

THE STRUCTURE OF THE COMPOUNDS $\text{Na}_{24}\text{As}_2\text{Z}_{22}\text{O}_{83}$ AND ITS RELATIONSHIP TO THE STRUCTURE OF $\text{Na}_2\text{Z}_2\text{O}_7$ ($\text{Z} = \text{Mo}, \text{W}$)

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X-ray study of the structure of the compounds $\text{Na}_{24}\text{As}_2\text{Z}_{22}\text{O}_{83}$ ($\text{Z} = \text{Mo}, \text{W}$) indicated that these compounds and the compounds $\text{Na}_2\text{Z}_2\text{O}_7$ are all isomorphous. They crystallize in the orthorhombic system with a space group of *Cmca*. The compound $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$ is formed by replacing part of the Mo atoms by As in the centres of the oxygen tetrahedra in the structure of $\text{Na}_2\text{Mo}_2\text{O}_7$. This substitution $\text{As} \rightarrow \text{Mo}$ results in loss of one oxygen atom for every two arsenic atoms in the $\text{Na}_2\text{Mo}_2\text{O}_7$ structure so that two AsO_4 tetrahedra are joined through an oxygen apex to form a $\text{As}-\text{O}-\text{As}$ bond. The exact atomic ratio $\text{As} : \text{Mo} = 1 : 11$ in the studied compounds was also sufficiently confirmed by study of the phase diagrams $\text{NaAsO}_3-\text{Na}_2\text{Z}_2\text{O}_7$.

This work deals with the solution of the structure of the compound $\text{Na}_{24}\text{As}_2\text{Z}_{22}\text{O}_{83}$, where $\text{Z} = \text{Mo}$ or W and its relationship to the structure of the compound $\text{Na}_2\text{Z}_2\text{O}_7$. These heteropolyanions were originally determined potentiometrically in a nitrate melt medium¹ and were first isolated from this medium as the sodium salts². Their compositions were refined by studying parts of the phase diagrams in the $\text{Na}_4\text{As}_2\text{O}_7-\text{Z}_2\text{O}_3-\text{NaZO}_4$ (ref.³) system. Single crystals were grown from the fused substances⁴.

EXPERIMENTAL

Preparation of the Initial Substances

Sodium trioxoarsenate was prepared from crystalline diarsenic acid (Merck, p.a.) by neutralization with sodium hydroxide (Lachema, p.a.) and dehydration of the $\text{Na}_2\text{H}_2\text{As}_2\text{O}_7$ obtained at 200°C. Its purity was controlled by gravimetric determination of arsenic as $\text{Mg}_2\text{As}_2\text{O}_7$ (calculated 51.34%, found 51.5% As).

Sodium dimolybdenate was prepared by fusing an equimolar mixture of MoO_3 (Lachema, Brno, p.a.) and Na_2MoO_4 , obtained by dehydration of the dihydrate (Lachema, Brno, p.a.). Fusion was carried out at a temperature of 650°C for 3 days. Reaction was controlled by measuring the melting point which continuously increased up to a value of 612°C, close to the tabulated value for the melting point of $\text{Na}_2\text{Mo}_2\text{O}_7$ ($615 \pm 3^\circ\text{C}$) (ref.⁵).

Sodium ditungstate was prepared similarly to the dimolybdenate, but fusion occurred at a temperature of 750°C and the product obtained had a melting point of 735°C, compared to the tabulated value of $740 \pm 5^\circ\text{C}$ (ref.⁵).

Single crystals of the compound $\text{Na}_{24}\text{As}_2\text{Z}_{22}\text{O}_{83}$ ($Z = \text{Mo}, \text{W}$) were prepared by the procedure given in the previous work⁴.

Apparatus and Methods

The powder diffraction patterns from ref.³ were compared with the JCPDS data basis implemented on the SIEMENS 7536 computer at the Institute of Physics of the Czechoslovak Academy of Sciences, describing the state of the art up to 1976 (ref.⁶).

