

Synthesis, Structure, and Characterization of Bis(diethyldithiocarbamato)(diethylthiocarbamyl)sulfidoniobium(V) and Its Tantalum Analogue

P. F. Gilletti, D. A. Femec,[†] F. I. Keen,[‡] and T. M. Brown*

Department of Chemistry and Biochemistry, Bateman Science Center, Arizona State University, Tempe, Arizona 85287-1604

Received December 2, 1991

The compounds $MS(\eta^2\text{-SCNEt}_2)(\eta^2\text{-S}_2\text{CNEt}_2)_2$ ($M = \text{niobium or tantalum}$) have been prepared from the reaction of $\text{NaS}_2\text{CNEt}_2$ with $\text{M}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$. These new compounds were characterized using spectroscopic methods and X-ray crystallography. $\text{NbS}(\text{SCNEt}_2)(\text{S}_2\text{CNEt}_2)_2 \cdot 1/4\text{C}_6\text{H}_6$ crystallizes in the triclinic space group, $P\bar{1}$, with cell parameters of $a = 10.390(4) \text{ \AA}$, $b = 14.002(3) \text{ \AA}$, $c = 18.314(11) \text{ \AA}$, $\alpha = 104.39(4)^\circ$, $\beta = 93.13(4)^\circ$, $\gamma = 90.11(3)^\circ$, $V = 2576(2) \text{ \AA}^3$, and $Z = 4$. The coordination sphere of the metal(V) atom consists of a lone sulfur atom, two chelating dithiocarbamate ligands, and one thiocarbamyl ligand bound through both the carbon and the sulfur atoms. The resulting structure is a seven-coordinate pentagonal bipyramid having the lone sulfur atom and a sulfur from one of the dithiocarbamate ligands occupying the polar positions. The formation of a sulfur ligand and thiocarbamyl ligand, SCNEt_2^- , corresponds to the oxidative addition of one C-S bond to the metal(III) center with concomitant cleavage of the dimer. A dimeric compound with bridging tridentate dithiocarbamate ligands is proposed as a necessary intermediate for the oxidative addition reaction to occur.

Introduction

The dimeric face-sharing bioctahedral niobium(III) and tantalum(III) compounds $\text{M}_2(\mu\text{-Cl})_2(\mu\text{-L})\text{Cl}_4\text{L}_2$ (**1**) [$\text{L} = \text{tetrahydrothiophene (THT)}$ or dimethyl sulfide]¹⁻⁴ have been shown to be viable starting materials for a large number of diverse reactions leading to a variety of products. Reactions with neutral bidentate ligands have resulted in the substitution of the neutral L ligands to form edge-sharing bioctahedral complexes $\text{M}_2(\mu\text{-Cl})_2\text{Cl}_4\text{B}_2$ ($\text{B} = \text{neutral bidentate ligand such as 1,2-bis(dimethylphosphino)methane, 1,2-bis(dimethylphosphino)ethane, 1,2-bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 2,5-dithiahexane, 2,2'-bipyridine}$).³⁻¹⁰ In each of these compounds only the neutral ligands are replaced while the metal centers remain in a +3 oxidation state and participate in a metal-metal double bond.

The dimeric starting materials **1** have also been found to react with substituted acetylenes to form a wide variety of products including monomers, dimers, trimers, and polymers.¹¹⁻¹⁴ Two examples of the dimeric compounds formed are $\text{Nb}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{THT})_2(\text{MeCC-}t\text{-Bu})_2$ ¹⁵ and $\text{Ta}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{THT})_2(\text{PhCCPh})_2$.¹⁶ In these compounds the metal centers are now in the +5 oxidation state and there is no longer any metal-metal interaction.

$\text{Ta}_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)\text{Cl}_4(\text{SMe}_2)_2$ has been found to undergo an oxidative-addition reaction with diphenyl disulfide (PhSSPh) to form the edge-sharing bioctahedral complex, $\text{Ta}_2(\mu\text{-SPh})_2\text{Cl}_6(\text{SMe}_2)_2$ with the oxidation state of each tantalum changing from III to IV.¹⁷ The reaction of $\text{Ta}_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)\text{Cl}_4(\text{SMe}_2)_2$ with diethyl disulfide forms the mixed oxidation state Ta(III)-Ta(IV) dimer $\text{Ta}_2(\mu\text{-SEt})_2(\mu\text{-Cl})\text{Cl}_4(\text{SMe}_2)_2$ and $\text{Nb}_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)\text{Cl}_4(\text{SMe}_2)_2$ reacted with tetraethylthiuram disulfide results in the monomeric seven-coordinate complex $\text{NbCl}_3(\text{S}_2\text{CNEt}_2)_2$.¹⁸

Although **1** has displayed a rich chemistry in which the neutral THT or SMe_2 ligands have been systematically replaced by neutral monodentate or bidentate ligands, the complete substitution of both the halide and the neutral ligands in the starting material has not been thoroughly studied. The diethyldithiocarbamate ligand was selected as a potential reactant to replace both the neutral and halide ligands in the starting material **1**. Our attempt to prepare $\text{M}_2(\text{S}_2\text{CNEt}_2)_6$ has led to the isolation of the oxidative addition products $\text{MS}(\text{SCNEt}_2)(\text{S}_2\text{CNEt}_2)_2$. The results of these reactions are reported herein.

Experimental Section

Materials and Methods. All manipulations were performed using standard vacuum line techniques or in a dry N_2 atmosphere. The $\text{M}_2\text{Cl}_6(\text{THT})_3$ starting compounds were prepared according to literature methods.^{1,2} Sodium diethyldithiocarbamate was purified by recrystallization from ethanol and dried under a dynamic vacuum for 48 h at 50 °C.

