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A Diphenylamido–Bromide Complex of Niobium: Dibromo[tris(diphenylamido)]niobium(V) Tetrahydrofuran Solvate

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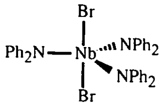
Abstract

$NbBr_5$ reacts with three equivalents of Me_3SiNPh_2 in ether to give the title compound, $[NbBr_2(C_{12}H_{10}N)_3].C_4H_8O$. $Nb(NPh_2)_3Br_2$ has trigonal bipyramidal geometry with axial bromide ligands.

Comment

Several diethylamido–chloride and –fluoride complexes of niobium have been prepared from NbX_5 and trimethylsilyldiethylamine, including $Nb(NEt_2)_3Cl_2$, $[Nb(NEt_2)_2Cl_3]_2$, $Nb(NEt_2)F_4$ and $Nb(NEt_2)_2F_3$ (Chao, Polson & Wigley, 1990; Fuggle, Sharp & Winfield, 1972; Fowles & Pleass, 1957). We were interested in preparing similar amido–bromide derivatives to obtain a selection of complexes available for reduction studies (Hoffman & Rangarajan, 1993; Bott, Hoffman & Rangarajan, 1995). In this paper we describe the preparation and structure of $Nb(NPh_2)_3Br_2$, (I).



(I)

$NbBr_5$ reacts with three equivalents of Me_3SiNPh_2 or $LiNPh_2$ in ether to give $Nb(NPh_2)_3Br_2$. The compound crystallizes from thf/CH_3CN as dark red needles, but it is difficult to isolate cleanly from one or two persistent unidentified contaminates. The preparation based on Me_3SiNPh_2 more consistently gives clean crystalline material than the one using $LiNPh_2$. Proton NMR spectra for $Nb(NPh_2)_3Br_2$ show only resonances arising from one kind of phenyl group, consistent with the solid-state structure.

$Nb(NPh_2)_3Br_2$ crystallizes with one molecule of thf in the lattice. The $Nb(NPh_2)_3Br_2$ molecules are trigonal bipyramidal with axial bromide ligands (Fig. 1). A crystallographic threefold axis passes through the Nb and Br atoms. The amido ligand NC_2 'blades' deviate by less than 4° from the trigonal plane defined by the three N atoms. In this configuration the amido N $p\pi$-donor orbitals can interact only with niobium $d_{xz,yz}$ and not at all with $d_{xy,x2-y2}$. This is expected since d_{xy} and d_{x2-y2} are involved in Nb—N σ bonding and would be too high in energy for an effective interaction with the $p\pi$ orbitals of nitrogen.

The Nb—N bond lengths [1.935 (8) Å] are similar to those in $Nb(NMe_2)_5$ [1.977 (17)–2.044 (14) Å]

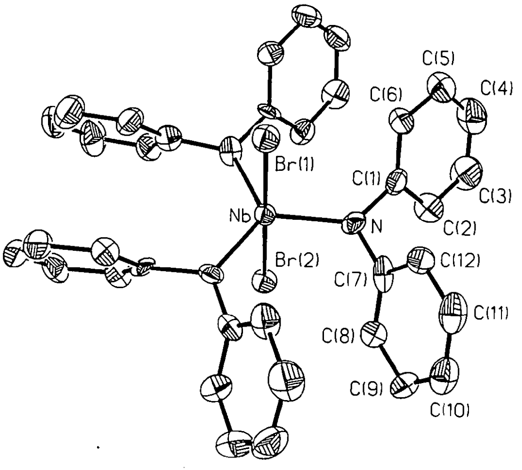


Fig. 1. View of $Nb(NPh_2)_3Br_2$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 40% probability level.

(Heath & Hursthouse, 1971; Bradley & Thomas, 1962). The Nb—Br bond lengths [2.637 (4) and 2.647 (4) Å] are within the range of terminal Nb—Br distances observed in other neutral complexes {*e.g.* $[NbBr_4(\mu\text{-}Br)]_2$ [2.403 (3), 2.462 (2) Å] (Müller & Klingelhöfer, 1983), $NbBr_4(PMe_2Ph)_3$ [2.541 (4)–2.621 (4) Å], $NbBr_3(PMe_2Ph)_3$ [2.554 (1)–2.573 (1) Å] (Cotton, Diebold & Roth, 1985) and $Nb_2Br_6(SC_4H_8)_3$ [2.604 (7)–2.648 (6) Å] (Templeton, Dorman, Clardy & McCarley, 1978)}.

