0.15, 0.12) is consistent with the preceding discussion, but, because of the presence of other peaks about oxygen, some larger than those just mentioned, no more can be said on this basis.

The infrared spectrum supports the proposed hydrogen-bond arrangement. The 2800–4000-cm$^{-1}$ portion of the infrared spectrum of solid tetraphenylantimony hydroxide is given in Figure 3. Two bands are observed in the OH stretching region: a broad band at $\sim$3320 cm$^{-1}$, whose shape and relatively low wave number indicate a hydrogen-bonded OH group, and a sharp peak at 3620 cm$^{-1}$ which corresponds to a free OH group. Sharp peaks in the range 3609–3677 cm$^{-1}$ have been reported for dilute solutions of $(C_6H_5)_3MOH$ compounds of group IVb elements in nonpolar solvents, where no association of any sort is believed to occur.[9] Although the assignment of this band has been questioned for $(C_6H_5)_3SnOH$,[10] the present results definitely support the assignment of the higher wave number sharp peak to the free hydroxyl group. In addition to these bands and those due to the phenyl rings listed by Doak, *et al.*,[20] two peaks at 795 (m, broad) and 528 cm$^{-1}$ (m) were obtained for $(C_6H_5)_4SbOH$, examined in a KBr disk from 400 to 1200 cm$^{-1}$. The second of these bands lies close to the position of the Sb–O stretching mode[21] for $[SbF_5OH]^-$, while the band at 795 cm$^{-1}$ is perhaps due to the Sb–O–H bending mode. In the spectrum of bis(tetraphenylantimony) oxide, the peaks at 3620 and 3320 cm$^{-1}$ are absent while those at 795 and 528 cm$^{-1}$ are replaced by a strong doublet at 652 and 660 cm$^{-1}$. Bands in the range 672–736 cm$^{-1}$ for $[(C_6H_5)_3Sb\text{–}O\text{–}Sb(C_6H_5)_3]Y_2$ (where Y is a common inorganic anion) have been assigned to the Sb–O–Sb asymmetric stretching mode.[20]

(20) G. O. Doak, G. G. Long, and L. D. Freedman, *J. Organometal. Chem.*, 4, 82 (1965).

(21) L. Kolditz and B. Nussbücker, *Z. Anorg. Allgem. Chem.*, **337**, 191 (1965).

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# The Stereochemistry of the Hexaoxo-μ-ethylenediaminetetraacetato-dimolybdate(VI) Ion in the Crystalline Sodium Salt and in Aqueous Solution[1,2]

**J. J. Park, M. D. Glick, and J. L. Hoard**[3]

*Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850.*
*Received July 23, 1968*

**Abstract:** A quantitative stereochemical description of the binuclear anion consisting of two molybdenum trioxide moieties that are bridged and stabilized through a complexing ethylenediaminetetraacetate ion ($A^{4-}$) emerges from the determination by X-ray analysis of the atomic arrangement in the crystalline sodium salt, $Na_4(O_3MoAMoO_3)\cdot 8H_2O$. The $MoO_3$ moiety in the octahedral coordination group of each Mo(VI) atom exhibits full double bonding with angles approaching the regular tetrahedral values, whereas the complexing links to nitrogen and carboxylate oxygen atoms carry, at most, bond orders of unity. The $O_3MoAMoO_3{}^{4-}$ complex, required in the crystal to possess a center of inversion, departs rather little from the higher symmetry of $C_{2h}$-2/m. The unit cell of the monoclinic crystals containing $2Na_4(O_3MoAMoO_3)\cdot 8H_2O$ has $a = 8.50$, $b = 11.56$, $c = 13.36$ Å, and $\beta = 87.25$; calculated and measured densities are 2.057 and 2.05 g/cc, respectively. The space group is $P2_1/c$. Some 3857 independent nonvanishing reflections, approximately 1.3 times the number comprised within the Cu K$\alpha$ limiting sphere, were photographically recorded with Mo K$\alpha$ radiation; intensities were visually estimated. Structure determination utilized Patterson and Fourier methods followed by anisotropic full-matrix least-squares refinement; a conventional $R$ of 0.090 was obtained.

Pecsok and Sawyer[4] have presented polarographic evidence for the existence in aqueous solution of a binuclear anionic complex in which two molybdenum(VI) atoms presumably are bridged through an ethylenediaminetetraacetate ion ($A^{4-}$). Following crystallization and chemical analysis of the sodium salt, $Na_4(O_3MoAMoO_3)\cdot 8H_2O$, they proposed a pattern for the connexity of the atoms within the complex that puts the Mo(VI) atoms into octahedral coordination. A subsequent proton magnetic resonance (pmr) study by Chan, *et al.*,[5] suggests that in aqueous solution, pH 3–8, the chelate exists predominantly in a single stereoisomeric form that gives just one sharp resonance for the four protons of the central ethylene radical and one resonance quartet of AB type for the eight methylenic protons adjacent to carboxylate groups. When considered in conjunction with the postulated connexity of the atoms, the pmr data are consistent with any of several stereoisomeric forms of the $O_3MoAMoO_3{}^{4-}$ ion having the effective symmetry of either $C_{2v}$ or $C_{2h}$.

The *a priori* identification of a single $C_{2h}$ stereoisomer and of a single $C_{2v}$ stereoisomer that can have octahedrally coordinated Mo(VI) atoms while fully observing the stringent stereochemical constraints that

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(2) The abbreviation, EDTA, and the short formula, $AH_4$, are used throughout for ethylenediaminetetraacetic acid.

(3) The author to whom correspondence should be addressed.

(4) R. L. Pecsok and D. T. Sawyer, *J. Am. Chem. Soc.*, 78, 5696 (1956).

