

# Crystal and Molecular Structure of a Seven-Coordinate Titanium Compound, Chlorotrtris(*N,N*-dimethyldithiocarbamato)titanium(IV)<sup>1</sup>

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**Abstract:** The crystal and molecular structure of chlorotrtris(*N,N*-dimethyldithiocarbamato)titanium(IV),  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$ , has been determined by single-crystal X-ray diffraction and has been refined (anisotropically on Ti, Cl, and S) by least-squares methods to  $R_1 = 0.047$  and  $R_2 = 0.063$ . The compound crystallizes in the orthorhombic space group  $Pn2_1a$  (nonstandard setting of  $Pna2_1$ ) with four molecules in a unit cell of dimensions  $a = 9.208$  (4),  $b = 13.829$  (5), and  $c = 14.803$  (6) Å ( $\rho_{\text{obsd}} = 1.59$  (2),  $\rho_{\text{calcd}} = 1.561$  g cm<sup>-3</sup>). The intensities of 2382 independent reflections having  $2\theta \leq 54.86^\circ$  were measured on a Picker four-circle diffractometer using the  $\theta$ - $2\theta$  scan technique and Mo K $\alpha$  radiation. A total of 1722 reflections having  $|F_o| \geq 2\sigma(|F_o|)$  was used in the determination and refinement of the structure. The crystal contains discrete seven-coordinate molecules which have a pentagonal bipyramidal structure of approximate symmetry  $C_{2v}$ . The chlorine atom occupies one axial position (Ti-Cl = 2.305 (3) Å), dithiocarbamate ligand a spans the other axial position and one equatorial position, and dithiocarbamate ligands b and c take the remaining equatorial positions. The average Ti-S bond length is 2.512 Å. Extreme crowding in the equatorial plane is evidenced by notably short interligand S...S contacts (2.95-3.10 Å). The observed distortions from ideal pentagonal bipyramidal geometry are discussed with reference to the eight-coordinate, dodecahedral structure of  $\text{Ti}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_4$ .

Apart from the oxo-bridged dinuclear peroxodipicolinato complex  $[\text{TiO}_{0.5}(\text{O}_2)(\text{C}_7\text{H}_3\text{O}_4\text{N})(\text{H}_2\text{O})]_2^{2-}$ ,<sup>2a</sup> coordination number seven for titanium(IV) has not yet been established by X-ray diffraction though it has been demonstrated for titanium(III) in  $\text{Ti}_2(\text{H}_2\text{O})_6(\text{C}_4\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ <sup>2b</sup> and has been suggested for a few titanium(IV) complexes ( $\text{Ti}(\text{tropolonate})_3\text{Cl}$ ,<sup>3</sup>  $\text{Ti}(\text{oxine})_3\text{Cl}$ ,<sup>4</sup> and  $\text{TiCl}_4(\text{triarsine})$ <sup>5</sup>). X-Ray studies have established eight-coordination for titanium(IV) in  $\text{TiCl}_4(\text{diarsine})_2$ ,<sup>6</sup>  $\text{Ti}(\text{NO}_3)_4$ ,<sup>7</sup> and the *N,N*-diethyldithiocarbamate complex  $\text{Ti}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_4$ .<sup>8</sup> In general, however, coordination numbers greater than six for first-row transition elements are still quite rare.<sup>9</sup>

Recently, a series of *N,N*-dialkyldithiocarbamate complexes of the type  $\text{Ti}(\text{S}_2\text{CNR}_2)_3\text{X}$  (R = Me, Et, *i*-Pr, *i*-Bu; X = Cl or Br) have been reported<sup>10-12</sup> which appear to be seven-coordinate on the basis of molecular weight, conductance, and infrared data. A single-crystal X-ray study of a representative complex of this

type,  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$ , was carried out in order to confirm the coordination number and establish the geometry of the coordination polyhedron.

## Experimental Section

Tris(dimethyldithiocarbamato)titanium(IV) chloride was prepared by the method of Bhat, *et al.*<sup>11</sup> Dark red crystals, suitable for X-ray diffraction work, were grown by cooling a saturated solution of the complex in dichloromethane-hexane (~3:1 v/v). Prismatic crystals were sealed, under nitrogen, in Lindemann glass capillaries.

