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ORGANOMETALLIC IONOPHORE FOR ALKALI METAL CATIONS

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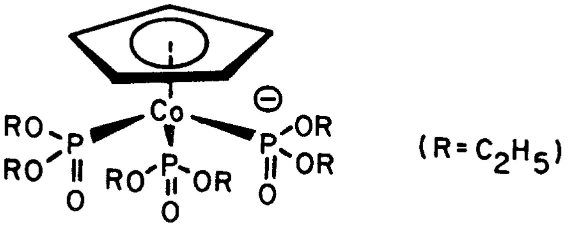
Abstract. Complexes of a novel synthetic organometallic ionophore with lithium and sodium cations have been characterized by single-crystal X-ray diffraction. The crystal structure of the lithium complex consists of cation-ligand dimers with a tetrahedral coordination around Li. The sodium complex reveals a different structure type consisting of cation-ligand trimers, with water molecules being included between the trimeric entities. The coordination sphere around the Na ions has a distorted octahedral symmetry. It is anticipated that the observed structures of dinuclear Li and trinuclear Na complexes represent possible modes of aggregation of the cation-ligand entities in lipophilic media.

1. INTRODUCTION

Synthetic ionophore ligands, mostly based on cyclic and branched polyethers, have been widely used in the last decade to study carrier facilitated cation transport across membranes. It has recently been observed that the organometallic ligand $(C_5H_5)Co[PO(OC_2H_5)_2]_3^-$ also has



efficient ionophoric properties for alkali metal cations, with a specificity toward Li^+ [1]. The association constants in aqueous [3] as well as methanol [2] solutions follow the trend $H^+ > Li^+ > Na^+ > K^+$. The rate of transport of the ions across a lipid membrane was monitored by ^{23}Na and ^{7}Li nuclear magnetic resonance, revealing a significant preference for Li^+ over Na^+ [1]. In order to elucidate the structural basis of the ionophoric behaviour we analysed crystallographically the lithium and sodium complexes of this ligand.

2. EXPERIMENTAL DATA

Single crystals of both compounds suitable for the crystallographic study were obtained from water as well as from wet n-heptane and iso-butylacetate solutions. Diffraction data were measured at ca. 18°C on a CAD4 diffractometer, using MoKα radiation. The crystal data are:

Lithium complex: triclinic, space group $P\bar{1}$, a=11.944(3), b=12.154(6), c=20.468(3) Å, α=92.79(3), β=91.05(1), γ=118.07(4)°, R=0.094 for 3694 observations above $3\sigma(I)$ out to $2\theta_{max}=46°$.

Sodium complex: monoclinic, space group $P2_1/c$, a=10.828(5), b=25.008(3), c=31.307(6) Å, β=98.76(2)°, R=0.091 for 3005 observations above $3\sigma(I)$ out to $2\theta_{max}=40°$.

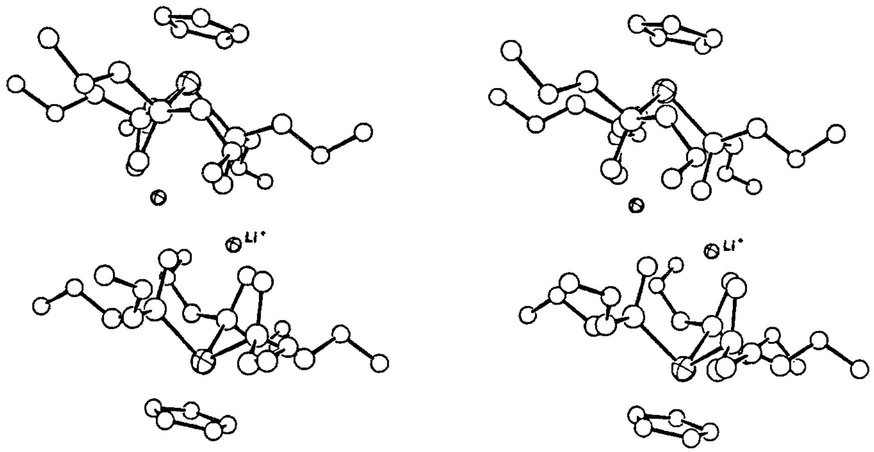
The asymmetric unit of the lithium compound contains two units of the 1:1 complex, while that of the sodium compound contains three units of the 1:1 complex and four molecules of water. The sodium compound was found also to crystallize from water in a different polymorphic form [monoclinic, a=10.969(5), b=53.226(4), c=14.731(3) Å, β=103.38(3)°], but good crystal of this phase could not be grown.

The two structures were solved by a combination of direct methods and Fourier techniques (MULTAN80). Their refinements were carried out by large block least-squares (SHELX76), including the positional and thermal parameters of all the nonhydrogen atoms. The refinement calculations indicated clearly that both structures are partially disordered. In the sodium compound the disorder is confined to the peripheral OEt groups of the ligand. In the lithium compound an additional twofold orientational disorder of an entire phosphonate group is present.

