lecular complexes as with niobium phosphate. The spacings for amines $C_nH_{2n+1}NH_2$ with $n > 5$ plotted vs. n (Figure 2) follow a straight line. The increase $\Delta d_L/\Delta n = 1.3$ Å indicates a nearly perpendicular chain orientation. The absolute spacings are slightly smaller than those for $NbOPO_4{\cdot}3H_2O$; the amine end groups are packed closer to the $\{VO(H_2O)PO_4\}$ layers than to the $\{NbO(H_2O)PO_4\}$ layers. In equilibrium with diluted ethanolic solutions (≤ 0.05 M) the interlayer amines lie flatly on the vanadium phosphate layers.

The different reactivities of vanadium and niobium phosphate may be related to differently distorted $[MO_6]$ octahedra. It should be noted that the distortion of the $[VO_6]$ octahedra in $VOPO_4{\cdot}2H_2O$ is maintained during thermal dehydration (below 220 °C) to α_{II}-$VOPO_4$. This compound differs from α_I-$VOPO_4$ (obtained by heating of the mixtures of the oxides) by the position of the vanadium atoms within the octahedra.[15]

The ease with which vanadium phosphate $VOPO_4{\cdot}2H_2O$ and niobium phosphate $Nb_2(OH)_2(HPO_4)(PO_4)_2{\cdot}4.4H_2O$ intercalate long-chain alkanol molecules distinguishes both phosphates from nearly all other layered host compounds, even from α-$H_2[Zr(PO_4)_2]{\cdot}H_2O$.[16]

Acknowledgment. We thank the "Fonds der chemischen Industrie" for financial support.

Registry No. $NbOPO_4$, 15593-35-8; $Nb_2O_5{\cdot}1.5P_2O_5$, 85116-29-6; $VOPO_4$, 12359-27-2; H_3PO_4, 7664-38-2; NMFA, 123-39-7; DMFA, 68-12-2; Me_2SO, 67-68-5; KSCN, 333-20-0; $NaNO_3$, 7631-99-4; Na_2SO_4, 7757-82-6; KI, 7681-11-0; $C_4H_9NH_2$, 109-73-9; $C_5H_{11}NH_2$, 110-58-7; $C_6H_{13}NH_2$, 111-26-2; $C_7H_{15}NH_2$, 111-68-2; $C_8H_{17}NH_2$, 111-86-4; $C_9H_{19}NH_2$, 112-20-9; $C_{10}H_{21}NH_2$, 2016-57-1; $C_{11}H_{23}NH_2$, 7307-55-3; $C_{12}H_{25}NH_2$, 124-22-1; $C_{13}H_{27}NH_2$, 2869-34-3; $C_{14}H_{29}NH_2$, 2016-42-4; $C_{16}H_{33}NH_2$, 143-27-1; di-*n*-butylamine, 111-92-2; 2-aminobutane, 13952-84-6; (3-methylbutyl)amine, 107-85-7; methylbutylamine, 110-68-9; methyl-*sec*-butylamine, 7713-69-1; methylisobutylamine, 625-43-4; dimethylbutylamine, 927-62-8; 4-amino-2-butanol, 39884-48-5; ephedrine, 299-42-3; cyclohexylamine, 108-91-8; piperazine, 110-85-0; aniline, 62-53-3; pyridine, 110-86-1; trimethylamine *N*-oxide, 1184-78-7; formamide, 75-12-7; ethylene glycol, 107-21-1; glycerol, 56-81-5; butanol, 71-36-3; decanol, 112-30-1; urea, 57-13-6; *N*-methylurea, 598-50-5; sulfuric acid, 7664-93-9; niobium, 7440-03-1.

