in IV shows an unusually long S–S bond at 2.154 (7) Å. A similarly long bond (2.136 (6) Å) was found previously for the same ligand in the $[(\eta^2\text{-}S_2)MoS(MoS_4)]^{2-}$ anion.[1] In the structures of IV, VI, $[(\eta^2\text{-}S_2)MoS(MoS_4)]^{2-}$, and $[(S_4)MoS(MoS_4)]^{2-}$, the two terminal Mo–S bond lengths within the "MoS_4" ligands are significantly different. In all cases, the bonds syn to the "$Mo^{IV}{=}X_t$" unit are shorter than those in the anti orientation.

The chemical reactivity of the various coordinated ligands in III–VI and of the same ligands in the analogous thio complexes currently are under investigation in systematic reactivity studies.

Acknowledgment. The support of this work by a grant (CH-79-0389) from the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Listings of positional and thermal parameters for the $[Ph_4P]^+$ salts of $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$ (III), $[(\eta^2\text{-}S_2)MoO(MoS_4)]^{2-}$ (IV), $[(S_4)MoX(\mu\text{-}S)_2MoX(\eta^2\text{-}S_2)]^{2-}$ (X = S, O) (V), and $[(S_4)MoO(MoS_4)]^{2-}$ (VI) (Tables S1–S4) (20 pages); listings of structure factors (Tables S5–S8) (56 pages). Ordering information is given on any current masthead page.

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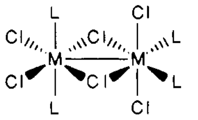
Received August 3, 1988

An Equilibrium Involving Edge- and Face-Shared Bioctahedral d^3–d^3 Ditungsten Complexes: $W_2Cl_6(PEt_3)_4$ and $W_2Cl_6(PEt_3)_3$

Sir:

There is now a diverse chemistry surrounding W_2^{6+}-containing compounds for which the green crystalline salt $NaW_2Cl_7(THF)_5$[1] provides an excellent starting material. (1) Metathetic reactions employing LiO-*t*-Bu or $LiNMe_2$ give access to $X_3W{\equiv}WX_3$ compounds.[2] (2) Addition of neutral donor ligands such as pyridine[3] and PMe_3[4,5] give edge-shared bioctahedral complexes of type I.



I

The latter finding prompted us to question why the $W_2Cl_7(THF)_2^-$ anion[6] did not exist in THF (tetrahydrofuran) solution as $W_2Cl_6(THF)_4$.[7] Could there be an equilibrium involving edge-shared bioctahedra and face-shared bioctahedra and, if so, what factors influence the equilibrium? We describe here our discovery of an equilibrium of the above type, eq 1, and our structural characterization of both W_2^{6+}-containing compounds.

$$W_2Cl_6(PEt_3)_4 \rightleftarrows W_2Cl_6(PEt_3)_3 + PEt_3 \qquad (1)$$

Addition of PEt_3 (>4 equiv) to a solution of $NaW_2Cl_7(THF)_5$ in THF leads to $W_2Cl_6(PEt_3)_4$, which can be crystallized from toluene. The molecular structure determined from a single-crystal X-ray diffraction study[8] showed this to be a member of a now fairly extensive family of edge-shared bioctahedra[9] of structural type I with W–W = 2.7397 (7) Å.[10] The terminal W–L axial bond distances are slightly shorter than the terminal W–L equatorial distances; cf. W–Cl = 2.41 (1) (axial) vs 2.45 (1) Å, and W–P = 2.56 (1) (axial) vs 2.61 (1) Å.

