High-co-ordination-number Compounds of Niobium and Tantalum: Reactions of Niobium and Tantalum Halides and Sulphido-halides with Sodium Diethyldithiocarbamate. The Crystal Structures of $[Nb(S_2CNEt_2)_4]Br$, $Nb(S_2CNEt_2)_3S$, and $Ta(S_2CNEt_2)_3(S_2)$*

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The reactions of $Na(S_2CNEt_2)$ with niobium(v) halides lead to the formation of a mixture from which $[Nb(S_2CNEt_2)_4]Br$, (**1**), and $Nb(S_2CNEt_2)_3S$, (**2**), can be separated. The corresponding reactions with tantalum sulphido-halides gave $Ta(S_2CNEt_2)_3S$ and $Ta(S_2CNEt_2)_3(S_2)$, (**3**). The products (**1**)—(**3**) have been characterised by single-crystal *X*-ray structure determinations: (**1**), monoclinic, space group $P2_1/a$, $a = 11.100(8)$, $b = 27.910(18)$, $c = 10.680(9)$ Å, $\beta = 92.8(1)°$, and $Z = 4$; (**2**), triclinic, space group $P\bar{1}$, $a = 16.892(14)$, $b = 9.868(8)$, $c = 15.747(14)$ Å, $\alpha = 91.0(1)$, $\beta = 78.1(1)$, $\gamma = 85.8(1)°$, and $Z = 4$; (**3**), monoclinic, space group $C2/c$, $a = 16.319(9)$, $b = 10.887(8)$, $c = 30.322(25)$ Å, $\beta = 88.0(1)°$, and $Z = 8$. For compound (**1**), 2 612 above-background data were collected on a diffractometer and the structure refined to R 0.081; for (**2**) and (**3**) the corresponding values are 5 058, $R = 0.054$ and 1 814, $R = 0.099$ respectively. The structure of (**1**) is ionic and contains the $[Nb(S_2CNEt_2)_4]^+$ cation in which the metal is eight-co-ordinate with *mmmm* dodecahedral symmetry. The Nb–S distances range from 2.511(5) to 2.593(4) Å. The structure of (**2**) comprises two crystallographically distinct seven-co-ordinate monomers of $Nb(S_2CNEt_2)_3S$ of similar geometry, both with a multiple Nb=S bond [2.164(3) and 2.112(3) Å] and three chelating S_2CNEt_2 ligands. In both molecules the metal geometry is pentagonal bipyramidal with the multiple bond in an axial position. The structure of (**3**) contains discrete molecules of $Ta(S_2CNEt_2)_3(S_2)$ which are eight-co-ordinate with the metal in a distorted dodecahedral environment. Four *m* edges are occupied by three S_2CNEt_2 ligands and a side-on bonded disulphide group. The Ta–S distances range from 2.375(12) to 2.598(10) Å with a S–S distance of 2.074(17) Å.

Increasing interest has recently been shown in the formation of dithiocarbamate complexes of the Group 5A metals.[1] This has led to the preparation and characterisation of a variety of new complexes. Many of the compounds that have been isolated show interesting stereochemistries or redox properties.

The most obvious route to dialkyldithiocarbamate complexes of niobium- and tantalum-(v) is *via* the reactions of the pentahalides with anhydrous sodium diethyldithiocarbamate $Na(S_2CNEt_2)$. A wide variety of compounds can be isolated depending upon the nature of the solvent, stoicheiometry of the reagents, and reaction temperature.[2,3] It is not appropriate to give all the various reaction products and relevant conditions but a few are given by way of illustration.[2] Thus in benzene solution, with metal to ligand ratios of 1:4 or 1:5, mixtures of the compounds $M(S_2CNEt_2)_4X$ and $M(S_2CNEt_2)_3S$ (M = Nb or Ta, X = Cl or Br) were isolated, while under the same conditions, but with metal to ligand ratios of 1:3 or 1:2, $M(S_2CNEt_2)_3X_2$ and $M(S_2CNEt_2)_2X_3$ were obtained respectively.

However the reaction in CH_2Cl_2 with a 1:4 or 1:5 metal to ligand ratio led, after a short time, to the isolation of $M(S_2CNEt_2)_4X$ while prolonged reaction afforded $M(S_2CNEt_2)_2X_3$. There are other routes to diethyldithiocarbamates. For example, CS_2 can be inserted into tantalum(v) pentamides to give $Ta(S_2CNEt_2)_5$, whereas niobium(v) pentamides are reduced to $Nb(S_2CNEt_2)_4$ and a thiuram disulphide.[4]

The compounds $M(S_2CNEt_2)_3S$ (M = Nb or Ta) are of particular interest as these are formed *via* sulphur-abstraction reactions from $S_2CNEt_2^-$. Both compounds were reported as being green and air-stable.[2] However, other workers[5] reported the tantalum compound $Ta(S_2CNEt_2)_3S$ as being yellow. An *X*-ray study on these yellow crystals of $Ta(S_2CNEt_2)_3S$ (**4**) which are monoclinic revealed that the metal was in a seven-co-ordinate distorted pentagonal-bipyramidal environment with a terminal Ta=S group in an axial position and three chelating S_2CNEt_2 ligands.[5] It is interesting to note that the cell dimensions of these monoclinic crystals (**4**) are consistent with the *X*-ray powder data for the green forms of both $Ta(S_2CNEt_2)_3S$ and $Nb(S_2CNEt_2)_3S$ given in ref. 2.

As part of our studies into species containing Nb=S or Ta=S terminal bonds we decided to investigate fully the reactions of various niobium(v) and tantalum(v) halides and sulphide halides with $Na(S_2CNEt_2)$. The aim of the work was to investigate in particular the sulphur-abstraction reactions from $S_2CNEt_2^-$ and the ambiguities that exist in the literature regarding the colour of $Ta(S_2CNEt_2)_3S$.

Results and Discussion

From the Experimental section and the Scheme it can be seen that the reactions of MX_5 (M = Nb or Ta, X = Cl, or Br) with $Na(S_2CNEt_2)$ in MeCN do not give single products. The reactions of $TaCl_3S$ with $Na(S_2CNEt_2)$ are also complex. The elemental analyses and selected data from the i.r. spectra of the products are given in Table 1. For most of the products C, H, and N analyses do not distinguish between two possible products and indeed from the experimental figures obtained it is

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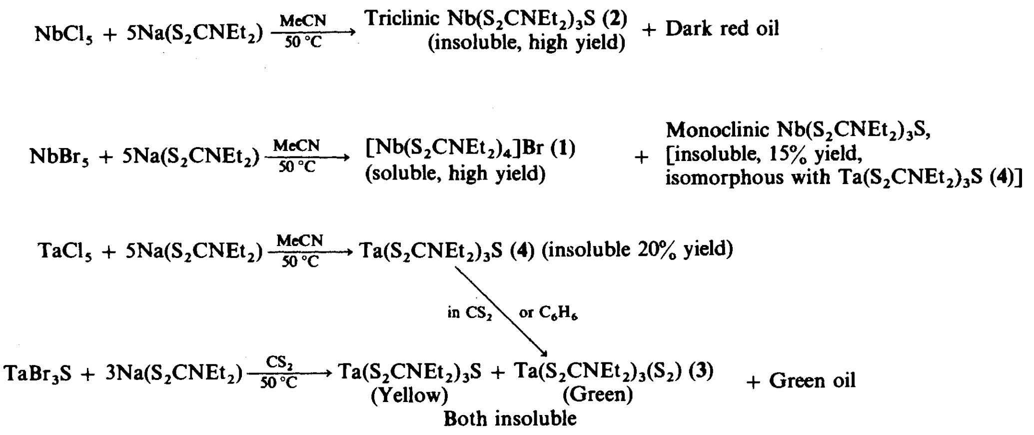
* Tetrakis(diethyldithiocarbamato-*SS'*)niobium(v) bromide, tris(diethyldithiocarbamato-*SS'*)sulphidoniobium(v), and tris(diethyldithiocarbamato-*SS'*)(disulphido-*SS'*)tantalum(v).

