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Chemical Shift Range of Thioether-Bridged Face-Sharing Bioctahedral Complexes: A Tungsten-183 NMR Study

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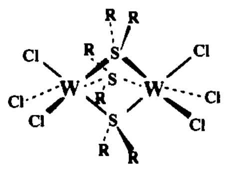
Introduction

Recently, we reported the syntheses and structures of some d^3–d^3 face-sharing bioctahedral (FBO) complexes of tungsten having two and three bridging thioether ligands (A–C).[1,2]



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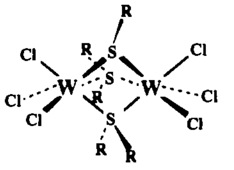

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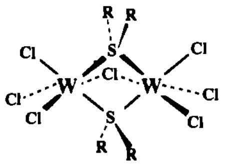

C

B is accessible from **A** by reacting **A** with nucleophiles. A facile S–C bond cleavage occurs, leading to the formation of mixed thioether–thiolate complexes, while retaining the FBO framework.[2] In the case of tetrahydrothiophene (THT) being in the bridging position, a ring-opening reaction leads to the mixed μ-THT-μ-butanethiolate cluster $[Cl_3W(\mu\text{-THT})_2(\mu\text{-S-}(CH_2)_4R)WCl_3]^-$. Concomitantly, the formation of a bridging thiolate results in a shortening of the W–W distance by about 0.02 Å.

The reactivity of these complexes can be interpreted as a result of the extremely acute M–S–M angles in these complexes as a result of the very short W–W bonds. In addition, the demonstrated ability of bridging thioethers to act as weak π-acceptor ligands using their vacant σ^* orbitals[3,4] will contribute to the activation of the S–C bonds in these complexes. According to calculations on molybdenum FBO systems,[3] changing the bridging ligands from thioethers to chlorides or thiolates is expected to dramatically influence the electronic structure of the FBO. As pointed out previously,[3] the presence of a bridging chloride within the FBO framework will lead to a repulsive interaction with the occupied W–W bonding orbitals. A bridging thioether, on the other hand, having one lone pair less than chloride can act as a π acceptor. As a result of strong intermetallic attraction within the $[W{\equiv}W]^{6+}$ core, the structural and electronic influences of the bridging thioether are less significant than those reported for molybdenum FBO complexes.[5,6] Most of the structural changes can indeed be explained in terms of steric influences within the FBO framework. Clearly, the electronic influence of thioether ligands is rather small in tungsten FBO complexes compared to the molybdenum systems. It was therefore necessary to apply a technique that is sensitive enough to detect minute electronic changes about the tungsten centers. It was thought that ^{183}W NMR spectroscopy should be a very sensitive probe for the chemical and electronic environments of each tungsten center.

Although the advent of Fourier transform NMR spectrometers and high-field superconducting magnets has made possible the observation of metal nuclei of low receptivity, such as ^{183}W (0.059 relative to ^{13}C), at natural abundance, ^{183}W NMR spectroscopy is still far away from being a routine technique.[7] Troubled by a low resonance frequency and a low receptivity, investigations have largely been restricted to highly soluble complexes. Over the past decade, 1- and 2-dimensional ^{183}W NMR techniques have been applied successfully for structural assignments in polytungstates.[8] In fact, according to the latest review, most of the information gathered is on W(VI) polytungstate complexes.[9]

Although information on intermediate-oxidation-state complexes is still scarce, it has been pointed out that there is no simple correlation between oxidation state and ^{183}W chemical shifts. To a first approximation, the nuclear shielding decreases as the oxidation state increases. However, the shift will be influenced to a large extent by the chemical environment around the metal center. The observation of odd-electron systems, such as W(I), W(III), and W(V), by ^{183}W NMR spectroscopy will be restricted to metal–metal-bonded species.

