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## Crystal and Molecular Structure and the Kinetics of Ligand Exchange of Tris(*N,N*-dimethyldithiocarbamato)thallium(III)

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The crystal structure of tris(*N,N*-dimethyldithiocarbamato)thallium(III) monohydrate,  $\text{Tl}(\text{Me}_2\text{dtc})_3 \cdot \text{H}_2\text{O}$ , has been solved from three-dimensional counter data in order to determine the detailed structural parameters of the  $\text{TlS}_6$  core. The structure was determined because ligand-exchange kinetic studies by PMR and solution infrared data suggested that the coordination number may be less than 6. The space group is  $P2_1/c$  with lattice constants  $a = 9.143$  (5) Å,  $b = 19.201$  (16) Å,  $c = 12.429$  (7) Å,  $\beta = 109.1$  (1)°, and  $Z = 4$ . The data were refined by least-squares to a conventional  $R$  of 0.080. The average Tl-S distance is 2.659 Å and all six Tl-S distances are within 0.046 Å or  $5\sigma$  of the average; hence the Tl atom is six-coordinate. The geometry of the  $\text{TlS}_6$  core is typical of other  $\text{M}(\text{dtc})_3$  complexes in that a geometry intermediate between trigonal antiprismatic and trigonal prismatic is found with approximate  $D_3$  symmetry. The average twist angle,  $\phi$ , and the average propeller pitch angle,  $\psi$ , are 33.2 and 26.5°, respectively. In addition a significant  $C_2$  distortion is superimposed on the trigonally twisted geometry of the  $\text{TlS}_6$  core. The geometry of the  $\text{TlS}_6$  core is compared to other  $\text{M}(\text{dtc})_3$  complexes and is analyzed in light of Kepert's electrostatic repulsive potential calculations of ground-state geometry for  $\sim D_3$   $\text{M}(\text{bidentate})_3$  complexes as a function of ligand bite angle. Several short intermolecular contacts are found: S-S of 3.43 (2) Å and methyl-methyl of 3.32 (6) Å but these do not appear to affect the geometry of the  $\text{TlS}_6$  core. A total line shape analysis of exchange broadened PMR spectra for  $\text{Tl}(\text{Me}_2\text{dtc})_3$  has also been carried out. The coalescence of the methyl doublet ( $J(\text{Tl-H}) = 10$  Hz at  $-50^\circ$ ) results from a first-order dissociative ligand-exchange reaction with  $\Delta H^\ddagger = 6.2 \pm 1.0$  kcal/mol and  $\Delta S^\ddagger = -28 \pm 10$  eu.

### Introduction

During our investigation of the dynamic stereochemistry of tris(*N,N*-disubstituted-dithiocarbamato)metal complexes,  $\text{M}(\text{R}_1\text{R}_2\text{dtc})_3$ ,<sup>1-4</sup> some new analogs were synthesized where  $\text{M} = \text{thallium(III)}$  and found to have several unusual properties in solution. The PMR spectrum of  $\text{Tl}(\text{Me}_2\text{dtc})_3$ <sup>5</sup> in various noncoordinating solvents showed a well-separated methyl doublet below ca.  $-38^\circ$ . This doublet which is due to  $(203)205\text{Tl-H}$  coupling<sup>6,7</sup> with  $J = 10$  Hz in  $\text{CD}_2\text{Cl}_2$  solution at  $-50^\circ$  collapses into a sharp singlet at ca.  $0^\circ$ . Rapid ligand exchange best accounts for the coalescence of the doublet because the exchange-broadened spectra were accurately computer simulated using this model (vide infra). In addition the rate of ligand exchange which is independent of complex concentration ( $k_1 = 15 \pm 1$  sec<sup>-1</sup> at  $-19^\circ$ ) probably results from ligand dissociation. Such fast dissociative ligand-exchange rates are unusual for chelated dithiocarbamato complexes<sup>1-4,8</sup> and possibly suggest a coordination number lower than 6. Further support for this possibility comes from  $\text{CS}_2$  and  $\text{CH}_2\text{Cl}_2$  solution infrared data which show a splitting of the band between 950 and 1000  $\text{cm}^{-1}$  which has often been attributed to monodentate coordination of the dithiocarbamato ligand.<sup>9,10</sup> The analogous six-coordinate  $\text{Fe}(\text{Me}_2\text{dtc})_3$  complex does not show such a splitting in  $\text{CS}_2$  solution. In the solid (KBr disk), however,  $\text{Tl}(\text{Me}_2\text{dtc})_3$  does not show a distinct split band in this region which suggests a coordination number change between the solution and solid phase. It was decided

to undertake an X-ray analysis of this new complex in order to establish the mode of coordination in the solid state. In addition it should be of interest to see how the  $\text{MS}_6$  core of a tris(dithiocarbamato) complex of a sixth-row metal is distorted relative to other  $\text{M}(\text{dtc})_3$  complexes. A trend has recently been established for this type of complex which shows that the smaller the bite angle the larger the distortion from trigonal-antiprismatic toward trigonal-prismatic geometry.<sup>1,11</sup>  $\text{Tl}(\text{Me}_2\text{dtc})_3$  is expected to have the smallest bite angle of any  $\text{M}(\text{dtc})_3$  complex thus far examined.

### Experimental Section

**Preparation of the Complex.** Tris(*N,N*-dimethyldithiocarbamato)thallium(III) monohydrate,  $\text{Tl}(\text{Me}_2\text{dtc})_3 \cdot \text{H}_2\text{O}$ , was synthesized by the reaction of thallium trichloride (3.1 g in ca. 25 ml of acetonitrile) with  $\text{Me}_2\text{dtcNa} \cdot x\text{H}_2\text{O}$  (5.0 g in ca. 50 ml of absolute ethanol). The yellow precipitate which formed immediately on mixing the two solutions was filtered and washed with ethanol. Yellow crystals were obtained after several crystallizations from  $\text{CH}_2\text{Cl}_2$ -heptane solution. The product was vacuum-dried and stored under nitrogen.

