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Variability of Niobium=Sulfur Multiple Bond Lengths: The Molecular Structures of Sulfido-tris(N,N-diethyldithiocarbamato)niobium(V)

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Abstract

In a further examination of the multiply bonded Nb=S group, the structure of $NbS(S_2CNEt_2)_3$ has been determined. The compound crystallizes in triclinic space group $P\bar{1}$ with a = 9.870(1), b = 15.743(2), c = 16.804(3) Å, α = 101.69(1)°, β = 93.51(1)°, γ = 91.12(1)°, and Z = 4. With use of 6709 unique data ($F_o^2 > 3\sigma(F_o^2)$) the structure was refined to $R(R_w)$ = 3.1(3.5%). The crystal contains two inequivalent molecules with distorted pentagonal bipyramidal coordination in which a sulfide atom occupies an axial position. The molecules are differentiated by ethyl group orientations and significantly different Nb=S bond lengths of 2.122(1) and 2.168(1) Å. Full structural details are reported. The results fall within the *ca.* 2.09–2.20 Å interval established with other molecules and emphasize the variability in bond length of the Nb=S group. Stretching frequencies and bond lengths show a rough inverse dependence. For square pyramidal $[NbSCl_4]^{1-}$, with a relatively high Nb=S bond order, $\nu_{Nb=S}$ = 552 cm^{-1} is associated with a bond length of 2.085(5) Å and an overlap population of 0.64.

Introduction

Whereas terminal metal–oxo bonds with orders exceeding one abound in compounds containing highly oxidized transition metals, authenticated examples of the corresponding sulfido unit, written as M=S, are not extensive. To a substantial degree this situation has arisen because of the lack of good preparative routes to the M=S group, its hydrolytic sensitivity, and the apparent tendency of the group to revert to a bridging sulfido structure, *e.g.*, $M(\mu_2\text{-}S)_2M$. The Mo=S group, found in a variety of Mo(V, VI) complexes, is the most widespread specific example. In the earlier transition elements the M=S group is infrequently encountered. However, methods are emerging for its synthesis, particularly by the direct conversion M=O → M=S. A case in point is VS(acen)**, which has been prepared from VO(acen) by reaction with B_2S_3 in dichloromethane [1] or $(Me_3Si)_2S$ in acetonitrile [2]. A short V=S distance (2.061(1) Å) has been established by X-ray analysis [3]. Similarly, the conversion of $NbO(S_2CNEt_2)_3$ [2, 4] to $NbS(S_2CNEt_2)_3$ in 52% yield by reaction with $(Me_3Si)_2S$ has been accomplished [2].

Shown in Fig. 1 are the structurally established cases of the Nb=S group, found in $NbSCl_3(SPPh_3)$ (1) [5, 6], $[NbSCl_3(SPPh_3)]_2$ (2) [5, 6], $NbSBr_3(THT)_2$ (3)† [7], $[NbSCl_4]^{1-}$ (4) [8], and [Nb₆-

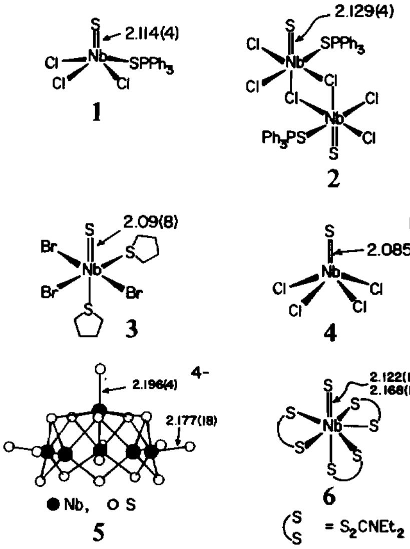

Fig. 1. Schematic depictions of structurally characterized Nb=S complexes 1–6. Reported bond lengths (Å) and e.s.d. values are given; for 5 the value (18) is the e.s.d. of the mean of five equatorial Nb=S bonds.

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**acen = N,N'-ethylenebis(acetylacetoneiminato) dianion.

†THT = tetrahydrothiophene.

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TABLE I. Summary of Crystal Data, Intensity Collection and Structure Refinement for $NbS(S_2CNEt_2)_3$.

formula (mol. wt.)	$C_{15}H_{30}N_3NbS_7$ (569.68)
a (Å)	9.870(1)
b (Å)	15.743(2)
c (Å)	16.804(3)
α (deg)	101.69(1)
β (deg)	93.51(1)
γ (deg)	91.12(1)
crystal system	triclinic
V (Å^3)	2551(1)
Z	4
d_{calcd} (obs) (g/cm^3)	1.48 (1.49[a])
space group	$P\bar{1}$
crystal dimensions (mm)	0.46 × 0.60 × 0.25
radiation	Mo Kα (λ = 0.71069 Å)
absorption coefficient, μ (cm^{-1})	10.1
scan speed (deg/min)	2.0–29.3 ($\theta/2\theta$ scan)
2θ limits	$3° \leqslant 2\theta \leqslant 54°$
scan range (deg)	$1.2 + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$
background/scan time ratio	0.25
data collected	9575 ($+h, \pm k, \pm l$)
unique data ($F_o^2 > 3\sigma(F_o^2)$)	6709
no. of variables	469
goodness of fit (GOF)[b]	1.17
R (R_w)[c] (%)	3.1 (3.5)