Infrared spectra were recorded on a Nicolet MX-1 FT spectrophotometer. Mass spectra were measured and recorded on a Varian MAT 312 double focusing spectrometer using a 70-eV ionizing voltage and a 225 °C temperature source. Elemental analyses were performed by either Galbraith Laboratories of Knoxville, TN, or by Guelph Chemical Laboratories Ltd. of Guelph, Ontario, Canada.

Synthesis. $\text{NbS}(\text{SCNEt}_2)(\text{S}_2\text{CNEt}_2)_2 \cdot \text{Nb}_2\text{Cl}_6(\text{THT})_3$ (0.5 g, 0.75 mmol) and $\text{NaS}_2\text{CNEt}_2$ (0.77 g, 4.5 mmol) were placed in an extraction vessel. Approximately 50 mL of toluene was distilled onto the reaction mixture and the resulting solution was stirred overnight, during which time the solution underwent a color change from purple to brown. The reaction mixture was filtered to remove the insoluble NaCl produced as

[†] Present address: EG & G Idaho Inc., Idaho Falls, ID.

[‡] Present address: Department of Chemistry, Clarion College, Clarion, PA.

- (1) Maas, E. T.; McCarley, R. E. *Inorg. Chem.* 1973, 12, 1096.
- (2) Templeton, J. T.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* 1978, 17, 1263.
- (3) Allen, A. D.; Naito, S. *Can. J. Chem.* 1976, 54, 2948.
- (4) Hubert-Pfalzgraf, L. G.; Tsunoda, M.; Riess, J. G. *Inorg. Chim. Acta* 1980, 41, 283.
- (5) Clay, M. E.; Brown, T. M. *Inorg. Chim. Acta* 1983, 72, 75.
- (6) Cotton, F. A.; Roth, W. J. *Inorg. Chim. Acta* 1983, 71, 175.
- (7) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* 1983, 22, 3654.
- (8) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chem.* 1983, 22, 375.
- (9) Cotton, F. A.; Duraj, S. A.; Falvello, L. R.; Roth, W. J. *Inorg. Chem.* 1985, 24, 4389.
- (10) Chakravarty, A. R.; Cotton, F. A.; Diebold, M. P.; Lewis, D. B.; Roth, W. J. *J. Am. Chem. Soc.* 1986, 108, 971.
- (11) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* 1979, 101, 5094.
- (12) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* 1980, 19, 2354.
- (13) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Organometallics* 1982, 1, 1640.
- (14) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* 1981, 14, 233.
- (15) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* 1981, 20, 1285.
- (16) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* 1984, 85, 17.

(17) Campbell, G. C.; Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Haw, J. F. *Inorg. Chem.* 1986, 25, 287.

(18) Canich, J. A. M.; Cotton, F. A. *Inorg. Chim. Acta* 1989, 159, 163.

Table I. Crystallographic Parameters for NbS(SCNET₂)(S₂CNET₂)₂·1/4C₆H₆

$a = 10.390 (4) \text{ \AA}$	space group: $P\bar{1}$
$b = 14.002 (3) \text{ \AA}$	$\mu = 9.2 \text{ cm}^{-1}$
$c = 18.314 (11) \text{ \AA}$	$\rho_{\text{calc}} = 1.44 \text{ g cm}^{-3}$
$\alpha = 104.39 (4)^\circ$	$\rho_{\text{obs}} = 1.50 \text{ g cm}^{-3}$
$\beta = 93.13 (4)^\circ$	transm coeff = 0.604–0.557
$\gamma = 90.10 (3)^\circ$	$\lambda = 0.710 73 \text{ \AA}$
$V = 2576 (2) \text{ \AA}^3$	$R = 5.51\%$ ^a
$Z = 4$	$R_w = 4.80\%$ ^b
$fw = 577.27$	goodness of fit = 1.4552
$T = 23^\circ \text{C}$	

^a $R = \sum |F_o| - |F_c| / \sum F_o$. ^b $R_w = \sum w(F_o - F_c)^2 / \sum w(F_o)^2$. $W = 1.000 / [\sigma^2(F) + \dots + 0.000325(F^2)]$.

a byproduct and the toluene was distilled off leaving a brown oil. The oil was solidified by stirring with hexanes (~50 mL) for 24 h. The hexanes were filtered off and the product dried under a dynamic vacuum for 24 h to yield a brown flaky solid. The brown product was extracted three times with 10 mL of cold benzene, leaving behind a bright yellow crystalline material (40–50% yield). The yellow crystalline material was dissolved in benzene and layered with hexanes, and after several hours crystals suitable for single-crystal X-ray studies were obtained. IR (KBr): $\nu(\text{C}=\text{N})$ 1504 and 1491 cm^{-1} ; $\nu(\text{C}-\text{S})$ 1000 cm^{-1} (all were strong). Anal. Calcd for NbS₆N₃C₁₅H₃₀: C, 33.51; N, 5.62; H, 7.81. Found: C, 33.35; N, 5.52; H, 7.81.

TaS(SCNET₂)(S₂CNET₂)₂. The above procedure was repeated using stoichiometric amounts of Ta₂Cl₆(THT)₃ and NaS₂CNET₂. The solution underwent a color change from brown to dark green, and after treatment with hexanes and extraction with cold benzene a yellow product was obtained (~20% yield). IR (KBr): $\nu(\text{C}=\text{N})$ 1506 and 1493 cm^{-1} ; $\nu(\text{C}-\text{S})$ 1000 cm^{-1} (all were strong). Anal. Calcd for TaS₆N₃C₁₅H₃₀: C, 28.79; N, 6.72; H, 4.83. Found: C, 28.70; N, 6.33; H, 4.86.

