when coordinated to main-group acids involves ca. 12° increases in $\sum$OPO. Since the OPO angle enlargements upon coordination of **4** and **9** are approximately the same, there appears to be no substantial evidence for the basicity order **9** > **4** to arise from OPO angle differences.

A detailed σ/π analysis for phosphates as presented for the aminophosphine oxides[2] is precluded by the fact that the phosphoryl and ester n_O IE's overlap. However, the simple σ-donor model appears to hold for X = S, where the n_S e orbitals ionize in order of energies **9b** < **4b**. The corresponding IE in **6b** implies that **6** lies between **4** and **9** in base strength, a conclusion reached independently from gas-phase proton affinity data obtained from ion cyclotron resonance experiments.[39] For X = Se, the basicity trend also seems to hold except that the IE range spanned is much smaller and the difference between **9c** and **4c** is negligible.

Acknowledgment. J.G.V. and A.H.C. thank the National Science Foundation and M.L. and A.H.C. thank the Robert A. Welch Foundation for grant support of this work. We also thank D. A. Lesch and L. E. Carpenter for experimental assistance.

Registry No. **1**, 18818-32-1; **1a**, 18818-34-3; **1b**, 18818-33-2; **2**, 91711-76-1; **3**, 280-45-5; **4**, 1449-91-8; **4b**, 3196-56-3; **4c**, 67471-54-9; **4d**, 6867-41-0; **5**, 1005-93-2; **6**, 281-33-4; **6a**, 875-12-7; **6b**, 58299-37-9; **7**, 22223-55-8; **8**, 536-97-0; **9**, 121-45-9; **9a**, 512-56-1; **9b**, 152-18-1; **9c**, 152-19-2; **10**, 816-80-8; **10a**, 681-71-0; **11**, 3862-19-9; $BrCH_2CH{=}CH_2$, 106-95-6; $BrCH_2CHBrCH_2Br$, 96-11-7; $HSCH_2CH(SH)CH_2SH$, 4756-13-2; $P(NMe_2)_3$, 1608-26-0.

Supplementary Material Available: PE spectra of **1b**, **4c**, **4d**, **5**, **6**, **6a**, **6b**, **8**, and **11** (9 pages). Ordering information is given on any current masthead page.

---

[39] Hodges, R. V.; Houle, F. A.; Beauchamp, J. L.; Montag, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1980**, *102*, 932.

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

Preparation of the Crystalline β (Bridged) Isomer of $Mo_2Cl_4(dppe)_2$ and Determination of Its Crystal Structure

PRADYOT A. AGASKAR and F. ALBERT COTTON*

Received December 12, 1983

It has been found that the α and β isomers of $Mo_2Cl_4(dppe)_2$, dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, can be prepared by the reaction of $Mo_2(O_2CCF_3)_4$ with $(CH_3)_3SiCl$ and dppe. The isomer obtained is controlled by reaction conditions, primarily the solvent. It has also been found possible to obtain both isomers in crystalline form. The crystal structure of the β isomer, in which the dppe ligands bridge the Mo$\overset{4}{-}$Mo unit, has been determined. It forms crystals in space group $P2_1/n$ with a = 23.103 (45) Å, b = 13.258 (75) Å, c = 16.792 (62) Å, β = 107.19 (7)°, V = 4913 (11) Å^3, and Z = 4. The midpoints of the Mo–Mo quadruple bonds reside on a set of general positions. At each position there are two orientations, a principal one (87%) and a minor one (13%). In the principal orientation the helical molecule consists of two fused rings with chair conformations and a mean angle of twist about the Mo–Mo axis of 30.5°. In the minor orientation, the fused rings have twist conformations and the sense of the helix about the Mo–Mo bond is opposite to the one in the principal molecule with an angle of 27.7°. In the principal molecule, the Mo–Mo distance is 2.183 (3) Å and the mean Mo–P and Mo–Cl distances are 2.579 (8) and 2.385 (7) Å, respectively.

Introduction

It is now well established that in compounds of the type $M_2X_4(R_2EYE'R_2)_2$, where M may be Mo, W, or Re, R may be phenyl or methyl, E and E′ are usually P but in one instance we have E = P and E′ = As, and Y may be CH_2CH_2, CH_2CHMe, CHMeCHMe, or $(CH_2)_3$, there are two isomers and that in most cases both isomers are formed. The two isomers have the chelated, α, and bridged, β, structures, shown schematically in Figure 1. The pioneering work on these systems was done by Walton and his students who first discovered that there are isomeric forms of $Re_2Cl_4(dppe)_2$, dppe = $Ph_2PCH_2CH_2PPH_2$, and who offered a correct conjecture as to their nature.[1] Since then, structural assignments based on X-ray crystallography have been made for several compounds. The detailed structural results heretofore published are collected in Table I.

