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Preparation, Characterization, and the Crystal and Molecular Structure of Two Salts Containing the Eight-Coordinate Tetrakis(*N*,*N*-dimethyldithiocarbamato)tantalum(V) Cation

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Two new *N*,*N*-dimethyldithiocarbamato complexes of composition $\mathrm{Ta(S_2CN(CH_3)_2)_4Cl\cdot CH_2Cl_2}$ (**1**) and $\mathrm{Ta(S_2CN(CH_3)_2)_2Cl_3\cdot {}^1/_4CH_2Cl_2}$ (**2**) have been isolated following reaction of $\mathrm{TaCl_5}$ with anhydrous $\mathrm{NaS_2CN(CH_3)_2}$. Both have been formulated as salts containing the $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$ cation, viz., $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]\mathrm{Cl\cdot CH_2Cl_2}$ (**1**) and $[\mathrm{Ta(S_2CN(CH_3)_2)_4}][\mathrm{TaCl_6}]\cdot{}^1/_2\mathrm{CH_2Cl_2}$ (**2**), on the basis of conductance, ^{1}H NMR, infrared, and x-ray diffraction data. Compound **1** crystallizes in the monoclinic space group $C2/c$ with four formula units in a unit cell of dimensions a = 12.055 (5) Å, b = 18.473 (8) Å, c = 12.794 (5) Å, and β = 94.71 (3)° ($\rho_{\mathrm{obsd}} = 1.83 \pm 0.02$, $\rho_{\mathrm{calcd}} = 1.829$ g cm^{-3}). The structure was solved by the heavy-atom method and was refined (anisotropically on the atoms of the cation) by least-squares methods to $R_1 = 0.063$ and $R_2 = 0.086$ using 2455 independent diffractometer-recorded reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} \leq 54.86°$ and $|F_o| > 2\sigma(|F_o|)$. Compound **2** crystallizes in the space group $C2/c$ with eight molecules in a unit cell of dimensions a = 30.97 (1) Å, b = 9.537 (4) Å, c = 25.95 (1) Å, and β = 117.17 (3)° ($\rho_{\mathrm{obsd}} = 2.11 \pm 0.02$, $\rho_{\mathrm{calcd}} = 2.139$ g cm^{-3}). Its structure was refined (anisotropically on Ta, Cl, and S) to $R_1 = 0.096$ and $R_2 = 0.065$ using 3317 independent diffractometer data having $2\theta_{\mathrm{Mo}K\bar{\alpha}} \leq 35.93°$ and $|F_o| > 2\sigma(|F_o|)$. In both **1** and **2** the eight-coordinate $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$ cation adopts a structure in which the bidentate dithiocarbamate ligands span the m edges of an idealized D_{2d}-$\bar{4}2m$ dodecahedron. Although packing relations in **1** and **2** are quite different, dimensions of the $\mathrm{TaS_8}$ coordination polyhedra in the two salts are closely similar and averaged dimensions are almost identical (Ta–S$_\mathrm{A}$ = 2.590, Ta–S$_\mathrm{B}$ = 2.521, a = 2.974, b = 3.648, m = 2.843, and g = 3.276 Å in the more accurately determined structure of compound **1**). The structure of $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$ is of special interest because it is the first eight-coordinate tetrakis chelate which has been reported to be stereochemically rigid on the NMR time scale.

Introduction

By virtue of their low charge and relatively small "bites" (~2.8–2.9 Å), *N*,*N*-dialkyldithiocarbamate ligands[1] are especially well suited for stabilization of higher coordination complexes of early transition metals. As an extension of our studies of seven- and eight-coordinate titanium(IV) *N*,*N*-dialkyldithiocarbamates,[2-4] we have begun to investigate the *N*,*N*-dialkyldithiocarbamate complexes of niobium and tantalum.

Reaction of anhydrous sodium *N*,*N*-dimethyldithiocarbamate with tantalum(V) chloride in dichloromethane affords two new compounds of composition $\mathrm{Ta(S_2CN(CH_3)_2)_4Cl\cdot CH_2Cl_2}$ (**1**) and $\mathrm{Ta(S_2CN(CH_3)_2)_2Cl_3\cdot {}^1/_4CH_2Cl_2}$ (**2**). The *N*,*N*-diethyldithiocarbamato analogues have been prepared by Heckley et al.[5] and have been formulated as salts containing the $[\mathrm{Ta(S_2CN(C_2H_5)_2)_4}]^+$ cation, viz., $[\mathrm{Ta(S_2CN(C_2H_5)_2)_4}]\mathrm{Cl}$ and $[\mathrm{Ta(S_2CN(C_2H_5)_2)_4}][\mathrm{TaCl_6}]$, respectively, on the basis of molecular weight, conductance, and infrared evidence. We have confirmed this formulation for the *N*,*N*-dimethyl compounds by an x-ray diffraction study which establishes that compounds **1** and **2** contain the $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]^+$ cation, which exists in both salts as the eight-coordinate, dodecahedral *mmmm*-D_{2d} stereoisomer. The structure of this complex is of special interest because it is the first eight-coordinate tetrakis chelate which has been reported to be stereochemically rigid on the NMR time scale.[6]

Experimental Section

Preparation and Characterization. A. Tetrakis(*N*,*N*-dimethyldithiocarbamato)tantalum(V) Chloride–Dichloromethane (1). This compound was prepared by reaction of tantalum(V) chloride with dry sodium *N*,*N*-dimethyldithiocarbamate (1:5.1 molar ratio) in refluxing anhydrous dichloromethane under a dry nitrogen atmosphere. After 24 h, the solution was filtered and yellow crystals of $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]\mathrm{Cl\cdot CH_2Cl_2}$ (**1**) were grown by addition of dry hexane. These crystals are extremely air sensitive and, upon exposure to the atmosphere, the faces rapidly turn cloudy, presumably due to loss of solvent of crystallization and/or hydrolysis. The presence of 1 mol of dichloromethane of crystallization/mol of Ta was established by x-ray diffraction (vide infra). Prior to analysis, the crystals were dried by pumping in vacuo for 2 h at room temperature; the pumping process destroys the crystallinity owing to rapid loss of the dichloromethane. Anal. Calcd for $\mathrm{Ta(C_3H_6NS_2)_4Cl}$: C, 20.67; H, 3.47; Cl, 5.08; N, 8.03; S, 36.79; Ta, 25.95. Found: C, 20.76; H, 3.74; Cl, 5.19; N, 7.73; S, 36.50; Ta, 26.04. Molar conductance (5.6 × 10^{-4} *M* $\mathrm{CH_2Cl_2}$ solution, 25.1 °C): 98 Ω^{-1} cm^2 mol^{-1}. NMR ($\mathrm{CH_2Cl_2}$ solution, 37 °C): −3.40 ppm ($\mathrm{CH_3}$) relative to an internal reference of tetramethylsilane (1% by volume). Ir (Nujol mull): $\nu(\mathrm{C}\doteq\mathrm{N})$ 1557 cm^{-1}, $\nu(\mathrm{C}\doteq\mathrm{S})$ 992 cm^{-1}, ν(Ta—S) 358 cm^{-1}.

