the disordered ethyl group were not included in this calculation.

All hydrogen atoms except those of the disordered ethyl group were located from a difference Fourier synthesis; their coordinates and isotropic thermal parameters (assigned a value slightly larger than the isotropic thermal parameter of the carbon atom to which the hydrogen is bonded) were included in the subsequent least-squares calculations but were not refined.

After the refinement had converged using unit weights, three cycles of least-squares calculations were attempted using empirical weights $w = 1/\sigma^2$, where

$$\sigma = \sum_0^3 a_n |F_o|^n$$

The coefficients a_n of the polynomial were determined from a least-squares fit of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n |F_o|^n$$

The results of these three cycles of refinement were virtually identical with those of the unit-weighted refinement with no improvement in the R values; therefore, the results of the unit-weighted refinement were retained.

Upon convergence the R_1 and R_2 values for the unit-weighted refinement were 0.086 and 0.087, respectively, where

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$$

The quantity minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$; all of the observed data were used throughout the refinement. In the final cycle of refinement no coordinate shifted by more than 0.03σ; the average shift was 0.01σ. A final difference Fourier synthesis was essentially featureless with the seven largest peaks (0.37–0.84 e/Å^3) being located in the vicinity of the disordered ethyl group.

[Zr(Et$_2$mtc)$_4$]. A Fourier synthesis was calculated using the final atomic coordinates for [Ti(Et$_2$mtc)$_4$]; refinement then proceeded according to the scheme given in Table II. The disordered ethyl group was treated in a manner identical with that employed for the titanium compound. The final R_1 and R_2 values following unit-weighted refinement were 0.064 and 0.070, respectively. Two cycles of weighted refinement, using the empirical weighting scheme described above, reduced R_2 to 0.049. The bond lengths calculated at the conclusion

Table III. Final Atomic Fractional Coordinates for $[Ti(Et_2mtc)_4]^a$

atom	10^4x	10^4y	10^4z
Ti	5000^b	5751.0 (7)	2500^b
S_{1B}	3106 (1)	6103 (1)	2292 (1)
S_{2A}	4679 (1)	7222 (1)	1492 (1)
O_{1A}	4067 (2)	4526 (2)	2445 (2)
O_{2B}	4498 (2)	5430 (2)	1230 (2)
N_1	2311 (3)	4310 (3)	1972 (3)
N_2	3903 (3)	6258 (3)	1 (2)
C_1	3156 (3)	4877 (3)	2232 (3)
C_2	4332 (3)	6236 (3)	839 (3)
C_{11A}	2456 (4)	3272 (4)	1914 (5)
$C_{11B}{}^c$	1245	4675	1811
C_{21A}	3736 (5)	7164 (4)	−475 (3)
C_{21B}	3555 (4)	5365 (4)	−474 (3)
C_{12A}	2627 (7)	2991 (6)	1128 (6)
$C_{12B(2/3)}{}^c$	640	4765	959
$C_{12B(1/3)}{}^c$	753	4721	2159
C_{22A}	4599 (6)	7339 (6)	−816 (4)
C_{22B}	2426 (6)	5156 (6)	−623 (6)

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Required by the symmetry of the space group. [c] Coordinates calculated from a Fourier synthesis and not refined; therefore, no estimated standard deviations are available.

of the unit-weighted and empirically weighted refinements were virtually identical; the maximum difference between corresponding bond lengths was only 1σ. The final results of the empirically weighted refinement were therefore retained on the basis of the lower R_2 value.

Scattering factors were taken from Cromer and Mann[12] for Zr^0, Ti^0, S^0, O^0, N^0, and C^0 and from Stewart, Davidson, and Simpson[13] for H^0. Corrections for both the real and imaginary parts of the anomalous dispersion for Ti, Zr, and S were obtained from Cromer.[14] Calculations were performed on an IBM 370/168 computer and a PRIME 300 computer using the following programs: DIFFDATA, a local data reduction program; FOURIER, a local version of the Zalkin Fourier program; ORFLSE, a modified version of Busing, Martin, and Levy's original full-matrix, least-squares structure refinement program ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP, the C. K. Johnson thermal ellipsoid plotting program; and MEAN PLANES, a local least-squares mean-plane calculation program.

Results and Discussion

Final atomic coordinates and thermal parameters for $[Ti(Et_2mtc)_4]$ are presented in Tables III and IV, respectively; the hydrogen atom parameters are given in Table V. The corresponding parameters for $[Zr(Et_2mtc)_4]$ are listed in Tables VI–VIII. Tables of observed and calculated structure factor amplitudes are available.[15] Figure 1 shows a perspective view of the Ti complex, with the disordered ethyl group omitted for clarity; the Zr complex is isostructural. Atoms are labeled with a numerical and a literal subscript; the former identifies the particular *N*,*N*-diethylmonothiocarbamate ligand while the latter designates the dodecahedral coordination site.[3] Primed atoms are related to unprimed atoms by the crystallographic twofold axis.

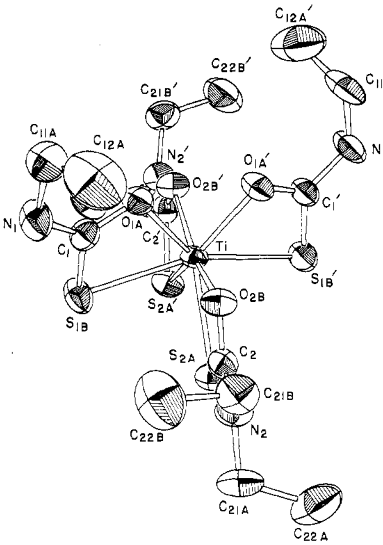


Figure 1. A model in perspective of the $[Ti(Et_2mtc)_4]$ molecule. The primed atoms are related to the unprimed atoms by a crystallographic twofold axis. The disordered ethyl group on ligand 1 has been omitted for clarity. The $[Zr(Et_2mtc)_4]$ molecule has a virtually identical structure.

