Preparation, Properties, and Crystal and Molecular Structures of the Cyanomethane Adducts of Niobium(IV) Chloride and Di-μ-sulphido-bis[dichloroniobium(IV)]

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The cyanomethane adduct of $NbCl_4$ analyses for $NbCl_4{\cdot}3CH_3CN$ (1). A crystal-structure determination of this species shows that it contains *cis* octahedral $[NbCl_4(NCMe)_2]$ and a solvent CH_3CN molecule. The unique bond lengths are Nb–N 2.220(13) Å and Nb–Cl 2.328(2), 2.343(6), and 2.349(4) Å. The crystals of (1) are orthorhombic with unit-cell dimensions a = 10.437(11), b = 13.883(12), c = 9.828(9) Å, Z = 4, and space group *Pnma*. A total of 729 reflections above background have been collected on a diffractometer and refined to R 0.051.

When the cyanomethane adducts of NbX_4 (X = Cl or Br) are treated with Sb_2S_3 in cyanomethane, adducts of NbX_2S (X = Cl or Br) are formed. The products contain $[\{NbX_2S(NCMe)_2\}_2]$ in which there is a $\overline{Nb–S–Nb–S}$ ring. The crystal structures of two compounds, (2) and (3), containing the $[\{NbCl_2S(NCMe)_2\}_2]$ dimeric unit have been determined. In (2) there are two molecules of occluded CH_3CN for each dimer while (3) has one. Both (2) and (3) are triclinic with space group $P\bar{1}$, with (2) having a = 9.031(7), b = 9.367(6), c = 8.360(8) Å, α = 108.72(9), β = 94.93(7), γ = 105.70(8)°, Z = 1 and (3) having a = 14.965(18), b = 8.838(17), c = 9.543(23) Å, α = 112.42(18), β = 84.39(28), γ = 103.65(21)°, Z = 2. For (2), 1 434, and for (3), 1 530, independent reflections above background have been collected on a diffractometer and refined to R 0.056 and 0.050 respectively.

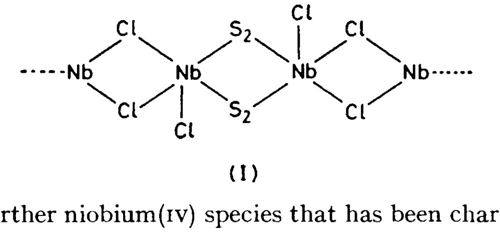
The dimer configurations in (2) and (3) are identical. The niobium atoms are in a pseudo-octahedral environment consisting of two *cis* sulphur [Nb–S 2.338(8)—2.349(7) Å], two *trans* chlorine [Nb–Cl 2.383(6)—2.403(5) Å], and two *cis* nitrogen atoms [Nb–N 2.286(26)—2.334(22) Å]. In addition, in each dimer there is a Nb–Nb single bond [2.862(2)—2.872(3) Å].

A RANGE of niobium(V) and tantalum(V) sulphido-halides has been readily prepared by the reaction of the metal pentahalides with antimony trisulphide at room temperature in the presence of carbon disulphide, equation (1) (X = Cl or Br).[1]

$$3\,MX_5 + Sb_2S_3 \xrightarrow[\text{room temperature}]{CS_2} 3\,MX_3S + 2\,SbX_3 \quad (1)$$

No such mild preparative conditions for the isolation of niobium(IV) sulphido-halides have been reported. The species $[Nb_2X_4Y_4]$ (Y = S or Se; X = Cl, Br, or I) have been prepared at high temperature. For example, $[Nb_2Cl_4S_4]$ was obtained by heating the metal and S_2Cl_2 at 480—500 °C in an evacuated sealed tube.[2]

A re-investigation of this preparation has shown a purer product is obtained by controlling the temperature range to 480—475 °C [3] and that the reaction gives rise to many niobium–sulphur phases. The niobium(IV) species $[Nb_2X_4S_4]$ (X = Cl, Br, or I) are all believed to have the structure depicted diagrammatically in (I) which has been established by single-crystal *X*-ray studies for $[Nb_2Cl_4S_4]$[3,4] and $[Nb_2Cl_4Se_4]$.[3]

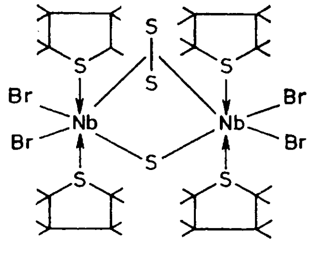


(I)

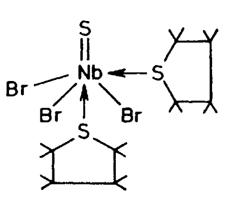
A further niobium(IV) species that has been characterised is $[Nb_2Br_4S(S_2)(tht)_4]$ (tht = tetrahydrothiophen).[5] It was isolated serendipitously from the reaction of $[NbBr_3S]$ with tht through a disproportionation reaction [equation (2)]. Evidence in support of the proposed

$$3\,[NbBr_3S] + 6\,tht \longrightarrow 3\,[NbBr_3S(tht)_2] \longrightarrow [Nb_2Br_4S(S_2)(tht)_4] + [NbBr_5(tht)] + tht \quad (2)$$

disproportionation reaction is provided by single-crystal *X*-ray studies on $[Nb_2Br_4S(S_2)(tht)_4]$[5] and



(II)



(III)

$[NbBr_3S(tht)_2]$[6] whose structures are depicted in (II) and (III) respectively.

