

The Crystal Structure of Caesium Oxobisoxalatobisaquoniobate(V) Dihydrate, Cs[NbO(C₂O₄)₂(H₂O)₂].2H₂O

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The structure of Cs[NbO(C₂O₄)₂(H₂O)₂].2H₂O has been determined from three-dimensional X-ray diffractometer data. The crystals are monoclinic with $a = 6.464(1)$, $b = 11.8697(9)$, $c = 7.9518(3)$ Å, $\beta = 98.911(3)^\circ$; the space group is $P2_1/m$. The coordination polyhedron around niobium is a pentagonal bipyramid. The ligands in the equatorial plane are two oxygen atoms from an oxalato group and their mirror-plane related pairs at distances of 2.104 and 2.124 Å, and one water molecule at 2.169 Å. The apices of the bipyramid are occupied by the double-bonded oxygen atom and one water molecule at 1.691 and 2.328 Å, respectively.

Introduction

Only one crystal structure determination of a niobium trisoxalato complex has been reported (Mathern & Weiss, 1971). The present structure determination is part of a structural investigation of niobium bisoxalato complexes (Galešić, Matković, Herceg & Šljukić, 1971) prepared recently (Brničević & Đorđević, 1971).

Experimental

The colourless crystals of Cs[NbO(C₂O₄)₂(H₂O)₂].2H₂O belong to the monoclinic holohedral class (Fig. 1) with:

$$a = 6.464(1)\text{Å}, b = 11.8697(9)\text{Å}, c = 7.9518(3)\text{Å},$$

$$\beta = 98.911(3)^\circ$$

$$V = 602.7\text{Å}^3$$

$$D_m = 2.66, D_c = 2.61\text{ g cm}^{-3}$$

$$Z = 2$$

Mo $K\alpha$ radiation, $\mu = 40.70\text{ cm}^{-1}$.

The space group was determined from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The diffraction symmetry and systematic absences indicated $P2_1$ or $P2_1/m$ as possible space groups. The structure was later refined successfully in $P2_1/m$.

The unit-cell dimensions were determined from a powder photograph recorded in a Guinier-Hägg XDC-700 focusing camera with Cr $K\alpha_1$ radiation ($\lambda = 2.28962$ Å), with silicon ($a = 5.43054$ Å at 25°C) as an internal standard. A least-squares treatment of the observed θ -values of 27 reflexions provided the final parameters. The density was measured at 25°C pycnometrically with decalin as the medium.

The intensity data were collected on a Stoe-Philips computer controlled four-circle diffractometer with a graphite monochromator using Mo $K\alpha$ radiation and the ω - 2θ scan. Different combinations of scan time and filter selection were used to measure all the reflexions with about the same precision. Three standard reflexions, measured at regular intervals to provide a check on crystal and instrumental stability, showed a slow decrease in intensity indicating radiation damage. A correction was applied to all the intensities based on the decrease of the standards; the maximum correction

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† Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

Table 1. Final coordinates and anisotropic thermal parameters ($\times 10^5$)

The thermal parameters refer to the expression: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	2091 (7)	25000	34356 (5)	1862 (13)	386 (4)	1083 (8)	0	552 (7)	0
Nb	38897 (7)	75000	22917 (5)	1108 (12)	173 (3)	494 (7)	0	269 (6)	0
O $W(1)$	55690 (70)	25000	3335 (52)	2121 (109)	250 (24)	723 (54)	0	797 (62)	0
O $W(2)$	96138 (68)	25000	89562 (59)	1323 (90)	513 (34)	1056 (69)	0	243 (63)	0
O	35371 (70)	25000	68806 (61)	1510 (92)	327 (27)	1110 (68)	0	35 (64)	0
O(1)	71595 (46)	14737 (23)	58552 (34)	1775 (65)	202 (15)	700 (37)	-34 (25)	523 (40)	16 (19)
O(2)	35640 (59)	9913 (26)	19838 (43)	2584 (86)	223 (17)	1088 (47)	11 (31)	897 (52)	44 (24)
O(3)	62129 (46)	8241 (23)	86556 (34)	1752 (64)	230 (16)	632 (35)	58 (26)	467 (38)	-16 (19)
O(4)	24421 (52)	2719 (25)	50731 (37)	2187 (75)	263 (18)	739 (39)	11 (30)	535 (46)	-93 (22)
O $W(3)$	11527 (53)	3776 (36)	82920 (43)	1723 (74)	701 (31)	1008 (50)	166 (38)	330 (48)	49 (31)
C(1)	71582 (56)	3863 (31)	59743 (43)	1237 (71)	239 (20)	569 (44)	-26 (30)	216 (45)	4 (24)
C(2)	34604 (59)	-7 (31)	23314 (45)	1360 (70)	222 (20)	660 (46)	-17 (31)	332 (46)	-7 (26)