The $[Ti(Et_2mtc)_4]$ and $[Zr(Et_2mtc)_4]$ complexes are eight-coordinate with four sulfur and four oxygen atoms bonded to the metal. The geometry of the coordination polyhedron is best described as a slightly distorted dodecahedron with the bidentate monothiocarbamate ligands spanning the *m* edges to give the *mmmm* stereoisomer.[3] This same stereoisomer has been found for $[Ti(Et_2dtc)_4]$[16] and $[Ta(Me_2dtc)_4]^+$[17] (Et_2dtc and Me_2dtc = *N*,*N*-diethyl- and *N*,*N*-dimethyldithiocarbamate, respectively), and it appears

Table IV. Final Thermal Parameters for $[Ti(Et_2mtc)_4]^a$

atom	anisotropic parameters						equiv isotropic B,[d] Å^2
	$\beta_{11}{}^{b,c}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	
Ti	32.1 (5)	22.8 (4)	22.3 (3)	0^e	4.2 (3)	0^e	2.10
S_{1B}	44 (1)	36 (1)	62 (1)	0 (1)	21 (1)	−7 (1)	3.62
S_{2A}	57 (1)	33 (1)	34 (1)	−3 (1)	6 (1)	4 (1)	3.28
O_{1A}	41 (2)	31 (1)	39 (1)	−6 (1)	8 (1)	2 (1)	2.97
O_{2B}	58 (2)	36 (1)	27 (1)	1 (1)	9 (1)	1 (1)	3.14
N_1	42 (2)	44 (2)	68 (3)	−15 (2)	17 (2)	−7 (2)	3.9
N_2	60 (3)	50 (2)	28 (1)	5 (2)	10 (2)	4 (1)	3.6
C_1	45 (2)	37 (2)	36 (2)	−8 (2)	14 (2)	−1 (2)	3.1
C_2	42 (2)	45 (2)	29 (2)	2 (2)	11 (2)	2 (2)	3.1
C_{11A}	60 (4)	42 (3)	81 (4)	−20 (3)	14 (3)	2 (3)	4.6
C_{11B}	33 (3)	76 (5)	198 (10)	−15 (3)	22 (5)	−5 (6)	6.4
C_{21A}	89 (5)	63 (3)	31 (2)	8 (3)	8 (2)	17 (2)	4.4
C_{21B}	72 (4)	66 (3)	31 (2)	1 (3)	10 (2)	−9 (2)	4.3
C_{12A}	143 (9)	75 (5)	96 (6)	7 (5)	29 (6)	−32 (4)	7.8
$C_{12B(2/3)}$	60 (7)	109 (10)	98 (8)	15 (6)	9 (6)	6 (7)	7.1
$C_{12B(1/3)}$	25 (8)	205 (29)	70 (11)	−15 (12)	29 (8)	−27 (15)	4.7
C_{22A}	115 (6)	95 (5)	55 (3)	−27 (5)	29 (4)	18 (3)	6.2
C_{22B}	78 (5)	84 (5)	96 (5)	−21 (4)	21 (4)	−21 (4)	6.8

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Values of β_{ij} are × 10^4. [d] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$. [e] Required by the symmetry of the space group.

Table V. Final Parameters for the Hydrogen Atoms of $[Ti(Et_2mtc)_4]$[a]

atom[b]	10^3x	10^3y	10^3z	B,[c] Å^2	distance, Å
H_1 (11A)	191	297	200	6.0	0.91
H_2 (11A)	308	303	232	6.0	0.94
H_3 (12A)	211	323	60	8.6	0.97
H_4 (12A)	290	237	111	8.6	0.95
H_5 (12A)	340	326	115	8.6	1.11
H_6 (21A)	382	774	−6	5.7	1.04
H_7 (21A)	305	709	−98	5.7	1.02
H_8 (22A)	471	673	−115	7.4	1.07
H_9 (22A)	474	789	−102	7.4	0.90
H_{10} (22A)	532	733	−31	7.4	1.05
H_{11} (21B)	369	543	−103	5.4	1.04
H_{12} (21B)	401	480	−15	5.4	1.02
H_{13} (22B)	214	584	−98	7.8	1.13
H_{14} (22B)	223	452	−99	7.8	1.07
H_{15} (22B)	207	510	−25	7.8	0.94

[a] Figure in parentheses is the number of the carbon atom to which the hydrogen is bonded at a distance given in the last column. [b] The hydrogen atoms bonded to carbon atoms 11B, 12B(2/3), and 12B(1/3) were not located. [c] Assigned at a value slightly larger than the isotropic thermal parameter of the carbon atom to which the hydrogen is bonded.

