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ABSTRACT

In addition to the more conventional methods used in hydrometallurgy to determine the stoichiometry of ligand–metal species formed in solvent extraction, a few research efforts have been done to establish some spectroscopic techniques which can provide that information "in situ." In this work, nuclear magnetic resonance is used to confirm the Cyanex 471X–silver ratio when the metal is extracted from a concentrated chloride medium on the basis of the "coordination shift" detected in some nucleus of the organic ligand upon complexation. The same approach has also been applied successfully to estimation of the composition of triphenylphosphine–silver chloride species synthesized in one phase.

INTRODUCTION

Nuclear magnetic resonance (NMR) is one of the spectroscopic techniques which has been occasionally applied to the analysis of metal–ligand species in solvent extraction (SX). Lockhart and coworkers reported that the ^{1}H-NMR signals of some crown ethers suffered significant deviations in the presence of metal ions such as sodium or potassium (1). Curiously, it was found that the observed shift had the sense of stronger magnetic fields for stoichiometries of ligand–metal of 2:1 and the inverse sense for 1:1 stoichiometries, regardless of the counterions tested. Moreover, for mixtures of free ligand and 1:1 and 2:1 complexes, the chemical shift of the average signal observed in ^{1}H-NMR spectra depended on the intrinsic ratios of the involved species (1).

More recently, Umetani and coworkers studied the interactions of pyrazolone derivatives and divalent cations by ^{1}H and ^{13}C NMR, concluding that there is an intrinsic connection between the pK_a values of the metallic complexes and the chemical shifts detected in ^{13}C NMR for the carbon nucleus attached to the oxygen atoms (2).

The above-mentioned NMR spectroscopies have also been used to estimate the extraction constants related with the extraction of monovalent and divalent cations by crown ethers [3]. It was found in this study that the exchange of ligands between complexed and free organic moieties is faster for monovalent than for divalent cations, allowing the identification of two independent NMR signals for the latter complexation situation (the absorptions related with the complexed and with the free organic ligand), whereas only a "coordination shift" in the signal of the free ligand is observed when a monovalent cation is involved (3).

Despite the lack of SX studies using ^{31}P NMR as a technique for an evaluation of the interactions of metal–phosphorus-bearing ligands, it is known that the phosphorus nucleus also suffer a "coordination shift" upon complexation (4). In this work, ^{31}P-NMR spectroscopy has been applied successfully to the analysis of metal–organic ligand interactions, allowing the estimation of the stoichiometries of the Cyanex 471X–silver chloride species formed in the organic phase after extraction of the metal from a concentrated chloride solution. Furthermore, the ^{31}P-NMR spectrum of an organic solution obtained by SX of silver from a similar aqueous phase by triphenylphosphine (TPP) allowed determination of the stoichiometries of TPP–Ag species synthesized by reaction of the organic ligand with silver chloride in methanol.

EXPERIMENTAL

Generally, SX experiments involving Cyanex 471X (kindly supplied by American Cyanamid Company) have been carried out following procedures reported elsewhere (5). The diluent used was deuterated chloroform or 1,2-dichloroethane.

For progressive loading of the organic solvent with silver, several contacts using an aqueous/organic volume ratio (A/O) of 10:1 were performed. Small aliquots of organic solution were taken for NMR analysis prior to the following extraction experiments.

To force effective saturation of the solvent with silver, a suspension of silver chloride in the 2 M HCl + 3 M NaCl aqueous phase, in which 0.25 g/L of the metal ($[Ag]_{total}$: 0.1 M) were dissolved, was shaken at a constant rate with a 0.1-M solution of Cyanex 471X in $CDCl_3$ for 24 hours in the dark. The ^{31}P-NMR spectra of the loaded organic phase was then recorded.

Extraction experiments involving TPP were carried out using similar experimental conditions as reported above (A/O = 10) (5). Analyses of the metal contents in the aqueous solutions were carried out by atomic absorption spectrophotometry (AAS). The amounts of silver in the organic phases were calculated by mass balance.