B. Tetrakis(*N*,*N*-dimethyldithiocarbamato)tantalum(V) Hexachlorotantalate(V)–Hemidichloromethane (2). This compound was obtained by further addition of hexane to the solution from which compound **1** had been isolated. Orange crystals of $[\mathrm{Ta(S_2CN(CH_3)_2)_4}][\mathrm{TaCl_6}]\cdot\mathrm{CH_2Cl_2}$ were separated mechanically under a dry nitrogen atmosphere (glovebag) from the yellow crystals of compound **1**. Anal. Calcd for $\mathrm{Ta(C_3H_6NS_2)_4TaCl_6\cdot CH_2Cl_2}$: C, 13.69; H, 2.30; Cl, 24.87; N, 4.91; S, 22.49. Found: C, 13.45; H, 2.32; Cl, 24.64; N, 4.96; S, 22.16. In the structure determination (vide infra) only half of the solvent of crystallization could be located; it seems likely that half of the dichloromethane was slowly expelled from the crystal during the months prior to x-ray data collection. Molar conductance (5.4 × 10^{-4} M $\mathrm{CH_2Cl_2}$ solution, 25.2 °C): 63 Ω^{-1} cm^2 mol^{-1}. NMR ($\mathrm{CH_2Cl_2}$ solution, 37 °C): −3.40 ppm ($\mathrm{CH_3}$) relative to an internal reference of tetramethylsilane. Ir (Nujol mull, after $\mathrm{CH_2Cl_2}$ had been removed by pumping): $\nu(\mathrm{C}\doteq\mathrm{N})$ 1552 cm^{-1}, $\nu(\mathrm{C}\doteq\mathrm{S})$ 1000 cm^{-1}, ν(Ta—S) 359 cm^{-1}, ν(Ta—Cl) 328 (sh) and 316 cm^{-1}.

Crystallography. A. $[\mathrm{Ta(S_2CN(CH_3)_2)_4}]\mathrm{Cl\cdot CH_2Cl_2}$ (1). Several well-formed crystals were sealed in Lindemann glass capillaries under an atmosphere of dry nitrogen. Attempts to determine their morphology using an optical goniometer were fruitless owing to interfering reflections from the internal and external surfaces of the capillary. The crystals are approximately described as octahedra elongated along the body diagonal which coincides with the crystallographic b axis. A crystal having dimensions ~0.15 × 0.25 × 0.15 mm along the body diagonals was mounted along the b axis and used for the diffraction experiment.

Preliminary precession photographs taken with nickel-filtered Cu Kα radiation indicated that the crystals are monoclinic. The observed systematic absences, hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$, are consistent with space groups Cc (C_s^4, No. 9) and $C2/c$ (C_{2h}^6, No. 15).[7] The following unit cell parameters were determined from the least-squares refinement of the setting angles for 12 reflections that had been automatically centered on a Picker FACS-I computer-controlled four-circle diffractometer using zirconium-filtered Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å): a = 12.055 (5) Å, b = 18.473 (8) Å, c = 12.794 (5) Å, β = 94.71 (3)°. The observed density of 1.83 ± 0.02 g cm^{-3}, measured by flotation in hexane–ethylene bromide, is in close agreement with the calculated density of 1.829 g cm^{-3} for four molecules of [Ta(S$_2$CN(CH$_3$)$_2$)$_4$]Cl·CH$_2$Cl$_2$ (mol wt 782.2) per unit cell.

Intensity data were recorded at ambient temperature using Zr-filtered Mo K$\bar{\alpha}$ radiation on a Picker FACS-I four-circle automated diffractometer. A total of 2675 independent reflections having $2\theta \leq 54.86°$ were collected. Each peak was scanned at the rate of 1° min^{-1} over a range in 2θ of 1.5° plus an allowance for the dispersion of Mo Kα_1 and Mo Kα_2 radiation. Background counts, each of 20-s duration, were taken at the limits of the scan. Reflections having counting rates in excess of 10 000 counts s^{-1} 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. Crystal and instrument stabilities were evaluated at intervals of 100 reflections by monitoring three "standard" reflections well separated in reciprocal space. In no case did the intensity of a standard reflection deviate from its mean by more than that value calculated on the basis of counting statistics.

The linear absorption coefficient is 49.3 cm^{-1} and for the crystal used in this experiment it is estimated that the maximum error due to neglect of an absorption correction is <12% in any intensity and <6% in any F. Since the morphology of the crystal could not be determined, it was felt that an absorption correction would at best be approximate and therefore of questionable value. Consequently, absorption corrections were ignored.

The intensity data were corrected for background, use of attenuators, and Lorentz and polarization factors (Lp). Standard deviations were calculated from

$$\sigma^2(|F_o|) = (C + k^2B)/4|F_o|^2(Lp)^2$$

wherein C is the count of the scan, B is the total background count, and k is the ratio of the scanning time to background time. Only these reflections (2455) having $|F_o| > 2\sigma(|F_o|)$ were considered observed.

Structure Determination and Refinement. The structure was solved in a straightforward manner by the use of Patterson and Fourier techniques.[8] The choice of space group $C2/c$ is justified on the basis of the successful refinement of the structure. As had been indicated by the lack of special conditions governing the distribution of strong reflections, the tantalum atom occupies special position 4e, which requires the complex to have twofold symmetry. Full-matrix least-squares refinement of the coordinates and isotropic thermal parameters of the 16 independent atoms was followed by full-matrix refinement using anisotropic temperature factors for the 13 independent atoms within the cation 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 neutral atoms were taken from Cromer and Mann.[9] Corrections for anomalous dispersion by Ta, Cl, and S were obtained from ref 10.

In the final cycle of refinement no variable changed by more than 0.41 (the average was 0.11) of its estimated standard deviation, and the discrepancy indices

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

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

were 0.063 and 0.086, respectively. A final difference Fourier showed no anomalous features.

B. [Ta(S$_2$CN(CH$_3$)$_2$)$_4$][TaCl$_6$]·$^1/_2$CH$_2$Cl$_2$ (2). An orange crystal having the shape of a parallelepiped was cut to a cube, ~0.15 mm on an edge, and mounted in a Lindemann glass capillary under a dry nitrogen atmosphere. Experimental procedures described for compound **1** were followed, and only deviations will be noted. Compound **2** crystallizes in the monoclinic system with systematic absences hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$ being consistent with space groups Cc (C_s^4, No. 9) and $C2/c$ (C_{2h}^6, No. 15).[7] The unit cell parameters are a = 30.97 (1) Å, b = 9.537 (4) Å, c = 25.95 (1) Å, and β = 117.17 (3)°. The observed density of 2.11 ± 0.02 g cm^{-3} is close to the calculated density of 2.139 g cm^{-3} for eight molecules of [Ta(S$_2$CN(CH$_3$)$_2$)$_4$][TaCl$_6$]·$^1/_2$CH$_2$Cl$_2$ (mol wt 1098.0) per unit cell.

