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^{183}W 2D NMR Assignments of All W–W Connectivities in Lacunary and in Vanadium(V)-Containing α_2-17-Tungstodiphosphates. Further Insights into Relation of Structure to ^{183}W Chemical Shifts

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All ^{183}W NMR signals and connectivities are unambiguously assigned by the 2D COSY spectrum of lacunary Wells–Dawson α_2-$[P_2W_{17}O_{61}]^{10-}$ and by the 2D INADEQUATE spectrum of monosubstituted Wells-Dawson α_2-$[P_2W_{17}VO_{62}]^{7-}$. These are the first 2D NMR studies of 17-tungsto species. The spectra show considerable differences from what might be expected on the basis of earlier results for substituted α-Keggin 11-tungsto species. The α_2 substitution in a Wells–Dawson structure apparently increases the electronic anisotropy for both structural types of W atoms adjacent to the substitution site more than is the case in monosubstituted α-Keggin complexes. The assignments for the 9-line spectrum of lacunary α_2-$[P_2W_{17}O_{61}]^{10-}$ confirm, with one minor interchange of assignments, those proposed previously on the basis of indirect evidence, but the spectrum of the V-substituted α_2-$[P_2W_{17}VO_{62}]^{7-}$ is completely different from that reported in an earlier paper. Since the latter spectrum was essential to the nearly correct assignment of the nine-line spectrum of the lacunary species, there is a strong possibility that another form of α_2-vanado-17-tungstodiphosphate exists, perhaps having an alkali-metal ion in the lacunary hole and a looser association of the vanadate.

This investigation unambiguously assigns all signals in the 2D ^{183}W NMR spectra of α_2-$[P_2W_{17}O_{61}]^{10-}$ and α_2-$[P_2W_{17}VO_{62}]^{7-}$, elucidating some issues presented by previous assignments for lacunary and monosubstituted derivatives of Keggin[1] and Wells–Dawson[2] heteropoly complexes. These are the first 2D ^{183}W NMR studies of 17-tungsto species. A hitherto unsuspected case for existence of a new but unclarified type of monosubstituted derivative is indicated.

Background

The original ^{183}W NMR work in our laboratory[3–7] indicated potentialities of the method and showed the power of simple integrated intensities to settle controversies and advance knowledge about polytungstates. Numerous important papers by others followed.[8] We elucidated various origins of ^{183}W NMR chemical shifts. Chemical shifts in Keggin species were correlated by the Jameson–Gutowsky equation.[6] It was proposed that magnitudes of chemical shifts in 17-tungsto and 11-tungsto lacunary species result from two factors:[3,6] "(1) The first is decreased availability of excited states in lacunary complexes with respect to their 18-tungsto and 12-tungsto parents, which provides a distinct upfield shift for all W's in the lacunary anion. (2) Superimposed on that effect is a downfield shift of approximately comparable magnitude for those W's that undergo an increase in electronic anisotropy owing to increased distortion of WO_6 octahedra introduced by removal of a nearby W atom." Thus it was proposed that the net effect produces minimal shift for W's near the vacancy and large upfield shifts for W's far from it. It was observed that quadrupolar ^{51}V in α_2-$[P_2W_{17}VO_{62}]^{7-}$ or α-$[PW_{11}VO_{40}]^{4-}$ greatly broadens ^{183}W NMR lines of W atoms adjacent to the substitution site.

The ^{183}W NMR spectrum of "α_2-$[P_2W_{17}VO_{62}]^{7-}$" presented in ref 6 is basically similar to that of α_2-$[P_2W_{17}O_{61}]^{10-}$, except that two lines of the lacunary anion's spectrum are missing from that of the V-substituted complex. All lines in the α_2-$[P_2W_{17}O_{61}]^{10-}$ spectrum were then assigned (1) by presuming that the two 2W lines arising from the four W's adjacent to the substitution site are broadened to invisibility by the V substitution and (2) by considering observed values of $^2J_{P\text{-}O\text{-}W}$ for the lacunary species and several related complexes. That original spectrum of α_2-$[P_2W_{17}O_{61}]^{10-}$ with the structure and that complete assignment of lines is shown in Figure 1 (upper spectrum).

