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The Compounds $\mathrm{KAs_4O_6}X$ (X = Cl, Br, I) and $\mathrm{NH_4As_4O_6}X$ (X = Br, I): Hydrothermal Syntheses and Structure Determinations

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The crystal structures of five isotypic hexagonal compounds with general formula $M\mathrm{As_4O_6}X$ [M = K, $\mathrm{NH_4}$; X = Cl, Br, I; space group: P622; Z = 1] were determined from ~ 370 single crystal X-ray data and refined to R values < 0.05. The structure type is characterized by neutral charged ${}^{2}_{\infty}[\mathrm{As_2O_3}]$ sheets arranged parallel (00.1). The As atoms of neighbouring two sheets point to each other and the sheets are combined by interlayered M and X atoms, respectively. The M atoms are coordinated to twelve oxygen atoms, the X atoms are coordinated to twelve arsenic atoms. In both cases the coordination polyhedron is a hexagonal prism. The compounds were synthesized by thermal treatments of cubic $\mathrm{As_2O_3}$ and potassium or ammonium haloids in a saturated aqueous solution of potassium acetate resp. ammonia [500 K, saturation vapour pressure].

(Keywords: $\mathrm{KAs_4O_6Cl}$; $\mathrm{KAs_4O_6Br}$; $\mathrm{KAs_4O_6I}$; $\mathrm{NH_4As_4O_6Br}$; $\mathrm{NH_4As_4O_6I}$; *Crystal structures; Crystal chemistry; Hydrothermal syntheses)*

Die Verbindungen $\mathrm{KAs_4O_6}X$ (X = Cl, Br, I) *und* $\mathrm{NH_4As_4O_6}X$ (X = Br, I): *Hydrothermalsynthese und Strukturbestimmung*

Die Kristallstrukturen der fünf isotypen hexagonalen Verbindungen mit der allgemeinen Formel $M\mathrm{As_4O_6}X$ [M = K, $\mathrm{NH_4}$; X = Cl, Br, I; Raumgruppe: P622; Z = 1] wurden anhand von ~ 370 Einkristall-Röntgendaten bestimmt und auf R-Werte < 0.05 verfeinert. Der Strukturtyp ist ausgezeichnet durch neutrale ${}^{2}_{\infty}[\mathrm{As_2O_3}]$-Schichten, die parallel (00.1) angeordnet sind. Die As-Atome zweier benachbarter Schichten weisen jeweils aufeinander zu, und die Schichten selbst werden durch zwischengelagerte M- bzw. X-Atome verbunden. Die M-Atome werden jeweils von zwölf O-Atomen, die X-Atome von zwölf As-Atomen umgeben. Das Koordinationspolyeder ist in beiden Fällen ein hexagonales Prisma. Die einzelnen Verbindungen wurden unter Hydrothermalbedingungen aus kubischem $\mathrm{As_2O_3}$ und dem jeweiligen Kalium- oder Ammoniumhalogenid in einer gesättigten wäßrigen Lösung von Kaliumacetat bzw. Ammoniak synthetisiert (500 K, Sättigungsdampfdruck).

Introduction

Within the series of compounds with the general formula $M\mathrm{As_4O_6}X$ with M = Na, K, NH_4 and X = Cl, Br, I, only the phase $NaAs_4O_6Br$, orthorhombic [1], as well as the hydrated member $(NH_4As_4O_6Cl)_2 \cdot H_2O$, hexagonal [2], have been described in literature, including reliable crystal structures. In connection with the syntheses of As(III)-oxygen compounds the five isotypic substances mentioned in the title of this article were obtained. The structure determinations of these hexagonal $M\mathrm{As_4O_6}X$ compounds were performed to learn about the crystal chemical behaviour of formal trivalent arsenic atoms in inorganic structures.

Experimental

The compounds $M\mathrm{As_4O_6}X$ were synthesized under following conditions: 2 g of an equimolar mixture of potassium haloid or ammonium haloid and cubic As_2O_3 were put into "teflon" coated vessels (~ 6 cm³ volume). The vessels were filled up to about 80% with concentrated aqueous solutions of potassium acetate or ammonia. After a reaction period of five days at 500(10) K and after cooling to room temperature during ~ 12 h the reaction products contain crystals of the title compounds as well as crystals of monoclinic As_2O_3 (claudetite – I [3]). For all individuums of the five chemical different title compounds only the crystallographic forms {00.1} and {11.0} were observed.

It is worth to mention that it was impossible to synthesize the compound $NH_4As_4O_6Cl$ under the given conditions. All investigations within the temperature range 300 to 500 K yielded crystals of $(NH_4As_4O_6Cl)_2 \cdot H_2O$ [2]. Experiments to synthesize the sodium analogues of $\mathrm{KAs_4O_6}X$ failed; only an orthorhombic modification of $NaAs_4O_6Br$ [1] was obtained showing a different atomic arrangement.

