this salt exhibits a medium to strong band at 1796 cm^{-1} (with a shoulder at 1813 cm^{-1}). This indicates bridging carbonyl groups not observed in the salt of the osmium analogue [C(NMe$_2$)$_3$][**3a**], whose carbonyl absorptions are essentially the same as those seen for the [PPN]$^+$ salt.[5b] A structural similarity is thus indicated with the 1,2-diazene complexes M$_3$(C$_4$H$_4$N$_2$)(CO)$_{10}$, M = Ru[21] or Os[22] (see Figure 1), which are isoelectronic with the μ-O=C(NMe$_2$)-substituted anions; the structure of Ru$_3$(C$_4$H$_4$N$_2$)(CO)$_{10}$ has been determined by X-ray diffraction.[21] Fluxional behavior is observed for each of the anions as also noted for the 1,2-diazene complexes but with a significant difference as explained below. For [C(NMe$_2$)$_3$][**6**] in THF a limiting spectrum is seen in the ^{13}C NMR[23a] at −95 °C with three peaks at 262.7, 257.6, and 246.1 ppm, confirming the presence of three carbonyl bridging groups.[23b] Coalescence of these resonances with those of the terminally bonded carbonyl groups occurs by various stages and is still not complete at +65 °C. By contrast, the osmium analogue [C(NMe$_2$)$_3$][**3a**] does not yield a limiting spectrum at −95 °C and shows averaging among all ten carbonyl groups at +26 °C.

The barrier for averaging of the carbonyl groups in the triosmium complex is thus *lower* than it is in the homologous triruthenium anion, a *reversal* in the relative barrier heights usually observed between cluster complexes of these two metals.[24] This is illustrated schematically in Figure 1. For the triruthenium anion, the ground state is known to be the bridged form, while for the triosmium anion the ground state is the all-terminal structure. The fluxional processes in these species are of course more complicated than can be represented by a single energy profile. We have simplified the diagram to make a point.

For neutral derivatives such as the 1,2-diazene complexes, the barrier height for tautomerism is higher in the triosmium cluster than in the triruthenium analogue. This is represented by the labeled vertical solid arrows in Figure 1. In the anions, the greater charge-carrying ability of the bridging carbonyls causes a stabilization of the bridged structure, represented by the dotted reaction coordinates falling at lower energy for the two bridged forms. The barrier toward the overall fluxional process is *increased* in the triruthenium anion but *decreased* in the triosmium anion relative to those in the corresponding neutral diazene complexes. This results in a *reversal* of the usual relationships between barriers to exchange in the complexes of these two metals, as represented by the vertical dashed double-arrows in Figure 1.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-79-08406), a NATO fellowship from the DAAD (German Academic Exchange Service) to A.M., and an NATO-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, 15696-40-9; [PPN][**2a**], 80800-43-7; [Li][**2b**], 80800-44-8; [PPN][**2c**], 80800-46-0; [PPN][**3a**], 80800-48-2; [C(NMe$_2$)$_3$][**3a**], 80822-54-4; [Li-cryptate][**3b**], 80822-25-9; [**3c**]$^-$, 80800-49-3; **4a**, 80800-50-6; **4b**, 65908-54-5; **4c**, 80800-51-7; **5**, 21559-15-9; [C(NMe$_2$)$_3$][**6**], 80845-41-6; Ru$_3$(CO)$_{12}$, 15243-33-1; Os$_3$(CO)$_{11}$(N≡CCH$_3$), 65702-94-5; LiNMe$_2$, 3585-33-9; MeLi, 917-54-4; C(NMe$_2$)$_4$, 10524-51-3; [**5**]$^-$, 80800-52-8.

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[22] Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 2820.

[23] (a) JEOL FX90Q F-T NMR spectrometer, ^{13}C with Cr(acac)$_3$ added as a paramagnetic relaxation agent, at 22.50 MHz relative to Me$_4$Si. (b) ^{13}C NMR for [C(NMe$_2$)$_3$][**6**]: at −95 °C, 262.7 (1 CO), 257.6 (1 CO), 246.1 (1 CO), 211.4 (1 CO), 210.6 [O=*C*N(CH$_3$)$_2$], 209.1 (1 CO), 206.0 (1 + 1 CO), 204.3 (1 + 1 CO), 202.7 (1 CO) ppm; at +65 °C, 220.7 (9 CO), 212.7 [O=*C*N(CH$_3$)$_2$], 211.2 (1 CO) ppm; for spectra at both temperatures 164.4 [*C*(NMe$_2$)$_3$], 41.0 (CH$_3$), 40.4 [C(N*Me*$_2$)$_3$], 33.6 (CH$_3$). (c) ^{13}C NMR for [C(NMe$_2$)$_3$][**3a**]: at −95 °C, 192.7 (1 CO), 190.5 (1 CO), 189.8 (1 CO), 189.0 [O=*C*N(CH$_3$)$_2$], 188.0 and 185.0 (both broad, 7 CO) ppm; at +26 °C, 190.6 [O=*C*N(CH$_3$)$_2$], 187.2 (10 CO); for spectra at both temperatures 164.2 [*C*(NMe$_2$)$_3$], 41.3 (CH$_3$), 40.2 [C(N*Me*$_2$)$_3$], 33.9 (CH$_3$).