Preliminary precession and Weissenberg photographs revealed Laue symmetry *mmm*. The observed systematic extinctions,  $0kl$  for  $k + l \neq 2n$  and  $hk0$  for  $h \neq 2n$ , are compatible with space groups  $Pnma$  (No. 62) and  $Pn2_1a$  (nonstandard setting of  $Pna2_1$ , No. 33).<sup>13</sup> Using zirconium-filtered Mo K $\alpha$  radiation ( $\lambda$  0.71069 Å) 12 reflections were centered in the counter window of a Picker FACS-I diffractometer, and the setting angles were used to determine least-squares values of the unit cell parameters. The results are  $a = 9.208$  (4),  $b = 13.829$  (5),  $c = 14.803$  (6) Å at  $20 \pm 1^\circ$ . The density calculated on the basis of four molecules of  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$  per unit cell is 1.561 g cm<sup>-3</sup>, which is in good agreement with the observed value of  $1.59 \pm 0.02$  g cm<sup>-3</sup> obtained by flotation in aqueous zinc chloride.

Intensity data were collected on a Picker FACS-I four-circle diffractometer employing a crystal mounted in a Lindemann glass capillary such that the *b* axis was parallel to  $\phi$ . The crystal was a parallelepiped of approximate dimensions  $0.20 \times 0.25 \times 0.20$  mm parallel to the *a*, *b*, and *c* axes, respectively. Mo K $\alpha$  radiation was used for data collection, and the diffracted beam was filtered through zirconium foil. A takeoff angle of  $\sim 2^\circ$  was employed. Intensities were gathered at room temperature ( $20 \pm 2^\circ$ ) using the  $\theta$ - $2\theta$  scan technique. The scan angle used was  $1.50^\circ$  plus an allowance for the dispersion of Mo K $\alpha_1$  and Mo K $\alpha_2$  radiation.<sup>14</sup>

Background counts, each of 20-sec duration, were taken at both ends of the scan. Reflections having counting rates greater than 10,000 cps were automatically attenuated by inserting 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 were monitored periodically at intervals of 100 reflections. No

(1) Presented in part before the Division of Inorganic Chemistry, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

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Table I. Final Atomic Positional Parameters for  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}^a$ 

Atom	$10^4x$	$10^4y$	$10^4z$
Ti	1668 (2)	2500 <sup>b</sup>	310.4 (9)
Cl	2652 (3)	3898 (2)	899 (2)
S <sub>a1</sub>	819 (3)	1188 (2)	-699 (2)
S <sub>a2</sub>	2343 (3)	2888 (2)	-1340 (1)
S <sub>b1</sub>	2282 (2)	1283 (2)	1495 (2)
S <sub>b2</sub>	4222 (2)	1854 (2)	106 (1)
S <sub>c1</sub>	-433 (2)	2406 (2)	1347 (1)
S <sub>c2</sub>	-430 (2)	3466 (2)	-298 (1)
N <sub>a</sub>	1355 (9)	1531 (7)	-2457 (6)
N <sub>b</sub>	4979 (9)	579 (6)	1389 (5)
N <sub>c</sub>	-2680 (8)	3522 (6)	843 (5)
C <sub>a</sub>	1491 (10)	1820 (7)	-1601 (6)
C <sub>b</sub>	3989 (9)	1155 (7)	1058 (6)
C <sub>c</sub>	-1376 (9)	3202 (6)	656 (6)
C <sub>a1</sub>	541 (15)	627 (11)	-2673 (9)
C <sub>a2</sub>	1991 (14)	2068 (10)	-3203 (9)
C <sub>b1</sub>	4658 (12)	-74 (8)	2144 (7)
C <sub>b2</sub>	6460 (12)	519 (8)	1009 (7)
C <sub>c1</sub>	-3418 (11)	3291 (8)	1717 (7)
C <sub>c2</sub>	-3443 (11)	4172 (8)	228 (6)

<sup>a</sup> Standard deviations in parentheses apply to the last significant figure. <sup>b</sup>  $y$  coordinate is arbitrary.