The structural data for the substances were found by using the (continuously brought up-to-date) data basis for inorganic substances ICSD (Inorganic Crystal Structure Data), containing data for more than 30 thousand structures (ref.⁷).

The intensities were measured using a single crystals with dimensions of $0.12 \times 0.15 \times 0.6$ mm using MoK_α radiation ($\lambda = 71.073$ pm) and a Zr filter on an automatic four-ring Hilger and Watts diffractometer (England) controlled by an M7000 computer (U.S.S.R.). The lattice parameters (Table I) were refined by the least squares method from a set of values of 32 triplets of set angles⁸. The fluctuations in the intensities of three standard reflections ($\pm 3\%$, $\pm 4\%$, $\pm 4\%$) controlled after every thirty measurements did not exhibit any significant change in the crystal during the experiment.

The measured data was corrected by the Lorentz polarization factor. As the linear absorption factor $\mu = 4.7 \text{ mm}^{-1}$ and the radius of an equivalent sample $r = 0.08$ mm, so that $\mu r = 0.83$, correction for absorption was not carried out. A total of 985 independent reflections were measured, of which 108 with intensity of $I < 1.96 \sigma(I)$ were considered as "unobserved".

The set of programs "Soubor programů HW" (ref.⁹) was employed to control the measurement, for reduction and correction of the measured values and for calculation of the values of the observed structural factors $|F_{\text{obs}}|$.

The studied substance is chemically similar to the compound $\text{Na}_2\text{Mo}_2\text{O}_7$ and has identical lattice parameters and extinction. It could be thus assumed that these two substances are isostructural. Using this assumption (which was later completely confirmed), the values of $|F_{\text{obs}}|$ were employed directly to refine the structural parameters by the least squares method using a SIEMENS (F.R.G.) computer and the TLS set of programs¹⁰. The values given in ref.¹¹ were taken as the input positional parameters of the atoms. Calculations were carried out considering secondary extinction for an equivalent spherical sample with radius 0.08 mm. The minimization function was $\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$, where weight $w = 1/(\sigma^2(F_{\text{obs}}) + (0.03F_{\text{obs}})^2)$. Refinement was carried out for the positional parameters, anisotropic temperature coefficients and relative contents (occupation) of the Mo and As atoms in the tetrahedral position (Mo(2) and As atoms

TABLE I

Parameters of the unit cell (pm) for the isomorphous compounds $\text{Na}_2\text{Mo}_2\text{O}_7$ (ref.¹⁴), $\text{Na}_2\text{W}_2\text{O}_7$ (ref.¹⁵) and $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$

Parameter	$\text{Na}_2\text{Mo}_2\text{O}_7$	$\text{Na}_2\text{W}_2\text{O}_7$	$\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$
<i>a</i>	716.4(6)	721.6(1)	718.1(5)
<i>b</i>	1 183.7(4)	1 189.9(1)	1 184.7(3)
<i>c</i>	1 471.6(3)	1 471.6(3)	1 472.2(9)

in Table II) with the bonding condition that the sum of the two occupation factors AI equals the relative frequency of these positions in the $Cmca$ space group.

The temperature phase conversions in the NaAsO₃-Na₂Z₂O₇ systems were found using an apparatus constructed at the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences. The output signal from the Ni, Ni-Cr thermocouple was digitized and recorded using a SINCLAIR ZX SPECTRUM Plus computer (England). The actual measurement was carried out using an MT 100 digital voltmeter (Metra, Blansko). The method permitted simultaneous measurement of three samples of the test substance together with comparative sample of Al₂O₃. Prior to entering the digital voltmeter, the individual signals from the thermocouple were switched using an MAB 24 integrated circuit (Tesla, Lanškroun). The data was transferred between the MT 100 and the computer through an interface for parallel data transfer, MHB 8255 (Tesla, Piešťany). The MT 100 digital voltmeter and measuring site switch were controlled by a program in BETABASIC v. 3.0. Measurements were carried out in a range of 150 mV, permitting temperature measurement with a sensitivity of 0.01 mV, i.e. about 0.5 to 1°C. In addition, this method permitted objective reading of the phase transition temperature as the intercept of the zero line on the DTA curve with the increasing branch of the peak.

