

an electrophilic attack to give the final chlorin product. Attempts are now underway to see if this is a general phenomenon for TPP complexes or is limited only to the case of reduced (TPP)Ru(CO).

Acknowledgment. The support of the National Science Foundation (Grant CHE-8515411) is gratefully acknowledged. We also acknowledge several helpful discussions with Royal B. Freas about the mass spectral data.

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Two-Dimensional ^{17}O - ^{51}V Heteronuclear Shift Correlation NMR Spectroscopy of the ^{17}O -Enriched Inclusion Complex $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$. Relationship of Cross-Peak Intensity to Bond Order

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Received September 13, 1990

Introduction

Two-dimensional NMR experiments are invaluable for the determination of molecular structures in solution,¹ and these techniques are most frequently applied to molecules possessing ^1H and ^{13}C nuclei. However, these methods are not limited to only spin $1/2$ nuclei in organic systems, as 2-D NMR techniques have also been applied to half-integer quadrupolar nuclei ($I > 1/2$) in order to characterize the structure of inorganic clusters in solution. For example, ^{11}B - ^{11}B ($I = 3/2$) homonuclear shift correlation spectroscopy (COSY) has been used to determine B-B connectivities in polyhedral boranes² and ^{51}V - ^{51}V ($I = 7/2$) COSY experiments have yielded connectivity patterns in $\text{V}_{10}\text{O}_{32}^{6-}$ and $\text{PV}_{14}\text{O}_{42}^{9-}$.³ Furthermore, it was noted in the borane study that ^{11}B - ^{11}B COSY cross-peaks are usually absent (or very weak) for nearest-neighbor boron atoms connected by a bridging hydrogen. Thus, cross-peak intensity provides information about the bonding in borane clusters.

This work demonstrates that heteronuclear shift correlation spectroscopy (HETCOR) is also feasible for half-integer quadrupolar nuclei by applying the technique to the ^{17}O -enriched inclusion complex $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$.⁴ The results not only allow the assignment of the ^{17}O ($I = 5/2$) and ^{51}V ($I = 7/2$) NMR resonances to the known crystal structure⁴ but also provide information about the nature of the various O-V bonds in the cluster on the basis of observed cross-peak intensities.

The idealized structure of the $\text{V}_{12}\text{O}_{32}^{4-}$ cluster is represented in Figure 1. The pseudo- C_4 axis is normal to the page as indicated. The vanadium and oxygen atoms are labeled to reflect the number of distinct peaks observed in 1-D ^{51}V and ^{17}O NMR spectra⁵ that agree with the approximate C_{4h} symmetry of the cluster.⁴ The structure is like a basket with four vanadium atoms (labeled V_1) in the bottom and eight vanadium atoms (V_2 and V_3) around the rim. Every vanadium atom has a terminal oxygen bonded to it. The four vanadiums in the bottom are connected via four doubly bridging oxygens (O_2), and the eight vanadiums in the rim are connected by eight doubly bridging oxygens (O_4). The vanadiums in the rim are connected to the vanadiums in the bottom by eight triply bridging oxygens (O_3). Thus, the ^{17}O - ^{51}V HETCOR spectrum is expected to yield many cross-peaks as a result of the different types of O-V bonds.

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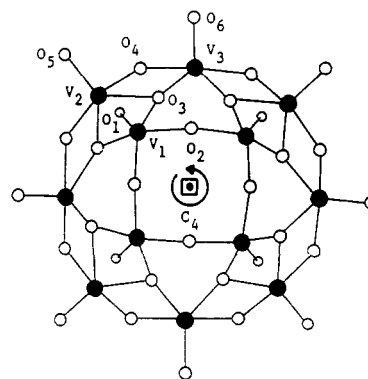


Figure 1. Idealized structure of the $\text{V}_{12}\text{O}_{32}^{4-}$ cluster showing the atom-numbering scheme. For clarity, the structure has been "flattened out". A perspective plot of the cluster can be found in ref 5.

