characterization of the common CO site exchange process first reported by Cotton in 1966.[6] It should however be stressed that all merry-go-round processes in carbonyl clusters are not necessarily concerted. Indeed, we have already shown that the merry-go-round process in $[Ir_4(CO)_8(\mu_2\text{-}CO)_3Br]^-$ does not pass through an unbridged intermediate or transition state. This can be related to the ground-state structure of this anion, which features two asymmetrical bridging CO's with shorter bonds to the same Ir atom.[14] Formation of an unbridged intermediate would require the rupture of one of the two shorter bonds and is, therefore, not the lowest activation energy process. On the other hand, a concerted process can take place in **1b**, as the three bridging CO's have equal Ir–CO distances.[7]

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Registry No. **1**, 127435-82-9.

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Lithium–Transition Metal Complexes Derived from *meso*-Octaethylporphyrinogen Which Display σ- and π-Bonding Modes

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Until recently,[2,3] *meso*-octaalkylporphyrinogens,[4] which are the precursors of porphyrin-type ligands,[5,6] have never been considered for metal complexation reactions. The anionic form of octaalkylporphyrinogen (Figure 1) has a number of characteristics which are virtually unique for a macrocyclic ligand: (i) The tetraanion should allow the stabilization of unusually high oxidation states for transition metals;[2] (ii) the pyrrolyl anion can function as a σ (2 e) or π (6 e) donor group;[3] (iii) the meso substituent should allow a variety of functionalities to be easily introduced into the macrocycle,[4] and at the same time the conformation of the metallacycle[7] may serve to force a special metal–hydrocarbon interaction.

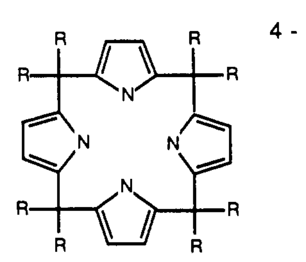

Figure 1.

Table I. Crystal Data for Complex **4**

formula	$C_{52}H_{80}CoLi_2N_4O_4$	*Z*	4
cryst system	monoclinic	no. of unique obsd data	3349
space group	*C*2/*c*		
cell params at 295 K		intens measmt	*a*
a/Å	20.698 (4)	struct refinement	*b*
b/Å	10.942 (4)	$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.043
c/Å	22.791 (4)		
β/deg	104.79 (2)		

[a] For intensities and background individual profiles were analyzed by the following: Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1974**, *A30*, 580. [b] Refinement was by blocked full-matrix least squares first isotropically and then anisotropically for all non-hydrogen atoms. The hydrogen atoms except those associated with THF molecules (which were ignored) were located from different Fourier maps and introduced as fixed contributors prior to the final stage of refinement.

Table II. Atomic Coordinates (×10[4]) and Thermal Parameters for Complex **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq},[a] Å[2]
Co	0	2259.1 (5)	2500	274 (2)
N1	842 (1)	2213 (2)	2300 (1)	305 (7)
N2	452 (1)	2190 (2)	3339 (1)	305 (6)
C1	969 (1)	1544 (3)	1831 (1)	344 (10)
C2	1654 (1)	1510 (3)	1897 (1)	448 (11)
C3	1956 (1)	2196 (3)	2422 (1)	448 (11)
C4	1443 (1)	2616 (3)	2663 (1)	344 (9)
C5	1465 (1)	3345 (3)	3235 (1)	366 (9)
C6	1082 (1)	2633 (3)	3609 (1)	361 (9)
C7	1247 (1)	2321 (3)	4217 (1)	485 (11)
C8	701 (1)	1654 (3)	4320 (1)	456 (10)
C9	226 (1)	1585 (3)	3781 (1)	334 (9)
C10	419 (1)	858 (3)	1388 (1)	347 (10)
C11	1125 (2)	4595 (3)	3062 (2)	477 (12)
C12	1457 (2)	5449 (3)	2701 (2)	656 (16)
C13	2203 (1)	3526 (4)	3594 (1)	542 (13)
C14	2336 (2)	4430 (4)	4120 (2)	808 (19)
C15	634 (2)	496 (3)	812 (1)	473 (12)
C16	813 (2)	1529 (4)	443 (2)	629 (15)
C17	259 (2)	−337 (3)	1696 (1)	492 (11)
C18	847 (2)	−1132 (4)	1993 (2)	927 (21)
Li	1472 (3)	3425 (6)	1561 (3)	697 (27)
O1S	859 (1)	4646 (2)	1139 (1)	726 (11)
C1S	175 (2)	4726 (4)	1176 (2)	844 (19)
C2S	−79 (3)	5951 (5)	929 (3)	1331 (32)
C3S	449 (3)	6509 (5)	686 (3)	1162 (31)
C4S	1050 (3)	5740 (5)	877 (3)	1321 (32)
O2S	2247 (1)	3849 (3)	1246 (1)	804 (11)
C5S	2811 (3)	4414 (7)	1634 (3)	1433 (36)
C6S	3368 (3)	4271 (8)	1348 (3)	1516 (39)
C7S	3060 (4)	3897 (9)	720 (4)	1962 (51)
C8S	2380 (3)	3535 (8)	679 (3)	1673 (43)