The densities of the crystals of the compound Na₂₄As₂Mo₂₂O₈₃ were measured pycnometrically in *p*-xylene p.a. at laboratory temperature.

RESULTS

It was found on the basis of the intensities of the diffraction lines and interplanar distances of the two isomorphous compounds of Na₂As₂Z₂₂O₈₃ given in ref.³ in the

TABLE II

The fractional atomic coordinates and equivalent isotropic temperature parameters B_{eq}^*

Atom	Position frequency	Wyckoff designation	Relative frequency (AI)	X	Y	Z	$B_{\text{eq}} \cdot 10^{-4}$ pm ²
Mo(1)	8	e	0.5	0.25	0.08185(3)	0.25	0.58(1)
Mo(2)	8	f	0.461(10)	0.039	0.24635(3)	0.08478(3)	0.59(1)
As			0.039				
Na(1)	8	d	0.5	0.2484(2)	0.0	0	1.30(5)
Na(2)	8	f	0.5	0	0.3177(2)	0.3430(2)	1.41(5)
O(1)	16	g	1	0.2015(4)	0.2311(2)	0.1551(2)	1.02(5)
O(2)	16	g	1	0.1997(4)	0.4919(3)	0.3375(2)	1.23(5)
O(3)	8	f	0.5	0	0.1216(3)	0.2825(2)	7.87(1)
O(4)	8	f	0.5	0	0.3759(3)	0.0316(3)	1.31(8)
O(5)	8	f	0.5	0	0.3594(3)	0.5021(3)	1.28(7)

* $B_{\text{eq}} = \sum_i \sum_j \beta_{ij} a_i a_j$ (ref.¹⁷).

JCPDS data bank that these substances have the same diffraction lines as the isomorphous dimolybdate and ditungstate compounds, $\text{Na}_2\text{Z}_2\text{O}_7$, with known structures.

The structure of $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$ was found on the basis of the literature data¹¹⁻¹⁶. It was found that, similar to $\text{Na}_2\text{Mo}_2\text{O}_7$ and $\text{Na}_2\text{W}_2\text{O}_7$, it crystallizes in a rhombohedral system with $Cmca$ space group. The elemental unit cell contains $2/3$ of a formula unit of $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$, analogous to 8 formula units of $\text{Na}_2\text{Z}_2\text{O}_7$. The measured density was $3.70(2) \text{ Mg m}^{-3}$ and the calculated density was $3.658(4) \text{ Mg m}^{-3}$. The unit cell volume $V = 1252(1) \cdot 10^6 \text{ pm}^3$.

In the final refinement cycle, the reliability factors $R = 0.027$ and $R_w = 0.047$ (from 877 observed reflections) and $R_z = 0.031$, $R_{wz} = 0.050$ (from all 985 reflections). The maximal ratio of the change to the error in an individual parameter was 0.01. The maximal residual electron density in the final differential Fourier synthesis was $0.87 \cdot 10^{-6} \text{ e pm}^{-3}$. Table II lists the absolute frequencies of the positions of the individual atoms in the $Cmca$ space group, their relative frequency (occupation factor AI), the fractional coordinates of the atoms and the equivalent isotropic temperature factors B_{eq} (ref¹⁶). Fig. 1 gives the characteristic part of the crystal structure. The view from the $[2\bar{7}1]$ direction reveals part of the chain formed by the MoO_6 octahedra and Mo(As)O_4 tetrahedra with common apices. Four such chains pass through the unit cell in the a direction. Table III gives the bonding distances and angles and the shortest distances between chains. In addition, the unit cell does not contain any Na^+ ions, compared to the number in the unit cell of sodium dimolybdenate.