was about 7%. 2411 independent reflexions with $\sin \theta/\lambda$ less than 0.7717 \AA^{-1} were recorded.

The intensities were corrected for Lorentz, polarization and absorption effects. The crystal was described by 11 planes and had a volume of 0.0142 mm^3 . The transmission factors were in the range 0.284 to 0.761.

Structure determination

The systematic absences indicated the space groups $P2_1$ or $P2_1/m$, but the Patterson map could only be interpreted in terms of $P2_1/m$. Since there are only two molecules of $\text{Cs}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ in the unit

Table 2. Observed and calculated structure factors

The columns are in the order $k, l, 10|F_o|$ and $10|F_c|$. Reflexions less than $3\sigma(F_o)$ are omitted.

k	l	$10 F_o $	$10 F_c $
0	0	1000	1000
0	1	1000	1000
0	2	1000	1000
0	3	1000	1000
0	4	1000	1000
0	5	1000	1000
0	6	1000	1000
0	7	1000	1000
0	8	1000	1000
0	9	1000	1000
0	10	1000	1000
0	11	1000	1000
0	12	1000	1000
0	13	1000	1000
0	14	1000	1000
0	15	1000	1000
0	16	1000	1000
0	17	1000	1000
0	18	1000	1000
0	19	1000	1000
0	20	1000	1000
0	21	1000	1000
0	22	1000	1000
0	23	1000	1000
0	24	1000	1000
0	25	1000	1000
0	26	1000	1000
0	27	1000	1000
0	28	1000	1000
0	29	1000	1000
0	30	1000	1000
0	31	1000	1000
0	32	1000	1000
0	33	1000	1000
0	34	1000	1000
0	35	1000	1000
0	36	1000	1000
0	37	1000	1000
0	38	1000	1000
0	39	1000	1000
0	40	1000	1000
0	41	1000	1000
0	42	1000	1000
0	43	1000	1000
0	44	1000	1000
0	45	1000	1000
0	46	1000	1000
0	47	1000	1000
0	48	1000	1000
0	49	1000	1000
0	50	1000	1000
0	51	1000	1000
0	52	1000	1000
0	53	1000	1000
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0	59	1000	1000
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0	62	1000	1000
0	63	1000	1000
0	64	1000	1000
0	65	1000	1000
0	66	1000	1000
0	67	1000	1000
0	68	1000	1000
0	69	1000	1000
0	70	1000	1000
0	71	1000	1000
0	72	1000	1000
0	73	1000	1000
0	74	1000	1000
0	75	1000	1000
0	76	1000	1000
0	77	1000	1000
0	78	1000	1000
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0	81	1000	1000
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0	83	1000	1000
0	84	1000	1000
0	85	1000	1000
0	86	1000	1000
0	87	1000	1000
0	88	1000	1000
0	89	1000	1000
0	90	1000	1000
0	91	1000	1000
0	92	1000	1000
0	93	1000	1000
0	94	1000	1000
0	95	1000	1000
0	96	1000	1000
0	97	1000	1000
0	98	1000	1000
0	99	1000	1000
0	100	1000	1000
1	0	1000	1000
1	1	1000	1000
1	2	1000	1000
1	3	1000	1000
1	4	1000	1000
1	5	1000	1000
1	6	1000	1000
1	7	1000	1000
1	8	1000	1000
1	9	1000	1000
1	10	1000	1000
1	11	1000	1000
1	12	1000	1000
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1	39	1000	1000
1	40	1000	1000
1	41	1000	1000
1	42	1000	1000
1	43	1000	1000
1	44	1000	1000
1	45	1000	1000
1	46	1000	1000
1	47	1000	1000
1	48	1000	1000
1	49	1000	1000
1	50	1000	1000
1	51	1000	1000
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1	57	1000	1000
1	58	1000	1000
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1	60	1000	1000
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1	64	1000	1000
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1	66	1000	1000
1	67	1000	1000
1	68	1000	1000
1	69	1000	1000
1	70	1000	1000
1	71	1000	1000
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1	73	1000	1000
1	74	1000	1000
1	75	1000	1000
1	76	1000	1000
1	77	1000	1000
1	78	1000	1000
1	79	1000	1000
1	80	1000	1000
1	81	1000	1000
1	82	1000	1000
1	83	1000	1000
1	84	1000	1000
1	85	1000	1000
1	86	1000	1000
1	87	1000	1000
1	88	1000	1000
1	89	1000	1000
1	90	1000	1000
1	91	1000	1000
1	92	1000	1000
1	93	1000	1000
1	94	1000	1000
1	95	1000	1000
1	96	1000	1000
1	97	1000	1000
1	98	1000	1000
1	99	1000	1000
1	100	1000	1000