X-ray Crystallography. A crystal of NbS(SCNET₂)(S₂CNET₂)₂ possessing approximately cubic dimensions (0.25 mm on edge) was selected and mounted in a 0.5-mm glass capillary and sealed under an N₂ atmosphere. Least-squares refinement of 15 reflections measured with a Nicolet R3m/V2000 autodiffractometer at room temperature yielded the cell parameters. The lattice and crystallographic parameters are listed in Table I. Standard P3 centering, indexing, and data collection programs were used. Four intensity standards were measured every 50 reflections showing no decomposition over the collection time. The structure was solved using the SHELXTL-Plus computing package. The positions of niobium atoms were revealed by direct methods and the positions of the other non-hydrogen atoms were found by subsequent least-squares refinement cycles. All non-hydrogen atoms were refined with anisotropic temperature factors, and hydrogen atoms were placed at calculated positions with fixed temperature factors.

Results and Discussion

Syntheses. The reaction between stoichiometric amounts of M₂Cl₆(THT)₃ and NaS₂CNET₂ in toluene results in brown (Nb) or green (Ta) products having the stoichiometry M₂(S₂CNET₂)₆. Repeated extractions over a 48-h period of the bulk material with cold benzene results in the separation of yellow crystalline monomeric compounds having the composition MS(SCNET₂)(S₂CNET₂)₂. The yield of the monomeric products can be increased if the bulk materials are allowed to remain in solution for greater lengths of time.

Description of the Structure of NbS(SCNET₂)(S₂CNET₂)₂. The compound crystallizes in the triclinic crystal system. A computer program utilizing the method of Howells et al. indicated the cell to be centric.¹⁹ The structure was solved in the $P\bar{1}$ space group and attempts at solving in the space group $P\bar{1}$ further confirmed the cell to be centric. There are two independent molecules in the asymmetric unit of the structure. A thermal ellipsoid plot of the molecular structure of NbS(SCNET₂)(S₂CNET₂)₂ is displayed in Figure 1 and a packing diagram is shown in Figure 2. Final atomic coordinates and temperature factors are listed

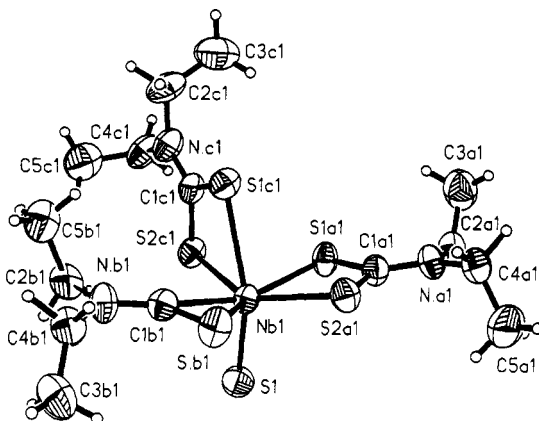


Figure 1. Thermal ellipsoid plot of one of the independent molecules NbS(SCNET₂)(S₂CNET₂)₂. Thermal ellipsoids are shown at 50% probability.

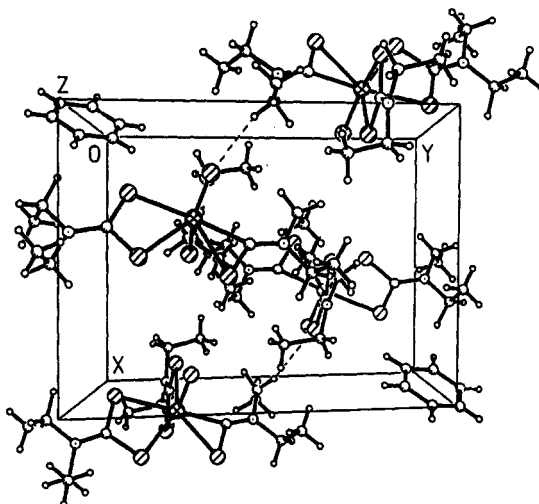


Figure 2. Packing diagram of NbS(SCNET₂)(S₂CNET₂)₂·1/4C₆H₆. Dashed lines indicate possible hydrogen bonding.

in Table II. Selected bond lengths and angles are listed in Tables III and IV, respectively.

The molecule has a distorted pentagonal bipyramidal structure with a dithiocarbamate ligand, the thiocarbamyl ligand, and one sulfur atom of the other dithiocarbamate ligand occupying the equatorial positions and forming the plane of the pentagonal girdle. The niobium atom lies approximately 0.38 Å out of the plane in the direction of the lone sulfur atom due to the Nb=S multiple bond. This effect is also observed in TaS(S₂CNET₂)₃,²⁰ NbS(S₂CNET₂)₃,²¹ and in the structurally analogous compound NbO(O₂C₇H₅)₃.²²

The lone sulfur atom and a sulfur of a dithiocarbamate ligand, S1c(*n*) (*n* = molecule 1 or 2), occupy the polar positions, but the average S(*n*)-Nb(*n*)-S1c(*n*) angle is ~156° instead of 180° since the dithiocarbamate ligand bite is too small to subtend 90° at the metal. A definite trans effect is seen here as the average Nb(*n*)-S1c(*n*) bond distance of 2.704 Å is at least 0.1 Å longer than any of the other niobium–dithiocarbamate sulfur bond lengths. This trans effect is also observed in TaS(S₂CNET₂)₃ and NbS(S₂CNET₂)₃ as well as in NbO(S₂CNET₂)₃²³ and NbO(O₂C₇H₅)₃.