The refined values of the occupation factors AI of the Mo2 and As atoms are $AI_{\text{Mo2}} = 0.461(10)$ and $AI_{\text{As}} = 0.039$ (Table II), which corresponds well to a ratio of 11 : 1 within the estimated error, i.e. $0.4583 : 0.0417$ (the sum of the occupation

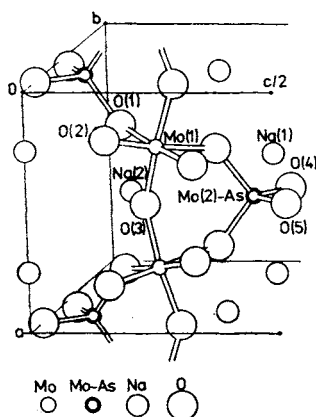


FIG. 1
Characteristic part of the crystal structure as viewed from the $[2\bar{7}1]$ direction

factors must equal 0.5, i.e. the relative frequency of their positions in the given space group).

To verify the empirical compositions of the studied compounds determined in the previous paper³ and especially the atomic ratio As/Mo , a study was carried out of parts of the phase diagrams of the NaAsO_3 – $\text{Na}_2\text{Z}_2\text{O}_7$ systems by the DTA method in the concentration range up to 25 mole% NaAsO_3 . The measured melting points correspond to the liquids curves for the compounds in this concentration range and are given in Fig. 2. The experimental points were fitted using the least squares method

TABLE III

The interatomic distances (pm), bonding angles ($^\circ$) and shortest intermolecular distances (pm). Designation of equivalent positions:

1) x, y, z	5) $-x, -y, -z$	9) $\frac{1}{2} + x, \frac{1}{2} + y, z$
2) $x, -y, -z$	6) $-x, y, z$	10) $\frac{1}{2} + x, \frac{1}{2} - y, -z$
3) $x, \frac{1}{2} - y, \frac{1}{2} + z$	7) $-x, \frac{1}{2} + y, \frac{1}{2} - z$	11) $\frac{1}{2} + x, -y, \frac{1}{2} + z$
4) $x, \frac{1}{2} + y, \frac{1}{2} - z$	8) $-x, \frac{1}{2} - y, \frac{1}{2} + z$	12) $\frac{1}{2} + x, y, \frac{1}{2} - z$
	13) $\frac{1}{2} - x, \frac{1}{2} - y, -z$	
	14) $\frac{1}{2} - x, \frac{1}{2} + y, z$	
	15) $\frac{1}{2} - x, y, \frac{1}{2} - z$	
	16) $\frac{1}{2} - x, -y, \frac{1}{2} + z$	

Bond length			Bond angles		
Mo(1)	—O(1) [1, 15]	228.0(3)	O(1) [1]	—O(1) [15]	78.3(1)
	—O(2) [4, 14]	171.0(3)		—O(2) [4]	89.4(1)
	—O(3) [1, 12]	191.7(1)		—O(2) [14]	167.6(1)
Mo(2), As	—O(1) [1, 6]	178.8(3)		—O(3) [1]	79.6(1)
	—O(4) [1]	172.3(4)		—O(3) [15]	78. (1)
	—O(5) [3]	174.7(4)	O(2) [4]—Mo(1)	—O(2) [14]	102.9(2)
Na(1)	—O(2) [3, 4]	242.0(3)		—O(3) [1]	98.2(1)
	—O(4) [9, 13]	237.5(3)		—O(3) [15]	99.4(1)
	—O(5) [3, 4]	244.1(3)	O(3) [1]—Mo(1)	—O(3) [15]	151.6(2)
Na(2)	—O(1) [12, 15]	237.7(3)	O(1) [1]—Mo(2), As—O(1) [6]		108.0(1)
	—O(2) [1, 6]	251.5(4)		—O(4) [1]	110.7(1)
	—O(3) [1]	248.8(4)		—O(5) [3]	109.3(1)
	—O(5) [1]	239.4(5)	O(4) [1]—Mo(2), As—O(5) [3]		108.8(2)