[a] Determined by the neutral buoyancy technique in CCl_4/n-hexane. [b] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$,

$S_{17}]^{4-}$ (5) [9]. Bond distances of this group are indicated; for the cage complex 5 the mean of five equatorial bond lengths under C_{5v} symmetry is given. The Nb=S distances are observed to vary substantially, by *ca.* 0.1 Å in the limited sample available. In order to examine further the range of such distances and their sensitivity to molecular and extrinsic factors, we report the structure of $NbS(S_2CNEt_2)_3$. This compound forms single crystals of high diffraction quality, which have the additional feature of containing two crystallographically inequivalent molecules.

Experimental

$NbS(S_2CNEt_2)_3$ was prepared as previously described [2].

Structure Determination of $NbS(S_2CNEt_2)_3$. Collection and Reduction of X-Ray Data

Yellow rectangular crystals were grown by slow cooling of concentrated acetonitrile solution. A suitable crystal was sealed in a glass capillary under dinitrogen. Diffraction studies were performed with a Nicolet R3m four-circle automated diffractometer and graphite-monochromatized Mo Kα radiation at ~23 °C. The final orientation matrix and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections having $20° \leqslant 2\theta \leqslant 25°$. Three standard reflections, monitored every 123 reflections, showed no signs of decay of intensities during the course of the data collection. Data collection was made to a diffraction angle 2θ of 54°. Details of the data collection and the crystal parameters are summarized in Table I. Data reduction was carried out with the program XTAPE of the SHELXTL structure determination program package (Nicolet XRD Corporation, Madison, Wisconsin, U.S.A.). An empirical absorption correction was applied with the program XEMP of the SHELXTL package. Maximum and minimum transmission factors were 0.94 and 0.75, respectively. After equivalent reflections were merged, R_{merg} was 2.5%. The intensity statistics suggested the centric space group $P\bar{1}$ (C_i [1], No. 2 [10]). Successful solution and refinement of the structure confirmed the space group assignment.

Solution and Refinement of the Structure

The direct methods program SOLV located two Nb atoms of two independent formula units that constitute the asymmetric unit. The remaining non-hydrogen atoms of two molecules were found by successive difference Fourier maps and blocked cascade least-squares refinements. Atom scattering factors were taken from a standard source [11].

TABLE II. Atom Coordinates ($\times 10^4$) for $NbS(S_2CNEt_2)_3$.

Atom[a]	x	y	z
Nb(1)	8208(1)[b]	7805(1)	5355(1)
Nb(2)	8558(1)	2444(1)	−57(1)
S(1)	9471(1)	8188(1)	6478(1)
S(2)	6107(1)	7385(1)	6065(1)
S(3)	6371(1)	8943(1)	5474(1)
S(4)	8774(1)	8918(1)	4505(1)
S(5)	10240(1)	7378(1)	4470(1)
S(6)	8517(1)	6203(1)	5379(1)
S(7)	6845(1)	6714(1)	4087(1)
S(8)	10183(1)	2379(1)	−835(1)
S(9)	8971(1)	4104(1)	451(1)
S(10)	9680(1)	2836(1)	1387(1)
S(11)	8658(1)	1068(1)	528(1)
S(12)	7213(1)	1153(1)	−978(1)
S(13)	7021(1)	3094(1)	−1045(1)
S(14)	6094(1)	2827(1)	504(1)
N(1)	4164(3)	8570(2)	6212(2)
N(2)	10923(3)	8578(2)	3611(2)
N(3)	7138(3)	5056(2)	4216(2)
N(4)	10437(3)	4511(2)	1886(2)
N(5)	7349(3)	−327(2)	−415(2)
N(6)	4498(3)	3385(2)	−615(2)
C(1)	5363(3)	8332(2)	5960(2)
C(2)	3630(4)	9422(3)	6116(3)
C(3)	4123(5)	10146(3)	6817(3)
C(4)	3286(4)	7999(3)	6560(2)
C(5)	3243(6)	8252(4)	7455(3)
C(6)	10112(4)	8324(2)	4118(2)
C(7)	10768(4)	9420(3)	3367(2)
C(8)	9845(5)	9360(3)	2618(3)
C(9)	12017(4)	8028(3)	3269(3)
C(10)	13321(5)	8215(4)	3803(4)
C(11)	7449(3)	5883(2)	4506(2)
C(12)	7676(4)	4370(2)	4628(3)
C(13)	6776(4)	4187(3)	5274(3)
C(14)	6167(4)	4760(3)	3512(2)
C(15)	6850(6)	4419(4)	2738(3)
C(16)	9791(3)	3916(2)	1324(2)
C(17)	10583(4)	5420(2)	1783(2)
C(18)	9569(5)[b]	6002(3)	2216(3)
C(19)	11103(4)	4305(3)	2629(2)
C(20)	12566(5)	4105(4)	2529(3)
C(21)	7690(3)	508(2)	−316(2)
C(22)	7787(4)	−846(2)	183(2)
C(23)	6758(4)	−865(3)	802(3)
C(24)	6521(4)	−776(2)	−1136(2)
C(25)	7378(5)	−1180(3)	−1805(3)
C(26)	5710(3)	3131(2)	−397(2)
C(27)	4168(4)	3560(3)	−1422(3)
C(28)	3614(5)	2768(3)	−2008(3)
C(29)	3398(4)	3490(3)	−46(3)
C(30)	3409(5)	4404(3)	451(3)