[a] U_{eq} is in the form $^{1}/_{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly

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Table III. Selected Bond Distances (Å) and Angles (deg) for Complex **4**[a]

Distances

Co–N1	1.911 (2)	C6–C7	1.383 (3)
Co–N2	1.904 (2)	C7–C8	1.414 (4)
N1–C1	1.375 (4)	C8–C9	1.366 (3)
N1–C4	1.379 (3)	C9–C10′	1.517 (3)
N2–C6	1.380 (3)	Li–C1	2.455 (7)
N2–C9	1.383 (4)	Li–C2	2.230 (7)
C1–C2	1.388 (3)	Li–C3	2.379 (7)
C1–C10	1.514 (3)	Li–C4	2.678 (7)
C2–C3	1.416 (4)	Li–N1	2.723 (8)
C3–C4	1.392 (4)	Li–O1S	1.923 (6)
C4–C5	1.519 (4)	Li–O2S	1.973 (7)
C5–C6	1.519 (4)		

Angles

N1–Co–N2	89.7 (1)	N2–Co–N2′	175.5 (1)
N1–Co–N2′	90.2 (1)	O1S–Li–O2S	98.6 (3)
N1–Co–N1′	177.0 (1)		

[a] A prime denotes a transformation of $-x$, y, $0.5 - z$.

distilled prior to use. Magnetic susceptibility measurements were carried out at room temperature using a Faraday balance. Syntheses of octaethylporphyrinogen[4] and the lithium salt were carried out as previously reported.[2,3]

Solid-State Structure of Dilithium Tetrakis(tetrahydrofuran)(α,β,γ,δ-octaethylporphyrinogenato)cobalt(II) (4). Crystallographic data, atomic coordinates, and selected bond distances and angles are shown in Tables I–III.

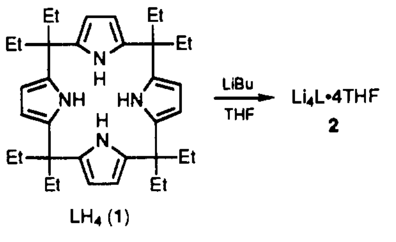
Preparation of Dilithium Tetrakis(tetrahydrofuran)(α,β,γ,δ-octaethylporphyrinogenato)iron(II) (3). Careful addition of $FeCl_2 \cdot 1.5THF$ (1.50 g, 6.4 mmol) to a solution containing lithium octaethylporphyrinogen (5.61 g, 6.5 mmol) in THF (150 mL), followed by stirring at room temperature for several hours, resulted in a clear orange solution. After evaporation of the solvent and shaking of the residue with toluene (150 mL), a white-beige solid was filtered off and dried in vacuo (5.00 g, 80%). Recrystallization of this powder from toluene yielded white cubic crystals. Anal. Calcd for $C_{52}H_{80}FeLi_2N_4O_4$: C, 69.79; H, 9.00; N, 6.26. Found: C, 69.54; H, 8.95; N, 6.32 $\mu_{eff} = 5.05\ \mu_B$ at 298 K.

Preparation of Dilithium Tetrakis(tetrahydrofuran)(α,β,γ,δ-octaethylporphyrinogenato)cobalt(II) (4). Addition of $CoCl_2 \cdot 1.5THF$ (0.80 g, 3.38 mmol) and lithium octaethylporphyrinogen (2.88 g, 4.06 mmol) to toluene (120 mL) resulted in a dark brown-black solution, which was stirred at room temperature for 2 days. Removal of LiCl by filtration and standing of the filtrate overnight at −20 °C furnished orange-amber rhomboids (2.14 g, 70%) which were suitable for X-ray crystallography. Anal. Calcd for $C_{52}H_{80}CoLi_2N_4O_4$: C, 69.55; H, 8.98; N, 6.24. Found: C, 69.73; H, 9.39; N, 6.27. $\mu_{eff} = 4.18\ \mu_B$ at 293 K.

