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Note

Preparation and Characterization of Some Sodium-, Rubidium-, Cesium- and Ammonium-Oxidiperoxoxalato-Molybdates (VI) and Tungstates (VI)

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INTRODUCTION

Potassium derivatives of oxidiperoxoxalato- molybdates and tungstates were prepared before^{1,2} studied by infrared³, Raman³ and X-ray methods^{4,5}. The crystal structure of corresponding molybdate with literature survey was published recently⁴. As a part of our interest on transition metal peroxo compounds, some sodium-, rubidium-, cesium- and ammonium- oxidiperoxoxalato- molybdates and corresponding rubidium- and cesium- tungstates were prepared and characterized by chemical analysis, i. r. spectra, X-ray and conductivity measurements. Rubidium, cesium and ammonium compounds are anhydrous, the sodium compound is trihydrate. Our attempts to prepare the anhydrous sodium compound failed so far. Compounds are sensitive on light.

EXPERIMENTAL

The crystals were obtained by similar methods as described before⁵. Their composition was proved by the determination of carbon, metals and peroxides. In the sodium compound hydrogen, and in the ammonium compound nitrogen was also determined.

Conductances were determined in water solutions using a 1000 cps conductivity bridge at $25.00 \pm 0.05^\circ\text{C}$ and bright platinum electrodes. The specific conductance of the water used was not greater than $3.0 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^2$.

I. r. spectra were obtained over the range $4000\text{--}400 \text{ cm}^{-1}$ on a Perkin-Elmer model 337 using Nujol or hexachlorobutadiene mulls.

The morphology of the crystals was determined with an optical goniometer. The lattice constants were obtained from oscillation and Weissenberg X-ray diffraction photographs with $\text{CuK}\alpha$ radiation; densities (D_m) by picnometer with decalin as liquid. No piezoelectric effect was detected. Systematic absences of reflections are as follows: a) for rubidium and ammonium compounds $h0l: h+l=2n+1$ and $0k0: k=2n+1$, these determine the space group as $\text{P}2_1/n$; b) for the cesium compounds $0kl: k+l=2n+1$ and $h0l: h=2n+1$, these determine the space group as $\text{P}na2_1$; c) for the sodium compound $0kl: k=2n+1$, $h0l: l=2n+1$ and $hk0: h=2n+1$, these determine the space group as $\text{P}bca$.

RESULTS AND DISCUSSION

The conductivity of sodium, rubidium, cesium and ammonium compounds was measured in water solutions over a range of concentrations from 10^{-2} to

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10^{-4} M. According to the graphical treatment of the data⁶ the complexes behave in aqueous solutions as though they are 2:1 electrolytes, because their molar conductivities for concentrations of 10^{-3} M are from 296 to 312 $\text{ohm}^{-1} \text{cm}^2$. In dilute solutions (less than 10^{-3} M) the conductivity increases rapidly, probably because of partial hydrolysis or decomposition of the complex anion.

TABLE I
Infrared Spectra

	M=O bands*	M(O ₂) bands*		
		(O—O)	M(O ₂) asym.	M(O ₂) sym.
Rb ₂ [MoO(O ₂) ₂ C ₂ O ₄]	973	874, 885	594	542
Cs ₂ [MoO(O ₂) ₂ C ₂ O ₄]	950	868, 875	588	540
(NH ₄) ₂ [MoO(O ₂) ₂ C ₂ O ₄]	965	862, 876	640	570
Na ₂ [MoO(O ₂) ₂ C ₂ O ₄] · 3 H ₂ O	965	860, 880		
Rb ₂ [WO(O ₂) ₂ C ₂ O ₄]	975	845, 860	593	540
Cs ₂ [WO(O ₂) ₂ C ₂ O ₄]	954	842, 860	587	544

(* values in cm^{-1})

I. r. spectra (Table I) are similar to those of the analogous potassium compounds³, but there are some differences in number and positions of bands, *e. g.* frequencies which belong to peroxo bands are splitted. The listed frequencies are assigned according to the values obtained for some other complexes of molybdenum and tungsten^{7,8}. Oxalato bands are not listed in Table I. By comparison with i. r. studies of other oxalato complexes⁹, oxalato ligands are bidentate. That was confirmed by crystal structure analysis of $\text{K}_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4]$, where oxalato and peroxo groups are bidentate and the molybdenum atom is seven coordinated⁴.

