Sheldrick, G. M. (1996). *SADABS User Guide*. University of Göttingen, Germany.

Siemens (1995a). *SAINT. Data Processing Software for the SMART System*. Version 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995b). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

$Cs_5Mo_{21}S_{23}$

S. Picard, P. Gougeon and M. Potel

Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS No. 1495, Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes CEDEX, France. E-mail: patrick.gougeon@univ-rennes1.fr

Abstract

Pentacaesium henicosamolybdenum tricosasulfur is isostructural with $Cs_5Mo_{21}Se_{23}$ and is the third member in the series $M_{2n-1}Mo_{6n+3}X_{6n+5}$ (M = Rb, Cs; X = S, Se, Te). Its crystal structure contains as the main building block an $Mo_{21}S_{23}$ cluster unit, the Mo core of which consists of six face-sharing Mo_6 octahedra. The decrease in the ionic radius of the chalcogen results in a shortening of the Mo—Mo intertriangle distances while the intratriangle ones do not change significantly. The shortest intercluster Mo—Mo distance also decreases from 3.342 (3) Å in $Cs_5Mo_{21}Se_{23}$ to 3.1687 (9) Å in $Cs_5Mo_{21}S_{23}$.

Comment

This work is part of our programme in search of new reduced molybdenum compounds in the Cs–Mo–S system. Until now, this study has led to the synthesis of six structure types by solid-state reaction: $Cs_{0.6}Mo_6S_7$ (Gougeon, Padiou, Potel, Sergent & Couach, 1984), which contains Mo_6 clusters; $Cs_6Mo_{24}S_{26}$ and $Cs_8Mo_{30}S_{32}$ (Gougeon, 1984), comprising condensed clusters built up from seven or nine Mo_6 clusters; and infinite chains of *trans*-face-shared Mo_6 octahedra in the quasi-one-dimensional compound $Cs_2Mo_6S_6$ (Potel, 1981). In addition, mixtures of Mo_6 and Mo_9 clusters ($Cs_2Mo_{15}S_{19}$; Gougeon, 1988), and Mo_9 and Mo_{12} clusters ($Cs_4Mo_{21}S_{25}$; Gougeon & Potel, 1993) have also been obtained. Here we present the crystal structure of a new compound belonging to the Cs–Mo–S system, $Cs_5Mo_{21}S_{23}$.

A view of the structure of $Cs_5Mo_{21}S_{23}$ is shown in Fig. 1. The basic structural unit is the $Mo_{21}S_{23}$ cluster

unit (Fig. 2) which can be thought of as six Mo_6S_8 units fused together sharing Mo_3S_3 faces, after removal of the capping S atoms. Consequently, the Mo atoms belonging to the outer Mo_3 triangles have an environment similar to that of the Mo atoms of the Mo_6S_8 cluster units (five S and four Mo), while those of the inner triangles are surrounded by six Mo atoms and four S atoms. In addition, all the S atoms which are coplanar with the shared octahedral faces bridge two triangular faces and the others bridge one triangular face.

As observed previously in $Cs_5Mo_{21}Se_{23}$ (Gougeon, Potel & Sergent, 1990) and compounds of the series $M_{2n-2}Mo_{6n}X_{6n+2}$ containing $Mo_{6n}X_{6n+2}$ cluster units (n = 2, 3, 4 and 5) (Gougeon, 1984), the distances between Mo atoms related through the threefold axis (intratriangle distances) lie in a narrow range [2.6587 (11)–2.6688 (8) Å] whereas those between adjacent Mo_3 triangles (intertriangle distances) vary from 2.6699 (6) to 2.7539 (7) Å. The intratriangle Mo—Mo distances are somewhat similar to those in $Cs_5Mo_{21}Se_{23}$ [2.652 (2)–2.669 (2) Å], and the intertriangle distances are smaller than comparable values in $Cs_5Mo_{21}Se_{23}$ [2.701 (2)–2.768 (2) Å], as expected from the smaller radius of the S atom. This contraction of the Mo_{21} cluster along its elongation axis is reflected in the spacings between Mo_3 triangles which are 2.275 Å for $\Delta(1)$–$\Delta(2)$, 2.194 Å for $\Delta(2)$–$\Delta(3)$ and 2.206 Å for $\Delta(3)$–$\Delta(4)$ in $Cs_5Mo_{21}S_{23}$
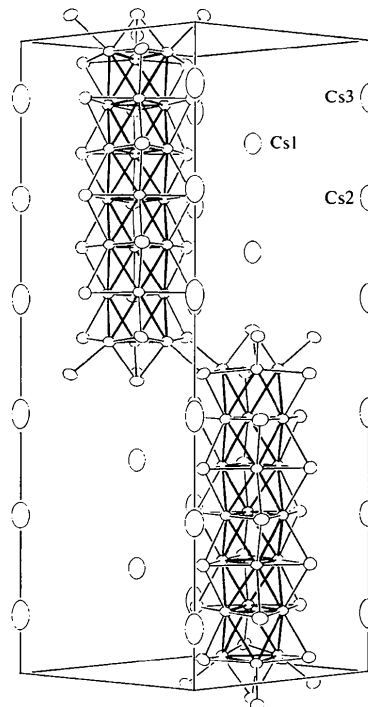