The accurate 2ϑ values for refinement of the lattice parameters (30–50 reflections) as well as the X-ray intensities were collected with a Stoe four-circle diffractometer AED2. The crystal data and the parameters of the data collection are compiled in Table 1. The X-ray intensities were corrected for absorption (*Gaußian* integration; empirical ψ scans for KAs_4O_6Cl) and for *Lorentz* and polarization effects. The atomic coordinates of the As atoms in KAs_4O_6Cl were found by a *Patterson* summation, subsequent *Fourier* syntheses gave the positions of the other atoms. The refined coordinates were used in starting sets of full-matrix least squares refinements for all the other four crystal structures. Complex neutral atomic scattering functions [4] were used. The finally obtained structure parameters are given in Table 2. Trials to locate the H atoms in the NH_4 groups failed; the reasons are the high value for F_{000} (~ 220) and the presumed splitting of each H atom position in three crystallographic different positions. Some important interatomic distances are summarized in Table 3.

Discussion

The structure type of the hexagonal compounds $M\mathrm{As_4O_6}X$ is characterized by layers parallel (00.1). These layers consist of neutral charged As_2O_3 sheets interlayered by M and X atoms. Each As_2O_3 sheet is formed

Table 1. *Summary of crystal data, data of X-ray intensity measurements and results of crystal structure refinements.* For all five compounds: space group P622-D_6^1; Z = 1 × $\{MAs_4O_6X\}$; graphite-monochromatized MoKα radiation; $2\theta/\omega$-scan mode with a step width of 0.03°; 0.5 to 3.0 s/step; range of data from 2° to 90° (2θ); 14 variables in refinement

	$NH_4As_4O_6Br$	$NH_4As_4O_6I$	KAs_4O_6Cl	KAs_4O_6Br	KAs_4O_6I
a (Å)	5.265(1)	5.290(1)	5.252(1)	5.257(1)	5.281(1)
c (Å)	9.148(2)	9.338(2)	8.880(2)	8.955(2)	9.169(2)
V (Å^3)	219.6	226.3	212.1	214.3	221.4
μ(MoKα) [cm^{-1}]	191.6	174.6	159.7	200.9	182.9
ρ_{calc} [g · cm^{-1}]	3.73	3.97	3.68	3.99	4.21
R	0.034	0.040	0.034	0.038	0.049
R_w; $w = [\sigma(F_0)]^{-2}$	0.0.30	0.033	0.030	0.027	0.042
Crystal dimension [mm^3]	0.20 × 0.20 × 0.06	0.20 × 0.20 × 0.04	0.08 × 0.08 × 0.12	0.16 × 0.16 × 0.04	0.10 × 0.10 × 0.02
Steps/reflection (+ α_1, α_2 splitting)	45	45	45	45	50
Measured reflections	1 200	796	3 736	2 969	1 489
Independent reflections	429	443	415	419	427
Reflections with $F_0 > 2\sigma_{F_0}$	385	376	386	360	367
g (sec. extinction [5])	$2.4(7) \cdot 10^{-5}$	$9.8(9) \cdot 10^{-5}$	$2.2(4) \cdot 10^{-5}$	$1.59(9) \cdot 10^{-4}$	$4.4(6) \cdot 10^{-6}$

Table 2. *Atomic fractional coordinates and anisotropic temperature parameters with e.s.d.'s in parentheses*. Space group $P622(D_6^1)$. The anisotropic temperature parameter ATF in $[pm^2]$ is of the form $\exp[-2\pi^2(\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^* a_j^* h_i h_j)]$. M = NH_4 or K; X = Cl, Br, or I

		$NH_4As_4O_6Br$	$NH_4As_4O_6I$	KAs_4O_6Cl	KAs_4O_6Br	KAs_4O_6I
1 *M* on 1(*b*) (0 0 1/2)	U_{11}	246(27)	245(33)	354(6)	293(8)	341(13)
	U_{33}	216(46)	210(67)	301(10)	289(15)	288(21)
4 As on 4(*h*) (1/3 2/3 *z*); etc.	Z	0.20346(6)	0.21063(8)	0.20533(5)	0.20796(6)	0.21503(9)
	U_{11}	88(1)	86(1)	150(1)	96(1)	97(2)
	U_{33}	167(2)	139(3)	172(2)	159(2)	188(3)
6 O on 6(*i*) (1/2 0 *z*); etc.	Z	0.3092(3)	0.3139(5)	0.3136(3)	0.3171(4)	0.3209(5)
	U_{11}	134(35)	159(61)	297(34)	157(48)	229(66)
	U_{22}	62(8)	60(11)	126(8)	79(10)	78(16)
	U_{33}	228(12)	191(16)	225(11)	209(14)	224(20)
	U_{12}	12(36)	48(59)	111(31)	21(49)	83(62)
1 *X* on 1(*a*) (000)	U_{11}	199(3)	149(2)	315(7)	196(3)	168(3)
	U_{33}	409(8)	227(5)	774(28)	413(8)	277(5)

