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Reduction and Deoxygenation of MoO^{3+}(aq) by Pyrrole-*N*-carbodithioate (L) To Yield Eight-Coordinate MoL_4: Crystal and Molecular Structure of Tetrakis(pyrrole-*N*-carbodithioato)molybdenum–Hemi(methylene chloride)[1]

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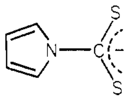
The reaction between $MoCl_5$ and potassium pyrrole-*N*-carbodithioate (K(pdc)) in an aqueous solution led to a surprising product with the stoichiometry $Mo(pdc)_4$. Optical spectra and infrared spectra suggested an eight-coordinate, nonoxygenated molybdenum product. A single-crystal structural study on this material recrystallized from CH_2Cl_2 was carried out, and the eight-coordinate geometry was confirmed. The crystal $Mo(pdc)_4\cdot{}^1/_2CH_2Cl_2$ crystallizes in the centrosymmetric space group $P\bar{1}$ with $a = 11.197$ (6) Å, $b = 11.220$ (5) Å, $c = 13.165$ (7) Å, $\alpha = 73.36$ (4)°, $\beta = 67.07$ (4)°, $\gamma = 66.75$ (4)°, $V = 1382$ (1) Å^3, and ρ(calcd) = 1.700 g cm^{-3} for mol wt 707.3 and $Z = 2$. A unique set of data ($h,\pm k,\pm l$; $3° < 2\theta < 45°$; Mo Kα) were collected with a Nicolet R3m automated diffractometer using graphite-monochromatized radiation. The structure was solved via a combination of Patterson, Fourier, and least-squares techniques. The final discrepancy indices were $R_F = 3.17\%$ and $R_{wF} = 3.26\%$ for the 2822 unique data with $F > 6\sigma(F)$. The molecule has approximate D_{2d} symmetry with the sulfurs located at the vertices of a D_{2d} dodecahedron. The average Mo–S bond lengths are 2.541 and 2.507 Å for the dodecahedral *a* and *b* sites, respectively.

Introduction

We have recently been very interested in exploring the range of chemical reactions exhibited by aromatic dithiocarbamates.[1] We were particularly interested in the reaction of pyrrole-*N*-carbodithioate (pdc) with the dimolybdenum acetate ($Mo_2(C_2H_3O_2)_4$) species to determine if it were possible to prepare a dithiocarbamate with the molybdenum(II) acetate structure, something not possible for dialkyldithiocarbamates.[1]



pdc

Early in our studies of the reaction of potassium pyrrole-*N*-carbodithioate (K(pdc)) with $Mo_2(Ac)_4$ we felt that a possibility existed that complexes of the formula $Mo_2O_3(pdc)_4$ were being obtained, based on the violet color of our compound. In order to test this idea, we attempted to synthesize $Mo_2O_3(pdc)_4$ by the method of Newton.[3] $MoCl_5$ was dissolved in water, and a THF solution of K(pdc) was added. After workup, a dark blue crystalline solid resulted. An infrared spectrum of this compound, however, revealed no Mo–O bonds were present.

We report here the characterization of this material.

Experimental Section

Potassium Pyrrole-*N*-carbodithioate. K(pdc) was prepared as previously reported.[4]

$Mo(pdc)_4\cdot{}^1/_2CH_2Cl_2$. $MoCl_5$ was dissolved in 25 mL of H_2O that had been degassed by three freeze–thaw cycles. About 4 equiv of K(pdc) was added slowly through a Schlenk frit. The solution first turned dark, and a dark brown solid precipitated. After several hours, the solution was filtered and evaporated to dryness under vacuum. The residue was extracted twice with 15–20 mL of CH_2Cl_2. The blue CH_2Cl_2 solutions were combined and filtered. Slow evaporation produced dark blue crystals. Anal. Calcd for $C_{20.5}H_{17}N_4S_8MoCl$: C, 34.79; H, 2.42; S, 36.24; Mo, 13.30. Found: C, 35.30; H, 2.55; S, 36.24; Mo. 13.30.