3. DISCUSSION OF RESULTS

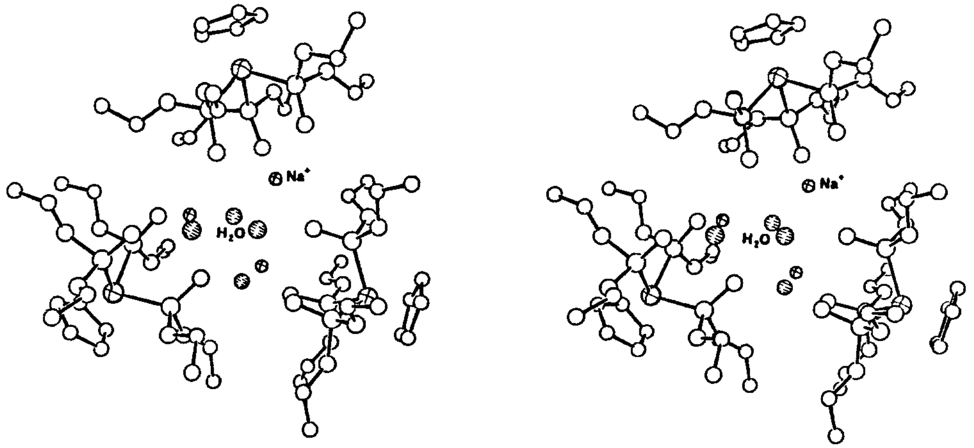
As stated at the outset, the organometallic ligand can transport alkali metal cations across phospholipid membranes. Since the molecular surface of the 1:1 complex is polar at one end and apolar at the other, it will be reasonable to assume that transfer of the cations through lipophilic media is more likely to occur in the form of polymeric cation-ligand aggregates than in the form of monomeric entities. The observed structures of the dinuclear Li^+ and the trinuclear Na^+ complexes may represent in fact two possible modes of such an aggregation during the process of transport.

The smaller Li^+ ions are sufficiently well enclosed within a cavity formed between two ligands, leading to the formation of dimers.

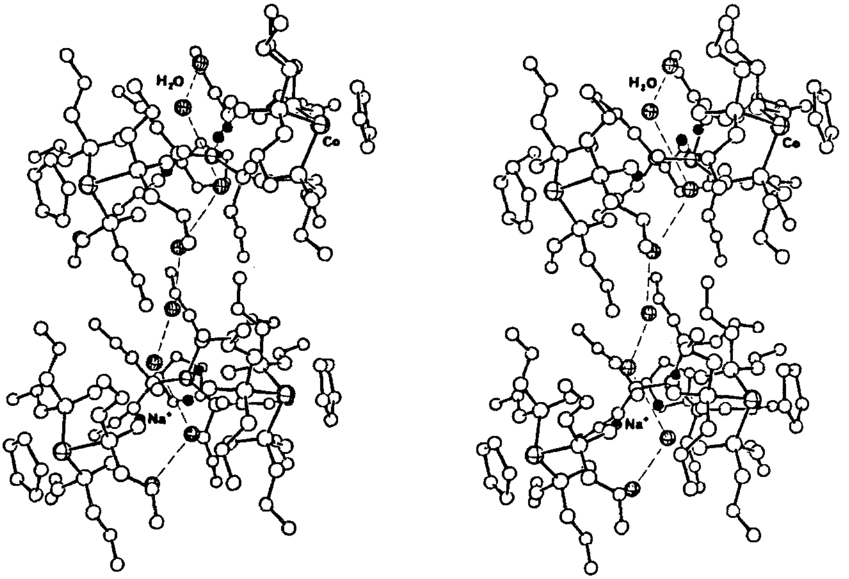


The Li^+ ions lie near the inversion centers of the crystal and bridge between the centrosymmetrically related ligands. They are tetracoordinated to four P=O ligating sites, three O-nucleophiles from one ligand and an additional P=O from the other part of the dimer. The Li-O distances vary from 1.88 to 1.95 Å in the ordered dimer and from 1.82 to 2.01 Å in the orientationally disordered entity. Within the dimers the distances between the two cations are 2.61 and 2.63 Å. The exterior surface of the dinuclear assembly consists of lipophilic OEt and cyclopentadienyl hydrocarbon groups, providing a lipophilic environment for the adjacent units in the crystal.

The sodium compound reveals a new structure type consisting of trimers. The trimeric entity is formed by triangularly arranged species of the ligand. It has a polar interior lined with P=O groups which provide a series of ion binding sites and an apolar exterior consisting of hydrocarbon fragments. The metal cations are contained within the central cavity of such unit. Each one of them is bound to four P=O groups, providing an effective bridge between adjacent molecules of the ligand. All Na-O bonds are within the 2.23-2.44 Å range; the distances between adjacent Na^+ ions within the trimeric unit vary from 3.26 to 3.42 Å.



In the crystal the trimeric cation-ligand assemblies are stacked one on top of the other, forming a channel-type structure. Molecules of water are included along the channels, linking between adjacent entities of the complex and supplementing the (pseudo octahedral) coordination sphere of the metal cations. Two of the water molecules lie in close proximity to the sodium ions, the corresponding Na^+-O(water) distances varying from 2.33 to 2.85 Å. The exterior of the stack consists of hydrocarbon fragments and is lipophilic; side packing of the stacked units is thus stabilized by van der Waals forces. In this respect the structure of the sodium complex (shown below) resembles a solid state model of a molecular channel similar to that of a functionalized macrocyclic polyether previously described in the literature [4]. The two crystal types contain channels with a hydrophilic interior which are suitable for the accommodation of polar species as metal cations and water.



It is important to note that molecular weight determinations for the sodium compound indicate the presence of trimeric aggregates in a benzene solution as well, which is consistent with the above discussion. Further structural investigations of related complexes and chemical modifications of the organometallic ligand are under way in order to improve the ionophoric properties of this type of molecular hosts.

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5. A short account of this work has been presented at the Tenth European Crystallographic Meeting, Wrocław (Poland), 7 August, 1986.
6. **Supplementary data:** The atomic coordinates of the two compounds are deposited with the British Library as Supplementary Publication No. SUP 82047.