Heteronuclear INDOR Spectra of some Tetrakis(fluorophosphine)-nickel(0) and -platinum(0) Complexes having the $[AX]_4(T_d)$ Spin System

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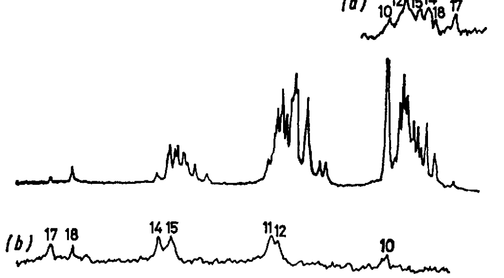
X-{A} INDOR spectra greatly simplify the analysis of tetrahedral $[AX]_4$ systems. The method is illustrated by the determination of the magnitudes and relative signs of ^1J(PF), ^3J(PF), ^2J(PP), and ^4J(FF) in complexes $[ML_4]$ [M = Ni or Pt; L = $F\overline{POC_6H_4O}$ or $PF(OPh)_2$].

MUCH attention has been focused on the evaluation of coupling constants, especially ^2J(PP), in square-planar and octahedral transition-metal complexes containing mutually *cis*- or *trans*-phosphine ligands.[1,2] In contrast, accurate data on tetrahedral systems have hitherto been confined to a number of nickel(0) fluorophosphine complexes [3,4] and in no case has the sign of ^2J(PP) been determined. Since ^{1}H-{^{31}P} INDOR has been used to determine the sign and magnitude of ^2J(PP) in square-planar complexes of spin systems $[AX_n]_2$ and $[AX_n]_4$,[2] we were interested in applying this technique to the problem of sign determination in a tetrahedral case. Complexes of the type $[ML_4]$ (L = a monofluorophosphine) have the simplifying features that $n = 1$ and J_{AX} is large although $J_{XX'}$ can no longer be assumed to be zero. We have examined the ^{19}F-{^{31}P} INDOR spectra of the previously reported [5,6] nickel(0) complexes of 2-fluoro-1,3,2-benzodioxaphosphole $F\overline{POC_6H_4O}$ and $PF(OPh)_2$ as well as the hitherto unreported platinum(0) analogues. {$[Ni(F\overline{POC_6H_4O})_4]$ was the subject of a previous analysis.[7]}

THEORY AND RESULTS

The matrix elements and general features of an $[AX]_4(T_d)$ spin system with large J_{AX} are described by Lynden-Bell.[7] One eighth of the total intensity of the X spectrum appears as a sharp doublet of separation $N = (J_{AX} + 3J_{AX'})$ arising from transitions in which $m_A = \pm 2$ and these 'N' lines are therefore particularly suitable for INDOR experiments. As in similar work on other spin systems,[2] we treated the X-{A} INDOR spectrum as that part of the A spectrum related to the six X transitions involved in the monitored line. On this basis, calculation of the INDOR spectrum from the matrix elements given by Lynden-Bell † yielded a group of 18 theoretically allowed transitions associated with each 'N' line of the X spectrum (Table 1). That the INDOR spectrum is only a fraction of the complete A spectrum arises because no states having E or T_1 symmetry in the T_d point group, or which have m_A equal to zero, are involved. From Table 1 it is apparent that four of the A_1 transitions comprise a series, $\nu_A + \frac{1}{2}N + n[\frac{1}{2}(J_{AA} + J_{XX}) - J_{AX'}]$ where $n = 0$—3, whilst the remaining four occur on the other side of ν_A with spacings of $\frac{1}{2}(J_{AA} + J_{XX}) + J_{AX'}$. If these lines can be identified, therefore, $(J_{AA} + J_{XX})$ and $J_{AX'}$ are immediately found with relative signs, while the sign and magnitude of J_{XX} follows from identification of lines (9) and (18).



