The Chemistry of Niobium and Tantalum Dithiocarbamato-complexes. Part 4.[1] The Co-ordination Isomers of $NbCl_3(S_2CNEt_2)_2$ and the *X*-Ray Crystal Structure of $[NbCl_3(S_2CNEt_2)_2]$†

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The co-ordination isomers $[NbCl_3(S_2CNEt_2)_2]$ and $[Nb(S_2CNEt_2)_4][NbCl_6]$ have been prepared by the reaction of $NbCl_5$ with $SiMe_3(S_2CNEt_2)$ in dichloromethane. The identity of the isomers has been established using a combination of *X*-ray crystallography, for the monomer, and ^{93}Nb n.m.r. spectroscopy.

The reactions of MCl_5 (M = Nb or Ta) with $Na(S_2CNEt_2)$ were studied some time ago,[2] but the structure of the mixed halidodithiocarbamato-complexes of empirical formula $MCl_3(S_2CNEt_2)_2$ was not clear at that time. Based on a combination of i.r. spectroscopy, conductivity measurements, and molecular-weight determinations the authors proposed that the material they isolated was $[M(S_2CNEt_2)_4][MCl_6]$. Herein we confirm this formulation using ^{93}Nb n.m.r. spectroscopy, but also show that, particularly under mild conditions, the co-ordination isomer $[NbCl_3(S_2CNEt_2)_2]$ can be isolated, and its identity has been confirmed by *X*-ray crystallography.

Results and Discussion

The reaction of $NbCl_5$ with 2 mol equivalents of $SiMe_3(S_2CNEt_2)$ in dichloromethane gave a mixture of bright red needles and a brown microcrystalline solid both of which, by elemental analysis (Table 1), had the same empirical formula, $NbCl_3(S_2CNEt_2)_2$. Previous studies on these systems had reported only the brown material, but using the relatively mild reagent $SiMe_3(S_2CNEt_2)$ the additional red isomer can be isolated. Certainly the formation of the red isomer is favoured by mild conditions since substantially higher yields of this material are obtained if the reaction is performed at 0 °C, but relatively little if the reaction is performed under ambient conditions when the brown solid predominates. The red needles were shown to be $[NbCl_3(S_2CNEt_2)_2]$ by *X*-ray crystallography.

Description of the Molecular Structure.—In crystals of $[NbCl_3(S_2CNEt_2)_2]$ the Nb atom has seven-fold pentagonal-bipyramidal co-ordination, Figure. The two S_2CNEt_2 ligands lie, with one Cl atom, in the equatorial plane, and the apical sites are occupied by the two remaining Cl atoms. A crystallographic mirror plane passes through the Nb and the three Cl atoms; the two S_2CNEt_2 ligands are related by this symmetry. This is the normal co-ordination pattern for $M(S_2CNEt_2)_2L_3$ complexes, as expected from the structures of similar complexes, *e.g.* $[NbCl(OMe)_2(S_2CNEt_2)_2]$[3] and $[NbCl_3(MeNCMeS)_2]$[4] and by prediction from chelate dimensions in ligand-repulsion-energy calculations.[5]

Atomic co-ordinates are listed in Table 2 and bond dimensions in Table 3. In this well resolved structure we note that the two Nb–S distances are distinctly different, and both are slightly shorter than those found in other niobium(v) seven-co-ordinate complexes, *e.g.* $[NbCl(OMe)_2(S_2CNEt_2)_2]$[3] and $[NbS(S_2CNEt_2)_3]$.[6] The S(2) ··· S(2′) distance is 2.970(1) Å, much shorter than the sum of van der Waals radii (3.7 Å), and also rather shorter than the S(1) ··· Cl(2) distance 3.045(1) Å (*cf.* the van der Waals distance here is 3.65 Å). In dodecahedral $[M(S_2CNEt_2)_4]^{n-}$ complexes the interligand S ··· S contacts within the trapezoidal planes have also been noted to be short.[7] Attractive forces between the S atoms of the coplanar S_2CNEt_2 ligands are suggested as responsible in both geometries for these short distances. The deployment of electrons in these (weak) interligand interactions results in a corresponding lengthening of the M–S contacts, hence the rather longer Nb–S(2) than Nb–S(1) bond in our complex.

