The Chemistry of Niobium and Tantalum Dithiocarbamato-complexes. Part 1. Synthesis, Structure, and Protonation of Dinitrogen-bridged Complexes†

Jonathan R. Dilworth, Richard A. Henderson,* Adrian Hills, David L. Hughes, Colin Macdonald, Alan N. Stephens, and David R. M. Walton
AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory and School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Convenient, 'single pot' syntheses of $[\{MCl_3(thf)_2\}_2(\mu-N_2)]$ (M = Nb or Ta, thf = tetrahydrofuran), using $(Me_3Si)_2NN(SiMe_3)_2$ and $Me_3SiNHNHSiMe_3$ respectively, have been achieved. The reaction of these dinitrogen complexes with an excess of $SiMe_3(S_2CNEt_2)$ gives the corresponding $[\{M(S_2CNEt_2)_3\}_2(\mu-N_2)]$, and the *X*-ray crystal structure of the complex with M = Nb has been determined. Treatment of the dithiocarbamato-complexes with an excess of anhydrous HX (X = Cl or Br) gives a stoicheiometric yield of hydrazine and the corresponding $[M(S_2CNEt_2)_3X_2]$; the crystal structure of one such example, M = Ta, X = Br, has been determined. Attempts to obtain crystals of $[NbCl_2(S_2CNEt_2)_3]$ suitable for *X*-ray crystallographic analysis resulted in the isolation of $[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$, whose identity was established crystallographically. Niobium-93 n.m.r. spectroscopy has been used to identify the nature of solution species in the reactions of $[\{Nb(S_2CNEt_2)_3\}_2(\mu-N_2)]$ with acid.

In the last two decades a detailed understanding of how dinitrogen can be activated towards protic attack at a mononuclear site has been developed.[1] However, relatively little is known about the analogous reactivity of binuclear complexes in which a dinitrogen ligand bridges two metal centres. This is particularly surprising since such a species has been suggested[1,2] as the binding mode adopted by the enzyme nitrogenase. Such proposals are, however, based on studies of multicomponent systems (sometimes catalytic) involving multistage reactions. Consequently detailed information about the intimate mechanisms of these reactions is limited, furthermore the identity and structure of reactants and products in these systems are poorly defined. In this paper we establish the structural and stoicheiometric chemistry for the reactions of acid with $[\{M(S_2CNEt_2)_3\}_2(\mu-N_2)]$ (M = Nb or Ta), which lay the foundations for a detailed mechanistic study.

Results and Discussion

Preparation of $[\{MCl_3(thf)_2\}_2(\mu-N_2)]$.—The complexes $[\{MCl_3(thf)_2\}_2(\mu-N_2)]$ (M = Nb or Ta) were first prepared by routes[3] involving several steps, with intermediate compounds which had to be isolated, purified, and which themselves are air-sensitive and in some cases thermally unstable. To circumvent these somewhat tortuous pathways we have developed the use of silylated hydrazines to prepare bridged dinitrogen complexes,[4] in a 'single pot' synthesis. Thus under ambient conditions in dichloromethane the reaction of $NbCl_5$ with $(Me_3Si)_2NN(SiMe_3)_2$ (tmsh) in the presence of a small excess of tetrahydrofuran (thf) gives $[\{NbCl_3(thf)_2\}_2(\mu-N_2)]$ in a 60% yield in only a few hours. However, tmsh does not react with $TaCl_5$ even under forcing conditions, but $Me_3SiNHNHSiMe_3$ does in the presence of a small excess of thf to give $[\{TaCl_3(thf)_2\}_2(\mu-N_2)]$ in 30% yield. The analogous reaction of $Me_3SiNHNHSiMe_3$ with $NbCl_5$ gives the niobium dinitrogen complex in about 20% yield. The dinitrogen complexes were characterised by elemental analysis and comparison of their i.r. spectra with those of materials prepared by an alternative route.[3]

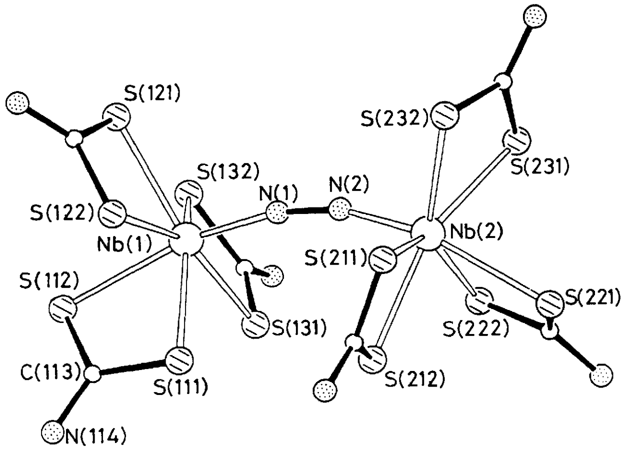

Figure 1. View of a molecule of $[\{Nb(S_2CNEt_2)_3\}_2(\mu-N_2)]$, indicating the atomic numbering scheme. The ethyl groups have been omitted for clarity

Preparation of $[\{M(S_2CNEt_2)_3\}_2(\mu-N_2)]$.—The reaction of $[\{MCl_3(thf)_2\}_2(\mu-N_2)]$ with an excess of $SiMe_3(S_2CNEt_2)$ in dichloromethane gives $[\{M(S_2CNEt_2)_3\}_2(\mu-N_2)]$ in about 80% yield as dark orange prisms (M = Ta) or dark red plates (M = Nb). The complexes were characterised by elemental analysis, ^1H n.m.r. spectroscopy (Table 1), analysis of hydrazine yields upon protonation (see below), and for the niobium complex by *X*-ray crystallography. It is important to emphasise that these complexes were *the first dinitrogen complexes in which the coligands are exclusively sulphurous*,[4] an important co-ordination environment in the light of the predominant sulphur ligation established for the enzyme nitrogenase.[5]

Description of the Molecule $[\{Nb(S_2CNEt_2)_3\}_2(\mu-N_2)]$.—Atomic co-ordinates and principal molecular dimensions are listed in Tables 2 and 3 respectively. In the crystal, the dinitrogen-bridging metal–nitrogen skeleton has a slightly

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Elemental and spectroscopic analysis of the complexes

Compound	Analysis[a]/% C	H	N	I.r.[b]/cm^{-1}	^{1}H N.m.r.[c]
[{NbCl$_3$(thf)$_2$}$_2$(μ-N$_2$)]	27.4	4.3	4.3	840	*d*
	(26.9)	(4.5)	(3.9)	[ν(NN)]	
[{TaCl$_3$(thf)$_2$}$_2$(μ-N$_2$)]	21.6	3.1	2.9	845	*d*
	(21.7)	(3.6)	(3.1)	[ν(NN)]	
[{Nb(S$_2$CNEt$_2$)$_3$}$_2$(μ-N$_2$)]	32.9	5.2	9.7	835	1.27(3) (t, Me, J_{HH} = 7.1)
	(32.7)	(5.4)	(10.2)	[ν(NN)]	3.80(2) (q, CH$_2$, J_{HH} = 7.2)
[{Ta(S$_2$CNEt$_2$)$_3$}$_2$(μ-N$_2$)]	27.6	4.3	8.5	850	1.27(3) (t, Me, J_{HH} = 6.9)
	(27.4)	(4.6)	(8.5)	[ν(NN)]	3.75(2) (q, CH$_2$, J_{HH} = 7.2)
[NbCl$_2$(S$_2$CNEt$_2$)$_3$]	30.5	4.9	7.1	—	1.27(3) (t, Me, J_{HH} = 6.9)
	(29.6)	(5.0)	(6.9)		3.80(2) (q, CH$_2$, J_{HH} = 7.0)
[NbBr$_2$(S$_2$CNEt$_2$)$_3$]	26.8	4.7	5.5	—	1.35(3) (t, Me, J_{HH} = 7.1)
	(25.8)	(4.3)	(6.0)		3.84(2) (q, CH$_2$, J_{HH} = 7.0)
[TaCl$_2$(S$_2$CNEt$_2$)$_3$]	25.7	4.5	6.5	—	1.26(3) (t, Me, J_{HH} = 7.1)
	(25.9)	(4.3)	(6.0)		3.76(2) (q, CH$_2$, J_{HH} = 7.2)
[TaBr$_2$(S$_2$CNEt$_2$)$_3$]	23.3	3.7	5.1	—	1.24(3) (t, Me, J_{HH} = 7.0)
	(22.9)	(3.8)	(5.3)		3.80(2) (q, CH$_2$, J_{HH} = 7.0)
[TaI$_2$(S$_2$CNEt$_2$)$_3$]	20.8	3.2	4.8	—	1.22(3) (t, Me, J_{HH} = 7.2)
	(20.5)	(3.4)	(4.8)		3.76(2) (q, CH$_2$, J_{HH} = 7.0)

