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A Nuclear Magnetic Resonance Study of Metal Complexes of Nonamethylimidodiphosphoramide

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The ligand exchange on nonamethylimidodiphosphoramide (NIPA) complexes in inert nonaqueous solvents is found to be exceptionally slow compared to reactions of analogous unidentate ligands. The rates determined by ^1H or ^{31}P NMR spectroscopy are $k(25\ °C) = 1.35 \times 10^4\ M^{-1}\ s^{-1}$, $4.3 \times 10^{-3}\ s^{-1}$, $3.2 \times 10^1\ M^{-1}\ s^{-1}$, $3.7 \times 10^4\ M^{-1}\ s^{-1}$, $1.8 \times 10^2\ s^{-1}$, and $2.4 \times 10^1\ M^{-1}\ s^{-1}$ for Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, and Cd^{2+} cations, respectively. For the Al^{3+}, Ga^{3+}, In^{3+}, and Be^{2+} ions no exchange could be detected by ^1H NMR spectroscopy up to 120 °C, indicating rates lower than about 10^{-3}–$10^{-4}\ s^{-1}$. The terminal *N*-methyl substituents are shown to be diastereotopic in hexacoordinated Al(III), Ga(III), In(III), and Mg(II) complexes, thus revealing a D_3 symmetry. Two mechanisms, both involving the breaking of a metal–ligand bond as a first step, are postulated to account for first-order (Mg^{2+}, Zn^{2+}) or second-order (Li^+, Ca^{2+}, Sr^{2+}, Cd^{2+}) kinetics. Higher activation parameters are associated with the first process, e.g., $\Delta H^{\ddagger} = 15.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -12.9$ eu for the Mg(II) complex, compared to 5.5 kcal mol^{-1} and -18.9 eu in the case of the Cd(II) system. The change in mechanism is assigned to steric reasons.

Introduction

Organophosphorus extractants have proved to be very useful for the extraction of a wide variety of metal species. The compounds used for this purpose include acidic organophosphates as well as neutral organophosphorus ligands, all containing the phosphoryl P=O solvating link, such as alkyl phosphates (e.g., trimethyl phosphate, TMPA), phosphonates, phosphites, phosphoramides (e.g., hexamethylphosphorotriamide, HMPA), and phosphine oxides.[1] These ligands and their solvation complexes with some metal ions (Al^{3+}, Ga^{3+}, In^{3+}, Be^{2+}) have been previously examined in our laboratory by NMR spectroscopy.[2-4] This method has been widely used to investigate the first solvation shell in cation–solvent systems for which the NMR exchange between the signals S_b and S_f of bound and free solvent molecules is slow on the NMR time scale.[5] A great deal of information was thus obtained concerning the structure of these labile complexes, the mechanisms of ligand exchange, the mobility of the ligands involved, and their solvating abilities toward metallic cations.[2-4]

However, the scope of this method is sharply restricted to a few cation–solvent systems on account of the NMR time scale. A first extension of possible cation–solvent systems was obtained by an expansion of the NMR time scale by using the resonance of heteronuclei: phosphorus-31,[6,7] carbon-13,[8,9] aluminum-27,[2,10] gallium-71.[4] Organophosphorus ligands have been successfully used in this respect since 1969.[6-8,11-14] The chemical shift difference $\Delta\delta$ between signals S_b and S_f is intrinsically larger for ^{31}P than for ^1H nuclei, this difference being still enhanced by a closer proximity of phosphorus atoms to the solvating site (i.e., the oxygen atom of the phosphoryl bond). Moreover, an interesting feature of these complexes is the possibility of observing the coupling $^2J_{^{31}P-M}$ between the metal cation M^{n+} and the surrounding phosphorus nuclei,[6,7] this being the route to information about the structure of these complexes in solution.

A second extension is now investigated in which the ligand exchange is slowed down by using the chelate effect anticipated for complexes of bidentate organophosphorus ligands.[15] Such complexes, e.g., with octamethylpyrophosphoramide (OMPA),[16] nonamethylimidodiphosphoramide (NIPA),[17-19] octamethylmethylenediphosphonic diamide (PCP), or tetraisopropyl methylenediphosphonate (IPCP)[20] as ligands, were already known in the solid state. They have however never been examined in solution.

Table I. Temperatures of Coalescence (°C) of the ^1H Signals of Unidentate (TMPA, HMPA) or Bidentate (NIPA) Organophosphorus Ligands in Solutions of Some Complexes in Nitromethane (NM) or Propylene Carbonate (PC) or a 2:1 v/v Methylene Chloride–Nitromethane Mixture ("C_2N")

	ligand		
cation	NIPA	TMPA	HMPA
Al^{3+}	>>120 (PC)	30 (NM)[a]	−30[a,e,g]
Ga^{3+}	>>120 (PC)	~0 (NM)[b]	
In^{3+}	>>120 (PC)	~0 (NM)[b,e]	
Be^{2+}	>>120 (PC)	5 (NM)[c,e]	95 (PC)[c]
Mg^{2+}	80 (NM)	−90 (CH_2Cl_2)[d]	
Ca^{2+}	−10, +35 (C_2N)[e]	<<−93 (CH_2Cl_2)[d]	
Sr^{2+}	−94, −50 (C_2N)[e,f]		
Zn^{2+}	25 (NM)		
Cd^{2+}	25, 45 (NM)[e]		
Li^+	−47, −1 (C_2N)[e,f]		

[a] Reference 2. [b] Reference 4. [c] Reference 3. [d] Reference 12. [e] Concentration dependent. [f] From ^{31}P NMR. [g] From ^{27}Al NMR.