Table II. Final Thermal Parameters for  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}^a$ 

Atom	Anisotropic parameters						Equiv isotropic $B, \text{\AA}^2$	Isotropic parameters			
	$\beta_{11}^{b,c}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$		Atom	$B, \text{\AA}^2$	Atom	$B, \text{\AA}^2$
Ti	74 (2)	35 (1)	22 (1)	-3 (1)	-2 (1)	0 (1)	2.37 (1)	N <sub>a</sub>	4.0 (2)	C <sub>a1</sub>	6.1 (3)
Cl	114 (3)	45 (1)	41 (1)	-19 (2)	-2 (1)	-7 (1)	3.50 (3)	N <sub>b</sub>	3.2 (1)	C <sub>a2</sub>	5.4 (3)
S <sub>a1</sub>	126 (3)	38 (1)	36 (1)	-12 (2)	-1 (2)	-4 (1)	3.33 (3)	N <sub>c</sub>	3.0 (1)	C <sub>b1</sub>	4.2 (2)
S <sub>a2</sub>	120 (3)	48 (1)	26 (1)	-14 (2)	7 (1)	3 (1)	3.20 (3)	C <sub>a</sub>	3.2 (2)	C <sub>b2</sub>	4.0 (2)
S <sub>b1</sub>	84 (3)	53 (1)	32 (1)	9 (2)	7 (1)	10 (1)	3.10 (3)	C <sub>b</sub>	2.7 (1)	C <sub>c1</sub>	4.1 (2)
S <sub>b2</sub>	81 (2)	47 (1)	33 (1)	0 (2)	8 (1)	0 (1)	3.02 (3)	C <sub>c</sub>	2.6 (1)	C <sub>c2</sub>	3.7 (2)
S <sub>c1</sub>	78 (2)	54 (1)	34 (1)	7 (2)	3 (1)	14 (1)	3.05 (3)				
S <sub>c2</sub>	99 (3)	51 (1)	29 (1)	9 (2)	0 (1)	9 (1)	3.14 (3)				

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the last significant figure. <sup>b</sup> Anisotropic temperature factors are of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>c</sup> Values of  $\beta_{ij}$  are  $\times 10^4$ . <sup>d</sup> Isotropic thermal parameter calculated from  $B = 4[V^2 \det(\beta_{ij})]^{1/3}$ .

significant fluctuations were observed, and for each reflection the deviation of the maximum and minimum observed intensity, expressed as a percentage of the mean, was  $< 2.68\%$ .

A total of 2382 reflections having  $2\theta \leq 54.86^\circ$  was collected. The data were corrected for background, use of attenuators, and Lorentz and polarization factors (Lp). The linear absorption coefficient for Mo  $K\alpha$  radiation is  $12.35 \text{ cm}^{-1}$ , and it is calculated that the maximum error resulting from neglect of absorption corrections is  $< 5\%$  in any intensity or  $< 3\%$  in any amplitude for the crystal used. For this reason it was felt that absorption corrections would not significantly improve the reliability of the data.

Standard deviations were calculated from

$$\sigma^2(|F_o|) = (C_s + k^2B)/4|F_o|^2(\text{Lp})^2$$

wherein  $C_s$  is the count of the scan,  $k$  is the ratio of scanning time to background time, and  $B$  is the total background count. A reflection with  $|F_o| < 2\sigma(|F_o|)$  was considered unobserved, which left a total of 1722 observed reflections that were subsequently used in the determination and refinement of the structure.

**Structure Determination and Refinement.** The structure was solved in a straightforward manner by the application of Patterson and Fourier techniques.<sup>15</sup> The choice of the noncentric space

(15) Calculations were performed on an IBM 360/65 computer using the following programs: DIFFDATA, a local data reduction program; FOURIER, a local version of the Zalkin Fourier program; ORFLS, the Busing-Martin-Levy structure factor calculation and least-squares refinement program; WEIGHT, a local program to calculate the coefficients of a polynomial weighting scheme; ORFEE, the Busing-Martin-Levy molecular geometry and error function program; ORTEP, the Johnson thermal ellipsoid plotting program; and MEAN PLANES, a local best planes program.

group  $Pn2_1a$  was made from an examination of the Patterson map and was substantiated by the success of the subsequent refinement. Full-matrix least-squares refinement of the coordinates and isotropic thermal parameters of the 20 atoms was followed by anisotropic full-matrix refinement of the heavy atoms (Ti, Cl, S) using all the observed data and empirical weights  $w = 1/\sigma^2$  calculated from

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

the  $a_n$  being coefficients from the least-squares fitting of the curve

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

Scattering factors for  $\text{Ti}^0$ ,  $\text{Cl}^0$ ,  $\text{S}^0$ ,  $\text{N}^0$ , and  $\text{C}^0$  were taken from Cromer and Mann.<sup>16</sup> Corrections for the effects of anomalous dispersion for Ti, Cl, and S were obtained from the International Tables.<sup>17</sup>

In the final cycle of refinement no parameter varied by more than 0.17 (the average was 0.05) of its estimated standard deviation, and the discrepancy indices

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

and

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

were 0.047 and 0.063, respectively. A final difference Fourier showed no anomalous features.

