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[11] Crystal structure analysis of **2**: $C_{56}H_{46}O_8 \cdot 3\,CHCl_3$, $M_r = 1205.11$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.389(3)$, $b = 19.630(4)$, $c = 10.790(2)$ Å, $\alpha = 90.45(2)$, $\beta = 108.78(1)$, $\gamma = 67.71(1)°$, $V = 2831(1)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.41\ \text{g cm}^{-3}$, colorless crystals from $CHCl_3$/EtOH, crystal dimensions $0.25 \times 0.30 \times 0.45\ \text{mm}^3$, $\theta$-$2\theta$ scan ($2\theta_{max} = 124.2°$), $F(000) = 1240$, room temperature. Of 9285 measured reflections, 8908 were independent ($R_{int} = 0.068$). Data were collected with a Rigaku AFC5R diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation and a 12 kW rotating anode generator. The data were corrected for Lorentzian and polarization effects, and an empirical absorption correction was applied to intensities based on azimuthal scans of several reflections; $\mu(Cu_{K\alpha}) = 45.27\ \text{cm}^{-1}$, no decay correction. The structure was solved by direct methods with the program SIR 92.[12] Non-hydrogen atoms were refined anisotropically[13] except for one solvent molecule refined isotropically because of disorder. All hydrogen atoms (apart from OH) were positioned geometrically (riding model). Final refinements were carried out according to the full-matrix least-squares method based on 4189 observed reflections with $F_o > 10\,\sigma(F_o)$ and 665 variable parameters. $R = 0.117$, $R_w = 0.121$, $w = (\sin\theta/\lambda)^2$, $S = 1.38$. Maximum and minimum peaks of the final difference Fourier map: 2.20 and $-1.03\ \text{e Å}^{-3}$; these residual electron densities could not be assigned to any chemically sensible moiety. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100536. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44)1223-336033; e-mail: deposit@chemcrys.cam.ac.uk).

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## Lanthanide-Assisted Self-Assembly of an Inert, Metal-Containing Nonadentate Tripodal Receptor**

Stéphane Rigault, Claude Piguet,*
Gérald Bernardinelli, and Gérard Hopfgartner

Recent fascinating applications of lanthanide, $Ln^{III}$, complexes as contrast agents for medical resonance imagining (MRI), luminescent stains for fluoroimmunoassays, and catalysts for the selective cleavage of RNA and DNA require close and tunable control of the coordination sphere to enhance specific structural and electronic properties.[1] The development of tailored receptors for $Ln^{III}$ remains a challenge for synthetic chemists, since $Ln^{III}$ ions do not display pronounced stereochemical preferences for particular bonding modes.[2] Highly preorganized macrobicyclic cryptands allow only partial control of the coordination of $Ln^{III}$ ions,[3] and their tedious preparation has encouraged the development of $Ln^{III}$-assisted template syntheses of macrocyclic Shiff base complexes.[4] However, the nondirectional Ln–ligand bonds and the high sensitivity of $Ln^{III}$ to basic conditions severely limit their use as template ions in the preparation of macrobicycles[5] and self-assembled metal-containing supramolecular compounds.[6]

A recent approach uses the segmental ligands $L^1$ and $L^2$, which are predisposed for the selective recognition of f-block metal ions. The self-assembled homotopic triple-stranded helicates $[Ln_2(L^1)_3]^{6+}$ result from the reaction of $L^1$ with $Ln(ClO_4)_3$,[7] while equimolar mixtures of $Ln(ClO_4)_3$ and $M(ClO_4)_2$ ($M = Zn$, Fe) produce head-to-head heterotopic

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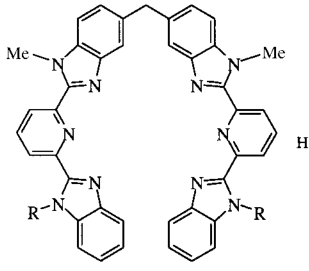
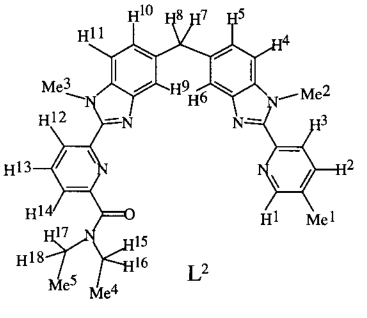
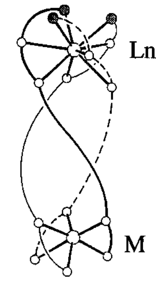