[a] Calculated values shown in parentheses. [b] Spectra recorded as Nujol mulls. [c] Chemical shifts *versus* SiMe$_4$, *J* values in Hz. All spectra recorded in CDCl$_3$; t = triplet and q = quartet. [d] Poor solubility precludes measurement of n.m.r. spectrum.

Table 2. Final atomic co-ordinates (fractional × 10^4) for [{Nb(S$_2$CNEt$_2$)$_3$}$_2$(μ-N$_2$)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nb(1)	506.0(9)	7 641.0(6)	5 259.5(6)	N(1)	−853(8)	7 609(5)	5 156(5)
Nb(2)	−2 893.6(9)	7 204.8(6)	4 489.8(6)	N(2)	−1 743(8)	7 514(5)	4 959(5)
S(111)	694(3)	7 292(2)	4 003(2)	S(211)	−2 977(3)	8 010(2)	3 421(2)
S(112)	2 354(3)	7 596(2)	5 034(2)	S(212)	−1 840(3)	6 744(2)	3 569(2)
C(113)	1 948(10)	7 387(7)	4 201(7)	C(213)	−2 174(9)	7 455(7)	3 071(7)
N(114)	2 538(9)	7 310(6)	3 716(6)	N(214)	−1 909(9)	7 561(7)	2 441(7)
C(115)	2 184(12)	7 062(10)	3 022(8)	C(215)	−1 262(11)	7 070(8)	2 136(8)
C(116)	2 436(15)	6 301(11)	2 929(8)	C(216)	−1 800(14)	6 504(10)	1 719(8)
C(117)	3 566(12)	7 479(9)	3 833(8)	C(217)	−2 258(16)	8 171(10)	2 012(9)
C(118)	3 751(13)	8 228(10)	3 584(9)	C(218)	−1 551(18)	8 748(11)	2 009(13)
S(121)	856(3)	8 698(2)	6 094(2)	S(221)	−4 222(3)	6 376(2)	3 770(2)
S(122)	605(3)	8 836(2)	4 616(2)	S(222)	−2 631(3)	5 892(2)	4 797(2)
C(123)	975(10)	9 238(7)	5 393(7)	C(223)	−3 632(9)	5 696(7)	4 213(7)
N(124)	1 342(8)	9 877(6)	5 454(6)	N(224)	−3 910(9)	5 002(6)	4 109(6)
C(125)	1 559(12)	10 277(7)	4 830(8)	C(225)	−4 848(13)	4 820(9)	3 667(9)
C(126)	2 477(11)	10 043(8)	4 575(9)	C(226)	−4 593(18)	4 585(11)	2 967(11)
C(127)	1 621(11)	10 202(7)	6 146(8)	C(227)	−3 322(12)	4 409(7)	4 460(8)
C(128)	2 665(12)	10 066(8)	6 421(8)	C(228)	−3 651(13)	4 287(9)	5 147(9)
S(131)	520(3)	6 270(2)	5 287(2)	S(231)	−3 942(3)	7 004(2)	5 493(2)
S(132)	1 027(3)	7 130(2)	6 478(2)	S(232)	−3 941(3)	8 286(2)	4 735(2)
C(133)	806(10)	6 276(7)	6 146(8)	C(233)	−4 388(12)	7 836(8)	5 416(8)
N(134)	881(10)	5 710(7)	6 542(7)	N(234)	−5 051(11)	8 141(9)	5 783(7)
C(135)	664(15)	4 989(8)	6 271(9)	C(235)	−5 534(16)	7 692(12)	6 310(11)
C(136)	−371(16)	4 762(9)	6 342(11)	C(236)	−4 913(17)	7 798(13)	6 946(11)
C(137)	1 064(21)	5 762(13)	7 352(15)	C(237)	−5 456(16)	8 866(10)	5 645(12)
C(138)	2 026(25)	5 606(19)	7 451(16)	C(238)	−4 862(16)	9 394(12)	6 121(13)

curved shape (Figure 1). The two niobium atoms are each seven-co-ordinate, with pentagonal-bipyramidal arrangements. About each metal, there are two S$_2$CNEt$_2$ ligands in the equatorial plane, and a third straddles an equatorial and an apical site. The opposite apical position is occupied by an N atom of the end-on bridging dinitrogen molecule.

This is a very similar pattern to that recorded for mononuclear [M(S$_2$CNEt$_2$)$_3$X] complexes, *e.g.* X = S, M = Nb[6] or Ta[7]; X = O, M = Nb or V,[8] and is that predicted by Kepert[9] from ligand-repulsion-energy calculations. In the mononuclear complexes having an M=X double bond, the M–S$_{ax}$ distances are considerably longer (*ca.* 0.12–0.18 Å) than the mean M–S$_{eq}$ lengths; in our complex, the Nb–S$_{ax}$ distances are longer by only 0.05 and 0.10 Å and indicate Nb–N bond orders of less than two[10] (see also below).

The atoms of the main S–Nb–N–N–Nb–S axis are approximately coplanar and form a smooth arc. The normals to the mean planes of the two equatorial planes are 42° apart. The S$_2$CNEt$_2$ ligands are arranged for minimal contact between the two equatorial planes; the CNEt$_2$ groups of the ligands of S(131) and S(212), near where the two planes come closest together, point in opposite directions, and the only contact less than 4 Å between non-hydrogen atoms in the two halves is that between S(111) and S(212) at a normal van der Waals distance

Table 3. Selected molecular dimensions (lengths in Å, angles in °) for $[\{Nb(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ with e.s.d.s in parentheses