(5) S. I. Chan, R. J. Kula, and D. T. Sawyer, *ibid.*, **86**, 377 (1964).

are imposed by multidentate chelation[6] is quite straightforward, but is most readily discussed in connection with the results of our X-ray analysis (*vide infra*). Inasmuch as either roughly scaled models or approximate calculations serve to demonstrate that the two halves of the $C_{2v}$ stereoisomer (or of any close approximation thereto) must interpenetrate one another in a wholly inadmissible fashion, the published data suggest that the $C_{2h}$ configuration is uniquely well-suited to satisfy all of the stereochemical requirements. We note further that published structural data for molybdate(VI) complexes[7,8] enable us to predict approximate values for both the lengths and the orders of the bonds within the octahedral coordination groups. Thus each $MoO_3$ moiety is expected to retain double bonding with bond angles that approach the regular tetrahedral value, whereas the complexing links to nitrogen and carboxylate oxygen atoms are expected to be single bonds.[7,8]

The results of our structure determination for crystalline $Na_4(O_3MoAMoO_3)\cdot 8H_2O$ will be seen to support the foregoing expectations except that the complex in the crystal is limited to $C_i$ symmetry—a center of inversion. It is necessary, consequently, to consider the possibility that the molecular conformation having exact $C_{2h}$ symmetry corresponds to a small energy maximum between two energy minima representing a pair of enantiomorphic conformers each having $C_i$ symmetry, and that, in solution, these conformers undergo rapid intraconversion to give the pmr data effective $C_{2h}$ symmetry.

## Experimental Section

The monoclinic crystals of $Na_4(O_3MoAMoO_3)\cdot 8H_2O$ used for structure determination were kindly supplied by Professor R. J. Kula. The unit cell has $a$ = 8.498 ± 0.008, $b$ = 11.56 ± 0.01, $c$ = 13.36 ± 0.01 Å, $\beta$ = 87.25 ± 0.10°, and a content of $2Na_4(O_3MoAMoO_3)\cdot 8H_2O$; calculated and measured densities are 2.057 and 2.05 g/cc, respectively. The pattern of systematically absent X-ray reflections and the negative tests for piezoelectricity support the unique choice of $P2_1/c$-$C_{2h}^5$ as the space group.[9] Sixteen layers of Weissenberg equiinclination data obtained with rotation about the $b$ axis and six layers of precession data along the other two axes were recorded with Mo K$\alpha$ radiation; intensities were visually estimated. Some 3857 independent nonvanishing reflections, approximately 1.3 times the number theoretically obtainable with Cu K$\alpha$ radiation, were recorded and used in the structure analysis; 763 reflections were directly involved in cross-correlating the intensity data. The crystal specimen, of prismatic shape, carried edge lengths of 0.18, 0.25, and 0.25 mm. With a linear absorption coefficient of the crystal for Mo K$\alpha$ radiation of only 1.1 mm$^{-1}$, no corrections for absorption were deemed necessary. Nor were extinction corrections included in the subsequent evaluation of calculated reflection amplitudes. The intensity data were reduced to a set of relative squared amplitudes, $|F_{hkl}|^2$, by applying the standard Lorentz and polarization factors.

The atomic arrangement in the crystal was readily determined by Patterson and Fourier methods.[10] Full-matrix least-squares refinement[11] that excluded hydrogen atoms, but assigned individual anisotropic thermal parameters to all other atoms, gave a conventional $R$ of 0.090 and a weighted $R$ of 0.122. The function minimized was $\Sigma w|k|F_o| - |F_c||^2$ wherein $F_o$ and $F_c$ are the respective observed and calculated structure amplitudes, $k$ is the scale constant, and $w$ is the weight assigned to each independent reflection. A slightly modified version of the Hughes weighting scheme, with the break point taken at 3.2 times the minimum intensity, was employed. No positional coordinate or thermal parameter changed by more than 0.4 of its standard deviation during the last cycle of refinement. A final difference synthesis gave no reliable indications of the positions of hydrogen atoms and was otherwise free of noteworthy features.[12]

The atomic coordinates within the unit cell of the asymmetric structural entity, half a chemical formula weight, are given in Table I, and the associated thermal parameters are listed in Table II. All atoms are placed in the general positions[9] of $P2_1/c$: $\pm(x, y, z)$; $\pm(x, {}^1/_2 - y, {}^1/_2 + z)$.

**Table I.** Atomic Coordinates in Crystalline $Na_4(O_3MoAMoO_3)\cdot 8H_2O^a$

| Atom type | Coordinates $10^4x$ | $10^4y$ | $10^4z$ |
|---|---|---|---|
| $O_1$ | −651 (6) | 6833 (6) | 2591 (4) |
| $O_2$ | 1016 (7) | 8078 (5) | 3948 (5) |
| $O_3$ | 1930 (7) | 8187 (6) | 1941 (5) |
| $O_4$ | 2129 (7) | 5796 (5) | 1946 (4) |
| $O_5$ | 3742 (7) | 7031 (6) | 3232 (4) |
| $O_6$ | 3055 (8) | 4007 (5) | 1821 (4) |
| $O_7$ | 5423 (6) | 6579 (6) | 4384 (4) |
| N | 1435 (6) | 5600 (5) | 3967 (3) |
| $C_1$ | 2353 (9) | 4795 (7) | 2295 (5) |
| $C_2$ | 4096 (7) | 6517 (7) | 4035 (4) |
| $C_3$ | 1695 (10) | 4549 (7) | 3343 (5) |
| $C_4$ | 2803 (8) | 5838 (7) | 4599 (5) |
| $C_5$ | −50 (8) | 5500 (6) | 4622 (4) |
| $Na_1$ | 3374 (4) | 2042 (3) | 2286 (3) |
| $Na_2$ | 6227 (5) | 8787 (4) | 4988 (3) |
| $W_1^b$ | 4758 (9) | 2706 (8) | 3674 (6) |
| $W_2^b$ | 3468 (8) | 9147 (7) | 5010 (5) |
| $W_3^b$ | 8709 (9) | 8373 (10) | 5469 (6) |
| $W_4^b$ | 3642 (11) | 99 (7) | 2774 (7) |
|  | $10^5x$ | $10^5y$ | $10^5z$ |
| Mo | 12,438 (5) | 72,290 (4) | 28,666 (4) |

$^a$ Figures in parentheses are the estimated standard deviations. $^b$ Symbols used for water molecules.

