

Raveau, 1982). Cette appellation n'a pas été utilisée dans les publications très récentes, mais il est comode de la conserver pour différencier les deux types les plus répandus de pyrophosphates.

De plus, l'étude de la série $A^I AlAs_2O_7$ ($A^I = Na, K, Rb, Cs, Tl$) a révélé que les quatre composés (K, Rb, Cs, Tl) $AlAs_2O_7$ sont isotypes et que $NaAlAs_2O_7$ (Driss & Jouini, 1992) possède une structure originale dans laquelle les deux tétraèdres AsO_4 du groupement pyro pointent dans la même direction comme dans les phosphates isotypes de $NaFeP_2O_7$.

En conclusion nous avons établi la première structure de pyroarséniate et mis en évidence dans les arsénates $A^I M^{III} As_2O_7$ deux formes correspondant à deux conformations différentes du groupement As_2O_7 , comme dans les phosphates de formulation analogue, sans qu'il y ait isotypie entre les composés de l'arsenic et ceux du phosphore.

Bibliographie en rapport. Le composé étudié possède une structure très similaire aux pyrophosphates de type I isotypes de $KAlP_2O_7$ (Nam Ng & Calvo, 1973); $CsMoP_2O_7$, (Lii & Haushalter, 1987); $KFeP_2O_7$ (Riou, Labbe & Goreaud, 1988); $KMoP_2O_7$ (Leclaire, Borel, Grandin & Raveau, 1989); $RbMoP_2O_7$ (Riou, Leclaire, Grandin & Raveau, 1989); $CsVP_2O_7$ (Wang & Lii, 1989); $A^I TiP_2O_7$ ($A^I = K, Rb, Cs$) (Wang & Hwu, 1991); $(Rb, Cs)FeP_2O_7$ (Millet & Mentzen, 1991); KVP_2O_7 (Benhamada, Grandin, Borel, Leclaire & Raveau, 1991). $NaAlAs_2O_7$ présente des analogies structurales avec les pyrophosphates de type II isotypes ou semblables à $NaFeP_2O_7-II$ (Gabelica-Robert, Goreaud, Labbe & Raveau, 1982; Moya-Pizarro, Salmon, Fournes, Le Flem, Wanklyn & Hagemuller, 1984); $NaMoP_2O_7$ (Leclaire, Borel, Grandin & Raveau, 1988); $\beta-NaTiP_2O_7$ (Leclaire, Benmoussa, Borel, Grandin & Raveau, 1988); $NaVP_2O_7$ (Wang, Lii & Wang, 1989). Autres types de structures connues de pyrophosphates: $LiFeP_2O_7$ (Genkina, Maksimov, Timofeeva, Bykov & Mel'nikov, 1985) et

$\alpha-NaTiP_2O_7$ (Leclaire, Benmoussa, Borel, Grandin & Raveau, 1988) qui a d'étroites analogies avec la cristobalite.

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$Cs_4Mo_{21}S_{25}$: a New Structure Type Containing Mo_9 and Mo_{12} Condensed Clusters

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Abstract. $Cs_4Mo_{21}S_{25}$, $M_r = 3347.96$, trigonal, $R\bar{3}c$, $a(\text{rh.})$ (rh. = rhombohedral, hex. = hexagonal) = 28.265 (1) Å, $\alpha(\text{rh.}) = 19.256 (1)^\circ$, $V(\text{rh.}) =$

2146.8 (2) Å³, $Z(\text{rh.}) = 2$, $a(\text{hex.}) = 9.4543 (5) \text{ \AA}$, $c(\text{hex.}) = 83.20 (1) \text{ \AA}$, $V(\text{hex.}) = 6440 (1) \text{ \AA}^3$, $Z(\text{hex.}) = 6$, $D_x = 5.179 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, μ

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= 102.6 cm⁻¹, $F(000)(\text{rh.}) = 3004$, $F(000)(\text{hex.}) = 9012$, $T = 295$ K, $R = 0.029$ for 1412 observed reflections. The structure of the title compound consists of Mo₉S₁₁ and Mo₁₂S₁₄ cluster units interconnected three-dimensionally by S bridges. The Mo—Mo distances in the clusters range from 2.638 (1) to 2.7806 (8) Å and the shortest Mo—Mo intercluster distance is 3.278 (1) Å. The Cs⁺ ions occupy the cavities created by the Mo₉S₁₁ and Mo₁₂S₁₄ cluster units in tetracapped trigonal prismatic S environments.

