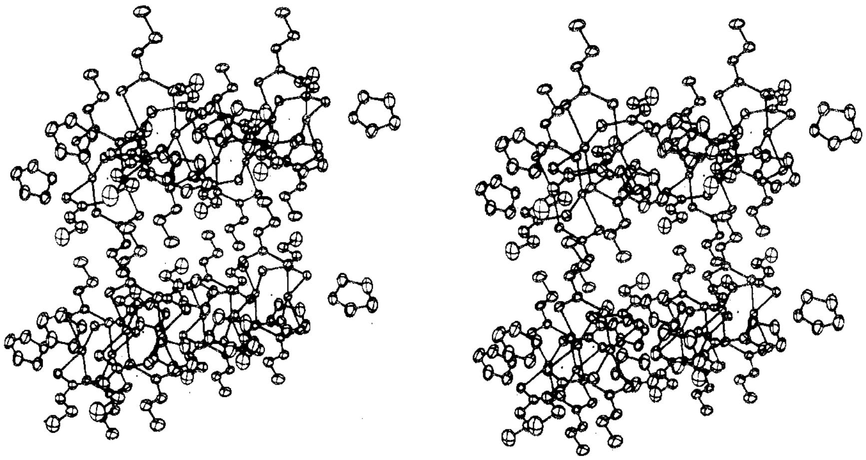

Figure 3. Stereoview of the crystal packing.

aging of the crystals and the observed weight loss.

Conclusion

The aim of this study was to investigate the generality of the carbon-sulfur bond cleavage recently observed in the reaction of $Mo_2(O_2CCH_3)_4$ with $NH_4S_2CN(C_3H_7)_2$. The main product of the reaction between $KS_2COC_2H_5$ and $Mo_2(O_2CCH_3)_4$ is now shown to have a transition metal carboxylate structure. However, one of the reaction products is not yet fully characterized. The green compound of probable composition Mo_2Xan_4 mentioned earlier has a most puzzling behavior. Recent studies indicate that it reacts in the manner expected of an alkoxycarbonyl complex[15,16] and its nmr spectrum indicates the presence of two electronically nonequivalent ligands, as does that of the thiocarboxamido complex. The stability of this complex is affected by the polarity of solvents used and it rearranges to the red complex whose structure is described here. We are presently completing our studies of the green compound, in view of ascertaining the possible occurrence of C-S bond cleavage in this compound.

Registry No. Mo_2Ac_4, 14221-06-8; KXan, 140-89-6; Mo_2Xan_4, 39301-35-4; $Mo_2Xan_4(C_4H_8O)_2$, 40694-45-9.

Acknowledgments. The authors wish to thank L. Sajus and coworkers of the Institut Francais du Petrole for their sustained interest in this work. L. R. wishes to thank the Sous-Commission quebecoise a la Recherche Scientifique et Technologique for a postdoctoral fellowship.

[15] L. Ricard and R. Weiss, unpublished results.

[16] An excellent review of this subject has been published by R. J. Angelici, *Accounts Chem. Res.*, 5, 335 (1972).

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Formation of a Thiocarboxamidomolybdenum Complex by Oxidative Bond Cleavage. Crystal and Molecular Structure of Bis[μ-sulfido-thiocarboxamido(di-*n*-propyldithiocarbamato)molybdenum], $[MoS(SCN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$

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The alleged compound $[Mo(S_2CN(C_3H_7)_2)_2]_2$ has been shown by three-dimensional X-ray structure analysis to contain one dithiocarbamate per metal atom, the second one having been cleaved at a C-S bond to yield a thiocarboxamidomolybdenum moiety; the presence of a short Mo-C bond (2.069 Å) indicates the carbene character of the Mo-C interaction. The remaining sulfur atom bridges two molybdenum atoms of the dimer; the Mo-Mo distance of 2.705 Å and the S-Mo-S and Mo-S-Mo angles of 106.5 (1) and 72.3 (1)°, respectively, indicate a Mo-Mo interaction. The crystals are monoclinic, space group C_2/c, with $a = 11.920$ (3), $b = 14.485$ (3), and $c = 24.713$ (6) Å and $\beta = 101.82$ (2)°. There are four molecules in the unit cell and the complex contains a crystallographic twofold symmetry axis. The intensities were collected by counter techniques using Mo Kα radiation. The structure was refined by least squares to an R factor of 0.050 using 2049 reflections. All atoms were given anisotropic temperature factors.