It was against this background that a study was commenced with the aim of preparing at ambient temperature some niobium(IV) sulphido-halides. We now report the synthesis and properties of cyanomethane adducts of [NbX_2S] (X = Cl or Br) and *X*-ray crystal structural studies of the cyanomethane adducts of [$NbCl_2S$] and $NbCl_4$.

RESULTS AND DISCUSSION

Initially attempts were made to synthesise [$NbCl_2S$] by allowing niobium(IV) chloride to react in a sealed evacuated tube at high temperatures with antimony trisulphide. This reaction mixture, it has been claimed, leads, at 200 °C, to the desired product,[7] but despite many attempts all our efforts to repeat the published process failed. Some reaction took place and quantities of $SbCl_3$ were produced but none of the reactions went to completion. The failure to obtain the desired product may be caused by the formation of surface layers of [$NbCl_2S$] on the $NbCl_4$ particles which prevent further reaction. Treatment of $NbCl_4$ with Sb_2S_3 in CS_2 solution was also unsuccessful.

TABLE 1

Important bond distances (Å) and angles (°) for [$NbCl_4(NCMe)_2$]·CH_3CN (1), [{$NbCl_2S(NCMe)_2$}$_2$]·2CH_3CN (2), and [{$NbCl_2S(NCMe)_2$}$_2$]·CH_3CN (3) *

	(1) (*j* = 1)	(2) (*j* = 1)	(3) (*j* = 1)	(3) (*j* = 2)
Nb(*j*)–Nb(*j*′)		2.862(2)	2.872(3)	2.864(3)
Nb(*j*)–Cl(*j*1)	2.349(4)	2.383(5)	2.388(5)	2.403(5)
Nb(*j*)–Cl(*j*2)	2.343(6)	2.383(5)	2.385(5)	2.383(6)
Nb(*j*)–Cl(*j*3)	2.328(7)			
Nb(*j*)–S(*j*)		2.349(5)	2.349(7)	2.344(6)
Nb(*j*)–S(*j*′)		2.341(3)	2.338(8)	2.338(6)
Nb(*j*)–N(*a*)	2.220(13)	2.312(12)	2.286(26)	2.334(22)
Nb(*j*)–N(*b*)		2.322(16)	2.308(19)	2.298(22)
Cl(*j*1)–Nb(*j*)–Cl(*j*1′)	92.47(16)			
Cl(*j*1)–Nb(*j*)–Cl(*j*3)	97.53(16)			
Cl(*j*1)–Nb(*j*)–Cl(*j*2)	95.56(15)	157.56(15)	157.34(24)	158.00(25)
Cl(*j*2)–Nb(*j*)–Cl(*j*3)	161.03(23)			
Cl(*j*1)–Nb(*j*)–N(*a*)	89.0(4)	81.29(41)	81.55(45)	82.56(49)
Cl(*j*1)–Nb(*j*)–N(*a*′)	178.1(4)			
Cl(*j*2)–Nb(*j*)–N(*a*)	83.1(4)	84.22(35)	80.18(45)	80.34(49)
Cl(*j*3)–Nb(*j*)–N(*a*)	83.4(4)			
S(*j*)–Nb(*j*)–Nb(*j*′)		52.27(9)	52.04(19)	52.20(16)
S(*j*)–Nb(*j*)–S(*j*′)		104.78(14)	104.44(24)	104.59(23)
S(*j*)–Nb(*j*)–Cl(*j*1)		98.53(16)	96.57(18)	96.67(20)
S(*j*)–Nb(*j*)–Cl(*j*2)		97.04(17)	96.25(19)	96.01(20)
S(*j*)–Nb(*j*)–N(*a*)		84.51(42)	88.5(5)	86.6(5)
S(*j*)–Nb(*j*)–N(*b*)		165.80(31)	169.8(6)	169.3(5)
Nb(*j*′)–Nb(*j*)–S(*j*′)		52.51(12)	52.39(15)	52.39(16)
Nb(*j*′)–Nb(*j*)–Cl(*j*1)		101.26(10)	101.33(17)	101.64(19)
Nb(*j*′)–Nb(*j*)–Cl(*j*2)		101.04(11)	101.29(17)	100.34(17)
Nb(*j*′)–Nb(*j*)–N(*a*)		136.74(42)	140.56(48)	138.7(5)
Nb(*j*′)–Nb(*j*)–N(*b*)		141.85(31)	138.1(6)	138.55(49)
S(*j*′)–Nb(*j*)–Cl(*j*1)		95.16(15)	97.26(21)	97.51(20)
S(*j*′)–Nb(*j*)–Cl(*j*2)		96.38(14)	97.54(22)	96.59(19)
S(*j*′)–Nb(*j*)–N(*a*)		170.50(45)	167.0(5)	168.7(6)
S(*j*′)–Nb(*j*)–N(*b*)		89.36(33)	85.7(6)	86.2(5)
Cl(*j*1)–Nb(*j*)–N(*b*)		81.10(38)	81.98(38)	81.87(46)
Cl(*j*2)–Nb(*j*)–N(*b*)		79.86(38)	82.11(40)	82.32(49)
N(*a*)–Nb(*j*)–N(*a*′)	89.4(5)			
N(*a*)–Nb(*j*)–N(*b*)		81.40(51)	81.3(7)	82.7(7)
Nb(*j*)–S(*j*)–Nb(*j*′)		75.22(14)	75.56(20)	75.41(17)

