Contribution from the Chemistry Departments, University of Kentucky,
Lexington, Kentucky 40506-0055, and Bloomsburg University, Bloomsburg, Pennsylvania 17815

Preparations and Structures of *cis*-[$Mo_2(S_2CNC_4H_4)_2(O_2CCH_3)_2OPPh_3$] and [$Mo_2(S_2PEt_3)(O_2CCH_3)_3OPEt_3$]($BF_4$): Two Quadruply Bonded Dimers Involving Dithio Acid Ligands

DONALD M. BAIRD,[†] PHILLIP E. FANWICK,*[‡] and TOM BARWICK[†]

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The dithiocarbamate of pyrrole (pdc) reacts with molybdenum acetate and triphenylphosphine oxide to give *cis*-[$Mo_2(pdc)_2(O_2CCH_3)_2OPPh_3$], which crystallizes from benzene with $1^1/_2$ molecules of solvent per dimer in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 11.777$ (2) Å, $b = 16.690$ (2) Å, $c = 11.535$ (3) Å, $\alpha = 95.4$ (2)°, $\beta = 102.07$ (2)°, $\gamma = 84.23$ (1)°, $V = 2197.9$ Å^3, and $Z = 2$. The reaction of molybdenum acetate with the zwitterionic S_2CPEt_3 in the presence of HBF_4 yields the dimer [$Mo_2(S_2CPEt_3)(O_2CCH_3)_3OPEt_3$]($BF_4$), which crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 13.186$ (2) Å, $b = 14.403$ (3) Å, $c = 17.882$ (4) Å, $\beta = 106.97$ (1)°, $V = 3248.3$ Å^3, and $Z = 4$. In both dimers, one molybdenum is axially coordinated to the oxygen of the phosphine oxide and the other to the oxygen of an acetate on an adjacent dimer. The Mo–O distances for the oxygen of the phosphine oxide are the shortest observed for axial coordination. Both sulfur ligands are in the dithio acid resonance form.

Introduction

Quadruply bonded molybdenum dimers have been synthesized with a wide variety of bridging ligands. Almost any three-atom group will bridge the metal–metal bond, and the list of ligand atoms includes carbon, nitrogen, oxygen, phosphorus, and sulfur.[1] In addition to compounds in which both ligand atoms are identical, a wide variety of mixed-ligand species is known. In general, the properties of the dimer are not particularly sensitive to the organic framework attached to the ligating atoms. The most notable exception is the dithio acid ligands. The tetrakis(*O*-ethyl dithiocarbonato)dimolybdenum(II) dimer was prepared and structurally characterized in 1973.[2] It had the usual geometry of a quadruply bonded dimer. One unusual property of this compound was that it was readily oxidized by bromine or iodine.[3] However, this was not a simple oxidative addition to the metal–metal bond. Instead, two S_2COEt ligands became tridentate with the two sulfurs situated at the midpoint of the metal–metal bond while the carbon was also strongly coordinated. The Mo–Mo bond order had been reduced to 1. The first dithiocarboxylate dimer was prepared[4] at about the same time the dithioxanthate compound was reported. While these dimers also reacted with halogens, no readily characterized products were obtained.[5]

The reaction of dithiocarbamates with quadruply bonded molybdenum dimers produced quite different products from those of the other dithio acids. While the stoichiometry was consistent with [$Mo_2(S_2CNR_2)_4$], the crystal structure revealed that this was not the product. Two dithiocarbamates had oxidatively added across the quadrupole bond to produce [$Mo_2S_2(SCN(C_3H_7)_2)_2(S_2CN(C_3H_7)_2)_2$].[6] These dithiocarbamates had become thiocarboxamido ligands that coordinated through both the sulfur and carbon. A later report suggested that a true dithiocarbamate dimer was synthesized by using the dithiocarbamate of pyrrole (pdc).[7] Because of the differences in behavior of the various dithio acid ligands it was important to structurally characterize the pdc compound and to prepare and characterize other dimers involving the dithio acid group. In this paper the preparations and crystal structures of [$Mo_2(pdc)_2(OAc)_2OPPh_3$]·$1^1/_2C_6H_6$ (where OAc is the acetate ion) and [$Mo_2(S_2CPEt_3)(OAc)_3OPEt_3$]($BF_4$) are reported.

Experimental Section

The ligands Kpdc[8] and S_2CPEt_3[9] were synthesized as previously described. All syntheses were conducted under an inert atmosphere except when noted.

Preparation of [$Mo_2(pdc)_2(OAc)_2OPPh_3$]. Freshly prepared molybdenum acetate (1 g) was reacted with 4 equiv of Kpdc (1.7 g) in 20 mL of THF for 1 h at room temperature. The resulting solution was filtered to remove the potassium acetate, and an equal volume of hexane was added. After several days at −20 °C, the dark red parent compound was filtered off. This compound was redissolved in a minimum of THF, and 2 equiv of triphenylphosphine oxide was added. The solvent was removed under vacuum, and the residue was extracted with benzene. This benzene solution was filtered and allowed to stand for 4 or 5 days, after which crystals had formed. The crystals are air sensitive.

