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Dithiophosphinate Complexes of the Actinides, III. An NMR Study of Uranyl Dithiophosphinates. Nuclear Spin–Spin Coupling ($^4J_{PP}$) through the Uranyl Center as Evidence for Metal–Ligand π Bonding

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In the complexes $[UO_2(S_2PR_2)_2 \cdot Cl]^-$ *(R = Me, OMe, OEt, OPr^i, Ph) and* $UO_2\{S_2P(OPr^i)_2\}_2 \cdot EtOH$ *the nmr spectra of the protons closest to phosphorus exhibit second order features due to appreciable spin–spin coupling between the* ^{31}P *nuclei through the metal center. These spectra have been analysed, if necessary with the aid of homonuclear decoupling, to yield values of* $^4J_{PP}$ *ranging from 9 to 19 Hz. Additional features are observed in the spectrum for R = OEt as the methylene protons are diastereotopic. A mechanism for the transmission of spin information via π orbitals is proposed.*

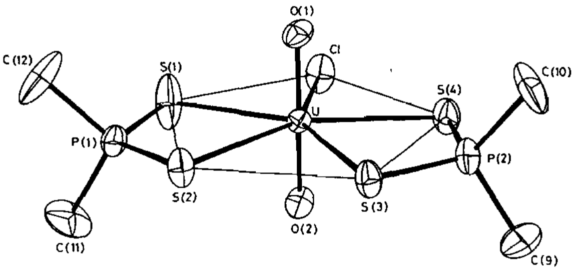

Fig. 1. A perspective view of the complex $[UO_2(S_2PMe_2)_2Cl]^-$.

Introduction

We have recently reported [1] the synthesis and characterisation of a number of pentagonal bipyramidal dithiophosphinate uranyl complexes of the general formula $UO_2(S_2PR_2)_2 \cdot L$, where L is a monodentate ligand (Cl^-, R′OH, R_3′PO). In discussing the proton nmr of these complexes we noted that they were not always first order, even at high field (360 MHz). These second order effects were attributed to substantial spin–spin coupling between the two phosphorus nuclei. We have thus carried out a detailed study of these spectra in the hope of obtaining additional information to characterise the bonding between these sulphur donor ligands and uranium (VI).

Experimental

The complexes were prepared as described [1] and their ^1H nmr spectra obtained from CD_2Cl_2 solutions at room temperature with a Brucker WH 360 spectrometer. Where more than one type of proton exists, the part of the spectrum of interest was simplified by homonuclear decoupling. Iterative fitting of the observed and calculated spectra was carried out with the program PANIC [2]. Reported chemical shifts are in ppm relative to $SiMe_4$, and coupling constants in Hz.

Results

In the solid state, the complexes $UO_2(S_2PR_2)_2 \cdot L$ have been shown to be pentagonal bipyramidal [1]. One example is shown in Fig. 1. In most cases the pentagonal plane is significantly puckered. This puckering implies that the two R substituents at phosphorus should be chemically inequivalent. In solution this puckering must be dynamic as only one chemical environment is observed by nmr (fluxional averaging).

The spectra that we wish to discuss are, at least to a first approximation, of the type $X_nAA'X_n'$. The theoretical treatment of this type of spectrum is well known [3]. For all the spectra considered here, good starting values for the coupling constants were

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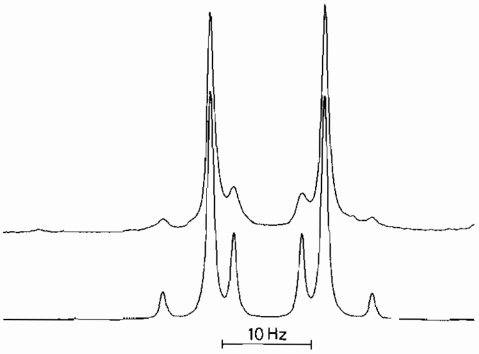


Fig. 2. Experimental (upper) and calculated (lower) ^{1}H nmr spectrum of [UO$_2$(S$_2$PMe$_2$)$_2$Cl]$^-$.