* Less important dimensions are given in SUP 23021. Primed atoms are those related to the *x,y,z* set by the mirror plane [in (1)] and the centre of symmetry [in (2) and (3)]. The transformations are: (1) $x, \frac{1}{2} - y, z, a = 1$; (2) $-x, -y, -z, a = 1, b = 2$; (3) $-x, 1 - y, 1 - z, j = 1, a = 2, b = 1$; (3) $1 - x, -y, 1 - z, j = 2, a = 3, b = 4$.

To overcome the problem of incomplete reaction it was decided to synthesise some well characterised adducts of $NbCl_4$ and allow them to react with Sb_2S_3. Surprisingly, no simple adducts of niobium(IV) chloride appear to have been fully characterised by *X*-ray crystallography. Initially we chose for our reactions the anion [$NbCl_6$]$^{2-}$ as it has been stated that these anions 'are undoubtedly monomeric and octahedral.'[8] Although a reaction took place in CS_2 solution between [$NbCl_6$]$^{2-}$ and Sb_2S_3 we were unable to separate the various products.

Antimony(III) chloride forms an adduct with cyanomethane that is soluble in the ligand so it was decided to synthesise the cyanomethane adduct of niobium(IV) chloride and treat it with Sb_2S_3. The analysis of the adduct we obtained from $NbCl_4$–CH_3CN corresponded to $NbCl_4$·3CH_3CN. Complex reactions quite frequently occur when early transition-metal halides are allowed to react with alkyl cyanides[9] and MCl_4–CH_3CN (M = Nb or Ta) mixtures can give rise to species containing M=NR fragments.[10] The results of physico-chemical measurements did not suggest that any redox reaction had occurred in the preparation. We could not eliminate the possible existence of an ionic compound and because of the lack of structural information on adducts of $NbCl_4$ we decided to ascertain the structure of $NbCl_4$·3CH_3CN.

The Structure of [$NbCl_4(NCMe)_2$]·CH_3CN, (1).—The unit cell of (1) contains discrete *cis*-[$NbCl_4(NCMe)_2$]

molecules together with a solvent CH_3CN molecule. Significant bond lengths and angles of $[NbCl_4(NCMe)_2]$ are given in Table 1 and bond lengths are included in Figure 1. The adduct (Figure 1) has a crystallographically imposed mirror plane through the Cl(13), Nb, Cl(12) atoms. The niobium–chlorine bond lengths [Nb–Cl 2.328(7), 2.343(6), 2.349(4) Å] are all equal within experimental error, and comparable to the length of the terminal Nb–Cl bonds in $NbCl_4$[11][2.291(2) Å] and those in $[\{NbCl_2S(NCMe)_2\}_2]$ (see later). There appears to be little change in Nb–Cl bond length with oxidation state as the Nb–Cl lengths in $[NbCl_3O(NCMe)_2]$[12] [2.313(9)—2.377(8) Å] and three of the lengths in $[NbCl_5O]^{2-}$ [13] [2.345(4), 2.396(3), 2.397(3) Å] are close to those reported here. The niobium–nitrogen distance [2.220(13) Å] is similar to the short niobium–nitrogen distance in $[NbCl_3O(NCMe)_2]$[12] [2.245(9) Å] and the related distance in $[NbBr_4(NCMe)_2]$ [14] (2.0 Å).