Table VI. Final Atomic Fractional Coordinates for $[Zr(Et_2mtc)_4]$[a]

atom	10^4x	10^4y	10^4z
Zr	5000[b]	5760.6 (3)	2500[b]
S_{1B}	3001 (1)	6052 (1)	2287 (1)
S_{2A}	4659 (1)	7239 (1)	1444 (1)
O_{1A}	4027 (2)	4504 (2)	2443 (2)
O_{2B}	4468 (2)	5446 (2)	1167 (2)
N_1	2294 (2)	4252 (2)	1959 (2)
N_2	3872 (3)	6289 (2)	−32 (2)
C_1	3110 (3)	4837 (2)	2222 (2)
C_2	4312 (3)	6256 (2)	805 (2)
C_{11A}	2467 (4)	3236 (3)	1901 (3)
C_{11B}[c]	1218	4640	1662
C_{21A}	3706 (4)	7191 (3)	−493 (3)
C_{21B}	3532 (4)	5413 (3)	−506 (3)
C_{12A}	2663 (6)	2981 (5)	1122 (5)
$C_{12B(2/3)}$[c]	625	4723	943
$C_{12B(1/3)}$[c]	702	4684	2008
C_{22A}	4570 (5)	7381 (5)	−827 (4)
C_{22B}	2426 (5)	5189 (5)	−633 (4)

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Required by the symmetry of the space group. [c] Coordinates calculated from a Fourier synthesis and not refined; therefore, no estimated standard deviations are available.

to be the preferred stereoisomer for complexes of the type ML_4, where L is a bidentate ligand of short bite.[18] The metal atom is located on a crystallographic twofold axis which is coincident with the $\bar{4}$ axis of the idealized D_{2d}-$\bar{4}$2m dodecahedron; only two of the four ligands are unique.

The deviations of the two complexes from idealized dodecahedral geometry can be measured by the methods of Lippard and Russ[19] and Porai-Koshits and Aslanov.[20] For $[Ti(Et_2mtc)_4]$ and $[Zr(Et_2mtc)_4]$ the interpenetrating BAAB trapezoids are very nearly perpendicular (dihedral angles = 87.4 and 86.9°, respectively), while the maximum deviation from the plane of a trapezoid defined by the metal atom and the four donor atoms is 0.06 Å for the Ti complex and 0.07 Å for the Zr complex. In the idealized dodecahedron the atoms which define the trapezoids are coplanar and the dihedral angle between the trapezoids is 90.0°. Porai-Koshits and Aslanov[20] have defined δ and ϕ shape parameters which measure the extent to which an observed coordination polyhedron approximates the idealized polyhedron. The δ shape parameters are 29.5° for the D_{2d} dodecahedron, 0.0, 21.8, and 48.2° for the C_{2v} bicapped-trigonal prism, 0.0 and 52.4° for the D_{4d} square antiprism, 26.3 and 34.8° for $[Ti(Et_2mtc)_4]$, and 27.8 and 36.6° for $[Zr(Et_2mtc)_4]$. The ϕ shape parameters are 0.0° for the D_{2d} dodecahedron, 14.1° for the C_{2v} bicapped-trigonal prism, 24.5° for the D_{4d} square antiprism, 3.6 and 3.8° for $[Ti(Et_2mtc)_4]$, and 3.4 and 3.7° for $[Zr(Et_2mtc)_4]$. Thus, the coordination polyhedra of the two complexes most closely approximate a dodecahedron.

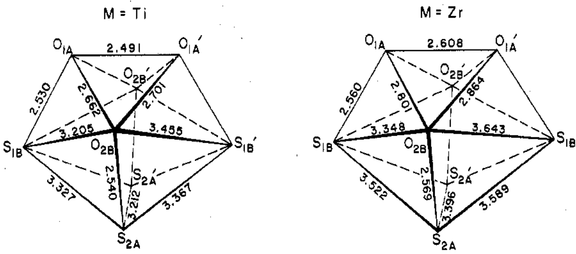


Figure 2. Perspective views (adapted from computer-drawn diagrams) of the dodecahedral coordination polyhedra in $M(Et_2mtc)_4$ (M = Ti or Zr).

Bond distances, polyhedral edge lengths, and bond angles in the MS_4O_4 coordination groups are presented in Table IX. Perspective views of the coordination polyhedra are shown in Figure 2. Values of the polyhedron-shape parameters defined by Hoard and Silverton[21] are compared with theoretical values in Table X; also included in Table X are shape parameters for the analogous $[Ti(Et_2dtc)_4]$ complex.[16] Differences between the observed and theoretical values of a, b, m, g, θ_A, and θ_B may be ascribed primarily to the short bite of the monothiocarbamate ligand (average values: 2.535 Å in $[Ti(Et_2mtc)_4]$ and 2.565 Å in $[Zr(Et_2mtc)_4]$ vs. 2.84 Å in $[Ti(Et_2dtc)_4]$[16]).

The most interesting feature of the structure is that the sulfur and oxygen atoms do *not* sort between the A and B sites, as suggested by Orgel's rule[2] but rather partially sort so that two of the sulfur atoms are in A sites and two are in B sites (Figures 1 and 2). Thus the complexes exist as the pseudo-C_{2v} stereoisomer instead of one of the two possible D_{2d} stereoisomers in which the donor atoms are completely sorted. In seeking reasons why Orgel's rule is not obeyed in this case, it was noted that the four sulfur atoms are located on one side of the molecule in an all-cis arrangement, with the four oxygen atoms on the other side. This situation is reminiscent of the preference for cis stereochemistry in octahedral[22] and square-planar[23-29] monothio-β-diketonate complexes. Moreover, in the Ti compound, the five S···S contacts along the a and the four g edges (3.212–3.367 Å; cf. Table IX) are relatively short compared with the van der Waals contact of 3.45 Å for two sulfur atoms.[30] Since the completely sorted D_{2d} stereoisomers have fewer short S···S contacts than the C_{2v} stereoisomer, it appeared initially[1a] that the observed stereoisomer might be stabilized by weakly attractive S···S interactions of the sort suggested for stabilization of cis monothio-β-diketonate complexes[22,29a] and trigonal-prismatic dithiolene complexes.[31]

It was to test this hypothesis that the structure of the Zr complex was determined. Because of longer metal–ligand distances in $[Zr(Et_2mtc)_4]$, the S···S contacts should be longer than in $[Ti(Et_2mtc)_4]$, with the result that the Zr complex might exist as one of the completely sorted D_{2d} stereoisomers, in accord with Orgel's rule. Such a result would provide indirect evidence for the importance of attractive S···S interactions in the Ti complex. Alternatively, if attractive S···S interactions were important in both the Ti and the Zr complexes, the short S···S contacts in the C_{2v} stereoisomer should be retained on going from $[Ti(Et_2mtc)_4]$ to $[Zr(Et_2mtc)_4]$.