Room-temperature intensity data were collected for 4676 reflections having $2\theta \leq 35.93°$. In the course of monitoring three "standard" reflections it was observed that there was a slow diminution in the intensity of these standards; this diminution proceeded at a different rate during five distinct periods of the data collection. Since the deterioration of the crystal, judged by the effect upon the intensity of the standards, appeared to be isotropic and to amount to less than 15% over the course of the experiment, it was decided to bring the intensities of the reflections to a common basis during each of the five periods. This was accomplished by a simple least-squares procedure that estimated the rate of decay during each period, whereupon the intensities of the reflections were adjusted accordingly. Standard reflections collected during any one of the periods of decomposition and adjusted in the above manner were then at variance by no more than 3% of their mean and in most cases by much less. To accommodate the five decomposition periods, five scale factors were used during the refinement, the particular scale factor applying to a given reflection being dependent upon the time period during which that reflection was measured. The cause of the decomposition remains somewhat uncertain; however, because the rate of decay appeared to correlate with the ambient humidity, we suspect that a submicroscopic crack in the Lindemann capillary may have led to partial hydrolysis.

The linear absorption coefficient is 77.9 cm^{-1} which could give a maximum error from neglect of absorption corrections of <15% in any intensity and <7% in any F for the crystal used. The error for the vast majority of reflections would be <4% in any F. It was felt that absorption corrections would not significantly improve the reliability of the data. The intensity data were corrected for the other factors as before, and 3317 reflections having $|F_o| > 2\sigma(|F_o|)$ were considered observed.

Structure Determination and Refinement. The structure was solved using Patterson and Fourier techniques, the choice of the centric space group $C2/c$ being substantiated by the successful refinement of the structure. No crystallographic symmetry is imposed on either the cation or the anion. Owing to the large number of atoms in the asymmetric unit, the least-squares refinement was accomplished in two matrix blocks. The first contained the scale factors and positional and thermal parameters for the atoms in the anion and the solvent of crystallization; the second contained the scale factors and the positional and thermal parameters for the atoms in the cation. Anisotropic temperature factors were used only for the heavy atoms (Ta, Cl, S). Reflections were given weights equal to $[\sigma(|F_o|)]^{-2}$. In each of the matrix blocks in the last cycle of refinement no parameter varied by more than 0.8 (the average was 0.08) of its estimated standard deviation. The final discrepancy indices were R_1 = 0.096 and R_2 = 0.065. A final difference Fourier showed no anomalous features.

Results and Discussion

Air-sensitive, yellow crystals of composition Ta(S$_2$CN(CH$_3$)$_2$)$_4$Cl·CH$_2$Cl$_2$ (**1**) and orange crystals of composition Ta(S$_2$CN(CH$_3$)$_2$)$_2$Cl$_3$·$^1/_4$CH$_2$Cl$_2$ (**2**) have been isolated following reaction of tantalum(V) chloride with anhydrous sodium *N*,*N*-dimethyldithiocarbamate (1:5.1 molar ratio) in refluxing dichloromethane. Both new compounds are 1:1 electrolytes in dichloromethane, and both exhibit a single methyl resonance at τ 6.60 in ^{1}H NMR spectra of dichloromethane solutions at 37 °C. Infrared spectra of the two compounds are closely similar except that compound **2** exhibits additional strong bands at 328 (sh) and 316 cm^{-1} attributable[5,11] to the TaCl$_6^-$ anion. These data suggest that compounds **1** and **2** should be formulated as [Ta(S$_2$CN(CH$_3$)$_2$)$_4$]Cl·CH$_2$Cl$_2$ and [Ta(S$_2$CN(CH$_3$)$_2$)$_4$][TaCl$_6$]·$^1/_2$CH$_2$Cl$_2$, respectively, in accord with a previous study of the analogous *N*,*N*-diethyldithiocarbamate complexes.[5] The presence of the eight-coordinate [Ta(S$_2$CN(CH$_3$)$_2$)$_4$]$^+$ cation in both crystalline salts has been confirmed by x-ray diffraction.

Final atomic positional and thermal parameters for compounds **1** and **2** are presented in Tables I–IV.[12] The molecular

Table I. Final Atomic Fractional Coordinates for $[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$[a]

Atom	10^4x	10^4y	10^4z
Ta	0	1592.1 (3)	2500
S_{1A}	1925 (2)	1005 (1)	2986 (2)
S_{1B}	515 (2)	669 (2)	1163 (2)
S_{2A}	−912 (2)	2167 (2)	795 (2)
S_{2B}	1232 (2)	2523 (2)	1752 (2)
N_1	2438 (7)	−35 (5)	1647 (7)
N_2	469 (9)	3068 (5)	−110 (8)
C_1	1745 (8)	462 (5)	1892 (7)
C_2	303 (9)	2651 (6)	688 (8)
C_{1A}	3453 (10)	−209 (7)	2338 (10)
C_{1B}	2261 (10)	−468 (8)	677 (11)
C_{2A}	−412 (14)	3186 (7)	−981 (10)
C_{2B}	1540 (14)	3423 (7)	−201 (14)
Cl	0	5000	0
Cl_S	−1170 (7)	8423 (4)	2063 (7)
C_S	0	8893 (33)	2500

[a] Standard deviations in parentheses apply to the last significant figure.

geometry and the atom-numbering schemes for the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation in the two salts are illustrated in Figures 1 and 2. Each atom is represented by an ellipsoid consistent with the thermal parameters in Tables II and IV and is labeled with a numerical and a literal subscript. The numerical subscript identifies the particular *N*,*N*-dimethyldithiocarbamate ligand; the literal subscript designates the dodecahedral coordination sites according to the nomenclature of Hoard and Silverton.[13] Atoms labeled with a prime in Figure 1 are related to the corresponding unprimed atoms by a crystallographic twofold axis.

The packing of the ions and dichloromethane of crystallization within one unit cell of compounds **1** and **2** is illustrated in Figures 3 and 4, respectively. In $[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$ the tantalum atoms (four per cell) occupy special positions 4e of space group *C*2/*c*, and the cation is therefore required to have twofold symmetry. The chloride ions occupy centers of symmetry (special positions 4b), while the dichloromethane molecules are located on twofold axes. In $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$ the cations (eight per cell) occupy general positions of space group *C*2/*c*, and there is no imposed crystallographic symmetry. The $TaCl_6^-$ anions also occupy general positions, but the dichloromethane molecules are required to lie on crystallographic twofold axes.