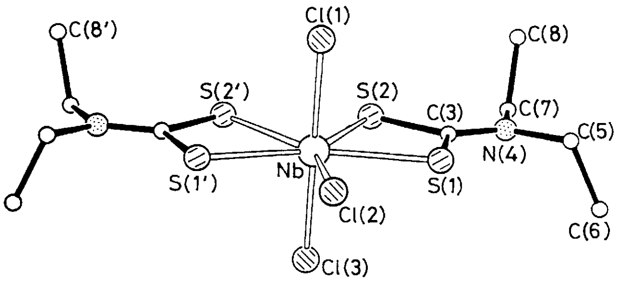

Figure. View and atomic labelling scheme of a molecule of $[NbCl_3(S_2CNEt_2)_2]$. A mirror plane of symmetry, passing through the Nb and Cl atoms, relates S(1) with S(1′), *etc.*

The Nb–Cl(2) distance of 2.419(1) Å is also slightly shorter than that found in $[NbCl(OMe)_2(S_2CNEt_2)_2]$[3] but is the same as the Nb–Cl_{eq} distance in $[NbCl_3(MeNCMeS)_2]$.[4] The two Nb–Cl_{ax} distances in our molecule are each considerably shorter than the Nb–Cl_{eq} distance; this is a feature common in $[MCl_3(L–L)_2]$ complexes (M = Nb or Ta; L–L = a bidentate ligand),[4,8–10] and less steric restraint on the axial ligands is thought to account for these differences. However, we note that there is a significant difference between the two Nb–Cl_{ax} distances in our complex, *viz.* 2.377(1) and 2.327(1) Å; similar differences (although none quite so large) have been observed in other pentagonal bipyramidal complexes of Nb and Ta,[4,8–10] and have been related to interligand contacts. In our complex, there are no such controlling intramolecular contacts, but Cl(3) has one intermolecular contact, 3.584(4) Å, to a methyl C(6) atom, slightly closer than Cl(1), nearest neighbours C(7) and C(8) at 3.665(3) and 3.723(3) Å, and this may account for the shorter Nb–Cl(3) bond.

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† Trichlorobis(diethyldithiocarbamato-*SS′*)niobium.

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	Colour	Analysis[a]/% C	H	N	I.r.[b]/cm^{-1}	Λ_M[c]/ ohm^{-1} cm^{-1} mol^{-1}	^{1}H N.m.r.[d]	^{93}Nb N.m.r.[e] (p.p.m.)
$[NbCl_3(S_2CNEt_2)_2]$	Red	24.8 (24.2)	4.0 (4.1)	5.6 (5.7)	1 515s, ν(CN); 1 000m, 980 m, 915m, ν(CS); 350s, ν(NbCl)	0.0[f]	1.39(3) (t, Me, J_{HH} = 7.1), 3.95(2) (q, CH$_2$, J_{HH} = 7.0)	−418($\Delta\nu_{\frac{1}{2}}$ = 5.2 kHz)
$[Nb(S_2CNEt_2)_4][NbCl_6]$	Brown	24.3 (24.2)	4.1 (4.1)	5.6 (5.7)	1 525s, 1 505s, ν(CN); 1 000w, 980vw, 915w, 340s, ν(NbCl)	135 ± 3	1.28(3) (t, Me, J_{HH} = 7.0), 3.80(2) (q, CH$_2$, J_{HH} = 6.9)	0($\Delta\nu_{\frac{1}{2}}$ = 0.2 kHz) $[NbCl_6]^-$ −325($\Delta\nu_{\frac{1}{2}}$ = 4.7 kHz) $[Nb(S_2CNEt_2)_4]^+$
$[Nb(S_2CNEt_2)_4]Cl$	Brown	33.5 (33.3)	5.2 (5.6)	7.5 (7.8)	1 530s, 1 515s, ν(CN); 995m, 915w, ν(CS)	150 ± 5	1.27(3) (t, Me, J_{HH} = 6.9), 3.80(2) (q, CH$_2$, J_{HH} = 6.9)	−325($\Delta\nu_{\frac{1}{2}}$ = 5.3 kHz)

