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A Bioctahedral NbIV Cluster with Bridging Sulfides: $[\text{Nb}_2(\mu\text{-S})_2\text{Cl}_4(\text{thf})_4]$

M. Yoon
Iowa State University

V. Young
Iowa State University

Gordon J. Miller
Iowa State University, gmiller@iastate.edu

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A Bioctahedral NbIV Cluster with Bridging Sulfides: $[\text{Nb}_2(\mu\text{-S})_2\text{Cl}_4(\text{thf})_4]$

Abstract

The title compound, tetrachloro-1,2,2',2'-tetrakis-(tetrahydrofuran-O)-1,2,2',2'-di-μ-thio-1,2,2',2'-dinio-bium(IV)(Nb-Nb), $[\text{Nb}_2\text{Cl}_4\text{S}_2(\text{C}_4\text{H}_8\text{O})_4]$, was obtained by the reaction of $\text{NbCl}_5(\text{thf})_2$ (thf is tetrahydrofuran) with $\text{S}(\text{SiMe}_3)_2$ (hexamethyldisilathiane) in tetrahydrofuran. The compound forms edge-sharing bioctahedral clusters with bridging sulfide ligands and terminal chloride and thf ligands. All thf ligands coordinate in the equatorial plane formed by the Nb-S-Nb-S cycle. Two independent half dimers are found in the asymmetric unit about independent inversion centers located at the midpoints of the Nb-Nb bonds. Distance ranges are: Nb-Nb 2.865(1)-2.869(1), Nb-Cl 2.370(2)-2.388(2) and Nb-S 2.324(2)-2.336(2), 4.

Disciplines

Materials Chemistry | Other Chemistry | Physical Chemistry

Comments

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$S = 1.030$
 7144 reflections
 614 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 3.3805P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

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Table 1. Selected geometric parameters (\AA , $^\circ$)

Re—O4	1.688 (5)	P—C51	1.800 (5)
Re—O2	1.697 (4)	Si—C21	1.877 (4)
Re—O3	1.699 (5)	Si—C41	1.878 (4)
Re—O1	1.709 (4)	Si—C31	1.879 (4)
S—P	2.074 (2)	Si—C11	1.887 (4)
S—C12	1.797 (5)	C77—C12	1.692 (9)
P—C61	1.787 (4)	C77—C11	1.726 (10)
P—C71	1.788 (5)		
O4—Re—O2	109.6 (3)	C41—Si—C11	109.8 (2)
O4—Re—O3	111.4 (4)	C31—Si—C11	108.8 (2)
O2—Re—O3	108.8 (3)	C61—P—C71	109.5 (2)
O4—Re—O1	109.0 (2)	C61—P—C51	110.4 (2)
O2—Re—O1	110.8 (2)	C71—P—C51	109.1 (2)
O3—Re—O1	107.1 (3)	C61—P—S	116.3 (2)
C12—S—P	105.98 (14)	C71—P—S	110.8 (2)
C21—Si—C41	114.2 (2)	C51—P—S	100.3 (2)
C21—Si—C31	105.9 (2)	C22—C21—Si	123.3 (4)
C41—Si—C31	108.6 (2)	C26—C21—Si	120.3 (4)
C21—Si—C11	109.3 (2)	C12—C77—C11	114.4 (5)

All non-H atoms were refined with anisotropic displacement parameters. Phenyl H atoms were refined isotropically. The two H atoms of the dichloromethane solvate molecule did not refine to reasonable positions and therefore were included in calculated positions and not refined. One peak of height 1.1 e \AA^{-3} was found in the final Fourier difference map, at a distance of 0.956 \AA from the Re atom. This peak was assigned to an accumulation of errors arising from series termination, non-quadratic thermal movements and imprecision in the rhenium scattering factor. No other difference peaks were of absolute height greater than 0.6 e \AA^{-3} .

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1433). Services for accessing these data are described at the back of the journal.