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Preparation and Structure of the Bridged Form of $Mo_2Cl_4[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$. Dependence of the Mo_2 Quadruple Bond Length on Torsional Angle

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Received July 9, 1982

The reaction of $Mo_2Cl_4(PEt_3)_4$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$, dmpe, in toluene gave a ca. 90% yield of the red-brown bridged (β) form of $Mo_2Cl_4(dmpe)_2$, as well as a small amount of a blue solid presumed to be the chelated (α) form. The bridged form was characterized by X-ray crystallography. It crystallizes in space group $P2_12_12$ with two molecules in a unit cell of the following dimensions: $a = 12.743$ (3) Å, $b = 11.497$ (2) Å, $c = 8.553$ (2) Å, $V = 1253.0$ (8) Å^3. The molecule has a rigorous twofold symmetry axis that is a perpendicular bisector of the Mo–Mo bond, but two other noncrystallographic twofold axes (one collinear with the Mo–Mo bond) are present, giving virtual D_2 molecular symmetry. The most significant features of the structure are a mean twist angle about the Mo–Mo axis of 40.0 (1)° and an Mo–Mo bond length of 2.183 (3) Å. When these data are combined with results for $Mo_2Cl_4(dppm)_2$ and $Mo_2Br_4(arphos)_2$, it is found that a linear relationship exists between cos (2χ) (where χ is the angle of twist away from the perfectly eclipsed conformation) and the Mo–Mo distance. The extrapolated Mo–Mo distance for $\chi = 45°$ is 2.193 ± 0.001 Å.

Introduction

There are relatively few occasions in chemistry where bonding theory reliably predicts a simple relationship between one structure parameter and another and where it is also feasible to obtain experimental confirmation of the relationship, free of other, complicating factors. This report is concerned with one such case.

From the established description of the $\sigma^2\pi^4\delta^2$ quadruple bond[1] it is straightforwardly predictable that the δ^2 contribution to the bond strength is sensitive to the angle of internal rotation, while the $\sigma^2\pi^4$ contribution is invariant with respect to this angle. Moreover, since the magnitude of the δ overlap varies as the cosine of 2χ, χ being the angle of rotation away from an eclipsed conformation, it is reasonable to expect a monotonic (perhaps even linear) relationship between the Mo–Mo distance and cos (2χ).

With the preparation and structural characterization of the title compound, $Mo_2Cl_4(dmpe)_2$, we now have sufficient data to test this prediction experimentally and to establish quantitatively the relationship between the bond length and the internal twist angle under conditions where there is no significant interference from any other factor.

Experimental Section

General Procedures. All manipulations were carried out in an atmosphere of dry, oxygen-free argon. Toluene was purified by distillation from sodium–potassium/benzophenone under argon.

Starting Materials. $Mo_2Cl_4(PEt_3)_4$ was prepared according to a previously reported procedure.[2] Bis(1,2-dimethylphosphino)ethane (dmpe) was purchased from Strem Chemicals and used without further purification.

Preparation. $Mo_2Cl_4(PEt_3)_4$, 2.57 g (3.19 mmol), and 1.00 g (6.66 mmol) of dmpe were dissolved in 150 mL of toluene to give a deep blue solution. Overnight (12 h) reflux resulted in a reddish brown

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[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; Chapters 1 and 8.

[2] Glicksman, H. D.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205.

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Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for β-$Mo_2Cl_4(dmpe)_2$

formula	$Mo_2Cl_4[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$
formula weight	633.97
space group	$P2_12_12$
a, Å	12.743 (3)
b, Å	11.497 (2)
c, Å	8.553 (2)
V, Å^3	1253.0 (8)
Z	2
d_{calcd}, g/cm^3	1.68
cryst size, mm	0.15 × 0.25 × 0.40
μ(Mo Kα), cm^{-1}	16.57
data collection instrument	Enraf-Nonius CAD-4
radiation	Mo Kα (graphite-monochromated) $\lambda_\alpha = 0.710\,73$ Å
scan method	2θ–ω
data collection range	$0° \leqslant 2\theta \leqslant 50°$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	874
no. of parameters refined	104
R^a	0.0699
$R_w{}^b$	0.0903
quality-of-fit indicator^c	2.316
largest shift/esd, final cycle	0.01

[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 $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$.

solution and a small amount (0.11 g) of blue solid. This mixture was filtered and the filtrate cooled at −10 °C for 1 week to afford a nice crop of reddish brown crystals suitable for X-ray crystallography.