Experimental

The synthesis was carried out under an inert atmosphere. To a dark brown solution of $NbBr_5$ (1.00 g, 2.03 mmol) in ether, Me_3SiNPh_2 (1.43 g, 6.09 mmol) was added slowly over a period of 10 min. The colour of the solution changed immediately to reddish brown. The reaction mixture was stirred for 48 h. The mixture was then stripped *in vacuo*, and the brown residue was extracted with 30 cm^3 of toluene and the extracts filtered through celite. The red–brown filtrate was stripped *in vacuo*, and the residue was extracted with thf/CH_3CN (4:1 ratio; 15 cm^3). The volume of the extract was reduced *in vacuo* to 5 cm^3. The solution was stored for 1 d at 237 K. This produced dark red needles. Yield: 1.32 g, 88%. The sample for analysis was washed with 20 cm^3 of hexane and dried *in vacuo*. Analysis: calculated for $NbBr_2N_3C_{36}H_{30}$ C 57.09, H 3.99, N 5.54%; found C 57.75, H 3.73, N 5.40%. ^1H NMR (C_6D_6): δ 7.65 (*d*, 6H, *p*-H), 6.64 (*t*, 12H, *m*-H), 6.49 p.p.m. (*t*, 12H, *o*-H).

Crystal data

$[NbBr_2(C_{12}H_{10}N)_3].C_4H_8O$
$M_r = 829.54$
Hexagonal
$P6_3$
$a = 13.671 (3)$ Å
$c = 11.400 (3)$ Å
$V = 1845$ $Å^3$
$Z = 2$
$D_x = 1.49$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 15–29°$
$\mu = 2.49$ mm^{-1}
$T = 223$ K
Hexagonal column
0.70 × 0.20 × 0.20 mm
Blood red

Data collection

Nicolet *R*3*m*/*V* diffractometer
ω-scan technique
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1987)
$T_{min} = 0.529$, $T_{max} = 0.565$
1153 measured reflections
1153 independent reflections

728 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 13$
2 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on *F*
$R = 0.029$
$wR = 0.026$
$S = 2.2$
728 reflections
146 parameters
Only H-atom *U*'s refined
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{max} = 0.3$
$\Delta\rho_{max} = 0.4$ e $Å^{-3}$
$\Delta\rho_{min} = -0.2$ e $Å^{-3}$
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus*
Absolute configuration: Rogers (1981) parameter = 0.93

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Nb	1/3	2/3	0.3000	0.031 (1)
Br(1)	1/3	2/3	0.5313 (4)	0.044 (1)
Br(2)	1/3	2/3	0.0678 (4)	0.041 (1)
N	0.2776 (5)	0.7719 (5)	0.2986 (13)	0.038 (2)
C(1)	0.1609 (6)	0.7434 (6)	0.3056 (17)	0.043 (2)
C(2)	0.1195 (7)	0.7728 (8)	0.2048 (10)	0.053 (2)
C(3)	0.0077 (8)	0.7457 (9)	0.2038 (13)	0.076 (2)
C(4)	−0.0609 (7)	0.6888 (8)	0.2940 (16)	0.077 (2)
C(5)	−0.0218 (9)	0.6582 (8)	0.3941 (12)	0.077 (2)
C(6)	0.0918 (7)	0.6856 (7)	0.3976 (11)	0.056 (2)
C(7)	0.3578 (6)	0.8932 (6)	0.2988 (15)	0.041 (2)
C(8)	0.4268 (7)	0.9438 (7)	0.2038 (10)	0.048 (2)
C(9)	0.5015 (8)	1.0612 (7)	0.2073 (10)	0.055 (2)
C(10)	0.5072 (7)	1.1226 (7)	0.3071 (17)	0.060 (2)
C(11)	0.4409 (8)	1.0714 (8)	0.4010 (12)	0.058 (2)
C(12)	0.3642 (7)	0.9541 (7)	0.3979 (10)	0.044 (2)
C(13)†	1.014 (2)	0.956 (2)	0.528 (2)	0.102 (2)
C(14)†	0.955 (2)	0.958 (2)	0.3846 (12)	0.102 (2)
C(15)†	0.893 (2)	0.920 (2)	0.437 (2)	0.102 (2)
C(16)†	0.908 (2)	0.872 (2)	0.482 (2)	0.102 (2)
C(17)†	0.930 (3)	0.988 (3)	0.529 (3)	0.102 (2)
C(18)†	0.963 (3)	0.895 (2)	0.503 (3)	0.102 (2)

† Partial occupancy (see below).

