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The Structures of Potassium, Rubidium and Caesium Molybdate and Tungstate

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The compounds K_2MoO_4, K_2WO_4, Rb_2MoO_4 and Rb_2WO_4 are monoclinic and isomorphous; Cs_2MoO_4 and Cs_2WO_4 are isomorphous with orthorhombic β-K_2SO_4. Cell constants and atomic parameters are calculated from powder data, and the powder patterns are given.

Introduction

The normal molybdates and tungstates of the alkali metals consist of MoO_4^{2-} and WO_4^{2-} anions and alkali cations. In the anions, the molybdenum and tungsten ions form the centres of oxygen tetrahedra, and since the ionic radii of Mo^{6+} and W^{6+} are nearly equal, a compound A_2MoO_4 may be expected to be isomorphous with A_2WO_4. At room temperature this is indeed the case. At elevated temperatures, however, one or more transition points occur in all of the compounds under consideration. Moreover there are temperature intervals in which one of the alkali compounds is changed into its high-temperature form, while the other with the same cation is still in the low-temperature modification.

We have undertaken a research program to study the polymorphism of the alkali molybdates and tungstates and in this paper we present results, obtained at room temperature, for those compounds for which no reliable data have been published previously. In a separate paper we will report on the transitions and high temperature modifications.

Lithium tungstate has the hexagonal phenacite structure (Zachariasen & Plettinger, 1961), and sodium tungstate is a spinel (Sadikov & Shishakov, 1965). The corresponding molybdates are isomorphous with the tungstates (Zachariasen, 1926; Lindqvist, 1950). The crystal structures of potassium molybdate and tungstate were determined by Gatehouse & Leverett (1969) and Koster, Kools & Rieck (1969) respectively, and it appeared that these compounds are monoclinic and isomorphous within fairly small limits. We report here those structures of the rubidium and caesium compounds that are sufficiently stable at room temperature to be analysed, and a comparison is made with the potassium salts. As single crystals are rather difficult to obtain and all structure types were known, we used powder diagrams as the basis for refinement of all cell constants and some atomic parameters. The powder data of the potassium salts were also refined as a check.

Experimental

In order to obtain reliable powder diffractograms of the pure compounds, a sample of a convenient particle size and free from extinction and texture is necessary. These requirements are not always met by the simple method of preparation of the compounds, *viz.* heating for half an hour at 900–1000 °C equivalent amounts of pure molybdenum oxide, MoO_3, or tungsten oxide, WO_3, and the pure alkali carbonate. So a subsequent treatment was necessary.

Potassium molybdate and tungstate and rubidium tungstate

These compounds are isomorphous. The crude product decrepitates into very small fragments on passing one of the transition points (at approximately 320 °C for K_2MoO_4, 370 °C for K_2WO_4, 240 °C for Rb_2WO_4). The resulting powder is very suitable for diffractometry, but sometimes contains a second phase, as indicated by extra peaks. After removing this phase by additional recrystallization from water at 50 °C, the resulting product consists of platelets which introduce a certain amount of texture into the diffractometer specimen, which persists even if the sample is carefully powdered.

Table 1. *Cell constants, standard deviations and cell volume, at* 25 °C

	a	b	c	β	V
K_2MoO_4	12·345 (2) Å	6·078 (1) Å	7·535 (1) Å	115·73 (1)°	509·3 Å^3
K_2WO_4	12·380 (2)	6·117 (1)	7·554 (1)	115·96 (1)	514·4
Rb_2MoO_4(I)	12·821 (2)	6·253 (1)	7·842 (1)	115·64 (1)	566·8
Rb_2WO_4	12·841 (2)	6·285 (1)	7·854 (1)	115·82 (1)	570·5
Rb_2MoO_4(II)	6·375 (2)	11·112 (3)	8·097 (2)		573·6
Cs_2MoO_4	6·551 (2)	11·586 (2)	8·499 (2)		645·2
Cs_2WO_4	6·598 (2)	11·647 (3)	8·513 (2)		654·2

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This is indicated by over strong 00*l* reflexions in the diffractometer diagram. However, by heating the sample to about 30°C above the transition point and allowing it to disintegrate upon cooling once more, the preferred orientation, due to platelets, is avoided.