Fig. 1. View of the unit cell of $Cs_5Mo_{21}S_{23}$. Mo_{21} clusters are emphasised by thick lines. Mo—S bonds are shown as thin lines. Unconnected ellipsoids represent the Cs^+ cations. Displacement ellipsoids are drawn at the 95% probability level.
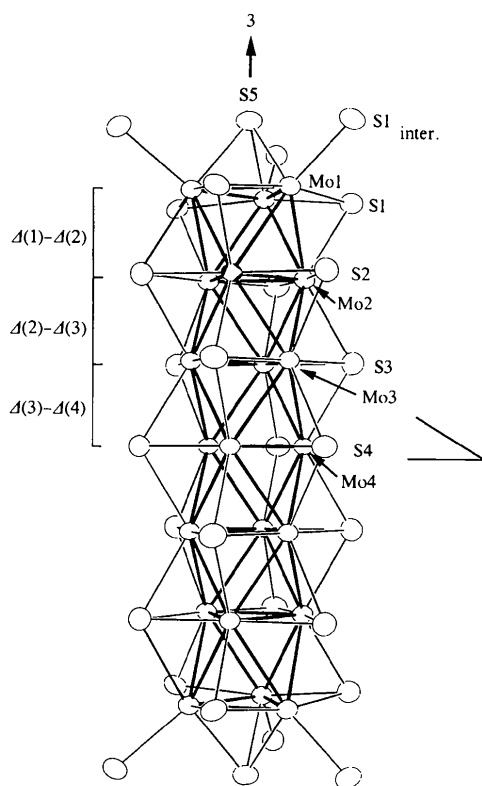
Fig. 2. The $Mo_{21}S_{23}$ cluster unit showing the atom-numbering scheme.

into a pellet and loaded in a molybdenum crucible which was sealed under a low argon pressure using an arc welding system. The crucible was heated at a rate of 300 K hr^{-1} to 2200 K and held there for 15 min, then cooled at 100 K hr^{-1} to 1300 K and finally furnace cooled to room temperature.

Crystal data

$Cs_5Mo_{21}S_{23}$	Mo $K\alpha$ radiation
$M_r = 3416.67$	$\lambda = 0.71073$ Å
Hexagonal	Cell parameters from 25
$P6_3/m$	reflections
$a = 9.3529$ (8) Å	$\theta = 7.21–19.52°$
$c = 29.292$ (4) Å	$\mu = 10.827$ mm^{-1}
$V = 2219.1$ (4) Å^3	$T = 293$ (2) K
$Z = 2$	Irregular
$D_x = 5.113$ Mg m^{-3}	$0.12 \times 0.08 \times 0.07$ mm
D_m not measured	Black

Data collection

Enraf–Nonius CAD-4 diffractometer	1553 reflections with $I > 2\sigma(I)$
$\omega–2\theta$ scans	$R_{int} = 0.030$
Absorption correction:	$\theta_{max} = 29.93°$
refined from ΔF	$h = 0 \to 13$
(*DIFABS*; Walker &	$k = 0 \to 13$
Stuart, 1983)	$l = 0 \to 41$
$T_{min} = 0.286$, $T_{max} = 0.469$	3 standard reflections
2562 measured reflections	frequency: 90 min
2189 independent reflections	intensity decay: <1%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 2.84$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{min} = -1.57$ e Å^{-3}
$wR(F^2) = 0.091$	Extinction correction:
$S = 1.107$	*SHELXL*93 (Sheldrick,
2189 reflections	1993)
79 parameters	Extinction coefficient:
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2$	0.00005 (3)
$+ 5.5132P]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	*International Tables for*
$(\Delta/\sigma)_{max} = 0.001$	*Crystallography* (Vol. C)