The remaining solution was removed from the crystals by cannula and its volume reduced under vacuum to ca. 3 mL in order to obtain more of the crystalline product. The isolated yield of the slightly air-sensitive solid was 92%. An infrared spectrum of the product (Nujol mull) revealed the presence of coordinated dmpe and no PEt_3; the molecular formula was assumed to be $Mo_2Cl_4(dmpe)_2$.

X-ray Data Collection and Reduction. A crystal of approximate dimensions 0.15 × 0.25 × 0.40 mm was coated with epoxy cement and sealed in a glass capillary tube. Routine 2θ–ω data collection was carried out at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with Mo Kα graphite-monochromated X radiation. The scan range in ω was calculated as (1.0 + 0.35 tan θ)° with a 25% extension on either end for background determination.

The data was processed by standard computer programs.[3] Lorentz and polarization corrections were applied, but neither decay nor absorption corrections were necessary. Only those data with $I \geq 3\sigma(I)$ were retained as observed and used in the refinement of the structure. Pertinent crystallographic data are summarized in Table I.

Solution and Refinement of the Structure. Systematic absences revealed the space group as $P2_12_12$. The Mo position was determined from the top three peaks of a three-dimensional Patterson map. The remaining non-hydrogen atoms were located by a sequence of alternating least-squares refinements and difference Fourier maps. Anisotropic refinement converged with discrepancy indices of R = 0.096 and R_w = 0.123.

At this point it was observed that the top two peaks in the difference Fourier were positioned halfway between the two Mo atoms of the dimer in a manner indicative of the type of disorder previously observed in similar structures (e.g., $Mo_2Br_4(arphos)_2$,[4] $Re_2Cl_4(dppe)_2$,[5] and the $Mo_2Cl_8{}^{4-}$ ion[6]). The intensities of the two peaks suggested occupancies of about 10% each, and since the peaks were on a two-fold axis, they were isotropically refined as Mo atoms at a fixed multiplicity of 0.05. This resulted in a significant lowering of the residuals to R = 0.074 and R_w = 0.096.

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo	−0.0692 (1)	−0.0560 (2)	−0.2368 (2)	2.42 (3)
Cl(1)	−0.0773 (5)	−0.1670 (6)	−0.4752 (8)	5.0 (1)
Cl(2)	−0.1710 (5)	−0.0341 (6)	−0.0028 (8)	5.1 (1)
P(1)	0.0126 (5)	−0.2344 (5)	−0.1180 (8)	4.1 (1)
P(2)	−0.1979 (5)	0.0855 (5)	−0.3594 (8)	3.8 (1)
C(11)	0.125 (2)	−0.297 (2)	−0.226 (3)	4.6 (6)
C(12)	0.055 (3)	−0.232 (3)	0.087 (3)	9 (1)
C(13)	−0.087 (2)	−0.353 (2)	−0.125 (3)	5.7 (7)
C(21)	−0.215 (2)	0.227 (2)	−0.246 (4)	5.1 (6)
C(22)	−0.187 (2)	0.126 (3)	−0.566 (3)	6.7 (8)
C(23)	−0.328 (2)	0.018 (3)	−0.344 (3)	7.7 (9)
Mo(3)	0.000	0.000	−0.116 (3)	1.5 (5)[b]
Mo(4)	0.000	0.000	−0.366 (4)	1.8 (5)[b]