Rubidium molybdate

This compound is isomorphous with rubidium tungstate. The corresponding transition however, occurs at only slightly elevated temperature and is extremely sluggish on cooling. Samples kept for two years still contained the high-temperature form. So the last stage of the preparation method described in the preceding paragraph could not be performed, and a sample crystallized from water was used. The transition point was determined at about 100°C, by keeping the sample at various temperatures for one hour and checking by means of diffractometry, whether or not the transition had taken place.

Caesium molybdate and tungstate

These compounds are orthorhombic and isomorphous with β-K_2SO_4 at room temperature. They were purified by crystallization from water at 10°C.

Determination of cell constants

The cell constants were calculated from the 2θ values of a powder diffraction pattern, obtained by means of a Philips PW 1050 diffractometer, using Ni-filtered copper $K\alpha$ radiation.

By comparing this pattern with a completely indexed diagram of K_2WO_4 or K_2SO_4 the main reflexions could be indexed, and these reflexions were used in a least-squares calculation of the cell constants. Generally the diagram was indexed up to $2\theta \simeq 65°$. About 40–50 non-overlapping reflexions were the basis of the cell constants calculation. The $K\alpha_1$–$K\alpha_2$ doublet was resolved at 2θ angles greater than about 35°; below this limit, $K\alpha$ was used. A zero-point correction was applied where necessary. The results of the least-squares calculations are given in Table 1. The values for the potassium salts do not differ significantly from the single-crystal values. The high temperature form of rubidium molybdate, Rb_2MoO_4(II), was still present at room temperature, and its diagram could be indexed completely on the basis of the orthorhombic β-K_2SO_4 lattice.

Determination of atomic parameters

As a final check of the structure type, the powder intensities were used to carry out a parameter refinement. The oxygen atom parameters were not refinable from these data but the positions of the metal ions were found. We used an ALGOL 60 program for the least-squares calculations with overlapping reflexions (Rietveld, 1966). The number of reflexions was about 120. The oxygen atom positions were taken from single-crystal work. The temperature factor was taken to be isotropic; its estimated value was (in Å^2) 2·5 for K^+, 2·0 for Rb^+, 1·5 for Cs^+, 1·8 for Mo^{6+} and 1·0 for W^{6+}.

The reliability of the refinement of the metal ion parameters was investigated by means of a calculation on potassium tungstate. For this purpose small but significant shifts were applied to the atomic parameters of the K and W ions, which were already accurately known from the single-crystal investigation by Koster, Kools & Rieck (1969). During refinement, these parameters did indeed converge to their original values. The powder data refinement was employed on K_2MoO_4 before the single-crystal work by Gatehouse & Leverett (1969) became available; their results were in agreement with ours. Table 2 gives the atomic coordinates of the rubidium compounds. It is clear that the parameters do not vary significantly between the various compounds.

Table 2. *Atomic parameters and estimated standard deviations (in parentheses)*

(Space group *C*2/*m*)

		x	*y*	*z*
Rb_2MoO_4	Mo	0·174 (2)	0	0·227 (4)
	Rb(1)	0·015 (3)	½	0·237 (6)
	Rb(2)	0·348 (3)	½	0·269 (5)
Rb_2WO_4	W	0·175 (1)	0	0·227 (2)
	Rb(1)	0·017 (3)	½	0·243 (4)
	Rb(2)	0·346 (3)	½	0·262 (4)

In the case of Cs_2MoO_4 and Cs_2WO_4 the starting point was the set of parameters of β-K_2SO_4, to which small shifts were likewise applied. It appeared that during refinement most of the original parameters were approached (Table 3). The final *z* parameter of the Mo and W atoms, however, shows a significant deviation from that in the β-K_2SO_4 model. This deviation is the same in Cs_2MoO_4 and $CsWO_4$, which indicates a correlation with the ionic radii. The parameters of β-K_2SO_4 were those given by Robinson (1958).