Crystal data are listed in Table II along with the data for potassium derivatives^{4,5} for comparison. Crystals of molybdenum derivatives are yellow, prismatic, those of tungsten derivatives colourless, transparent and prismatic. All are elongated along the *c* axis. Figures 1—4 represent their crystal habits. Compounds, listed in Table II, except sodium, which is hydrate, have similar values of lattice constants. Volumes of their unit cells increase from smaller to larger cations. Rubidium and ammonium compounds are monoclinic with the same systematic absences of reflections as potassium compounds; cesium compounds are orthorhombic. Similar values of lattice constants and the same space group extinctions suggest isomorphism between molybdenum and tungsten derivatives of the same type and either isomorphism or close structural relationship between potassium, ammonium and rubidium compounds. The differences in space groups between cesium and rubidium, ammonium or potassium compounds can be attributed to the packing rearrangement of the cations and anions without change of anion configuration. The crystal structure determinations on $\text{Na}_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4] \cdot 3 \text{H}_2\text{O}$, $(\text{NH}_4)_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4]$ and $\text{Cs}_2[\text{WO}(\text{O}_2)_2\text{C}_2\text{O}_4]$ are in course.

TABLE II
Crystal data

	a (Å)	b (Å)	c (Å)	β	V (Å ³)	Z	Space group	Dm (g. cm ⁻³)	Dx (g. cm ⁻³)	Ref.
K ₂ [MoO(O ₂) ₂ C ₂ O ₄]	13.721 (2)	8.835 (1)	6.885 (1)	92° 26 (6)'	833.9	4	P2 ₁ /n	2.68	2.725	(4)
K ₂ [WO(O ₂) ₂ C ₂ O ₄]	13.66 (1)	8.894 (8)	6.937 (7)	93° 05 (5)'	841.4	4	P2 ₁ /n	3.37	3.396	(5)
(NH ₄) ₂ [MoO(O ₂) ₂ C ₂ O ₄]	14.07 (2)	9.14 (1)	7.06 (1)	90° 25 (5)'	907.9	4	P2 ₁ /n	2.19	2.20	This work
Rb ₂ [MoO(O ₂) ₂ C ₂ O ₄]	14.33 (1)	9.13 (1)	6.97 (1)	90° 25 (2)'	911.9	4	P2 ₁ /n	3.16	3.17	"
Rb ₂ [WO(O ₂) ₂ C ₂ O ₄]	14.13 (4)	9.18 (2)	7.02 (1)	91° 42 (5)'	910.2	4	P2 ₁ /n	3.78	3.82	"
Cs ₂ [MoO(O ₂) ₂ C ₂ O ₄]	7.43 (1)	13.16 (2)	9.62 (1)	Ortho- rhombic	940.6	4	Pna2 ₁	3.74	3.74	"
Cs ₂ [WO(O ₂) ₂ C ₂ O ₄]	7.41 (1)	13.15 (2)	9.60 (1)	"	935.4	4	Pna2 ₁	4.38	4.39	"
Na ₂ [MoO(O ₂) ₂ C ₂ O ₄] · 3 H ₂ O	18.62 (3)	16.38 (2)	6.85 (1)	"	2089.2	8	Pbca	2.29	2.32	"

(Errors are in parentheses)

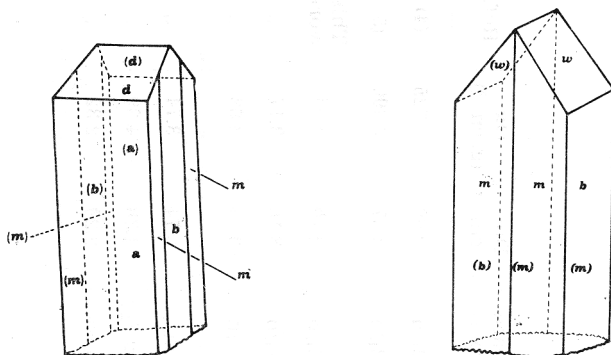


Fig. 1. Crystal habit of $\text{Na}_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4] \cdot 3 \text{H}_2\text{O}$. The combination of crystal forms is: $a\{100\}$, $b\{010\}$, $m\{110\}$, $d\{101\}$.