Introduction. As part of our program on the synthesis of new reduced Mo compounds in the system Cs—Mo—S, we have previously synthesized ternary sulfides containing Mo clusters of different sizes: Mo₆ octahedra in Cs_{0.6}Mo₆S₇ (Gougeon, Padiou, Potel, Sergent & Couach, 1984), condensed clusters built up of 6, 7 and 9 *trans*-face-shared Mo₆ octahedra in Cs₅Mo₂₁S₂₃ (Gougeon, 1990), Cs₆Mo₂₄S₂₆ and Cs₈Mo₃₀S₃₂ (Gougeon, 1984), as well as infinite chains of *trans*-face-shared Mo₆ octahedra in Cs₂Mo₆S₆ (Potel, 1981). Moreover a mixture of Mo₆ and Mo₉ clusters has also been obtained in Cs₂Mo₁₅S₁₉ which is isostructural with In₂Mo₁₅Se₁₉ (Potel, Chevrel & Sergent, 1981). Herein, we describe the crystal structure of Cs₄Mo₂₁S₂₅ containing simultaneously, for the first time, the two Mo₉ and Mo₁₂ condensed clusters.

Experimental. Single crystals were obtained by heating a mixture of overall composition 'Cs₃Mo₁₅S₁₇' (starting materials: Cs₂MoS₄, MoS₂ and Mo) in a sealed molybdenum crucible at about 2000 K for 1 h. The crucible was then cooled at a rate of 100 K h⁻¹ to 1300 K and finally furnace-cooled to room temperature.

A crystal with dimensions 0.16 × 0.16 × 0.24 mm was selected for the intensity data collection carried out on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo K α radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $15 \leq 2\theta \leq 30^\circ$. The systematic absence (hhl , $l = 2n + 1$) allowed the space group to be $R\bar{3}c$ or $R3c$; the former was assumed and confirmed by the successful analysis. 2750 reflections were recorded in the range $2 \leq 2\theta \leq 60^\circ$ with $h - 39 \rightarrow 39$, $k - 39 \rightarrow 39$, $l 0 \rightarrow 39$, $k > h$ and $|l| > |k|$ (rhombohedral setting). The ω - 2θ scan mode was used with scan width $\Delta\omega = (1.00 + 0.35\tan\theta)^\circ$ and counter aperture $\Delta l = (2 + 0.5\tan\theta)$ mm. Three orientation and three intensity control reflections were checked every 250 reflections and every hour, respectively, and showed no significant variation. Data were transformed into the hexagonal setting and corrected for Lorentz-polarization. An empirical

absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The minimum and maximum correction factors were 0.735 and 1.358. After averaging ($R_{\text{int}} = 0.026$), 2095 unique data were used to solve the structure with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. The function minimized in the least-squares program was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$. The refinement of all atoms anisotropically and an extinction coefficient (78 variables) converged to $R = 0.029$, $wR = 0.045$, $S = 1.002$ for 1412 reflections with $F_o^2 > 2\sigma(F_o^2)$. The largest shift/e.s.d. was < 0.01 . Maximum and minimum electron densities in the final difference Fourier map were 0.59 and -1.36 e Å⁻³, respectively; the final value of g was 6.73×10^{-8} (Stout & Jensen, 1968). A refinement of the occupancy factors for the Cs sites confirmed that they were fully occupied. Scattering factors for neutral atoms and f' , f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed with the *SDP* (B.A. Frenz & Associates, Inc., 1985) programs on a Digital MicroVAX 3100. Final atomic coordinates and B_{eq} values are reported in Table 1 and selected interatomic distances in Table 2.*