Subsequently, Lefebvre et al.,[9] using a higher frequency spectrometer, observed, as ~7% satellites, $^2J_{W\text{-}O\text{-}W}$ homonuclear couplings in several heteropolytungstates. ^{183}W ($I = {}^1/_2$) has very convenient natural abundance (14.3%) for the much more powerful 2D methods, allowing unambiguous assignments of connectivities and of signals. COSY[10,11] and INADEQUATE[10,12] 2D NMR pulse sequences were applied by Domaille[13,14] and by Brevard et al.[15] to assign completely ^{183}W NMR spectra of several lacunary and transition-metal-substituted α-Keggin anions, which shed new light on origins of chemical shifts. It turned out that certain lacunary species (PW_{11}) and the Pb^{2+}-substituted Keggin structure follow the rules quoted above,[6] but lacunary $[SiW_{11}O_{39}]^{8-}$ and several other diamagnetic-transition-metal-substituted (Zn, Ti, V) Keggin structures do not.[13,14,16] It thus became evident that more data were needed to understand clearly ^{183}W NMR chemical shifts in these heteropolytungstates.

Experimental Section

A D_2O solution of α_2-$Na_{10}[P_2W_{17}O_{61}]$ was prepared from 0.7 M α-$Na_6[P_2W_{18}O_{62}]$ by the method previously described.[3,6] The solution's ^{183}W NMR spectrum (Figure 2) is identical to that previously described[6]

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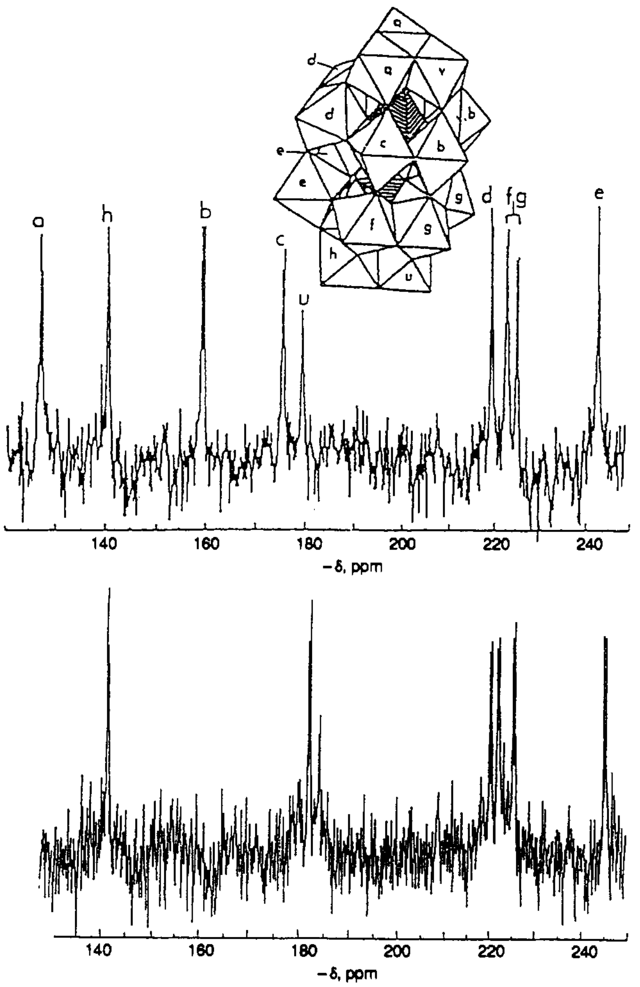

Figure 1. ^{183}W NMR spectra of 0.6 M α_2-$Na_{10}[P_2W_{17}O_{61}]$ in D_2O (upper spectrum) and of 0.46 M "α_2-$Li_7[P_2W_{17}VO_{62}]$" in D_2O (lower spectrum), each obtained on a Bruker WH/HFX-90 (Electromagnet) spectrometer and showing the structure of the α-$[P_2W_{18}O_{62}]^{6-}$ complex. [Reprinted with permission of ref 6. Copyright 1982 American Chemical Society.] Note the close correspondence of the two spectra except for the complete absence of lines a and b from the lower spectrum. In the structure shown, each vertex of a polyhedron locates the center of a close-packed O atom. The P atoms are at the centers of the interior hatched tetrahedra. Every octahedron contains a W atom. The α_2 isomer of lacunary $[P_2W_{17}O_{61}]^{10-}$ has a structure identical with that illustrated except that one W atom (labeled "v" in the figure) and its unshared O atom have been removed from the 3-fold W_3O_{13} cap on the top of the complex. α_2-$[P_2W_{17}VO_{62}]^{7-}$ also has the structure illustrated, except that a V^{5+} has replaced the one W^{6+} at site "v". The structurally unique W in the 17-tungsto derivatives is labeled "u" in the figure. Each member of a pair of structurally equivalent W's in the 17-tungsto derivatives is designated by a given letter, identical for those two W's. The lines in each spectrum are labeled with letters corresponding to the W's to which they were assigned in ref 6.