Table I. Crystallographic Data

	a	*b*
formula	$Mo_2S_4PO_5N_2C_{41}H_{38}$	$Mo_2S_2P_2F_4O_7C_{19}BH_{39}$
fw	995.8	784.3
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.777 (2)	13.186 (2)
b, Å	16.690 (2)	14.403 (3)
c, Å	11.535 (3)	17.882 (4)
α, deg	95.94 (2)	90
β, deg	102.07 (2)	106.97 (1)
γ, deg	84.23 (1)	90
vol, Å^3	2197.9	3248.3
Z	2	4
ρ_{calcd}, g/cm^3	1.51	1.60
cryst dimens, mm	0.33 × 0.23 × 0.13	0.52 × 0.32 × 0.18
temp, °C	22	22
radiation	Mo Kα	Mo Kα
μ, cm^{-1}	8.25	10.4
2θ range, deg	2.5–45	2.5–45
no. of indep reflcns	5911	4238
no. of reflcns used ($I > 3\sigma(I)$)	3245	3652
final *R*	0.051	0.046
final R_w	0.053	0.071

[a] [$Mo_2(S_2CNC_4H_4)_2(O_2CCH_3)_2OPPh_3$]·$1^1/_2C_6H_6$. [b] [$Mo_2(S_2CPEt_3)(O_2CCH_3)_3OPEt_3$]($BF_4$).

Preparation of [$Mo_2(S_2CPEt_3)(OAc)_3OPEt_3$]($BF_4$). Freshly prepared $Mo_2(OAc)_4$ (0.5 g) and 2 equiv of S_2CPEt_3 (0.45 g) were dissolved in 20 mL of THF. To this was added 0.1 mL of 48% HBF_4. Upon addition

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* To whom correspondence should be addressed at the Department of Chemisty, Purdue University, West Lafayette, IN 47907.

[†] Bloomsburg University.

[‡] University of Kentucky.

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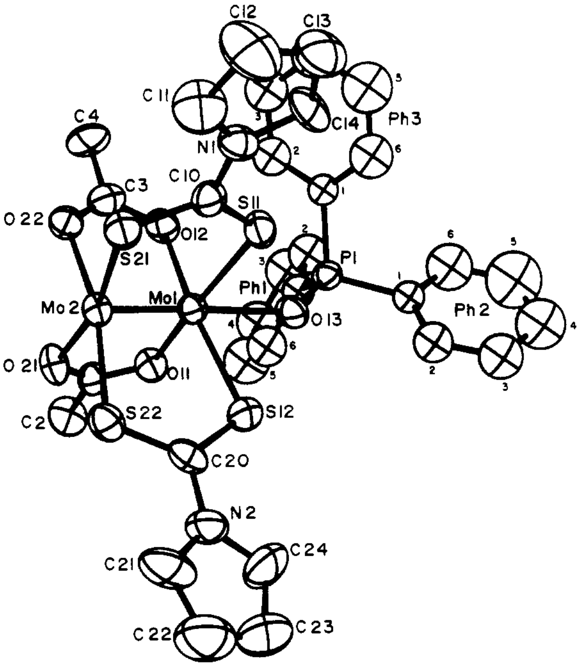

Figure 1. ORTEP drawing of *cis*-$[Mo_2(pdc)_2(OAc)_2OPPh_3]$. The ellipsoids are drawn at the 50% probability level.

of the acid the solution immediately turned purple. After 1 h the solution was filtered in air and a layer of pentane was floated on top of it. Large crystals formed after several days.

Crystallography. Crystals were aligned and indexed, and data were collected on an Enraf-Nonius CAD-4 diffractometer. Crystals of $[Mo_2(pdc)_2(OAc)_2OPPh_3]\cdot 1^1/_2C_6H_6$ were handled in deoxygenated Nujol and were mounted surrounded by epoxy resin in a glass capillary. The procedures used for data collection and refinement have been described previously.[10] The crystallographic data for the two structures are reported in Table I.

Results and Discussion

The synthesis of $[Mo_2(pdc)_2(OAc)_2]$ was different fronm that reported previously for $Mo_2(pdc)_4$[7] in several respects. First, only 4 equiv of ligand was used instead of a large excess. Second, the ligand was not dissolved and added dropwise to the molybdenum acetate suspension. The compound $Mo_2(pdc)_2(OAc)_2$ is only sparingly soluble in THF, and the more concentrated solutions used here may be responsible for the reaction stopping at the substitition by two pdc ligands per dimer. It is clear that the compound characterized as $Mo_2(pdc)_4$ is not the same as the one reported here. Elemental analyses reported for $Mo_2(pdc)_4$ are only consistent with four pdc ligands. In addition, the electronic spectra of the two compounds are different. The lowest energy band in the visible spectrum occurred at 510 nm for THF solutions of $Mo_2(pdc)_4$ while it was at 499 nm in $Mo_2(pdc)_4(OAc)_2$ dissolved in THF. This band shifted to 510 nm only after the addition of triphenylphosphine oxide. Since the potassium acetate formed in the reaction was removed before the phosphine oxide was added, the recomplexation by acetate can be ruled out.

Attempts were made to grow crystals of $Mo_2(pdc)_2(OAc)_2$ without the phosphine oxide. Slow diffusion of hexane into THF solutions produced long needles. Even the largest of these did not diffract well enough to allow data collection. However, the unit cell was determined to be orthorhombic with unit cell parameters $a = 19.990$ (5) Å, $b = 25.120$ (6) Å, $c = 8.893$ (6) Å, and $V = 4466$ Å^3. Observed absences: hkl, $h + k = 2n + 1$; $hk0$, $h = 2n + 1$. The space group is either *Cmma* or *Cm*2*a* (standard group *Abm*2). While a variety of potential axial ligands were tried in order to produce better crystals, triphenylphosphine oxide worked best. The solubility of the dimer after reaction with the phosphine oxide was increased greatly. In fact, $Mo_2(pdc)_2(OAc)_2$ is nearly insoluble in benzene yet the crystals of the axial adduct were grown from this solvent and contain $1^1/_2$ benzene molecules per dimer.

