Self-Assembly and Crystal Structure of a Novel Octadecametallic Square Box Composed of 52 Single Components**

Rolf W. Saalfrank,* Ingo Bernt, and Frank Hampel[a]

Dedicated to Professor Robert Weiß on the occasion of his 60th birthday

Abstract: Reaction of *divalent hexacoordinate* metal ions with either *tetradentate N*-(2-piridylmethyl)iminodiethanol (**3**; H_2L^4) or *tridentate N*-(2-chlorobenzyl)iminodiethanol (**5**; H_2L^5) resulted in the formation of two completely different products. Starting from nickel(II) acetate and *tetradentate* **3**, linear trinuclear complex $[\{Ni(HL^4)\}_2Ni(OAc)_2(HCO_2)_2]$ (**4**) was formed. However, when *tridentate* **5** was allowed to react with cobalt(II) acetate, the novel octadecametallic square box $[Na_2\{Co_4(HL^5)_3(OAc)_5\}_4(HCO_2)_2]$ (**6**) was isolated. Chiral **6** has D_2-molecule symmetry and crystalizes with both enantiomers in the unit cell. The structures of all new compounds were determined unequivocally by single-crystal X-ray analyses.

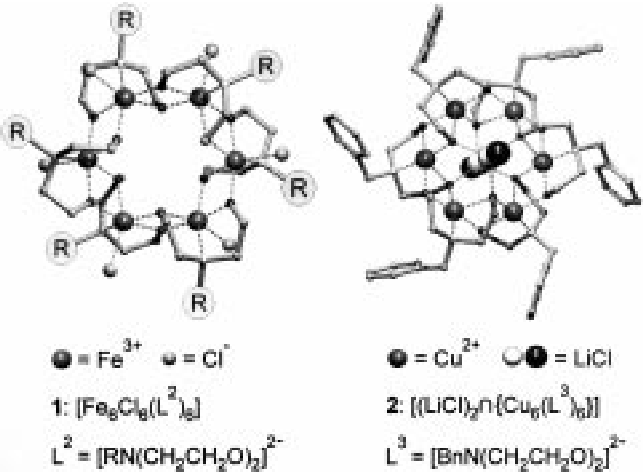
Keywords: cobalt · coordination modes · nickel · oligomers · self-assembly · supramolecular chemistry

Introduction

Design and synthesis of supramolecular inorganic structures exhibiting novel properties have provided exciting new prospects.[1] We reported on the template-mediated self assembly of six-membered $[Na \subset \{Fe_6(L^1)_6\}]^+$ and eight-membered $[Cs \subset \{Fe_8(L^1)_8\}]^+$ iron coronates, which were accessible in a one-pot reaction from triethanolamine (H_3L^1; $L^1 = [N(CH_2CH_2O)_3]^{3-}$) with iron(III) chloride and sodium hydride or caesium carbonate, respectively.[2] A common feature of these complexes is, that the hexanuclear structure is determined by two ethanolate μ_2-O donors alone. The μ_1-O donors of $(L^1)^{3-}$ are not involved in the linkage of the hexa- or octanuclear structures and function exclusively as ligands for coordinative saturation of the iron centers.

Consequently, reaction of *N*-substituted diethanolamines (H_2L^2; $L^2 = [RN(CH_2CH_2O)_2]^{2-}$) with iron(III) chloride yielded the void-neutral iron cryptands $[Fe_6Cl_6(L^2)_6]$ (**1**) with [12]metallacrown-6 structure.[3] Compared with the complexes generated with triethanolamine, in **1** the lacking μ_1-O ethanolate ligands are replaced by *extra chloride donors* to achieve charge compensation and octahedral coordination at iron (Scheme 1).

In extension of the afore-mentioned strategy, starting with *N*-substituted diethanolamines (H_2L^2) and *pentacoordinate divalent* metals instead of *hexacoordinate trivalent* iron, neutral-void hexanuclear wheels *without extra co-ligands* were expected. This hypothesis proved to be correct, and it was shown, that reaction of *N*-benzyliminodiethanol (H_2L^3; $L^3 = [BnN(CH_2CH_2O)_2]^{2-}$) with lithium hydride and copper(II) chloride yielded $[(LiCl)_2 \cap \{Cu_6(L^3)_6\}]$ (**2**).[4] In **2**, two additional molecules of lithium chloride are bound exohedrally on opposite sides of the six-membered copper wheel (Scheme 1).