With all of these compounds, perhaps most severely with those of molybdenum, one encounters difficulties because of insolubility. This makes it difficult to control the course of the syntheses so as to obtain the desired products and frequently denies access to useful single crystals unless these form directly from the synthetic reaction, which, by good fortune, is sometimes the case.

Table I. Previously Reported Crystal Structures for Compounds of the Type $M_2X_4(R_2ECH_2CH_2E'R_2)$

M	X	$R_2EXE'R_2$	M-M dist, Å	% minor orientation	ref
Re	Cl	$Ph_2PCH_2CH_2PPh_2$	2.244 (1)	6.5	*a*
Mo	Br	$Ph_2PCH_2CH_2AsPh_2$	2.167 (4)	23	*b*
W	Cl	$Ph_2PCH_2CH_2PPh_2$	2.314 (1)	7	*c*
Mo	Cl	$Me_2PCH_2CH_2PMe_2$	2.183 (3)	8	*d*

[a] Cotton, F. A.; Stanley, G. G.; Walton, R. A. *Inorg. Chem.* 1978, *17*, 2099. [b] Cotton, F. A.; Fanwick, P. E.; Fitch, J. W.; Glicksman, H. D.; Walton, R. A. *J. Am. Chem. Soc.* 1979, *101*, 1752. [c] Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* 1981, *20*, 3880. [d] Cotton, F. A.; Powell, G. L. *Inorg. Chem.* 1983, *22*, 1507.

In this paper we report the successful result of a deliberate effort to isolate the β (bridged) isomer of $Mo_2Cl_4(dppe)_2$ in crystalline form and determine its structure. From this prototypal compound in the field it was expected that lessons could be learned about both the synthesis and structure that would have wider implications. Since the original synthetic method of Best, Smith, and Walton[2,3] is not appropriate for the pro-

---

(1) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

0020-1669/84/1323-3383$01.50/0

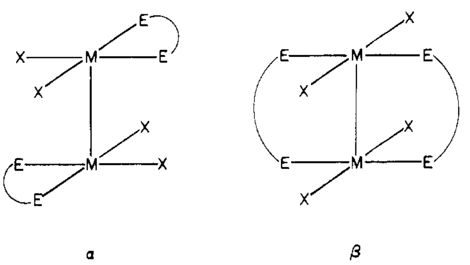

Figure 1. Schematic representations of the two isomers of an $M_2X_4(R_2EYER_2)_2$ molecule: the α, or chelated form, and the β, or bridged, form. The latter has been shown for simplicity with an eclipsed conformation about the M–M bond, whereas in reality for most connecting groups X, other than CH_2, there is a helical twist.

duction of a crystallographically useful product, we have developed an entirely different synthetic procedure, which is described herein. Advantage is taken of the general reaction (1) to give a preparative method represented by reaction 2. The employment of Me_3SiCl in this type of synthetic reaction was first described by McCarley[4] and has also been used in other preparations.[5]

$$M{-}O_2CR + Me_3SiCl \rightarrow M{-}Cl + Me_3Si{-}O_2CR \quad (1)$$

$$Mo_2(O_2CCF_3)_4 + 4Me_3SiCl + 2dppe \rightarrow Mo_2Cl_4(dppe)_2 + 4Me_3SiO_2CF_3 \quad (2)$$

Experimental Procedures

Preparative reactions and other handling of materials were conducted in an inert atmosphere using Schlenk technique, unless otherwise noted. $Mo_2(O_2CCF_3)_4$ was prepared by the literature method.[6]

Preparation A. $Mo_2(O_2CCF_3)_4$ (40 mg) was dissolved in 10 mL of toluene. dppe (50 mg) was added, followed by 0.5 mL of Me_3SiCl. A green precipitate, which formed over a period of 2–3 h, was filtered off in air and dried by pumping. A UV–visible spectrum was recorded on a mineral oil mull sample, and it showed maxima at 660, 475, and 390 nm. This should be the α isomer,[2] and it was obtained in approximately 40% yield.

Preparation B. $Mo_2(O_2CCF_3)_4$ (80 mg) was dissolved in 10 mL of tetrahydrofuran (THF) and 0.1 mL of Me_3SiCl added. This mixture was stirred for about 12 h, and then 100 mg of dppe was added. The reaction mixture first turned green, but a light brown precipitate soon began to form. After several hours this was isolated by filtration and dried under vacuum. A mull spectrum showed maxima at 785, 575, and 475 nm. This product appears to be essentially pure β isomer, and the yield is about 30%. Unfortunately, it is not crystalline.

Preparation C. $Mo_2(O_2CCF_3)_4$ (80 mg) was dissolved in a mixture of toluene (9 mL) and THF (1 mL), and Me_3SiCl (0.1 mL) was added. This solution was stirred for about 12 h. A layer of toluene (5 mL) was gently introduced over the red-orange solution, and then 5 mL of toluene containing 100 mg of dppe was placed above the toluene layer; some mixing of the two toluene layers occurred as this was done. During the following period of about 12 h both green and brown crystals were formed. A brown crystal (β isomer) was used for the X-ray study.