in contrast to 2.290, 2.230 and 2.248 Å, respectively, in $Cs_5Mo_{21}Se_{23}$. Another consequence of the smaller size of the chalcogen is the decrease in the Mo—Mo intercluster distance from 3.342 (3) Å in $Cs_5Mo_{21}Se_{23}$ to 3.1687 (9) Å in $Cs_5Mo_{21}S_{23}$. The Mo—S bond distances range from 2.407 (2) to 2.6012 (14) Å with the shortest of these involving the terminal S5 atom which is only linked to three Mo atoms. These values are similar to those observed in the other ternary reduced molybdenum sulfides.

The Cs$^+$ cations occupy either large twin cavities between the $Mo_{21}S_{23}$ cluster units (Cs1) or tunnels running along the c axis (Cs2 and Cs3). Cs1 is ten-coordinate with six S atoms (three S2 and three S4) forming a trigonal prism, three capping the three rectangular faces (three S3) and one the triangular face (S5). For this site the Cs1—S bond lengths range from 3.5380 (14) to 3.9085 (15) Å. The Cs2 and Cs3 polyhedra are distorted tricapped trigonal prisms with $\bar{6}$ and 3 symmetry, respectively. For these two sites, the Cs—S distances range from 3.530 (2) to 3.7223 (13) Å and from 3.4950 (13) to 3.8623 (15) Å, respectively.

Experimental

Single crystals were obtained from a stoichiometric mixture of Cs_2MoS_4, MoS_2 and Mo. The reactants were cold-pressed

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cs1	2/3	1/3	0.16415 (3)	0.0222 (2)
Cs2	0	0	1/4	0.0274 (2)
Cs3	0	0	0.09169 (3)	0.0306 (2)
Mo1	0.51247 (5)	0.16047 (5)	0.52210 (2)	0.00841 (12)
Mo2	0.68359 (5)	0.17780 (5)	0.599788 (15)	0.00795 (12)
Mo3	0.51254 (5)	0.15971 (5)	0.674669 (14)	0.00771 (12)
Mo4	0.68659 (7)	0.18008 (7)	3/4	0.00765 (14)
S1	0.0493 (2)	0.3482 (2)	0.47085 (4)	0.0102 (2)
S2	0.6204 (2)	−0.0136 (2)	0.09876 (4)	0.0114 (2)
S3	0.7058 (2)	0.0477 (2)	0.67475 (4)	0.0109 (2)
S4	0.6187 (2)	−0.0078 (2)	1/4	0.0106 (3)
S5	2/3	1/3	0.45888 (8)	0.0113 (4)

Table 2. *Selected bond lengths (Å)*

Cs1—S3^i	3.5380 (14)	Mo2—S1^{vii}	2.4390 (14)
Cs1—S2	3.6025 (14)	Mo2—S2^x	2.4649 (14)
Cs1—S5^{ii}	3.604 (2)	Mo2—S2^{xiii}	2.4773 (14)
Cs1—S4	3.9085 (15)	Mo2—S3	2.5688 (14)

Cs2—S4'"	3.530 (2)	Mo2—Mo2x'	2.6673 (8)
Cs2—S3'x	3.7223 (13)	Mo2—Mo3	2.6699 (6)
Cs3—S2'"	3.4950 (13)	Mo2—Mo3x'	2.6907 (6)
Cs3—S1v	3.5603 (13)	Mo3—S3'"	2.4775 (14)
Cs3—S3v'	3.8623 (15)	Mo3—S3	2.5017 (14)
Mo1—S5	2.407 (2)	Mo3—S4x"	2.5789 (11)
Mo1—S1v"	2.4634 (13)	Mo3—S2x	2.5805 (14)
Mo1—S1v"'	2.4634 (13)	Mo3—Mo3'"	2.6688 (8)
Mo1—S1'x	2.4847 (13)	Mo3—Mo4'"	2.6877 (6)
Mo1—S2x	2.6012 (14)	Mo3—Mo4	2.6916 (6)
Mo1—Mo1x'	2.6621 (8)	Mo4—S4x"	2.480 (2)
Mo1—Mo2	2.7398 (7)	Mo4—S4x'v	2.504 (2)
Mo1—Mo2'"	2.7539 (7)	Mo4—S3	2.5781 (13)
Mo1—Mo1x"'	3.1687 (9)	Mo4—Mo4x'	2.6587 (11)