(*a*) About the Nb atoms

Nb(1)–N(1)	1.858(12)	Nb(2)–N(2)	1.825(10)
Nb(1)–S(111)	2.565(4)	Nb(2)–S(211)	2.562(4)
Nb(1)–S(112)	2.632(4)	Nb(2)–S(212)	2.580(4)
Nb(1)–S(121)	2.577(4)	Nb(2)–S(221)	2.670(4)
Nb(1)–S(122)	2.589(4)	Nb(2)–S(222)	2.563(4)
Nb(1)–S(131)	2.587(4)	Nb(2)–S(231)	2.582(5)
Nb(1)–S(132)	2.573(4)	Nb(2)–S(232)	2.573(4)
N(1)–Nb(1)–S(111)	95.9(3)	N(2)–Nb(2)–S(211)	99.6(3)
N(1)–Nb(1)–S(112)	163.9(3)	N(2)–Nb(2)–S(212)	85.9(3)
S(111)–Nb(1)–S(112)	68.0(1)	S(211)–Nb(2)–S(212)	67.4(1)
N(1)–Nb(1)–S(121)	101.7(3)	N(2)–Nb(2)–S(221)	161.3(3)
S(111)–Nb(1)–S(121)	139.7(1)	S(211)–Nb(2)–S(221)	87.8(1)
S(112)–Nb(1)–S(121)	91.0(1)	S(212)–Nb(2)–S(221)	81.2(1)
N(1)–Nb(1)–S(122)	94.9(3)	N(2)–Nb(2)–S(222)	95.9(3)
S(111)–Nb(1)–S(122)	75.5(1)	S(211)–Nb(2)–S(222)	138.8(1)
S(112)–Nb(1)–S(122)	80.9(1)	S(212)–Nb(2)–S(222)	76.1(1)
S(121)–Nb(1)–S(122)	67.2(1)	S(221)–Nb(2)–S(222)	67.9(1)
N(1)–Nb(1)–S(131)	88.6(3)	N(2)–Nb(2)–S(231)	101.5(3)
S(111)–Nb(1)–S(131)	76.2(1)	S(211)–Nb(2)–S(231)	136.1(1)
S(112)–Nb(1)–S(131)	88.1(1)	S(212)–Nb(2)–S(231)	151.8(1)
S(121)–Nb(1)–S(131)	139.5(1)	S(221)–Nb(2)–S(231)	84.2(1)
S(122)–Nb(1)–S(131)	151.7(1)	S(222)–Nb(2)–S(231)	76.1(1)
N(1)–Nb(1)–S(132)	104.7(3)	N(2)–Nb(2)–S(232)	97.2(3)
S(111)–Nb(1)–S(132)	136.7(1)	S(211)–Nb(2)–S(232)	72.9(1)
S(112)–Nb(1)–S(132)	88.4(1)	S(212)–Nb(2)–S(232)	140.1(1)
S(121)–Nb(1)–S(132)	72.7(1)	S(221)–Nb(2)–S(232)	101.4(1)
S(122)–Nb(1)–S(132)	138.1(1)	S(222)–Nb(2)–S(232)	142.1(1)
S(131)–Nb(1)–S(132)	66.8(1)	S(231)–Nb(2)–S(232)	66.6(1)

(*b*) In the ligands

N(1)–N(2)	1.252(16)		
S(111)–C(113)	1.732(14)	S(211)–C(213)	1.719(13)
S(112)–C(113)	1.692(13)	S(212)–C(213)	1.686(13)
C(113)–N(114)	1.321(19)	C(213)–N(214)	1.331(19)
S(121)–C(123)	1.722(14)	S(221)–C(223)	1.697(14)
S(122)–C(123)	1.709(13)	S(222)–C(223)	1.717(12)
C(123)–N(124)	1.308(18)	C(223)–N(224)	1.372(18)
S(131)–C(133)	1.665(15)	S(231)–C(233)	1.685(16)
S(132)–C(133)	1.749(14)	S(232)–C(233)	1.742(16)
C(133)–N(134)	1.311(19)	C(233)–N(234)	1.351(22)
Nb(1)–N(1)–N(2)	166.8(9)	Nb(2)–N(2)–N(1)	163.1(9)
Nb(1)–S(111)–C(113)	88.4(5)	Nb(2)–S(211)–C(213)	89.3(5)
Nb(1)–S(112)–C(113)	87.1(5)	Nb(2)–S(212)–C(213)	89.5(5)
S(111)–C(113)–S(112)	116.4(8)	S(211)–C(213)–S(212)	113.8(8)
S(111)–C(113)–N(114)	120.7(10)	S(211)–C(213)–N(214)	122.0(10)
S(112)–C(113)–N(114)	122.9(10)	S(212)–C(213)–N(214)	124.0(10)
Nb(1)–S(121)–C(123)	89.5(5)	Nb(2)–S(221)–C(223)	85.5(5)
Nb(1)–S(122)–C(123)	89.3(5)	Nb(2)–S(222)–C(223)	88.6(5)
S(121)–C(123)–S(122)	112.8(8)	S(221)–C(223)–S(222)	118.0(8)
S(121)–C(123)–N(124)	123.2(10)	S(221)–C(223)–N(224)	122.6(9)
S(122)–C(123)–N(124)	124.0(11)	S(222)–C(223)–N(224)	119.4(10)
Nb(1)–S(131)–C(133)	90.8(5)	Nb(2)–S(231)–C(233)	91.5(6)
Nb(1)–S(132)–C(133)	89.4(5)	Nb(2)–S(232)–C(233)	90.5(5)
S(131)–C(133)–S(132)	112.6(8)	S(231)–C(233)–S(232)	111.3(9)
S(131)–C(133)–N(134)	125.0(11)	S(231)–C(233)–N(234)	127.7(13)
S(132)–C(133)–N(134)	122.5(11)	S(232)–C(233)–N(234)	120.9(12)

of 3.64 Å. It is likely that this binuclear complex is quite flexible in solution and falls into this conformation only on crystallisation. Packing in the crystal is at normal van der Waals distances.

The N–N bond length, 1.25(2) Å, is that of an N=N double bond. It is, however, only slightly shorter than the N–N bond in the bridged binuclear complexes $[\{TaCl_3[P(CH_2Ph)_3]_2(thf)\}_2(\mu\text{-}N_2)]$[11] and $[\{Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2\}_2(\mu\text{-}N_2)]$[12] in which the bridging ligand was described as a hydrazido(4−)-group Ta=N–N=Ta. Our Nb–N distances, mean 1.842 Å, are of the same order as the Ta–N lengths in those complexes, 1.796(5) and (mean of two) 1.840(3) Å, and these suggest that there is a bond order of rather more than unity in the Nb–N bond, and therefore rather less than two in the N–N bond.

Protonation of $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$.—The reaction of an excess of anhydrous HCl, HBr, or HI with $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ in a variety of solvents (thf, CH_2Cl_2, or MeCN) gives hydrazine, in greater than 90% yield, and the corresponding $[Ta(S_2CNEt_2)_3X_2]$, as shown in Equation (1).

$$[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)] + 4HX \longrightarrow 2[Ta(S_2CNEt_2)_3X_2] + N_2H_4 \quad (1)$$

The complexes, $[Ta(S_2CNEt_2)_3X_2]$ (X = Cl, Br, or I) have been isolated as microcrystalline, yellow to orange solids, and characterised by elemental analysis, ^1H n.m.r. spectroscopy (Table 1), and, for the bromo-complex, by *X*-ray crystallography (see below). Crude samples of these complexes all exhibit small additional ethyl ^1H n.m.r. signals which, by comparison with an authentic sample, were shown to be due to contamination by $[NH_2Et_2]Cl$, presumably formed by protic attack on the dithiocarbamato-ligand. The impurity represents about 8% of the total material (integration of the ^1H n.m.r. spectrum), but can be removed by careful recrystallisation from a dichloromethane–diethyl ether mixture.

Like their parent dinitrogen complex, $[Ta(S_2CNEt_2)_3X_2]$ exhibit only a single set of ethyl signals in the ^1H n.m.r. spectrum. This fluxional behaviour was maintained to −60 °C.

Incidentally, the reaction of acid with $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ is the only pathway to $[Ta(S_2CNEt_2)_3X_2]$: the reactions of TaX_5 with an excess of either $SiMe_3(S_2CNEt_2)$ or $Na(S_2CNEt_2)$ result only in $[Ta(S_2CNEt_2)_2X_3]$.[13]

Description of the Molecule $[TaBr_2(S_2CNEt_2)_3]$.—The molecules of $[TaBr_2(S_2CNEt_2)_3]$ exist as discrete entities in the crystal (Figure 2), with the Ta atom showing eight-co-ordination in the dodecahedral pattern as described by Hoard and Silverton.[14] Two S_2CNEt_2 ligands span the two *m* edges of one A_2B_2 trapezoid plane, the third spans the *a* edge of the other trapezoid plane, in which the two B sites are occupied by the two bromide ligands. A pseudo-two-fold symmetry axis passes through the midpoints of S(4a) ··· S(4b) and S(3b) ··· S(5b), and relates, approximately, not only the atoms of the co-ordination sphere, but also the outer atoms of the S_2CNEt_2 ligands. The atomic co-ordinates and principal molecular dimensions are shown in Tables 4 and 5 respectively.