This paper is devoted to an NMR study of complexes of nonamethylimidodiphosphoramide (NIPA), $(NMe_2)_2P(O)NMeP(O)(NMe_2)_2$, in solution. The complexes are prepared in the solid state and are then dissolved in an inert solvent, either nitromethane (NM) or propylene carbonate (PC), or a 2:1 v/v mixture of methylene chloride and nitromethane ("C_2N"). In this manner, we tried to simulate a situation analogous to that of a cation surrounded by a first solvation shell only, dissolved in an inert liquid. Moreover we may add known quantities of extra organophosphorus ligand in the solution so as to promote the chemical exchange between free (NIPA*) and bound (NIPA) molecules on the metal cation M^{n+}

$$M(NIPA)_m^{\,n+} + NIPA^* \overset{k}{\rightleftharpoons} M(NIPA)_{m-1}(NIPA^*)^{n+} + NIPA \qquad (1)$$

This substitution reaction is accompanied by the NMR site exchange

$$S_b \overset{k_{NMR}}{\rightleftharpoons} S_f \qquad (2)$$

which is the one actually observed.

These investigations proved to be much more than a straightforward extension of our previous studies of unidentate organophosphorus ligands. We found indeed that the ligand-exchange rate is dramatically decreased in NIPA complexes, this property allowing us to study complexes of cations that are usually beyond the scope of NMR on account of too fast ligand exchanges, namely, of divalent cations (Mg^{2+}, Zn^{2+}, Cd^{2+}), alkaline-earth cations (Ca^{2+}, Sr^{2+}), and even a monovalent alkaline cation (Li^+). The coalescence temperatures of these complexes are reported in Table I and are compared

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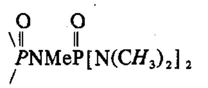
with those of complexes of the same cations with the unidentate organophosphorus ligands TMPA and HMPA. A second interesting aspect of our investigation is that it provides information on the exchange of bidentate ligands, which is less well understood than the exchange of monodentate ligands.

Experimental Section

Materials. Nonamethylimidodiphosphoramide has been synthesized starting from hexamethylphosphorotriamide (HMPA) and phosphorus oxychloride, $OPCl_3$, by a reported method,[21] using an improved variant due to De Bolster and Groeneveld.[22] The resulting product was purified by distillation and recrystallization from petroleum ether. The compound, a white solid at room temperature, is extremely hygroscopic and should be handled in a glovebox under purified argon. Its purity was checked by NMR and IR spectra and by elemental analysis. Anal. Calcd for $C_9H_{27}P_2N_5O_2$: C, 36.12; H, 9.09; P, 20.70; N, 23.40. Found: C, 36.08; H, 8.93; P, 20.52; N, 23.61. The metal complexes were prepared in the solid state from the hydrated perchlorates according to a procedure first described by Van Leeuwen.[18,23,24] The metallic perchlorates were obtained from Fluka [$Al(ClO_4)_3 \cdot 8H_2O$ (purum), $Mg(ClO_4)_2 \cdot 2H_2O$ (puriss.), $Ca(ClO_4)_2 \cdot 4H_2O$ (purum), $LiClO_4$ (anhydrous)] or from Alfa Inorganics [$Ga(ClO_4)_3 \cdot 6H_2O$, $In(ClO_4)_3 \cdot 11H_2O$, $Sr(ClO_4)_2 \cdot 6H_2O$]. Beryllium perchlorate was prepared by reaction of the metal (Fluka, puriss.) with 70% aqueous perchloric acid. Most of these complexes had already been prepared in the solid state[17,18] with the exception of $Be(NIPA)_2^{2+},2ClO_4^-$ and $Ga(NIPA)_3^{3+},3ClO_4^-$. All of them gave satisfactory elemental analyses. Data are reported for the two newly prepared complexes only. Anal. Calcd for $[Ga(NIPA)_3](ClO_4)_3$: Ga, 5.46; C, 25.45; H, 6.44; P, 14.44. Found: Ga, 5.51; C, 25.62; H, 6.45; P, 14.68. Calcd for $[Be(NIPA)_2](ClO_4)_2$: Be, 1.12; C, 26.80; H, 6.75; P, 15.36; Cl, 8.79. Found: Be, 1.12; C, 26.67; H, 6.64; P, 15.20; Cl, 8.72. The solvents used to dissolve these complexes, i.e., nitromethane (Fluka), dichloromethane (Prolabo), and propylene glycol carbonate (Fluka), were distilled and stored in the dark at 0 °C over molecular sieves.

NMR Spectroscopy. Proton spectra were taken on a JEOL C60-HL spectrometer operating at 60 MHz or with a Cameca 250 apparatus at 250 MHz with Me_4Si as an internal reference. The spectrum of pure NIPA cannot be analyzed simply by assuming first-order couplings between phosphorus nuclei and *N*-methyl protons, i.e., as a doublet for the terminal or a triplet for the bridging *N*-methyl protons. The expected lines are indeed observed but are broadened as a result of second-order effects due to long-range couplings $^5J_{^{31}P-^1H}$ between the italic nuclei:



$$\diagdown\overset{\displaystyle O}{\overset{\|}{\mathit{P}}}\mathrm{NMe}\overset{\displaystyle O}{\overset{\|}{P}}[N(C\mathit{H}_3)_2]_2$$

This is clearly shown by decoupling the phosphorus nuclei, in which case the ^1H spectrum is reduced to two sharp singlets a and b at 2.66 and 2.71 ppm downfield from TMS, the ratio of their intensities being 8:1 as expected from the 24 and 3 protons of the terminal and the bridging *N*-methyl groups respectively. ^1H spectra of NIPA complexes were therefore obtained in this way, and all ^{31}P spectra were proton decoupled. Phosphorus-31 Fourier transform spectroscopy was performed with a Bruker HX-90 apparatus at 36.43 MHz (128–8192 scans of 4K/8K points over a frequency range of 3–6 kHz) using 85% H_3PO_4 in D_2O as an external reference and lock. The ^{31}P chemical shift of free NIPA is located at 20.0 ppm downfield from this reference.