L$^1$



L$^2$



(HHH)-[LnM(L$^2$)$_3$]$^{5+}$

triple-stranded helicates (HHH)-[LnM(L$^2$)$_3$]$^{5+}$ (HHH = head-to-head helicate),[6] which are referred to as noncovalent lanthanide podates.[8] In the latter complexes, the facial pseudo-octahedral d-block and the pseudo-tricapped trigonal prismatic 4f-block ions display synergic structural and electronic effects that allow the design of supramolecular "devices" with predictable and tunable properties (luminescence, magnetism).[8] Here we report the selective formation of an inert, nine-coordinate metal-containing tripodal receptor by means of a related self-assembly process with Ln$^{III}$ ions as template and subsequent modification[9] of the resulting helicate.

Cobalt is ideally suited to the preparation of inert d-block tripods since the pseudo-octahedral high spin d$^7$ Co$^{II}$ ion coordinated to $\alpha,\alpha'$-diimine donors is expected to be labile. This allows the strict self-assembly of the supramolecular complex [LnCo(L$^2$)$_3$]$^{5+}$; its subsequent oxidation gives the inert low-spin d$^6$ Co$^{III}$ complex with the cobalt ion in a similar pseudo-octahedral environment.[10] Electrospray (ES) MS titrations of L$^2$ with an equimolar mixture of Ln(ClO$_4$)$_3\cdot n$H$_2$O and Co(ClO$_4$)$_2\cdot$6H$_2$O in acetonitrile show formation of the expected complexes [LnCo(L$^2$)$_3$]$^{5+}$ (Ln = La, Eu, Lu) together with traces of [Co(L$^2$)$_2$]$^{2+}$, as previously observed for [LnM(L$^2$)$_3$]$^{5+}$ (M = Zn, Fe).[8] Spectrophotometric titrations under the same conditions can be satisfactorily fitted to the equilibria of Equations (1) and (2) to give the stability constants $\lg(\beta_{113}^{\mathrm{LnCo}}) = 21.7(6)$ (Ln = La), 23.2(9) (Ln = Eu), and 23.9(6) (Ln = Lu), which resemble those found for [LnFe(L$^2$)$_3$]$^{5+}$ ($\lg(\beta_{113}^{\mathrm{LnFe}}) = 23.0(8)$, 24.6(9), and 23.6(7) for Ln = La, Eu, Lu, respectively).[8]

$$\mathrm{Co}^{2+} + 2\,\mathrm{L}^2 \rightleftharpoons [\mathrm{Co}(\mathrm{L}^2)_2]^{2+} \qquad \lg(\beta_{12}^{\mathrm{Co}}) = 14.4(6) \qquad (1)$$

$$\mathrm{Ln}^{3+} + \mathrm{Co}^{2+} + 3\,\mathrm{L}^2 \rightleftharpoons [\mathrm{LnCo}(\mathrm{L}^2)_3]^{5+} \qquad \lg(\beta_{113}^{\mathrm{LnCo}}) \qquad (2)$$