Since only one form of data ( $hkl$ ) had been collected, two cycles of refinement were run in which ( $hkl$ ) was replaced by ( $\bar{h}\bar{k}l$ ). This refinement converged at values of  $R_1 = 0.048$  and  $R_2 = 0.064$ . Application of a significance test<sup>18</sup> on the ratio of the  $R_2$  factors indicates that the ( $hkl$ ) structure is preferred at a confidence level greater than 99.5% assuming that systematic errors are absent.

## Results

Final atomic positional and thermal parameters for  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$  are presented in Tables I and II, respectively.<sup>19</sup> The molecular geometry and the atom numbering scheme are shown in Figure 1. Each atom is represented by an ellipsoid consistent with the thermal parameters in Table II and is labeled with a literal and a numerical subscript; the literal subscript identifies the particular  $N,N$ -dimethyldithiocarbamate ligand (a, b, or c). The characteristic parameters of the coordination polyhedron are presented in Table III, and bond lengths and angles within the dithiocarbamate ligands are given in Table IV.

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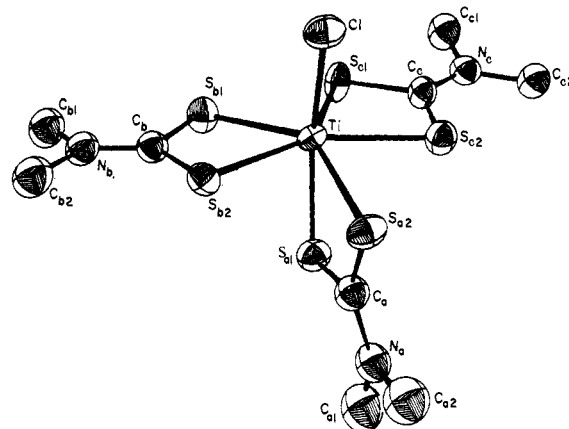
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**Table III.** Bond Distances, Polyhedral Edge Lengths, and Bond Angles in the Coordination Group<sup>a</sup>

Atoms	Length, Å	Atoms	Angle, deg
Ti-Cl	2.305 (3)	Cl-Ti-S <sub>a1</sub>	165.03 (12)
Ti-S <sub>a1</sub>	2.477 (3)		
Ti-S <sub>a2</sub>	2.577 (3)		
Ti-S <sub>b1</sub>	2.496 (3)		
Ti-S <sub>b2</sub>	2.533 (3)		
Ti-S <sub>c1</sub>	2.473 (3)		
Ti-S <sub>c2</sub>	2.516 (3)		
Cl...S <sub>a2</sub>	3.608 (4)	Cl-Ti-S <sub>a2</sub>	95.12 (10)
Cl...S <sub>b1</sub>	3.738 (4)	Cl-Ti-S <sub>b1</sub>	102.17 (11)
Cl...S <sub>b2</sub>	3.385 (4)	Cl-Ti-S <sub>b2</sub>	88.65 (10)
Cl...S <sub>c1</sub>	3.573 (4)	Cl-Ti-S <sub>c1</sub>	96.72 (11)
Cl...S <sub>c2</sub>	3.399 (4)	Cl-Ti-S <sub>c2</sub>	89.53 (10)
S <sub>a1</sub> ...S <sub>a2</sub> <sup>b</sup>	2.898 (4)	S <sub>a1</sub> -Ti-S <sub>a2</sub>	69.92 (9)
S <sub>a1</sub> ...S <sub>b1</sub>	3.519 (4)	S <sub>a1</sub> -Ti-S <sub>b1</sub>	90.08 (10)
S <sub>a1</sub> ...S <sub>b2</sub>	3.476 (4)	S <sub>a1</sub> -Ti-S <sub>b2</sub>	87.84 (10)
S <sub>a1</sub> ...S <sub>c1</sub>	3.653 (4)	S <sub>a1</sub> -Ti-S <sub>c1</sub>	95.10 (10)
S <sub>a1</sub> ...S <sub>c2</sub>	3.406 (4)	S <sub>a1</sub> -Ti-S <sub>c2</sub>	86.02 (10)
S <sub>a2</sub> ...S <sub>b2</sub>	3.101 (4)	S <sub>a2</sub> -Ti-S <sub>b2</sub>	74.72 (9)
S <sub>a2</sub> ...S <sub>c2</sub>	3.088 (4)	S <sub>a2</sub> -Ti-S <sub>c2</sub>	74.63 (9)
S <sub>b1</sub> ...S <sub>b2</sub> <sup>b</sup>	2.836 (4)	S <sub>b1</sub> -Ti-S <sub>b2</sub>	68.65 (8)
S <sub>b1</sub> ...S <sub>c1</sub>	2.951 (4)	S <sub>b1</sub> -Ti-S <sub>c1</sub>	72.86 (9)
S <sub>c1</sub> ...S <sub>c2</sub> <sup>b</sup>	2.844 (4)	S <sub>c1</sub> -Ti-S <sub>c2</sub>	69.49 (9)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the last significant figure. <sup>b</sup> The "bite" of the ligand.