Comparison of the high-frequency halves of the ^{31}P Fourier-transform n.m.r. spectrum of $[Pt(F\overline{POC_6H_4O})_4]$ and the ^{19}F-{^{31}P} INDOR spectra observing (*a*) the strong high-frequency ^{19}F line and (*b*) the strong low-frequency ^{19}F line

The Figure illustrates how the ^{19}F-{^{31}P} INDOR spectrum of $[Pt(F\overline{POC_6H_4O})_4]$ is related to the directly observed ^{31}P spectrum. Only 14 out of the 18 possible transitions were observed. Lines (4), (7), (13), and (16) are almost forbidden when $J_{AA} \gg J_{XX}$, but these four lines should in principle be observable with greater irradiating power.[8] In most cases, broadening of nearby features at increased power levels precluded detection of these weak lines, but for the two platinum complexes line (7) was sufficiently distant to be observed at *ca.* 25 dB higher irradiating power than that used in the Figure. Calculation of ^2J(PP) and ^4J(FF) from lines (8), (9), (17), and (18) in the INDOR spectrum of $[Pt(F\overline{POC_6H_4O})_4]$ yielded values within 0.1 Hz of those in Table 2 but ^3J(PF) was in error by >2 Hz. This is a consequence of the approximate nature of the expressions in Table 1 which hold well for the nickel but less so for the platinum complexes where the value of ^2J(PP) is much larger. The errors in the calculated line positions [*ca.* 5—8 Hz with opposite signs for lines (2)—(9) and (11)—(18) respectively] largely cancel in the evaluation of J_{AA} and J_{XX} but not for $J_{AX'}$. Accurate values of ^3J(PF) were obtained by including the mixing

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† In Table 4 of ref. 7, for both types of function with $m_A = 1$ and $m_X = 0$, the X entries of H_1ii should be $-\frac{1}{2}$ and the diagonal matrix elements of H_2 for the T_1 species should be $\frac{1}{2}(X - A)$ and $\frac{1}{2}A$.

[1] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

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between the two A_1 spin functions of the ($m_A = 1$, $m_X = 1$) and ($m_A = 1$, $m_X = -1$) matrices, leading to expressions (i) and (ii) for the relevant transition energies.

$$(17),\ (2)\quad J_{AX'} + J_{AA} + J_{XX} \pm \tfrac{1}{2}[(N - 2J_{AX'} + J_{AA} + J_{XX})^2 - 4(N - 3J_{AX'})(J_{AX'} + J_{AA} + J_{XX}) + 3(J_{AA} + J_{XX})^2]^{\frac{1}{2}} \qquad \text{(i)}$$

$$(11),\ (8)\quad -J_{AX'} + J_{AA} + J_{XX} \pm \tfrac{1}{2}[(-N + 2J_{AX'} + J_{AA} + J_{XX})^2 + 4(N - 3J_{AX'})(-J_{AX'} + J_{AA} + J_{XX}) + 3(J_{AA} + J_{XX})^2]^{\frac{1}{2}} \qquad \text{(ii)}$$

The parameters obtained by this method are sufficiently accurate for most purposes, but they were refined by fitting a computed spectrum (using the program LACX [9]) to the proton-decoupled phosphorus spectrum. The complete set of data for the four complexes is given in Table 2. The signs of the coupling constants are based on the assumption that ^1J(PF) is negative.[3]

The relative intensities of the INDOR lines showed considerable deviations from those of the same lines in the directly observed or computed spectra. One factor which has to be taken into account is that the intensity of an INDOR resonance depends on the square root of the intensity of the perturbed transition; [8] thus the reason why lines (1) and (10) are relatively weak may be that they are, respectively, regressively or progressively connected to X transitions of intensity 4 while line (2), for example, is regressively connected to an X transition of intensity 6 and also progressively connected to one of intensity 4. We have not considered the matter further, but note that in all the INDOR spectra the A_1 transitions are more intense than those between T_2 states rather than the reverse.

DISCUSSION

The application of INDOR to complexes with the spin system $[AX]_4(T_d)$ not only yields valuable sign information but also greatly simplifies the analysis. This technique should therefore be particularly valuable in cases where the analysis of single resonance spectra is made difficult by poor resolution resulting from many overlapping lines, as often happens with the fluorine spectra of fluorophosphine complexes (particularly $[Ni\{PF(OPh)_2\}_4]$ where there is significant broadening from the phenoxy-protons). It should similarly be

