for assistance, and Johnson, Matthey Ltd. for the loan of ruthenium. The work is a contribution from the Bioinorganic Chemistry Group.

Registry No. **1**·CH_2Cl_2, 76584-43-5; **2**, 76584-44-6; **3**, 76584-50-4; **4**, 76584-45-7; $[Ru(TPP)(dpb)]_n$, 76584-48-0; $Ru(OEP)(dpm)_2$, 76584-46-8; Ru(TPP)(CO)(EtOH), 41654-56-2; Ru(OEP)(CO)(EtOH), 55059-73-9.

Supplementary Material Available: Table IV, a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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$[Mo_2S_{10}]^{2-}$, a Complex with Terminal Sulfido, Bridging Sulfido, Persulfido, and Tetrasulfido Groups

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The complex $[Mo_2S_{10}]^{2-}$ has been isolated as one product of the reaction between $[NH_4]_2[Mo_2S_{12}]$ and PhSNa (1:16) in $MeOH/Me_2SO$ (10:1). $[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN$ crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$), with $a = 10.489$ (2) Å, $b = 11.756$ (2) Å, $c = 21.856$ (4) Å, $\alpha = 77.11$ (2)°, $\beta = 85.46$ (2)°, and $\gamma = 77.92$ (2)°. The structure has been determined from 6774 X-ray counter intensities by Patterson and Fourier techniques and refined by full-matrix least-squares methods to $R = 0.054$ (0.064 weighted). The anion has a terminal sulfido group bonded to each of the molybdenum atoms ($\overline{\mathrm{Mo{-}S}} = 2.110$ (2) Å) which are bridged by two μ-sulfido groups (Mo–S = 2.289 (2)–2.351 (2) Å); one of the molybdenum atoms is also coordinated to a persulfido group ($\overline{\mathrm{Mo{-}S}} = 2.395$ (3), S–S = 2.071 (3) Å) whereas the other is bonded to a tetrasulfido group ($\overline{\mathrm{Mo{-}S}} = 2.406$ (3) Å). The two central atoms of the tetrasulfido group are disordered and this disorder has been refined in terms of an 80–20% distribution of two components; in each case the length of the S–S bond involving the noncoordinated sulfur atoms (1.970 (6) Å for the major component) is significantly shorter than those involving a coordinated sulfur atom (2.018 (5) and 2.116 (5) Å for the major component).

Introduction

There is much current interest in the study of complexes containing molybdenum and sulfur, not least because of the probable coordination of molybdenum by a group of sulfur atoms in each of the molybdenum-containing enzymes.[2] This generally held view has received considerable support from the interpretations presented for the EXAFS details, associated with the molybdenum *K* edge, for nitrogenase,[3] sulfite oxidase,[4] and xanthine oxidase.[5,6] In nitrogenase, the molybdenum appears to be incorporated into an assembly of iron and sulfur atoms,[3] whereas in sulfite oxidase[4] and xanthine oxidase[5,6] the molybdenum is apparently coordinated by three or four sulfur atoms, which are presumably derived from methioninyl and/or cysteinyl residues of a polypeptide. Furthermore, a comparison of the EXAFS data obtained for active and desulfo xanthine oxidase,[6] indicates that the sulfur atom lost upon the cyanolysis which converts the former to the latter,[7] is immediately adjacent to the molybdenum; the interpretation of these data provides some support for the view[8] that this atom is present as a terminal sulfido group.

Recent developments in molybdenum–sulfur chemistry serve to demonstrate the structural diversity possible for combinations of these elements.[11-29] One interesting aspect developed[12-16] and discussed[17,18] by Müller et al. is the formation of molybdenum–persulfide complexes; $[Mo_2S_{12}]^{2-}$ provides a good example of this ligand's ability to function as a terminal and a bridging group.[12] Herein, we report that $[NH_4]_2[Mo_2S_{12}]$ reacts with PhSNa to give, as one of the products, $[Mo_2S_{10}]^{2-}$; this anion contains two terminal sulfido groups, two μ-sulfido groups, one persulfido group, and one tetrasulfido

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group and epitomizes the versatility of molybdenum–sulfur couplings.

