tion functions, to average images of the helical repeat, and to reconstruct a three-dimensional model from the weighted back projection algorithm.[22]

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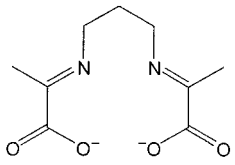
Template Assembly of Metal Aggregates by Imino-Carboxylate Ligands**

Dan M. J. Doble, Colin H. Benison, Alexander J. Blake, Dieter Fenske, Matthew S. Jackson, Richard D. Kay, Wan-Sheung Li, and Martin Schröder*

The aggregation of soft metal centers to form covalently bonded clusters is well known,[1–3] and there are well-established theories regarding the structure and bonding in these polynuclear complexes, for example Ru– and Os – carbonyl[2] and Au clusters.[3] In contrast, hard metal cations do not readily form metal – metal bonds, and usually require bridging ligands such as carboxylate,[4] oxide,[5] or hydroxide ligands[5] to induce aggregation. These ligands have enabled one-pot syntheses of some spectacular high-nuclearity aggregates, often with interesting magnetic and electronic properties.[4, 5] However, such ligands can adopt a variety of coordination modes, which, together with the often unpredictable coordination geometries of the metals concerned, makes it very difficult to rationalize the structures of the resulting aggregates. Recent developments in self-assembly have shown how metal – ligand frameworks can be sucessfully templated about a substrate anion[6] or cation.[7] Our approach has been to use the tetradentate ligand $(L)^{2-}$ [8] to chelate the four equatorial sites of a potentially octahedral metal ion M^{II} ($M^{II} = Ni^{II}$, Mn^{II}), leaving two free axial sites at the metal center for aggregation by interaction with the carboxylate oxygen donors of neighboring [M(L)] units.[9] Thus, each planar [M(L)] moiety has available two acceptor sites on M^{II} to form a 180° junction, and two carboxylates donors forming 90° junctions to one another and to the acceptor sites on M^{II}.



$(L)^{2-}$

Slow codiffusion of methanolic solutions of [Ni(L)][10a] and $La(ClO_4)_3 \cdot 6H_2O$ results in the growth of brown, columnar crystals of **1**. A single-crystal X-ray structure determination[11]

$[\{Ni(L)\}_6La](ClO_4)_3$ **1**

reveals a highly unusual[12] heptanuclear $[\{Ni(L)\}_6La]^{3+}$ cluster (Figure 1) in which a La^{III} center is located at the center of the

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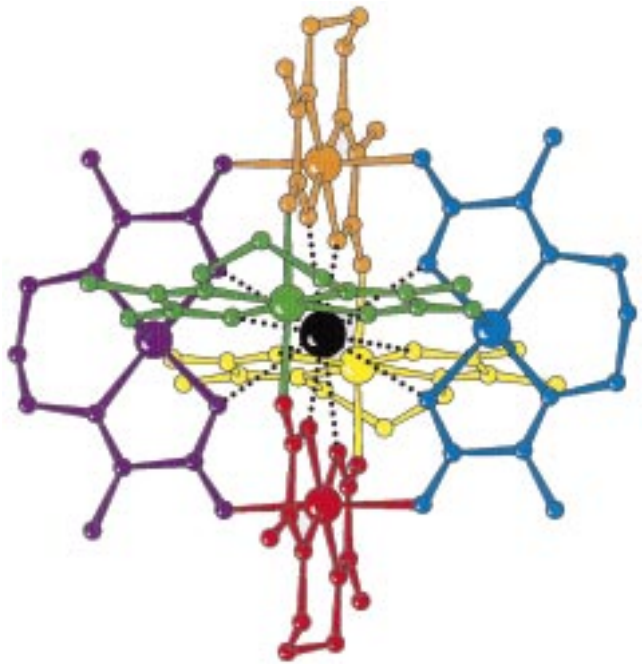

Figure 1. Crystal structure of **1**. The [Ni(L)] units are shown in different colors. The interstitial La^{III} cation is represented by a black sphere, and its icosahedral coordination sphere is indicated by dotted lines. The ClO_4^- anions and all hydrogen atoms are omitted for clarity.