Table 2. *Selected geometric parameters (Å, °)*

Nb—Br(1)	2.637 (4)	Nb—Br(2)	2.647 (4)
Nb—N	1.935 (8)	N—C(1)	1.444 (11)
N—C(7)	1.461 (8)		
Br(2)—Nb—N	89.5 (4)	Br(1)—Nb—N	90.5 (4)
Nb—N—C(1)	126.3 (4)	Nb—N—C(7)	119.5 (5)
C(1)—N—C(7)	114.0 (7)		

During the final stages of refinement, a diffuse area of residual electron density, characteristic of included solvent, was located around a threefold axis. On the basis of NMR data, the solvent in the crystals was assumed to be thf. As thf has so many possible configurations, however, it was impossible to refine it as a rigid body. Thus, the positions in the difference map having the highest electron density were each refined as C atoms having population factors of 0.333 (C13–C16) or 0.222 (C17 and C18). To determine the chirality of the molecule in the crystal, a coefficient multiplying $\Delta f''$ was refined, and this indicated that the absolute structure reported herein is correct.

Data collection: *SHELXTL-Plus* (Sheldrick, 1987). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: local program.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Potassium Aqua(3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetato)ferrate(III)–Water (1/1.5)

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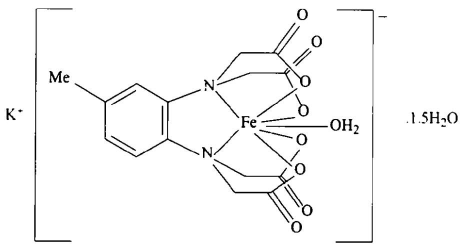
Abstract

The ligand 3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetate in the title compound, $K[Fe(C_{15}H_{14}N_2O_8)(H_2O)].1.5H_2O$, is hexadentate, but the central iron(III) ion is seven-coordinate, with one coordinated water molecule. The complex has roughly pentagonal-bipyramidal geometry. The Fe—N bond lengths are 2.304 (3) Å in the *para* position and 2.349 (3) Å in the *meta* position with respect to the methyl group. The presence of the CH_3 group increases the basicity of the N atom in the *para* position, shortening the length of the Fe—N bond.

Comment

The preparation of coordinating agents derived from aromatic diamines is of special interest since the use of N atoms for coordination to a single cation is directly related to their situation in *ortho*, *meta* or *para* positions. Thus, in the case of diaminetetramethylenecarboxylic acids, derived from *o*-phenylenediamines, the closer proximity of the N atoms permits the simultaneous coordination of both to the same metal cation, as has been established by the X-ray crystallographic determination of the structures of the complexes of *o*-phdta acid (*ortho*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) with Co^{II} (McCandlish, Michael, Neal, Lingafelter & Rose, 1978), Mn^{II} (Nakasuka, Azuma, Katayama, Honda, Tanaka & Tanaka, 1985), Zn^{II} (Azuma, Nakasuka & Tanaka, 1986), Cu^{II} (Nakasuka, Azuma & Tanaka, 1986*a*), Cd^{II} (Nakasuka, Azuma & Tanaka, 1986*b*), Mg^{II} (Nakasuka & Shiro, 1989) and Fe^{III} (Mizuno, Funahashi, Nakasuka & Tanaka, 1991). Contrary to this is the behaviour of diaminetetramethylenecarboxylic acids derived from *meta*- or *para*-phenylenediamines, which can only coordinate one N atom of the ligand to the same metallic cation. Therefore, these ligands can bridge metal ions, as has been proven by the preparation of bimetallic species M_2L for *p*-phdta acid (*para*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) (Ruíz-Pérez, Rodríguez, Rodríguez Romero, Mederos, Gili & Martín-Zarza, 1990) and dimer species M_2L_2 for *m*-phdta acid (*meta*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) (Mederos *et al.*, 1990).

In the present work, the solid crystalline complex $K[Fe(H_2O)(3,4\text{-tdta})].1.5H_2O$, (I), was prepared and characterized. 3,4-tdta (3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) is a potentially hexacoordinating ligand, analogous to *o*-phdta and edta.



(I)

The determination by X-ray diffraction of the structure of the complex $[Fe(OH_2)(o\text{-phdta})]^-$ (Mizuno, Funahashi, Nakasuka & Tanaka, 1991) shows that Fe^{III} is heptacoordinate, with roughly bipyramidal pentagonal