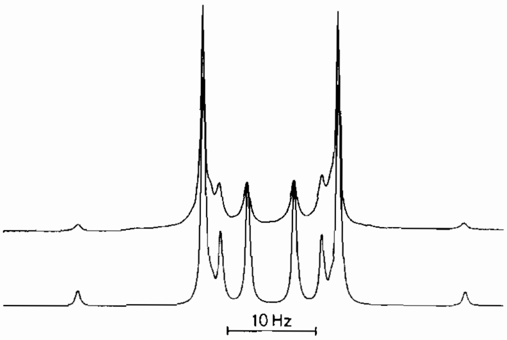


Fig. 3. Experimental (upper) and calculated (lower) ^{1}H nmr spectrum of [UO$_2${S$_2$P(OMe)$_2$}$_2$Cl]$^-$.

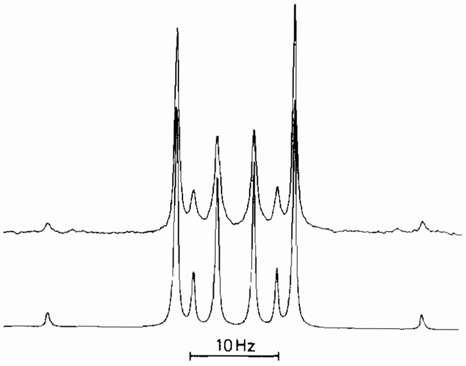


Fig. 4. Experimental (upper) and calculated (lower) ^{1}H nmr spectrum of [UO$_2${S$_2$P(OPr^i)$_2$}$_2$Cl]$^-$, decoupled CH region only.

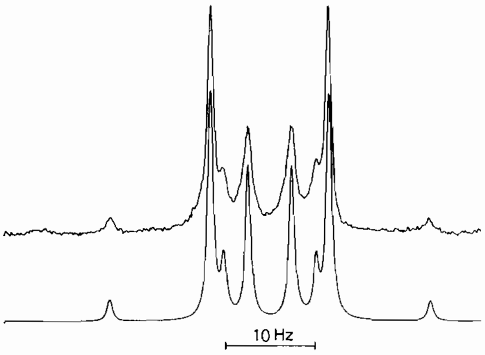


Fig. 5. Experimental (upper) and calculated (lower) ^{1}H nmr spectrum of UO$_2${S$_2$P(OPr^i)$_2$}$_2$·EtOH, decoupled CH region only.

obtained by inspection and best values obtained by iterative fitting to the obserbed digitised spectra. The spectra will be presented in order of increasing complexity, and the derived parameters discussed at the end.

[UO$_2$(S$_2$PMe$_2$)$_2$Cl]$^-$

The experimental (upper) and calculated (lower) spectra are presented in Fig. 2. The line widths of the calculated spectrum are fixed artificially to approximate the experimental spectrum and have no physical significance. The multiplet (δ = 2.23) is clearly not a simple first order doublet. Inspection of the symmetrical multiplet using the expressions set out by Harris [3] indicate that there is an appreciable phosphorus–phosphorus (A–A′) coupling ($^4J_{PP}$ ≈ 8 Hz), but that the long range proton–phosphorus coupling ($^6J_{PH}$) is small. The main doublet (N = $^2J_{PH}$ + $^6J_{PH}$) is hence almost exactly $^2J_{PH}$ (≈13 Hz). The values obtained from the iterative fitting procedure are given in the table. The signs of the couplings are only relative, no effort having been made to obtain absolute values.

[UO$_2${S$_2$P(OMe)$_2$}$_2$Cl]$^-$

The experimental and calculated spectra are presented as before in Fig. 3. The multiplet centered at δ = 3.86 is of a similar type to that obtained above. The magnitude of $^4J_{PP}$ is clearly larger (≈19 Hz) and the main doublet (N = $^3J_{PH}$ + $^7J_{PH}$) is ≈15 Hz, but the long range $^7J_{PH}$ is again close to zero. The iterated values are presented in the table.

[UO$_2${S$_2$P(OPr^i)$_2$}$_2$Cl]$^-$

The methyl protons of the isopropyl group are observed as a simple first order doublet at δ = 1.39, $^3J_{HH}$ = 6.3 Hz. The signal of the CH proton (δ = 4.93) is however complex. Although at a rapid glance it could be thought to be a badly-resolved doublet ($^3J_{PH}$) of septets ($^3J_{HH}$), the resolution of the rest of the spectrum suggested this to be unlikely. Hence the septet structure was removed by irradiation of the methyl protons, and the typical second order pattern shown in Fig. 4 obtained. The spectrum was analysed as before, the starting values for $^4J_{PP}$ (19 Hz), $^3J_{PH}$ (13 Hz) and $^7J_{PH}$ (0 Hz) being obtain-