The infrared spectrum of the solid (KBr disk) was very similar to other six-coordinate  $\text{M}(\text{Me}_2\text{dtc})_3$  complexes but the  $\text{CS}_2$  and  $\text{CH}_2\text{Cl}_2$  solution spectra revealed a splitting of the band at ca. 975  $\text{cm}^{-1}$  which is characteristic of a monodentate dtc ligand;<sup>9,10</sup> the analysis of the vacuum-dried anhydrous complex is as follows. Anal. Calcd for  $\text{TlC}_9\text{H}_{18}\text{N}_3\text{S}_6 \cdot \text{H}_2\text{O}$ : C, 19.53; H, 3.46. Found: C, 19.01; H, 3.11. The experimental average molecular weight by vapor pressure osmometry in  $\text{CHCl}_3$  solvent is 558 in the concentration range  $1 \times 10^{-2}$

Table I. Positional and Thermal Parameters<sup>a</sup>

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Tl	0.0021 (2)	0.2229 (1)	0.6490 (2)	118 (3)	15 (1)	80 (2)	-1 (2)	5 (2)	-2 (1)
S(A1)	0.8402 (12)	0.2587 (7)	0.4414 (8)	131 (21)	40 (6)	60 (10)	17 (8)	25 (11)	-7 (7)
S(A2)	0.7634 (13)	0.3055 (6)	0.6426 (9)	152 (23)	24 (5)	57 (11)	8 (8)	11 (12)	-5 (6)
S(B1)	0.2420 (13)	0.3060 (6)	0.6613 (9)	162 (23)	26 (5)	67 (12)	1 (8)	25 (13)	1 (6)
S(B2)	0.1659 (12)	0.2501 (5)	0.8623 (8)	127 (21)	21 (5)	70 (11)	-11 (7)	16 (11)	1 (6)
S(C1)	0.1540 (13)	0.1087 (6)	0.6228 (10)	146 (24)	25 (5)	104 (14)	-13 (9)	41 (14)	-3 (7)
S(C2)	0.8554 (13)	0.1062 (6)	0.6727 (10)	132 (23)	19 (5)	121 (14)	4 (8)	53 (14)	2 (7)

Atom	x	y	z	$B, \text{\AA}^2$	Atom	x	y	z	$B, \text{\AA}^2$
C(A1)	0.7374 (44)	0.3069 (20)	0.5049 (32)	3.6 (1)	C(B3)	0.4424 (43)	0.3248 (22)	0.0044 (33)	4.0 (10)
N(A)	0.6027 (37)	0.3395 (18)	0.4320 (27)	4.3 (1)	C(C1)	0.0078 (54)	0.0607 (21)	0.6540 (37)	4.9 (9)
C(A2)	0.5640 (50)	0.3419 (25)	0.3066 (36)	5.8 (12)	N(C)	0.0272 (39)	-0.0090 (17)	0.6667 (28)	4.4 (8)
C(A3)	0.4986 (49)	0.3843 (22)	0.4778 (33)	4.5 (11)	C(C2)	0.1629 (48)	-0.0456 (24)	0.6498 (33)	5.2 (11)
C(B1)	0.2835 (45)	0.2992 (20)	0.8057 (32)	3.8 (10)	C(C3)	0.8957 (49)	-0.0478 (24)	0.6928 (35)	5.5 (11)
N(B)	0.4087 (37)	0.3300 (17)	0.8796 (26)	3.8 (8)	O	0.8485 (25)	0.5016 (12)	0.5005 (18)	2.9 (5)
C(B2)	0.5063 (51)	0.3764 (22)	0.8332 (36)	5.2 (11)					

<sup>a</sup> Anisotropic thermal parameters have been multiplied by  $10^4$ . Estimated standard deviations are given in parentheses. Anisotropic temperature factors are of the form  $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ .

to  $1 \times 10^{-1} M$  compared to 583 calculated for  $\text{TlC}_9\text{H}_{18}\text{N}_3\text{S}_6 \cdot \text{H}_2\text{O}$ .

**X-Ray Analysis.** Crystals of  $\text{Tl}(\text{Me}_2\text{dtc})_3 \cdot \text{H}_2\text{O}$  suitable for X-ray work were obtained by slow evaporation from  $\text{CH}_2\text{Cl}_2$ -heptane solution under nitrogen. The crystals were not vacuum-dried as this made them unsuitable for X-ray work. The crystals slowly decomposed in air. A hexagonal crystal was selected for data collection and had dimensions of 0.25, 0.29, 0.29, and 0.31 mm between flat faces with the longest dimension parallel to *a*, the spindle axis. The crystal was thinly coated with epoxy resin to minimize decomposition presumably due to  $\text{H}_2\text{O}$  loss.

The systematic absences were obtained from Weissenberg film data (Cu  $K\alpha$  radiation) and are  $h0l, l = 2n + 1$ , and  $0k0, k = 2n + 1$ , which indicate the space group to be  $P2_1/c$ . This space group was used for solution and refinement of the structure. The unit cell dimensions are  $a = 9.143 (5) \text{\AA}$ ,  $b = 19.201 (16) \text{\AA}$ ,  $c = 12.429 (7) \text{\AA}$ , and  $\beta = 109.1 (1)^\circ$  and were determined by least-squares refinement using the  $\theta$  angle values for 11 Mo  $K\alpha$  peaks scanned with a diffractometer at room temperature. The measured density is  $1.90 \text{ g/cm}^3$  from flotation which is in good agreement with the calculated value of  $1.878 \text{ g/cm}^3$ , with four molecules per unit cell.

