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Short Communication

Crystal Structure of Ammonium Diaquadioxalatooxoniobate(V) Dihydrate, $NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_2$

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In a number of articles Raman spectroscopy studies of oxoniobate complexes in alkaline and acidic oxalate solutions,[1] as well as in the solid state,[2,3] have been discussed. One of the compounds studied was $NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_2$. This compound has been reported to be isostructural[4] with the corresponding cesium compound,[5] but no single-crystal study has been made. Among the reported coordination compounds between Nb and oxalate studied by single-crystal diffraction techniques, there are cases where Nb is coordinated by two oxalate groups[5–8] or three oxalate groups.[9] All of these compounds are either oxooxalates or peroxooxalates. In order to provide accurate structure data for comparison with Raman studies, a single-crystal X-ray diffraction study of the title compound was made.

Experimental

Ammonium diaquadioxalatooxoniobate(V) dihydrate was provided by Prof. Israel Wachs, Leigh University, Bethlehem, PA, USA. Its X-ray powder diffraction pattern was recorded with a focusing Guinier–Hägg camera, using Si ($a = 5.43059$ Å)[10] as internal standard. The photograph was measured with an automatic single-beam densitometer[11] and was indexed by the program TREOR.[12] All lines were indexed with a high figure of merit [$M(20) = 38$], indicating a single-phase sample. The resulting cell was $a = 6.3804(9)$, $b = 11.7582(12)$, $c = 7.9296(8)$ Å and $\beta = 98.233(13)°$, which is in good agreement with previously reported values.[4] Thermogravimetrical decomposition to Nb_2O_5 in oxygen gave a weight loss of 66.0%, in agreement with the expected value (64.5%). Systematic absences $0k0: k = 2n+1$ indicated space groups $P2_1$ or $P2_1/m$. Information on the data collection is given in Table 1. Three standard reflections measured every 120 min during data collection showed no sign of crystal deterioration. The data were corrected for Lorenz and polarization effects and also for absorption using numerical integration. The scattering factors for C, H, N and O were those included in SHELX,[13] and the scattering factor function for Nb was taken from Ref. 14. The structure of $Cs[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_2$ (Ref. 5) was used as a starting model for the full-matrix least-squares refinement with SHELX. A conventional R-value of 0.057 was reached with isotropic displacement parameters. After a few cycles of refinement with anisotropic displacement parameters, the hydrogens could be located from difference Fourier maps, using low-angle 2θ-reflections. All hydrogens in the water molecules were restrained to the refined average distance to the water oxygen, within a simulated standard deviation of 0.05 Å, and all hydrogens in the ammonium group were restrained to an average distance to the nitrogen atom, within an 0.05 Å standard deviation. All non-hydrogen atoms were refined with anisotropic displacement factors, and the hydrogens were refined with isotropic displacement factors. The largest shift in any of the 122 refined parameters was 0.006σ in the last cycle. The weighting scheme used was $1/\sigma^2(|F|) + 0.0001\,|F|^2)$. Crystal data for $NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_2$ are given in Table 1, positional parameters and displacement parameters in Table 2, bond lengths in Table 3 and bond angles in Table 4. A perspective ORTEP plot[15] of the structure is shown in Fig. 1.

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Table 1. Crystal data and data collection parameters.

Formula	$NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$
Diffractometer	Siemens STOE/AED2
Radiation	Mo $K\alpha$ ($\lambda = 0.7107$ Å)
Space group and cell content	$P2_1/m$, $Z = 2$
a/Å	6.331(3)
b/Å	11.754(6)
c/Å	7.900(4)
β/°	99.26(2)
V/Å^3	580.2(9)
D_x/g cm^{-3}	2.147(3)
Crystal dimensions/mm	0.12, 0.18, 0.12
μ(Mo K_α)/cm^{-1}	9.8
Range of data /°, method	$2 \leqslant 2\theta \leqslant 70$, $\omega/2\theta$-scan
Scan speed /° s^{-1}	0.01–0.03
Basic scan width /°	1.2
Temperature of data collection/K	153
Measured reflections	2642
Unique observed reflections ($I \geqslant 1.5\sigma I$)	2280
Transmission factors	0.77–0.82
No. of parameters	122
$R = \Sigma \mid \lvert F_o \rvert - \lvert F_c \rvert \mid m / \Sigma \lvert F_o \rvert$	0.033
$R_w = [\Sigma\, w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma\, w \lvert F_o \rvert^2]^{1/2}$	0.044