Supplementary data available (No. SUP 56264, 9 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



Scheme.

Table 1. Analytical and i.r. data for products

Reactants	Product	Analysis (%) M	C	H	N	I.r. bands (cm^{-1})[a] ν(C–N)	ν(C–S)	ν(M=S)	ν(M–S)
$NbCl_5 + 5Na(S_2CNEt_2)$	Insoluble	—	32.3	5.6	7.6	1 502s	1 009m, 1 000m	500vs	361s
$NbBr_5 + 5Na(S_2CNEt_2)$	Insoluble	16.0	31.5	5.5	7.5	1 510s, br	1 008m, 999m	497s	360s, br
		(16.3)	(31.6)	(5.3)	(7.4)[b]				
$NbBr_5 + 5Na(S_2CNEt_2)$	Soluble	—	32.2	5.7	7.6	1 510s, br	1 005m (sh), 995m	497w	362vs
		(—)	(31.3)	(5.2)	(7.3)[c]				
$TaCl_5 + 5Na(S_2CNEt_2)$	Insoluble	27.4	27.2	5.1	6.3	1 515s, br	1 009m, 1 002m	479s	357s, br
		(27.5)	(27.4)	(4.6)	(6.4)[d]				
$TaCl_3S + 3Na(S_2CNEt_2)$	Soluble	21.7	29.7	5.1	6.9	1 508m	980m	471s	360m
	Insoluble	22.5	29.8	5.0	7.0	1 509m, 1 495m	1 005m, 996m	471s	360m
$TaBr_3S + 3Na(S_2CNEt_2)$	Insoluble	—	26.0	4.4	6.2	1 500s	1 007m, 999m	473m	355m
	Soluble	—	27.5	4.7	6.1	1 500s	1 010m	473m	355m
		(26.2)	(26.1)	(4.4)	(6.1)[e]				
		(13.5)	(35.0)	(5.8)	(8.2)[f]				

[a] Nujol mulls. [b] Required for $Nb(S_2CNEt_2)_3S$. [c] Required for $[Nb(S_2CNEt_2)_4]Br$. [d] Required for $Ta(S_2CNEt_2)_3S$. [e] Required for $Ta(S_2CNEt_2)_3(S_2)$. [f] Required for $Nb(S_2CNEt_2)_4$.

apparent that some of the products are mixtures. The details of how the various products were isolated are given in the Experimental section.

From what has been reported in the literature and the results reported here it is evident that the abstraction of sulphur from $S_2CNEt_2^-$ by niobium- or tantalum-(v) halides is a facile process and irrespective of the reaction conditions leads to a mixture of products one of which is $M(S_2CNEt_2)_3S$ (M = Nb or Ta). It was hoped that by replacing MX_5 (M = Nb or Ta) by species containing a sulphur atom bound to niobium or tantalum, namely MCl_3S (M = Nb or Ta), the reaction would proceed more simply giving just one product. From the data given for the reactions with $TaCl_3S$ (Table 1 and Experimental section) it can be seen that this was not the case.

The reaction with $NbCl_3S$ was very complex. A visual inspection showed that several different soluble and insoluble products had been formed. Perhaps this is not surprising as $NbCl_3S$ has been shown to undergo a fascinating internal redox process.[6] The reaction was not investigated further because of the complicated nature of the products formed.

It has been reported that in MeCN the reactions of $NbCl_4$ and $TaCl_5$ with $Na(S_2CNEt_2)$ give $Nb(S_2CNEt_2)_4$ and $Ta(S_2CNEt_2)_5$ respectively.[3] In common with other workers (who used the pentahalides as starting materials) we found no evidence for the formation of $Ta(S_2CNEt_2)_5$, but unlike them did not detect the formation of the purple species $Nb(S_2CNEt_2)_4$.[2] That reduction should occur in the reaction of $NbCl_5$ with $Na(S_2CNEt_2)$ in benzene and dichloromethane solutions and yet fail to occur in our systems using MeCN at 50 °C is surprising as many reactions are known in which high-oxidation-state early transition-metal species are reduced in MeCN solution. However trace amounts of $Nb(S_2CNEt_2)_4$ may have been formed, as highly coloured oils were obtained in a number of the reactions that yielded niobium(v) compounds and $[Nb(S_2CNEt_2)_4]^+X^-$ and $Nb(S_2CNEt_2)_3S$ are known to be lightly coloured.

From the reaction of NbX_5 (X = Br or Cl) with $Na(S_2CNEt_2)$ we isolated as the insoluble products two crystallographically different forms of $Nb(S_2CNEt_2)_3S$ depending upon whether $NbCl_5$ or $NbBr_5$ was used in the preparation (see Scheme). As stated in the Experimental section, the product from the reaction with the bromide was isomorphous with monoclinic $Ta(S_2CNEt_2)_3S$ (4),[5] whereas the product from the reaction with the chloride [shown to be $Nb(S_2CNEt_2)_3S$ (2)] had a triclinic unit cell. The results of the single-crystal *X*-ray study of (2) are given below. The existence of two crystal forms was not observed previously and indeed it had been reported[2] that *X*-ray powder data on niobium- and tantalum-(v) diethyldithiocarbamate species were equivalent. However, in the previous work, C_6H_6 and CH_2Cl_2 were used as solvent whereas we used MeCN.

A further difference between the reactions involving the niobium(V) halides concerns the soluble products. With the chloride the major product was the insoluble one, namely $Nb(S_2CNEt_2)_3S$, with a small amount of soluble product whose character proved impossible to determine. In contrast, for the bromide $NbBr_5$ the major product was the soluble one, namely $[Nb(S_2CNEt_2)_4]Br$ (**1**), which is the subject of a single-crystal study (see later).

The reactions of the tantalum(V) halides with $Na(S_2CNEt_2)$ led to the formation of the yellow species $Ta(S_2CNEt_2)_3S$ (in 20% yield), whereas from the reaction of $TaCl_3S$ with $Na(S_2CNEt_2)$ the major products (>90%) were a mixture of $Ta(S_2CNEt_2)_3S$ and $Ta(S_2CNEt_2)_3(S_2)$. The latter is green. Both routes that led to $Ta(S_2CNEt_2)_3S$ gave compounds that were isomorphous with the known monoclinic form (**4**),[5] by contrast with niobium where two crystal forms of $M(S_2CNEt_2)_3S$ were isolated.