The overall geometry of the thiocarbamyl ligand is largely unchanged from that of the dithiocarbamate ligand; however,

(19) (a) Program written by Thomas L. Groy, Arizona State University. (b) Howells, E. R.; Phillips, D. C.; Rogers, D. *Acta Crystallogr.* **1950**, *3*, 210.

(20) Peterson, E. J.; Von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1978**, *17*, 1410.

(21) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1985**, 1821.

(22) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *Inorg. Chim. Acta* **1986**, *118*, 165.

(23) Dewan, J. C.; Kepert, D. L.; Raston, C. L.; Taylor, D.; White, A. H.; Maslen, E. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2082.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{NbS}(\text{SCNET}_2)(\text{S}_2\text{CNET}_2)_2 \cdot 1/4\text{C}_6\text{H}_6$

	x	y	z	U(eq)
Nb(1)	902 (1)	2369 (1)	2796 (1)	40 (1)
S(1)	-559 (2)	2826 (1)	3618 (1)	57 (1)
S(1a1)	310 (2)	499 (1)	2418 (1)	51 (1)
S(2a1)	2559 (2)	1365 (1)	3309 (1)	49 (1)
C(1a1)	1648 (6)	306 (4)	2941 (3)	48 (2)
N.a(1)	1978 (5)	-557 (4)	3058 (3)	53 (2)
C(2a1)	1079 (9)	-1423 (6)	2816 (5)	70 (3)
C(3a1)	1428 (9)	-2074 (6)	2084 (5)	90 (4)
C(4a1)	3240 (7)	-696 (6)	3442 (5)	64 (3)
C(5a1)	3139 (8)	-602 (7)	4263 (4)	93 (4)
S.b(1)	2650 (2)	3610 (1)	3321 (1)	58 (1)
C(1b1)	1481 (6)	3841 (5)	2719 (3)	48 (2)
N.b(1)	1352 (5)	4659 (4)	2501 (3)	57 (2)
C(2b1)	300 (7)	4770 (6)	1937 (5)	61 (3)
C(3b1)	1720 (8)	6145 (5)	3543 (5)	81 (4)
C(4b1)	2180 (7)	5537 (6)	2825 (5)	61 (3)
C(5b1)	797 (7)	4723 (6)	1186 (4)	72 (3)
S(1c1)	1888 (2)	1942 (1)	1418 (1)	51 (1)
S(2c1)	-809 (2)	2257 (1)	1714 (1)	48 (1)
C(1c1)	334 (6)	1995 (4)	1057 (3)	43 (2)
N.c(1)	64 (5)	1856 (4)	323 (3)	56 (2)
C(2c1)	1074 (7)	1659 (7)	-239 (4)	68 (4)
C(3c1)	1371 (9)	602 (7)	-510 (5)	98 (5)
C(4c1)	-1302 (8)	1892 (7)	23 (4)	67 (3)
C(5c1)	-1618 (8)	2889 (6)	-72 (4)	89 (4)
Nb(2)	6350 (1)	-3133 (1)	1862 (1)	46 (1)
S(2)	7840 (2)	-3607 (2)	1064 (1)	72 (1)
S(1a2)	7262 (2)	-1396 (1)	2549 (1)	65 (1)
S(2a2)	5075 (2)	-1766 (1)	1489 (1)	62 (1)
C(1a2)	6084 (6)	-898 (5)	2078 (4)	51 (3)
N.a(2)	5920 (5)	71 (4)	2180 (3)	57 (2)
C(2a2)	6819 (8)	792 (6)	2692 (5)	71 (4)
C(3a2)	6337 (8)	1141 (7)	3471 (5)	101 (4)
C(4a2)	4879 (8)	475 (6)	1785 (5)	70 (4)
C(5a2)	5269 (9)	656 (7)	1057 (5)	118 (5)
S.b(2)	4396 (2)	-4070 (1)	1199 (1)	60 (1)
C(1b2)	5464 (6)	-4599 (5)	1680 (3)	47 (2)
N.b(2)	5483 (5)	-5504 (4)	1743 (3)	54 (2)
C(2b2)	6540 (7)	-5875 (6)	2154 (5)	61 (3)
C(3b2)	6187 (8)	-6061 (6)	2881 (5)	89 (4)
C(4b2)	4482 (7)	-6237 (6)	1372 (5)	63 (3)
C(5b2)	4764 (8)	-6783 (6)	597 (4)	84 (4)
S(1c2)	5161 (2)	-2960 (1)	3164 (1)	53 (1)
S(2c2)	7832 (2)	-3457 (1)	2945 (1)	54 (1)
C(1c2)	6620 (6)	-3178 (4)	3567 (4)	50 (3)
N.c(2)	6803 (6)	-3149 (4)	4291 (3)	60 (2)
C(2c2)	5748 (10)	-2831 (7)	4823 (5)	79 (4)
C(3c2)	5000 (9)	-3680 (7)	4915 (5)	113 (5)
C(4c2)	8078 (8)	-3351 (6)	4612 (4)	68 (3)
C(5c2)	8305 (8)	-4429 (6)	4554 (5)	92 (4)
C(3)	86 (8)	870 (6)	4791 (5)	73 (4)
C(2)	-677 (8)	-772 (6)	4537 (4)	75 (4)
C(1)	-591 (8)	97 (7)	4331 (4)	73 (4)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