The synthesis of TPP–Ag species was performed by shaking a mixture of silver chloride (10^{-3} mol) with a solution of TPP in methanol (2.2×10^{-3} M) until there was complete dissolution of the residue. The solvent was then evaporated and the remaining solid suitably dried. A small amount was then dissolved in 1,2-dichloroethane to obtain the respective ^{31}P-NMR spectrum.

^{1}H- and ^{13}C-NMR spectra were recorded in a Bruker FT 200 spectrometer, working at 200 MHz for ^{1}H and at 50 MHz for ^{13}C. Deuterated chloroform was used as the diluent and TMS as the reference.

^{31}P-NMR spectra were recorded in a Bruker FT 300 operating at 121.5 MHz. Tributylphosphate (TBP) was the external reference, and $CDCl_3$ or 1,2-dichloroethane was the chosen diluent. For the latter case, the introduction of an external standard of $CDCl_3$ in the spectrometer was necessary.

RESULTS AND DISCUSSION

The ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra of Cyanex 471X (whose active ingredient is triisobutylphosphine sulfide, TIBPS, 95% purity) are displayed in Fig. 1, and the respective data are interpreted below.

^{1}H NMR:
δCH_3 = 1.08 ppm (18 H, dd, $JH_3\text{-}H$ = 6.6 Hz, $JH_3\text{-}P$ = 0.33 Hz)
δCH_2 = 1.78 ppm (6H, dd, $JH\text{-}H_2$ = 6.2 Hz, JH_2 = 10.95 Hz)
δCH = 2.21 ppm (3H, m, JH = $JH\text{-}H_3$ = 6.5 Hz, JH = 12 Hz)
^{13}C NMR (noise decoupled):
δCH_2 = 41.2 ppm (d, $J^{13}C\text{-}P$ = 48 Hz)
δCH = 24.8 ppm (d, $J^{13}C\text{-}P$ = 5 Hz)
δCH_3 = 24.1 ppm (d, $J^{13}C\text{-}P$ = 3.5 Hz)
^{31}P NMR (proton decoupled and proton coupled):
δP = 45.98 ppm (m, $JP\text{-}H$ = $JP\text{-}H_2$ = 11.5 Hz)

