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Preliminary communication

HYPOTHESIS OF A BOND ALTERNATION MECHANISM FOR CHARGE DELOCALIZATION WHICH DETERMINES ^{183}W CHEMICAL SHIFTS IN α-[(η^5-C_5H_5)Ti($PW_{11}O_{39}$)]$^{4-}$

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Summary

A *trans* bond alternation mechanism for charge transmission in the α-[(η^5-C_5H_5)Ti($PW_{11}O_{39}$)]$^{4-}$ anion is proposed which provides a self-consistent interpretation of ^{183}W NMR chemical shifts observed for the anion. Chemical shift data for the α-$PW_{12}O_{40}{}^{3-}$, α-$SiW_{12}O_{40}{}^{4-}$, β-$SiW_{12}O_{40}{}^{4-}$ and $W_6O_{19}{}^{2-}$ anions show, however, that ^{183}W NMR chemical shifts are extremely sensitive to environmental and structural perturbations, and that interpretation of chemical shift values can be made on the basis of charge distribution arguments only when close structural analogy is maintained.

The remarkable hydrolytic stability of the recently reported [1,2] α-[(η^5-C_5H_5)Ti($PW_{11}O_{39}$)]$^{4-}$ anion (I) has been attributed in part to a relatively uniform surface charge distribution [1]. Although ^{17}O NMR data reflect this uniformity [1], the data fail to provide insight into the mechanism of charge delocalization due to incomplete spectral resolution. We have therefore measured the ^{183}W NMR spectrum of anion I and propose here an interpretation of the fully resolved spectrum which involves a bond alternation mechanism for charge transmission in the anion. This mechanism, should it prove to be valid for other metal oxide systems, may provide a partial explanation for the enhanced stability of organometallic species bound to oxide supports.

A Bruker WH-180 NMR spectrometer operating at a nominal 7.50 MHz was employed to obtain the spectrum shown in Figure 1 and the chemical shift data recorded in Table 1. Direct ^{183}W NMR investigations are limited to

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TABLE 1

7.50 MHz ^{183}W NMR CHEMICAL SHIFT DATA

Anion [a]	Chemical shifts [b]
α-$(\eta^5$-$C_5H_5)Ti(PW_{11}O_{39})^{4-}$ (I) [c,d]	-117.7 [e], -112.3 [e], -100.4 [e] -94.8 [e], -93.6 [f], -78.3 [e]
α-$(\eta^5$-$C_5H_5)Ti(PW_{11}O_{39})^{4-}$ (I) [d,g]	-115.1 [e], -109.5 [e], -97.7 [e] -92.3 [e], -90.9 [f], -76.7 [e]
α-$PW_{12}O_{40}^{3-}$ (II) [g]	-86.7
α-$SiW_{12}O_{40}^{4-}$ (III) [g]	-92.1
β-$SiW_{12}O_{40}^{4-}$ (V) [g]	-120.5 [f], -104.0 [e], -103.5 [f]
$W_6O_{19}^{2-}$ (VI) [g]	$+58.9$

[a] Spectra measured from 7±1 g tetra-n-butylammonium salts in 10 ml solution. [b] Positive chemical shifts in parts per million downfield from 2 *M* Na_2WO_4 in D_2O whose precise resonance frequency (D_2O lock) was determined to be 7501444 Hz in a magnetic field at which TMS in $CDCl_3$ resonates at exactly 180045289 Hz. [c] In CD_3CN solution. [d] All resonances are doublets with $J(^{31}P$—$^{183}W) \sim 1$ Hz. [e] Relative intensity of two. [f] Relative intensity of one. [g] 20 volume % CD_3CN in $(CH_3)_2NCHO$.

