Nuclear Spin–Spin Coupling to ^{89}Y. A Model to investigate the Question of Covalent Bonding in Lanthanoid Dithiophosphinate Complexes

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The observation of spin–spin coupling between ^{89}Y and ^{31}P nuclei in the complex $[Y(S_2PR_2)_4]^-$, R = OEt, is interpreted as evidence for covalent bonding. The magnitude of the reduced coupling constant $^2K_{Y-P}$ is of the same order as $^2K_{Rh-P}$ and $^2K_{Pt-P}$ in $[Rh(S_2PR_2)_3]$ and $[Pt(S_2PR_2)_2]$ indicating similarity in the covalent contribution to their bonds. This result is extrapolated to the chemically similar lanthanoid complexes. The mechanism of hyperfine coupling in paramagnetic lanthanoid complexes, the nephelauxetic effect and the intensities of observed *f–f* transitions are discussed with respect to the above model.

THE co-ordination of sulphur donor ligands to lanthanoid ions is by now well established, especially for dithiophosphinate [1-8] and dithiocarbamate [9-11] ligands. We have previously discussed the question of the nature of the bonding in the dithiophosphinate compounds on the basis of structural data,[2-4] i.r. spectra,[5] u.v.–visible spectra,[5] and the hyperfine coupling observed between the ^{31}P nuclei and the unpaired electrons in the paramagnetic complexes.[6] Bonding parameters were found to be comparable to those in analogous transition-metal complexes,[2-4] as were the ν(M–S) frequencies,[5] suggesting a similarity in the bonding. Although the nephelauxetic effect observed for the *f—f* transitions is greatest for sulphur–donor ligands,[5] the effect is much smaller than for *d—d* transitions suggesting that there is little participation of the *f* orbitals in the bonding. The hyperfine coupling constants observed from n.m.r. spectral shifts of the paramagnetic species were shown to be two orders of magnitude less than for analogous transition-metal complexes, but significantly larger than for oxygen-donor ligands.[6]

None of the above results is able to answer the question of whether there is a significant covalent contribution to the metal–ligand bond, or whether we must accept a purely electrostatic model. We have thus chosen to study directly the interaction between the ^{89}Y and ^{31}P nuclei by n.m.r. methods to try and shed some light on the question.

EXPERIMENTAL

The compounds $[AsPh_4][Y(S_2PR_2)_4]$, $[Rh(S_2PR_2)_3]$, and $[Pt(S_2PR_2)_2]$ (R = OEt) were prepared by minor modifications of the literature methods.[5,12] Samples for n.m.r. measurements were prepared in 10-mm tubes by the addition of CD_2Cl_2 to the crystalline complexes. For the hygroscopic yttrium salt the operation was carried out under dry argon. The ^{31}P n.m.r. spectra of the rhodium and platinum compounds were recorded at room temperature and for the yttrium analogue at -50 °C, at 24.3 and/or 36.5 MHz using Bruker WP-60 and HX-90 instruments. The spectrometers were operated in the Fourier-transform mode with broadband proton decoupling, and for the WP-60, quadrature detection. Chemical shifts are reported relative to external 85% H_3PO_4.

RESULTS AND DISCUSSION

If a covalent bond exists between two nuclei which have non-zero spin in a diamagnetic compound they will be coupled to one another. This nuclear spin–spin coupling will be measurable from the n.m.r. spectrum of either nucleus.[13] However, if either nuclear spin is $>\frac{1}{2}$ the signals will be too broad in most situations to observe small couplings due to additional relaxation pathways.[14] The same problem exists for paramagnetic compounds where broad signals are invariably observed.[14] As the only diamagnetic lanthanoid ions, La and Lu, both have nuclear spins $I = 7/2$, this type of study is not possible for the lanthanoids themselves.