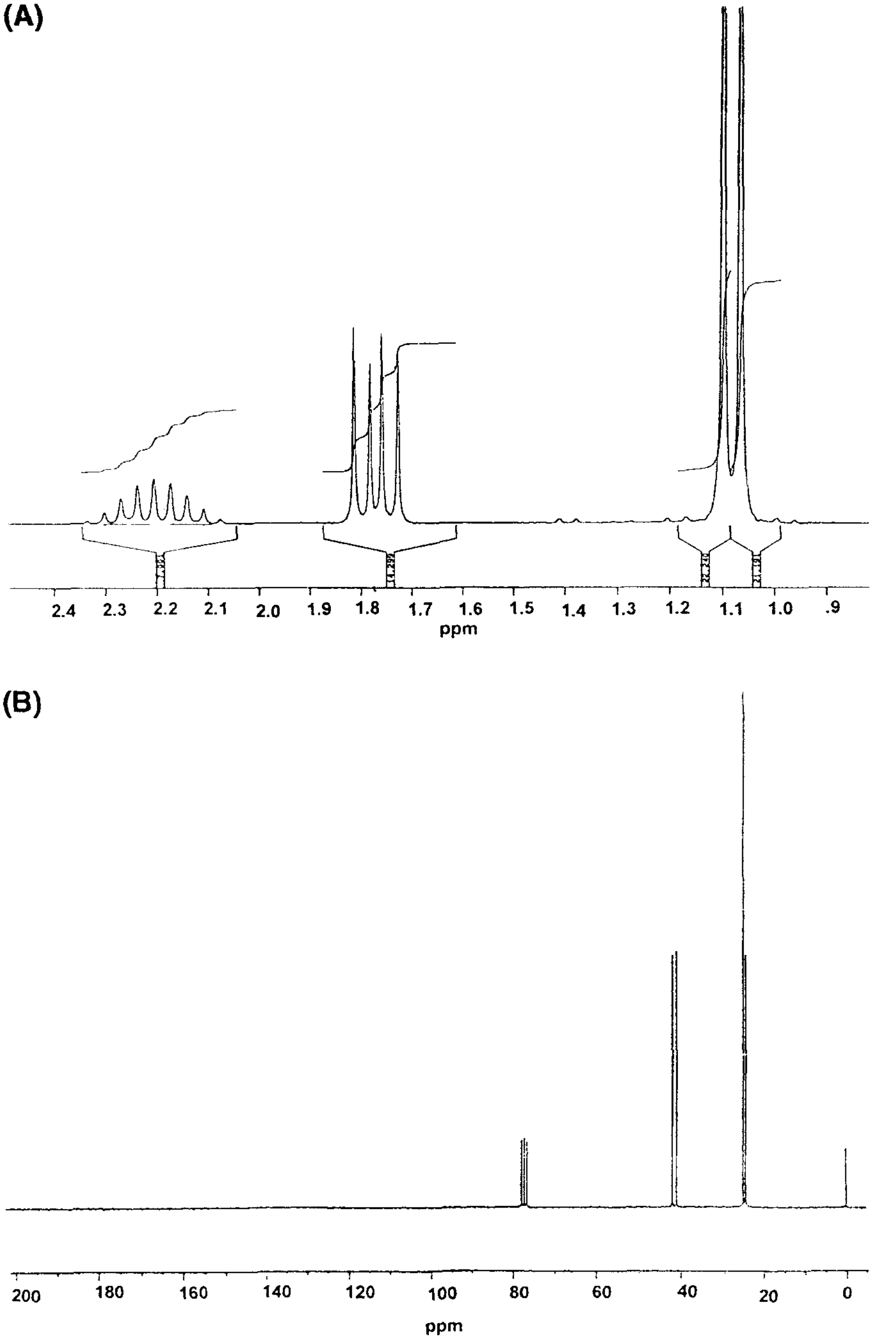

FIG. 1 ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra of TIBPS (field intensities: 200, 50, and 121 MHz, respectively; extractant dissolved in $CDCl_3$, references TMS and TBP).