X-ray Diffraction Procedures. The crystal was mounted with epoxy cement on a glass fiber. No special effort was made to protect it from air. Table II summarizes basic crystallographic information. The unit cell was defined and the crystal orientation deduced by centering 15 reflections with 2θ values in the range of 10–30°. The crystal lattice was found to be dimensionally consistent with the monoclinic system, and subsequent observation of systematic absences showed the space group to be $P2_1/n$. Corrections were made for Lorentz and polarization effects and for an overall 4.3% linear decline in the intensities of three standard reflections (checked after every 100 measurements), over a period of 191.5 h of X-ray exposure time. Because of the low X-ray absorption coefficient, no absorption correction was made.

Table II. Crystallographic Data and Data Collection Procedures

formula	$Mo_2Cl_4((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2$
fw	1130.55
space group	$P2_1/n$
syst absences	$h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$
a, Å	23.103 (45)
b, Å	13.258 (75)
c, Å	16.792 (62)
α, deg	90.0
β, deg	107.19 (7)
γ, deg	90.0
V, Å^3	4913 (11)
Z	4
d_{calcd}, g/cm^3	1.528
cryst size, mm	0.3 × 0.2 × 0.5
μ(Mo Kα), cm^{-1}	8.808
data colln instrum	Syntex $P\bar{1}$
radiation (monochromated in incident beam)	Mo Kα
no. of orientation reflcns; range (2θ), deg	15; 10–30
temp, °C	22
scan method	ω/2θ
data colln range (2θ), deg	2.5, 50.0
no. of unique data	6163
$F_o^2 > 3\sigma(F_o^2)$	1861
no. of parameters refined	305
R^a	0.0729
$R_w{}^b$	0.0887
quality-of-fit indicator^c	1.364
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	0.659

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

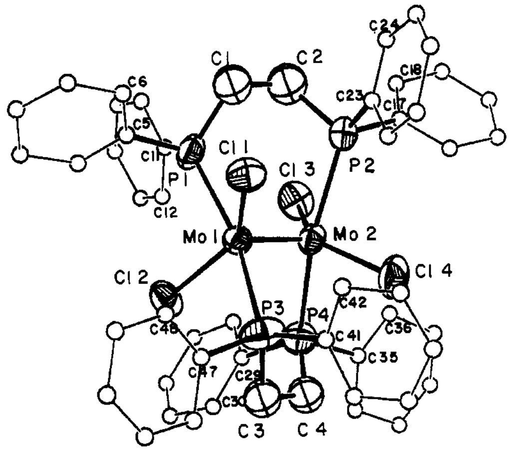

Figure 2. View of the entire molecule including the molybdenum atoms that occupy the dominant positions. The carbon atoms of the phenyl groups are represented by spheres of arbitrarily small size to reduce overlap of more significant parts of the structure.

Solution and Refinement of the Structure.[7] Comparison of the unit cell for this compound with that previously reported for $Re_2Cl_4(dppe)_2$ (see Table I for the reference) immediately suggested that the atomic positional parameters were likely to be very similar in the two cases, and it was, accordingly, noted that three of the four highest peaks in the three-dimensional Patterson function were consistent with this assumption. The entire structure was solved and refined on this basis. As in the case of the rhenium compound and virtually all M_2X_8 type

---

(2) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.

(3) It has recently been found (R. D. Peacock, Glasgow University, private communication) that by starting with the method of ref 2 it is possible to obtain pure β isomer since it is evidently the thermodynamically stable one. Suitable crystals, however, were not so obtained.

(4) McCarley, R. E.; Ryan, T. R.; Torardi, C. C. "Reactivity of Metal–Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC 1981; ACS Symp. Ser. No. 155, p 48.

(5) (a) Arenivar, J. D.; Mainz, V. V.; Ruben, H.; Anderson, R. A.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2649. (b) Agaskar, P.; Cotton, F. A. *Inorg. Chim. Acta* **1984**, *83*, 33.

(6) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161.

(7) All computations were carried out with the program in the Enraf-Nonius structure determination package on a PDP-11/60 computer.