[a]See Fig. 2 for labelling schemes of molecules in this and following tables. [b]Estimated standard deviation in parentheses in this and following tables.

Although data collection was made to a 2θ angle of 54°, only 8062 data collected between $3° \leqslant 2\theta \leqslant 48°$ were employed in order to minimize computation time. With use of 6709 unique data, convergence was reached at R = 7.8% for isotropic, and at R = 4.3% for anisotropic, refinement of all non-hydrogen atoms. After hydrogen atoms were included in the two molecules at 0.96 Å from, and with isotropic thermal parameters 1.2x that of, the bonded carbon atom during the final stages of refinement, the weighting scheme was introduced and optimized. A final difference Fourier map revealed two weak peaks (0.47 $e^-/Å^3$) near the Nb atoms and several random features elsewhere ($\leqslant 0.42$ $e^-/Å^3$). Final R factors and other data are included in Table I. Positional and thermal parameters are collected in Tables II and III, respectively.

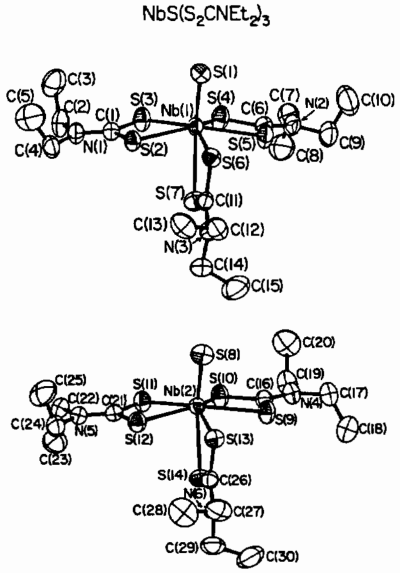

Fig. 2. Structures of the two independent $NbS(S_2CNEt_2)_3$ molecules, showing the atom numbering scheme and 50% probability ellipsoids.

Results and Discussion

Structures of the two independent molecules in the asymmetric unit are depicted in Fig. 2. The NbS_7 coordination units are shown in two views in Fig. 3. Bond distances and angles within these units are collected in Table IV. The two molecules are oriented such that the dihedral angle between planes S(2–6) and S(9–13) is 90.5°. The Nb atom is seven-coordinate, with the ligand atoms arranged in the form of a distorted pentagonal bipyramid (PBP)

TABLE III. Anisotropic Temperature Factors ($Å^2 \times 10^3$) for $NbS(S_2CNEt_2)_3$.