Scheme 1.

Results and Discussion

In this communication we report on our studies on the reaction of *divalent hexacoordinate* metal ions with either *tetradentate N*-(2-piridylmethyl)iminodiethanol (**3**; H_2L^4) or *tridentate N*-(2-chlorobenzyl)iminodiethanol (**5**; H_2L^5) (Schemes 2 and 3).

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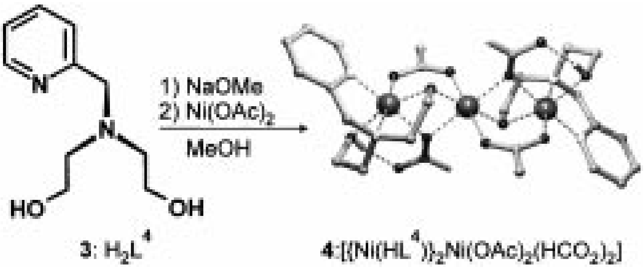
[**] Chelate Complexes, Part 18; for Part 17 see reference [4].

Following the synthesis of the ferric wheels $[Fe_6Cl_6(L^2)_6]$ (**1**), generated from iron(III) chloride and *tridentate* *N*-substituted diethanolamines (H_2L^2), starting from nickel(II) acetate and *tetradentate* *N*-(2-piridylmethyl)iminodiethanol (**3**; H_2L^4), we expected the formation of hexanuclear $[Ni_6(L^4)_6]$. In this case, the neutral 2-pyridylmethyl groups should take on the role of the chloride donors in **1**. However, the FAB (fast atom bombardment) data of the isolated blue microcrystalinic material **4** were not in agreement with a hexanuclear system. In order to unequivocally determine the structure of complex **4**, we carried out a single-crystal X-ray analysis. According to this investigation, $[\{Ni(HL^4)\}_2Ni(OAc)_2(HCO_2)_2]$ (**4**; $L^4 = [PymN(CH_2CH_2O)_2]^{2-}$) is present in the crystal as a trinuclear,[5] rather than hexanuclear cluster (Scheme 2).

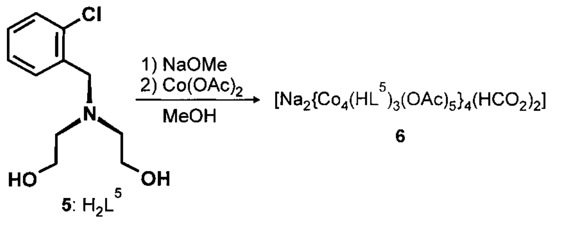


Scheme 2.

Linear **4** comprises two terminal $\{Ni(HL^4)\}^+$ subunits, in which each $(HL^4)^-$ ligand coordinates to the nickel centres by one μ_1-O, one μ_2-O, and two nitrogen donors. These terminal building blocks are each linked to a central nickel cation through the μ_2-oxygen of $(HL^4)^-$, one μ_1-bridging acetate, and one μ_2-bridging formate. In addition, a hydrogen bond is found between each of the uncoordinated formate oxygens and the μ_1-OH groups of the ligands. The formation of structure **4** is evidently governed by the presence of the strong co-ligands, acetate and formate, preventing the assembly of a hexanuclear nickel wheel $[Ni_6(L^4)_6]$.

In the light of the reaction of *tetradentate* ligand **3** with hexacoordinating divalent nickel, an even more challenging problem should arise from the reaction of *tridentate* *N*-substituted diethanolamines (H_2L^2) with hexacoordinate divalent metal ions. Assuming that a hexanuclear coronand $[M_6(L^2)_6]$ is formed, the twelve positive charges stemming from the M^{2+} ions would be compensated by the six ligands $(L^2)^{2-}$. However, tridentate $(L^2)^{2-}$ would leave each metal center in $[M_6(L^2)_6]$ only pentacoordinate. In order to guarantee both coordinative saturation and charge compensation at the metal centers, a more complex assembly rather than a hexanuclear one was expected.