Line-Shape Measurements. Two types of exchange are reported in this paper: ^1H exchange between two doublets; ^{31}P exchange between two singlets. The corresponding line shapes are computed according to a matrix formulation due to Anderson,[25] Kubo,[26] and Sack.[27] All calculations were performed by using the program TRECH[3] on a Texas Instruments 980A minicomputer, equipped with a digital plotter, Hewlett-Packard 7210A.

Results and Discussion

Structure of the Complexes. The solutions of metal complexes with a known quantity of free NIPA were examined by $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ spectroscopy. Separate signals were obtained for free and bound NIPA molecules except for the protons of Li(I) and Sr(II) complexes, even at −80 °C. These two complexes could however be distinguished from the free ligand by ^{31}P spectroscopy where the chemical shifts are intrinsically larger and the NMR time scale is quite different. The ^1H or ^{31}P signals of NIPA in all these complexes were found downfield relative to those of the free ligand. The measured chemical shift differences $\Delta\delta$ are reported in Table II.

Table II. ^1H and ^{31}P Chemical Shift Differences $\Delta\delta(^1H)$ and $\Delta\delta(^{31}P)$[a] and ^{31}P Line Widths ($\Delta\nu_{1/2}$, Hz) at 30 °C

	$\Delta\delta(^1H)$			
complex	terminal NMe_2	bridging NMe	$\Delta\delta(^{31}P)$	$\Delta\nu_{1/2}$
$Li(NIPA)_2^+$			2.85[b]	12[b,c]
$Be(NIPA)_2^{2+}$	0.19	0.21	6.25	13
$Mg(NIPA)_3^{2+}$	0.13	0.11	1.75	4.5
$Ca(NIPA)_3^{2+}$	0.13[d]	0.0	3.05	4.5
$Sr(NIPA)_3^{2+}$			2.90[e]	4.5
$Zn(NIPA)_3^{2+}$	0.12	0.0	2.35	4.5
$Cd(NIPA)_3^{2+}$	0.12	0.04	4.20	4.5
$Al(NIPA)_3^{3+}$	0.22[f]	0.30	1.70	26
$Ga(NIPA)_3^{3+}$	0.23[f]	0.31	3.05	4.5
$In(NIPA)_3^{3+}$	0.22[f]	0.28	5.60	4.5

[a] Ppm downfield from free NIPA as a reference. [b] At −65 °C. [c] Line width at 30 °C: 5.2 Hz. [d] At −25 °C. [e] At −75 °C. [f] Mean of two components (see the text).

From the ratio of areas of the two signals, *coordination numbers* of 6 ± 0.3 and of 4 ± 0.2 were determined for Al(III), Ga(III), In(III), Mg(II), Ca(II), Sr(II), Zn(II), and Cd(II) complexes, on the one hand, and for Be(II) and Li(I) complexes, on the other. These numbers do not change on dissolving the solid complexes, thus suggesting identical structures of the metal complexes in both states.

As to the *hexacoordinated complexes* $M(NIPA)_3^{n+}$, their crystal structure has not been described to date. However they are reported to be isomorphous[28] with the $(OMPA)_3$ complexes of known structure,[16,17] so that we may reasonably assume (i) a D_3 site symmetry of the metal ions, (ii) the planarity of the chelate rings, and (iii) the coplanarity of the chelate rings with the metal ion.

The presence of such structures in solution is supported by our observing a splitting of signal a into two components a_1 and a_2, chemically shifted from each other by 0.01, 0.004, and 0.005 ppm in Al(III), Ga(III), and In(III) complexes, respectively. D_3 complexes are dissymmetric, and the solution contains equal quantities of two chiral configurations Δ and Λ,[30] which yield identical NMR spectra. Within each configuration however, the set A of the terminal four *N*-methyl substituents can be divided into two equal subsets A_1 and A_2, which are not interchanged by any symmetry operation (C_3, $3C_2$) of the D_3 symmetry group. This situation may be easily visualized by a projection of the set of oxygen, phosphorus, and nitrogen atoms of the complexes along the C_3 symmetry axis (Figure 1). The protons within the two subsets A_1 and A_2 are therefore diastereotopic[30] and thus give rise to separate signals a_1 and a_2 of equal intensities (Figure 2a). Magnetic nonequivalence is also found for the carbon atoms of the terminal *N*-methyl substituents. The two signals are located, in the case of the Al(III) complex, at 37.00 and 36.86 ppm downfield from an internal Me_4Si reference or at 0.52 and 0.38 ppm downfield from the corresponding single resonance of the free ligand (Figure 2b). A further point to be considered in this respect is the presence of one signal only, at 25 °C, for the hexacoordinated complexes of the other cations investigated: Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, and Cd^{2+}. This apparent inconsistency may be easily removed by taking into account *an inversion of configuration* Δ ⇄ Λ as it has been observed by Jurado and Springer in the tris(diisobutyrylmethanide) complex of aluminum(III) by DNMR at 100–150 °C.[31] This process is accompanied by an NMR exchange between sites a_1 and a_2. The exchange at 25 °C is slow on the NMR time