At a complex concentration of 5 mM, [LnCo(L$^2$)$_3$]$^{5+}$ (Ln = La, Eu, Lu) is the only species present in acetonitrile, and the $^1$H NMR spectrum displays 22 signals typical of a $C_3$-symmetrical head-to-head arrangement of the three strands. These are spread over a region of 100 ppm as a result of the paramagnetic Co$^{II}$ center ($\mu_{\mathrm{eff}} = 4.99(3)$ and 4.93(4) BM for [LaCo(L$^2$)$_3$]$^{5+}$ and [LuCo(L$^2$)$_3$]$^{5+}$, respectively, in CD$_3$CN at 298 K; Figure 1a).[11] Intra- and interstrand nuclear Overhauser effects (NOEs) clearly establish that (HHH)-[LnCo(L$^2$)$_3$]$^{5+}$ adopts the expected triple-helix structure[8] in which Co$^{II}$ occupies the facial pseudo-octahedral site produced by the three wrapped bidentate binding units, and Ln$^{III}$ the remaining nine-coordinate site. It is noteworthy that the reaction of L$^2$ (3 equiv) with Co(ClO$_4$)$_2\cdot$6H$_2$O (1 equiv) in the absence of Ln$^{III}$ provides mainly the 1:3 complex [Co(L$^2$)$_3$]$^{3+}$, in which the Co$^{II}$ ion is coordinated by the three bidentate binding sites of the ligands. However, the latter complex exists in solution as a 4:1 mixture of the $C_1$-symmetrical *mer* and $C_3$-symmetrical *fac* isomers according to the integration of the $^1$H NMR signals (expected statistical ratio 3:1).

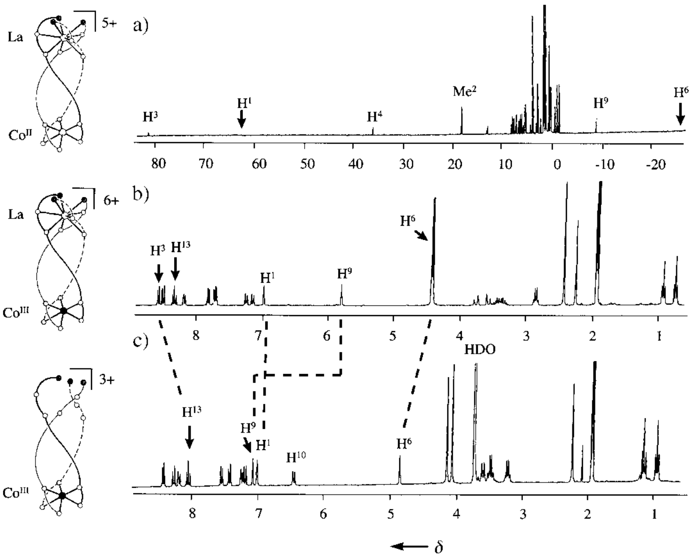


Figure 1. $^1$H NMR spectra (CD$_3$CN) of a) (HHH)-[LaCo(L$^2$)$_3$]$^{5+}$, b) (HHH)-[LaCo(L$^2$)$_3$]$^{6+}$, and c) *fac*-[Co(L$^2$)$_3$]$^{3+}$ (12 M D$_2$O).

Cyclic voltammograms of (HHH)-[LnCo(L$^2$)$_3$]$^{5+}$ (Ln = La, Eu, Lu) show a quasi-reversible Co$^{II}$/Co$^{III}$ oxidation wave at 0.42 V vs. SCE in acetonitrile/0.1 M NBu$_4$PF$_6$ in agreement with analogous Co$^{II}$ complexes.[11] Oxidation with bromine in acetonitrile gives quantitatively the poorly soluble complexes (HHH)-[LnCo(L$^2$)$_3$]$^{6+}$ (Ln = La, Lu), whose $^1$H NMR spectra exhibit 22 signals in the range $\delta = 0-10$, which is characteristic of diamagnetic Co$^{III}$. ES mass spectra confirm the exclusive formation of [LnCo(L$^2$)$_3$]$^{6+}$ (Ln = La, Eu, Lu) in solution, while specific NOEs (intrastrand: Me$^2$–H$^3$, Me$^3$–H$^{12}$, H$^{14}$–H$^{17,18}$; interstrand: Me$^2$–H$^{10}$, Me$^3$–H$^5$) imply that the head-to-head triple-helix structure is retained for (HHH)-[LnCo$^{III}$(L$^2$)$_3$]$^{6+}$. Precipitation with diethyl ether afforded the microcrystalline complex [LaCo(L$^2$)$_3$](ClO$_4$)$_5$Br$\cdot$(H$_2$O). Recrystallization by slow diffusion of diisopropyl ether into a concentrated solution of the complex in acetonitrile/water (25/1) gave extremely fragile X-ray quality crystals of **1**.

