

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[pyH⁺]₂[CdNb₂(py)₄O₂F₁₀]²⁻

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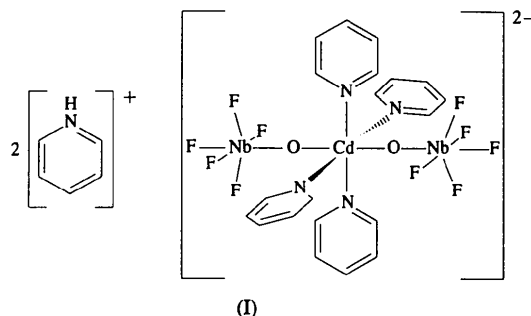
Abstract

A new Cd^{II}/Nb^V compound, bis(pyridinium) decafluoro-2κ⁵F₃κ⁵F-di-μ-oxo-1:2κ²O;1:3κ²O-tetrakis(pyridine-N)-cadmiumdiniobium(2-), (C₅H₆N)₂[CdNb₂F₁₀O₂(C₅H₅-N)₄], has been synthesized. The complex contains [CdNb₂(py)₄F₁₀O₂]²⁻ anions (py is pyridine) linked *via* the pyridinium cation through N—H⁺···F hydrogen bonding. The anion is composed of two [NbF₅O_{1/2}]⁻ octahedra connected by O²⁻ to a central [Cd(py)₄O_{2/2}]²⁻ octahedron.

Comment

The new mixed metal compound, [pyH⁺]₂[CdNb₂(py)₄O₂F₁₀]²⁻, (I), is isostructural with [pyH⁺]₂[CuNb₂(py)₄O₂F₁₀]²⁻ (Halasyamani *et al.*, 1996). The title metal complex contains anionic [CdNb₂(py)₄O₂F₁₀]²⁻ clusters linked *via* the pyridinium cation through hydrogen bonding. Each cluster is composed of two [NbF₅O_{1/2}]⁻ octahedra connected through O²⁻ to a central [Cd(py)₄O_{2/2}]²⁻

octahedron. The niobium cations are displaced from the center of the [NbF₅O_{1/2}]⁻ octahedra towards the bridging O atoms (Goodenough & Longo, 1970) in an anti-parallel manner.



Single crystal diffraction data revealed only three unique atoms in the asymmetric unit for pyridinium, indicating disorder. Owing to a number of possible disorder constraints, the probable N(3)—H⁺···F hydrogen-bonding interactions were used to disorder N(3) and C(9). Only one hydrogen-bonding interaction, however, occurs for each ring. The large *U*₃₃ value observed for the F(3) atom is due to the possible hydrogen-bonding interactions.

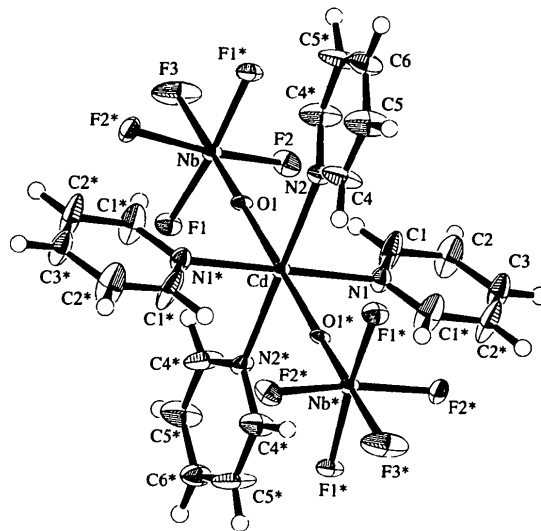


Fig. 1. ORTEP (Johnson, 1976) plot (50% probability ellipsoids) of the polynuclear anion [CdNb₂(py)₄O₂F₁₀]²⁻.

The bond lengths of (I) compare well with other compounds. For example, the Nb—O/F distances, Nb—F_{trans} 2.097 (6), Nb—O 1.747 (7) and Nb—F_{eq} 1.935 (4) Å, compare well to the Nb—O/F distances of Nb—F_{trans} 2.095 (2), Nb—O 1.765 (2) and Nb—F_{eq} 1.925 (2)–1.974 (2) Å in Na₂[NbF₅O] (Stomberg, 1983). In addition, the average Cd—N distance of 2.35 (1) Å is in good agreement with the Cd—N distance of 2.341 (5) Å in [Cd(NH₃)₄(I₂)₂] (Tebbe & Plewa, 1982).

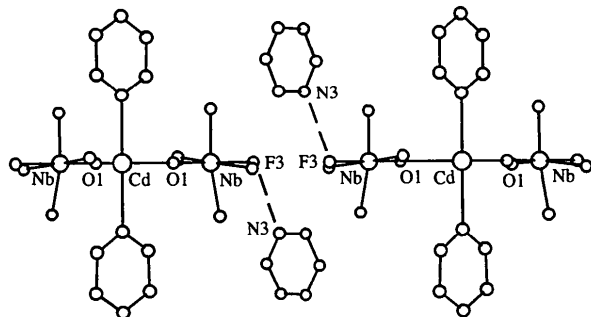


Fig. 2. Ball-and-stick diagram of $[pyH^+]_2[CdNb_2(py)_4O_2F_{10}]^{2-}$, with dashed lines indicating hydrogen bonding.