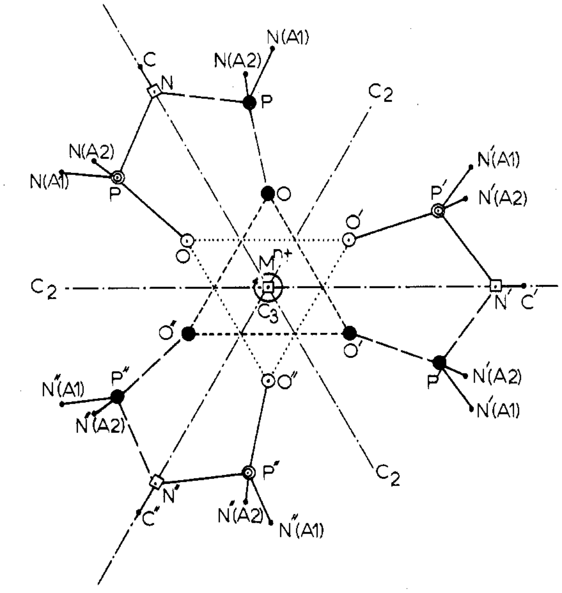


Figure 1. A projection of the tris-bidentate NIPA complex of a metal ion M^{n+} along the C_3 rotation axis showing the nonequivalence of the terminal nitrogen atoms (A1 and A2). Oxygen and phosphorus atoms of the chelate rings are drawn in either of two ways [(1) open and circled circles; (2) solid and shaded circles] depending on whether they are located above or below the mean molecular plane defined by the central metal ion M^{n+} and the three bridging nitrogen atoms (open squares).

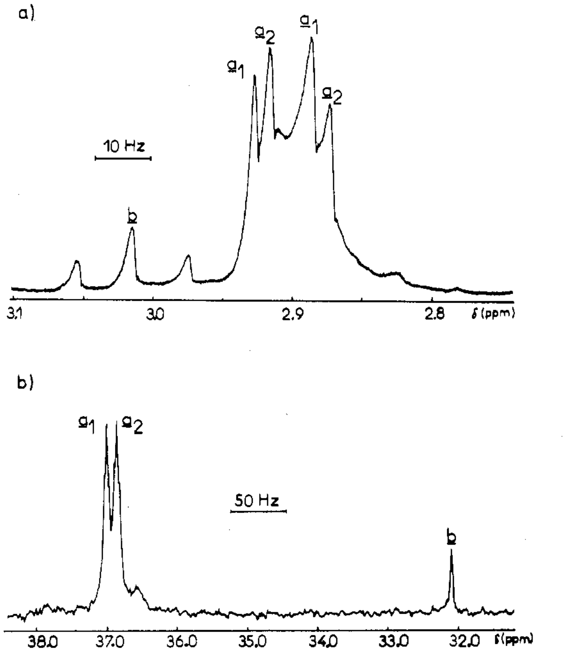


Figure 2. 250-MHz ^{1}H (a) and 62.8-MHz $^{13}C\{^1H\}$ (b) spectra of the $Al(NIPA)_3{}^{3+}$ complex at 30 °C revealing the anisochrony of the terminal $-NMe_2$ groups (signals a_1 and a_2) of the coordinated NIPA molecule. The other lines (b) are due to the single resonance of the bridging *N*-methyl group. The proton spectrum is not decoupled from ^{31}P.

scale in the case of the $(NIPA)_3$ complexes of Al(III), Ga(III), and In(III) and is very fast for the other compounds. This point was checked in either of two ways. First, a_1 and a_2 in the ^{1}H spectrum of the In(III) complex were brought to coalescence on increasing the temperature to 40–60 °C. Second, the ^{13}C spectrum of the Mg(II) complex was taken at −60 °C. Separate signals at 37.01 and 37.10 ppm for the A_1 and A_2 groups were effectively observed as a result of a slower exchange at this temperature.

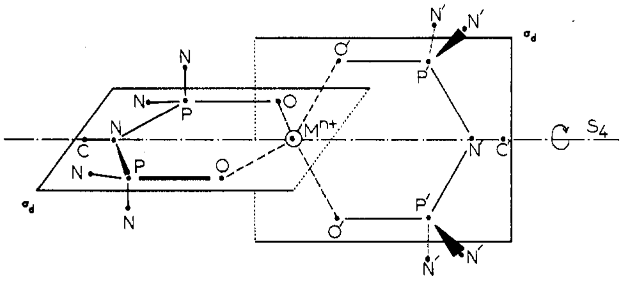


Figure 3. A perspective projection of the D_{2d} bis-bidentate NIPA complex of a metal ion M^{n+} showing the equivalence of the terminal *N,N*-dimethyl substituents. The symmetry elements S_4, σ_d are shown for convenience; the two $C_2{}'$ axes are omitted.

Table III. ^{31}P Chemical Shifts in Unidentate (TMPA, HMPA) and Bidentate (NIPA) Complexes[a]

	TMPA	HMPA	NIPA
Be^{2+}	-5.8^b	-3.1^b	6.3
Al^{3+}	-7.3^c	1.7^c	1.7
Ga^{3+}	-8.2^d		3.05
In^{3+}	-6.1^d		5.6

[a] Ppm downfield from the free ligand as a reference. [b] Reference 3. [c] Reference 2. [d] Reference 4.