Introduction

The study of compounds containing strong multiple metal-metal bonds has recently drawn much interest. Among these compounds, the molybdenum carboxylates received particular attention.[2] Contrary to other transition metal carboxylates, however, very few studies of the reactivity of these com-

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[2] F. A. Cotton and J. G. Norman Jr., *J. Amer. Chem. Soc.*, 94, 5697 (1972), and references cited therein.

plexes were attempted. Aside from the preparation of a variety of chloro complexes and that of molybdenum trifluoroacetate,[3] molybdenum(II) acetate has not been used as starting material in the preparation of other molybdenum complexes. In view of the fact that this molecule is coordinatively unsaturated, one would expect it to react fairly easily, under mild conditions, with a variety of ligands. We were very interested when the Institut Francais du Petrole[4] reported the easy substitution of acetate by a dithiocarbamate to form a molybdenum dithiocarbamate, presumably $Mo_2(dtc)_4$. In view of the current interest in the dithiocarbamates of transition metals and the absence of structural data on molybdenum(II)-sulfur complexes, we decided to undertake a structural study of this compound.

Experimental Section

Suitable crystals of $[MoS(SCN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$ were given by Dr. Seree de Roch of the Institut Francais du Petrole.[4] The compound was prepared by reacting Mo_2Ac_4 with $NH_4S_2CN(C_3H_7)_2$ in alcohol under argon.

Crystal Data. The complex is monoclinic with $a = 11.920$ (3), $b = 14.485$ (3), $c = 24.713$ (6) Å; $\beta = 101.82$ (2)°; $V = 4176.5$ Å^3; $d_{obsd} = 1.42$ g/cm^3, for $Z = 4$ $d_{calcd} = 1.426$ g/cm^3; $\mu = 9.95$ cm^{-1}. Precession photographs showed systematic absences for hkl reflections with $(h + k)$ odd and for $h0l$ reflections with l odd, indicating that possible space groups are C_2/c or Cc. The centrosymmetric space group was preferred for interpretation of the three-dimensional Patterson map and was confirmed by successful structure solution and refinement. This space group requires molecular symmetry C_i or C_2.

The unit cell dimensions and their estimated standard deviations were obtained at room temperature (20 ± 2°) with Mo Kα radiation ($\lambda = 0.70926$ Å) using the method outlined by Busing for four-circle diffractometers.[5] The experimental density was measured by flotation in aqueous KI.

Data Collection. A crystal was cut to a cube of 200-μ edge. This fragment was sealed under nitrogen in a Lindemann glass capillary and mounted on a rotation[6] free goniometer head. All quantitative data were obtained from a Picker four-circle diffractometer controlled by a PDP-8I computer, using graphite monochromated Mo Kα radiation. The monochromator was set at a 2θ angle of 11.68° ($\theta = 5.45°$). The refined parameters listed above and the orientation matrix were obtained using standard Picker supplied routines.

Intensity data were collected by use of the θ-2θ scan technique with a scan range of 2.0° and a scan rate of 2°/min. Stationary background counts (10 sec) were recorded at each end of the scan. Attenuators were used whenever the scan count exceeded 7000 counts/sec. The intensities of three standard reflections were monitored throughout the data collection at intervals of 50 measurements. Despite all precautions, the intensities of these standards steadily dropped so that three crystals were required to collect the whole data set. A crystal was discarded when the intensities of the standards had dropped by 10%. The data were prescaled by least squares to allow for the drop in intensity and the change of crystal using a local program.[7] All subsequent calculations were conducted using one scale factor. A standard deviation was assigned to each measured intensity using the expression

$$(I) = [C + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are respectively scan and background times, and p is an empirical coefficient of the net count I.[8] The factor p was given an initial value of 0.06. A total of 3860 independent reflections were recorded in the range $2\theta < 45°$; 2049 of these had $\sigma(I)/I$ less than 0.33 and were retained. No absorption corrections were applied in view of the small crystal dimensions and linear absorption coefficient.