Table I. Details of Data Collection for $Mo(pdc)_4\cdot{}^1/_2CH_2Cl_2$

A. Crystal Parameters at 20.5 °C

cryst size: 0.25 mm × 0.25 mm × 0.40 mm
cryst syst: triclinic
space group: $P\bar{1}$

$a = 11.197$ (6) Å	$\alpha = 73.36$ (4)°
$b = 11.220$ (6) Å	$\beta = 67.07$ (4)°
$c = 13.165$ (7) Å	$\gamma = 66.75$ (4)°
$V = 1382$ (1) Å^3	mol wt: 707.3
$Z = 2$	ρ(calcd) = 1.700 g cm^{-3}

B. Measurement of Intensity Data

diffractometer: Nicolet R3m
radiation: Mo Kα ($\bar{\lambda} = 0.710\,69$ Å)
monochromator: highly ordered graphite
reflctns measd: $h,\pm k,\pm l$
scan type: coupled θ(cryst)–2θ(counter)
scan speed: (4–30)° min^{-1}
scan width: $[2\theta(\text{MoK}\alpha_1) - 1.0]°$–$[2\theta(\text{MoK}\alpha_2 + 1.0]°$
bkgd measmt: stationary cryst and counter, at beginning and end of scan—each for half the time taken for the 2θ scan
std reflctns: 3 measd every 97 reflctns; no significant dev from the mean obsd
abs coeff: $\mu = 11.61$ cm^{-1}
abs cor: none, $T_{max}/T_{min} = 1.10$
reflctns collected: 3831 total, yielding 2822 indep reflctns
data averaging: $R(I) = 1.57\%$ for 2822 unique reflctns

Optical and NMR Spectra. These data were obtained as before.[4]

Crystal Data Collection. A single crystal of the title compound was mounted on the tip of a glass fiber which was fixed into a brass pin and mounted in an eucentric goniometer. The crystal was transferred to a Nicolet R3m automated diffractometer. The crystal was set up for data collection in a manner analogous to that of Churchill et al.[5] Details are outlined in Table I.

Following correction of these data for Lorentz and polarization effects, a three-dimensional Patterson map quickly revealed the position of the molybdenum atom. Subsequent difference-Fourier syntheses and least-squares refinement cycles yielded all non-hydrogen atom positions. Hydrogen atoms were included in their idealized positions with d(C–H) = 0.96 Å.[6] The inclusion of a grossly disordered methylene chloride molecule yielded final discrepancy indices of $R_F = 3.17\%$ and $R_{wF} = 3.26\%$, where w is a weight defined by $w = (\sigma^2(F) + gF^2)^{-1}$ with g being an ignorance factor equal to 0.0005. Final positional parameters for all atoms are given in Table II. A final

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(1) This is part 25 in the series Coordination Chemistry of New Sulfur-Containing Ligands. Part 24: R. D. Bereman, D. M. Baird, and C. Moreland, submitted for publication.

