That the LiH unit is attached to $AlH_3$ and not to $(C_2H_5)_3N$ is demonstrated by the ability of $LiH \cdot AlH_3 \cdot N(C_2H_5)_3$ to act as if the $LiH \cdot AlH_3$ were a molecular entity in its reaction with commercial grade LiH in benzene to give $Li_3AlH_6$.[1] Under the same condition $LiAlH_4$ will not react with LiH.

When triethylamine was added to a diethyl ether solution of $LiAlH_4$, we obtained results similar to those reported by Peters[3] except that the soluble portion was $LiH \cdot AlH_3 \cdot N(C_2H_5)_3$ rather than $(C_2H_5)_3N \cdot AlH_3$. An attempt to prepare $NaAlH_4 \cdot N(C_2H_5)_3$ in benzene was unsuccessful.

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## Inner- and Outer-Sphere Complex Formation in Aqueous Solutions of Nickel(II)–Methyl Phosphate[1]

BY HANS BRINTZINGER AND GORDON G. HAMMES

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The relative amounts of outer-sphere ion pairs ($ML_o$) and inner-sphere coordination compounds ($ML_i$) present in solutions of metal complexes are difficult to assess experimentally. A knowledge of the relative amounts is of particular interest in biological systems involving mono- and diphosphate esters. We present here a direct measurement of the ratio $(ML_o)/(ML_i)$ for $Ni^{2+}$ complexes of methyl phosphate (MP) by use of the temperature-jump method. Methyl phosphate was selected for study because its metal complexes are considerably more soluble than those of most monophosphate esters (*e.g.*, adenosine 5′-monophosphate). Some of the related kinetic constants also have been obtained.

### Experimental Section

All solutions were 0.1 $M$ in NaCl and $2 \times 10^{-5}$ $M$ in chlorophenol red at pH 6.8. The $NiCl_2$ used was standard reagent grade; the methyl phosphate was prepared as previously described.[2] The temperature-jump apparatus and experimental procedure have been described in detail elsewhere.[3,4] The change in pH resulting from the shift in concentrations of the reactants was followed by observing the absorbancy changes at 573 mμ and the final temperature was 25°.

### Results and Treatment of Data

Relaxation effects were observed only when the total nickel and ligand concentrations were in the range 0.005 to 0.1 $M$. The relaxation times were evaluated from a plot of the logarithm of the signal amplitude *vs.* time; the straight line obtained indicates a single relaxation process is being observed. The relaxation times obtained and the total metal and ligand concentrations used are summarized in Table I.

TABLE I
RELAXATION TIMES AND TOTAL METAL AND LIGAND CONCENTRATIONS

| $\tau$, μsec | $10^2\Sigma Ni$, $M$ | $10^2\Sigma MP$, $M$ |
|---|---|---|
| 85 | 10.0 | 10.0 |
| 95 | 4.00 | 4.00 |
| 100 | 1.60 | 1.60 |
| 120 | 0.64 | 0.64 |

The generally accepted mechanism of complex formation between $Ni^{2+}$ and a ligand $L^{2-}$ is (*cf.* ref 3 and 5)

$$\underset{M}{Ni(H_2O)_n{}^{2+}} + L^{2-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{ML_o}{Ni(H_2O)_nL} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{ML_i}{Ni(H_2O)_{n-x}L} + xH_2O \quad (1)$$

(Methyl phosphate, in the pH range under consideration, is either a mono- or divalent anion, but only the divalent species is assumed to react with $Ni^{2+}$.) For all of the Ni complexes studied thus far, with the temperature-jump method, the concentration of $ML_o$ has been assumed to be very small compared to $ML_i$ and the formation of the outer-sphere complex has been assumed to be rapid compared to the rate of expulsion of water molecules from the inner coordination sphere of the metal ion. In this case the relaxation time is given by[3]

$$1/\tau = K_{12}k_{23}[(M)/(1 + \alpha) + (L)] + k_{32} \quad (2)$$

where $K_{12} = k_{12}/k_{21}$ and $\alpha$ is a known factor which takes into account the rapid protolytic reactions also occurring. The concentration dependence of the relaxation times observed in the present cases is not consistent with eq 2. However, if we assume that the concentration of $ML_0$ is not negligible, but that ion-pair formation and adjustment of protolytic equilibria are still rapid compared to dissociation of the water molecules, the slow relaxation time for eq 1 is (a general procedure for calculating relaxation times is given in ref 6)

$$1/\tau = k_{32} + \cfrac{k_{23}}{1 + \cfrac{1 + \alpha'}{K_{12}(L) + \alpha' K_{12}[(M) + (L)]}}$$

with (3)

$$\alpha' = \cfrac{(L)/(H)}{1 + \cfrac{K_I(In)}{1 + K_I(H)}} + \frac{1}{K_A(H)}$$

where $K_I$ is the acid association constant of the indicator ($10^{6.2}$ $M^{-1}$ for chlorophenol red), $K_A$ is that of the