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

Table III. Interatomic Distances and Angles for β-$Mo_2Cl_4(dmpe)_2$

	Distances, Å		
Mo–Mo′	2.183 (3)	P(2)–C(21)	1.90 (2)
–Cl(1)	2.407 (5)	–C(22)	1.84 (2)
–Cl(2)	2.398 (4)	–C(23)	1.84 (2)
–P(1)	2.514 (5)	C(11)–C(21)′	1.41 (2)
–P(2)	2.538 (5)	Mo(3)–Mo(4)	2.13 (3)
–Mo(3)	1.50 (2)	–Cl(2)	2.42 (1)
–Mo(4)	1.55 (2)	–P(1)	2.700 (4)
P(1)–C(11)	1.85 (2)	Mo(4)–Cl(1)	2.35 (1)
–C(12)	1.83 (2)	–P(2)	2.707 (4)
–C(13)	1.86 (2)		
	Angles, deg		
Mo′–Mo–Cl(1)	110.3 (1)	P(1)–C(11)–C(21)′	117 (1)
–Cl(2)	112.0 (1)	P(2)–C(21)–C(11)′	117 (1)
–P(1)	98.5 (1)	Mo′–Mo(3)–Mo	93 (1)
–P(2)	98.2 (1)	Mo′–Mo(4)–Mo	89 (1)
–Mo(3)	43.4 (6)	Mo(3)–Mo–Mo(4)	88.7 (7)
–Mo(4)	45.3 (6)	Mo(3)–Mo(4)–Cl(1)	113.4 (5)
Cl(1)–Mo–Cl(2)	137.6 (2)	–P(2)	88.8 (5)
–P(1)	85.9 (2)	Mo(4)–Mo(3)–Cl(2)	113.7 (5)
–P(2)	87.8 (2)	–P(1)	89.7 (5)
Cl(2)–Mo–P(1)	88.4 (2)	Cl(2)–Mo(3)–Cl(2)′	133 (1)
–P(2)	85.9 (2)	–P(1)	83.9 (2)
P(1)–Mo–P(2)	163.3 (2)	–P(1)′	96.4 (3)
Mo–P(1)–C(11)	115.9 (7)	P(1)–Mo(3)–P(1)′	179 (1)
–C(12)	119.7 (8)	Cl(1)–Mo(4)–Cl(1)′	133 (1)
–C(13)	107.6 (6)	–P(2)	85.1 (2)
C(11)–P(1)–C(12)	105 (1)	–P(2)′	95.8 (3)
–C(13)	103.0 (8)	P(2)–Mo(4)–P(2)′	178 (1)
C(12)–P(1)–C(13)	104 (1)	Mo(3)–P(1)–C(11)	116.0 (7)
Mo–P(2)–C(21)	114.1 (6)	Mo(3)–P(1)–C(12)	89.8 (9)
–C(22)	121.0 (7)	–C(13)	133.7 (6)
–C(23)	106.4 (8)	Mo(4)–P(2)–C(21)	115.1 (6)
C(21)–P(2)–C(22)	107 (1)	–C(22)	90.3 (8)
–C(23)	103 (1)	–C(23)	133.5 (8)
C(22)–P(2)–C(23)	104.1 (9)		

Several series of refinements were then performed by first allowing the multiplicities of the disordered Mo atoms to vary independently, secondly fixing these multiplicities at the average of their refined values, and thirdly setting the multiplicity of the principal Mo atom at 1 minus twice the average multiplicity of the disordered atoms. The best residuals (R = 0.0702, R_w = 0.0909) and quality-of-fit indicator (2.332) were obtained with occupancies of 8.0% for the disordered metal atoms and 92.0% for the principal metal atom. No attempt was made to locate disordered positions for lighter atoms.

Finally, least-squares refinement was carried out for the other enantiomorph. At convergence the residuals had values of R = 0.0699 and R_w = 0.0903, and the quality-of-fit indicator was 2.316. Since no significant shifting of any positional or thermal parameters occurred, this was assumed to be the correct enantiomorph. A final difference Fourier map contained three peaks between 1.08 and 1.91 e/Å^3, but each was within 1.5 Å of the principal Mo atom. All other peaks had intensities below 0.84 e/Å^3.

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(3) Computing was done with the Enraf-Nonius Structure Determination Package on a PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX.

(4) Cotton, F. A.; Fanwick, P. E.; Fitch, J. W.; Glicksman, H. D.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 1752.

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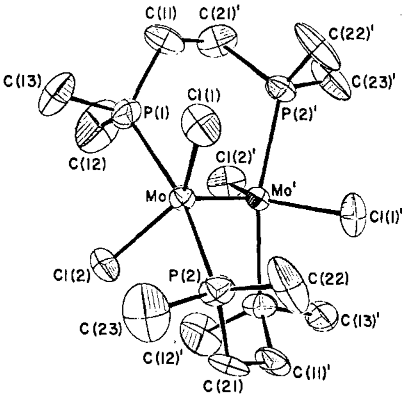

Figure 1. Complete molecular geometry and atom-labeling scheme for β-$Mo_2Cl_4(dmpe)_2$.