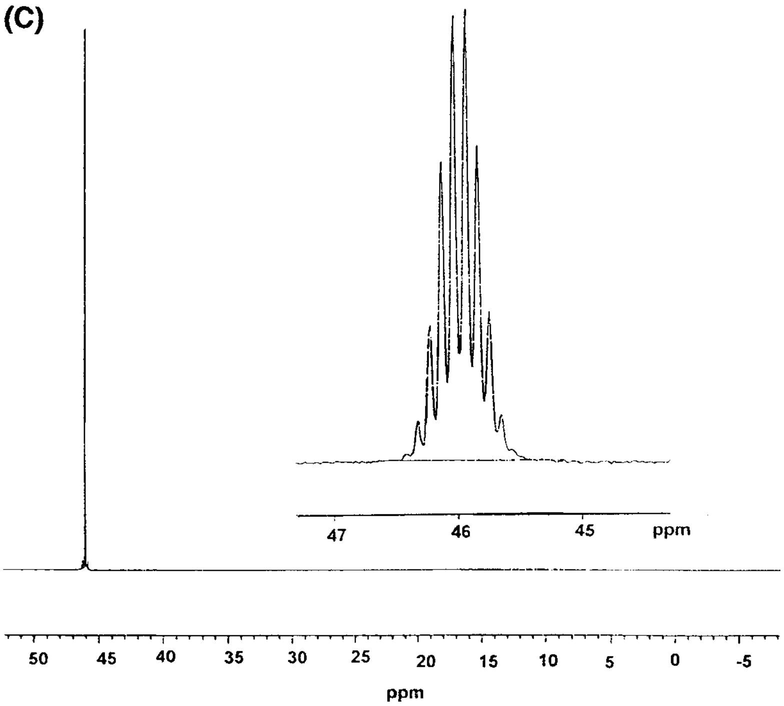

FIG. 1 Continued

H, H_2, and H_3 are the protons related with the —CH, —CH_2, and —CH_3 groups, respectively.

The presence of silver in solutions of TIBPS causes a deviation in the chemical shift related with some nucleus of the organic molecule. Table 1 presents such deviations observed in spectra obtained for the three different sorts of NMR spectroscopy mentioned above, and as a function of increasing concentrations of the metal. Silver has been sequentially introduced in a solution of 0.5 M TIBPS in $CDCl_3$ by suitable extraction experiments.

Analysis of the data in Table 1 suggests that the "coordination shifts" observed for the protons and carbon-13 nucleus are very low if compared with the respective values obtained for the phosphorus-31 nucleus. Therefore, it was decided to continue the investigation considering only this latter sort of NMR spectroscopy.

TABLE 1

Deviations in Chemical Shifts (δ) of the Protons, Carbon-13 and Phosphorus-31 Nucleus of TIBPS Caused by the Presence of Increasing Silver Concentrations (—, not perceptible; $\Delta\delta = \delta_{TIBPS+Ag} - \delta_{TIBPS}$, in ppm)

	^1H RMN			^{13}C RMN			
$[Ag]_{org}$/M	$\Delta\delta CH_2$	$\Delta\delta CH$	$\Delta\delta CH_3$	$\Delta\delta CH_2$	$\Delta\delta CH$	$\Delta\delta CH_3$	^{31}P RMN, $\Delta\delta P$
0.016	+0.02	—	—	−0.08	−0.01	—	+0.26
0.026	+0.03	—	—	−0.15	−0.02	−0.01	+0.42
0.032	+0.04	—	—	−0.19	−0.02	−0.01	+0.53
0.037	+0.04	<0.01	—	−0.20	−0.02	−0.01	+0.61

A plot of the ΔδP displayed in Table 1 as a function of the silver concentrations in the organic phase (determined by AAS) is presented in Fig. 2. It can be seen that there is a very good linear correlation between the two variables considered. From the known silver concentrations in the organic phase, it would be possible, in principle, to investigate what the best linear correlation between the ΔδP observed and the percentage of complexed phosphorus for each stoichiometry ligand–metal of 1:1, 2:1, and 3:1 would be. However, the correlation values obtained for the three types of complexes were all equally good (correlation coefficients > 0.9998). Thus, obtaining the exact ligand–metal stoichiometry by such a treatment is meaningless. This result is probably due to the low concentration of

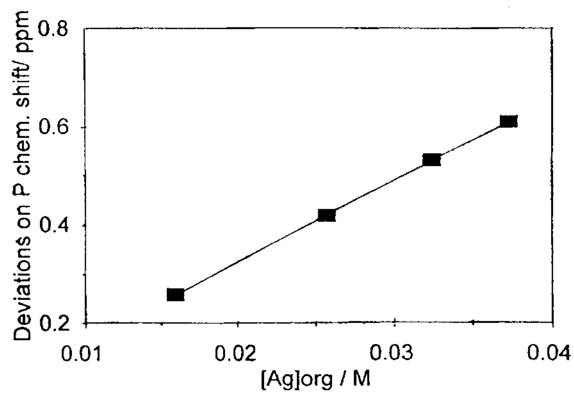

FIG. 2 Dependence of ΔδP on increasing concentrations of silver in the organic phase (0.5 M TIBPS in $CDCl_3$).

complexed phosphorus, even for the more concentrated silver solution, when compared with the concentration of free ligand.