Shortest intermolecular distances

O(1) [1]—O(2) [15]	317.2(4)	O(4) [1]—O(4) [2]	308.4(5)
O(2) [1]—O(4) [12]	320.2(4)	O(5) [1]—O(5) [2]	333.2(5)
—O(5) [1]	322.4(5)		

similarly as in ref.³ to yield concentration maximum positions corresponding to 15.17 mole % NaAsO₃ for the system in which Z = Mo and 15.23 mole % NaAsO₃ for the system in which Z = W. The calculated value of the atomic ratio As : Mo = 1 : 11, i.e. for compounds with composition Na₂₄As₂Z₂₂O₈₃ equals 15.38 mole % NaAsO₃. The determined melting points for the pure compounds are 587°C for Z = Mo and 688°C for Z = W, which is in satisfactory agreement with the results in the previous paper³.

DISCUSSION

Solution of the structure of Na₂₄As₂Mo₂₂O₈₃ indicated that it is isomorphic with sodium dimolybdate and ditungstate, Na₂Z₂O₇. The dimensions of the unit cells in these compounds differ only negligibly (Table I). If the empirical formula of the studied compounds is compared with twelve times the formula unit of Na₂Z₂O₇, i.e. Na₂₄Mo₂₄O₈₄, it can be seen that the number of sodium atoms is identical, the sum of the numbers of As + Mo atoms is also identical and the number of oxygen atoms differs by one, i.e. by 2/3 of an oxygen atom per unit cell, which contains eight formula units of Na₂Mo₂O₇ and corresponds to 2/3 of a formula unit of Na₂₄As₂Mo₂₂O₈₃. Thus, two of three unit cells contain two molybdenum atoms that are surrounded by tetrahedra of oxygen atoms, which are replaced by two arsenic atoms; this arrangement is probably regular over large distances. In addition, two of three unit cells contain one oxygen atom less and these oxygen vacancies are also ordered regularly over large distances.

It can be seen from Table III that the Mo(As)—O bonding distances in the tetrahedra are very similar, as are the O—Mo(As)—O bonding angles which are also close to the ideal tetrahedral angle value $\tau = 109.47^\circ$; i.e. the tetrahedra are almost regular.

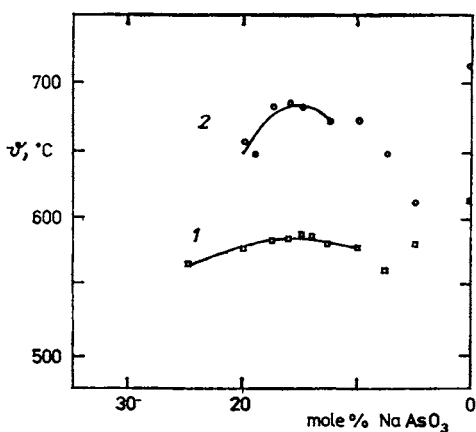


FIG. 2

The liquidus curve for the compound Na₂₄As₂Z₂₂O₈₃ in part of the phase diagram of Na₂Z₂O₇-NaAsO₃; 1 Z = Mo, 2 Z = W

In contrast, the Mo—O bonding distances in the octahedra differ widely, as do the angles which (with a single exception, see Table III) differ greatly from the ideal value of 90° . Thus, the octahedra are strongly distorted. These results are in complete agreement with the results obtained by Seleborg for $\text{Na}_2\text{Mo}_2\text{O}_7$ (ref.¹⁵) and by Okady et al. for $\text{Na}_2\text{W}_2\text{O}_7$ (ref.¹⁶). It is most probable that two AsO_4 tetrahedra will be joined through the O(4) atom of one tetrahedron and through the O(4) atom of the second tetrahedron.