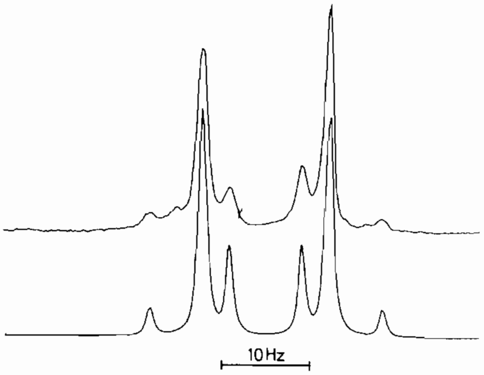


Fig. 6. Experimental (upper) and calculated (lower) ^1H nmr spectrum of $[UO_2(S_2PPh_2)_2Cl]^-$, decoupled ortho proton region only.

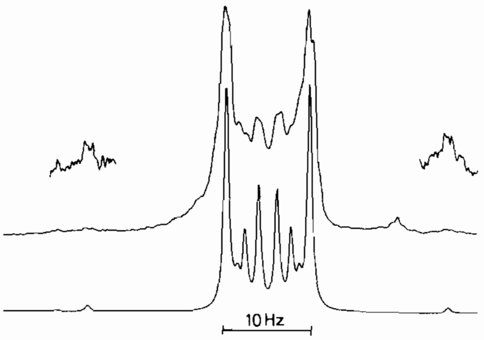


Fig. 7. Experimental (upper) and calculated (lower) ^1H nmr spectrum of $[UO_2\{S_2P(OEt)_2\}_2Cl]^-$, decoupled CH_2 region only.

TABLE I. Coupling Constants for the Complexes $UO_2(S_2PR)_2 \cdot L$.[a]

R	L	$^4J_{PP}$	J_{PH}	$J_{PH'}$
Me	Cl^-	7.90	13.11	−0.25
OMe	Cl^-	19.06	15.08	0.02
OPr^i	Cl^-	19.00	13.25	0.06
OPr^i	EtOH	15.60	13.35	−0.03
Ph	Cl^-	9.05	14.63	−0.07
OEt	Cl^-	19.20	9.28	0.14

[a] The only protons considered are those closest to phosphorus.

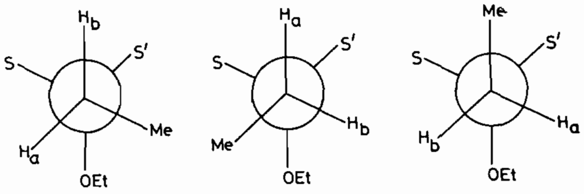


Fig. 8. Newman projection of the methylene group of one ethyl substituent in the complex $[UO_2\{S_2P(OEt)_2\}_2Cl]^-$.

ed by inspection, and the values obtained after iteration are reported as before.

$UO_2\{S_2P(OPr^i)_2\}_2 \cdot EtOH$

A similar situation exists here as in the chloro-complex above. The methyl signal (δ = 1.39) is a simple doublet ($^3J_{HH}$ = 5.9 Hz), but the CH signal (δ = 4.92) is complex. After decoupling in the same way, the CH signal was simplified to give the spectrum in Fig. 5. Inspection yields the starting values of 15 Hz ($^4J_{PP}$), 13 Hz ($^3J_{PH}$) and 0 Hz ($^7J_{PH}$), and the final values are given in the Table.

$[UO_2\{S_2PPh_2\}_2Cl]^-$

The protons of the phenyl rings give rise to two signals at δ = 7.44 (3H) and δ = 8.06 (2H). These signals are complex due in part to the inherent magnetic inequivalence of the protons in monosubstituted phenyl rings. Because the signals are well separated we were able to irradiate the high field signal (*meta* and *para* protons) and thus simplify the low field signal (*ortho* protons) to that shown in Fig. 6. The experimental spectral quality is not good here, no doubt due to the closeness of the decoupling frequency. The fact that we distinguish only one type of *ortho* proton implies that the phenyl rings must rotate freely about the P–C bond. The starting values of the coupling constants were 8.8 Hz ($^4J_{PP}$), 14.5 Hz ($^3J_{PH}$) and 0 Hz ($^7J_{PH}$) and the iterated values are reported in the table.

