Introduction
The synthesis of alkali metal salts of the organometallic anion \([\text{C}_{5}\text{H}_{2}\text{Co}(\text{P}(\text{O})(\text{OC}_{2}\text{H}_{5})_{2})_{2}]^{-}\) has recently been reported [1]. This anion and analogous complexes of the type \([\text{C}_{5}\text{H}_{2}\text{Co}(\text{P}(\text{O})(\text{OR})_{2})_{2}]^{-}\) readily form 2:1 adducts with metal ions \(M^{n+}\), \(n = 2, 3\) [1-4]. From X-ray structural investigations it is evident that in such adducts the complexes \([\text{C}_{5}\text{H}_{2}\text{Co}(\text{P}(\text{O})(\text{OR})_{2})_{2}]^{-}\) act as tridentate oxygen ligands by using the three phosphoryl groups as oxygen donors [5, 6].

In \(\text{CoL}_{2}\) the central cobalt(II) ion is octahedrally coordinated by the 6 oxygen atoms of the two ligands \(L^{-}\) and the same MO coordination can be postulated in all complexes of the type \([\text{ML}_{2}]^{(n-1)+}\). Such compounds can be prepared with a large variety of metal ions \(M^{n+}\), including main group as well as transition metal ions, small ions (e.g. \(\text{Mg}^{2+}\), \(r = 0.65\,\text{Å}\)) and large ones like \(\text{Ba}^{2+}\) (\(r = 1.35\,\text{Å}\)). All the known metal complexes of \(L^{-}\) are very easily isolated and it is of interest whether these complexes are also stable in solution. The ligand itself is not sensitive to air oxidation and is not hydrolysed by water or aqueous acids. As the complexes are not readily soluble in water the equilibria \(M^{n+} + \text{ML}_{2}^{(n-1)+} \rightleftharpoons \text{ML}_{2}^{(n-2)+}\) cannot be studied in aqueous solution, but it is possible to follow most of the complex formation reactions in 95% methanol/water solutions.

Experimental
The complex formation was investigated by following the change in pH during alkalimetric titrations of the protonated ligand in the presence of a metal ion. The formation of the complex causes a change in concentration of \(L^{-}\) and also in the pH. The ligand \(L^{-}\) is a weak base giving a protonated
species HL with $pK_a = 8.82$ and therefore the direct pH method [7] could be used. L$^-$ was available only as the sodium salt. This introduced minor problems with the evaluation of the stability constants in cases where the expected complex ML is formed together with NaL (see Table I). The ionic strength of the solutions was maintained at 0.1 M by using tetramethylammonium chloride, an electrolyte which shows no tendency to associate with the ligand L$^-$. By adding the necessary amount of dry methanol the water content was always kept at exactly 5 ml per 100 ml of the final solutions. This proved necessary because the pH value depends strongly on the composition of the solution. The cell was calibrated by titration of an HCl solution with 0.1 M tetramethylammonium hydroxide in 95% methanol/water. In this solvent at 25 °C the ionic product $[\text{H}^+][\text{OH}^-]$ was found to be 10$^{-15.99}$ M$^2$. The measurements were made using the microprocessor/analyzer Orion 901, glass electrodes Beckman 40498 and Philips GA 110, and a 0.1 M calomel electrode containing 0.1 M (CH$_3$)$_4$NCI in 95% methanol/water. For each evaluation of the stability constant 40 experimental points from each curve were considered for a particular equilibrium. The data were analysed using a CDC 6500-6400 computer. The methods of calculation have recently been described [8].

Results

Table I contains the measured log $K_1$ and log $K_2$ values. In the case of divalent cations only the stability constants $K_1$ have been obtained since L$^-$ is introduced as the sodium salt and the total ligand concentration is used to form ML. The error in the logarithm of the stability constants is estimated to be lower than 0.1 for log $K_1 < 7$ but increases to 0.3 for log $K_1 > 9$. A large log $K_1$ value means that the complex ML$^+_1$ is already formed in the solution before it is titrated, consequently causing a relatively larger error in log $K_1$.

The formation of a solid phase in the Ni$^{2+}$ system does not allow an exact determination of $K_2$. It is worth noting that with most metal ions the complex formation is fast. However the attainment of a constant pH value was extremely slow with Pb$^{2+}$ and one titration takes several days. In the initial solution Hg$^{2+}$ seems to be present already as Hg(OH)L, therefore its formation cannot be followed by alkalimetric titration. Addition of Ag$^+$ to the acidified solution of NaL produces some turbidity, which increases upon neutralisation with 0.1 M tetramethylammonium hydroxide. The stability of AgL therefore cannot be measured with certainty.

The complex formation of L$^-$ with H$^+$, Mg$^{2+}$, and La$^{3+}$ has been investigated calorimetrically and the obtained thermodynamic parameters are given in Table II.