Discussion

$NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_2$ is isostructural with the compound $Cs[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_2$. Most of the interatomic distances are the same for both compounds within a few hundredths of an ångström, except those involving the cesium atom and the ammonium group. Since the structure of $Cs[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_2$ has been described in detail by Kojić-Prodić *et al.*,[5] we will only give a schematic description here. The discussion will be concentrated on the differences between the two compounds. The Nb atom is coordinated to two bidentate oxalate groups, two water molecules and one oxygen atom, forming a pentagonal bipyramid. The distance between the latter oxygen atom and the niobium atom is only 1.704(3) Å, indicating a double bond, while the distance to the

Table 2. Positional parameters, equivalent isotropic displacement factors for all non-hydrogen atoms and isotropic displacement factor for hydrogen atoms, with estimated standard deviations.

Atom	X	Y	Z	$U_{eq}{}^a/U_{iso}$
Nb	0.37928(5)	0.75	0.22684(4)	0.0083(1)
OW1	0.4336(4)	0.75	−0.0365(3)	0.0144(6)
OW2	0.0254(4)	0.75	0.0931(4)	0.0162(7)
O	0.6436(4)	0.75	0.3131(3)	0.0144(6)
O1	0.2707(3)	0.8531(1)	0.4151(2)	0.0122(4)
O2	0.3544(3)	0.1045(2)	0.2022(2)	0.0169(5)
O3	0.3709(3)	0.9197(1)	0.1331(2)	0.0117(4)
O4	0.2389(3)	0.0314(2)	0.5105(2)	0.0144(4)
OW3	0.8859(3)	0.9626(2)	0.1686(2)	0.0197(5)
C1	0.2761(3)	0.9625(2)	0.4028(3)	0.0102(5)
C2	0.3392(3)	0.0031(2)	0.2337(3)	0.0112(5)
N	0.9530(5)	0.75	0.6355(4)	0.0178(8)
H1	0.492(6)	0.697(3)	−0.070(5)	0.030(10)
H2	−0.047(6)	0.705(3)	0.107(5)	0.043(13)
H3	0.835(6)	0.964(4)	0.260(4)	0.029(10)
H4	0.810(6)	0.998(4)	0.109(5)	0.042(13)
H5	0.065(7)	0.75	0.589(7)	0.028(14)
H6	0.992(10)	0.75	0.750(6)	0.048(19)
H7	0.867(6)	0.808(3)	0.611(5)	0.046(13)

[a] ($U_{eq} = \frac{1}{3}\Sigma U_{ii}$).

Table 3. Interatomic distances (in Å) with estimated standard deviations in parentheses.

Nb polyhedron:		Oxalate group:	
Nb–O	1.704(3)	C1–O1	1.290(3)
Nb–2O1	2.117(2)	C1–O4	1.225(3)
Nb–2O3	2.125(2)	C2–O2	1.225(3)
Nb–OW1	2.162(3)	C2–O3	1.298(3)
Nb–OW2	2.318(3)	C1–C2	1.531(3)
O1–O3	2.536(3)	O2–O3	2.246(3)
O1–O1′	2.424(3)	O1–O4	2.247(3)
O3–OW1	2.470(2)		
Ammonium group:		**Water molecules:**	
N–O	2.953(5)	OW1–2O3	2.470(2)
N–2O4	2.993(3)	OW1–2O2	2.647(3)
N–2O2	3.026(4)	OW2–2OW3	2.748(3)
N–2O1	3.111(4)	O4–OW3	2.775(3)
N–OW2	3.570(5)		
Interatomic distances to hydrogen atoms:			
OW1–2H1	0.79(3)	O3–H1	2.33(4)
OW2–2H2	0.72(4)	O1–H5	2.37(4)
OW3–H4	0.75(4)	OW2–H6	2.69(5)
OW3–H3	0.83(4)	O–2H2	2.79(4)
N–H5	0.85(5)	H1–H1	1.24(7)
N–2H7	0.88(4)	H2–H2	1.05(8)
N–H6	0.90(5)	H3–H4	1.24(6)
O2–H1	1.88(4)	H5–H6	1.42(7)
O4–H3	1.95(4)	H5–2H7	1.47(6)
OW3–H2	2.09(4)	H6–2H7	1.42(6)
O4–2H7	2.17(4)	H7–H7	1.37(8)

Table 4. Bond angles (in °) with estimated standard deviation in parentheses.