In a recent study, ^{183}W chemical shifts were reported for five W(III) binuclear complexes of the general formula M_2L_6, having a formal W–W triple bond. Enemark and co-workers have presented evidence that the nuclear deshielding in M_2L_6 complexes is related to the nature of the metal–metal bond itself.[10] The nature of this metal–metal bond, on the other hand, is strongly dependent on the nature of the terminal ligands in the two ML_3 fragments forming the M_2L_6 complex. Nuclear shielding was found to increase in the order $[M{\equiv}M]^{6+}$ ($\sigma^2\pi^4$) < $[M{\equiv}M]^{6+}$ ($\pi^4\delta^2$).

In this study, we are not solely concerned with the influence of the metal–metal bond on the shielding. The overall metal–metal-bonding situtation in $Cl_3W(\mu\text{-}L)_3WCl_3$ systems ($\sim\sigma^2\delta^4$)[11] will not change dramatically when changes in the bridging region occur, but are expected to be very subtle in nature. This work represents the first systematic study of d^3–d^3 confacial bioctahedral complexes by ^{183}W NMR spectroscopy and, to our knowledge, is the first attempt to evaluate the effect of the bridging ligands on nuclear shielding.

Results and Discussion

Before discussing our results in detail, it will be necessary to briefly introduce the main features of heavy-nuclei NMR spectroscopy.

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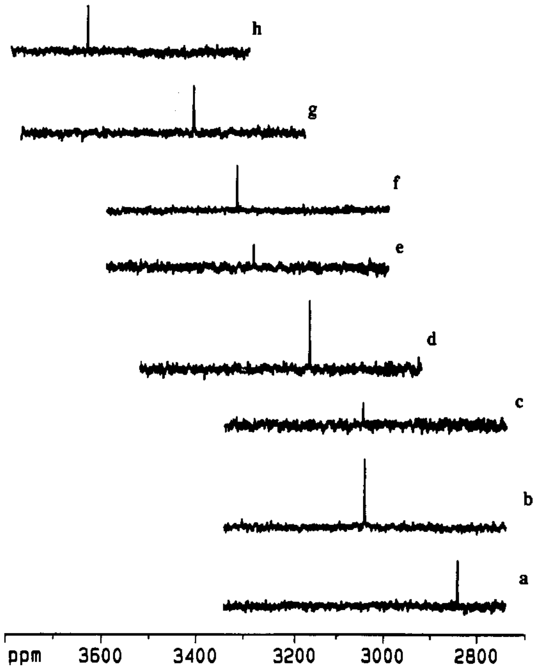

Figure 1. ^{183}W chemical shifts: (a) $Cl_3W(\mu\text{-THT})_3WCl_3$ (**8**), 23 000 scans; (b) $(Ph_4P)[Cl_3W(\mu\text{-}S(CH_2)_4SC_6H_4CH_3\text{-}4)(\mu\text{-THT})_2WCl_3]$ (**9**), 1000 scans; (c) $Cl_3W(\mu\text{-}SEt_2)_3WCl_3$ (**7**), 15 300 scans; (d) $(Ph_4P)[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]$ (**6**), 1000 scans; (e) $(Ph_4P)[Cl_3W(\mu\text{-}Cl)(\mu\text{-THT})_2WCl_3]$ (**3**), 13 000 scans; (f) $(Ph_4P)[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SMe_2)_2WCl_3]$ (**5**), 17 000 scans; (g) $(Ph_4P)[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SEt_2)_2WCl_3]$ (**4**), 14 000 scans; (h) $(NH_4)_2WS_4$ (**2**), 2000 scans.