The inversion may proceed by either of two types of reaction pathways:[32–35] the so-called twist mechanism and the bond rupture mechanism (TBP transition state of Gordon and Holm[33]). We may notice that inversion takes place on NIPA complexes which rapidly exchange their ligands with the free NIPA molecules (Table I). This parallelism strongly suggests an initial step common to both processes (i.e., the intramolecular and intermolecular exchanges), namely, the rupture of one metal–ligand bond (cf. the kinetic results below), thus ruling out the twist mechanism for inversion. This conclusion is also supported by structural considerations: the close packing of bound NIPA molecules hinders the various twist motions of the chelate rings; a bond rupture mechanism, on the contrary, is accompanied by a release of steric strain.

In the case of the tetracoordinated complex $Be(NIPA)_2{}^{2+}$, one signal is observed at any temperature for either the terminal or the bridging *N*-methyl substituents, as expected for a configuration with D_{2d} symmetry (Figure 3).

NMR Parameters. *Complexation shifts the ^{1}H signals to lower fields.* The shifts Δδ of the terminal *N*-methyl groups are nearly constant for trivalent (0.20 ppm) or divalent (0.10 ppm) hexacoordinated cation complexes (Table II). These observations suggest a predominant deshielding effect of the electrical field of the cation.[7,36] The same conclusions hold for the bridging *N*-methyl group.

Complexation of NIPA shifts the $^{31}P\{^1H\}$ signals to lower fields in all cases, contrary to TMPA or HMPA solutions[2–4] (Table III). Strong variations of Δδ are observed according to the nature of the cation and of the ligand. These variations are not related in a simple manner to the charge or the radius of the cation but are presumably due to antagonistic effects. There is indeed an important d_π–p_π bonding between the phosphorus and the nitrogen atoms of the ligand, as evidenced by the planarity of the chelate ring in the isomorphous OMPA complexes,[16] on the one hand, and by the flattening of the terminal *N*-dimethylamino groups and the shortening of the bond distances in analogous OMPA[16] and HMPA[37] complexes (in the solid state), on the other. This suggests that the hybridization at the nitrogen atoms approximates sp^2. Variable d_π–p_π interactions between phosphorus and oxygen atoms under the influence of the coordinated cation M^{n+} (with eventually a d_π–p_π delocalization in turn between M^{n+} and the chelate ring), on the one hand, and between phosphorus and nitrogen atoms, on the other, may produce unexpected charge

Table IV. Experimental Conditions for Kinetic Measurements: Salt and Free Ligand Concentrations (C_s and C_f), Number of Investigated Temperatures (in Parentheses) over the Specified Range, and Correlation Coefficients in Least-Squares Arrhenius Plots

cation/ solvent	concn, M		temp range, °C	R
	C_s	C_f		
Li^+/C_2N	0.111	0.296	−47 to −1 (6)	0.99729
	0.116	0.159	−47 to −1 (6)	0.99710
Mg^{2+}/NM	0.102	0.156	67 to 97 (6)	0.99993
	0.102	0.302	67 to 97 (6)	0.99598
	0.150	0.297	67 to 97 (6)	0.99959
Ca^{2+}/C_2N	0.148	0.218	−10 to +19 (6)	0.99985
	0.070	0.276	0 to 45 (7)	0.99655
	0.099	0.150	0 to 35 (8)	0.99821
	0.100	0.326	−11 to +26 (7)	0.99886
	0.072	0.103	11 to 30 (5)	0.99861
	0.071	0.208	0 to 30 (7)	0.99853
Sr^{2+}/C_2N	0.109	0.305	−94 to −49 (6)	0.99175
	0.098	0.1655	−80 to −49 (5)	0.99879
Zn^{2+}/NM	0.0626	0.185	−10 to +31 (5)	0.9996
	0.0508	0.302	−10 to +31 (5)	0.9986
	0.067	0.336	−10 to +31 (5)	0.9980
Cd^{2+}/NM	0.142	0.187	20 to 42 (6)	0.9975
	0.070	0.159	20 to 42 (6)	0.9998
	0.068	0.434	20 to 42 (6)	0.9816

densities and simultaneously local magnetic anisotropies at the various atoms. These two factors have to be combined with the deshielding effect of the electric field of the cation to obtain the resulting chemical shift $\Delta\delta$ of the observed nuclei, which consequently is not expected to obey any simple law.

