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$(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2]\cdot 2H_2O$, a Novel Sulfur-Rich Coordination Compound with Two Nonequivalent Complex Anions Having the Same Point Group but Different Structures: Crystal and Molecular Structures

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Disulfur complexes[2] have been obtained mainly only accidentally. A compound containing only S_2 groups as ligands was not known up to now. S_2 complexes and clusters are interesting because of their bioinorganic relevance. Also from the structural point of view the chemistry of S_2 coordination compounds is fascinating as there is no other ligand so versatile in its mode of coordination.[3] Despite the above-mentioned aspects our knowledge of S_2 as a ligand is very limited.[4] A compound containing only S_2 groups as ligands is of interest as a S_2 generator. In this paper the molecular and crystal structure of $(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$ will be reported.

Experimental Section

$(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$ was prepared with the method described in ref 5.

X-ray Structure Determination. The molecular structure of the $[Mo_2(S_2)_6]^{2-}$ ion was determined from a single-crystal X-ray structure analysis. A summary of crystal data and details on the intensity collection are given in Table I. The space group was uniquely determined from systematic extinctions; the unit cell parameters were obtained from least-squares refinement of the diffractometer coordinates of 15 high-angle reflections. Intensity data were collected on a Syntex P2$_1$ four-circle diffractometer. As it was not possible to obtain larger single crystals, a relatively large portion of the reflections measured (36%, see Table I) were below the significant level. No absorption correction was made, the minimum and maximum transmission factors being 0.87 and 0.94.

The structure was solved with Patterson methods; after initial location of the Mo atoms, the lighter atoms were obtained from subsequent ΔF syntheses. Full-matrix least-squares refinement with isotropic thermal parameters for all nonhydrogen atoms gave residuals of $R_1 = 0.088$ and $R_2 = 0.079$ for the 1854 significant reflections, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. With anisotropic temperature factors final residuals were obtained: $R_1 = 0.054$ and $R_2 = 0.052$, the final standard deviation of an observation of unit weight being 1.70 e. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics. The atomic scattering factors for Mo, S, O, and N were taken from ref 6. The final ΔF map contained no significant peaks; hydrogen atom positions could not be determined uniquely.[7]

A partial disorder at the sites of the ammonium ions and the water molecules had to be assumed in order to avoid direct NH_4^+–NH_4^+ contacts. Variation of the occupancy factors for the four light-atom sites suggested, to a first approximation, the model of two ordered and two 1:1 disordered positions; this model resulted also in a reasonable equalization of the temperature factors. The final positional and thermal parameters are given in Table II. A list of observed and calculated structure factors is available.[8]

Table I. Summary of Crystal Data and Intensity Collection

formula	$(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$
fw	648.76
a	21.614 (4) Å
b	13.127 (3) Å
c	12.576 (3) Å
V	3568 Å^3
Z	8
density	2.415 g/cm^3 (calcd), 2.41 (1) g/cm^3 (exptl)
space group	$Pnna$-D_{2h}^6
systematic absences	$0kl$, $k + l = 2n$; $h0l$, $h + l = 2n$; $hk0$, $h = 2n$
cryst size	0.18 × 0.04 × 0.06 mm
radiation	Mo Kα; λ(Kα_1) 0.709 26 Å, λ(Kα_2) 0.713 54 Å; graphite monochromator
abs coeff	25.5 cm^{-1}
data collectn	takeoff angle 5°; 2θ scan speed 2–20°/min depending on intensity, θ–2θ mode, bkgd:scan time ratio 1:1, scan from 1.0° below Kα_1 to 1.0° above Kα_2 in 2θ; reference reflctn every 50 reflctns
no. of reflctns	2893 in the range $(\sin\theta)/\lambda \leq 0.58$ Å^{-1} 1854 of which with $I > 2\sigma(I)$ (one octant)

