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Note

The Crystallographic Data of Potassium-, Ammonium-, and Rubidium-Oxo-bis-Oxalato-bis-Aquo-Niobates(V) Di- and Trihydrates

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The crystallographic data for $K[NbO(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$, $NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$, and $Rb[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ has been obtained by X-ray diffraction methods. On the basis of similar values of unit cell parameters and the same space group extinctions, an isostructural relationship has been found among dihydrates of Cs-salt (with known crystal structure from previous work[2]) and NH_4- and Rb-salts, as well as between trihydrates of NH_4-salt (with crystal structure[3] solved previously too) and K-salt.

INTRODUCTION

A series of oxo-bis-oxalato-bis-aquo-niobates (V) di- and trihydrates has been recently prepared and characterized by chemical analysis, conductivity measurements and infrared absorption spectra[1]. The crystal structure of $Cs[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ has been determined by X-ray diffraction analysis[2]. The crystal structure of $NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ has been solved by X-ray diffraction methods[3], and the location of the hydrogen atoms by neutron diffraction is in due course. In this paper the investigation of the structural data is extended to three more compounds, $NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$, $Rb[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$, and $K[NbO(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$.

EXPERIMENTAL

The rough estimates of unit cell parameters were done previously using oscillation and Weissenberg photographs taken with CuKα radiation (in the already published paper[3] the parameters of $NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ were obtained only by this method). The precise values were then deduced from zero-layer rotation patterns of single crystals taken in asymmetric (Straumanis) position and indexed by means of corresponding Weissenberg patterns. The rotation patterns were obtained in a precise Debye-Scherrer camera (diameter 114.6 mm) fitted with a goniometer head. The asymmetric position of the films provided determination of the effective film radius, including the shrinkage effect. The errors due to absorption and beam divergence normal to the specimen rotation axis were minimized by using the smallest possible specimens. Having in mind that most of systematic errors vanish as diffraction angle Θ approaches 90^0 no additional corrections were undertaken as reflexions at highest diffraction angles were considered. Therefore the unit cell parameters were deduced from pairs or triplets of *hk0* and *h0l* reflexions with $\Theta > 75^0$. In order to ensure similar accuracies of all parameters the groups of reflexions were chosen in such a way that Σh^2 was comparable with Σk^2 in case of *hk0* reflexions, and Σh^2 with Σl^2 in case of *h0l* reflexions.

The measured densities (D_m) were obtained pycnometrically using decalin as liquid.

TABLE I

Crystal Data

	a (Å)	*b* (Å)	*c* (Å)	β (°)	V (Å^3)	M	D_m D_x (gcm^{-3})		Z	Space group	Ref.
$NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot 3\,H_2O$	6.578 (2)	16.368 (3)	12.308 (3)	92.63 (2)	1323.8 (8)	393.065	1.89	1.97	4	$P2_1/n$	(3) and this work
K[„] $\cdot 3\,H_2O$	6.445 (2)	16.390 (3)	12.069 (2)	93.35 (1)	1272.7 (6)	414.128	2.19	2.16	4	$P2_1/n$	this work
NH_4[„] $\cdot 2\,H_2O$	6.381 (1)	11.755 (1)	7.931 (1)	98.29 (1)	588.7 (2)	375.049	2.16	2.12	2	$P2_1/m$ ($P2_1$)	„
Rb[„] $\cdot 2\,H_2O$	6.377 (2)	11.749 (2)	7.937 (2)	98.49 (1)	588.1 (3)	442.480	2.57	2.50	2	$P2_1/m$ ($P2_1$)	„
Cs[„] $\cdot 2\,H_2O$	6.464 (1)	11.870 (1)	7.952 (1)	98.91 (1)	602.7 (2)	489.920	2.66	2.61	2	$P2_1/m$	(2)

Unit cell dimensions, *a*, *b*, *c*, monoclinic angle β, volume V of the unit cell, molecular weight M. measured, D_m, and calculated, D_x, densities, number of molecules Z in the unit cell, and spaces group. Numbers in parenthesis are the estimated errors in the least significants digits.

RESULTS AND DISCUSSION

Crystal data are listed in Table I, together with the data for Cs-salt[2]. The presence of *h0l* reflexions only for $h + l = 2n$, and *0k0* reflexions only for $k = 2n$ indicates the monoclinic space group $P2_1/n$ for trihydrate salts. The presence of *0k0* reflexions only for $k = 2n$ indicates the monoclinic space group $P2_1/m$ or $P2_1$ for dihydrate salts.

Similar values of unit cell parameters and the same space group extinctions suggest that there is a close structural relationship among dihydrate salts on one hand and between the trihydrate salts on the other hand. Therefore, the most probable space group of NH_4- and Rb-dihydrate salts will be $P2_1/m$, the same as the space group of the completely solved structure of Cs-salt[2], and not $P2_1$. For this reason a complete crystal structure determination of $K[NbO(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$, $NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ and $Rb[NbO(C_2O_4)_2H_2O)_2] \cdot 2H_2O$ is not planned.

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IZVOD

Kristalografski podaci kalij-, amonij- i rubidij-oksodioksalatodiakvo niobata(V) di- i trihidrata

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Postupcima ogiba rendgenskih zraka određeni su kristalografski podaci za $K[NbO(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$, $NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ i $Rb[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$. Na temelju sličnih parametara jediničnih ćelija i istih prostornih grupa ustanovljena je izostrukturnost između dihidrata Cs-soli (koje je kristalna struktura određena ranije[2]) i NH_4- i Rb-soli, te trihidrata NH_4-soli (koje je kristalna struktura također određena ranije[3]) i K-soli.

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