Fig. 2. Crystal habit of $\text{Cs}_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4]$. The combination of crystal forms is: $b\{010\}$, $m\{110\}$, $w\{011\}$. Crystals of $\text{Cs}_2[\text{WO}(\text{O}_2)_2\text{C}_2\text{O}_4]$ have a similar habit.

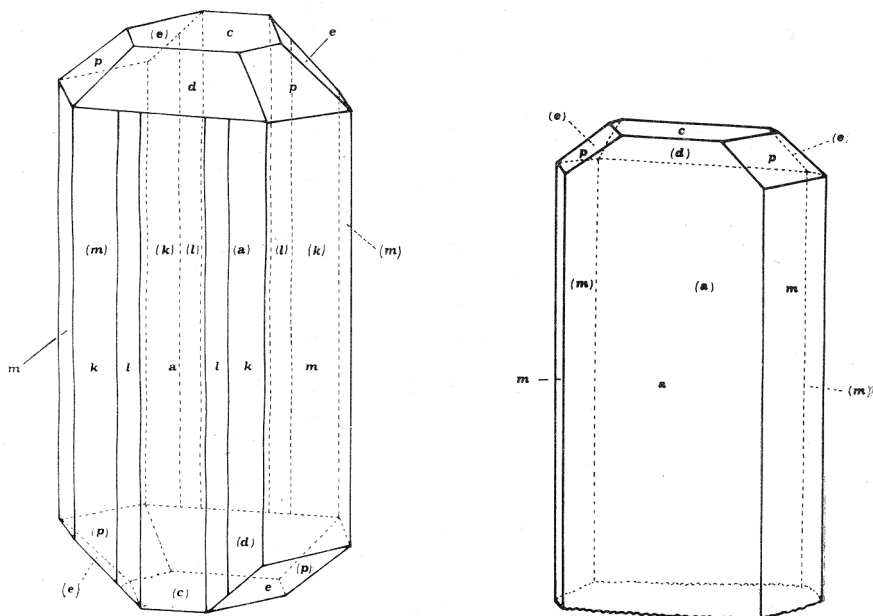


Fig. 3. Crystal habit of $\text{Rb}_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4]$. The combination of crystal forms is: $c\{001\}$, $a\{100\}$, $m\{110\}$, $k\{210\}$, $l\{310\}$, $p\{111\}$, $e\{111\}$, $d\{301\}$. Crystals of $(\text{NH}_4)_2[\text{MoO}(\text{O}_2)_2\text{C}_2\text{O}_4]$ have a similar habit.

Fig. 4. Crystal habit of $\text{Rb}_2[\text{WO}(\text{O}_2)_2\text{C}_2\text{O}_4]$. The combination of crystal forms is: $c\{001\}$, $a\{100\}$, $m\{110\}$, $p\{111\}$, $e\{111\}$, $d\{301\}$.

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IZVOD

Preparacija i karakterizacija nekih natrium-, rubidium-, cesium- i amonium-oksodiperoksooksalato- molibdata (VI) i volframata(VI)

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Priredeni su: M_2^I [$MoO(O_2)_2C_2O_4$], $M^I = Rb, Cs, NH_4$; M_2^I [$WO(O_2)_2C_2O_4$], $M^I = Rb, Cs$ i $Na_2[MoO(O_2)_2C_2O_4] \cdot 3H_2O$. Formule tih spojeva određene su na temelju kemijskih analiza. Iz rezultata dobivenih mjerenjem vodljivosti ustanovljeno je da se navedeni spojevi ponašaju u vodenim otopinama u koncentracijama većim od 10^{-3} M kao 2 : 1 elektroliti. Izmjereni su infracrveni spektri i uspoređeni sa spektrima analognih kalijevih spojeva. Metodama rendgenske difrakcije određeni su kristalografski podaci (tabela II). Na temelju sličnih dimenzija elementarnih ćelija i istih prostornih grupa ustanovljen je izomorfizam između molibdenovih i volframovih derivata iste vrste. Rubidijevi i amonijevi spojevi su izostrukturalni s odgovarajućim kalijevim spojevima koji su ispitani prije.

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