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A Bioctahedral Nb^{IV} Cluster with Bridging Sulfides: $[\text{Nb}_2(\mu\text{-S})_2\text{Cl}_4(\text{thf})_4]$

MYUNGOK YOON,[†] VICTOR YOUNG JR[‡] AND GORDON J. MILLER

Department of Chemistry, Iowa State University, Ames, IA 50011, USA. E-mail: gmiller@iastate.edu

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Abstract

The title compound, tetrachloro- $1\kappa^2\text{Cl}, 2\kappa^2\text{Cl}$ -tetrakis-(tetrahydrofuran- O)- $1\kappa^2O, 2\kappa^2O$ -di- μ -thioxo- $1:2\kappa^4S$ -dinio-bium(IV)($Nb-Nb$), $[\text{Nb}_2\text{Cl}_4\text{S}_2(\text{C}_4\text{H}_8\text{O})_4]$, was obtained by the reaction of $\text{NbCl}_4(\text{thf})_2$ (thf is tetrahydrofuran) with $\text{S}(\text{SiMe}_3)_2$ (hexamethyldisilathiane) in tetrahydrofuran. The compound forms edge-sharing bioctahedral clusters with bridging sulfide ligands and terminal chloride and thf ligands. All thf ligands coordinate in the equatorial plane formed by the Nb—S—Nb—S cycle. Two independent half dimers are found in the asymmetric unit about independent inversion centers located at the midpoints of the Nb—Nb bonds. Distance ranges are: Nb—Nb 2.865 (1)–2.869 (1), Nb—Cl 2.370 (2)–2.388 (2) and Nb—S 2.324 (2)–2.336 (2) \AA .

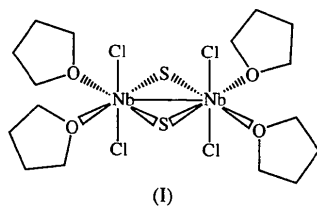
Comment

Metal–metal bonded edge-sharing bioctahedral complexes, $M_2(\mu\text{-X})_2Y_4L_4$, are interesting structural systems to investigate in order to study the interactions between two adjacent metal atoms by changing the types of metal atoms M , bridging ligands X , and terminal ligands Y and L (Cotton, 1987). Several group V transition metal

[†] Current address: Department of Chemistry, University of Oregon, Eugene, OR 97403-1253, USA.

[‡] Current address: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA.

complexes of this type have been structurally characterized (Benton, Drew, Hobson & Rice, 1981; Boyd, Nielson & Rickard, 1987; Drew, Rice & Williams, 1985; Babaian-Kibala, Cotton & Kibala, 1990; Babaian-Kibala & Cotton, 1991). The molecular structure of the title compound, (I), is isotopic with Nb₂(μ-S)₂Cl₄L₄ [L = NCCH₃, SC₄H₈, P(CH₃)₃]. It is rather surprising to find out that an OC₄H₈ (thf) analogue of the trimethylphosphine complex has not been structurally characterized yet, since both dinuclear compounds have been prepared from the same mononuclear Nb^{IV} compound which has terminal thf ligands, NbCl₄(thf)₂. According to our results, these two dimeric complexes are not isomorphous to each other.



The complex Nb₂(μ-S)₂Cl₄(thf)₄ is another example of an edge-sharing bioctahedron, and the molecules reside on crystallographic inversion centers lying at the

midpoint of the Nb—Nb bond. Fig. 1 illustrates the two independent molecules. The Nb₂S₂Cl₄O₄ core has nearly *D*_{2h}(*mmm*) point symmetry. Bond distances between the Nb atoms and its six ligands average 2.345 Å and lie within 0.1 Å of each other. The Cl—Nb—Cl bond angles of 158.2(1)–160.2(1)° indicate significant deviation from regular octahedral geometry. Furthermore, the S—Nb—S angles of 104.0(1)–104.1(1)° and (thf)—Nb—(thf) angles of 78.9(1)–82.5(1)° point out that this deviation arises when the Nb atoms are shifted towards each other to form an Nb—Nb bond. Molecular orbital calculations (Shaik, Hoffmann, Fisel & Summerville, 1980) and simple electron counting assigns this Nb—Nb interaction as a single bond. The Nb—Nb bond distances in these complexes are very close to the reported values of 2.84–2.87 Å for the tetrahydrothiophene (SC₄H₈) and trimethylphosphine [P(CH₃)₃] analogs, and support the previous observation that Nb—Nb bond distances are not dependent on the terminal equatorial ligands (Babaian-Kibala & Cotton, 1991).