As already indicated, X-ray analysis establishes the same C_{2v} stereoisomer for both $[Ti(Et_2mtc)_4]$ and $[Zr(Et_2mtc)_4]$.

Table VII. Final Thermal Parameters for $[Zr(Et_2mtc)_4]^a$

atom	anisotropic parameters $\beta_{11}{}^{b,c}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	equiv isotropic B,[d] Å^2
Zr	31.5 (2)	24.5 (2)	23.7 (2)	0[e]	3.8 (2)	0[e]	2.23
S_{1B}	43 (1)	38 (1)	66 (1)	0 (1)	18 (1)	−7 (1)	3.83
S_{2A}	58 (1)	35 (1)	34 (1)	−4 (1)	5 (1)	5 (1)	3.44
O_{1A}	38 (1)	33 (1)	37 (1)	−4 (1)	5 (1)	3 (1)	3.01
O_{2B}	58 (2)	37 (1)	25 (1)	2 (1)	7 (1)	−1 (1)	3.17
N_1	44 (2)	45 (2)	63 (2)	−9 (2)	12 (2)	−3 (2)	4.1
N_2	59 (2)	60 (2)	25 (1)	1 (2)	7 (1)	4 (1)	3.7
C_1	41 (2)	38 (2)	35 (2)	−10 (1)	10 (2)	−1 (1)	3.1
C_2	40 (2)	44 (2)	29 (2)	3 (1)	9 (1)	5 (1)	3.1
C_{11A}	65 (3)	41 (2)	75 (3)	−14 (2)	14 (2)	−1 (2)	4.8
C_{11B}	35 (3)	72 (3)	195 (8)	−14 (2)	30 (4)	−17 (4)	6.2
C_{21A}	84 (3)	70 (3)	32 (2)	10 (3)	8 (2)	15 (2)	4.6
C_{21B}	72 (3)	69 (3)	28 (2)	3 (2)	8 (2)	−7 (2)	4.3
C_{12A}	143 (6)	77 (4)	91 (4)	0 (4)	31 (4)	−29 (3)	7.9
$C_{12B(2/3)}$	61 (6)	135 (9)	101 (7)	7 (6)	−9 (5)	−8 (6)	7.9
$C_{12B(1/3)}$	54 (9)	118 (14)	62 (9)	−24 (9)	14 (8)	−8 (9)	5.9
C_{22A}	116 (5)	99 (4)	56 (3)	−19 (4)	31 (3)	17 (3)	6.6
C_{22B}	86 (4)	94 (4)	87 (4)	−26 (3)	17 (3)	−28 (3)	7.1

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Values of β_{ij} are × 10^4. [d] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$. [e] Required by the symmetry of the space group.

Table VIII. Final Parameters for the Hydrogen Atoms of $[Zr(Et_2mtc)_4]^a$

atom[b]	10^3x	10^3y	10^3z	B,[c] Å^2	distance, Å
H_1 (11A)	192	298	199	6.1	0.90
H_2 (11A)	301	302	234	6.1	0.90
H_3 (12A)	205	308	65	8.7	0.94
H_4 (12A)	267	245	117	8.7	0.75
H_5 (12A)	333	346	104	8.7	1.18
H_6 (21A)	369	763	−6	5.8	0.98
H_7 (21A)	301	708	−98	5.8	1.04
H_8 (22A)	472	683	−111	7.3	0.98
H_9 (22A)	451	801	−119	7.3	1.07
H_{10} (22A)	500	739	−51	7.3	0.64
H_{11} (21B)	368	552	−109	5.6	1.10
H_{12} (21B)	402	485	−25	5.6	1.03
H_{13} (22B)	204	574	−94	8.0	0.99
H_{14} (22B)	213	463	−94	8.0	0.96
H_{15} (22B)	215	514	−17	8.0	0.99

[a] Figure in parentheses is the number of the carbon atom to which the hydrogen is bonded at a distance given in the last column. [b] The hydrogen atoms bonded to carbon atoms 11B, 12B(2/3), and 12B(1/3) were not located. [c] Assigned at a value slightly larger than the isotropic thermal parameter of the carbon atom to which the hydrogen is bonded.

