Nuclear Magnetic Triple Resonance Studies of Silver Shielding in Organo-phosphite Complexes

By IAN J. COLQUHOUN and WILLIAM MCFARLANE*
(*Chemistry Department, City of London Polytechnic, Jewry Street, London* EC3N 2EY)

Summary $^{31}P-\{^{107}Ag, ^{1}H\}$ magnetic triple resonance experiments allied to difference spectroscopy and two-dimensional presentation give rapid and unequivocal assignments of resonances from mixtures of silver complexes and permit the study of trends in silver-107 shielding.

SILVER has two isotopes (^{107}Ag, $I = \frac{1}{2}$, natural abundance 52%; ^{109}Ag, $I = \frac{1}{2}$, natural abundance 48%) with properties which would be well suited to n.m.r. study were it not for their poor sensitivities which are only 3.4×10^{-5} and 4.9×10^{-5} of the proton's. Furthermore, as a result generally of chemical exchange, spin coupling to protons has almost never been observed,[1] so that the otherwise attractive $^{1}H-\{X\}$ double resonance method[2] is inapplicable, and there have been remarkably few reports of silver n.m.r. spectroscopy in spite of its potential value in many areas of silver chemistry.[3]

We now report the use of $^{31}P-\{^{107}Ag\}$ experiments with proton decoupling to identify unequivocally complex species in solutions containing silver salts and organophosphites, and to study silver shielding and coupling constants. These experiments succeed because at low temperatures the rate of exchange in many labile silver complexes is slow enough for $^{1}J(^{107/109}Ag-^{31}P)$ (typically[4] several hundred Hz) to be resolved. They utilise pulsed Fourier transform techniques, proton decoupling, and the relatively high sensitivity of phosphorus-31 [6.4% of the proton sensitivity] to attain a good signal-to-noise ratio. It is not normally possible to obtain true INDOR spectra on a Fourier transform spectrometer, and instead selective irradiation and difference spectroscopy must be used to produce pseudo INDOR spectra in which spin population transfer effects generate the observed responses.[5] Since $|\gamma(^{107/109}Ag)|$ is much less than $|\gamma(^{31}P)|$ the spin population transfer effects possible in $^{31}P-\{^{107/109}Ag,H\}$ experiments are very small, and therefore in the present work amplitudes of $\gamma(^{107/109}Ag)B_2$ large enough to produce spin tickling (line splitting) effects were used.[6] Under conditions of broadband proton decoupling this leads to pseudo-INDOR spectra in which each response is a triplet [splitting $\gamma(^{107}Ag)B_2/4\pi$] with outer components of opposite phase to the central one which may itself be of zero intensity. A satisfactory presentation is achieved by performing the spectral subtraction prior to Fourier transformation to give a power $[(u^2 + v^2)^{1/2}]$ spectrum, the free induction decay being exponentially weighted sufficiently to give a resolution of *ca.* $\gamma(^{107}Ag)B_2/4\pi$. By stepping $\nu(^{107}Ag)$ through an appropriate range this procedure yields a montage in which phosphorus and silver chemical shifts are correlated, and in which valuable information on the spin coupling interactions is retained. The Figure shows the $^{31}P/^{107}Ag$ two-dimensional spectrum obtained in this way from a solution containing the complex ions $[(EtO)_3P]_nAg^+$