There are two crystallographically inequivalent molecules which crystallize in the unit cell in equal amounts. As Fig. 1 indicates, the primary difference between these two molecules is the orientation of the terminal thf ligands, which is linked mostly to packing effects.

Experimental

The title compound was obtained by reacting a suspension of NbCl₄(thf)₂ (1.78 g, 4.7 mmol) in 30 ml of tetrahydrofuran with S(SiMe₃)₂ (0.35 ml, 1.7 mmol) for 12 h. Tetrahydrofuran and S(SiMe₃)₂ were distilled over NaK and CaH₂, respectively, prior to use, and all manipulations were carried out under dry Ar using Schlenk techniques. After the unreacted NbCl₄(thf)₂ was removed by filtration, the brown-green filtrate was concentrated (to ca 15 ml) under reduced pressure and left undisturbed at ambient temperature for 24 h yielding brown-green crystals of the title compound [0.076 g, 0.11 mmol; 13% yield based on S(SiMe₃)₂].

Crystal data

[Nb₂Cl₄S₂(C₄H₈O)₄]

*M*_r = 680.16

Monoclinic

*P*2₁/*c*

a = 16.540 (1) Å

b = 15.605 (2) Å

c = 10.445 (1) Å

β = 104.90 (1)°

V = 2605.3 (4) Å³

Z = 4

*D*_x = 1.734 Mg m⁻³

*D*_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10.3–14.4°

μ = 1.469 mm⁻¹

T = 293 (2) K

Prism

0.40 × 0.30 × 0.20 mm

Brown-green

Data collection

Enraf–Nonius CAD-4
diffractometer

3226 reflections with
I > 2σ(*I*)

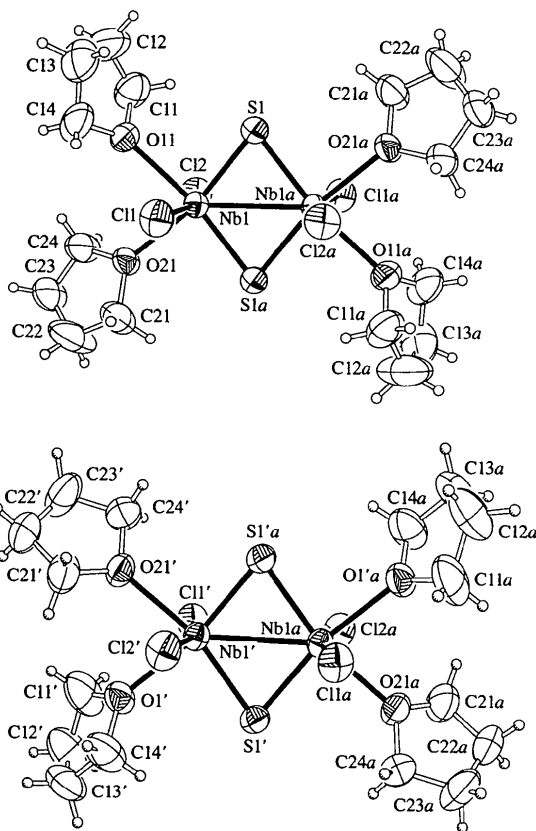


Fig. 1. Molecular structures of the two equivalent molecules showing 50% probability displacement ellipsoids.