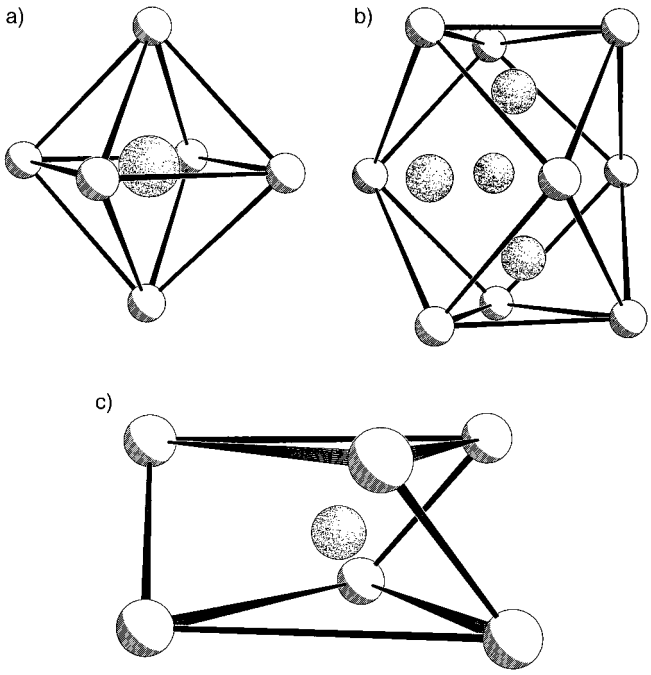

Figure 2. Polyhedra formed by connection of the metal centers of adjoining [M(L)] complex units in a) **1**, b) **2**, and c) **3**. Interstitial atoms are shown as speckled spheres.

octahedral cage formed by six [Ni(L)] moieties, and is bound by an icosahedron of twelve carboxylate groups (La–O 2.665(5), 2.710(5) Å), two from each [Ni(L)] unit. The La^{III} center lies on a crystallographic $\bar{3}$ axis so that all six [Ni(L)] units are equivalent. The octahedral Ni^{II} centers are bound equatorially by $(L)^{2-}$ (Ni–O 1.997(5), 2.002(5); Ni–N 1.976(6), 1.997(5) Å). The axial sites are occupied by the carboxylate oxygen atoms of two neighboring [Ni(L)] units (Ni–O 2.122(6), 2.160(5) Å). Thus, each [Ni(L)] unit is joined to four other [Ni(L)] units such that the six Ni^{II} centers lie at the vertices of a near-perfect octahedron with La^{III} at its center (Figure 2a).

By contrast, crystallization of [Ni(L)] from MeOH/Et_2O in the presence of $NaClO_4$ yields purple crystals of **2**, containing

$$[\{Ni(L)\}_9Na_4(H_2O)(MeOH)(ClO_4)](ClO_4)_3 \cdot Et_2O \cdot 6.5\,MeOH \cdot 0.15\,H_2O \quad \mathbf{2}$$

a highly novel Ni_9Na_4 cluster in which four Na^+ cations are encapsulated within a nine-membered $[\{Ni(L)\}_9]$ cage[11] (Figure 3). The cage is made up of [Ni(L)] units which are related by an approximate, noncrystallographic, threefold axis. As in **1**, all the Ni^{II} centers are octahedral, with the equatorial sites bound by $(L)^{2-}$ (Ni–O 2.010(3)–2.077(3), Ni–N 1.996(3)–2.054(3) Å) and the axial sites bound by the carboxylate oxygen atoms of neighboring complexes (Ni–O 2.051(3)–2.134(3) Å). The Ni^{II} centers are arranged in a tricapped trigonal prism, although connection of the Ni^{II} centers of adjoining [Ni(L)] units gives a polyhedron with three square faces and eight triangular faces, with each [Ni(L)] moiety connected to four other [Ni(L)] fragments (Figure 2b). All the carboxylate oxygen atoms are orientated inwards, encapsulating a core of four Na^+ cations (Na–O 2.265(3)–2.459(3) Å), of which two are five-coordinate and two are