## Discussion of the Structural Results

A scaled model of the $O_3MoAMoO_3^{4-}$ ion as it exists in the crystal is illustrated in the perspective drawing of Figure 1. The midpoint of the central bond connecting the pair of ethylenic carbon atoms is a required center of inversion ($C_i$-$\bar{1}$). The manifest possibility that the free ion might achieve the higher symmetry of $C_{2h}$-2/m, with a "backbone" comprised of the two ethylenic carbon, the two nitrogen, the two molybdenum, and two of the oxide-oxygen atoms ($O_3$ and $O_3'$) lying in the mirror plane, is best considered in the light of data given in Table III. Listed therein are the equations, fitted by least-squares procedures, of the mean plane A for the backbone of the entire complex and of the mean plane B for the backbone of the asymmetric unit (just half) of the complex together with the displace-

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(6) *Cf.* J. L. Hoard, E. W. Silverton, and J. V. Silverton, *J. Am. Chem. Soc.*, **90**, 2300 (1968), for a listing of all pertinent references.

(7) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397(1964).

(8) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 867 (1965).

(9) "International Tables for X-Ray Crystallography," Vol. I, "Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, pp 98–99.

(10) Modified versions of Blount's Fourier programs for the CDC 1604 computer were employed; see J. F. Blount, Ph.D. Thesis, University of Wisconsin, 1965.

(11) Slightly modified versions of the Busing–Martin–Levy ORFLS and ORFFE programs were employed in the final stages of refinement. Atomic form factors were from D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965), with dispersion corrections to the form factor of Mo(VI) from C. H. Dauben and D. H. Templeton, *ibid.*, **8**, 841 (1955).

(12) A table of observed and calculated structure amplitudes from this refinement has been deposited as Document No. NAPS-00135 with the ASIS National Auxiliary Publications Service, % CCM Information Sciences, Inc., 22 West 34th St. New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $3.00 for photoprints or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to ASIS-NAPS.

Table II. Thermal Parameters in Crystalline $Na_4(O_3MoAMoO_3) \cdot 8H_2O$[a]

| | Anisotropic parameters, Å$^2$ | | | | | | |
|---|---|---|---|---|---|---|---|
| Atom type | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ | $B$,[b] Å$^2$ |
| Mo | 1.08 (2) | 0.73 (2) | 1.14 (2) | 0.07 (2) | −0.08 (1) | 0.24 (2) | 0.94 |
| $O_1$ | 1.4 (2) | 2.7 (2) | 2.1 (2) | 0.0 (1) | −0.5 (2) | 0.6 (2) | 1.9 |
| $O_2$ | 2.3 (2) | 1.6 (2) | 2.7 (2) | 0.1 (2) | −0.1 (3) | −0.7 (1) | 2.1 |
| $O_3$ | 2.4 (2) | 2.0 (2) | 2.5 (2) | 0.3 (2) | 0.2 (2) | 1.5 (2) | 1.9 |
| $O_4$ | 2.8 (2) | 1.4 (2) | 1.5 (2) | 0.3 (2) | 0.5 (2) | 0.3 (1) | 1.7 |
| $O_5$ | 1.7 (2) | 2.5 (2) | 1.8 (2) | −0.2 (2) | −0.2 (3) | 1.1 (1) | 1.8 |
| $O_6$ | 2.9 (2) | 1.5 (2) | 1.8 (2) | 0.2 (2) | 0.5 (2) | 0.1 (1) | 2.0 |
| $O_7$ | 1.3 (2) | 3.0 (2) | 1.6 (2) | 0.4 (1) | 0.0 (2) | 0.1 (1) | 1.8 |
| N | 1.2 (2) | 0.7 (2) | 0.8 (2) | −0.1 (2) | 0.5 (1) | −0.0 (1) | 0.8 |
| $C_1$ | 2.3 (2) | 1.4 (2) | 1.1 (2) | 0.1 (2) | −0.1 (2) | −0.2 (1) | 1.5 |
| $C_2$ | 1.1 (2) | 1.7 (2) | 1.0 (1) | 0.0 (2) | −0.3 (2) | 0.3 (2) | 1.1 |
| $C_3$ | 3.1 (3) | 1.0 (2) | 1.2 (2) | −0.4 (2) | 0.5 (3) | −0.0 (2) | 1.5 |
| $C_4$ | 1.6 (2) | 1.6 (2) | 1.5 (2) | −0.5 (2) | −0.3 (2) | 0.9 (2) | 1.3 |
| $C_5$ | 1.3 (2) | 1.0 (2) | 1.6 (2) | 0.2 (2) | 0.2 (2) | 0.4 (2) | 1.3 |
| $Na_1$ | 1.9 (1) | 1.5 (1) | 2.2 (1) | 0.2 (1) | 0.1 (1) | −0.1 (1) | 1.8 |
| $Na_2$ | 2.3 (2) | 3.2 (2) | 3.8 (2) | 0.4 (2) | 0.3 (2) | 1.7 (2) | 2.7 |
| $W_1$ | 2.8 (3) | 5.4 (4) | 2.6 (3) | 1.0 (3) | −0.7 (3) | −1.0 (2) | 3.2 |
| $W_2$ | 2.8 (2) | 3.6 (3) | 2.1 (2) | 0.1 (2) | −0.3 (2) | −0.4 (2) | 2.8 |
| $W_3$ | 3.0 (3) | 6.6 (6) | 3.3 (3) | 1.5 (3) | −0.6 (3) | −0.0 (3) | 3.8 |
| $W_4$ | 4.0 (3) | 2.3 (3) | 6.8 (4) | −0.1 (3) | −1.5 (4) | 0.7 (3) | 3.8 |