Intensity data were collected at room temperature on a four-circle Hilger and Watts automatic diffractometer. The incident beam was Zr-filtered Mo  $K\alpha$  radiation. The scan was one-hundred  $0.01^\circ$  steps in  $\theta$  and  $\omega$  from  $-0.50$  to  $+0.50^\circ$  with respect to the calculated setting. The step time was 2 sec and the background was counted for 50 sec at each limit of the scan while crystal and counter were stationary. A total of 2330 independent reflections were collected over one quadrant for  $\theta$  between  $0$  and  $20^\circ$ . The number of nonzero reflections (i.e., with  $F_o^2 > 2\sigma(F_o^2)$ ) used in the structure determination was 1190. Two standard reflection intensities were checked at intervals of 30 sequential reflections. A 35% decay of the initial intensities of both standard reflections was observed during data collection and attributed to a combination of decomposition and X-ray tube deterioration. Scale factors were adjusted on the assumption that all reflections decreased at the same rate.

The data were processed in a manner described by Corfield, Doedens, and Ibers;<sup>12</sup> the value of 0.04 was used for  $\rho$  in the  $\sigma(I)$  equation. The intensity data were corrected for Lorentz and polarization effects and for absorption ( $\mu = 85.78 \text{ cm}^{-1}$ ) using the program DATAP2.<sup>13</sup> A grid size of  $4 \times 4 \times 4$  was used for the absorption correction.

The thallium and two sulfur atoms were located from a three-dimensional Patterson map.<sup>14</sup> The subsequent three-dimensional Fourier map, phased by the thallium and two sulfur atoms, showed the remaining sulfur atoms. A second Fourier map, phased on the thallium and six sulfur atoms, showed all but one of the remaining carbon atoms and all nitrogen atoms. Three cycles of isotropic full-matrix least-squares refinement followed by a three-dimensional difference Fourier showed the remaining carbon atom and an unexpected oxygen atom from a water molecule of solvation. The presence of the water molecule was confirmed by NMR spectroscopy. Three cycles of full-matrix least-squares refinement with all 20 atoms thermally isotropic yielded  $R = 0.124$  and  $r = 0.056$ .<sup>15</sup> Four more cycles of full-matrix least-squares refinement with the thallium and

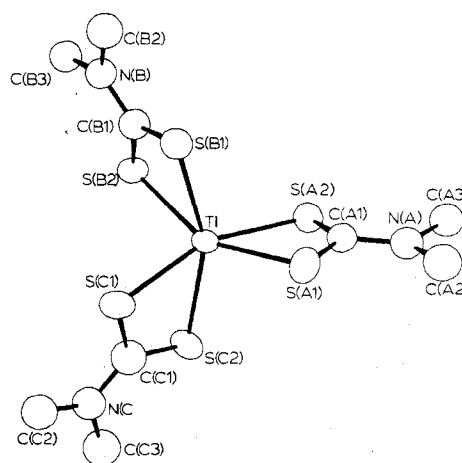


Figure 1. Drawing of the  $\text{Tl}(\text{Me}_2\text{dtc})_3$  molecule viewed along the  $C_3$ -ref axis (see text) showing the labeling scheme.

six sulfur atoms thermally anisotropic yielded a final  $R = 0.080$  and  $r = 0.026$ . The numbers of observations and variables are respectively 1190 and 116 in the final refinements.

The final atomic coordinates with their standard deviations and the final anisotropic and isotropic thermal parameters with their standard deviations are given in Table I. A table of observed and calculated structure factors is available.<sup>16</sup>

**PMR Measurements.** PMR spectra were recorded using a Varian XL-100-15-FT NMR spectrometer equipped with a variable-temperature probe and deuterium lock. Temperatures were measured by a thermocouple mounted in an NMR tube and are accurate to  $\pm 1^\circ$ . All spectra were recorded using  $\text{CD}_2\text{Cl}_2$  solvent and chemical shifts were measured relative to the  $^2\text{H}$  internal lock frequency and are reported in ppm relative to  $\text{CHDCl}_2$ . All spectra were recorded using Fourier transform techniques. The number of transients recorded for each spectrum usually varied between 100 and 200.

## Results and Discussion

**TlS<sub>6</sub> Core.** The numbering system is shown in Figure 1 and the interatomic distances and angles are listed in Table II.

The mean Tl-S distance is  $2.659 \text{\AA}$  with all six Tl-S distances within  $5\sigma$  or  $0.046 \text{\AA}$  of the mean. Tl-S(A1) and Tl-S(B2) distances are notably shorter than the others and these two sulfur atoms are involved in surprisingly short intermolecular S-S contacts (vide infra and Figure 4). The three ligands are therefore bidentate with all Tl-S distances shorter than the sum of either atomic or ionic radii.<sup>17</sup> The Tl-S<sub>6</sub> polyhedron will therefore be analyzed like other tris-bidentate complexes with approximate  $D_3$  symmetry.