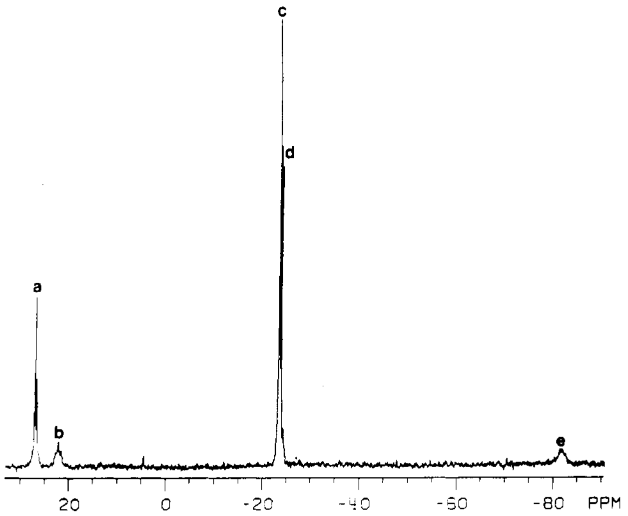
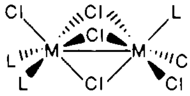


Figure 1. ^{31}P NMR spectrum of a single crystal of $W_2Cl_6(PEt_3)_4$ dissolved in toluene-d_8 at −80 °C and 146.2 MHz showing the presence of free PEt_3, δ −22.1 s (c), and signals due to the equilibrium involving I, δ 23.2 t (b), and −81.4 t (e), J_{P-P} = 87 Hz, and II, δ 27.8 t (a), and −22.3 d (d), J_{P-P} = 44 Hz. Tungsten satellites are resolved for II but not for I. Chemical shifts are in ppm relative to H_3PO_4 (85% aqueous) external reference.

The ^{31}P NMR spectrum of a crystalline sample of $W_2Cl_6(PEt_3)_4$ dissolved in toluene-d_8 is temperature dependent, and only at low temperatures are signals present that can be correlated with a compound of structural type I, namely two triplets of equal intensity. The major species present in solution gives rise to a doublet and a triplet in the intensity ratio 2:1, respectively. This is consistent with the presence of a confacial bioctahedral isomer having a mirror plane of symmetry as shown in II. In addition there



II

is a singlet assignable to free PEt_3 (see Figure 1). The equilibrium

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(1) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *26*, 3182.

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(6) Bergs, D. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Stahl, K. A. *Inorg. Chem.* **1988**, *27*, 2950.

(7) I.e., as originally suggested in ref 4.

(8) Crystal data for $W_2Cl_6(PEt_3)_4$ at −144 °C: a = 11.220 (2) Å, b = 18.462 (3) Å, c = 18.519 (3) Å, β = 98.32 (1)°, Z = 4, d_{calcd} = 1.843 g cm^{-3}, and space group $P2_1/n$. Of 6359 reflections collected (6° ≤ 2θ ≤ 45°), 4975 were unique and the 4288 reflections having $F > 3\sigma(F)$ were used in the refinement. Hydrogen atoms were placed in idealized positions during the final refinement. All non-hydrogen atoms were refined anisotropically. Final residuals are $R(F)$ = 0.0397 and $R_w(F)$ = 0.0397. Crystal data for $W_2Cl_6(PEt_3)_3{\cdot}CH_2Cl_2$ at −144 °C: a = 14.097 (2) Å, b = 12.992 (2) Å, c = 18.798 (3) Å, β = 97.96 (1)°, Z = 4, d_{calcd} = 1.987 g cm^{-3}, and space group $P2_1/n$. Of 6111 reflections collected, 4324 were unique and the 4125 reflections that had $F > 3\sigma(F)$ were used in the full least-squares refinement. Hydrogen atoms were introduced in fixed, calculated positions; all other atoms were refined anisotropically, leading to $R(F)$ = 0.0437 and $R_w(F)$ = 0.0445. General operating procedures and listings of programs have been given: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(9) For a review of edge-shared bioctahedra for d^n–d^n complexes where n = 0–5, see: Cotton, F. A. *Polyhedron* **1987**, *6*, 677. Evidence for an equilibrium involving mononuclear octahedral Mo(III) and a confacial bioctahedral dimer

$$2MoCl_3(THF)_3 \rightleftarrows Mo_2Cl_6(THF)_3 + 3THF$$

has been reported previously: Boyd, I. W.; Wedd, A. G. *Aust. J. Chem.* **1976**, *29*, 1829. We thank Professor R. A. Walton for bringing this to our attention.

