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Contribution from the Department of Chemistry,
 Bateman Science Center, Arizona State University, Tempe, Arizona 85281

Synthesis, Characterization, and Molecular Structure of Sulfidotris(*N,N*-diethyldithiocarbamato)tantalum(V)

E. J. PETERSON, R. B. VON DREELE,* and T. M. BROWN*

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The synthesis of the title compound has been accomplished and classical physical methods have been employed to characterize the complex. The crystal and molecular structures have also been determined from single-crystal x-ray intensity data collected by the θ - 2θ scan technique. The molecule is monomeric with seven sulfur atoms bound to the Ta(V) atom at the corners of a distorted pentagonal bipyramid. The monodentate sulfur atom, doubly bonded to the tantalum atom, occupies one axial position (Ta-S = 2.181 (1) Å), one diethyldithiocarbamate ligand spans the other axial position and one equatorial position, and two diethyldithiocarbamate ligands occupy the remaining equatorial positions. The bond distance between the tantalum and the axial sulfur atom opposite Ta=S is ca. 0.13 Å longer than the average length of the five equatorial bonds (Ta-S_{eq} = 2.556 Å). Because of the extremely close S...S contacts in the equatorial plane, the pentagonal girdle of sulfur atoms is appreciably puckered. The observed distortions from the ideal pentagonal-bipyramidal geometry are considered in relation to steric effects. The structure was solved by standard heavy-atom techniques and refined by full-matrix least squares to a final *R* value of 0.037 for 5055 independent observed reflections. The compound crystallized in the monoclinic space group $P2_1/c$, $Z = 4$, and has lattice parameters $a = 9.647$ (4) Å, $b = 17.214$ (7) Å, $c = 15.442$ (6) Å, and $\beta = 96.78$ (3)° ($\rho_{\text{calcd}} = 1.704$ g cm⁻³; $\rho_{\text{obsd}} = 1.703$ g cm⁻³).

Introduction

Tantalum, as well as the other early transition metals, exhibits a marked preference for higher coordination numbers, and coordination number seven for it has recently been established by x-ray diffraction studies. A tetragonal face capped trigonal prism geometry, with a chloride as the capping ligand, has been used to describe the coordination polyhedron in Me₃TaCl₂(bpy).¹ Orthorhombic and monoclinic forms of the acetamidates TaCl₃(C₆H₁₁N=C(Me)NC₆H₁₁)₂ and TaCl₃(C₆H₁₁N=C(Me)NC₆H₁₁)(C₆H₁₁NC(NHC₆H₁₁)=O) have recently been found to adopt this same geometry.²⁻⁵ However, another acetamidate complex, MeTaCl₂(C₆H₁₁N=C(Me)NC₆H₁₁)₂, has the two bidentate ligands mutually perpendicular, and the molecular geometry could not be related to any idealized polyhedron.⁶ In contrast, the diarsine complex of tantalum(V) originally formulated⁷ as a seven-coordinate complex, TaBr₅(diars), has recently been found by x-ray diffraction⁸ to be [TaBr₄(diars)]₂⁺[TaBr₆]⁻.

Sulfidotris(*N,N*-diethyldithiocarbamato)tantalum(V), TaS(S₂CNEt₂)₃, was first reported by Heckley et al.⁹ These authors isolated a green crystalline compound which they analyzed by classical characterization techniques to be a seven-coordinate complex. The work described in this paper was undertaken when a yellow compound was isolated from a different preparation and was also formulated as TaS(S₂CNEt₂)₃. The yellow crystalline compound was examined by the single-crystal x-ray diffraction technique, as well as by classical methods, in order to unequivocally confirm the coordination number and to establish the geometry of the coordination polyhedron.

Experimental Section

Due to the sensitivity of starting materials to hydrolysis, it was necessary to rigorously exclude water during preparation, handling, and storage. In order to maintain these conditions, standard inert-atmosphere and vacuum techniques were employed. The reac-

tion-extraction vessel used in the preparation was described previously.¹⁰ The vessel was evacuated and heated prior to use to remove residual traces of water.

Materials. Tantalum(V) chloride obtained from Research Inorganic Chemicals was purified by sublimation. Sodium diethyldithiocarbamate trihydrate was obtained from Aldrich Chemical Co., washed with three 50-mL portions of hot diethyl ether, and dried at 60 °C in vacuo before use. Analytical reagent grade acetonitrile, obtained from Mallinckrodt Chemical Works, was dried and outgassed over phosphorus pentoxide and stored over Linde type 4A molecular sieves. Immediately prior to use, the acetonitrile was vacuum distilled onto CaH₂ and again outgassed in order to ensure anhydrous conditions.

Preparation and Characterization of TaS(S₂CNEt₂)₃. In a typical preparation, 2 g of TaCl₅ (0.0056 mol) and 4.77 g of sodium diethyldithiocarbamate (0.0279 mol) were placed in one end of the reaction-extraction vessel. Approximately 60 mL of acetonitrile was vacuum distilled onto the reactants, and stirring was initiated and continued for a period of 3 h at ambient temperature. The vessel was then inverted and the brown solution was filtered away from the insoluble NaCl. This solution was allowed to stand undisturbed in vacuo for a period of several weeks. During this time, a yellow crystalline compound separated from the acetonitrile solution (which remained brown) and was isolated by filtration. The formation of the yellow compound could be accelerated by heating the acetonitrile solution to reflux. The yellow crystals appeared to resist hydrolysis indefinitely. Anal. Calcd for TaS₇C₁₅N₃H₃₀: C, 27.41; H, 4.57; N, 6.40; S, 34.09. Found: C, 27.44; H, 4.47; N, 6.33; S, 33.61. NMR (CD₃CN solution, 35 °C): 1.20 ppm (triplet, CH₃) and 3.70 ppm (quartet, CH₂) relative to an internal reference of tetramethylsilane. IR (Nujol mull): ν (C=N) 1520 cm⁻¹, ν (NC₂) 1155 cm⁻¹, ν (C=S) 1010 cm⁻¹, ν (Ta=S) 905 cm⁻¹, ν (Ta-S) 360 cm⁻¹ (all assigned bands were strong and sharp).