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Table II. Final Positional and Isotropic Thermal Parameters, with Esd's, for $Mo(pdc)_4\cdot{}^1/_2CH_2Cl_2$ [b]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.21696 (4)	0.17368 (4)	0.19659 (3)
S(1)	0.18048 (13)	0.04449 (13)	0.39064 (10)
S(2)	0.44035 (14)	0.02471 (14)	0.23333 (11)
S(3)	0.14485 (12)	0.34654 (13)	0.04370 (10)
S(4)	0.41234 (13)	0.17894 (13)	0.01517 (10)
S(5)	0.24599 (28)	−0.02411 (29)	0.12584 (25)
S(6)	−0.00985 (29)	0.14653 (30)	0.22499 (26)
S(7)	0.30000 (31)	0.33040 (31)	0.23137 (26)
S(8)	0.02485 (13)	0.34872 (13)	0.30551 (11)
N(1)	0.4117 (5)	−0.1024 (4)	0.4442 (4)
N(2)	0.3427 (4)	0.3582 (5)	−0.1555 (3)
N(3)	0.0133 (4)	−0.0628 (4)	0.1484 (3)
N(4)	0.1040 (4)	0.5308 (4)	0.3348 (3)
C(1)	0.3502 (5)	−0.0214 (5)	0.3663 (4)
C(2)	0.5512 (6)	−0.1466 (6)	0.4299 (5)
C(3)	0.5691 (7)	−0.2193 (6)	0.5260 (5)
C(4)	0.4401 (8)	−0.2210 (7)	0.6019 (5)
C(5)	0.3459 (7)	0.1492 (7)	0.5514 (5)
C(6)	0.3037 (5)	0.3026 (5)	−0.0448 (4)
C(7)	0.4747 (6)	0.3275 (5)	−0.2296 (4)
C(8)	0.4690 (6)	0.4016 (6)	−0.3282 (5)
C(9)	0.3322 (7)	0.4804 (7)	−0.3167 (5)
C(10)	0.2552 (6)	0.4550 (6)	−0.2105 (5)
C(11)	0.0759 (5)	0.0111 (5)	0.1650 (4)
C(12)	−0.1255 (6)	−0.0354 (6)	0.1714 (5)
C(13)	−0.1413 (9)	−0.1306 (8)	0.1409 (6)
C(14)	−0.0132 (7)	−0.2212 (6)	0.0998 (5)
C(15)	0.0810 (7)	−0.1796 (6)	0.1049 (5)
C(16)	0.1402 (6)	0.4175 (6)	0.2943 (5)
C(17)	0.1938 (8)	0.5864 (7)	0.3361 (5)
C(18)	0.1188 (9)	0.6988 (7)	0.3791 (6)
C(19)	−0.0200 (7)	0.7143 (6)	0.4053 (5)
C(20)	−0.0270 (7)	0.6120 (6)	0.3775 (5)
C(21)	0.5751 (9)	0.4281 (8)	−0.0125 (8)
Cl[a]	0.5295 (69)	0.4446 (63)	−0.0483 (77)
Cl′[a]	0.6351 (6)	0.3944 (6)	0.0813 (5)
Cl″[a]	0.5913 (10)	0.4416 (10)	0.0390 (10)

[a] The chlorine atoms are set with site occupancies of $^1/_3$ to account for the disorder found in the solvent molecule. [b] Hydrogen atoms are in idealized positions 0.960 Å from the attached carbon. Isotropic thermal parameters were assigned (at the time of entry) the value $U_{iso}(H) = 1.2U_{iso}(C)$.[2]

difference-Fourier synthesis showed no unexpected features, and the structure was deemed complete.

All calculations were performed in-house with the SHELXTL structure solution package[7] and a NOVA computer (32K memory) with associated disk systems. For structure-factor calculations we used analytical scattering factors[8b] for neutral Mo, Cl, S, N, C, and H atoms; both the $\Delta f'$ and $\Delta f''$ contributions[8c] were included for all non-hydrogen atoms. Atomic absorption coefficients are found in ref 8a. No correction for extinction was applied. A table of observed and calculated structure factors is available as supplementary material. Tables of ligand bond lengths (Table V) and bond angles (Table VI) have been deposited as supplementary material.

Results and Discussion

A ^1H NMR spectrum of $Mo(pdc)_4$ proved to be very informative in suggesting the structure of this compound. The fact that an NMR spectrum was obtainable suggested either a Mo(IV) monomer or a Mo–Mo dimer as the structure of this molecule. Resonance lines representing the α- and β-protons of the pyrrole ring were detected at 7.4 and 6.25 ppm (referenced to Me_4Si), respectively, as well as a third line at 5.3 ppm representing the $^1/_2$ CH_2Cl_2 associated with the compound in the crystal lattice.