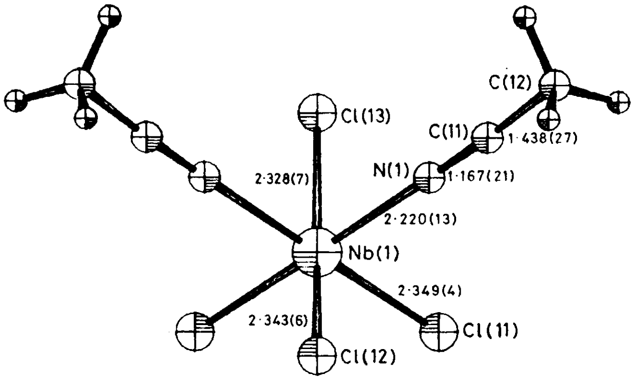


FIGURE 1 The structure of $[NbCl_4(NCMe)_2]$

Some of the angles subtended at the niobium atom deviate quite considerably from the ideal 90° and 180°. This deviation is caused by the *trans* chlorine atoms Cl(13) and Cl(12) being bent back [Cl(13)–Nb–Cl(12) 161.03(23)°] away from the other two chlorine atoms. This gives an increase (above 90°) in the Cl(13)–Nb–Cl(11) [97.53(16)] and Cl(12)–Nb–Cl(11)[95.56(15)°] angles and values below 90° for the Cl(13)–Nb–N(11) [83.4(4)°] and Cl(12)–Nb–N(11) [83.1(4)°] angles. These deviations are probably caused by intramolecular rather than intermolecular forces. The unco-ordinated cyanomethane molecule is disordered with the methyl carbon atom being on the mirror plane. There are no contacts less than the van der Waals radii between the lattice CH_3CN molecule and the $[NbCl_4(NCMe)_2]$ unit. The shortest distance is 3.50 Å (Table 2).

TABLE 2

Intermolecular distances less than 3.5 Å

(*a*) In (1)			
$C(12) \cdots N(5)^{I}$	3.50	$N(5) \cdots C(11)^{II}$	3.50
(*b*) In (2)			
$N(5) \cdots C(21)^{III}$	3.45	$C(12) \cdots N(5)^{IV}$	3.10
$N(5) \cdots C(22)^{II}$	3.41	$C(51) \cdots C(21)^{V}$	3.49
(*c*) In (3)			
$N(5) \cdots C(21)^{III}$	3.44	$N(5) \cdots N(1)^{I}$	3.48
$N(5) \cdots C(22)^{III}$	3.43	$N(5) \cdots C(11)^{I}$	3.27
$N(5) \cdots C(42)^{VI}$	3.18	$C(51) \cdots C(21)^{III}$	3.40

Roman superscripts refer to the symmetry operations that relate the second atom to the x,y,z set of the first. The transformations are: I $x,y,1+z$; II $x,y,-1+z$; III x,y,z; IV $1-x, 1-y, 1-z$; V $1-x, -y, 1-z$; VI $x, 1+y, z$.

Preparation and Structure of $[\{NbX_2S(NCMe)_2\}_2]$ (X = Cl *or* Br).—Having fully characterised (1), it was allowed to react with Sb_2S_3 in cyanomethane solution for 2 d at 50 °C. During the reaction period a green precipitate was formed whose analysis corresponded to that of $[NbCl_2S(NCMe)_2]$. A similar reaction using $[NbBr_4(NCMe)_2]$ yielded a brown product that analysed for $[NbBr_2S(NCMe)_2]$.

The chloride containing species $[NbCl_2S(NCMe)_2]$ was recrystallised from cyanomethane solution and two distinctly different crystal types were obtained, one being brown parallelopipeds (2) and the other consisting of green rectangular platelets (3). Both species were examined by single-crystal *X*-ray techniques.

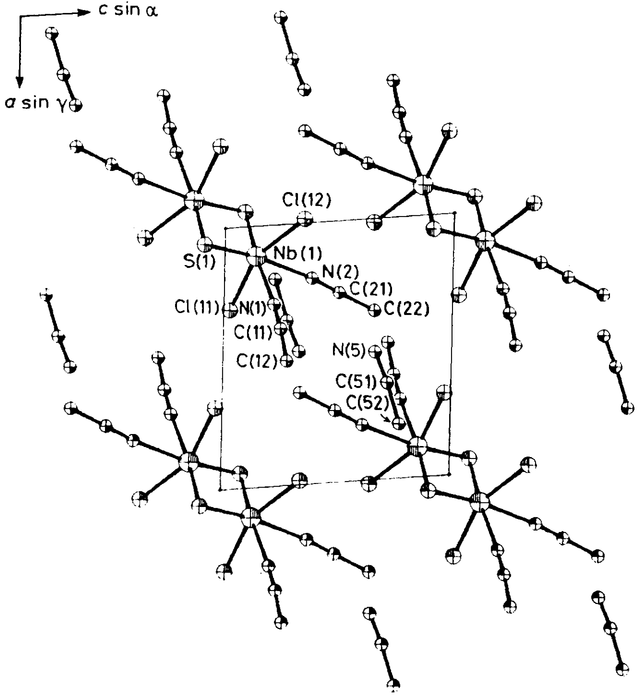


FIGURE 2 The unit cell of $[\{NbCl_2S(NCMe)_2\}_2]\cdot 2CH_3CN$, (2), in the *b* projection

Discussion of Structures (2) *and* (3).—The unit cells of the brown (2) and green (3) crystals are shown in Figures 2 and 3 respectively together with the atomic numbering schemes. In both compounds the $[\{NbCl_2S(NCMe)_2\}_2]$ dimer is present. The only significant difference between the two structures is in the number of occluded cyanomethane molecules, there being two for each $[\{NbCl_2S(NCMe)_2\}_2]$ dimer in (2) and one in (3).