Table 3. *Atomic parameters and estimated standard deviations (in parentheses)*

(Space group *Pmcn*)

		x	*y*	*z*
β-K_2SO_4	S	¼	0·416 (16)	0·236 (4)
	K(1)	¼	0·418 (13)	0·677 (3)
	K(2)	¼	0·705 (2)	0·988 (2)
Cs_2MoO_4	Mo	¼	0·416 (2)	0·224 (2)
	Cs(1)	¼	0·418 (1)	0·671 (1)
	Cs(2)	¼	0·707 (1)	0·991 (1)
Cs_2WO_4	W	¼	0·418 (1)	0·226 (1)
	Cs(1)	¼	0·420 (1)	0·671 (2)
	Cs(2)	¼	0·709 (1)	0·990 (2)

Powder patterns

The powder patterns are given in Tables 4 and 5. The pattern of K_2MoO_4 given in the ASTM index is essentially correct, but no cell constants and indices are given. Of the other compounds investigated here,

Table 4. *Powder patterns of monoclinic phases*

	K_2MoO_4		K_2WO_4		Rb_2MoO_4		Rb_2WO_4	
hkl	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1
001	6·79	4	6·79	4	7·07	5	7·07	4
$\bar{2}01$	5·68	21	5·70	25	5·90	3	5·91	20
200	5·56	12	5·57	28	—	—	5·78	7
110	5·33	14	5·36	28	—	—	5·52	9
$\bar{1}11$	4·70	45	4·72	54	4·85	6	4·87	27
111	3·82	25	3·83	30	—	—	3·97	11
$\bar{2}02$	3·70	11	3·71	13	3·85	5	3·85	8
201	3·60	12	3·60	13	—	—	3·75	6
002, $\bar{3}11$	3·394	53	3·404	41	3·53	72	3·53	70
310	3·165	100	3·172	100	3·280	100	3·285	100
$\bar{4}01$	3·085	5	3·094	13	—	—	—	—
020	3·039	55	3·058	58	3·126	60	3·143	51
$\bar{3}12$	2·915	65	2·928	43	3·023	90	3·033	83
$\bar{4}02$	2·838	6	—	—	—	—	—	—
400	2·780	10	2·783	7	—	—	2·890	5
$\bar{2}21$	2·679	5	2·695	9	—	—	—	—
$\bar{3}13$	2·284	9	2·293	8	2·372	20	2·378	7
022	2·264	52	2·273	37	2·342	60	2·349	45
$\bar{5}12$	2·231	6	2·239	6	—	—	2·320	5
$\bar{6}02$	2·042	21	2·048	9	2·121	16	2·125	14
312	1·978	30	1·978	21	2·056	38	2·056	28
$\bar{1}31$	—	—	1·966	7	—	—	—	—
$\bar{6}03$	1·892	5	—	—	1·965	10	1·970	7
131	1·873	4	—	—	—	—	—	—
600	1·854	14	1·855	18	1·926	17	1·927	11
$\bar{3}14$	1·799	15	1·804	12	1·870	28	1·874	17
330	1·778	17	1·787	16	1·833	28	1·841	14
$\bar{3}32$	1·730	14	1·740	9	1·784	20	1·792	15
004	—	—	—	—	1·767	10	1·767	8
$\bar{6}22$	1·695	19	1·702	8	1·755	18	1·760	13

the ASTM index gives only patterns of Rb_2MoO_4 and Cs_2MoO_4, both of which are incorrect.

Table 5. *Powder patterns of orthorhombic phases*

	Cs_2MoO_4		Cs_2WO_4	
hkl	*d*	I/I_1	*d*	I/I_1
020	—	—	5·82	3
110	—	—	5·74	2
021	—	—	4·81	8
111	—	—	4·76	12
002	4·25	4	4·26	10
012	3·99	9	4·00	7
121	3·87	17	3·89	10
102	3·57	14	3·58	15
031	3·52	8	3·53	5
022, 112	3·42	100	3·43	100
130	3·33	80	3·35	80
200	3·28	46	3·30	40
122	3·306	9	3·048	9
032	2·857	10	2·869	12
013	2·752	11	2·757	4
132	—	—	2·631	8
212, 113, 141	2·530	22	2·544	27
042, 231	2·395	11	2·408	13
222	2·368	24	2·380	29
051	2·236	6	2·247	4
232	2·154	9	2·165	10
004	2·125	5	2·128	6
213	2·107	5	2·115	3
104	2·021	6	2·026	12
114	1·991	8	1·996	4
152, 302	1·942	4	1·953	7
143, 242, 060	1·934	18	1·942	19
312	1·916	10	1·927	11
330	1·901	14	1·914	16

Discussion

When comparing the cell dimensions of the molybdate and the tungstate of the same alkali metal, we notice that in all cases the molybdate cells are the smallest. As we may conclude from the atomic parameters that the packing is the same, the difference in size can be attributed to the size of the $[XO_4]$ complex. It follows then that the radius of the Mo^{6+} ion is somewhat smaller than the radius of the W^{6+} ion; this is in contradiction to the data of Shannon & Prewitt (1969), who state that r_{eff} (Mo^{6+}, 4-coordinated) $= 0·42$ Å and r_{eff} (W^{6+}, 4-coordinated) $= 0·41$ Å. From the data presented here, we can assume the difference to be approximately 0·02 Å, which is in agreement with the value of Gatehouse & Leverett (1969) for the average Mo–O distance: $1·76 \pm 0·01$ Å, and the finding of Koster, Kools & Rieck (1969) that the average W–O distance is $1·79 \pm 0·01$ Å.