Atom	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb(1)	37(1)	40(1)	44(1)	7(1)	10(1)	0(1)
Nb(2)	39(1)	38(1)	42(1)	10(1)	3(1)	1(1)
S(1)	50(1)	76(1)	64(1)	4(1)	2(1)	−4(1)
S(2)	42(1)	45(1)	54(1)	15(1)	14(1)	2(1)
S(3)	53(1)	50(1)	73(1)	24(1)	25(1)	10(1)
S(4)	67(1)	54(1)	71(1)	22(1)	33(1)	8(1)
S(5)	55(1)	55(1)	77(1)	12(1)	30(1)	6(1)
S(6)	44(1)	44(1)	55(1)	11(1)	0(1)	3(1)
S(7)	65(1)	55(1)	44(1)	13(1)	−1(1)	1(1)
S(8)	57(1)	76(1)	88(1)	13(1)	9(1)	2(1)
S(9)	67(1)	42(1)	50(1)	15(1)	−12(1)	−3(1)
S(10)	69(1)	43(1)	53(1)	17(1)	−11(1)	−5(1)
S(11)	55(1)	41(1)	53(1)	13(1)	−5(1)	−3(1)
S(12)	53(1)	46(1)	49(1)	8(1)	−3(1)	−1(1)
S(13)	49(1)	52(1)	42(1)	16(1)	4(1)	5(1)
S(14)	47(1)	64(1)	42(1)	14(1)	7(1)	9(1)
N(1)	43(1)	53(2)	61(2)	11(1)	15(1)	6(1)
N(2)	60(2)	64(2)	59(2)	4(1)	29(1)	−11(1)
N(3)	46(2)	47(2)	64(2)	1(1)	7(1)	0(1)
N(4)	60(2)	48(2)	41(1)	13(1)	−3(1)	−8(1)
N(5)	44(1)	39(1)	58(2)	5(1)	6(1)	1(1)
N(6)	46(2)	57(2)	64(2)	21(1)	−0(1)	10(1)
C(1)	41(2)	46(2)	46(2)	6(1)	6(1)	2(1)
C(2)	57(2)	79(3)	88(3)	27(2)	27(2)	29(2)
C(3)	108(4)	58(3)	113(4)	12(3)	38(3)	14(2)
C(4)	46(2)	63(2)	81(3)	11(2)	21(2)	−5(2)
C(5)	147(5)	116(4)	84(3)	25(3)	36(3)	−53(4)
C(6)	54(2)	55(2)	57(2)	3(2)	17(2)	−8(2)
C(7)	75(3)	74(3)	66(2)	14(2)	25(2)	−21(2)
C(8)	103(4)	104(4)	73(3)	22(3)	15(3)	−14(3)
C(9)	69(3)	88(3)	87(3)	5(2)	37(2)	−7(2)
C(10)	69(3)	114(4)	147(5)	24(4)	29(3)	−6(3)
C(11)	43(2)	42(2)	49(2)	2(1)	14(1)	1(1)
C(12)	55(2)	44(2)	103(3)	8(2)	6(2)	4(2)
C(13)	73(3)	72(3)	107(4)	34(3)	−5(2)	−6(2)
C(14)	66(2)	65(2)	68(2)	−6(2)	2(2)	−10(2)
C(15)	136(5)	121(5)	69(3)	−5(3)	25(3)	−22(4)
C(16)	48(2)	42(2)	44(2)	12(1)	4(1)	−0(1)
C(17)	73(2)	50(2)	51(2)	12(2)	−3(2)	−11(2)
C(18)	100(4)	63(3)	117(4)	14(3)	12(3)	9(2)
C(19)	81(3)	63(2)	50(2)	18(2)	−13(2)	−13(2)
C(20)	80(3)	113(4)	89(3)	39(3)	−25(3)	1(3)
C(21)	38(2)	44(2)	49(2)	7(1)	8(1)	4(1)
C(22)	55(2)	40(2)	69(2)	13(2)	6(2)	6(1)
C(23)	85(3)	82(3)	89(3)	36(2)	28(2)	3(2)
C(24)	59(2)	49(2)	71(2)	6(2)	−3(2)	−4(2)
C(25)	100(4)	97(4)	86(3)	−28(3)	−3(3)	17(3)
C(26)	46(2)	40(2)	48(2)	10(1)	2(1)	0(1)
C(27)	57(2)	97(3)	90(3)	49(3)	−4(2)	12(2)
C(28)	102(4)	125(4)	63(3)	40(3)	−13(2)	−5(3)
C(29)	43(2)	84(3)	94(3)	32(2)	8(2)	13(2)
C(30)	98(4)	90(3)	133(5)	34(3)	50(3)	42(3)

[a] The anisotropic temperature factor exponent takes the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

whose apical positions are occupied by sulfide atoms S(1,8) and atoms S(7,14) from dithiocarbamate ligands spanning axial and equatorial sites. The remaining two dithiocarbamate ligands lie in the equatorial plane. Ligand structural information is provided in Table V. The molecular configuration

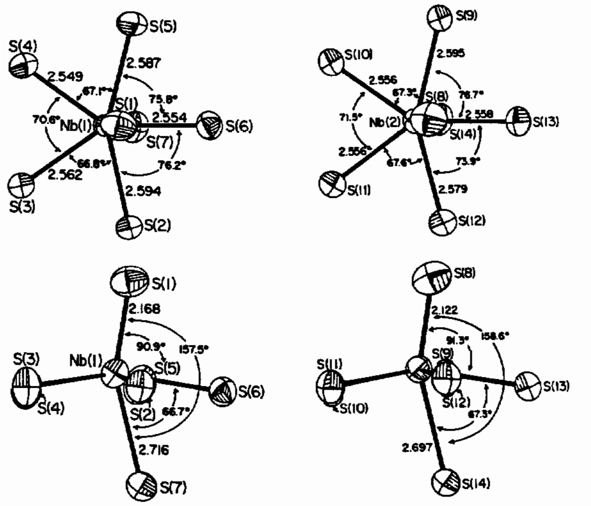

Fig. 3. Views showing the orientation of the Nb=S group of the two independent $NbS(S_2CNEt_2)_3$ molecules with respect to the least-squares planes S(2–6) and S(9–13) (top), and Nb(1)S(1,6,7) and Nb(2)S(8,13,14) (bottom).