Experimental Section

Preparation of $[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN$. All manipulations were carried out under an atmosphere of purified dinitrogen with use of dry solvents previously purged with this gas. Sodium (0.56 g, 24.7 mmol) was dissolved in MeOH (30 cm^3), and benzenethiol (Aldrich; 2.54 cm^3, 24.7 mmol) was added. The addition of a solution of $[NH_4]_2[Mo_2S_{12}]$[12] (0.95 g, 1.55 mmol) in Me_2SO/MeOH (1:4; 25 cm^3) gave no immediate reaction but, after the mixture was stirred overnight at room temperature, a red-violet solution was obtained. The addition of $[AsPh_4]Cl$ (Aldrich; 1.6 g, 3.9 mmol) in MeOH (10 cm^3) to this solution produced an immediate crystalline precipitate which was collected by filtration, washed with MeOH, and dried in vacuo. The crude solid was dissolved in Me_2SO (10 cm^3) at 50 °C and the solution filtered and diluted with MeCN (30 cm^3) at 50 °C. Addition of MeOH (10 cm^3) to incipient crystallization, followed by slow cooling to −5 °C, gave the product as large, black, diamond-shaped needles: yield 0.97 g (ca. 50%); mp 215–216 °C. Anal. Calcd for $[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN = C_{49}H_{41.5}N_{0.5}As_2Mo_2S_{10}$: C, 45.3; H, 3.2; N, 0.5; As, 11.5; Mo, 14.8; S, 24.7. Found: C, 45.4; H, 3.3; N, 0.6; As, 11.1; Mo, 15.0; S, 24.5. Some of these crystals were suitable for x-ray crystallographic studies.

Crystal Structure Determination

All crystallographic measurements were made at room temperature, with a Stoe-Siemens AED diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å), from a crystal mounted in a glass capillary. Unit cell dimensions, derived from 50 accurately centered reflections with $20 < 2\theta < 25°$, are a = 10.489 (2) Å, b = 11.756 (2) Å, c = 21.856 (4) Å, α = 77.11 (2)°, β = 85.46 (2)°, γ = 77.92 (2)°, and V = 2567.5 Å^3 (this is the Niggli reduced cell). The space group is $P\bar{1}$, with Z = 2.

Intensities were collected for $7 < 2\theta < 50°$, in the θ/ω scan mode, by means of a profile-fitting procedure.[30,31] A total of 9010 reflections were measured. After application of Lp and absorption corrections, 6772 unique reflections with $I > 2\sigma(I)$ were used for structure solution and refinement. Absorption corrections were of the Gaussian integration type, with μ = 21.4 cm^{-1} and 120 grid points. The dominant crystal faces were ±(011), and the sides corresponded approximately to faces ±(100) and ±(0$\bar{1}$6); dimensions were 0.096 × 0.270 × 0.384 mm.

The structure was solved by conventional Patterson and Fourier synthesis methods and refined to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F_o) + 0.001F_o^2$]. Scattering factors were taken from ref 32. Hydrogen atoms were included in the refinement, constrained to lie on the external bisectors of C–C–C angles, with C–H = 0.96 Å. They were assigned isotropic thermal parameters, fixed at 1.2 times the equivalent isotropic thermal parameters of the corresponding carbon atoms. Anisotropic thermal parameters were refined for all other atoms.

After refinement of the atoms of the anion and both cations, a difference synthesis contained peaks which could be assigned to the disorded MeCN solvent molecule and to a minor disorder component of the S_4^{2-} ligand. Two disorder components of the ligand were refined with occupancy factors of 0.80 (2) and 0.20 (2), and the solvent molecule was refined as a rigid group with C–C = 1.47 Å, C–N = 1.15 Å, C–C–N = 180°, and an occupancy factor of 0.5; hydrogen atoms were not included. This removed the remaining significant difference synthesis peaks and reduced R from 0.0644 to 0.0538 and R_w from 0.0801 to 0.0644 [$R = \sum|\Delta|/\sum|F_o|$; $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$]. The rms deviation of a reflection on an absolute scale of F_o [$=(\sum w\Delta^2/\sum w)^{1/2}$] was 2.31 electrons and showed no systematic trends as a function of indices, sin θ, or F_o.

Observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom parameters are available as supplementary material. Structural results are given in the tables: atomic coordinates in Table I, bond lengths and angles in Table II, and selected planes through atomic positions in Table III.

Table I. Atomic Coordinates ($\times 10^4$)[a]