Moreover, in the Zr complex, the four S···S contacts along the *g* edges (Table IX) are no longer short compared with the van der Waals contact of 3.45 Å and the S···S distance along the *a* edge is only marginally short. Comparison of the increases in the *a* and *g* edge lengths and the corresponding ligand–metal–ligand angles (Table IX) indicates that on going from the Ti complex to the Zr complex the structure opens up to a greater extent on the sulfur side of the coordination group. Thus, the O···O distances along the *a* and *g* edges increase by only 0.12–0.16 Å, while the corresponding S···S distances increase by 0.18–0.22 Å. The corresponding O–M–O angles open by 0.3–1.1°, while the S–M–S angles open by 1.6–2.3°. If the S···S interactions were attractive, one would have expected the structure to open up on the oxygen side of the coordination group, with the S···S distances remaining short. It seems very unlikely, therefore, that the observed C_{2v} stereoisomer can be attributed to attractive S···S interactions.[32]

Other factors which could influence the donor atom sorting pattern and choice of stereoisomer include steric effects, σ-electronic effects, and crystal-packing effects. However, none of these factors provides a simple rationale for the preferred stability of the C_{2v} stereoisomer. Steric effects favor the D_{2d} stereoisomer with the larger sulfur atoms in the less sterically hindered B sites.[21] Molecular orbital calculations on model ML_8 dodecahedral complexes[33] predict that the less electronegative (better σ donor) sulfur atoms will prefer the A sites. Stabilization of the C_{2v} stereoisomer in the solid state by crystal-packing effects seems unlikely since dipole moment

Table IX. Bond Distances, Polyhedral Edge Lengths, and Bond Angles in the Coordination Groups of $[M(Et_2mtc)_4]$ (M = Ti or Zr)[a]

		length, Å			angle, deg	
atoms	edge[b]	M = Ti	M = Zr	atoms	M = Ti	M = Zr
$M-S_{1B}$		2.533 (1)	2.669 (1)			
$M-S_{2A}$		2.609 (1)	2.689 (1)			
$M-O_{1A}$		2.117 (3)	2.200 (2)			
$M-O_{2B}$		2.061 (3)	2.180 (2)			
$O_{1A}\cdots O_{1A}'$	*a*	2.491 (6)	2.608 (5)	$O_{1A}-M-O_{1A}'$	72.07 (17)	72.71 (12)
$S_{2A}\cdots S_{2A}'$	*a*	3.212 (2)	3.396 (2)	$S_{2A}-M-S_{2A}'$	75.99 (6)	78.31 (4)
$S_{1B}\cdots O_{2B}$	*b*	3.205 (3)	3.348 (3)	$S_{1B}-M-O_{2B}$	87.86 (10)	86.72 (7)
$S_{1B}\cdots O_{2B}'$	*b*	3.455 (3)	3.643 (3)	$S_{1B}-M-O_{2B}'$	96.99 (10)	96.88 (7)
$S_{1B}\cdots O_{1A}{}^c$	*m*	2.530 (3)	2.560 (2)	$S_{1B}-M-O_{1A}$	65.21 (9)	62.57 (6)
$S_{2A}\cdots O_{2B}{}^c$	*m*	2.540 (3)	2.569 (2)	$S_{2A}-M-O_{2B}$	64.66 (9)	62.66 (7)
$S_{1B}\cdots S_{2A}$	*g*	3.327 (2)	3.522 (2)	$S_{1B}-M-S_{2A}$	80.62 (5)	82.18 (3)
$S_{1B}\cdots S_{2A}'$	*g*	3.367 (2)	3.589 (1)	$S_{1B}-M-S_{2A}'$	81.80 (4)	84.10 (3)
$O_{1A}\cdots O_{2B}$	*g*	2.662 (4)	2.801 (3)	$O_{1A}-M-O_{2B}$	79.17 (12)	79.49 (9)
$O_{1A}\cdots O_{2B}'$	*g*	2.701 (4)	2.864 (3)	$O_{1A}-M-O_{2B}'$	80.55 (12)	81.66 (9)

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Edge nomenclature is defined in ref 3. [c] The "bite" of the ligand.

Table X. Average Polyhedron-Shape Parameters

shape parameter[a]	$[Ti(Et_2mtc)_4]$	$[Zr(Et_2mtc)_4]$	$[Ti(Et_2dtc)_4]$[b]	MFP[c]	HSM[d]
a	1.22	1.23	1.17	1.17	1.20
b	1.43	1.44	1.42	1.49	1.50
m	1.09	1.05	1.11	1.17	1.20
g	1.29	1.31	1.29	1.24	1.20
θ_A, deg	37.0	37.8	35.1	35.2	36.9
θ_B, deg	78.1	79.7	77.5	73.5	69.5
$M-S_A/M-S_B$	1.030	1.007	1.033	1.03	1.00
$M-O_A/M-O_B$	1.027	1.009		1.03	1.00

[a] *a*, *b*, *m*, and *g* are averaged lengths of the dodecahedral edges[21] in units of the averaged metal-ligand bond distance (2.330 Å for $[Ti(Et_2mtc)_4]$, 2.435 Å for $[Zr(Et_2mtc)_4]$, and 2.564 Å for $[Ti(Et_2dtc)_4]$). θ_A and θ_B are the averaged angles which metal-ligand bonds directed toward the A and B sites, respectively, make with the $\bar{4}$ axis of the idealized dodecahedron. [b] Reference 16. [c] Most favorable coordination polyhedron for a dodecahedral ML_8 complex, calculated[21] to minimize the closed-shell ligand repulsive energy. [d] Hard-sphere model.

and NMR evidence[9] strongly suggest that the C_{2v} isomer is also the principal species in solution.

It is possible that the observed stereoisomer may be stabilized by a trans influence of the sulfur atoms. The classical polarization theory of the trans effect[34] favors a structure which locates the more polarizable sulfur atoms on one side of the molecule and the oxygen atoms on the other side. However, from an orbital point of view,[35] application of the trans effect to dodecahedral complexes is not as straightforward as in the case of square-planar and octahedral complexes. For example, it is not clear why the observed C_{2v} stereoisomer is favored over the C_2 isomer which has a cis arrangement of sulfur atoms in the pseudo-square-planar B sites.