is the same in essential details as those of other structurally characterized members of the seven-coordinate series $[MX(S_2CNR_2)_3]^{0,Z+}$. This extensive series includes $Ti(S_2CNEt_2)_3Cl$ [12], $VO(S_2CNEt_2)_3$ [13], $Mo(NO)(S_2CN(n\text{-}Bu)_2)_3$ [14], $[MoO(S_2CNEt_2)_3]^+$ [15], $Mo(SH)(S_2CNEt_2)_3$ [16], $[Mo(N_2PhEt)(S_2CN(CH_2)_5)_3]^+$ [17], $Re(CO)(S_2CNEt_2)_3$ [18], $RuCl(S_2CNEt_2)_3$ [19], $RuI(S_2CNMe_2)_3$ [20], and, most pertinent to the present work, $NbO(S_2CNEt_2)_3$ [13] and $TaS(S_2CNEt_2)_3$ [21]. The $MoN(S_2CNEt_2)_3$ portions of $[Mo_3N_2(S_2CNEt_2)_9]^{3+}$ [22] and either $MoO(S_2CNEt_2)_3$ fragment of the μ-oxo complex $[Mo_2O(S_2CNEt_2)_6]^+$ [23] also have distorted PBP structures, as do $Mo(SO_2)(S_2CNEt_2)_3$ [24] and $Ta(S_2)(S_2CNEt_2)_3$ [25] if the η^2-SO_2 and η^2-S_2 ligands are approximated as unidentate. Kepert's stereochemical model accommodates this configuration as a potential energy minimum [26]. In view of this treatment and the useful analysis of $TaS(S_2CNEt_2)_3$ by Peterson *et al.* [21], a brief description of the structure of $NbS(S_2CNEt_2)_3$ is provided.

TABLE IV. Interatomic Distances (Å) and Angles (deg) for the NbS_7 Coordination Sphere of $NbS(S_2CNEt_2)_3$.

Nb(1)–S(1)	2.168(1)	Nb(2)–S(8)	2.122(1)
Nb(1)–S(2)	2.594(1)	Nb(2)–S(9)	2.595(1)
Nb(1)–S(3)	2.562(1)	Nb(2)–S(10)	2.556(1)
Nb(1)–S(4)	2.549(1)	Nb(2)–S(11)	2.556(1)
Nb(1)–S(5)	2.587(1)	Nb(2)–S(12)	2.579(1)
Nb(1)–S(6)	2.554(1)	Nb(2)–S(13)	2.558(1)
Nb(1)–S(7)	2.716(1)	Nb(2)–S(14)	2.697(1)
S(1)–Nb(1)–S(7)	157.5(1)	S(8)–Nb(2)–S(14)	158.6(1)
S(1)–Nb(1)–S(6)	90.9(1)	S(8)–Nb(2)–S(13)	91.3(1)
S(1)–Nb(1)–S(2)	94.4(1)	S(8)–Nb(2)–S(9)	91.6(1)
S(1)–Nb(1)–S(5)	94.1(1)	S(8)–Nb(2)–S(12)	93.8(1)
S(1)–Nb(1)–S(3)	104.0(1)	S(8)–Nb(2)–S(10)	105.1(1)
S(1)–Nb(1)–S(4)	105.1(1)	S(8)–Nb(2)–S(11)	105.8(1)
S(2)–Nb(1)–S(3)	66.8(1)	S(9)–Nb(2)–S(10)	67.3(1)
S(4)–Nb(1)–S(5)	67.1(1)	S(11)–Nb(2)–S(12)	67.6(1)
S(6)–Nb(1)–S(7)	66.7(1)	S(13)–Nb(2)–S(14)	67.4(1)
S(3)–Nb(1)–S(4)	70.6(1)	S(10)–Nb(2)–S(11)	71.5(1)
S(2)–Nb(1)–S(6)	76.2(1)	S(9)–Nb(2)–S(13)	76.7(1)
S(5)–Nb(1)–S(6)	75.8(1)	S(12)–Nb(2)–S(13)	73.9(1)
S(2)–Nb(1)–S(5)	150.8(1)	S(9)–Nb(2)–S(12)	150.2(1)
S(2)–Nb(1)–S(4)	136.3(1)	S(9)–Nb(2)–S(11)	138.2(1)
S(3)–Nb(1)–S(5)	137.1(1)	S(10)–Nb(2)–S(12)	138.3(1)
S(3)–Nb(1)–S(6)	140.8(1)	S(10)–Nb(2)–S(13)	140.4(1)
S(4)–Nb(1)–S(6)	140.3(1)	S(11)–Nb(2)–S(13)	138.5(1)
S(2)–Nb(1)–S(7)	79.8(1)	S(9)–Nb(2)–S(14)	81.7(1)
S(5)–Nb(1)–S(7)	81.8(1)	S(12)–Nb(2)–S(14)	82.7(1)
S(3)–Nb(1)–S(7)	93.7(1)	S(10)–Nb(2)–S(14)	91.1(1)
S(4)–Nb(1)–S(7)	93.6(1)	S(11)–Nb(2)–S(14)	92.4(1)

TABLE V. Selected Interatomic Distances (Å) and Angles (deg) for the S_2CNEt_2 Ligands of $NbS(S_2CNEt_2)_3$.