The structure of $Ta(S_2CNEt_2)_3(S_2)$ (**3**), a product which has not been previously identified, is detailed below. When first reported $Ta(S_2CNEt_2)_3S$ was described as green,[2] but when its structure was determined it was reported to be yellow.[5] It is probable that the first sample contained some $Ta(S_2CNEt_2)_3(S_2)$ which accounts for the reported green colour. When yellow $Ta(S_2CNEt_2)_3S$ was dissolved in CS_2 or C_6H_6 a yellow solution was formed. Over a period of 5 h the solution slowly turned green. Evaporation of the solvent led to the isolation of large rectangular green crystals and a smaller amount of a lighter green material. The green crystals were separated manually; the cell dimensions were similar but significantly different* from those of compound (**3**). It is regrettable that the nature of the second product from the benzene solutions of $Ta(S_2CNEt_2)_3S$ could not be determined as it may contain tantalum-(IV) or -(III).

Selected data from the i.r. spectra of the compounds are given in Table 1. The occurrence of a single ν(C–S) mode around 1 000 cm^{-1} is said to indicate the presence of bidentate S_2CNEt_2 while two bands are indicative of unidentate co-ordination.[7] In the spectra of pure samples of $Nb(S_2CNEt_2)_3S$ and $Ta(S_2CNEt_2)_3S$ two bands were detected and yet only chelating S_2CNEt_2 was shown by *X*-ray methods to be present. The ν(Ta=S) mode in $Ta(S_2CNEt_2)_3S$ has been previously assigned to a band at 905 cm^{-1} which is at very high energy for such a mode.[5] A strong band near 475 cm^{-1} is present in the spectra of all the tantalum products in Table 1 and this is believed to be the ν(Ta=S) stretch. Similarly in the spectra of the niobium compounds a band near 498(2) cm^{-1} is assigned to ν(Nb=S). These values are in accord with those observed for various compounds of the sulphido-halides MCl_3S (M = Nb or Ta).

The Crystal Structures of Compounds (**1**)—(**3**).—The structure of compound (**1**) contains discrete $[Nb(S_2CNEt_2)_4]^+$ and Br^- ions. The cation, shown in Figure 1 with the atomic numbering scheme, consists of a central Nb^V atom co-ordinated by eight sulphur atoms from the four bidentate S_2CNEt_2 ligands. These chelates span the four *m* edges of an idealised D_{2d} dodecahedron giving the *mmmm* isomer that is common for tetrakis(dithiocarbamate) complexes of the early transition elements[8,9] {*e.g.* $[Mo(S_2CNEt_2)_4]^+$,[10] $Ta(S_2CNMe_2)_4$,[11] and $[W(S_2CNEt_2)_4]^+$[12]}. The polyhedron shape parameters for compound (**1**) [and also (**3**)] are given in Table 2 along with values for these related species and the calculated dodecahedron.

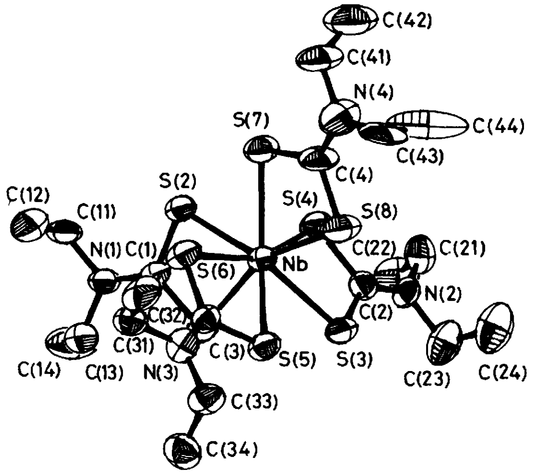


Figure 1. The structure of compound (**1**)

The root mean square (r.m.s.) deviation from ideal geometry of 0.013 Å is particularly small[8] and indicates very little distortion within the cation. Atoms S(2), S(3), S(5), and S(7) occupy the A sites in the dodecahedron and S(1), S(4), S(6), and S(8) the B sites. The average $Nb-S_A$ distance (2.579 Å) is longer than that of $Nb-S_B$ (2.530 Å). This reflects the greater repulsion energy experienced by the atoms at the A sites and is a common feature of the *mmmm* dodecahedron (Table 2).

The thermal parameters for the bromide anion are large and anisotropic indicating considerable freedom for the anion within the cation matrix, the closest Br···C approach being 3.60(2) Å. Attempts to refine the bromide ion in disordered positions with fractional occupancy were unsuccessful. Similarly, atom C(44) shows anomalous thermal motion suggesting some unresolved disorder.

The *X*-ray powder data for the species $[Nb(S_2CNEt_2)_4]X$ (X = Cl or Br) obtained by Heckley *et al.*[2] fit well with the cell dimensions of (**1**).

The yellow crystals of compound (**2**) were found to be a triclinic form of $Nb(S_2CNEt_2)_3S$. The asymmetric unit consists of two crystallographically distinct monomers, denoted by (**2A**) and (**2B**). The molecules have similar geometries but with some significant differences; Figure 2 shows molecule (**2A**) with the common numbering system. In the molecules, the metal is seven-co-ordinate with a distorted pentagonal-bipyramidal environment. The terminal sulphur atom occupies an axial position, a unique S_2CNEt_2 ligand spans the other axial position and an equatorial, position while the two remaining S_2CNEt_2 ligands occupy four equatorial sites. This geometry is also found in $Ta(S_2CNEt_2)_3S$,[5] $Nb(S_2CNEt_2)_3O$,[13] and $V(S_2CNEt_2)_3O$.[13] It is the most favoured seven-co-ordinate geometry for molecules containing a multiple bond and three chelating ligands.[14]

The r.m.s. deviations[14] from ideal pentagonal-bipyramidal geometry are 0.158 (**2A**) and 0.155 Å (**2B**). These deviations follow a similar pattern to those observed in $Ta(S_2CNEt_2)_3S$, $Nb(S_2CNEt_2)_3O$, and $V(S_2CNEt_2)_3O$ and occur because of the *trans* influence of the multiple bond and the fact that the 'bite' of the unique S_2CNEt_2 ligand [S(3) and S(4)] is too small to subtend 90° at the metal. The Nb=S multiple bond produces a steric effect as the metal atom is displaced towards it from the S_5 equatorial plane by 0.35(1) Å in molecule (**2A**) and 0.33(1) Å in (**2B**) (Table 3) and the Nb–S(4) bond distances *trans* to S(7) have a mean value of 2.71 Å, about 0.13 Å longer than the mean Nb–S distance to the other atoms. Similar deviations are observed in the other three compounds,[5,13] for example in $Ta(S_2CNEt_2)_3S$ the axial Ta–S(4) bond length is 2.682(1) Å, the

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* Both crystals were monoclinic, space group *C2/c*, with *Z* = 8. The cell dimensions of the new form were *a* = 16.909(12), *b* = 10.000(11), *c* = 33.28(2) Å, β = 108.6(1)° compared to *a* = 16.319(9), *b* = 10.887(8), *c* = 30.322(25) Å, and β = 88.0(1)° for (**3**). A structure determination showed that the crystals also contained $Ta(S_2CNEt_2)_3(S_2)$ with a dodecahedral structure similar to (**3**), but the data were not of sufficient quality to merit reporting here.