In both salts, the eight-coordinate $[Ta(S_2CN(CH_3)_2)_4]^+$ cation adopts a structure in which the bidentate dithiocarbamate ligands span the *m* edges of an idealized D_{2d}-$\bar{4}2m$ dodecahedron to give the *mmmm*-D_{2d} stereoisomer.[13] The crystallographic twofold axis in compound **1** passes through

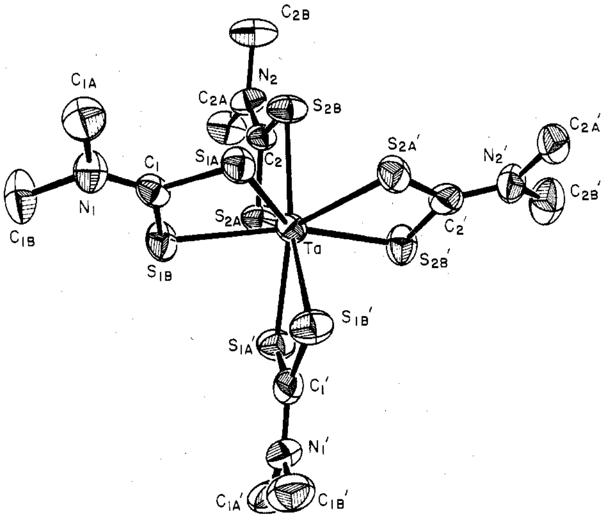

Figure 1. Model in perspective of the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation in crystalline $[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$ (**1**). A crystallographic twofold axis passes midway between atoms S_{1B} and S_{1B}' and atoms S_{2B} and S_{2B}'.

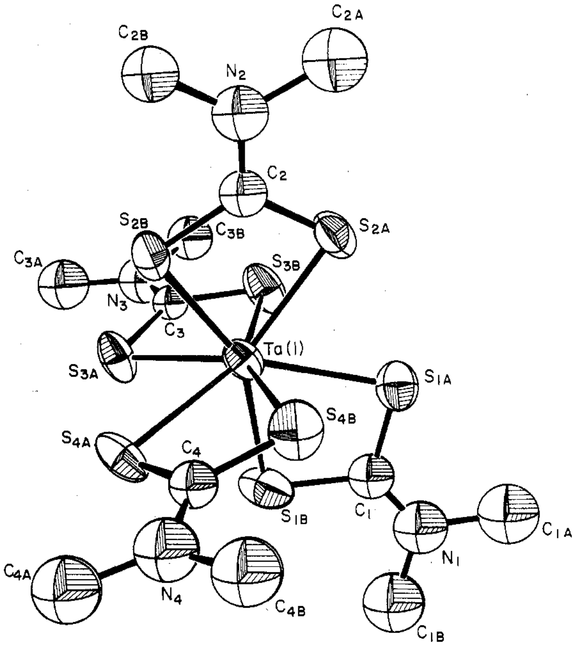

Figure 2. Model in perspective of the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation in crystalline $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$ (**2**).

Table II. Final Thermal Parameters for $[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$[a]

	Anisotropic parameters						Equiv isotropic	Isotropic parameters	
Atom	β_{11}[b,c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B,[d] Å^2	Atom	B, Å^2
Ta	50.2 (5)	21.6 (2)	37.1 (4)	0	−7.7 (3)	0	2.72 (2)	Cl	5.25 (8)
S_{1A}	55 (2)	29 (1)	44 (1)	4 (1)	−11 (1)	−5 (1)	3.20 (5)	Cl_S	10.5 (2)
S_{1B}	66 (2)	33 (1)	52 (2)	9 (1)	−20 (1)	−12 (1)	3.61 (5)	C_S	16.0 (17)
S_{2A}	71 (2)	30 (1)	48 (2)	−3 (1)	−13 (1)	7 (1)	3.66 (5)		
S_{2B}	63 (2)	31 (1)	68 (2)	−5 (1)	−6 (1)	11 (1)	3.97 (5)		
N_1	55 (6)	27 (3)	62 (6)	−3 (3)	2 (5)	−9 (3)	3.6 (2)		
N_2	97 (8)	22 (3)	63 (6)	7 (4)	15 (6)	10 (3)	3.9 (2)		
C_1	51 (6)	26 (3)	37 (5)	−7 (3)	−4 (5)	−2 (3)	2.9 (2)		
C_2	75 (8)	23 (3)	52 (6)	10 (4)	3 (6)	−2 (4)	3.5 (2)		
C_{1A}	56 (8)	42 (4)	77 (9)	13 (5)	−11 (7)	−1 (5)	4.4 (3)		
C_{1B}	70 (9)	46 (5)	79 (9)	10 (5)	−5 (7)	−31 (6)	4.6 (3)		
C_{2A}	141 (14)	29 (4)	60 (8)	−1 (6)	−29 (9)	13 (5)	4.7 (3)		
C_{2B}	99 (12)	34 (5)	104 (13)	4 (5)	39 (10)	16 (5)	5.2 (3)		

[a] Numbers in parentheses are estimated standard deviations 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 $\times 10^4$. [d] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Final Atomic Fractional Coordinates for $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$[a]

Atom	10^4x	10^4y	10^4z
Ta(1)	1427.4 (4)	288 (1)	3276.6 (5)
S_{1A}	2118 (3)	−1554 (8)	3796 (3)
S_{2A}	2214 (3)	1200 (8)	3301 (3)
S_{3A}	564 (2)	80 (9)	2408 (3)
S_{4A}	804 (3)	1353 (8)	3572 (3)
S_{1B}	1131 (3)	−1848 (8)	3592 (3)
S_{2B}	1341 (3)	2771 (8)	2906 (3)
S_{3B}	1423 (3)	−1083 (8)	2451 (3)
S_{4B}	1812 (3)	1139 (8)	4306 (3)
N_1	1823 (10)	−3895 (28)	4149 (10)
N_2	2130 (9)	3790 (26)	2853 (10)
N_3	542 (9)	−1500 (24)	1538 (10)
N_4	1184 (10)	1990 (27)	4698 (11)
C_1	1691 (9)	−2598 (29)	3873 (10)
C_2	1917 (9)	2774 (27)	2985 (10)
C_3	809 (10)	−853 (27)	2069 (11)
C_4	1249 (10)	1618 (28)	4266 (12)
C_{1A}	2322 (12)	−4415 (33)	4342 (12)
C_{1B}	1415 (11)	−4581 (35)	4197 (12)
C_{2A}	2600 (11)	3641 (33)	2864 (12)
C_{2B}	1843 (10)	5113 (31)	2583 (11)
C_{3A}	−16 (11)	−1256 (33)	1242 (13)
C_{3B}	774 (9)	−2298 (29)	1253 (11)
C_{4A}	689 (12)	2261 (35)	4621 (13)
C_{4B}	1590 (12)	2079 (36)	5301 (15)
Ta(2)	1060.4 (5)	2776 (1)	720.6 (6)
Cl(1)	1545 (3)	4782 (10)	1002 (4)
Cl(2)	1430 (4)	2057 (13)	200 (4)
Cl(3)	555 (4)	787 (9)	437 (5)
Cl(4)	678 (4)	3417 (12)	1248 (4)
Cl(5)	1634 (4)	1671 (10)	1548 (4)
Cl(6)	502 (4)	3960 (9)	−90 (4)
Cl_s	−146 (7)	5202 (26)	2924 (9)
C_s	0	5313 (108)	2500

[a] Standard deviations in parentheses apply to the last significant figure.

the midpoints of the opposite dodecahedral *b* edges defined by atoms S_{1B} and S_{1B}' and by atoms S_{2B} and S_{2B}' (Figure 1). The same dodecahedral structure has been found for tetrakis(*N*,*N*-diethyldithiocarbamato)titanium(IV),[14] titanium(IV) nitrate,[15] and the tetrakis(oxalato)zirconate(IV) ion.[16] In the absence of steric constraints, this structure appears to be a preferred configuration for complexes of the type $M(XX)_4$.

