Paramagnetic ^{183}W N.M.R. Chemical Shifts in Heteropolytungstates

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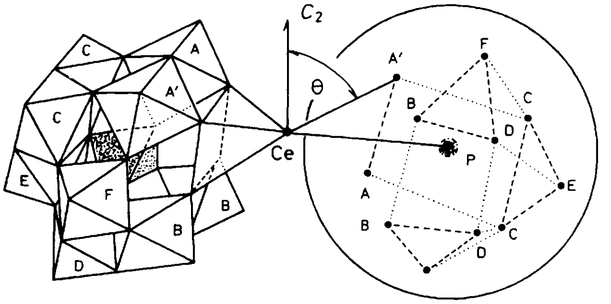
The intensity and position of the resonances in the ^{183}W n.m.r. spectra of the paramagnetic $Ce^{3+}(PW_{11}O_{39})_2^{11-}$ and the diamagnetic $Ce^{4+}(PW_{11}O_{39})_2^{10-}$ complex anions, which have a different solid-state structure, indicate that they also have different structures in aqueous solution; a high degree of electron delocalization from Ce^{3+} to the four adjacent tungsten atoms is deduced from the significant ^{183}W chemical shifts.

Some years ago Peacock and Weakley[1] reported a new category of heteropoly-complexes formed by f-elements and the 'unsaturated' $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$ acting as macroligands. Single-crystal *X*-ray crystal structure determinations have shown that the anions α-$GeW_{11}O_{39}^{8-}$ (see Figure 1) and $P_2W_{17}O_{61}^{10-}$ form a square antiprism around U^{4+} (ref. 2) and Ce^{4+} (ref. 3), respectively. Later, from the ^{31}P n.m.r. chemical shifts for solutions containing complex paramagnetic anions, a slightly different configuration was assumed in which the two ligands were rotated relative to each other to a greater extent than was indicated by the *X*-ray studies.

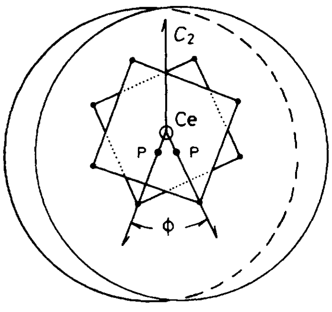
Recently, direct ^{183}W n.m.r. shifts have proved to be very sensitive to the structural non-equivalence of the tungsten atoms.[5] Encouraged by the possibility of observing the ^{31}P n.m.r. spectra of paramagnetic heteropoly complexes, we have now measured the ^{183}W n.m.r. spectra of paramagnetic Ce^{3+} and diamagnetic Ce^{4+} complexes.

Natural abundance ^{183}W spectra were recorded, relative to 2M aqueous Na_2WO_4, at 300 K on a Bruker CXP 300 Fourier transform spectrometer at 12.5 MHz for saturated solutions of $K_{10}Ce^{4+}(PW_{11}O_{39})_2$ and $K_{11}Ce^{3+}(PW_{11}O_{39})_2$ prepared according to the method in ref. 1. All high-field shifts are negative.

In the well known Keggin structure $XW_{12}O_{40}^{x-8}$ all the tungsten atoms are identical, as shown by a single resonance in the ^{183}W n.m.r. spectra within the relatively small range of -98 to -130 p.p.m. depending on X.[5] Removal of one W–O group reduces the symmetry of the anion from T_d to C_s and the expected six-line pattern is observed in the ^{183}W n.m.r. spectrum.[5,6] For the complexes Z(ligand)$_2$ the solid-state structure[2] has a C_2 axis and the two ligand anions are identical but each anion loses its symmetry plane resulting in non-equivalence of all the tungsten atoms. Also, the projections of the Z–P vectors on the plane perpendicular to



(a) $Ce(PW_{11}O_{39})_2^{n-}$



(b)

Figure 1. (a) Schematic representation of the complex anion $Ce(PW_{11}O_{39})_2{}^{n-}$ based on ref. 2 for $U^{4+}(GeW_{11}O_{39})_2{}^{12-}$. (Letters denote differing tungsten atoms.) (b) Side view of the complex showing the rotation angle ϕ.

the C_4 axis of the square antiprism form an angle ϕ of *ca.* 45° (see Figure 1a and b). This staggered conformation found in the two complexes Z(ligand)$_2$ is rather strained and governed by crystal packing forces.[2,3] Other rotational isomers may be possible in solution.

From the emission spectra of some lanthanoid polytungstates it was deduced that the effective point group around Z is close to D_4, four oxygen atoms from each of the two anion ligands leading to a cubic co-ordination around Z.[7,8] Comparison of the emission spectra of the crystalline salts with those of their aqueous solutions has shown that the geometry around Z does not change on dissolution in water.[8]

The ^{31}P n.m.r. spectra and calculation of dipole interaction chemical shifts allowed the assumption that upon dissolution the geometry of the complex $U^{4+}(P_2W_{17}O_{61})^{16-}$ changes towards a more rotated configuration with $135 \leqslant \phi \leqslant 180°$.[4] However for the Ce^{3+}(ligand)$_2$ complex this effect was not so evident owing to the small range of the paramagnetic shifts, but analysis of the ^{31}P n.m.r. spectra of $Dy(P_2W_{17}O_{61})_2{}^{17-}$ and $Ho(P_2W_{11}O_{61})_2{}^{17-}$, which show two-line patterns with chemical shifts of −21.7 and −95.1 p.p.m., and −21.4 and −92.6 p.p.m., respectively, leads to $\phi = 90°$ assuming a cubic co-ordination around Ln^{3+}.