**Figure 1.** Model in perspective of the  $\text{Ti}[\text{S}_2\text{CN}(\text{CN})_2]_3\text{Cl}$  molecule.

of the type  $\text{M}(\text{chelate})_3\text{X}$  when X is a ligand which forms a relatively strong, covalent  $\text{M}-\text{X}$  bond.<sup>23</sup> A closely similar structure has been found for chlorotris-(acetylacetonato)zirconium(IV), but the  $C_s-m$  symmetry of the  $\text{ZrO}_6\text{Cl}$  coordination group does not extend to the entire molecule because the acetylacetonate ligands exhibit an unsymmetric wrapping pattern.<sup>23</sup>

**Table IV.** Bond Lengths (Å) and Bond Angles (deg) in the *N,N*-Dimethyldithiocarbamate Ligands<sup>a</sup>

Bond	Ligand a	Ligand b	Ligand c	Av <sup>b</sup>	Angle	Ligand a	Ligand b	Ligand c	Av <sup>b</sup>
S <sub>1</sub> ...S <sub>2</sub> <sup>c</sup>	2.898 (4)	2.836 (4)	2.844 (4)	2.840 (6) <sup>d</sup>	S <sub>1</sub> -C-S <sub>2</sub>	115.4 (5)	111.5 (5)	111.7 (5)	111.6 (1) <sup>d</sup>
C-S <sub>1</sub>	1.712 (10)	1.709 (9)	1.736 (9)	1.716 (13)	C-S <sub>1</sub> -Ti	89.0 (3)	90.6 (3)	89.5 (3)	89.6 (7) <sup>d</sup>
C-S <sub>2</sub>	1.717 (10)	1.722 (9)	1.699 (9)		C-S <sub>2</sub> -Ti	85.7 (3)	89.1 (3)	89.0 (3)	
C-N	1.33 (1)	1.31 (1)	1.31 (1)	1.32 (1)	S <sub>1</sub> -C-N	123.7 (8)	124.2 (7)	123.2 (7)	124.2 (7) <sup>d</sup>
					S <sub>2</sub> -C-N	120.9 (8)	124.2 (7)	125.0 (7)	
C <sub>1</sub> -N	1.49 (2)	1.47 (1)	1.50 (1)	1.48 (2)	C <sub>1</sub> -N-C	120.1 (10)	121.4 (8)	121.8 (8)	121.6 (8)
C <sub>2</sub> -N	1.45 (2)	1.48 (1)	1.46 (1)		C <sub>2</sub> -N-C	122.1 (9)	122.4 (8)	121.1 (8)	
					C <sub>1</sub> -N-C <sub>2</sub>	117.8 (10)	116.2 (8)	116.9 (7)	117.0 (8)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the last significant figure. <sup>b</sup> The number in parentheses following each averaged value is the standard deviation in a single measurement (obtained from the spread of the values); the averaging assumes  $C_2$  symmetry for each ligand. <sup>c</sup> The bite of the ligand. <sup>d</sup> Average for ligands b and c.