atom	x	y	z
Mo(1)	4976 (1)	6053 (1)	2290 (1)
Mo(2)	4256 (1)	7906 (1)	2964 (1)
S(1)	5512 (2)	7951 (2)	2056 (1)
S(2)	4297 (2)	5908 (2)	3342 (1)
S(3)	2343 (2)	8739 (2)	2693 (1)
S(4)	5344 (2)	9283 (2)	3267 (1)
S(5)	4643 (2)	8096 (2)	3998 (1)
S(6)	3323 (2)	6148 (2)	1774 (1)
S(7)	6896 (2)	5892 (3)	1613 (1)
S(8a)	7849 (3)	4091 (4)	1707 (2)
S(8b)	6829 (15)	4441 (12)	1215 (6)
S(9a)	6398 (4)	3245 (3)	1975 (2)
S(9b)	7337 (13)	3572 (18)	2050 (7)
S(10)	5771 (2)	3976 (2)	2724 (1)
As(1)	1274 (1)	986 (1)	867 (1)
C(11)	183 (6)	−38 (6)	1338 (3)
C(12)	374 (6)	−1207 (6)	1289 (3)
C(13)	−436 (8)	−1915 (7)	1654 (4)
C(14)	−1378 (7)	−1475 (7)	2043 (4)
C(15)	−1588 (7)	−299 (8)	2076 (3)
C(16)	−793 (7)	442 (7)	1738 (3)
C(21)	263 (6)	2235 (5)	288 (3)
C(22)	−1047 (7)	2254 (6)	223 (3)
C(23)	−1760 (7)	3181 (7)	−199 (4)
C(24)	−1181 (8)	4071 (7)	−549 (4)
C(25)	126 (8)	4031 (6)	−491 (4)
C(26)	860 (7)	3120 (6)	−70 (3)
C(31)	2015 (6)	1746 (5)	1402 (3)
C(32)	1258 (8)	2783 (6)	1535 (4)
C(33)	1753 (10)	3359 (7)	1940 (4)
C(34)	2971 (12)	2878 (9)	2173 (4)
C(35)	3686 (10)	1876 (9)	2054 (5)
C(36)	3204 (8)	1280 (7)	1655 (4)
C(41)	2559 (6)	84 (6)	411 (3)
C(42)	2653 (6)	383 (6)	−238 (3)
C(43)	3573 (7)	−280 (7)	−560 (4)
C(44)	4414 (7)	−1261 (7)	−249 (4)
C(45)	4345 (6)	−1565 (6)	403 (3)
C(46)	3420 (6)	−907 (6)	733 (3)
As(2)	286 (1)	2174 (1)	5583 (1)
C(51)	539 (6)	3140 (5)	6134 (3)
C(52)	1689 (7)	3538 (7)	6114 (3)
C(53)	1872 (7)	4244 (7)	6519 (4)
C(54)	874 (8)	4555 (7)	6937 (4)
C(55)	−307 (8)	4164 (6)	6966 (3)
C(56)	−468 (7)	3468 (6)	6567 (3)
C(61)	264 (6)	600 (6)	6054 (3)
C(62)	1341 (7)	−32 (7)	6380 (3)
C(63)	1338 (10)	−1160 (7)	6734 (4)
C(64)	217 (11)	−1633 (7)	6764 (4)
C(65)	−862 (9)	−993 (7)	6449 (4)
C(66)	−869 (7)	121 (6)	6090 (3)
C(71)	−1317 (6)	2819 (6)	5162 (3)
C(72)	−1647 (7)	2231 (7)	4730 (4)
C(73)	−2798 (8)	2660 (8)	4424 (4)
C(74)	−3592 (7)	3684 (8)	4523 (4)
C(75)	−3251 (7)	4272 (7)	4943 (4)
C(76)	−2109 (6)	3842 (6)	5260 (3)
C(81)	1670 (6)	2156 (6)	4954 (3)
C(82)	2642 (7)	1155 (7)	4944 (4)
C(83)	3620 (7)	1219 (9)	4474 (4)
C(84)	3625 (8)	2259 (9)	4036 (4)
C(85)	2662 (9)	3197 (8)	4037 (4)
C(86)	1680 (8)	3173 (7)	4495 (4)
C(1*S*)[b]	4623 (18)	4492 (15)	295 (6)
C(2*S*)[b]	5573	5186	394
N(1*S*)[b]	3879	3949	217

[a] Estimated standard deviations in the last place of figures are given in parentheses. [b] S = solvent.

Results and Discussion

The dimensions obtained for the $[AsPh_4]^+$ cation (Table II) do not differ significantly from the corresponding details re-

