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.

(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.
(13) Watson, W. H.; Waser, J. *Acta Crystallogr.* **1958**, *11*, 689.

Department of Chemistry and Molecular Structure Center
Indiana University
Bloomington, Indiana 47405

Stephanie T. Chacon
Malcolm H. Chisholm*
William E. Streib
William Van Der Sluys

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.

(1) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.
(2) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.
(3) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Fontaine, X. L. R.; Fowles, E. H.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1988**, 482. (c) Electrochemical data: Costello, M.T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563.
(4) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780.
(5) Cotton, F. A.; Luck, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1277.
(6) Cotton, F. A.; Luck, R. L. Submitted for publication in *Inorg. Chem.*

0020-1669/89/1328-0006$01.50/0

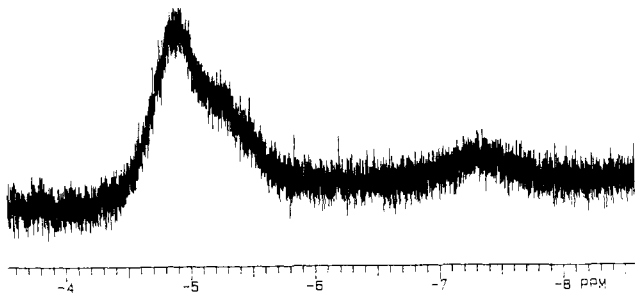


Figure 1. ^1H NMR spectrum in the hydride region of $ReH_5(PPh_3)_3$ (**1**) at −100 °C and 400 MHz in a 20:80 CD_2Cl_2/CF_2Cl_2 mixture.

signal assigned as containing the two remaining hydride ligands that were magnetically equivalent down to −155 °C.[7] The X-ray structural determination of the $ReH_5(PPh_3)_3$ complex showed that the complex may be viewed as having an irregular geometry apparently with two hydride ligands above and three below the approximate plane described by the rhenium atom and the three phosphorus atoms.[7]

Thus, we decided to obtain variable-temperature T_1 measurements on the $ReH_5(PR_3)_3$ (PR_3 = PPh_3 (**1**), $PMePh_2$ (**2**)) and $ReH_7(PPh_3)_2$ (**3**) complexes in order to compare them to the NMR and X-ray data that were obtained previously.[3a,7] The T_1 data for these complexes are listed in Table I, and in the case of **1** and **3**, the data at two different magnetic fields are also included. The ^1H NMR spectrum of **1** at room temperature is a quartet as reported previously.[8] Figure 1 displays the ^1H NMR spectrum, in the hydride region only, for **1** in a 20:80 CD_2Cl_2/CF_2Cl_2 mixture at −100 °C. The spectrum consists of a band at δ −5.0 with a shoulder on the right at δ −5.3 and a bump at δ −7.4. Unfortunately attempts to obtain the spectrum at lower temperatures were unsuccessful as the solvent mixture separated with the yellow solution of **1** in CD_2Cl_2 floating on top of clear CF_2Cl_2. However, the same pattern was observed with acetone-d_6 as the solvent at −90 °C at 200 MHz and −95 °C at 400 MHz (see Table I). The NMR T_1 values for **1** attain a minimum of 123 ms around −60 °C at 400 MHz and 46 ms at −80 °C and 200 MHz. The shoulder at δ −5.3 in Figure 1 was not resolved in the 200-MHz spectrum at −80 °C, and thus the T_1 value reported is a composite of the two. It is generally accepted that T_1 values in the range 4–100 ms are typical of nonclassical species[1] and $ReH_5(PPh_3)_3$ should therefore be formulated as a nonclassical complex, presumably $Re(H_2)H_3(PPh_3)_3$. Finally, at temperatures of ca. −95 °C, the hydride resonances appear to be separating out into a pattern attributable to three equivalent hydrogen atoms that resonate at δ −5.0 and two hydrogen atoms that are resolved, with one at δ −5.3 and the other at δ −7.4.