[24] A similar situation exists for the anions [M$_3$(μ-H,μ-CO)(CO)$_{10}$]$^-$, where the range from a single resonance to a limiting spectrum is −50 to −105 °C for M = Os, but +32 to −115 °C for M = Ru. Cf. respectively: Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1978**, 1358. Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Süss, G. *Ibid.* **1979**, 1356.

Synthesis of Edge Double-Bridged Ru$_3$(μ-H,μ-X)(CO)$_{10}$, X = O=C(Me), Cl, Br, I, and of Ru$_3$(μ-H,μ_3-I)(CO)$_9$: A New Series of Reactive Complexes for Triruthenium Cluster Chemistry. Crystal and Molecular Structure of Ru$_3$(μ-H,μ-Br)(CO)$_{10}$

Sir:

Recent studies of the stepwise formation of edge double-bridged trinuclear cluster complexes[1] led us to the synthesis of the new acyl derivative Ru$_3$[μ-H,μ-O=C(Me)](CO)$_{10}$ (**1**).[2,3] In this work we consistently observed a minor product that eluted, together with unreacted Ru$_3$(CO)$_{12}$, ahead of the main product. Trial and error led us to a procedure in which the yield of the minor product was optimized to 30%,[4,5] sufficient

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[1] Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.*, companion paper in this issue.

[2] (a) Ru$_3$(CO)$_{12}$ in THF at −30 °C is treated with MeLi stabilized with ca. 22.5% LiBr (1.5 M in diethyl ether, Alfa Products, Thiokol/Ventron Division). IR spectra in a cell precooled to −50 °C under a dry-dinitrogen atmosphere indicate an anionic η^1-C(O)Me complex, identified by the characteristic carbonyl stretch at 1575 cm^{-1}; the other bands in the carbonyl stretching region are at 2080 w, 2061 w, 2012 vs, 1990 vs, and 1962 br, sh cm^{-1}. The mixture is permitted to warm to 0 °C over a 15-min period and stirred for an additional 1 h. The reaction is acidified with CF$_3$SO$_3$H (dropwise) and the solvent removed under oil pump vacuum. Extraction of the residue was performed in hexane and elution through a silica gel column (Merck 60). (b) IR and ^{1}H NMR for **1** are given in Table I. ^{13}C NMR (relative to internal Me$_4$Si, in C$_6$D$_6$/Cr(acac)$_3$): O=*C*Me 285.1; CO groups 206.1 (1), 205.9 (1), 200.5 (1), 200.2 (1), 195.1 (1), 194.0 (1), 190.7 (1 + 1), 188.4 (1), 183.9 (1); Me 46.8.

[3] The reaction of phenyllithium with Ru$_3$(CO)$_{12}$ has been previously reported to give the unusual orthometalated carbene complex HRu$_3$[C$_6$H$_4$-*o*-C(Ph)](CO)$_{10}$ in low yield: Parkins, A. W.; Fischer, E. O.; Huttner, G.; Regler, D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 633. Also mentioned was an orange oil. In repeating this work, we confirm this observation; through preliminary spectroscopic studies we believe this material to be the acyl derivative HRu$_3$[μ-O=C(Ph)](CO)$_{10}$.

[4] (a) Treatment of THF solutions of Ru$_3$(CO)$_{12}$ with MeLi/LiBr[2a] at −30 °C followed within 5 min by acidification with excess CF$_3$SO$_3$H results in a mixture that upon workup gives **1** in 20% yield and **2a** in 30% yield. Spectroscopic data are presented in Table I. Less than 5% of the starting material is recovered; the balance represents various polynuclear species among which we could identify [HRu$_6$(CO)$_{18}$]$^-$.[4b] (b) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383.