Application of the test of Lippard and Russ[17] to the TaS_8 coordination group demonstrates that the choice of coordination polyhedron (D_{2d}-$\bar{4}2m$ dodecahedron or D_{4d}-$\bar{8}2m$ square antiprism) is unambiguous. The dihedral angle between the two interpenetrating trapezoidal least-squares planes defined by atoms Ta, S_{1A}, S_{1B}, S_{2A}', and S_{2B}' and by atoms Ta, S_{1A}', S_{1B}', S_{2A}, and S_{2B} in compound **1** (Figure 1) is 89.4°. These planes are perpendicular in a perfect D_{2d} dodecahedron, whereas they intersect at an angle of 77.4° in an idealized D_{4d} square antiprism. In compound **2** (Figure 2) the dihedral angle between the trapezoidal planes defined by atoms Ta, S_{1A}, S_{1B}, S_{2A}, and S_{2B} and by atoms Ta, S_{3A}, S_{3B}, S_{4A}, and S_{4B} is 89.0°. Values of d_T, the average displacement of ligand atoms from the trapezoidal best planes, are 0.03 Å for both planes in compound **1** and 0.05 and 0.04 Å for the two planes in compound **2**; d_T is 0.0 Å for a perfect dodecahedron.[18]

Bond distances, polyhedral edge lengths, and bond angles in the TaS_8 coordination group are presented in Tables V and VI. Although packing relations in compounds **1** and **2** are quite different, corresponding dimensions of the coordination polyhedra in the two salts are closely similar and averaged dimensions (Tables V and VI) are almost identical. Such differences as are observed relate to distortions from the idealized D_{2d} symmetry characteristic of the *mmmm* stereoisomer. In compound **1** the coordination group has crystallographically imposed C_2 symmetry, and D_{2d} symmetry is closely approximated. In compound **2**, where the cation occupies a general position, there is somewhat more variation in the lengths of the *b* and *g* polyhedral edges. Nevertheless, the same polytopal form and ligand wrapping pattern are maintained. It appears that the energy preference of $[Ta(S_2CN(CH_3)_2)_4]^+$ for the *mmmm*-D_{2d} stereoisomer is sufficiently large so that the gross stereochemistry of the cation is not altered by the effects of crystal packing.[20] It is also likely that the cation has the same stereochemistry in solution.[6]

Average polyhedron-shape parameters for $[Ta(S_2CN(CH_3)_2)_4]^+$, derived from the results in Tables V and VI, are compared with theoretical values in Table VII. Also included in Table VII are corresponding shape parameters for the isostructural titanium(IV) complex, $Ti(S_2CN(C_2H_5)_2)_4$.[14] It is evident that the dodecahedral coordination polyhedron conforms reasonably well with expectations based on the analysis of Hoard and Silverton.[13] Differences between the observed and theoretical lengths of the *m*, *b*, and *g* edges may be ascribed to the rigidity of the dithiocarbamate ligand; the *m* edge in $[Ta(S_2CN(CH_3)_2)_4]^+$ is constrained by the bite of the ligand to an average value of 2.843 Å (Table VI), which

Table IV. Final Thermal Parameters for $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$[a]

	Anisotropic parameters						Equiv isotropic	Isotropic parameters	
Atom	β_{11}[b,c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B,[d] Å^2	Atom	B, Å^2
Ta(1)	10.4 (2)	78 (2)	18.3 (3)	3.7 (5)	4.4 (2)	5.7 (7)	3.37 (4)	N_1	6.9 (7)
S_{1A}	13 (1)	100 (11)	25 (2)	14 (3)	2 (1)	12 (4)	4.2 (2)	N_2	6.1 (6)
S_{2A}	11 (1)	96 (11)	33 (2)	13 (3)	8 (2)	14 (4)	4.2 (2)	N_3	5.6 (6)
S_{3A}	9 (1)	232 (16)	21 (2)	8 (4)	2 (1)	−16 (5)	4.8 (3)	N_4	7.1 (7)
S_{4A}	13 (1)	131 (12)	26 (2)	−5 (4)	9 (2)	−4 (4)	4.7 (2)	C_1	4.2 (6)
S_{1B}	20 (2)	99 (12)	36 (3)	2 (4)	15 (2)	18 (4)	5.0 (3)	C_2	3.4 (6)
S_{2B}	13 (1)	103 (11)	34 (2)	10 (3)	7 (1)	22 (4)	4.6 (2)	C_3	4.4 (7)
S_{3B}	10 (1)	172 (14)	23 (2)	10 (4)	6 (1)	−3 (4)	4.5 (2)	C_4	4.8 (7)
S_{4B}	20 (2)	139 (13)	20 (2)	13 (4)	4 (2)	2 (4)	5.3 (3)	C_{1A}	7.6 (9)
Ta(2)	21.5 (3)	93 (2)	26.3 (4)	−0.8 (6)	6.3 (3)	2.5 (7)	5.25 (5)	C_{1B}	7.7 (9)
Cl(1)	32 (2)	170 (16)	55 (3)	−38 (5)	0 (2)	9 (6)	8.6 (4)	C_{2A}	7.1 (9)
Cl(2)	48 (3)	440 (28)	50 (4)	26 (8)	29 (3)	32 (9)	12.6 (5)	C_{2B}	5.9 (8)
Cl(3)	54 (3)	129 (16)	64 (4)	−53 (6)	12 (3)	−26 (6)	8.9 (4)	C_{3A}	7.3 (9)
Cl(4)	34 (2)	367 (24)	53 (3)	−33 (6)	22 (2)	−21 (8)	11.0 (4)	C_{3B}	5.5 (7)
Cl(5)	54 (3)	190 (17)	42 (3)	18 (6)	−2 (3)	50 (6)	9.3 (4)	C_{4A}	8.2 (9)
Cl(6)	40 (2)	132 (14)	42 (3)	−3 (5)	−12 (2)	11 (5)	8.4 (4)	C_{4B}	8.9 (10)
								Cl_s	11.9 (7)
								C_s	24 (4)

[a] *Numbers in parentheses are estimated standard deviations 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 $\times 10^4$. [d] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

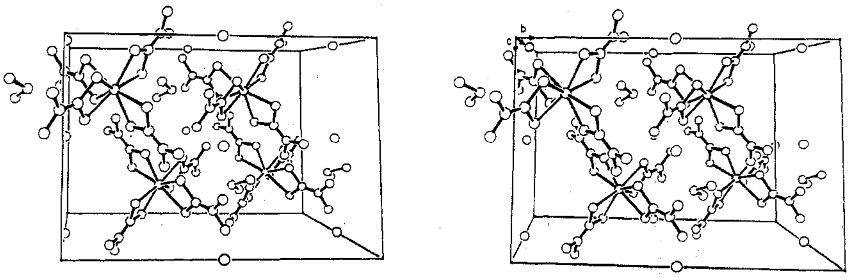

Figure 3. Stereoscopic view of the packing in one unit cell of $[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$ (1). The front face is the (100) plane.