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Table II

	Bond Lengths (Å)		
Mo(1)–S(1)	2.351 (2)	Mo(2)–S(1)	2.289 (2)
Mo(1)–S(2)	2.332 (2)	Mo(2)–S(2)	2.303 (2)
Mo(1)–S(6)	2.112 (2)	Mo(2)–S(3)	2.108 (2)
Mo(1)–S(7)	2.403 (3)	Mo(2)–S(4)	2.394 (3)
Mo(1)–S(10)	2.409 (2)	Mo(2)–S(5)	2.395 (3)
S(4)–S(5)	2.071 (3)	S(7)–S(8a)	2.115 (5)
S(8a)–S(9a)	1.970 (6)	S(9a)–S(10)	2.019 (5)
S(7)–S(8b)	2.096 (16)	S(8b)–S(9b)	1.936 (19)
S(9b)–S(10)	2.169 (14)	Mo(1)· · ·Mo(2)	2.837 (1)
As(1)–C(11)	1.912 (6)	As(2)–C(51)	1.896 (7)
As(1)–C(21)	1.900 (6)	As(2)–C(61)	1.910 (6)
As(1)–C(31)	1.915 (8)	As(2)–C(71)	1.910 (6)
As(1)–C(41)	1.896 (6)	As(2)–C(81)	1.919 (6)
C(11)–C(12)	1.373 (10)	C(51)–C(52)	1.377 (10)
C(11)–C(16)	1.404 (9)	C(51)–C(56)	1.412 (9)
C(12)–C(13)	1.394 (11)	C(52)–C(53)	1.390 (13)
C(13)–C(14)	1.348 (11)	C(53)–C(54)	1.378 (11)
C(14)–C(15)	1.371 (13)	C(54)–C(55)	1.401 (13)
C(15)–C(16)	1.385 (11)	C(55)–C(56)	1.362 (12)
C(21)–C(22)	1.388 (10)	C(61)–C(62)	1.369 (9)
C(21)–C(26)	1.385 (10)	C(61)–C(66)	1.407 (11)
C(22)–C(23)	1.385 (9)	C(62)–C(63)	1.379 (11)
C(23)–C(24)	1.372 (11)	C(63)–C(64)	1.393 (16)
C(24)–C(25)	1.376 (13)	C(64)–C(65)	1.363 (13)
C(25)–C(26)	1.384 (9)	C(65)–C(66)	1.368 (10)
C(31)–C(32)	1.385 (10)	C(71)–C(72)	1.390 (12)
C(31)–C(36)	1.361 (10)	C(71)–C(76)	1.361 (9)
C(32)–C(33)	1.414 (14)	C(72)–C(73)	1.373 (11)
C(33)–C(34)	1.372 (15)	C(73)–C(74)	1.362 (12)
C(34)–C(35)	1.325 (14)	C(74)–C(75)	1.376 (14)
C(35)–C(36)	1.413 (15)	C(75)–C(76)	1.375 (10)
C(41)–C(42)	1.384 (9)	C(81)–C(82)	1.389 (9)
C(41)–C(46)	1.400 (8)	C(81)–C(86)	1.380 (9)
C(42)–C(43)	1.363 (10)	C(82)–C(83)	1.394 (11)
C(43)–C(44)	1.374 (9)	C(83)–C(84)	1.375 (13)
C(44)–C(45)	1.389 (11)	C(84)–C(85)	1.331 (12)
C(45)–C(46)	1.372 (10)	C(85)–C(86)	1.378 (12)
	Bond Angles (Deg)		
S(1)–Mo(1)–S(2)	100.7 (1)	S(1)–Mo(2)–S(2)	103.4 (1)
S(1)–Mo(1)–S(6)	107.6 (1)	S(1)–Mo(2)–S(3)	106.4 (1)
S(2)–Mo(1)–S(6)	107.5 (1)	S(2)–Mo(2)–S(3)	108.3 (1)
S(1)–Mo(1)–S(7)	74.4 (1)	S(1)–Mo(2)–S(4)	90.9 (1)
S(2)–Mo(1)–S(7)	142.4 (1)	S(2)–Mo(2)–S(4)	132.5 (1)
S(1)–Mo(1)–S(10)	144.4 (1)	S(1)–Mo(2)–S(5)	133.5 (1)
S(2)–Mo(1)–S(10)	78.2 (1)	S(2)–Mo(2)–S(5)	89.4 (1)
S(6)–Mo(1)–S(7)	109.5 (1)	S(3)–Mo(2)–S(4)	110.5 (1)
S(6)–Mo(1)–S(10)	106.5 (1)	S(3)–Mo(2)–S(5)	111.6 (1)
S(7)–Mo(1)–S(10)	85.1 (1)	S(4)–Mo(2)–S(5)	51.2 (1)
Mo(1)–S(1)–Mo(2)	75.4 (1)	Mo(1)–S(2)–Mo(2)	75.5 (1)
Mo(2)–S(4)–S(5)	64.4 (1)	Mo(2)–S(5)–S(4)	64.4 (1)
Mo(1)–S(7)–S(8a)	110.5 (2)	Mo(1)–S(7)–S(8b)	104.0 (4)
Mo(1)–S(10)–S(9a)	105.0 (1)	Mo(1)–S(10)–S(9b)	100.3 (5)
S(7)–S(8a)–S(9a)	102.1 (2)	S(7)–S(8b)–S(9b)	81.5 (9)
S(8a)–S(9a)–S(10)	97.1 (3)	S(8b)–S(9b)–S(10)	109.7 (8)
C(11)–As(1)–C(21)	109.9 (3)	C(51)–As(2)–C(61)	109.2 (3)
C(11)–As(1)–C(31)	111.1 (3)	C(51)–As(2)–C(71)	110.3 (3)
C(21)–As(1)–C(31)	105.9 (3)	C(61)–As(2)–C(71)	110.0 (3)
C(11)–As(1)–C(41)	108.5 (3)	C(51)–As(2)–C(81)	109.2 (3)
C(21)–As(1)–C(41)	108.8 (3)	C(61)–As(2)–C(81)	110.6 (3)
C(31)–As(1)–C(41)	112.6 (3)	C(71)–As(2)–C(81)	107.6 (3)
As(1)–C(11)–C(12)	120.5 (5)	As(2)–C(51)–C(52)	120.9 (5)
As(1)–C(11)–C(16)	117.7 (5)	As(2)–C(51)–C(56)	119.8 (5)
C(12)–C(11)–C(16)	121.7 (6)	C(52)–C(51)–C(56)	119.3 (7)
C(11)–C(12)–C(13)	117.8 (6)	C(51)–C(52)–C(53)	120.7 (7)
C(12)–C(13)–C(14)	121.5 (8)	C(52)–C(53)–C(54)	118.9 (8)
C(13)–C(14)–C(15)	120.3 (8)	C(53)–C(54)–C(55)	121.5 (8)
C(14)–C(15)–C(16)	120.9 (7)	C(54)–C(55)–C(56)	118.8 (7)
C(11)–C(16)–C(15)	117.6 (7)	C(51)–C(56)–C(55)	120.8 (7)
As(1)–C(21)–C(22)	120.5 (5)	As(2)–C(61)–C(62)	119.2 (6)
As(1)–C(21)–C(26)	118.8 (5)	As(2)–C(61)–C(66)	120.2 (4)
C(22)–C(21)–C(26)	120.7 (6)	C(62)–C(61)–C(66)	120.5 (6)
C(21)–C(22)–C(23)	119.1 (6)	C(61)–C(62)–C(63)	120.2 (8)
C(22)–C(23)–C(24)	120.6 (7)	C(62)–C(63)–C(64)	119.0 (8)
C(23)–C(24)–C(25)	119.9 (7)	C(63)–C(64)–C(65)	120.7 (8)
C(24)–C(25)–C(26)	120.8 (7)	C(64)–C(65)–C(66)	121.0 (9)
C(21)–C(26)–C(25)	118.9 (7)	C(61)–C(66)–C(65)	118.6 (7)
As(1)–C(31)–C(32)	116.5 (5)	As(2)–C(71)–C(72)	118.0 (5)
As(1)–C(31)–C(36)	122.2 (6)	As(2)–C(71)–C(76)	122.0 (6)
C(32)–C(31)–C(36)	121.2 (8)	C(72)–C(71)–C(76)	119.9 (6)
C(31)–C(32)–C(33)	118.5 (7)	C(71)–C(72)–C(73)	119.7 (7)
C(32)–C(33)–C(34)	118.5 (8)	C(72)–C(73)–C(74)	120.3 (9)
C(33)–C(34)–C(35)	123.0 (11)	C(73)–C(74)–C(75)	119.7 (7)
C(34)–C(35)–C(36)	119.3 (10)	C(74)–C(75)–C(76)	120.5 (7)
C(31)–C(36)–C(35)	119.4 (8)	C(71)–C(76)–C(75)	119.8 (8)
As(1)–C(41)–C(42)	120.9 (4)	As(2)–C(81)–C(82)	122.2 (5)
As(1)–C(41)–C(46)	119.9 (5)	As(2)–C(81)–C(86)	118.3 (5)
C(42)–C(41)–C(46)	119.2 (6)	C(82)–C(81)–C(86)	119.5 (6)
C(41)–C(42)–C(43)	120.4 (6)	C(81)–C(82)–C(83)	118.6 (7)
C(42)–C(43)–C(44)	120.8 (7)	C(82)–C(83)–C(84)	120.4 (8)
C(43)–C(44)–C(45)	119.6 (7)	C(83)–C(84)–C(85)	120.3 (8)
C(44)–C(45)–C(46)	120.1 (6)	C(84)–C(85)–C(86)	121.1 (7)
C(41)–C(46)–C(45)	119.9 (6)	C(81)–C(86)–C(85)	120.0 (7)