there are some differences. The average S-C-N angle of the thiocarbamyl ligands is 127.3° compared to the related S-C-N angles of the dithiocarbamate ligands, which average 123.0° . The Nb-C-N angle of the thiocarbamyl ligand is 153° (average). An M-C-N angle of this magnitude is not observed in either of the two reported molybdenum thiocarbamyl-containing compounds which are formed from dithiocarbamates, $\{\text{Mo}(\mu\text{-S})[\eta^2\text{-SCN}(\text{C}_3\text{H}_7)_2][\eta^2\text{-S}_2\text{CN}(\text{C}_3\text{H}_7)_2]\}_2^{24}$ and $\text{Mo}_2(\mu\text{-S})(\mu\text{-EtCCEt})(\eta^2\text{-SCNMe}_2)(\eta^2\text{-S}_2\text{CNMe}_2)_3$.²⁵ In the molybdenum complexes the Mo-C-N angles are 146.6 and 145.0° , respectively, and are comparable to the 145° observed in CS_2 bonding to platinum in $\text{Pt}(\text{PPh}_3)_2\text{CS}_2$.²⁶ The distortion to $\sim 153^\circ$ appears to be due to

Table III. Selected Bond Lengths (\AA) for $\text{NbS}(\text{SCNET}_2)(\text{S}_2\text{CNET}_2)_2$

molecule 1		molecule 2	
Nb(1)-S(1)	2.180 (2)	Nb(2)-S(2)	2.178 (3)
Nb(1)-S(1a1)	2.601 (2)	Nb(2)-S(1a2)	2.596 (2)
Nb(1)-S(2a1)	2.511 (2)	Nb(2)-S(2a2)	2.539 (3)
Nb(1)-S.b(1)	2.491 (2)	Nb(2)-S.b(2)	2.499 (2)
Nb(1)-C(1b1)	2.185 (7)	Nb(2)-C(1b2)	2.189 (7)
Nb(1)-S(1c1)	2.705 (2)	Nb(2)-S(1c2)	2.702 (3)
Nb(1)-S(2c1)	2.564 (2)	Nb(2)-S(2c2)	2.574 (3)
S(1a1)-C(1a1)	1.705 (7)	S(1a2)-C(1a2)	1.707 (7)
S(2a1)-C(1a1)	1.726 (6)	S(2a2)-C(1a2)	1.721 (6)
C(1a1)-N.a(1)	1.321 (9)	C(1a2)-N.a(2)	1.335 (9)
S.b(1)-C(1b1)	1.681 (7)	S.b(2)-C(1b2)	1.666 (7)
C(1b1)-N.b(1)	1.308 (9)	C(1b2)-N.b(2)	1.300 (9)
S(1c1)-C(1c1)	1.720 (6)	S(1c2)-C(1c2)	1.710 (7)
S(2c1)-C(1c1)	1.711 (6)	S(2c2)-C(1c2)	1.725 (7)
C(1c1)-N.c(1)	1.324 (8)	C(1c2)-N.c(2)	1.320 (9)

Table IV. Selected Bond Angles (deg) for $\text{NbS}(\text{SCNET}_2)(\text{S}_2\text{CNET}_2)_2$

molecule 1		molecule 2	
S(1)-Nb(1)-S(1a1)	97.2 (1)	S(2)-Nb(2)-S(1a2)	99.5 (1)
S(1)-Nb(1)-S(2a1)	109.1 (1)	S(2)-Nb(2)-S(2a2)	108.9 (1)
S(1a1)-Nb(1)-S(2a1)	68.0 (1)	S(1a2)-Nb(2)-S(2a2)	67.8 (1)
S(1)-Nb(1)-S.b(1)	101.4 (1)	S(2)-Nb(2)-S.b(2)	103.1 (1)
S(1a1)-Nb(1)-S.b(1)	144.8 (1)	S(1a2)-Nb(2)-S.b(2)	144.6 (1)
S(2a1)-Nb(1)-S.b(1)	77.7 (1)	S(2a2)-Nb(2)-S.b(2)	79.1 (1)
S(1)-Nb(1)-C(1b1)	97.4 (2)	S(2)-Nb(2)-C(1b2)	95.0 (2)
S(1a1)-Nb(1)-C(1b1)	161.2 (2)	S(1a2)-Nb(2)-C(1b2)	160.5 (2)
S(2a1)-Nb(1)-C(1b1)	117.7 (2)	S(2a2)-Nb(2)-C(1b2)	119.4 (2)
S.b(1)-Nb(1)-C(1b1)	41.5 (2)	S.b(2)-Nb(2)-C(1b2)	41.0 (2)
S(1)-Nb(1)-S(1c1)	156.5 (1)	S(2)-Nb(2)-S(1c2)	156.1 (1)
S(1a1)-Nb(1)-S(1c1)	82.6 (1)	S(1a2)-Nb(2)-S(1c2)	82.9 (1)
S(2a1)-Nb(1)-S(1c1)	92.7 (1)	S(2a2)-Nb(2)-S(1c2)	94.1 (1)
S.b(1)-Nb(1)-S(1c1)	91.5 (1)	S.b(2)-Nb(2)-S(1c2)	87.3 (1)
C(1b1)-Nb(1)-S(1c1)	79.3 (2)	C(1b2)-Nb(2)-S(1c2)	78.6 (2)
S(1)-Nb(1)-S(2c1)	90.3 (1)	S(2)-Nb(2)-S(2c2)	91.0 (1)
S(1a1)-Nb(1)-S(2c1)	77.7 (1)	S(1a2)-Nb(2)-S(2c2)	76.3 (1)
S(2a1)-Nb(1)-S(2c1)	142.1 (1)	S(2a2)-Nb(2)-S(2c2)	141.1 (1)
S.b(1)-Nb(1)-S(2c1)	131.3 (1)	S.b(2)-Nb(2)-S(2c2)	129.7 (1)
C(1b1)-Nb(1)-S(2c1)	90.5 (2)	C(1b2)-Nb(2)-S(2c2)	90.4 (2)
S(1c1)-Nb(1)-S(2c1)	66.6 (1)	S(1c2)-Nb(2)-S(2c2)	66.3 (1)
Nb(1)-S(1a1)-C(1a1)	88.1 (2)	Nb(2)-S(1a2)-C(1a2)	88.6 (2)
Nb(1)-S(2a1)-C(1a1)	90.7 (2)	Nb(2)-S(2a2)-C(1a2)	90.1 (3)
S(1a1)-C(1a1)-S(2a1)	112.9 (4)	S(1a2)-C(1a2)-S(2a2)	113.5 (4)
S(1a1)-C(1a1)-N.a(1)	124.6 (5)	S(1a2)-C(1a2)-N.a(2)	123.5 (5)
S(2a1)-C(1a1)-N.a(1)	122.4 (5)	S(2a2)-C(1a2)-N.a(2)	123.0 (5)
Nb(1)-S.b(1)-C(1b1)	59.5 (2)	Nb(2)-S.b(2)-C(1b2)	59.5 (2)
Nb(1)-C(1b1)-S.b(1)	79.0 (3)	Nb(2)-C(1b2)-S.b(2)	79.6 (3)
Nb(1)-C(1b1)-N.b(1)	155.0 (5)	Nb(2)-C(1b2)-N.b(2)	151.5 (5)
S.b(1)-C(1b1)-N.b(1)	125.8 (5)	S.b(2)-C(1b2)-N.b(2)	128.8 (5)
Nb(1)-S(1c1)-C(1c1)	86.7 (2)	Nb(2)-S(1c2)-C(1c2)	87.5 (2)
Nb(1)-S(2c1)-C(1c1)	91.5 (2)	Nb(2)-S(2c2)-C(1c2)	91.5 (2)
S(1c1)-C(1c1)-S(2c1)	115.2 (4)	S(1c2)-C(1c2)-S(2c2)	114.4 (4)
S(1c1)-C(1c1)-N.c(1)	121.5 (5)	S(1c2)-C(1c2)-N.c(2)	123.0 (5)
S(2c1)-C(1c1)-N.c(1)	123.3 (5)	S(2c2)-C(1c2)-N.c(2)	122.6 (5)