cell, the caesium and niobium atoms and the oxo atom were assumed to occupy twofold special positions. From a three-dimensional Patterson map the x and z coordinates of the caesium and niobium atoms situated in the mirror plane [position 2(e)] were established. In addition to the caesium, niobium and double-bonded oxygen atoms, the oxygen atoms of the two coordinated water molecules $OW(1)$ and $OW(2)$, were also found to occupy special positions in the mirror plane. The remaining atoms, those of the oxalato group and the non-coordinated water molecule, occupy general four-fold positions.

Refinement

The structure was refined by minimizing the function $\sum w(|F_o| - |F_c|)^2$ using the full matrix least-squares pro-

gram *LINUS*. Each reflexion was assigned a weight inversely proportional to the estimated variance of the observation $w = 1/\sigma^2(F)$ where $\sigma^2(F) = \sigma_{\text{count}}^2(F^2)/4F^2 + k \cdot F^2$. The first term is based on counting statistics and the second is an empirical correction term to take account of other errors in the data. The constant k was chosen to be 0.0004. The refinement was based on 2165 reflexions with intensities greater than $3\sigma_{\text{count}}$. The parameters refined consisted of 31 positional and 62 anisotropic thermal parameters, one overall scale factor and one extinction parameter.

The atomic scattering factors used for Cs^+ , Nb, O and C were those calculated by Hanson, Herman, Lea & Skillman (1964). The scattering factors of Cs^+ and Nb were corrected for anomalous dispersion according to Cromer (1965). The final agreement values were

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.046$$

and

$$R_w = \left| \frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2} \right|^{1/2} = 0.080.$$

The standard deviation of an observation of unit weight $\sigma_1 = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ was 2.24, where m is the total number of observations and n the number of varied parameters.

The atomic positional and thermal parameters obtained from the refinement are listed in Table 1 and observed and calculated structure factors in Table 2.

The observed F values were corrected for extinction using the expression:

$$|F_o|_{\text{corr}} = |F_o| \left(1 + \frac{T p |F_c|^2 g \lambda^3}{12.593 V^2 \sin 2\theta} \right)^{1/4}$$

where λ is in Å, V is the unit cell volume in Å³ and $p = 2(1 + \cos^4 2\theta) / (1 + \cos^2 2\theta)$, [which is strictly valid only for unpolarized X-rays (Coppens & Hamilton, 1970)]. The mean path length through the crystal, T , for

Table 3. *Interatomic distances and angles*

(a) Distances

Within the Nb polyhedron

Nb—O(1)	2.104 (3) Å
Nb—O(3)	2.124 (3)
Nb—O $W(1)$	2.169 (4)
Nb—O $W(2)$	2.328 (4)
Nb—O	1.691 (5)
O(1)—O(1')	2.436 (4)
O(1)—O(3)	2.520 (4)
O(3)—O $W(1)$	2.466 (4)