Table III. Equations of Planes through Atomic Positions, in the Form $ax + by + cz = d$ (Crystal Coordinates)

plane	atoms	*a*	*b*	*c*	*d*
1	Mo(1), S(1), S(2)	9.3520	−1.9311	5.7686	4.8057
2	Mo(2), S(1), S(2)	8.9969	2.5638	12.5798	9.5846
3	Mo(2), S(4), S(5)	7.8463	−5.7883	−1.8733	−1.7919
4	Mo(1), S(7), S(10)	6.5739	6.1088	17.1918	10.9058

planes	dihedral angle, deg	planes	dihedral angle, deg
2–3	52.2	1–2	26.8
1–4	53.0		

atom	dev from plane 4, Å	atom	dev from plane 4, Å
S(8a)	0.312 (5)	S(9a)	1.322 (5)
S(8b)	1.615 (16)	S(9b)	0.377 (18)

ported for this species in other crystallographic studies of a similar precision.[33]

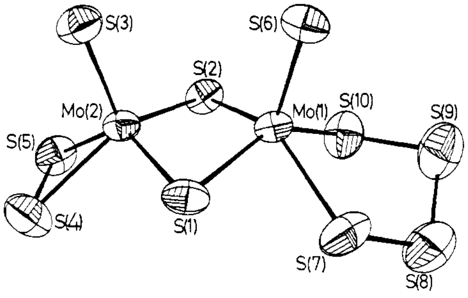

Figure 1. Atomic arrangement within the $[Mo_2S_{10}]^{2-}$ anion.