(Figure 1). This solution was used to obtain the COSY spectrum (Figure 2), using a Bruker WM 400 NMR spectrometer.

The potassium salt of α_2-$[P_2W_{17}VO_{62}]^{7-}$ was prepared from α_2-K_{10}-$[P_2W_{17}O_{61}]$ by reaction with $VOSO_4$ according to the method reported by Acerete[3] and by Harmalker et al.,[17] followed by Br_2 oxidation of V^{IV} to V^V. This was redissolved and converted to the more soluble lithium salt by a sulfonic acid type cation-exchange resin (Dowex 50), regenerated in the Li form, and washed as described previously.[18] Evaporation yielded crystals of the Li salt, which were dissolved in D_2O to form a 0.7 M solution. The INADEQUATE spectrum was obtained using a Bruker AM300 WB NMR spectrometer and the Mareci–Freeman–Turner modification[19] of the 2D INADEQUATE pulse sequence.

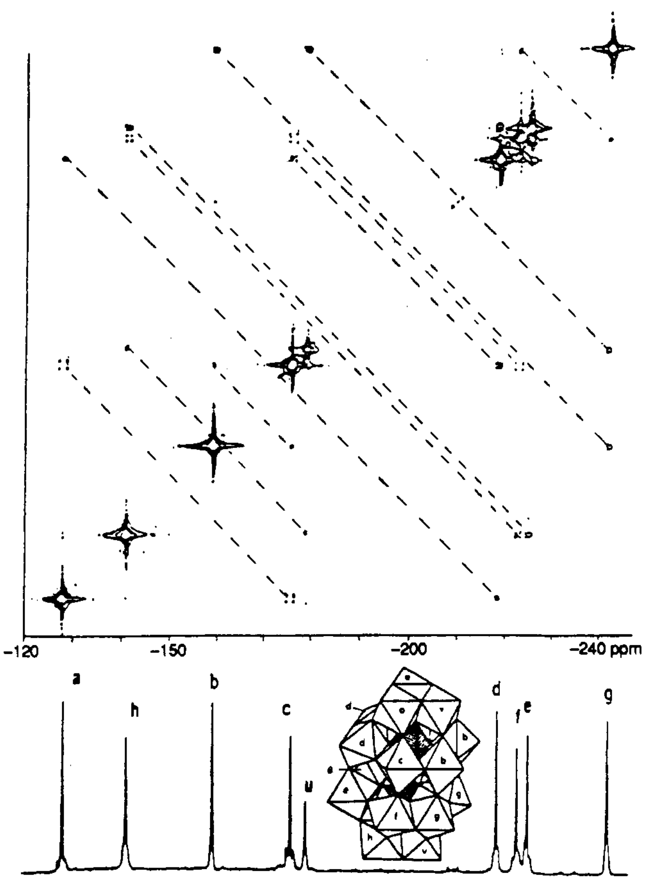

Figure 2. ^{183}W 2D COSY contour plot for α_2-$[P_2W_{17}O_{61}]^{10-}$ and the structure of that anion, obtained on a Bruker WM 400 NMR spectrometer. The connectivity pattern is shown by dashed lines. The peaks are labeled with letters corresponding to the W's to which they are assigned. Note that the assignment is identical to that given in Figure 1 except for interchange of W_e and W_g in the lower 6W belt. The experiment was run as 256 × 1K spectra (960 scans each) with negative (N) peak type selection. Data were apodized in both dimensions by a cosine-bell function. Temperature = 25 °C, total data collection time = 34 h.

Results

1. The ^{183}W 2D NMR COSY Experiment on α_2-$[P_2W_{17}O_{61}]^{10-}$. Figure 2 represents the COSY contour plot. The coupled W sites are easily detected via their square patterns. The designations of W atoms used in ref 6 and shown in Figure 1 are retained in the following discussion.

The structure has eight nonequivalent pairs of structurally identical W atoms plus a single structurally unique W. Its spectrum therefore has eight signals of equal intensity plus one signal having half that intensity. The signal from that unique W (W_u) at -179 ppm is easily assigned on the basis of intensity. It shows couplings to signals at -141 and -242 ppm, one of which must be from W_h and the other from W_g. Each of these shows two other connectivities: the signal at -141 ppm to the signals at -223 and -225 ppm and the signal at -242 ppm to the signals at -160 and -223 ppm. The signal at -223 ppm is then unambiguously assigned to W_f, which is the only W (besides W_u) to which both W_h and W_g are coupled. Of the two other signals showing couplings to the signals at -141 and -242 ppm (located at -160 and -225 ppm), one must be from W_b and the other from W_e. The signal at -160 ppm is unambiguously assigned to W_b because it shows only two connectivities (to the lines at -176 and -242 ppm) and clearly is *not* coupled to the signal of W_f. The signal at -225 ppm is then assigned to W_e. While the last signal shows only two connectivities clearly (to the lines at -219 and -141 ppm), its expected third connectivity (to the signal at -223 ppm) is not visible owing to the close proximity of these two peaks (at -223 and -225 ppm) and overlap of very intense diagonal signals with off-diagonal peaks. On the basis of the last two assignments, the signal at -242 ppm (coupled to the signal of W_b) is assigned to W_g, and the signal at -141 ppm