As a temperature as low as −30°C did not change the appearance of the NMR spectrum of the more concentrated silver solution, a method to force an effective saturation of the organic phase was then carried out (see Experimental Section). The ^{31}P NMR spectrum obtained is presented in Fig. 3.

Two absorption signals appear in the new spectrum: one related with the free ligand at 46 ppm, another at 50 ppm (this latter with 82.5% of the whole, calculated by the spectrum integration), corresponding to the complex TIBPS–Ag. Therefore, in these conditions the concentration of uncomplexed phosphorus is small enough to avoid (or decrease) the rate

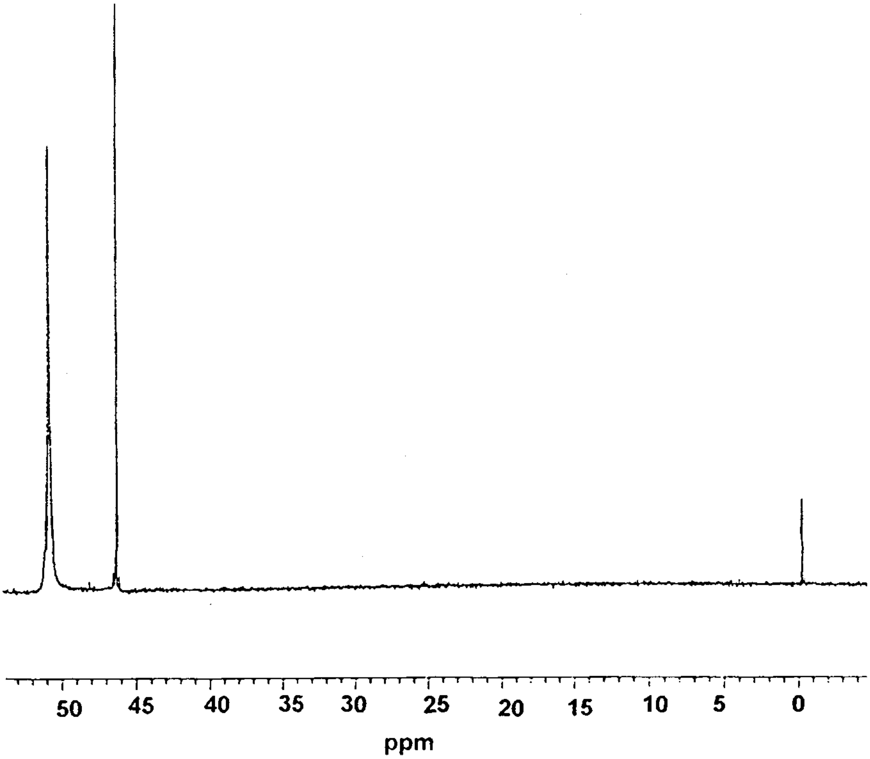

FIG. 3 ^{31}P-NMR spectrum of TIBPS after prolonged extraction of silver (field intensity: 121 MHz).

TABLE 2
Values of $\Delta\delta P$ Calculated for Different Stoichiometries of TIBPS–Ag and the Respective Experimental Values Obtained

TIBPS–Ag species	Calcd $\Delta\delta P$ (ppm)	Exp $\Delta\delta P$ (ppm)
1:1	8.2	
2:1	4.1	4.58
3:1	2.7	

of exchange of ligands between the free and complexed species, allowing the identification of two distinct absorption peaks on the NMR time scale.

Knowledge of the exact chemical shift of the complexed species helps in determination of the stoichiometry of the ligand–metal in the solutions presented in Table 1, if it is assumed that these species are the same in all the available organic silver phases. In fact, calculation of the percentages of complexed phosphorus for each of the three stoichiometries allows estimation of the chemical shift expected for each stoichiometry, and these can then be compared with the experimental value of $\Delta\delta P$ obtained for the isolated complex. The results of this calculation, as well as the experimental value obtained, are presented in Table 2.