Several spectra at different temperatures are shown for **2** in Figure 2. Again at room temperature the spectrum for the hydrogen atoms consists of a quartet. However at −20 °C this changes into a broad bump that is resolved at −60 °C into two resonances in an intensity ratio of 2:3 at δ −5.76 and δ −6.6, respectively. At −80 °C the resonance at δ −5.76 collapses and is then resolved at −95 °C into two peaks, a broad bump at δ −5.63 and a triplet at δ −6.1, and the broad resonance at δ −6.6. The last spectrum in Figure 2, obtained at −110 °C, shows that the two resonances at δ −5.3 and −6.1 are now a complex multiplet and a triplet, respectively, and that the resonance at δ −6.6 due to the three magnetically equivalent hydrogen atoms is now collapsing. It was not possible to obtain the spectrum at lower temperatures with this solvent (CD_2Cl_2). The T_1 data for **2** are given in Table I, and the position where the T_1 was measured is given in parentheses. The room-temperature measurement is 100 ms greater than the value obtained for **1**. This can be attributed to the steric and/or electronic differences between the PPh_3 ligands in **1** and the $PMePh_2$ ligands in **2**. Others have also found steric

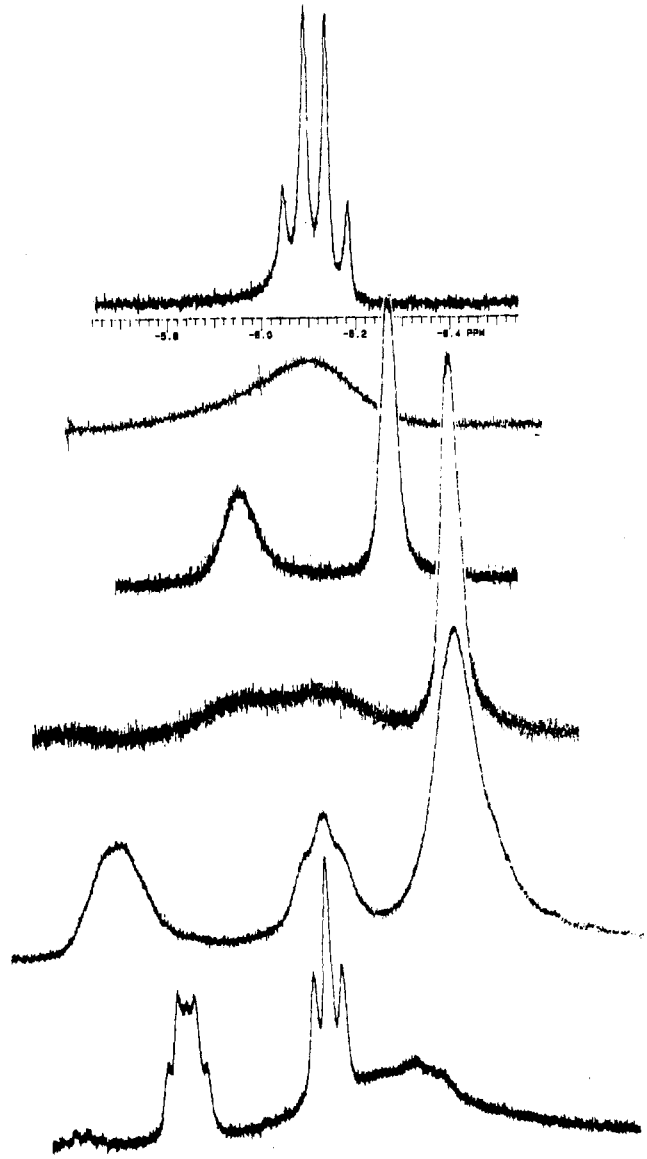


Figure 2. Spectra of $ReH_5(PMePh_2)_3$ (400 MHz, CD_2Cl_2 solvent) at several temperatures. The temperatures from top to bottom, are +22, −20, −60, −80, −95, and −110 °C. The chemical shift scale, given precisely for the +22 °C spectrum is also approximately applicable to the others.

effects on T_1 measurements upon changing the tertiary phosphine ligands.[9] At −40 °C, the spectrum consists of the 2:3 intensity pattern, and T_1 values of 96 ms for the peak at δ −5.8, indicating an η^2-H_2 component at this temperature, and 145 ms for the peak at δ −6.5 are obtained. At −80 °C the spectrum consists of a 1:1:3 intensity pattern, and the T_1 values have increased substantially for the two magnetically inequivalent hydrogen atoms; however, that for the three magnetically equivalent ones at δ −6.6 has not changed significantly. This is in keeping with the fact that hydridic hydrogen atoms should have greater T_1 values than those that are either nonclassical or rapidly fluxional. Our conclusion that **2** is classical in solution at −110 °C is in accord with the neutron diffraction structure reported for the solid.[10]