$Ce^{3+}(PW_{11}O_{39})_2^{11-}$ **(1)** $Ce^{4+}(PW_{11}O_{39})_2^{10-}$ **(2)**

As in the ^{31}P n.m.r. spectra, the resonances in the ^{183}W n.m.r. spectrum of the paramagnetic complex **(1)** (Figure 2a) are fairly sharp, and the spectrum is unexpectedly very simple, comprising a six-line pattern. This suggests that the complex **(1)** should have a symmetry plane, as for the uncomplexed ligand. This configuration is only possible with $\phi = 0$ or 180°. Molecular models favoured a more rotated isomer with the C_2 axis perpendicular to the symmetry plane in which the close approach of four terminal oxygen atoms bonded to the tungsten atoms of B-type of the two anions is avoided.

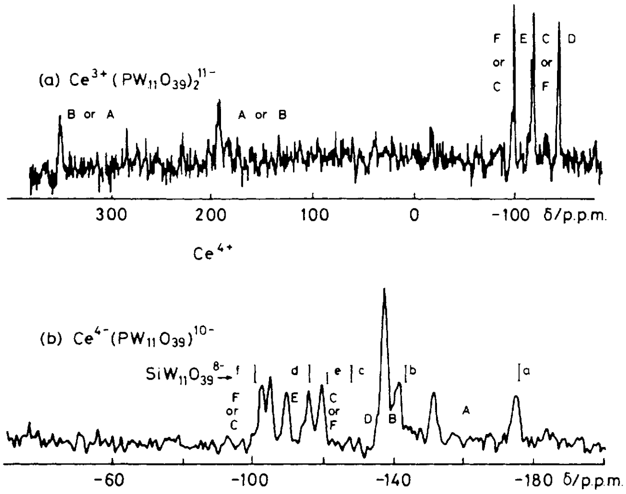


Figure 2. (a) ^{183}W N.m.r. spectrum of $Ce^{3+}(PW_{11}O_{39})_2{}^{11-}$ **(1)** (δ +349, +193, −114.8, 116.7, and 141.5 p.p.m.) and tentative assignments. (b) ^{183}W N.m.r. spectrum of $Ce^{4+}(PW_{11}O_{39})_2{}^{10-}$ **(2)** (δ −105.8, −110.3, −116.6, −120.5, −138.0, −142.3, −152.3, and −175.7 p.p.m.) and position of the resonances in the ^{183}W n.m.r. spectrum of $SiW_{11}O_{39}{}^{8-}$ taken from ref. 5, with the assignment taken from ref. 6.

A rather complicated ^{183}W n.m.r. spectrum is observed for the diamagnetic complex **(2)**, indicating a somewhat different structure. The spectrum (Figure 2b) corresponds to one of three possible isomers with ϕ = 45, 90, or 135°. In view of the tendency of the complexes to have a more rotated configuration and cubic co-ordination around the lanthanoid atom the isomers with ϕ — 45 and 135° may be ruled out. The spectrum clearly shows that the symmetry plane for each ligand anion is absent and that one of the four W atoms (type A′) near the vacancy has an unusual co-ordination (δ −175 p.p.m.). The chemical shifts for the complex **(2)** are similar to those found for the 'unsaturated' $SiW_{11}O_{39}{}^{8-}$ (ref. 5).

As far as is known[9] the isotropic n.m.r. shifts of paramagnetic complexes may result from either or both of two different mechanisms. One produces a contact interaction leading directly to the spin densities in the s orbitals of the magnetic nuclei. Usually these orbitals do not overlap with spin-containing metal ligands and they acquire unpaired electron density indirectly from other ligand orbitals. The second mechanism gives rise to a dipolar or pseudocontact interaction between electronic and nuclear spins. The dipolar shift δ_d for a complex with axial symmetry is often expressed by equation (1), where K is a product of constants for a given

$$\delta_d = -K.\mathbf{R}^{-3}(3\cos^2\theta - 1) \qquad (1)$$

complex, and θ is the angle between the vector **R** (distance between the resonating nucleus and central paramagnetic atom) and the principal symmetry axis of the whole complex.

For the complex **(1)** if we take into account a ^{31}P n.m.r. δ_d for **(1)** and $La(PW_{11}O_{39})_2{}^{11-}$ of −6.1 p.p.m., calculations of the chemical shifts due to only Ce–W dipolar interaction show that the range of δ_d does not exceed a few p.p.m. The resonance assigned to tungsten atoms F should undergo a down-field shift and those due to the remaining tungsten atoms an up-field shift due to dipole interaction. If we use the mean value of the split resonances for (**2**) as a reference, only two lines undergo an up-field shift. The remaining resonances are shifted to low field. If contact interaction results in paramagnetic shifts, especially for the tungsten atoms A and B owing to f-electron delocalisation, some electron transfer should also take place onto neighbouring tungsten atoms. This would be most likely for atoms C and F since they have a quasilinear (150°) W_C–O–W_A bridge as opposed to atoms D which have a bent (120°) bridge W_B–O–W_D. The larger angle is more favourable for electron transfer. On this assumption the observed resonances should be assigned as indicated in Figure 2a.

A more detailed picture may emerge as more results are obtained for paramagnetic complexes in which the configuration of the complex anion is rigid, *e.g.*, $U^{4+}(Ce^{3+})$-$W_{10}O_{36}{}^{8-}$($^{9-}$). These, as well as the complexes $U^{4+}(P_2W_{17}$-$O_{61})_2{}^{16-}$ and $U^{4+}(PW_{11}O_{39})_2{}^{10-}$ which show high paramagnetic shifts in their ^{183}W n.m.r. spectra, are being studied.

The ^{183}W n.m.r. spectra of paramagnetic complexes thus clearly show electron transfer from the central atom onto the tungsten atoms through oxygen bridges having a high degree of covalent character. This provides a new way of studying electron delocalisation in reduced polytungstates.

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