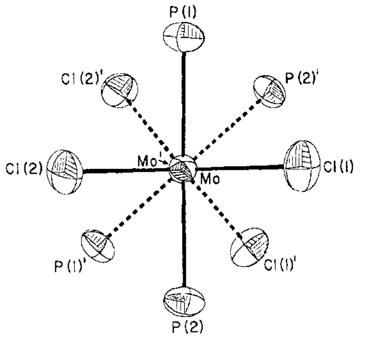

Figure 2. Central portion of the β-$Mo_2Cl_4(dmpe)_2$ molecule viewed down the Mo–Mo axis.

The final atomic positional and isotropic-equivalent thermal parameters are given in Table II. Tables of observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material.

Discussion

The Structure. Figure 1 illustrates the complete molecular geometry and gives the atom-labeling scheme for the red-brown $Mo_2Cl_4(dmpe)_2$. Table III gives the important bond lengths and bond angles. The molecule resides on a twofold axis that perpendicularly bisects the Mo–Mo bond, and thus the crystallographic symmetry of the molecule is C_2. However, the molecule possesses idealized D_2 symmetry. The crystallographic C_2 axis bisects not only the Mo–Mo axis but also the two lines that can be drawn between the pairs of nongeminal chlorine atoms. A second C_2 axis, which is also a perpendicular bisector of the Mo–Mo bond, bisects the two C–C bonds of the bridging dmpe ligands and is approximately vertical in Figure 1. The third C_2 axis is coincident with the Mo–Mo bond and is approximately horizontal in Figure 1. The idealized D_2 symmetry may be visualized more easily by the view down the Mo–Mo axis given in Figure 2.

Figure 2 also clearly illustrates the most significant structural aspect of β-$Mo_2Cl_4(dmpe)_2$, namely that it exists in an almost completely staggered conformation as in β-$W_2Cl_4(dppe)_2$[7] and $Re_2Cl_4(dppe)_2$.[5] Table IV lists the smallest torsion angles in the molybdenum dimer and shows that their average value is 40.0 (1)°. The mean torsion angles in β-$W_2Cl_4(dppe)_2$, $Re_2Cl_4(dppe)_2$, and $Mo_2Br_2(arphos)_2$ are 45, 39, and 30°, respectively.

The small amount of blue solid obtained early in the preparation of the title compound is apparently the α or chelated isomer of $Mo_2Cl_4(dmpe)_2$, a compound first reported[8] by San Filippo and co-workers. The formation of both chelated and bridged isomers for molecules of this sort is apparently common. It has been observed previously for $Mo_2Cl_4(dppe)_2$[9] and for $W_2Cl_4(dppe)_2$.[7,10] In the case of San Filippo's previous work, a different preparative reaction, in which $[Mo_2Cl_8]^{4-}$ was treated with dmpe, was used. This led exclusively to a blue product which was formulated, on the basis of indirect evidence, as the chelated (α) structure. The present results add considerable support to that assignment since the β isomer is now shown to be red-brown.

Table IV. Torsion Angles in β-$Mo_2Cl_4(dmpe)_2$

plane 1	plane 2	angle, deg
Mo'-Mo-P(1)	Mo-Mo'-Cl(2)'	40.1
Mo'-Mo-Cl(1)	Mo-Mo'-P(2)'	39.9
		av 40.0 (1)
Mo(4)-Mo(3)-P(1)	Mo(3)-Mo(4)-Cl(1)	30.6
Mo(4)-Mo(3)-Cl(2)	Mo(3)-Mo(4)-P(2)	31.5
		av 31.0 (4)

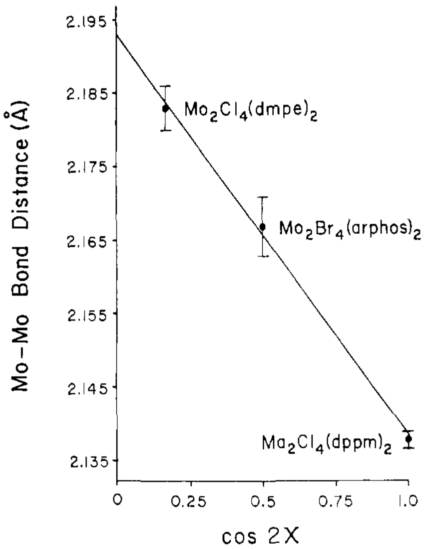

Figure 3. Plot of Mo–Mo bond length vs. the cosine of twice the torsion angle (χ) for three similar dimolybdenum molecules. Esd's for the bond lengths are represented by vertical bars.