In Table 1 are given the important bond angles and distances for the three distinct $[\{NbCl_2S(NCMe)_2\}_2]$ dimers. Two of these dimers occur in (3) and one in (2). All three dimers have crystallographically imposed centres of symmetry with the two niobium, two sulphur, and four nitrogen atoms forming a plane that is at right angles to a plane formed by the two niobium and four chlorine atoms. In the dimers the two niobium atoms are bridged by two *cis* sulphur atoms [Nb–S 2.338(8)—2.349(7) Å] and in addition each metal is bonded to two *trans* chlorine atoms [Nb–Cl 2.383(6)—2.403(5) Å] and two *cis* nitrogen atoms [Nb–N 2.286(26)—2.334(22) Å]. These six bonds form an octahedral environment that is distorted primarily by the existence of a niobium–niobium interaction [Nb–Nb 2.862(2)—2.872(3) Å]. These Nb–Nb distances are similar to a number of other such distances to which have been attributed single-bond character {2.871(4) Å [$Nb_2Cl_4S_4$],[3] 2.973(4) Å [$Nb_2Cl_4Se_4$],[3] 2.8371(7) Å [$Nb_2Br_4S(S_2)(tht)_4$] [5]}. Among the effects brought about by the metal–metal bond are the increase from 90° of the S–Nb–S angles [104.44(24)—104.78(14)°] together with small Nb–S–Nb angles [75.22(14)—75.56(20)°] and the bending away from the metal–metal bond of the chlorine atoms [Cl-Nb-Nb 100.34(17)—101.64(19)°]. A similar bending away of the halogens from the Nb–Nb bond was seen in [$Nb_2Br_4S(S_2)(tht)_4$] [Br–Nb–Nb 103.1(2)—109.3(2)°].[6]

The distances in the Nb–S–Nb bridges [2.338(8)—2.349(7) Å] are similar to those found in other niobium(IV)-sulphur compounds {2.333(11) Å in [$Nb_2Br_4S(S_2)(tht)_4$],[5] 2.488(4)—2.432(4) Å in $Nb^{IV}S(S_2)$[15]} while the niobium–nitrogen distances are in accordance with those in [$NbCl_3O(NCMe)_2$] [2.245(9) Å *trans* to Cl] and in [$NbCl_4(NCMe)_2$] [2.220(13) Å]. Similarly, the niobium–chlorine distances are within the range of other known Nb^{IV}–Cl distances {2.291(2) Å $NbCl_4$,[11] 2.328(7)—2.349(4) Å [$NbCl_4(NCMe)_2$], see earlier}.

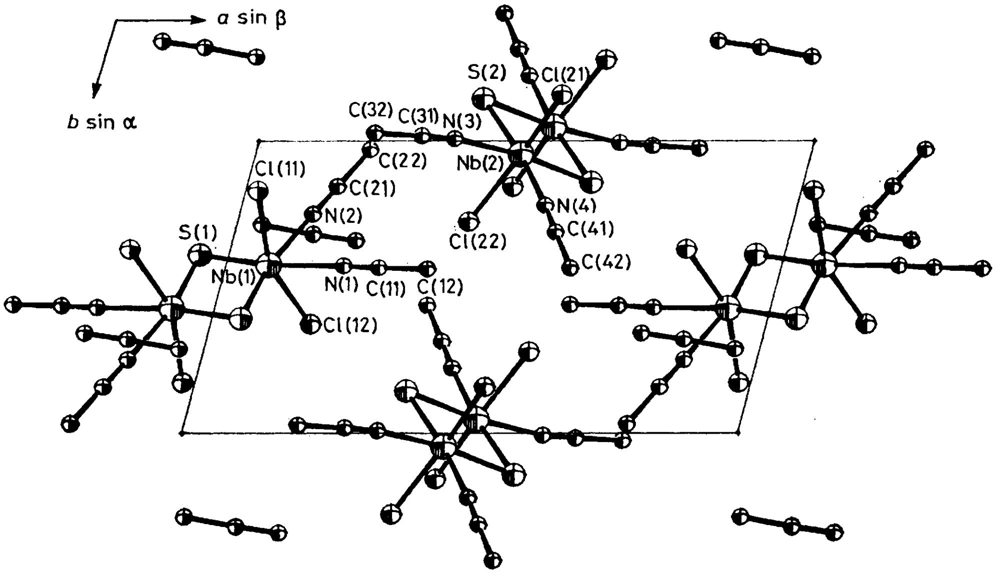


FIGURE 3 The unit cell of [$\{NbCl_2S(NCMe)_2\}_2$]·CH_3CN, (3), in the *c* projection

The Nb–N–C angles are close to 180° [173(2)—177(2)°] and there are no close contacts between the occluded cyanomethane molecules and the dimers, the minimum distances being 3.10 Å in (2) [C(12) ··· N(5)] and 3.18 Å in (3) [N(5) ··· C(42)]. Interatomic distances less than 3.5 Å are given in Table 2.

The i.r. spectral data of [$\{NbX_2S(NCMe)_2\}_2$] (X = Cl or Br) in the region 500 to 200 cm^{-1} are given in Table 3.