[5] (a) Nucleophilic attack of coordinated carbonyl groups by MeLi followed by protonation has been shown to generate carbyne, vinylidine, and hydroxycarbene complexes, as shown in ref 5b, 5c, and 5d, respectively. In the synthesis of **2a** one such type of complex may well be an intermediate susceptible to substitution by bromide ion in the presence of excess acid. (b) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620. (c) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1120. (d) Fisher, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156. Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979**, *171*, 65. Chatt, J.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *Ibid.* **1980**, *184*, C64.

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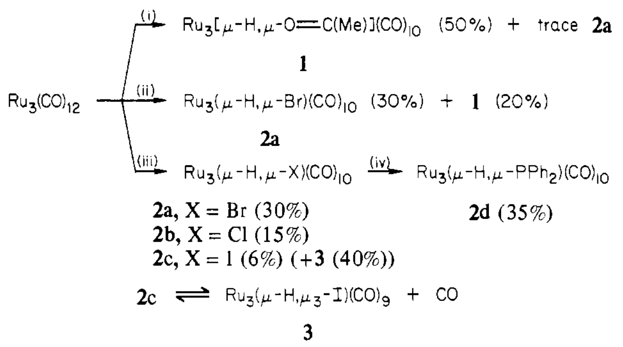
Scheme I[a]



[a] Key to reactions: (i) MeLi/LiBr at −30 °C, warm-up, acidification;[2] (ii) MeLi/LiBr, followed in 5 min by acidification, both at −30 °C;[4,5] (iii) [Li] [X]/THF + 2 mol of Me_3NO (1 h) followed by acidification;[8] (iv) $LiPPh_2$/THF.

Table I. Spectroscopic Data for $Ru_3(\mu\text{-H},\mu\text{-X})(CO)_{10}$ (X = O=C(Me), **1**; X = Br, **2a**; X = Cl, **2b**; X = I, **2c**; X = PPh_2, **2d**) and $Ru_3(\mu\text{-H},\mu_3\text{-I})(CO)_9$ (**3**)

compd	$\nu(CO)^a/cm^{-1}$	δ(Ru–*H*–Ru)
1	2105 w, 2068 vs, 2055 vs, 2030 s, 2021 m, 2009 m, 2004 m, 1992 vw, 1989 w[b]	−13.88[c]
2a	2112 w, 2076 s, 2069 s, 2029 vs, 2024 sh, 2013 vw, 2004 w, 1999 vw, 1996 m	−14.39[d]
2b	2113 w, 2077 s, 2070 s, 2034 sh, 2030 vs, 2014 vw, 2005 w, 2000 vw, 1997 m	−13.89[d]
2c	2109 w, 2072 s, 2066 s, 2028 vs, 2021 sh, 2012 vw, 2003 w, 2001 vw, 1995 m	−15.02[d]
2d	2099 m, 2055 vs, 2050 s, 2022 vw, 2004 m, 1999 m, 1990 w	−15.87[d,e]
3	2096 m, 2069 vs, 2049 vs, 2017 vs, 2002 w, 1988 m, 1978 w	−17.67[d]

[a] Hexane solution. [b] $\nu(C{=}O\cdots Ru)$ 1519 w cm^{-1}, C_2Cl_4 solution. [c] $CDCl_3$ solution; CH_3, 2.57 ppm. [d] C_6D_6 solution. [e] Doublet, $J_{^{31}P-H} = 30.5$ Hz.

for it to be isolated in a pure crystalline state and characterized as $Ru_3(\mu\text{-H},\mu\text{-Br})(CO)_{10}$ (**2a**) (see (ii) in Scheme I; see also Table I).

The chemistry of carbonyl halide clusters is of special interest at the present. It has, for instance, been shown that iodide is a promoter in the $Ru_3(CO)_{12}$-catalyzed conversion of syngas to mixtures of methanol and ethylene glycol,[6] a result also observed by use of $Ru_3(CO)_{12}$ in melts containing the salts of various quaternary halides.[7] We were thus led to the synthesis of **2a** as well as the chloro and iodo derivatives, **2b** and **2c**, respectively, through route (iii) shown in Scheme I.[8] Complex **2c** is prone to carbonyl loss to give $Ru_3(\mu\text{-H},\mu_3\text{-I})(CO)_9$ (**3**), a reaction which is reversible under 1 atm of CO. Treatment of **2a** with $LiPPh_2$ results in a bridged diphenylphosphido derivative, **2d** (see Scheme I and Table I).

