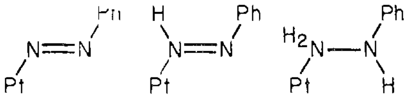
**Table V.** Comparison of Structural Parameters of Compounds I, II, and III.



| | I | II | III |
|---|---|---|---|
| Pt-P, Å | 2.302 (4) | 2.320 (6) | 2.328 (2) |
| Pt-Cl, Å | 2.413 (6) | 2.291 (2) | 2.303 (2) |
| Pt-N(1), Å | 1.975 (28) | 1.973 (7) | 2.081 (7) |
| N(1)-N(2), Å | 1.17 (3) | 1.235 (10) | 1.436 (11) |
| N(2)-C(1), Å | 1.49 (3) | 1.412 (12) | 1.408 (11) |
| Pt-N(1)-N(2), deg | 118.3 (20) | 125.3 (6) | 113.2 (5) |
| N(1)-N(2)-C(1), deg | 117.8 (23) | 120.0 (8) | 114.4 (7) |

ligand.[12] The Pt-Cl bond length in II of 2.291 (2) Å can be taken as an indication that the aryldiazene ligand has little trans influence.[1] Protonation therefore may tend to decrease the metal-to-ligand bonding in the aryldiazo group. The aryldiazo ligand then might be expected to form a shorter Pt-N bond than either the diazene or hydrazine moieties.

The N(1)-N(2) bond shows a smooth increase in length from I to II to III but in view of the errors the difference between I and II is not significant. The N(1)-N(2) bond length in I of 1.17 (3) Å is intermediate between a double and a triple bond. Compounds II and III have N-N bond lengths corresponding respectively to double and single bonds. The Pt-N(1)-N(2) and N(1)-N(2)-C(1) angles are also consistent with this reduction of the N-N bond order. The N-N bond length found here is identical with that in a previously reported structure containing a doubly bent aryldiazo group.[8]

Compounds I, II, and III differ basically in the degree of N-N bond reduction. This is clearly indicated by the trends in N-N bond lengths and bond angles about each of the nitrogen atoms.

Although complexes of the type $Pt(NO)X(PR_3)_2$, X = halide or pseudohalide, have not yet been isolated, on the basis of their very close electronic resemblance to the present complex we anticipate that they will have square-planar coordination about the Pt atom and that the Pt-N-O angle will be bent. This geometry is to be contrasted with the pseudotetrahedral arrangement in $Ni(NO)(N_3)(PPh_3)_2$.[13]

**Acknowledgment.** We wish to thank the U. S. National Institutes of Health for their support of this work and Matthey-Bishop, Inc. for the generous loan of platinum used in this study.

**Registry No.** I, 55722-66-2.

**Supplementary Material Available.** Table II, the idealized hydrogen atom parameters, Table III, the root-mean-square amplitudes of vibration, and Table IV, a listing of structure amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50289N-9-75.

## References and Notes

(1) S. D. Ittel and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4804 (1974).

(2) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, **14**, 636 (1975).

(3) (a) G. W. Parshall, *J. Am. Chem. Soc.*, **89**, 1822 (1967); (b) *ibid.*, **87**, 2133 (1965); (c) *Inorg. Synth.*, **12**, 26 (1970).

(4) R. J. Doedens and J. A. Ibers, *Inorg. Chem.* **6**, 204 (1967).

(5) In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program. Our full-matrix least-squares program NUCLS, in its nongroup form, closely resembles the Busing-Levy ORFLS program. Our absorption program is AGNOST.

(6) Scattering factors are from D. T. Cromer and J. T. Waber in "International Tables for X-Ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974.

(7) Second harmonic generation test performed by Dr. J. Dougherty of Phillips Lab, Briarcliff Manor, N. Y.

(8) A. P. Gaughan, Jr., B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, Jr., and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 6859 (1973).

(9) Supplementary material.

(10) W. E. Carroll, M. E. Deane, and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1837 (1974).

(11) R. Mason, K. N. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Am. Chem. Soc.*, **96**, 260 (1974).

(12) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(13) J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971).

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## Formation and Crystal Structure of μ-Dioxo-bis(oxodiethyldithiocarbamatomolybdenum(V))

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It is well known that the dithiocarbamato ligand confers apparently unique properties to transition metal complexes, probably because of its important electron transfers to the metal. This may account in part for the renewed interest in the study of oxomolybdenum dithiocarbamates.[1]

Newton and coworkers have recently shown that molybdenum(IV) oxodithiocarbamates oxidatively add to organic molecules containing activated multiple bonds.[2] We have previously reported the crystal structure of the tetracyanoethylene complex[3] which is, as expected, heptacoordinate. In the course of these studies, we noticed that all solutions were readily decomposing, leading to purplish oils. We wish to report an analogous investigation on the behavior of the $MoO(Et_2NCS_2)_2$ addition to dimethyl acetylenedicarboxylate.

