

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

Gang Zhu and Zong-Xun 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

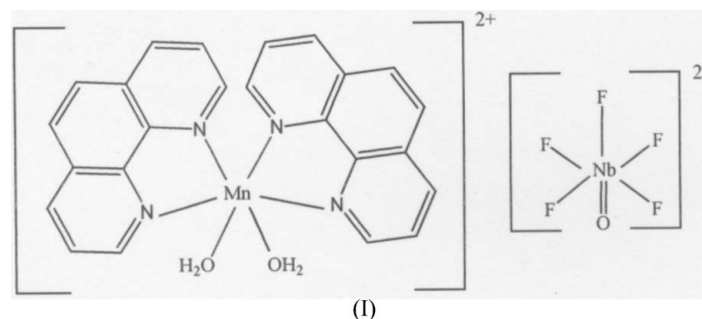
Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.033
 wR factor = 0.092
Data-to-parameter ratio = 12.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2][\text{NbOF}_5]$, each of the Mn^{II} and Nb^{V} atoms has a distorted octahedral coordination. In the $[\text{NbOF}_5]^{2-}$ anion, a characteristic short terminal $\text{Nb}=\text{O}$ bond and a longer $\text{Nb}-\text{F}$ bond are observed, which result in the out-of-center distortion of the octahedron, a manifestation of the second-order Jahn–Teller effect.

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Comment

Early transition metal oxofluoro anions, such as $[\text{NbOF}_5]^{2-}$ and $[\text{TaOF}_5]^{2-}$, interest researchers because their inherent distortions mimic those in the $[\text{NbO}_{6/2}]^-$ octahedra in LiNbO_3 , an excellent solid-state non-linear optical material. In the $[\text{NbOF}_5]^{2-}$ anion, the Nb atom is displaced from the center of the octahedron towards the O atom, forming a short $\text{Nb}=\text{O}$ bond and a longer $\text{Nb}-\text{F}$ bond. The distortion can be exploited when designing new materials that exhibit important structure-dependent properties, such as piezoelectricity, second-order non-linear optical activity and ferroelectricity (Heier *et al.*, 1998; Welk *et al.*, 2002). Here the synthesis and crystal structure of a mixed-metal complex, diaquabis(1,10-phenanthroline)manganese(II) pentafluorooxoniate, (I), which incorporates the $[\text{NbOF}_5]^{2-}$ anion, is reported.



The crystal structure of (I) consists of Mn^{II} complex cations and Nb^{V} complex anions (Fig. 1). The Mn^{II} atom has an octahedral coordination, formed by two 1,10-phenanthroline(phen) and two water molecules. The Nb^{V} atom assumes a distorted octahedral coordination, formed by 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 has also been observed in previously reported structures (Halasyamani *et al.*, 1996; Norquist *et al.*, 1999; Izumi *et al.*, 2005).

Bond-valence sums (Izumi *et al.*, 2005) show that some of the F atoms are heavily underbonded (Table 3), and this is compensated by substantial hydrogen bonding (Table 2) to the complex cations. For example, the F atom (F5) *trans* to the

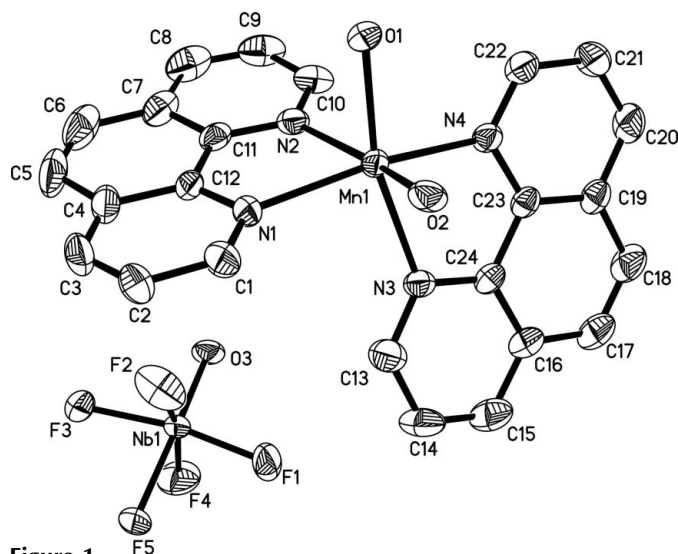


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level. All H atoms have been omitted. **[Please provide revised figure with no parentheses in labels]**