It should be noticed that the ^{31}P signal of the complex appears either as a sharp singlet or doublet or as a single broad line, depending upon the isotopic composition of the metal and the spin numbers I of the various isotopes. The predominant isotopes of magnesium, calcium, strontium, and zinc have no magnetic moment, and the phosphorus signal of their complexes is therefore a sharp singlet (line width $\Delta\nu_{1/2} = 4.5$ Hz; cf. Table II). Cadmium has two magnetically active isotopes, ^{111}Cd and ^{113}Cd, of closely similar abundance (12.75 and 12.26%), both with spin $^1/_2$. As their gyromagnetic ratios are nearly identical (within 4%), only one coupling constant is observed: $^2J_{^{31}P-Cd} = 27$ Hz. The ^{31}P signal of the Cd^{2+} complex therefore consists of one main line (75% of the total intensity) accompanied by two satellites of equal intensities ($\simeq$12.5%) at ±13.5 Hz. Various line shapes may be found in the case of isotopes with $I > {}^1/_2$. The expected ^{31}P multiplet can be observed only if the quadrupolar relaxation rate of the cation is small with respect to the coupling constant between the phosphorus and metal nuclei.[4] The corresponding spectra have been observed for complexes of beryllium(II) and aluminum(III)[2,3] with unidentate ligands where the cubic symmetry leads to a zero electrical field gradient at the metal nucleus. This is not the case for NIPA complexes however which belong to D_3 or D_{2d} symmetry groups. The multiplet may be averaged to one sharp singlet if quadrupolar relaxation is fast. This is observed in the case of the Ga(III), In(III), and Li(I) complexes at 30 °C. Alternatively the quadrupolar relaxation rate may be moderately fast so that the multiplet coalesces into a broad line, as observed for the Al(III) and Be(II) complexes at 30 °C and for the Li(I) complex at −60 °C. In the latter cases, the coupling constants may be calculated from the spectra according to a procedure previously described:[4] $^2J_{^9Be-^{31}P} = 2.6 \pm 0.4$; $^2J_{^{27}Al-^{31}P} = 19 \pm 3$; $^2J_{^7Li-^{31}P} = 2 \pm 0.5$ Hz. The values do not differ very much from those obtained with unidentate organophosphorus ligands, e.g., $^2J_{^9Be-^{31}P} = 5.0$ and $^2J_{^{27}Al-^{31}P} = 19.9$ Hz in $Be(TMPA)_4{}^{2+}$ and $Al(TMPA)_6{}^{3+}$ complexes.[3,4]

Finally, the NMR signals of the metal nuclei have been observed in the case of the Al(III) and Be(II) complexes. The ^{27}Al spectrum consists of a broad singlet ($\Delta\nu_{1/2} \simeq 150$ Hz) located at 13.7 ppm upfield from an external $Al(H_2O)_6{}^{3+}$ reference, instead of the sharp heptuplet[2] observed at 19.9 ppm for the complex $Al(TMPA)_6{}^{3+}$. In a similar manner, the ^9Be signal is a single line showing a width, $\Delta\nu_{1/2}$, of 13 Hz. For the $Be(HMPA)_4{}^{2+}$ complex in contrast, a sharp quintuplet is observed.[3] The line broadening is consistent with a moderately fast quadrupolar relaxation rate, as mentioned above.

Kinetic Measurements. The coalescence of NMR spectra on increasing the temperature yields the rate constant k_{NMR} of eq 2. Measurements are carried out by using various concentrations of salt C_s and of free added ligand C_f and taking spectra at different temperatures (Table IV, Figure 4). *No exchange can be detected for the Be(II), Al(III), Ga(III), and In(III) complexes* at temperatures up to 120 °C, thus indicating rate constants lower than 10^{-3}–10^{-4} s^{-1} if we assume an activation enthalpy of 15–20 kcal mol^{-1}. *The NMR site exchange around the Mg(II) and Zn(II) cations is found to be independent of* C_f and is accordingly equal to the chemical rate constant k_e for a mechanism involving the dissociation of the complex as the first step. *On the contrary, the kinetic law is first-order with respect to the concentration* C_f *for the Li(I), Ca(II), Sr(II), and Cd(II) complexes*; we define a concentration-independent rate constant $k_e = k_{NMR}/C_f$ (Table V). The values of the activation parameters for the various sets of concentrations C_s and C_f agree satisfactorily. Their mean values $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are given in Table V, together with the mean deviations, which are assumed to represent the errors to be expected in $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

The values thus obtained show clearly that NIPA is a powerful complexing agent. This is shown by a comparison with unidentate ligands; e.g., $k_e = 1.5$ M^{-1} s^{-1}, 0.38 s^{-1}, 5.0 s^{-1}, and 7.2 M^{-1} s^{-1} at 25 °C for the trimethyl phosphate complexes of Be(II), Al(III), Ga(III), and In(III)[4] instead of less than ca. 10^{-3}–10^{-4} s^{-1} for the NIPA compounds; $k_e = 7.2 \times 10^5$ or 4.7×10^3 s^{-1} for ligand exchange on $Mg(TMPA)_6{}^{2+}$[12] or $Mg(CH_3OH)_6{}^{2+}$[38] instead of 4.3×10^{-2} s^{-1} with NIPA as ligand.

Table V. Kinetic Parameters for Ligand Exchange on NIPA Complexes

complex	ionic radius, A	ionic charge density[a]	kinetic order[b]	k_e(25 °C), s^{-1} or M^{-1} s^{-1}	$\Delta H^\ddagger$(25 °C), kcal mol^{-1}	$\Delta S^\ddagger$(25 °C), eu
$Be(NIPA)_2{}^{2+}$	0.35	10.27	no exchange up to 120 °C			
$Al(NIPA)_3{}^{3+}$	0.51	7.25				
$Ga(NIPA)_3{}^{3+}$	0.62	4.91				
$In(NIPA)_3{}^{3+}$	0.81	2.87				
$Li(NIPA)_2{}^+$	0.68	1.36	one	1.35×10^4	7.9 ± 0.1	−12.9 ± 0.6
$Mg(NIPA)_3{}^{2+}$	0.66	2.89	zero	4.3×10^{-2}	15.7 ± 0.2	−11.9 ± 0.6
$Ca(NIPA)_3{}^{2+}$	0.99	1.28	one	3.2×10	7.3 ± 0.5	−27.0 ± 2.1
$Sr(NIPA)_3{}^{2+}$	1.12	1.00	one	3.7×10^4	5.5 ± 0.1	−18.9 ± 0.3
$Zn(NIPA)_3{}^{2+}$	0.74	2.30	zero	1.8×10^2	12.7 ± 0.3	−5.6 ± 1.0
$Cd(NIPA)_3{}^{2+}$	0.97	1.40	one	2.4×10	9.6 ± 1.0	−20.0 ± 3.7

[a] Relative to that of Sr^{2+}. [b] With respect to the free ligand.