[a] Calculated values shown in parentheses. [b] Spectra recorded as Nujol mulls. [c] Conductivities measured in MeCN. [d] Chemical shifts *versus* SiMe$_4$. Spectra recorded in CD$_2$Cl$_2$; variable-temperature n.m.r. spectroscopic studies did not reveal any change of the spectrum from that at room temperature. [e] Chemical shifts *versus* $[NbCl_6]^-$. Spectra recorded in CH$_2$Cl$_2$–CD$_2$Cl$_2$. For broad lines ($\Delta\nu_{\frac{1}{2}}$ > 1 kHz)δ ± 4 p.p.m., for other lines δ ± 2 p.p.m. [f] Conductivity slowly increases over a period of several hours.

Table 2. Final atomic co-ordinates (fractional × 10^4) for $[NbCl_3(S_2CNEt_2)_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Nb	1 000.6(2)	2 500	1 666.4(3)
S(1)	621.6(4)	4 068.6(3)	1 396.4(8)
S(2)	2 320.4(3)	3 451.6(3)	2 401.1(7)
C(3)	1 676(1)	4 344(1)	2 045(2)
N(4)	1 960(1)	5 130(1)	2 251(2)
C(5)	1 396(2)	5 875(1)	1 827(3)
C(6)	957(2)	6 270(2)	3 284(5)
C(7)	2 856(2)	5 309(2)	2 884(3)
C(8)	3 537(3)	5 475(3)	1 627(5)
Cl(1)	1 508.7(7)	2 500	−1 024(1)
Cl(2)	−542.3(5)	2 500	789(1)
Cl(3)	568.9(7)	2 500	4 337(1)

Table 3. Selected molecular dimensions (lengths in Å, angles in °) with e.s.d.s in parentheses

(*a*) About the Nb atom; e.s.d.s of angles less than 0.05°

Nb–S(1)	2.523(1)	Nb–Cl(2)	2.419(1)
Nb–S(2)	2.544(1)	Nb–Cl(3)	2.327(1)
Nb–Cl(1)	2.377(1)		
S(1)–Nb–S(2)	68.2	S(2)–Nb–Cl(3)	89.0
S(1)–Nb–Cl(1)	89.2	Cl(1)–Nb–Cl(3)	177.5
S(2)–Nb–Cl(1)	89.0	Cl(2)–Nb–Cl(3)	91.6
S(1)–Nb–Cl(2)	76.1	S(1)–Nb–S(1′)	152.0
S(2)–Nb–Cl(2)	144.3	S(1)–Nb–S(2′)	139.7
Cl(1)–Nb–Cl(2)	90.9	S(2)–Nb–S(2′)	71.5
S(1)–Nb–Cl(3)	91.4		

(*b*) In the S$_2$CNEt$_2$ ligands

S(1)–C(3)	1.720(2)	N(4)–C(7)	1.466(3)
S(2)–C(3)	1.719(2)	C(5)–C(6)	1.516(4)
C(3)–N(4)	1.310(2)	C(7)–C(8)	1.486(4)
N(4)–C(5)	1.479(3)		
Nb–S(1)–C(3)	90.5(1)	C(3)–N(4)–C(5)	121.3(2)
Nb–S(2)–C(3)	89.8(1)	C(3)–N(4)–C(7)	121.5(2)
S(1)–C(3)–S(2)	111.4(1)	C(5)–N(4)–C(7)	117.2(2)
S(1)–C(3)–N(4)	124.9(2)	N(4)–C(5)–C(6)	111.9(2)
S(2)–C(3)–N(4)	123.6(2)	N(4)–C(7)–C(8)	113.7(2)

Within the S$_2$CNEt$_2$ ligand the bond dimensions are as expected. The S–C distances are identical, at 1.719(2) Å, the S$_2$CNC$_2$ fragment is almost planar [with a rotation of 3.5(1)° about the C–N bond], and the outer methyl groups are directed on opposite sides of, and almost straight out from, that plane [the C–N–C–C torsion angles are 101.1(3) and 96.1(3)°].