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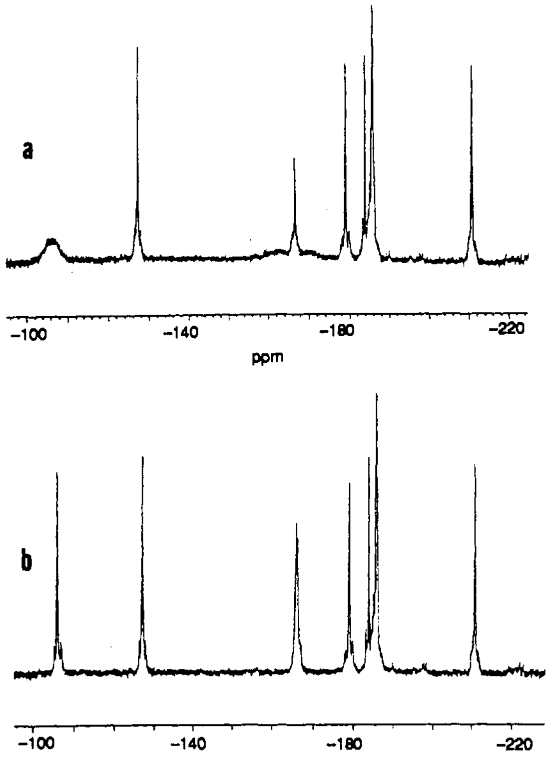

Figure 3. Spectra obtained on a Bruker AM 300WB NMR spectrometer: (a) ^{183}W NMR spectrum of 0.7 M α_2-Li$_7$[P$_2$W$_{17}$VO$_{62}$] in D$_2$O; (b) ^{51}V-Decoupled ^{183}W NMR spectrum of 0.7 M α-Li$_7$[P$_2$W$_{17}$VO$_{62}$] in D$_2$O. Conditions for each spectrum: 8192 scans, recycle delay 1 s (recycle delay plus acquisition time = ~5 s), temperature 25 °C. For spectrum b the CW decoupling power was 4 W.

(coupled to the signal of W$_e$) is assigned to W$_h$. Of the three remaining unassigned signals (at -128, -176, and -219 ppm) only one, at -176 ppm, is coupled to the signal of W$_b$, and so it is assigned to W$_c$. Finally the signal at -128 ppm is assigned to W$_a$, because it shows only two connectivities (to the signals of W$_c$ and W$_d$), and the signal at -219 ppm is assigned to W$_d$, on the basis of its two clearly visible connectivities to the signals of W$_c$ and W$_a$ and the third, less clearly visible, connectivity (owing to above-mentioned overlap of diagonal and off-diagonal peaks) to the signal of W$_e$.

The assignment is completely unambiguous, even though one connectivity (W$_e$-W$_f$) is not visible and one connectivity (W$_d$-W$_e$) is not very clearly visible. The missing connectivities are buried under diagonal signals and all other connectivities are completely self-consistent. The fact that edge-linked WO$_6$ octahedra produce markedly smaller W-O-W coupling constants ($J \approx 7$ Hz) than corner-linked WO$_6$ octahedra do ($J \approx 20$ Hz) may be used as an assignmnt tool.[12-14] The off-diagonal peaks originating from corner-sharing WO$_6$ octahedra appear as multiple patterns in the COSY contour plot, while the off-diagonal peaks originating from edge sharing WO$_6$'s appear as single signals. It is not, however, always possible to distinguish between "large" and "small" couplings in 2D contour plots of lacunary anions. Apparently, the changes in W-O-W angles (after removal of a W atom) are sufficient to make the two types of couplings more similar to each other, which can be seen clearly in the case of the W$_b$-W$_c$ and W$_a$-W$_d$ connectivities. The first connectivity originates from edge-sharing octahedra, while the latter represents corner-sharing octahedra. Both connectivities appear, however, as practically identical single peaks. It is worth noticing that both W$_a$ and W$_b$ are located as immediate neighbors to the vacancy. A similar phenomenon is observed, although the authors did not comment on it, in the connectivity pattern of Na$_7$[PW$_{11}$O$_{39}$].[15]

All connectivities and the complete assignment of peaks are shown in Figure 2. Comparison of Figures 1 and 2 reveals almost complete agreement between the earlier signal assignments for α_2-[P$_2$W$_{17}$O$_{61}$]$^{10-}$ and the certain assignment derived from the COSY experiment. Only one pair of signals needs to be interchanged (W$_e$ and W$_g$), which are those for W's far from the lacunary site. The original assignment of the nine lines was very good indeed in view of the fact that it was based on indirect evidence.