Crystal Data and Data Collection. Because of the apparent insensitivity of the crystals to moisture, a suitable crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm was mounted in a random orientation on the end of a glass fiber. On the basis of precession photographs, the lattice was assigned to the monoclinic system. The systematic absences of $0k0$ for k odd and $h0l$ for l odd are consistent with the centrosymmetric space group $P2_1/c$ (C_{2h}^2).¹¹ There were 57 strong

Table I. Fractional Coordinates^a (×10⁴) and Thermal Parameters^{a,b} (×10³) for TaS[S₂CN(C₂H₅)₂]₃

Atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ta	7045.7 (2)	945.6 (1)	2126.1 (1)	35.3 (1)	37.0 (1)	39.5 (1)	-0.5 (1)	9.1 (1)	-2.2 (1)
S	5927.5 (15)	1968.6 (8)	1581.8 (10)	51.1 (8)	51.8 (8)	59.8 (9)	3.1 (6)	8.4 (7)	1.7 (6)
S(a1)	8154.3 (14)	-98.7 (7)	3298.3 (9)	53.6 (8)	42.0 (7)	44.8 (7)	10.2 (6)	8.4 (6)	-4.6 (5)
S(a2)	6836.0 (15)	1354.9 (7)	3683.9 (9)	53.2 (8)	43.7 (7)	45.8 (7)	10.3 (6)	10.9 (6)	-6.7 (5)
S(b1)	6298.9 (15)	-149.4 (8)	1073.8 (9)	55.6 (8)	47.5 (7)	47.3 (7)	-12.8 (6)	20.1 (6)	-9.3 (6)
S(b2)	4814.2 (14)	242.9 (8)	2494.3 (9)	44.4 (7)	53.3 (8)	49.2 (7)	-6.3 (6)	17.0 (6)	-8.2 (6)
S(c1)	8885.5 (16)	755.8 (9)	1096.2 (11)	47.0 (8)	66.2 (9)	64.7 (9)	-11.5 (7)	23.5 (7)	-17.4 (7)
S(c2)	9341.5 (15)	1662.0 (8)	2639.1 (10)	45.1 (8)	56.1 (8)	57.7 (8)	-10.2 (6)	8.1 (6)	-7.0 (7)
C(a)	7636 (5)	503 (3)	4074 (3)	35 (3)	43 (3)	49 (3)	1 (1)	9 (2)	-4 (2)
N(a)	7770 (5)	344 (2)	4920 (3)	52 (3)	49 (2)	41 (2)	1 (2)	11 (2)	-2 (2)
C(a1)	8310 (6)	-405 (3)	5268 (4)	65 (4)	57 (3)	52 (3)	5 (3)	7 (3)	7 (3)
C(a2)	7322 (7)	903 (4)	5559 (4)	65 (4)	75 (4)	40 (3)	2 (3)	16 (3)	-12 (3)
C(a3)	7152 (9)	-981 (4)	5367 (5)	98 (6)	66 (4)	88 (5)	-13 (4)	35 (5)	7 (4)
C(a4)	8479 (7)	1481 (4)	5847 (5)	73 (5)	71 (4)	72 (4)	4 (3)	4 (4)	-24 (3)
C(b)	4923 (5)	-378 (3)	1645 (3)	40 (3)	44 (3)	43 (3)	-4 (2)	5 (3)	3 (2)
N(b)	4100 (5)	-976 (2)	1441 (3)	48 (3)	47 (2)	46 (2)	-10 (2)	10 (3)	-2 (2)
C(b1)	4258 (6)	-1474 (3)	686 (4)	64 (4)	53 (3)	47 (3)	-14 (3)	2 (3)	-9 (2)
C(b2)	3040 (6)	-1216 (4)	2003 (4)	56 (4)	64 (3)	61 (4)	-15 (3)	14 (3)	7 (3)
C(b3)	5331 (7)	-2105 (4)	898 (5)	74 (4)	51 (3)	103 (6)	-14 (3)	19 (4)	-9 (4)
C(b4)	1666 (9)	-833 (5)	1739 (7)	58 (5)	137 (8)	114 (7)	-4 (5)	21 (5)	28 (6)
C(c)	10035 (6)	1343 (3)	1733 (4)	44 (3)	44 (3)	70 (4)	1 (2)	15 (3)	2 (3)
N(c)	11292 (5)	1517 (3)	1540 (4)	41 (3)	55 (3)	87 (4)	-6 (2)	22 (3)	-5 (3)
C(c1)	11746 (7)	1263 (4)	711 (6)	54 (4)	81 (5)	116 (7)	-9 (3)	43 (4)	-15 (5)
C(c2)	12257 (6)	2001 (6)	2129 (4)	37 (3)	65 (4)	96 (5)	-5 (3)	-2 (3)	11 (3)
C(c3)	11220 (9)	1770 (5)	-52 (6)	107 (7)	103 (6)	96 (6)	-19 (5)	53 (5)	-3 (5)
C(c4)	12244 (10)	2823 (5)	1890 (7)	124 (8)	62 (5)	154 (8)	-12 (5)	-44 (6)	16 (5)