[LaCo(L$^2$)$_3$](ClO$_4$)$_{5.5}$(OH)$_{0.5}\cdot$4CH$_3$CN$\cdot$2H$_2$O **1**

The crystal structure determination of **1** confirms the presence of a head-to-head triple-helical cation (HHH)-[LaCo(L$^2$)$_3$]$^{6+}$ of approximate $C_3$ symmetry, together with disordered anions and solvent molecules (see Experimental Section). Figure 2 shows an ORTEP[12] stereoview of the cation perpendicular to the helical axis, and Table 1 lists the

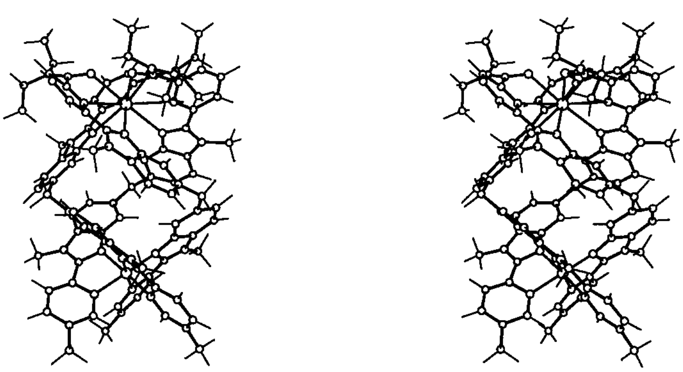


Figure 2. ORTEP[12] stereoview of the cation of **1** perpendicular to the helical axis.

Table 1. Distances [Å] and angles [°] in the coordination spheres of the Co$^{III}$ and La$^{III}$ atoms in **1**.

| | Average[a] | Minimum | Maximum |
|---|---|---|---|
| Co–N(py) | 2.03(2) | 2.01(2) | 2.04(2) |
| Co–N(bzim) | 1.96(3) | 1.94(2) | 2.00(2) |
| N(py)-Co-N(bzim)[b] | 80.9(11) | 79.5(8) | 82.4(9) |
| La–N(bzim) | 2.67(4) | 2.61(2) | 2.70(2) |
| La–N(py) | 2.74(3) | 2.72(2) | 2.78(2) |
| La–O(amide) | 2.50(2) | 2.48(2) | 2.53(2) |
| N(bzim)-La-N(py)[b] | 60.3(12) | 58.8(7) | 61.9(6) |
| N(py)-La-O(amide)[b] | 62.1(12) | 61.2(6) | 63.7(6) |

[a] Averaged for $C_3$ symmetry. [b] Chelate bite angles.

structural parameters obtained by averaging the distances and angles according to $C_3$ symmetry. The geometry around the Co$^{III}$ center is best described as a slightly distorted octahedron flattened along the pseudo-$C_3$ axis as a result of chelate bite angles smaller than 90° (Table 1). The average Co–N(py) distance is slightly larger than the Co–N(bzim) distances, but both are in good agreement with the reported standard values of 2.034 and 1.946 Å, respectively.[12] Comparison with the Co–N(py) (1.96(3) Å) and Co–N(bzim) (1.92(3) Å) distances in an analogous homotopic triple-stranded helicate[13] suggests that the Co–N bonds in **1** are slightly stretched. This is also evident in the similar Fe–N(py) (2.00(3) Å) and Fe–N(bzim) (1.95(2) Å) distances in (HHH)-[LnFe(L$^2$)$_3$]$^{5+}$[8] in spite of the about 12% larger ionic radius expected for low-spin d$^6$ Fe$^{II}$.[14] We attribute this distortion to steric constraints induced by the occupied pseudo-tricapped trigonal prismatic site. The La–Co distance is 8.865(4) Å, and detailed structural analysis of the complex indicates that (HHH)-[LaCo(L$^2$)$_3$]$^{6+}$ is structurally similar to (HHH)-[LaFe(L$^2$)$_3$]$^{5+}$, in which Fe$^{II}$ also has the stereochemically demanding low-spin d$^6$ configuration.[15]