Table III. Table of Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	B,[a] Å	atom	*x*	*y*	*z*	B,[a] Å
Mo(1)	0.3103 (1)	0.2997 (2)	−0.0126 (2)	3.51 (6)	C(21)	0.056 (1)	0.182 (3)	0.133 (2)	8.6 (9)*
Mo(2)	0.2516 (1)	0.2027 (2)	0.0349 (2)	3.68 (6)	C(22)	0.100 (1)	0.227 (2)	0.096 (2)	6.1 (8)*
Mo(3)	0.2424 (7)	0.289 (1)	−0.026 (1)	3*	C(23)	0.143 (1)	0.437 (2)	0.027 (2)	4.8 (7)*
Mo(4)	0.3199 (7)	0.231 (1)	0.065 (1)	3*	C(24)	0.118 (1)	0.510 (2)	0.070 (2)	7.3 (8)*
Cl(1)	0.2638 (3)	0.4593 (5)	−0.0611 (4)	5.0 (2)	C(25)	0.072 (1)	0.574 (2)	0.017 (2)	7.1 (8)*
Cl(2)	0.4056 (3)	0.2242 (6)	0.0019 (5)	5.6 (2)	C(26)	0.054 (1)	0.570 (2)	−0.068 (2)	6.0 (8)*
Cl(3)	0.2886 (3)	0.1701 (6)	0.1822 (4)	5.8 (2)	C(27)	0.080 (2)	0.492 (3)	−0.109 (2)	9 (1)*
Cl(4)	0.1635 (3)	0.1576 (6)	−0.0729 (5)	6.3 (2)	C(28)	0.122 (1)	0.428 (2)	−0.059 (2)	5.1 (7)*
P(1)	0.3552 (3)	0.4005 (6)	0.1222 (5)	4.8 (2)	C(29)	0.374 (1)	−0.006 (2)	0.052 (2)	5.2 (7)*
P(2)	0.1951 (3)	0.3452 (6)	0.0890 (5)	5.1 (2)	C(30)	0.410 (1)	−0.043 (2)	0.004 (2)	6.7 (8)*
P(3)	0.2841 (4)	0.2269 (6)	−0.1610 (5)	5.8 (2)	C(31)	0.472 (1)	−0.077 (2)	0.055 (2)	6.7 (8)*
P(4)	0.2951 (3)	0.0348 (6)	0.0023 (5)	4.9 (2)	C(32)	0.486 (1)	−0.079 (2)	0.137 (2)	6.5 (8)*
C(1)	0.296 (1)	0.480 (2)	0.148 (2)	6.3 (8)*	C(33)	0.450 (1)	−0.042 (2)	0.182 (2)	7.4 (9)*
C(2)	0.250 (1)	0.416 (2)	0.177 (2)	7.0 (8)*	C(34)	0.392 (1)	0.000 (2)	0.139 (2)	6.7 (8)*
C(3)	0.310 (1)	0.091 (2)	−0.158 (2)	5.8 (7)*	C(35)	0.251 (1)	−0.078 (2)	0.029 (2)	7.0 (8)*
C(4)	0.282 (1)	0.019 (2)	−0.111 (2)	5.5 (7)*	C(36)	0.213 (1)	−0.051 (3)	0.069 (2)	9 (1)*
C(5)	0.402 (1)	0.500 (2)	0.100 (2)	5.2 (7)*	C(37)	0.180 (2)	−0.149 (3)	0.087 (2)	10 (1)*
C(6)	0.381 (1)	0.596 (2)	0.076 (2)	6.6 (8)*	C(38)	0.200 (2)	−0.242 (3)	0.066 (2)	10 (1)*
C(7)	0.421 (1)	0.667 (3)	0.059 (2)	9 (1)*	C(39)	0.237 (2)	−0.262 (3)	0.021 (2)	10 (1)*
C(8)	0.482 (1)	0.647 (2)	0.072 (2)	6.9 (8)*	C(40)	0.269 (1)	−0.165 (2)	−0.003 (2)	7.7 (9)*
C(9)	0.504 (1)	0.550 (2)	0.088 (2)	9 (1)*	C(41)	0.210 (1)	0.237 (2)	−0.236 (2)	6.8 (8)*
C(10)	0.460 (1)	0.477 (2)	0.104 (2)	7.2 (8)*	C(42)	0.176 (1)	0.324 (2)	−0.234 (2)	5.3 (7)*
C(11)	0.405 (1)	0.355 (2)	0.218 (2)	6.0 (7)*	C(43)	0.112 (1)	0.334 (2)	−0.300 (2)	7.9 (9)*
C(12)	0.429 (1)	0.257 (2)	0.218 (2)	5.2 (7)*	C(44)	0.092 (1)	0.248 (2)	−0.346 (2)	7.9 (9)*
C(13)	0.472 (1)	0.216 (3)	0.290 (2)	9 (1)*	C(45)	0.130 (1)	0.169 (3)	−0.352 (2)	9 (1)*
C(14)	0.497 (1)	0.281 (3)	0.360 (2)	8.5 (9)*	C(46)	0.191 (1)	0.158 (3)	−0.294 (2)	9 (1)*
C(15)	0.473 (2)	0.374 (3)	0.357 (2)	10 (1)*	C(47)	0.330 (1)	0.283 (2)	−0.223 (2)	5.4 (7)*
C(16)	0.427 (2)	0.417 (3)	0.284 (2)	9 (1)*	C(48)	0.348 (1)	0.380 (3)	−0.209 (2)	8.2 (9)*
C(17)	0.147 (1)	0.289 (2)	0.141 (2)	5.3 (7)*	C(49)	0.381 (1)	0.430 (3)	−0.259 (2)	8 (1)*
C(18)	0.155 (1)	0.295 (2)	0.226 (2)	7.1 (8)*	C(50)	0.394 (1)	0.373 (3)	−0.322 (2)	9 (1)*
C(19)	0.111 (1)	0.254 (3)	0.264 (2)	9 (1)*	C(51)	0.376 (2)	0.275 (3)	−0.334 (2)	11 (1)*
C(20)	0.066 (1)	0.197 (3)	0.215 (2)	7.8 (8)*	C(52)	0.345 (2)	0.223 (3)	−0.281 (3)	13 (1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