Within the oxalato group

C(1)—O(1)	1.294 (5)
C(1)—O(4)	1.199 (5)
C(2)—O(3)	1.291 (5)
C(2)—O(2)	1.214 (5)
C(1)—C(2)	1.533 (5)

Caesium—oxygen distances ≤ 3.210 Å

Cs—O	3.210 (5)
Cs—O(1)	3.201 (3)
Cs—O(2)	3.165 (4)
Cs—O(4)	3.192 (3)

Hydrogen bonds O—H...O

O $W(1)$ H...O(2)	2.671 (6)
O $W(2)$ H...O $W(3)$	2.789 (5)
O $W(3)$ H...O(4)	2.815 (6)

(b) Angles

Within the Nb polyhedron

O—Nb—O $W(2)$	177.70 (20)°
O(1)—Nb—O(3)	73.17 (10)
O(1)—Nb—O(1')	70.78 (15)
O(3)—Nb—O $W(1)$	70.10 (07)
O(1')—O(1)—O(3)	107.82 (09)
O(1)—O(3)—O $W(1)$	108.40 (14)
O(3)—O $W(1)$ —O(3')	107.53 (20)

Within the oxalato group

O(1)—C(1)—O(4)	126.61 (34)
O(3)—C(2)—O(2)	125.17 (44)
O(4)—C(1)—C(2)	121.97 (34)
O(2)—C(2)—C(1)	121.38 (42)

Hydrogen bonded atoms

O(2)—O $W(1)$ —O(2')	84.19 (22)
O $W(3)$ —O $W(2)$ —O $W(3')$	129.19 (22)
O $W(2)$ —O $W(3)$ —O(4)	112.15 (22)

Atoms marked O(1') and O(3') are related by the mirror plane operation to O(1) and O(3).

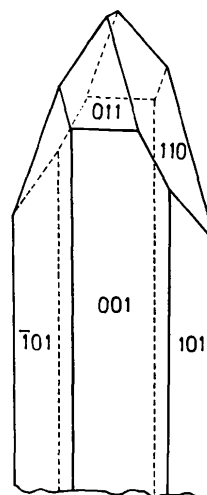


Fig. 1. Crystal habit of $\text{Cs}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.

a particular reflexion was appropriately corrected for absorption. The refined value of the isotropic extinction parameter is $g = 2017(422)$. This corresponds to a mosaic spread of approximately 28 sec or a domain size of $0.14 \mu\text{m}$, depending upon whether a Zachariasen (1967) type I or II description is assumed. The extinction correction factors as given above were in the range 0.82 to 1.00.

The calculations were carried out on the IBM 1800 and CDC 3600 computers in Uppsala using programs briefly described by Jönsson & Liminga (1971).

Description and discussion of the structure

The niobium atom is coordinated by two oxygen atoms, O(1) and O(3) from one oxalato group and their pairs related by a mirror plane [O(1') and O(3')], and by one water molecule OW(1), all situated at the corners of a nearly regular pentagon. The apices of the bipyramid are occupied by one oxo atom, O, and one water oxygen, OW(2). The coordination polyhedron around niobium is thus a pentagonal bipyramid (approximate D_{5h} symmetry, Fig. 2).

The crystal structure is a three dimensional network of pentagonal bipyramids connected by hydrogen bonds O-H...O, and also by means of Coulomb interactions between caesium ions and oxygen atoms.

Coordination around the niobium atom

The niobium–oxygen distances from the oxalato group of $2.104(3) \text{ \AA}$ and $2.124(2) \text{ \AA}$ are not significantly different from the values reported earlier, *e.g.* 2.114 to 2.157 \AA in $(\text{NH}_4)_3[\text{NbO}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$ (Mathern & Weiss, 1971) and 2.07 \AA to 2.12 \AA in $\text{NH}_4[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (Galešić, Matković, Herceg & Šljukić, 1971). Although the Nb–OW(1) distance of 2.169 \AA is somewhat longer than the corresponding niobium–oxygen distances from the oxalato group, these differences in the niobium–oxygen distances have a small influence on the regularity of the pentagonal plane. The mean

value of the O(1')–O(1)–O(3), O(1)–O(3)–OW(1) and O(3)–OW(1)–O(3') angles is 107.9° , which is almost equal to the value of 108° for a regular pentagon (Fig. 3).