Table II. Positional Parameters for the Nongroup Atoms of $[Mo_2(S_2CNC_4H_4)_2(O_2CCH_3)OPPh_3]\cdot 1^1/_2C_6H_6$

atom	x^a	y	z
Mo(1)	−0.05226 (8)	0.18593 (6)	0.21508 (9)
Mo(2)	0.04129 (8)	0.08848 (6)	0.13134 (9)
S(11)	0.0898 (3)	0.2095 (2)	0.4005 (3)
S(12)	0.0036 (3)	0.2985 (2)	0.1256 (3)
S(21)	0.2216 (3)	0.0760 (2)	0.2807 (3)
S(22)	0.1264 (3)	0.1618 (2)	0.0028 (3)
P(1)	−0.2365 (2)	0.3169 (2)	0.3901 (3)
O(11)	−0.1991 (6)	0.1743 (4)	0.0755 (7)
O(12)	−0.1289 (6)	0.1042 (5)	0.2988 (6)
O(21)	−0.1065 (7)	0.0703 (4)	−0.0086 (6)
O(22)	−0.0281 (7)	0.0027 (4)	0.2142 (7)
O(13)	−0.1603 (6)	0.2966 (4)	0.3019 (6)
N(1)	0.2962 (8)	0.1423 (5)	0.4995 (8)
N(2)	0.1244 (9)	0.3157 (6)	−0.0408 (9)
C(1)	−0.1977 (10)	0.1178 (7)	−0.005 (1)
C(2)	−0.3042 (9)	0.1108 (7)	−0.105 (1)
C(3)	−0.097 (1)	0.0285 (8)	0.282 (1)
C(4)	−0.147 (1)	−0.0313 (7)	0.348 (1)
C(10)	0.2061 (9)	0.1429 (6)	0.3990 (10)
C(11)	0.401 (1)	0.0906 (9)	0.512 (1)
C(12)	0.464 (1)	0.110 (1)	0.623 (1)
C(13)	0.396 (1)	0.1731 (9)	0.682 (1)
C(14)	0.294 (1)	0.1922 (8)	0.606 (1)
C(20)	0.0853 (9)	0.2613 (7)	0.0270 (9)
C(21)	0.209 (1)	0.2958 (9)	−0.111 (1)
C(22)	0.218 (2)	0.365 (1)	−0.162 (1)
C(23)	0.136 (2)	0.426 (1)	−0.125 (2)
C(24)	0.076 (2)	0.3965 (9)	−0.047 (2)
C(S1)	0.548 (1)	0.037 (1)	0.112 (1)
C(S2)	0.603 (1)	−0.0320 (10)	0.065 (2)
C(S3)	0.440 (1)	0.0686 (9)	0.046 (2)
C(S11)	0.603 (2)	0.333 (1)	0.773 (2)
C(S12)	0.685 (2)	0.348 (1)	0.874 (2)
C(S13)	0.686 (3)	0.416 (2)	0.935 (3)
C(S14)	0.590 (3)	0.482 (2)	0.878 (3)
C(S15)	0.512 (2)	0.462 (2)	0.781 (2)
C(S16)	0.513 (2)	0.387 (1)	0.726 (2)

[a] Estimated standard deviations in the last figure(s) are given in parentheses in this and all subsequent tables.

The structure of *cis*-$[Mo_2(pdc)_2(OAc)_2OPPh_3]\cdot 1^1/_2C_6H_6$ was refined by using rigid groups for the phenyl rings of the triphenylphosphine oxide (C–C = 1.41 Å) and anisotropic refinement for all other atoms except those of the benzenes of crystallization. The positional parameters and their errors for the nonrigid-group atoms are given in Table II. An ORTEP drawing of the dimer is shown in Figure 1, and bond distances and angles are given in Table III. The *cis*-$[Mo_2(pdc)_2(OAc)_2OPPh_3]$ dimer is located at a general position and therefore possesses no crystallographically imposed symmetry. One benzene is located at a general position, and the second is centered on an inversion center. This results in the unit cell containing three benzene molecules and two dimers.

The bond distances about the molybdenums are quite typical. It is difficult to compare the Mo–Mo distance of 2.134 (1) Å[11] with that of other dimers involving dithio acids because the observed distances cover a wide range. For example, the Mo–Mo distance was 2.125 (1) Å[2] in the ethyl xanthate dimer and averaged 2.138 [4] Å for the three crystallographically distinct dithiocarboxylates.[5] However, in the case of $Mo_2(S_2CCH_3)_4\cdot 2THF$ there were two independent molecules in the cell and their Mo–Mo distances were 2.141 (1) and 2.133 (1) Å. The difference in axial coordination may account for these variations. The Mo–S distances in $[Mo_2(pdc)_2(OAc)_2OPPh_3]$ are somewhat shorter than in any of the other dithio acids, averaging to 2.443 [4] Å as compared to 2.465 [8] Å in the dithiocarboxylates[5] and 2.478 [2] Å in the dithioxanthate.[2]

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(11) Errors in ( ) are the estimated standard deviations from the least squares. Errors in [ ] are the standard deviations of the means.