Correlation of Mo$\overset{4}{-}$Mo Bond Lengths with Twist Angles. The Mo–Mo distance we have found in β-$Mo_2Cl_4(dmpe)_2$, 2.183 (3) Å, is the longest one known in a compound of the $Mo_2X_4(PR_3)_4$ or $Mo_2X_4(P–P)_2$ type, where X is Cl or Br. At the same time the twist angle, χ, is the greatest, at 40.0 (1)°. The large twist angle was not planned or even anticipated. It results from the complex interplay of many nonbonded forces that determine the preferred conformations of the two six-membered rings that are fused along the Mo–Mo bond. These conformational preferences, working against the inherent tendency of the bond to have a twist angle of zero, lead to the observed equilibrium structure. The fact that the twist angle was not predicted is irrelevant to our present purpose, however. Given that certain twist angles exist, the question of interest is whether there is a systematic relationship between them and the corresponding bond lengths.

Together with the 40.0° twist angle in β-$Mo_2Cl_4(dmpe)_2$ we have previous angles of 0° in $Mo_2Cl_4(dppm)_2$[11] and 30° in $Mo_2Br_4(arphos)_2$.[4] In Figure 3 the cos (2χ) values corresponding to these angles are plotted against the associated bond lengths. A straight line with a correlation coefficient of

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–0.9990 (where –1 would characterize a perfect correlation) can be drawn. Clearly, the bond length is a linear function of cos (2χ), which means[4] that the bond lengthens in linear proportion to decreasing δ-bond strength. The line can be extrapolated to $\chi = 45°$ to predict a value of 2.193 ± 0.001 Å. The overall change, then, from a full δ bond to no δ bond is 0.055 (2) Å. This may well be the most unambiguous quantitative, experimental evaluation of how bond length depends on δ-bond order alone that it is possible to get. It has been obtained under circumstances where essentially no other factor such as ligand type, oxidation states, or atomic number of the metal atoms has been changed.

The Disorder. As is very common in compounds of this and related types, there is some disorder of the sort that leads to the observation of a second Mo–Mo unit perpendicular to the main one. Since the positional parameters for the secondary metal atoms (which are on the crystallographic 2 axis and thus crystallographically independent of each other) are not highly accurate and no ligand atoms belonging to this second orientation could be distinguished and refined, nothing can be said about the dimensions of this secondary molecule. The secondary Mo–Mo distance appears to be smaller, 2.13 (3) Å, but statistically the difference from the distance in the primary molecule is not significant.

Acknowledgment. We are grateful to the National Science Foundation for support and to Dr. Brian Kolthammer for his interest and advice.

Registry No. β-$Mo_2Cl_4(dmpe)_2$, 85115-86-2; $Mo_2Cl_4(PEt_3)_4$, 59780-36-8; Mo, 7439-98-7.

Supplementary Material Available: Complete tables of anisotropic thermal parameters, torsional angles for the central portion of the molecule, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 24.[1,2] Crystal Structures of the 60-Electron Cluster $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ and the 59-Electron Radical Cluster $(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$