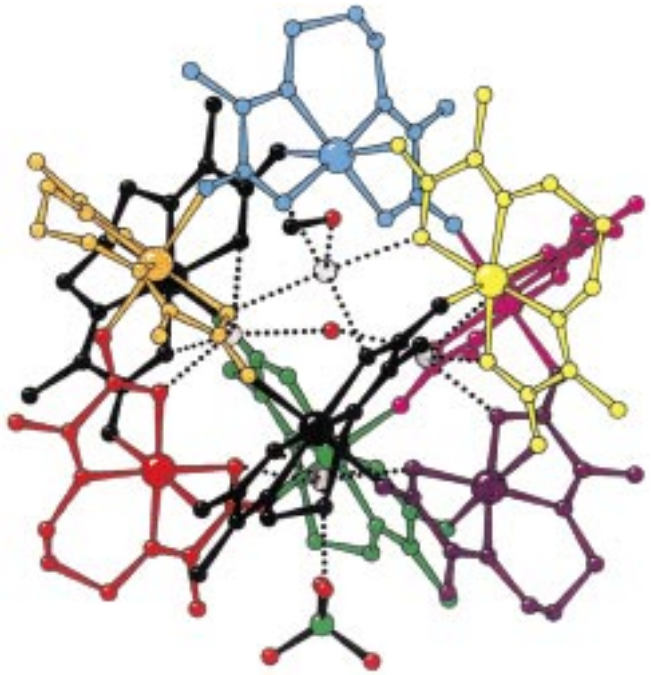

Figure 3. Crystal structure of **2**. The [Ni(L)] units are shown in different colors. The interstitial Na^+ cations are represented by grey spheres, and their coordination spheres are indicated by dotted lines. All hydrogen atoms, noncoordinated ClO_4^- anions, and solvent molecules are omitted for clarity.

four-coordinate. A water molecule is also bound within the Na_4 core (Na–O 2.392(3)–2.404(4) Å), and a ClO_4^- anion and a MeOH molecule protrude through two of the square faces of the $[\{Ni(L)\}_9]$ cage to bind to the Na^+ core (Na–O(ClO_4^-) 2.607(6)–2.774(8), Na–O(MeOH) 2.367(4) Å). The cation in

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2 is, to our knowledge, the first complex cage to have been assembled around a template of four metal centers.

Therefore, [Ni(L)] units aggregate into an octahedral cage in the presence of $La(ClO_4)_3 \cdot 6H_2O$ and into a tricapped trigonal-prismatic cage in the presence of $NaClO_4$. Since the same anion and solvent are present in each case, it appears that the difference in aggregation state results from a templating effect of the interstitial metal cations. A related example has been reported recently by Saalfrank and coworkers in which Group 1 metal ions were found to template the formation of a surrounding cage of [Fe(triethanolamine)] complexes.[7a] In this case, Na^+ templates the formation of a six-membered cage, whereas the larger Cs^+ cation templates the formation of an eight-membered cage. In contrast, [Ni(L)] forms a larger aggregate in the presence of Na^+ than in the presence of the larger La^{III} cation. We believe that the [Ni(L)] units adopt a cage geometry with an internal hole size that best matches the ionic radius of the metal ions available for encapsulation. Thus, while the rigid icosahedral cavity in the $[\{Ni(L)\}_6]$ octahedron accommodates a La^{III} center, it is too large for occupation by a single Na^+ center and too small to accommodate two Na^+ centers. Thus, the [Ni(L)] units assemble into a larger, nine-membered cage around four Na^+ centers.