[a] The number in parentheses that follows each $B_{ij}$ value is the estimated standard deviation in the last significant figure. The $B_{ij}$ in Å$^2$ are related to the dimensionless $\beta_{ij}$ employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Selected Mean Planes and Atomic Displacements Therefrom

| Least-Squares Mean Planes | |
|---|---|
| Atomic grouping[a] | Equation of mean plane[b] |
| A. "Backbone" ($O_3$–Mo–N–$C_5$–$C_5'$–N'–Mo'–$O_3'$) | $0.450X + 0.581Y + 0.678Z = 8.03$ |
| B. "Half-backbone" ($O_3$–Mo–N–$C_5$) | $0.434X + 0.582Y + 0.688Z = 8.05$ |
| C. Glycinato ring I (–Mo–$O_4$–$C_1$–$C_3$–N–) | $0.954X + 0.202Y + 0.220Z = 3.77$ |
| D. Glycinato ring II (–Mo–$O_5$–$C_2$–$C_4$–N–) | $-0.236X + 0.710Y + 0.664Z = 8.01$ |

| | Atomic Displacements from Mean Planes,[c] A | | | |
|---|---|---|---|---|
| Atom | Plane A | Plane B | Plane C | Plane D |
| $O_3$ | 0.02* | 0.01* | 0.40 | 0.01 |
| Mo | −0.02* | −0.01* | −0.05* | 0.17* |
| N | −0.01* | 0.00* | 0.11* | −0.25* |
| $C_5$ | −0.04* | 0.00* | −0.88 | 0.54 |
| $C_3$ | −1.20 | −1.20 | −0.14* | −1.70 |
| $C_1$ | −1.77 | −1.78 | 0.08* | −2.55 |
| $O_4$ | −1.50 | −1.52 | 0.01* | −1.99 |
| $O_6$ | −2.47 | −2.50 | 0.29 | −3.75 |
| $O_1$ | −1.27 | −1.24 | −1.78 | −0.01 |
| $C_4$ | 1.26 | 1.26 | 1.50 | 0.22* |
| $C_2$ | 1.68 | 1.66 | 2.51 | 0.03* |
| $O_5$ | 1.14 | 1.12 | 2.06 | −0.18* |
| $O_7$ | 2.56 | 2.52 | 3.72 | 0.12 |
| $O_2$ | 1.47 | 1.50 | 0.35 | 1.85 |

[a] Atoms listed are those used to determine the mean plane. [b] Referred to orthogonal coordinates ($X$, $Y$, $Z$) measured in Å along ($a$, $b$, $c^*$), respectively. [c] Displacements carrying asterisks are those of the atoms used in the determination of the mean plane. Note, however, that an additional four atoms ($O_3'$, Mo', N', $C_5'$), related to those listed by the inversion center, entered into the determination of the backbone plane A. The estimated standard deviations of the displacements are generally ~0.01 Å.

ments from these planes of the several atoms comprised within the asymmetric unit. Although the four backbone atoms used to determine plane B are virtually coplanar (Table III), this plane does not pass through the center of the complex (the center of inversion); the perpendicular separation of the symmetry-equivalent pair of parallel planes, B and B', for the two halves of the complex is 0.09 Å. Consequently, the dihedral angle between planes A and B (or B'), though small (1.1°), is not zero. These observations are mostly attributable to a twisting of ~3.7° around the central $C_5$–$C_5'$ bond taken in accord with $C_i$ symmetry. The fact that such pairings of atoms as $O_1$ with $O_2$ and $O_4$ with $O_5$ (Figure 1) do not approximate closely to $C_{2h}$ symmetry (Table III) is largely attributable to a twisting around the Mo–N bond in the coordination group that is associated with significant stereochemical variations between the pair of glycinato rings (*vide infra*).

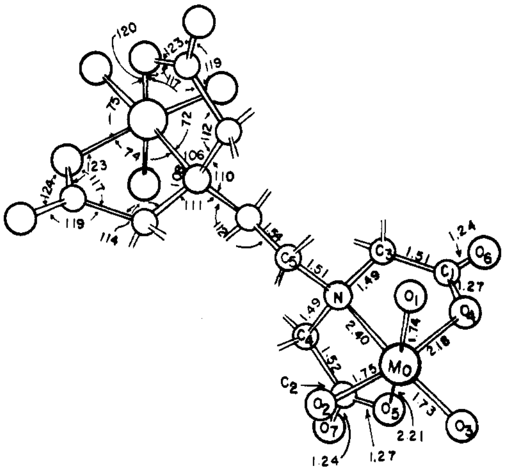

Figure 1. Model in perspective of the centrosymmetric $O_3MoAMoO_3^{4-}$ ion. The numbering of the atoms is that used throughout the text. More precise values of the stereochemical parameters are listed in Tables IV and V.

Exact $C_{2h}$ symmetry leads to numerous, but not extraordinarily short, H–H and H–O contacts in the scaled model of the complex. Whether small rotations about the several bonds can lead to a pair of $C_i$ enantiomers of slightly greater stability (a possibility favored by entropy considerations) is a question that cannot be answered. If so, however, the intraconversion of the $C_i$ enantiomers in solution should be quite rapid enough on the pmr time scale to give resonance spectra in agreement with $C_{2h}$ symmetry.[5]

In further description of the complex anion, it is convenient to use $O_o$ to designate any of the three oxide-oxygen atoms ($O_1$, $O_2$, $O_3$) of the $MoO_3$ moiety and either $O_c$ or $O_u$ for carboxylate oxygen atoms accordingly as these are ($O_4$, $O_5$) or are not ($O_6$, $O_7$) complexed to the Mo(VI) atom. Octahedral coordination about the Mo(VI) atom of each $MoO_3$ moiety is completed (Figure 1) by the complexing of a nitrogen and two $O_c$ atoms. Two glycinato rings are simultaneously formed with the nitrogen and the two $O_c$ atoms occupying contiguous vertices that define one face of the coordination polyhedron; the three vertices of the opposite face are occupied by the $O_o$ atoms of the $MoO_3$ moiety.

Reference to Table IV, in which the stereochemical parameters of the coordination group are listed, reveals that the edge lengths of the octahedron defined by the six ligand atoms approximate to dimensional regularity; the only notable distortion arises from the positioning of the nitrogen atom. Far from being centered in this polyhedron, the Mo(VI) atom is substantially displaced toward the three atoms of the $O_o$ face so as to maintain the dimensional integrity of the $MoO_3$ moiety within the complexed species. The averaged $O_oMoO_o$ bond angle of 105.6° (Table IV) is not far below the regular tetrahedral value of 109.5°, and the averaged $Mo{=}O_o$ bond length of 1.740 Å corresponds, according to the relation developed by Cotton and Wing,[8] to a bond order of 2. These bond parameters are virtually identical with those reported for the $MoO_3$ moiety as this exists within the mononuclear octahedrally coordinated trioxo(diethylenetriamine)molybdenum(VI) molecule[7] [$O_3Mo$(dien)]. As would then be expected from the earlier study, the lengths of the complexing bonds in the $O_3MoAMoO_3^{4-}$ ion, $Mo–O_c$ = 2.195 (average) and Mo–N = 2.399 Å, correspond to a bond order not exceeding unity.[8] The complexing bond lengths are quite similar to the values, Zr–O = 2.191 (average) and Zr–N = 2.439 Å, that characterize the eight-coordinate bis(nitrilotriacetato)zirconate(IV) ion, the differences in coordination number, oxidation state, and nuclear charge of the Mo(VI) and Zr(IV) atoms notwithstanding. The cited Zr–O distance, however, is the average for two bond types that differ in length (2.25 and 2.13 Å) because they differ in bond order (1 and $^{5}/_{4}$, respectively), as permitted by dodecahedral eight-coordination. This comparison serves to underline the generally pronounced tendency for the $\pi$ bonding in Mo(VI)[8] (and Mo(IV)[13]) complexes to be concentrated in the bonds formed with oxide oxygen at the expense of the bonds formed with other ligands that are present in a mixed complex.