The addition of D$_2$O to a 5 mM solution of (HHH)-[LnCo(L$^2$)$_3$]$^{6+}$ (Ln = La, Lu) in CD$_3$CN (total D$_2$O concentration 10 M) results in decomplexation of Ln$^{III}$, which can be monitored by ESMS and $^1$H NMR spectroscopy. The ESMS titration shows the exclusive formation of [Co(L$^2$)$_3$]$^{3+}$ ($m/z$ 563.4), and the $^1$H NMR spectrum still shows 22 signals corresponding to the quantitative formation of the C$_3$-symmetrical complex *fac*-[Co(L$^2$)$_3$]$^{3+}$. The $^1$H NMR signals of the bidentate binding units are not significantly shifted (except for that of H$^6$, which is located between the Co$^{III}$ and Ln$^{III}$ centers in (HHH)-[LnCo$^{III}$(L$^2$)$_3$]$^{6+}$), whereas the signals of the tridentate units are strongly shifted—the signal for H$^9$ is shifted downfield by $\Delta\delta = 1.3$ owing to unfolding of the strands.[16] The signals for H$^{12}$–H$^{14}$ are shifted to high field by $\Delta\delta \approx 0.3$, since the associated pyridine ring is no longer coordinated to a metal ion.[8] Finally, the disappearance of the intrastrand NOEs Me$^3$–H$^{12}$ and H$^{14}$–H$^{17,18}$ implies a *trans,trans* arrangement of the tridentate units, which is only compatible with the release of the Ln$^{III}$ ion from the coordination site. This assumption is further supported by the use of Eu$^{III}$ as a paramagnetic NMR probe in (HHH)-[EuCo(L$^2$)$_3$]$^{6+}$. Reaction of (HHH)-[EuCo(L$^2$)$_3$]$^{6+}$ with 12 M D$_2$O severely affects the signals of the protons and quantitatively produces the diamagnetic spectrum of *fac*-[Co(L$^2$)$_3$]$^{3+}$.

Treatment of (HHH)-[LaCo$^{III}$(L$^2$)$_3$]$^{6+}$ with a stoichiometric quantity of (NBu)$_4$EDTA · 6H$_2$O in acetonitrile/water (25/1) leads to formation of the insoluble salt NBu$_4$[La(EDTA)], which can be separated by filtration. The desired inert, metal-containing tripodal receptor *fac*-[Co(L$^2$)$_3$](ClO$_4$)$_3$(C$_4$H$_{10}$O)$_{0.4}$ · 6H$_2$O is obtained by fractional crystallization from diethyl ether as a red powder whose $^1$H NMR spectrum is identical to that of the complex prepared in situ. This complex is a novel tailored helical nine-coordinate receptor which is currently being investigated in our laboratory for the selective complexation of Ln$^{III}$. This self-assembly with post-processing and release of the template Ln$^{III}$ ion leads to the almost quantitative isolation of pure *fac*-[Co(L$^2$)$_3$]$^{3+}$, while direct bromine oxidation of the *mer*/*fac* mixture of [Co(L$^2$)$_3$]$^{2+}$ also gives a mixture containing only 20% of the desired *fac*-[Co(L$^2$)$_3$]$^{3+}$ and 80% of the *mer* isomer.