Table 2. Shape parameters for the *mmmm* dodecahedron found in compounds (**1**) and (**3**) and related species

Species	Ref.	Δ^a/Å	b^b	$\theta_A{}^c$/°	$\theta_B{}^c$/°	$(M-S_A)/(M-S_B)$
$[Nb(S_2CNEt_2)_4]Br$ (**1**)	This work	0.013	1.11	34.5	78.2	1.02
$Ta(S_2CNEt_2)_3(S_2)$ (**3**)	This work	0.079	1.10	34.6	79.1	1.01 for S_2CNEt_2
			0.86	42.4	86.9	1.05 for S_2
$[Mo(S_2CNEt_2)_4]Cl$	10	0.011	1.11	34.6	77.8	1.01
$[Mo(S_2CNEt_2)_4][Mo_6O_{19}]$	10	0.014	1.12	35.7	76.4	1.02
$Ta(S_2CNMe_2)_4 \cdot CH_2Cl_2$	11	0.015	1.11	35.0	77.4	1.03
$[Ta(S_2CNMe_2)_4][TaCl_6] \cdot 5CH_2Cl_2$	11	0.045	1.11	34.7	77.6	
$[W(S_2CNEt_2)_4]Br$	12	0.015	1.11	34.7	77.6	1.01
Hard-sphere model	30	0.000	1.20	36.9	69.5	1.00
Most favoured polyhedron	30	0.000	1.17	35.2	73.5	1.03

[a] R.m.s. deviation from ideal polyhedron, ref. 14. [b] Normalised bite distance. [c] θ_A and θ_B are the angles between the $\bar{4}$ axis and the $M-S_A$ and $M-S_B$ bonds respectively.

Table 3. Least-squares planes and contacts in compound (**2**). Values for molecule A precede those for molecule B

Atom	Deviation (Å) from S_5 plane*	S(7)–Nb–S(*n*) angle (°)	S(4)–Nb–S(*n*) angle (°)	S(7) ··· S(*n*) distance (Å)
Nb(1)	0.35, 0.33	—	—	—
S(1)	0.08, 0.10	94.3, 93.8	81.5, 82.9	3.35, 3.44
S(3)	−0.07, −0.12	91.1, 90.9	66.7, 67.8	3.38, 3.34
S(5)	0.04, 0.11	94.1, 91.4	80.2, 81.7	3.51, 3.39
S(2)	−0.06, −0.03	105.4, 106.2	93.1, 92.1	3.77, 3.74
S(6)	0.01, −0.06	103.3, 105.5	94.1, 90.5	3.71, 3.72
S(4)	−2.43, −2.35	157.8, 158.6	—	—
S(7)	2.63, 2.44	—	—	—

* Plane through atoms S(1), S(2), S(3), S(5), and S(6).

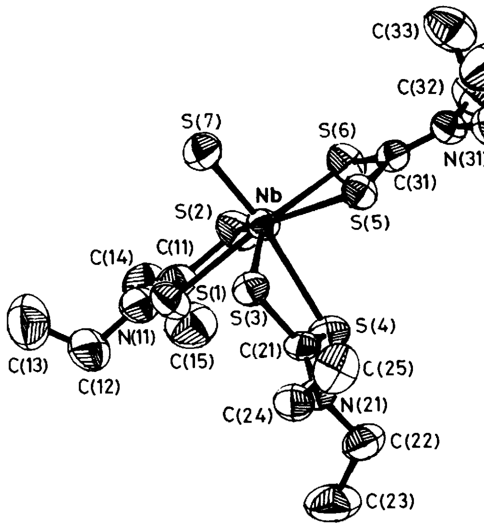

Figure 2. The structure of compound (**2A**)

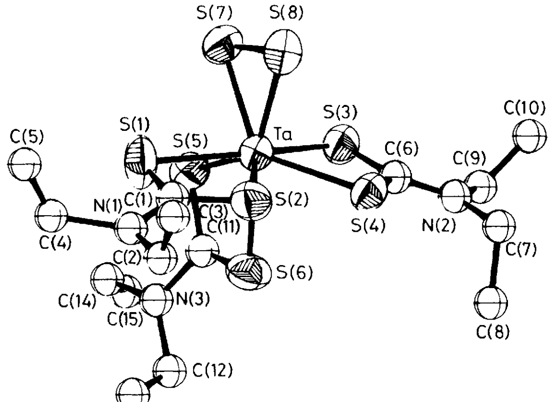

Figure 3. The structure of compound (**3**)

unique equatorial Ta–S(3) bond length is 2.538(1) Å, and the mean Ta–S(S_2CNEt_2) bond length 2.561 Å.[5]

The small bite causes both atoms S(3) and S(4) to be bent out of their ideal positions towards each other (see Table 3); though S(3) is bent only slightly out of the equatorial plane, the axial atom S(4) is much displaced so that distances to S(1) and S(5) [the atoms adjacent to S(3)] are considerably shorter than those to S(2) and S(6). This is expected but the distortion in the position of the terminal sulphur atom is remarkable because it is displaced from the ideal axial position in such a way as to decrease S ··· S distances rather than increase them. Thus it is tilted towards the unique equatorial atom S(3) and forms a close contact with it [3.38 Å in (**2A**), 3.34 Å in (**2B**)], see Table 3, and this is despite S(3) being on the other side of the equatorial plane. This tilt brings S(7) into close contact with two other sulphur atoms S(1) and S(5) in the equatorial plane. The presence of short S ··· S interligand distances is a feature of some S_2CNEt_2 structures [notably in trigonal-prismatic $M(S_2CNR_2)_3$ (R = alkyl)[9]] and has been ascribed to some weak attractive interaction. Whatever the cause of the axial displacement, steric repulsions cannot be the only relevant factor. These distortions are also observed, though to a lesser degree, in $Ta(S_2CNEt_2)_3S$.[5]

There is a significant difference between the Nb=S bond lengths in molecule (**2A**) [2.164(3) Å] and in (**2B**) [2.112(3) Å]. The latter is remarkably short in view of known distances for the six-co-ordinate species $(NbCl_3S \cdot SPPh_3)_2$ 2.129(4)[15] and