Table V. Bond Distances in the Coordination Group of $[Ta(S_2CN(CH_3)_2)_4]^{+}$ [a]

$[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$		$[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot {}^1/_2CH_2Cl_2$	
Bond	Length, Å	Bond	Length, Å
$Ta\text{-}S_{1A}$	2.591 (3)	$Ta\text{-}S_{1A}$	2.617 (7)
$Ta\text{-}S_{2A}$	2.589 (3)	$Ta\text{-}S_{2A}$	2.559 (6)
$Ta\text{-}S_{1B}$	2.528 (3)	$Ta\text{-}S_{3A}$	2.602 (6)
$Ta\text{-}S_{2B}$	2.513 (3)	$Ta\text{-}S_{4A}$	2.588 (6)
		$Ta\text{-}S_{1B}$	2.520 (7)
		$Ta\text{-}S_{2B}$	2.523 (7)
		$Ta\text{-}S_{3B}$	2.505 (6)
		$Ta\text{-}S_{4B}$	2.511 (6)
Average Values[b]			
$Ta\text{-}S_A$	2.590 (3, 1, 1)	$Ta\text{-}S_A$	2.591 (6, 18, 32)
$Ta\text{-}S_B$	2.521 (3, 8, 8)	$Ta\text{-}S_B$	2.515 (7, 7, 10)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The numbers in parentheses following each averaged value are the root-mean-square estimated standard deviation for an individual datum and the mean and maximum deviation from the average value.

is in accord with the intraligand S···S distances found in other dithiocarbamate structures.[1,4,14,22-24] Bonds to the dodecahedral A sites, $Ta\text{-}S_A$ (average value 2.590 Å in the more accurately determined structure of compound **1**), are longer than bonds to the B sites, $Ta\text{-}S_B$ (average 2.521 Å in compound **1**), by 0.07 Å. Similar differences in the $M\text{-}L_A$ and $M\text{-}L_B$ bond lengths have been observed for $Ti(S_2CN(C_2H_5)_2)_4$ ($\sim$0.08 Å),[14] $Zr(C_2O_4)_4^{4-}$ ($\sim$0.06 Å),[16] and $Zr(acac)_2(NO_3)_2$ ($\sim$0.03 Å),[25] all of which have an *mmmm* dodecahedral structure. The ratio of the averaged bond distances, $Ta\text{-}S_A/Ta\text{-}S_B$, in $[Ta(S_2CN(CH_3)_2)_4]^+$ is 1.03 (Table VII), a value which is identical with that calculated[13] for the "most favorable polyhedron" which minimizes closed-shell ligand repulsions. Because the B sites of a dodecahedron are somewhat more "open" than the A sites, ligand repulsions can be relieved by a slight lengthening (relative to the hard-sphere model) of the $M\text{-}L_A$ bonds and a slight shortening of the $M\text{-}L_B$ bonds. As suggested by Colapietro et al.[14] for $Ti(S_2CN(C_2H_5)_2)_4$, π bonding (S_B $p\pi \rightarrow$ metal $d_{x^2-y^2}$) could also contribute to the difference between the $M\text{-}L_A$ and $M\text{-}L_B$ bond lengths. The averaged length of all eight Ta–S bonds in $[Ta(S_2CN(CH_3)_2)_4]^+$ is 2.556 Å in compound **1** and 2.553 Å in compound **2**.

Averaged dimensions of the TaS_8 coordination polyhedron (Tables V and VI) are remarkably similar to corresponding averaged dimensions of the TiS_8 dodecahedron in $Ti(S_2CN(C_2H_5)_2)_4$; averaged M–S bond lengths in the tantalum and titanium complexes agree within 0.016 Å, and averaged polyhedral edge lengths agree within 0.03 Å.[6] This structural similarity stands in sharp contrast to a striking difference between the kinetic properties of the Ti(IV) and Ta(V) complexes. $Ti(S_2CNR_2)_4$ complexes are stereochemically nonrigid at very low temperatures,[3,26] whereas $[Ta(S_2CN(CH_3)_2)_4]^+$ is stereochemically rigid on the NMR time scale at temperatures below −62 °C.[6] It is evident that the charge

Table VI. Polyhedral Edge Lengths and Bond Angles Subtended at the Ta(V) Atom in the Coordination Group of $[Ta(S_2CN(CH_3)_2)_4]^{+}$ [a]