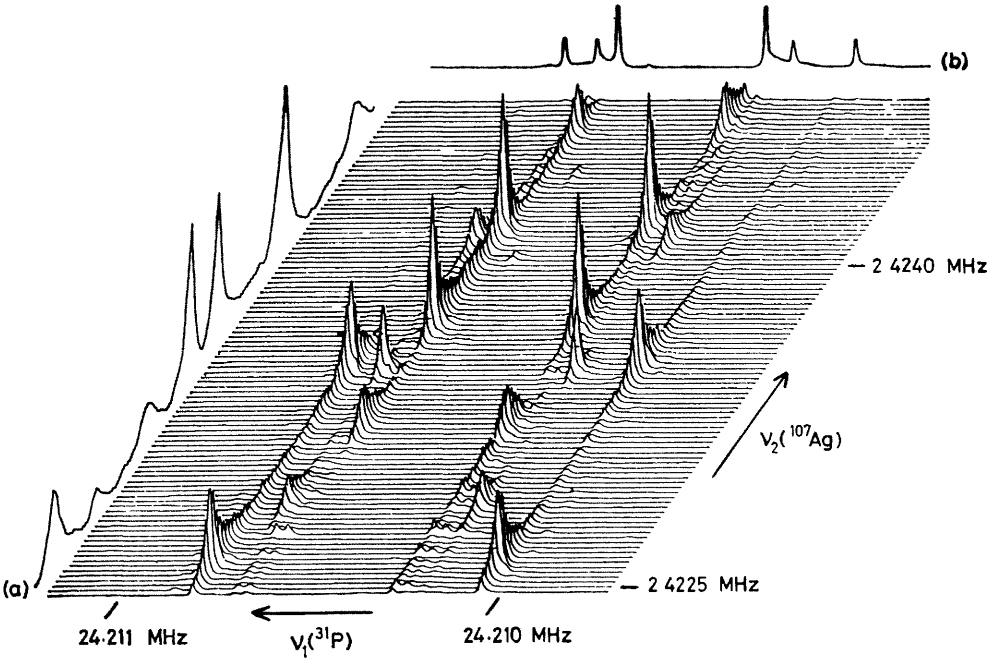

FIGURE. $^{31}P/^{107}Ag$ Two-dimensional spectrum of $(EtO)_3P$–AgSCN mixture in CH_2Cl_2 at −80 °C with proton noise decoupling using a JEOL FX-60 spectrometer with phosphorus probe operating at a detecting frequency of 24·2 MHz. Each trace was obtained by subtracting 50 normal ^{31}P free induction decays from the same number obtained with irradiation ($\gamma(^{107}Ag)B_2/2\pi = 10$ Hz) at the appropriate $\nu(^{107}Ag)$ followed by Fourier transformation and conversion to a power spectrum. Two projections are also shown: (a) the ^{107}Ag spectrum from the various species present; (b) the ^{31}P spectrum from the various species containing ^{107}Ag (but not ^{109}Ag).

(n = 1—4) made by dissolving silver thiocyanate and triethyl phosphite in dichloromethane at −80 °C. In the Figure, dispersal of the phosphorus chemical shifts and coupling patterns is achieved in one dimension, and those of silver in the other, so that problems of overlapping are essentially eliminated and assignments become easy. The projection of the 2D spectrum on to the ν_1 axis yields the total ^{31}P spectrum only from species containing ^{107}Ag (*i.e.* signals from ^{109}Ag-containing ions have been eliminated, a feature of much more importance for nuclei of low natural abundance), while the projection onto the ν_2 axis gives the ^{107}Ag spectrum. Cross sections parallel to either axis are the spectra from individual species; for example, those parallel to the ν_2 axis and passing through $\nu(^{31}P)$ = 24·21025 and 24·21065 MHz are silver spectra with a 1:3:3:1 quartet multiplicity and so must arise from the species $[(EtO)_3P]_3Ag^+$ for which $^1J(^{107}Ag–^{31}P)$,$\delta(^{31}P)$, and $\delta(^{107}Ag)$ can thus be obtained directly. $^{31}P/^{109}Ag$ two-dimensional spectra can be got similarly, but add no further chemical information, although they have provided a value of 0·8698373 ± 0·0000004 for the ratio $\gamma(^{107}Ag)/\gamma(^{109}Ag)$ which agrees well with that obtained by direct observation.[7]

The Table shows the trends in silver shielding as n changes in the species with thiocyanate and nitrate as counter-ion. Co-ordination of silver by nitrate ion will be weak and so the changes in $^1J(^{107}Ag–^{31}P)$ and $\delta(^{107}Ag)$ as n increases follow the change in silver hybridization from *sp* to sp^3. For thiocyanate as counter-ion however, the silver hybridization will have less s-character, even when n is low and this is reflected in smaller values of the coupling constants and reduced silver shielding. In conformity with this $\delta(^{107}Ag)$ and $^1J(^{107}Ag–^{31}P)$ are almost independent of X when n = 4 since the silver is then fully co-ordinated by the phosphite ligands.

TABLE ^{31}P and ^{107}Ag N m r. parameters of $[\{(EtO)_3P\}_nAg]^+$-X^{-}[a] ($X{=}SCN,NO_3$) in CH_2Cl_2 solution at −80 °C

	$\delta(^{107}Ag)$[b]		$J(^{107}Ag - {^{31}P})$[c]		$\delta(^{31}P)$[d]	
n	SCN^-	NO_3^-	SCN^-	NO_3^-	SCN^-	NO_3^-
1	−350	−904	794·1	1059·0	130·5	125·2
2	−191	−593	535·3	689·4	132·0	126·8
3	− 33	−212	402·2	454·1	132·4	132·8
4	+ 1	0	341·8	340·8	130·2	130·9

[a] In solution there is rapid equilibrium between $[\{(EtO)_3P\}_n$-$Ag]^+X^-$ and $[\{(EtO_3P\}_nAgX]$ and for any particular value of n the observed parameters are an average. [b] In p.p.m. to high frequency of $\{(EtO)_3P\}_4Ag^+NO_3^-$ which is selected as the species least susceptible to the effects of counter-ion, concentration, and temperature [c] In Hz This coupling constant is probably negative. [d] In p.p m. to high frequency of 85% H_3PO_4.

The two dimensional spectrum of the Figure was obtained by a time/frequency domain experiment, but is in many respects similar to $^{13}C/^1H$ ones produced by double Fourier transformation[8] from double time domain experiments. It is important to realise that in these latter experiments the advantage in sensitivity of Fourier transform n.m.r. spectroscopy is achieved in one dimension only, and so the approach described here can yield a comparable signal-to-noise ratio in a given time, since it too uses Fourier transformation for one of its dimensions. In one respect this time/frequency domain method places higher demands upon instrumentation, since ideally a programmable frequency synthesizer is required, but this is offset by drastically reduced demands upon computer memory as there is no need to store all the spectra. Indeed, its lack of dependence upon magnetization transfer makes it superior for nuclei of very low magnetic moment and we are currently applying it to complexes of a number of such nuclei including ^{57}Fe, ^{103}Rh, and ^{183}W.

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