^a Value in parentheses is the estimated standard deviation in the last significant figure given in this and all following tables. ^b The thermal parameters are expressed in the form $T = \exp[-2\pi^2(U_{11}h^2a^*2 + \dots + 2U_{23}klb^*c^*)]$, where the U_{ij} values are in Å².

reflections within the angular range $5^\circ \leq 2\theta \leq 60^\circ$ for Mo K α radiation which were automatically centered on a Syntex P1 auto-diffractometer; a least-squares refinement of the angular settings yielded the lattice parameters $a = 9.647$ (4) Å, $b = 17.214$ (7) Å, $c = 15.442$ (6) Å, and $\beta = 96.78$ (3)° which for $Z = 4$ gives $\rho_{\text{calc}} = 1.704$ g/cm³ ($\rho_{\text{obsd}} = 1.703$ g/cm³, by flotation in CCl₄-CBr₄ solution).

An irregularly shaped crystal bounded by the faces (100), (111), (011), (001), (010), (010), (010), and (201) was used in the data collection. The distances of the faces from the center of the crystal were as follows: (100), 0.18 mm; (111), 0.22 mm; (011), 0.14 mm; (001), 0.20 mm; (010), 0.19 mm; (010), 0.13 mm; (201), 0.11 mm. Intensity data were collected with the crystal mounted on a glass fiber roughly perpendicular to the (010) face. Examination of a number of low-order ω scans suggested that the crystal was single and of excellent quality.

Diffraction intensities were measured for 6704 independent reflections within the angular range $3^\circ \leq 2\theta \leq 55^\circ$ with monochromated Mo K α radiation using θ - 2θ scans of variable rate and range. The scanning rate was 1°/min for most reflections, but was increased up to 12°/min for those of higher intensity. The base scan range of 1.4° was varied slightly to take account of spectral dispersion, and background measurements lasting 0.25 of the scan time were made at each end of the scan. Periodic monitoring of three reflections showed no decrease in intensity throughout the entire data collection. A total of 5055 reflections were retained as objectively observed with $|F_o| > 0.675\sigma_F$, $\sigma_F = 0.025|F_o| + [C + (B_1 + B_2)k^2]^{1/2}R/2|F_o|Lp$, where C is the total count in a scan taken at the rate R and k (=4) is the ratio of scanning time to the time for each background count B_1 and B_2 . The usual Lorentz and polarization corrections for monochromated radiation¹² were applied and analytical absorption corrections¹³ were made for a linear absorption coefficient of 51.1 cm⁻¹.

Structure Solution and Refinement. The atomic scattering factors for Ta(0), S(0), N(0), and C(0) from published tables¹⁴ were used with real and imaginary anomalous dispersion corrections¹⁴ applied for Ta and S. The function minimized during all least-squares refinement processes was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. Discrepancy indices used below are defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_w = \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}$$

A three-dimensional Patterson synthesis¹⁵ provided the location of the tantalum atoms in the unit cell. A Fourier synthesis using the tantalum position indicated positions for the seven sulfur atoms. These eight atoms were refined isotropically to give a standard residual of $R = 0.315$ and a weighted residual of $R_w = 0.396$. A series of Fourier syntheses (each successive one being phased by an increasing number of atoms) led to the location of all nonhydrogen atoms. Three cycles of large-block least-squares refinement of an anisotropic model (with scale factor, tantalum atom, and sulfido ligand in one block and each dithiocarbamate ligand contained in its own block) converged to give residuals $R = 0.054$ and $R_w = 0.078$. At this point, hydrogen atoms were placed at idealized positions with an isotropic temperature factor of $U = 0.05$ Å². A difference Fourier synthesis based on the least-squares results had showed peaks between 0.4 and 0.7 e/Å³ at all of these positions. Four final cycles of the large-block least-squares refinement, varying all nonhydrogen positional and anisotropic thermal parameters and fixing all hydrogen parameters, converged with $R = 0.037$ and $R_w = 0.041$. On the final refinement cycle, no parameter shift to esd ratio was greater than 0.25 (root-mean-square average was 0.06). A difference Fourier synthesis using these final parameters showed no peaks greater than 0.17 e/Å³. Listings of final values of $|F_o|$ and $|F_c|$ (in electrons × 5) and phases of the reflections used in the refinement of the structure are available as supplementary material.

Results and Discussion

A yellow crystalline compound, formulated as TaS(S₂CNEt₂)₃, has been isolated from acetonitrile solutions of a 1:5 mixture of TaCl₅ and NaS₂CNEt₂. This is in contrast to the report of Heckley et al.,⁹ who reported a green compound isolated from benzene solution and formulated as above. The yellow solid isolated in this study from acetonitrile is an air-stable compound, and it exhibits typical resonances for an ethyl group (δ 1.20, triplet; δ 3.70, quartet) in CD₃CN solutions at 35 °C. The infrared spectrum is closely similar to those of other diethyldithiocarbamate complexes;¹⁶ the strong band at 1005 cm⁻¹ is assigned to ν (C-S) and indicates that all dithiocarbamate ligands are bidentate.¹⁷ The absorption bands at 905 and 360 cm⁻¹ have been assigned as ν (Ta=S) and ν (Ta-S), respectively. The preceding conclusions concerning the formation and characterization of the yellow solid have been confirmed by single-crystal x-ray diffraction studies.