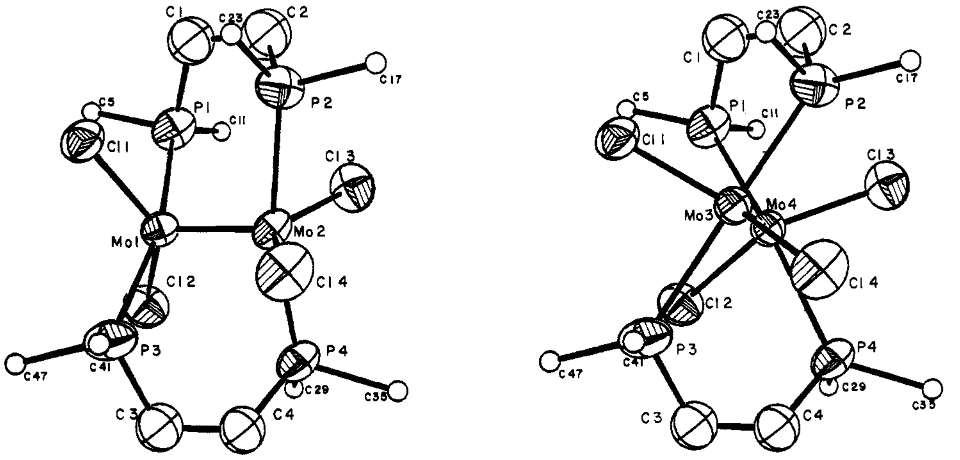

Figure 3. Drawings of the inner part of the structure showing how the Mo(1)–Mo(2) and Mo(3)–Mo(4) units can each form bonds to sets of *trans*-P_2Cl_2 ligands, despite their orthogonal orientations.

species, there was a disorder such that a minority of the molecules are tipped approximately 90° relative to the majority. Beginning at a stage of refinement where $R_1 = 11\%$, the occupancy of the main Mo positions was set at 0.90 and a second pair of Mo positions with occupancy of 0.10 was introduced at coordinates indicated by a difference Fourier map. At convergence these occupancies had values of 0.87 and 0.13.

Results

The observed and calculated structure factors as well as the elements of the anisotropic thermal vibration tensors are available as supplementary material. The atomic positions and isotropic (or equivalent) thermal parameters are listed in Table III. Only the 10 atoms Mo(1), Mo(2), Cl(1)–Cl(4), and P(1)–P(4) were refined anisotropically, and for these the isotropic thermal parameter calculated to be equivalent to the full tensor is listed in Table III.

The entire molecule with the major molybdenum atoms, Mo(1) and Mo(2), is depicted in Figure 2, where the atom-numbering scheme is also given. For each of the phenyl rings, only two atoms are numbered but the remaining numbers follow in an obvious sequence therefrom. Figure 3 shows two drawings of the central region only, in which the positons of all the non-molybdenum atoms, and all bonds within the dppe ligands, are the same in both parts. In one part the Mo(1)–Mo(2) unit and its bonds to the chlorine and phosphorus atoms are drawn in, while in the other part the Mo(3)–Mo(4) unit and its bonds to the lignads are drawn in. From these drawings it is clear that the disorder, however unlikely it might seem at first, is indeed structurally feasible. Table IV lists the important interatomic (bonded) distances and angles; a complete list of bond lengths and angles is available as supplementary material.

Table IV. Principal Bond Distances and Bond Angles

Bond Distances, Å			
Mo(1)-Mo(2)	2.183 (3)	Mo(3)-Mo(4)	2.13 (2)
-Cl(1)	2.404 (6)	-Cl(1)	2.41 (2)
-Cl(2)	2.366 (6)	-Cl(4)	2.48 (2)
-P(1)	2.569 (7)	-P(2)	2.60 (2)
-P(3)	2.572 (8)	-P(3)	2.83 (2)
Mo(2)-Cl(3)	2.405 (7)	Mo(4)-Cl(2)	2.51 (2)
-Cl(4)	2.367 (7)	-Cl(3)	2.43 (2)
-P(2)	2.607 (8)	-P(1)	2.48 (2)
-P(4)	2.568 (7)	-P(4)	2.80 (2)

