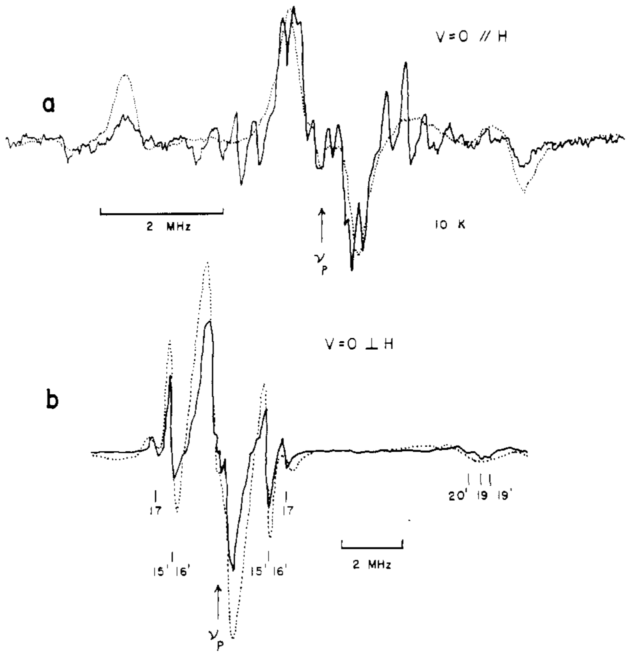

Figure 2. ENDOR spectra of $VO(H_2O)_5^{2+}$ in $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ powder (solid line) and in frozen aqueous solution (dotted line). The solution was 0.1 N in HCl, and glycerol was added to ensure glass formation.[4] Spectra were recorded at about 10 K; the experimental details have been reported before.[4,8] Spectra were taken with the magnetic field set on (a) the low-field turning point and (b) the $^3/_2 \perp {}^{51}V$ 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 $^3/_2 \perp {}^{51}V$ 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 V=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 data[3] 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 $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ 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 $NH_4Al(SO_4)_2 \cdot 12H_2O$ obtained with $H \perp$ V=O is very similar to the spectra shown in Figure 2b. (Unfortunately, signal to noise problems prevented a recording of the $H \parallel$ V=O spectrum.) This finding is in accordance with crystallographic data[2,10] that show that the $Cu(H_2O)_6^{2+}$ and $Al(H_2O)_6^{3+}$ structures are very similar.

The salient feature of the structure of the hexaaquo complexes[2,10] is that the planes of adjacent water molecules are more or less perpendicular to each other. The ENDOR data show that $VO(H_2O)_5^{2+}$ has a similar geometry and that it is retained in aqueous solution. This observation leads to the conclusion that the $VO(H_2O)_5^{2+}$ 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 hexaaquo complexes and $VO(H_2O)_5^{2+}$ and the lack of a pronounced solvent effect on the structure of $VO(H_2O)_5^{2+}$ may be due to the fact that these internal hydrogen bonding forces play a dominant role in determining the geometry.

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Registry No. $VO(H_2O)_5^{2+}$, 15391-95-4; $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 7785-18-4.

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[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 study[3] shows that this assignment must be incorrect.

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An Accurately Characterized Diplatinum(III) Bond: The Structure of $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$

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 $Re_2Cl_4(PR_3)_4$ or $Os_2(hp)_4Cl_2$. 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

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[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

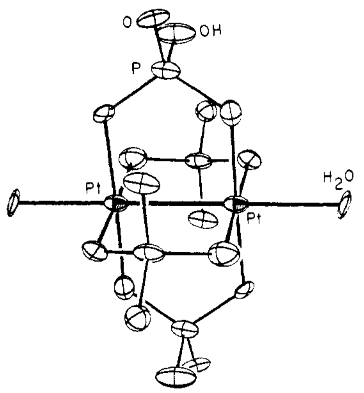

Figure 1. The $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ ion. This drawing represents both the essentially identical, centrosymmetric anions found in the unit cell.