C(1)–S(2)	1.710(3)	C(16)–S(9)	1.712(3)
C(1)–S(3)	1.721(3)	C(16)–S(10)	1.727(3)
C(6)–S(4)	1.718(4)	C(21)–S(11)	1.732(3)
C(6)–S(5)	1.714(4)	C(21)–S(12)	1.703(3)
C(11)–S(6)	1.734(3)	C(26)–S(13)	1.736(3)
C(11)–S(7)	1.707(3)	C(26)–S(14)	1.702(3)
N(1)–C(1)	1.317(4)	N(4)–C(16)	1.311(4)
N(1)–C(2)	1.486(5)	N(4)–C(17)	1.481(5)
N(1)–C(4)	1.466(5)	N(4)–C(19)	1.472(5)
N(2)–C(6)	1.316(5)	N(5)–C(21)	1.324(4)
N(2)–C(7)	1.474(6)	N(5)–C(22)	1.469(5)
N(2)–C(9)	1.469(5)	N(5)–C(24)	1.465(4)
N(3)–C(11)	1.317(4)	N(6)–C(26)	1.322(4)
N(3)–C(12)	1.486(5)	N(6)–C(27)	1.456(6)
N(3)–C(14)	1.468(5)	N(6)–C(29)	1.481(5)
C(2)–C(3)	1.513(6)	C(17)–C(18)	1.492(6)
C(4)–C(5)	1.479(6)	C(19)–C(20)	1.496(6)
C(7)–C(8)	1.493(6)	C(22)–C(23)	1.501(6)
C(9)–C(10)	1.512(6)	C(24)–C(25)	1.493(6)
C(12)–C(13)	1.513(7)	C(27)–C(28)	1.494(6)
C(14)–C(15)	1.508(6)	C(29)–C(30)	1.509(6)
Nb(1)–S(2)–C(1)	90.4(1)	Nb(2)–S(9)–C(16)	89.6(1)
Nb(1)–S(3)–C(1)	91.2(1)	Nb(2)–S(10)–C(16)	90.6(1)
Nb(1)–S(4)–C(6)	91.2(1)	Nb(2)–S(11)–C(21)	90.0(1)
Nb(1)–S(5)–C(6)	89.9(1)	Nb(2)–S(12)–C(21)	89.8(1)
Nb(1)–S(6)–C(11)	91.6(1)	Nb(2)–S(13)–C(26)	90.1(1)
Nb(1)–S(7)–C(11)	86.9(1)	Nb(2)–S(14)–C(26)	86.3(1)
S(2)–C(1)–S(3)	111.6(2)	S(9)–C(16)–S(10)	112.1(2)
S(4)–C(6)–S(5)	111.7(2)	S(11)–C(21)–S(12)	112.5(2)
S(6)–C(11)–S(7)	114.8(2)	S(13)–C(26)–S(14)	116.1(2)
S(2)–C(1)–N(1)	124.8(3)	S(9)–C(16)–N(4)	125.0(3)
S(3)–C(1)–N(1)	123.5(3)	S(10)–C(16)–N(4)	122.9(3)
S(4)–C(6)–N(2)	123.0(3)	S(11)–C(21)–N(5)	122.7(3)
S(5)–C(6)–N(2)	125.2(3)	S(12)–C(21)–N(5)	124.8(2)
S(6)–C(11)–N(3)	120.8(3)	S(13)–C(26)–N(6)	120.1(3)
S(7)–C(11)–N(3)	124.4(2)	S(14)–C(26)–N(6)	123.8(3)

The MS_7 coordination units are set out in detail in Fig. 3 and are further defined by the atom deviations from and dihedral angles between the least-squares planes in Table VI. The two nearly perfect planes 2 and 7, containing the chelate rings spanning axial and equatorial sites, behave as quasi-mirror planes across which the equatorial ligands are nearly symmetrically disposed. Equatorial bond angles deviate somewhat from the 72° value of a perfect PBP. For the equatorial ligands of the two molecules, the bite angles (66.8(1)–67.6(1)°) and S···S bite distances (2.839(2)–2.857(2) Å) fall into narrow ranges. Distances between equatorial sulfur atoms not in the same chelate ring, *e.g.*, S(3)···S(4) = 2.954(2) Å, S(2)···S(6) = 3.177(2) Å, and S(5)···S(6) = 3.159(2) Å, are larger than the bite distances. Atoms deviate significantly from the equatorial planes, the extremes being −0.064 (S(6)) to +0.069 Å (S(5)) in plane 1 and −0.123 (S(13)) to +0.111 (S(9)) in plane 2. Bond lengths in these planes average to 2.569(20) Å and 2.569(18) Å, respectively.

Another clear deviation from regular PBP geometry is found in the axial bond angles S(1)–

TABLE VI. Dihedral Angles (deg) between and Atom Position Deviations (Å) from Selected Unweighted Least-Squares Planes of $NbS(S_2CNEt_2)_3$.