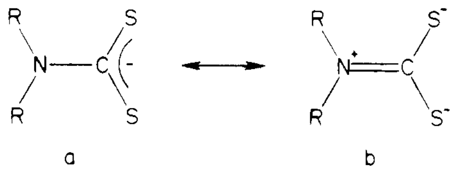
Table III. Bond Distances (Å) and Angles (deg) for $[Mo_2(S_2CNC_4H_4)_2(O_2CCH_3)_2OPPh_3]\cdot 1^1/_2C_6H_6$

Mo(1)-Mo(2)	2.134 (1)		
-O(11)	2.111 (7)	Mo(2)-O(21)	2.135 (7)
-O(12)	2.120 (7)	-O(22)	2.115 (7)
-O(13)	2.370 (7)	-S(21)	2.445 (3)
-S(11)	2.447 (3)	-S(22)	2.438 (3)
-S(12)	2.442 (3)	-O(21)′[a]	2.980 (7)
S(11)-C(10)	1.68 (1)	S(12)-C(20)	1.67 (1)
S(21)-C(10)	1.70 (1)	S(22)-C(20)	1.69 (1)
C(10)-N(1)	1.40 (1)	C(20)-N(2)	1.43 (1)
N(1)-C(11)	1.43 (1)	N(2)-C(21)	1.40 (2)
C(11)-C(12)	1.36 (2)	C(21)-C(22)	1.38 (2)
C(12)-C(13)	1.46 (2)	C(22)-C(23)	1.43 (2)
C(13)-C(14)	1.36 (2)	C(23)-C(24)	1.40 (2)
C(14)-N(1)	1.41 (1)	C(24)-N(2)	1.41 (2)
O(11)-C(1)	1.26 (1)	O(12)-C(3)	1.29 (1)
O(21)-C(1)	1.27 (1)	O(22)-C(3)	1.26 (1)
C(1)-C(2)	1.52 (1)	C(3)-C(4)	1.55 (1)
O(13)-P(1)	1.484 (7)	P(1)-CPh(21)	1.783 (9)
P(1)-CPh(11)	1.778 (9)	P(1)-CPh(31)	1.791 (9)
C(S1)-C(S2)	1.38 (2)		
-C(S3)	1.42 (2)		
C(S2)-C(S3)	1.37 (2)		
C(S11)-C(S12)	1.37 (2)	C(S14)-C(S15)	1.33 (3)
C(S12)-C(S13)	1.28 (3)	C(S15)-C(S16)	1.34 (3)
C(S13)-C(S14)	1.58 (3)	C(S16)-C(S11)	1.38 (2)
Mo(2)-Mo(1)-O(11)	90.5 (2)	Mo(1)-Mo(2)-O(21)	91.3 (2)
-O(12)	91.1 (2)	-O(22)	91.4 (2)
-O(13)	177.9 (2)	-O(21)′	163.0 (1)
-S(11)	99.34 (8)	-S(21)	100.43 (8)
-S(12)	99.36 (9)	-S(22)	100.34 (8)
O(11)-Mo(1)-O(12)	85.3 (3)	O(21)-Mo(2)-O(22)	90.1 (2)
-O(13)	87.8 (3)	-O(21)′	76.8 (3)
-S(11)	168.8 (2)	-S(21)	166.7 (2)
-S(12)	90.4 (2)	-S(22)	90.1 (2)
O(12)-Mo(1)-O(13)	89.9 (3)	O(22)-Mo(2)-O(21)′	75.5 (3)
-S(11)	89.1 (2)	-S(21)	89.3 (2)
-S(12)	168.7 (2)	-S(22)	167.1 (2)
O(13)-Mo(1)-S(11)	82.4 (2)	O(21)′-Mo(2)-S(21)	90.4 (2)
-S(12)	79.4 (2)	-S(22)	91.9 (2)
S(11)-Mo(1)-S(12)	93.2 (1)	S(21)-Mo(2)-S(22)	93.8 (1)
Mo(1)-S(11)-C(10)	108.8 (4)	Mo(1)-S(12)-C(20)	108.6 (4)
Mo(2)-S(21)-C(10)	107.7 (4)	Mo(2)-S(22)-C(20)	107.6 (4)
S(11)-C(10)-S(21)	123.5 (7)	S(12)-C(20)-S(22)	124.0 (7)
S(11)-C(10)-N(1)	118.8 (8)	S(12)-C(20)-N(2)	118.9 (9)
S(21)-C(10)-N(1)	117.7 (8)	S(22)-C(20)-N(2)	117.1 (8)
C(10)-N(1)-C(11)	126 (1)	C(20)-N(2)-C(21)	125 (1)
-C(14)	124 (1)	-C(24)	122 (1)
C(11)-N(1)-C(14)	110 (1)	C(21)-N(2)-C(24)	113 (1)
N(1)-C(11)-C(12)	107 (1)	N(2)-C(21)-C(22)	106 (1)
C(11)-C(12)-C(13)	108 (1)	C(21)-C(22)-C(23)	108 (1)
C(12)-C(13)-C(14)	109 (1)	C(22)-C(23)-C(24)	111 (2)
C(13)-C(14)-N(1)	107 (1)	C(23)-C(24)-N(2)	103 (1)
Mo(1)-O(13)-P(1)	142.3 (4)	CPh(11)-P(1)-CPh(21)	108 (1)
O(13)-P(1)-CPh(11)	111.9 (9)	-CPh(31)	106 (1)
-CPh(21)	109.7 (9)	CPh(21)-P(1)-CPh(31)	107 (1)
-CPh(31)	113.4 (9)		
Mo(1)-O(11)-C(1)	119.6 (7)	Mo(1)-O(12)-C(3)	117.4 (7)
Mo(2)-O(21)-C(1)	117.3 (7)	Mo(2)-O(22)-C(3)	118.0 (7)
O(11)-C(1)-O(21)	121 (1)	O(12)-C(3)-O(22)	122 (1)
-C(2)	119 (1)	-C(4)	120 (1)
O(21)-C(1)-C(2)	120 (1)	O(22)-C(3)-C(4)	118 (1)
C(S2)-C(S1)-C(S3)	118 (1)		
C(S1)-C(S2)-C(S3)	122 (1)		
C(S1)-C(S3)-C(S2)	119 (1)		
C(S16)-C(S11)-C(S12)	126 (2)	C(S13)-C(S14)-C(S15)	120 (3)
C(S11)-C(S12)-C(S13)	122 (3)	C(S14)-C(S15)-C(S16)	123 (3)
C(S12)-C(S13)-C(S14)	114 (3)	C(S15)-C(S16)-C(S11)	116 (2)