Therefore, we treated *tridentate* *N*-(2-chloro-benzyl)-iminodiethanol (**5**; H_2L^5) with cobalt(II) acetate. After workup a pink material was isolated, which was identified on the basis of a single-crystal X-ray structure analysis as the novel octadecametallic square box $[Na_2\{Co_4(HL^5)_3(OAc)_5\}_4(HCO_2)_2]$ (**6**) (Scheme 3).[5]



Scheme 3.

Although **6** represents a rather complex assembly of 52 single components, its "building plan" is rather straightforward. Supramolecule **6** consists of four trigonal pyramidal modules, corner-linked by two sodium cations and two formate anions (Figure 1).

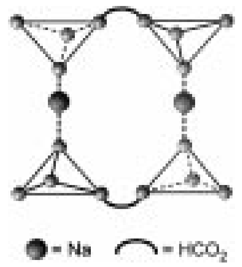


Figure 1. Pictorial representation of molecular box **6**.

The basic modules of **6** are four trigonal pyramids $\{Co_4(HL^5)_3(OAc)_5(HCO_2)_{1/2}\}$. Each of the three tridentate ligands $(HL^5)^-$ connects two cobalt centers from the base of the pyramid with the apical cobalt cation through an ethanolate μ_3-O donor. In addition, one nitrogen and one μ_1-OH donor from the ligand is bound to a cobalt cation in the base. Moreover, the three cobalt centers in the base are coordinated by two non-bridging acetate ions and one formate ion, which acts as a clamp to link the two halves of structure **6** (Figure 2, top).

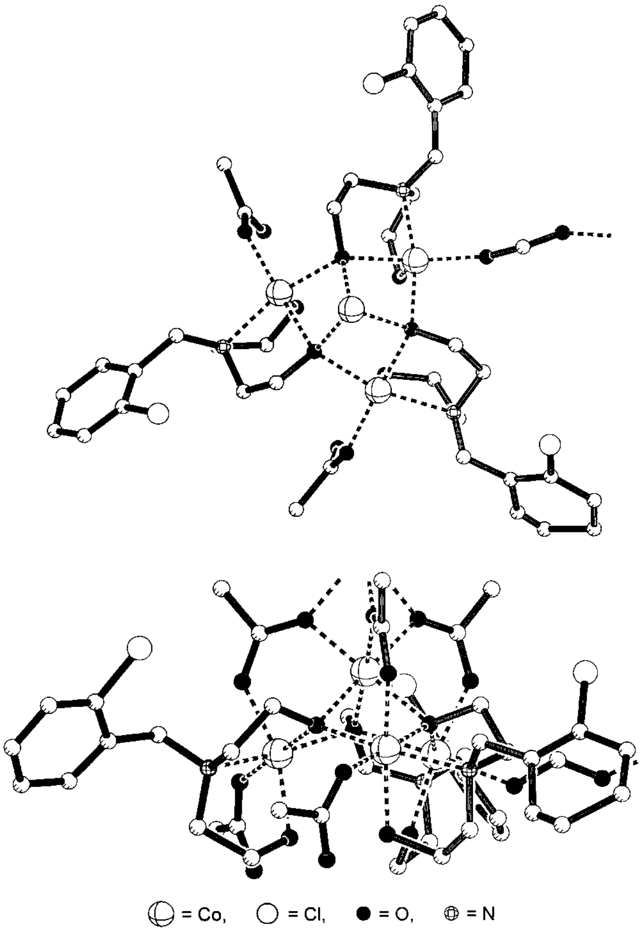


Figure 2. Top: Top view of the reduced basic pyramidal module. Bottom: Side view of the complete basic pyramidal module. (PLUTON presentation; hydrogen atoms omitted for clarity.)