Plane	Deviation[a] (±)	Angle	
1.S(2–6)	0.045(26)	1/2	90.4
2.Nb(1)S(1,6,7)	0.009(5)	1/3	90.6
3.Nb(1)S(1,6,7)C(11)	0.017(9)	1/4	8.3
4.Nb(1)S(2,3)C(1)	0.004(1)	1/5	8.4
5.Nb(1)S(4,5)C(6)	0.014(5)	1/6	90.2
6.S(9–13)	0.085(39)	2/3	0.6
7.Nb(2)S(8,13,14)	0.018(9)	6/7	90.0
8.Nb(2)S(8,13,14)C(26)	0.025(9)	6/8	90.2
9.Nb(2)S(9,10)C(16)	0.043(13)	6/9	7.1
10.Nb(2)S(11,12)C(21)	0.014(4)	6/10	7.8
		7/8	0.6

[a] Mean value for all atoms in the plane; standard deviation from the mean is given in parentheses.

Nb(1)–S(7) = 157.5(1)° and S(8)–Nb(2)–S(14) = 158.6(1)°. This feature and the nonplanarity of the equatorial sulfur atoms leads to the large range in angles S(1)–Nb(1)–S(2–6) = 90.9(1)–105.1(1)° and S(8)–Nb(2)–S(9–13) = 91.3(1)–105.8(1)°. Atoms Nb(1) and Nb(2) are displaced by 0.33 Å from their equatorial least-squares planes in the direction of the terminal sulfide ligands. The distances to these ligands, Nb(1)–S(1) = 2.168(1) Å and Nb(2)–S(8) = 2.122(1) Å, are short and are experimentally distinguishable. As expected, the bonds opposite S(1,8) are lengthened by the usual trans influence of multiply bonded terminal ligands. Relative to mean equatorial bond lengths, bond elongations are 0.15 Å for Nb(1)–S(7) and 0.13 Å for Nb(2)–S(14).

Comparison of the metric data in Tables IV and V reveals that, excluding the Nb=S groups, corresponding values for the two inequivalent molecules of $NbS(S_2CNEt_2)_3$ differ at most by 0.02 Å and 3°, and usually by less. The molecules appear to be significantly distinguished only by the orientations of the ethyl groups (Fig. 2). In the Nb(1) molecule the two equatorial ligands have *syn* and *anti* arrangements at N(1) and N(2), respectively. In the Nb(2) molecule an *anti* orientation obtains at both N(4) and N(5). An *anti* arrangement also occurs in the axial-equatorial ligand of each molecule. Neither $NbO(S_2CNEt_2)_3$ [13] nor $TaS(S_2CNEt_2)_3$ [21] is isomorphous with $NbS(S_2CNEt_2)_3$ or otherwise crystallizes in a form with inequivalent molecules; their structures (excluding the Nb=O group) are nearly isometric with that of the latter. These observations underscore the unexpected result of this investigation: the occurrence of two Nb=S groups whose bond lengths differ by 0.046 Å in the same molecular species, crystallographic differentiation of which appears otherwise to involve orientation of ethyl substituents at some distance from the coordination sphere. Given that Nb(V) and Ta(V) have identical seven-coordinate Shannon radii (0.84 Å) [27], bond distances very close to 2.181(1) Å for the Ta=S group of $TaS(S_2CNEt_2)_3$ [21] were expected. We are unable to discern a clear origin for the appreciable difference in Nb=S bond lengths, or for the pairing of the longer (shorter) Nb=S distance with the longer (shorter) *trans* Nb–S bond.

The Nb=S bond distances of $NbS(S_2CNEt_2)_3$ (**6**) fall within the *ca.* 2.09–2.20 Å range already established with **1**–**5** (Fig. 1) but are more precise. Comparable or slightly smaller distance intervals for other M=X groups, *e.g.*, Mo=O [28] and Mo=S [29], with the metal in a fixed oxidation state in different molecules, are not unknown but a ~0.05 Å difference such as observed with **6** is not anticipated. The larger e.s.d. values for other species in Fig. 1 tend to obscure any structural effects on Nb=S bond lengths. At the 3σ level of significance five-coordinate **1** and **4**, which might be expected to have the shortest Nb=S distances and highest bond orders owing to the absence of *trans* ligands, are just distinguishable but **1** and six-coordinate **2** are not. This is reflected by the $\nu_{Nb=S}$ frequencies of 536 (**1**) and 537 (**2**) cm^{-1} [6]. Values of $\nu_{Nb=S}$ cover the 552–483 cm^{-1} range [2, 6, 8, 9, 30–33] and show a rough parallel with Nb=S distances. The highest value is found with **4** [8] (and $NbSCl_3$ [30]), and the lowest with $[Nb_6S_{17}]^{4-}$ [9], whose bond lengths are the longest reported. The single resolvable feature of **6**, at 493 cm^{-1} (also reported at 502 cm^{-1} [31]), falls near the lower end of the scale. Extended Hückel calculations for **4**, which from distance and frequency results appear to have the highest bond order, were carried out in C_{4v} symmetry with the Nb atom 0.057 Å above the basal plane [8]. The Nb–Cl and Nb–S overlap populations are 0.37 and 0.64, respectively. The latter value is somewhat larger than those for the axial (0.58) and equatorial (0.60) groups of **5**, which were calculated by the same procedure [9]. The collective results of bond distances, stretching frequencies, and overlap populations demonstrate a real variability in the multiple bond order of the Nb=S group, which, however, will require additional structural data for proper clarification.