Edge type[b]	$[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$				$[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot {}^1/_2CH_2Cl_2$			
	Atoms	Length, Å	Atoms	Angle, deg	Atoms	Length, Å	Atoms	Angle, deg
a	$S_{1A}\text{-}S_{2A}'$	2.974 (4)	$S_{1A}\text{-}Ta\text{-}S_{2A}'$	70.07 (8)	$S_{1A}\text{-}S_{2A}$	2.997 (9)	$S_{1A}\text{-}Ta\text{-}S_{2A}$	70.7 (2)
a					$S_{3A}\text{-}S_{4A}$	3.017 (7)	$S_{3A}\text{-}Ta\text{-}S_{4A}$	71.1 (2)
b	$S_{1B}\text{-}S_{2B}$	3.597 (4)	$S_{1B}\text{-}Ta\text{-}S_{2B}$	91.05 (11)	$S_{1B}\text{-}S_{3B}$	3.544 (7)	$S_{1B}\text{-}Ta\text{-}S_{3B}$	89.7 (2)
b	$S_{1B}\text{-}S_{1B}'$	3.733 (6)	$S_{1B}\text{-}Ta\text{-}S_{1B}'$	95.19 (15)	$S_{1B}\text{-}S_{4B}$	3.525 (11)	$S_{1B}\text{-}Ta\text{-}S_{4B}$	89.0 (2)
b	$S_{2B}\text{-}S_{2B}'$	3.664 (6)	$S_{2B}\text{-}Ta\text{-}S_{2B}'$	93.60 (15)	$S_{2B}\text{-}S_{3B}$	3.904 (10)	$S_{2B}\text{-}Ta\text{-}S_{3B}$	101.9 (2)
b					$S_{2B}\text{-}S_{4B}$	3.593 (8)	$S_{2B}\text{-}Ta\text{-}S_{4B}$	91.1 (2)
m	$S_{1A}\text{-}S_{1B}$[c]	2.840 (4)	$S_{1A}\text{-}Ta\text{-}S_{1B}$	67.38 (8)	$S_{1A}\text{-}S_{1B}$[c]	2.869 (10)	$S_{1A}\text{-}Ta\text{-}S_{1B}$	67.9 (2)
m	$S_{2A}\text{-}S_{2B}$[c]	2.846 (4)	$S_{2A}\text{-}Ta\text{-}S_{2B}$	67.78 (9)	$S_{2A}\text{-}S_{2B}$[c]	2.841 (10)	$S_{2A}\text{-}Ta\text{-}S_{2B}$	68.0 (2)
m					$S_{3A}\text{-}S_{3B}$[c]	2.838 (9)	$S_{3A}\text{-}Ta\text{-}S_{3B}$	67.5 (2)
m					$S_{4A}\text{-}S_{4B}$[c]	2.825 (11)	$S_{4A}\text{-}Ta\text{-}S_{4B}$	67.3 (2)
g	$S_{1A}\text{-}S_{2B}$	3.293 (4)	$S_{1A}\text{-}Ta\text{-}S_{2B}$	80.33 (9)	$S_{1A}\text{-}S_{3B}$	3.185 (8)	$S_{1A}\text{-}Ta\text{-}S_{3B}$	76.9 (2)
g	$S_{1A}\text{-}S_{1B}'$	3.278 (4)	$S_{1A}\text{-}Ta\text{-}S_{1B}'$	79.64 (9)	$S_{1A}\text{-}S_{4B}$	3.225 (10)	$S_{1A}\text{-}Ta\text{-}S_{4B}$	77.9 (2)
g	$S_{2A}\text{-}S_{1B}$	3.271 (4)	$S_{2A}\text{-}Ta\text{-}S_{1B}$	79.46 (9)	$S_{2A}\text{-}S_{3B}$	3.266 (10)	$S_{2A}\text{-}Ta\text{-}S_{3B}$	80.3 (2)
g	$S_{2A}\text{-}S_{2B}'$	3.261 (4)	$S_{2A}\text{-}Ta\text{-}S_{2B}'$	79.45 (10)	$S_{2A}\text{-}S_{4B}$	3.365 (7)	$S_{2A}\text{-}Ta\text{-}S_{4B}$	83.1 (2)
g					$S_{3A}\text{-}S_{1B}$	3.313 (9)	$S_{3A}\text{-}Ta\text{-}S_{1B}$	80.6 (2)
g					$S_{3A}\text{-}S_{2B}$	3.348 (10)	$S_{3A}\text{-}Ta\text{-}S_{2B}$	81.6 (2)
g					$S_{4A}\text{-}S_{1B}$	3.210 (11)	$S_{4A}\text{-}Ta\text{-}S_{1B}$	77.9 (2)
g					$S_{4A}\text{-}S_{2B}$	3.195 (8)	$S_{4A}\text{-}Ta\text{-}S_{2B}$	77.4 (2)
Average Values[d]								
a	S···S	2.974 (4, 0, 0)	S–Ta–S	70.1 (1, 0, 0)	S···S	3.007 (8, 10, 10)	S–Ta–S	70.9 (2, 2, 2)
b	S···S	3.648 (5, 51, 85)	S–Ta–S	92.7 (1, 17, 25)	S···S	3.642 (9, 131, 262)	S–Ta–S	92.9 (2, 45, 90)
m	S···S	2.843 (4, 3, 3)	S–Ta–S	67.6 (1, 2, 2)	S···S	2.843 (10, 13, 26)	S–Ta–S	67.7 (2, 3, 4)
g	S···S	3.276 (4, 10, 17)	S–Ta–S	79.7 (1, 3, 6)	S···S	3.263 (9, 60, 102)	S–Ta–S	79.5 (2, 19, 36)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Edge nomenclature is defined in ref 13. [c] The "bite" of the ligand. [d] The numbers in parentheses following each averaged value are the root-mean-square estimated standard deviation for an individual datum and the mean and maximum deviation from the average value.

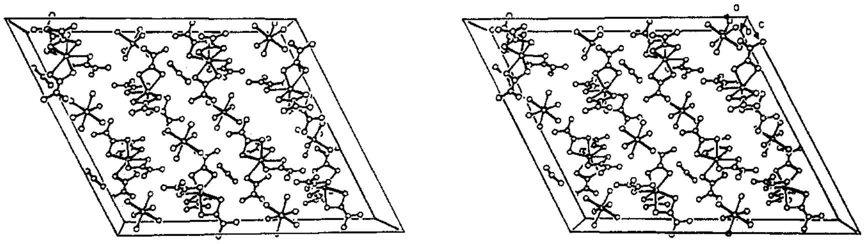

Figure 4. Stereoscopic view of the packing in crystalline $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$ (2). The contents of one unit cell are viewed normal to the (010) plane.

Table VII. Average Polyhedron-Shape Parameters for Dodecahedral $M(S_2CNR_2)_4$ Molecules

	$[Ta(S_2CN(CH_3)_2)_4]^+$				
Shape parameter[a]	Compd 1[b]	Compd 2[b]	$Ti(S_2CN(C_2H_5)_2)_4$[c]	MFP[d]	HSM[e]
a	1.16	1.18	1.17	1.17	1.20
b	1.43	1.43	1.42	1.49	1.50
m	1.11	1.11	1.11	1.17	1.20
g	1.28	1.28	1.29	1.24	1.20
θ_A, deg	35.0	35.4	35.1	35.2	36.9
θ_B, deg	77.4	76.6	77.5	73.5	69.5
$M-S_A/M-S_B$	1.027	1.030	1.033	1.03	1.00

[a] *a, b, m,* and *g* are averaged lengths of the dodecahedral edges[13] in units of the averaged M-S bond distance (2.556 and 2.553 Å in compounds 1 and 2, respectively, for M = Ta; 2.564 Å for M = Ti). θ_A and θ_B are the averaged angles which the $M-S_A$ and $M-S_B$ bonds, respectively, make with the $\bar{4}$ axis of the idealized dodecahedron. [b] This work. [c] Reference 14. [d] Most favorable coordination polyhedron, calculated[13] to minimize the closed-shell ligand repulsive energy. [e] Hard-sphere model.

on the Ta(V) complex plays an important role in slowing the rate of rearrangement.

Bond distances and angles within the dithiocarbamate ligands (Table VIII) are comparable to values that have been found in other dithiocarbamate structures.[1,4,14,22-24] Merlino[27] has observed that the geometry of the dithiocarbamate ligand is not particularly sensitive to the oxidation state and coordination number of the metal atom to which it is attached. However, exceptions do occur in cases where there is a marked disparity in the metal–sulfur bond lengths.[28-30] The C–N and C–S distances (average values 1.31 and 1.722 Å, respectively, in compound **1**) are intermediate between the sum of the Pauling single-bond and double-bond radii (C—N = 1.47 Å, C═N = 1.27 Å, C—S = 1.81 Å, C═S = 1.61 Å),[31] indicative of delocalized π bonding in the S_2CN portion of the ligand. Consistent with this view, the six atoms of the S_2CNC_2 ligand skelton show only minor departures from planarity. Thus the average displacement of the 24 atoms of the four ligands from their respective mean planes is 0.028 Å in both compounds; maximum displacements are 0.055 Å for compound **1** and 0.073 Å for compound **2**. The small deviations from planarity involve primarily a slight twisting of the ligands about the C–N bond; dihedral angles between the S_2CN and CNC_2 mean planes vary from 1.5 to 4.7°. A similar twisting was noted in the structures of $Ti[S_2CN(CH_3)_2]_3Cl$[4] and $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$.[24] The tantalum atom in both salts is slightly displaced from the ligand planes, which implies a small folding of the chelate rings about the *m* edges (S···S) of the dodecahedron. In compound **1** chelate rings on the same BAAB trapezoid are folded toward each other such that the ligand planes make an angle of 10.3°; the direction of the ring folding is such as to bring the uncoordinated parts of ligands 1 and 2′ closer to ligand 1′ (cf. Figure 1). Dihedral angles between the ligand planes and the appropriate S–Ta–S groups are 4.2 and 6.4° for rings 1 and 2, respectively, while the corresponding displacements of the Ta(V) atom from the ligand planes are 0.15 and 0.23 Å, respectively. Similar distortions are evident in three of the chelate rings in compound **2**. Thus, ligand 2 is folded toward ligand 3, and ligands 3 and 4 are folded toward ligand 1 (cf. Figure 2). Dihedral angles between the ligand planes and the appropriate S–Ti–S group are 5.6, 3.1, and 8.7° for rings 2, 3, and 4, respectively; corresponding displacements of the Ta(V) atom from the ligand planes are 0.20, 0.12, and 0.34 Å, respectively. The Ta(V) atom lies in the plane of ligand 1.