Bond Angles, deg			
Mo(2)-Mo(1)-Cl(1)	112.3 (2)	Cl(3)-Mo(2)-P(4)	91.2 (3)
-Cl(2)	111.9 (2)	-P(2)	92.5 (3)
-P(1)	96.7 (2)	-P(4)	85.4 (2)
-P(3)	98.0 (2)	P(2)-Mo(2)-P(4)	166.0 (3)
Cl(1)-Mo(1)-Cl(2)	135.8 (3)	Mo(4)-Mo(3)-Cl(1)	108.9 (8)
-P(1)	82.2 (2)	-Cl(4)	110.7 (8)
-P(3)	92.8 (2)	-P(2)	90.8 (7)
Cl(2)-Mo(1)-P(1)	90.4 (2)	-P(3)	93.3 (7)
-P(3)	83.5 (2)	Cl(1)-Mo(3)-Cl(4)	140.0 (8)
P(1)-Mo(1)-P(3)	165.2 (3)	-P(2)	94.4 (6)
Mo(1)-Mo(2)-Cl(3)	114.3 (2)	-P(3)	86.5 (5)
-Cl(4)	110.8 (2)	Cl(4)-Mo(3)-P(2)	90.2 (5)
-P(2)	97.5 (2)	-P(3)	86.2 (5)
-P(4)	96.2 (2)	P(2)-Mo(3)-P(3)	175.3 (7)
Mo(3)-Mo(4)-Cl(2)	107.9 (8)	Cl(2)-Mo(4)-Cl(3)	142.4 (7)
-Cl(3)	108.5 (7)	-P(1)	89.2 (6)
-P(1)	93.5 (7)	-P(4)	84.6 (5)
-P(4)	91.8 (7)	Cl(3)-Mo(4)-P(1)	97.6 (6)
Cl(3)-Mo(2)-Cl(4)	134.8 (3)	-P(4)	85.4 (5)
-P(2)	80.5 (3)	P(1)-Mo(4)-P(4)	172.9 (7)

Only for the molecule containing Mo(1)–Mo(2) are the principal distance and angles obtained with the customary precision and useful accuracy. The Mo(1)–Mo(2) distance is 2.183 (3) Å. The mean Mo–P and Mo–Cl distances are 2.579 (8) and 2.385 (7) Å, respectively. It should be noted that there is a sizeable spread in each set, the Mo–Cl distances ranging from 2.366 (6) to 2.405 (7) Å, while the Mo–P distances run from 2.568 (7) to 2.607 (8) Å. The mean Mo–Cl distance here is not significantly different from that in the $Mo_2Cl_4(dmpe)_2$ molecule, 2.403 [4] Å, but there does seem to be a genuine difference between the dppe and dmpe molecules with respect to the Mo–P distances. In the dmpe case the two independent ones are 2.514 (5) and 2.538 (5) Å, both of which are quite significantly shorter than the average value here, 2.579 (8) Å, and both are significantly shorter, by at least 0.030 (8) Å, than the shortest one in the dppe case. This is probably attributable to the fact that the $-CH_2PPh_2$ unit is both less basic and more hindered than the $-CH_2PMe_2$ unit.

All of the possible torsion angles about the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond have been calculated, and a complete table is available for both Mo(1)–Mo(2) and Mo(3)–Mo(4) in the supplementary material. For purposes of the present discussion only the P–Mo(1)–Mo(2)–Cl and Cl–Mo(1)–Mo(2)–P type angles are of interest. They have the values 30.8, 30.3, 29.3, and 31.6°, which gives an average of 30.5°.

The present structure invites comparison with the structure of $Mo_2Br_4(arphos)_2$, where arphos = $Ph_2PCH_2CH_2AsPh_2$. In that structure the phosphorus and arsenic atoms were randomly disordered. The greater size of the arsenic and bromine atoms might be expected to lead to some conformational differences in the rings, in the twist angle about the Mo–Mo bond, and in the distribution of molecules over the primary and secondary orientations. Some such differences are indeed found. The Mo–Mo bond length, 2.167 (4) Å, is shorter in the arphos case than it is here, viz., 2.183 (3) Å. The occupation of the secondary orientation (23%) was greater in the arphos case than here (13%). However, the mean torsion angles about the Mo–Mo bond (to be discussed in detail below) are essentially the same in both cases. Figure 4 gives a view of $Mo_2Cl_4(dppe)_2$ looking straight down the Mo(1)–Mo(2) axis, showing very clearly the way in which this molecule is twisted into a helical conformation. It must be kept in mind that there are equal numbers of right- and left-hand helices present in the crystal because there are crystallographic inversion centers between the molecules.