The T_1 values for all three resonances increase as the temperature is further lowered and at −110 °C clearly indicate that $ReH_5(PMePh_2)_3$ is classical. This separation of the hydrogen resonances as the temperature is lowered is similar to what was reported for $ReH_5(PEtPh_2)_3$.[7] However, it is interesting that the

(7) Ginsberg, A. P.; Abrahams, S. C.; Jamieson, P. B. *J. Am. Chem. Soc.* **1973**, *95*, 4751.
(8) Chatt, J.; Coffey, R. S. *J. Chem. Soc., A*, **1969**, 1963.
(9) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4056.
(10) Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012.

variable-temperature pattern for **1** differs from that obtained for **2** and $ReH_5(PEtPh_2)_3$. The reasons for this are not clear and may be either electronic or steric in origin.

The T_1 data obtained for the complex $ReH_7(PPh_3)_2$ are given in Table I. This complex exhibits a triplet in the hydride region, for the seven magnetically equivalent hydrogen atoms, which is still clearly defined down to −90 °C. However, as reported previously, the T_1 values at the low temperatures do indicate a fluxional process with involvement of nonclassical hydrogen atoms accounting for the low T_1 values.[3a]

Finally, we have made the first T_1 observations on a complex of the type $Re_2H_8(PR_3)_4$, namely, the one where $PR_3 = PPh_3$ (**4**).[11] We find for **4** that T_1(min) = 65 ms in CD_2Cl_2 at −40 °C and 200 MHz. The related complex with $PR_3 = PEtPh_2$ (**4'**) is known[12] to have four μ_2-H^- and four terminal H^- ligands. Thus, it is uncertain whether a low T_1 value is necessarily diagonistic of the ligand H_2. If it is, the structure of **4** in solution must differ from that of **4'**.

In summary, the above results (a) require reclassification of **1** as nonclassical, probably as $Re(H_2)H_3(PPh_3)_3$, (b) show that even a slight change in auxiliary ligands (from PPh_3 to $PMePh_2$) can alter the behavior of the H atoms, and (c) raise a question as to the rigor of always ascribing low T_1 values to the presence of H_2 as a ligand.

Acknowledgment. We thank Professor R. H. Morris for helpful comments. Support by the National Science Foundation is gratefully acknowledged.

Note Added in Proof. More resolved low-temperature spectra for **1**, which are also consistent with our assignment of a nonclassical formulation for this complex, were recently obtained in CD_2Cl_2.

(11) Cotton, F. A.; Luck, R. L. Unpublished work. The crystal structure shows disorder sufficient to make it impossible to observe the hydrogen atoms.
(12) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3873.

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

F. Albert Cotton*
Rudy L. Luck

Received September 7, 1988

Oxomolybdenum(V) Complexes with Sulfide and Hydrogensulfide Ligands: Models for the Molybdenum(V) Centers of Xanthine Oxidase and Xanthine Dehydrogenase

Sir:

Recent evidence from EXAFS and EPR studies of xanthine oxidase (XO) and xanthine dehydrogenase indicates their molybdenum(VI) centers have both terminal oxo and terminal sulfide ligands.[1] Upon reduction by substrate to the molybdenum(IV) state, the sulfide group is apparently protonated to SH;[1b-d] one-electron reoxidation to the molybdenum(V) state generates the Very Rapid[1e] and Rapid[1b,c] EPR signals, which are thought to arise from Mo^VOS and $Mo^VO(SH)$ centers, respectively. No model oxomolybdenum(V) complexes with these ligands have been isolated, although their presence in solution has been convincingly demonstrated.[2,3]

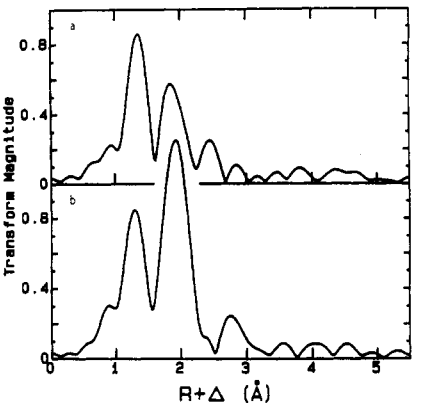


Figure 1. K-edge EXAFS transforms (transform k range 4–15 $Å^{-1}$): (a) $[Ph_4P][MoOSL]$ (**1**); (b) *trans*-MoO(SH)L (**2**).