**Table IV.** Parameters of the Coordination Octahedron

A. Bond and Edge Lengths[a]

| Type | Length, Å | Type | Length, Å |
|---|---|---|---|
| $Mo–O_1$ | 1.731 (6) | $N–O_1$ | 2.977 (8) |
| $Mo–O_2$ | 1.749 (6) | $N–O_2$ | 2.887 (9) |
| $Mo–O_3$ | 1.739 (6) | Average | 2.932 |
| Average[b] | 1.740 | | |
| | | $O_1–O_2$ | 2.759 (9) |
| $Mo–O_4$ | 2.176 (6) | $O_2–O_3$ | 2.758 (10) |
| $Mo–O_5$ | 2.213 (6) | $O_3–O_1$ | 2.799 (9) |
| Average[c] | 2.195 | $O_1–O_4$ | 2.751 (9) |
| | | $O_2–O_5$ | 2.744 (9) |
| Mo–N[c] | 2.399 (5) | $O_3–O_4$ | 2.769 (9) |
| | | $O_3–O_5$ | 2.717 (8) |
| $N–O_4$ | 2.746 (7) | $O_4–O_5$ | 2.664 (9) |
| $N–O_5$ | 2.713 (8) | Average | 2.745 |
| Average[c] | 2.730 | | |

B. Bond Angles Subtended at the Mo(VI) Atom[a]

| Type | Angle, deg | Type | Angle, deg |
|---|---|---|---|
| $O_1MoO_2$ | 104.9 (3) | $O_1MoO_4$ | 88.7 (3) |
| $O_2MoO_3$ | 104.5 (4) | $O_2MoO_5$ | 86.8 (3) |
| $O_3MoO_1$ | 107.5 (3) | $O_3MoO_4$ | 89.3 (3) |
| Average[b] | 105.6 | $O_3MoO_5$ | 86.0 (3) |
| | | Average | 87.7 |
| $NMoO_4$ | 73.6 (2) | | |
| $NMoO_5$ | 71.9 (2) | $NMoO_1$ | 90.8 (2) |
| Average[c] | 72.8 | $NMoO_2$ | 86.7 (3) |
| | | Average | 88.7 |
| $O_4MoO_5$[d] | 74.7 (2) | | |

[a] Figures in parentheses are the estimated standard deviations. [b] Within the $MoO_3$ moiety. [c] Within glycinato rings. [d] Between glycinato rings.

It is evident that trigonal-pyramidal geometry for the $MoO_3$ moiety must be accompanied by the observed *cis* positioning of the complexing $O_c$ atoms in the octahedral coordination group, and that *trans* positioning either of two $O_o$ atoms or of the two $O_c$ atoms demands *trans* positioning of the other pair. Although the bond parameters of the observed *cis*-stereoisomeric form of the $O_3MoAMoO_3^{4-}$ (or of the $O_3Mo$(dien)) complex suggest the particularly effective use of $\pi$ bonding in stabilizing the species, the possibility is not precluded that the presently hypothetical *trans* stereoisomer might do as well in this respect. But even if double bonding could play a comparable role in the *trans* isomer, the steric superiority of the *cis* isomer in most, if not all, respects is demonstrable. The bond parameters of the chelation framework that are listed in Table V are pertinent in this connection.

As indicated by the subheadings carried by the double columns in Table V, the bond parameters of the chelation framework are tabulated in categories that, with the aid of Figure 1 and Table III, facilitate discussion of the stereochemical relations. The comparison of corresponding bond lengths within the glycinato rings I and II reveals just one objectively significant difference: the complexing $Mo–O_5$ bond in ring II is ~0.04 Å longer than the analogous $Mo–O_4$ bond in ring I. Inasmuch as the complexing bonds afford a principal repository for cumulative ring strain, the greater length of the $Mo–O_5$ bond suggests an enhancement of strain in ring II, a conclusion that is confirmed by analysis of the bond angle data (*vide infra*). With the exception noted, the bond lengths in the glycinato rings are very similar to those observed in a series of aminepolycarboxylate complexes.[6] We remark, however, that the small doubtfully significant difference between $C–O_c$ and $C–O_u$ bond lengths in the $O_3MoAMoO_3^{4-}$ chelate provides further evidence for comparatively weak $Mo–O_c$ bonds.

Bond angles at nitrogen and at carbon atoms (Table V), whether in or between glycinato rings, display variations from the ideal values for the characteristic