ω - 2θ scans
Absorption correction:
empirical via ψ scans
(*XPREP* in *SHELXTL-Plus*; Sheldrick, 1990)
 $T_{\min} = 0.640$, $T_{\max} = 0.710$
6000 measured reflections
4572 independent reflections

$R_{\text{int}} = 0.0298$
 $\theta_{\text{max}} = 25.01^\circ$
 $h = -19 \rightarrow 19$
 $k = -18 \rightarrow 0$
 $l = -12 \rightarrow 3$
3 standard reflections
frequency: 60 min
intensity decay: 12%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.111$
 $S = 1.034$
4571 reflections
253 parameters
H atoms riding with C—H =
0.96 Å

$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 3.8139P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.001$
 $\Delta\rho_{\text{max}} = 0.440 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.664 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Nb1—O21	2.289 (4)	Nb1'—O21'	2.303 (4)
Nb1—S1'	2.324 (2)	Nb1'—S1'	2.330 (2)
Nb1—S1	2.336 (2)	Nb1'—S1''	2.331 (2)
Nb1—Cl1	2.370 (2)	Nb1'—O1'	2.335 (4)
Nb1—Cl2	2.3747 (15)	Nb1'—Cl2'	2.377 (2)
Nb1—O11	2.385 (4)	Nb1'—Cl1'	2.3879 (15)
Nb1—Nb1'	2.8685 (10)	Nb1'—Nb1''	2.8647 (10)
S1'—Nb1—S1	104.02 (5)	S1'—Nb1'—S1''	104.14 (5)
Cl1—Nb1—Cl2	158.20 (6)	O21'—Nb1'—O1'	78.88 (15)
O21—Nb1—O11	82.55 (14)	Cl2'—Nb1'—Cl1'	160.19 (6)
Nb1'—S1—Nb1	75.97 (5)		

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $2 - x, 1 - y, -z$.

The structure was solved using direct methods with the program *SHELXTL-Plus* (Sheldrick, 1990). According to systematic absences, the space group $P2_1/c$ was selected. All non-H atoms were located directly from the E map and refined with anisotropic displacement parameters. All H atoms were treated as riding atoms with C—H distances of 0.96 Å and with individual group isotropic displacement parameters.

Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

This work was supported by the Chemical Sciences Division, Office of Basic Energy Sciences, US Department of Energy, under Contract W-7405-Eng-82.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1039). Services for accessing these data are described at the back of the journal.

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Tris(8-hydroxyquinolinato)iron(III) Ethanol Solvate

LUCIA PECH,^a YURI A. BANKOVSKY,^a ANDREJS KEMME^b
AND JANIS LEJEJS^a

^a*Institut of Inorganic Chemistry, Latvian Academy of Sciences, 34 Miera Street, Salaspils, LV-2169, Latvia, and*
^b*Latvian Institute of Organic Synthesis, 21 Aizkraukles Street, Riga, LV-1006, Latvia. E-mail: director@iic.iph.sal.lv*

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Abstract

The title compound, tris(8-quinolinolato-*N,O*)iron(III) ethanol solvate, $[\text{Fe}(\text{C}_9\text{H}_6\text{NO})_3] \cdot \text{C}_2\text{H}_5\text{OH}$, has a slightly distorted octahedral coordination about the central Fe atom which bonds to the N and O atoms of each of the three 8-hydroxyquinoline ligands. The ethanol solvate molecule forms a hydrogen bond with the O atom which is least strongly bound to Fe. The Fe—O and Fe—N bond distances are in the ranges 1.936 (5)–1.996 (5) and 2.125 (6)–2.172 (5) Å, respectively.

Comment

The present study is part of systematic crystallographic research of internal complexes of 8-hydroxyquinoline and its derivatives with transition metals (Bankovsky, Belsky, Pech & Ashaks, 1993; Kuzmina *et al.*, 1995).

The monomeric iron complex, (I), crystallizes together with an ethanol molecule which is not included in the coordination sphere of iron. The O and N atoms of the bidentate ligands form three five-membered chelate rings. The Fe atom thereby attains a distorted octahedral coordination. The intra-ligand bond angles at the Fe atom are in the range 78.9–79.5°, whereas all inter-ligand angles at Fe are greater than 87° (see Table 1). Similar results have been obtained in the case of tris(8-quinolinolato) complexes of chromium(III) (Foltling, Cox, Moore & Merritt, 1968) and manganese(III) (Hems & Mackay, 1975; Xiong, You, Wu & Huang, 1995).