

nance of the carbonyl groups trans to the hydride. At ambient temperature the two signals assigned to the in-plane carbonyl groups collapse, indicating exchange of these four ligands. This is in contrast to the osmium analogues $\text{Os}_3(\mu\text{-H}, \mu\text{-X})(\text{CO})_{10}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SEt}, \text{etc.}$) in which polytopal rearrangement of the carbonyl groups on the unique osmium is the only discernible dynamic process above 70°C in toluene solutions.¹³

The triruthenium cluster complexes synthesized in this work as well as the carboxamido complex $\text{Ru}_3[\mu\text{-H}, \mu\text{-O}=\text{C}(\text{NMe}_2)](\text{CO})_{10}$ (**4**)¹⁴ display interesting reactivity at ambient temperature. Preliminary experiments (monitored by ^1H NMR) show that ethylene reacts reversibly with **2a**, forming within 45 min an isomeric mixture of complexes that contain an η^2 -ethylene group. Complexes **2a** and **4** also react with diphenylacetylene or -but-2-yne to give (σ - π)-coordinated vinyl derivatives. The edge double-bridged osmium analogues are unreactive under these conditions. Complexes **1**, **2a-c**, and **4** thus provide extensions into cluster chemistry for ruthenium analogous to that provided for osmium through the reactive cluster $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$, whose ruthenium analogue has not yet been isolated or observed.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-79-08406) and an SERC Fellowship to N.M.B. Computing costs were supported in part by an intramural grant from the UCLA Academic Computing Center.

Registry No. **1**, 80800-53-9; **2a**, 80800-54-0; **2b**, 80800-55-1; **2c**, 80800-56-2; **2d**, 80800-57-3; **3**, 80800-58-4; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; MeLi, 917-54-4; LiBr, 7550-35-8; LiCl, 7447-41-8; LiI, 10377-51-2.

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Received November 16, 1981

Structure of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ in Tutton Salt and in Frozen Aqueous Solution

Sir:

Crystallographic studies of Tutton salts^{1,2} ($\text{M}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, where M can be Mg, Zn, or Cu) reveal a unique structure for the $\text{M}(\text{H}_2\text{O})_6^{2+}$ complex. A single-crystal proton ENDOR study of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ in $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$,³ where VO^{2+} substitutes for Mg^{2+} in the lattice, shows that this complex has a similar geometry. The question arises whether hydrogen bonding with sulfate ions^{1,2} plays a dominant role in determining the positions of the water molecules or whether the geometry is determined primarily by binding forces within the aquo complex itself. Results of the single-crystal ENDOR study³ suggest that the answer to this question can be given by a comparison of the ENDOR data from $\text{VO}(\text{H}_2\text{O})_5^{2+}$ in Tutton salt powder and in frozen aqueous solution. This consideration prompted us to reexamine⁴ the ENDOR spectra of the complex in the two media.

Single-crystal measurements³ show that the traceless components of hyperfine tensors in $\text{VO}(\text{H}_2\text{O})_5^{2+}$, to a good approximation, can be accounted for by assuming that they stem

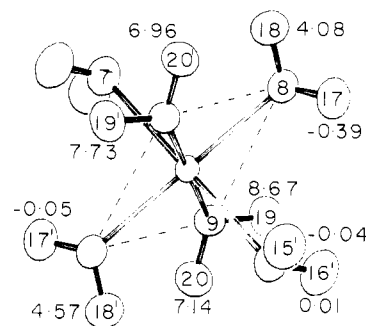


Figure 1. Structure of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex in Tutton salt.² In VO^{2+} -doped $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ the vanadyl oxygen is positioned along the $\text{M}-\text{O}_7$ direction. Of particular interest are the positions and isotropic hyperfine splittings (given in MHz) of the protons (labeled 17 through 20) of the equatorial water molecules. The equatorial plane is indicated by the dashed line.

from point dipole interactions between the protons and an electron spin at the metal nucleus. This is consistent with the conclusion that the unpaired electron is localized virtually completely in the $3d_{xy}$ AO.^{5,6} The positions of the hydrogen atoms, deduced from the magnitudes and orientations of the axial components of the traceless tensors,³ agree quite well with those given by crystallographic studies of Tutton salts.^{1,2}