It is interesting to note that bis(cyclotetramethylenemonothiocarbamato)bis(pyrrolidine)cobalt(II), $Co[SOCN(C_2H_8)]_2(NC_4H_9)_2$,[36] and tris(N,N-dimethylmonothiocarbamato)iron(III), $Fe(mtc)_3$,[37] also adopt solid-state molecular structures in which the sulfur atoms occupy cis positions.

Metal–sulfur and metal–oxygen bond distances in $[Ti(Et_2mtc)_4]$ and $[Zr(Et_2mtc)_4]$ (Table IX) are closely similar to corresponding averaged bond distances in other dodecahedral molecules. Thus, the $Ti-S_A$ and $Ti-S_B$ distances of 2.609 (1) and 2.533 (1) Å agree very well with the corresponding average distances of 2.606 and 2.522 Å in $[Ti(Et_2dtc)_4]$.[16] The $Ti-O_A$ and $Ti-O_B$ bond lengths of 2.117 (3) and 2.061 (3) Å differ only slightly from the corresponding average bond lengths in $Ti(NO_3)_4$ (2.076 and 2.059 Å),[38] while the $Zr-O_A$ and $Zr-O_B$ bond distances of 2.200 (2) and 2.180 (2) Å are comparable to corresponding averaged distances in $[Zr(C_2O_4)_4]^{4-}$ (2.230 and 2.168 Å).[39] As is generally observed in dodecahedral structures, the bonds to the A sites are longer than the bonds to the B sites. The ratios $M-S_A/M-S_B$ and $M-O_A/M-O_B$ in the Ti compound (Table X) are equal to the theoretical value of 1.03 for the "most favorable polyhedron", the D_{2d} dodecahedron which minimizes closed-shell ligand repulsions.[21] The corresponding ratios in the Zr complex are smaller (1.01), probably because of less crowding in the coordination group of the Zr compound.

Averaged bond lengths and bond angles within the monothiocarbamate ligands (Table XI) are remarkably consistent for the two complexes. The only notable differences are in the S···O intraligand contact (the bite of the ligand), where the average distance is 2.535 Å in the more crowded $[Ti(Et_2mtc)_4]$ and 2.565 Å in $[Zr(Et_2mtc)_4]$, and in the S–C–O angle, where the angle closes from 116.7° for the Zr complex to 114.8° for the Ti complex. Relatively little structural data for monothiocarbamates are available for comparison. In one case the monothiocarbamate ligands are monodentate, bonding through the sulfur atom only,[40] while in other cases the monothiocarbamate ligands are bidentate but the sulfur atoms are bridging two metal atoms.[41,42] In $Co[SOCN(C_2H_8)]_2(NC_4H_9)_2$[36] and $Fe(Me_2mtc)_3$,[37] however, the monothiocarbamate ligands are bidentate and nonbridging; bond distances within the ligand have been reported for the former complex (C–S = 1.735 (6), C–O = 1.283 (7), C–N = 1.342 (7) Å),[36] and all agree quite well with the corresponding average distances given in Table XI.

Table XI. Bond Lengths (Å) and Bond Angles (deg) in the *N,N*-Diethylmonothiocarbamate Ligands[a]

	$[Ti(Et_2mtc)_4]$			$[Zr(Et_2mtc)_4]$		
atoms	ligand 1	ligand 2	av[b]	ligand 1	ligand 2	av[b]
			(a) Distances			
S···O[c]	2.530 (3)	2.540 (3)	2.535 (3, 5, 5)	2.560 (2)	2.569 (2)	2.565 (2, 5, 5)
C–S	1.718 (4)	1.723 (5)	1.721 (5, 3, 3)	1.727 (4)	1.726 (4)	1.727 (4, 1, 1)
C–O	1.264 (5)	1.285 (5)	1.275 (5, 11, 11)	1.270 (4)	1.280 (4)	1.275 (4, 5, 5)
C–N	1.337 (5)	1.328 (5)	1.333 (5, 5, 5)	1.335 (4)	1.343 (5)	1.339 (5, 4, 4)
$C_{1A}-N$	1.472 (7)	1.475 (6)	1.472 (7, 2, 4)	1.461 (6)	1.471 (5)	1.469 (5, 9, 16)
$C_{1B}-N$	1.474[d]	1.468 (7)		1.485[d]	1.460 (5)	
$C_{1A}-C_{2A}$	1.490 (11)	1.513 (9)	1.501 (10, 12, 12)	1.496 (9)	1.511 (8)	1.499 (8, 8, 12)
$C_{1B}-C_{2B}$	1.386[d,e]	1.501 (9)		1.216[d,e]	1.490 (7)	
	1.047[d,e]			1.073[d,e]		
			(b) Angles			
S–C–O	115.2 (3)	114.4 (3)	114.8 (3, 4, 4)	116.6 (2)	116.7 (3)	116.7 (3, 1, 1)
C–S–M	75.8 (2)	74.5 (2)	75.2 (2, 7, 7)	75.4 (1)	75.3 (1)	75.4 (1, 1, 1)
C–O–M	102.4 (3)	106.2 (3)	104.3 (3, 19, 19)	103.8 (2)	105.2 (2)	104.5 (2, 7, 7)
S–C–N	124.2 (4)	125.6 (4)	124.9 (4, 7, 7)	123.6 (3)	124.5 (3)	124.1 (3, 5, 5)
O–C–N	120.6 (4)	120.0 (4)	120.3 (4, 3, 3)	119.8 (3)	118.8 (3)	119.3 (3, 5, 5)
$C_{1A}-N-C$	119.0 (4)	121.8 (4)	120.8 (4, 13, 18)	119.5 (3)	121.9 (3)	120.3 (3, 8, 16)
$C_{1B}-N-C$	122.3[d]	119.9 (4)		120.1[d]	119.7 (3)	
$C_{1A}-N-C_{1B}$	118.5[d]	118.3 (4)	118.4 (4, 1, 1)	120.3[d]	118.4 (3)	119.4 (3, 10, 10)
$N-C_{1A}-C_{2A}$	112.9 (6)	111.2 (5)	111.8 (5, 7, 11)	112.4 (4)	111.3 (4)	111.8 (4, 4, 6)
$N-C_{1B}-C_{2B}$	113.5[d,e]	111.4 (5)		127.4[d,e]	111.6 (4)	
	135.5[d,e]			127.1[d,e]		