Discussion. Cs₄Mo₂₁S₂₅ contains an equal mixture of the two Mo₉S₁₁ and Mo₁₂S₁₄ condensed cluster units with Cs⁺ ions inserted between the latter (Figs. 1 and 2). Its structure derives from that of Cs₂Mo₁₅S₁₉, which also crystallizes in the space group $R\bar{3}c$ and is built up from Mo₆S₈ and Mo₉S₁₁ units in equal proportion, by merely replacing the Mo₆S₈ cluster units by the Mo₁₂S₁₄ condensed cluster unit having the same local symmetry ($\bar{3}$). The Mo₉S₁₁ unit is structurally identical in both structure types and has $3/m$ symmetry. The Mo₉S₁₁ and Mo₁₂S₁₄ units result from the linear condensation of two and three basic Mo₆S₈ units, respectively, by sharing of Mo₃S₃ faces, and were first observed in Cs₂Mo₁₅S₁₉ and Tl₂Mo₉S₁₁ (Potel, Chevrel & Sergent, 1980) in which they cocrystallize with Mo₆S₈ units. The environments of the terminal Mo(1) and Mo(3) atoms of both cluster types are similar and consist of four Mo atoms and four S atoms forming a quasi-planar square. In addition, they are bonded to a fifth S atom belonging to an adjacent Mo₉S₁₁ or Mo₁₂S₁₄ cluster unit. The internal Mo(2) and Mo(4) atoms are connected at six

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55488 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1004]

Table 1. *Positional parameters (hexagonal setting) and equivalent isotropic thermal parameters (\AA^2)*

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

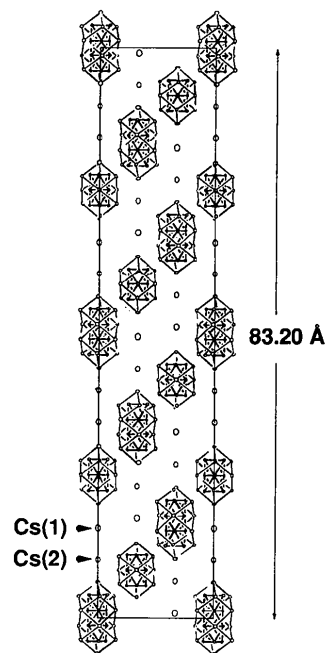
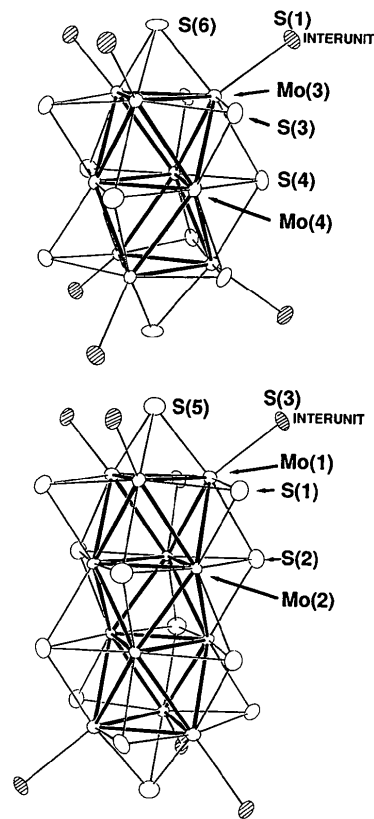
	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Mo(1)	0.14945 (8)	-0.02117 (8)	0.45973 (1)	0.28 (1)
Mo(2)	-0.01714 (8)	-0.17204 (8)	0.48705 (1)	0.20 (1)
Mo(3)	0.16015 (8)	-0.00661 (8)	0.22263 (1)	0.26 (1)
Mo(4)	-0.1641 (1)	0.000	0.250	0.26 (2)
S(1)	0.2826 (2)	0.3204 (2)	0.03793 (2)	0.42 (4)
S(2)	0.6992 (2)	0.0492 (2)	0.31964 (3)	0.51 (4)
S(3)	0.3029 (2)	0.2890 (2)	0.22534 (2)	0.37 (3)
S(4)	0.3011 (3)	0.000	0.250	0.48 (6)
S(5)	0.000	0.000	0.06249 (4)	0.58 (4)
S(6)	0.000	0.000	0.20032 (4)	0.54 (4)
Cs(1)	0.000	0.000	0.15783 (1)	1.40 (1)
Cs(2)	0.000	0.000	0.10254 (1)	1.02 (1)

Table 2. *Selected interatomic distances (\AA)*

$|\text{Mo}-\text{Mo}|_{\Delta}$ is the distance between Mo atoms related through the threefold axis and thus forming an Mo_3 triangle perpendicular to this axis; called the intratriangle distance in the text. $\text{Mo}_{\Delta}-\text{Mo}_{\Delta}$ is the distance between Mo atoms of different Mo triangles and is called the intertriangle distance.