Of particular interest to us are the Fermi contact contributions. For the eight equatorial protons, these range from about zero to +8.67 MHz.³ The diversity can be understood by considering the geometry of the $\text{VO}(\text{H}_2\text{O})_5^{2+}$ complex. According to the ENDOR data,³ the structure of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex in $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$,² shown in Figure 1, gives a fairly good presentation of the structure of $\text{VO}(\text{H}_2\text{O})_5^{2+}$. The figure indicates that there is a correlation between the magnitude of the Fermi contact term and the distance between proton and nearest nodal plane of the $3d_{xy}$ AO. The isotropic component is attributed³ to a direct admixture of hydrogen 1s AO into the orbital of the unpaired electron. The admixture increases with increasing overlap of the 1s and $3d_{xy}$ AO's, accounting for the observed correlation between hydrogen atom position and magnitude of the Fermi contact term.

If the structure shown in Figure 1 stems primarily from the effects of crystal packing forces, one may expect pronounced changes in hydrogen atom positions upon a medium change. According to the discussion presented above, this should have a pronounced effect on the isotropic coupling constants. Such an effect should be evident in the ENDOR spectra given by $\text{VO}(\text{H}_2\text{O})_5^{2+}$.

Figure 2 presents the ENDOR spectra of the aquo complex in two media. The spectra in Figure 2a were obtained with the magnetic field (H) set on the low-field turning point in the solid-solution ESR spectrum. This field setting gives an ENDOR spectrum of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ molecules that have their $\text{V}=\text{O}$ axis approximately along H .⁴ Ideally, this field setting should generate single-crystal type spectra.^{7,8} In this case, the large number of protons involved and the rather large values of some of the hyperfine components reduce the magnetoselectivity. Since a relatively broad range of orientations is probed, both spectra exhibit some powder-spectrum features. The frozen aqueous solution spectrum has rather broad lines, so that much of the spectral resolution present in the Tutton salt spectrum is lost. This could be indicative of some disorder in the geometry of the complex. However, it is clear that the spectra do not show evidence of a pronounced medium effect

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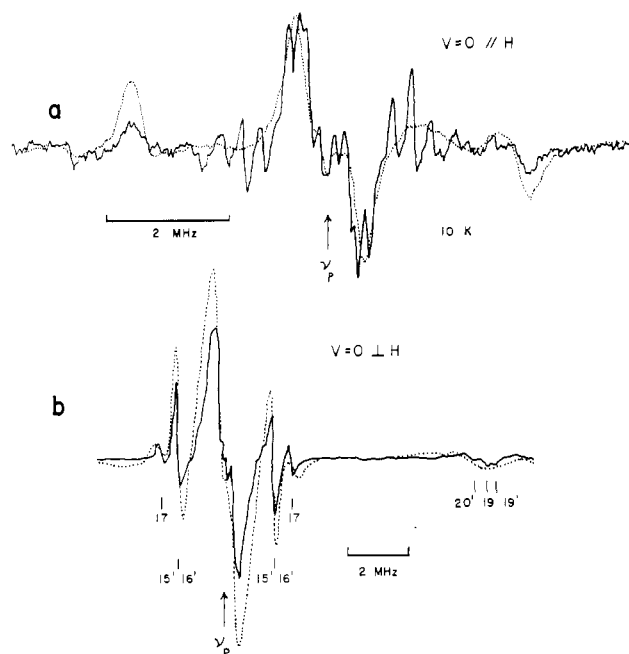


Figure 2. ENDOR spectra of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ in $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ powder (solid line) and in frozen aqueous solution (dotted line). The solution was 0.1 N in HCl, and glycerol was added to ensure glass formation.⁴ Spectra were recorded at about 10 K; the experimental details have been reported before.^{4,8} Spectra were taken with the magnetic field set on (a) the low-field turning point and (b) the $3/2 \perp ^{51}\text{V}$ hyperfine line in the ESR spectrum.⁴

on the magnitude of the hyperfine splitting constants.

The ENDOR spectra shown in Figure 2b, obtained with H set on the $3/2 \perp ^{51}\text{V}$ hyperfine peak in the ESR spectrum, also do not exhibit significant changes associated with the medium change. Here the ENDOR spectrum is due to those molecules that have the $\text{V}=\text{O}$ bond approximately perpendicular to H .⁴ Therefore, the spectra give information on the magnitudes of the hyperfine tensor components in the equatorial plane of the aquo complex. An interpretation of the salient features in terms of the single-crystal data³ will serve to illustrate that the spectra shown in Figure 2b provide a particularly sensitive probe of changes in structure.