There is good, tight packing of molecules in the crystal, with several interactions at less than van der Waals distances. In addition to the Cl ··· C contacts noted above, we find, for example, Cl(2) ··· C(5) 3.585(3), C(3) ··· C(7) 3.595(3), and C(5) ··· C(8) 3.823(5) Å, each to a different neighbouring molecule.*

Niobium-93 N.M.R. Spectroscopy and the Identity of $[Nb(S_2CNEt_2)_4][NbCl_6]$.—We were unable to grow crystals of the brown isomer suitable for *X*-ray crystallography. Furthermore, neither i.r. nor ^{1}H n.m.r. spectroscopy were sufficiently diagnostic to establish the identity of either isomer. However ^{93}Nb n.m.r. spectroscopy was able to define the nature of the brown isomer. A major drawback in using ^{93}Nb n.m.r. spectroscopy is that the signals are often broad ($\Delta\nu_{\frac{1}{2}}$ of the order of kHz) because of an increased electric field gradient caused by an unsymmetrical group of ligands.[11] However the spectral range that the dithiocarbamato-complexes cover (δ = −300 to −500 p.p.m., *versus* $[NbCl_6]^-$) allows easy identification of the complexes.

In dichloromethane the ^{93}Nb n.m.r. spectrum of the brown isomer shows two signals: one at δ = 0 p.p.m., corresponding to $[NbCl_6]^-$, and another at δ = −325 p.p.m., $\Delta\nu_{\frac{1}{2}}$ = 4.7 kHz. This latter signal is that of $[Nb(S_2CNEt_2)_4]^+$ as established by the independent preparation of $[Nb(S_2CNEt_2)_4]Cl$.[2] The signal attributable to $[NbCl_3(S_2CNEt_2)_2]$ in the ^{93}Nb n.m.r. spectrum occurs at −418 p.p.m., $\Delta\nu_{\frac{1}{2}}$ = 5.2 kHz.

Thus we have established, by a combination of *X*-ray crystallography and ^{93}Nb n.m.r. spectroscopy, the co-ordination isomers $[NbCl_3(S_2CNEt_2)_2]$ and $[Nb(S_2CNEt_2)_4][NbCl_6]$. It is tempting to speculate that the pathways for the formation of these two isomers, from common precursors, may be associated with attack of dithiocarbamato-groups at two niobium centres in the dimeric $[Nb_2Cl_{10}]$ (established in the solid state)[12] as shown in the Scheme.

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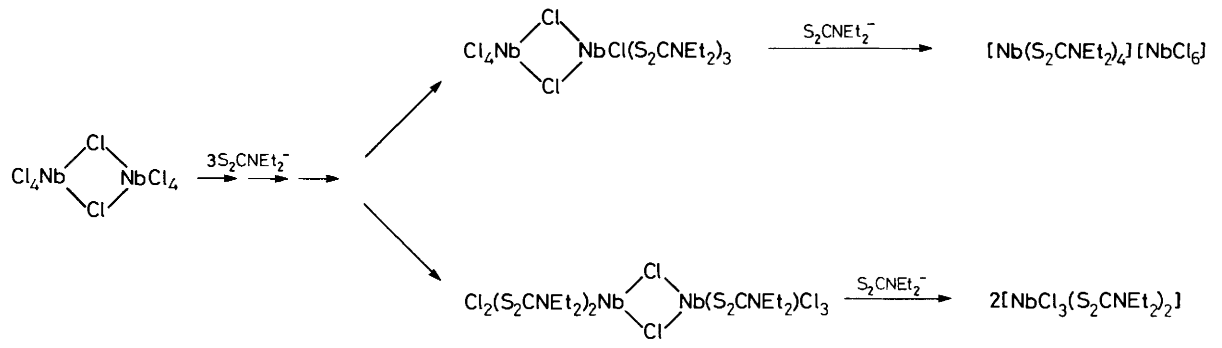
* *Note added at proof.* The crystal structure of $[NbCl_3(S_2CNEt_2)_2]$, prepared by a different route, has recently been reported (J. A. M. Cannich and F. A. Cotton, *Inorg. Chim. Acta*, 1989, **159**, 163). The data reported therein are in good agreement with ours.



Scheme.