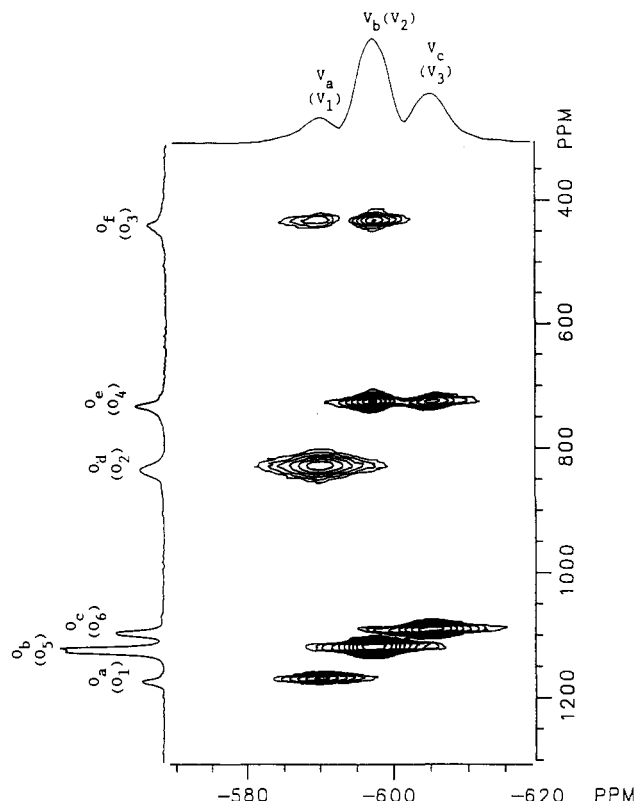


Figure 2. Contour plot of the ^{17}O - ^{51}V HETCOR NMR spectrum obtained for $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$ along with projections across the ^{17}O and ^{51}V frequency axes showing the peak-labeling scheme. Atom assignments to the structure in Figure 1 are given in parentheses.

Experimental Section

The 10% ^{17}O -enriched $[\text{CH}_3\text{CN}\cdot(\text{V}_{12}\text{O}_{32}^{4-})]$ inclusion cluster was dissolved in CD_3CN , and the solution was transferred to a 10-mm NMR tube under nitrogen. The ^{17}O - ^{51}V HETCOR experiment⁶ was performed on a General Electric GN300WB spectrometer utilizing a custom-built 10-mm ^{17}O frequency probe (General Electric) possessing a broad-band (^{93}Nb - ^{51}V) decoupling channel. The very basic pulse sequence $[\pi/2-(^{51}\text{V})](t_1)-[\pi/2(^{51}\text{V})][\pi/2(^{17}\text{O})](t_2)$ acquire ^{17}O was used without phase cycling. The observation frequencies for ^{17}O and ^{51}V were 40.7 and 78.9 MHz, respectively. A sweep width of 62 500 Hz (dwell time 16 μs) was

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used in the ^{17}O (t_2) dimension, and a sweep width of 20 000 Hz (dwell time 50 μs) was used in the ^{51}V (t_1) dimension. There were 256 time increments, and 2048 data points were collected during acquisition. A total of 512 scans were averaged for each time increment, with a 0.4-s delay between acquisitions. The t_1 dimension was zero-filled to 512 points before the Fourier transform. An exponential line broadening of 50 Hz was used in the t_2 dimension, and 100 Hz was used in the t_1 dimension. The ^{17}O chemical shifts are referenced to tap water (0 ppm), and the ^{51}V chemical shifts are referenced to neat VOCl_3 (0 ppm).

Results

A contour plot of the ^{17}O - ^{51}V HETCOR experiment is shown in Figure 2. Projections of the data across the ^{17}O and ^{51}V frequency axes are included in the figure and show the peak labeling scheme used for the following discussion. The intensities of the peaks in the projections are distorted with respect to the normal 1-D ^{17}O and ^{51}V NMR spectra, which will be discussed later in the text.

Discussion

The structure assignment can be made by starting with the O_d resonance in the bridging region of the spectrum, which only shows a single cross-peak with the V_a resonance as expected from the structure. A relative intensity of 4 is observed for the O_d resonance in the 1-D ^{17}O spectrum, verifying this initial assignment. Thus, the V_a resonance is assigned to vanadium atom V_1 in the "bottom" of the basket structure. The O_d resonance is assigned to the connecting O_2 double bridges, and the other V_a resonance cross-peak indicates that the O_a signal is due to the terminal O_1 oxygens attached to the V_1 vanadiums. The V_a resonance also shows a weak cross-peak with the O_f resonance, indicating that O_f is the triply bridging resonance due to O_3 in the structure. The O_f resonance has a relative intensity of 8 in the 1-D ^{17}O spectrum, as expected for the eight triply bridging oxygens; however, only two cross-peaks with vanadium resonances are observed instead of three. It should be noted that even if all three cross-peaks were observable, the V_2 and V_3 vanadiums could not be assigned due to their similar connectivities. In order to complete the assignment, factors affecting cross-peak intensities need to be considered.