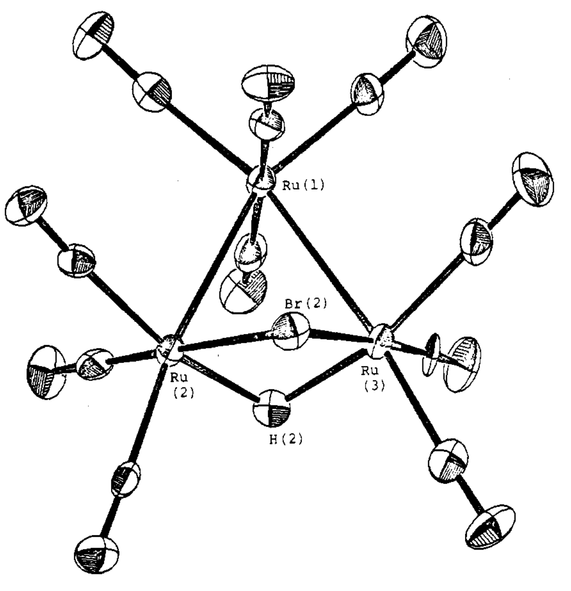


Figure 1. ORTEP projection for $Ru_3(\mu\text{-H},\mu\text{-Br})(CO)_{10}$ (**2a**) for one molecule in the group in which hydrogen was located.[9] Thermal ellipsoids are shown at 50% probability. Metal atom separations are given in the text. Other selected separations are as follows (Å): Ru(2)–Br(2) = 2.559 (2); Ru(3)–Br(2) = 2.561 (2); Ru(2)–H(2) = 1.776 (1); Ru(3)–H(2) = 1.790 (1).

An X-ray study of **2a** was undertaken at −158 °C;[9] an ORTEP projection is shown in Figure 1. The double-bridged Ru(2)–Ru(3) distance is found to be 2.819 (1) Å, close to the unbridged distances Ru(2)–Ru(1), 2.813 (1) Å, and Ru(3)–Ru(1), 2.802 (1) Å, and also close to the average separation of 2.854 (8) Å found in $Ru_3(CO)_{12}$.[10] This distance represents single-bond order for all separations mentioned.[11] The structure of **2a** is analogous to that of $Os_3(\mu\text{-H},\mu\text{-Br})(CO)_{10}$[12] but, by contrast, shows different fluxional behavior[13] and is also possessed of a remarkably high reactivity along with other edge double-bridged complexes of this metal, both discussed as follows.

Proton-decoupled ^{13}C NMR of **2b** in $CD_2Cl_2/Cr(acac)_3$, at −25 °C, showed the following resonances in the carbonyl region: δ 204 (1), 203 (1), 198 (2), 191 (2 + 2), 181 (2). In the proton-coupled spectrum, shoulders appear on the resonance at 191 ppm, indicating this signal to contain the reso-

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(7) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959.

(8) (a) The reactions of $Ru_3(CO)_{12}$ with lithium chloride, bromide, or iodide in THF in the presence of 2 mol equiv of trimethylamine *N*-oxide proceed to about 50% conversion within about 1 h. On protonation all three halohydrides are isolated; the ratio of **3** to **2c** is increased by the presence of a CO atmosphere. Addition of further amounts of Me_3NO in the first step does not lead to any better yields of isolated products. Characterization of **2b**, **2c**, and **3** by mass spectroscopy and elemental analysis is under way; our assignments thus far are based on the IR carbonyl absorptions and ^1H NMR, which are analogous to those of **2a** or the complex $Os_3(\mu\text{-H},\mu_3\text{-I})(CO)_9$, respectively (see Table I). The latter complex was not isolated but in turn characterized by analogy to the absorptions in $Os_3(\mu\text{-H},\mu_3\text{-SR})(CO)_9$.[8b] A similar adventitious discovery of a carbonyl halide cluster followed by a more direct synthesis has been reported for $[PPN][Ru_4(\mu\text{-Cl})(CO)_{13}]$.[8c] (b) Johnson, B. F. G.; Lewis, J.; Pippard, D. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (c) Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2985.