Final atomic coordinates and anisotropic thermal parameters for the nonhydrogen atoms are presented in Table I along with

Table II. Fractional Coordinates ($\times 10^3$) for the Hydrogen Atoms^a

H atom on	x	y	z
C(a1)	889	-33	585
C(a1)	894	-64	486
C(a2)	706	63	608
C(a2)	648	120	528
C(a3)	751	-147	561
C(a3)	653	-74	579
C(a3)	657	-106	481
C(a4)	817	186	627
C(a4)	932	121	612
C(a4)	874	178	533
C(b1)	455	-115	20
C(b1)	334	-172	47
C(b2)	338	-109	263
C(b2)	291	-180	197
C(b3)	542	-244	38
C(b3)	626	-188	109
C(b3)	505	-245	137
C(b4)	94	-98	212
C(b4)	178	-24	178
C(b4)	131	-95	112
C(c1)	1279	126	76
C(c1)	1141	73	58
C(c2)	1200	196	275
C(c2)	1325	179	216
C(c3)	1153	160	-61
C(c3)	1155	233	5
C(c3)	1017	179	-13
C(c4)	1292	313	229
C(c4)	1131	304	187
C(c4)	1255	286	128

^a Hydrogen atoms placed at idealized positions 1 Å from their respective carbon atoms.

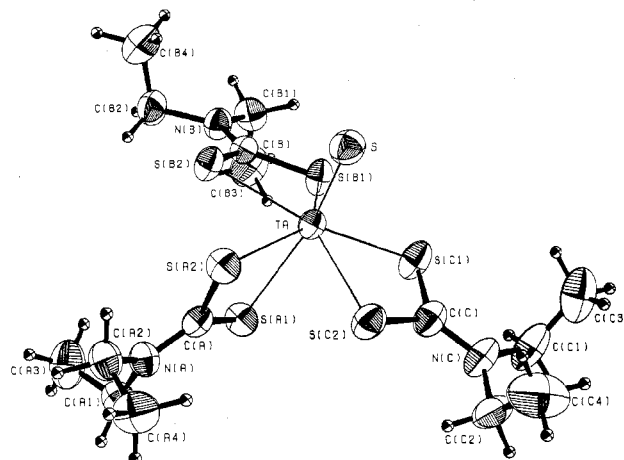
Table III. Bond Distances, Spherical Polar Coordinates,^a and Bond Angles in the Coordination Group

Bond	Dist, Å	θ , deg	ϕ , deg
Ta-S	2.181 (1)	0.0	0.0
Ta-S(a1)	2.682 (1)	160.18	6.11
Ta-S(a2)	2.538 (1)	92.84	0.0
Ta-S(b1)	2.537 (1)	105.27	143.85
Ta-S(b2)	2.591 (1)	94.34	76.26
Ta-S(c1)	2.541 (1)	102.29	-143.05
Ta-S(c2)	2.576 (1)	95.73	-75.02

Atoms	Angle, deg	Atoms	Angle, deg
S-Ta-S(a1)	160.18 (5)	S(a1)-Ta-S(a2)	67.46 (4)
S-Ta-S(a2)	92.84 (12)	S(a1)-Ta-S(b1)	89.68 (4)
S-Ta-S(b1)	105.27 (10)	S(a1)-Ta-S(b2)	79.28 (4)
S-Ta-S(b2)	94.34 (12)	S(a1)-Ta-S(c1)	94.83 (13)
S-Ta-S(c1)	102.29 (12)	S(a1)-Ta-S(c2)	81.61 (5)
S-Ta-S(c2)	95.73 (12)	S(a2)-Ta-S(b2)	76.09 (4)
S(b1)-Ta-S(b2)	67.26 (4)	S(a2)-Ta-S(c2)	74.82 (5)
S(c1)-Ta-S(c2)	67.36 (5)	S(b1)-Ta-S(c1)	70.72 (4)

^a The spherical polar coordinate system is defined relative to a Cartesian coordinate system oriented with the monodentate ligand on the z axis. The angle θ is that between the x axis and the M-L vector, and ϕ is the angle from the projection of the Ta-S(a2) vector onto the x-y plane to that of the M-L vector.

the estimated standard deviations derived from the least-squares analysis. Atomic coordinates for the hydrogen atoms are given in Table II. The perspective view shown in Figure 1 shows the essential features of the molecule. Each atom is represented by an ellipsoid consistent with the anisotropic thermal parameters in Table I and each atom is labeled consistent with the atom names in Table I. A stereoscopic view of the molecular packing and unit cell contents for TaS-(S₂CNET₂)₃ is shown in Figure 2. The list of bond distances and angles in the coordination group is given in Table III, and the polyhedral edge lengths and interfacial dihedral angles as described by Muettterties and Guggenberger¹⁸ are listed in

**Figure 1.** A perspective representation of the structure of TaS-(S₂CNET₂)₃. Hydrogen atoms on C(a1), C(b3), and C(c1) are hidden from view.**Table IV.** Polyhedral Edge Lengths and Interfacial Dihedral Angles (δ) in the Coordination Group

Atoms	Edge, Å	δ , deg
S-S(a2)	3.427 (2)	56.91
S-S(b1)	3.756 (2)	45.86
S-S(b2)	3.510 (2)	60.57
S-S(c1)	3.684 (2)	52.24
S-S(c2)	3.538 (2)	56.53
S(a1)-S(a2) ^a	2.901 (2)	62.48
S(a1)-S(b1)	3.681 (2)	48.82
S(a1)-S(b2)	3.364 (2)	54.00
S(a1)-S(c1)	3.847 (2)	42.84
S(a1)-S(c2)	3.437 (2)	54.04
S(a2)-S(b2)	3.161 (2)	68.21
S(a2)-S(c2)	3.107 (2)	70.45
S(b1)-S(b2) ^a	2.840 (2)	85.75
S(c1)-S(c2) ^a	2.838 (2)	87.85
S(b1)-S(c1)	2.939 (2)	91.89

^a The "bite" of the ligand.