Structural parameters for some complexes of approximate  $D_3$  symmetry containing the  $\text{MS}_6$  core are summarized in

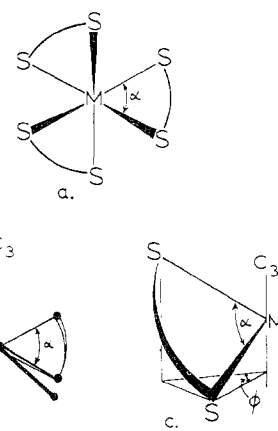
**Table II.** Interatomic Distances and Angles within the  $TlS_6$  Polyhedron

Distances, Å			
Tl-S(A1)	2.613 (10) <sup>a</sup>	S(C1)-S(C2)	2.990 (17)
Tl-S(A2)	2.677 (11)	S(A1)-S(B1)	3.904 (16)
Tl-S(B1)	2.676 (12)	S(A1)-S(C1)	4.170 (17)
Tl-S(B2)	2.637 (10)	S(B1)-S(C1)	3.869 (17)
Tl-S(C1)	2.672 (12)	S(A2)-S(B2)	3.947 (16)
Tl-S(C2)	2.677 (12)	S(A2)-S(C2)	3.908 (17)
S(A1)-S(A2)	2.948 (15)	S(B2)-S(C2)	4.108 (17)
S(B1)-S(B2)	3.001 (15)		
Angles, Deg			
S(A1)-Tl-S(A2)	67.7 (3)	S(B2)-Tl-S(C2)	101.3 (4)
S(B1)-Tl-S(B2)	68.8 (3)	S(A1)-Tl-S(C2)	100.7 (4)
S(C1)-Tl-S(C2)	68.0 (4)	S(B1)-Tl-S(A2)	107.1 (4)
S(A1)-Tl-S(B1)	95.1 (4)	S(C1)-Tl-S(B2)	97.9 (3)
S(A1)-Tl-S(C1)	104.2 (4)	S(A1)-Tl-S(B2)	153.3 (4)
S(A2)-Tl-S(B2)	95.9 (3)	S(B1)-Tl-S(C2)	157.5 (4)
S(A2)-Tl-S(C2)	93.8 (3)	S(C1)-Tl-S(A2)	159.0 (4)
S(B1)-Tl-S(C1)	92.7 (4)		

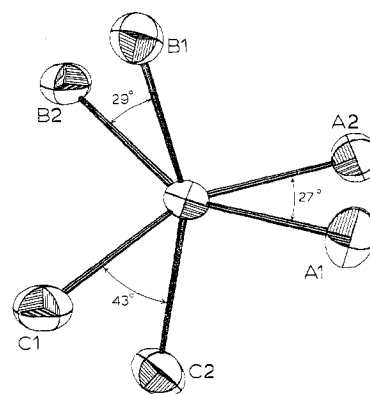
<sup>a</sup> Estimated standard deviations are given in parentheses.

Table III and defined in Figure 2. These parameters have been discussed before and completely characterize the  $MS_6$  polyhedron. The parameters  $r$ ,  $d$ , and  $\alpha$  are calculated directly from the crystallographic coordinates whereas  $\phi$  and  $\psi$  depend on the definition of the  $\sim C_3$  symmetry axis. This axis is crystallographically defined only for complex IX which has crystallographic  $D_3$  symmetry, however, the other compounds have approximate  $D_3$  symmetry and therefore are analyzed by defining a  $C_3$  reference axis hereafter denoted  $C_3$ -ref.<sup>18</sup> For these complexes the  $C_3$ -ref axis is defined as follows. The midpoints of the lines connecting the ligating sulfur atoms of each bidentate chelate were calculated and the plane containing these three midpoints constructed. The  $C_3$ -ref axis is defined as the normal to this plane which contains the metal ion. The parameters  $\phi$  and  $\psi$  are then calculated for each chelate ring individually (see Figure 2).

It can be readily seen from Tables II and III that the three values of  $d$  and  $\alpha$  which refer to the three chelate rings for  $Tl(Me_2dte)_3$  are nearly identical as is true for all entries in Table III. However,  $Tl(Me_2dte)_3$  has two small values and one large value of  $\phi$  and  $\psi$  which indicates a significant distortion from  $D_3$  symmetry. In fact the complex is best described as having  $\sim C_2$  symmetry with the  $\sim C_2$  axis bisecting chelate ring 3 (in Table III) or C (in Figures 1 and 3) and containing the thallium atom. A similar distortion but not as pronounced is noted in complexes II and III. The other complexes listed in Table III in general do not show this distortion especially when using values of the propeller pitch angle  $\psi$ ; however, complexes VI and VII do show a similar but smaller distortion. This distortion can be seen in Figure 3 which shows an ORTEP view down the  $C_3$ -ref axis and includes the values of the three twist angles. There is no a priori reason



**Figure 2.** Various views of the  $MS_6$  coordination core of a tris-chelate complex which define the bite angle  $\alpha$ , the pitch angle  $\psi$ , the twist angle  $\phi$ , the bite distance  $d$ , and the metal-ligand distance  $r$ . Note that  $\phi$  is the projection of  $\alpha$  into a plane normal to the  $C_3$  axis.



**Figure 3.** ORTEP drawing of the  $TlS_6$  core showing the anisotropic thermal ellipsoids. Ellipsoids are 50% probability surfaces. The values of the three twist angles are shown.