According to the Ramsay model of nuclear shielding for heavy nuclei, the total shielding can be analyzed in terms of two components, a diamagnetic, σ_d, and a paramagnetic component, σ_p.[12] The paramagnetic component, σ_p (eq 1), will be the dominant factor in determining the ^{183}W chemical shift.

$$\sigma_p \simeq (-\mu_0/4\pi)(4\mu^2{}_B/\Delta E)[\langle r^{-3}\rangle_{np}\mathbf{P}_i + \langle r^{-3}\rangle_{nd}\mathbf{D}_i] \quad (1)$$

Since mixing of excited states into the electronic ground state is responsible for the paramagnetic term, it is not surprising that it contains an inverse dependence on the lowest allowed energy transition, ΔE. $\mathbf{P}_i$ and $\mathbf{D}_i$ are the imbalances of electron density of the valence electrons in p and d orbitals relative to the free-atom values $\langle r^{-3}\rangle_{np}$ and $\langle r^{-3}\rangle_{nd}$. For our qualitative discussion, this can be simplified to

$$\sigma_p \propto -\text{constant}(k^2\langle r^{-3}\rangle)/\Delta E \quad (2)$$

k contains the electron imbalance factors $\mathbf{P}_i$ and $\mathbf{D}_i$ and is called the "orbital reduction factor". It describes the degree of covalency of the metal–ligand bond, where a small k describes a large ligand contribution to the molecular orbital.

Transition metal complexes can show a dependency on either of two effects: (a) in cases where the HOMO–LUMO separation determines the shielding, the shielding will follow the spectrochemical series (i.e., the shielding increases as the ligand field strength increases); (b) if the $k^2\langle r^{-3}\rangle$ factor is dominant, the shielding will follow the nephelauxetic effect of the ligand. This means that as the bond between metal and ligand increases in covalency, the shielding of the metal will increase.

In theoretical studies of group 11 and 12 d^{10} and d^5 Mn complexes,[13] the shielding of the metal nuclei has been related to ligand properties, such as the π-donating ability of the ligand. Nakatsuji and co-workers[13] emphasized that for open-shell systems, such as Mn(I), the contributions from the d orbitals to the paramagnetic term will be by far the most important contributions to the paramagnetic term.

In binuclear complexes, the strong interaction of the partially filled d orbitals on the metal with the neighboring metal center and hence the presence of a metal–metal bond will lead to a deshielding of the nuclear shift, as reported for ^{95}Mo binuclear complexes[14a] and for ^{183}W bi-[14b] and trinuclear complexes.[10] This deshielding effect increases as the metal–metal bond order increases. $W_2(CF_3COO)_4$, having a formal quadruple bond, is the most deshielded tungsten complex known to date and gives a signal at 6760 ppm.[15] Reducing the bond order to 3 will shift the signal upfield. The W_2L_6 systems and their derivatives, investigated by Enemark and co-workers, formally contain a W–W triple bond. They give signals ranging from δ 4736 ($W_2(O^iPr)_6(dmpe)$) to δ 2653 ($W_2(O_2CMe)_4(CH_2CMe_3)_2$).[10]

The shifts of the d^3–d^3 confacial bioctahedral clusters **3**–**13** are summarized in Table I, where it is seen that their ^{183}W chemical shifts fall within the range established by Enemark and co-workers. They are well shielded compared to the unsubstituted parent complex $[Cl_3W(\mu\text{-}Cl)_3WCl_3]^{3-}$ (**14**) and cover a range from 2850 to 3415 ppm (*versus* 2 M Na_2WO_4 in H_2O). The ^{183}W NMR spectra of some of the thioether-bridged confacial bioctahedral complexes together with the spectrum of Na_2WS_4 are shown in Figure 1. As expected, each complex shows one signal for the two magnetically equivalent tungsten nuclei.

As discussed by Summerville and Hoffmann,[16] a short intermetallic separation in M_2L_9 systems, as found in $W_2Cl_9{}^{3-}$ and in its derivatives, will result in a strong metal–metal interaction. The interactions of the bridging ligands with the metal centers are of lesser importance. This means that in our FBO complexes, the fundamental bonding situation with respect to the metal–metal bond does not change. Therefore, it is understandable that no significant influence of the bridging ligands on the electronic transitions of the complexes was found.[1,2] Hence, we are in the fortunate situation of being able to evaluate the influence of the bridging ligand on the ^{183}W shielding. The shielding will be related only to the ligand's properties and the covalency of the metal–ligand bond.