Table V. Bond Lengths and Bond Angles in the *N,N*-Diethyldithiocarbamate Ligands

Bond	Ligand a	Ligand b	Ligand c	Av ^a
S ₁ -S ₂ ^b	2.901 (2)	2.840 (2)	2.838 (2)	2.860 (36)
C-S ₁	1.703 (5)	1.724 (5)	1.720 (6)	1.716 (11)
C-S ₂	1.731 (5)	1.705 (5)	1.711 (6)	
C-N	1.326 (6)	1.315 (6)	1.317 (7)	1.319 (6)
N-C ₁	1.468 (7)	1.470 (7)	1.470 (8)	1.474 (5)
N-C ₂	1.480 (7)	1.477 (7)	1.479 (7)	
C ₁ -C ₃	1.515 (9)	1.510 (9)	1.503 (12)	1.500 (22)
C ₂ -C ₄	1.521 (9)	1.492 (10)	1.461 (9)	

Angle	Ligand a	Ligand b	Ligand c	Av ^a
S ₁ -Ta-S ₂	67.46 (4)	67.26 (4)	67.36 (5)	67.36 (10)
Ta-S ₁ -C	86.6 (2)	91.1 (7)	91.0 (8)	89.8 (17)
Ta-S ₂ -C	90.7 (7)	89.7 (2)	90.0 (8)	
S ₁ -C-S ₂	115.2 (6)	111.9 (6)	111.6 (7)	112.9 (20)
S ₁ -C-N	124.4 (8)	122.4 (8)	123.5 (9)	123.6 (19)
S ₂ -C-N	120.4 (8)	125.7 (7)	124.9 (8)	
C-N-C ₁	122.1 (8)	121.9 (8)	120.5 (10)	121.4 (6)
C-N-C ₂	121.3 (8)	121.3 (9)	121.2 (10)	
N-C ₁ -C ₃	110.4 (12)	109.1 (11)	113.7 (15)	111.3 (20)
N-C ₂ -C ₄	111.0 (12)	110.0 (13)	113.8 (12)	
C ₁ -N-C ₂	116.5 (8)	116.6 (8)	118.2 (9)	117.1 (10)

^a The number in parentheses following each average value is the standard deviation in a single observation obtained from the averaged values. ^b The bite of the ligand.

Table IV. The bond lengths and angles characterizing the dithiocarbamate ligands are given in Table V.

Crystalline TaS(S₂CNET₂)₃ consists of discrete molecules in which the tantalum atoms have a coordination number of

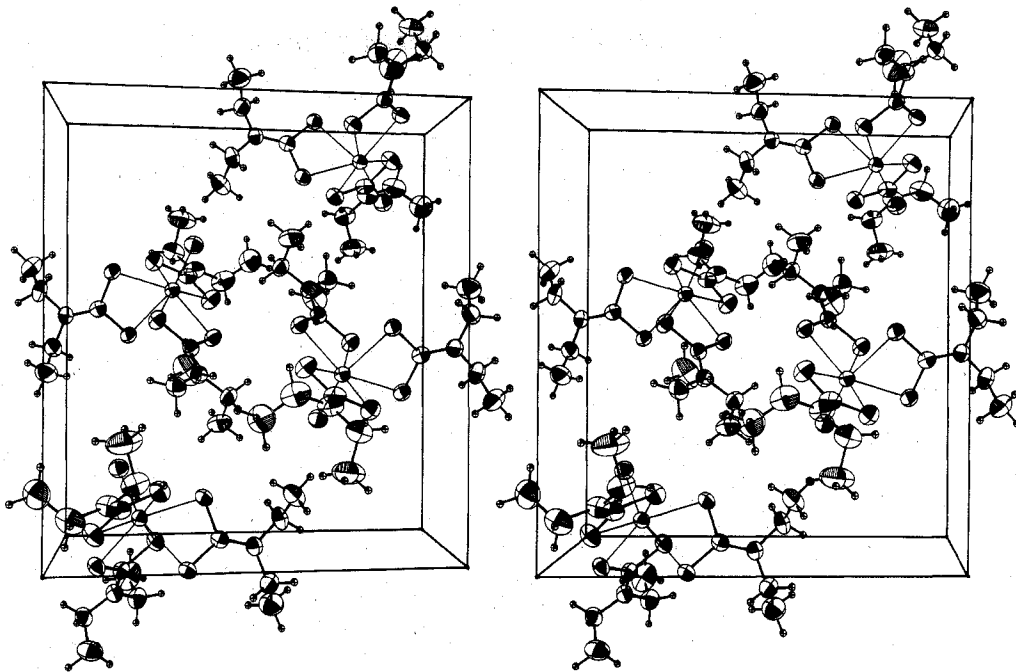


Figure 2. A stereodiagram of the unit cell and four molecules of $\text{TaS}(\text{S}_2\text{CNET}_2)_3$ viewed along the a axis.

seven arranged in a somewhat distorted pentagonal bipyramid. Recently, Muetterties and Guggenberger¹⁸ have developed a method for describing real molecules by referencing them to idealized polyhedra via geometric reaction pathways, which are characterized by the set of interfacial dihedral angles (δ) in the coordination polyhedron. Although their discussion is based upon a unidentate ML_7 system instead of a $\text{ML}(\text{AA})_3$ system and hence would be of limited usefulness in the present case,¹⁹ the dihedral angles given in Table IV are similar to those for an idealized pentagonal bipyramid. However, the dihedral angles are difficult to interpret in establishing the mode of distortion from an idealized pentagonal bipyramid in this $\text{ML}(\text{AA})_3$ case; therefore, we shall examine other parameters for this purpose.