### Experimental Section

All manipulations were carried out under argon, using solvents dried and stored under the same gas. Dimethyl acetylenedicarboxylate (Fluka) was degassed under vacuum and flash distilled prior to use. The dimethyl acetylenedicarboxylate-oxomolybdenumbis(diethyldithiocarbamate) complex was prepared after the procedure described by Newton and coworkers.[2]

The initially clear yellow solutions invariably darkened within a few hours.[2] Storing in the dark or at −28° did not inhibit this reaction. In all cases, small, well formed crystals appeared after 1 or 2 days. These were identified from infrared spectra as a μ-dioxo-molybdenum complex[4] and their structure was investigated in order to confirm this result.

Crystals of μ-dioxo-bis(diethyldithiocarbamatomolybdenum(V)) are triclinic, space group $P\bar{1}$ with $a = 8.121$ (2) Å, $b = 9.260$ (1) Å, $c = 13.921$ (1) Å, $\alpha = 107.77$ (2)°, $\beta = 101.54$ (2)°, $\gamma = 94.55$ (3)°, $V = 965.65$ Å$^3$, $M = 552$. The calculated density (1.898 g/cm$^3$) for $Z = 2$ is in good agreement with the observed density of 1.905 g/cm$^3$.

A rhombic crystal fragment having edges of 125 × 125 × 100 microns was used to record the intensity data in the range $6° < 2\theta < 75°$, using Mo K$\alpha$ radiation. Data collection and structure refinement were conducted as previously described[5] and absorption corrections were applied using the program DATAPP.[6] Refinement of the structure using anisotropic temperature factors for all nonhydrogen atoms and isotropic temperature factors for the 20 hydrogen atoms lead to a conventional $R$ factor of 0.032.[7]

### Results and Discussion

The geometry of the complex is shown in Figure 1 and interatomic distances are listed in Table I.

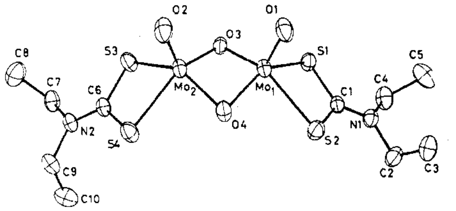

**Figure 1.** The molecular geometry of $Mo_2O_4(Et_2NCS_2)_2$.

**Table I.** Molecular Dimensions in $Mo_2O_4(S_2CNEt_2)_2$[a]

| | Bond lengths, Å | | Bond lengths, Å |
|---|---|---|---|
| Mo1-O1 | 1.677 (2) | Mo2-O2 | 1.680 (2) |
| Mo1-O3 | 1.940 (2) | Mo2-O3 | 1.940 (2) |
| Mo1-O4 | 1.940 (2) | Mo2-O4 | 1.943 (2) |
| Mo1-S1 | 2.457 (1) | Mo2-S3 | 2.459 (1) |
| Mo1-S2 | 2.447 (1) | Mo2-S4 | 2.456 (1) |
| C1-S1 | 1.728 (3) | C6-S3 | 1.732 (3) |
| C1-S2 | 1.729 (3) | C6-S4 | 1.731 (3) |
| C1-N1 | 1.306 (5) | C6-N2 | 1.302 (4) |
| N1-C2 | 1.484 (4) | N2-C7 | 1.471 (3) |
| N1-C4 | 1.475 (4) | N2-C9 | 1.486 (4) |
| C2-C3 | 1.510 (6) | C7-C8 | 1.498 (7) |
| C4-C5 | 1.492 (7) | C9-C10 | 1.498 (7) |
| Mo1-Mo2 | 2.580 (1) | C-H | 0.9 ± 2[b] |
| | Important angles, deg | | Important angles, deg |
| Mo1-O3-Mo2 | 83.37 (7) | O3-Mo1-O4 | 91.97 (11) |
| Mo1-O4-Mo2 | 83.28 (7) | O3-Mo2-O4 | 91.89 (11) |

[a] Numbers in parentheses are standard deviations unless otherwise noted. [b] Maximum deviation from the mean.

The geometry of $\mu$-dioxo-bis(diethyldithiocarbamatomolybdenum(V)) is very close to that of other di-$\mu$-bridged complexes, namely the L-cysteine complexes previously described by Kay and Drew,[8] and the $\mu$-dithio-bis(thiodi-$n$-buthyldithiocarbamatomolybdenum(V)) complex studied by Spivack and Dori.[9] The terminal and bridging Mo–O bond lengths are identical in all complexes. The short Mo–Mo distance of 2.580 Å and the obtuse $O_b$–Mo–$O_b$ angles may indicate a direct metal–metal interaction.

Examination of the least-squares plane data, however, shows a major difference between the present complex and most other di-$\mu$-bridged molybdenum(V) complexes (see Table II).

