

Pseudosymmetry in pyridinium tetrachloro(oxo)pyridineniobate(V) pyridine solvate¹

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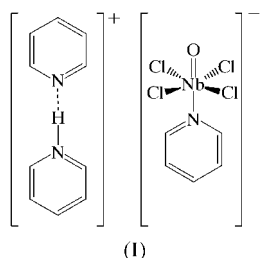
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The title compound, (C₅H₅N)[NbCl₄O(C₅H₅N)]·C₅H₅N, crystallizes as discrete ions, with a very strong linear N—H···N hydrogen-bonding interaction between the cation and the solvate pyridine molecule [N···N 2.755 (5) Å]. All chemical species occupy crystallographic twofold axes. The ligated and solvate pyridines form *ABABAB* stacks in the lattice. There is pseudosymmetry which emulates a centred unit cell in *Amm2*, but it is not supported by the diffraction pattern, which is consistent with the correct space group *Pnc2*. Three crystallographic software packages suggested space group *Amm2* over *Pnc2*, while a fourth indicated *Pnc2*, a subgroup of *Amm2*.

Comment

The title compound, (I), crystallizes in an orthorhombic space group, *Pnc2* (*Z* = 2), and refines to an *R* factor of 0.020 [*wR*(*F*²) = 0.054], with expected interatomic bond distances, low s.u. values and normal atomic anisotropic displacement parameters. Geometric details are given in Table 1.



Program *XPREP* of the *SHELXTL* software package (Sheldrick, 1997a) suggested two probable space groups, *Pmna* and *Pnc2*, but only the latter non-centrosymmetric space group yielded chemically reasonable and computationally stable refinement results. All chemical moieties reside on crystallographic twofold axes.

¹ This paper is dedicated to the memory of Bob Sparks.

Upon completion of the refinement, *PLATON* (Spek, 1991) was used to verify the correctness of the structure and a new space group, *Amm2*, was suggested. Refinement in this space group also proved to be reasonable, with all chemical entities possessing *mm2* (*C_{2v}*) site symmetry. However, the *R* factor was slightly higher [*R* = 0.024 and *wR*(*F*²) = 0.063] and the displacement ellipsoids were elongated in a direction perpendicular to the crystallographic mirror planes. The bond distances differed slightly from the corresponding distances in the structure refined in *Pnc2*, but fell into the expected ranges with low s.u. values. Nonetheless, these s.u. values were twice as large as those determined in *Pnc2*. The *checkCIF* software also suggested the higher symmetry space group *Amm2*, but this is not surprising as it employs the same algorithms as *PLATON*.

The late Bob Sparks kindly analyzed the structure with the program *FINDSYMM* (not commercially available from Bruker AXS at the time) to discover that, again, space group *Amm2* was chosen over *Pnc2*. Interestingly, the centred structure was never suggested by *XPREP*. Table 3 contains the *XPREP* output of a statistical analysis of the current data set. It is clear from the statistics that *A*-centring is not present.

The correct assignment of the space group came down to an analysis of the actual X-ray diffraction pattern by eye, which may not often be performed nowadays, since fast computers and elaborate programs are readily available. Space groups *Pnc2* and *Amm2* have the same reflection conditions for two sets of reflections *0kl* and *h0l*. However, *Amm2* has an extra reflection condition, *hkl* (*k* + *l* = even). While reflections with *k* + *l* = odd (*hkl*) were not very strong, their observed presence substantiated the correct assignment of the space group as

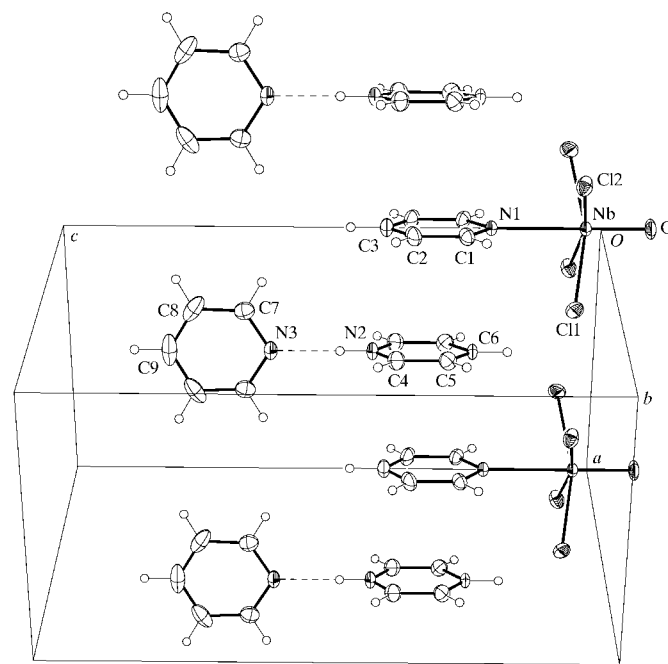


Figure 1

The spatial arrangement of ions and solvate molecules in the structure of (I). Only one of the disordered H-atom sites between N2 and N3 is shown.