Table 4. Crystal data and refinement details

Formula	$[Nb(S_2CNEt_2)_4]Br$ $C_{20}H_{40}BrN_4NbS_8$	$Nb(S_2CNEt_2)_3S$ $C_{15}H_{30}N_3NbS_7$	$Ta(S_2CNEt_2)_3(S_2)$ $C_{15}H_{30}N_3S_8Ta$
M	765.6	569.6	689.7
Crystal system	Monoclinic	Triclinic	Monoclinic
a/Å	11.100(8)	16.892(14)	16.319(9)
b/Å	27.910(18)	9.868(8)	10.887(8)
c/Å	10.680(9)	15.747(14)	30.322(25)
α/°	(90)	91.0(1)	(90)
β/°	92.8(1)	78.1(1)	88.0(1)
γ/°	(90)	85.8(1)	(90)
Space group	$P2_1/a$	$P\bar{1}$	$C2/c$
Systematic absences	$h0l; h = 2n + 1$ $0k0; k = 2n + 1$	—	$hkl; h + k = 2n + 1$ $h0l; l = 2n + 1$ $0k0; k = 2n + 1$
U/Å^3	3 304.7	2 560	5 383.8
Z	4	4	8
D_m/g cm^{-3}	1.5(1)*	1.44(5)	1.75(5)
D_c/g cm^{-3}	1.54	1.48	1.70
μ/cm^{-1}	23.2	12.5	49.0
λ(Mo-K_α)/Å	0.7017	0.7017	0.7017
F(000)	1 568	1 176	2 736
Crystal size (mm)	0.50 × 0.35 × 0.20	1.0 × 0.2 × 0.70	1.0 × 0.50 × 0.30
Rotation axis	a	a	a
Independent data measured	5 572	8 568	3 359
Data used in refinement [$I > 3\sigma(I)$]	2 612	5 058	1 814
R	0.081	0.054	0.099
R'	0.085	0.054	0.095

* Crystal dissolved quickly.

$NbCl_4S^-$ 2.09 Å,[16] and indeed is as short as that in the five-co-ordinate species $NbCl_3S{\cdot}SPPh_3$ [2.114(4) Å].[15] There seem to be no significantly short intermolecular contacts in molecule (**2A**) or (**2B**) to account for this difference, although S(7B) is involved in three contacts less than 3.75 Å [*viz.* S(7B) ··· C(24B) (x, 1 + y, z) 3.58 Å, S(7B) ··· C(15A) (2 − x, 1 − y, 1 − z) 3.60 Å, S(7B) ··· C(14B) (1 − x, 1 − y, 1 − z) 3.44 Å] and S(7A) only two [S(7A) ··· C(14A) (2 − x, 1 − y, 1 − z) 3.74 Å and S(7A) ··· C(13B) (x, y, z) 3.64 Å]. The distances of the sulphur atoms from the respective equatorial planes and the lengths of the *trans* Nb=S bonds are both consistent with the relative Nb=S bond lengths, see Table 3. It would thus seem that both the length and orientation of the Nb=S bonds are governed by subtle electronic and steric effects.

The structure of compound (**3**) consists of discrete monomers of $Ta(S_2CNEt_2)_3(S_2)$, Figure 3. The metal atom is eight-co-ordinate with a *mmmm* dodecahedral environment. The four edges are occupied by three chelating S_2CNEt_2 groups and one from a 'side-on' bonded disulphide group. As shown in Table 2, this geometry is well suited to the tetrakis(dithiocarbamates) of the early transition metals which have bites of *ca.* 1.11 (S–M–S angles *ca.* 66°). In compound (**3**) however one S_2CNEt_2 is replaced by a S_2 ligand with a normalised bite of 0.86 (S–M–S *ca.* 51°) and this causes considerable distortion in the polyhedron so that the r.m.s. deviation from ideal geometry is 0.079 Å.[8]

In the *mmmm* dodecahedron with bites of *ca.* 1.1 it is usually found that bonds to atoms in the A sites are longer than to those in the B sites and this was indeed observed in compound (**1**). In (**3**) however, bond lengths to A-site atoms are Ta–S(2) 2.598(10), Ta–S(4) 2.583(9), Ta–S(5) 2.514(11), and Ta–S(7) 2.451(11) Å and to B-site atoms are Ta–S(1) 2.560(10), Ta–S(3) 2.527(10), Ta–S(6) 2.577(12) Å, and Ta–S(8) 2.375(12) Å. The bond lengths to A sites are greater than those to B sites for two of the S_2CNEt_2 chelates and also for the S_2 group. For the remaining S_2CNEt_2 ligands, S(5) and S(6), the effect is reversed with $Ta{-}S_B > Ta{-}S_A$ by 0.063 Å. This discrepancy is probably due to the difference in ligand 'bites' between S_2CNEt_2 and S_2 as this S_2CNEt_2 ligand is in the same trapezoid as the S_2 group.

The presence of the disulphide group co-ordinated in a 'side-on' mode [S(7)–S(8) 2.07(2) Å] is the most interesting feature of structure (**3**). Such co-ordination has been observed previously for the Group 5A cyclopentadienyl (cp) compounds $[V(cp)_2(S_2)]$,[17] $[Nb(cp)_2(S_2)X]$ [X = Me,[18] Cl,[19] or $S_2P(OEt)_2$[20]]. The asymmetry of the S_2 co-ordination [Ta–S(7) 2.451(11), Ta–S(8) 2.375(12) Å] is common for this mode of co-ordination of S_2[21,22] (as indeed it is for the *mmmm* dodecahedron) and is also seen in analogous dioxygen complexes.[23] The S(7)–S(8) distance of 2.07(2) Å is slightly longer than those seen in other Group 5A compounds (1.93—2.03 Å)[17–20] but is typical of disulphide complexes of other early transition metals.[24] However, it is shorter than in ionic Na_2S_2 (2.13 Å)[25] and longer than in S_2 (1.89 Å),[26,27] suggesting the presence of some π^* to d_π, S_2 to Ta donation.

Conclusions

The pentahalides of niobium and tantalum undergo complex reactions with S_2CNEt_2. From the products the species $[Nb(S_2CNEt_2)_4]Br$ and $Nb(S_2CNEt_2)_3S$ have been isolated and characterised by *X*-ray analysis. The ionic nature of the former product has been confirmed, but crystals of the latter have a triclinic structure and are not isomorphous with the analogous tantalum complex. Reactions of the sulphido-halides with S_2CNEt_2 have led to the isolation of $Ta(S_2CNEt_2)_3(S_2)$ in which the metal is eight-co-ordinate with a side-on bonded disulphide group.

Experimental

All manipulations involved in the preparation and isolation of the products were carried out using an all-glass vacuum line.