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The heteronuclear hydrido–metal-cluster complexes $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ (**1**) and $(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (**2**), previously synthesized by Shore and co-workers,[3] have been characterized via single-crystal X-ray diffraction studies. Crystal data are as follows: **1**, space group *Pcam* (No. 57), a = 14.554 (3) Å, b = 17.845 (3) Å, c = 15.008 (3) Å, V = 3898 (1) Å^3, Z = 8, R_F = 5.3%, R_{wF} = 4.9% for all 2683 independent data with 2θ = 3.5–45.0° (Mo Kα); **2**, space group *Pcam* (No. 57), a = 14.632 (3) Å, b = 17.872 (5) Å, c = 14.991 (3) Å, V = 3920 (2) Å^3, Z = 8, R_F = 5.2%, R_{wF} = 5.0% for all 1937 data with 2θ = 4.0–40.0° (Mo Kα). **1** and **2** are isomorphous; each contains two independent sites of C_s symmetry for the constituent molecules. The molecular configurations in the two sites are identical, but there is a conformational charge in the $(\eta^5\text{-}C_5H_5)$ ligand that is rotated by π radians from one site to the other. Each molecule contains an apical $(\eta^5\text{-}C_5H_5)M$ (M = Ni, Co) fragment of approximate C_{5v} symmetry bonded in an apparently symmetrical fashion to a basal $(\mu\text{-H})_3Os_3(CO)_9$ moiety of approximate C_{3v} symmetry. Osmium–nickel bond lengths in **1** range from 2.562 (2) through 2.578 (3) Å (average 2.567 Å), while osmium–cobalt bond lengths in **2** range from 2.578 (3) through 2.597 (4) Å (average 2.585 Å). The hydrido-bridged osmium–osmium distances are 2.859 (1)–2.874 (1) Å (average 2.871 Å) in **1** and 2.864 (1)–2.891 (1) Å (average 2.879 Å) in **2**.

Introduction

We have become interested in the structural chemistry of tetrahedral hydrido cluster species based on the Os_3M core (M = first-row transition metal) and have recently published reports on the structures of $(\mu\text{-H})_2Os_3Fe(CO)_{13}$[2] and $(\mu\text{-H})_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$.[4] Entry into this chemical area has been greatly facilitated by the discovery by Shore and co-workers that $(\mu\text{-H})_2Os_3(CO)_{10}$ provides a good starting material for the triosmium fragment.[5] More recently, it has been found that hydride-rich products can be obtained in excellent yield by including molecular dihydrogen in the synthesis.[3]

Thus, $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ can be synthesized in 93% yield as shown in eq 1. In similar fashion, the reaction of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with $(\mu\text{-H})_2Os_3(CO)_{10}$ under H_2 yields a mixture of $(\mu\text{-H})_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$ (4%), *paramagnetic* $(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (33%), and $(\mu\text{-H})_4Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (32%).

$$[(\eta^5\text{-}C_5H_5)Ni(CO)]_2 + 2(\mu\text{-H})_2Os_3(CO)_{10} + H_2 \xrightarrow[90\,°C,\ 10\,h]{\text{toluene}} 2(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5) + 4CO \quad (1)$$

We now report the results of single-crystal X-ray diffraction studies on two new trihydrido clusters—the diamagnetic 60-electron species $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ and the paramagnetic 59-electron species $(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$. A preliminary report of this work has appeared previously.[3]

Experimental Section

Samples of the two complexes were kindly provided by Professor S. G. Shore of The Ohio State University. They had previously been characterized fully via infrared and exact mass spectroscopy, ^1H NMR (Os_3Ni complex), and ESR (Os_3Co complex)—cf. ref 3.

$(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ (1). An irregular opaque dark crystal of average diameter 0.2 mm was mounted and aligned on our Syntex P2$_1$ automated four-circle diffractometer; diffraction data were collected as described previously,[6] details being given in Table I. All

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(1) Part 23 ($(\mu\text{-H})(\mu\text{-}O_2CH)Os_3(CO)_{10}$): Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.*, **1982**, *21*, 3295–3303.

(2) Part 22 ($(\mu\text{-H})_2Os_3Fe(CO)_{13}$): Churchill, M. R.; Bueno, C.; Hsu, W. L.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1958–1963.

(3) Shore, S. G.; Hsu, W. L.; Weisenberger, C. R.; Caste, M. L.; Churchill, M. R.; Bueno, C. *Organometallics* **1982**, *1*, 1405–1407.

(4) Part 20 ($(\mu\text{-H})_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$): Churchill, M. R.; Bueno, C.; Kennedy, S.; Bricker, J. C.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 627–633.

(5) Plotkin, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 6156–6157.

(6) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

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