Crystallization of [Mn(L)][10b] from $MeOH/Et_2O$ in the presence of $Mn(ClO_4)_2 \cdot 6H_2O$ gave colorless, cube-shaped crystals of **3**. Single-crystal X-ray diffraction analysis[11] reveals a novel heptanuclear $[\{Mn(L)\}_6Mn]^{2+}$ cluster lying

$[\{Mn(L)\}_6Mn(H_2O)_{2.25}(MeOH)_{0.75}](ClO_4)_2 \cdot 1.75\,MeOH \cdot 0.5\,H_2O$ **3**

on a crystallographic threefold axis (Figure 4). All seven Mn^{II} centers are approximately octahedral with six outer Mn^{II} centers bound by $(L)^{2-}$ in the equatorial plane (Mn–O 2.163(9) – 2.200(9), Mn–N 2.220(12) – 2.269(12) Å) and an interstitial Mn^{II} center bound by six carboxylate oxygen atoms from surrounding [Mn(L)] units (Mn–O 2.187(9), 2.232(10) Å). Unlike **1** and **2**, in which each [Ni(L)] unit is joined to four others through carboxylate bridges, the [Mn(L)] units in **3** are only joined to three neighboring units, with the axial sites on the Mn^{II} centers bound either by carboxylate oxygens atoms of neighboring [Mn(L)] complexes (Mn–O 2.137(9) – 2.138(10) Å) or terminal H_2O molecules (disordered with MeOH; Mn–O 2.185(9) Å). Connection of the Mn^{II} centers of adjoining [Mn(L)] units gives a twisted Mn_6 trigonal-prismatic cage with a twist angle of 42.23° in which only one carboxylate O-donor from each [Mn(L)] unit binds to the interstitial Mn^{II} ion (Figure 2c).

In conclusion, we have shown that the aggregation of [M(L)] into polynuclear cages can be templated by main group, lanthanide, and transition metal ions. The nuclearity and geometry of these cages is influenced by the size and coordination requirements of the template metal centers. Thus, in **1** an icosahedral La^{III} ion templates an octahedral cage and binds to two carboxylate donors from each [M(L)] moiety; in **2** four Na^+ centers template a tricapped trigonal prismatic cage with four- and five-coordinate Na^+ centers; and in **3** an octahedral Mn^{II} ion templates the formation of a twisted trigonal prismatic cage and binds to one carboxylate donor from each [M(L)] fragment. Preliminary experiments confirm the self-assembly of [M(L)] units at Ba^{2+}, Cs^+, and K^+.

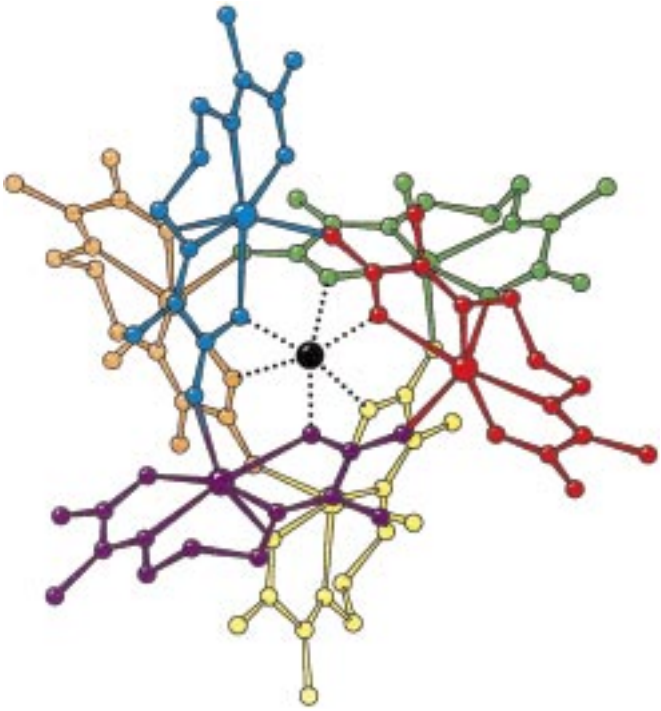

Figure 4. Crystal structure of **3**, viewed down the crystallographic threefold axis. The [Mn(L)] units are shown in different colors. The interstitial Mn^{II} center is represented by a black sphere, and its distorted trigonal-prismatic coordination sphere is indicated by dotted lines. All hydrogen atoms, ClO_4^- anions, and noncoordinated solvent molecules are omitted for clarity.