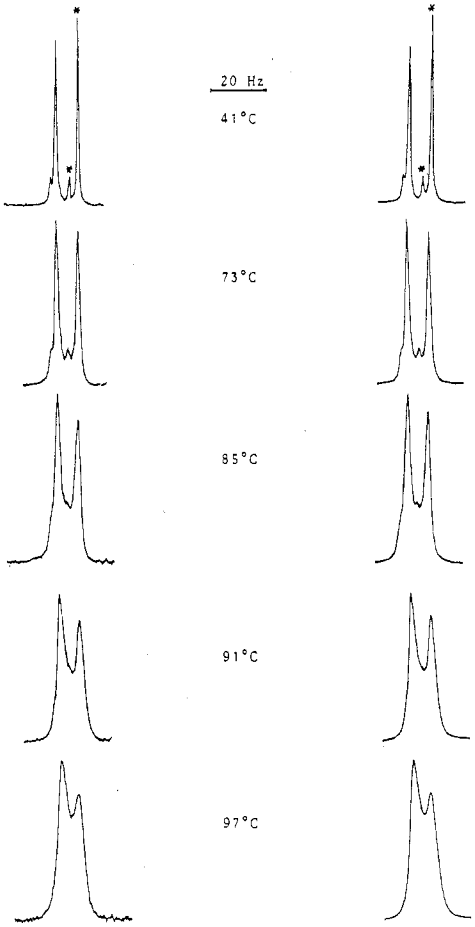


Figure 4. Experimental (left) and calculated (right) 60-MHz $^1H\{^{31}P\}$ spectra for the Mg–NIPA system. Concentrations are 0.102 M of complex salt and 0.302 M of free ligand. (The signals of free NIPA are marked by an asterisk.)

Compared to the Eigen mobility scale[39] for aquo complexes of cations, exchange rates are thus shifted to much lower values, e.g., 10^{-2} s^{-1} for Mg^{2+} and 10–10^4 M^{-1} s^{-1} for Ca^{2+}, Sr^{2+}, and Li^{+}[40] instead of 10^5 s^{-1} and 10^7–10^9 M^{-1} s^{-1}. A more striking fact however is that NIPA also appears to give exceptionally stable complexes if compared with other *neutral* bidentate ligands. In fact it should be compared to multidentate ligands, such as EDTA ($k_e = 1.2 \times 10^2$ and 1.1×10^3 M^{-1} s^{-1} for Ca^{2+} and Sr^{2+} complexes), antibiotic compounds (e.g., valinomycin[42]), crown ethers,[43] and cryptands.[44]

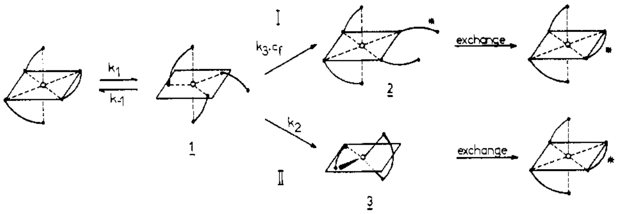
If we look at the stability of NIPA complexes as a function of the coordinated metal ion, we observe that the exchange grows faster *as the electrical charge of the cation is decreased and the ionic radius is increased.* Rate constants (or temperature ranges for coalescence) closely parallel the charge densities of the cations (with the exception of In(III) and Mg(II) complexes, which have quite different labilities in spite of almost equal ionic charge densities). This suggests that electrostatic forces are mainly responsible for complexation, as was already suggested to account for similar crystal structures of the OMPA complexes of Cu(II) and Mg(II) cations in spite of quite different electronic structures.[16]

Let us now examine *the mechanisms of ligand exchange in hexacoordinated NIPA complexes.* Two kinetic laws are obtained for the overall substitution reaction. A simultaneous decrease of activation enthalpies (from 12.7–15.7 to 5.5–9.6 kcal mol^{-1}) and entropies (from −5.6, −11.9 to −18.9, −27.0 eu) accompanies the change from first- to second-order kinetics. The magnitudes of activation parameters are consistent with an S_N2 mechanism in the terminology of Hughes and Ingold[45] or in the interpretation of Langford and Gray[46] with an associative or interchange mechanism (cf. the values found for the unidentate trimethyl phosphate complex of indium(III):[4] $\Delta H^{\ddagger} = 8.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -26.1$ eu). Another analogy with the case of uncharged organophosphorus ligands is the fact that an S_N2 mechanism is observed for the bigger cations (Sr^{2+}, Ca^{2+}, Cd^{2+}) only and not for Mg^{2+} and Zn^{2+}. However the three bulky NIPA molecules bound to the metal ion completely fill the space surrounding the cation, thus rendering the existence of a heptacoordinated transition state highly improbable. A simple dissociative S_N1 mechanism for the first-order processes encounters also serious objections: the corresponding activation entropies are clearly negative—$\Delta S^{\ddagger} = -11.9$ and -5.6 eu for Mg(II) and Zn(II) complexes, in contrast to the large and positive values observed for S_N1 mechanisms involving monodentate organophosphorus ligands, as described in a previous publication, e.g., $\Delta S^{\ddagger} = 18.2$ and 15.1 eu for trimethyl phosphate exchange in $Al(TMPA)_6{}^{3+}$ and $In(TMPA)_6{}^{3+}$ complexes.[4]

There exist in fact some examples of dissociative mechanisms being accompanied by an increase in entropy, but they seem to be restricted to cases where strongly interacting solvents[50] or charged ligands[51] are used, contrary to the conditions of our experiments.

