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Preparation and Crystal and Molecular Structure of Tetrakis(*O*-ethyl dithiocarbonato)dimolybdenum Bis(tetrahydrofuranate)

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The reaction of Mo_2Ac_4 with excess $KS_2COC_2H_5$ yielded two products which have been characterized by ir and nmr spectroscopy. A green compound, tentatively formulated as Mo_2Xan_4, structure unknown, rearranges into a red complex, tetrakis(*O*-ethyl dithiocarbonato)dimolybdenum. An X-ray crystal structure analysis revealed that this complex crystallizes in space group $P\bar{1}$, with $a = 8.391$ (3) Å, $b = 10.961$ (3) Å, $c = 11.345$ (3) Å, $\alpha = 88.84$ (2)°, $\beta = 112.19$ (2)°, $\gamma = 119.91$ (2)°, and $V = 818.9$ Å^3. The unit cell contains one centrosymmetric molecule, possessing close to ideal D_{4h} symmetry at the level of the Mo_2S_8 skeleton. Two THF molecules occupy the free axial positions of the molecule. The structure of the complex is that of a transition metal carboxylate, of general formula $M_2L_4 \cdot 2L'$. The intensities of 4559 reflections were collected by counter methods using Mo Kα radiation. Positional and anisotropic temperature factors for all nonhydrogen atoms were refined by least squares to a conventional *R* factor of 3.3%. All hydrogen atoms were located and included in the refinement. These were assigned fixed isotropic temperature factors.

Introduction

We have recently found that the reaction of ammonium dithiocarbamate with dimolybdenum tetraacetate, instead of leading to a *bona fide* molybdenum dithiocarbamate, yields a thiocarboxamido complex analogous to those recently described by Treichel.[2] This reaction can be likened to an oxidative addition reaction. In view of the current interest in these reactions, we have attempted to broaden the scope of the reaction observed with the dithiocarbamate ion. In order to show its generality, we tried ligands containing other heteroatoms than nitrogen. The first choice for this kind of work is obviously the xanthate molecule, since its overall properties are similar to those of a dithiocarbamate. The present is a report of the results obtained to date concerning the reaction of dimolybdenum tetraacetate with potassium *O*-ethyl dithiocarbonate.

Experimental Section

Molybdenum(II) acetate was prepared following the method of Wilkinson.[3] Potassium xanthate was obtained by slowly adding CS_2 to an alcoholic solution of KOH at 0° and used without further purification. All solvents were dried by conventional methods and the reactions were conducted under argon. Molybdenum analyses were effected by calcination to MoO_3 at 600°.

Preparation of the Red Mo_2Xan_4. Mo_2Ac_4 (1 g) was allowed to react, in alcohol at room temperature, with 4 g of KXan for 8 hr. The solution became green after a few minutes and a red compound crystallized after a few hours. This product may be contaminated by traces of a green product. It can be purified by washing with benzene. The compound is slightly soluble in aromatic solvents and fairly soluble in acetone and tetrahydrofuran. Its nmr spectrum in acetone-d_6 at 60 MHz shows only a quartet at τ 5.3 and a triplet at τ 8.5; the ir spectrum contains a complex band system between 1000 and 1200 cm^{-1}. Both spectra indicate that all acetates have been substituted. *Anal.* Calcd for Mo_2Xan_4: Mo, 28.40; S, 37.87; C, 21.30; H, 2.96. Found: Mo, 28.38; S, 36.28; C, 22.11; H, 2.90.

Structure of Tetrakis(*O*-ethyl dithiocarbonato)dimolybdenum Bis(tetrahydrofuranate). Crystal Data. Suitable crystals were obtained from tetrahydrofuran. They appeared to be solvated and this was later confirmed by the solution of the structure. Precession photographs showed the crystals to be triclinic, space group *P*1 or $P\bar{1}$. The crystal parameters are $a = 8.391$ (3) Å, $b = 10.961$ (3) Å, $c = 11.345$ (3) Å, $\alpha = 88.84$ (2)°, $\beta = 112.19$ (2)°, $\gamma = 119.91$ (2)°, and $V = 818.9$ Å^3.