Within the limits of experimental uncertainty all five equatorial oxygen atoms O(1), O(1'), O(3), O(3') and OW(1) lie in a plane [Table 4(a)] as determined by the least-squares method (Blow, 1960).

Table 4. Distances from the least-square planes

(a) Pentagonal plane	
O(1)	–0.004 (3) Å
O(1')	–0.004 (3)
O(3)	0.010 (3)
O(3')	0.010 (3)
OW(1)	–0.028 (4)
Nb	0.245
(b) Oxalato group	
O(4)	0.009 (3) Å
C(1)	0.011 (4)
O(1)	–0.002 (4)
O(2)	–0.011 (4)
C(2)	–0.015 (3)
O(3)	0.008 (3)

The niobium atom is displaced by 0.245 \AA from the equatorial plane in the direction of the apical oxo atom. The distances of the apical atoms from the equatorial plane are almost the same. Similar shifts of the niobium atom from the equatorial plane have been previously observed, *e.g.* in $(\text{NH}_4)_3[\text{NbO}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$, -0.18 \AA (Mathern & Weiss, 1971), in $\text{NH}_4[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, -0.21 \AA (Galešić, Matković, Herceg & Šljukić, 1971), in NbOPO_4 mentioned only qualitatively (Longo & Kierkegaard, 1966), and also in some other compounds such as $\text{K}_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4]$, -0.35 \AA (Stomberg, 1970). The length of the bond from niobium to the oxo atom of 1.691 \AA indicates its double-bond character and can be compared with the values 1.68 \AA in $[\text{NbOF}_5]^{2-}$ (Pinsker, 1966) and 1.710 \AA in $[\text{NbO}(\text{C}_2\text{O}_4)_3]^{3-}$ (Mathern & Weiss, 1971). The presence of such a niobium–oxy-

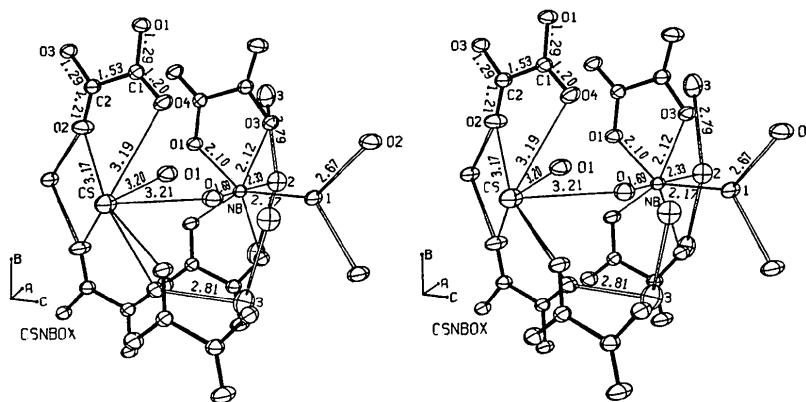


Fig. 2. Stereo pair showing the pentagonal bipyramid around niobium as well as the caesium environment in the $\text{Cs}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ structure. Water molecules OW(1), OW(2) and OW(3) are denoted by the numbers 1, 2, 3. All contacts less than 3.21 \AA are included. The ellipsoids are scaled to enclose 50% probability.

gen bond is in agreement with an IR stretching band at 952 cm^{-1} (Brničević & Đorđević, 1971) assigned as niobyl group stretching. The second apex of the bipyramid is occupied by the water oxygen, OW(2) at a distance of 2.328 Å from niobium.