In dodecahedral systems involving d^0 metal ions, steric factors are predominant in determining ligand arrangements and co-ordination dimensions.[15] The bromide ligands occupy B sites, where there is least crowding, and are almost *trans* to one another. The three bidentate S_2CNEt_2 groups are bound in the more symmetrical of the two possible arrangements, and the Ta–S_A distances (S_A is in an A site), mean value 2.575(5) Å, are,

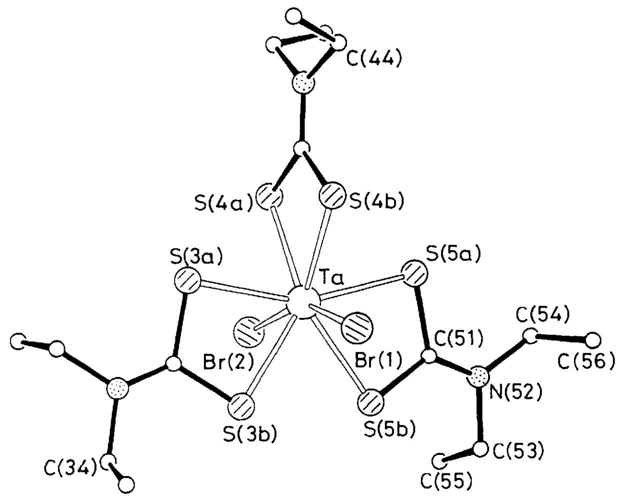

Figure 2. View of a molecule of $[TaBr_2(S_2CNEt_2)_3]$ showing the labelling system used in the text

Table 4. Final atomic co-ordinates (fractional × 10^4) for $[TaBr_2(S_2CNEt_2)_3]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ta	2 852.8(4)	2 445.8(3)	4 899.1(3)
Br(1)	4 463(1)	2 311.7(8)	3 730.2(8)
Br(2)	2 011(1)	2 208.1(9)	6 420.7(7)
S(3a)	3 382(2)	4 034(2)	5 317(2)
S(3b)	4 844(3)	2 555(2)	5 784(2)
C(31)	4 661(9)	3 664(7)	5 887(6)
N(32)	5 369(7)	4 175(6)	6 342(5)
C(33)	5 073(10)	5 139(7)	6 490(6)
C(34)	6 421(10)	3 818(8)	6 815(7)
C(35)	4 295(11)	5 259(9)	7 249(7)
C(36)	7 505(13)	3 815(11)	6 277(10)
S(4a)	758(2)	3 190(2)	4 994(2)
S(4b)	2 080(2)	3 184(2)	3 515(2)
C(41)	785(9)	3 503(6)	3 947(6)
N(42)	−114(8)	3 913(5)	3 542(5)
C(43)	−1 205(9)	4 189(9)	3 971(8)
C(44)	−127(10)	4 074(8)	2 623(7)
C(45)	−2 146(12)	3 450(9)	3 929(9)
C(46)	286(16)	5 009(11)	2 380(9)
S(5a)	1 558(2)	1 205(2)	4 252(2)
S(5b)	3 658(2)	879(2)	5 270(2)
C(51)	2 450(9)	411(7)	4 786(6)
N(52)	2 176(8)	−444(6)	4 819(5)
C(53)	2 901(9)	−1 049(6)	5 375(7)
C(54)	1 167(9)	−847(7)	4 337(6)
C(55)	2 425(12)	−1 027(9)	6 266(8)
C(56)	1 561(13)	−1 314(9)	3 551(7)

typically,[15,16] significantly longer than the Ta–S_B distances, mean 2.533(7) Å.

In the two S_2CNEt_2 ligands that lie on the *m* edges, the C–S_A distances are slightly shorter than the C–S_B values; this presumably corresponds to the difference in Ta–S distances but this feature is rarely noted in this type of complex.[15] In the third S_2CNEt_2 ligand the difference in C–S lengths is less marked. Each of the S_2CNEt_2 ligands has the dimensions (Table 5) and the nearly planar form expected for a delocalised π-electron system. The dimensions in the three ligands are very similar, and there are only small twists about the C(*n*1)–N(*n*2) bonds, of 4.2(4), 5.0(4), and 6.4(3)° for $n = 3$, 4, and 5 respectively. The distortions from planarity presumably result from intermolecular packing effects. In each ligand, also, the pair of outer methyl groups point outwards, one each side, from the S_2CNC_2 plane, with the C(*n*1)–N(*n*2)–C–C torsion angles in the range 85.5(11)—100.1(11)°.

The intermolecular contacts correspond to van der Waals interactions and are mainly between pairs of methyl groups.

Protonation of $[\{Nb(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$.—The reactions of an excess of anhydrous HCl or HBr with the niobium dinitrogen complex are also believed to give $[Nb(S_2CNEt_2)_3X_2]$, at least initially. Certainly stoicheiometric yields of hydrazine are produced. Elemental analysis and ^1H n.m.r. spectroscopy of the isolated metal-containing products (Table 1) are consistent with the formulation $[Nb(S_2CNEt_2)_3X_2]$, but both techniques are poorly diagnostic for this class of compound, particularly since contamination with $[NH_2Et_2]^+$ salts also occurs with these niobium compounds as it did for the tantalum series. Use of ^{93}Nb n.m.r. spectroscopy showed that only one ^{93}Nb n.m.r.-active product was formed in each reaction with HCl or HBr, and that these products showed signals in the same position as authentic samples of $[NbCl_2(S_2CNEt_2)_3]$ and $[NbBr_2(S_2CNEt_2)_3]$[8] respectively (Table 6). Furthermore the position of these signals is very different from that for $[Nb(S_2CNEt_2)_4]^+$ or the corresponding $[Nb(S_2CNEt_2)_2X_3]$ (X = Cl or Br).[17]

Attempts to grow crystals of $[NbCl_2(S_2CNEt_2)_3]$ by allowing diethyl ether to diffuse slowly into a saturated solution of the chloro-complex in dichloromethane resulted in the isolation of dark red needles of $[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$, a material whose identity was established by *X*-ray crystallography (see below). The approximate empirical formula of this material, '$NbCl_{1.7}(S_2CNEt_2)_{2.7}$' does not readily permit identification of its true nature without an *X*-ray crystallographic analysis. It is also clear, since this material was formed from an authentic sample of $[NbCl_2(S_2CNEt_2)_3]$, that in these systems reasonably facile redistribution and sulphur-abstraction processes occur.

Description of the Molecule $[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$.—There are two independent $[Nb(S_2CNEt_2)_4]^+$ cations and two independent $[NbCl_5S]^{2-}$ anions in the crystal. The anions each lie about a centre of symmetry and are therefore disordered; in each anion, four of the Cl atoms form a square plane with Cl ··· Cl diagonal distances in the range 4.757(14)—4.815(15) Å. In the axes normal to these planes, the remaining Cl and S atoms are arranged randomly in either of the two centrosymmetrically related positions, with Cl ··· S distances of 4.545(16) and 4.478(18) Å. The thermal ellipsoids of the Nb atoms in the anions are a little elongated along the Cl ··· S axis, and we suggest that the Nb atom is removed, say 0.16 Å from the crystallographic inversion centre towards the S atom so that Nb–S is *ca.* 2.09 Å and the *trans*-Nb–Cl distance is *ca.* 2.42 Å. This would then be in fair agreement with the dimensions in related complexes, *e.g.* $[NbCl_5O]$,[18] $[WCl_5S]$,[19] $[NbCl_4S]$,[20] and $[WCl_4S]$,[21] where the M–S distances are in the range 2.085(5)—2.132(13) Å, the *trans*-M–Cl in the two octahedral complexes are 2.555(4) and 2.461(12) Å, and the M–Cl equatorial distances are all *ca.* 2.30—2.40 Å. In the centrosymmetric, octahedral complex anions $[MCl_6]^-$ (M = Nb or Ta) the M–Cl distances have been found in the range 2.29—2.37 Å with mean values 2.33(1) and 2.35(1) Å for the complexes of Nb and Ta respectively.[22]