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] The figures in parentheses following each averaged value are the root-mean-square estimated standard deviation for an individual datum and the mean and the maximum deviation from the average value. [c] The "bite" of the ligand. [d] Distances and angles involving disordered carbon atoms. The coordinates of the disordered atoms were determined from a Fourier synthesis but were not refined; therefore, no estimated standard deviations are available. [e] Value not included in the average.

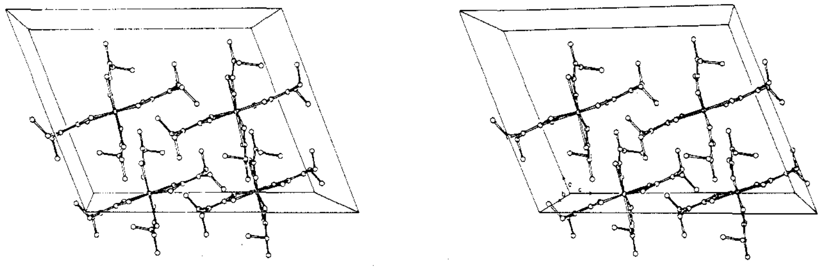
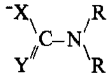


Figure 3. Stereoscopic view of the packing in one unit cell of [Ti(Et$_2$mtc)$_4$]. The front face is the (010) plane. The methyl carbon atom of the disordered ethyl group has been omitted.

A most interesting and unexpected feature of the structure of the monothiocarbamate ligand is the essential identity of the C–S and C–N bond lengths to those in dithiocarbamate ligands, even though a more electronegative oxygen atom has been substituted for a sulfur atom. For a large number of dithiocarbamate complexes,[16,17,31,43-56] the average C–S bond distance is about 1.70–1.73 Å and the average C–N distance is about 1.30–1.35 Å; the C–S and C–N distances in [Ti(Et$_2$mtc)$_4$] and [Zr(Et$_2$mtc)$_4$] (Table XI) fall well within that range. Similarly, the C–O and C–N distances in the monothiocarbamate complexes are nearly identical with the corresponding averaged distances (1.272 and 1.352 Å) in the carbamate complex [Ti(NMe$_2$)$_2$(O$_2$CNMe$_2$)$_2$].[57] It appears that the relative importance of the three resonance structures **1**–**3** (X = Y = O; X = O, Y = S; X = Y = S) is surprisingly



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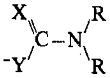

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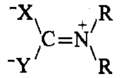

3

similar for bidentate carbamate, monothiocarbamate, and dithiocarbamate. The delocalization of π electrons within the SOCN portion of the monothiocarbamate ligand, implied by resonance structures **1**–**3**, is supported by the C–N, C–S, and C–O bond distances (Table XI) which are intermediate between the sum of the Pauling single-bond and double-bond radii (C—N = 1.47, C=N = 1.27, C—S = 1.81, C=S = 1.61, C—O = 1.43, C=O = 1.21 Å).[58]

The OSCNC$_2$ ligand skeleton is nearly coplanar with an average deviation from the plane for the 12 independent atoms of 0.037 Å for [Ti(Et$_2$mtc)$_4$] and of 0.022 Å for [Zr(Et$_2$mtc)$_4$]. The maximum deviations are 0.058 Å for the Ti complex and 0.049 Å for the Zr complex. There is a slight twist about the C–N bond of the ligands for both complexes. For the Ti complex the dihedral angle between the OSCN and CNC$_2$ mean planes is 5.0° for ligand 1 and 4.2° for ligand 2; for the Zr complex the corresponding dihedral angles are 1.6 and 3.9°. Furthermore, there is a small folding of the chelate rings about the *m* edges of the dodecahedron. The dihedral angle between the ligand and MOS mean planes is 12.2° for ligand 1 and 6.3° for ligand 2 in the Ti complex and 15.6° for ligand 1 and 6.5° for ligand 2 in the Zr complex. Thus, the metal atoms are not located in the plane of the ligands, being displaced by 0.38 Å from the ligand 1 plane and by 0.18 Å from the ligand 2 plane in [Ti(Et$_2$mtc)$_4$] and by 0.55 Å from the ligand 1 plane and 0.21 Å from the ligand 2 plane in [Zr(Et$_2$mtc)$_4$].