Our results show that the molecule contains two vertical mutually perpendicular planes, planes 3 and 4. The first one contains the two molybdenum and the two terminal oxygen atoms; the second contains the two bridging oxygen atoms and the points defined by the average of the Mo1–Mo2 and O1–O2 coordinates.

Whereas the metal environment in the L-cysteine complexes is best described as trigonal bipyramidal and the complexes may at most possess $C_2$ virtual symmetry, the dithiocarbamate is best represented by two "square pyramids" sharing an edge, the basal planes being bent at an angle of 148.2 (3)° along the common edge. The Mo atoms sit 0.73 Å above the planes and the Mo–$O_t$ lines are respectively perpendicular to the basal planes and coplanar. The overall geometry of the complex is thus very close to $C_{2v}$. This result is confirmed by those of Spivack and Dori on the complex $Mo_2S_4(n\text{-}Bu_2NCS_2)_2$.[9]

The reaction leading to the formation of a $\mu$-dioxomolybdenum(V) complex starting from a heptacoordinate molybdenum(VI) species remains as yet unexplained. It is however probable that it arises from a dismutation reaction similar to that recently reported by Mitchell and Scarle.[10] This and recent results obtained in our and other laboratories show the ready interconvertibility of all oxodithiocarbamatomolybdenum species and may open the way to an extensive and interesting chemistry.

**Table II.** Least-Squares Planes in the Molecule[a]

Least-Squares Planes

1. (A) $0.5035x - 0.8622y - 0.0554z = 0.0732$
   (B) S1 −3, 7 (9), S2 5 (1), O3 27 (2), O4 −30 (2)
   (C) Mo1 −0.730 (1), O1 −2.407 (3)
2. (A) $0.7614x - 0.5155y - 0.3930z = -0.4786$
   (B) S3 −8.6 (9), S4 10 (1), O3 58 (2), O4 −65 (2)
   (C) Mo2 −0.739 (1), O2 −2.419 (3)
3. (A) $-0.5660x - 0.2787y - 0.7831z = -2.8134$
   (B) Mo1 0.0 (3), Mo2 0.0 (3), O1 4 (3), O2 −4 (3)
   (C) S1 1.427 (1), S3 1.430 (1), O3 1.387 (2), N1 −0.052 (3), C1 −0.020 (3) S2 −1.448 (1), S4 −1.446 (1), O4 −1.403 (3), N2 −0.025 (3), C6 −0.019 (3)
4. (A) $0.4975x + 0.6422y - 0.5831z = -0.8889$
   (B) O3 0 (2), O4 0 (2), ⟨Mo1 − Mo2⟩ −1 (11), ⟨O1 − O2⟩ 0 (11)
   (C) Mo1 1.289 (1), O1 1.776 (3), S1 2.891 (1), S2 2.847 (1), N1 4.874 (3), C1 3.726 (3), Mo2 −1.291 (1), O2 −1.775 (3), S3 −2.902 (1), S4 −2.823 (1), N2 −4.774 (3), C6 −3.684 (3)

Angles between the Planes, deg

1-2 31.8 (3), 1-3 89.8 (3), 1-4 105.7 (3),
2-3 83.4 (3), 2-4 73.9 (3), 3-4 89.9 (3)

[a] The equations of the planes are listed under A and the atoms defining it under B along with their esd. and distances from the planes (A × 1000); the distances of selected atoms from the planes are listed under C; notice the symmetry of these values for planes 3 and 4.

**Registry No.** Dimethyl acetylenedicarboxylate–oxomolybdenumbis(diethyldithiocarbamate), 55723-31-4; $Mo_2O_4(Et_2NCS_2)_2$, 55780-89-7.

**Supplementary Material Available.** Listings of structure factors (Table III) and atomic coordinates (Table IV) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC502826-9-75.

## References and Notes

(1) See for instance: (a) J. Chatt and J. R. Dilworth, *J. Less-Common Met.*, **36**, 513 (1974); (b) M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Organomet. Chem.*, **73**, C59 (1974); (c) W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, **13**, 1100 (1974).

(2) (a) P. M. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **94**, 8640 (1972). (b) Our observations were confirmed in a personal communication by W. E. Newton.

(3) L. Ricard and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **10**, 217 (1974).

(4) R. M. Wing and K. P. Callahan, *Inorg. Chem.*, **8**, 871 (1969).

(5) L. Richard, J. Estienne, and R. Weiss, *Inorg. Chem.*, **12**, 2182 (1973).

(6) DATAPP, by P. Coppens, Buffalo.

(7) Supplementary material.

(8) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1846, 1851 (1971).

(9) B. Spivack and Z. Dori, submitted to *J. Chem. Soc., Chem. Commun.*, and personal communication.

(10) P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 110 (1975).