[a] A prime represents an atom related by an inversion center.

The terminal coordination in $[Mo_2(pdc)_2(OAc)_2OPPh_3]\cdot 1^1/_2C_6H_6$ is quite interesting. Even though 2 equiv of triphenylphosphine oxide was added, there is only one coordinated to each dimer in the crystal. The Mo–O distance is very short for an axial adduct being only 2.370 (7) Å. This can be compared to the values of 2.703 [3] Å for the Mo–O of THF in $Mo_2(S_2CR)_4(THF)_2$ or 2.548 (8) Å for the Mo–N of $[Mo_2(O_2CCF_3)_4(NC_5H_5)_2]$.[12] The molybdenum not bound to the phosphine

Scheme I



oxide appears to be weakly coordinated to O(21) of an acetate of a neighboring dimer related by the crystallographic inversion center. While this Mo(2)–O(21)′ distance of 2.980 (7) Å is only slightly shorter than the average of 3.03 [3] Å for the other Mo–O′ contacts, there are two indications that the interaction with O(21) is significant. First, by the Mo(2)–O(21) distance of 2.135 (7) Å is longer than the average of 2.115 [4] Å for the other Mo–O distances. Second, the Mo(1)–Mo(2)–O(21)′ angle is 163.0 (1)° while all the other oxygens make angles less than 50°, which is not chemically reasonable. This type of axial coordination by carboxylate oxygens has been observed in many of these dimers.[13]

The most important question to be answered by this structure is why pdc does not oxidatively add across the quadruple bond like the other dithiocarbamates. It has been suggested previously that this is due to the pyrrole ring stabilizing the less stable resonance form.[14,15] The two possible forms are shown in Scheme I. The form labeled "a" will be called the dithio acid form while that labeled "b" is the 1,1-dithiolate form. The two forms are readily distinguished structurally by three tests. First, in 1,1-dithiolates the carbon–sulfur bonds are single bonds and generally have lengths greater than 1.71 Å. A more sensitive test is the length of the carbon–nitrogen bond. In the 1,1-dithiolate structure this is essentially a double bond and typically has a length of less than 1.35 Å. Third, if the carbon–nitrogen double bond is formed, then the planes defined by S–C–S and by NR_2 must be coplanar. These features can be observed in the structure of $NaS_2CNEt_2 \cdot 3H_2O$, which is typical of the 1,1-dithiolate form.[16] The carbon–sulfur bond lengths are 1.712 (7) and 1.729 (6) Å. The carbon–nitrogen bond length is 1.344 (8) Å, and the molecule is essentially planar with the exception of the terminal methyl groups. However, in order for pdc to be in the dithiolate form, the aromaticity of the pyrrole ring must be destroyed. Thus, pdc exists in the dithio acid form and its properties are frequently different from those of other dithiocarbamates.[14,15]

The two pdc ligands in *cis*-$[Mo_2(pdc)_2(OAc)_2OPPh_3] \cdot 1^1/_2C_6H_6$ are typical for the dithio acid configuration. These two pdc ligands will be referred to as pdcI (which is composed of S(11), S(12), N(1), and C(10)–C(14)) and pdcII. The pyrrole groups for both pdc ligands are quite planar, the largest deviation from the best plane being 0.012 Å. In previous structures there has only been a slight deviation from planarity for the entire ligand. In $Fe(pdc)_3$ the torsional angle between the pyrrole ring and the SCS plane varied from 5.4 to 8.5°[14] while in $Mo(pdc)_4$ this angle averaged to 4.1°.[15] The torsional angle in pdcI is only 1.8° while in pdcII it is 12.9°. The the N–C bond lengths are 1.40 (1)–1.43 (1) Å. These are slightly longer than the mean value of 1.377 [6] Å observed in $Mo(pdc)_4$, and the value of 1.43 Å is the longest value yet observed. In fact, it is quite close to the 1.47 Å observed in *N*-methylpyrrole,[17] suggesting there is almost no C–N double-bond character. In addition, the smaller variance in the carbon–carbon bond distances in pdcII suggests that the pyrrole ring is much closer to the idealized aromatic structure. The carbon–sulfur distances for both pdc ligands are also typical for the dithio acid form.