TABLE 1

Transitions of the A nuclei of an $[AX]_4(T_d)$ spin system which are related to the X line at $(\nu_X + \frac{1}{2}N)$ [a] (with approximations following from J_{AX} being large)

	m_X	Symmetry [b]	Energy [c]	Intensity [d]
(1)	2	A_1	$\frac{1}{2}N$	4
(2)	1	A_1	$\frac{1}{2}N - J_{AX'} + \frac{1}{2}J_{AA} + \frac{1}{2}J_{XX}$	3
(3)	1	T_2	$\frac{1}{2}N - J_{AX'} + \frac{5}{4}J_{AA} - \frac{3}{4}J_{XX} - \frac{1}{4}R$	$\frac{3}{2}(3 + g)$
(4)	1	T_2	$\frac{1}{2}N - J_{AX'} + \frac{5}{4}J_{AA} - \frac{3}{4}J_{XX} + \frac{1}{4}R$	$\frac{3}{2}(3 - g)$
(5)	0	A_1	$\frac{1}{2}N - 2J_{AX'} + J_{AA} + J_{XX}$	2
(6)	0	T_2	$\frac{1}{2}N - 2J_{AX'} + \frac{3}{2}J_{AA} - \frac{1}{4}J_{XX} - \frac{1}{4}S$	$3(1 + h)$
(7)	0	T_2	$\frac{1}{2}N - 2J_{AX'} + \frac{3}{2}J_{AA} - \frac{1}{4}J_{XX} + \frac{1}{4}S$	$3(1 - h)$
(8)	−1	A_1	$\frac{1}{2}N - 3J_{AX'} + \frac{3}{2}J_{AA} + \frac{3}{2}J_{XX}$	1
(9)	−1	T_2	$\frac{1}{2}N - 3J_{AX'} + \frac{3}{2}J_{AA} - \frac{1}{2}J_{XX}$	3
(10)	−2	A_1	$-\frac{1}{2}N$	4
(11)	−1	A_1	$-\frac{1}{2}N + J_{AX'} + \frac{1}{2}J_{AA} + \frac{1}{2}J_{XX}$	3
(12)	−1	T_2	$-\frac{1}{2}N + J_{AX'} + \frac{5}{4}J_{AA} - \frac{3}{4}J_{XX} - \frac{1}{4}R$	$\frac{3}{2}(3 + g)$
(13)	−1	T_2	$-\frac{1}{2}N + J_{AX'} + \frac{5}{4}J_{AA} - \frac{3}{4}J_{XX} + \frac{1}{4}R$	$\frac{3}{2}(3 - g)$
(14)	0	A_1	$-\frac{1}{2}N + 2J_{AX'} + J_{AA} + J_{XX}$	2
(15)	0	T_2	$-\frac{1}{2}N + 2J_{AX'} + \frac{3}{2}J_{AA} - \frac{1}{4}J_{XX} - \frac{1}{4}S$	$3(1 + h)$
(16)	0	T_2	$-\frac{1}{2}N + 2J_{AX'} + \frac{3}{2}J_{AA} - \frac{1}{4}J_{XX} + \frac{1}{4}S$	$3(1 - h)$
(17)	1	A_1	$-\frac{1}{2}N + 3J_{AX'} + \frac{3}{2}J_{AA} + \frac{3}{2}J_{XX}$	1
(18)	1	T_2	$-\frac{1}{2}N + 3J_{AX'} + \frac{3}{2}J_{AA} - \frac{1}{2}J_{XX}$	3

$N = J_{AX} + 3J_{AX'}$
$R = [(J_{AA} + J_{XX})^2 + 8(J_{AA} - J_{XX})^2]^{\frac{1}{2}}$
$S = [(2J_{AA} - J_{XX})^2 + 8J_{XX}^2]^{\frac{1}{2}}$
$g = [(J_{AA} + J_{XX}) + 8(J_{AA} - J_{XX})]/R$
$h = (2J_{AA} - J_{XX})/S$

[a] Transitions related to $(\nu_X - \frac{1}{2}N)$ are obtained by reversing the signs of the terms in J_{AA} and J_{XX}. [b] T_2 is used where ref. 7 has T_1. [c] Term in ν_A omitted. [d] In the directly observed A spectrum, relative to a total intensity of 1 024.