The density of crystals freshly taken from the solution is 1.92 g/cm^3. This density requires the presence of four THF molecules in the unit cell ($d_{\text{calcd}} = 1.922$ g/cm^3). However, the crystals appeared to be rapidly loosing weight for a few hours. Their density decreases to 1.70 g/cm^3. A molybdenum analysis performed on these crystals yielded a Mo content of 23.46 %. The presence of a two-THF adduct of Mo_2Xan_4 in the unit cell requires a density of 1.664 g/cm^3. The molybdenum content of this compound would be 23.39%. Since the aged crystals remained transparent and suitable for diffraction measurements, it was decided to use these crystals to record the intensities.

The unit cell dimensions and their estimated standard deviations were obtained at room temperature (20 ± 2°) with Mo Kα radiation (λ 0.70926 Å) using the procedure outlined by Busing.[4] The experimental densities were measured by flotation in a mixture of CCl_4 and $CHBr_3$.

Data Collection. A crystal was cut to a cube of 175-μ edge. This fragment was sealed under nitrogen in a Lindemann glass capillary and mounted on a rotation-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 11.84° ($\theta = 5.57°$). The refined parameters listed above and the orientation matrix were obtained using standard Picker routines.

Intensity data were collected by use of the θ–2θ scan technique with a scan range of 1.8° and a scan rate of 2°/min. Stationary-background counts of 20 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. Since the crystals were slowly decomposing, the intensities of these standards steadily dropped, so that four crystals were required to collect the whole data set. A crystal was discarded when the intensities of the three standards had dropped by 16%. The data were prescaled by least squares to allow for the drop in intensity and the change of crystal using a local program.[5] One scale factor was then used for most subsequent calculations. A standard deviation was assigned to each measured intensity using the expression $\sigma(I) = |C + (t_c/t_b)^2(B_1 + B_2) + (pI)^2|^{1/2}$, where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are scan and background times, respectively, and p is an empirical coefficient of the net count I.[6] The p value was initially set at 0.05. A total of 8116 independent reflections were recorded in the range $2\theta < 70°$; 4559 of these had $\sigma(I)/I$ less than 0.40 and were retained. No absorption corrections were applied in view of the small crystal dimensions and linear absorption coefficient ($\mu = 13.0$ cm^{-1}).

Structure Solution and Refinement. A three-dimensional Patterson map revealed that the crystal is centrosymmetric, space

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[2] (a) L. Ricard, J. Estienne, and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 906 (1972); (b) to be submitted for publication; (c) P. M. Treichel and W. K. Dean, *J. Chem. Soc., Chem. Commun.*, 804 (1972); (d) R. Barral, C. Bocard, I. Seree de Roch, and L. Sajus, private communication.

[3] A. B. Brignole, F. A. Cotton, Z. Dori, and G. Wilkinson, *Inorg. Syn.*, 13, 87 (1972).

[4] W. R. Busing, "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 319.

[5] J. Fischer, unpublished data.