Three additional acetate ions each bridge the cobalt centers in the basis with the cobalt center in the apex of the trigonal pyramid.[6] This leads to hexacoordination at all four cobalt centers of module $\{Co_4(HL^5)_3(OAc)_5(HCO_2)_{1/2}\}$. However, the three oxygen donors on top of the pyramid represent a sticky end, ready for further linkages (Figure 2, bottom).

The three acetate oxygens on top of the module form a regular triangle parallel to the basis of the trigonal pyramid. A sodium cation links two modules across these three distinct oxygen donors. The pyramids are apex-linked and rotated by approximately 180° relative to each other; this results in a columnlike dimer $\{Na[Co_4(HL^5)_3(OAc)_5]_2(HCO_2)\}$ (Figure 3).

Two of these dimers are joined by the two formate anion clamps at the cobalt centers in the triangular base of the modules $\{Co_4(HL^5)_3(OAc)_5(HCO_2)_{1/2}\}$ to give the neutral molecular box $[Na_2\{Co_4(HL^5)_3(OAc)_5\}_4(HCO_2)_2]$ (**6**). In terms of the cobalt distances and the over-all size, the dimensions of box **6** are approximately 10 × 14 and 16 × 28 Å, respectively (Figure 4).

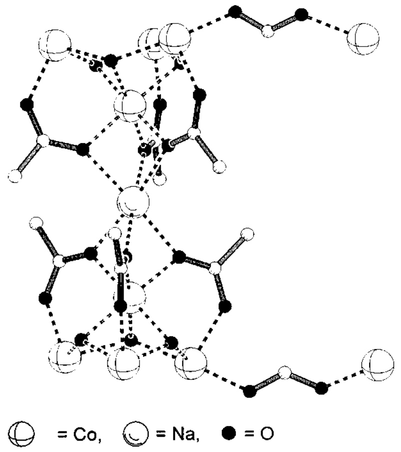


Figure 3. Simplified presentation of the connectivity of two basic pyramidal modules via sodium, together with the formate linkers. (PLUTON presentation: For clarity, only the μ_3-O donors of the ligands $(HL^5)^-$ are depicted. Hydrogen atoms and non-bridging acetate groups omitted).

It is worth noting, that the spontaneous assembly of 52 simple achiral building blocks yielded a racemic mixture of chiral, supramolecule **6** with idealized D_2-molecule symmetry. As depicted in Figure 5, both enantiomers of cluster **6** are present in the crystal.