In the paper by Brničević & Đorđević (1971), the following formula was suggested: $\text{CsH}[\text{NbO}(\text{OH})(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$, and according to this formulation an OH group would be expected in the coordination polyhedron. But in the vicinity of the oxygen atom located at the apex of the bipyramid, two symmetrical contacts of 2.789 Å to the crystalline water OW(3) are found, which can be attributed to $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds between coordinated water molecules and crystalline water molecules. The water molecule, OW(1) situated in the equatorial position is hydrogen bonded to the uncoordinated oxalato oxygens O(2) and

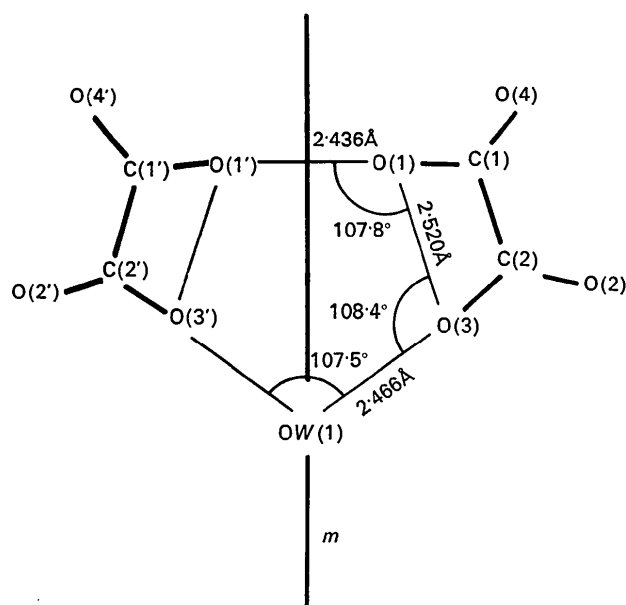


Fig. 3. The ligands in the equatorial plane of the bipyramid disposed at the corners of a pentagon.

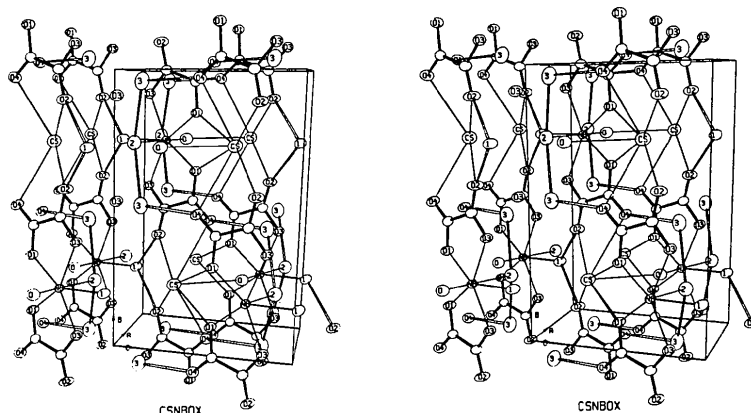


Fig. 4. Stereo pair, drawn by the program ORTEP, showing the structure of $\text{Cs}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$. All contacts less than 3.21 Å are included.

O(2') at two equal distances of 2.671 Å . The crystalline water OW(3) is hydrogen bonded to the uncoordinated oxalato oxygen O(4) at distance of 2.815 Å .

The n.m.r. spectra of caesium oxobisoxalatobisaquoniobate(V) dihydrate at room-temperature and also at -110°C were recorded by Dr J. Herak, Institute 'Ruder Bošković', and from them the presence of four water molecules (two coordinated + two crystalline) was established. The neutron diffraction study (Matković & Galešić, to be published) of some oxobisoxalatobisaquoniobate(V) salts with the same seven coordinated niobium anion described in the present paper also confirms the existence of two coordinated water molecules. The correct formulation of the present compound is thus $\text{Cs}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.

Oxalato group

The oxalato group is asymmetrical; the C(1)-O(1) and C(2)-O(3) distances are $1.294(5)\text{ Å}$ and $1.291(5)\text{ Å}$, respectively. They are significantly longer than the C(1)-O(4) bond of $1.199(5)\text{ Å}$ and the C(2)-O(2) of $1.214(5)\text{ Å}$. The C(1)-O(4) and C(2)-O(2) distances are characteristic of carbon-oxygen double bonds.