The electronic spectrum of this compound was complex, showing at least six bands in the optical region. Even though a spectrum of this complexity could not be interpreted, it was very useful when compared to the spectrum of $Mo(dtb)_4$ (dtb = dithiobenzoate).[9] The similarity of these two electronic spectra led us to formulate the new blue compound as eight-coordinate $Mo(pdc)_4$ and, on the basis of the NMR and elemental analysis, to include half of a molecule of CH_2Cl_2 per molecule of $Mo(pdc)_4$.

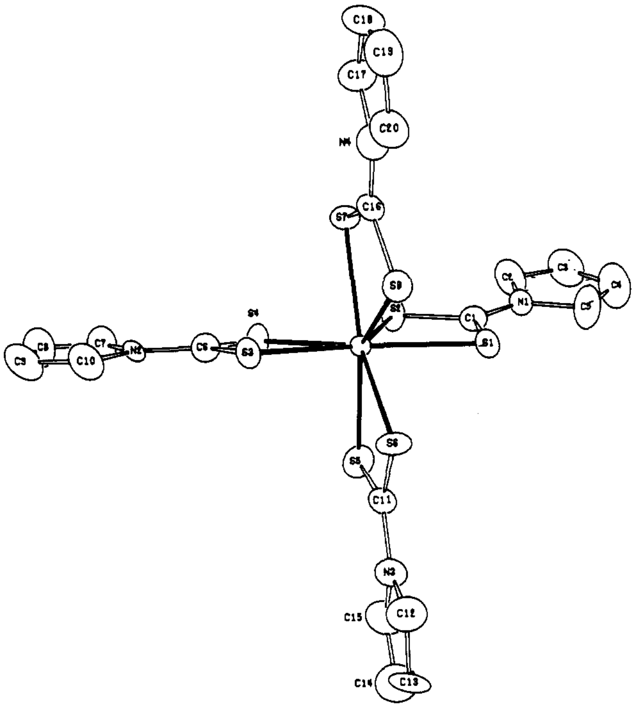

Figure 1. Labeling of atoms in $[Mo(pdc)_4]$.

The stoichiometry of this compound is not unusual since several Mo(IV) dithiocarbamates have been reported. However, the conditions under which this compound is stable is remarkable since with every dialkyldithiocarbamate reacted under these conditions, a Mo_2O_3 core has resulted.[1] The apparent product of the reducing agent is likely the disulfide derived from two pyrrole-*N*-carbodithioate ligands. The fate of the oxygen atom on the molybdenum(V) unit is unknown. In a previous study, we had shown that VO^{2+} reacted with pdc in *nonaqueous* solvents to yield eight-coordinate VL_4.[10] We speculated then that the π-structure of the four-membered VS_2C chelate ring was obviously very important and removed π-density from the V=O unit to such an extent that the V–O bond became labile. However, that reaction occurred in anhydrous CH_3CN. To observe a similar reaction in an aqueous medium is very surprising. It may be that chemical reduction occurs first ($MoO^{3+} \rightarrow MoO^{2+}$) followed by the oxygen labilization since Mo^{IV}=O species are not as common as the Mo^V=O unit.

The production of $Mo(pdc)_4$ again demonstrates the unusual reactivities of the aromatic dithiocarbamates.[1,4] It appears that pyrrole-*N*-carbodithioate will be more likely to mimic dithiobenzoate (dtb) than other dithiocarbamates. In other words, like dithio acids, and xanthates, the aromatic dithiocarbamates will tend to stabilize lower oxidation states while the dialkyl species tend to stabilize higher oxidation states. Yet, even the eight-coordinate complex, $Mo(dtb)_4$, was isolated from the *oxidation* of $MoCl_6^{3-}$.[11] The eight-coordinate dialkyldithiocarbamate complexes that have been prepared were

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[7] "Structure Determination Operation Manual", Nicolet XRD Corp., Cupertino, CA, 1980.

[8] "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1973: (a) p 55; (b) p 99; (c) p 149.