observations of a few simple binary compounds [3,4] and to a very recent spectral description [5] of six heteropolytungstates related to those described herein. The ^{183}W NMR spectrum of anion I as the tetra-n-butylammonium salt in CD_3CN is shown as Fig. 1. The observed six doublets of intensity ratios 2:1:2:2:2:2: and with $J(^{31}P$—$^{183}W) = 1$ Hz are consistent with the structure of C_s symmetry proposed in ref. 1. Only the low intensity doublet is assignable by inspection, but the reasonable assumption that chemical shifts of these quite chemically similar W^{VI} atoms are increasingly screened (shifted upfield) by increased negative charge densities at structurally analogous metal centers allows self-consistent assignment of all resonances. This assumption is derived from comparison of reported [5] tungsten chemical shifts for the isostructural aqueous anions α-$PW_{12}O_{40}^{3-}$ (II), -98.83 ppm; α-$SiW_{12}O_{40}^{4-}$ (III), -103.83 ppm; and α-$BW_{12}O_{40}^{5-}$ (IV), -130.39 ppm. Bonding at each of the twelve symmetry-equivalent tungsten centers in anion II is represented in Scheme 1a. Here, hexavalence at tungsten is satisfied by a double bond to the terminal oxygen O_t (d(W—O_t) = 1.7 Å [6]) and four single bonds to the bridging oxygens O_b (d(W—O_b) = 1.9 Å [6]). Due to the weakness of bonds to the central phosphate oxygens O_c (d(W—O_c) = 2.4 Å [6]) the anion may be viewed as a PO_4^{3-} anion which is encapsulated by the neutral $W_{12}O_{36}$ cage represented schematically in Figure 2a. Anions III and IV are derived from anion II by replacing the central PO_4^{3-} unit with the more highly charged

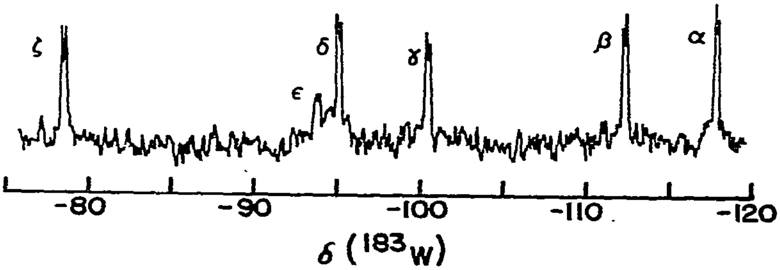


Fig. 1. The 7.50 MHz ^{183}W NMR spectrum of $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}(\eta^5\text{-}C_5H_5)Ti(PW_{11}O_{39})]$ in CD_3CN observed by obtaining ca. 16000 scans in a period of 8 hours. For spectral data see Table 1.

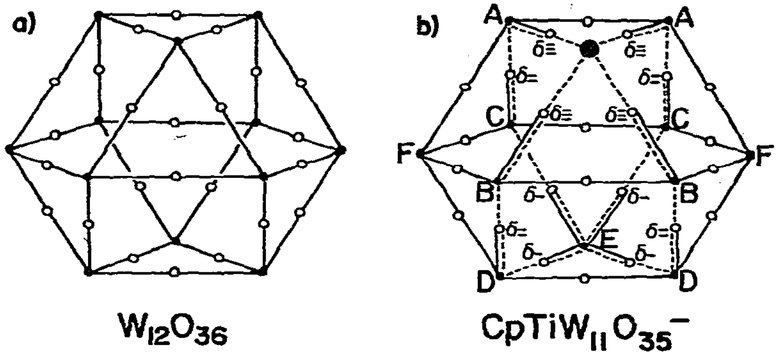
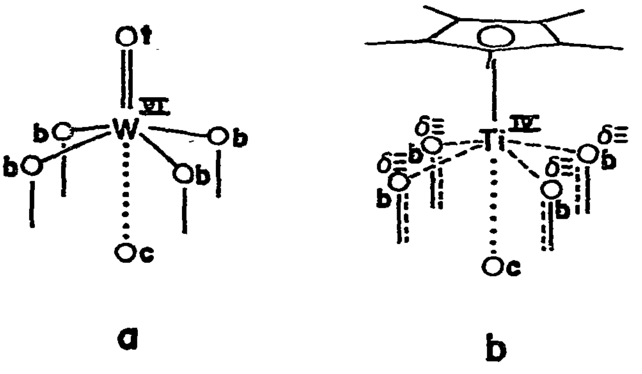


Fig. 2. Bonding schemes for (a) the T_d α-$W_{12}O_{36}$ cage in α-$PW_{12}O_{40}{}^{3-}$ and (b) the C_s α-(η^5-C_5H_5)-$TiW_{11}O_{35}{}^-$ cage in [α-(η^5-C_5H_5)Ti($PW_{11}O_{39}$)]$^{4-}$. Open circles represent oxygen atoms, small filled circles represent $W{=}O_t$ units, and the large filled circle represents a Ti(C_5H_5) unit. In (b), symmetry equivalent tungsten centers are provided with identical labels.