## *Experimental Section*

[LaCo(L$^2$)$_3$](ClO$_4$)$_5$Br · H$_2$O: Elemental analysis calcd for LaCoC$_{99}$H$_{101}$N$_{21}$O$_{24}$Cl$_5$Br: C 49.05, H 4.20, N 12.13, Br 3.30; found C 48.98, H 4.28, N 12.11, Br 3.00. $^1$H NMR (300 MHz, CD$_3$CN, TMS, 298 K): $\delta = 0.73$ (t, J = 7 Hz, 9H), 0.91 (t, J = 7 Hz, 9H), 2.25 (s, 9H), 2.86 (q, J = 7 Hz, 6H), 3.35 (pseudo-sext., J = 15, 7 Hz, 3H), 3.42 (pseudo-sext., J = 15, 7 Hz, 3H), 3.55 (d, J = 16 Hz, 3H), 3.75 (d, J = 16 Hz, 3H), 4.41 (s, 9H), 4.44 (s, 3H), 4.44 (s, 9H), 5.78 (s, 3H), 6.97 (s, 3H), 7.15 (d, J = 8 Hz, 3H), 7.23 (d, J = 8 Hz, 3H), 7.69 (d, J = 8 Hz, 3H), 7.71 (d, J = 8 Hz, 3H), 7.80 (d, J = 8 Hz, 3H), 8.15 (d, J = 8 Hz, 3H), 8.31 (t, J = 8 Hz, 3H), 8.48 (d, J = 8 Hz, 3H), 8.55 (d, J = 8 Hz, 3H); ESMS (10$^{-4}$ M, CH$_3$CN): $m/z = 304.8$ [LaCo(L$^2$)$_3$]$^{6+}$ (60%), 385.8 [LaCo(L$^2$)$_3$(ClO$_4$)]$^{5+}$ (100%), 506.7 [LaCo(L$^2$)$_3$(ClO$_4$)$_2$]$^{4+}$ (99%), 708.9 ([LaCo(L$^2$)$_3$(ClO$_4$)$_3$]$^{3+}$ (43%), 1113.3 ([LaCo(L$^2$)$_3$(ClO$_4$)$_4$]$^{2+}$ (5%).

[Co(L$^2$)$_3$](ClO$_4$)$_3$ · 0.4(C$_4$H$_{10}$O) · H$_2$O. Elemental analysis: calcd for CoC$_{100.6}$H$_{115}$N$_{21}$O$_1$8.4Cl$_3$: C 56.84, H 5.45, N 13.84; found C 56.92, H 5.30, N 13.86. $^1$H NMR (300 MHz, CD$_3$CN, TMS, 298 K): $\delta = 1.00$ (t, J = 7 Hz, 9H), 1.20 (t, J = 7 Hz, 9H), 2.35 (s, 9H), 3.28 (q, J = 7 Hz, 6H), 3.50 (q, J = 7 Hz, 6H), 3.55 (d, J = 16 Hz, 3H), 3.60 (d, J = 16 Hz, 3H), 4.13 (s, 9H), 4.15 (s, 9H), 4.98 (s, 3H), 6.59 (d, J = 8 Hz, 3H), 6.93 (s, 3H), 7.23 (d, J = 8 Hz, 3H), 7.30 (s, 3H), 7.32 (d, J = 8 Hz, 3H), 7.48 (d, J = 8 Hz, 3H), 7.52 (d, J = 8 Hz, 3H), 8.02 (t, J = 8 Hz, 3H), 8.17 (d, J = 8 Hz, 3H), 8.41 (d, J = 8 Hz, 3H), 8.44(d, J = 8 Hz, 3H). ESMS (10$^{-4}$ M, CH$_3$CN): $m/z = 563.4$ [Co(L$^2$)$_3$]$^{3+}$ (95%), 894.2 [Co(L$^2$)$_3$(ClO$_4$)]$^{2+}$ (15%).

Crystal structure determination of **1**: A fragile red-orange crystal (0.18 × 0.30 × 0.32 mm) was mounted from the mother liquor on a quartz fiber with perfluoropolyether oil RS 3000. $M_r = 2584.6$, monoclinic, $C2/c$, $a = 53.638(7)$, $b = 23.068(5)$, $c = 21.885(7)$ Å, $\beta = 92.78(1)°$, $V = 27047(11)$ Å$^3$ (by least-squares refinement of 20 reflections in the range $35 \leq 2\theta \leq 44°$), $Z = 8$, $\rho_{calcd} = 1.27$ g cm$^{-3}$, $F(000) = 10640$, $\mu(Cu_{K\alpha}) = 4.986$ mm$^{-1}$. *Data collection and processing:* Stoe STADI4 diffractometer, $T = 200$ K, $\omega - 2\theta$ scan, scan width $1.05 + 0.35 \tan\theta$, scan speed 0.13° s$^{-1}$, Cu$_{K\alpha}$ radiation ($\lambda = 1.5418$ Å); 15658 measured reflections ($3 \leq 2\theta \leq 104°$, $-53 < h < 53$, $0 < k < 23$,