Table 5. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) Compound (**1**)							
Nb	−1 769(1)	4 044(0)	2 581(1)	C(24)	−3 303(25)	2 229(8)	203(24)
Br	−5 990(2)	3 192(1)	−2 590(3)	S(5)	−3 533(3)	3 925(1)	4 032(4)
S(1)	−3 287(3)	4 621(1)	1 530(4)	S(6)	−1 594(3)	4 575(2)	4 513(4)
S(2)	−760(3)	4 793(1)	1 705(4)	N(3)	−3 418(12)	4 481(5)	6 055(11)
N(1)	−2 314(10)	5 479(4)	1 037(12)	C(3)	−2 913(12)	4 351(5)	5 028(14)
C(1)	−2 161(11)	5 030(5)	1 352(13)	C(31)	−2 882(14)	4 862(6)	6 864(15)
C(11)	−1 277(13)	5 814(6)	1 111(19)	C(32)	−2 257(17)	4 691(7)	7 985(17)
C(12)	−1 081(18)	6 021(8)	2 377(25)	C(33)	−4 521(13)	4 247(7)	6 463(15)
C(13)	−3 515(14)	5 693(6)	736(17)	C(34)	−5 634(17)	4 483(7)	5 970(18)
C(14)	−3 678(19)	5 863(9)	−570(21)	S(7)	548(3)	4 019(1)	3 030(4)
S(3)	−3 298(3)	3 430(1)	1 660(4)	S(8)	−1 073(4)	3 302(2)	3 735(5)
S(4)	−1 176(3)	3 721(2)	499(4)	N(4)	1 287(14)	3 268(6)	4 355(17)
N(2)	−2 604(11)	3 025(4)	−473(12)	C(4)	391(13)	3 487(7)	3 762(16)
C(2)	−2 419(12)	3 332(5)	386(14)	C(41)	2 528(14)	3 443(8)	4 365(20)
C(21)	−1 858(17)	2 981(6)	−1 559(16)	C(42)	3 287(19)	3 249(11)	3 339(29)
C(22)	−2 349(18)	3 253(8)	−2 678(17)	C(43)	997(18)	2 830(11)	5 415(39)
C(23)	−3 654(20)	2 704(7)	−473(18)	C(44)	1 154(23)	2 513(17)	4 518(29)
(*b*) Compound (**2**)							
Nb(1A)	9 640(0)	3 221(1)	2 807(0)	C(15A)	12 397(7)	4 834(15)	4 319(10)
Nb(1B)	5 050(0)	3 564(1)	7 443(0)	C(21A)	10 487(5)	2 454(9)	890(6)
S(1A)	10 517(2)	5 264(3)	2 374(2)	C(22A)	11 490(6)	1 186(12)	−235(7)
S(2A)	10 498(2)	3 786(3)	3 912(2)	C(23A)	12 268(8)	1 899(17)	−584(10)
S(3A)	9 608(1)	3 524(3)	1 204(2)	C(24A)	10 384(7)	2 669(11)	−630(6)
S(4A)	10 909(1)	1 866(3)	1 714(2)	C(25A)	9 733(8)	1 737(13)	−810(8)
S(5A)	8 932(1)	1 114(2)	2 388(1)	C(31A)	9 030(5)	373(9)	3 328(6)
S(6A)	9 520(2)	1 382(3)	3 943(2)	C(32A)	8 868(7)	−1 373(11)	4 416(7)
S(7A)	8 515(2)	4 482(3)	3 201(2)	C(33A)	8 198(9)	−929(15)	5 155(8)
S(1B)	5 971(1)	2 226(3)	6 146(2)	C(34A)	8 433(7)	−1 697(10)	3 004(7)
S(2B)	4 464(1)	3 666(3)	6 071(2)	C(35A)	7 550(8)	−1 729(18)	3 240(11)
S(5B)	4 543(1)	3 974(3)	9 107(2)	C(11B)	5 291(5)	2 700(9)	5 501(6)
S(6B)	3 606(1)	4 678(3)	7 844(2)	C(12B)	6 125(7)	1 515(12)	4 224(7)
S(3B)	6 044(1)	2 031(3)	8 086(2)	C(13B)	6 802(8)	2 416(15)	3 811(10)
S(4B)	4 495(1)	1 087(3)	7 828(2)	C(14B)	4 810(7)	2 797(11)	4 148(6)
S(7B)	5 814(2)	5 177(4)	7 380(2)	C(15B)	4 188(7)	1 751(14)	4 149(8)
N(11A)	11 394(5)	5 932(9)	3 563(6)	C(21B)	5 405(5)	722(10)	8 130(6)
N(21A)	10 768(5)	2 144(8)	55(5)	C(22B)	6 446(7)	−838(13)	8 545(8)
N(31A)	8 795(5)	−836(8)	3 575(5)	C(23B)	7 018(8)	−1 408(17)	7 763(10)
N(11B)	5 399(4)	2 364(8)	4 674(5)	C(24B)	5 038(7)	−1 644(11)	8 484(9)
N(21B)	5 615(5)	−498(8)	8 375(5)	C(25B)	4 556(9)	−1 601(15)	9 406(9)
N(31B)	3 114(5)	5 433(8)	9 533(5)	C(31B)	3 681(5)	4 772(10)	8 925(6)
C(11A)	10 864(6)	5 117(10)	3 313(8)	C(32B)	3 223(6)	5 581(11)	10 432(6)
C(12A)	11 701(7)	7 044(12)	3 013(8)	C(33B)	2 811(9)	4 566(14)	11 020(9)
C(13A)	11 229(11)	8 333(15)	3 185(11)	C(34B)	2 375(6)	6 127(12)	9 317(7)
C(14A)	11 641(7)	5 787(12)	4 403(7)	C(35B)	2 477(8)	7 580(14)	9 114(9)
(*c*) Compound (**3**)							
Ta	3 686(1)	5(2)	1 196(0)	C(3)	895(32)	1 227(43)	−23(20)
S(1)	2 157(6)	178(14)	1 404(4)	C(4)	462(39)	1 205(57)	1 159(17)
S(2)	2 833(7)	931(11)	569(3)	C(5)	14(34)	213(24)	1 128(14)
S(3)	5 195(6)	−149(11)	1 348(3)	C(6)	5 438(35)	477(36)	872(13)
S(4)	4 648(6)	766(9)	558(3)	C(7)	6 353(25)	1 425(37)	305(13)
S(5)	3 669(8)	356(9)	2 016(3)	C(8)	6 323(28)	2 896(37)	387(15)
S(6)	3 814(9)	2 294(11)	1 399(4)	C(9)	6 935(23)	667(41)	1 012(16)
S(7)	3 559(8)	−2 063(11)	1 509(4)	C(10)	7 486(63)	−307(81)	835(26)
S(8)	3 651(7)	−1 918(11)	827(4)	C(11)	3 719(54)	1 885(43)	1 900(22)
N(1)	1 258(21)	1 449(35)	802(15)	C(12)	3 504(50)	4 192(45)	2 140(20)
N(2)	6 213(18)	847(31)	744(11)	C(13)	2 752(40)	4 638(92)	1 994(24)
N(3)	3 439(39)	2 833(49)	2 252(13)	C(14)	3 266(40)	2 432(60)	2 725(16)
C(1)	2 020(23)	869(14)	893(14)	C(15)	3 944(50)	2 666(62)	3 043(20)
C(2)	1 171(28)	2 027(59)	361(21)				

Solvents were first dried with P_2O_5 then twice distilled under vacuum onto further quantities of the appropriate dehydrating agent.