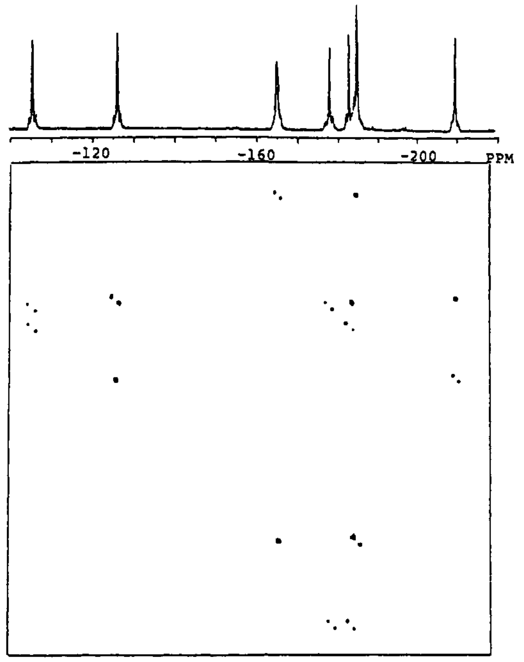

Figure 4. 2D INADEQUATE ^{183}W NMR spectrum of ^{51}V-Decoupled 0.7 M α_2-Li$_7$[P$_2$W$_{17}$VO$_{62}$] in D$_2$O run on a Bruker AM 300WB spectrometer. Run as 128 × 2K spectra (1792 scans each) with positive (P) peak type selection. D1 relaxation delay was such that AQT + D1 = 1.5 s, the matrix was symmetrized, FID data were processed with apodization by a square sine-bell function in the F2 dimension (SSB2 = 4.0), there was no apodization in F1 dimension, and total data collection time = ~91 h.

2. ^{183}W NMR and ^{51}V-Decoupled ^{183}W NMR Spectra of α_2-[P$_2$W$_{17}$VO$_{62}$]$^{7-}$. The ^{183}W NMR spectrum of 0.7 M α_2-[P$_2$W$_{17}$VO$_{62}$]$^{7-}$ in D$_2$O is shown in Figure 3a. The spectrum consists of seven sharp lines at chemical shifts -127.4, -166.6, -179.9, -184.2, -186.0, -186.3, and -211.2 ppm, with the integration ratios 2:1:2:2:2:2:2, and two much broader lines: one clearly visible at chemical shift ≈-106 ppm ($\Delta\nu_{1/2} \approx 70$ Hz) and the other broadened almost to unobservability at ≈-166 ppm. Each sharp line is a doublet owing to ^{31}P-O-^{183}W coupling. The lines at -186.0 and -186.3 ppm partially overlap but are clearly distinguished as a pair of doublets when the spectrum is expanded. ^{51}V decoupling (frequency = 78.9002 MHz) sharpens both broad signals (Figure 3b). The signal at -166.2 ppm overlaps with the signal at -166.6 ppm. The overlapping signals integrate as three tungstens.

The two signals which sharpen after ^{51}V decoupling (at -106.3 and -166.2 ppm) are assigned to the W atoms adjacent to the substitution site. These signals are broadened in the undecoupled spectrum by interaction with quadrupolar ^{51}V.

3. 2D NMR INADEQUATE Study of α_2-[P$_2$W$_{17}$VO$_{62}$]$^{7-}$. Figure 4 shows the 2D INADEQUATE ^{183}W NMR spectrum of ^{51}V-decoupled α_2-Li$_7$[P$_2$W$_{17}$VO$_{62}$]. Single-quantum transitions along the diagonal are not visible, and only off-diagonal peaks which represent coupling between corresponding signals show up on the contour plot. The magnitudes of the $^2J_{\text{W-O-W}}$ values are clear from the contour map because the edge couplings appear as unresolved "ovals" owing to their large line widths, whereas the stronger corner couplings produce "dumbbells" for all four resolved components of the AX spin system. The same phenomenon was observed previously for transition-metal-substituted Keggin heteropoly tungstates.[13,15]