$0 < l < 22$), 15138 unique reflections ($R_{\mathrm{int}} = 0.095$ for equivalent reflections) of which 8318 were observed $[|F_o| > 4\sigma(F_o)]$. Two reference reflections were measured every 45 min and showed a total decrease in intensity of 15.3%. All intensities were corrected for this drift. Data were corrected for Lorentzian, polarization, and absorption effects[17] ($A^*_{\min} = 2.916$, $A^*_{\max} = 5.163$). The structure was solved by direct methods with the program MULTAN 87;[18] all other calculations were performed with the XTAL[19] system and ORTEP II[12] programs. Full-matrix least-squares refinements on $F$ with weights of $w = 1/(\sigma2(\mathrm{Fo}) + 0.0005\,F_o^2)$ gave final values $R = 0.125$ and $R\mathrm{w} = 0.128$ for 1460 variables and 8318 reflections. The five perchlorate ions and the four acetonitrile molecules were refined with 64 restraints on bond distances and angles. The remaining "half" perchlorate i was located in special position 4*c* and was fully disordered. Five atomic sites (of which two were in special position 4*e*) were observed for the water molecules and the half hydroxide anion. Two oxygen atoms of the perchlorate i, the carbon and nitrogen atoms of two acetonitrile molecules, and the five oxygen atoms of the water molecules were refined with isotropic displacement parameters (13 atoms), and all the other atoms (157) with anisotropic displacements parameters. The mean ratio of shift to error on the last cycle was 0.058. Hydrogen atoms were placed in calculated positions and included in $F_c$ calculations. The final Fourier difference synthesis showed a maximum of $+1.44$ and a minimum of $-2.06\,\mathrm{e\,Å^{-3}}$. Complex **1** is isostructural with $[\mathrm{LaFe(L^2)_3}](\mathrm{ClO_4})_{0.5}(\mathrm{CF_3SO_3})_{4.5} \cdot \mathrm{CH_3CN} \cdot 4\,\mathrm{H_2O}$ and $[\mathrm{EuZn(L^2)_3}](\mathrm{ClO_4})(\mathrm{CF_3SO_3})_4 \cdot 4\,\mathrm{CH_3CN}$.[8] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100482. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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## Crown Ethers, Double-Decker, and Sandwich Complexes: Cation-Mediated Formation of Metallatopomer Coronates**

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Crown ethers, [2]cryptands, and [3]cryptands selectively complex alkali metal ions.[1] This discovery led to the construction of novel supramolecular architectures[2] capable of recognizing neutral as well as cationic or anionic substrates with formation of well-defined host–guest compounds. Recently we pointed out the structural analogy between coronates and cryptates[3] and their topologically equivalent metallacoronates and metallacryptates.[4] If one applies the knowledge of crown ethers to the chemistry of metallacrown ethers (MC),[5] the complexation of differently sized cations by metallacrown ethers should lead to metallacoronates of varying structures. Since the ionic radii of alkaline and alkaline earth metal cations differ significantly (whereas the diameter of the metallacrowns essentially does not change) the inclusion of small cations such as $\mathrm{Na^+}$ or $\mathrm{Ca^{2+}}$ should lead to a metallacoronate with 1:1 stoichiometry, and, in contrast, encapsulation of the larger $\mathrm{K^+}$ ions to a metallacrown ether sandwich complex ($\mathrm{K^+}$:MC = 1:2).

Reaction of diethyl ketipinate[6] $\mathrm{H_2L^1}$ with copper(II) acetate in the presence of calcium nitrate leads to green microcrystals of **1** (Scheme 1) after crystallization from tetrahydrofuran/diethyl ether. According to elemental analysis and FAB-MS data (FAB = fast atom bombardment, $m/e = 977$) **1** is a metallacoronate. Compound **1** is a neutral, trinuclear metal cluster (Figure 1), as determined by X-ray

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