Analysis of Table 2 suggests that the stoichiometry of the TIBPS–Ag species must be 2:1, which is in accordance with the data obtained by conventional methods using 1,2-dichloroethane as diluent (5).

In order to investigate the influence of the diluent in the $\Delta\delta P$ observed, a similar sequential silver loading of a TIBPS solution in 1,2-dichloroethane has also been carried out. The results, presented in Table 3, show that there is also a good linear correlation between the two parameters

TABLE 3
Deviations Caused in Chemical Shifts (δ) of the Phosphorus-31 Nucleus of TIBPS by the Presence of Increasing Silver Concentrations (0.5 M TIBPS in 1,2-dichloethane, $\Delta\delta P = \delta P_{(TIBPS+Ag)} - \delta P_{(TIBPS)}$, in ppm)

$[Ag]_{org}$/M	$\Delta\delta P$ (ppm)
0.014	0.40
0.022	0.70
0.027	0.92
0.030	1.11

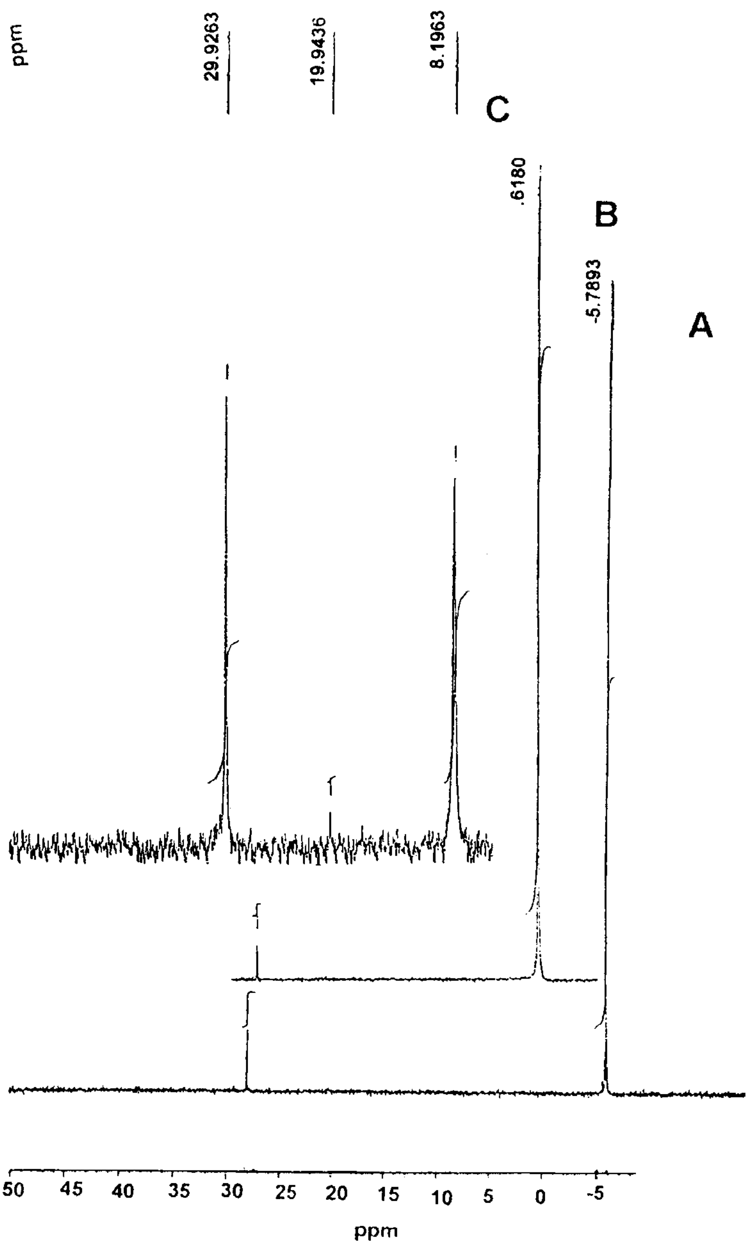

FIG. 4 ^{31}P-NMR spectra of TPP in 1,2-dichloroethane (A), of TPP after extraction of silver (B), and of the crystals obtained by reaction of TPP with silver chloride (C) (field intensities: 121 MHz; all spectra decoupled from protons).