The chemistry of yttrium is directly comparable to that of the lanthanoids, especially to that of terbium.[15] For the purpose of n.m.r. investigations yttrium is very tractable because it is diamagnetic, with the isotope ^{89}Y having a spin, $I = \frac{1}{2}$, and a natural abundance of 100%. Hence, yttrium complexes may be used as models for their lanthanoid analogues in n.m.r. studies. Due to the low value of the gyromagnetic ratio for ^{89}Y, $\gamma = 1.3107$ rad T^{-1} s^{-1}, it is evident that the yttrium resonance will be difficult to observe because of its low sensitivity. The magnitude of the spin–spin coupling to other nuclei will also be small but of the same order as couplings to ^{103}Rh, $\gamma = 0.841\,95$ rad T^{-1} s^{-1}, in similar complexes. Since there are no available *f* orbitals in yttrium complexes it is possible to consider the influence of *s*, *p*, and *d* orbitals alone. For the above reasons we have investigated the ^{31}P n.m.r. spectrum of the dithiophosphinate complex $[Y(S_2PR_2)_4]^-$ (R = OEt) and its Pt^{II} and Rh^{III} analogues.

^{31}P N.m.r. parameters for dithiophosphinato-complexes

Metal	Atomic number	δ/ p.p.m.	$^2J_{M-P}$/ Hz	$^2K_{M-P}$/ 10^{20} N A^2 m^{-3}	C.N.
Y	39	98.8	5.1	2.14	8
Rh	45	96.1	13.3	8.69	6
Pt	78	100.5	447.1	42.77	4

At room temperature the broadband-decoupled ^{31}P n.m.r. spectrum of the yttrium complex is a broad singlet. On cooling to -50 °C a well resolved doublet (Table) was observed for the ^{31}P resonance. We attribute this behaviour to chemical exchange between the complex and a trace of free ligand impurity in the solution. This conclusion is supported by a separate variable-temperature n.m.r. experiment where a small quantity of free ligand added to the solution was shown to be in rapid exchange with the complex at room temperature. This behaviour contrasts with that of the lanthanoid analogues, which were shown to be stable, with respect to exchange of the ligand, in methylene chloride solution.[6]

The crystal structure[2] of the $[Pr(S_2PMe_2)_4]^-$ ion indicates the probable chemical equivalence of the four phosphorus atoms; however, it is known that $[Ln\{S_2P(OEt)_2\}_4]^-$ ions exist in two different structural configurations in solution.[6] For this reason the coupling constant was measured at two field strengths to confirm that the splitting is due to spin–spin coupling rather than some chemical non-equivalence of the phosphorus nuclei.

The treatment of nuclear spin–spin coupling constants given by Ramsey and expanded by Pople and Santry[13] implies that the magnitude of the observed coupling between two nuclei yields information about the covalency of the intervening bonds. If the contact mechanism is dominant in spin–spin coupling, then all that is required is a contribution of *s* orbitals to the bonds. If dipolar or orbital effects also contribute then higher orbitals and multiple bonding must be invoked. It is outside the scope of this work to state, quantitatively, the covalency and contribution due to each valence orbital. However, the measured Y–P coupling can be compared to analogous transition-metal couplings. To this end we have also evaluated the J couplings between ^{31}P and ^{195}Pt and ^{103}Rh in $[Pt\{S_2P(OEt)_2\}_2]$ and $[Rh\{S_2P(OEt)_2\}_3]$ (Table). To effect the comparison, the measured spin–spin couplings must be corrected for the different gyromagnetic ratios.[13,16] This is done by calculating the reduced coupling constant, $K_{ij} = J_{ij}(4\pi^2/h\gamma_i\gamma_j)$. The values of $^2K_{M-P}$ measured for M = Y, Rh, and Pt can now be compared to each other. Within the framework of the Pople–Santry formalism of coupling constants,[13] the contact contribution to $^2K_{M-P}$ should be proportional to the square of the valence-shell *s* orbital density at the nucleus, $\psi^2(0)$, and the dipolar and orbital contributions proportional to the mean value of r^{-3} for the atomic orbitals in the valence shell. Calculated values for $\psi^2(0)$ and $\langle r^{-3}\rangle$ have recently been tabulated.[17] The values for Y, Rh, and Pt in atomic units are $\psi^2(0) = 4.616$, 6.414, and 12.53, and $\langle r^{-3}\rangle = 2.373$, 7.179, and 12.81 respectively. From these figures it is clear that $^2K_{M-P}$ must be in the order Pt > Rh > Y as observed, irrespective of the mechanism. A further point to consider is the change in co-ordination number (C.N.) which implies a change in the relative metal *s*-orbital contribution to the M–S bond, with Pt > Rh > Y, and the contact contribution to the reduced coupling constant should be greater to the ligand with the greater metal *s*-orbital contribution. Hence, the above effects all reduce the apparent differences in $^2K_{M-P}$ for the different metals. Thus we suggest that the Y–S bond has covalent character similar to that found in analogous transition-metal complexes. We may now extrapolate this result to the lanthanoids and state that covalent bonds probably exist without any need to invoke the contribution of the *f* orbitals, and from this point of view comment on previous structural, i.r., n.m.r., and u.v.–visible spectral results.