In $\text{TaS}(\text{S}_2\text{CNET}_2)_3$, seven-coordination is achieved by placing the monodentate sulfido ligand at the axial position of a distorted pentagonal bipyramid; one dithiocarbamate ligand spans the other axial position and an equatorial site. The remaining four equatorial sites are then taken by the other two dithiocarbamate ligands. A study of the repulsive energy for $\text{ML}(\text{AA})_3$ complexes by Kepert²⁰ shows a broad minimum in the potential energy surface near the position that corresponds to a pentagonal bipyramid. Given that the normalized bite²¹ for the equatorial dithiocarbamate ligands is 1.11 in $\text{TaS}(\text{S}_2\text{CNET}_2)_3$, these calculations predict that the pentagonal bipyramid will be distorted but still retain C_s - m symmetry. The Ta atom, the monodentate sulfido ligand, and one dithiocarbamate ligand would be in the mirror plane and the other two dithiocarbamate ligands would be symmetrically disposed across the mirror plane.

In the structure of $\text{TaS}(\text{S}_2\text{CNET}_2)_3$, the principal distortion from a pentagonal bipyramid takes the form predicted by Kepert; the root-mean-square displacement of Ta, S, S(a1), and S(a2) from the quasi-mirror plane is $\pm 0.021 \text{ \AA}$. The equatorial plane Ta, S(a2), S(b1), S(b2), S(c1), and S(c2) is closely perpendicular (88.7°) to the quasi-mirror plane but the atoms involved are displaced appreciably (root-mean-square displacement is $\pm 0.142 \text{ \AA}$) from the plane. As can be seen in Figure 3, which is a projection of the coordination group onto the quasi-mirror plane, these displacements do not disturb the approximate mirror relationships between the equatorial dithiocarbamate ligands. A similar coordination

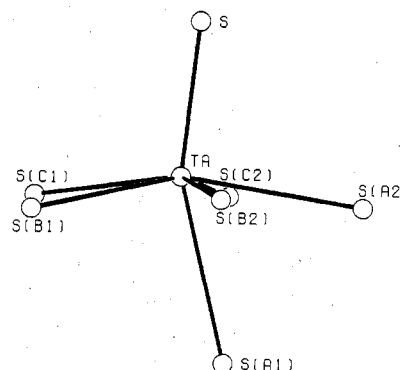


Figure 3. A projection of the coordination group onto the best plane through atoms Ta, S, S(a1), and S(a2).

geometry is adopted by many seven-coordinate complexes including η^5 -cyclopentadienyltris(hexafluoroacetylacetonato)zirconium(IV),²² chloro- and hydroxotris(tropolonato)tin(IV),²³ nitrosyltris(*N,N*-di-*n*-butyldithiocarbamato)molybdenum(IV),²⁴ and chlorotris(*N,N*-dimethyldithiocarbamato)titanium(IV)²⁵ and appears to be the preferred conformation for complexes of the type $\text{M}(\text{AA})_3\text{X}$ when X is a ligand which forms a relatively strong $\text{M}-\text{X}$ bond. Because the axial positions experience less repulsion energy, the monodentate X ligand is invariably in this position.²⁰ Also, a recent molecular orbital exploration¹⁹ of the seven-coordinate geometries suggests that in pentagonal-bipyramidal structures the axial positions are preferred by π -donor ligands for d^0 cases and by π -acceptor ligands for d^4 cases which is consistent with these structures.

An alternate distortion that did not reveal itself as a minimum in the potential energy surface²⁰ is that exhibited by chlorotris(acetylacetonato)zirconium(IV).²⁶ The coordination group in this structure displays approximate C_s - m symmetry with an oxygen atom for one of the equatorial acetylacetonate ligands in the quasi-mirror plane. Thus, the quasi-mirror symmetry does not extend to the carbon framework of the acetylacetonate ligands in contrast with the cases listed above. There is some tendency toward this type of distortion in $\text{TaS}(\text{S}_2\text{CNET}_2)_3$; of the five sulfur atoms in the pentagonal girdle, S(b2) is most displaced (0.090 \AA) from the

best plane rather than S(a2) as might be expected from the C_s - m geometry studied by Kepert.