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**Table V.** Bond Parameters of the Chelation Framework

| Bond Lengths,[a] Å | | | | | | | |
|---|---|---|---|---|---|---|---|
| In ring I | | In ring II | | Ring average | | Between rings | |
| Bond | Length | Bond | Length | Bond | Length | Bond | Length |
| $Mo–O_4$ | 2.176 (6) | $Mo–O_5$ | 2.213 (6) | $Mo–O_c$ | 2.195 | $C_5–C_5'$ | 1.539 (13) |
| $O_4–C_1$ | 1.264 (9) | $O_5–C_2$ | 1.275 (8) | $C–O_c$ | 1.270 | $N–C_5$ | 1.506 (8) |
| $C_1–C_3$ | 1.511 (10) | $C_2–C_4$ | 1.521 (9) | C–C | 1.516 | | |
| $C_3–N$ | 1.484 (9) | $C_4–N$ | 1.495 (9) | C–N | 1.490 | | |
| N–Mo | 2.399 (5) | N–Mo | 2.399 (5) | N–Mo | 2.399 | | |
| $C_1–O_6$ | 1.245 (9) | $C_2–O_7$ | 1.243 (8) | $C–O_u$ | 1.244 | | |

| Bond Angles,[a] Deg | | | | | | | |
|---|---|---|---|---|---|---|---|
| In ring I | | In ring II | | Ring average | | Between rings | |
| Type | Value | Type | Value | Type | Value | Type | Value |
| $MoO_4C_1$ | 122.8 (4) | $MoO_5C_2$ | 120.1 (4) | $MoO_cC$ | 121.5 | $NC_5C_5'$ | 111.6 (7) |
| $O_4C_1C_3$ | 117.3 (6) | $O_5C_2C_4$ | 117.6 (6) | $O_cCC$ | 117.5 | $C_5NC_3$ | 111.2 (5) |
| $C_1C_3N$ | 113.9 (6) | $C_2C_4N$ | 112.2 (5) | CCN | 113.1 | $C_5NC_4$ | 109.8 (5) |
| $C_3NMo$ | 108.1 (4) | $C_4NMo$ | 106.2 (4) | CNMo | 107.2 | $C_5NMo$ | 109.7 (4) |
| $NMoO_4$ | 73.6 (2) | $NMoO_5$ | 71.9 (2) | $NMoO_c$ | 72.8 | $C_3NC_4$ | 111.6 (6) |
| $O_4C_1O_6$ | 124.0 (6) | $O_5C_2O_7$ | 123.0 (6) | $O_cCO_u$ | 123.5 | $O_4MoO_5$ | 74.7 (2) |
| $C_3C_1O_6$ | 118.7 (7) | $C_4C_2O_7$ | 119.4 (6) | $CCO_u$ | 119.0 | | |

[a] The number in parentheses following a parameter value is the estimated standard deviation in the last significant figure.

types that fall within the range observed for other aminepolycarboxylate chelates.[6] The largest deviations from the ideal values, as much as 4°, are in angles at methylene- and carboxylate-carbon atoms in the glycinato rings. (It is seen, however, that the sum of the angles subtended at each carboxylate-carbon atom comes out to be 360.0°.) Angular ring strain of this description is required in combination with folding and/or puckering of the glycinato ring in order (1) that long complexing bonds can be accommodated (any bond length above 2.0 Å certainly is "long" in this connection), (2) that the metal–nitrogen distance can be small enough to represent a real complexing interaction, (3) that the bond angle at the metal atom need not be restricted to an unduly small value, and (4) that the "bite" or ring span can remain within acceptable limits. In an aminepolycarboxylate complex all of the bond angles at the tertiary nitrogen atom(s) generally remain near the regular tetrahedral value (109.5°) whereas, at the other extreme, the ring angle at a complexed oxygen ($O_c$) atom behaves rather as a dependent variable within, at least, the range from 110 to 132°. A significant expansion of the ring angle at methylene carbon above the regular tetrahedral value is quite usual whenever long complexing bonds are involved because this provides one effective means, along with folding and puckering of the ring, for maintaining an acceptable balance between the metal–nitrogen and metal–oxygen bond lengths. That the glycinato ring resists unduly large folding and puckering, as well as undue distortion of critical angles, is supported by the observation that the difference between the M–N and M–O bond lengths is relatively large (0.15–0.35 Å) whenever the M–O distance is large.[6,14]

The comparison, using objective criteria, of corresponding angles within the two glycinato rings of the $O_3MoAMoO_3^{4-}$ ion (Table V) shows that every angle in ring II is as small as, or smaller than, the corresponding angle in ring I; the cumulative effect of these differences is to make the sum of the interior angles in ring II only 528.0°, as compared with 535.7° for ring I and 540° for a planar conformation. Ring II, consequently, must display more pronounced out-of-plane distortions than does ring I. The data listed in Table III for the displacements of the atoms in rings I and II from their respective mean planes C and D yield an averaged displacement of 0.08 Å for the five atoms of ring I and 0.17 Å for those of ring II. Residual strain tends, of course, to be distributed throughout the ring, but it is most likely to become objectively evident in the complexing bond lengths and, especially, in the bond angle at the central atom. Thus the larger strain carried by ring II is manifest in a significantly less favorable bond angle at the Mo(VI) atom and, as noted above, in a significantly longer $Mo–O_c$ bond length; it is also to be noted that the Mo–N bond along which the glycinato rings are fused together is 0.07–0.08 Å longer than the Mo–N bonds in the $O_3Mo(dien)$ molecule.[7] A qualitative criterion of relative strain in the glycinato rings is seen to be provided by the sum of the interior angles or, more properly, by the magnitude of the deviation of this sum from the 540° maximum.[14]

*trans* Positioning of the $O_c$ atoms of two glycinato rings calls for greater out-of-plane distortions of the rings than does the *cis* arrangement. This is largely because the dihedral angle between either of the planes containing a ring N–C bond and the plane in which the *trans* $O_c$–Mo bonds ideally would lie to close both rings is 30°, whereas the corresponding angle for ring closure in *cis* positions is only 15°. Using the averaged bite (2.73 Å) and complexing bond distances observed in the *cis* stereoisomer of the $O_3MoAMoO_3^{4-}$ ion, one calculates an $O_cMoO_c$ angle of 145° for the unobserved *trans* isomer. This calculation, however, does not allow for the enhancement of strain in the glycinato rings; redistribution and minimization of strain appear to call for some increase in the Mo–N distance and, probably, for some reduction in the bite (and in the $O_cMoO_c$ angle). We then point out that in the bis(nitrilotriacetato)zirconate(IV) ion[6] two of the three glycinato rings[15] formed by each chelating anion provide

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[14] Some discussion of the points made in this paragraph is given in ref 6 and in earlier papers cited therein. A more comprehensive appraisal of the interdependent roles played by the factors cited and by such others as coordination number and nonbonding repulsions in determining chelate stereochemistry is in preparation.

[15] The third glycinate ring, positioned *cis* to the others, is apparently the least strained of the three.