steric reasons as a model built to scale of the seven-coordinate niobium compound shows the ethyl groups of the thiocarbamyl ligand to come into contact with the ethyl groups of the axial to equatorial coordinated dithiocarbamate ligand (ligand C) when rotated about the N-C bonds. In addition, there is some evidence of possible hydrogen bonding between a methyl hydrogen of the thiocarbamyl ligand and a sulfur atom of a dithiocarbamate ligand of another molecule as shown by the dashed lines in Figure 2. This observation is not without precedence; the S-H distance of $\sim 2.87 \text{\AA}$ is within the established range for hydrogen bonding,^{27,28} and the S-H-C angle is almost linear (167°) which is the preferred geometry for hydrogen bonding. The acute S-Nb-C angle of $\sim 41^\circ$ is due to the short S-C distance

(24) Richard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182.

(25) Herrick, R. S.; Nietzer-Burmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2599.

(26) Mason, R.; Rae, A. I. *J. Chem. Soc. A* **1970**, 1767.

(27) Cotton, F. A.; Wilkinson, J. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988; pp 89-94.

(28) Krebs, B. *Agnew. Chem., Int. Ed. Engl.* **1983**, *22*, 113.

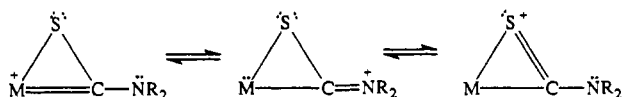
Table V. Characteristic Mass Spectral Data of Bulk Reaction Product and MS(SCNET₂)(S₂CNET₂)₂ (M = Ta or Nb)

bulk reaction product ^a		NbS(SCNET ₂)(S ₂ CNET ₂) ₂	
m/e (rel intens)	assignt	m/e (rel intens)	assignt
685 (2)	NbL ₄ ⁺		
653 (4)	Nb(SCNET ₂)L ₃ ⁺		
621 (0.5)	Nb(SCNET ₂) ₂ L ₂ ⁺		
569 (15)	NbSL ₃ ⁺		
537 (62)	NbL ₃ ⁺	537 (100)	NbS(SCNET ₂)L ₂ ⁺
505 (12)	Nb(SCNET ₂)L ₂ ⁺	505 (9)	Nb(SCNET ₂)L ₂ ⁺
453 (21)	NbS ₂ L ₂ ⁺	453 (2)	NbS ₂ L ₂ ⁺
421 (58)	NbSL ₂ ⁺	421 (66)	NbSL ₂ ⁺
389 (18)	NbL ₂ ⁺	389 (17)	NbL ₂ ⁺

bulk reaction product ^a		TaS(SCNET ₂)(S ₂ CNET ₂) ₂	
m/e (rel intens)	assignt	m/e (rel intens)	assignt
657 (16)	TaSL ₃ ⁺		
625 (39)	TaL ₃ ⁺	625 (67)	TaS(SCNET ₂)L ₂ ⁺
593 (2)	Ta(SCNET ₂)L ₂ ⁺	593 (13)	Ta(SCNET ₂)L ₂ ⁺
541 (19)	TaS ₂ L ₂ ⁺	541 (2)	TaS ₂ L ₂ ⁺
509 (72)	TaSL ₂ ⁺	509 (100)	TaSL ₂ ⁺
477 (10)	TaL ₂ ⁺	477 (18)	TaL ₂ ⁺