We note that the monochloro-bridged complexes **3**–**5** are more deshielded than the mixed thioether–thiolate-bridged complexes **6** and **9**–**13**. The triply thioether-bridged systems **7** and **8** are on the high-field side of the shift range defined by the FBO complexes. From the data presented here, it is not possible to give a quantitative correlation between bridging ligand and chemical shift. However, we note a trend in the shielding following the order $(\mu\text{-}Cl)(\mu\text{-}SR_2)_2 < (\mu\text{-}SR)(\mu\text{-}SR_2)_2 < (\mu\text{-}SR_2)_3$. The chloro-bridged systems under investigation show a signal in region δ 3600–3300. The mixed thiolate–thioether systems are more shielded and give signals in the region δ 3200–3000. And, finally, the triply thioether-bridged systems resonate in the region δ 3050–2800. This means that the ^{183}W shielding increases in the order $Cl^- < SR^- < SR_2$. This can be explained in terms of the nephelauxetic effect of the ligand. Ligands with large nephelauxetic effects, i.e. soft ligands with a tendency to form covalent rather than ionic bonds, will influence the shielding mainly through the $k^2\langle r^{-3}\rangle$ term and will have a shielding effect. According to Jørgensen's classification,[17] chloride will be less effective in delocalizing electron density away from the metal center than a sulfur-based ligand. In fact, the interaction between the bridging

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Table I. ^{183}W Chemical Shifts of d^3–d^3 Confacial Bioctahedral Complexes Having Bridging Sulfur Ligands and Some Reference Complexes

complex	no.	solvent	δ^a (ppm)	T_1 (s)	d(W–W) (Å)
$Na_2WO_4{}^a$	**1**	H_2O	0	31.4	
$(NH_4)_2WS_4$	**2**	DMF	3639		
$(Ph_4P)[Cl_3W(\mu\text{-}Cl)(\mu\text{-}THT)_2WCl_3]$	**3**	MeCN	3288		
$(Ph_4P)[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SEt_2)_2WCl_3]$	**4**	MeCN	3415		
$(Ph_4P)[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SMe_2)_2WCl_3]$	**5**	MeCN	3324		2.4752(8)
$(Ph_4P)[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]$	**6**	MeCN	3167		2.474(1)
$Cl_3W(\mu\text{-}SEt_2)_3WCl_3$	**7**	MeCN	3050		2.4990(9)
$Cl_3W(\mu\text{-}THT)_3WCl_3$	**8**	CH_2Cl_2	2850		
$(Ph_4P)[Cl_3W(\mu\text{-}S(CH_2)_4S\textit{p}tol)(\mu\text{-}THT)_2WCl_3]$	**9**	MeCN	3046	0.44	2.4846^b
$(Ph_4P)[Cl_3W(\mu\text{-}S(CH_2)_4STIP)(\mu\text{-}THT)_2WCl_3]$	**10**	MeCN	3046	0.44	
$(Ph_4P)[Cl_3W(\mu\text{-}S(CH_2)_4SPh)(\mu\text{-}THT)_2WCl_3]$	**11**	MeCN	3046		
$(Ph_4P)[Cl_3W(\mu\text{-}S(CH_2)_4SePh)(\mu\text{-}THT)_2WCl_3]$	**12**	MeCN	3046		
$(Ph_4P)[Cl_3W(\mu\text{-}S(CH_2)_4SH)(\mu\text{-}THT)_2WCl_3]$	**13**	MeCN	3047		
$K_3[Cl_3W(\mu\text{-}Cl)_3WCl_3]$	**14**	CD_3CN	3539^c		2.44^c

^{a} 2 M Na_2WO_4 in H_2O; ν = 16.671 210 6 MHz. ^{b} The crystal structure of the analogous complex $(Ph_4P)[Cl_3W(\mu\text{-}S(CH_2)_4Cl)(\mu\text{-}THT)_2WCl_3]$ exhibits a W–W bond length of 2.4846(8) Å; see ref 2. ^{c} from ref 14b.

chlorides and the metal centers will be a 4e–2-orbital interaction, and hence, it will be destabilizing.[3] Thiolates, being softer ligands, will have a shielding effect comparable to that of chloride. Thioether ligands will be even softer due to the ability of the thioether to use its empty σ^* orbitals to accept electron density.

