# Di-μ-chloro-μ-(dimethyl sulfide)-bis[dichloro-(dimethyl sulfide)niobium(III)]

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**Key indicators**

Single-crystal X-ray study
$T = 173$ K
Mean $\sigma$(S–C) = 0.003 Å
$R$ factor = 0.023
$wR$ factor = 0.056
Data-to-parameter ratio = 28.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Nb_2Cl_6(C_2H_6S)_3]$, contains an $Nb^{III}$═$Nb^{III}$ double bond [2.6880 (3) Å]. Each Nb atom has a distorted octahedral coordination environment formed by two terminal and two bridging $Cl^-$ ions, and one monodentate and one bridging $Me_2S$ ligands.

## Comment

Transition metal complexes containing solvent as a ligand are utilized as precursors in various substitution reactions. As part of a systematic investigation of the properties of niobium complexes which contains solvent as ligands, we have recently reported the crystal structure of $[Nb_2(\mu\text{-}Cl)_2Cl_4(CH_3CN)_4]\cdot 2CH_3CN$, (II), which contains an $Nb^{III}$═$Nb^{III}$ double bond (Kakeya *et al.*, 2004). We report here the structure of the title compound, (I), which is a triply bridged dinuclear niobium complex containing solvent dimethyl sulfide as ligands. The synthesis of (I) has been previously reported by Tsunoda & Hubert-Pfalzgraf (1982) as a precursor to other niobium complexes with $\mu$-Cl ligands.



(I)
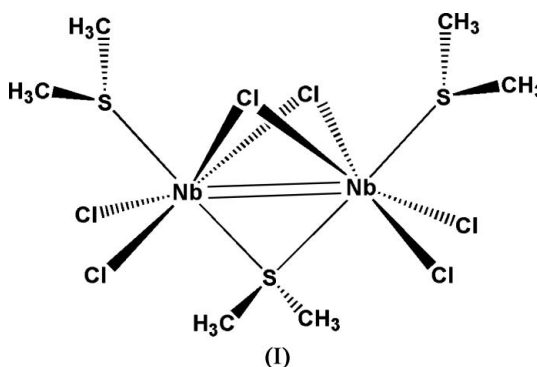
Compound (I) contains a dinuclear unit $[Nb_2(\mu\text{-}Cl)_2(\mu\text{-}Me_2S)]$ with the terminal $Me_2S$ ligands in a *trans* orientation to the bridging one (Fig. 1 and Table 1). The average $Nb-(\mu\text{-}Cl)$ and $Nb-(\mu\text{-}Me_2S)$ distances of 2.498 (6) and 2.425 (2) Å, respectively, fall within the range of those for $[Nb_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-}Me_2S)(C_4H_8O)_2]$, which has the same bridging unit (Cotton *et al.*, 1985). The terminal Nb—Cl and Nb—S bond lengths are shorter and longer, respectively, than the corresponding distances to the bridging atoms. The Nb—S—Nb bond angle is slightly larger than the Nb—Cl—Nb angles. These differences may arise from the difference in the nature of the coordination bonds. On the $Me_2S$—Nb—$SMe_2$ axis, the bridging bonding is favorable, while the terminal polarized Cl—Nb bond is stronger than the bridging Cl—Nb bond on the Cl—Nb—Cl axis. Other geometrical parameters also lie
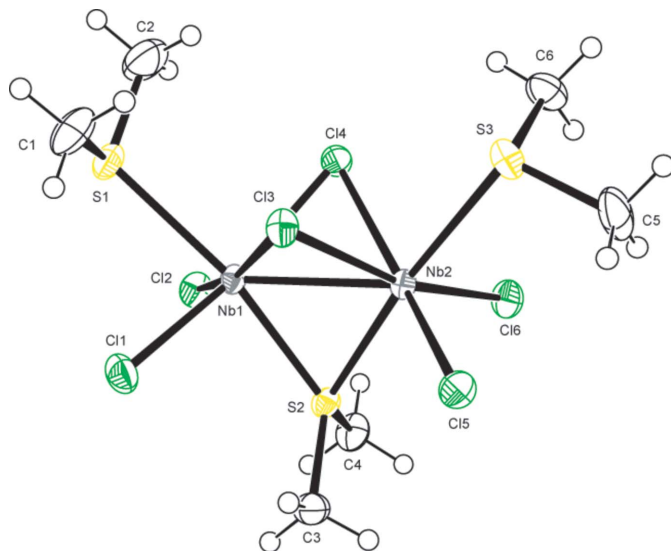
**Figure 1**
A perspective view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

within the same ranges as in analogous dinuclear niobium complexes (Babaian-Kibala *et al.*, 1991; Cotton *et al.*, 1984, 1985).