Symmetry codes: (i) $1 + y, 1 - x + y, z - \frac{1}{4}$; (ii) $1 - x + y, 1 - x, \frac{1}{2} - z$; (iii) $1 - x + y, 1 - x, z$; (iv) $x - y - 1, x - 1, z - \frac{1}{4}$; (v) $-y, x - y, \frac{1}{2} - z$; (vi) $y, 1 - x + y, z - \frac{1}{4}$; (vii) $1 + x - y, x, 1 - z$; (viii) $y, -x + y, 1 - z$; (ix) $-x + y, -x, z$; (x) $1 - x, -y, \frac{1}{2} + z$; (xi) $1 - y, x - y, z$; (xii) $1 - x, -y, 1 - z$; (xiii) $1 + y, 1 - x + y, \frac{1}{2} + z$; (xiv) $1 + y, 1 - x + y, 1 - z$.

Data were corrected for Lorentz–polarization effects and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The structure was solved with *MULTAN*11/82 (Main *et al.*, 1982) and subsequent difference Fourier syntheses. The largest positive peak in the final difference Fourier map was 2.69 Å from Cs3, while the largest negative peak was 1.25 Å from Mo4. Refinement of the occupancy factors for the Cs sites confirmed that they are fully occupied. Calculations were performed on a Digital Pentium Celebris 590 FP for *SHELXL*93 (Sheldrick, 1993) and on a Digital MicroVAX 3100 for the *MolEN* (Fair, 1990) programs.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MUL-TAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *OR-TEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

References

Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Gougeon, P. (1984). Thesis, University of Rennes, France.

Gougeon, P. (1988). Unpublished result.

Gougeon, P., Padiou, J., Potel, M., Sergent, M. & Couach, M. (1984). *Ann. Chim. Fr.* **9**, 1083–1086.

Gougeon, P. & Potel, M. (1993). *Acta Cryst.* C**49**, 427–430.

Gougeon, P., Potel, M. & Sergent, M. (1990). *Acta Cryst.* C**46**, 2284–2287.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.

Potel, M. (1981). Thesis, University of Rennes, France.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Cadmium Thiosulfate Dihydrate

Sergio Baggio,[a] María I. Pardo,[a] Ricardo Baggio[b] and Oscar González[c]

[a]*Universidad Nacional de la Patagonia, Sede Puerto Madryn, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, [b]Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, and [c]Laboratorio de Cristalografía, Facultad de Química, Universidad de la República, Montevideo, Uruguay. E-mail: baggio@cnea.edu.ar*

Abstract

The polymeric structure of the title compound, $CdS_2O_3.2H_2O$, consists of tightly woven two-dimensional networks interconnected by hydrogen bonds. The Cd^{2+} environment is octahedral and each thiosulfate ion binds to four different cationic sites, in simple as well as in bridging mode.

Comment

So far, few structures of complexes of cadmium(II) with thiosulfate have been reported. Two have been solved only recently, namely $Cd_2(S_2O_3)_2(C_{14}H_{12}N_2)_2$, (1) (Baggio, Baggio, Pardo & Garland, 1996), and $Cd(S_2O_3)(C_{10}H_8N_2)$, (2) (Baggio, Pardo, Baggio & Garland, 1997), and in both these compounds the anions present unusual types of coordination: in (1) the thiosulfate group acts both as a bridging and as a bidentate ligand, binding two metal centers to form a dimeric moiety; in (2) the anion, acting as a bridge, binds to three Cd atoms through S atoms and one O atom.

The interesting results obtained so far have prompted us to attempt the X-ray structural study of cadmium thiosulfate dihydrate, (3), a compound in which the coordination around the metal atom, as well as the type of bonding displayed by the thiosulfate group, could not be predicted by stoichiometric arguments alone; also, no X-ray structural data seemed to be available, except for preliminary spectroscopic work by Gabelica (1973).

Fig. 1 shows the interactions in the unit cell, as well as the labeling scheme. The Cd ion displays a rather distorted octahedral environment, coordinating to O1, O2, O1W, O2W [range 2.293 (4)–2.340 (4) Å] and to two symmetry-related S1 atoms, arranged in the *cis* mode [2.581 (1) and 2.627 (1) Å]. Cd—O distances in the Cd coordination polyhedron are normal, with no significant differences, irrespective of the source of the O atoms (water or thiosulfate). Furthermore, their mean value [2.32 (4) Å] is surprisingly close to that reported by Bürgi & Dunitz (1994) [2.32 (6) Å]