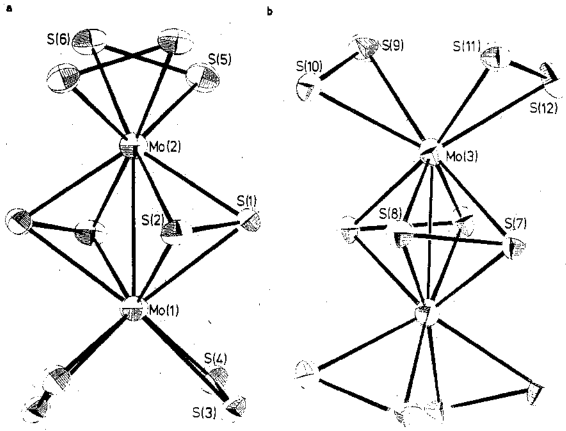

Figure 1. The two crystallographically independent $[Mo_2(S_2)_6]^{2-}$ ions in the title compound with the twofold axis (a) in the direction of the Mo–Mo bond or (b) in the direction perpendicular to it (approximately along S(7)···S(8)); 50% probability ellipsoids are drawn.

Results and Discussion

The crystal structure contains discrete dimeric $[Mo_2(S_2)_6]^{2-}$ ions besides NH_4^+ cations and two hydrate water molecules per formula unit. A remarkable result of the crystal structure is the existence of two independent anions in the asymmetric unit, both with exact C_2 symmetry. The first has its twofold axis along Mo(1)–Mo(2) (parallel to crystallographic *c*); in the second case it is perpendicular to Mo(3)–Mo(3)^{II} (parallel to crystallographic *a*). Figure 1 shows the two different $[Mo_2(S_2)_6]^{2-}$ anions with atom designation. In Table III bond lengths and bond angles are given.

In the novel dimeric ion, each Mo(V) is coordinated "side on" by four S_2^{2-} groups in a distorted dodecahedral arrangement, two of which are bridging and two of which are terminal. There is no significant difference in the mean Mo–S bond lengths between bridging and terminal groups (Mo–S 2.444 vs. 2.459 Å). The coordination of the S_2^{2-} groups to Mo is asymmetric, especially in the bridge bonds (mean values of the "short" and "long" Mo–S bonds 2.391 and 2.497 Å, re-

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(1) (a) University of Bielefeld. (b) University of Münster.
(2) In the text they are often noted as disulfur complexes in agreement with the notation of dioxygen complexes, though it is chemically more reasonable to define the known ones as S_2^{2-} complexes (see ref 3).
(3) A. Müller and W. Jaegermann, *Inorg. Chem.*, **18**, 2631 (1979).
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(6) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 99 ff.
(7) In addition to local programs for the IBM 360/158 and Data General Nova 1200 computers, programs of the Syntex XTL system and C. Johnson's ORTEP were employed.
(8) Supplementary material.