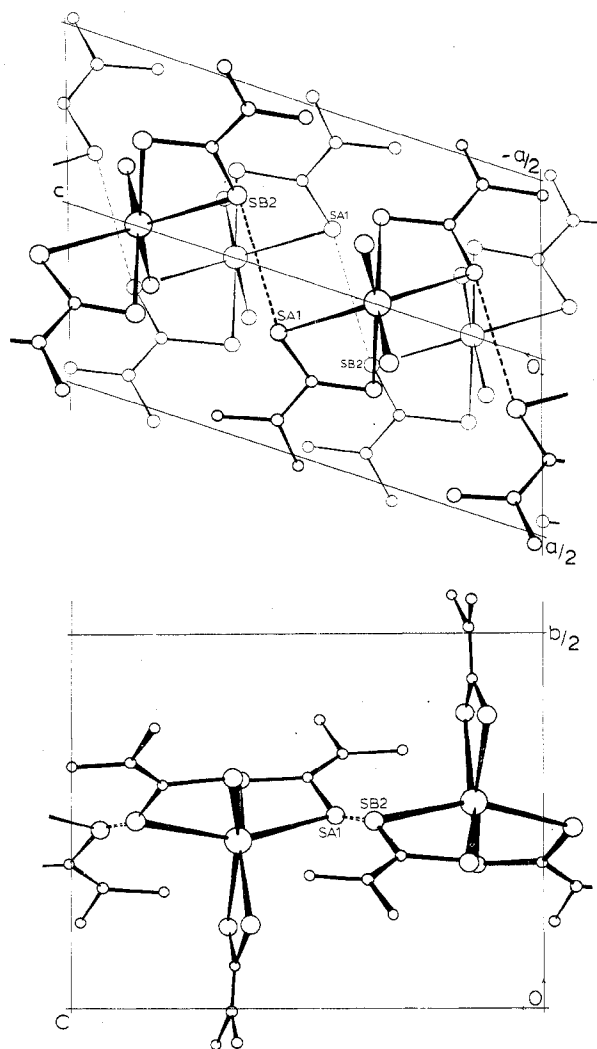
for this distortion. In  $Tl(Me_2dte)_3$  S(A1), S(B2), C(C2), C(C3), C(B1), and C(B2) are involved in short intermolecular S-S and C-C contacts (vide infra and Figure 4) which may influence the relative pitch of the chelate propeller blades to give the observed distortion; however, no short intermolecular contacts are found in compounds II and III. It is interesting that the three complexes which show the significant  $C_2$  distortion have the longest metal-sulfur distances and therefore the smallest ligand bite angles. More examples are needed with large metal ions in order to test the generality of this distortion.

In view of the non- $D_3$  geometry observed in compounds I-III it is perhaps not meaningful to include these in a discussion

**Table III.** Crystallographic Parameters<sup>a</sup> of the  $MS_6$  Core for Some Tris-Bidentate Complexes<sup>b</sup>

Complex	$\bar{r}$ , Å <sup>b</sup>	$\bar{d}$ , Å	$\bar{\alpha}$ ( $\alpha_1, \alpha_2, \alpha_3$ ), deg <sup>c</sup>	$\bar{\phi}$ ( $\phi_1, \phi_2, \phi_3$ ), deg <sup>c</sup>	$\bar{\psi}$ ( $\psi_1, \psi_2, \psi_3$ ) deg <sup>c</sup>	Ref
$Tl(Me_2dte)_3$ , I	2.66	2.98	68.2 (67.7, 68.8, 68.0)	33.2 (27.3, 29.1, 43.2)	26.5 (21.2, 22.3, 35.9)	e
$In(S_2C_2Ph)_3$ , II <sup>d</sup>	2.60	2.94	68.6 (69.4, 68.3, 68.2)	36.1 (33.6, 33.8, 40.9)	28.6 (25.8, 26.7, 33.4)	f
$In[(CH_2)_2dte]_3$ , III	2.59	2.95	69.4 (69.3, 69.6, 69.3)	32.8 (31.6, 28.4, 38.5)	25.3 (24.2, 21.4, 30.3)	g
$Ru(Et_2dte)_3$ , IV	2.38	2.83	73.0 (72.9, 72.9, 73.2)	38.1 (37.5, 39.5, 37.2)	27.8 (27.4, 29.1, 26.9)	h
$Fe(Et_2dte)_3$ , V	2.36	2.84	74.2 (74.1, 74.2, 74.4)	37.6 (37.4, 38.7, 36.8)	26.8 (26.6, 27.7, 26.0)	i
$Fe[(CH_2)_2dte]_3$ , VI	2.41	2.91	74.4 (73.6, 74.2, 75.5)	37.4 (34.7, 35.0, 42.4)	26.5 (24.7, 24.6, 30.1)	j
$Fe(Me, Ph(dte))_3$ , VII	2.31	2.82	75.1 (75.2, 74.9, 75.2)	40.7 (36.2, 43.2, 42.6)	28.9 (25.1, 31.1, 30.4)	j
$Co(Et_2dte)_3$ , VIII	2.26	2.79	76.2 (75.9, 75.9, 76.8)	43.7 (43.6, 43.6, 43.9)	30.7 (30.8, 30.8, 30.6)	k
$Ni(Bu_2dte)_3^+$ , IX	2.26	2.79	76.3 (76.3, 76.3, 76.3)	45.3 (45.3, 45.3, 45.3)	32.1 (32.1, 32.1, 32.1)	l

<sup>a</sup> Parameters are defined in Figure 2 and text; the bar refers to the average value. <sup>b</sup> Each complex listed has all M-S distances within 0.03 Å of its mean except for I (see text). <sup>c</sup> The three values given in parentheses correspond to the three ligands where the subscripts identify specific ligands in each complex. <sup>d</sup> Dithiophenylacetato ligand. <sup>e</sup> This work. <sup>f</sup> M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *Ann. Chim. (Rome)*, **60**, 664 (1970). <sup>g</sup> Reference 22. <sup>h</sup> Reference 1. <sup>i</sup> J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973). <sup>j</sup> Reference 23. <sup>k</sup> S. Merlino, *Acta Crystallogr., Sect. B*, **24**, 1441 (1968). <sup>l</sup> J. P. Fackler, Jr., A. Avdeef, and R. G. Fischer, Jr., *J. Am. Chem. Soc.*, **95**, 774 (1973).