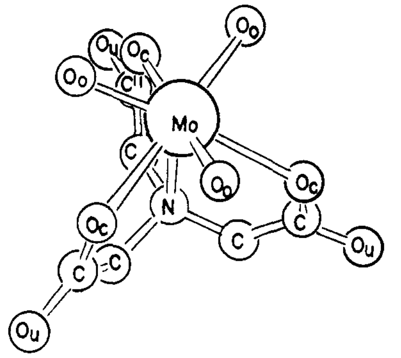

Figure 2. Model in perspective for a seven-coordinate trioxonitrilotriacetatomolybdate(VI) ion that utilizes the monocapped octahedron as the coordination polyhedron. The model shown has $C_{3v}$ symmetry; the more probable twisted model of $C_3$ symmetry is discussed in the text.

an example of the *trans* configuration with quantitative features much like those anticipated for a *trans* stereoisomer of the $O_3MoAMoO_3^{4-}$ ion. The pertinent parameters are Zr–$O_c$ (av) = 2.193 (8), Zr–N = 2.439 (9), and an averaged bite of 2.65 (1) Å. The $O_cZrO_c$ angle of 141° fits in beautifully with the dodecahedral eight-coordination group of the zirconate(IV) chelate, but it is an awkward value for a *trans* arrangement of the complexing bonds in octahedral coordination.

It is clear that the steric requirements of the chelating agent are better satisfied by the observed *cis* arrangement of the bonds in the $O_3MoAMoO_3^{4-}$ ion than they are in the *trans* alternative. It is also clear that the steric requirements of the $MoO_3$ moiety are better handled by the observed trigonal-pyramidal geometry than is possible with the planar form that is specified in the *trans* stereoisomer. An $O_oMoO_o$ bond angle of 90°, the ideal value for the planar $MoO_3$ moiety in the octahedral coordination group, together with the double-bond Mo–$O_o$ distance of 1.74 Å gives an $O_o$–$O_o$ separation of only 2.46 Å, much below the corresponding separation of 2.76 Å in the trigonal-pyramidal moiety and the van der Waals diameter of 2.80 Å. In these circumstances, an $O_oMoO_o$ angle approaching 100°, probably accompanied by some increase in the Mo–$O_o$ bond length, would seem to be required for stabilization of the planar moiety.

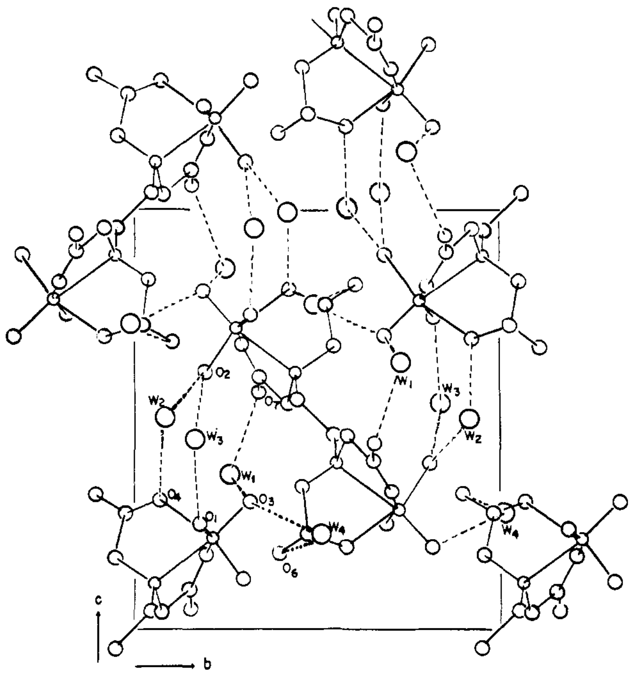

Figure 3. Packing diagram of an anionic layer in the crystalline arrangement showing the hydrogen bonding of $O_3MoAMoO_3^{4-}$ ions with water molecules. Stabilization of such layers is provided by interleaving "puckered sheets" of sodium ions; see text.

The trioxonitrilotriacetatomolybdate(VI) ion is still another species in which the $MoO_3$ moiety is stabilized by chelation, in this case by the potentially quadridentate nitrilotriacetate ion ($Z^{3-}$) to form the 1:1 complex.[5] The structural considerations presented herein suggest that it is both stereochemically and energetically plausible for the complexing agent to use all four of its "teeth" to give a seven-coordinate species that utilizes the monocapped octahedron as the coordination polyhedron. A model of the $O_3MoZ^{3-}$ ion, accorded the full symmetry of $C_{3v}$ in agreement with the observation that in aqueous solution (pH 3–8) the species gives a single sharp pmr signal attributable to the methylene hydrogen atoms, is illustrated in the perspective drawing of Figure 2. With use of the trigonal-pyramidal $MoO_3$ moiety described earlier, an $O_c$–Mo bond length of 2.20 Å, standard $O_c$–C, C–C, and C–N bond lengths, and ideal angles at the nitrogen and carbon atoms, each (necessarily flat) glycinato ring in the $C_{3v}$ model has an unduly long Mo–N distance approaching 3.0 Å and an unduly small $NMoO_c$ angle of 59°. Some improvement in the values of these critical parameters, probably quite insufficient for stabilization of a $C_{3v}$ model, is given by the redistribution of angular strain within the flat ring; a twisting of the chelation framework around the threefold axis that introduces foldings and puckerings into the glycinato rings also is needed if the Mo–N distance and the $NMoO_c$ angle are to have values near those observed in the $O_3MoAMoO_3^{4-}$ ion. The combined out-of-plane and angular distortion required of each glycinato

**Table VI.** Intermolecular Distances and Angles in the Crystal

A. Interatomic Distances Involving the Sodium Ions[a]

| Bond | Length, Å | Bond | Length, Å |
|---|---|---|---|
| $Na_1$–$O_1$ | 2.325 (7) | $Na_2$–$W_2$ | 2.381 (8) |
| $Na_1$–$O_5$ | 2.515 (7) | $Na_2$–$W_3$ | 2.285 (9) |
| $Na_1$–$O_6$ | 2.374 (7) | $Na_2$–$O_6$ | 2.476 (7) |
| $Na_1$–$O_7$ | 2.468 (7) | $Na_2$–$O_7$ | 2.772 (9) |
| $Na_1$–$W_1$ | 2.370 (9) | $Na_2$–$W_1$ | 2.595 (11) |
| $Na_1$–$W_4$ | 2.353 (9) | $Na_2$–$W_2'$ | 2.403 (10) |