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Table II. Atomic Coordinates and Thermal Parameters (Å^2) for $(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O^a$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.25	0.5	0.03111 (12)	1.81 (7)	2.11 (8)	1.59 (7)	−0.14 (7)	0	0
Mo(2)	0.25	0.5	−0.19373 (11)	1.39 (6)	2.04 (8)	1.79 (7)	−0.07 (6)	0	0
Mo(3)	0.00585 (5)	0.24308 (9)	0.13789 (8)	1.55 (4)	2.32 (5)	2.04 (4)	−0.09 (6)	0.11 (5)	0.15 (5)
S(1)	0.2155 (2)	0.3596 (3)	−0.0894 (3)	2.09 (15)	1.98 (16)	1.71 (14)	−0.36 (14)	−0.11 (14)	0.22 (15)
S(2)	0.1583 (1)	0.4821 (3)	−0.0731 (3)	1.34 (13)	2.83 (19)	1.58 (13)	−0.27 (13)	0.02 (13)	0.20 (15)
S(3)	0.2141 (1)	0.3813 (3)	0.1710 (2)	2.50 (16)	2.39 (17)	1.77 (15)	−0.75 (15)	0.44 (13)	0.40 (14)
S(4)	0.3054 (2)	0.3683 (3)	0.1299 (3)	2.33 (16)	1.97 (17)	2.19 (16)	0.36 (14)	−0.44 (14)	0.17 (15)
S(5)	0.3152 (1)	0.3768 (3)	−0.2870 (2)	2.14 (15)	2.64 (18)	2.11 (15)	0.35 (15)	0.18 (12)	−0.37 (14)
S(6)	0.3265 (1)	0.5243 (3)	−0.3371 (3)	1.24 (13)	3.24 (20)	1.71 (14)	0.05 (14)	0.26 (12)	0.22 (14)
S(7)	0.0548 (1)	0.1213 (3)	0.2654 (3)	1.57 (13)	1.94 (16)	2.39 (18)	0.39 (13)	−0.12 (13)	−0.10 (15)
S(8)	−0.0397 (1)	0.1185 (3)	0.2526 (3)	1.66 (13)	1.71 (15)	1.90 (14)	−0.49 (12)	−0.07 (15)	−0.05 (16)
S(9)	−0.0316 (2)	0.3563 (3)	−0.0062 (3)	3.11 (18)	2.89 (20)	2.08 (16)	0.70 (16)	0.49 (15)	0.82 (16)
S(10)	−0.0947 (1)	0.2520 (3)	0.0495 (3)	1.50 (13)	4.51 (20)	2.10 (16)	0.13 (18)	−0.21 (13)	0.17 (17)
S(11)	0.0373 (1)	0.1161 (3)	0.0043 (3)	2.41 (16)	2.39 (18)	2.16 (16)	0.01 (16)	0.01 (14)	−0.71 (16)
S(12)	0.1020 (1)	0.2254 (3)	0.0359 (3)	1.63 (14)	2.60 (19)	3.26 (18)	−0.13 (14)	1.07 (14)	0.03 (16)
O(1)	0.1610 (4)	−0.0053 (7)	0.1246 (6)	3.05 (38)	2.96 (44)	2.89 (34)	1.14 (35)	0.57 (32)	−0.06 (42)
N(1)	0.2594 (4)	0.1523 (7)	0.0341 (7)	2.48 (49)	1.88 (45)	2.46 (42)	0.74 (42)	−0.40 (42)	−0.10 (39)
O,N(1)	0.4317 (4)	0.1574 (7)	0.1955 (7)	2.48 (41)	3.88 (50)	2.83 (43)	−0.13 (40)	0.30 (41)	0.20 (43)
O,N(2)	0.5551 (4)	0.3507 (8)	0.2237 (7)	2.55 (42)	4.01 (54)	2.93 (52)	−0.36 (41)	−0.11 (39)	1.01 (41)

[a] The anisotropic temperature factor used is defined as $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Bond Lengths (Å) and Bond Angles (Deg) in the Two $[Mo_2(S_2)_6]^{2-}$ Ions of the Asymmetric Unit^a

Mo(1)–S(1)	2.499 (4)	(2×)	Mo(3)–S(7)	2.499 (4)
Mo(1)–S(2)	2.388 (3)	(2×)	Mo(3)–S(7)^{II}	2.401 (4)
Mo(1)–S(3)	2.475 (4)	(2×)	Mo(3)–S(8)	2.393 (4)
Mo(1)–S(4)	2.443 (4)	(2×)	Mo(3)–S(8)^{II}	2.483 (4)
Mo(2)–S(1)	2.382 (4)	(2×)	Mo(3)–S(9)	2.480 (4)
Mo(2)–S(2)	2.507 (3)	(2×)	Mo(3)–S(10)	2.444 (4)
Mo(2)–S(5)	2.445 (4)	(2×)	Mo(3)–S(11)	2.463 (4)
Mo(2)–S(6)	2.467 (4)	(2×)	Mo(3)–S(12)	2.454 (4)
Mo(1)–Mo(2)	2.828 (2)		Mo(3)–Mo(3)^{II}	2.826 (2)
S(1)–S(2)	2.038 (5)		S(7)–S(8)	2.048 (5)
S(3)–S(4)	2.047 (5)		S(9)–S(10)	2.056 (5)
S(5)–S(6)	2.050 (5)		S(11)–S(12)	2.043 (5)

Mo(1)