Table IV. Positional Parameters for the Atoms of $[Mo_2(S_2CPEt_3)(O_2CCH_3)_3OPEt_3](BF_4)$

atom	*x*	*y*	*z*
Mo(1)	0.57285 (4)	0.59437 (4)	0.95232 (3)
Mo(2)	0.58677 (5)	0.74105 (4)	0.97102 (3)
S(11)	0.7360 (1)	0.5407 (1)	1.0384 (1)
S(21)	0.7557 (1)	0.7435 (1)	1.0674 (1)
P(11)	0.9339 (1)	0.6132 (1)	1.1461 (1)
P(21)	0.6572 (2)	0.9883 (1)	0.9722 (1)
O(11)	0.4237 (4)	0.6089 (3)	0.8669 (3)
O(12)	0.6365 (4)	0.6025 (3)	0.8579 (3)
O(13)	0.4849 (4)	0.5837 (3)	1.0349 (3)
O(21)	0.4383 (4)	0.7618 (3)	0.8847 (3)
O(22)	0.6519 (4)	0.7549 (3)	0.8771 (3)
O(23)	0.4995 (4)	0.7367 (3)	1.0525 (3)
O(24)	0.6013 (4)	0.9027 (3)	0.9875 (3)
C(S)	0.8045 (5)	0.6356 (5)	1.0811 (4)
C(111)	0.3894 (6)	0.6900 (6)	0.8517 (4)
C(112)	0.2826 (8)	0.7037 (7)	0.7902 (6)
C(121)	0.6611 (6)	0.6820 (6)	0.8390 (4)
C(122)	0.7012 (8)	0.6918 (8)	0.7686 (6)
C(131)	0.4638 (6)	0.6582 (5)	1.0663 (4)
C(132)	0.3922 (8)	0.6528 (7)	1.1176 (6)
C(11)	0.9891 (6)	0.0577 (6)	0.4101 (5)
C(12)	0.8737 (9)	0.0362 (8)	0.3610 (6)
C(21)	0.9221 (7)	0.5331 (6)	1.2218 (5)
C(22)	0.8405 (9)	0.5631 (8)	1.2593 (6)
C(31)	0.9941 (6)	0.7191 (6)	1.1934 (5)
C(32)	0.9710 (8)	0.2860 (7)	0.3611 (6)
C(41)	0.5774 (7)	1.0497 (7)	0.8873 (5)
C(42)	0.5478 (9)	0.9860 (8)	0.8150 (6)
C(51)	0.6802 (7)	1.0713 (6)	1.0515 (5)
C(52)	0.7448 (9)	1.0274 (8)	1.1298 (7)
C(61)	0.7830 (7)	0.9582 (6)	0.9588 (5)
C(62)	0.8517 (9)	1.0415 (8)	0.9493 (6)
B	0.949 (1)	0.271 (1)	0.0905 (9)
F(1)	0.9327 (10)	0.1905 (6)	0.1159 (4)
F(2)	0.966 (1)	0.3332 (6)	0.1452 (5)
F(3)	0.875 (1)	0.2903 (9)	0.0253 (6)
F(4)	1.034 (1)	0.263 (1)	0.0698 (8)

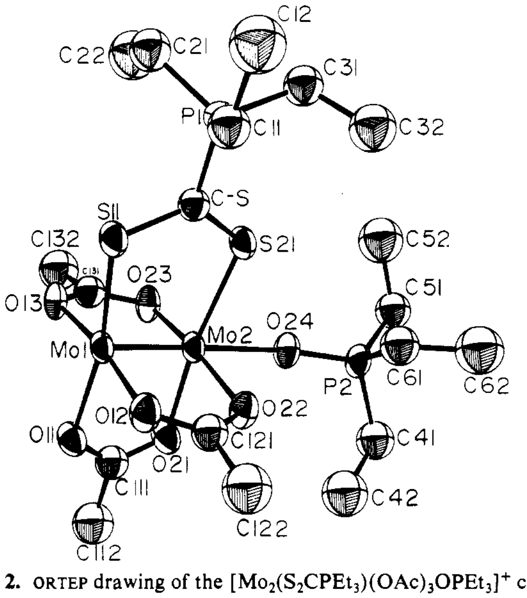


Figure 2. ORTEP drawing of the $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3]^+$ cation.

$[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$. The initial impetus for using the dithiocarboxylatophosphonium zwitterion was to prepare cationic dimers involving dithio acid ligands. The coordination chemistry of this ligand has received much attention lately.[18-21]

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Table V. Bond Distances (Å) and Angles (deg) for $[Mo_2(S_2CPEt_3)(O_2CCH_3)_3OPEt_3](BF_4)$