Pnc2. This example illustrates that blindly relying upon modern software can lead to incorrect space-group assignment, which in turn results in flawed structures.

A molecular packing diagram for (I) is shown in Fig. 1. The absence of C_{2v} symmetry in the structure is further evidenced by two structural parameters. Firstly, the orientation of the coordinated N1 pyridine ring relative to the Cl atoms is noteworthy. The Cl1—Nb—N1—Cl dihedral angle is $51.7(2)^\circ$, rather than the 45° which would correspond to the expected ideally staggered conformation. The observed deviation from idealized geometry is attributed to packing forces. Secondly, the dihedral angle between the pyridine rings of the two solvate pyridine molecules participating in the hydrogen-bonding interaction is $82.16(2)^\circ$. This value is consistent with the observed C_2 symmetry but contradicts C_{2v} symmetry, for which angles of 0 or 90° are required.

The $[\text{NbOCl}_4(\text{py})]^-$ anion (py is pyridine) exhibits a distorted octahedral geometry, with the pyridine ring *trans* to the oxo ligand. The Nb^V centre is displaced by $-0.303(2)$ Å toward the O atom and away from the equatorial plane defined by the four Cl[−] ligands. Similar geometrical features have been observed in related compounds, such as $\text{PPh}_3\text{Me}[\text{NbOCl}_4(\text{CH}_3\text{CN})]^-$ (Hiller *et al.*, 1984), and compounds of the form $[\text{X}]^+[\text{NbOCl}_4(\text{H}_2\text{O})]^-$, where X is $[(\text{H}_2\text{dafone})\text{Cl}]$ (dafone is 4,5-diazafluoren-9-one; Balagopalakrishna *et al.*, 1996), PPh_4 (Klingelhofer & Muller, 1984) or 1,2,3-tris(dimethylamino)cyclopropenylum (Schafer *et al.*, 1991).

The Nb—Cl distances in (I) [mean $2.400(4)$ Å] compare well with the average Nb—Cl bond length of $2.35(5)$ Å obtained by averaging 261 Nb—Cl distances found in 57 complexes reported in the Cambridge Structural Database (CSD, Version 1.2 for Windows; Allen & Kennard, 1993). The Nb=O formal double bond in (I) [$1.708(3)$ Å] is in good agreement with the average Nb=O separation of $1.72(3)$ Å calculated by averaging 20 relevant distances in 15 complexes in the CSD. The Nb—N(py) coordinative bond is generally observed to vary in length depending on the ligand *trans* to the pyridine. In cases where the pyridine is opposite a doubly bound ligand, the bond is considerably longer than in the instances when the pyridine is *trans* to a singly bound group, a typical manifestation of the *trans* influence. Thus, the Nb—N(py) distances in $(i\text{PrN})\text{NbCl}_3\text{py}_2$, (II) (Chiu *et al.*, 1998), $(\text{BuN})\text{NbCl}_3\text{py}_2$, (III) (Chiu *et al.*, 1998), and *cis-mer*- $[\text{NbCl}_3(\text{OC}_6\text{H}_3^i\text{Pr-2,6})_2(\text{py})]$ (Clark *et al.*, 1997) are, respectively, $2.307(3)$, $2.313(4)$ and $2.331(4)$ Å to the pyridines *trans* to single M—ligand bonds, while the Nb—N(py) distances to the pyridines *trans* to the imido ligands in (II), (III) and $[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{Nb}(\text{N}^i\text{Bu})\text{Cl}_4(\text{py})]\cdot\text{CH}_2\text{Cl}_2$ (Clegg *et al.*, 1991) are $2.463(3)$, $2.480(4)$ and $2.479(4)$ Å, respectively. The Nb—N1 bond length in (I) [$2.488(4)$ Å] compares well with the latter three values, which is in accord with the slight concomitant compression of the Nb=O double bond.