Lastly, the present and other recent results provide definition of the nature of three of the four members of the set $MX(S_2CNR_2)_3$ (M = Nb(V), Ta(V); X = O, S). Pure $NbS(S_2CNEt_2)_3$ and $TaS(S_2CNEt_2)_3$ are yellow [2, 21, 25], not green [31], with $\nu_{M=S}$ = 493 (Nb) [2] and 479 (Ta) cm^{-1} [25]. The value $\nu_{Ta=S}$ = 905 cm^{-1} [21] is incorrect. In the Ta system, a green component has been shown to be $Ta(S_2)(S_2CNEt_2)_3$ [25]. Earlier preparations of $MS(S_2CNEt_2)_3$ were apparently contaminated with the η^2-persulfide complexes. $NbO(S_2CNEt_2)_3$ [13], $NbS(S_2CNEt_2)_3$, and $TaS(S_2CNEt_2)_3$ [25] are isostructural. The remaining member, $TaO(S_2CNR_2)_3$, has not been reported.

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References

1 K. P. Callahan and P. J. Durand, *Inorg. Chem., 19,* 3211 (1980).
2 Y. Do, E. D. Simhon and R. H. Holm, *Inorg. Chem., 22,* 3809 (1983).
3 M. Sato, K. M. Miller, J. H. Enemark, C. E. Strouse and K. P. Callahan, *Inorg. Chem., 20,* 3571 (1981).
4 A. T. Casey, D. J. Mackey, R. L. Martin and A. H. White, *Aust. J. Chem., 25,* 477 (1972).
5 M. G. B. Drew, G. W. A. Fowles, R. J. Hobson and D. A. Rice, *Inorg. Chim. Acta, 20,* L35 (1976).
6 M. G. B. Drew and R. J. Hobson, *Inorg. Chim. Acta, 72,* 233 (1983).
7 M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc., Dalton Trans.,* 2251 (1983).
8 U. Muller and P. Klingelhofer, *Z. Anorg. Allg. Chem., 510,* 109 (1984).
9 J. Sola, Y. Do, J. M. Berg and R. H. Holm, *J. Am. Chem. Soc., 105,* 7794 (1973); *Inorg. Chem.,* in press.
10 'International Tables for X-ray Crystallography, Vol. III', Kynoch Press, Birmingham, 1973.
11 D. T. Cromer and J. T. Waber (eds.), 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.
12 D. F. Lewis and R. C. Fay, *J. Am. Chem. Soc., 96,* 3843 (1974).
13 J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White and E. N. Maslen, *J. Chem. Soc., Dalton Trans.,* 2082 (1973).
14 T. F. Brennan and I. Bernal, *Inorg. Chim. Acta, 7,* 283 (1973).
15 J. Dirand, L. Ricard and R. Weiss, *Transition Met. Chem., 1,* 2 (1975–76).
16 N. Dupré, H. M. J. Hendriks and J. Jordanov, *J. Chem. Soc., Dalton Trans.,* 1463 (1984).
17 F. C. March, R. Mason and K. M. Thomas, *J. Organomet. Chem., 96,* C43 (1975).
18 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.,* 486 (1974).
19 K. W. Given, B. M. Mattson and L. H. Pignolet, *Inorg. Chem., 15,* 3152 (1976).
20 B. M. Mattson and L. H. Pignolet, *Inorg. Chem., 16,* 488 (1977).
21 E. J. Peterson, R. B. Von Dreele and T. M. Brown, *Inorg. Chem., 17,* 1410 (1978).
22 M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse and M. Motevalli, *J. Chem. Soc., Chem. Commun.,* 780 (1976).
23 J. A. Broomhead, M. Sterns and C. G. Young, *Inorg. Chem., 23,* 729 (1984).
24 J. A. Broomhead, N. S. Gill, B. C. Hammer and M. Sterns, *J. Chem. Soc., Chem. Commun.,* 1234 (1982).
25 M. G. B. Drew, D. M. Williams and D. A. Rice, *Inorg. Chim. Acta, 89,* L19 (1984).
26 D. L. Kepert, *Prog. Inorg. Chem., 25,* 41 (1979).
27 R. D. Shannon, *Acta Crystallogr., Sect. A:, 32,* 751 (1976).
28 F. A. Schröder, *Acta Crystallogr., Sect. B:, 31,* 2294 (1975).
29 J. T. Hueneke and J. H. Enemark, *Inorg. Chem., 17,* 3698 (1978).
30 G. W. A. Fowles, R. J. Hobson, D. A. Rice and K. J. Shanton, *J. Chem. Soc., Chem. Commun.,* 552 (1976).
31 P. R. Heckley, D. G. Holah and D. Brown, *Can. J. Chem., 49,* 1151 (1971).
32 A. O. Baghlaf and A. Thompson, *J. Less-Common Met., 53,* 291 (1977).
33 D. A. Rice, *Coord. Chem. Rev., 25,* 199 (1978).