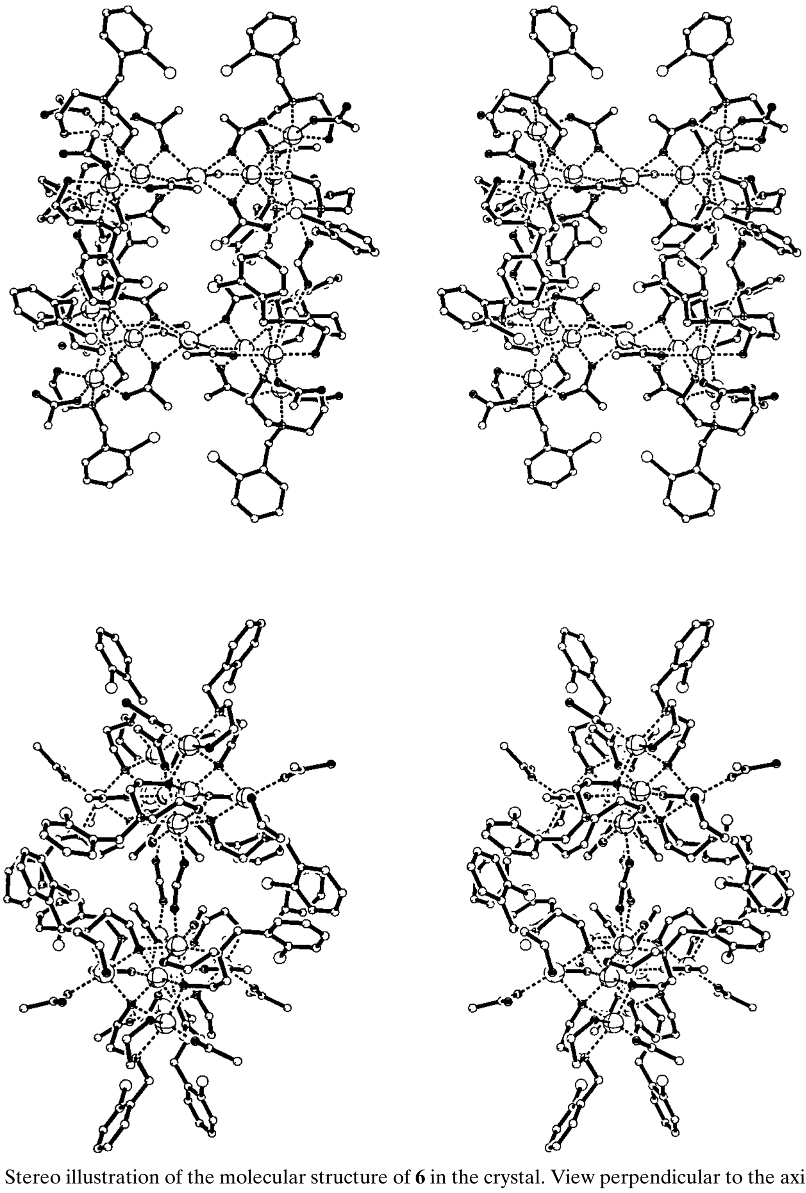


Figure 4. Stereo illustration of the molecular structure of **6** in the crystal. View perpendicular to the axis running through the two sodium cations, highlighting the linkage by sodium (top) and by formate (bottom). (PLUTON presentation; solvent molecules and hydrogen atoms omitted for clarity).

Conclusion

The predictable nature of our investigations on hexanuclear metalla cryptates is based on the careful selection of matching metal-ligand combinations. Our findings prompted us to tackle non-matching metal–ligand combinations as well. This approach has led to the isolation of unpredictable molecular box **6**.

Experimental Section

General techniques: Reagents and metal salts were used as obtained from Aldrich. Ligands **3** and **4** were prepared by standard procedures. IR spectra were recorded from KBr pellets on a Bruker IFS25 spectrometer. FAB-MS spectra were recorded on a Micromass ZabSpec-E spectrometer. Elemental analyses were performed on a EA1110 CHNS-Microautomat.

Preparation of $[Ni_3(HL^4)_2(OAc)_2(HCO_2)_2]$ (4): $Ni(OAc)_2 \cdot 4H_2O$ (0.75 g, 3 mmol) and NaOMe (0.32 g, 6 mmol) were added to a solution of

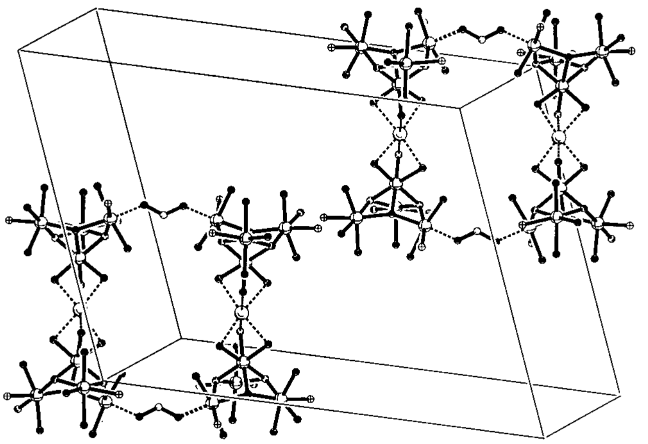


Figure 5. Depicted is the crystal packing of two enantiomers of **6** in the unit cell. (PLUTON presentation; solvent molecules omitted; for clarity only the coordination polyhedra of the cobalt centers and the bridging sodium and formate ions are shown).