Table 3. *Some selected interatomic distances (Å) and angles (°); e.s.d.'s in parentheses*

	$NH_4As_4O_6Br$	$NH_4As_4O_6I$	KAs_4O_6Cl	KAs_4O_6Br	KAs_4O_6I
M—O (12 ×)	3.158(1)	3.165(2)	3.104(3)	3.097(2)	3.109(2)
As—O (3 ×)	1.801(1)	1.806(2)	1.795(2)	1.805(2)	1.807(2)
O—O (3 ×)	2.632(1)	2.645(2)	2.626(2)	2.629(2)	2.640(2)
X—As (12 ×)	3.564(1)	3.632(2)	3.538(3)	3.561(2)	3.631(2)
O—As—O (3 ×)	93.87(9)	94.15(8)	94.01(9)	93.45(9)	93.86(9)

by AsO_3 pyramids—with point symmetry 3 of the As atoms—which are connected over three common oxygen atom corners. The As—O distances and O—As—O angles in the MAs_4O_6X compounds are in good agreement with crystal chemical experience [6, 7]. The As—O distances and the O—O edges increase from Cl to Br to I containing compounds; for the two Br resp. the two I compounds these values are equal within limits of error. The O atoms of a As_2O_3 sheet are exactly coplanar arranged due to space group requirements. All the apices of the AsO_3 pyramids, the As atoms, lie at the same side with respect to the basal plane defined by the oxygen atoms. The connection of the AsO_3 groups compares with that in the structure of $(NH_4As_4O_6Cl)_2 \cdot H_2O$ [2] only. As_2O_3 sheets have been determined in the crystal structures of claudetite I and II (monoclinic modifications of As_2O_3 [8–10]): In both these modifications of As_2O_3 the basal planes of the AsO_3 groups are mutually tilted within one sheet and the As atoms are arranged alternately at both sides of the sheet (ratio 1 : 1). In the structure type of the title compounds neighbouring sheets are inverted with respect to each other. The result is that on the one hand the As atoms and on the other hand the O atoms of adjacent sheets are pointing to each other.

The As_2O_3 sheets in the compounds MAs_4O_6X are connected by the M and the X atoms. The M atoms are coordinated to twelve O atoms in the form of a regular hexagonal prism. As expected, the distances K—O are somewhat shorter than the distances NH_4—O. The M atom has the point symmetry 622 which is incomensurable with the symmetry of an NH_4

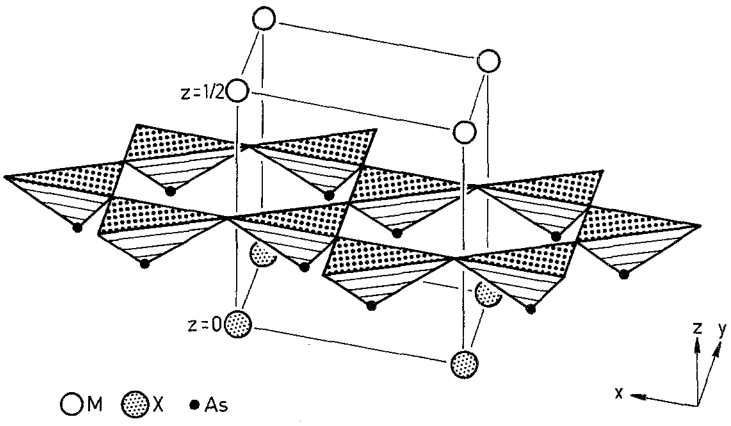

Fig. 1. A $\overset{2}{\infty}$ [As_2O_3] sheet at $z \sim 1/4$ built up by AsO_3 pyramids connected over common corners (shadowed). Additionally, the M = K, NH_4 resp. X = Cl, B, I atoms at both sides of this sheet are indicated

molecule. Therefore it is presumed that the H atoms are statistically distributed over at least three positions. The apices of the As_2O_3 sheets, the As atoms, point towards the X atoms, and twelve As atoms form the first coordination sphere around the X atoms (hexagonal prism). Vice versa the X atoms complete the coordination of the AsO_3 pyramids to strongly distorted "octahedra" with As—X from 3.54 to 3.63 Å. The completion of trigonal pyramidal $As(III)O_3$ polyhedra by three additional O atoms to a distorted octahedral coordination is well known in crystal chemistry [7]. Now this crystal chemical feature is also extended to haloids and As—X bonds. As expected the X—As bond length increases from Cl to Br and to I and for ammonia as well as for potassium compounds the distances Br—As and I—As are equal within the given e.s.d.'s. Figure 1 gives a survey over the atomic arrangement of the structure type MAs_4O_6X.

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