Mo(1)-Mo(2)	2.1384 (8)		
Mo(1)-O(11)	2.119 (5)	Mo(2)-O(21)	2.131 (5)
-O(12)	2.097 (5)	-O(22)	2.107 (5)
-O(13)	2.132 (5)	-O(23)	2.105 (5)
-S(11)	2.380 (2)	-S(21)	2.386 (2)
-O(13)′	2.704 (6)	-O(24)	2.348 (5)
S(11)-C(S)	1.692 (7)	S(21)-C(S)	1.673 (7)
C(S)-P(11)	1.792 (7)	P(11)-C(21)	1.819 (9)
P(11)-C(11)	1.809 (8)	-C(31)	1.811 (9)
O(11)-C(111)	1.253 (9)	C(11)-C(12)	1.55 (1)
O(21)-C(111)	1.270 (9)	C(21)-C(22)	1.49 (1)
C(111)-C(112)	1.53 (1)	C(31)-C(32)	1.53 (1)
O(12)-C(121)	1.263 (9)	O(13)-C(131)	1.280 (9)
O(22)-C(121)	1.276 (9)	O(23)-C(131)	1.277 (9)
C(121)-C(122)	1.41 (1)	C(131)-C(132)	1.50 (1)
O(24)-P(21)	1.502 (5)		
P(21)-C(41)	1.806 (9)	C(41)-C(42)	1.54 (1)
-C(51)	1.812 (9)	C(51)-C(52)	1.55 (1)
-C(61)	1.797 (9)	C(61)-C(62)	1.54 (1)
B(1)-F(1)	1.29 (2)	B(1)-F(3)	1.31 (2)
-F(2)	1.30 (2)	-F(4)	1.28 (2)
Mo(2)-Mo(1)-O(11)	92.0 (1)	Mo(1)-Mo(2)-O(21)	90.4 (1)
-O(12)	92.0 (1)	-O(22)	90.3 (1)
-O(13)	90.1 (1)	-O(23)	92.3 (1)
-S(11)	101.52 (5)	-S(21)	98.45 (4)
-O(13)′	159.6 (1)	-O(24)	178.3 (1)
O(11)-Mo(1)-O(12)	85.8 (2)	O(21)-Mo(2)-O(22)	84.9 (2)
-O(13)	85.9 (2)	-O(23)	86.2 (2)
-S(11)	166.4 (1)	-S(21)	171.1 (1)
-O(13)′	86.0 (2)	-O(24)	88.6 (2)
O(12)-Mo(1)-O(13)	171.1 (2)	O(22)-Mo(2)-O(23)	170.7 (2)
-S(11)	92.3 (1)	-S(21)	93.6 (1)
-O(13)′	108.1 (2)	-O(24)	88.2 (2)
O(13)-Mo(1)-S(11)	95.8 (1)	O(23)-Mo(2)-S(21)	94.8 (1)
-O(13)′	69.5 (2)	-O(24)	89.0 (2)
S(11)-Mo(1)-O(13)′	82.0 (2)	S(21)-Mo(2)-O(24)	82.5 (1)
Mo(1)-S(11)-C(S)	107.0 (2)	Mo(2)-S(21)-C(S)	109.3 (2)
S(11)-C(S)-S(21)	123.5 (4)	C(11)-P(11)-C(21)	108.5 (4)
-P(11)	115.4 (4)	-C(31)	113.0 (4)
S(21)-C(S)-P(11)	121.0 (4)	C(21)-P(11)-C(31)	107.9 (4)
C(S)-P(11)-C(11)	107.6 (3)	P(11)-C(11)-C(12)	113.0 (6)
-C(21)	108.9 (4)	-C(21)-C(22)	112.4 (7)
-C(31)	110.9 (4)	-C(31)-C(32)	113.8 (6)
Mo(1)-O(11)-C(111)	116.7 (5)	Mo(1)-O(13)-C(131)	118.4 (4)
Mo(2)-O(21)-C(111)	117.2 (5)	Mo(2)-O(23)-C(131)	117.8 (4)
O(11)-C(111)-O(21)	123.7 (7)	O(13)-C(131)-O(23)	121.2 (6)
-C(112)	118.5 (7)	-C(132)	118.9 (7)
O(21)-C(111)-C(112)	117.7 (7)	O(23)-C(131)-C(132)	119.9 (7)
Mo(1)-O(12)-C(121)	117.4 (5)		
Mo(2)-O(22)-C(121)	118.1 (4)		
O(12)-C(121)-O(22)	122.1 (7)		
-C(122)	119.2 (7)		
O(22)-C(121)-C(122)	118.7 (7)		
Mo(2)-O(24)-P(21)	144.8 (3)	C(41)-P(21)-C(61)	109.9 (4)
O(24)-P(21)-C(41)	111.0 (4)	C(51)-P(21)-C(61)	108.2 (4)
-C(51)	112.2 (3)	P(21)-C(41)-C(42)	110.9 (7)
-C(61)	110.3 (4)	-C(51)-C(51)	111.2 (7)
C(41)-P(21)-C(51)	105.0 (4)	-C(61)-C(62)	115.0 (7)
F(1)-B(1)-F(2)	111 (1)	F(2)-B(1)-F(3)	116 (1)
-F(3)	110 (1)	-F(4)	108 (2)
-F(4)	106 (1)	F(3)-B(1)-F(4)	104 (1)

When molybdenum(II) acetate was reacted with 2 equivalents of S_2CPEt_3 for 24 h in refluxing THF, there was no reaction. However, adding a small amount of any acid (in this case HBF_4) to the solution immediately resulted in a color change to dark purple. This reaction solution was placed in a test tube, and a layer of hexane was floated on top and allowed to diffuse. Large purple-black crystals of $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$ grew at the boundary. The phosphine oxide results from the reaction of the water in the acid with the ligand. If the reaction solutions were allowed to stand for several months, a second dark red crystal formed at the bottom of the tube. The compound is deliquescent and must be protected from air. An X-ray data set was collected on these crystals, which had a *C*-centered, orthorhombic unit cell of $a = 24.423$ (3) Å, $b = 27.298$ (4) Å, and $c = 13.997$ (3) Å. Refinement of this data set has not been satisfactory (lowest *R* values $R = 12.2$, $R_w = 16.0$), and the final structure will be reported later. However, it is clear that the cation is *cis*-[Mo₂-

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$(S_2CPEt_3)_2(OAc)_2(THF)_2]^{2+}$. When 4 equiv of S_2CPEt_3 was reacted with $Mo_2(O_2CCH_3)_4$ in the presence of 4 equiv of acid, the same purple-red solution was produced. After several days of reaction, a layer of hexane was floated on top, immediately resulting in the precipitation of the excess ligand.