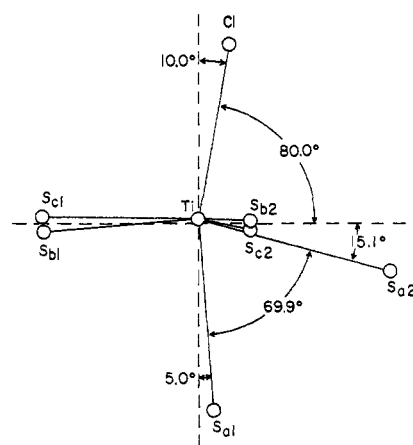
## Discussion

Crystalline  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$  contains discrete seven-coordinate molecules which have a somewhat distorted pentagonal bipyramidal structure (Figure 1). The chlorine atom is located at one axial position, dithiocarbamate ligand a spans the other axial position and one equatorial position, and dithiocarbamate ligands b and c take the remaining equatorial positions. The molecules (four per unit cell) occupy general positions of the space group  $Pn2_1a$  and are not required to have any symmetry. However, the maximum permissible symmetry for this configuration,  $C_s-m$ , is closely approximated, with the metal atom, monodentate ligand, and bidentate ligand a lying in the mirror plane, and bidentate ligands b and c being symmetrically disposed about this plane. This same pentagonal bipyramidal structure is adopted by  $\pi$ -cyclopentadienyltris(hexafluoroacetylacetonato)zirconium(IV),<sup>20</sup> chloro- and hydroxotris(tropolonato)tin(IV),<sup>21</sup> and nitrosyltris(*N,N*-di-*n*-butyldithiocarbamato)molybdenum<sup>22</sup> and appears to be the preferred configuration for complexes

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**Figure 2.** Projection of the  $\text{TiS}_6\text{Cl}$  coordination group of  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$  on the quasi-mirror plane.

The principal distortions from ideal pentagonal bipyramidal geometry in  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$  can be seen from Figure 2, which is a projection of the  $\text{TiS}_6\text{Cl}$  coordination group onto the quasi-mirror plane contain-

(23) R. B. VonDreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, **93**, 2887 (1971).

ing the atoms Ti, Cl, S<sub>a1</sub>, and S<sub>a2</sub>; the mean displacement of these atoms from the quasi-mirror plane is 0.004 Å. The atoms Ti, S<sub>b1</sub>, S<sub>b2</sub>, S<sub>c1</sub>, and S<sub>c2</sub> are nearly coplanar (displacements ≤ 0.10 Å; mean displacement 0.07 Å), and the dihedral angle between this plane, subsequently referred to as the equatorial plane, and the quasi-mirror plane is 89.3° (90° for an ideal pentagonal bipyramid). Sulfur atom S<sub>a1</sub> is located slightly off the quasi-fivefold axis (5.0°) and S<sub>a2</sub> is appreciably below the equatorial plane (0.61 Å), because the 2.9-Å "bite" of the dithiocarbamate ligand does not permit it to span a 90° bond angle. The more surprising distortion is the positioning of the chlorine atom 10.0° off the quasi-fivefold axis. From a steric point of view, this distortion is counterproductive since it increases the nonbonded repulsions by making the Cl···S<sub>b2</sub> and Cl···S<sub>c2</sub> contacts (~3.39 Å) about 0.14 Å less than the van der Waals contact<sup>24-27</sup> and 0.26 Å less than the averaged value of the Cl···S<sub>b1</sub> and Cl···S<sub>c1</sub> contacts. Park, *et al.*,<sup>21</sup> have noted the same sort of distortion in SnT<sub>3</sub>X (T = tropolonate; X = Cl or OH) and have suggested that the geometry resembles that expected for the corresponding eight-coordinate complex SnT<sub>4</sub> with the monodentate ligand taking the place of one bidentate ligand in the *mmmm* dodecahedral stereoisomer.<sup>28</sup> It is interesting to apply the description of Park, *et al.*,<sup>21</sup> to Ti[S<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl since the corresponding tetrakis(diethylthiocarbamate), Ti[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, has been shown to have the *mmmm* dodecahedral structure.<sup>8</sup> The arrangement of ligands b and c in Ti[S<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl ( $\theta_A = 36.4^\circ$ ,  $\theta_B = 74.5^\circ$ <sup>29</sup>) is closely similar to the arrangement in the trapezoidal planes of Ti[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> ( $\theta_A = 35.1^\circ$ ,  $\theta_B = 77.5^\circ$ ). The 10.0° rotation of the Ti-Cl bond off the quasi-fivefold axis (Figure 2) puts this bond within 11° of the axis bisecting the fourth dithiocarbamate ligand in Ti[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, and the 15.1° rotation of Ti-S<sub>a2</sub> out of the equatorial plane takes ligand a nearly halfway to its position in Ti[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>.