**Figure 4.** Projection views showing the packing of the  $\text{Tl}(\text{Me}_2\text{dtc})_3$  molecules along the  $b$  (top view) and  $a$  (bottom view) crystallographic axes. The dashed line shows the short S-S contact (see text). Several carbon atoms are omitted near the  $\pm a/2$  axes of the top view for clarity. The bottom view only shows one chain of tris-chelate molecules which corresponds to the lower layer of the top view. The carbon and nitrogen atoms of the C ligands (those with planes approximately parallel to the  $b$  axis) have been omitted in the top view.

of the extent of distortion from octahedral toward trigonal-prismatic geometry. Recent interest<sup>1-4,11,19-21</sup> in this type of distortion for complexes with  $\sim D_3$  symmetry and the importance of small bite angle chelates in these analyses, however, makes such a comparison important. Therefore the average twist angle,  $\bar{\phi}$ , and pitch angle,  $\bar{\psi}$ , will be used as a measure of this distortion as has been done by others,<sup>1,4,11,19-23</sup> even for complexes I-III. The results of this analysis will therefore be valid in an average sense for complexes not possessing strict  $D_3$  symmetry of the  $\text{MS}_6$  core.

Octahedral geometry is usually assumed for six-coordinate tris-bidentate complexes and is characterized by  $\alpha = 90^\circ$ ,  $\phi = 60^\circ$ ,  $\psi = 35.3^\circ$ , and orthogonal chelate rings.<sup>24</sup> Since  $\text{M}(\text{dtc})_3$  complexes have  $\alpha \ll 90^\circ$ , this geometry is impossible. It is therefore of interest to determine exactly what distortion is found in these complexes. If the small bite angle ligands retain their orthogonality, the pitch angle will remain at  $35.3^\circ$ ; however, the twist angle will significantly decrease below  $60^\circ$ . For example, in a complex with  $\alpha = 70^\circ$  and  $\psi = 35.3^\circ$  the value of  $\phi$  is  $44.1^\circ$ . Although the  $\text{M}(\text{dtc})_3$  complexes could retain orthogonal chelate rings, they do not as clearly evidenced in Table III. All of these complexes are truly distorted toward

**Table IV.** Experimental and Calculated Twist Angles

Complex <sup>a</sup>	$\bar{b} = \bar{d}/\bar{r}$	$\bar{\phi}_{\text{exptl}}$ , deg <sup>b</sup>	$\bar{\phi}_{\text{calcd}}$ , deg <sup>c</sup>
I	1.12	33.2	28 (33)
II	1.13	36.1	29 (34)
III	1.14	32.8	31 (35)
IV	1.19	38.1	37 (38)
V	1.20	37.6	38 (40)
VI	1.21	37.4	39 (40)
VII	1.22	40.7	40 (42)
VIII	1.23	43.7	41 (43)
IX	1.23	45.3	41 (43)

<sup>a</sup> See Table III for complex definition. <sup>b</sup> Experimental twist angles were computed using crystallographic coordinates and  $C_3$ -ref axis as defined in text; for references see Table III. <sup>c</sup> Twist angles obtained from Figure 3 of ref 11; the numbers refer to  $n = 1$  ( $n = 6$ ) in the electrostatic repulsive potential function  $U = Xr^{-n}$  where  $X$  is dependent on the geometry of the complex.<sup>11</sup>

trigonal-prismatic geometry ( $\phi = \psi = 0^\circ$ ) from the  $\psi = 35.3^\circ$  orthogonal limit. In several papers<sup>4,19-22</sup> the twist angle criterion has been used exclusively as a measure of this distortion. Thus a value of  $60^\circ$  for  $\phi$  corresponds to trigonal-antiprismatic geometry found for the  $O_h$  case. It is unreasonable to assume that a value of  $60^\circ$  for  $\phi$  is to be expected for complexes with small bite angle ligands since  $\phi$  is naturally  $< 60^\circ$  for values of  $\alpha < 90^\circ$  even if the ligands remain orthogonal. The  $\psi$  criterion is a truer measure of distortions toward trigonal-prismatic geometry. By either criterion, however,  $\text{Tl}(\text{Me}_2\text{dtc})_3$  is one of the closest to trigonal-prismatic  $\text{M}(\text{dtc})_3$  complexes known. Only compound III is slightly closer to trigonal prismatic. Again it should be pointed out that compounds I-III which are most distorted toward trigonal prismatic also show the largest superimposed  $C_2$  distortion (vide supra).

Kepert<sup>11</sup> has recently calculated the trigonal-twist distortions for a number of  $\sim D_3$   $\text{M}(\text{bidentate})_3$  complexes using a simple electrostatic repulsive potential between the six donor atoms of the  $\text{ML}_6$  core. In the calculation it is assumed that the interaction between the two ends of each coordinated bidentate ligand is constant and that the repulsion between each pair of donor atoms is inversely proportional to the  $n$ th power of the distance between them. The positions of the donor atoms are allowed to move within  $D_3$  symmetry to the energy minimum. The results are summarized in Figure 3 of ref 11 which shows calculated plots of  $\phi_{\text{min}}$  (twist angle of minimum repulsive energy) as a function of  $d/r$  (Kepert's<sup>11</sup> parameter  $b$  which equals  $2 \sin(\alpha/2)$ ) for  $n = 2, 4$ , and  $6$ . Experimental values of  $\bar{\phi}$  and  $\bar{d}/\bar{r}$  show surprising agreement with the calculated values. The principal conclusions of Kepert's analysis are as follows: (i) tris-bidentate complexes with small bite angle ligands ( $\alpha \ll 90^\circ$ ) are distorted toward trigonal-prismatic geometry; (ii) the distortion can be attributed solely to the small bite angle of the ligands; and (iii) the extent of the distortion can quite accurately be calculated by assuming a simple electrostatic repulsive model.<sup>25</sup> Most of the complexes in Table III were not available to Kepert so Table IV shows the comparison of  $\bar{\phi}_{\text{exptl}}$  with  $\bar{\phi}_{\text{calcd}}$  for these complexes. The values of  $\bar{\phi}_{\text{calcd}}$  were estimated from Figure 3 of ref 11. Best agreement is actually obtained with the  $n = 6$  form of the repulsive potential (especially for complexes I-III) which contains the smallest values for  $\bar{d}/\bar{r}$  or  $\bar{\alpha}$ . Kepert's original plot does not contain examples with  $\bar{d}/\bar{r} < 1.19$ .<sup>11,25</sup> In addition complexes I-III show a significant  $C_2$  distortion superimposed on the trigonal-twist distortion (vide supra). It would be interesting to perform the electrostatic repulsive calculation within  $C_2$  symmetry rather than  $D_3$  to see if the observed  $\sim C_2$  distortion is predicted.<sup>27</sup>