The compound $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$ crystallized in a monoclinic cell with four molecules per cell. The cation is situated at a general position and contains no crystallographically imposed symmetry. The positional parameters and their errors are given in Table IV, and the bond distances and angles, in Table V. Figure 2 is an ORTEP drawing of the cation.

The general features of the cation are quite similar to those of $[Mo_2(pdc)_2(OAc)_2OPPh_3]$. The Mo-Mo distance is 2.1384 (8) Å. Again one molybdenum is tightly bound to the oxygen of the phosphine oxide. This Mo-O distance of 2.348 (5) Å is the shortest bond length observed for any axially coordinated, quadruply bonded molybdenum dimer. The other molybdenum is again coordinated to an oxygen of an acetate on a neighboring dimer related by an inversion center. In this case the Mo-O axial bond is much shorter than in the pdc dimer. In addition, the Mo-Mo-O′ angle is 159.6 (1)°, in agreement with the 163.0 (1)° for the pdc dimer. It appears that the net positive charge on the dimer results in these shorter distances because all the Mo-S bonds are also shorter than in $[Mo_2(pdc)_2(OAc)_2OPPh_3]$.

The dithiocarboxylato group in S_2CPEt_3 is required to exist in the dithio acid resonance form. The C-S distances are typical for this form and agree with those observed in the pdc dimer. In general, the two ligands pdc and S_2CPEt_3 seem to behave in a very similar fashion toward dimolybdenum dimers. The inability of S_2CPEt_2 to completely replace the acetates may have to do with trying to form a 4+ cation in an organic solvent.

Registry No. $[Mo_2(pdc)_2(OAc)_2OPPh_3]\cdot 1^1/_2C_6H_6$, 98244-72-5; $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$, 98218-58-7; $[Mo_2(pdc)_2(OAc)_2]$, 98218-59-8; $[Mo_2(S_2CPEt_3)_2(OAc)_2(THF)_2]^{2+}$, 98218-60-1; Mo, 7439-98-7.

Supplementary Material Available: Tables of least-squares planes, thermal parameters, rigid-group parameters, and observed and calculated structure factors for *cis*-$[Mo_2(pdc)_2(OAc)_2OPPh_3]\cdot 1^1/_2C_6H_6$ and tables of thermal parameters and observed and calculated structure factors for $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$ (48 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Geometrical Isomers of $[Ph_2P(CH_2)_2AuX_2]_2$. Crystal and Molecular Structures of *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$ and *cis,trans*-$[Ph_2P(CH_2)_2AuCl_2]_2$

DOUGLAS S. DUDIS and JOHN P. FACKLER, JR.*

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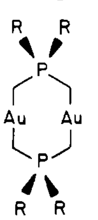
The X-ray structure of the dinuclear gold(III) ylide complex *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$ has been determined. This is the first completely characterized dimer of this type. While no metal-metal bond is suggested for the compound in its eclipsed configuration, there is an unusual "semibridging" halide. When the same compound stands in $CDCl_3$ for prolonged periods, the geometrical isomer with a cis,trans configuration is formed. The chloride analogue of this cis,trans compound, formed by reaction of the gold(II) dimer with $SnCl_2\cdot 2H_2O$ in $CDCl_3$, has been characterized structurally and is reported here. For *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2\cdot CDCl_3$, $a = 11.657$ (2) Å, $b = 13.244$ (3) Å, $c = 26.374$ (5) Å, $\beta = 120.299$ (13)°, $Z = 4$, and $V = 3515.4$ (1.1) Å^3 for the yellow crystals which conform to a monoclinic $C2/c$ space group. The *cis,trans*-$[PhP_2(CH_2)_2AuCl_2]_2\cdot 2CDCl_3$ product crystallizes in $P2_1/c$ with $a = 12.695$ (2) Å, $b = 24.198$ (5) Å, $c = 13.2279$ (2), $\beta = 108.523$ (11)°, $V = 3852.8$ (1.0) Å^3, and $Z = 4$.

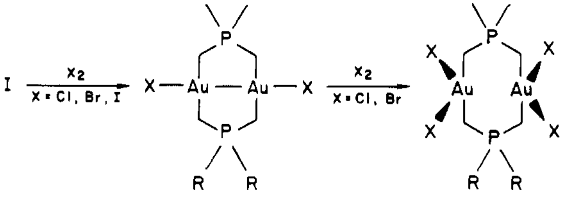
Introduction

The oxidation of the dinuclear gold(I) ylide complexes I with



I, R = alkyl or aryl

X_2 (X = Cl, Br) occurs[1] stepwise to give gold(II) and gold(III) products (eq 1). The structures of I and II-X_2 have been confirmed for a variety of alkyl substituents and halogens.[2-6] Upon oxidation from I to II-X_2, the Au-Au distance decreases from 3.0 to 2.6 Å. No crystallographic studies for the gold(III) derivatives, III-X_4, have been reported. Thus, the Au···Au separation (and presumably any experimental data regarding the Au···Au interaction) was, heretofore, unknown. These III-X_4 compounds are known to contain gold(III) on the basis of ^{197}Au Mössbauer and photoelectron spectra,[7] but the suggested structures are described as "tentative". Metathesis of I and III-X_4 gives[8] II-X_2, which supports the formulation of III-X_4. This reaction of a M(I) and M(III) compound to yield a stable M(II) species is unprecedented in mononuclear gold chemistry. Recently, we were able to obtain single crystals of III-Br_4 (R = Ph for all gold compounds described hereafter) and an isomeric form of the chloro derivative,[9]



(1)

II-X_2 III-X_4

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