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

Table I. Positional and Thermal Parameters for the Nonhydrogen Atoms in $Mo_2(S_2COC_2H_5)\cdot 2C_4H_8O$ ($\times 10^5$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	15,361 (2)	4,469 (1)	6,761 (1)	1291 (6)	659 (2)	644 (2)	510 (2)	291 (2)	67 (1)
S(1)	−19,947 (8)	14,945 (5)	−1,166 (5)	1659 (13)	867 (7)	885 (6)	744 (8)	232 (7)	−79 (5)
S(2)	23,472 (8)	27,603 (5)	17,469 (5)	1601 (14)	754 (6)	951 (6)	592 (8)	157 (7)	−110 (5)
S(3)	10,290 (8)	−5,276 (7)	25,817 (5)	1619 (13)	1014 (7)	693 (6)	608 (8)	357 (7)	182 (5)
S(4)	−32,916 (8)	−18,381 (7)	6,556 (5)	1471 (13)	1093 (8)	835 (6)	601 (8)	453 (7)	263 (5)
C(1)	2,267 (33)	28,052 (23)	10,594 (21)	1784 (51)	734 (24)	744 (22)	686 (30)	413 (28)	46 (18)
C(2)	−13,577 (43)	41,273 (29)	10,620 (29)	2652 (73)	1144 (35)	1246 (33)	1274 (44)	598 (41)	52 (27)
C(3)	−7,642 (59)	54,906 (35)	18,359 (37)	4369 (115)	1297 (42)	1686 (47)	1719 (62)	1133 (61)	46 (35)
C(4)	−15,021 (34)	−15,488 (23)	21,361 (22)	1832 (53)	800 (25)	742 (22)	677 (31)	565 (29)	187 (19)
C(5)	−41,269 (43)	−30,753 (31)	28,229 (29)	2224 (67)	1191 (36)	1118 (32)	583 (41)	898 (39)	343 (27)
C(6)	−41,941 (56)	−34,108 (46)	40,878 (37)	3245 (104)	2408 (71)	1292 (42)	738 (69)	1295 (57)	624 (44)
C(7)	62,642 (52)	5,992 (40)	27,763 (33)	2850 (89)	1896 (55)	1271 (39)	1537 (61)	223 (47)	−130 (36)
C(8)	83,641 (57)	14,286 (48)	38,066 (35)	3135 (101)	2570 (73)	1228 (41)	1861 (75)	112 (51)	−89 (43)
C(9)	85,130 (71)	26,627 (50)	44,322 (43)	4564 (146)	2178 (70)	1661 (54)	2078 (89)	−744 (69)	−618 (49)
C(10)	65,010 (56)	25,217 (43)	37,238 (35)	3421 (106)	1943 (58)	1220 (40)	1460 (67)	268 (52)	−274 (38)
O(1)	4,051 (27)	39,925 (17)	15,379 (17)	2096 (44)	812 (20)	1049 (20)	827 (25)	336 (24)	−99 (16)
O(2)	−19,949 (27)	−21,319 (20)	30,824 (17)	2050 (44)	1191 (24)	847 (19)	666 (27)	712 (24)	359 (17)
O(3)	54,889 (28)	15,082 (22)	25,541 (19)	2185 (49)	1595 (31)	904 (21)	1158 (33)	195 (25)	26 (20)

Table II. Positional and Thermal Parameters for the Hydrogen Atoms in $Mo_2(S_2COC_2H_5)\cdot 2C_4H_8O$

	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	B, Å^2
H(2-1)	−1679 (69)	4188 (48)	187 (74)	6.00
H(2-2)	−2205 (76)	3479 (52)	1230 (46)	6.00
H(5-1)	−4786 (67)	−2532 (49)	2489 (44)	6.00
H(5-2)	−4683 (68)	−3857 (52)	2189 (43)	6.00
H(3-1)	−1887 (79)	5567 (55)	1598 (50)	7.30
H(3-2)	265 (87)	6132 (60)	1770 (54)	7.30
H(3-3)	−392 (87)	5472 (58)	2645 (55)	7.30
H(6-1)	−5564 (95)	−3817 (68)	4017 (57)	9.00
H(6-2)	−3554 (92)	−2437 (66)	4622 (57)	9.00
H(6-3)	−3743 (100)	−3855 (71)	4351 (66)	9.00
H(7-1)	5631 (80)	115 (58)	3297 (51)	7.00
H(7-2)	6069 (77)	242 (57)	2048 (51)	7.00
H(8-1)	9002 (89)	1767 (67)	3341 (56)	8.40
H(8-2)	8746 (85)	788 (60)	4400 (56)	8.40
H(9-1)	9271 (112)	3091 (79)	5263 (71)	11.90
H(9-2)	9324 (110)	3690 (78)	4240 (68)	11.90
H(10-1)	6845 (94)	3311 (67)	3431 (57)	8.40
H(10-2)	6199 (91)	2056 (63)	4370 (55)	8.40

group $P\bar{1}$, and readily yielded the position of the molybdenum atom and that of the four independent sulfur atoms. The R factor at this stage was 0.31. A Fourier map computed using these positions revealed that of all other nonhydrogen atoms in the molecule and of two THF molecules. In all structure factor calculations, the atomic scattering factors used were those tabulated by Moore[7] for neutral atoms, using the development of Pepinsky.[8] 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 ref 9. After three cycles of refinement using isotropic temperature factors, the atomic coordinates and individual anisotropic temperature factors were refined by full-matrix least squares using the program SFLS-5.[10] In all least-squares computation, 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 equals $1/\sigma^2(|F_o|)$. The refinement converges to a discrepancy factor $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ equal to 0.052. A difference Fourier map computed at this stage revealed the positions of all hydrogen atoms in the molecule. These were assigned isotropic temperature factors using the expression $B_H = 1.6B_C - 2.0$, but only their positional parameters were varied.