The question arises of why the empirical composition expressed by the formula $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$ corresponds to the sufficiently large lattice energy of a stable, congruently melting compound. It is probable that substitution of the molybdenum or tungsten atom in the tetrahedral cavities of the $\text{Na}_2\text{Z}_2\text{O}_7$ structure by arsenic atoms increases the lattice energy and thus also the stability of the structure. This substitution occurs at the cost of the loss of an oxygen atom from two out of three unit cells, which labilizes the structure (probably as a result of increased bond strain); thus all the molybdenum or tungsten atoms cannot be replaced by arsenic atoms in the tetrahedral cavities. The substitution of arsenic for two molybdenum or tungsten atoms with the loss of an oxygen atom from two thirds of the unit cells is probably an optimal compromise leading to the most stable structure. It can be expected that, for the same reason, further compounds with composition $\text{Na}_{24}\text{X}_2\text{Z}_{22}\text{O}_{83}$ will be formed for other combinations of $X = \text{P}, \text{As}, \text{V}$ and $Z = \text{Mo}, \text{W}$, as suggested by the results of ref.¹. To verify the empirical formula $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$ and especially the atomic ratio $\text{As} : \text{Mo} = 1 : 11$, a subsequent study was carried out on the NaAsO_3 – $\text{Na}_2\text{Z}_2\text{O}_7$ phase diagram ($Z = \text{Mo}, \text{W}$). Originally, the empirical formula $\text{Na}_{24}\text{As}_2\text{Z}_{22}\text{O}_{83}$ was derived by studying parts of the phase diagrams of the $\text{Na}_4\text{As}_2\text{O}_7$ – ZO_3 – Na_2ZO_4 system (for $Z = \text{Mo}, \text{W}$), especially five cross-sections with constant concentration of $\text{Na}_4\text{As}_2\text{O}_7$ (ref.³). This empirical formula can also be expressed as the sum $2\text{NaAsO}_3 + 11\text{Na}_2\text{Z}_2\text{O}_7$ and the corresponding compound should appear as

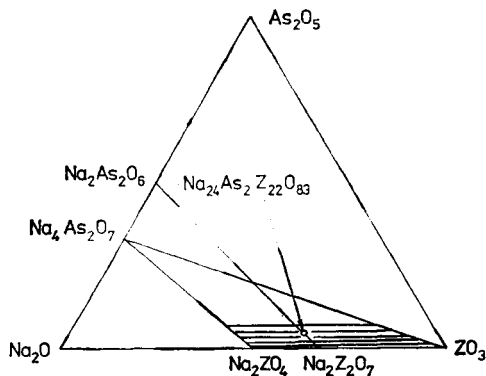


FIG. 3

The relationship between the phase diagrams of the Na_2O – ZO_3 – As_2O_5 and $\text{Na}_4\text{As}_2\text{O}_7$ – ZO_3 – Na_2ZO_4 systems and the studied cross-sections through these diagrams. The circle designates the image point for the compound $\text{Na}_{24}\text{As}_2\text{Z}_{22}\text{O}_{83}$

a melting point maximum in the $\text{NaAsO}_3\text{-Na}_2\text{Z}_2\text{O}_7$ system (Fig. 3). The position of the maximum on the liquids curves on this cross-section through the $\text{As}_2\text{O}_5\text{-ZnO}_3\text{-Na}_2\text{O}$ is far more sensitive to a change in the atomic ratio As/Z than in the procedure employed to determine the empirical formula in ref.³. Study of the liquidus curves in parts of these cross-sections using sophisticated measuring techniques completely confirmed the atomic ratio $\text{As/Z} = 1/11$ and thus the validity of the empirical formula $\text{Na}_{24}\text{As}_2\text{Z}_{22}\text{O}_{83}$ for both compounds ($\text{Z} = \text{Mo, W}$).

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