Comparison of the cell volumes of the two forms of Rb_2MoO_4, both obtainable at room temperature, demonstrates that the high temperature β-K_2SO_4 modification is more loosely-packed than the low temperature K_2MoO_4-type modification, in contradiction to a statement by Gatehouse & Leverett.

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Etude Cristallographique de Composés Nématogènes. II. Structure Cristalline du 4,4′-Azodiphénétole

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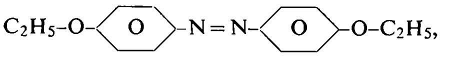
The crystal structure of 4,4′-azodiphenetole, C_2H_5–O–C_6H_4–N=N–C_6H_4–O–C_2H_5, has been determined from three-dimensional data collected on a single-crystal diffractometer with Cu $K\alpha$ radiation. The crystals are monoclinic, space group $P2_1/c$, with $a=9{\cdot}77$, $b=7{\cdot}59$, $c=20{\cdot}57$ Å, $\beta=104°$, $Z=4$. The structure was refined by least-squares methods and the final R is 0·086. The compound is nematogenic; the molecules are aligned parallel to [401] and the packing shows that dipole–dipole interactions exist in the crystalline state.

La détermination de la structure du 4,4′-azodiphénétole,



a été effectuée dans le cadre de l'étude d'un ensemble de produits présentant une phase nématique à la fusion.

Partie experimentale

Le 4,4′-azodiphénétole donne assez difficilement de bons cristaux. Les seuls cristaux acceptables ont été obtenus par refroidissement lent d'une solution de ce produit dans le toluène. Ils avaient la forme de plaquettes, mais un clivage assez facile nous a permis d'obtenir un cristal de 0,3 × 0,4 × 1 mm.

Données cristallographiques

$a=9{,}77\pm0{,}01$ Å
$b=7{,}59\pm0{,}01$
$c=20{,}57\pm0{,}02$
$\beta=104\pm0{,}1°$

$V=1483$ Å^3
$M=270$
$Z=4$

Groupe spatial $P2_1/c$ (d'après les extinctions systématiques)

Densité mesurée $D_m=1{,}10$ g.cm^{-3}
Densité calculée $D_c=1{,}13$
Coefficient linéaire d'absorption $\mu_l=5{,}96$ cm^{-1}.

La densité a été mesurée par 'flottation' dans une solution de nitrate d'argent. Les mesures de paramètres et la détermination du groupe spatial ont été effectuées sur des clichés de chambre de Weissenberg et de chambre à précession de Buerger. Les paramètres ont été précisés sur le diffractomètre semi-automatique Enraf–Nonius qui a servi à mesurer les intensités de toutes les réflexions. Ces mesures ont été effectuées à la température ambiante avec la radiation Cu $K\alpha$, par la méthode du balayage $\theta/2\theta$, la vitesse de balayage étant de 1°.minute^{-1}. Les temps de comptage étaient de 100 secondes pour le pic et de 20 secondes de part et d'autre de ce dernier pour le fond continu (toujours en balayage $\theta/2\theta$).

Les 2570 réflexions de $\sin\theta/\lambda<0{,}6$ (limite mécanique pour Cu $K\alpha$) ont été explorées; pour 1150 d'entre elles, l'erreur statistique relative $\sigma(I)/I$ était inférieure à 2,5% et pour 500 autres elle était comprise entre 2,5 et 5%. Nous n'avons utilisé pour les affinements que les 1 150 intensités connues avec le plus de précision.

Les corrections de Lorentz–polarisation et d'absorption ont été effectuées, cette dernière au moyen d'un programme permettant de traiter des cristaux prismatiques.

Détermination de la structure

Tous les calculs nécessaires à la détermination, l'affinement et l'interprétation de la structure, ont été effectués