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A long Nb═O double bond in bis(pyridinium) tetrachlorooxo(pyridine-*κN*)niobate(V) chloride

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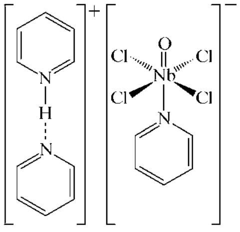
The asymmetric unit of the title compound, $(C_5H_6N)_2$-$[NbCl_4O(C_5H_5N)]Cl$ or $(pyH)_2[O{=}NbCl_4(py)]Cl$ (py is pyridine), contains a discrete anionic niobium(V) complex, $[O{=}NbCl_4(py)]^-$, and two protonated pyridine molecules, which form medium–strong hydrogen bonds with the Cl^- counter-ion. The Nb═O distance of 1.7643 (17) Å is the longest among those in congener niobium complexes reported to date. Extensive density functional theory studies of conformations of $[O{=}NbCl_4(py)]^-$ and structural data mining raise doubts regarding the reliability of the length of this Nb═O double bond.

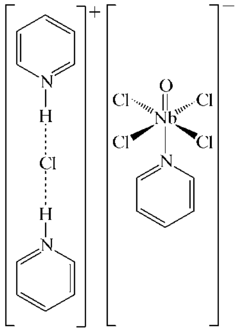
Comment

Recently, we reported a niobium(V) complex, *viz.* $(pyH)[O{=}NbCl_4(py)]\cdot py$ (py is pyridine), (I) (see scheme) (Guzei *et al.*, 2002), which posed an interesting crystallographic problem. The assignment of the space group was problematic due to pseudosymmetry, and a careful differentiation between space groups *Pnc*2 and *Pmna* was necessary. We have since isolated the title compound, $(pyH)_2[O{=}NbCl_4(py)]Cl$, (II), which presents a different issue, in that the Nb═O double bond is considerably longer than that in (I), and we report here a discussion of this fact based on the results of crystallographic data mining and theoretical computations.

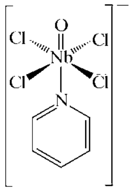
The asymmetric unit of (II) contains four discrete ions: the niobium(V) anion $[O{=}NbCl_4(py)]^-$, (III), two pyridinium cations and a Cl^- anion (Fig. 1). The pyridinium cations form two unequal hydrogen-bonding interactions with the Cl^- counter-ion. The N2—H2N···Cl5 interaction is somewhat weaker than the N3—H3N···Cl5 bond, as revealed by the donor–acceptor distances and N—H···Cl angles (Table 2). The charge-assisted hydrogen bonds are medium–strong and agree well with the average N···Cl separation [3.05 (5) Å] calculated for 18 hydrogen-bonding contacts between pyridinium and Cl^- in 13 relevant structures reported to the Cambridge Structural Database (CSD, Version 5.27, update of May 2006; Allen, 2002). The N—H···Cl angle in these complexes averaged 164 (8)°.



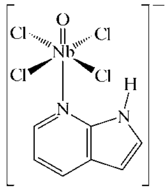
(I)



(II)



(III)



(IV)

Compound (II) is a congener of complexes (I) and $(H_2aza$-$aza)[O{=}NbCl_4(Haza)]\cdot 0.5CH_2Cl_2$ (Haza is 7-azaindole; Poitras & Beauchamp, 1994). We have also optimized the geometry of the C_{2v} symmetrical $[O{=}NbCl_4(py)]^-$ anion at the pbe1pbe/SDD level of theory using *GAUSSIAN03* (Frisch *et al.*, 2004) and will refer to it as (III-DFT) (DFT is density functional theory).

In compounds (I), (II), (III-DFT) and (IV), the Nb metal center is in a distorted octahedral environment, with the equatorial plane formed by four Cl atoms. The Nb—Cl distances average 2.400 (4), 2.404 (6), 2.50 and 2.387 (8) Å, respectively. The experimental values are typical and in accord with each other. However, the theoretical value is ~4% larger. The Nb atom is displaced from the equatorial plane toward the oxo ligand by 0.303 (2), 0.3014 (4), 0.37 and 0.261 (2) Å, respectively. The Nb—N bond lengths are 2.486 (4), 2.5119 (19), 2.52 and 2.534 (11) Å, respectively. The experimental bonds are all statistically different, and the theoretical value is within the range of the observed bond lengths. The somewhat longer Nb—N distance in (IV) is probably a result of intramolecular hydrogen-bonding interactions between the coordinated aza ligand and two equatorial Cl atoms (see scheme).