The two axial bonds are not perpendicular to the equatorial plane although the Ta=S bond is nearly perpendicular (88.88°) to the plane Ta, S(a2), S(b2), S(c2) (root-mean-square deviation ± 0.092 Å). The position of S(a1) is determined by the small bite of the dithiocarbamate ligand which cannot permit a S-Ta-S bond angle of 90° . At first glance the position of the sulfido ligand is very sterically counterproductive. The S-S contacts to one side are much greater, 3.756 and 3.684 Å to S(b1) and S(c1), respectively, than on the other, 3.510 and 3.538 Å to S(b2) and S(c2), respectively. A calculation following Kepert²⁰ was made of the geometric part of the interligand repulsion energy as a function of the angular position of the monodentate sulfur atom relative to the pentagonal girdle. For both the $n = 6$ and $n = 12$ potentials the energy minimum was found for a rotation of the Ta=S bond of 5.5° directly away from S(a2) giving reductions of 1.9% and 7.2%, respectively, in the contribution to the molecular repulsion energy for the sulfido ligand. This is a displacement of the sulfido ligand of 0.200 Å from its observed position. A similar calculation for $TiCl(S_2CNMe)_3$ gives a rotation of 3.5° for the TiCl bond in exactly the same direction resulting in 0.6% and 2.25% reductions, respectively, in the potential energy and corresponds to a displacement of 0.121 Å for the Cl atom. This counterproductive distortion is quite common at least for dithiocarbamate complexes and frequently takes place as described for $TaS(S_2CNEt_2)_3$ but other directions for the displacement can occur.²⁷ It is not clear why these counterproductive distortions occur but the change in the repulsive energy is quite small and could result from an energetically minor electronic effect.

The Ta-S bond distance of 2.181 Å to the sulfido ligand is indicative of a multiple bond, a fact already inferred from infrared data. The electronic requirements of the metal atom and the sulfur suggest a bond order of 2. Unfortunately, there are no structures available which contain Ta-S multiple bonds, and, thus, direct comparison is not possible. The bond distance between the tantalum and the other axial sulfur, Ta-S(a1), is ca. 0.13 Å longer than the average length of the five equatorial bonds, 2.557 (25) Å, much in contrast to several other reports.^{23,25,27} However, in a report of a similar structure, $NbO(S_2CNEt_2)_3$, Dewan et al.²⁸ noted that the axial M-S bond is appreciably longer than the equatorial bonds. This is undoubtedly due to a shift in the electron density toward the metal-ligand multiple bond, which causes a weakening of the opposite axial M-S bond.

The equatorial Ta-S bonds are all similar and average to 2.557 (25) Å. Using the Slater²⁹ atomic radius for tantalum, an average sulfur atom radius of 1.11 Å is obtained which is in close agreement with sulfur radii in other seven-coordinate dithiocarbamate complexes.²⁷ The bonds Ta-S(b2) and Ta-S(c2) are ca. 0.05 Å longer than their counterparts Ta-S(b1) and Ta-S(c1) and may be a result of the relatively close contacts $S\cdots S(b2)$ and $S\cdots S(c2)$ as compared with $S\cdots S(b1)$ and $S\cdots S(c1)$. Curiously the shortest contact $S\cdots S(a2)$, 3.427 Å, involves the sulfur atom with a short Ta-S bond, 2.538 Å.

The $S\cdots S$ contacts in the equatorial plane are extremely short with an average interligand $S\cdots S$ distance of 3.07 (12) Å. This is 0.50 Å shorter than the sum of Pauling's³⁰ van der Waals radii of 1.80 Å and 0.30 Å shorter than the sum of radii suggested by van der Helm et al.³¹ and is a common feature of all seven-coordinate dithiocarbamate complexes. Interligand $S\cdots S$ distances of ca. 3.07 Å in trigonal-prismatic tris(1,2-dithiolene) complexes have been interpreted in terms of interdonor bonding forces³² and are consistent with the results of the molecular orbital calculations which show positive overlap between ligand orbitals.¹⁹ However, this type of

interaction does not seem to be possible with dithiocarbamate complexes.^{25,32} The bites of the dithiocarbamate ligands in both the equatorial and axial planes are normal, 2.839 Å average and 2.901 Å, respectively, and are appropriate for the Ta-S distances found in the complex.²⁷

The bond distances and angles within the dithiocarbamate ligands agree well with other reported structures which contain this ligand.^{32,33} The dimensions of the two equatorial dithiocarbamate ligands b and c are almost identical but ligand a, which spans an axial and an equatorial position, shows the effects of a somewhat larger bite and asymmetric Ta-S bonding. The largest effect is in the S-C-S angles, 115.2° for ligand a compared to a 111.7° average for ligands b and c, with smaller effects in the Ta-S-C and S-C-N angles. The C=N (average value 1.319 (6) Å) and the C-S (average value 1.716 (11) Å) distances are intermediate between the sum of the Pauling single-bond radii and the double-bond radii (C-N = 1.47 Å, C=N = 1.27 Å, C-S = 1.81 Å, C=S = 1.61 Å)³⁰ and indicate that there is considerable delocalized π bonding in the S_2CN portion of the ligands. In addition, the six atoms of the S_2C-NC_2 dithiocarbamate skeleton are coplanar in all three ligands with root-mean-square deviations of ± 0.040 , ± 0.045 , and ± 0.035 Å for ligands a, b, and c, respectively. The primary distortion in these planes is a slight twisting about the C=N bond; the angles between the S_2C and NC_2 planes are 5.63, 6.87, and 4.20° , respectively, for the ligands a, b, and c. In each case the Ta atom is slightly out of the plane of the ligand and the distortion is ascribed to a folding of the ligand at the S-S bite; the angles between the TaS_2 and S_2C planes are 2.20, 3.07, and 2.26° , respectively. The orientation of the ethyl groups in ligand c is syn while for ligands a and b they are anti. A syn ligand a was observed³⁴ in $Te(S_2CNEt_2)_3(C_6H_5)$ but all other seven-coordinate diethyldithiocarbamate complexes have anti ligands.