OW2–Nb–OW1	81.5(1)	O3–Nb–O	96.2(1)
O–Nb–OW1	95.0(1)	O3–Nb–O1	73.4(1)
O–Nb–OW2	176.5(1)	O4–C1–O1	126.6(2)
O1–Nb–OW1	142.7(1)	C2–C1–O1	113.0(2)
O1–Nb–OW2	85.5(1)	C2–C1–O4	120.4(2)
O1–Nb–O	97.4(1)	C1–C2–O2	121.4(2)
O3–Nb–OW1	70.3(1)	C1–C2–O3	112.7(2)
O3–Nb–OW2	82.7(1)		

opposite water oxygen (OW2) is very long: 2.318(3) Å. These values are very close to those found in the Cs analogue: 1.691 and 2.328 Å, respectively. The remaining Nb–O distances are between 2.117(2) and 2.162(3) Å, which is the same range as in the Cs compound, within 0.01 Å. The ammonium group is surrounded by seven oxygen atoms in a irregular arrangement. Six of them belong to the oxalate group and one to the niobyl group. The hydrogen atoms in the ammonium group are oriented towards 2 × O1, OW2 and O4, but the rather long N–O distances indicate only very weak hydrogen bonding. This view is also supported by a relatively long average N–O interatomic distance, 3.030 Å, which is longer than found in $NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ (2.952 Å),[6] where the existence of hydrogen bonds has been confirmed by neutron diffraction. The short average N–O distances in $(NH_4)_3NbO(C_2O_4)_3\cdot H_2O$ (2.996, 2.917 and 2.979 Å)[9] and $(NH_4)_3Nb(O_2)_2(C_2O_4)_2\cdot H_2O$ (2.947, 2.997 and 3.000 Å)[7] also indicate hydrogen bonds. The N–O distance here is significantly shorter than the corresponding distance in the Cs compound, 3.190 Å. It is noteworthy that the cavity around NH_4^+ is slightly different from the cavity around Cs^+. The shortest distance within the N–O polyhedron [2.955(5) Å] in the ammonium compound corresponds to the longest in the Cs–O polyhedron (3.210 Å) in the Cs analogue. This can be expected from a comparison of the ionic radii of NH_4^+ and Cs^+, 1.46 and 1.67 Å,[16] respectively. The cavity needed for the ammonium ion is thus significantly smaller than that required by the cesium ion. The size difference fully explains the 22.5 Å^3 difference in unit-cell volume between the two compounds. The niobyl bond distance of 1.704(3) Å here reported fits well with that obtained from Raman spectroscopy. According to the formula $\nu(\mathrm{cm}^{-1}) = 25922\exp(-1.9168\,R)$ (R = bond length),[3] the measured wavenumber, 960 cm^{-1},[2] corresponds to $R = 1.72$ Å, in good agreement with the observed distance. A list of observed and calculated structure-factor amplitudes and anisotropic displacement parameters may be requested from one of the authors (L. Eriksson).

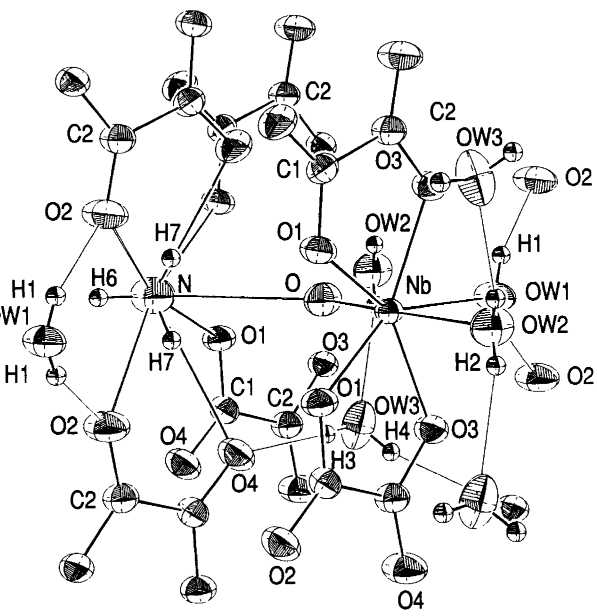

Fig. 1. Perspective view of the structure.

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