N-(2-piridylmethyl)iminodiethanol (**3**; 0.59 g, 3 mmol) in methanol (50 mL). After stirring for one day at 20 °C and subsequent filtration, the solvent was evaporated. The remaining blue solid was extracted with dichloromethane (50 mL). The solvent was then evaporated and the remaining blue solid was re-crystallised from methanol/diethyl ether to give $\mathbf{4}\cdot 2\,CH_3OH$ (yield: 0.40 g, 48 %). Blue needles were obtained from methanol by diffusion of diethyl ether. Elemental analysis calcd (%) for $C_{26}H_{38}N_4Ni_3O_{12}$: C 40.31, H 4.94, N 7.23; found C 40.11, H 5.20, N 7.24; m.p. > 220 °C (decomp); IR (KBr): $\tilde{\nu} = 2850, 1583, 1419\ cm^{-1}$; FAB-MS (3-nitrobenzyl alcohol-matrix): *m*/*z*: 505 $[Ni_2(HL^4)(L^4)]^+$.

Preparation of $\{Na_2[Co_4(HL^5)_3(OAc)_5]_4(HCO_2)_2\}$ (6): $Co(OAc)_2\cdot 4\,H_2O$ (0.75 g, 3 mmol) and NaOMe (0.32 g, 6 mmol) were added to a solution of *N*-(2-chlorobenzyl)iminodiethanol (**5**; 0.69 g, 3 mmol) in methanol (50 mL). After stirring for two days at 20 °C and subsequent filtration, the solvent was evaporated. The remaining pink solid was extracted with dichloromethane (50 mL). Evaporation of the solvent gave compound **6** as a pink powder (yield: 0.66 g, 49 %). Crystals of $\mathbf{6}\cdot 3\,C_6H_6\cdot 2\,Et_2O\cdot 2\,H_2O$ suitable for X-ray analysis were grown from a benzene solution by diffusion of diethylether. Elemental analysis calcd (%) for $C_{174}H_{242}Cl_{12}Co_{16}N_{12}Na_2O_{68}$: C 41.76, H 4.87, N 3.36; found C 42.35, H 4.91, N 3.14; m.p. > 220 °C (decomp); IR (KBr): $\tilde{\nu} = 3066, 2925, 2874, 1580, 1440\ cm^{-1}$; FAB-MS (3-nitrobenzyl alcohol-matrix): *m*/*z*: 978 $[Co_4(L^5)_3(OAc)]^+$.

Single-crystal X-ray structure analyses: Details for crystal data, data collection, and refinement are given in Table 1. X-ray data were collected on a Nonius Kappa CCD area detector using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were employed. The structures were solved by direct methods with SHELXS-97[8] and refined with full-matrix least-squares against F^2 with SHELXL-97.[9] Three of the chlorobenzyl groups show disorder at the chlorine atoms with an occupation ratio of 85:15 and 77:23 %. Hydrogen atoms were attached in idealised positions and refined using the riding model.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155065 (**4**) and CCDC-155066 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Details of X-ray structure determinations.

	4	6
formula	$C_{26}H_{38}N_4Ni_3O_{12}$ $\cdot 2\,H_3COH$	$C_{174}H_{242}Cl_{12}Co_{16}N_{12}Na_2O_{68}$ $\cdot 3\,C_6H_6\cdot 2\,C_4H_{10}O\cdot 2\,H_2O$
M_r	838.82	5422.77
crystal size [mm]	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.25
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
T [K]	173(2)	173(2)
a [Å]	11.0196(2)	19.63620(10)
b [Å]	12.2153(3)	25.38720(10)
c [Å]	13.4086(3)	30.5720(2)
α [°]	90	73.8460(10)
β [°]	101.179	88.8500(10)
γ [°]	90	67.8140(10)
V [Å^3]	1770.66(7)	13492.83(12)
Z	2	2
ρ_{calcd} [M g m^{-3}]	1.573	1.329
θ range [°]	2.19 to 27.46	1.13 to 25.06
reflections collected	6812	83999
unique reflections	4035	44884
[R_{int}]	0.0215	0.0307
reflections observed [$I > 2\sigma(I)$]	3445	32531
parameters	289	2851
final $R1$ [$I > 2\sigma(I)$]	0.0325	0.0670
$wR2$ (all data)	0.0814	0.2322
largest residuals [e Å^{-3}]	0.544/ − 0.457	2.324/ − 0.890

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