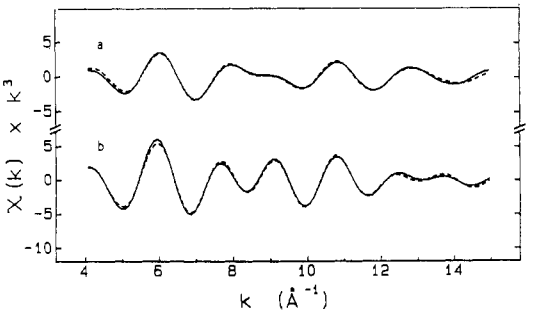


Figure 2. EXAFS curve fits: (a) $[Ph_4P][MoOSL]$ (**1**); (b) *trans*-MoO(SH)L (**2**).

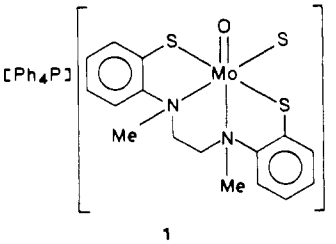
Table I. EXAFS Curve-Fitting Results

	Mo=O		Mo—S		Mo—N/O[a]	
complex	bond length, Å[b]	N[c]	bond length, Å[b]	N[c]	bond length, Å[b]	N[c]
$[Ph_4P][MoOSL]$ (**1**)	1.68	1	2.36	2–3	2.02	~1
trans-MoO(SH)L (**2**)	1.66	1	2.39	3–4	2.02	~1

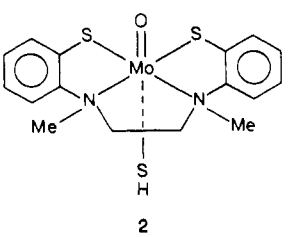
[a] Mo—N/O: Mo—N or Mo—O bonds, not distinguished by EXAFS. [b] Uncertainty ±0.03 Å. [c] Number of bonds.

The synthesis and characterization of $Mo^{VI}O_2L$ (L = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptophenyl)ethylenediamine) has recently been reported from this laboratory.[2] One-electron electrochemical reduction of MoO_2L in MeCN, followed by addition of $[n\text{-}Bu_4N]SH$, generates $[MoOSL]^-$ in solution. Protonation of $[MoOSL]^-$ at low temperature (<−40 °C) gives *cis*-MoO(SH)L, which appears to rearrange to *trans*-MoO(SH)L at room temperature. The latter species is also obtained in solution by treatment of *trans*-MoOClL with $[n\text{-}Bu_4N]SH$ at room temperature.[2]

We report here the synthesis and characterization of complexes formulated as $[Ph_4P][MoOSL]$ (**1**) and *trans*-MoO(SH)L (**2**), apparently the first oxomolybdenum(V) complexes with sulfide and hydrogensulfide ligands to be isolated.



1



2

(1) (a) Hille, R.; Massey, V. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley: New York, 1985; p 443. (b) Cramer, S. P. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 259. (c) Cramer, S. P.; Wahl, R. C.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721. (d) George, G. N.; Bray, R. C.; Cramer, S. P. *Biochem. Soc. Trans.* **1986**, *14*, 651. (e) Bray, R. C.; George, G. N. *Biochem. Soc. Trans.* **1985**, *13*, 560. (f) Bray, R. C.; Gutteridge, S.; Storter, D. A.; Tanner, S. J. *Biochem. J.* **1979**, *177*, 357. (g) Bray, R. C. *Q. Rev. Biophys.* **1988**, *21*, 299.

(2) Dowerah, D.; Spence, J. T.; Singh, R.; Wedd, A. G.; Wilson, G. L.; Farchione, F.; Enemark, J. H.; Kristofzski, J.; Bruck, M. *J. Am. Chem. Soc.* **1987**, *109*, 5655.
(3) Hinshaw, C. J.; Spence, J. T. *Inorg. Chim. Acta* **1986**, *125*, L17.

0020-1669/89/1328-0008$01.50/0