Since some important correlations appeared in the least-squares matrix, the refinement of the structure was continued by dividing the molecule into two parts. The coordinates of all nonhydrogen atoms were first refined using the hydrogen atoms as fixed factors; then, the refinements of the Mo and 4 S atoms were blocked and all carbon and hydrogen atoms were refined. After a few cycles of this proce-

Table IV. Molecular Dimensions in $Mo_2Xan_4\cdot 2THF$

(a) Bond Lengths, Å

Mo–Mo	2.125 (1)	O(2)–C(5)	1.458 (3)
Mo–S(1)	2.477 (1)	C(5)–C(6)	1.490 (5)
Mo–S(2)	2.480 (1)	Mo–O(3)	2.795 (1)
Mo–S(3)	2.479 (1)	O(3)–C(7)	1.412 (6)
Mo–S(4)	2.475 (1)	O(3)–C(10)	1.409 (4)
C(1)–S(1)	1.688 (1)	C(7)–C(8)	1.479 (4)
C(1)–S(2)	1.678 (3)	C(8)–C(9)	1.468 (8)
C(1)–O(1)	1.336 (3)	C(9)–C(10)	1.497 (7)
O(1)–C(2)	1.454 (4)	C–H[a]	0.909 (20)
C(2)–C(3)	1.495 (5)	O(3)· · ·S′(1)	3.420 (3)
C(4)–S(3)	1.692 (2)	O(3)· · ·S(2)	3.378 (3)
C(4)–S(4)	1.679 (2)	O(3)· · ·S(3)	3.278 (3)
C(4)–O(2)	1.333 (3)	O(3)· · ·S′(4)	3.512 (3)

(b) Bond Angles, Deg

Mo–Mo–O(3)	176.40 (6)	S(3)–C(4)–S(4)	124.94 (6)
S(1)–Mo–S(3)	90.03 (2)	S(3)–C(4)–O(2)	113.74 (9)
S(1)–Mo–S(4)	88.42 (2)	S(4)–C(4)–O(2)	121.32 (10)
S(2)–Mo–S(3)	87.65 (2)	C(4)–O(2)–C(5)	119.66 (19)
S(2)–Mo–S(4)	86.95 (2)	O(2)–C(5)–C(6)	107.06 (21)
S(1)–C(1)–S(2)	125.23 (6)	C(7)–O(3)–C(10)	107.15 (25)
S(1)–C(1)–O(1)	120.68 (10)	O(3)–C(7)–C(8)	107.90 (22)
S(2)–C(1)–O(1)	114.08 (9)	C(7)–C(8)–C(9)	104.75 (27)
C(1)–O(1)–C(2)	119.22 (19)	C(8)–C(9)–C(10)	106.51 (26)
O(1)–C(2)–C(3)	107.52 (19)	C(9)–C(10)–O(3)	106.24 (24)

[a] Average C–H bond length and deviation from the mean.

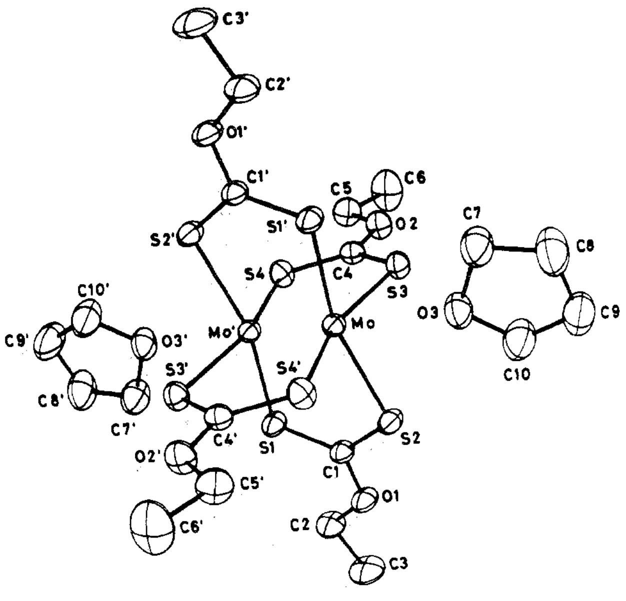

Figure 1. Molecular geometry of the complex $Mo_2(S_2COC_2H_5)_4\cdot 2C_4H_8O$.