In an earlier study by Grimes et al.,^{2b} 2-D ^{11}B COSY NMR spectroscopy was utilized to make ^{11}B NMR assignments in boron cage structures. The workers specified four conditions for the observation of cross-peaks in 2-D experiments: (1) enough electron density must be present between the two nuclei to allow scalar coupling, (2) the two nuclei must not be decoupled by a T_1 that is short compared to the reciprocal of the coupling constant (i.e., $2\pi J T_1 \ll 1$), (3) T_2 values must be long enough to allow the cross-peaks to be detected during t_2 , and (4) the individual peaks must be resolvable in 1-D spectra. The results of 1-D $^{17}\text{O}\{^{51}\text{V}\}$ selective decoupling experiments⁵ demonstrate that resonances are observed for each crystallographically distinct oxygen and vanadium atom and that the ^{17}O signals are broadened by ^{51}V coupling. In fact, ^{51}V splitting can be observed in two of the terminal ^{17}O signals (O_b and O_c) in 1-D spectra. These observations indicate that conditions 1 and 4 above are met. Additionally, all the ^{17}O and ^{51}V resonances are relatively sharp, so that T_2 should not prevent cross-peak observation during t_2 . Thus, the amount of electron density between the ^{17}O - ^{51}V pairs should be the major factor controlling cross-peak intensity. In other words, the absence of an observable cross-peak between an ^{17}O - ^{51}V pair would suggest the absence of sufficient electron density to yield a sufficiently strong coupling.

In the $\text{V}_{12}\text{O}_{32}^{4-}$ structure, weak internuclear electron density would most likely be present around the triply bridging oxygens due to their reduced bond order. The expected trend in cross-peak intensity with respect to bond order is present in the 2-D ^{17}O - ^{51}V HETCOR spectrum and is more easily seen in a stack plot of the data shown in Figure 3. Although individual cross-peak intensities within a group can vary significantly, the overall trend for terminal, doubly bridging, and triply bridging cross-peak intensity is clear. The most intense cross-peaks occur for the terminal ^{17}O - ^{51}V bonds (especially for the terminal ^{17}O resonances, which exhibit ^{51}V splittings), the next intense for doubly bridging ^{17}O - ^{51}V bonds,

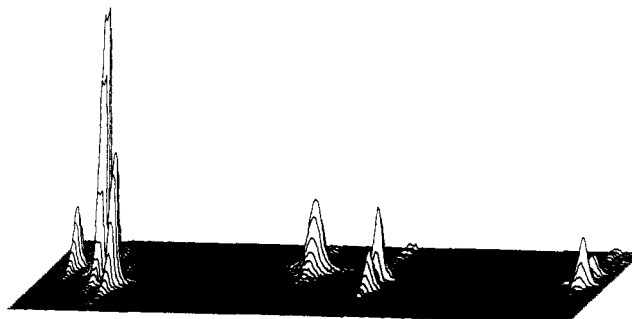


Figure 3. Stack plot representation of the ^{17}O - ^{51}V HETCOR NMR spectrum of $[\text{CH}_3\text{CNC}(\text{V}_{12}\text{O}_{32}^{4-})]$.

and the weakest for triply bridging ^{17}O - ^{51}V bonds. In fact, as noted earlier, one of the ^{17}O - ^{51}V cross-peaks is missing for one of the triply bridging bonds. However, the triply bridging bond lengths do not differ by more than ca. 0.04 Å. Thus, the absence of one of the triply bridging cross-peaks is not expected from bond length considerations alone.

An assumption can be made that maximum orbital overlap occurs between oxygen and vanadium for a tetrahedral V-O-V bonding angle. Inspection of the various V-O-V angles around the triply bridging oxygen shows that a nearly tetrahedral angle of ca. 104° is present in the $\text{V}_2\text{-O}_3\text{-V}_1$ bonds. Therefore, favorable orbital overlap is predicted between O_3 and V_1 . This observation is consistent with the observed cross-peak for the triply bridging oxygen in the HETCOR experiment. Favorable overlap is also expected between V_2 and O_3 , which allows the assignment of the V_b resonance to V_2 on the basis of the observed cross-peak for this resonance. This results in the assignment of V_c to V_3 . The angles $\text{V}_3\text{-O}_3\text{-V}_1$ (ca. 148°) and $\text{V}_3\text{-O}_3\text{-V}_2$ (ca. 95°) would not permit a good overlap between V_3 and O_3 , which accounts for the lack of an observable cross-peak. Thus, O_3 is not a perfect triply bridging oxygen and most of the electron density is skewed toward V_2 and V_1 in the structure.