TABLE 3

Infrared spectral data (cm^{-1}) of [$\{NbX_2S(NCMe)_2\}_2$] (X = Cl or Br) *

[$\{NbCl_2S(NCMe)_2\}_2$]	[$\{NbBr_2S(NCMe)_2\}_2$]	Assignment
476, 470s, doublet	468s	$\overline{\mathrm{Nb{-}S{-}Nb{-}S}}$
408w	417, 405w, doublet	Nb–N
	360vw	ν_8 of CH_3CN ?
	343w	
340v br, s		Nb–Cl
330 (sh)	321s	$\overline{\mathrm{Nb{-}S{-}Nb{-}S}}$
284vs	302vvw	Nb–Cl
	254vbr, s	Nb–Br
212br, m	214br, vs	Nb–N? Nb–Br

* s = Strong, m = medium, w = weak, sh = shoulder, br = broad, v = very.

The [$\{NbX_2S(NCMe)_2\}_2$] dimers have D_{2h} symmetry and so six stretching modes of the $Nb_2X_4S_2N_2$ skeleton will be i.r.-active. Assignment of the vibrations given in Table 3 is made easier by the fact that the free ligand has only one mode at 364.7 cm^{-1}, below 500 cm^{-1}.[16] Metal–nitrogen modes in alkyl cyanide complexes have proved notoriously difficult to assign so the assignments given for the Nb–N modes in Table 3 must be regarded as tentative. In fact the bands in the 408—417 cm^{-1} region [which we suggest as one of the ν(NbN) modes and that are common in RCN complexes] have been assigned to the δ(C–C≡N) mode that occurs at 364.7 cm^{-1} in the free ligand.[17] However, comparison of the two spectra does allow us to assign with great confidence bands to the $\overline{\mathrm{Nb{-}S{-}Nb{-}S}}$ and Nb–X modes. Both the

[$\{NbX_2S(NCMe)_2\}_2$] compounds are diamagnetic and e.s.r. inactive.

EXPERIMENTAL

All the preparations were carried out using an all-glass vacuum line. Samples for crystallography and other physical measurements were prepared in a dinitrogen dry-box. Infrared measurements were made on Nujol mulls using a Nicolet 7 000 Fourier-transform i.r. spectrophotometer and e.s.r. spectra measured with a Varian E3 spectrometer.

TABLE 4

Crystal data[a]

	(1) $C_6H_9Cl_4N_3Nb$	(2) $C_{12}H_{18}Cl_4N_6Nb_2S_2$	(3) $C_{10}H_{15}Cl_4N_5Nb_2S_2$
M	357.88	638.07	597.02
Class	Orthorhombic	Triclinic	Triclinic
a/Å	10.437(11)	9.031(7)	14.965(18)
b/Å	13.883(12)	9.367(6)	8.838(17)
c/Å	9.828(9)	8.360(8)	9.543(23)
α/°	(90)	108.72(9)	112.42(18)
β/°	(90)	94.93(7)	84.39(28)
γ/°	(90)	105.70(8)	103.65(21)
U/Å^3	1 424.05	633.13	1 133.76
D_c/g cm^{-3}	1.79	2.016	1.749
D_m/g cm^{-3}	1.76	*b*	*b*
Z	4	1	2
Space group	*Pnma*	$P\bar{1}$	$P\bar{1}$
$2\theta_{min.}$	6.04	5.19	4.96
No. of data	978	1 645	2 133
$2\theta_{max.}$	45	45	45
Data used in refinement	729	1 434	1 530
Size of crystal/mm	0.7 × 0.4 × 0.4	0.6 × 0.6 × 0.1	0.75 × 0.45 × 0.05
Planes parallel to alignment axis	100	113	310
F^* in weighting scheme	65.0	23.0	118.0
R	0.051	0.056	0.050
μ/cm^{-1}	21.12	23.51	21.71
F(000)	700	314	584

[a] $\lambda(Mo\text{-}K_\alpha) = 0.7107$ Å. [b] Not measured owing to crystal decomposition.

Niobium pentahalides were prepared by halogenation of niobium sheet. The tetrahalides were prepared by heating (250 °C in 7 d) in a sealed tube niobium pentahalide (14 g) with aluminium strip (molar ratio 3.1 : 1). After the initial 7 d period the aluminium halide and excess of niobium(V) halide were sublimed from the reaction mixture by keeping the product at 200 °C, and the other end of the tube at room temperature.

The cyanomethane adducts (1) and [$NbBr_4(NCMe)_2$] were prepared by treating the tetrahalide (10 g) with a four-fold excess of dry degassed cyanomethane. The reaction was carried out in a sealed ampoule, the mixture being stirred at room temperature for 7 d. The adducts are soluble in cyanomethane so the reaction mixture was filtered on a vacuum line and the product obtained by removing the excess of ligand at the pump (Found: Cl, 40.8; Nb, 26.7. Calc. for $NbCl_4{\cdot}2CH_3CN$: Cl, 39.6; Nb, 26.0%. Found: Br, 64.4; Nb, 18.6. Calc. for $NbBr_4{\cdot}2CH_3CN$: Br, 64.6; Nb, 18.8%).