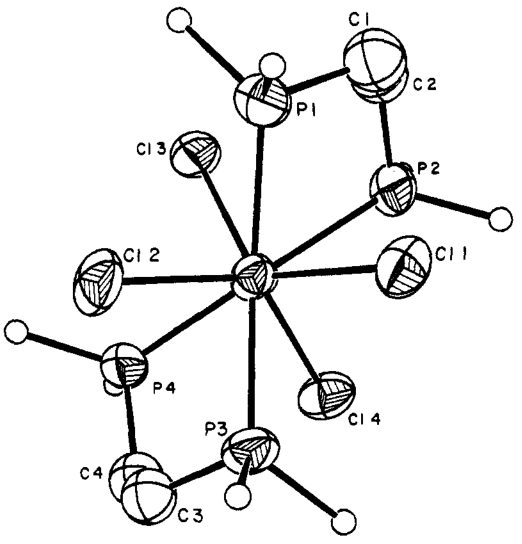

Figure 4. View of the central part of the molecule containing Mo(1) and Mo(2) directly down the Mo(1)–Mo(2) axis.

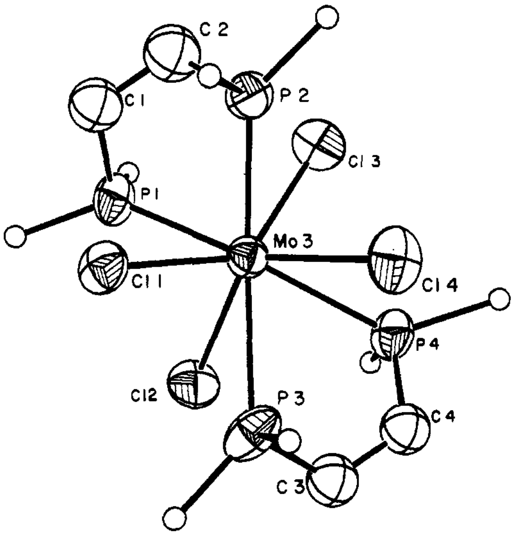

Figure 5. View of the central part of the molecule containing Mo(3) and Mo(4) directly down the Mo(3)–Mo(4) axis.

Discussion

While the structure of the Mo(1)–Mo(2) containing molecule is not in itself particularly remarkable, the comparison of this with its partner Mo(3)–Mo(4) molecule on the same site reveals some features that have not previously been discussed and that are important with respect to work we shall soon be reporting on the chirality and optical activity of molecules of this general class. Turning first to Figure 3, it is clear that for both molecules the ring fusion is akin to that in *cis*-decalin. However, there is also a considerable configurational difference between the two molecules. In the principal molecule, each ring has a nearly ideal chair conformation. This is particularly apparent in Figure 4, where it is obvious that the C(1)–C(2), C(3)–C(4), and Mo(1)–Mo(2) bonds are very nearly, though not exactly, parallel. On the other hand, in the minor molecule both rings have a twist conformation.

The structure with both rings in the twist conformation would be expected to be less stable than the one with two chair conformations. Since there is, in fact, a significant percentage (13%) of the former present, it is evident that while it is less stable, it is not a great deal less stable. The percentage here is near the center of the range previously known (Table I) of 6–23%.

The conformations of the six-membered rings can also be designated as δ or λ, just as in the case of five-membered chelate rings[8] if the center of the Mo–Mo bond is supposed to occupy the position of the single metal atom in the mononuclear chelate complex. It will be seen that all rings in Figure 3 have the λ conformation.

When we compare Figure 4 with Figure 5, one more remarkable and important fact becomes clear. The two molecules partially occupying a given site have *opposite chiralities.* In the case chosen, the principal molecule has a clockwise or right-hand helicity (Δ), while the minor molecule has a counterclockwise or left-hand helicity (Λ). Thus, the two molecules shown in Figures 4 and 5 could be designated as $\lambda\Delta\lambda$ and $\lambda\Lambda\lambda$, respectively. Those related to them by inversion would be $\delta\Lambda\delta$ and $\delta\Delta\delta$. Besides these four, two other possibilities can be envisioned, $\delta\Delta\lambda$ and $\delta\Lambda\lambda$, but we know of no evidence for their existence.

It is interesting that, in the minor molecule shown in Figure 5, the P–Mo–Mo–Cl type torsion angles, though opposite in sign to those of the principal molecule, are very similar in magnitude, viz., 27.5, 27.0, 31.7, and 24.6°, for a mean value of 27.7° as compared to 30.5° for the principal molecule.

Acknowledgment. We thank the National Science Foundation for the support of this work.

Registry No. β-$Mo_2Cl_4(dppe)_2$, 64508-32-3; α-$Mo_2Cl_4(dppe)_2$, 64490-77-3; $Mo_2(O_2CCF_3)_4$, 36608-07-8; Mo, 7439-98-7.

Supplementary Material Available: Tables of anisotropic thermal vibration parameters, bond distances, bond angles, torsion angles, and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

---

(8) See, for example: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 78.