Crystal data

$(C_5H_6N)_2[CdNb_2F_{10}O_2(C_5H_5N)_4]$

$M_r = 996.83$

Tetragonal

$I4_122$

$a = 11.490(2) \text{ \AA}$

$c = 30.906(3) \text{ \AA}$

$V = 4080.2(9) \text{ \AA}^3$

$Z = 4$

$D_x = 1.62 \text{ Mg m}^{-3}$

$D_m = 1.61(1) \text{ Mg m}^{-3}$

D_m measured by flotation pycnometry

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10.01\text{--}12.08^\circ$

$\mu = 1.148 \text{ mm}^{-1}$

$T = 153.2 \text{ K}$

Faceted

$0.386 \times 0.258 \times 0.172 \text{ mm}$

Colorless

Data collection

Enraf-Nonius CAD-4

diffractometer

ω/θ scans

Absorption correction:

analytical (de Meulenaer & Tompa, 1965)

$T_{\min} = 0.632$, $T_{\max} = 0.836$

2043 measured reflections

1098 independent reflections

982 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.0378$

$\theta_{\max} = 24.97^\circ$

$h = -13 \rightarrow 0$

$k = -13 \rightarrow 0$

$l = -36 \rightarrow 0$

3 standard reflections

monitored every 90

reflections

intensity decay: 1.15%

Refinement

Refinement on F

$R = 0.0245$

$wR = 0.0289$

$S = 2.350$

982 reflections

116 parameters

H-atom parameters not refined

Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\max} = 0.218$

$\Delta\rho_{\max} = 0.60 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.57 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1968) type

2, Gaussian isotropic

Extinction coefficient:

0.85668

Atomic scattering factors

from *International Tables for X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

U_{iso} for N(3) and C(9), $U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$ for all others.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Cd	1/2	1/2	1/2	0.01311 (9)
Nb	0.75125 (4)	x	1/2	0.01439 (8)
F(1)	0.8800 (3)	0.6446 (3)	0.4933 (1)	0.0245 (9)
F(2)	0.7785 (3)	0.7516 (3)	0.56182 (9)	0.0279 (9)
F(3)	0.8802 (3)	x	1/2	0.058 (1)
O(1)	0.6436 (4)	x	1/2	0.0142 (8)
N(1)	1/2	1/2	0.5755 (1)	0.022 (2)
N(2)	0.3548 (5)	$1-x$	1/2	0.019 (1)
N(3)†	0.9593 (7)	0.9576 (8)	0.4160 (2)	0.034 (1)
C(1)	0.5700 (8)	0.5685 (8)	0.5978 (2)	0.045 (2)
C(2)	0.573 (1)	0.571 (1)	0.6425 (2)	0.052 (3)
C(3)	1/2	1/2	0.6652 (2)	0.037 (4)
C(4)	0.2428 (5)	0.6198 (5)	0.4941 (4)	0.042 (2)
C(5)	0.1552 (5)	0.7016 (6)	0.4951 (4)	0.051 (2)
C(6)	0.1839 (5)	$1-x$	1/2	0.034 (1)
C(7)	0.9201 (9)	0.9135 (9)	0.3785 (2)	0.046 (2)
C(8)	0.959 (1)	0.957 (1)	0.3399 (2)	0.062 (5)
C(9)†	0.9593	0.9576	0.4160	0.034

† Site occupancy = 0.5.

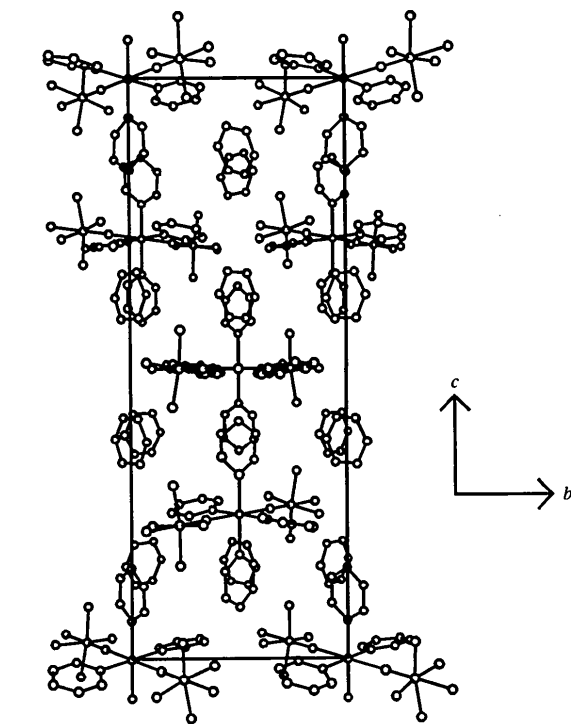


Fig. 3. Packing diagram of $[pyH^+]_2[CdNb_2(py)_4O_2F_{10}]^{2-}$.