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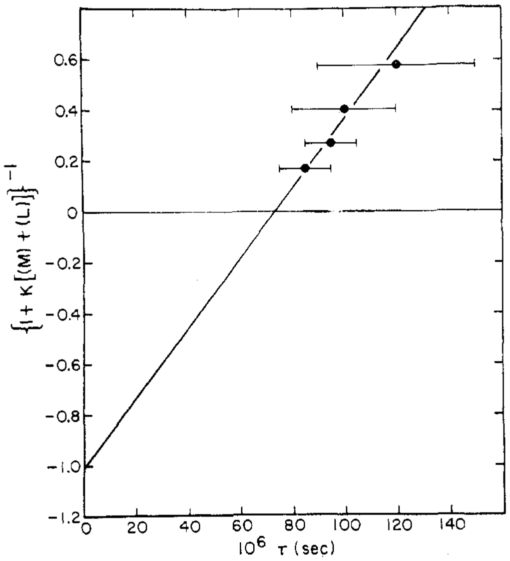

Figure 1.—Plot of $\{1 + K[(\mathrm{M}) + (\mathrm{L})]\}^{-1}$ *vs.* the relaxation time, $\tau$.

ligand ($10^{6.2}$ $M^{-1}$ for methyl phosphate), and (In) is the concentration of the indicator anion. Since $\alpha' >> 1$ for all experiments reported here

$$1/\tau \cong k_{32} + \frac{k_{23}}{1 + \dfrac{1}{K_{12}[(\mathrm{M}) + (\mathrm{L})]}} \qquad (4)$$

Equation 4 can be rearranged to give

$$\{1 + K[(\mathrm{M}) + (\mathrm{L})]\}^{-1} = \tau k_{32}(K_{32} + 1) - K_{32} \qquad (5)$$

where $K$ is the over-all association constant, $[(\mathrm{ML_o}) + (\mathrm{ML_i})]/(\mathrm{M})(\mathrm{L})$, which is 81.3 $M^{-1}$,[2] and $K_{32} = k_{32}/k_{23}$.

A plot of $\{1 + K[(\mathrm{M}) + (\mathrm{L})]\}^{-1}$ *vs.* $\tau$ should be linear, and determination of the intercept and slope permits $k_{23}$ and $k_{32}$ to be evaluated. A plot of the data according to eq 5 is given in Figure 1, and the rate and equilibrium constants obtained are $k_{23} = k_{32} = 0.7 \times 10^4$ sec$^{-1}$, $K_{32} = 1$, and $K_{12} = 41$ $M^{-1}$. The experimental uncertainty in the constants is about ±30%.

## Discussion

The value of $k_{23}$ is in reasonable agreement with the values found for other $\mathrm{Ni^{2+}}$ complexes[5] and with the rate of exchange of water from the inner hydration sphere of $\mathrm{Ni^{2+}}$;[7] it is also in agreement with the idea that expulsion of water molecules from the inner hydration sphere is rate determining in the over-all complex formation.[5] In the case of $\mathrm{Ni^{2+}}$ complexes with trivalent pyrophosphate,[8] tetravalent tripolyphosphate,[8] and tetravalent adenosine 5'-triphosphate,[9] the ratios of inner-sphere to outer-sphere complexes can be estimated to be 35, 150, and 260, respectively (±30% at least). The ratio $(\mathrm{ML_i})/(\mathrm{ML_o})$ correlates roughly with the charge on the phosphates; that is, the lower the charge, the more predominant are outer-sphere complexes. It is also worth noting that the oxygen atoms of the $\mathrm{PO_3}$ pyramid just match the hydrogens on a trigonal face of the octahedrally hydrated metal ion so that stabilization of the outer-sphere complex might occur through hydrogen bonding. An appreciable amount of outer-sphere complexes has also been found for $\mathrm{NiSO_4}$ complexes.[10] Other divalent metals would be expected to have ratios of $(\mathrm{ML_o})/(\mathrm{ML_i})$ similar to the complexes of $\mathrm{Ni^{2+}}$ with MP, but the associated rates are too rapid to measure with the temperature-jump method. The relative amounts of inner- and outer-sphere complexes may be of importance in biological systems where divalent monophosphates and singly charged phosphate diesters are quite prevalent.

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# O,O'-Diphenyldithiophosphatotetracarbonylmanganese(I) and Related Compounds

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The versatility of the dialkyldithiophosphato group and its similarity to the acetylacetonato group as a uninegative bidentate ligand for transition metal atoms has been pointed out,[1,2] and complexes of the related dialkyl- or diaryldithiophosphinato group have been described.[3] Sulfur-bonded tetracarbonylmanganese chelates of diethyldithiocarbamato,[4] dithiobenzoato,[5] and maleonitriledithiolato[6] groups are known, as well as bromotricarbonylmanganese chelates of uncharged dithioethers.[7] The preparation and properties of mixed complexes containing Lewis bases and halo- or pseudohalocarbonylmanganese(I) groups have been of continuing interest.[8-15]

We have prepared O,O'-diphenyldithiophosphatotetracarbonylmanganese(I), $[\mathrm{MnS_2P(OC_6H_5)_2(CO)_4}]$, and investigated its reactions with Lewis bases. Some-

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