$[UO_2\{S_2P(OEt)_2\}_2Cl]^-$

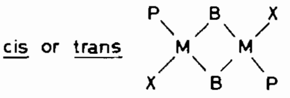
The methyl protons give rise to a simple first order triplet (δ = 1.38, $^3J_{HH}$ = 7.0 Hz), however the methylene proton signal (δ = 4.25) has the form of two overlapping quartets with additional structure. The quartet structure was removed by irradiating at the methyl frequency, and the upper trace of Fig. 7 was obtained. The lower trace is the spectrum calculated from the iterated values (Table 1) assuming the two methylene protons to be chemically equivalent (starting values $^4J_{PP}$ = 19 Hz, $^3J_{PH}$ = 9.5 Hz, $^7J_{PH}$ = 0 Hz). Although this model gives an overall reasonable fit, it is clear that there is additional structure in the experimental spectrum. This is due to a small chemical shift difference between the methylene protons which may be understood by consideration of the possible rotamers shown in Fig. 8. For clarity, the projections have been drawn as if the P–O–C angle were linear. We can thus see that H_a and H_b have been rendered diastereotopic by the chemical equivalence of the sulphur atoms. The sulphur atoms lie in a pentagonal plane, one having chlorine as nearest neighbour and the other sulphur from the second ligand (see Fig. 1).

We have not attempted to analyse this spectrum further as the resolution is not sufficient; however, the chemical shift difference is small as all additional splittings in the spectrum are less than 1 Hz even at 360 MHz.

Discussion

The most important point to discuss is the observed coupling between the phosphorus nuclei, $^4J_{PP}$. We will first consider this in terms of the coupling itself, and then in terms of the uranyl center.

Spin–spin coupling between phosphorus nuclei has been of interest for a number of years and there have been several reviews on the subject [4]. In general coupling constants are rapidly attenuated by the number of intervening bonds, and the few values of $^4J_{PP}$ known are rather small. To our knowledge, the only observation of this coupling through a metal center concerns bimetallic systems I where the coupling is $^4J(PMBMP)$ [5, 6]. The metal (M) is usually platinum or palladium. The bridge (B) may be RS, R_2P or H, and the couplings are generally < 10 Hz. However, a value of 15 Hz was obtained for *cis*-$Pt_2I_4(PF(OPh)_2)_2$ [6] and for the hydride bridged heterometallic species II a coupling of 43 Hz was observed [7].



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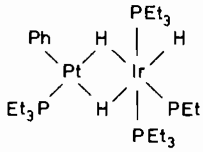

II

A few long-range phosphorus–phosphorus couplings have also been reported ($^5J_{PP}$–$^9J_{PP}$) but these are all for highly conjugated molecules and are transmitted by π electrons [8].

Very little information exists in the literature concerning the nmr spectra of dithiophosphinate complexes of the d transition metals. The most detailed study was carried out by Nanjo [9], but no mention was made of second order effects or of phosphorus–phosphorus coupling.

The values of $^4J_{PP}$ obtained here (8–19 Hz) are hence surprisingly large, and the first example of spin information transmitted by an f transition element. The fact that the most electronegative substitutents at phosphorus give the largest values for $^4J_{PP}$ suggest that the sign of the coupling is positive. Bent [10] has demonstrated that the s contribution to orbitals is highest towards the most electropositive substituents. We would thus expect the Fermi contact contribution to the coupling to increase as the electronegativity of the substituents on the other side of the phosphorus increases.

If the transmission of spin information across the metal center was passed uniquely by the σ bonding scheme, we would expect at least equally large couplings to be observed in diamagnetic d transition metal analogues, and this does not appear to be the case. We are thus tempted to postulate transmission mainly by a π mechanism. It is known that the of the highest occupied π orbital of 'odd' π orbital ligands (*e.g.* 1,1 dithiols) is a non-bonding orbital which has a net zero overlap with metal d orbitals for symmetry reasons [11]. However, using similar arguments, this orbital has the correct symmetry to interact with $5f_{xyz}$ or $5f_{zx^2}$ orbitals. In addition, this would allow both of the ligands to interact with the same f orbitals which would thus give rise to π delocalisation across the metal center and a possible mechanism for the transmission of spin information.

We thus suggest that the present nmr results are consistent with the presence of a π contribution to the covalent bonding scheme in these uranyl complexes.

Acknowledgements

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