The two cations show virtually identical conformations about the Nb atoms. Each Nb atom has eight-fold co-ordination by four bidentate S_2CNEt_2 ligands in a dodecahedral arrangement, Figure 3. Each S_2CNEt_2 ligand spans an *m* edge of the dodecahedron,[14] and the Nb–S distances follow the normal

Table 5. Selected molecular dimensions (lengths in Å, angles in °) for $[TaBr_2(S_2CNEt_2)_3]$ with e.s.d.s in parentheses

(*a*) About the Ta atom; e.s.d.s for all angles less than 0.1°

Ta–Br(1)	2.615(1)	Ta–Br(2)	2.625(1)
Ta–S(3a)	2.527(3)	Ta–S(3b)	2.580(3)
Ta–S(4a)	2.585(3)	Ta–S(4b)	2.567(3)
Ta–S(5a)	2.540(3)	Ta–S(5b)	2.567(3)
Br(1)–Ta–Br(2)	154.7		
Br(1)–Ta–S(3a)	95.6	Br(1)–Ta–S(3b)	78.0
Br(1)–Ta–S(4a)	135.2	Br(1)–Ta–S(4b)	69.6
Br(1)–Ta–S(5a)	93.0	Br(1)–Ta–S(5b)	81.4
Br(2)–Ta–S(3a)	88.6	Br(2)–Ta–S(3b)	80.7
Br(2)–Ta–S(4a)	70.0	Br(2)–Ta–S(4b)	135.7
Br(2)–Ta–S(5a)	93.1	Br(2)–Ta–S(5b)	78.5
S(3a)–Ta–S(3b)	67.2		
S(3a)–Ta–S(4a)	77.4	S(3a)–Ta–S(4b)	83.4
S(3a)–Ta–S(5a)	156.1	S(3a)–Ta–S(5b)	136.2
S(3b)–Ta–S(4a)	134.2	S(3b)–Ta–S(4b)	133.5
S(3b)–Ta–S(5a)	136.6	S(3b)–Ta–S(5b)	69.5
S(4a)–Ta–S(4b)	65.7		
S(4a)–Ta–S(5a)	80.8	S(4a)–Ta–S(5b)	133.3
S(4b)–Ta–S(5a)	78.7	S(4b)–Ta–S(5b)	133.6
S(5a)–Ta–S(5b)	67.3		

(*b*) In the S_2CNEt_2 ligands

S(3a)–C(31)	1.745(10)	S(3a)–C(31)–S(3b)	111.2(5)
S(3b)–C(31)	1.679(10)	S(3a)–C(31)–N(32)	124.5(8)
C(31)–N(32)	1.294(12)	S(3b)–C(31)–N(32)	124.2(8)
N(32)–C(33)	1.498(14)	C(31)–N(32)–C(33)	121.5(8)
N(32)–C(34)	1.465(14)	C(31)–N(32)–C(34)	121.7(9)
C(33)–C(35)	1.508(16)	C(33)–N(32)–C(34)	116.4(8)
C(34)–C(36)	1.493(18)	N(32)–C(33)–C(35)	111.8(9)
S(4a)–C(41)	1.717(10)	N(32)–C(34)–C(36)	110.9(9)
S(4b)–C(41)	1.679(11)	S(4a)–C(41)–S(4b)	110.7(6)
C(41)–N(42)	1.317(13)	S(4a)–C(41)–N(42)	123.7(8)
N(42)–C(43)	1.465(14)	S(4b)–C(41)–N(42)	125.5(8)
N(42)–C(44)	1.467(13)	C(41)–N(42)–C(43)	122.1(9)
C(43)–C(45)	1.519(18)	C(41)–N(42)–C(44)	122.4(9)
C(44)–C(46)	1.523(20)	C(43)–N(42)–C(44)	115.3(9)
S(5a)–C(51)	1.744(10)	N(42)–C(43)–C(45)	110.7(10)
S(5b)–C(51)	1.674(10)	N(42)–C(44)–C(46)	113.9(10)
C(51)–N(52)	1.316(13)	S(5a)–C(51)–S(5b)	111.7(6)
N(52)–C(53)	1.479(13)	S(5a)–C(51)–N(52)	123.5(8)
N(52)–C(54)	1.462(13)	S(5b)–C(51)–N(52)	124.8(8)
C(53)–C(55)	1.516(16)	C(51)–N(52)–C(53)	119.7(8)
C(54)–C(56)	1.499(16)	C(51)–N(52)–C(54)	123.6(8)
		C(53)–N(52)–C(54)	116.7(8)
		N(52)–C(53)–C(55)	109.7(9)
		N(52)–C(54)–C(56)	112.4(9)

Table 6. ^{93}Nb N.m.r. chemical shifts of dithiocarbamato-complexes

Compound	Chemical shift[a]/p.p.m.	$\Delta\nu_{\frac{1}{2}}$/kHz
$[NbCl_2(S_2CNEt_2)_3]$	−315[b]	5.0
$[NbBr_2(S_2CNEt_2)_3]$	−545[c]	2.6
$[NbCl_3(S_2CNEt_2)_2]$	−418	2.8
$[Nb(S_2CNEt_2)_4]Cl$	−325	5.3
$[\{NbCl_3(thf)_2\}_2(\mu-N_2)]$[d]	−532	4.6

[a] All chemical shifts *versus* $[NbCl_6]^-$, $\delta \pm 4$ p.p.m. [b] Identical signals obtained from samples prepared *via* the reaction of $NbCl_5$ with $SiMe_3(S_2CNEt_2)$, or the protonation of $[\{Nb(S_2CNEt_2)_3\}_2(\mu-N_2)]$ with HCl. [c] Identical signals obtained from samples prepared *via* the reaction of $NbBr_5$ with $SiMe_3(S_2CNEt_2)$, or the protonation of $[\{Nb(S_2CNEt_2)_3\}_2(\mu-N_2)]$ with HBr. [d] Weak signal only observed after 43 000 scans. No signal obtained for $[\{Nb(S_2CNEt_2)_3\}_2(\mu-N_2)]$.

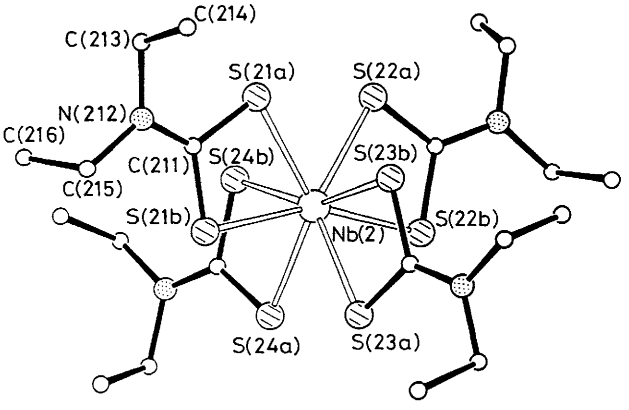

Figure 3. View of one of the two virtually identical cations in the crystal of $[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$; for the disordered ethyl groups only one of the orientations is shown

pattern,[15,16] *i.e.* the Nb–S_A (where S_A is at an A site of the dodecahedron) bond lengths, mean 2.575(3) Å, are rather longer than the Nb–S_B distances, mean 2.514(3) Å. Since, in similar complexes, no systematic differences in the C–S_A and C–S_B dimensions have been noted (and the same is found in our cations), it has been suggested that the differences in Nb–S dimensions arise principally from steric effects.

Some of the ethyl groups in the S_2CNEt_2 ligands have unique arrangements and are well resolved, others are disordered but clearly resolved in two orientations. There are further S_2CNEt_2 ligands which are poorly resolved and probably disordered in a random arrangement. There appear to be several improbably short contacts between cations, but these all involve atoms of disordered groups; the arrangement of an ethyl group in one ligand is determined by the arrangement of an ethyl group in an adjacent cation, which, in turn, is influenced by its neighbours.

Atomic co-ordinates are listed in Table 7 and selected molecular dimensions are in Table 8.