The atomic arrangement within the $[Mo_2S_{10}]^{2-}$ anion is shown in Figure 1. This represents a rare example of a discrete complex in which molybdenum is coordinated exclusively by sulfur *atoms*; i.e., *none* of the latter are bound to organic or other groups. Each metal atom of this anion is bonded to one terminal sulfido and two μ-sulfido groups; the fourth and fifth coordination sites of Mo(2) are occupied by the sulfur atoms of a bidentate persulfido group while the corresponding sites of Mo(1) are occupied by two sulfur atoms of a bidentate tetrasulfido group. Each metal atom of this anion is considered to be in the +V oxidation state on the basis of the ionic formulation $[(Mo^{5+})_2(S^{2-})_4(S_2^{2-})(S_4^{2-})]^{2-}$.

The central portion of $[Mo_2S_{10}]^{2-}$ (i.e., omitting S(8) and S(9)) has a structure which resembles that observed for the majority of complexes known to contain $\{Mo_2(X)_2(\mu\text{-}Y)_2\}$ (X, Y = O or S) units[2,22-24] and can be considered to consist of

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Table IV. Structural Parameters[a] of the $\{(S,S)Mo^V(S)(\mu\text{-}S)_2(S)Mo^V(S,S)\}$ Portion of Selected Complexes

parameter[b]	syn-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$	$[Mo_2S_4(S_2CNEt_2)_2]$	$[Mo_2S_{10}]^{2-}$		
Mo–Mo, Å	2.863 (2)	2.814 (1)	2.837 (1)		
Mo–S_t, Å	2.100 (12)	2.092 (2)	2.110 (2)		
Mo–S_b, Å	2.320 (3)	2.309 (11)	2.32 (3)	2.296 (7)[g]	2.341 (10)[h]
Mo–S, Å	2.406 (3)	2.453 (6)	2.400 (9)	2.395 (3)[g]	2.406 (3)[h]
S_b–S_b, Å	3.550 (4)	3.570 (2)	3.605 (3)		
Mo–S_b–Mo, deg	76.22 (6)	75.1 (1)	75.5 (1)		
S_b–Mo–S_b, deg	99.9 (1)	101.3 (1)	102.1 (1.4)	103.4 (1)[g]	100.7 (1)[h]
Mo–Mo–S_t, deg	103.9 (1.5)	104.8 (5)	105.1 (1)	105.0 (1)[g]	105.2 (1)[h]
dihedral angle,[c] deg	146.9 (1)	147.9 (1)	153.2 (2)		
Mo displacement,[d] Å	0.72	0.72	0.74 (2)	0.75[g]	0.72[h]
ref	*e*	*f*	*i*		

[a] Value in parentheses represents the esd if a single value or the maximum deviation from the mean if more than one value, with reference to the last significant figure(s). [b] S_t = terminal sulfido group; S_b = bridging sulfido group; S = sulfur atom cis to S_t and trans to S_b. [c] Between $Mo(S_b)_2$ planes; 180° minus that in ref 23. [d] Above the S_b,S_b,S,S plane. [e] Reference 23. [f] Reference 24. [g] Persulfido side of the complex. [h] Tetrasulfido side of the complex. [i] Average value; this work.