$\text{Mo}_{12}\text{S}_{14}$ unit		Mo_9S_{11} unit	
$ \text{Mo}(1)-\text{Mo}(1) _{\Delta}$	2.638 (1) $\times 2$	$ \text{Mo}(3)-\text{Mo}(3) _{\Delta}$	2.678 (1) $\times 2$
$\text{Mo}(1)_{\Delta}-\text{Mo}(2)_{\Delta}$	2.727 (1) $\times 2$	$\text{Mo}(3)_{\Delta}-\text{Mo}(4)_{\Delta}$	2.7278 (8) $\times 2$
	2.762 (1) $\times 2$		2.7806 (8)
$\text{Mo}(2)_{\Delta}-\text{Mo}(2)_{\Delta}$	2.655 (1) $\times 2$	$ \text{Mo}(4)-\text{Mo}(4) _{\Delta}$	2.687 (2) $\times 2$
$ \text{Mo}(2)-\text{Mo}(2) _{\Delta}$	2.688 (1) $\times 2$		
$\text{Mo}(1)-\text{Mo}(3)_{\text{intercluster}}$	3.278 (1)		
$\Delta(1)-\Delta(2)$	2.273	$\Delta(3)-\Delta(4)$	2.277
$\Delta(2)-\Delta(2)$	2.155		
$\text{Mo}(1)-\text{S}(5)$	2.395 (3)	$\text{Mo}(3)-\text{S}(6)$	2.416 (3)
$\text{Mo}(1)-\text{S}(3)_{\text{interunit}}$	2.452 (2)	$\text{Mo}(3)-\text{S}(3)$	2.432 (2)
$\text{Mo}(1)-\text{S}(1)$	2.483 (2)		2.448 (2)
	2.501 (2)	$\text{Mo}(3)-\text{S}(1)_{\text{interunit}}$	2.520 (2)
$\text{Mo}(1)-\text{S}(2)$	2.580 (2)	$\text{Mo}(3)-\text{S}(4)$	2.624 (2)
$\text{Mo}(2)-\text{S}(1)$	2.460 (2)	$\text{Mo}(4)-\text{S}(3)$	2.403 (2) $\times 2$
$\text{Mo}(2)-\text{S}(2)$	2.469 (2)	$\text{Mo}(4)-\text{S}(4)$	2.469 (3) $\times 2$
	2.479 (3)		
	2.570 (2)		
Cs—S			
$\text{Cs}(1)-\text{S}(6)$	3.535 (4)	$\text{Cs}(2)-\text{S}(3)$	3.282 (2) $\times 3$
$\text{Cs}(1)-\text{S}(2)$	3.564 (2) $\times 3$	$\text{Cs}(2)-\text{S}(5)$	3.332 (4)
$\text{Cs}(1)-\text{S}(2)$	3.625 (2) $\times 3$	$\text{Cs}(2)-\text{S}(4)$	3.679 (2) $\times 3$
$\text{Cs}(1)-\text{S}(1)$	3.904 (2) $\times 3$	$\text{Cs}(2)-\text{S}(1)$	3.759 (2) $\times 3$

Mo and four S atoms. The Mo—Mo distances within the Mo_9 and Mo_{12} clusters can be classified into two groups, as usual. The first corresponds to the distances within the Mo_3 triangles formed by the Mo atoms related through the threefold axis (intra-triangle distances) and which are equal to 2.678 (1) and 2.687 (2) \AA in the Mo_9 cluster and to 2.638 (1) and 2.688 (1) \AA in the Mo_{12} cluster. The second group comprises the Mo—Mo bonds between these Mo_3 triangles (intertriangle distances) which range from 2.7278 (8) to 2.7806 (8) \AA in the Mo_9 cluster and from 2.655 (1) to 2.762 (1) \AA in the Mo_{12} cluster. The mean Mo—Mo distances within the Mo_9 and Mo_{12} clusters are 2.723 and 2.694 \AA , respectively. The shortest distance between the Mo_9 and Mo_{12}