(9) Red crystals of **2a** are monoclinic, space group $P2_1/c$, with $a = 8.297$ (2) Å, $b = 11.549$ (5) Å, $c = 34.957$ (5) Å, $\beta = 93.62$ (2)°, $V = 3342.95$ Å^3, $Z = 8$, $\rho_{calcd} = 2.750$ (Mo Kα = 0.71069 Å). The structure was solved and refined with use of 4528 observed $[I \geq 3[\sigma(I)]]$ independent reflections measured on a Syntex P$\bar{1}$ automated diffractometer in the range $0° \leq 2\theta \leq 50°$. The ruthenium atoms were located by direct methods, and the structure was subsequently refined by Fourier difference maps and least-squares techniques, anisotropic thermal corrections being applied to all nonhydrogen atoms. The unit cell consists of two crystallographically independent quartets of molecules, although the bridging hydrogen was only located on one set of symmetry related molecules; $R_F = 0.048$ and $R_{wF} = 0.061$.

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(11) (a) The conventional vector between metal atoms of the double-bridged edge is omitted from our structure representations of trinuclear complexes because we believe this better reflects the octahedral coordination around the metal atoms in question. Bonding interactions between the metal atoms along a double-bridged edge are believed to take place through orbitals involving the bridging atoms.[11b,c] (b) Mason, R.; Mingos, D. W. P. *J. Organomet. Chem.* **1973**, *50*, 53. (c) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Ibid.* **1974**, *70*, 413.

(12) (a) The osmium analogues are best prepared from the reaction of $Os_3(\mu\text{-H})_2(CO)_{10}$ with allyl halides,[12b] a route unavailable for ruthenium. X-ray structures of $Os_3(\mu\text{-H},\mu\text{-X})(CO)_{10}$ (X = Cl,[12c] Br[12d]) have been reported. (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313. (c) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926. (d) Churchill, M. R.; Lashewycz, R. A. *Ibid.* **1979**, *18*, 3261.

(13) Bryan, E. G.; Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1978**, 196.

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 $Os_3(\mu\text{-}H,\mu\text{-}X)(CO)_{10}$ (X = Cl, Br, I, SEt, 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 $Ru_3[\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)](CO)_{10}$ (**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 and 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 $Os_3(\mu\text{-}H)_2(CO)_{10}$, 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; $Ru_3(CO)_{12}$, 15243-33-1; MeLi, 917-54-4; LiBr, 7550-35-8; LiCl, 7447-41-8; LiI, 10377-51-2.

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(14) Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243.

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Structure of $VO(H_2O)_5{}^{2+}$ in Tutton Salt and in Frozen Aqueous Solution

Sir:

Crystallographic studies of Tutton salts[1,2] ($M(NH_4)_2(SO_4)_2{\cdot}6H_2O$, where M can be Mg, Zn, or Cu) reveal a unique structure for the $M(H_2O)_6{}^{2+}$ complex. A single-crystal proton ENDOR study of $VO(H_2O)_5{}^{2+}$ in $Mg(NH_4)_2(SO_4)_2{\cdot}6H_2O$,[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 study[3] suggest that the answer to this question can be given by a comparison of the ENDOR data from $VO(H_2O)_5{}^{2+}$ in Tutton salt *powder* and in frozen aqueous solution. This consideration prompted us to reexamine[4] the ENDOR spectra of the complex in the two media.

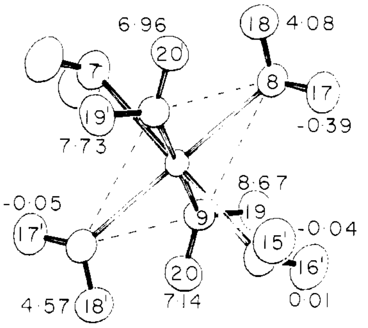

Figure 1. Structure of the $Cu(H_2O)_6{}^{2+}$ complex in Tutton salt.[2] In VO^{2+}-doped $Mg(NH_4)_2(SO_4)_2{\cdot}6H_2O$ the vanadyl oxygen is positioned along the M–O_7 direction. Of particular interest are the positions and isotropic hyperfine splittings (given in MHz) of the protons (labeled 17 through 20′) of the equatorial water molecules. The equatorial plane is indicated by the dashed line.

Single-crystal measurements[3] show that the traceless components of hyperfine tensors in $VO(H_2O)_5{}^{2+}$, to a good approximation, can be accounted for by assuming that they stem 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 $VO(H_2O)_5{}^{2+}$ complex. According to the ENDOR data,[3] the structure of the $Cu(H_2O)_6{}^{2+}$ complex in $Cu(NH_4)_2(SO_4)_2{\cdot}6H_2O$,[2] shown in Figure 1, gives a fairly good presentation of the structure of $VO(H_2O)_5{}^{2+}$. 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 attributed[3] 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 $VO(H_2O)_5{}^{2+}$.

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 $VO(H_2O)_5{}^{2+}$ molecules that have their V=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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