two square-pyramidal MoS_5 units, in the syn[23] conformation, linked by edge sharing (over S(1) and S(2)). Mo(2) is 0.75 Å above the pyramidal base of the bridging atoms and the persulfide atoms S(4) and S(5), and Mo(1) is 0.72 Å above the pyramidal base of the bridging atoms and the S(7) and S(10) of the tetrasulfido group. As with other complexes of this type,[2,22-24] the molybdenum atom is situated slightly (ca. 0.15 Å) above the center of gravity of the five ligand donor atoms. Enemark et al.[22-24] have provided a comprehensive documentation of the structural parameters obtained in crystallographic characterizations of complexes containing $\{Mo^V(\mu\text{–}S)_2Mo^V\}$ moieties; Table IV provides a comparison between the values of these parameters for $[Mo_2S_{10}]^{2-}$ and two other complexes, $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$[23] and $[Mo_2S_4(S_2CNEt_2)_2]$,[24] containing a syn $\{(S,S)Mo^V(S)(\mu\text{-}S)_2(S)Mo^V(S,S)\}$ arrangement. It is seen that there is good agreement between the values of the majority of these parameters for all three complexes; the principal difference for $[Mo_2S_{10}]^{2-}$ is that the bridging region is slightly asymmetric, doubtless because of the different environments of Mo(1) and Mo(2). The Mo(1)–S_b bonds (average length 2.341 Å) are significantly longer than the Mo(2)–S_b bonds (average length 2.296 Å); the S_b–Mo(1)–S_b interbond angle (103.4 (1)°) is significantly larger than the S_b–Mo(2)–S_b interbond angle (100.7 (1)°). However, the average values of these parameters, in particular that of $\overline{\text{Mo–S}_b}$, agree well with the corresponding values for *syn*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ and $[Mo_2S_4(S_2CNEt_2)_2]$.[24] Similarities also extend to the average distance of the S---S "nonbonded" contacts about the molybdenum atoms in these three dimers. For *syn*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ and $[Mo_2S_4(S_2CNEt_2)_2]$ the sides of the S_5 square pyramids are of length 3.537–3.674 Å (*average 3.61* Å) and 3.568–3.669 Å (*average 3.61* Å), respectively; the lengths of the edges of the base of these pyramids are 2.960–3.546 Å (*average 3.17* Å) and 2.844–3.570 Å (*average 3.18* Å), respectively. For $[Mo_2S_{10}]^{2-}$, the lengths of the sides are 3.587–3.691 Å (*average 3.63* Å) and 3.521–3.727 Å (*average 3.63* Å), for the S_5 pyramids about Mo(1) and Mo(2), respectively; the corresponding lengths for the edges of the bases are 2.873–3.605 Å (*average 3.18* Å) and 2.071–3.605 Å (*average 3.08* Å). Thus, despite the very different sulfur-donor ligands involved in these three molybdenum(V) dimers and the wide variation in the length of the S---S contacts, particularly for the edges of the pyramidal base, the average external dimensions of each S_5 pyramid are remarkably invariant. The magnitude of these external dimensions appear to be determined by the Mo–S bond lengths plus the consideration that the S---S contacts corresponding to the side of the pyramid (i.e., those involving the terminal sulfur atom) be near the van der Waals distance (ca. 3.7 Å)[34] for two sulfur atoms. The latter criterion holds despite some remarkably short S---S nonbonded contacts (between S_b and S of the chelating ligand) at the base of the pyramid. Given the previous comments, it follows that these S_b---S contacts will decrease as the bite (S---S) of the chelate increases: $[Mo_2S_{10}]^{2-}$, persulfide portion, S---S = 2.071 (3) Å, S_b---S = 3.32 Å; $[Mo_2S_4(S_2CNEt_2)_2]$, S---S = 2.844 (6) Å, S_b---S = 3.16 (2) Å; *syn*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$, S---S = 3.125 (4) Å, S_b---S = 3.00 (3) Å; $[Mo_2S_{10}]^{2-}$, tetrasulfide portion, S---S = 3.253 (3) Å, S_b---S = 2.93 (6) Å. As has been noted earlier,[35,36] S---S contacts of ca. 3 Å are sufficiently close for the occurrence of a bonding interaction which may lead to the stabilization of a particular structure. However, in the systems discussed above, the short S---S nonbonded contacts appear to arise as a consequence of other attractive and repulsive influences, rather than as factor which influences the structure in its own right.

The length of the terminal sulfido–molybdenum (Mo–S_t) bond is of interest, in view of earlier discussion[24,37] in this respect. The value obtained here, 2.110 (2) Å, agrees well with those reported by Enemark et al.,[22-24] and, therefore, this appears to be the typical Mo–S_t bond length in $\{Mo_2S_4(S,S)_2\}$ complexes.

The dimensions of the bidentate persulfido–molybdenum group, with Mo–S = 2.395 (3) Å, S–S = 2.071 (3) Å, and S–Mo–S = 51.2 (1)°, are in good agreement with the dimensions reported by Müller et al.[12-18] for this moiety in other complexes.

The arrangement of the tetrasulfido group is not symmetrical. In the major component of the disorder, one of the two central sulfur atoms, S(8a), is 0.31 (1) Å above (i.e., toward S(6)) the plane of the Mo(1), S(7), and S(10) atoms while the other such atom, S(9a), is 1.32 (1) Å above this plane. The length of the central sulfur bond (1.970 (6) Å) is appreciably shorter than that for the other two S–S bonds of this group. Also, the S(9a)–S(10) bond (2.018 (3) Å) is significantly shorter than the S(8a)–S(7) bond (2.116 (5) Å) and the interbond angles subtended at these central sulfur atoms also differ, with S(8a)–S(9a)–S(10) and S(7)–S(8a)–S(9a) having values of 97.1 (3) and 102.1 (2)°, respectively. In the minor component of the disordered tetrasulfido group, the displacements of the atoms S(8b) and S(9b) from the Mo(1), S(9), S(10) plane are the reverse of their *a* counterparts. However, a similar, though less precisely defined, pattern in the relative magnitudes of the S–S bond lengths and S–S–S

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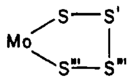
Table V. Dimensions (Å, deg) within Molybdenum Tetrasulfide Moieties



	$[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN$[c]		$[(\eta^5\text{-}C_5H_5)_2\text{-}MoS_4]$[d]
	a	*b*	
Mo-S	2.409 (2)		2.455
Mo-S'''	2.403 (3)		2.451
S-S'	2.019 (5)	2.169 (14)	2.085
S'''-S''	2.115 (5)	2.096 (16)	2.081
S'-S''	1.970 (6)	1.936 (19)	2.018
S-Mo-S'''	85.1 (1)		88.2
Mo-S-S'	105.0 (1)	100.3 (5)	108.4
Mo-S'''-S''	110.5 (2)	104.0 (4)	108.8
S-S'-S''	92.1 (3)	109.7 (8)	99.9
S'''-S''-S'	102.1 (2)	81.5 (9)	100.8
dist from MoS'S''' plane S'	1.322 (5)	0.377 (18)	−0.65
dist from MoS'S''' plane S''	0.312 (5)	1.615 (16)	0.53