	Mo(2)	S(1)^I	S(1)	S(2)^I	S(2)	S(3)^I	S(3)	S(4)^I
S(1)	52.7	105.4						
S(2)	56.7	89.3	49.2	113.4				
S(3)	135.3	171.4	82.7	135.5	93.9	89.4		
S(4)	120.6	133.2	86.2	86.7	128.0	86.0	49.2	118.9

Mo(2)

	Mo(1)	S(1)^I	S(1)	S(2)^I	S(2)	S(5)^I	S(5)	S(6)^I
S(1)	56.6	113.1						
S(2)	52.8	89.3	49.2	105.6				
S(5)	118.7	126.5	86.2	84.1	133.2	122.7		
S(6)	137.0	95.3	135.4	84.3	169.8	87.2	49.3	86.1

Mo(3)

	Mo-(3)^{II}	S(7)	S(7)^{II}	S(8)	S(8)^{II}	S(9)	S(10)	S(11)
S(7)	53.2							
S(7)^{II}	56.4	87.9						
S(8)	56.1	49.5	112.5					
S(8)^{II}	53.1	106.2	49.5	90.1				
S(9)	133.7	172.1	94.0	135.7	80.6			
S(10)	116.8	134.3	125.9	86.6	82.2	49.4		
S(11)	136.4	83.6	136.5	93.6	169.5	89.9	88.2	
S(12)	121.9	85.2	87.8	126.8	134.0	87.2	121.4	49.1

[a] In the bond angle tables the central atom is given at the top center. Atom designations correspond to Figure 1 and Table I, the primed atoms being generated by the intramolecular twofold axes through Mo(1)–Mo(2) (I = 0.5 − x, −y, z) and approximately along S(7)···S(8) (II = x, 0.5 − y, 0.5 − z). Esd's of all bond angles are 0.1° (0.09–0.11° for MoMoS, 0.12–0.14° for SMoS angles).

spectively) but to a smaller extent also in the terminal ones (2.446 vs. 2.471 Å). The central Mo–Mo distance of 2.827 Å is to be regarded as a single bond length,[9] in accordance with the magnetic measurements. The observed S–S bond lengths in the disulfide groups (average 2.047 Å) are very close to those in other S_2 complexes.[3]

All intermolecular contacts within the structure are normal. The shortest NH_4^+–$H_2O(NH_4^+)$ and H_2O–H_2O distances are O,N(2)–O,N(2) = 2.725 (16), O,N(1)–O,N(1) = 2.791 (15), O(1)–N(1) = 2.825 (14), O,N(1)–O,N(2) = 2.857 (14), O(1)–O,N(1) = 2.965 (14), and O(1)–N(1) = 3.178 (14) Å; the closest contacts of NH_4^+ and H_2O to S atoms are N(1)–S(4) = 3.237 (10), O(1)–S(3) = 3.252 (8), N(1)–S(1) = 3.274 (10), O,N(2)–S(9) = 3.316 (9), O(1)–S(7) = 3.343 (9), N(1)–S(5) = 3.355 (9), O,N(2)–S(6) = 3.359 (10), and O,N(1)–S(10) = 3.371 (10) Å, indicating an extensive N–H···S and O–H···S hydrogen system.

The central unit $\{Mo_2(S_2)_2\}$ of the $[Mo_2(S_2)_6]^{2-}$ anion is the same as that in the solid-state structure of $[Mo_2(S_2)_2Cl_4Cl_{4/2}]$.[10] The corresponding homologous cluster of Mo^{IV} (d^2), the novel species $[Mo_3S(S_2)_6]^{2-}$, which is the first binary discrete metal–sulfur cluster, could also be obtained.[11] $[Mo_3S(S_2)_6]^{2-}$ contains the same central unit as the solid-state structure $[Mo_3S(S_2)_3Cl_2Cl_{4/2}]$.[10] It is remarkable that in all these substances the central units $\{Mo_2(S_2)_2\}$ and $\{Mo_3S(S_2)_3\}$ only contain tricoordinated sulfur[13] and asymmetrically coordinated S_2^{2-}. Comparable bonds of these central units are of nearly the same length except the Mo–Mo distances, which are shorter for the Mo^{IV} than for Mo^V species, as expected.

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Supplementary Material Available: A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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