$SiO_4{}^{4-}$ and $BO_4{}^{5-}$ units, and the increased negative charge introduced into the tungsten coordination spheres is reasonably presumed to be responsible for the observed upfield displacements of ^{183}W chemical shift values.

Anion I is derived from anion II by replacement of a single tetravalent $[WO_t]^{4+}$ unit with a trivalent $[Ti(\eta^5\text{-}C_5H_5)]^{3+}$ unit, leading to increased negative charge on the O_b oxygens (see Scheme 1b). We assign therefore the pair of doublets α and β which appear furthest upfield in the ^{183}W NMR spectrum of I (see Fig. 1) to the tungstens labeled A and B (or B and A) in Fig. 2b, which are structurally adjacent to the $[Ti(\eta^5\text{-}C_5H_5)]^{3+}$ unit in anion I. Since ^{17}O NMR data shown, however, that this negative charge is delocalized [1], a mechanism for charge transmission must be provided which accounts for the values of the remaining tungsten chemical shifts. Such charge delocalization may be effected by strengthening the bonds from W_A and W_B to the oxygens bridging to the titanium center and weakening predominantly the *trans* W—O bonds as indicated in Fig. 2b. This bond weakening in turn generates increased negative charge on the oxygens bridging W_A and W_C as well as the oxygens bridging W_B and W_D centers. The effect of this increased negative charge is an upfield shift of the W_C and W_D resonances which are there-



SCHEME 1

fore associated with the pair of doublets γ and δ (or δ and γ). The emerging pattern of charge transmission via *trans* bond alternation is terminated by weakening of the bonds connecting W_C and W_D to the bridging oxygens bonded to W_E, generating negative charge in the coordination sphere of the unique tungsten, W_E. Note that the doublet ϵ, which is unambiguously assigned to W_E on the basis of intensity, is displaced only slightly downfield from the δ and γ doublets in comparison to the larger downfield displacement of the δ and γ doublets relative to the β and α doublets. This smaller displacement reflects the fact that negative charge has accumulated on all four bridging oxygens in the W_E coordination sphere whereas only two of the bridging oxygens in the W_A, W_B, W_C, and W_D coordination spheres have been perturbed. Note also that the current assignments imply by default that the downfield ζ doublet be assigned to the W_F tungstens. This assignment is implied by the *trans* bond alternation scheme which fails to direct negative charge to the W_F center (see Figure 2b). Here and above, we do not mean to imply that *cis* effects are negligible, only that *trans* effects predominate. X-ray crystallographic studies of several related Group VIa polyoxoanions have revealed precisely this type of bond alternation [7,8].

The bond alternation scheme just outlined does provide a selfconsistent interpretation of the ^{183}W NMR spectrum of I, yet it fails to account for the fact that the -78.3 ppm doublet for I lies downfield relative to the -98.83 ppm doublet for II reported in ref. 5. Since this downfield relationship cannot be accounted for by the influence of charge distribution on chemical shift values, we have addressed the question of whether the 20.5 ppm difference in chemical shifts represents a deficiency in our analysis or whether it simply reflects an extreme sensitivity of ^{183}W NMR chemical shift to environmental effects or a lack of sufficiently strict structural analogy between the compounds under consideration. First, environmental effects were probed by considering the spectra of anions I, II, and III in CD_3CN/DMF and comparing the observed chemical shifts with those obtained for I in CD_3CN and II and III in water. Data given in Table 1 show that the solvent effects are substantial, with the largest effect being observed for anion II whose chemical shift value is displaced 12.1 ppm by changing solvent and counterion. Second, the effect of structural variation was investigated by examining spectra of other polytungstates containing tungsten centers in the local environment depicted in Scheme 1a, namely, the β-$SiW_{12}O_{40}^{4-}$ (V) and $W_6O_{19}^{2-}$ (VI) anions (see Table 1). The large variation in observed chemical shift values demonstrates that charge distribution may be safely inferred from ^{183}W NMR chemical shift values only when a very strict structural analogy exists between the tungsten centers in question.

Acknowledgement

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