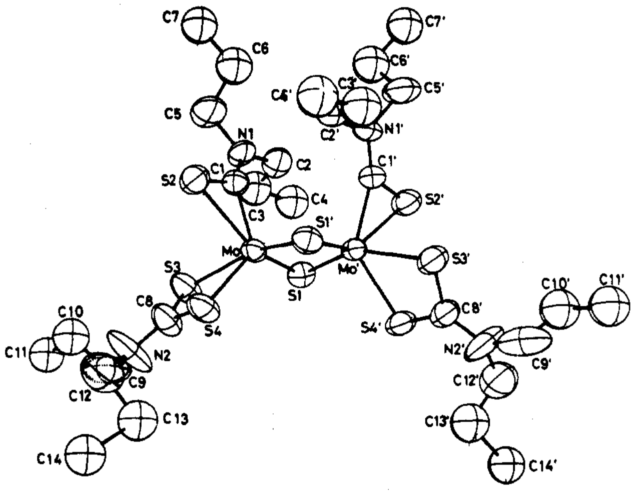

Figure 1. The $[MoS(SCN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$ molecule.

Structure Solution and Refinement. A three-dimensional Patterson map readily yielded the position of the molybdenum atom. The R factor at this stage was 0.41. A Fourier map computed using this position revealed the coordinates of all other nonhydrogen atoms.

In all structure-factor calculations, the atomic scattering factors used were those tabulated by Moore[9a] for neutral atoms using Pepinsky's development.[9b] The effects of anomalous dispersion were included for the molybdenum and sulfur atoms; the values of $\Delta f'$ and $\Delta f''$ are those given in the "International Tables for X-Ray Crystallography."[10] Atomic coordinates and individual anisotropic thermal parameters were refined by full-matrix least squares using the program SFLS-5.[11] In all least-squares computations, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors. The weight w was taken as $1/\sigma^2(F_o)$. A p value of 0.10 was used in the last cycles of refinement. The refinement converges to a discrepancy factor $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ equal to 0.050 and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ equal to 0.071. Thirty-one low-intensity reflections having ΔF greater than $3.0\sigma(F_o)$ were omitted from the final refinement cycles resulting in R values, $R_1 = 0.047$ and $R_2 = 0.065$. The standard deviation of a unit weight observation was 1.05.

A Fourier difference map computed at this stage revealed the positions of some of the hydrogen atoms, but these were not refined. No other peaks higher than 0.6 e/Å^3 were detected. All computations were conducted on a Univac 1108 computer. Other programs used were ORTEP, by C. K. Johnson[12] for drawings, and local programs by Fischer[7] for Fourier and least-squares planes. Final positional and thermal parameters for all nonhydrogen atoms are listed in Table I. Table II contains the observed and computed structure factors for all 2049 reflections used in the refinement.[13] Table III contains a list of selected bond lengths and angles.

Results and Discussion

The crystal structure analysis has confirmed that the global composition of the complex is indeed $Mo_2(dtc)_4$. However, it has shown that the molecule is not a simple dithiocarbamate, as could be expected from elemental analysis. Figure 1 shows, along with the numbering scheme adopted, the

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(3) (a) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 9, 346 (1970), and references cited therein; (b) G. B. Allison, I. R. Anderson, and J. C. Sheldon, *Aust. J. Chem.*, 22, 1091 (1969); (c) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, 1, 161 (1972).

(4) R. Barral, C. Bocard, I. Seree de Roch, and L. Sajus, private communication.

(5) W. R. Busing, "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 319.

(6) In order to improve the stability of the crystal mounting, a special head, comprising only three translations, is used currently in this lab, following an original design of W. Peter, E.T.A., Zurich, private communication.

(7) J. Fischer, unpublished results.

(8) O. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(9) (a) F. M. Moore, *Acta Crystallogr.*, 16, 1169 (1963); (b) V. Vand, P. F. Eiland, and R. Pepinsky, *ibid.*, 10, 303 (1957).

(10) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, 215.

(11) C. T. Prewitt, a FORTRAN IV full-matrix crystallographic least-squares program, SFLS5, 1966.

(12) C. K. Johnson, Program ORTEP, ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(13) Table II, listing structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N. W., Washington D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2182.