[a] Major component of disorder. [b] Minor component of disorder. [c] This work. [d] Reference 29.

interbond angles is observed. The dimensions of these tetrasulfido groups are listed in Table V, which contains a comparison with the corresponding details for $[(\eta^5\text{-}C_5H_5)_2MoS_4]$.[29] The conformation of the tetrasulfido group characterized here differs from that identified for $[(\eta^5\text{-}C_5H_5)_2MoS_4]$ and its tungsten analogue.[38] Thus, for $[(\eta^5\text{-}C_5H_5)_2MoS_4]$, the central sulfur atoms lie at approximately equal distances (0.53 and 0.65 Å) from, and on opposite sides of, the plane containing the molybdenum and two coordinated sulfur atoms. Nevertheless, the pattern that the central S-S bond is shorter than the other two S-S bonds is also manifest for both of these $[(\eta^5\text{-}C_5H_5)_2MoS_4]$ molecules, albeit to a smaller extent than in $[Mo_2S_{10}]^{2-}$.

The mechanism for the formation of $[Mo_2S_{10}]^{2-}$, from the reaction between $[Mo_2S_{12}]^{2-}$ and PhSNa (1:16) described in the Experimental Section, presumably involves the abstraction by the benzenethiolate of sulfur atoms from some of the persulfido groups of the initial complex, with some subsequent insertion of two sulfur atoms into one of the remaining terminal persulfido groups. However, why the particular complex should be formed is not clear.

Conclusions

The complex $[Mo_2S_{10}]^{2-}$, which contains terminal sulfido, bridging sulfido, persulfido, and tetrasulfido groups has been isolated and characterized by X-ray crystallography; the respective Mo-S bond lengths are 2.110 (2), 2.32 (2), 2.395 (3), and 2.406 (3) Å.

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Registry No. $[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN$, 76550-05-5; $[NH_4]_2[Mo_2S_{12}]$, 68417-00-5.

Supplementary Material Available: Tables of thermal parameters and structure factors (43 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Low-Temperature Crystal Spectra of Dicesium Dichlorotetraaquochromium(III) Chloride

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$Cs_2CrCl_5\cdot 4H_2O$ has been found by X-ray diffraction to belong to the monoclinic space group $C2/m$ with $a = 17.604$ Å, $b = 6.140$ Å, $c = 6.979$ Å, $\beta = 106.04°$, and $Z = 2$. The compound contains *trans*-$[CrCl_2(H_2O)_4]^+$ groups. The principal bond lengths are as follows: Cr-Cl, 2.302; Cr-O, 1.925; O-H···Cl, 3.006 and 3.062 Å. The latter values indicate strong hydrogen bonding in the crystal. The bands at 16.63, 21.76, 23.04, and 35.13×10^3 cm^{-1} in the polarized crystal spectra have been assigned to spin-allowed transitions. Since the chromophore has almost exact D_{4h} symmetry, selection rules of this group have been used to label the transitions. The decrease of the band areas on cooling indicates that vibronic coupling is the principal source of band intensity. Two extensive sets of sharp, weak bands starting at 14.43×10^3 and 20.69×10^3 cm^{-1} are assigned as spin-forbidden transitions to states originating from octahedral $^2E_g + {}^2T_{1g}$ and $^2T_{2g}$, respectively. A σ-polarized band at 19.70×10^3 cm^{-1} is due to coupling of ν(O-H) to a component of the lowest spin-allowed band; upon deuteration of the compound the band shifts to lower energy by the expected amount. An iron(III) impurity causes the appearance of bands at 28.18×10^3 cm^{-1} (π) and 31.01×10^3 cm^{-1} (σ). The former is most probably a Cl → Fe charge-transfer band of the *trans*-$[FeCl_2(H_2O)_4]^+$ group; the latter has not been assigned.

Introduction

A large number of halo-aquo complexes of the first-row transition metals are known, and the crystal structures of many have been determined by X-ray diffraction.[2] A significant number of these contain the *trans*-$[MX_2(H_2O)_4]^{n+}$ chromophore, among which are $CrCl_3\cdot 6H_2O$ (green isomer),[3] $MCl_3\cdot 6H_2O$ (M = Ti, V, Fe),[4] $VBr_3\cdot 6H_2O$,[4] $CoCl_2\cdot 6H_2O$,[5] $NiCl_2\cdot 6H_2O$,[6] and $FeCl_2\cdot 4H_2O$.[7] Although these compounds show varying degrees of deviation from tetragonal symmetry, they provide a rather extensive series of chromophores of approximate D_{4h} symmetry. In cases where single crystals of

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