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(7) F. M. Moore, *Acta Crystallogr.*, 16, 1169 (1963).

(8) V. Vand, P. F. Eiland, and R. Pepinsky, *Acta Crystallogr.*, 10, 303 (1957).

(9) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216.

(10) C. T. Prewitt, SFLS-5, a Fortran IV full-matrix least-squares program, 1966.

Table V. Weighted Least-Squares Planes in the Mo_2S_8 Skeleton

Plane	Atoms	Equation of the plane	Angles between the normals to the planes, deg
1	Mo, S(1), S(2), C(1)	$0.3969x + 0.6001y - 0.6945z + 0.0174 = 0$	90.43
2	Mo, S(3), S(4), C(4)	$0.5853x - 0.7516y - 0.3042z - 0.0231 = 0$	88.96
3	S′(1), S(2), S(3), S′(4)	$-0.7228x - 0.2410y - 0.6475z + 1.4935 = 0$	92.58

Plane	Distances of atoms from the planes, Å × 10^4
1	Mo, 0 (2); S(1), −3 (7); S(2), −4 (7); C(1), 78 (25)
2	Mo, −0 (2); S(3), 5 (8); S(4), 4 (8); C(4), −92 (27)
3	S′(1), −4 (8); S(2), −4 (8); S(3), 4 (8); S′(3), 4 (8)

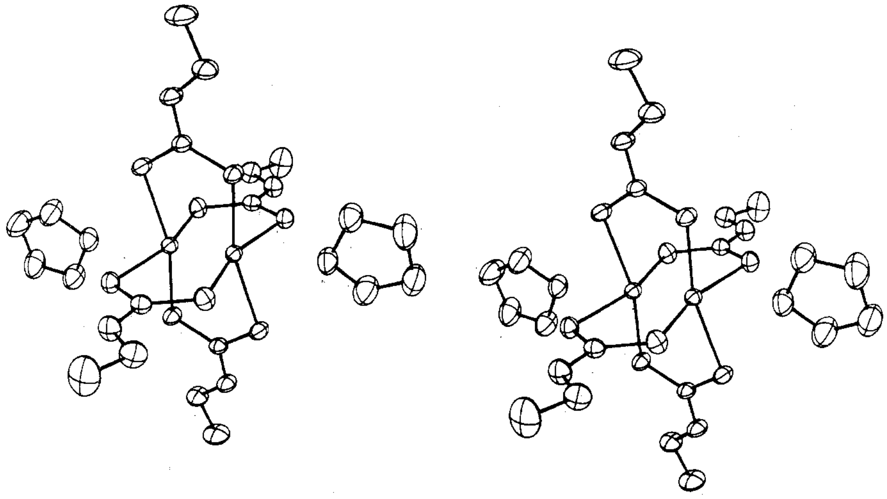

Figure 2. Stereoview of the complex $Mo_2(S_2COC_2H_5)_4 \cdot 2C_4H_8O$.

dure, the distribution of the $w|\Delta F|^2$ appeared inappropriate and the *p* value was reduced to 0.03. Moreover, four scale factors were used from then on to correct some inadequacies of the distribution of residuals $\Delta(F_o - F_c)$ over the whole space.

The refinement thus converged to a final R_1 value of 0.033 and $R_2 = (\Sigma w(|F_o - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ equal to 0.035. Seventy-five low-intensity reflections having $\Delta F > 3.0\sigma(|F_o|)$ were omitted from the final refinement cycles, yielding the values $R_1 = 0.031$ and $R_2 = 0.030$, respectively. The estimated standard deviation of a unit weight observation was 0.96; consequently, all esd's on bond lengths and angles are slightly underestimated. A Fourier difference map computed at this point revealed no other peaks higher than 0.3 e/Å^3, with the exception of maxima of 0.5 e/Å^3 located in the plane of the ligands, between the Mo and S atoms.