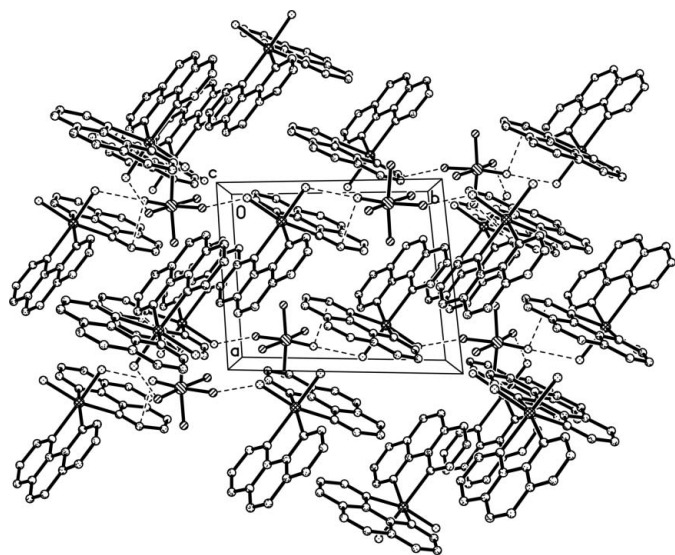


Figure 2
The molecular packing of (I), viewed along the *c* axis. For clarity, all H atoms have been omitted. Dashed lines indicate O–H...F hydrogen-bonding interactions.

short Nb=O bond (F5) accepts three hydrogen bonds; F4 accepts two. Atom O3 is hydrogen-bonded to one OH group. All H atoms of the water molecules and some H atoms of phen are involved in hydrogen bonding. The complex hydrogen-bonding scheme results in the crystal packing shown in Fig. 2.

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 being cooled to room temperature, MnSO₄·H₂O (0.169 g, 1 mmol), phen (0.396 g, 2 mmol) and H₂O (10 ml) were added to the above solution. The pH of the mixture was adjusted to about 6 by KOH. The mixture was then heated under autogenous hydrothermal conditions at 403 K for 3 d. After cooling to room temperature, the mixture was filtered. Yellow single crystals of (I) were obtained from the filtrate after several days.

Crystal data

[Mn(C ₁₂ H ₈ N ₂) ₂ (H ₂ O) ₂][NbF ₅ O]	<i>V</i> = 1278.62 (9) Å ³
<i>M_r</i> = 655.29	<i>Z</i> = 2
Triclinic, <i>P</i> $\bar{1}$	<i>D_x</i> = 1.702 Mg m ⁻³
<i>a</i> = 9.6242 (4) Å	Mo <i>K</i> α radiation
<i>b</i> = 11.3971 (5) Å	<i>μ</i> = 1.01 mm ⁻¹
<i>c</i> = 13.0605 (5) Å	<i>T</i> = 273 (2) K
<i>α</i> = 72.341 (2)°	Block, yellow
<i>β</i> = 70.054 (3)°	0.31 × 0.20 × 0.07 mm
<i>γ</i> = 79.686 (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	12791 measured reflections
<i>φ</i> and <i>ω</i> scans	4530 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	3265 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.746, <i>T_{max}</i> = 0.937	<i>R_{int}</i> = 0.033
	<i>θ_{max}</i> = 25.1°

Refinement

Refinement on <i>F</i> ²	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.033	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0507 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.092	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 1.03	(Δ/σ) _{max} = 0.001
4530 reflections	Δρ _{max} = 0.46 e Å ⁻³
360 parameters	Δρ _{min} = -0.53 e Å ⁻³

Table 1

Selected bond lengths (Å).

Nb1—O3	1.756 (2)	Mn1—O2	2.137 (3)
Nb1—F2	1.885 (3)	Mn1—O1	2.149 (2)
Nb1—F1	1.892 (2)	Mn1—N4	2.245 (3)
Nb1—F4	1.927 (3)	Mn1—N1	2.254 (3)
Nb1—F3	1.964 (2)	Mn1—N2	2.281 (3)
Nb1—F5	2.0516 (19)	Mn1—N3	2.286 (3)

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—H1C...F3 ⁱ	0.85 (3)	1.81 (3)	2.660 (3)	176 (4)
O1—H1D...O3 ⁱⁱ	0.83 (3)	1.83 (3)	2.649 (3)	175 (5)
O2—H2C...F5 ⁱⁱⁱ	0.84 (2)	1.72 (2)	2.552 (3)	172 (3)
O2—H2D...F4 ⁱ	0.82 (3)	2.31 (4)	2.947 (4)	135 (4)
O2—H2D...F5 ⁱ	0.82 (3)	2.25 (3)	3.028 (3)	157 (5)
C1—H1A...F1 ⁱⁱⁱ	0.93	2.48	3.064 (4)	121
C3—H3...F1 ^{iv}	0.93	2.46	3.283 (6)	147
C5—H5...O1 ^v	0.93	2.59	3.330 (6)	137
C17—H17...F4 ^{vi}	0.93	2.43	3.278 (6)	152
C18—H18...F5 ^{vii}	0.93	2.44	3.344 (6)	166

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

Table 3
Bond-valence parameters.

	S_i	$V-S_i$
Nb1–O3	1.52	0.48
Nb1–F2	0.84	0.16
Nb1–F1	0.83	0.17
Nb1–F4	0.75	0.25
Nb1–F3	0.68	0.32
Nb1–F5	0.54	0.46

Water H atoms were located in a different Fourier map and refined with a restrained O–H bond length of 0.85 (2) Å and 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: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 2002); software used to prepare material for publication: *SHELXTL*.

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