(10) The distance in the closely related d^2–d^2 complex $Ta_2Cl_6(PMe_3)_4$ is 2.721 (1) Å: Sattelberger, A. P.; Wilson, B. R. Jr.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 2392.

in eq 1 is not rapid on the NMR time scale.

The existence of the equilibrium in eq 1 allows for the preparation of $W_2Cl_6(PEt_3)_3$ from $W_2Cl_6(PEt_3)_4$ by the application of a dynamic vacuum to the equilibrium mixture.[11] Recrystallization of the nonvolatile residue from methylene chloride layered with diethyl ether gave a crystalline sample: $W_2Cl_6(PEt_3)_3 \cdot CH_2Cl_2$. The molecule of solvent CH_2Cl_2 was well behaved in the crystal, and the X-ray structural determination[8] confirmed the confacial bioctahedral isomer of type II for the $W_2Cl_6(PEt_3)_3$ molecule: W–W = 2.4705 (7) Å; W–P = 2.55 (1) Å (average). The W–Cl bonds trans to the W–P bonds are longer than those trans to W–Cl bonds, and most notably and in contrast to $W_2Cl_6(PEt_3)_4$, the terminal W–Cl bond distances, 2.38 (1) Å (averaged), are shorter by 0.1 Å than the W–Cl bridging distances.

The discovery of the equilibrium involving edged-shared and face-shared bioctahedra leads us to the question posed in our introduction: What factors influence such an equilibrium? To our knowledge this is the first time the existence of this equilibrium has been seen for any d^n–d^n compound where $n = 1$–5.[9] Aside from the obvious considerations of metal–ligand enthalpies and entropy, the d^3–d^3 case offers the clearest preference for the confacial bioctahedral geometry in terms of the difference in metal–metal bonding.[12] In the edge-shared bioctahedra the M–M bonding may be formulated as $\sigma^2\pi^2\delta^{*2}$ whereas in the confacial bioctahedral there can formally be a M–M triple bond of configuration $\sigma^2\pi^4$ as a result of the t_{2g}^3–t_{2g}^3 d-orbital interactions. The M–M distance in $W_2Cl_6(PEt_3)_4$, 2.74 (1) Å, compared with 2.47 (1) Å in $W_2Cl_6(PEt_3)_3$ gives a clear indication of the stronger M–M bonding in the latter compound. However, in comparing the M–M distances in the d^3–d^3 confacial bioctahedra in $W_2Cl_9^{3-}$,[13] $W_2Cl_7(THF)_2^-$,[1,6] and $W_2Cl_6(PEt_3)_3$ we see an increase from 2.40 (1) to 2.47 (1) Å upon phosphine substitution. This suggests that W–PEt$_3$ bond formation results in a weakening of the M–M bonding in the d^3–d^3 face-shared bioctahedra thus enthalpically favoring the edge-shared bioctahedra. Further studies are clearly warranted, however, before any detailed knowledge of such matters can be reliably claimed.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: A table of fractional coordinates and complete listings of bond distances and angles together with VERSORT drawings (10 pages). Ordering information is given on any current masthead page.

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(11) Satisfactory analytical data have been obtained for $W_2Cl_6(PEt_3)_4$ and $W_2Cl_6(PEt_3)_3$.

(12) For a discussion of the bonding in compounds of structural type I see ref 9 and see: Shaik, R. H.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

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Received September 29, 1988

Variable-Temperature T_1 Studies on $ReH_5(PR_3)_3$ (PR_3 = $PMePh_2$, PPh_3), $ReH_7(PPh_3)_2$, and $Re_2H_8(PPh_3)_4$: Classical or Nonclassical Hydrides?