All computations were conducted on a UNIVAC 1108 computer. Other programs used include ORTEP by Johnson[11] and local modifications of standard Fourier and least-squares planes programs by Fischer.[5]

Final positional and thermal parameters are listed in Table I for nonhydrogen atoms and in Table II for hydrogen atoms. Table III contains the observed and computed structure factors for all 4559 reflections used in the refinement.[12] Table IV is a list of selected bond lengths and angles.

Results and Discussion

The structure of the complex is represented in Figure 1, along with the numbering scheme adopted. A stereoview is included in Figure 2. This study has shown that the structure of the red (*O*-ethyl dithiocarbonato)molybdenum complex is the same as that of transition metal carboxylates of general formula $M_2L_4 \cdot 2L'$ [13] and, in particular, that it closely resembles that of $Mo_2(O_2CCF_3)_4 \cdot 2C_5H_5N$, recently described by Cotton and Norman.[14] The least-squares planes listed in Table V show that the complex Mo_2S_8 skeleton possesses very close to ideal D_{4h} symmetry. The substitution of oxygen by sulfur, a softer base, seems to have little bearing on the Mo–Mo distance; the observed distance of 2.125 (1) Å is the same as that reported by Cotton and Norman (2.129 (2) Å[14]). These distances are identical and there seems to be little effect of the axial ligands. The Mo–O_3 distance, equal to 2.795 (5) Å, could indicate a weak interaction between molybdenum and tetrahydrofuran. It is however difficult to estimate the strength of that interaction on that basis, since O_3 is in close contact with the four sulfur atoms.

We have already mentioned in the Experimental Section that four molecules of THF are required to account for the density of fresh crystals. However, the crystals aged rapidly with a corresponding loss of THF. The solution of the crystal structure has shown that these aged crystals do indeed contain only two THF molecules per dimer. As shown in Figure 3, the crystal cohesion is partly ensured by strong contacts between a CH_3 group and an O atom of neighboring ligands; as a result of this interaction, it was possible to resolve satisfactorily the hydrogen atoms of the methyl groups. Interactions between the THF molecules complete the packing. This geometry of the packing leaves a large canal throughout the crystal, running in a direction approximately parallel to the *c* axis. This cavity would be large enough to contain THF molecules and we believe that it is indeed the case in the fresh crystals. These molecules would however be very weakly held in the crystal. This would explain the rapid

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[11] C. K. Johnson, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

[12] Table III, a listing of 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 St., N.W., Washington, D. C. 20036. Remit check or money money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2179.

[13] (a) D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 87, 921 (1965); (b) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, 1, 161 (1972).

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

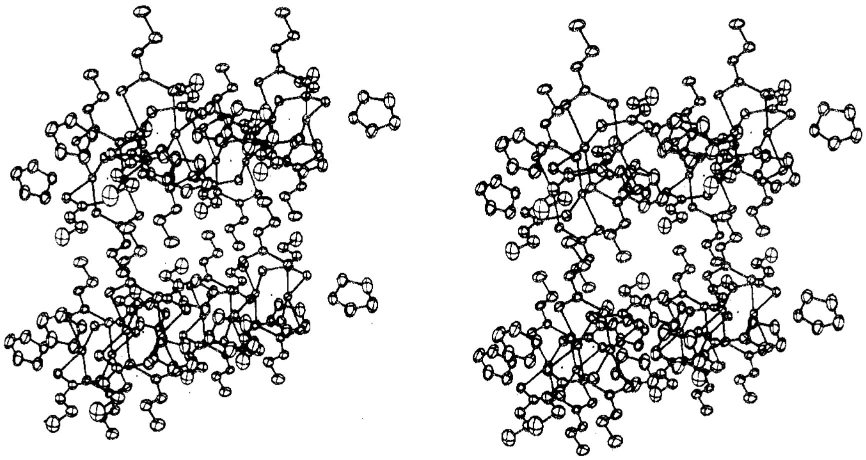

Figure 3. Stereoview of the crystal packing.

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.

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[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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[1] Laboratoire de Cristallochimie associe au CNRS.

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