## Experimental

Reactions were carried out under an atmosphere of purified argon using standard Schlenk techniques. A mixture of $Nb_2Cl_{10}$ (2.3 g, 4.3 mmol), dimethyl sulfide (1.71 ml, 23.4 mmol), and Mg (0.57 g, 23.4 mmol) was dissolved in a mixture of $CH_2Cl_2$ (75 ml) and $Et_2O$ (11.5 ml) at room temperature. The mixture was stirred for 2 days at room temperature. A precipitate formed which was removed by suction filtration. The resultant filtrate was concentrated to dryness, leaving a purple powder. The crude product was washed with hexane and dried under reduced pressure. Compound (I) was recrystallized from $CH_2Cl_2$–hexane (1:7) to give purple crystals (2.2 g, 88% yield). $^1H$ NMR ($CDCl_3$): δ 3.33 (6H, $\mu$-$Me_2S$), 2.63 (12H, terminal-$SMe_2$); $^{13}C$ NMR ($CDCl_3$): δ 30.0 (2C, $\mu$-$Me_2S$), 22.7 (4C, terminal $Me_2S$); $^{93}Nb$ NMR ($CDCl_3$): δ −495 ($W_{1/2}$ = 1320 Hz); elemental analysis calculated for $C_6H_{18}Cl_6Nb_2S_3$: C 12.38, H 3.10%; found: C 12.32, H 2.93%.

### Crystal data

| | |
|---|---|
| $[Nb_2Cl_6(C_2H_6S)_3]$ | $D_x = 2.020$ Mg m$^{-3}$ |
| $M_r = 584.90$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 7953 |
| $a = 8.0002$ (8) Å | reflections |
| $b = 11.3868$ (11) Å | $\theta = 2.6$–27.9° |
| $c = 21.446$ (2) Å | $\mu = 2.33$ mm$^{-1}$ |
| $\beta = 100.040$ (2)° | $T = 173$ (2) K |
| $V = 1923.7$ (3) Å$^3$ | Block, violet |
| $Z = 4$ | $0.41 \times 0.40 \times 0.39$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART APEX CCD area-detector diffractometer | 4586 independent reflections |
| | 4293 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.022$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 27.9°$ |
| | $h = -7 \rightarrow 10$ |
| $T_{min} = 0.390$, $T_{max} = 0.403$ | $k = -13 \rightarrow 14$ |
| 13709 measured reflections | $l = -28 \rightarrow 25$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0255P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.023$ | $+ 0.7014P]$ |
| $wR(F^2) = 0.056$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.10$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 4586 reflections | $\Delta\rho_{max} = 0.40$ e Å$^{-3}$ |
| 160 parameters | $\Delta\rho_{min} = -0.62$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cl1—Nb1 | 2.3853 (6) | Cl6—Nb2 | 2.3756 (6) |
| Cl2—Nb1 | 2.3715 (6) | Nb1—S2 | 2.4262 (6) |
| Cl3—Nb1 | 2.5043 (6) | Nb1—S1 | 2.6409 (6) |
| Cl4—Nb1 | 2.5026 (6) | Nb1—Nb2 | 2.6880 (3) |
| Cl3—Nb2 | 2.5168 (6) | Nb2—S2 | 2.4233 (6) |
| Cl4—Nb2 | 2.4920 (6) | Nb2—S3 | 2.6477 (6) |
| Cl5—Nb2 | 2.3845 (6) | | |
| Nb1—Cl3—Nb2 | 64.735 (15) | S2—Nb1—Nb2 | 56.285 (14) |
| Nb2—Cl4—Nb1 | 65.120 (15) | S2—Nb2—S3 | 173.66 (2) |
| S2—Nb1—S1 | 169.14 (2) | | |

The H atoms were placed in calculated positions, with C—H = 0.98 Å for $CH_3$, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms.

Data collection: *SMART-W2K/NT* (Bruker, 2003); cell refinement: *SAINT-W2K/NT* (Bruker, 2003); data reduction: *SAINT-W2K/NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2003); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

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