Sir:

The NMR T_1 method[1] has recently been shown to be of great use in evaluating whether complexes containing two or more hydrogen atoms among their ligands also contain one or more molecular hydrogen (H_2) ligands.[2,3a,b] Several polyhydride complexes have had their structures reassigned in keeping with the low NMR T_1 measurements, for example, $Re(H_2)H_5(PPh_3)_2$,[3] $Re(H_2)H_5(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$),[3a] $Fe(H_2)H_2L_3$,[3a] $Ru(H_2)H_2L_3$,[3a] $[Os(H_2)H_3(PPh_3)_3]^+$,[3a] and $[Ru(H_2)H(dppe)_2]^+$.[4]

However, we were surprised at the assignment of $ReH_5(PPh_3)_3$ (**1**) as containing only classical hydride ligands.[3a] The complexes $Re(H_2)Cl(PMePh_2)_4$[5] and $ReH_7(PPh_3)_2$[2,3a] are both believed to contain molecular hydrogen ligands in view of their very short NMR T_1 relaxation times (25 ms in CD_2Cl_2 (−50 °C, 200 MHz) and 70 ms in toluene-d_8 (−73 °C, 250 MHz), respectively) in sharp contrast to the value of 540 ms reported for **1** at −70 °C in toluene-d_8.[3a] The NMR T_1 values for the metal-bonded hydrogen atoms in the complex $ReH_3(PMePh_2)_4$ are also short (T_1(min) = 142 ms at −49 °C in CD_2Cl_2 at 400 MHz),[6] and this complex is presumably $Re(H_2)H(PMePh_2)_4$. Furthermore, the complexes $ReH_5(PEtPh_2)_3$ and $ReH_5(AsEtPh_2)_3$ have ^1H NMR spectra (at −135 °C) consisting of three separate hydride resonances and a

Table I. T_1 Measurements on $ReH_6(PPh_3)_3$, $ReH_5(PMePh_2)_3$, and $ReH_7(PPh_3)_2$ at 200 and 400 MHz and Various Temperatures[a]

T, °C	T_1, ms
	$ReH_5(PPh_3)_3$ (**1**)[b–d] in $(CD_3)_2CO$
	At 200 MHz
+19	175 (−5.23, q, J = 18 Hz)
−20	99 (−5.29, q, J = 18 Hz)
−50	71 (−5.37, br)
−80	46 (−5.2)
−90	59 (−5.1)
	At 400 MHz
+24	209 (−5.2, q, J = 18 Hz)
−20	141 (−5.3, q, J = 18 Hz)
−60	123 (−5.3, br)
−80	215 (−5.0), 18 (−5.3)[e]
−95	186 (−4.8), 7 (−5.3)[e]
	$ReH_5(PMePh_2)_3$ (**2**) in CD_2Cl_2
	At 400 MHz
+22	293 (−6.1, q, J = 18 Hz)
0	222 (−6.1, br)
−20	197 (−6.1)
−40	96 (−5.8), 145 (−6.5)
−60	140 (−5.7), 132 (−6.6)
−80	169 (−5.5), 176 (−5.9), 144 (−6.6)
−95	210 (−5.3), 199 (−6.1), 181 (−6.6)
−105	255 (−5.3), 228 (−6.1), 210 (−6.6)
−110	429 (−5.4), 340 (−6.2), 333 (−6.6)
	$ReH_7(PPh_3)_2$ (**3**) in CD_2Cl_2
	At 200 MHz
+19	672 (−4.94, t, J = 19 Hz)
−80	74 (−5.06, t, J = 18 Hz)[d]
	At 400 MHz
+24	738 (4.93, t, J = 19 Hz)
−80	113 (−5.06, t, J = 18 Hz)[f]
−90	103 (−5.07, t, J = 18 Hz)

[a] Following each T_1 is the chemical shift (δ) at which it was measured in parentheses. [b] This complex was prepared by three different routes, two of which are in ref 8, and the third was adapted from the preparation of $ReH_5(PMe_2Ph)_3$ as reported in: *Inorg. Synth.* **1977**, *17*, 64. All routes results in yellow $ReH_5(PPh_3)_3$ exhibiting the same T_1 values for the metal-bonded hydrogen atoms within experimental error. [c] In ref 3 a value of 540 ms measured in toluene-d_8 at −70 °C is reported, but the frequency of measurement is not stated. [d] In ref 3 a value of 79 ms at −70 °C and 250 MHz is reported. [e] T_1 measurement of dubious accuracy due to the low intensity of the signal. [f] In ref 3 a value of 110 ms at −70 °C and 500 MHz is reported.

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