The last assignments of the oxygen resonances, O_b , O_c , and O_e , to the terminal O_5 , O_6 , and doubly bridging O_4 oxygens, respectively, can be made on the basis of the observed cross-peaks with the assigned vanadium resonances. The NMR assignments are indicated in parentheses in Figure 2.

Conclusion

In conclusion, ^{17}O - ^{51}V HETCOR NMR spectroscopy has enabled the assignments of the ^{17}O and ^{51}V NMR resonances in accord with the known crystal structure of the ^{17}O -enriched inclusion complex $[\text{CH}_3\text{CNC}(\text{V}_{12}\text{O}_{32}^{4-})]$. The intensities of the observed cross-peaks in the experiment depend on the bond order, with the largest cross-peaks occurring for terminal O-V bonds, the next most intense for doubly bridging O-V bonds, and the weakest for triply bridging O-V bonds, thus providing information about the bonding within the cluster.

It should be emphasized that T_2 (or more appropriately T_2^*) is an important consideration in determining the feasibility of the experiment described in this work, as quadrupolar nuclei notoriously yield broad signals (i.e., short T_2). For best results, the J couplings between the nuclei of interest must be large enough to permit cross-peak detection during t_2 (which will be limited due to short T_2 's). The ideal case is $J \geq T_2^{-1}$.

As is normally done in ^1H - ^{13}C HETCOR experiments, improvements could be made to the basic pulse sequence used in this work to include heteronuclear decoupling during t_1 and t_2 to yield narrower line widths and appropriate phase cycling to avoid unwanted axial peaks and allow for quadrature detection in ν_1 . This technique should prove useful in characterizing larger, more complex transition-metal clusters, many of which contain half-integer quadrupolar nuclei in their frameworks.

Acknowledgment. I thank Professor Walter Klemperer and Mr. Omar Yaghi for the ^{17}O -enriched $[\text{CH}_3\text{CNC}(\text{V}_{12}\text{O}_{32}^{40-})]$ sample and also for many helpful discussions. Discussions with Dr. Vera Mainz are also gratefully acknowledged.

Registry No. $[\text{CH}_3\text{CNC}(\text{V}_{12}\text{O}_{32}^{4-})]$, 132699-16-2; ^{17}O , 13968-48-4; ^{51}V , 7440-62-2.

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Intramolecular O-H...Cl Hydrogen Bonding in Titanium Chloride Alkoxides of the Formula $[\text{TiCl}_2(\text{OCH}_2\text{CH}_2\text{X})_2\cdot\text{HOCH}_2\text{CH}_2\text{X}]_2$ (X = Cl, Br, I). Crystal Structure of $[\text{TiCl}_2(\text{OCH}_2\text{CH}_2\text{Cl})_2\cdot\text{HOCH}_2\text{CH}_2\text{Cl}]_2$

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Received October 29, 1990

Despite the fact that titanium alkoxides have been known for over 50 years, relatively little is known about their molecular geometries due to a paucity of structural data.¹ The limited solid-state studies that are available point to an impressive array of possible molecular compositions, including polymers,^{1,2a} hexamers,^{2b} tetramers,^{2c} dimers,^{3,4} and monomers.^{1,5} The general picture is further clouded by the existence of complex equilibria that can occur *in solution*.⁶ As part of our program relating to the development of new routes to early-transition-metal materials, we have been exploring the synthesis of new titanium complexes that contain oxygen ligands. We now report the preparation and properties of titanium chloride alkoxides of the general formula $[\text{TiCl}_2(\text{OCH}_2\text{CH}_2\text{X})_2\cdot\text{HOCH}_2\text{CH}_2\text{X}]_2$ (X = Cl, Br, I), which exist as dimers in the solid state. The dimeric structure appears to be strongly favored by intramolecular O-H...Cl hydrogen bonding, which constitutes a general structural feature of these complexes.

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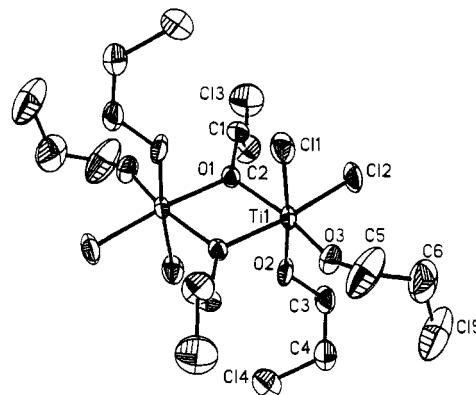


Figure 1. Perspective view of **1**.