The signal from the unique W$_u$, at -166.6 ppm, is easily assigned by its intensity in the undecoupled spectrum. One of the two signals broadened by the presence of ^{51}V (at -106.3 and -166.2 ppm) must belong to W$_a$ and the other to W$_b$. The signal at -106.3 ppm is assigned to W$_a$ because it shows two "large" couplings (to signals at -179.3 and -184.2 ppm). The couplings of the signal located at -166.2 ppm are indistinguishable from couplings of W$_u$ (-166.6 ppm) because these two signals are located too close to each other. Additionally, both W$_u$ and W$_b$ are expected to show coupling to W$_g$. Two expected couplings of W$_u$

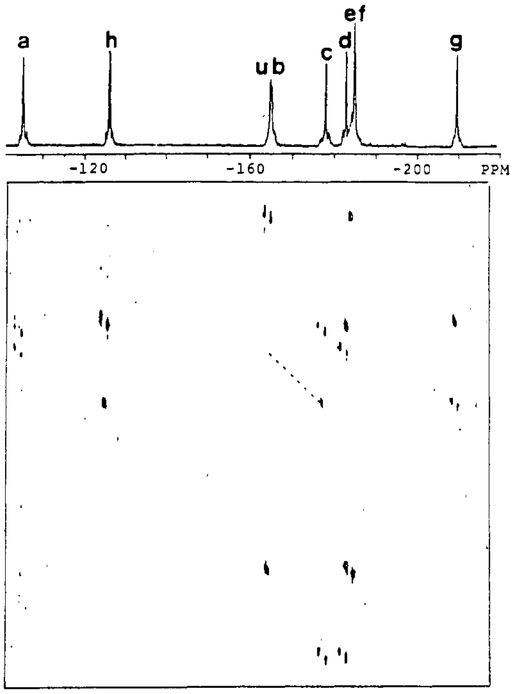

Figure 5. Same as for Figure 4 except 2D data were processed without symmetrization. The peaks are labeled with letters corresponding to the labeling in Figures 1 and 2.

(one "large", to the signal at −211.2 ppm, and one "small", to the signal at −127.4 ppm) are observed. No additional coupling of W_b is observable in the *symmetrized* INADEQUATE contour plot, but after processing of the data *without* symmetrization of the matrix, half of the missing connectivity does appear on the contour plot (Figure 5) as the "oval" at chemical shift −179.9 ppm. This connectivity is identified as W_b–W_c and is indicated in Figure 5 by a dashed line. The reason for the unsymmetrical appearance of that connectivity is incomplete ^{51}V decoupling from W_b, which is corner-shared to vanadium. Domaille[14] recently found that V–O–W coupling is 2–3 times larger for corner-sharing VO_6 and WO_6 octahedra than for edge-sharing octahedra, and INADEQUATE plots of vanadium-substituted Keggin heteropoly anions show only "halves" of expected couplings for tungsten atoms which share only one oxygen with vanadium (corner sharing). The second expected coupling of W_b (to W_g) coincides with one of the couplings of W_u. The pair of "dumbbells" at chemical shifts of W_b and W_u and at −211.2 ppm identifies the signal at −211.2 ppm as belonging to W_g. Next, the signal at −127.4 ppm (through its "small" coupling to W_u) is identified as W_h, and the signal at −184.2 ppm is assigned to W_d, based on its observed couplings to W_a and W_c. The two overlapping signals at −186.0 and −186.3 ppm are assigned to W_e and W_f. The signals are too close to be separately assigned unambiguously. Out of thirteen expected connectivities only one, between W_c and W_f, is not visible on the contour plot, possibly because of overlap with W_c–W_d connectivity. (Owing to the very similar chemical shifts of W_d and W_e, the connectivity between those two W's shows as a single "oval" *midway* between their chemical shifts *on the diagonal*, representing a very characteristic AB pattern. See Figure 4.)

Conclusions

The two-dimensional connectivity studies presented herein yield the first direct assignments of ^{183}W signals in 17-tungsto lacunary or transition-metal-substituted Wells–Dawson heteropoly anions. Assignment of ^{183}W NMR signals in the α_2 lacunary anion by the COSY 2D method confirmed the assignment of Acerete et al.[3,6] with only one minor pair of signals interchanged.

The 2D INADEQUATE study of vanadium-substituted α_2-17-tungstodiphosphate shows *both* pairs of W atoms near the substitution site (corner- *and* edge-sharing with vanadium) to have been shifted *downfield* relative to the unsubstituted Wells–Dawson anion (α-$[P_2W_{18}O_{62}]^{6-}$). Edge-sharing tungstens are shifted by ≈22 ppm (from −128.1 to −106.3 ppm), and corner-sharing tungstens are shifted by ≈8 ppm (from −173.8 to −166.2 ppm). This effect was explained by Acerete et al.[3,6] for lacunary α_2-$[P_2W_{17}O_{61}]^{10-}$ as arising from an increase in electronic anisotropy for the W atoms near the vacancy. The results presented herein confirm that vanadium substitution in a Wells–Dawson anion increases electronic anisotropy for *both* types of W's near the substitution site.