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Table III. Selected Bond Lengths (Å), with Esd's,[a] for $Mo(pdc)_4 \cdot {}^1/_2CH_2Cl_2$

Mo-S(1)	2.515 (1)	Mo-S(5)	2.508 (4)
Mo-S(2)	2.544 (1)	Mo-S(6)	2.547 (4)
Mo-S(3)	2.503 (1)	Mo-S(7)	2.500 (4)
Mo-S(4)	2.539 (1)	Mo-S(8)	2.532 (1)
Mo-S_A(av)[b]	2.541 (6)	Mo-S_B(av)	2.507 (6)

[a] σ(av) is the esd on the average value calculated by $\sigma(\text{av}) = [\Sigma(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the ith measurement, $\bar{d}$ is the average of all measurements, and N is the total number of measurements. [b] The subscripts A and B refer to the *a* and *b* sites of the dodecahedron.

Table IV. Selected Bond Angles (deg) for $Mo(pdc)_4 \cdot {}^1/_2CH_2Cl_2$

(A) Sulfur-Molybdenum-Sulfur			
S(1)-Mo-S(2)	67.3 (1)	S(3)-Mo-S(5)	98.7 (1)
S(1)-Mo-S(3)	155.0 (1)	S(3)-Mo-S(6)	87.7 (1)
S(1)-Mo-S(4)	138.1 (1)	S(3)-Mo-S(7)	79.9 (1)
S(1)-Mo-S(5)	89.0 (1)	S(3)-Mo-S(8)	78.3 (1)
S(1)-Mo-S(6)	81.3 (1)	S(4)-Mo-S(5)	78.2 (1)
S(1)-Mo-S(7)	95.7 (1)	S(4)-Mo-S(6)	127.0 (1)
S(1)-Mo-S(8)	80.2 (1)	S(4)-Mo-S(7)	81.7 (1)
S(2)-Mo-S(3)	137.2 (1)	S(4)-Mo-S(8)	134.0 (1)
S(2)-Mo-S(4)	71.3 (1)	S(5)-Mo-S(6)	67.0 (1)
S(3)-Mo-S(5)	81.3 (1)	S(5)-Mo-S(7)	154.4 (1)
S(2)-Mo-S(6)	135.6 (1)	S(5)-Mo-S(8)	138.2 (1)
S(2)-Mo-S(7)	77.4 (1)	S(6)-Mo-S(7)	138.6 (1)
S(2)-Mo-S(8)	128.8 (1)	S(6)-Mo-S(8)	71.5 (1)
S(3)-Mo-S(4)	67.0 (1)	S(7)-Mo-S(8)	67.3 (1)
(B) Sulfur-Carbon-Sulfur			
S(1)-C(1)-S(2)	112.9 (3)	S(5)-C(11)-S(6)	112.7 (5)
S(3)-C(6)-S(4)	112.4 (3)	S(7)-C(16)-S(8)	112.2 (4)
S-C-S(av) = 112.6 (3)[a]			
(C) Molybdenum-Sulfur-Carbon			
Mo-S(1)-C(1)	90.4 (2)	Mo-S(5)-C(11)	90.8 (3)
Mo-S(2)-C(1)	89.2 (2)	Mo-S(6)-C(11)	89.5 (3)
Mo-S(3)-C(6)	91.0 (2)	Mo-S(7)-C(16)	90.9 (3)
Mo-S(4)-C(6)	89.7 (2)	Mo-S(8)-C(16)	89.4 (2)
Mo-S-C(av) 90.1 (8)[a]			

[a] See footnote *a* of Table III.

isolated from the CS_2 addition to $Mo(NMe_2)_4$.[12]

Figure 1 shows a general view of the $Mo(pdc)_4$ molecule. Interatomic distances and angles for the coordination sphere about Mo are listed in Tables III and IV, respectively. The remaining distances and angles are listed in Tables V and VI, deposited as supplementary material.