Preparations of [$Nb(S_2CNEt_2)_4$]Br (**1**), $Nb(S_2CNEt_2)_3S$ (**2**), *and* $Ta(S_2CNEt_2)_3(S_2)$ (**3**).—Sodium diethyldithiocarbamate trihydrate (Aldrich Chemicals) was dehydrated by pumping first for 24 h at room temperature and then for a further 48 h at 40 °C. The metal halides and sulphido-halides were prepared as described previously.[6,28] The metal halide or sulphido-halide (*ca.* 2 g) was placed in a glass apparatus comprising two bulbs linked by a glass sinter. Dry $Na(S_2CNEt_2)$ was added to the

Table 6. Molecular dimensions in the metal co-ordination sphere (distances in Å, angles in °)

(*a*) Compound (**1**)

Nb–S(1)	2.550(4)	S(1)–Nb–S(2)	67.46(12)	S(1)–Nb–S(6)	90.68(14)	S(5)–Nb–S(7)	131.38(14)
Nb–S(2)	2.570(4)	S(1)–Nb–S(3)	80.94(13)	S(2)–Nb–S(6)	78.67(14)	S(6)–Nb–S(7)	80.19(14)
Nb–S(3)	2.573(4)	S(2)–Nb–S(3)	133.91(14)	S(3)–Nb–S(6)	136.22(14)	S(1)–Nb–S(8)	156.47(14)
Nb–S(4)	2.517(5)	S(1)–Nb–S(4)	91.91(14)	S(4)–Nb–S(6)	156.04(14)	S(2)–Nb–S(8)	136.06(13)
Nb–S(5)	2.578(4)	S(2)–Nb–S(4)	80.37(14)	S(5)–Nb–S(6)	67.49(13)	S(3)–Nb–S(8)	79.65(14)
Nb–S(6)	2.541(4)	S(3)–Nb–S(4)	67.64(14)	S(1)–Nb–S(7)	136.53(14)	S(4)–Nb–S(8)	92.89(17)
Nb–S(7)	2.593(4)	S(1)–Nb–S(5)	80.86(13)	S(2)–Nb–S(7)	69.08(13)	S(5)–Nb–S(8)	79.81(14)
Nb–S(8)	2.511(5)	S(2)–Nb–S(5)	132.95(14)	S(3)–Nb–S(7)	133.04(14)	S(6)–Nb–S(8)	94.17(16)
		S(3)–Nb–S(5)	68.76(13)	S(4)–Nb–S(7)	81.59(14)	S(7)–Nb–S(8)	66.99(14)
		S(4)–Nb–S(5)	136.40(14)				

(*b*) Compound (**2**)

	A	B		A	B
Nb–S(1)	2.606(3)	2.574(2)	Nb–S(5)	2.613(3)	2.599(2)
Nb–S(2)	2.563(3)	2.555(3)	Nb–S(6)	2.560(3)	2.551(3)
Nb–S(3)	2.557(3)	2.552(3)	Nb–S(7)	2.164(3)	2.112(3)
Nb–S(4)	2.707(3)	2.716(3)			
S(1)–Nb–S(2)	66.76(10)	67.44(8)	S(2)–Nb–S(6)	71.27(9)	71.56(8)
S(1)–Nb–S(3)	76.16(9)	74.17(8)	S(3)–Nb–S(6)	140.42(9)	140.26(8)
S(2)–Nb–S(3)	140.14(9)	138.59(8)	S(4)–Nb–S(6)	94.11(8)	90.54(8)
S(1)–Nb–S(4)	81.51(8)	82.93(8)	S(5)–Nb–S(6)	66.61(9)	67.24(8)
S(2)–Nb–S(4)	93.06(9)	92.09(9)	S(1)–Nb–S(7)	94.34(10)	93.78(11)
S(3)–Nb–S(4)	66.75(8)	67.84(8)	S(2)–Nb–S(7)	105.36(11)	106.20(13)
S(1)–Nb–S(5)	150.88(9)	150.34(9)	S(3)–Nb–S(7)	91.10(10)	90.90(12)
S(2)–Nb–S(5)	136.61(9)	138.20(8)	S(4)–Nb–S(7)	157.84(11)	158.62(13)
S(3)–Nb–S(5)	75.86(9)	76.58(8)	S(5)–Nb–S(7)	94.09(10)	91.44(12)
S(4)–Nb–S(5)	80.23(8)	81.67(9)	S(6)–Nb–S(7)	103.31(10)	105.50(12)
S(1)–Nb–S(6)	137.43(10)	138.13(9)			

(*c*) Compound (**3**)

Ta–S(1)	2.560(10)	S(1)–Ta–S(2)	66.98(36)	S(1)–Ta–S(6)	87.54(47)	S(5)–Ta–S(7)	76.00(40)
Ta–S(2)	2.598(10)	S(1)–Ta–S(3)	155.21(36)	S(2)–Ta–S(6)	81.35(37)	S(6)–Ta–S(7)	143.38(44)
Ta–S(3)	2.527(10)	S(2)–Ta–S(3)	135.25(34)	S(3)–Ta–S(6)	86.16(41)	S(1)–Ta–S(8)	98.12(44)
Ta–S(4)	2.583(9)	S(1)–Ta–S(4)	136.28(36)	S(4)–Ta–S(6)	79.40(37)	S(2)–Ta–S(8)	88.61(38)
Ta–S(5)	2.514(11)	S(2)–Ta–S(4)	69.87(35)	S(5)–Ta–S(6)	67.39(33)	S(3)–Ta–S(8)	93.83(40)
Ta–S(6)	2.577(12)	S(3)–Ta–S(4)	65.63(31)	S(1)–Ta–S(7)	84.41(44)	S(4)–Ta–S(8)	87.41(36)
Ta–S(7)	2.451(11)	S(1)–Ta–S(5)	76.59(39)	S(2)–Ta–S(7)	126.84(40)	S(5)–Ta–S(8)	126.81(36)
Ta–S(8)	2.375(12)	S(2)–Ta–S(5)	132.58(37)	S(3)–Ta–S(7)	86.45(38)	S(6)–Ta–S(8)	165.55(37)
S(7)–S(8)	2.074(17)	S(3)–Ta–S(5)	78.84(37)	S(4)–Ta–S(7)	128.76(40)	S(7)–Ta–S(8)	50.87(43)
		S(4)–Ta–S(5)	132.57(34)				

metal halide (5:1) or sulphido-halide (3:1 molar ratio). Onto the reactants was distilled dry solvent (*ca.* 40 cm^3; acetonitrile for MX_5, CS_2 for MX_3S reactions) and the apparatus sealed. The reactants were stirred for 24 h at room temperature. The insoluble sodium halide formed during this stage was removed by drawing the solution through the sinter into the second bulb. This bulb was then sealed and transferred to an oil-bath at 50 °C where it was allowed to remain undisturbed for 6 months. The products were then filtered on the vacuum line, and the solvent was vacuum distilled from the filtrate to isolate the soluble products.

(*a*) *Products of the reaction of* $NbCl_5$ *with* $Na(S_2CNEt_2)$ (*molar ratio* 1:5). The insoluble product had an analysis close to that required for $Nb(S_2CNEt_2)_3S$ (see Table 1) and consisted mainly of dark yellow crystals together with a small amount of light yellow powder. The i.r. spectrum of the product had a band at 500 cm^{-1} in the position expected for a Nb=S stretch.[15] A compound of formulation $Nb(S_2CNEt_2)_3S$ synthesised recently is reported to have ν(Nb=S) at 493 cm^{-1}.[29] One of the dark yellow crystals was selected for single-crystal studies and thus shown to be $Nb(S_2CNEt_2)_3S$ (**2**). The filtrate from the reaction was red and on removal of the solvent a dark red oil was obtained. Treatment of the oil with CCl_4 gave a mixture of red and yellow powders that were not separable.