Table I. Fractional Atomic Coordinates and Thermal Parameters ($\times 10^5$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	992 (5)	7,694 (3)	19,645 (2)	1020 (6)	455 (3)	229 (1)	−62 (3)	139 (1)	−32 (1)
S_1	15,723 (16)	6,111 (14)	26,855 (8)	840 (15)	611 (11)	273 (4)	14 (10)	118 (6)	−27 (5)
S_2	−7,403 (26)	19,181 (15)	12,280 (10)	1863 (30)	608 (12)	234 (4)	−98 (15)	−14 (9)	0 (6)
S_3	14,922 (22)	2,946 (16)	13,652 (10)	1448 (25)	780 (14)	373 (6)	−340 (15)	394 (10)	−217 (7)
S_4	−7,331 (21)	−4,848 (14)	13,320 (10)	1352 (22)	556 (10)	325 (5)	−208 (12)	226 (9)	−138 (6)
C_1	3,145 (80)	21,422 (50)	17,778 (34)	1494 (96)	452 (39)	226 (17)	−163 (47)	198 (33)	−36 (21)
C_2	17,692 (95)	29,636 (65)	24,238 (43)	1494 (110)	699 (54)	297 (23)	−253 (62)	87 (41)	−1 (28)
C_3	29,535 (118)	27,172 (112)	23,093 (65)	1433 (126)	1587 (124)	497 (41)	−331 (103)	35 (60)	378 (57)
C_4	37,093 (181)	26,836 (151)	28,914 (93)	2649 (266)	1907 (182)	686 (65)	−731 (175)	−335 (109)	136 (88)
C_5	7,823 (142)	37,175 (76)	15,368 (54)	2908 (206)	557 (58)	404 (33)	−232 (87)	52 (64)	56 (34)
C_6	1,841 (161)	44,717 (110)	17,424 (78)	2637 (231)	1138 (110)	565 (46)	286 (118)	203 (81)	191 (60)
C_7	1.066 (216)	53,193 (106)	13,333 (84)	4410 (357)	918 (93)	663 (57)	−532 (152)	22 (111)	362 (63)
C_8	4,862 (93)	−4,926 (67)	10,680 (44)	1462 (104)	760 (56)	323 (22)	−274 (58)	305 (39)	−208 (29)
C_9	19,597 (132)	−12,479 (89)	5,630 (74)	2303 (188)	719 (74)	598 (49)	−14 (92)	97 (78)	7 (48)
C_{10}	17,490 (174)	−6,327 (113)	1,196 (63)	3102 (269)	1225 (118)	404 (38)	93 (133)	−321 (81)	−285 (54)
C_{11}	30,564 (152)	−8,426 (144)	−774 (84)	2200 (201)	2662 (221)	794 (67)	−1276 (173)	907 (103)	−903 (102)
C_{12}	−3,641 (166)	−16,530 (121)	3,830 (89)	3003 (256)	1245 (115)	823 (67)	−885 (146)	761 (111)	−756 (80)
C_{13}	−2,456 (179)	−24,970 (152)	6,295 (131)	2252 (234)	1320 (144)	1419 (133)	−122 (161)	294 (142)	−681 (118)
C_{14}	−11,543 (168)	−31,541 (122)	1,468 (126)	2456 (246)	1017 (111)	1373 (117)	−355 (133)	−255 (131)	−365 (91)
N_1	8,903 (72)	28,971 (41)	19,133 (29)	1775 (93)	377 (31)	249 (16)	−232 (43)	89 (31)	28 (18)
N_2	6,460 (104)	−10,933 (80)	6,876 (52)	2050 (129)	1326 (79)	628 (38)	−687 (87)	689 (60)	−629 (49)