Conclusion

Although there are many examples in the literature of complexes which contain a dinitrogen ligand bridging two metal centres very few are susceptible to protic attack to give hydrazine, and none of them gives ammonia. Our ultimate aim is to define the protonation chemistry of a bridging dinitrogen ligand and the systems described in this paper are uniquely suited for such a mechanistic study: the molecule contains a single dinitrogen ligand which bridges two identical '$M(S_2CNEt_2)_3$' cores wherein the coligands act as spectators to the protonation reactions occurring at the bridge. Furthermore the protonation reactions are essentially quantitative. In the following five papers we will elucidate more fully the protonation chemistry of $[\{M(S_2CNEt_2)_3\}_2(\mu-N_2)]$ and related complexes.

Experimental

All manipulations were routinely performed under an atmosphere of dinitrogen using standard Schlenk techniques. Solvents were freshly distilled from the necessary drying agent immediately prior to use. The reagents, $(Me_3Si)_2NN(SiMe_3)_2$,[23] $Me_3SiNHNHSiMe_3$,[23] and $SiMe_3(S_2CNEt_2)$[24] were prepared by the literature methods, as was $[Nb(S_2CNEt_2)_3X_2]$ (X = Cl or Br).[13]

Solutions of anhydrous HX (X = Cl or Br) were prepared in

Table 7. Final atomic co-ordinates (fractional × 10^4) for $[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	S.o.f.[a]	Atom	*x*	*y*	*z*	S.o.f.[a]
Nb(1)	2 578.6(9)	1 736.4(7)	348(1)		Nb(2)	2 402.3(8)	−1 699.5(8)	−364(1)	
S(11a)	2 500(3)	1 320(2)	−1 526(4)		S(21a)	1 794(2)	−1 037(2)	−1 516(4)	
S(11b)	3 300(3)	1 001(3)	131(5)		S(21b)	1 417(3)	−1 566(2)	307(4)	
C(111)	3 034(9)	899(8)	−1 156(16)		C(211)	1 246(11)	−1 115(9)	−695(18)	
N(112)	3 236(8)	530(7)	−1 777(15)		N(212)	748(10)	−851(9)	−853(19)	
C(113)	2 953(10)	440(9)	−2 931(14)		C(213)	666(11)	−425(14)	−1 682(21)	
C(114)	2 448(11)	55(10)	−2 981(23)		C(214)	908(16)	113(11)	−1 249(28)	
C(115)	3 675(13)	112(10)	−1 354(18)		C(215)	287(16)	−955(17)	−50(31)	
C(116)	4 262(10)	283(12)	−1 548(21)		C(216)	−133(16)	−1 337(18)	−717(43)	
S(12a)	1 717(3)	2 140(2)	−745(4)		S(22a)	2 910(3)	−1 433(2)	−2 054(4)	
S(12b)	2 076(3)	2 425(3)	1 386(5)		S(22b)	3 409(3)	−2 065(3)	−372(6)	
C(121)	1 627(11)	2 534(10)	333(18)		C(221)	3 499(11)	−1 751(9)	−1 577(17)	
N(122)	1 237(12)	2 925(11)	275(19)		N(222)	4 036(9)	−1 680(9)	−1 956(17)	
C(123)	889(17)	3 044(16)	−771(27)		C(223)	4 076(11)	−1 398(11)	−2 980(21)	
C(124)	348(20)	2 709(19)	−768(33)		C(224)	3 974(14)	−1 764(15)	−3 885(23)	
C(125)	1 144(31)	3 307(20)	1 192(43)	0.5	C(225)	4 533(14)	−1 975(16)	−1 403(24)	
C(126)	719(23)	2 998(24)	1 817(35)	0.5	C(226)	4 914(13)	−1 510(17)	−677(28)	
C(128)	1 380(32)	3 438(22)	893(59)	0.5	S(23a)	2 699(3)	−1 695(3)	1 651(4)	
C(129)	961(24)	3 469(22)	1 752(46)	0.5	S(23b)	2 803(3)	−815(2)	264(4)	
S(13a)	2 687(3)	1 339(3)	2 246(4)		C(231)	2 987(10)	−1 085(8)	1 484(16)	
S(13b)	1 824(3)	1 050(3)	668(5)		N(232)	3 352(9)	−847(8)	2 197(14)	
C(131)	2 125(12)	975(9)	1 957(19)		C(233)	3 407(17)	−1 063(16)	3 317(21)	0.6
N(132)	1 880(12)	617(9)	2 677(18)		C(234)	2 914(17)	−944(16)	4 026(33)	0.6
C(133)	2 151(17)	597(14)	3 791(20)		C(238)	3 626(25)	−1 180(21)	3 096(36)	0.4
C(134)	1 954(25)	1 044(20)	4 518(46)	0.5	C(239)	4 027(28)	−1 639(25)	2 855(58)	0.4
C(139)	2 612(29)	183(31)	3 619(72)	0.5	C(235)	3 574(12)	−311(11)	2 024(22)	
C(135)	1 356(16)	306(11)	2 277(27)		C(236)	4 109(13)	−369(12)	1 469(24)	
C(136)	1 509(14)	−231(11)	1 916(22)		S(24a)	2 228(3)	−2 614(2)	478(4)	
S(14a)	3 438(3)	2 151(3)	1 425(5)		S(24b)	1 952(3)	−2 346(2)	−1 693(4)	
S(14b)	3 054(3)	2 452(3)	−677(4)		C(241)	1 882(9)	−2 789(8)	−669(14)	
C(141)	3 500(10)	2 582(9)	394(16)		N(242)	1 553(8)	−3 219(7)	−796(12)	
N(142)	3 903(8)	2 974(8)	432(16)		C(243)	1 462(13)	−3 593(11)	142(21)	
C(143)	4 315(10)	3 026(11)	1 430(21)		C(244)	973(20)	−3 394(18)	783(38)	0.6
C(144)	4 042(13)	3 398(11)	2 183(23)		C(249)	1 971(34)	−3 908(31)	254(61)	0.4
C(145)	3 926(12)	3 368(11)	−474(18)		C(245)	1 248(12)	−3 361(10)	−1 867(19)	
C(146)	4 401(18)	3 137(14)	−1 121(23)		C(246)	676(13)	−3 084(12)	−1 956(22)	
Nb(3)	5 000	0	5 000		Nb(4)	0	0	5 000	
Cl(31)	4 004(3)	−65(3)	5 281(5)		Cl(41)	996(3)	11(3)	5 561(6)	
S/Cl(32)[b]	5 053(3)	790(3)	5 892(6)		S/Cl(42)[b]	104(4)	771(3)	4 129(8)	
Cl(33)	4 757(3)	472(3)	3 392(5)		Cl(43)	−216(3)	508(3)	6 551(6)	

[a] Site occupancy factor, when less than 1.0. [b] Disordered S/Cl atom; refer to text.

any particular solvent by mixing equimolar amounts of Me_3SiX and MeOH to give the desired concentration of acid.

Hydrazine Analysis.[25]—Hydrazine produced from the reaction of $[\{M(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ with an excess of HX was determined by the following general method. The dinitrogen complex was treated with 10 mol equivalents of HX ($SiMe_3X$ with MeOH) in the required solvent and stirred at room temperature for 30 min. The solvent and all volatiles were then removed *in vacuo* and the residue extracted with water *ca.* 5 cm^3, filtered through Celite to remove any solid, and the filtrate accurately made up to 250.0 cm^3. To a 5.0-cm^3 aliquot of this solution was added a standard *p*-dimethylaminobenzaldehyde (pdmab) solution (10.0 cm^3) and the resulting solution made up to 25.0 cm^3. The absorbance of this solution at λ = 458 nm was measured on a Philips-Scientific SP1800 spectrophotometer. The concentration of the solution was determined by comparison using a calibration curve previously established for that batch of pdmab solution, using $[N_2H_5]HSO_4$ (A.R.) as a calibrant.