(*b*) *Products from the reaction of* $NbBr_5$ *and* $Na(S_2CNEt_2)$ (*molar ratio* 1:5). The insoluble product (15% based upon the amount of metal halide) had an analysis close to that required for $Nb(S_2CNEt_2)_3S$. The required C, H, and N figures for $Nb(S_2CNEt_2)_3S$ and $Nb(S_2CNEt_2)_4Br$ are very similar (see Table 1) but there is a major difference in the required percentage of niobium. A band in the i.r. spectrum of the insoluble products at 497 cm^{-1} is typical for Nb=S. This product was examined by *X*-ray powder photography and shown to be isomorphous with $Ta(S_2CNEt_2)_3S$ (**4**)[5] whose crystal structure has been determined. [(**4**) is monoclinic, space group $P2_1/c$, a = 9.647(4), b = 17.214(7), c = 15.442(6) Å, and β = 96.8(1)°]. The major product was obtained as a dark red mass by removing the solvent at the pump. A sample was taken up in a small amount of CH_2Cl_2 and a large amount of MeCN added. Slow evaporation of the solvent using the double-ampoule technique yielded orange crystals one of which was made the subject of a single-crystal study and shown to be $[Nb(S_2CNEt_2)]_4Br$ (**1**).

(*c*) *Products from the reaction of* $TaCl_5$ *with* $Na(S_2CNEt_2)$ (*molar ratio* 1:5). The yellow insoluble product which was obtained in 20% yield had analyses corresponding to $Ta(S_2CNEt_2)_3S$ and a band in its i.r. spectrum at 479 cm^{-1} which is assigned to ν(Ta=S). The compound was shown by *X*-

ray powder photography to be isomorphous with (**4**). From the dark brown filtrate a brown oily mass was obtained on evaporation of the solvent. All attempts to determine the nature of the soluble material proved abortive.

(*d*) *Products from the reactions of* TaX_3S (X = Cl *or* Br) *with* $Na(S_2CNEt_2)$ (*molar ratio* 1:3). The reaction with $TaCl_3S$ yielded a green insoluble powder and a green solution from which a small amount of green powder was isolated. The analyses for both products indicated that mixtures had been formed. With the bromide $TaBr_3S$ an insoluble mass consisting of a mixture of green and yellow crystals was obtained and from the green filtrate a green oil was isolated. Precession photographs revealed that the yellow crystals were (**4**) while the green crystals were shown by single-crystal methods to be $Ta(S_2CNEt_2)_3(S_2)$ (**3**).

Crystal Structure Determinations.—Crystal data for $[Nb(S_2CNEt_2)_4]Br$ (**1**), $Nb(S_2CNEt_2)_3S$ (**2**), and $Ta(S_2CNEt_2)_3(S_2)$ (**3**) are given in Table 4. Data were collected on a Stoe STADI2 diffractometer using variable width ω-scans. Background counts were 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$.

An absorption correction was applied in the case of compound (**3**) but not (**1**) or (**2**). In (**1**) the Nb and Br atomic positions were obtained by direct methods using SHELX 76.[30] In (**2**) and (**3**) the co-ordinates of the metal atoms were found from a Patterson function. For all three compounds, Fourier methods were used to locate the remaining non-hydrogen atoms and the structures were refined using full-matrix least-squares. All non-hydrogen atoms, except for the carbon atoms in (**3**) were refined anisotropically. In compounds (**1**) and (**2**) the hydrogen atoms were placed in tetrahedral positions around the appropriate carbon atoms. Common thermal parameters were applied to all the methylene hydrogen atoms in each ligand, and to all the hydrogen atoms of each methyl group. Hydrogen-atom positions were not included for (**3**).

The weighting schemes were chosen to give equivalent values of $w\Delta^2$ over ranges of $(\sin\theta)/\lambda$ where $w = 1/[\sigma^2(F) + 0.00XF^2]$ where $\sigma(F)$ was taken from counting statistics and X = 3, 0, and 1 for compounds (**1**), (**2**), and (**3**) respectively. Calculations were made at the University of Manchester Regional Computer Centre. Atomic co-ordinates are given in Table 5. Selected molecular dimensions are given in Table 6.

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References

1 R. P. Burns, F. P. McCullough, and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1980, **23**, 211.
2 P. R. Heckley, D. G. Holah, and D. Brown, *Can. J. Chem.*, 1971, **49**, 1151.
3 J. N. Smith and T. M. Brown, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 441.
4 D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1969, 1152.
5 E. J. Peterson, R. B. Von Dreele, and T. M. Brown, *Inorg. Chem.*, 1978, **17**, 1410.
6 M. G. B. Drew, D. A. Rice, and D. M. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 2251.
7 F. Bonati and R. Ugo, *J. Organomet. Chem.*, 1967, **10**, 257.
8 M. G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179.
9 D. L. Kepert, 'Inorganic Stereochemistry,' Springer, Berlin, 1982.
10 C. D. Garner, N. C. Howlader, F. E. Mabbs, A. T. McPhail, R. W. Miller, and K. D. Onan, *J. Chem. Soc., Dalton Trans.*, 1978, 1582.
11 D. F. Lewis and R. C. Fay, *Inorg. Chem.*, 1976, **15**, 2219.
12 J. G. Wijnhovan, *Cryst. Struct. Commun.*, 1973, **2**, 637.
13 J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White, and E. N. Maslen, *J. Chem. Soc., Dalton Trans.*, 1973, 2082.
14 M. G. B. Drew, *Prog. Inorg. Chem.*, 1977, **23**, 67.
15 M. G. B. Drew and R. J. Hobson, *Inorg. Chim. Acta*, 1983, **72**, 233.
16 U. Muller and P. Klingelhofer, *Z. Anorg. Allg. Chem.*, 1984, **510**, 109.
17 S. Gambarotta, C. Floriani, A. C. Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 184.
18 R. Mercier, J. Douglade, J. Amaudrut, J. Sala-Pala, and J. Guerchais, *Acta Crystallogr., Sect. B*, 1980, **36**, 2986.
19 R. Mattes and M. Bradtke, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1981, **157**, 95.
20 R. Mercier, J. Douglade, and B. Viard, *Acta Crystallogr., Sect. B*, 1981, **37**, 949.
21 W. Rittner, A. Muller, A. Neumann, W. Batker, and R. C. Sharma, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 530.
22 W. Clegg, N. Mohan, A. Muller, A. Neumann, W. Rittner, and G. M. Sheldrick, *Inorg. Chem.*, 1980, **19**, 2066.
23 A. Muller, R. Jostes, and F. A. Cotton, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 875.
24 A. Muller, W. Jaegermann, and J. H. Enemark, *Coord. Chem. Rev.*, 1982, **46**, 245.
25 H. Foppl, E. Busmann, and F. K. Frorath, *Z. Anorg. Allg. Chem.*, 1962, **314**, 12.
26 L. R. Maxwell, V. M. Mosley, and S. B. Hendricks, *Phys. Rev., B*, 1936, **50**, 41.
27 B. Meyer, *Chem. Rev.*, 1976, **76**, 367.
28 M. G. B. Drew, D. A. Rice, and D. M. Williams, *J. Chem. Soc., Dalton Trans.*, 1984, 845.
29 Y. Do, E. D. Simon, and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 3809.
30 SHELX 76, Package for Crystal Structure Determination, G. M. Sheldrick, University of Cambridge, 1976.

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