Table III. Molecular Dimensions in $[MoS(SCNPr_2)(S_2CNPr_2)]_2$

Bond Lengths, Å			
Mo-Mo′	2.705 (2)	C_3-C_4	1.534 (25)
Mo-S_1	2.242 (2)	C_5-C_6	1.452 (23)
Mo-S_1′	2.340 (2)	C_6-C_7	1.581 (24)
Mo-S_2	2.517 (2)	C_8-S_3	1.708 (10)
Mo-S_3	2.536 (2)	C_8-S_4	1.711 (12)
Mo-S_4	2.469 (2)	C_8-N_2	1.323 (16)
Mo-C_1	2.069 (7)	N_2-C_9	1.672 (21)
C_1-S_2	1.683 (8)	N_2-C_{12}	1.518 (21)
C_1-N_1	1.298 (10)	C_9-C_{10}	1.395 (22)
N_1-C_2	1.469 (12)	C_{10}-C_{11}	1.752 (29)
N_1-C_5	1.498 (13)	C_{12}-C_{13}	1.360 (30)
C_2-C_3	1.538 (19)	C_{13}-C_{14}	1.724 (33)
Bond Angles, deg			
Mo-S_1-Mo′	72.3 (1)	C_1-N_1-C_5	122.3 (7)
S_1-Mo-S_1′	106.5 (1)	C_2-N_1-C_5	115.9 (7)
S_1′-Mo-S_2	95.1 (1)	N_1-C_2-C_3	110.3 (7)
S_1′-Mo-S_3	153.9 (1)	C_2-C_3-C_4	102.7 (9)
S_1′-Mo-S_4	84.2 (1)	N_1-C_5-C_6	111.4 (8)
S_1-Mo-S_2	140.6 (1)	C_5-C_6-C_7	109.2 (1.0)
S_1-Mo-S_3	86.4 (1)	Mo-S_3-C_8	86.9 (2)
S_1-Mo-S_4	125.1 (1)	Mo-S_4-C_8	89.1 (3)
S_2-Mo-S_3	88.2 (1)	S_3-C_8-S_4	114.1 (2)
S_2-Mo-S_4	88.9 (1)	S_3-C_8-N_2	123.6 (5)
S_3-Mo-S_4	69.9 (1)	S_4-C_8-N_2	122.2 (5)
S_1′-Mo-C_1	109.3 (2)	C_8-N_2-C_9	119.7 (8)
S_1-Mo-C_1	59.1 (2)	C_8-N_2-C_{12}	119.3 (1.0)
S_2-Mo-C_1	41.6 (2)	C_9-N_2-C_{12}	121.0 (9)
S_3-Mo-C_1	90.3 (2)	N_2-C_9-C_{10}	92.0 (8)
S_4-Mo-C_1	128.2 (2)	C_9-C_{10}-C_{11}	94.6 (1.0)
Mo-C_1-N_1	146.7 (4)	N_2-C_{12}-C_{13}	105.0 (1.1)
S_2-C_1-N_1	129.7 (4)	C_{12}-C_{13}-C_{14}	101.2 (1.2)
C_1-N_1-C_2	121.6 (6)		
Important Intramolecular Contact Distances, Å			
C_1-S_1	3.289 (10)	S_1′-S_4	3.227 (3)
C_1-S_1′	3.600 (10)	S_1-S_3	3.277 (3)
C_1-S_3	3.280 (10)	S_1-S_1′	3.672 (3)
S_2-S_1′	3.587 (3)	S_3-S_4	2.869 (3)
S_2-S_4	3.490 (3)		

geometry of the complex and Figure 2 is a stereoview of the molecule. As expected from the density measurements, the molecule is dimeric and contains a crystallographic twofold axis. The ligand containing sulfur atoms S_3 and S_4 is a normal dithiocarbamate. The second ligand, however, has lost a sulfur atom. This resulted in the formation of a thiocarboxamido moiety bonded to molybdenum both through carbon C_1 and sulfur S_2. The sulfur atom S_1 liberated by the cleavage of a dithiocarbamate C-S bond bridges the two molybdenum atoms of the dimer.

Table IV. Least-Squares Planes in the Molecule. The Equation has the Form $Ax + By + Cz - D = 0$

	A	B	C	D	Atoms[a]	Distance from the plane, Å × 10^3
Plane 1	0.2682	−0.6745	0.6879	−2.2810	Mo	0 (1)
					S_3	−0 (3)
					S_4	−0 (2)
					C_8	−7 (10)
					N_2	14 (11)
Plane 2	0.7325	−0.3195	−0.6011	−3.8469	Mo	−6 (1)
					S_1	37 (2)
					S_2	69 (3)
					C_1	−142 (9)
					N_1	−218 (7)
Plane 3	0.8027	−0.2659	−0.5338	−3.5352	Mo	0 (1)
					S_1[b]	246 (3)
					S_2	1 (3)
					C_1	−34 (9)
					N_1	13 (7)

[a] All atoms mentioned are included in the computation unless otherwise noted. [b] Not included in the computation of plane 3.