The lengthening of the C(1)-O(1) and C(2)-O(3) bonds are due to the coordination to the metal atom. These bond lengths are in agreement with the values found in some other coordinated oxalato complexes, e. g. in $(\text{NH}_4)_3[\text{NbO}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$, (Mathern & Weiss, 1971) and $\text{K}_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4]$, (Stomberg, 1970). The C(1)-C(2) bond of length $1.533(5)\text{ Å}$ can be compared with that in ethane (1.536 Å). The oxalate ion is planar within the limits of the experimental error [Table 4(b)].

Caesium environment

The neighbourhood around caesium is composed of seven oxygen atoms O(2) and O(2') at 3.165 Å , O(4) and O(4') at 3.192 Å , O(1) and O(1') at 3.201 Å and the oxo atom at 3.210 Å in an arrangement which cannot be described by any polyhedron. The caesium atom, as a large positive cation, merely serves to join the niobium polyhedra together (Fig. 4). The pentagonal bi-

pyramids are also connected by hydrogen bonds between the oxalato oxygen atoms and equatorial water, and between the crystalline and apical coordinated water molecules.

Available data about hepta-coordination are rather limited and it is not reasonable to draw any general conclusion upon this subject at this time. The seven-coordinated geometry was discussed by Muetterties & Wright (1967), based on the three idealized polyhedra: pentagonal bipyramid- D_{5h} , capped trigonal prism- C_{2v} and capped octahedron- C_{3v} . (A fourth type of geometry, the tetragonal base-trigonal base- C_s has also been mentioned.)

Other authors have tried to evaluate relative stabilities of the idealized seven-coordinated polyhedra (Duffey, 1950; Gillespie, 1960; Britton, 1963; Claxton & Benson, 1966) but these results are not applicable to seven-coordinated species with different ligands.

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The Crystal Structure of $HgMoO_4$ and Related Compounds

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Mercuric molybdate crystallizes in the monoclinic system, space group $C2/c$ with $a = 11.282$ (2), $b = 6.055$ (1), $c = 5.154$ (1) Å, $\beta = 112.27$ (1)°, and $Z = 4$. The structure was determined from single-crystal counter data by Patterson and Fourier methods. A full-matrix least-squares refinement with anisotropic thermal parameters resulted in a conventional R value of 0.023 for 849 reflections (unobserved included). The Hg atom is coordinated by two oxygen atoms forming a linear O-Hg-O arrangement with oxygen-mercury distances of 2.03 Å. Four more oxygens are further away at 2.67 ($2 \times$) and 2.77 ($2 \times$) Å, completing an approximately octahedral grouping. The oxygen environment of Mo is essentially octahedral with Mo-O distances between 1.72 and 2.23 Å indicating bond orders from two to one respectively. A qualitative description of bonding in the $HgMoO_4$ structure is given. Mercuric tungstate, $HgWO_4$ has the same structure with $a = 11.375$ (2), $b = 6.007$ (1), $c = 5.145$ (1) Å, $\beta = 113.20$ (1)°. The structure of $HgMoO_4$ and $HgWO_4$ is closely related to the structure of $CdWO_4$ (Ni WO_4 -type). Results for solid solutions such as $CdWO_4$ - $HgWO_4$ prepared at 65 kbar are reported.

Introduction

$HgMoO_4$ and $HgWO_4$ have been reported by Swindell (1951), Gupta & Saxena (1958), and Saxena & Gupta (1959), who prepared these substances by precipitation from aqueous solutions. Large (mm size) crystals can be

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grown by reaction of $HgCl_2$ with $Na_2MoO_4 \cdot 2H_2O$ or $Na_2WO_4 \cdot 2H_2O$ respectively at 700°C in collapsible gold tubes under 3 kbar pressure. They have been characterized as monoclinic, space group $C2/c$ or Cc , with the lattice constants given in Table 1 (Sleight & Licis, 1971). Preliminary results of a structure determination of $HgMoO_4$ were also reported (Jeitschko & Sleight, 1972). This paper gives a full account of the crystal

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