B. Hydrogen-Bonding Parameters[a]

| Bond | Length, Å | Bond angle | Deg |
|---|---|---|---|
| $W_1$–$O_7$ | 2.721 (9) | | |
| | | $O_3W_1O_7$ | 102.6 (3) |
| $W_1$–$O_3$ | 2.947 (10) | | |
| $W_2$–$O_4$ | 2.776 (8) | | |
| | | $O_2W_2O_4$ | 101.4 (3) |
| $W_2$–$O_2$ | 2.857 (10) | | |
| $W_3$–$O_2$ | 2.777 (11) | | |
| | | $O_1W_3O_2$ | 122.9 (3) |
| $W_3$–$O_1$ | 2.921 (10) | | |
| $W_4$–$O_3$ | 2.897 (11) | | |
| | | $O_3W_4O_6$ | 103.2 (3) |
| $W_4$–$O_6$ | 3.148 (11) | | |

[a] The estimated standard deviations are given in parentheses.

ring in a $C_3$ stereoisomer of the $O_3MoZ^{3-}$ ion should be quite comparable with that which characterizes the averaged ring in the $O_3MoAMoO_3{}^{4-}$ complex. A pair of $C_3$ enantiomers that undergo sufficiently rapid intraconversion on the pmr time scale to give effective $C_{3v}$ symmetry are the probable species in solution.

Table VI lists data that pertain to the atomic arrangement in crystals of $Na_4(O_3MoAMoO_3)\cdot 8H_2O$. The rather high stability of the crystalline phase, reflected in relatively small values of the effective thermal parameters for all of the atoms (Table II), is attributable to the efficient use of both the sodium ions and the water molecules in tying the bulky anions into the three-dimensional framework. A sodium ion of either structural class is surrounded by six oxygen atoms that delineate an irregular octahedron; Na–O distances range from 2.29 to 2.77 Å (Table VI). A sodium ion $Na_1{}^+$ coordinates one oxide-oxygen, two water-oxygen, and three carboxylate-oxygen atoms; the other sodium ion $Na_2{}^+$ coordinates four water-oxygen and two carboxylate-oxygen atoms. Each carboxylate-oxygen atom that is not complexed to the Mo(VI) atom is coordinated to two sodium ions, one of each class, and every water molecule is coordinated to at least one sodium ion. The water molecules are also involved in hydrogen bonding (Table V) with carboxylate-oxygen and oxide-oxygen atoms. Separations between pairs of sodium ions range upward from 3.50 Å.

The crystalline arrangement may be described as layered along the *a* axis. A negatively charged layer of the type illustrated in Figure 3 consists of complex anions that are hydrogen bonded with and through water molecules. Such layers are interleaved by, and alternate with, puckered sheets of sodium ions. The description is quite formal because the layers and sheets have no clear planes of demarcation. Furthermore, the bonding between layer and sheet clearly is much stronger than it is within either layer or sheet.

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# The Crystal and Molecular Structure of Thio-*p*-toluoyldisulfidobis(dithio-*p*-toluato)iron(III)

**Dimitri Coucouvanis and Stephen J. Lippard**[1]

*Contribution from the Department of Chemistry, Columbia University, New York, New York 10027.*

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**Abstract:** The crystal and molecular structure of thio-*p*-toluoyldisulfidobis(dithio-*p*-toluato)iron(III), $Fe(CH_3C_6H_4CS_3)(CH_3C_6H_4CS_2)_2$, Fe(TTD)(DTT)$_2$, has been determined by a three-dimensional X-ray crystallographic analysis. The compound crystallizes as dark violet prisms in space group $P2_1/c$ with unit cell dimensions $a$ = 18.23 (2), $b$ = 7.64 (1), $c$ = 24.12 (2) Å, $\beta$ = 125.4 (1)°. The density of 1.43 g/cm$^3$ calculated for four molecules per unit cell agrees well with the observed density of 1.42 ± 0.01 g/cm$^3$. From approximately 1225 independent nonzero reflections estimated visually from Weissenberg photographs, the structure was solved by the use of conventional Patterson, Fourier, and least-squares refinement techniques to a final value of the discrepancy index, $R$, of 0.085. The geometry about the iron atom consists of a distorted octahedron of sulfur atoms contributed by two essentially equivalent bidentate dithioacid ligands and a third bidentate ligand containing an extra sulfur atom to form the structural grouping I, shown in the text. The average of four Fe–S distances in the four-membered rings is 2.32 ± 0.02 Å whereas the two Fe–S distances in the five-membered ring are 2.18 and 2.24 ± 0.01 Å, respectively. These differences may be understood in terms of simple ring constraint and valence-bond resonance arguments. The S–S distance in the five-membered chelate ring is 2.09 ± 0.01 Å. An analysis of the geometry reveals some evidence for electron delocalization between the iron atom and the ligand molecules. A brief discussion of the possible relevance of this work to nonheme iron protein systems is set forth.

In recent years there has been a growing interest in a series of electron-transfer proteins containing sulfur-bound iron atoms in a nonheme environment.[2,3] Of special interest is a class of nonheme iron proteins (NHIP) which is characterized by the presence of two or more iron atoms per mole of protein, relatively low redox potentials, a biologically unique form of sulfur which can be released as $H_2S$ upon acidification (the so-called "acid-labile" sulfur), and bonds between the iron atoms and the mercaptide function of the amino acid cysteine. Examples include the plant and bacterial ferredoxins.[2,3]

The stability and unusual electronic properties of the sulfur-coordinated iron atoms in the ferredoxins appear to be related to the presence of the acid-labile sulfur, the nature of which has not yet been established. Two likely possibilities are either that this sulfur is present as sulfide, $S^{2-}$, and perhaps functions as a bridging ligand,[4] or that the R–S–S–Fe linkages exist.[3] Recent investigations in our laboratory[5] have been designed to produce iron–sulfur complexes of possible relevance to ferredoxin systems in general and, in particular, to

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