^a 100% intensity obtained for [SCNET₂]. L = S₂CNET₂.

and leads to the distortion in the pentagonal plane in which the C1b(n)-Nb(n)-S2c(n) interligand angle is $\sim 90^\circ$ compared to $\sim 77^\circ$ found between the other ligands within the plane. The C-N bond and the S-C bonds of the thiocarbamyl ligand are ~ 0.02 and ~ 0.04 Å shorter than the average of those found in the dithiocarbamate ligands. In addition, the Nb-C bond length of 2.187 Å (average) is shorter than typical niobium-alkyl carbon bond lengths which are generally greater than 2.3 Å.²⁹⁻³¹ This general trend of shorter bond lengths was also observed in the two thiocarbamyl-containing molybdenum complexes. The short Nb-C bond distances suggest multiple bond character comparable to metal carbene bonding. The overall display of shorter bond lengths involving the thiocarbamyl carbon can be explained via the resonance structures discussed by Templeton and co-workers²⁵ and shown in the following resonance scheme:



Mass Spectrometry. In Table V appears a listing of the characteristic mass spectral data for the initial bulk reaction products and the MS(SCNET₂)(S₂CNET₂)₂ complexes along with their peak assignments. A molecular ion peak is not observed for either of the expected M₂(S₂CNET₂)₆ complexes in the bulk reaction products. This is somewhat to be expected since mass spectral work done on the related tungsten complex, W₂(S₂CNET₂)₆,³² also failed to give a peak for the molecular ion with the largest mass/charge peak observed being [W(S₂CNET₂)₂S₂]⁺. The mass spectral data of both the niobium and the tantalum bulk products display mass/charge peaks larger than M(S₂CNET₂)₃. This, taken in conjunction with the observed diamagnetism and elemental analysis of these bulk products, suggests that the expected dinuclear species may be present. These products also most likely contain some of the MS(SCNET₂)(S₂CNET₂)₂ species since the oxidative addition reaction occurs slowly in solution.

The mass spectral data of the two MS(SCNET₂)(S₂CNET₂)₂ compounds are almost identical and can be readily explained. A

molecular ion, MS(SCNET₂)(S₂CNET₂)₂⁺, is observed for each compound. The next high mass/charge peak observed is assigned to M(SCNET₂)(S₂CNET₂)₂⁺ and corresponds to the loss of a sulfur atom. The mass/charge peak assigned to MS₂(S₂CNET₂)₂⁺ is formed by the loss of a CNET₂ group from the molecular complex and probably from the thiocarbamyl ligand. The next mass peak is assigned to MS(S₂CNET₂)₂⁺, corresponding to either a loss of a sulfur from the MS₂(S₂CNET₂)₂⁺ ion or to the loss of the thiocarbamyl species from the molecular ion.

Infrared Spectroscopy. It is significant to note that although the infrared spectra of the initially formed bulk products and the reported thiocarbamyl-containing monomers are very similar; there is an important difference in the C=N stretching absorption band which occurs around the 1500-cm⁻¹ region. In the bulk products this band is a single band (1493 cm⁻¹ for Nb and 1500 cm⁻¹ for Ta), but in the monomeric thiocarbamyl compounds, this band appears as two peaks separated by more than 10 cm⁻¹ (for Nb, 1505 and 1491 cm⁻¹; for Ta, 1506 and 1495 cm⁻¹). The occurrence of two bands is due to the fact that the C=N bond of the thiocarbamyl ligand is no longer equivalent to the C=N bond found in the dithiocarbamate ligands and the stretching band attributed to the former is shifted to higher energy since the carbon atom is strongly bonded to the metal atom. Perhaps this band could be useful in studying other dithiocarbamate compounds in which this type of ligand transformation is possible.

It is somewhat surprising that the C-S band appearing at ~ 1000 cm⁻¹ is a single peak in the infrared spectra of the thiocarbamyl containing monomers since there are two different C-S environments and this band is often used to indicate whether the dithiocarbamate ligand is coordinated in a monodentate or bidentate mode.³³ It is conceivable that a second band is masked by another band. However, in the compounds NbS(S₂CNET₂)₃ and TaS(S₂CNET₂)₃, two ν (C-S) bands were detected (1009 and 1000 cm⁻¹ for NbS(S₂CNET₂)₃ and 1009 and 1002 cm⁻¹ for TaS(S₂CNET₂)₃), yet only chelating ligands were shown by X-ray methods to be present.^{20,21} Therefore, it appears that the ν (C-S) mode occurring around 1000 cm⁻¹ is not a good criteria for detecting the mode of coordination. This is in agreement with a study by Kellner et al.³⁴ on the IR and laser Raman spectra of a number of metal-dithiocarbamate complexes. At this point in time it appears that the only reliable method to determine the coordination mode of the ligand is by single-crystal X-ray studies.

Conclusions. The compounds MS(SCNET₂)(S₂CNET₂)₂ have been prepared in reproducible yields by the oxidative addition reactions of M₂Cl₆(THT)₃ with 6 equiv of NaS₂CNET₂. A comparison of the mass spectral data (Table V) for the bulk material initially formed and the data for the subsequent crystalline metal-thiocarbamyl products obtained shows that a single reaction product is not obtained in the initial reaction since mass/charge peaks of greater mass than the thiocarbamyl complexes are found in the spectra of the bulk materials but not in the spectra of the thiocarbamyl species. It is conceivable that the expected dimeric product, M₂(S₂CNET₂)₆, is initially formed with the metal in a +3 oxidation state. This metal-dithiocarbamate dimer then undergoes a self-induced oxidative addition reaction to form the monomeric MS(SCNET₂)(S₂CNET₂)₂ complexes with the metal in the +5 oxidation state.