In all probability, the ring folding and $S_2C\text{–}NC_2$ twisting result from crystal packing forces. There are six intermolecular

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

	$[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$			$[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$				
Atoms	Ligand 1	Ligand 2	Av[b]	Ligand 1	Ligand 2	Ligand 3	Ligand 4	Av[b]
				(a) Distances				
$S_A\cdots S_B$[c]	2.840 (4)	2.846 (4)	2.843 (4, 3,3)	2.869 (10)	2.841 (10)	2.838 (9)	2.825 (11)	2.843 (10, 13, 26)
$C\text{-}S_A$	1.722 (9)	1.732 (12)	1.722 (10, 8, 16)	1.74 (3)	1.76 (3)	1.66 (2)	1.72 (2)	1.72 (3, 3, 6)
$C\text{-}S_B$	1.728 (9)	1.706 (11)		1.70 (3)	1.70 (2)	1.71 (3)	1.76 (3)	
C-N	1.30 (1)	1.31 (1)	1.31 (1, 1, 1)	1.39 (4)	1.30 (3)	1.39 (2)	1.28 (2)	1.34 (3, 5, 6)
$C_A\text{-}N$	1.49 (1)	1.49 (2)	1.48 (2, 1, 2)	1.48 (4)	1.45 (3)	1.56 (3)	1.48 (4)	1.49 (4, 3, 7)
$C_B\text{-}N$	1.48 (1)	1.46 (2)		1.48 (4)	1.52 (4)	1.46 (2)	1.50 (4)	
				(b) Angles				
$S_A\text{-}C\text{-}S_B$	110.8 (6)	111.7 (6)	111.3 (6, 5, 5)	113 (1)	111 (1)	115 (1)	109 (1)	112 (1, 2, 3)
$C\text{-}S_A\text{-}Ta$	89.9 (3)	88.5 (4)	89.2 (4, 7, 7)	87.6 (9)	89.5 (8)	87.8 (9)	91.0 (8)	89.0 (9, 13, 20)
$C\text{-}S_B\text{-}Ta$	91.8 (3)	91.6 (4)	91.7 (4, 1, 1)	91.6 (9)	91.9 (9)	90.0 (7)	92.6 (7)	91.5 (8, 8, 15)
$S_A\text{-}C\text{-}N$	124.6 (7)	123.4 (9)	124.4 (8, 5, 10)	121 (2)	123 (2)	124 (2)	126 (2)	124 (2, 2, 3)
$S_B\text{-}C\text{-}N$	124.6 (7)	124.9 (9)		127 (2)	127 (2)	121 (1)	125 (2)	
$C_A\text{-}N\text{-}C$	121.7 (9)	121.7 (11)	121.7 (10, 3, 6)	119 (2)	123 (2)	117 (1)	120 (2)	119 (2, 3, 7)
$C_B\text{-}N\text{-}C$	122.3 (9)	121.2 (11)		112 (2)	119 (2)	122 (1)	123 (2)	
$C_A\text{-}N\text{-}C_B$	116.0 (9)	117.1 (11)	116.6 (10, 6, 6)	129 (2)	118 (2)	121 (1)	117 (2)	121 (2, 4, 8)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The numbers 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.

Table IX. Bond Lengths (Å) and Bond Angles (deg) in the Hexachlorotantalate(V) Anion[a]

Lengths

Ta-Cl(1)	2.334 (9)	Ta-Cl(4)	2.265 (8)
Ta-Cl(2)	2.241 (8)	Ta-Cl(5)	2.322 (9)
Ta-Cl(3)	2.354 (10)	Ta-Cl(6)	2.317 (8)

Angles

Cl(1)-Ta-Cl(3)	178.5 (3)	Cl(2)-Ta-Cl(5)	91.9 (3)
Cl(2)-Ta-Cl(4)	177.8 (4)	Cl(2)-Ta-Cl(6)	88.7 (3)
Cl(5)-Ta-Cl(6)	177.8 (3)	Cl(3)-Ta-Cl(4)	87.1 (3)
Cl(1)-Ta-Cl(2)	90.4 (3)	Cl(3)-Ta-Cl(5)	92.4 (3)
Cl(1)-Ta-Cl(4)	91.7 (3)	Cl(3)-Ta-Cl(6)	89.7 (3)
Cl(1)-Ta-Cl(5)	88.3 (3)	Cl(4)-Ta-Cl(5)	87.4 (3)
Cl(1)-Ta-Cl(6)	89.6 (3)	Cl(4)-Ta-Cl(6)	92.1 (3)
Cl(2)-Ta-Cl(3)	90.9 (3)		

[a] Numbers in parentheses are estimated standard deviations in the last significant figure.

contacts in compound **1** and five in compound **2** which are 0.1–0.3 Å shorter than the sum of the van der Waals radii. All but one of these involve dithiocarbamate methyl groups, and the shortest contacts involve those methyl groups which are farthest displaced from the planes of the ligands.

Bond distances and bond angles in the hexachlorotantalate(V) anion of compound **2** are set out in Table IX. The geometry of the anion is close to regular octahedral; however, two trans Ta–Cl bonds (Ta–Cl(2) and Ta–Cl(4), average length 2.253 Å) appear to be somewhat shorter than the other four Ta–Cl bonds (average length 2.332 Å). The origin of this distortion is not fully understood although a close intermolecular contact between Cl(2) and a dithiocarbamate methyl group (3.53 Å) would tend to decrease the shortest bond, Ta–Cl(2). Because Ta(V) has electronic configuration d^0, the isolated $TaCl_6^-$ ion should be undistorted. Preiss[32] has reported the structure of $[PCl_4][TaCl_6]$ in which the Ta–Cl bond distances vary from 2.30 to 2.37 Å (average value 2.33 Å). The averaged value of all six Ta–Cl distances in $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$ is 2.306 Å.

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Registry No. **1**, 57483-74-6; **2**, 57526-19-9.

Supplementary Material Available: Listings of structure factor amplitudes (30) pages. Ordering information is given on any current masthead page.

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