In the literature the problem of the substitution of two unidentate molecules in a hexacoordinated solvation complex by one bidentate ligand molecule is rather well documented,[47] but information on the symmetrical substitution of bidentate ligands around metal ions is very limited.

Lanier and Pearson[48] proposed mechanisms I and II for solvent-assisted symmetrical exchange of bidentate ligands such as that of glycine on cations of transition metals. Recently, such mechanisms have been suggested to describe the ligand exchange on tris(acetylacetonato)aluminum(III) and -gallium(III) complexes in aqueous or nonaqueous organic solvents.[49] Both mechanisms involve as a first step the release of one end of the chelate by a dissociative process. The intermediate **1** thus obtained was assumed to remain hexacoordinated in Lanier and Pearson's scheme, the sixth coordination site being temporarily occupied by one water molecule. A similar situation with a nitromethane molecule occupying a sixth coordination site in intermediate **1** in spite of its weak solvating power is unlikely since it cannot account for the intramolecular process $\Delta \rightleftarrows \Lambda$ observed in our case. We therefore identify **1** with the TBP pentacoordinated transition state[33] already proposed for the bond rupture inversion of the configuration of $M(NIPA)_3$ complexes (see above). Ligand exchange and inversion of configuration would thus have this intermediate in common. The intramolecular return from intermediate **1** to the initial complex molecule or to its enantiomer (rate constant k_{-1}) would compete either with the attachment of the free end of an external ligand molecule (mechanism I with a second hexacoordinated intermediate **2**) or with the release of both ends of one chelate molecule to yield a tetracoordinated D_{2d} intermediate, **3**, which then rapidly combines with an external ligand molecule (mechanism II). The intermediate **3** is represented as having a tetrahedral D_{2d} structure, which seems to be the energetically most favorable arrangement since it reduces the repulsions between the two remaining ligands to a minimum. A hexacoordinated structure where two nitromethane molecules occupy two coordination



sites is discarded by analogy to intermediate **1**.

Mechanism I as well as mechanism II would lead to NMR site exchange (a statistical factor of $^1/_2$ should be introduced for mechanism I). Applying a steady-state treatment gives the final result for the rate of exchange (with the notations shown on the scheme)

$$k_{\mathrm{NMR}} = \frac{k_1(k_2 + \frac{1}{2}k_3C_f)}{k_{-1} + k_2 + k_3C_f} \qquad (3)$$

Two limiting rate laws are obtained according to the relative magnitudes of k_{-1}, k_2, and k_3C_f: *a first-order kinetic law* in either of two ways (a) $k_e = k_1/2$ if $k_3C_f \gg k_2$ and k_{-1} or $k_e = k_1$ if $k_3C_f \ll k_{-1} \ll k_2$ or (b) $k_e = Kk_2/2$, with $K = k_1/k_{-1}$, if $k_3C_f \ll k_2 \ll k_{-1}$; *a second-order kinetic law* (c) $k_e = Kk_3/2$ if $k_2 \ll k_3C_f \ll k_{-1}$. The rate laws described in (a) are not consistent with the experimental observation that the inversion of configuration is much faster than the ligand exchange so that $k_e \ll k_1$. Therefore we assign mechanism II to first- and mechanism I to second-order kinetics with $k_e = Kk_2/2$ and $k_e = Kk_3/2$, respectively. This conclusion is consistent with the decrease of activation entropy on passing from first- to second-order processes; this results from a gain of entropy on going from intermediate **1** to **3** in mechanism I (by the release of a ligand molecule) in contrast to a loss of entropy between **1** and **2** in mechanism II (for the opposite reason). The fact that first-order kinetics are observed for the smaller cations is explained by a closer packing of the ligands around these cations, thus compelling one ligand molecule to leave the complex completely (i.e., with both its ends) before an external ligand molecule can approach the metal ion.

As to the *tetracoordinated complexes*, the stability of the beryllium(II) complex was not unexpected since a coalescence temperature of 95–115 °C had been observed previously for the HMPA complex.[4] The lithium(I) complex follows a second-order kinetic law, which may be tentatively accounted for by a simple associative S_N2 mechanism.

In conclusion, the bidentate phosphoramide ligands might constitute a new class of neutral sequestering agents challenging the well-known crown ethers and cryptands on account of their greater ease of preparation.

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Registry No. $Li(NIPA)_2^+$, 47788-17-0; $[Be(NIPA)_2](ClO_4)_2$, 71000-97-0; $Mg(NIPA)_3^{2+}$, 47889-95-2; $Ca(NIPA)_3^{2+}$, 47889-75-8; $Sr(NIPA)_3^{2+}$, 47890-02-8; $Zn(NIPA)_3^{2+}$, 47890-05-1; $Cd(NIPA)_3^{2+}$, 47889-79-2; $Al(NIPA)_3^{3+}$, 47889-70-3; $[Ga(NIPA)_3](ClO_4)_3$, 71031-55-5; $In(NIPA)_3^{3+}$, 47889-92-9.

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