Table V. Bond Lengths (Å) and Bond Angles (deg) in Some MoS_2 Units

	This study	$(C_5H_5$-$MoOS)_2$	$[(C_4H_8NO_2S)$-$MoOS]_2$
Mo-Mo	2.705 (2)	2.894 (5)	2.804 (4)
Mo-S_1	2.242 (2)	2.317 (3)	2.299 (13)
Mo-S_1′	2.340 (2)	2.317 (3)	2.315 (13)
S_1-S_1′	3.672 (3)	3.616 (9)	3.58
Mo-S_1-Mo′	72.3 (1)	77.3 (1)	74.8 (4)
S_1-Mo-S_1′	106.5 (1)	102.7 (1)	101.8 (5)
Angle between the MoS_2 planes	160.7	0.0	149.1
Environment of the metal	Deformed octahedral	Octahedral	Trigonal bipyramidal

The outstanding feature of this molecule is the occurrence, during its formation, of a carbon–sulfur bond cleavage. This reaction is similar to the well-known oxidative addition reaction which, though frequent with d^8 and d^{10} metals, is not at all common with a d^4 metal such as Mo^{II}. One example is the addition of Cl_2 to π-$C_5H_5Mo(CO)_3Cl$ to yield π-$C_5H_5Mo(CO)_2Cl_3$.[14] The thiocarboxamido moiety formed

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(14) M. L. H. Green and W. E. Lindsell, *J. Chem. Soc. A*, 686 (1967).

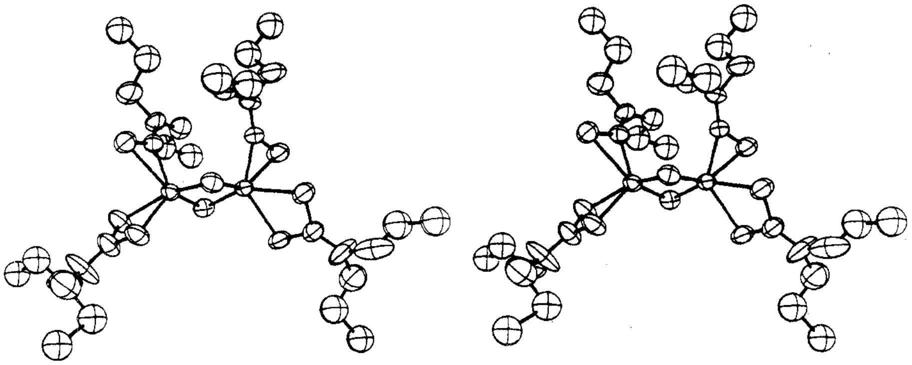

Figure 2. Stereoview of the molecule.

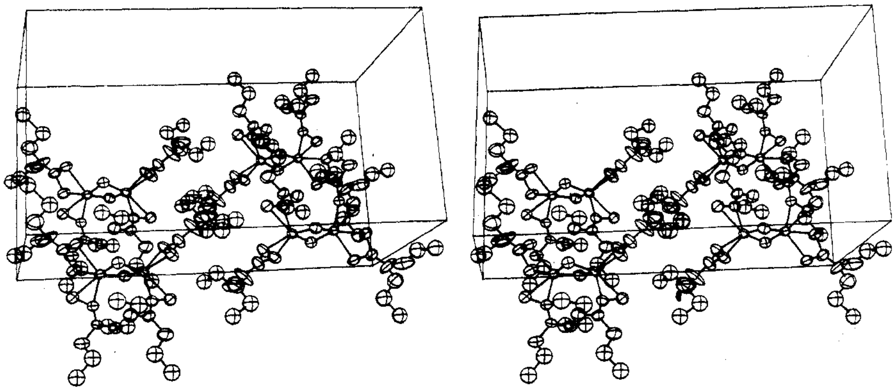

Figure 3. Molecular content of the unit cell of $[MoS(SCN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$.

in this reaction is, in many respects, unusual. This ligand is bonded to the Mo atom through both sulfur and carbon atoms, as Treichel and coworkers recently suggested.[15] The Mo-S_2 bond has a length of 2.517 (2) Å. This value is similar to that found in the normal dithiocarbamate present in this molecule (*cf.* Table III). The carbon atom C_1 is very strongly bonded to molybdenum, the bond length being 2.069 (7) Å. This is considerably shorter than that found in most alkylmolybdenum derivatives[16] and similar to the value of 2.092 (12) Å reported in the nitrogenomolybdenum carbene chelate $\pi\text{-}C_5H_5(CO)_2\overline{MoNHNCCO_2C_2H_5C}OH$.[17] Such a short Mo-C bond is generally regarded as due to multiple bonding arising from the presence of a carbene. According to the work of Cotton, *et al.*,[18] the bond order would be approximately 1.5. For the purpose of electron counting, we will later consider it as a double bond.