A stereoscopic packing diagram for [Ti(Et$_2$mtc)$_4$] is presented in Figure 3. One of the ethyl groups on monothiocarbamate ligand 1 (see Figure 1) is disordered, occupying two sites in the ratio of two-thirds to one-third. The disorder is apparently caused by rather severe intermolecular contacts involving the methyl carbon atoms. For example, the $C_{12B(1/3)}$–$C_{12B(1/3)}$ intermolecular contact ($C_{12B(1/3)}$ is the disordered methyl carbon in the site of one-third occupancy) is a very short 2.71 Å and the $C_{12B(2/3)}$–$C_{12B(2/3)}$ intermolecular contact ($C_{12B(2/3)}$ is the disordered methyl carbon in the site of two-thirds occupancy) is only 3.16 Å. By comparison, the shortest C–C intermolecular contact involving ordered methyl carbon atoms is 3.96 Å. Note also the larger folding of the chelate ring about the dodecahedral *m* edge for ligand 1 compared to that for ligand 2, as mentioned above. Disorder among the ethyl groups of dithiocarbamate ligands has also been observed.[54,56]

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Registry No. [Ti(Et$_2$mtc)$_4$](coordination form), 61359-07-7; [Zr(Et$_2$mtc)$_4$](coordination form), 66758-39-2; [Ti(Et$_2$mtc)$_4$](salt form), 61372-28-9; [Zr(Et$_2$mtc)$_4$](salt form), 66750-63-8.

Supplementary Material Available: A listing of structure factor amplitudes (37 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes[1]

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The synthesis of the seven-coordinate $[\mathrm{ML_7}]^{2+}$ and $[\mathrm{ML_6X}]^+$ cations, where M = Mo or W, L = alkyl (usually *tert*-butyl) isocyanide, and X = Cl, Br, or I, is described. These complexes are best prepared by oxidative addition of the metal hexacarbonyl with halogen in the presence of the isocyanide ligand, although other routes are available. The X-ray crystal structure analysis of $[(t\text{-}\mathrm{C_4H_9NC})_6\mathrm{MoBr}]\mathrm{Br}$ is presented. This complex, like the iodide analogue described previously, has a C_{2v} capped trigonal-prismatic structure with the bromide ion as the capping ligand. All six molybdenum and tungsten $[\mathrm{ML_6X}]\mathrm{X}$ salts are isomorphous and presumably have this structure. The familiar pattern of metal–ligand bond lengths is observed. There are two short Mo–C distances, 2.05 Å, involving the two isocyanide ligands on the unique edge, four longer Mo–C distances, 2.12 Å, involving the four isocyanide ligands on the quadrilateral, capped face, and a molybdenum–bromine bond of 2.673 (2) Å. Solution conductivity data confirm electrolytic behavior expected for heptacoordinate cations $[\mathrm{MoL_7}]^{2+}$ and $[\mathrm{MoL_6I}]^+$. Temperature-dependent proton and $^{13}\mathrm{C}$ NMR spectral results suggest fluxional structures. Infrared (solids) and solution electronic spectral bands are reported.

Although numerous seven-coordinate transition metal complexes have been prepared and structurally characterized,[3] relatively few of these contain only monodentate ligands. Apart from heptafluorides, the class of geometrically characterized $\mathrm{ML_7}$ complexes is limited to $[\mathrm{V(CN)_7}]^{4-}$,[4] $[\mathrm{Mo(CN)_7}]^{5-}$,[5] and $[\mathrm{Mo(CNR)_7}]^{2+}$, R = *tert*-butyl.[6] The last of these has a C_{2v} capped trigonal-prismatic structure, as does the related $[\mathrm{Mo(CNR)_6I}]^+$ complex in which iodide is the capping ligand.[7] Compounds of general formula $\mathrm{Mo(CNR)_5X_2}$ have also been reported,[8] but their structures are unknown.

The $[\mathrm{Mo(CNR)_7}]^{2+}$ and $[\mathrm{Mo(CNR)_6X}]^+$ complexes provide an opportunity to examine the effects of charge and ligand steric factors on the geometry of seven-coordinate species in the absence of any constraints imposed by chelating ligands. Structural information of this kind is important to test the predictions of theoretical discussions of the bonding in seven-coordination.[9] The present paper provides geometric data for bromohexakis(*tert*-butyl isocyanide)molybdenum(II) bromide, which is isomorphous with the iodide analogue. Moreover, since the original synthesis of $[\mathrm{Mo(CNR)_6I}]^+$ was serendipitous and difficult to reproduce,[7] a more rational approach was devised.[10] Here we report further improvement of the synthetic method and preparative details for the complete series of complexes $[\mathrm{M(CNR)_7}]^{2+}$ and $[\mathrm{M(CNR)_6X}]^+$, where M = Mo or W, X = Cl, Br, or I, and R = alkyl, generally *tert*-butyl. Analogous aryl isocyanide complexes $[\mathrm{M(CNPh)_6Cl}]^+$, M = Mo or W, may be obtained by irradiation of $[\mathrm{M(CNPh)_6}]$ in chloroform.[11] The reductive coupling of isocyanide ligands in $[\mathrm{Mo(CNR)_6I}]^+$ and related cations to form $[\mathrm{Mo(CNR)_4(RHN{=}C{=}C{=}NHR)X}]^+$ has been briefly described[2] and will be reported in detail elsewhere.[12]

Experimental Procedure

Synthetic Work. All complexes were prepared and stored under an atmosphere of dinitrogen using anhydrous solvents. Methyl isocyanide and *tert*-butyl isocyanide were prepared by standard methods[13] and purified by distillation prior to use. Potassium octacyanomolybdate(IV) dihydrate was synthesized by a literature procedure.[14] Other starting materials were commercially available. Microchemical analyses were preformed by Galbraith Laboratories, Knoxville, Tenn.

Heptakis(alkyl isocyanide)molybdenum(II) and -tungsten(II) Salts. $[(\mathrm{CH_3NC})_7\mathrm{Mo}]\mathrm{I_2}$. A mixture containing 2 mmol (0.528 g) of mo-

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