TABLE 2

Fluorine-19, ^{31}P, and ^{195}Pt n.m.r. parameters of $[ML_4]$ [M = Ni or Pt; L = $FPOC_6H_4O$ or $PF(OPh)_2$]

	δ(F) [a]	δ(P) [b]	^1J(PF)	^3J(PF)	^2J(PP)	^4J(FF)	δ(Pt) [c]	^1J(PtP)	^2J(PtF)
$[Ni(FPOC_6H_4O)_4]$ [d]	14.0	−158.1	−1 288.3 ± 0.5	+29.2	+17.7	+5.8			
$[Ni\{PF(OPh)_2\}_4]$ [e]	29.9 [f]	−140.2	−1 205.8 ± 1	+34.7 ± 0.2	+21.7 ± 0.2	+5.1 ± 0.2			
$[Pt(FPOC_6H_4O)_4]$ [f]	13.8	−117.4	−1 359.3 ± 0.5	+34.2	+100.7	+8.4	−1 096 [g]	+6 096 ± 1	445.1
$[Pt\{PF(OPh)_2\}_4]$ [e]	22.5 [f]	−106.7	−1 269.4 ± 0.5	+40.3	+102.5	+7.8	−1 057 [f]	+5 981 ± 1	371.6 [f]

Coupling constants are accurate to ±0.1 Hz except where indicated.

[a] In p.p.m. upfield from $CFCl_3$. [b] In p.p.m. upfield from H_3PO_4. [c] In p.p.m. to high frequency of 21.4 MHz when corrected to $SiMe_4$ = 100 MHz. [d] In benzene. [e] In $CDCl_3$. [f] In CH_2Cl_2. [g] In tetrahydrofuran.

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[9] C. W. Haigh, *Ann. Rev. N.M.R. Spectroscopy*, 1971, **4**, 346; N.M.R. Computer Program Library Manual, Science Research Council.

possible to partition complex spectra of other spin systems of high symmetry.

The values of ^2J(PP) in the two platinum(0) complexes are much higher than any reported for a nickel(0) complex.[3,4] It is interesting to note that they lie midway between typical values for *cis* (*ca.* −20 Hz) and *trans* (>+250 Hz) platinum(II) complexes.[2] Further discussion does not seem profitable in the absence of data on platinum(II) systems with this type of ligand.

EXPERIMENTAL

Phosphorus-31 n.m.r. spectra were recorded on a JEOL PFT 100 Fourier-transform spectrometer, using an internal deuterium lock and broad-band proton decoupling. INDOR spectra were recorded as previously described.[10] All the measurements were made at ambient magnet temperature (*ca.* 300 K). For measurements on [Pt($FPOC_6H_4O)_4$], which decomposes slowly both in solution and the solid state, fresh saturated solutions in dichloromethane were used except that tetrahydrofuran, in which it is more soluble but decomposes more rapidly, was the solvent for the δ(Pt) determination. The other complexes were examined as *ca.* 0.4 mol dm^{-3} solutions in a suitable solvent.

Tetrakis(2-*fluoro*-1,3,2-*benzodioxaphosphole*)*platinum*(0).—A 10% excess of $FPOC_6H_4O$ [5] was added, at −50 °C under nitrogen, to a solution of [Pt(cod)$_2$] [11] (cod = cyclo-octa-1,5-diene) (0.51 g, 1.2 mmol) in dry toluene (20 cm^3). Stirring was continued until the mixture reached room temperature. After filtration and the addition of pentane, the product crystallized as colourless blocks (0.88 g, 86%), m.p. 151—153 °C (Found: C, 34.9; H, 2.05. $C_{24}H_{16}F_4O_8P_4Pt$ requires C, 34.85; H, 1.95%).

The complex [Pt{PF(OPh)$_2$}$_4$] was prepared similarly from [Pt(cod)$_2$] and PF(OPh)$_2$ [12] but could not be crystallized or sublimed (Found: C, 50.8; H, 3.45. $C_{48}H_{40}F_4O_8P_4Pt$ requires C, 50.6; H, 3.55%). The previous preparations of the two nickel complexes [5,6] started from [Ni(CO)$_4$]. We prepared them in good yield from [Ni(cod)$_2$] in the manner described above. The complex [Ni($FPOC_6H_4O)_4$] crystallized as white plates, m.p. 129—130 °C (Found: C, 41.65; H, 2.3. $C_{24}H_{16}F_4NiO_8P_4$ requires C, 41.7; H, 2.35%) and had similar n.m.r. parameters to those previously reported.[3] Like the previous workers, we could isolate [Ni{PF(OPh)$_2$}$_4$] only as an oil; the ^{19}F and ^{31}P chemical shifts were similar to the published values.[6]

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