Despite the *a priori* important perturbation induced in the ligand by the formation of the Mo-C bond, there is no apparent change in the S_2-C_1 and C_1-N_1 bond lengths compared to analogous bonds in the dithiocarbamate. As shown in Table III, the angles formed between the atoms Mo, S_2, C_1, and N_1 are comparable to those observed in the complex $Pt(PPh_3)_2CS_2$, so that the bonding of the thiocarboxamido moiety to molybdenum is reminiscent of that of CS_2 to platinum.[19] Finally, it should be noted that the atoms Mo, S_1, S_2, C_1, N_1, C_2, and C_5 are nearly coplanar, as it is the case in a normal dithiocarbamate (Table IV).

Extensive studies of cluster systems involving molybdenum and sulfur have recently been published.[20] In doubly bridging sulfur complexes, the Mo-S and Mo-Mo distances have nearly constant values of 2.31 and 2.81 Å, respectively. These values do not seem to be affected by the formal oxidation state of the metal. Whenever there is a metal-metal interaction, the M-S-M angle is acute and the angle between the M-S_2 planes depends on the environment of the metal.[21] Two molybdenum(V) complexes are of particular interest in the present instance. The data concerning the title compound, the complex $(\pi\text{-}C_5H_5MoOS)_2$[22] and (L-cysteinato-$MoOS)_2$,[23] are summarized in Table V.

Our results confirm the essential invariance of the Mo-bridging sulfur distance. On the other hand, referring to Table V, one sees that the Mo-Mo distance in the present complex is remarkably short. This shortening of the Mo-Mo bond results in a significant lengthening of the S_1-S_1' nonbonded distance, a decrease of the Mo-S_1-Mo$'$ angle and a corresponding opening of the S_1-Mo-S_1' angle.

The above values indicate that there still exists a very strong metal-metal interaction in the thiocarboxamido complex and, in view of the values observed in the other complexes, one would expect it to be stronger in the present complex. As a result of the oxidative C-S bond cleavage, the molybdenum atom can be formally regarded as molybdenum(IV). If we assume single Mo-S bonds and a double Mo-C bond, the electron count leads to 16 electrons around a given molybdenum atom. This is two electrons short of the "ideal" 18 electrons and, hence, we can consider that we

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have a double Mo-Mo bond in the complex.[24] This is to be compared to the weak interaction proposed by Dahl in the complex $(\pi\text{-}C_5H_5MoOS)_2$ and the strong bond suggested by Drew's results.

The rest of the molecule, namely, the dithiocarbamato ligand and the propyl chains of both ligands, present the usual geometries and bond lengths taking into account some imprecision of carbon-carbon bond lengths. This may result from the strong thermal motions of these atoms. As shown in Figure 3, the crystal cohesion is mainly ensured by contacts between the propyl chains and there are only weak interactions between the molecules. This may be responsible for some lack of precision in the resolution of the structure at the level of the propyl chains.

Registry No. $[MoS(SCN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$, 40631-71-8.

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[24] The Mo-S_1 bond order is probably more than 1.0. If we use, as Drew suggests, an Mo-S_1 bond order of 1.5, bond orders of 1.0 for all other sulfurs, and a bond order of 1.5 for Mo-C_1, we get a bond order of 1 for the thiocarboxamido complex. However, the value of 1.5 for the Mo-S_1 bond order is probably overestimated. A value of 1.3, similar to that suggested by Cotton[25] in the Mo_2O_2 system, seems more reasonable and leads to essentially the same results as above.

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Notes

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Phenylimino Quaternization of Birdcage Phosphorus Compounds

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One of the less explored areas of phosphorus chemistry consists of the broad group of structures[2-4] in which each phosphorus atom is bonded only to nitrogen atoms. This group has received relatively little attention as compared to the massive body of work[4,5] on the compounds in which each phosphorus is bonded only to oxygen atoms. In the study reported here, a series of birdcage structures is described in which four phosphorus atoms are bridged by nitrogen and each tetracoordinate phosphorus is surrounded by four nitrogen atoms. Some related chemistry is also discussed.