Fig. 1. Projection of the structure of $\text{Cs}_4\text{Mo}_{21}\text{S}_{25}$ onto the hexagonal (110) plane.Fig. 2. Mo_9S_{11} and $\text{Mo}_{12}\text{S}_{14}$ cluster units with their numbering scheme. Hatched S atoms belong to neighbouring cluster units.

clusters is 3.278 (1) Å [Mo(1)—Mo(3)]. The S atoms bridge either one [S(1), S(3), S(5) and S(6)] or two [S(2) and S(4)] Mo triangular faces of the clusters. Moreover, the S(1) and S(3) atoms are linked to an Mo atom of a neighbouring cluster. The Mo—S bond distances range from 2.403 (3) to 2.624 (2) Å within the Mo₉S₁₁ unit and from 2.395 (3) to 2.580 (2) Å within the Mo₁₂S₁₄ unit.

The Cs⁺ ions occupy large intersecting channels which run parallel to the axes of the rhombohedral unit cell. Both are located on special 12(c) positions and are each surrounded by ten S atoms. Six of them form a trigonal prism and the remaining four cap the three rectangular and one triangular face. The Cs—S distances range from 3.535 (4) to 3.904 (2) Å (mean value 3.681 Å) for the Cs(1) site and from 3.282 (2) to 3.759 (2) Å (mean value 3.549 Å) for the Cs(2) site.

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Structure of (NH₄)₃H(SeO₄)₂ in High-Temperature Phases I and II

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Abstract. Triammonium hydrogenbis(tetraoxoselenate), (NH₄)₃H(SeO₄)₂, *M_r* = 341.04, *Z* = 3, $\lambda(\text{Mo } K\bar{\alpha}) = 0.71073 \text{ \AA}$, *F*(000) = 498. Phase I: trigonal, *R* $\bar{3}m$, *a* = 6.090 (1), *c* = 22.759 (5) Å, *V* = 731.0 (2) Å³, *D_x* = 2.32 g cm⁻³, $\mu = 68.7 \text{ cm}^{-1}$, *T* = 355 K, *R* = 0.0336 for 241 unique reflections with *I* > 4σ(*I*). Phase II: trigonal, *R* $\bar{3}$, *a* = 6.064 (1), *c* = 22.904 (5) Å, *V* = 729.4 (2) Å³, *D_x* = 2.33 g cm⁻³, $\mu = 68.8 \text{ cm}^{-1}$, *T* = 310 K, *R* = 0.0374 for 397 unique reflections with *I* > 4σ(*I*). In both phases, SeO₄ tetrahedra are linked by a dynamic system of symmetrically disordered hydrogen bonds in planes perpendicular to the trigonal axis. In phase II, SeO₄ tetrahedra deviate from the (210) plane owing to a small rotation of about 4° about the trigonal axis. In phase I, owing to symmetry enhancement, both orientations of SeO₄ tetrahedra are equally probable on both sides of (210), which is therefore a mirror plane.

Introduction. Triammonium hydrogenbis(tetraoxoselenate) (TAHSe) is a member of the isomorphic series with the general formula *A*₃H(*B*O₄)₂, where *A* = NH₄, K, Rb or Cs and *B* = S or Se. Unlike other isomorphic compounds with a single high-temperature trigonal superionic phase, TAHSe has two trigonal superionic phases. TAHSe undergoes four successive phase transitions at 332, 302–305, 276–279 and 181 K, with phases denoted I, II, III, IV and V in order of descending temperature (Osaka, Makita & Gesi, 1979; Baranov, Tregubtchenko, Shuvalov & Shagina, 1987). Phase V is ferroelectric, phases II and I are superionic conductors. Recently, Merinov, Antipin, Baranov, Tregubtchenko, Shuvalov & Struchkov (1991) obtained crystals of TAHSe with the III–II phase-transition temperature lowered to 291 K and determined the crystal structure of TAHSe at 295 K in phase II. We have performed a detailed study of the crystal structure of