Discussion

Within the series of the alkali and earth alkali cations the stability constant $K_1$ increases with decreasing ionic radius of the cation as expected for an electrostatic interaction of two spheres of opposite charge. The very small difference between the $K_1$(Mg$^{2+}$) and $K_1$(Ca$^{2+}$) values is unexpected however. This may be due to the low ligand charge and the relatively rigid ligand geometry. It is interesting to note in this context that L$^-$ is the first known

Table II. Thermodynamic data of reactions from direct calorimetric measurements at $T = 25 °C$, $I = 0.1$ M [(CH$_3$)$_4$N]Cl.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ [kcal/mol]</th>
<th>log $K$</th>
<th>$\Delta G$ [kcal/mol]</th>
<th>$\Delta S$ [kcal/mol]</th>
<th>$\Delta S$ [cal/mol · K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$ + L$^-$ → HL</td>
<td>0.0</td>
<td>8.82</td>
<td>-12.0</td>
<td>12.0</td>
<td>40.2</td>
</tr>
<tr>
<td>Na$^+$ + L$^-$ → NaL</td>
<td>-0.5</td>
<td>4.2</td>
<td>-5.7</td>
<td>6.2</td>
<td>20.8</td>
</tr>
<tr>
<td>Mg$^{2+}$ + 2 L$^-$ → MgL$_2$</td>
<td>0.0</td>
<td>15.9</td>
<td>-21.7</td>
<td>21.7</td>
<td>72.7</td>
</tr>
<tr>
<td>La$^{3+}$ + 2 L$^-$ → LaL$_2^+$</td>
<td>-9.5</td>
<td>18.7</td>
<td>-25.5</td>
<td>16.8</td>
<td>57.2</td>
</tr>
</tbody>
</table>
example of a monoanionic tridentate oxygen ligand with $C_3v$ symmetry [9]. The stability constant $K_i$ of NaL in water is more than 100 times lower than in 95% methanol/water. Lehn has observed a similar influence of the solvent on the $K_i$ values of alkali metal cryptate complexes [11]. $L^-$ forms a stronger sodium complex in both aqueous methanol and water than the known crown ether compounds [12, 13] whereas the cryptands form more stable sodium complexes than $L^-$ [11]. The ligand $L^-$ and tripolyphosphate (log $K_1 = 1.75$ for Na$^+$ in aqueous solution) have about the same tendency for complex formation with Na$^+$. Estimates of the $K_i$ values of $L^-$ with divalent cations in water can be obtained by subtracting 3 log units from the values in Table I. This clearly shows that $L^-$, probably because of the low charge, forms less stable complexes with M$^{2+}$ ions than the highly charged ligand tripolyphosphate (log $K_1 = 9.3$ for Cu$^{2+}$, 8.35 for Zn$^{2+}$, in aqueous solution). The stability constants $K_1$ of complexes of tripolyphosphate with M$^{2+}$ ions in water are similar to those obtained with $L^-$ in 95% methanolic solutions. $L^-$ forms not only 1:1 but also 1:2 complexes with all divalent and trivalent cations investigated so far. Generally $K_2$ is 100 to 1000 times lower than $K_1$. The two constants are of the same order of magnitude only for Ca$^{2+}$. Steric hindrance prevents the formation of 1:3 complexes.

Among the log $K_i$ values of the divalent 3d cations the Ni(II) value is remarkably low although the same general trend Mn$^{2+} >$ Co$^{2+} >$ Ni$^{2+} <$ Cu$^{2+} >$ Zn$^{2+}$ is found for the corresponding tripolyphosphate complexes. This trend has been analysed in detail by thermodynamic measurements. In the case of the tripolyphosphate complexes all complex formation reactions are endothermic and the stability of its complexes arises from a large positive $\Delta S$ of reaction [14]. We have not yet been able to measure the thermodynamics of the complex formation of $L^-$ with 3d metal ions. The formation of the complexes HL, NaL, MgL$_2$, and LaL$_2^+$ however has been examined calorimetrically. The values given in Table II show that the solvent molecules are exchanged for $L^-$ in the formation of the neutral complexes ML$_n$ without evolution of heat. The favorable thermodynamics of the reaction are solely due to the entropy term $\Delta S$. It is well known that ions in solution act as good "organizers" of the solvent, and it is the loss of organization of the solvent that favors the formation of the neutral complexes ML$_n$. In the formation of the charged complex LaL$_2^+$ this effect is less pronounced making $\Delta S$ slightly less positive and $\Delta H$ more negative with respect to the thermodynamic parameters of MgL$_2$.

It seems very probable that the complex stability constants of $L^-$ with 3d transition metal ions are also dominated by the entropy term and that this is the reason for the non-adherence to the Irving-Williams series. The thermodynamic parameters given in Table II are in complete agreement with this interpretation.

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[9] The only other type of tripod ligands with the same charge and symmetry are the trispyrazolylborates, a novel class of nitrogen ligands studied by Trofimenko. See e.g. ref. [10].