to give a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration. Real systems that might be expected to exemplify such bonding are Rh^{II}_2, Ir^{II}_2, Pd^{III}_2, and Pt^{III}_2, but only for the first and the last are there reported examples. In contrast to the many compounds known for Rh^{II}_2,[2] the results for Pt^{III}_2 are meager.[2,3] Indeed, the anion we report here is the first one having fourfold symmetry to be structurally characterized fully and precisely, although there is a very terse report listing average bond lengths (with no error estimates) for the $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ ion.[4] The first mention of compounds containing, or likely to contain, the $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ ion occurred in 1980,[5] although the preparation and structural characterization of comparable compounds containing molybdenum(III)[6] had been reported earlier, and a similar rhodium(II) compound is also known.[7]

Crystals of the sodium compound $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$ were obtained in the course of preparing and recrystallizing other compounds containing the same or a similar anion. It has been difficult to obtain other compounds in suitably crystalline form for X-ray work, so we gladly took advantage of this fortunate accident. The yellow crystals were handled by the crystallographic procedures normally used in this laboratory.[8] There are two crystallographically independent anions residing on inversion centers at 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. The Na^+ ions are on general positions.[9]

The two anions show only small random differences from each other, and Figure 1 presents the structure characteristic of both. The Pt-Pt unit is bridged by four $PO_3(OH)^{2-}$ ions so that four five-membered rings with the Pt-Pt bond in common are formed. Each ring has an envelope conformation with the phosphorus atom bent out of the Pt_2O_2 plane. All such bends are in the same sense about the Pt-Pt axis as are the orientations of the O=P—OH groups. The $Pt_2(HPO_4)_4$ unit thus has effectively C_{4h} symmetry. A water molecule is coordinated at each axial position.

Some of the important dimensions, averaged[10] over all chemically equivalent ones of each type in both anions, are as follows: Pt—Pt, 2.486 [2] Å; Pt—O(phosphate), 2.006 [7] Å; Pt—O(H_2O), 2.151 [11] Å; P—O(coordinated), 1.543 [5] Å; P—OH, 1.549 [6] Å; P—O, 1.505 [6] Å; ∠Pt—Pt—O, 90.8 [1]°; ∠Pt—Pt—O(H_2O), 177.9 [4]°. The two independent Pt—Pt distances are 2.485 (1) and 2.487 (2) Å. In each HPO_4 ligand, the P=O and P—OH distances differ by 0.016–0.072 Å, the average difference being 0.044 [12] Å. Each Na^+ ion is surrounded by a distorted octahedron of phosphate oxygen atoms with Na–O distances ranging from 2.79 (2) to 3.16 (2) Å with an average value of 2.96 Å.

The structure of the $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ ion is qualitatively similar to those of other $M_2(HPO_4)_4L_2$ and $M_2(SO_4)_4L_2$ species; it shows no significant differences from them other than those arising in some cases from the differences in the M–M bond lengths. The Pt–Pt bond length is very similar to that reported[4] in $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$, 2.466 (?) Å, and to the Rh–Rh bond length[7] in $Rh_2(H_2PO_4)_4(H_2O)_2$, 2.485 (1) Å. It is also interesting to compare the present Pt–Pt distance with those in some other compounds having qualitatively different structures but also having Pt–Pt bonds of order 1. Two moderately closely related structures are those of $(p\text{-}CH_3C_5H_4N)_2Pt_2(CH_3)_4(O_2CCF_3)_2$[11] and $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_3)(H_2O)](NO_3)_3\cdot H_2O$[12] in which the Pt–Pt distances are 2.557 (1) and 2.539 (1) Å, respectively, i.e., considerably longer than in the present case. In the tetranuclear molecule[13] $Pt_4(O_2CCH_3)_8$ there are four bonds of average length 2.495 [4] Å; here the formal oxidation number is only 2, but the total valence could be considered 4, as in the present case. There is also a class of mixed-oxidation-state compounds[14] with longer Pt–Pt bonds, for the discussion of which the present structure and those most closely related to it may form a useful point of reference.

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Registry No. $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$, 80963-04-8.

Supplementary Material Available: Tables of general temperature factor expressions, positional and thermal parameters, structure factors, rms amplitudes of thermal vibration, and bond angles and distances (19 pages). Ordering information is given on any current masthead page.

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[9] Tables of positional parameters, thermal parameters, and structure factors are available as supplementary material.

[10] A number in parentheses is an esd for a given individual value while a number in brackets is equal to $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith value in a set of n such values from the arithmetic mean of the n values.

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