μ-Dinitrogen-bis[trichlorobis(tetrahydrofuran)niobium].—To a rapidly stirred slurry of $NbCl_5$ (1.03 g, 3.81 mmol) in dichloromethane (*ca.* 50 cm^3) was added thf (0.55 cm^3, 7.6 mmol) and $(Me_3Si)_2NN(SiMe_3)_2$ (0.61 g, 1.88 mmol). The solution rapidly darkened to a red-purple and was stirred for a total of 4 h. The solvent was removed *in vacuo* until the purple microcrystalline solid started to precipitate. The solution was set aside at −20 °C overnight then removed by filtration, washed with ice-cold dichloromethane, and dried *in vacuo* to give $[\{NbCl_3(thf)_2\}_2(\mu\text{-}N_2)]$ (0.92 g, 1.19 mmol, 62.5%) of analytically pure solid.

μ-Dinitrogen-bis[trichlorobis(tetrahydrofuran)tantalum].—To a suspension of $TaCl_5$ (2.1 g, 5.86 mmol) in dichloromethane (*ca.* 30 cm^3) at −70 °C was added $Me_3SiNHNHSiMe_3$ (0.6 cm^3, 3.37 mmol) dropwise. Whilst maintaining rapid stirring the mixture was allowed to warm to room temperature during which time the solution turned dark red. After stirring for *ca.* 1 h the solution was filtered, the filtrate recooled to −70 °C, and thf (3.0 cm^3, 41.5 mmol) added slowly. Upon allowing the solution to warm to room temperature, and maintaining the stirring, red microcrystalline $[\{TaCl_3(thf)_2\}_2(\mu\text{-}N_2)]$ (0.86 g, 0.91 mmol, 31%) was deposited after 2—3 h. The solid was removed by filtration, washed with diethyl ether, and dried *in vacuo* to give analytically pure product.

Table 8. Selected molecular dimensions (lengths in Å, angles in °) for $[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$ with e.s.d.s in parentheses

(*a*) In the cations			
Nb(1)–S(11a)	2.572(5)	Nb(1)–S(11b)	2.523(7)
Nb(1)–S(12a)	2.570(6)	Nb(1)–S(12b)	2.499(7)
Nb(1)–S(13a)	2.583(6)	Nb(1)–S(13b)	2.513(7)
Nb(1)–S(14a)	2.568(7)	Nb(1)–S(14b)	2.507(7)
Nb(2)–S(21a)	2.569(6)	Nb(2)–S(21b)	2.526(6)
Nb(2)–S(22a)	2.586(6)	Nb(2)–S(22b)	2.524(7)
Nb(2)–S(23a)	2.584(6)	Nb(2)–S(23b)	2.510(6)
Nb(2)–S(24a)	2.565(6)	Nb(2)–S(24b)	2.508(6)
S(11a)–C(111)	1.674(21)	S(11b)–C(111)	1.714(20)
S(12a)–C(121)	1.699(24)	S(12b)–C(121)	1.657(24)
S(13a)–C(131)	1.620(27)	S(13b)–C(131)	1.733(25)
S(14a)–C(141)	1.700(22)	S(14b)–C(141)	1.680(21)
S(21a)–C(211)	1.707(25)	S(21b)–C(211)	1.719(23)
S(22a)–C(221)	1.668(24)	S(22b)–C(221)	1.731(23)
S(23a)–C(231)	1.687(21)	S(23b)–C(231)	1.704(20)
S(24a)–C(241)	1.665(19)	S(24b)–C(241)	1.714(20)
C(111)–N(112)	1.318(27)	C(211)–N(212)	1.34(3)
C(121)–N(122)	1.34(4)	C(221)–N(222)	1.38(3)
C(131)–N(132)	1.42(3)	C(231)–N(232)	1.336(28)
C(141)–N(142)	1.358(30)	C(241)–N(242)	1.326(27)
S(11a)–Nb(1)–S(11b)	67.3(2)	S(21a)–Nb(2)–S(21b)	67.7(2)
S(11a)–Nb(1)–S(12a)	70.3(2)	S(21a)–Nb(2)–S(22a)	68.7(2)
S(11b)–Nb(1)–S(12b)	154.1(2)	S(21b)–Nb(2)–S(22b)	156.8(2)
S(12a)–Nb(1)–S(12b)	68.2(2)	S(22a)–Nb(2)–S(22b)	67.3(2)
S(13a)–Nb(1)–S(13b)	67.4(2)	S(23a)–Nb(2)–S(23b)	67.4(2)
S(13a)–Nb(1)–S(14a)	69.0(2)	S(23a)–Nb(2)–S(24a)	68.8(2)
S(13b)–Nb(1)–S(14b)	155.5(2)	S(23b)–Nb(2)–S(24b)	155.6(2)
S(14a)–Nb(1)–S(14b)	68.0(2)	S(24a)–Nb(2)–S(24b)	68.2(2)
Nb(1)–S(11a)–C(111)	89.6(7)	Nb(2)–S(21a)–C(211)	89.7(8)
Nb(1)–S(11b)–C(111)	90.4(7)	Nb(2)–S(21b)–C(211)	90.9(9)
Nb(1)–S(12a)–C(121)	86.3(8)	Nb(2)–S(22a)–C(221)	89.6(8)
Nb(1)–S(12b)–C(121)	89.5(9)	Nb(2)–S(22b)–C(221)	90.3(9)
Nb(1)–S(13a)–C(131)	88.8(9)	Nb(2)–S(23a)–C(231)	88.0(7)
Nb(1)–S(13b)–C(131)	88.7(9)	Nb(2)–S(23b)–C(231)	90.1(7)
Nb(1)–S(14a)–C(141)	87.5(7)	Nb(2)–S(24a)–C(241)	87.6(7)
Nb(1)–S(14b)–C(141)	90.0(8)	Nb(2)–S(24b)–C(241)	88.4(7)
S(11a)–C(111)–S(11b)	112.8(12)	S(21a)–C(211)–S(21b)	111.8(14)
S(12a)–C(121)–S(12b)	115.9(15)	S(22a)–C(221)–S(22b)	112.8(14)
S(13a)–C(131)–S(13b)	115.1(14)	S(23a)–C(231)–S(23b)	113.0(12)
S(14a)–C(141)–S(14b)	114.1(13)	S(24a)–C(241)–S(24b)	114.6(12)
(*b*) In the anions			
Nb(3)–Cl(31)	2.382(6)	Nb(4)–Cl(41)	2.388(6)
Nb(3)–S/Cl(32)	2.273(8)	Nb(4)–S/Cl(42)	2.239(9)
Nb(3)–Cl(33)	2.378(7)	Nb(4)–Cl(43)	2.409(8)
Cl(31)–Nb(3)–S/Cl(32)	90.5(3)	Cl(41)–Nb(4)–S/Cl(42)	90.0(3)
Cl(31)–Nb(3)–Cl(33)	88.7(2)	Cl(41)–Nb(4)–Cl(43)	90.3(2)
S/Cl(32)–Nb(3)–Cl(33)	89.4(3)	S/Cl(42)–Nb(4)–Cl(43)	88.6(3)

μ-*Dinitrogen-bis*[*tris*(*diethyldithiocarbamato*)*tantalum*].—To a stirred suspension of $[\{TaCl_3(thf)_2\}_2(\mu\text{-}N_2)]$ (1.4 g, 1.48 mmol) in dichloromethane (*ca.* 20 cm^3) was added $SiMe_3(S_2CNEt_2)$ (1.8 cm^3, 8.1 mmol). The mixture was stirred for 3 h at room temperature to yield an orange-red solution. The solvent was removed *in vacuo* to yield a sticky solid. Addition of thf (*ca.* 20 cm^3) precipitated $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ as an orange microcrystalline solid (1.66 g, 1.30 mmol, 88%). The solid was removed by filtration, washed with a small amount of thf, and dried *in vacuo*. The material can be recrystallised from dichloromethane–thf.