considered, which suggests that the same type of complex must be formed in both situations, at least when the two diluents tested are used.

A similar type of approach, based on ^{31}P-NMR "coordination shifts," revealed its usefulness for the determination of the composition of TPP–Ag species formed by reaction of this organic ligand with silver chloride in methanol. To investigate if the method developed could also be applied with this aim, the ^{31}P-NMR spectra of a solution of TPP in 1,2-dichloroethane of a solution with the same extractant containing 1.97 g/L of silver and a third one containing the crystals synthesized, dissolved in 1,2-dichloroethane, are presented in Fig. 4.

As expected, the presence of silver in the solution of TPP causes a deviation on the chemical shift of the phosphorus nucleus of the free ligand in the sense of lower magnetic fields (spectrum B). In addition to the main absorption, a low signal (δ = 27 ppm) is also observed in the spectrum of TPP, and it is probably related with the small amount of triphenylphosphine oxide (TPPO) which usually exists in TPP samples. When passing from A to B (Fig. 4), this small signal suffers a shift to higher magnetic fields.

By calculation of the expected $\Delta\delta P$ for the three different stoichiometries of TPP–Ag, based on the amount of silver present in the corresponding solution of spectrum B, it is possible to compare those values with the real chemical shifts observed for the crystals synthesized (Table 4).

It can be concluded from Table 4 that species TPP–Ag 1:1 is present in the sample ($\delta P_{\text{calcd and expl}}$ = 29.8 and 29.9 ppm, respectively). The other experimental value of δP = 8.20 ppm is located between the calculated ones for the 2:1 and 3.1 stoichiometries (δP = 12.0 and 6.1 ppm, respectively), which suggests that the two forms may exist in equilibrium. In fact, the exchange of ligands between the two species must be faster than the NMR time scale, a feature that can explain the appearance of only one broad signal whose chemical shift depends on the proportion of

TABLE 4

Values of δP and $\Delta\delta P$ Calculated by the Text Method and Those of δP Experimentally Obtained (in ppm)

TPP and Ag:TPP complexes	$\Delta\delta P_{\text{calcd}}$	δP_{calcd}	δP_{expl}
TPP	—	—	−5.79
1:1	35.6	29.8	29.9
1:2	17.8	12.0	
1:3	11.9	6.1	8.20

the involved species. It can be assumed, however, that the crystals probably have a TPP:Ag ratio of 2:1, but in solution they dissociate to give a mixture of the three stoichiometries, with a fast exchange between the 2:1 and 3:1 stoichiometries.

Confirmation of the proposed composition of TPP–Ag species using suitable techniques (x-ray diffraction and mass spectroscopy–FAB) is currently in progress.

CONCLUSIONS

^{31}P NMR proved to be a useful technique for estimation of the stoichiometries of the TIBPS–Ag and TPP–Ag species contained in organic phases coming from solvent extraction procedures and involving concentrated chloride media. The same type of "coordination shift" in the chemical shift of the phosphorus nucleus was observed for the ^{31}P-NMR spectra of organic silver solutions containing nitrate as the counteranion, which suggests the potential wide application of the method for analysis of industrial organic samples arising from different solvent extraction plants and sources. The main interest of the method lies in the possibility of observing the effect of cation binding to the ligand even if several species are involved. This is useful for both mechanism elucidation and tailoring of new extracting agents.

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