Clearly we would now expect that structural parameters should show the same trends whether the central ion is a lanthanoid or a transition metal. The same conclusion may be reached with regard to their i.r. spectra. This is in complete agreement with experience.[2-5] Properties which depend on the presence of *f* electrons must however be discussed differently. There are two possible mechanisms to produce the electron–nuclear hyperfine coupling deduced from the n.m.r. spectra of the paramagnetic lanthanoid complexes.[18] Both mechanisms require a covalent bond between the metal and the ligand. One possible bonding scheme directly involves the *f* orbitals of the metal ion; however, the *f* orbitals in the lanthanoids are effectively shielded from direct overlap with the ligand orbitals by the filled 5*s* and 5*p* orbitals. Alternatively, the bonding may take place by using the unfilled 6*s*, 6*p*, and 5*d* orbitals, and the hyperfine coupling is accomplished by configuration interaction. Since this work has demonstrated that nuclear spin–spin coupling is as important in yttrium complexes as in transition-metal analogues, it is reasonable to propose that the electron–nuclear hyperfine coupling in lanthanoid complexes is due to a mechanism involving the 6*s*, 6*p*, and 5*d* orbitals. This proposal is also consistent with our observation, reported earlier,[6] that the hyperfine coupling for $[Ln\{S_2P(OEt)_2\}_4]^-$ is orders of magnitudes smaller than for transition-metal analogues, but greater than for less polarisable, and presumably less covalent, oxygen-donor ligands.

We may also consider the u.v.–visible spectra of lanthanoid complexes in a similar way. The nephelauxetic effect[19] requires that the *f* orbitals should expand on complex formation. The introduction of the ligand electrons into the outer orbitals of the lanthanoid ion will reduce the effective nuclear charge and thus allow the required expansion. This is, of course, a smaller effect than observed for *d* orbitals in transition metals, because the *d* electrons are at about the same distance from the nucleus as the orbitals used for bond formation, whereas the *f* orbitals lie closer to the nucleus.

A further phenomenon observed in these spectra is the increase in the oscillator strengths of the formally forbidden *f*—*f* transitions on complexation.[5,8,11] According to the Judd–Ofelt theory,[20] these transitions become weakly allowed due to some mixing of excited states of opposite parity into the ground state (configuration interaction). This small mixing may be increased on complexation if the energy of the excited state is lowered. The most likely states to be affected in this way are those derived from configurations involving the 5*d* orbitals or the molecular orbitals formed from them on complexation. These are just those which we have proposed as part of the covalent bonding scheme. Additional intensity may also be gained by the mixing of ligand and metal wavefunctions due to the orbital overlap. This is in agreement with previous reports[5,8,11] that the intensities of the *f*—*f* transitions, especially those of the hypersensitive bands, are significantly larger for sulphur-donor ligands than for the less polarisable oxygen and nitrogen donors.

Conclusions.—We have shown that yttrium is a useful model for investigating the nature of bonding in lanthanoid complexes by n.m.r. studies on the bound ligand. The bonding contains an important covalent contribution involving the 6*s*, 6*p*, and 5*d* orbitals. The electron–nuclear hyperfine coupling observed in paramagnetic complexes of the lanthanoids is probably due to configuration interaction rather than a direct bonding interaction. Nephelauxetic parameters may be explained by a covalent model which reduces the effective nuclear charge and allows the *f* orbitals to expand. Covalent bonds increase the mixing of states of opposite parity required to relax the selection rules for *f*—*f* transitions, thus increasing their intensity.

We thank Professors G. Brunisholz, A. Merbach, and D. Schwarzenbach for their encouragement to pursue this investigation, and the Swiss National Science Foundation for financial support.

[8/1386 *Received, 25th July*, 1978]

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