As has been observed in other structures of the M(chelate)<sub>3</sub>X type,<sup>21,23</sup> the bond to the axial ligand, Ti-S<sub>a1</sub> (2.477 Å), is somewhat shorter (by ~0.04 Å) than the averaged length of the five equatorial bonds. However, the equatorial bond lengths (Table III) vary considerably, Ti-S<sub>b2</sub> and Ti-S<sub>c2</sub> being ~0.04 Å longer than Ti-S<sub>b1</sub> and Ti-S<sub>c1</sub>, and Ti-S<sub>a2</sub> being longer still by an additional 0.05 Å. The variation in equatorial bond lengths may reflect the off-axis positioning of the chlorine atom. As expected, the mean length of the six Ti-S bonds (2.512 Å) is shorter than the mean Ti-S bond distance (2.564 Å) in the eight-coordinate Ti[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>.<sup>8,30</sup>

(24) We take the Cl···S and S···S van der Waals contacts to be about 3.53 and 3.45 Å, respectively, based on a van der Waals radius for sulfur of 1.72-1.73 Å.<sup>25</sup> The Pauling value (1.85 Å)<sup>26</sup> appears to be too large.<sup>21</sup>

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(27) R. E. Marsh, *Acta Crystallogr.*, **8**, 91 (1955); H. L. Yakel, Jr., and E. W. Hughes, *ibid.*, **7**, 291 (1954); J. Donohue, *J. Amer. Chem. Soc.*, **72**, 2701 (1950).

(28) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(29) See ref 28 for a definition of the dodecahedral shape parameters.

(30) In Ti[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, the Ti-S<sub>B</sub> bonds are ~0.08 Å shorter than the Ti-S<sub>A</sub> bonds.<sup>8</sup> That the Ti-S<sub>b2</sub> and Ti-S<sub>c2</sub> distances in Ti[S<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl are ~0.04 Å longer than the Ti-S<sub>b1</sub> and Ti-S<sub>c1</sub> distances is considered especially significant since, with reference to a dodecahedral

The Ti-Cl bond length (2.305 Å) is in the range found for Ti-Cl distances in neutral, six-coordinate complexes (2.20-2.32 Å)<sup>31</sup> and is appreciably shorter than the Ti-Cl bond in the eight-coordinate *o*-phenylenebis(dimethylarsine) complex, TiCl<sub>2</sub>(diarsine)<sub>2</sub> (2.46 Å).<sup>6</sup> The relatively short Ti-Cl bond in Ti[S<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl is in keeping with the axial position of the chlorine atom.

A striking feature of this structure is the extreme crowding in the equatorial plane. The bites of the equatorial dithiocarbamate ligands (2.84 Å) are normal,<sup>32</sup> but the interligand S···S distances (2.95-3.10 Å) are as much as 0.5 Å less than the sum of the van der Waals radii.<sup>24</sup> Similarly short interligand S···S contacts have been reported for the pentagonal girdle of Mo(NO)[S<sub>2</sub>CN(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>]<sub>3</sub><sup>22</sup> and the dodecahedral *a* edges of Ti[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>.<sup>8</sup> Evidently the "soft" sulfur donor atoms are easily deformed, or else higher coordination complexes having MS<sub>6</sub>X and MS<sub>8</sub> cores would not be stable for a metal atom as small as Ti(IV). Interligand S···S distances of ~3.07 Å in trigonal prismatic tris(1,2-dithiolene) complexes have been interpreted in terms of interdonor atom bonding forces; however, this type of interaction is not possible in dithiocarbamate complexes.<sup>32</sup>