The 2D INADEQUATE studies of transition-metal-substituted α-Keggin heteropoly anions[13-16] showed, however, that it is only edge-sharing W's that are shifted downfield relative to the unsubstituted α-Keggin species. Corner-sharing W's *always* shift upfield in α isomers of $[PW_{11}VO_{40}]^{4-}$, $[SiW_{11}VO_{40}]^{5-}$, $[BW_{11}VO_{40}]^{6-}$, $[PW_{11}TiO_{40}]^{5-}$, $[PW_{11}Zn(H_2O)O_{39}]^{5-}$, and $[SiW_{11}Zn(H_2O)O_{39}]^{6-}$. The only anion that showed corner-sharing W's shifting downfield was $[PW_{11}Pb(H_2O)O_{39}]^{5-}$, but W atoms corner-sharing with Pb^{2+} in this compound are believed[15] to be involved in some kind of dynamic exchange process and the geometry of the substitution site[20] is completely different from that of all other substituted Keggin anions).

These observations clearly show the difference in ^{183}W NMR chemical shift patterns in mono(transition-metal)-substituted (including vanadium) α-Keggin species versus monovanadium-substituted α_2-Wells–Dawson heteropoly complexes. Apparently, the electronic anisotropy term is larger for W atoms sharing corners with transition-metal atoms in α_2-Wells–Dawson anions than it is in α-Keggin anions. More experimental data are needed, however, before further conclusions can be drawn.

An Unresolved Problem

The 25 °C ^{183}W NMR spectrum of α_2-$[P_2W_{17}VO_{62}]^{7-}$ reported herein does not match the 25 °C spectrum reported for that complex by Acerete et al.[3,6] (Figure 1, lower spectrum). The complex prepared in that investigation was therefore not identical to the α_2-$[P_2W_{17}VO_{62}]^{7-}$ used in the present work. It is striking, however, that the ^{183}W NMR spectrum of the vanadium compound prepared by Acerete et al. was essential in leading those authors to almost faultless assignment of all nine signals in the lacunary species,[6] α-$[P_2W_{17}O_{61}]^{10-}$ (Figure 1, upper spectrum). It is very improbable that this could have happened fortuitously.

This situation leads to the conclusion that there are probably two α_2-17-tungstovanado derivatives which can result from reaction with the lacunary species. One gives a spectrum closely related to, but somewhat different from, that of the α_2 lacunary complex, but missing the two lines (a and b, Figure 1) for the two pairs of W atoms adjacent to the V substitution site). Compare the spectra in Figure 1. The other complex gives an entirely different spectrum which also has two 2W lines broadened almost to nonobservability. Possibly, the vanadium in the first complex is located close enough to the lacunary site to broaden specifically the signals from the two pairs of adjacent W atoms but too far away to affect very greatly the chemical shift pattern of all the remaining lines. Another possibility would involve an exchange mechanism for the vanadium, perhaps similar to that postulated[15,20] for $[PW_{11}Pb(H_2O)O_{39}]^{5-}$.

In each investigation the vanadium complexes were prepared in a similar way,[17] from a solution of the lacunary α_2-17-tungstodiphosphate. The products in the two cases are extremely similar, both being microcrystalline salts of the same shade of yellow and both being soluble and recrystallizable. Several subsequent attempts to prepare another sample which gives the first-reported spectrum have all led only to the α_2-$[P_2W_{17}VO_{62}]^{7-}$ species reported herein. The preparative attempts involved (1) reacting the lacunary complex with vanadate and (2) reaction of the lacunary species with vanadyl (followed by oxidation of V(IV)), as used in the present work.

Contant and Ciabrini[21] have concluded that lacunary sites may

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(21) A recent paper,[22] submitted a year subsequent to this one, presents a correct undecoupled 1D ^{183}W NMR spectrum of α_2-$[P_2W_{17}VO_{62}]^{7-}$ and gives some partially substantiated speculations about assignments of groups of lines (based on coupling constants) and about directions of chemical shift changes in substituted Wells–Dawson species as contrasted with substituted Keggin complexes. Because our work in the present paper unambiguously assigns all lines as well as presenting the V-decoupled spectrum, its reasoning and conclusions on these points are fully established.

be variously filled, or associated with, different alkali-metal ions, forming equilibrium mixtures between such adducts and true lacunary species. The preparations involved in the present work and in that reported earlier by Acerete et al.[6] have involved a variety of concentrations of K^+, Na^+, and Li^+ ions at various stages. There may be conditions where a V atom or a vanadate attaches to an alkali-metal-containing lacunary differently from the way it attaches to a true lacunary. We have not investigated possible effects of various concentrations of different alkali-metal ions during the preparation.