The niobium analogue, $[\{Nb(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$, was prepared in an identical manner from $[\{NbCl_3(thf)_2\}_2(\mu\text{-}N_2)]$ except that the reaction was heated under reflux for 1 h to ensure complete substitution. Yield 85%.

Dibromotris(*diethyldithiocarbamato*)*tantalum*.—To a solution of $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (0.30 g, 0.23 mmol) in dichloromethane (*ca.* 20 cm^3) was added a solution of anhydrous HBr (MeOH, 2.3 mmol + $SiMe_3Br$, 2.3 mmol). There was an immediate reaction and the bright orange solution was stirred for a further hour. The mixture was filtered through Celite to remove $[N_2H_5]Br$, and the filtrate evaporated to dryness *in vacuo* to yield an oily material. This was dissolved in the minimum of dichloromethane and crystallised slowly by the addition of diethyl-ether, to yield orange-red prisms of $[TaBr_2(S_2CNEt_2)_3]$ (0.25 g, 0.32 mmol, 67%). The complexes, $[Ta(S_2CNEt_2)_3X_2]$ (X = Cl or I) and $[Nb(S_2CNEt_2)_3X_2]$ (X = Cl or Br) were prepared in an analogous manner.

Niobium-93 *N.M.R. Spectroscopy*.—All ^{93}Nb n.m.r. spectra were recorded in 10-mm n.m.r. tubes using dichloromethane as the solvent, containing dichlorodideuteriomethane (5% v/v) to act as the field/frequency lock. All spectra were recorded under ambient conditions, and externally referenced against the relatively sharp ($\Delta\nu_{\frac{1}{2}}$ = 30 Hz) signal of $[NbCl_6]^-$ in acetonitrile.

Spectra were recorded on a JEOL FX-90Q or a Bruker WM360 spectrometer. In particular, for the JEOL FX-90Q machine we encountered the familiar problem of acoustic ringing. The source of this disturbance is electromagnetic generation and detection of ultrasonic waves in the receiver coil, cables, and filters immediately after the high-power excitation pulse.[26] Free induction decays (f.i.d.s) which were both weak and of short duration resulted in problems of distinguishing between the n.m.r. signal and baseline rolling (measured linewidths were of the order 1–5 kHz). Pre-acquisition delays were generally employed, the favourable abundance and sensitivity of the ^{93}Nb nucleus compensating for the associated loss of n.m.r. signal. Where this was unsatisfactory a pulse sequence of the type $(90°_{1/3B1}\text{–f.i.d.}^{(+)})_3\text{–}(270°_{B1}\text{–f.i.d.}^{(-)})$ (where B1 is the power of the exciting R.F. field) was used;[27] field attenuation was performed through the spin-locking unit of the JEOL FX-90Q driven by the pulse programmer.

Using the JEOL FX-90Q spectrometer, spectra were scanned at 21.86 MHz with a frequency sweepwidth of 36 kHz and the number of scans varied from 1 K to 10 K. The pulse width was 20 μs, which is equivalent to a 90° pulse. A pre-acquisition delay of 500 μs was employed to remove some of the acoustic ringing responses and a post-acquisition delay of 0.1 s was used to allow the re-establishment of equilibrium. A maximum resolution of 8.5 Hz on 4 K of data points was used, and a line-broadening factor of 6—100 Hz (depending on the width of the line being recorded).

Using the Bruker WM360 spectrometer, spectra were scanned at 88.147 MHz with a frequency sweep width of up to 250 kHz. A pulse width of 15 μs was used and the number of scans varied from 1.2 K to 10 K.

Crystal Structure Analyses.—The *X*-ray analysis of $[TaBr_2(S_2CNEt_2)_3]$ is described; the analyses of the other two complexes followed very similar courses. For the three complexes, crystal data are in Table 9, and experimental details in Table 10.

A selected crystal of $[TaBr_2(S_2CNEt_2)_3]$ was mounted, in air, on a glass fibre, and, after preliminary photographic examination, transferred to our Enraf-Nonius CAD4 diffractometer [with monochromated radiation, $\lambda(\text{Mo-}K_{\bar{\alpha}})$ = 0.710 69 Å] for measurement of accurate cell dimensions and diffraction intensities. During processing, the data were corrected for Lorentz-polarisation effects, slight deterioration, absorption (by semi-empirical ψ-scan methods), and negative intensities (by

Table 9. Crystal data

Compound	$[\{Nb(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$	$[TaBr_2(S_2CNEt_2)_3]$	$[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$
Formula	$C_{30}H_{60}N_8Nb_2S_{12}$	$C_{15}H_{30}Br_2N_3S_6Ta$	$2(C_{20}H_{40}N_4NbS_8)\cdot Cl_5NbS$
M	1103.4	785.5	1 674.1
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	13.758(2)	11.096(1)	23.367(4)
b/Å	18.870(6)	14.947(3)	25.025(6)
c/Å	19.391(4)	15.754(2)	12.571(5)
β/°	96.80(2)	91.86(1)	93.70(3)
U/Å^3	4 998.6	2 611.4	7 335.4
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (equiv. to no. 14)	$P2_1/c$ (no. 14)
Z	4	4	4
D_c/ g cm^{-3}	1.466	1.998	1.516
F(000)	2 280	1 520	3 424
μ(Mo-K_α)/cm^{-1}	9.5	76.6	11.2

Table 10. Experimental details of the X-ray analyses

Compound	$[\{Nb(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$	$[TaBr_2(S_2CNEt_2)_3]$	$[Nb(S_2CNEt_2)_4]_2[NbCl_5S]$
Crystal colour, shape	Deep red plates	Orange-red, short rectangular prisms	Dark red, flat needles
Crystal size (mm)	0.38 × 0.26 × 0.02	0.17 × 0.20 × 0.30	0.07 × 0.21 × 0.57
Mounting	On glass fibre	On glass fibre, coated in silicone grease	On glass fibre
On CAD4 diffractometer			
For cell dimension, θ/°	8—9	10—11	10—11
Maximum θ/°	20	25	20
No. of independent reflections	4 665	4 584	6 807
During processing, corrections made for			
Lorentz polarisation	Yes	Yes	Yes
Deterioration	No	Yes	Yes
Absorption	Yes	Yes	Yes
Negative intensities	No	Yes	No
Structure solved by	Direct methods (EEES) in SHELX	Automated Patterson routine (PATT) in SHELXS + subsequent Fourier difference maps	Automated Patterson (PATT) and tangent expansion (TEXP) routines in SHELXS
Final R (ref. 28)	0.074	0.074	0.092*
Final R' (ref. 28)	0.066	0.076	0.095
No. of reflections in refinement	3 540	4 584	4 012
With $I > n\sigma_I$, where n	1	0	1.5
Weighted $w = (\sigma^2_F + gF^2)^{-1}$ where g	0.000 87	0.002 29	0.003 95
Highest peaks in final difference map (eÅ^{-3})	0.6	2.7	0.8
Found near	Disordered Et groups	Ta and Br atoms	Disordered Et groups or cationic Nb atoms

* This crystal has very few observable reflections at θ = 20° and a generally weak data set overall; presumably these arise principally from the disorder in the S_2CNEt_2 ligands, and result in the rather high R factor here.

Bayesian statistics). The data were then entered into the SHELX program system[28] for structure determination by the automated Patterson routines in SHELXS[29] (for the Ta atom) and successive difference maps for the remaining non-hydrogen atoms. Hydrogen atoms were included in idealised positions; the methyl groups were refined with geometrical restraints, and the methylene groups as rigid entities. All non-hydrogen atoms were allowed anisotropic thermal parameters. Refinement by large-block-matrix least-squares methods converged with $R = 0.074$, $R' = 0.076$ for all data weighted $w = (\sigma^2_F + 0.002\,29F^2)^{-1}$.

Scattering curves were taken from ref. 30. Computer programs, in addition to those noted above, have been listed in Table 4 of ref. 31, and were run on the AFRC's VAX 11/750 machine at IHR-Glasshouse Crops Research Institute, Littlehampton.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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