Preparation of Dilithium Tetrakis(tetrahydrofuran)(α,β,γ,δ-octaethylporphyrinogenato)copper(II) (5). Anhydrous $CuCl_2$ (0.65 g, 4.81 mmol) was added to toluene (150 mL), followed by the lithium octaethylporphyrinogen (3.84 g, 4.50 mmol). The resulting orange-red solution was stirred overnight at room temperature and then evaporated to dryness. The residue was shaken with a mixture of hexane (100 mL) and THF (3 mL) and stirred for 1 h, after which time the orange microcrystalline powder was filtered off and dried in vacuo (2.97 g, 77%). Recrystallization of this powder from hexane/THF gave orange cubic crystals. Anal. Calcd for $C_{52}H_{80}CuLi_2N_4O_4$: C, 69.19; H, 8.93; N, 6.21. Found: C, 68.88; H, 9.27; N, 6.07. $\mu_{eff} = 1.80\ \mu_B$ at 298 K.

Results and Discussion

Among the meso-substituted porphyrinogens, *meso*-octaethylporphyrinogen is noteworthy due to its facile synthesis.[2] So far we have only expored its nonaqueous chemistry with transition metals. The ligand is easily converted by reaction with BuLi in tetrahydrofuran (THF) (reaction 1) to the crystalline tetralithium derivative **2**, whose structure is currently under investigation.



LH_4 (**1**) $\xrightarrow[\mathrm{THF}]{\mathrm{LiBu}}$ $Li_4L \cdot 4THF$ **2** (1)

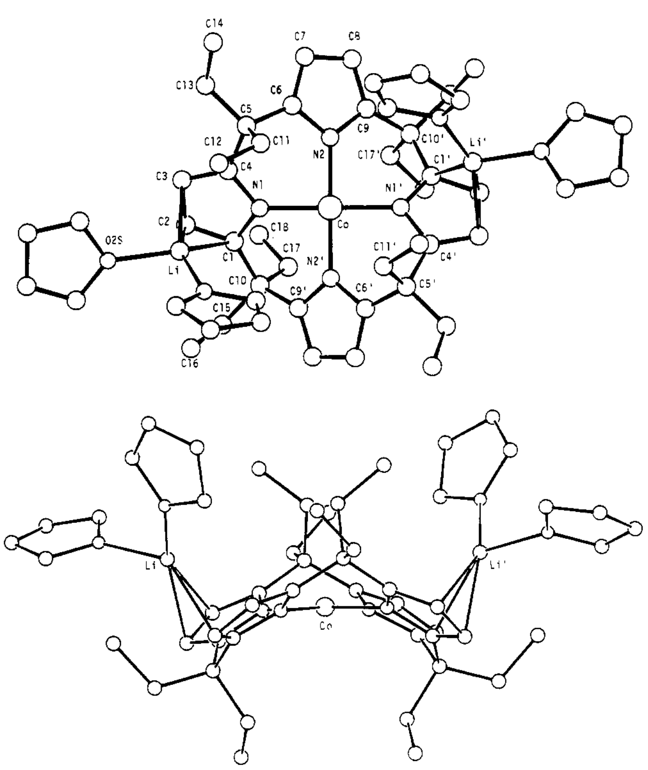


Figure 2. (a) Top: SCHAKAL drawing of complex **4**. (b) Bottom: Side view of complex **4**.