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Registry No. ^{183}W, 14265-81-7; α_2-$[P_2W_{17}O_{61}]^{10-}$, 12412-89-4; α_2-$[P_2W_{17}VO_{62}]^{7-}$, 85585-35-9.

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Bond-Stretch Isomers of Transition-Metal Complexes. Do They Exist?

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The existence of bond-stretch isomers of transition-metal complexes and the electronic mechanisms explaining these isomers are investigated with ab initio calculations. For $(LWOCl_2)^+$ (L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane) complexes, only the $^2A'$ state can be identified as a ground state. $^2A''$ is an excited state, and the orbital crossing mechanism cannot explain the occurrence of two stable isomers. For *cis-mer*-$MoOCl_2(PR_3)_3$ complexes, the second-order Jahn-Teller effect is too weak to cause the bond-stretch phenomenon. On both molecular systems, our calculations support the structure of the blue "isomer" as the stable compound and preclude the existence of any other isomer with a long M-O bond and similar energy.

Introduction

The term "bond-stretch isomerism" was proposed by Jean et al.[1] to describe complexes that have the same composition and geometry but differ only in the length of certain bonds. This phenomenon was first reported for the blue and green crystal structures of *cis-mer*-$MoOCl_2(PR_3)_3$.[2,3] The main differences between these two isomers are in the lengths of the Mo-O and Mo-$Cl_{(\text{trans-to-O})}$ bonds (Figure 1). Since only the blue isomer was observed in solution, it appeared that the stability of the green one in the solid phase was simply caused by a packing effect. The recent discovery of the blue and green structures of $(LWOCl_2)^+$ complexes (L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane),[4] where the W isomers differ most significantly in the W-O bond length (Figure 2), seems to belie these explanations. Both isomers appear to be stable in acetonitrile solution, as well as in the solid state.

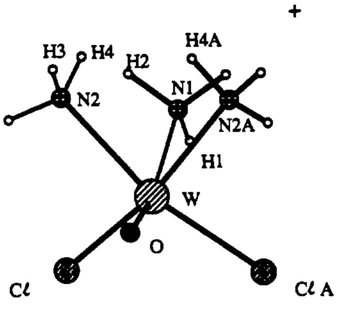
Two electronic mechanisms were proposed to explain these results.[1] "A real electronic crossing of filled and empty orbitals"[1] was used to explain the existence of the W isomers, which are d^1 transition-metal complexes. "The reorganization of the d-π bonding through a second-order Jahn-Teller effect"[1] was proposed to explain the structures of the Mo isomers, which are d^2 transition-metal complexes. These two explanations were supported by extended Hückel calculations.[1] This work promoted us to determine if these explanations could also be supported by ab initio calculations.

At first our inability to reproduce the experiment results with ab initio methods lead us to look for inadequacy in the method. Thus, we explored a variety of model ligands, since most of the experimental results have ligands which are too large for accurate calculations. We also explored partial vs full geometry optimizations, basis sets, and various levels of electron correlation. Finally, we began to question the experimental results.

In the recently reported reexamination of the crystallography of the Mo isomers, Yoon, Parkin, and Rheingold found that the "bond-stretch" phenomenon in the Mo systems is due to a composition disorder.[5] Only the blue "isomer" corresponds to pure $Mo(PMe_2Ph)_3OCl_2$, while the green "isomer" is the compound contaminated with $Mo(PMe_2Ph)_3Cl_3$. Although most of our calculations were completed when we received a preprint of ref 5, the work gave us sufficient courage to describe briefly our most critical calculations. These calculations confirm the results of Yoon et al. on the d^2 Mo complexes[2] and suggested that a similar problem exists for the d^1 W complexes.[4]

Calculational Details

Three model compounds were used. For the tungsten isomers, the model compound is **1**, where three NH_3 groups were used to substitute *N,N',N''*-trimethyl-1,4,7-triazacyclononane. Model compounds **2** and **3** were used to examine the experimental structures of the molybdenum isomers and the second-order Jahn-Teller effect, respectively. PH_3 ligands were substituted for the PR_3 ligands found in the actual complexes. In the three models, the NH_3 and PH_3 groups were fixed by using



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