An ORTEP drawing of the  $\text{TlS}_6$  core viewed along the  $C_3$ -ref axis is shown in Figure 3.

**Geometry of the Ligands.** The numbering system is shown

Table V. Interatomic Distances and Angles within the Ligands<sup>a</sup>

	Ligand A	Ligand B	Ligand C
Distances, Å			
S(1)-C(1)	1.69 (4)	1.71 (4)	1.77 (5)
S(2)-C(1)	1.65 (4)	1.74 (4)	1.72 (5)
C(1)-N	1.41 (5)	1.35 (4)	1.35 (4)
N-C(2)	1.48 (6)	1.50 (5)	1.50 (6)
N-C(3)	1.52 (6)	1.48 (5)	1.54 (6)
Angles, Deg			
Tl-S(1)-C(1)	85 (1)	85 (1)	87 (1)
Tl-S(2)-C(1)	83 (1)	86 (1)	87 (2)
S(1)-C(1)-S(2)	124 (2)	121 (2)	118 (2)
S(1)-C(1)-N	116 (3)	122 (3)	118 (4)
S(2)-C(1)-N	118 (3)	117 (3)	125 (4)
C(1)-N-C(2)	123 (4)	119 (3)	122 (4)
C(1)-N-C(3)	122 (3)	122 (4)	115 (4)
C(2)-N-C(3)	114 (3)	120 (3)	123 (3)

<sup>a</sup> For numbering systems see Figure 1.

in Figure 1 and the ligand interatomic distances and angles are summarized in Table V. The distances and angles are similar to those found in other bidentate chelated dithiocarbamate complexes. The rather short S<sub>2</sub>C-N bond distances (average 1.37 Å) are typical of dithiocarbamate ligands and indicate significant double-bond character.<sup>1,2,28,29</sup> Hindered rotation about this bond has been observed by PMR in many dithiocarbamate complexes<sup>28</sup> including unsymmetrically substituted Tl(R<sub>1</sub>R<sub>2</sub>dtc)<sub>3</sub> complexes.<sup>30</sup> The three chelate rings were tested for planarity. The grouping TlS<sub>2</sub>CNC<sub>2</sub> for ligands A and B is planar within experimental error; however a significant deviation from planarity is found for ligand C. The distortion is best described as a fold about the S-S or chelate bite axis. The S<sub>2</sub>CNC<sub>2</sub> part of the ligand is planar within experimental error and the dihedral angle between this plane and the TlS<sub>2</sub> plane is 6°. This distortion presumably results from crystal packing forces because both methyl groups in this ligand, C(C2) and C(C3), are involved in short intermolecular contacts (vide infra).

**Intermolecular Distances.** There are several short intermolecular carbon-carbon contacts with distances less than 3.60 Å which is the sum of the van der Waals radii for carbon. The shortest of these is a methyl-methyl contact of 3.32 (6) Å found for C(C2)-C(B2)' where prime denotes a different molecule. This contact involves nearly coaxial N-CH<sub>3</sub> bonds and is not uncommonly short for such methyl-methyl intermolecular distances.<sup>31-34</sup> In addition a distance of 3.37 (6) Å is found for C(C3)-C(B1)". This distance is not surprisingly short if the van der Waals radii for the methyl hydrogen atoms and the S<sub>2</sub>CN carbon atom are used to define the closest nonbonded carbon-carbon contact. Since both of these short distances involve chelate rings B and C, it is not obvious that they have any effect on distortions of the TlS<sub>6</sub> core (vide supra).

The presence of a water molecule of hydration is surprising since the final recrystallizations took place from a CH<sub>2</sub>Cl<sub>2</sub>-heptane mixture; however the PMR spectrum in CDCl<sub>3</sub> solvent of freshly crystallized complex verified the existence of one H<sub>2</sub>O per Tl(Me<sub>2</sub>dtc)<sub>3</sub> molecule. The water molecule is well removed from the Tl(Me<sub>2</sub>dtc)<sub>3</sub> molecular unit. The shortest contact involving oxygen and Tl(Me<sub>2</sub>dtc)<sub>3</sub> is 3.88 Å for O-C(C3). The water molecule is hydrogen bonded to another water molecule because the O-O' distance of 2.78 (5) Å is quite close to that of 2.76 Å found in ice.<sup>35</sup>

A short sulfur-sulfur intermolecular distance is found and shown in the projection view of the unit cell (Figure 4) as a dashed line. The S(A1)-S(B2)' distance of 3.43 (2) Å is shorter than the sum of the van der Waals radii for sulfur which is 3.7 Å. This is of some significance as it represents one of the shortest intermolecular sulfur-sulfur contacts observed for any monomeric M(dtC)<sub>3</sub> complex including highly

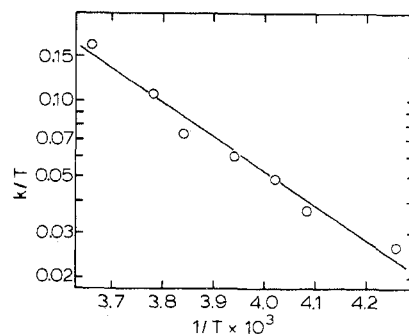
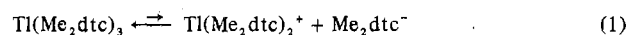


