

Di- μ -chloro-bis[diacetonitriledichloro-niobium(III)] acetonitrile disolvate

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Key indicators

Single-crystal X-ray study

$T = 297$ K

Mean $\sigma(\text{C}-\text{C}) = 0.012$ Å

R factor = 0.053

w R factor = 0.136

Data-to-parameter ratio = 25.4

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

The title compound, $[\text{Nb}_2(\mu\text{-Cl})_2\text{Cl}_4(\text{CH}_3\text{CN})_4] \cdot 2\text{CH}_3\text{CN}$, is a centrosymmetric dinuclear niobium complex containing an $\text{Nb}^{\text{III}}=\text{Nb}^{\text{III}}$ double bond [2.8577 (9) Å]. The Nb atom has a distorted octahedral coordination environment formed by two terminal Cl atoms [Nb—Cl = 2.3761 (14) and 2.3853 (15) Å], two acetonitrile ligands [Nb—N = 2.301 (4) and 2.309 (4) Å] and two $\mu\text{-Cl}$ atoms [Nb—Cl = 2.3356 (13) and 2.3358 (13) Å].

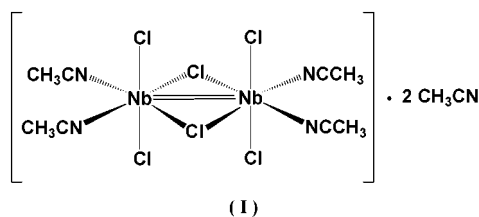
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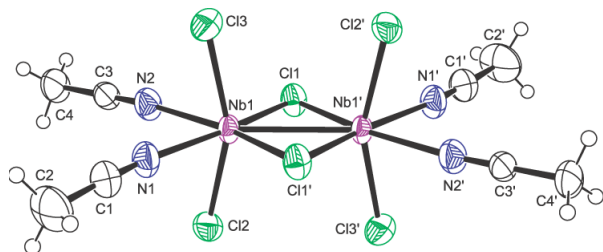
Transition metal complexes containing acetonitrile (CH_3CN) as a ligand are utilized as precursors in various substitution reactions. Previously reported niobium complexes with coordinated CH_3CN include mononuclear $[\text{NbCl}_4(\text{CH}_3\text{CN})_2]$ (Benton, Drew & Rice 1981), dinuclear $[\text{Nb}_2\text{Cl}_4(\mu\text{-OCH}_3)_2(\text{OCH}_3)_2(\text{CH}_3\text{CN})_2]$ (Cotton *et al.*, 1987) and tetranuclear $[\text{Nb}_4\text{Br}_4(\mu\text{-Br})_6(\mu\text{-Se})_3(\text{CH}_3\text{CN})_4]$ (Benton, Drew, Hobson & Rice, 1981). We report here the title compound, (I), which is a dinuclear niobium complex with four terminal CH_3CN ligands.



The Nb complex in (I) is centrosymmetric and contains the dinuclear unit $[\text{Nb}_2(\mu\text{-Cl})_2]$ (Fig. 1 and Table 1). In general, the $\text{Nb}^{\text{IV}}-\text{Nb}^{\text{IV}}$ distance is greater than 2.86 Å. On the other hand, the $\text{Nb}^{\text{III}}=\text{Nb}^{\text{III}}$ bond distance is in the range 2.60–2.86 Å. The Nb1—Nb(− x , 1 − y , − z) distance of 2.8577 (9) Å in (I) indicates an Nb= Nb double bond, as found in a previously reported dinuclear Nb^{III} complex, $[\text{Nb}_2\text{Cl}_4(\mu\text{-OCH}_3)_2(\text{OCH}_3)_2(\text{CH}_3\text{CN})_2]$, (II) (Cotton *et al.*, 1987). The terminal Nb—Cl bond lengths [2.3761 (14) and 2.3853 (15) Å] are shorter than those in (II) [mean 2.445 (5) Å]. The Nb—($\mu\text{-Cl}$) bond lengths are 2.3356 (13) and 2.3358 (13) Å. The geometric parameters for coordinated CH_3CN ligands in (I) are comparable with the values reported for related compounds.

Experimental

Reactions were carried out under an atmosphere of purified argon, using standard Schlenk techniques. To a 100 ml Schlenk tube containing NbCl_5 (2.9 g, 0.011 mol) and Mg (0.90 g, 0.037 mol) was added acetonitrile (30 ml, 0.93 mol). The solution changed from yellow to black after stirring for 17 h at room temperature. The


Figure 1

A view of the complex molecule in (I), with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. Atoms labeled with a prime are at the symmetry position $(-x, 1-y, -z)$.

resulting precipitate was removed by filtration and the filtrate was concentrated to dryness, leaving a black powder. The crude product was washed with hexane (3×10 ml) and dried under reduced pressure. Compound (I) thus obtained was recrystallized from acetonitrile–toluene–diethyl ether (5 : 2 : 2 v/v) at 253 K to give black crystals (1.0 g, 17% yield). IR (KBr, cm^{-1}): 2230 ($\text{C}\equiv\text{N}$); ^1H NMR (400 MHz, CDCl_3 , TMS_{int} , p.p.m.): 2.00 (s, 3H, CH_3CN).

Crystal data

$[\text{Nb}_2\text{Cl}_6(\text{C}_2\text{H}_3\text{N})_4] \cdot 2\text{C}_2\text{H}_3\text{N}$
 $M_r = 644.84$
 Triclinic, $P\bar{1}$
 $a = 8.331$ (2) Å
 $b = 8.997$ (2) Å
 $c = 9.341$ (2) Å
 $\alpha = 105.851$ (4)°
 $\beta = 108.501$ (4)°
 $\gamma = 94.671$ (4)°
 $V = 627.8$ (2) Å³

$Z = 1$
 $D_x = 1.706$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1556 reflections
 $\theta = 2.4$ – 27.7 °
 $\mu = 1.56$ mm⁻¹
 $T = 297$ (2) K
 Block, black
 $0.45 \times 0.32 \times 0.24$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.540$, $T_{\text{max}} = 0.691$
 4583 measured reflections

3077 independent reflections
 2457 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 28.3$ °
 $h = -11 \rightarrow 9$
 $k = -11 \rightarrow 11$
 $l = -11 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.136$
 $S = 1.06$
 3077 reflections
 121 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.0314P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.34 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.97 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Nb1–N1	2.301 (4)	Nb1–Cl2	2.3761 (14)
Nb1–N2	2.309 (4)	Nb1–Cl3	2.3853 (15)
Nb1–Cl1 ⁱ	2.3356 (13)	Nb1–Nb1 ⁱ	2.8577 (9)
Nb1–Cl1	2.3358 (13)		
N1–Nb1–N2	81.22 (17)	Cl1 ⁱ –Nb1–Cl1	104.57 (4)
N1–Nb1–Cl1 ⁱ	84.86 (12)	Cl1 ⁱ –Nb1–Cl2	98.70 (5)
N2–Nb1–Cl1 ⁱ	166.01 (12)	Cl2–Nb1–Cl3	157.44 (5)
N1–Nb1–Cl1	170.38 (12)	Nb1 ⁱ –Cl1–Nb1	75.43 (4)
N2–Nb1–Cl1	89.39 (12)		

Symmetry code: (i) $-x, 1-y, -z$.

All H atoms were placed in calculated positions, with C–H = 0.96 Å, and refined in a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

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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