Experimental

All manipulations were routinely performed under an atmosphere of dinitrogen using the standard Schlenk-tube technique. Solvents were freshly distilled from the appropriate drying agents immediately prior to use. The compound $NbCl_5$ (Aldrich) was used as received and $SiMe_3(S_2CNEt_2)$ was prepared by the literature method,[13] as was $[Nb(S_2CNEt_2)_4]Cl$.[2]

Trichlorobis(diethyldithiocarbamato)niobium.—To a suspension of $NbCl_5$ (1.56 g, 5.77 mmol) in dichloromethane (*ca.* 20 cm^3) at 0 °C was added $SiMe_3(S_2CNEt_2)$ (2.56 g, 11.55 mmol), slowly with constant vigorous stirring of the solution. There was an immediate colour change from yellow to orange-brown and the solution was stirred for a further 2 h. Upon leaving the solution to stand overnight bright red needles of $[NbCl_3(S_2CNEt_2)_2]$ deposited from the brown solution. They were removed by filtration, washed with diethyl ether, then dried *in vacuo*. The sparingly soluble red needles can be recrystallised from a dichloromethane–diethyl ether mixture.

Tetrakis(diethyldithiocarbamato)niobium Hexachloroniobate.—This isomer can be isolated from the filtrate after removing $[NbCl_3(S_2CNEt_2)_2]$ in the preparation described above. The volume of the filtrate was reduced to about 15 cm^3 *in vacuo* and then diethyl ether (*ca.* 40 cm^3) layered on top of the solution. After 3 d the small dark brown plates of $[Nb(S_2CNEt_2)_4][NbCl_6]$ were removed by filtration, washed with diethyl ether, then dried *in vacuo*. Contamination by a small amount of the red isomer can be removed manually or by dissolving the brown solid in the minimum volume of dichloromethane, quickly filtering to remove the poorly soluble red isomer, then layering with diethyl ether to recrystallise slowly the brown isomer. Higher yields of the brown isomer can be obtained (at the expense of the red isomer) if the reaction of $NbCl_5$ and $SiMe_3(S_2CNEt_2)$ is performed at room temperature.

Niobium-93 N.M.R. Spectroscopy.—All ^{93}Nb n.m.r. spectra were recorded using the parameters and conditions described before.[14]

Crystal Structure Analysis of $[NbCl_3(S_2CNEt_2)_2]$.—*Crystal data.* $C_{10}H_{20}Cl_3N_2NbS_4$, $M = 495.8$, orthorhombic, space group *Pnma* (no. 62), $a = 14.935(1)$, $b = 15.607(1)$, $c = 8.373(1)$ Å, $U = 1\,951.6$ Å^3, $Z = 4$, $D_c = 1.687$ g cm^{-3}, $F(000) = 1\,000$, $\mu(\text{Mo-}K_\alpha) = 14.1$ cm^{-1}, $\lambda(\text{Mo-}K_{\bar{\alpha}}) = 0.710\,69$ Å.

From a sample of beautiful, large, red prismatic crystals, a small specimen 0.20 × 0.25 × 0.40 mm was selected and mounted on a glass fibre. After photographic examination, which showed the crystal to diffract very well, the crystal was transferred to our Enraf-Nonius CAD4 diffractometer for measurement of accurate cell dimensions (refined from the settings of 25 centred reflections having θ *ca.* 19°) and diffraction intensities (to $\theta_{max.} = 30°$). After correction for Lorentz and polarisation effects, absorption, and negative intensities, 2 933 unique reflections were entered into the SHELX program system.[15]

The structure was determined by the heavy-atom method and was refined by full-matrix least-squares methods. Hydrogen atoms were located in Fourier difference maps and were included as independent isotropic atoms in the refinement process; all other atoms were allowed anisotropic thermal parameters with constraints on some parameters of the Nb and Cl atoms which lie on crystallographic mirror planes. At convergence, $R = 0.035$ and $R' = 0.036$[15] for all data with the refined weighting scheme $w = (\sigma_F^2 + 0.000\,34F^2)^{-1}$.

In a final difference map, the highest peaks (to 0.70 e Å^{-3}) were close to the Nb atom.

Scattering curves were taken from ref. 16. Computer programs used in this analysis, in addition to SHELX, have been listed in Table 4 of ref. 17, 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 lengths and angles.

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