The $[Mo(pdc)_4]$ molecule adopts a structure in which the bidentate pdc ligands span the *m* edges of an idealized D_{2d}-$\bar{4}2m$ dodecahedron, giving the *mmm*-D_{2d} stereoisomer.[13] The same structure has been found for tetrakis(dithiobenzoato)molybdenum(IV).[11]

The Mo coordination sphere consists of eight sulfur donor atoms from the pdc ligands. The MoS_8 coordination group displays a geometry consistent with an unambiguous choice of the dodecahedral coordination polyhedron, D_{2d}-$\bar{4}2m$ symmetry, as opposed to the square antiprism, D_{4d}-$\bar{8}2m$.[14] The dihedral angle between the planes generated by atoms Mo, S1, S2, S3, and S4 and by atoms Mo, S5, S6, S7, and S8 is 88.7°, conforming to the limit of 90° in the idealized dodecahedron. These planes intersect at an angle of 77° in the idealized D_{4d} square antiprism. The *a* edges of the dodecahedron are defined by atoms S2, S4, S6, and S8 with an average Mo-S_A distance of 2.541 (6) Å, while the *b* edges are defined by S1, S3, S5, and S7 with an average Mo-S_B distance of 2.507 (6) Å. The pdc ligands are nearly planar, with these maximum deviations from planarity contributed by the dihedral angles between the planes defined by the NCS_2 grouping and the pyrrole ring NC_4, averaging 5.1° for the four ligand groups. The bond lengths and angles for the pdc ligand grouping suggest a significant contribution from resonance form I in Scheme I to the ligand geometry as suggested before.[10,15]

Scheme I

I II

Table VII. Selected C-S and C-N Average Bond Distances (Å) in Dithiocarbamates

	$Mo(pdc)_4$	$Fe(pdc)_3$	$Fe(pydc)_3$
C-S	1.678 (8)	1.686 (5)	1.712 (9)
C-N	1.377 (6)	1.365 (13)	1.317 (5)

Table VII summarizes the average C-S and C-N distances for this $Mo(pdc)_4$ complex, for the $Fe(pdc)_3$[15] complex, and for the tris(pyrrolidine-*N*-carbodithioato)iron(III)[16] complex. These data clearly support resonance form I above since the C-S bonds are shorter here (more π-bonding in the four-membered chelate ring) than in the alkyl analogue of pyrrolidine-*N*-carbodithioate. This latter complex was suggested by us to be the *extreme* example of a low-spin Fe(III) dithiocarbamate complex on the basis of the unusually short C-S distances and long C-N distances when compared to the average for *all* iron(III) dithiocarbamates.

If we accept the structure of $Mo(pdc)_4$ as an ideal D_{2d} dodechedron, then the Mo-Sσ "hybridization" will use eight valence shell atomic orbitals of molybdenum, leaving only the $d_{x^2-y^2}$ orbital for potential π-bonding. Since the Mo-S_B distances are much shorter than the Mo-S_A distances, 2.507 vs. 2.541 Å, it is clear that the largest participating π-atomic orbital on molybdenum must be $4d_{x^2-y^2}$. However, for the structure of $Mo(dtb)_4$, where a clear distinction between Mo-S_A (2.545 (1) Å) and Mo-S_B (2.4750 (1) Å) bonds also exists, the difference between these distances $\Delta[d(\text{Mo-S}_A) - d(\text{Mo-S}_B)]$ of 0.068 Å is very much larger than that of 0.034 Å in $Mo(pdc)_4$. This supports more equitable Mo-S π-bonding between sites here than in $Mo(dtb)_4$.

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Registry No. $Mo(pdc)_4 \cdot {}^1/_2CH_2Cl_2$, 86261-13-4; $MoCl_5$, 10241-05-1.

Supplementary Material Available: Listings of structure factors, thermal parameters, ligand bond lengths (Table V), and ligand bond angles (Table VI) (21 pages). Ordering information is given on any current masthead page.

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