The negative charge on the Nb complex is balanced by an H atom located between the N atoms of the two pyridine solvate molecules residing on a crystallographic twofold axis. The N...N separation of $2.756(5)$ Å corresponds to a very strong

intermolecular N—H...N hydrogen-bonding interaction. For the initial structural refinement, the H atom was arbitrarily placed in an idealized position on atom N2, but it can be refined equally well on the other nitrogen, N3. Thus, for the final refinement, the H atom was refined as being equally disordered between the two positions. The resulting N—H...N hydrogen bonds are equivalent (Table 2). The N—H...N angle is linear due to symmetry considerations. A CSD search on intermolecular N—H...N interactions returned 4200 hits, with an N...N separation range of $2.634\text{--}3.754$ Å. The hydrogen-bonding interaction observed in (I) is among the 30 shortest reported to date.

The spatial arrangement of the molecules and ions in the lattice of (I) is such that the ligated pyridine and the N2 pyridine form stacks in an *ABABAB* fashion, with an interplanar distance of $3.56(3)$ Å. While the aromatic rings are not quite parallel, these π -stacking interactions are significant, as they fall within the sum of the van der Waals radii of the delocalized π -systems of aromatic rings, approximated to be 3.70 Å (Cotton & Wilkinson, 1972).

Experimental

Adventitious hydrolysis of Nb(=O)Cl_3 in the presence of pyridine yielded (I). Crystals of (I) were obtained from a pyridine/hexane solvent system (Saulys & Roberts, 2002).

Table 1

Selected geometric parameters (Å, °).

Nb—O	1.706 (3)	Nb—Cl2 ⁱ	2.4037 (5)
Nb—Cl1 ⁱ	2.3962 (5)	Nb—N1	2.486 (4)
O—Nb—Cl1 ⁱ	98.733 (18)	Cl2—Nb—Cl2 ⁱ	168.44 (3)
Cl1—Nb—Cl1 ⁱ	162.53 (4)	Cl1 ⁱ —Nb—N1	81.267 (18)
O—Nb—Cl2 ⁱ	95.782 (17)	Cl2 ⁱ —Nb—N1	84.218 (17)
Cl1 ⁱ —Nb—Cl2 ⁱ	89.113 (18)		
Cl1 ⁱ —Nb—N1—Cl1 ⁱ	51.70 (10)	Cl2 ⁱ —Nb—N1—Cl1 ⁱ	−38.29 (10)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2A...N3	0.88	1.88	2.756 (5)	180
N3—H3A...N2	0.88	1.88	2.756 (5)	180

Table 3

The *XPREP* statistical analysis of the diffraction data of (I).

8146 reflections; mean $(I/\sigma) = 15.74$.

Lattice exceptions	<i>P</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>F</i>	Obv	Rev	All
<i>N</i> (total)	0	4081	4082	4055	4054	6109	5421	5409	8146
<i>N</i> (<i>I</i> > 3σ)	0	3115	3594	3571	3402	5140	4753	4755	7174
Mean intensity	0.0	5.3	34.8	35.0	28.1	25.0	35.2	35.1	35.2
Mean <i>I</i> /σ	0.0	11.0	15.9	15.6	15.0	14.1	15.7	15.7	15.8

Notes: Obv and Rev are the obverse and reverse settings, respectively, for a rhombohedrally centred cell described with hexagonal axes.

Crystal data

(C₅H₆N)[NbCl₄O(C₅H₅N)]·C₅H₅N
 $M_r = 489.02$
 Orthorhombic, *Pnc2*
 $a = 7.3355$ (3) Å
 $b = 9.4033$ (4) Å
 $c = 14.1728$ (7) Å
 $V = 977.61$ (8) Å³
 $Z = 2$
 $D_x = 1.661$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 5722 reflections
 $\theta = 2-25^\circ$
 $\mu = 1.17$ mm⁻¹
 $T = 173$ (2) K
 Block, yellow
 $0.41 \times 0.32 \times 0.30$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Blessing, 1995)
 $T_{\min} = 0.646$, $T_{\max} = 0.721$
 7522 measured reflections

1048 independent reflections (plus 952 Friedel-related reflections)
 1975 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\max} = 26.4^\circ$
 $h = -9 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.054$
 $S = 1.04$
 2000 reflections
 115 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.0707P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.57$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³
 Absolute structure: Flack (1983)
 Flack parameter = -0.03 (4)

H atoms were treated as riding in idealized positions, with C—H = 0.95 Å and N—H = 0.88 Å. Displacement parameters for H atoms were assigned as $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the attached atom. H atoms on N atoms were treated as half populated.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine

structure: *SHELXTL* (Sheldrick, 1997a); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1359). Services for accessing these data are described at the back of the journal.

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