Contribution from the Laboratoire de Chimie des Mêtaux de Transition, ERA 608,
and Laboratoire de Chimie du Solide, LA 302, Universitê Pierre et Marie Curie, 75230 Paris, France

X-ray, ESR, and Optical Absorption Studies of Tetrakis(cyclohexylamine)copper(II) Nitrate: An Example of a Flattened-Tetrahedral Copper(II) Complex

J. GOUTERON,[†] S. JEANNIN,[†] Y. JEANNIN,*[†] J. LIVAGE,[‡] and C. SANCHEZ[‡]

Received November 29, 1983

The preparation, spectroscopic and redox properties, and crystal structure of $[Cu(C_6H_{11}NH_2)_4](NO_3)_2$ are described. Crystals are orthorhombic, space group $P2_12_12_1$, with a = 13.68 (4) Å, b = 16.21 (2) Å, c = 13.55 (1) Å, and Z = 4. The structure has been solved and refined to R = 0.066. The copper environment is a flattened tetrahedron, with the four amine nitrogens ligated to copper. Symmetry elements are not far from those of the D_{2d} symmetry group. Optical and ESR results suggest that the properties of Cu(II) are closer to those of a pseudoplanar geometry, since the ω distortion angle is 40° and since LCAO–MO calculations place the change from T_d to D_{4h} at 65°. Potential measurements in the solid state and in acetonitrile solution show a shift of potential toward more positive values.

Introduction

Blue copper proteins (BCP) exhibit unusual properties with respect to other copper complexes, i.e. a large extinction coefficient for the absorption near 17 000 cm^{-1}, an unusually small copper hyperfine coupling constant, and a markedly positive redox potential. Many authors have investigated the relation between these properties and the coordination geometry of copper(II);[1] among several suggestions, one assumes that a pseudotetrahedral geometry of copper environment allows an easier change from copper(II) to copper(I). Low-molecular-weight copper(II) complexes, such as CuS_4, CuS_2N_2, $CuSN_3$, CuN_4, can be useful models for these investigations.

The title compound is an example of a flattened-pseudotetrahedral environment and can be then proposed as a model for BCP. Several such examples have been already described and discussed; however, this one has the rare feature of having four monodentate ligands. The purpose of the present paper is to contribute to the above discussion, with careful study of the structural and spectral properties of this pseudotetrahedral CuN_4 complex.

Experimental Section

Synthesis. Eleven milliliters of a 5.2 mol L^{-1} ethanolic solution of cyclohexylamine was poured into 25 mL of a 1.3 × 10^{-3} mol L^{-1} ethanolic solution of $Cu(NO_3)_2 \cdot 6H_2O$. Slow evaporation under a nitrogen flow led to slightly air-unstable blue crystals suitable for X-ray analysis. Anal. Calcd for $Cu(C_6H_{11}NH_2)_4(NO_3)_2$: Cu, 10.88; H, 8.9; C, 49.36; N, 14.40; O, 16.45. Found: Cu, 10.57; H, 9.0; C, 49.0; N, 14.97; O, 16.6.

Electronic Spectra were recorded at room temperature on a Beckman 5240 UV–visible spectrophotometer, between 25 000 and 5000 cm^{-1}. For the solid compound, its concentration in KBr pellets was 0.013 mg/mg of KBr. Solutions of the compound in nitromethane and propylene carbonate were 0.55 and 0.64 mg mL^{-1}, respectively.

ESR Spectra were recorded on a Varian CST 104 spectrometer, working at 9.3 GHz (X band) with a 100-kHz field modulation and supplied with a variable-temperature accessory in the range 293–77 K. The components of the g tensor have been measured with respect to a DPPH sample (g = 2.0037). The magnetic field was checked with a NMR proton probe.

Redox Potential Measurements. Cyclic voltammetry was carried out in the solid state and in solution, with a Tacussel potentiostat. Potentials were referred to a saturated calomel electrode. For the solid compound, the electrode was made of carbon powder[2], with 1.45

[†] Laboratoire de Chimie des Mêtaux de Transition.

[‡] Laboratoire de Chimie du Solide.

(1) (a) D. C. Gould and A. Ehrenberg, in "Physiology and Biochemistry of Haemocyanins", F. Ghiretti, Ed., Academic Press, New York, 1968, p 95; (b) R. Malkin and B. Malmström, *Adv. Enzymol. Relat. Areas Mol. Biol.*, **33**, 177 (1970); (c) J. Peisach, P. Aisen, and W. E. Blumberg, "Biochemistry of Copper", Academic Press, New York, 1966; (d) E. I. Solomon, J. W. Hare, D. M. Dooley, J. H. Dawson, P. J. Stephens, and H. B. Gray, *J. Am. Chem. Soc.*, **102**, 168 (1980); (e) C. A. Bates, W. S. Moore, K. J. Standley, and K. W. Steven, *Proc. Phys. Soc., London*, **72**, 73 (1962); (f) H. Yokoi and A. W. Addison, *Inorg. Chem.*, **16** (6), 1341 (1977). (g) A. R. Amudsen, J. Whelan, and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6730 (1977).

0020-1669/84/1323-3387$01.50/0