The reaction of **2** (reaction 2) with anhydrous or THF-solvated forms of MCl_2 (M = Fe, Co, Cu) in THF gave the corresponding lithium–transition metal complexes, in a good to excellent yield (see Experimental Section).

$$\underset{\mathbf{2}}{\mathrm{Li_4L(THF)_4}} + \mathrm{MCl_2} \xrightarrow[\mathrm{THF}]{-\mathrm{LiCl}} \mathrm{Li_2ML(THF)_4} \quad (2)$$

$$\begin{array}{l} \mathbf{3},\ \mathrm{M} = \mathrm{Fe} \\ \mathbf{4},\ \mathrm{M} = \mathrm{Co} \\ \mathbf{5},\ \mathrm{M} = \mathrm{Cu} \end{array}$$

Excess of the metal halide should be avoided since a further metalation may occur (vide infra). In the case of iron, the use of excess $FeCl_2$ led to the iron(III) octaethylporphyrinogen derivative via a disproportionation reaction.[2] In complexes **3**–**5** the transition metal is high-spin. Comparison with other N_4 macrocyclic ligands may be interesting but not really very relevant. Porphyrins and phthalocyanines are conjugated aromatic ligands where the N_4 cavity size is determined by the planar conformation of the ligand itself. However, in porphyrinogen **1** there is no conjugation between the four pyrrols and hence various conformations are possible. A more reliable comparison can be made with tetramethyldibenzotetraazaannulene ($tmtaaH_2$)[8] in terms of its nonaromatic character and the flexibility of conformation. Some significant differences exist, however, between the two classes of compounds: [Co(tmtaa)] is a low-spin complex, while [Fe(tmtaa)] is of intermediate spin with $\mu_{eff} = 3.32\ \mu_B$.[9] The Co–N bond distances are significantly shorter in [Co(tmtaa)] [1.889 (3) Å][10] than in **4** (Table III). The four independent pyrrolyl anions therefore seem to induce a much weaker ligand field than four conjugate pyrroles, or, in general, conjugated nitrogen-donor systems. The ion-pair dimetallic nature of complexes **3**–**5** was revealed by X-ray analysis. The structure of the cobalt derivative **4** is shown in Figure 2a, the other two being isostructural.[11] A

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list of selected bond distances and angles is given in Table III. The molecular structure has an imposed C_2 symmetry. Cobalt is bonded to the four nitrogens in a square-planar geometry, the metal being only 0.063 (1) Å out of the N_4 plane. The six-membered chelate rings, which each have a boat conformation, tilt alternatively up and down giving rise to a double saddle-shaped conformation of the tetraanion. The pyrrole planes form dihedral angles of 34.0 (1) and 31.7 (1)° with the N_4 coordination plane. The dihedral angle between adjacent pyrroles is 123.3 (1)°, while those between the two pairs of opposite pyrroles are 112.1 (1) and 116.6 (1)°. The axial coordination sites around the metal are filled by the *meso*-methylene groups (Figure 2b). The two pairs of carbon atoms C11, C11′ and C17, C17′ cap the CoN_4 plane on both sides, their C···C separation ranging from 4.073 (4) Å for C17···C17′ to 4.707 (5) Å for C11···C11′. Four hydrogens, one from each of the aforementioned carbons, provide a flattened tetrahedral cage around the cobalt, and the Co···H distances are rather short [Co···H(112) = 2.69 Å, Co···H(172) = 2.79 Å]. The *meso*-alkyls of the porphyrinogen are forced by the conformation of the macrocycle to be in close proximity to the metal. This has been observed in the iron(III) and the oxomolybdenum(V) complexes.[2,3] The C–H bonds are able to protect and maintain unsaturated metal centers, in the meantime providing information on the C–H···metal interaction for a variety of metals and oxidation states. Such an interaction should be considered a preliminary stage in any aliphatic intramolecular C–H bond activation.[12]

There is a significant difference in the distances of the three similar Li–C bonds (Li–C1, Li–C2, Li–C3) and Li–C4 and Li–N1 (Table III), implying an η^3-bonding mode for the lithium cation to the pyrrolyl anion. The pyrrolyl anion can display thus either the σ- or π-bonding mode, depending on the electronic needs of the cation. This can occur with the central metal atom, as was found in the zirconium(IV) derivative,[3] or with cations binding at the periphery of the macrocycle, as was found in the structures of complexes **3**–**5**. We should emphasize the potential ability of the periphery of our macrocycle–metal complexes to bind metals. The structures of the zirconium(IV) complex[3] together with those of **3**–**5** show the electronic flexibility of the macrocyclic tetraanion **4**. With regard to this, in the syntheses of complexes **3**–**5** (reaction 2) the use of an excess of metal halide should be avoided, since complexes **3**–**5** react with metal halides.[13] These factors may lead us to the use of **2** for the construction of polymetallic systems. In addition, complexes **3**–**5** exemplify a bifunctional nature containing both an electron-rich transition metal and a Lewis acid in their structure. Their use for producing a significant polarization in small molecular substrates is very well-known.