Of primary interest are the differences in the Nb═O bond lengths, which are 1.706 (3), 1.7643 (17), 1.73 and 1.691 (9) Å, respectively. Theoretical DFT bond distances are typically longer than the observed ones by a few percent, which is the case for (I) (1.4%) and (IV) (2.3%). However, in the case of (III), the theoretical distance is shorter by 1.9%, or 0.034 Å. The Nb═O bond lengths in the chemically identical anions in (I) and (II) differ by 0.058 Å, a value exceeding the precision of a typical crystallographic experiment by a factor ~15. This 0.058 Å difference in the Nb═O bond lengths is in sharp contrast with the data observed for several related compounds. The corresponding difference for the $[O{=}NbCl_4$-

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$(NCMe)]^-$ monoanion in $[PPh_3Me][O{=}NbCl_4(NCMe)]$ (Hiller *et al.*, 1984) and $Na[O{=}NbCl_4(NCMe)]\cdot 2$(10-crown-5) (Ruhlandt-Senge & Müller, 1991) is 0.008 Å, for $[O{=}NbCl_4(THF)]^-$ (THF is tetrahydrofuran) in [chloro(η^5-cyclopentadienyl)tetrakis(*tert*-butylisocyanide)niobium]-$[O{=}NbCl_4(THF)]\cdot$THF (Aspinall *et al.*, 1984) and [hexakis(μ_2-acetato-*O*,*O*′)bis(μ_3-oxo)tris(tetrahydrofuran)triniobium]-$[O{=}NbCl_4(THF)]\cdot$THF (Cotton *et al.*, 1988) it is 0.017 Å, and for $[O{=}NbCl_4(H_2O)]^-$ in (4,5-diazoniafluoren-9-one)$_2$-$[O{=}NbCl_4(H_2O)]Cl$ (Balagopalakrishna *et al.*, 1996), [1,2,3-tris(dimethylamino)cyclopropenylium]$[O{=}NbCl_4(H_2O)]$ (Schäfer *et al.*, 1991) and $[PPh_4][O{=}NbCl_4(H_2O)]$ (Klingelhofer & Muller, 1984) the range is 0.038 Å.

It has been suggested that the standard uncertainites for atomic coordinates reported for individual crystallographic experiments are underestimated by a factor of 1.40–1.45 (Taylor & Kennard, 1986), but even if the s.u. values for the Nb═O bond distances in (I) and (II) are tripled, the bonds still remain statistically different. While both distances fall in the expected range for Nb═O double bonds of 1.66–1.77 Å (Nugent & Mayer, 1988), we sought to formulate an explanation for the length of the Nb═O double bond in (II).

Firstly, we observe that the Nb—Cl, C—C and C—N distances in (I) and (II) are statistically indistinguishable. Thus, a systematic error is unlikely. Secondly, we observe that both Nb═O and Nb—N bond distances in (II) are longer than those in (I). This cannot be attributed to a *trans* correlation, since the elongation of both bonds is simultaneous. An examination of intermolecular contacts in the crystal structure does not reveal the presence of weak C—H···O or C—H···Cl hydrogen-bonding interactions that could result in such elongations.

Our next step was an evaluation of energies attributable to the conformational changes of (III-DFT). We performed minimizations for (III-DFT) to discover that its staggered conformation (torsion angle Cl—Nb—N—C = 45°) is 1.5 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) more stable than the eclipsed conformation (torsion angle Cl—Nb—N—C = 0°). These dihedral angles are 38.29 (10)° in (I) and 35.51 (17)° in (II), and in both cases the molecular symmetry is approximately C_2 rather than C_{2v}.

A relaxed potential-energy surface scan of (III-DFT), in which the Nb═O distance was varied between 1.65 and 1.80 Å in 0.03 Å increments and the Nb—N distances were varied between 2.45 and 2.54 Å in 0.03 Å steps, demonstrated that the energy difference among all the optimized geometries did not exceed 4.3 kcal mol^{-1}. In particular, the optimized geometry of (III-DFT) with Nb═O and Nb—N distances constrained to be identical to those in (I) (1.706 and 2.486 Å, respectively) is 0.36 kcal more stable than the optimized geometry of (III-DFT) with the Nb═O and Nb—N distances constrained to equal those in (II) (1.7643 and 2.5119 Å, respectively). The strength of the N—H···Cl hydrogen bonds present in the lattice of (II) is estimated to be between 10 and 24 kcal mol^{-1}. Since the geometry of the $[O{=}NbCl_4(py)]^-$ anion in (I) and (II) differs from the idealized C_{2v} symmetric staggered conformation in both bond distances and torsion angles, it is proposed that the lattice energy and crystal forces that cause the deformation of the ideal geometry of $[O{=}NbCl_4(py)]^-$ also result in the extended axial bond distances about the Nb metal center. From the frequentist point of view, the probability that the two Nb═O bonds in question are equal is less than 0.01%. On the other hand, in view of the fact that the $[O{=}NbCl_4(py)]^-$ anions in (I) and (II) are chemically equivalent and the energy difference between them is small, the Bayesian approach is to conclude that this difference between two chemically equivalent Nb═O double bonds is inconsequential. Nonetheless, the fact that the Nb═O bond in (II) is longer than that in (III-DFT) and substantially longer than that in (I) is worrisome. Unfortunately, acquiring enough statistics for anion (III) by collecting several datasets on crystals of (I) and (II) was not feasible, due to the instability of the crystals and their scarce number. Complex (II) formed adventitiously and there is no established synthetic procedure for its preparation.