Preparation of [$\{NbX_2S(NCMe)_2\}_2$] (X = Cl or Br).—In an ampoule were placed [$NbX_4(NCMe)_n$] (X = Cl, n = 3 or X = Br, n = 2) (6 g) and Sb_2S_3 (molar ratio 3 : 0.98). Dry degassed cyanomethane (25 cm^3) was distilled into the ampoule. The reactants and solvents were sealed in the ampoule and the mixture stirred for 2 d at 50 °C. The desired products [$\{NbX_2S(NCMe)_2\}_2$] (X = Cl or Br) were obtained as precipitates and so were isolated by vacuum-line filtration. The filtrate contained a small amount of [$\{NbX_2S(NCMe)_2\}_2$], the excess of [$NbX_4(NCMe)_n$], and the antimony side product (Found: Cl, 25.6; Nb, 34.0. [$\{NbCl_2S(NCMe)_2\}_2$] requires Cl, 25.6; Nb, 33.4%. Found: Br, 43.5; Nb, 25.0. [$\{NbBr_2S(NCMe)_2\}_2$] requires Br, 43.6; Nb, 25.3%). The compounds are so air sensitive that it proved impossible to obtain reproducible C, H, N, and S analyses.

Crystal Preparation.—[$NbCl_4(NCMe)_2$]$\cdot CH_3CN$,(1). The powdered sample of (1) was recrystallised from cyanomethane using a double ampoule technique. Brown crystals were obtained.

[$\{NbCl_2S(NCMe)_2\}_2$]$\cdot nCH_3CN$. A saturated solution of [$NbCl_2S(NCMe)_2$] in cyanomethane was prepared in a double ampoule and the crystals obtained by slow removal of the solvent. Two distinct types of crystal were obtained, the first existed as brown parallelopipeds, (2), and the second as green rectangular platelets, (3).

TABLE 5

Final positional parameters (× 10^4 for Nb, Cl, C, N; × 10^3 for H) for [$NbCl_4(NCMe)_2$]$\cdot CH_3CN$, (1), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Nb(1)	5 573(2)	2 500(0)	5 182(2)
Cl(12)	4 179(5)	2 500(0)	7 052(6)
Cl(13)	7 451(6)	2 500(0)	3 905(7)
Cl(11)	4 500(4)	3 722(3)	3 985(4)
N(1)	6 583(12)	3 625(9)	6 377(14)
C(11)	7 121(16)	4 206(12)	7 018(17)
C(12)	7 831(20)	4 879(14)	7 836(24)
H(1)	875(13)	458(12)	776(13)
H(2)	737(13)	482(12)	879(13)
H(3)	760(13)	552(11)	727(13)
N(5)	5 326(49)	4 337(40)	20(54)
C(51)	5 592(48)	3 533(52)	196(56)
C(52)	5 873(38)	2 500(0)	358(43)

Crystal Data.—These are summarised in Table 4.

The diffractometer used for the study of all three crystals was a G.E. XRD 5 diffractometer and intensities were measured by the stationary-counter–stationary-crystal method (counting time of 10 s). The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Backgrounds were obtained from plots of background counts against 2θ. Details of the data collections for the three crystals are given in Table 4. Several standard reflections were monitored during the course of the experiments and these showed no significant change during the experimental period. Absorption corrections were not applied. Cell dimensions were calculated by least-squares refinement of 12 reflections with large 2θ values.

TABLE 6

Final positional parameters (× 10^4) for $[\{NbCl_2S(NCMe)_2\}_2]\cdot 2CH_3CN$, (2), with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Nb(1)	1 312(1)	588(2)	1 384(2)
S(1)	990(4)	1 516(4)	−879(5)
Cl(11)	2 847(5)	−1 062(5)	226(5)
Cl(12)	565(5)	2 535(5)	3 484(5)
N(1)	3 743(16)	2 512(17)	2 212(17)
C(11)	4 931(21)	3 405(21)	2 499(23)
C(12)	6 482(24)	4 582(25)	2 841(29)
N(2)	2 193(15)	205(16)	3 859(17)
C(21)	2 774(18)	100(21)	5 049(22)
C(22)	3 517(20)	−52(23)	6 577(21)
N(5)	6 064(33)	3 419(31)	6 656(34)
C(51)	7 378(31)	3 794(28)	7 207(31)
C(52)	9 096(29)	4 152(29)	7 765(31)

Structural Determination.—All three structures were solved by Patterson methods and successive Fourier maps were then calculated to determine the remaining non-hydrogen atom positions. All the atoms were refined anisotropically.

