

Diaquabis(1,10-phenanthroline- κ^2N,N')cadmium(II)
pentafluorooxoniate(V)

Gang Zhu and Zongxun Tang*

Department of Chemistry, Shaanxi Key
Laboratory of Physico-Inorganic Chemistry,
Northwest University, Xi'an, Shaanxi 710069,
People's Republic of China

Correspondence e-mail: tzxtq@163.com

Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.009$ Å
 R factor = 0.034
 wR factor = 0.092
Data-to-parameter ratio = 12.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the title compound, $[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2][\text{NbOF}_5]$, consists of Cd^{II} complex cations and Nb^{V} complex anions. The Cd^{II} and Nb^{V} atoms both have a distorted octahedral geometry. The $\text{Nb}-\text{F}$ bond *trans* to the $\text{Nb}=\text{O}$ bond is significantly longer than the other four $\text{Nb}-\text{F}$ bonds.

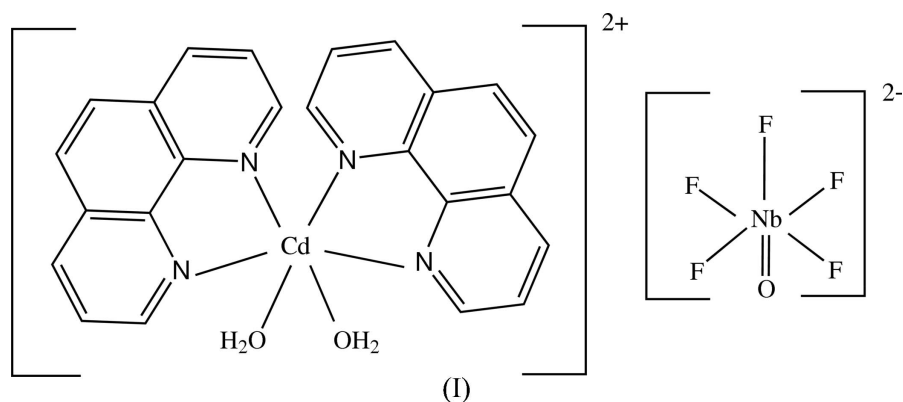
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Comment

Out-of-center 'primary' electronic distortions are inherent to oxide fluoride anions of the early d^0 transition metals. In the $[\text{NbOF}_5]^{2-}$ anion, the Nb^{V} atom deviates from the center of the octahedron toward the oxygen ligand, forming a short $\text{Nb}=\text{O}$ bond and long *trans* $\text{Nb}-\text{F}$ bond. The *trans*-directing property of the $[\text{NbOF}_5]^{2-}$ anion can be exploited when designing new materials that exhibit important structure-dependent properties such as piezoelectricity, second-order nonlinear optical activity and ferroelectricity (Heier *et al.*, 1998; Welk *et al.*, 2002). Here the synthesis, crystal structure and characterization of a mixed-metal complex $[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]^{2+} \cdot [\text{NbOF}_5]^{2-}$, (I), which incorporates the $[\text{NbOF}_5]^{2-}$ anion, is reported.



The molecular structure of (I) is shown in Fig. 1. The crystal structure of (I) is built up of Cd^{II} complex cations and Nb^{V} complex anions. The Cd^{II} atom has an octahedral coordination geometry with two 1,10-phenanthroline (phen) and two water molecules. The Nb^{V} atom assumes a distorted octahedral coordination with five F atoms and one O atom. The $\text{Nb}-\text{F}$ bond *trans* to the $\text{Nb}=\text{O}$ bond is significantly longer than the other four $\text{Nb}-\text{F}$ bonds in the same anion (Table 1). This feature was also observed in previously reported structures (Halasyamani *et al.*, 1996; Norquist *et al.*, 1999; Izumi *et al.*, 2005). The coordinated water molecules of the Cd^{II} complex cation form hydrogen bonds with the $[\text{NbOF}_5]^{2-}$ anion. Some phen H atoms also interact with the $[\text{NbOF}_5]^{2-}$ anion *via* C—H...F hydrogen bonds (Table 2).

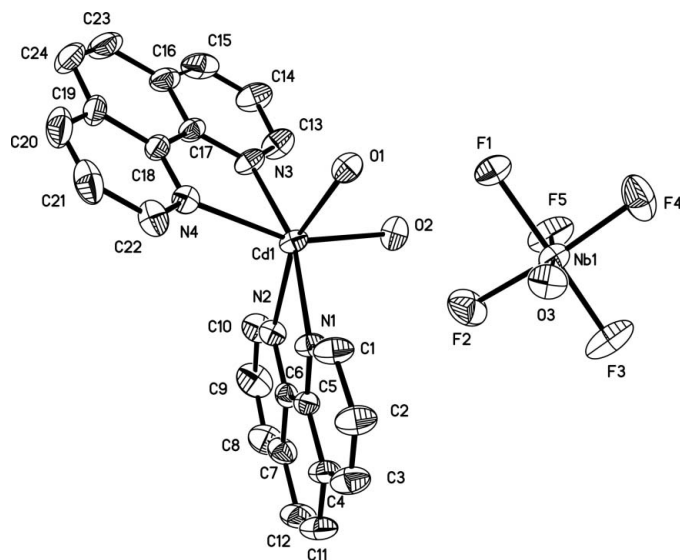


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. All H atoms have been omitted.