According to these data, the hyperfine splittings in the equatorial plane show a diversity in magnitude and anisotropy. The axial protons (15', 16') and one of the equatorial protons (17) (cf. Figure 1) have a relatively small hyperfine anisotropy in the plane. Therefore, they should give readily observable resonances with single-crystal features. The predicted splittings are ~ 3.0 MHz for the axial protons and ~ 5.0 MHz for the equatorial proton. Indeed, both spectra given in Figure 2b show two pairs of single-crystal type lines with splittings that are in reasonably close agreement with those predicted.⁹ The hyperfine splittings of the axial protons are not expected to be very sensitive to media changes since they will be almost completely point-dipolar in origin, irrespective of the orientation of the axial water molecule. On the other hand, the location and single-crystal appearance of the pair of lines attributed to proton 17 stem from its unique position. Namely, it lies almost in a nodal plane of the $3d_{xy}$ AO so that the Fermi contact term is small. Furthermore, it is located well below the equatorial plane, so that the hyperfine anisotropy in this plane is minimized. Clearly, if this location were to change, this should be observable in the ENDOR spectrum. A similar argument applies for the resonance peaks due to protons 19,

19', and 20'. Since, these protons are located close to the equatorial plane and far from the $3d_{xy}$ nodal planes, both the hyperfine anisotropy in the equatorial plane and the Fermi contact terms are large. The high-frequency turning points of the resonances due to these protons are found, as predicted by the single-crystal data,³ about 8.5 MHz above the free-proton frequency (ν_p). A change in the positions of these protons upon going from $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ powder to frozen aqueous solution would be accompanied by a change in position of these resonance peaks.

The ENDOR spectrum of VO^{2+} doped into $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ obtained with $H \perp \text{V}=\text{O}$ is very similar to the spectra shown in Figure 2b. (Unfortunately, signal to noise problems prevented a recording of the $H \parallel \text{V}=\text{O}$ spectrum.) This finding is in accordance with crystallographic data^{2,10} that show that the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ structures are very similar.

The salient feature of the structure of the hexaquo complexes^{2,10} is that the planes of adjacent water molecules are more or less perpendicular to each other. The ENDOR data show that $\text{VO}(\text{H}_2\text{O})_5^{2+}$ has a similar geometry and that it is retained in aqueous solution. This observation leads to the conclusion that the $\text{VO}(\text{H}_2\text{O})_5^{2+}$ structure is determined primarily by intramolecular forces. The unique orientation of the water molecules^{2,10} optimizes hydrogen bonding within the complexes. The similarity in structure of the hexaquo complexes and $\text{VO}(\text{H}_2\text{O})_5^{2+}$ and the lack of a pronounced solvent effect on the structure of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ may be due to the fact that these internal hydrogen bonding forces play a dominant role in determining the geometry.

Acknowledgment. We thank Dr. L. J. Zompa of the UMB for providing us with ORTEP plots of some aquo complexes. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $\text{VO}(\text{H}_2\text{O})_5^{2+}$, 15391-95-4; $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 7785-18-4.

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Received January 22, 1982

An Accurately Characterized Divalent Platinum(III) Bond: The Structure of $\text{Na}_2[\text{Pt}_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2]$

Sir:

With the well-established orbital scheme for the metal-metal quadruple bond, $\sigma^2\pi^4\delta^2$, as a point of departure, M-M bonds of other orders may be formed by deleting or adding electrons.¹ For example, addition of two electrons reduces the bond order to 3 ($\sigma^2\pi^4\delta^2\delta^{*2}$) as in $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ or $\text{Os}_2(\text{hp})_4\text{Cl}_2$. The ultimate degree of integral bond order reduction by addition of electrons, short of the entire abolishment of the bond, is to a bond order of unity by addition of six electrons

(9) Earlier the peaks now assigned to proton 17 were attributed to a proton hydrogen bonded to the oxygen atom of the vanadyl cation.⁴ The single-crystal study³ shows that this assignment must be incorrect.

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