To date, the Nb═O distance in (II) of 1.7643 (17) Å is the longest among those reported for ten six-coordinate monoanionic oxoniobium(V) complexes in the CSD.

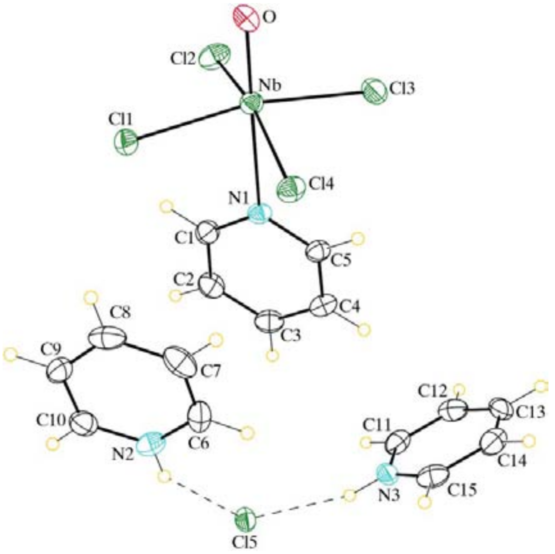

Figure 1
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen-bonding interactions are represented by dashed lines.

Experimental

Adventitious hydrolysis of $O{=}NbCl_3$ in the presence of pyridine yielded (II). Crystals of (II) were obtained from a pyridine–hexane solvent system.

Crystal data

$(C_5H_6N)_2[NbCl_4O(C_5H_5N)]Cl$
$M_r = 525.48$
Monoclinic, $P2_1/c$
$a = 7.6122$ (9) Å
$b = 20.091$ (2) Å
$c = 13.8061$ (16) Å
$\beta = 99.328$ (2)°
$V = 2083.5$ (4) Å^3

$Z = 4$
$D_x = 1.675$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.23$ mm^{-1}
$T = 100$ (2) K
Block, yellow
0.42 × 0.34 × 0.33 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
0.30° ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.60$, $T_{\max} = 0.66$
16884 measured reflections
4257 independent reflections
4097 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.025$
$\theta_{\max} = 26.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.079$
$S = 1.11$
4257 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 2.8236P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.96$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Nb1—O1	1.7643 (17)	Nb1—Cl2	2.4029 (7)
Nb1—Cl4	2.3992 (6)	Nb1—Cl1	2.4127 (6)
Nb1—Cl3	2.4002 (7)	Nb1—N1	2.5119 (19)

O1—Nb1—Cl4	98.45 (6)	Cl3—Nb1—Cl1	167.47 (2)
O1—Nb1—Cl3	96.52 (6)	Cl2—Nb1—Cl1	89.09 (2)
Cl4—Nb1—Cl3	88.77 (2)	O1—Nb1—N1	179.35 (8)
O1—Nb1—Cl2	97.97 (6)	Cl4—Nb1—N1	81.56 (5)
Cl4—Nb1—Cl2	163.50 (2)	Cl3—Nb1—N1	82.83 (5)
Cl3—Nb1—Cl2	90.97 (3)	Cl2—Nb1—N1	82.04 (5)
O1—Nb1—Cl1	95.87 (6)	Cl1—Nb1—N1	84.78 (5)
Cl4—Nb1—Cl1	87.63 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···Cl5	0.88	2.32	3.108 (2)	150
N3—H3N···Cl5	0.88	2.16	3.015 (2)	163

All H atoms were placed in idealized locations and refined as riding, with C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This manuscript was prepared using beta test version 1.0.1 of the program *publCIF* to be released by the IUCr and program *modiCIFer* to be released by the University of Wisconsin–Madison.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3030). Services for accessing these data are described at the back of the journal.

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