Experimental

The Cd analog was synthesized by placing CdO (0.128 g, 0.001 mol, Aldrich, 99.5%) and Nb_2O_5 (0.133 g, 0.0005 mol, Aldrich, 99.99%) in a teflon pouch (Gier & Stucky, 1991). To the pouch were added $(HF)_x$ -pyridine (0.51 g, 0.0015 mol, Aldrich, pyridinium polyhydrogen fluoride, 70% HF by weight), pyridine (0.8 g, 0.01 mol, Aldrich, 99%) and H_2O (0.036 g, 0.002 mol). The pouch was sealed and placed in a 2000 ml autoclave filled with H_2O (600 ml). The autoclave was heated for 24 h at 423 K and cooled to room temperature over an additional 24 h. The pouch was opened in air and the product, subsequently determined to be $[pyH^+]_2[CdNb_2(py)_4O_2F_{10}]^{2-}$, was recovered in about 40% yield based on CdO.

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cd—O(1)	2.333 (6)	Nb—F(2)	1.936 (3)
Cd—N(1)	2.335 (4)	Nb—F(3)	2.095 (4)
Cd—N(2)	2.359 (8)	Nb—O(1)	1.750 (6)
Nb—F(1)	1.932 (3)		
O(1)—Cd—N(1)	90.0	F(1)—Nb—O(1)	95.3 (1)
O(1)—Cd—N(2)	90.00 (1)	F(2)—Nb—F(2')	166.7 (2)
N(1)—Cd—N(2)	90.0	F(2)—Nb—F(3)	83.3 (1)
F(1)—Nb—F(1')	169.3 (2)	F(2)—Nb—O(1)	96.6 (1)
F(1)—Nb—F(2)	89.0 (1)	F(3)—Nb—O(1)	180.0
F(1)—Nb—F(2')	89.8 (1)	Cd—O(1)—Nb	180.0
F(1)—Nb—F(3)	84.7 (1)		

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

Neutral-atom scattering factors were taken from Cromer & Waber (1974). The coordinates and isotropic U values for the disordered N(3) and C(9) sites were constrained to be equal in the refinement.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *DIRDIF* (Beurskens *et al.*, 1992). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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$[(\text{CpTi})_6(\mu_3\text{-Te})_6(\mu_3\text{-O})_2]$

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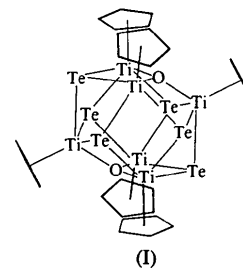
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Abstract

The X-ray crystal structure of the title cluster, hexakis[1,2,3,4,5,6(η^5)-cyclopentadienyl]-di- μ_3 -oxo-1:2:3 κ^3 O;4:5:6 κ^3 O-hexatelluriumhexatitanium(18 Te—Ti), $[(\text{CpTi})_6(\mu_3\text{-Te})_6(\mu_3\text{-O})_2]$, has been determined. The metric parameters for this cluster are compared with those of the closely related oxo cluster and other relevant titanium compounds.

Comment

The cluster $[(\text{CpTi})_6(\mu_3\text{-Te})_6(\mu_3\text{-O})_2]$, (1), where Cp is cyclopentadienyl, was obtained from the reaction of $\text{Cp}_2\text{Ti}(\text{TeSiPh}_3)_2$ with PPh_3 . Although we have little information as to how this compound is formed, it is most likely that the oxo ligands are introduced by trace amounts of water in the toluene solvent used.



An *ORTEP* (Johnson, 1976) diagram of the molecular structure of (1) viewed down the O—O vector is shown in Fig. 1. The structure of (1) is similar to the structure of $[(\text{CpTi})_6(\mu_3\text{-O})_6]$, (2), reported some time ago by Huffman, Stone, Krusell & Caulton (1977). The six Ti atoms form an octahedron with each of the faces capped by a chalcogen. Each individual Ti atom is coordinated in a distorted square-pyramidal geometry. The $L\text{—Ti—}L$ angles range from $75.1(1)$ to $86.8(2)^\circ$ for *cis* ligands and from $121.8(2)$ to $138.0(2)^\circ$ for *trans* ligands. Unlike cluster (2), the $\text{Ti}\cdots\text{Ti}$ distances [$3.273(2)$ – $3.990(2)$ \AA] in (1) do not suggest any degree of interaction between metal centres. The Ti—C distances (average 2.374 \AA) are identical to values found in both (2) and related titanocene derivatives. The $\text{Te}1\cdots\text{Te}3$ and $\text{Te}2\cdots\text{Te}3$ distances [$3.442(1)$ and $4.048(1)$ \AA , respectively] lie outside the range of bond lengths found for Te—Te covalent bonds (Du