Bond distances and angles within the dithiocarbamate ligands (Table IV) are in accord with the values found in other dithiocarbamate structures.<sup>32,33</sup> The dimensions of ligands b and c are virtually identical, but ligand a, which spans the axial and an equatorial position, has a somewhat larger bite (by ~0.06 Å), a larger S-C-S angle (by ~4°), and correspondingly smaller values for the S<sub>2</sub>-C-N and C-S<sub>2</sub>-Ti angles. These distortions probably reflect the positioning of sulfur atom S<sub>a2</sub> somewhat farther from the Ti(IV) atom (2.577 Å) so as to relieve nonbonded repulsions in the pentagonal girdle. The C-N (average value, 1.32 Å) and C-S (average value, 1.716 Å) distances are intermediate between the sum of the Pauling single-bond radii and double-bond radii (C-N, 1.47 Å; C=N, 1.27 Å; C-S, 1.81 Å; C=S, 1.61 Å)<sup>34</sup> and are indicative of delocalized  $\pi$  bonding in the S<sub>2</sub>CN portion of the ligand. Consistent with this picture, the six atoms of the S<sub>2</sub>CNC<sub>2</sub> dithiocarbamate skeleton show only minor departures from planarity; the average displacement of the 18 atoms of the three ligands from their respective mean planes is 0.029 Å (maximum displacement, 0.065 Å). The small deviations from planarity which are observed involve a slight twisting of the ligands about the C-N bond; dihedral angles between the S<sub>2</sub>CN and CNC<sub>2</sub> mean planes are 3.0, 4.7, and 2.2° for ligands a, b, and c, respectively. The Ti(IV) atom lies close to the plane of the ligands. However, there is a slight folding of the chelate rings about the edges (S···S) of the coordination polyhedron. Rings b and c are folded so as to bring the uncoordinated parts of the ligands

coordination polyhedron, S<sub>b2</sub> and S<sub>c2</sub> are located in the B sites and S<sub>b1</sub> and S<sub>c1</sub> in the A sites. The same sort of inequality in the equatorial bond lengths of SnT<sub>3</sub>X has been noted by Park, *et al.*<sup>21</sup>

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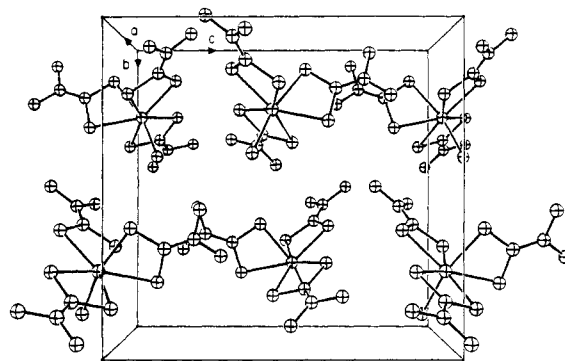
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(34) Reference 26, pp 224-229.

closer to the chlorine atom, while ring a is folded in the direction of ring c. The dihedral angles between the ligand planes and the appropriate S-Ti-S group are 2.9, 2.3, and 5.5° for rings a, b, and c, respectively; the corresponding displacements of the Ti(IV) atom from the ligand planes are 0.10, 0.04, and 0.19 Å, respectively. The departures from planarity are probably due to crystal packing; there are a number of relatively close intermolecular contacts but none is more than 0.2 Å less than the sum of the van der Waals radii. A packing diagram is presented in Figure 3.

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**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



**Figure 3.** Model in perspective to illustrate the packing of  $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$  molecules in the crystalline arrangement. One unit cell is outlined. The view is perpendicular to the (100) plane.

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## Electronic Structure of Square-Planar Transition Metal Complexes. I. The $\text{PtCl}_4^{2-}$ and $\text{PdCl}_4^{2-}$ Ions

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**Abstract:** Molecular orbital calculations using the self-consistent-field  $X\alpha$ -scattered wave (SCF- $X\alpha$ -SW) method have been carried out for the  $\text{PtCl}_4^{2-}$  and  $\text{PdCl}_4^{2-}$  ions. Optical transitions have been calculated and found to be in good agreement with the experimental absorption spectra. The calculated d-level ordering for these two complexes is  $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ , and the mixing among d orbitals and ligand orbitals is predicted to be considerably stronger than in previous calculations.

The electronic structure of square-planar transition metal complexes remains a topic of continuing interest and controversy, in spite of numerous spectral,<sup>2-8</sup> magnetic circular dichroism,<sup>9,10</sup> and photoelectron<sup>11-13</sup>

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studies and many theoretical investigations.<sup>14-19</sup> The controversy centers mainly on the ordering of the d-orbital energy levels in the various complexes, although definitive answers to questions such as the degree of covalency in the metal-ligand bonds and the amount of  $\pi$ -bonding occurring in such systems have yet to be presented.

In addition to the continuing interest in these complexes as molecular entities with their own characteristic spectral and chemical behavior, a more recent impetus to study the electronic structure of these complexes results from the unusual solid-state properties observed in certain crystalline compounds such as  $\text{Pt}(\text{NH}_3)_4\text{Pt}$ -

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