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Supplementary Material Available: For complex **4**, complete listings of crystallographic data, fractional atomic coordinates for hydrogen atoms, anisotropic thermal parameters, bond distances and angles, and equations of least-squares planes (5 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(11) The Cu and Fe derivatives are isostructural with that of Co. The unit cell parameters are as follows: $C_{52}H_{80}CuLi_2N_4O_4$, M_r = 902.7, monoclinic, space group *C2/c*, *a* = 20.808 (2) Å, *b* = 10.946 (1) Å, *c* = 22.811 (2) Å, β = 104.57 (2)°, *U* = 5028.5 (9) Å^3, *Z* = 4, D_c = 1.192/g cm^{-3}; $C_{52}H_{80}FeLi_2N_4O_4$, M_r = 895.0, monoclinic, space group *C2/c*, *a* = 20.749 (2) Å, *b* = 10.930 (1) Å, *c* = 22.797 (2) Å, β = 104.69 (2)°, *U* = 5001.1 (9) Å^3, *Z* = 4, D_c = 1.189 g cm^{-3}.

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Binding of Alkali-Metal Cations by Self-Assembling Ionophore Complexes of Nickel(II)

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The assembly of enzyme complexes to form binding sites not present in the separated subunits is an important mechanism of molecular recognition in biological systems.[1,2] Recently, a family of Ni(II) complexes has been reported that allows the self-assembly process to be modeled using small molecules.[3,4] In complexes such as **1** (Chart I), two Schiff base ligands (L = *N*-methyl-3-(2-ethoxymethoxy)salicylaldimine) containing flexible polyether chains are organized around a Ni^{2+} template to create an alkali-metal cation binding site. The complex transports picrate salts of alkali-metal cations from aqueous solution into chloroform.[3] It was shown that the complexes transport alkali-metal cations when 2 equiv of the ligand is mixed with 1 equiv of Ni^{2+}, demonstrating the self-assembly of the binding site in situ.

In a report by Gokel et al.,[4] it was shown that a related complex, **2**, is monomeric and square planar at low concentrations in chloroform solution but is octahedral in 1:1 $CHCl_3/CH_3OH$, presumably with two axial CH_3OH ligands. The binding of sodium picrate by **2** leads to a novel complex with the formula $L'_4Ni_2(H_2O)(Na(picrate))_2$ (L′ = *N*-methyl-3-methoxysalicylaldimine), which has been characterized by X-ray crystallography. Since studies thus far were performed either in methanol or by extraction from aqueous solution, it remains unclear whether a coordinating solvent is required to create the binding site or whether the presence of the alkali-metal cation alone can induce the association of the Ni complexes. Furthermore, the results of Gokel suggest that picrate anion is required for cation binding, suggesting that without a hydrophobic coordinating anion addition of the polyether chains to the complex is not sufficient for cation binding.[4] We report here three important features of complex **1**: (1) in acetone solution, the complex remains monomeric and square planar until *only* the dry alkali-metal salt is added; (2) cation binding occurs in the absence of picrate anion; (3) the binding constants for alkali-metal cations can be determined accurately in the absence of a standard using methods usually applied to biological self-assembly.

Experimental Section

Complex **1** was prepared as previously described.[3] $NaClO_4$ was recrystallized from ethanol and dried in a vacuum oven. Cyclic voltammetry was performed in acetonitrile with either 0.1 M tetrabutylammonium hexafluorophosphate or 0.1 M sodium hexafluorophosphate. Experiments were performed using a ferrocene standard in a drybox with a Pt button working electrode, Pt wire counter electrode, and a Ag wire pseudoreference electrode. Instrumental conditions were as previously described.[5a] Vapor pressure osmometry was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. A solution of 0.1 M $NaClO_4$ in acetone was used. This solution was initially calibrated using azobenzene, which gave an accurate molecular weight. Solution magnetic moments were determined in acetone-d_6 solution by the Evans method.[5b] UV–vis spectra were acquired in acetone solution using an HP8452 diode-array spectrophotometer.

Results and Discussion

The optical spectrum of **1** in acetone exhibits a d–d band at 615 nm (ϵ = 107 M^{-1} cm^{-1}) and an intense charge-transfer band at 416 nm (Figure 1). These solutions give diamagnetic proton NMR spectra, which can be readily assigned. These properties

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