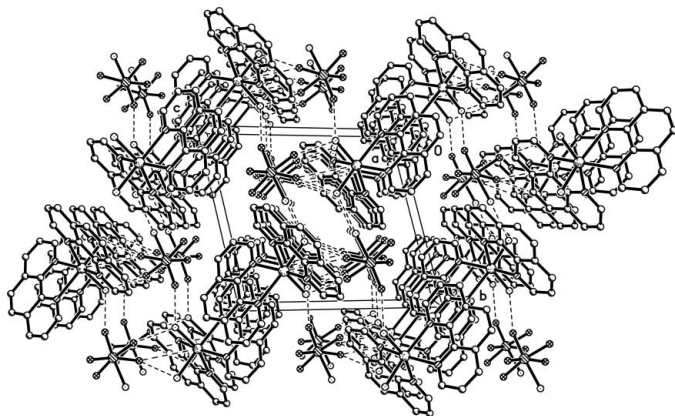


Figure 2
The molecular packing of (I), viewed along the *a* axis. For clarity, all H atoms have been omitted. Dashed lines indicate O—H...F hydrogen-bonding interactions.

Experimental

All reagents were of analytical grade from commercial sources and used without further purification. Nb₂O₅ (0.133 g, 0.5 mmol) was first dissolved in HF solution (1 ml, 42 wt% in H₂O) at 383 K for 2 h in a Teflon-lined stainless steel vessel. After the solution had been cooled to room temperature, 3CdSO₄·8H₂O (0.257 g, 0.33 mmol), phen (0.496 g, 2.5 mmol) and water (15 ml) were added. The pH of the mixture was adjusted to about 6 using KOH solution. The mixture was then heated under autogenous hydrothermal conditions at 413 K for 3 d. The mixture was filtered, then the solution was allowed to evaporate slowly. After 5 d, colorless single crystals suitable for X-ray diffraction were obtained. The crystals were dried in air. Elemental analysis: found: C 40.31, H 2.78, N 7.87%; calculated for C₂₄H₂₀CdF₅N₄NbO₃: C 40.34, H 2.82, N 7.85%.

Crystal data

[Cd(C₁₂H₈N₂)₂(H₂O)₂][NbOF₅]
M_r = 712.75
 Triclinic, *P* $\bar{1}$
a = 9.487 (4) Å
b = 11.537 (5) Å
c = 13.007 (5) Å
 α = 99.162 (6)°
 β = 109.646 (6)°
 γ = 100.661 (5)°
V = 1279.3 (9) Å³

Z = 2
D_x = 1.850 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2883 reflections
 θ = 2.2–27.2°
 μ = 1.35 mm⁻¹
T = 298 (2) K
 Block, colorless
 0.35 × 0.33 × 0.29 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
T_{min} = 0.650, *T_{max}* = 0.696
 6750 measured reflections

4464 independent reflections
 3413 reflections with *I* > 2σ(*I*)
R_{int} = 0.016
 θ_{\max} = 25.0°
h = -11 → 11
k = -13 → 13
l = -15 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.034
wR (*F*²) = 0.092
S = 1.00
 4464 reflections
 355 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 1.0033P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.79 \text{ e \AA}^{-3}$

Table 1
Selected bond lengths (Å).

Nb1—O3	1.764 (3)	Cd1—O2	2.279 (3)
Nb1—F4	1.882 (3)	Cd1—O1	2.296 (3)
Nb1—F3	1.903 (3)	Cd1—N1	2.317 (4)
Nb1—F2	1.935 (3)	Cd1—N3	2.324 (4)
Nb1—F1	1.966 (3)	Cd1—N4	2.364 (4)
Nb1—F5	2.046 (3)	Cd1—N2	2.364 (4)

Table 2
Hydrogen-bond 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>
O1—H25...O3 ⁱ	0.85 (4)	1.83 (4)	2.672 (5)	177 (5)
O1—H26...F1	0.84 (3)	1.84 (3)	2.679 (5)	172 (6)
O2—H27...F5 ⁱⁱ	0.85 (3)	1.74 (3)	2.582 (5)	171 (6)
O2—H28...F2	0.83 (3)	2.12 (5)	2.851 (5)	146 (5)
O2—H28...F5	0.83 (3)	2.44 (3)	3.130 (5)	142 (5)
C11—H11...F5 ⁱⁱⁱ	0.93	2.52	3.427 (7)	166
C12—H12...F2 ^{iv}	0.93	2.43	3.299 (7)	156
C13—H13...F3 ⁱⁱ	0.93	2.48	3.089 (7)	123
C15—H15...F3 ^v	0.93	2.33	3.224 (8)	161

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

The water H atoms were located in a difference Fourier map and refined with the O—H bond length restrained to 0.85 (2) Å, and assigned fixed isotropic displacement parameters of 0.08 Å². Other H atoms were placed at calculated positions and refined as riding, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXTL* (Siemens, 1995).

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References

- Bruker (2002). *SAINTE* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Halasyamani, P., Willis, M. J., Stern, C. L., Lundquist, P. M., Wong, G. K. & Poeppelmeier, K. R. (1996). *Inorg. Chem.* **35**, 1367–1371.
- Heier, K. R., Norquist, A. J., Wilson, C. G., Stern, C. L. & Poeppelmeier, K. R. (1998). *Inorg. Chem.* **37**, 76–80.
- Izumi, H. K., Kirsch, J. E., Stern, C. L. & Poeppelmeier, K. R. (2005). *Inorg. Chem.* **44**, 884–895.
- Norquist, A. J., Stern, C. L. & Poeppelmeier, K. R. (1999). *Inorg. Chem.* **38**, 3448–3449.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.
- Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Welk, M. E., Norquist, A. J., Arnold, F. P., Stern, C. L. & Poeppelmeier, K. R. (2002). *Inorg. Chem.* **41**, 5119–5125.