A close inspection of Table I shows that there is a substituent dependency of the chemical shift. First, we inspect the $Cl_3W(\mu\text{-}Cl)(\mu\text{-}SR_2)_2WCl_3$ systems. The shielding follows increases in the order $SEt_2 < SMe_2 <$ THT. Comparing the ^{183}W shift data with crystal data for some of the complexes[1,2] shows that a progressive opening of the C–S–C angle[18] from 96.2° (THT) to 102.6° (Me_2S) to 103.5° (Et_2S) leads to a decrease in the shielding. This trend is mirrored by the $Cl_3W(\mu\text{-}SR)(\mu\text{-}SR_2)_2WCl_3$ systems investigated. The μ-THT systems, **9**–**13**, are all more shielded (by about 110 ppm) than the μ-SEt system, **6**. Similarly, $Cl_3W(\mu\text{-}SEt_2)_3WCl_3$ is less shielded (by 200 ppm) than is $Cl_3W(\mu\text{-}THT)_3WCl_3$. From simple MO arguments it follows[19] that a decrease in the C–S–C angle will influence significantly the energy levels of the acceptor orbitals (σ^*), while those of the donor orbitals are influenced to a lesser extent. A decrease of the C–S–C angle will lower the energy of the σ^* orbital responsible for back-bonding in FBO complexes, which increases its acceptor ability. The THT ligand, having the smallest C–S–C angle, should therefore have a higher shielding effect compared to SEt_2 and SMe_2, which is in accordance with the observed behavior.

It is important to point out that $Cl_3W(\mu\text{-}SR_2)_3WCl_3$ systems have a longer W–W bond compared to $[Cl_3W(\mu\text{-}SR)(\mu\text{-}SR_2)_2WCl_3]^-$ and $[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SR_2)_2WCl_3]^-$ systems. For steric reasons the metal–metal bond lengthens if three thioethers are in the bridging region. A reduction in steric bulk of the three bridging ligands allows the two tungsten centers to come closer together, and this will deshield the ^{183}W nuclei. This also explains the trend in shielding: $Cl^- < SR^- < SR_2$.

Remote changes in the ligands, such as a substitution of –SPh for –SH, as shown by **9**–**13**, have no influence on the tungsten chemical shift.

Comments about the Probe and Solvent and Relaxation Effects

Generally, all spectra were recorded as an acetonitrile solution (0.01–0.05 M), using a horizontal coil arrangement. According to Drakenberg and Forsén,[20] the horizontal probe is far superior to the traditional saddle-shaped Helmholtz coil in terms of sensitivity; we have found an improvement of 3–4 times over a traditional 10-mm broad band probe. This allowed us to record spectra, even of dilute solutions with a good signal to noise ratio, in a reasonable amount of time.

The low solubility of **8** in acetonitrile made it necessary to record its spectrum in dichloromethane. Subsequent solutions of **7** and **9** in dichloromethane did not show a significant influence of the solvent on the chemical shift (~1 ppm), thus allowing us to compare chemical shifts recorded in CH_2Cl_2 with those recorded in CH_3CN. It is of interest to note that the concentration influence on the chemical shift for complexes **3**–**13** is also negligible (~1 ppm).