Figure 5. Eyring plot for first-order ligand exchange in Tl(Me<sub>2</sub>dtc)<sub>3</sub> (see text).

oxidized ones such as Fe[(CH<sub>2</sub>)<sub>4</sub>dtc]<sub>3</sub>ClO<sub>4</sub><sup>30</sup> and Mn-[(CH<sub>2</sub>)<sub>5</sub>dtc]<sub>3</sub>ClO<sub>4</sub>.<sup>37</sup> Short sulfur-sulfur distances could indicate partial ligand oxidation; however the distance observed here is too long to warrant this description.<sup>38</sup> The crystal structure consists of parallel chains of tris(chelate) molecules sharing edges as illustrated in Figure 4 in projection.

**Ligand Exchange.** The 100-MHz PMR spectrum of Tl-(Me<sub>2</sub>dtc)<sub>3</sub> shows a sharp singlet at 31° with a chemical shift of 1.94 ppm to high field of CHDCl<sub>2</sub> internal standard and a peak width at half-height of 1.3 Hz. As the temperature was lowered, the peak broadened and split into a doublet below ca. -20°. The frozen-out limit was reached at ca. -50°. The splitting of the doublet varied from 10.0 Hz at -51° to 9.3 Hz at -80° under slow-exchange conditions and was independent of NMR spectrometer frequency. Thallium noise decoupling resulted in collapse of the doublet. Therefore the doublet is due to <sup>(203)205</sup>Tl-<sup>1</sup>H spin-spin coupling<sup>6,7</sup> and its coalescence with increasing temperature results from rapid exchange of Me<sub>2</sub>dtc ligands. Exchange-broadened spectra were computer simulated employing eq 41 of ref 39 which was derived for the collapse of spin-spin coupling due to mutual exchange. Good fits to the experimental spectra were found in the temperature range +38 to +10°. Extrapolated values of J(Tl-H) from the slow-exchange limit (<-51°) (slope and intercept of linear J vs. 1/T plot are -1.01 × 10<sup>3</sup> Hz K<sup>-1</sup> and 14.5 Hz, respectively) and interpolated values of the line width at half-height, H<sub>1/2</sub>, from the fast (>30°) and slow (<-50°) exchange limits (slope and intercept of linear ln H<sub>1/2</sub> vs. 1/T plot are 4.31 × 10<sup>2</sup> ln Hz K<sup>-1</sup> and -1.20 ln Hz, respectively) were used in the calculation. Best fits of calculated line shapes at seven temperatures were visually selected. The rate constant for ligand exchange, k(sec<sup>-1</sup>), was assumed to be equal to 1/τ where τ is the mean lifetime in seconds of coordinated ligand which gives rise to spin-spin coupling. The rate constants are independent of complex concentration over the concentration range 1 × 10<sup>-3</sup> to 1 × 10<sup>-2</sup> M which indicates a first-order reaction. An Eyring plot of the data is shown in Figure 5 and ΔH<sup>‡</sup> = 6.2 ± 1.0 kcal/mol and ΔS<sup>‡</sup> = -28 ± 10 eu.

This is the first quantitative report of ligand-exchange reactions for M(R<sub>1</sub>R<sub>2</sub>dtc)<sub>3</sub> type complexes. The kinetic results suggest a dissociative mechanism. The solid-state structure gives no evidence for weak Tl-S bonding; however the solution ir data (see Experimental Section) suggest a lowering of the Tl-S coordination number which would facilitate dissociative ligand exchange. In addition the temperature dependence of J(Tl-H) (vide supra) may suggest a rapid monodentate-bidentate equilibrium in solution. Molecular weight data determined by vapor pressure osmometry in CHCl<sub>3</sub> solvent give no indication of ligand dissociation. It is most probable, therefore, that the rate-determining step is ligand dissociation given by eq 1 but that the equilibrium constant for this reaction



is undetectably small. Addition of an approximately equimolar

amount of  $\text{NEt}_4\text{Me}_2\text{dtc}$  to  $\text{Tl}(\text{Me}_2\text{dtc})_3$  below the coalescence temperature but in the region of exchange broadening did not cause a noticeable effect on the line shape of the methyl signal of coordinated ligand. This is consistent with the above mechanism.

Ligand-exchange experiments are being carried out for a number of  $\text{M}(\text{R}_1\text{R}_2\text{dtc})_3$  complexes. The exchange rate for  $\text{Tl}(\text{Me}_2\text{dtc})_3$  is faster than for analogous complexes of  $\text{M} = \text{Ga}(\text{III}), \text{In}(\text{III}), \text{Fe}(\text{III}), \text{Fe}(\text{IV}), \text{Co}(\text{III}), \text{Cr}(\text{III}), \text{Mn}(\text{III}),$  and  $\text{V}(\text{III})$ .<sup>30</sup>

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**Registry No.**  $\text{Tl}(\text{Me}_2\text{dtc})_3 \cdot \text{H}_2\text{O}$ , 55721-19-2.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50169F-9-75.

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- (15)  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$ ; the numerator of  $r$  was the function minimized; the weights were  $1/[\sigma(F^2)]^2$  where  $\sigma(F^2) = \sigma(I)/Lp$ . Atomic scattering factors were taken from "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A (S, C, O, N) and Table 3.3.1B (Tl). Anomalous dispersion corrections from the same source (Table 3.3.2C) were used for thallium:  $\Delta f' = -3.2$ ,  $\Delta f'' = 11.2$ .
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