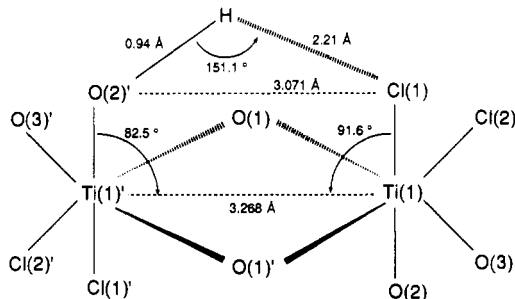


Figure 2. Bond lengths and angles about the Ti_2O_2 core of **1**.

Table I. Crystallographic Data for **1**

chem formula	$\text{C}_{12}\text{H}_{26}\text{Cl}_{10}\text{O}_6\text{Ti}_2$	fw	716.67
<i>a</i> , Å	8.9659 (7)	space group	<i>P1</i>
<i>b</i> , Å	9.2748 (8)	<i>T</i> , °C	15
<i>c</i> , Å	10.515 (1)	λ , Å	1.54178
α , deg	98.186 (7)	ρ_{calc} , g cm ⁻³	1.667
β , deg	111.001 (7)	μ , cm ⁻¹	139.0
γ , deg	112.435 (6)	transm coeff	0.493-0.160
<i>V</i> , Å ³	714.0 (1)	<i>R</i> (F_o)	0.061
<i>Z</i>	1	<i>R</i> _w (F_o)	0.070

Table II. Bond Lengths and Angles for **1**

Ti(1)-C(1)	2.326 (2)	C(1)-C(2)	1.499 (8)
Ti(1)-Cl(2)	2.284 (2)	C(2)-Cl(3)	1.754 (6)
Ti(1)-O(1)	2.087 (5)	O(2)-C(3)	1.455 (9)
Ti(1)-O(2)	2.102 (4)	C(3)-C(4)	1.48 (1)
Ti(1)-O3	1.746 (5)	C(4)-Cl(4)	1.78 (1)
Ti(1)-O(1)'	1.956 (4)	O(3)-C(5)	1.41 (1)
O(1)-C(1)	1.440 (6)	C(5)-C(6)	1.40 (2)
Ti(1)···Ti(1)'	3.268 (3)	C(6)-Cl(5)	1.73 (1)
O(2)···Cl(1)'	3.071 (6)		
Ti(1)-O(1)-C(1)	127.3 (4)	O(1)-Ti(1)-O(2)	86.0 (2)
Ti(1)-O(1)-Ti(1)'	107.9 (1)	O(1)-Ti(1)-O(3)	170.3 (2)
Ti(1)-O(2)-C(3)	130.9 (5)	O(1)-Ti(1)-O(1)'	72.1 (2)
Ti(1)-O(3)-C(5)	154.2 (4)	O(1)-C(1)-C(2)	108.7 (4)
Cl(1)-Ti(1)-Cl(2)	95.50 (7)	C(1)-O(1)-Ti(1)'	124.3 (5)
Cl(1)-Ti(1)-O(1)	88.5 (1)	C(1)-C(2)-Cl(3)	110.7 (4)
Cl(1)-Ti(1)-O(2)	174.0 (2)	O(2)-Ti(1)-O(3)	93.4 (2)
Cl(1)-Ti(1)-O(3)	91.6 (1)	O(2)-Ti(1)-O(1)'	81.8 (2)
Cl(1)-Ti(1)-O(1)'	94.3 (1)	O(2)-C(3)-C(4)	111.0 (6)
Cl(2)-Ti(1)-O(1)	91.7 (1)	C(3)-C(4)-Cl(3)	111.7 (7)
Cl(2)-Ti(1)-O(2)	87.0 (1)	O(3)-Ti(1)-O(1)'	98.2 (2)
Cl(2)-Ti(1)-O(3)	98.0 (2)	O(3)-C(5)-C(6)	114.9 (7)
Cl(2)-Ti(1)-O(1)'	160.8 (1)	C(5)-C(6)-Cl(5)	116.5 (7)
O(2)-H(O(2))···Cl(1)'	151.1 (4)		
Cl(1)-Ti(1)···Ti(1)'	91.61 (8)		
O(2)-Ti(1)···Ti(1)'	82.5 (2)		

Results and Discussion

In the course of our studies pertaining to the deposition of titanium dioxide thin films, we required titanium complexes that contained both chloride and alkoxide ligands. Our attention was