The short values for the longitudinal relaxation time, T_1, for **9** and **10** point to an effective scalar coupling of the second kind[21] of the ^{183}W with the quadrupolar nuclei ^{35}Cl and ^{37}Cl. The possibility of a dipolar relaxation mechanism due to the neighboring ^{183}W center will be remote (1.96% possibility of finding two neighboring ^{183}W). It is reasonable to assume that all Cl-containing complexes (**3**–**14**) have similarly short relaxation times. Hence, the recycle times could have been reduced allowing a faster data collection without sacrificing signal strength, making this a useful experimental technique for organometallic chemists. $WO_4{}^{2-}$ will have a long T_1, since no effective relaxation mechanism is present.

Conclusion

This study focused on d^3–d^3 face-sharing biocathedral complexes of tungsten having the overall formula $[Cl_3W(\mu\text{-}X)_n(\mu\text{-}SR_2)_{3-n}WCl_3]^{n-}$ (n = 0, 1), where X can be chloride, thiolate, or thioether. Since changes in the bridging region do not influence the fundamental bonding within the FBO framework, observed ^{183}W chemical shift changes are related only to ligand influences. It is observed that the ^{183}W shielding increases in the order $\mu\text{-}Cl^- < \mu\text{-}SR^- < \mu\text{-}SR_2$. Furthermore, a substituent influence exists, which can be related to the C–S–C angle of the thioether. Thioethers with a smaller C–S–C angle will shield the ^{183}W nuclear shift. Both tendencies have been explained using arguments based on the nephelauxetic effect. A correlation between increasing intermetallic distance and an increase in shielding is found. The two tungsten centers are kept further apart due to steric crowding within the bridging region of the FBO. Reducing the steric pressure allows the two metals to be closer together, and a deshielding is the result.

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(18) Given are the mean C–S–C angles from the complexes $(Ph_4P)[Cl_3W(\mu\text{-}THT)_3WCl_3]$, $Na[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]\cdot 3THF$, $Cl_3W(\mu\text{-}SEt_2)_3WCl_3$, and $(SMe_3)[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SMe_2)_2WCl_3]$. For a detailed crystallographic analysis, see refs 1 and 2.

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Experimental Procedure

Materials. Na_2WO_4 was purchased from Aldrich and was used without further purification. $(NH_4)_2WS_4$[22] and the FBO[1,2] complexes **3–13** were synthesized according to published procedures, and their purity was checked by ^1H NMR spectroscopy.

Sample Preparation. A 2 M solution of Na_2WO_4 in H_2O was used as the reference (δ 0.0 ppm; ν = 16.671 21 MHz). A saturated solution of $(NH_4)_2WS_4$ in dimethylformamide (DMF) was used as a secondary reference. Complexes **3–13** were used as saturated solutions in MeCN (0.01–0.05 M), prepared in air. **8** was used as a 0.01 M solution in CH_2Cl_2.

NMR Spectroscopy. ^{183}W NMR measurements were performed using a wide-bore Bruker AM-400 spectrometer operating at a resonance frequency of 16.7 MHz and equipped with a horizontal solenoid probe. The Pyrex glass sample tubes were of cylindrical shape with an o.d. of 17 mm and a length of about 4 cm.

The spectra were acquired at room temperature (21 ± 1 °C) using a pulse length of 20 μs (30° pulse), a delay between pulses of 3–4 s, and a sweep width of 10 kHz. The window was chosen so that the signal was approximately in the center of the window to ensure maximum excitation. A spectrometer dead time of 400 μs was used to ensure a flat base line. This did not cause any detectable loss of signal intensity. An exponential multiplication was applied to all data resulting in a line broadening of 10 Hz. Spectra with a signal to noise ratio of approximately 10 were obtained with several thousand scans.

Each sample was run twice to ensure that the signal was reproducible. The field stability of the Supercon made it possible to acquire all ^{183}W spectra unlocked. All spectra were referenced to external 2 M Na_2WO_4 in H_2O (δ (ppm) = $(\nu_{\text{sample}} - \nu_{Na_2WO_4}/\nu_{Na_2WO_4}) \times 10^6$). T_1 measurements were made with the inversion recovery sequence (π–τ–π/2–FID) and analyzed using standard Bruker software.

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