The atoms in the $TaS(S_2CNEt_2)_3$ molecule undergo thermal motion, with typical root-mean-square thermal displacements of 0.17–0.30 Å for the coordination sphere and somewhat greater, 0.17–0.36 Å, for the dithiocarbamate skeletons. The methyl groups experience substantial thermal motion with a maximum root-mean-square displacement for one of 0.46 Å. As a consequence, a riding correction³⁵ was applied to the bond lengths for these atoms. The corrected lengths are C(a1)–C(a3) = 1.543, C(a2)–C(a4) = 1.533, C(b1)–C(b3) = 1.527, C(b2)–C(b4) = 1.530, C(c1)–C(c3) = 1.517, and C(c2)–C(c4) = 1.515 Å which are more in accord with normal C–C single bonds than the uncorrected lengths.

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Registry No. $TaS(S_2CNEt_2)_3$, 31388-25-7.

Supplementary Material Available: A table listing observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Magnetic and Structural Characterization of Dibromo- and Dichlorobis(thiazole)copper(II)

WILLIAM E. ESTES, DIANE P. GAVEL, WILLIAM E. HATFIELD,* and DEREK J. HODGSON*

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The temperature dependence of the magnetic susceptibility and the electron paramagnetic resonance spectra of the thiazole complexes dichloro- and dibromobis(thiazole)copper(II) are reported, along with a complete three-dimensional x-ray structure analysis of the dichloro complex based on counter data. The dichloro complex, $\text{Cu}(\text{C}_2\text{H}_3\text{NS})_2\text{Cl}_2$, crystallizes in space group $P2_1/c$ of the monoclinic system with two independent formula units in a cell of dimensions $a = 7.332(6) \text{ \AA}$, $b = 3.853(4) \text{ \AA}$, $c = 17.493(17) \text{ \AA}$, and $\beta = 93.70(1)^\circ$. The structure has been refined by full-matrix least-squares methods using 1172 independent data to a final value of the conventional R factor (on F) of 0.028. The structure, which consists of infinite chains of doubly chloride-bridged copper(II) ions, is reminiscent of those of the pyridine analogues, with a Cu-Cu separation of $3.853(4) \text{ \AA}$ and bridging angle of $91.89(2)^\circ$. The magnetic data and interchain exchange interactions are discussed in the light of the structural properties of the systems.

Introduction

Current interest in one-dimensional exchange-coupled magnetic systems has recently stimulated a considerable number of theoretical and experimental studies as well as several comprehensive reviews.¹⁻⁵ Most of the theoretical work has centered on completely *isolated* one-dimensional models, while the experimental work has reflected the longer range interactions which always occur in real crystals.

From the theoretical standpoint, most of the investigations have centered on the use of the various forms of the spin-spin Hamiltonian (1), where J is the exchange integral, S_x , S_y , and

$$H = -2J \sum_{i < j} [a \hat{S}_z^i \cdot \hat{S}_z^j + b (\hat{S}_x^i \cdot \hat{S}_x^j + \hat{S}_y^i \cdot \hat{S}_y^j)] \quad (1)$$

S_z are the components of the total spin (S), the ratio a/b is an anisotropy parameter, and i and j label adjacent ions. For the case $a = 1$ and $b = 0$, the Ising model is obtained; and, in the special case for $S = 1/2$, an "exact" closed-form solution has been obtained for the magnetic and thermodynamic properties of a one-dimensional chain.⁴⁻⁶ If the spins are restricted to lie in the xy plane, i.e., $a = 0$ and $b = 1$, then the X-Y or planar Heisenberg model is obtained; and Katsura⁷ has obtained exact solutions for the $S = 1/2$ linear chain. Furthermore, when $a = b = 1$, the exchange interaction is isotropic and the Heisenberg model is obtained.⁸⁻¹⁰

Unfortunately, in the Heisenberg or isotropic limit, no closed-form solutions for magnetic or thermodynamic properties have yet been found; this being the case, almost all of the theoretical analyses have used some approximations to estimate the properties of linear chains.⁹ Bonner and Fisher⁸ studied the $S = 1/2$ antiferromagnetic Heisenberg chain and

performed computer calculations on finite rings and chains of isotropically interacting spins; they were able to estimate rather accurately the limiting behavior of the infinite linear system. Katsura and co-workers¹¹ have applied "linked-cluster" expansions via perturbation theory to estimate the various thermodynamic functions of interest. Finally, Baker, Rushebrooke, and co-workers^{9,10} have employed a high-temperature series-expansion method to study the magnetic and thermal properties of linear Heisenberg systems. Generally, the results of Bonner and Fisher have been most widely accepted.¹

Numerous experimental studies of linear-chain crystals have appeared in the literature.^{1-3,5} The results of these experiments have been analyzed in terms of the available one-dimensional (1-D) models. Transitions to the long-range, three-dimensional ordered state have also been observed for several of these systems. Since it is known from the theorems of Mermin and Wagner¹² that pure one- and two-dimensional isotropic systems cannot sustain long-range order at finite temperatures, considerable interest has been focused on linear Heisenberg complexes with small but finite *interchain* exchange.^{13,14}

Perhaps the most famous example of a nearly one-dimensional chain is provided by tetramethylammonium trichloromanganate(II) (TMMC), whose *intrachain* exchange is about 9 cm^{-1} with longer range *interchain* interactions being about 4 orders of magnitude smaller.¹⁶ For $S = 1/2$ complexes, copper tetraammine sulfate monohydrate (CTS) has been the most thoroughly studied,¹⁷⁻²¹ but some recently reported electron paramagnetic resonance results have been interpreted in terms of a quadratic rather than linear model.²² Finally, one of the best known examples of a $S = 1/2$ Heisenberg chain