TABLE 7

Final positional parameters (× 10^4) for $[\{NbCl_2S(NCMe)_2\}_2]\cdot CH_3CN$, (3), with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Nb(1)	775(1)	4 259(2)	4 878(2)
S(1)	−596(4)	3 908(7)	6 256(6)
Cl(11)	361(4)	1 718(6)	2 733(6)
Cl(12)	1 676(4)	6 282(7)	6 978(6)
N(1)	2 195(13)	4 287(21)	3 691(19)
C(11)	2 873(17)	4 353(23)	3 109(25)
C(12)	3 802(16)	4 389(28)	2 256(27)
N(2)	1 271(13)	2 511(26)	5 733(21)
C(21)	1 564(16)	1 571(31)	6 012(26)
C(22)	1 955(17)	310(29)	6 361(28)
Nb(2)	4 847(1)	471(2)	3 779(2)
S(2)	3 852(4)	−1 434(6)	4 693(6)
Cl(22)	4 141(4)	2 780(6)	5 118(6)
Cl(21)	5 434(4)	−1 576(7)	1 649(6)
N(3)	3 687(14)	−78(23)	2 074(22)
C(31)	3 128(20)	−174(30)	1 358(30)
C(32)	2 330(25)	−264(47)	449(34)
N(4)	5 604(12)	2 222(23)	2 572(22)
C(41)	5 949(15)	3 135(28)	2 017(26)
C(42)	6 428(17)	4 365(29)	1 309(26)
N(5)	1 909(25)	3 420(48)	9 868(36)
C(51)	1 120(33)	3 205(45)	9 799(34)
C(52)	162(25)	2 873(38)	9 587(34)

In (1) the unco-ordinated cyanomethane molecule is disordered between two positions with the carbon atom of the methyl group situated on the mirror plane. Appropriate atoms were given population parameters of 0.5.

All attempts to refine the hydrogen atoms in (2) and (3) were unsuccessful but by a difference-Fourier synthesis on the refined structure of (1) the positions of the hydrogen atoms on the co-ordinated cyanomethane molecules were determined. These were included in the structure-factor calculation with thermal parameters equivalent to their parent carbon atoms but their parameters were not refined.

The refinement of the three structures by least squares gave *R* values of 0.051 [for (1)], 0.056 [for (2)], and 0.050 [for (3)].

Calculations were made using the SHELX-76[18] system of programs at the University of Manchester Computer Centre while scattering factors were obtained from the International Tables.[19] In the last cycles of refinement shifts were less than 0.2σ; the final difference-Fourier maps showed no significant peaks and the zero-weighted reflections no serious discrepancies.

Bond lengths are given in Table 1, positional co-ordinates in Tables 5 [for (1)], 6 [for (2)], and 7 [for (3)]. Structure factor tables and anisotropic thermal parameters are in Supplementary Publication No. SUP 23021 (23 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

REFERENCES

[1] G. W. A. Fowles, R. J. Hobson, D. A. Rice, and K. J. Shanton, *J. Chem. Soc., Chem. Commun.*, 1976, 552.

[2] H. Schäfer and W. Beckmann, *Z. Anorg. Allg. Chem.*, 1966, **347**, 225.

[3] J. Rijnsdorp, Ph.D. Thesis, Rijksuniversiteit, Groningen, Holland, 1978.

[4] H. G. von Schnering and W. Beckmann, *Z. Anorg. Allg. Chem.*, 1966, **347**, 231.

[5] M. G. B. Drew, I. B. Baba, D. A. Rice, and D. M. Williams, *Inorg. Chim. Acta Lett.*, 1980, **44**, L217.

[6] D. M. Williams, unpublished work.

[7] I. S. Morozov and N. P. Dergacheva, U.S.S.R. P. 430,064/1974; *Otkrytiya Izobret., Prom. Obraztsy, Tovarnye Znaki*, 1974, **51**, 65 (*Chem. Abstr.*, 1975, **82**, 61374q).

[8] D. L. Kepert, 'The Early Transition Metals,' Academic Press, London and New York, 1972.

[9] G. W. A. Fowles, D. A. Rice, and K. J. Shanton, *J. Chem. Soc., Dalton Trans.*, 1977, 1212.

[10] P. A. Finn, M. S. King, P. A. Kilty, and R. E. McCarley, *J. Am. Chem. Soc.*, 1975, **97**, 220.

[11] D. R. Taylor, J. C. Calabrese, and E. M. Larsen, *Inorg. Chem.*, 1977, **16**, 721.

[12] C. Chavant, J. C. Daran, Y. Jeannin, G. Constant, and R. Morancho, *Acta Crystallogr., Sect. B*, 1975, **31**, 1828.

[13] U. Müller and I. Lorenz, *Z. Anorg. Allg. Chem.*, 1980, **463**, 110.

[14] T. A. Dougherty, *Diss. Abstr. B.*, 1967, **28**, 83B.

[15] J. Rijnsdorp and F. Jellinek, *J. Solid State Chem.*, 1978, **25**, 325.

[16] J. L. Duncan, D. C. McKean, F. Tullini, G. D. Nivellini, and J. Perez Pena, *J. Mol. Spectrosc.*, 1978, **69**, 123.

[17] R. A. Walton, *Can. J. Chem.*, 1968, **46**, 2347.

[18] G. M. Sheldrick, 1976, personal communication.

[19] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.