Experimental Section

Materials. Due to the sensitivity of the compounds to moisture and oxygen, all operations were carried out under dry nitrogen, with exclusion of light for P_4O_6 and its reaction products. The solvents were of Spectrograde quality and practically water free; prior to use they were saturated with dry nitrogen. High-purity tetraphosphorus hexaoxide was purchased from Albright & Wilson, Ltd., London, England, and tetraphosphorus hexamethylhexaimide was prepared by an improvement to the procedure given in ref 6. Phenyl azide was made according to the literature.[7]

Analyses. The ^{31}P nuclear magnetic resonance (nmr) spectra were run on a Varian XL-100-15 spectrometer at 40.55 MHz, with locking onto the deuterium resonance of D_2O which was contained in a 5-mm tube that was concentrically inserted into the 12-mm tube holding the sample. Broad-band decouplings of the protons were employed and chemical shifts are reported *vs.* external 85% H_3PO_4. The ^1H nmr spectra were obtained with a Varian A-60 spectrometer in $CDCl_3$ solution with tetramethylsilane as the internal-reference standard. Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz. Uncorrected melting points were obtained in sealed capillaries on a Mel-Temp unit.

Reactions. Sufficient birdcage compound $[P_4(NCH_3)_6$ or $P_4O_6]$ was dissolved in 10 ml of benzene to make a *ca.* 1.0 *M* solution and the desired amount of phenyl azide was pipetted in from a 3.5 *M* solution in benzene.

Isolation of Crystalline Species. The two compounds corresponding to one and four phenylimino groups being bonded to the tetraphosphorus hexamethylhexaimide birdcage molecule have been isolated in crystalline form. The first of these compounds, which might be named hexa-μ-methylimino-tetraphosphorus monophenylimide, was prepared by adding 1.88 g of $C_6H_5N_3$ in 10 ml of hexane to a solution of 4.70 g of $P_4(NCH_3)_6$ in 20 ml of hexane. Since $[P_4(NCH_3)_6]NC_6H_5$ is insoluble in hexane, a yellow precipitate formed within a few seconds, as would be predicted from the value presented for k_1 of eq 1. After stirring for 10 min, the resulting yellow crystals were filtered within a drybox and dried under vacuum; yield 4.88 g (61%); mp 96.5° dec. *Anal.* Calcd for $C_{12}H_{23}N_7P_4$: C, 37.03; H, 5.95; N, 25.19; P, 31.83. Found: C, 37.37; H, 5.66; N, 25.30; P, 31.29. The ^{31}P nmr data are presented in Table I and the ^1H data are the following: $\tau(C_6H_5)$ 2.58 (complex multiplet, 5 H), $\tau(CH_3)$ *ca.* 6.9 (middle of complex multiplet, 18 H).

The preparation of $[P_4(NCH_3)_6](NC_6H_5)_4$ was accomplished by adding 2.32 g of $C_6H_5N_3$ in 10 ml of benzene to a solution consisting of 1.5 g of $P_4(NCH_3)_6$ in 5 ml of benzene. After gentle reflux for 20 hr and then concentration to a total volume of about 7 ml, a yield was obtained of 1.1 g (34% of theory) of white crystals, mp 167°, which were filtered and dried under vacuum. *Anal.* Calcd for $C_{30}H_{38}N_{10}P_4$: C, 54.46; H, 5.79; N, 21.17; P, 18.72. Found: C, 54.58; H, 5.96; N, 20.91; P, 18.56. Again the ^{31}P nmr data for this compound are presented in Table I and the ^1H data are as follows: $\tau(C_6H_5)$ 3.00 (complex multiplet, 20 H); $\tau(CH_3)$ 6.82 (pseudotriplet, 18 H); $J(PNCH_3) = 10.3$ Hz.

Attempts to make the compounds $[P_4(NCH_3)_6](NC_6H_5)_2$ and $[P_4(NCH_3)_6](NC_6H_5)_3$ led to the formation of oily products which we were unable to crystallize. As can be seen from the kinetic calculations, the rate constants for the reactions of eq 1-4 are such that only $[P_4(NCH_3)_6](NC_6H_5)$ and the final product $[P_4(NCH_3)_6](NC_6H_5)_4$ can be made essentially pure. Presumably, the presence of some of the neighboring species of this series of compounds inhibits the crystallization of the two intermediate structures.

Results and Discussion

Quaternization of $P_4(NCH_3)_6$. When increasing amounts of phenyl azide are added at 40° to tetraphosphorus hexamethylhexaimide in a nonreactive organic solvent (benzene), periodic observation by ^{31}P nuclear magnetic resonance (nmr) shows that there is a stepwise addition of phenylimino groups

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