The proposed oxidative addition reaction is not unprecedented in the literature. Two examples of products formed by oxidative addition reactions occurring in metal-dithiocarbamate complexes are the dimeric molybdenum compounds^{24,25} shown in reactions 1 and 2. In each compound the thiocarbamyl ligand and the sulfur ligand are formed from a dithiocarbamate ligand by a reaction that can be considered as the oxidative addition of one C-S bond to the metal center. It appears that a dimeric

(29) Seitz, K.; Behrens, U. *J. Organomet. Chem.* **1985**, *294*, C9.

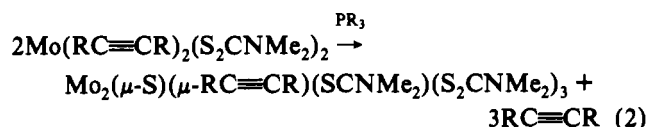
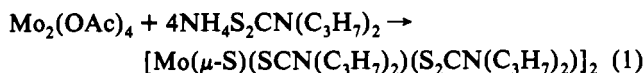
(30) Mercier, P. R.; Douglade, J.; Amaudrut, J.; Sala-Pala, J.; Guerschais, J. *Acta Crystallogr.* **1980**, *B36*, 2986.

(31) Drew, M. G. B.; Pu, L. S. *Acta Crystallogr.* **1977**, *B33*, 1207.

(32) Brown, D. A.; Glass, W. K.; Toma, H. J.; Waghorne, W. E. *J. Chem. Soc., Dalton Trans.* **1987**, 2531.

(33) Bonati, F.; Ugo, R. *J. Organomet. Chem.* **1967**, *10*, 257.

(34) Kellner, R.; St. Nikolov, G.; Trendafilova, N. *Inorg. Chim. Acta* **1983**, *84*, 233.

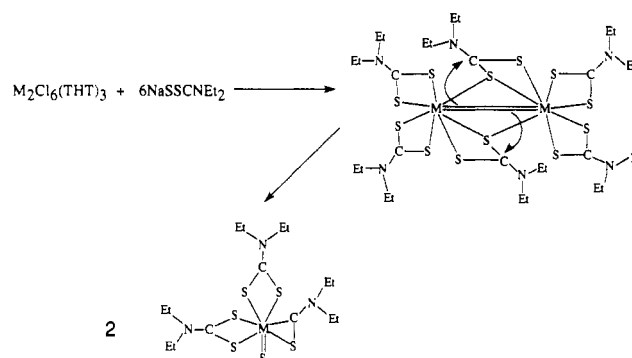


intermediate is involved in these reactions. It is reasonable that for the formation of the niobium and tantalum thiocarbamyls a dimeric intermediate structure of the type shown in Scheme I with bridging tridentate dithiocarbamate ligands is necessary for the oxidative addition reaction to occur.

The proposed coordination mode for the bridging ligands of the dimeric complexes shown in the reaction scheme is not without precedence in the literature. The ruthenium compound, $[\text{Ru}_2(\text{S}_2\text{CNEt}_2)_5]\text{BF}_4$,³⁵ has three bridging dithiocarbamate ligands. In the related molybdenum-xanthate complex, $\text{Mo}_2(\text{S}_2\text{COC}_2\text{H}_5)_4\text{I}_2$,³⁶ two tridentate bridging xanthate ligands with both sulfur atoms bridging and the carbon atom bonded to one of the metals, forming a total of five bonds for each ligand, are present. The bridging sulfur atom-metal bonds are essentially symmetrical with Mo-S bond lengths nearly equal to those found in the terminal ligands. The Mo-C bond distance of 2.302 (6) Å is indicative of strong bonding, and the Mo-Mo bond length of 2.723 (2) Å taken in accord with the electron counting scheme is considered indicative of a Mo-Mo bond order of 1.

In summary, $\text{M}_2(\mu\text{-Cl})_2(\mu\text{-L})\text{Cl}_4(\text{L})_2$ reacts with sodium diethylthiocarbamate with complete substitution of both the neutral and the halide ligands. Although it is apparent that the

Scheme I



expected $\text{M}_2(\text{S}_2\text{CNEt}_2)_6$ dimeric product is formed, this product is subject to an oxidative addition reaction which leads to the monomeric $\text{MS}(\text{SCNEt}_2)(\text{S}_2\text{CNEt}_2)_3$ product. This could occur as a nucleophilic attack of the metal-metal bond on the CS_2 carbon atom as shown in Scheme I. This type of attack has been suggested by Bereman and co-workers in the related molybdenum-dithiocarbamate compound (reaction 1).³⁷ It seems highly probable that this type of oxidative addition reaction will also occur in other dimeric metal systems. We are currently attempting to obtain crystals of the proposed metal dimer intermediates as well as investigating the related niobium and tantalum monothiocarbamate and xanthate systems.

Acknowledgment. D.A.F. wishes to thank W. S. Glaunsinger of the Arizona State University Chemistry Department for support of a postdoctoral research associateship. We are grateful to the Arizona State University X-ray facility for the use of their instrumentation.

Supplementary Material Available: Tables S1-S5, listing experimental details for the structural determination, thermal parameters, derived hydrogen parameters, and complete bond distances and angles (12 pages). Ordering information is given on any current masthead page.

(35) Mattson, B. M.; Heiman, J. R.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 564.

(36) Cotton, F. A.; Extine, M. W.; Niswander, R. H. *Inorg. Chem.* **1978**, *17*, 692.

(37) Bereman, R. D.; Baird, D. M.; Moreland, C. G. *Polyhedron* **1983**, *2*, 59.