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[10] a) Synthesis of [Ni(L)]: Reaction of 1,3-diaminopropane (0.074 g, 1 mmol) with sodium pyruvate (0.220 g, 2 mmol) and $Ni(BF_4)_2 \cdot 6H_2O$ (0.340 g, 1 mmol) in MeOH (40 mL) under reflux for 2 h resulted in a blue-green solution. This was reduced in volume and eluted through a Sephadex LH-20 column. Slow diffusion of Et_2O vapor into the resulting solution yielded green crystals of $[Ni(L)(MeOH)_2] \cdot 2MeOH$. The structure of this complex has been confirmed by single-crystal X-ray diffraction.[11b] b) The method for the synthesis of [Ni(L)] was also used in the synthesis of [Mn(L)].

[11] a) Satisfactory elemental analyses were obtained for **1**, **2**, and **3**. Single-crystal X-ray analyses: All fully occupied non-hydrogen atoms were refined using anisotropic displacement parameters, and disordered atoms were refined isotropically over partially occupied sites. All hydrogen atoms were allowed to ride on their respective parent atoms. **1**: $C_{54}H_{72}N_{12}O_{36}Cl_3Ni_6La$, $M_r = 2062.76$, trigonal, space group $P\bar{3}$, $a = 12.4549(11)$, $c = 12.736(2)$ Å, $V = 1711$ Å^3, $T = 150(2)$ K, $\rho_{calcd} = 2.002$ g cm^{-3}, $Z = 1$. Data were collected at 200(2) K on a Stoe Imaging Plate Diffractometer System (IPDS). Of the 2031 data collected ($2\theta_{max} = 50^\circ$, $-14 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 15$), 1988 were unique ($R_{int} = 0.140$) and 1670 had $F \ge 4\sigma(F)$. All non-hydrogen atoms were located using heavy-atom and difference-Fourier methods.[13] $R_1 = 0.0748$ ($F \ge 4\sigma(F)$), and $wR_2 = 0.226$ (all data) for 179 parameters, $(\Delta/\sigma)_{max} = 0.02$, the largest difference Fourier extrema of 3.04 and -1.53 e Å^{-3} both lay near the La atom. **2**: $C_{92.5}H_{150.3}N_{18}O_{61.65}Cl_4Na_4Ni_9$, $M_r = 3663.16$, monoclinic, space group $P2_1/n$, $a = 17.735(4)$, $b = 27.149(5)$, $c = 28.938(6)$ Å, $\beta = 100.22(3)^\circ$, $V = 13711(5)$ Å^3, $T = 200(2)$ K, $\rho_{calcd} = 1.581$ g cm^{-3}, $Z = 4$. Data were collected as for **1**. Of the 78620 data collected ($2\theta_{max} = 52.26^\circ$, $-21 \le h \le 21$, $-33 \le k \le 31$, $-35 \le l \le 35$), 25638 were unique ($R_{int} = 0.109$) and 20268 had $F \ge 4\sigma(F)$. All non-hydrogen atoms were located using direct and difference Fourier methods.[13] $R_1 = 0.0549$ ($F \ge 4\sigma(F)$), and $wR_2 = 0.1634$ (all data) for 1752 parameters, $(\Delta/\sigma)_{max} = 0.08$, largest Fourier extrema: 0.84 and -0.95 e Å^{-3}. **3**: $C_{58}H_{93}N_{12}O_{38.5}Cl_2Mn_6$, $M_r = 2029.92$, cubic, space group $Pa\bar{3}$, $a = 25.523(3)$ Å, $V = 16625.9$ Å^3, $T = 150(2)$ K, $\rho_{calcd} = 1.622$ g cm^{-3}, $Z = 8$. Data were collected as for **1**. Of the 8599 data collected ($2\theta_{max} = 50^\circ$, $0 \le h \le 30$, $0 \le k \le 21$, $0 \le l \le 30$), 4467 were unique ($R_{int} = 0.138$) and 2195 had $F \ge 4\sigma(F)$. All non-hydrogen atoms were located using direct and difference Fourier methods.[13] $R_1 = 0.1053$ ($F \ge 4\sigma(F)$), and $wR_2 = 0.249$ (all data) for 358 parameters, $(\Delta/\sigma)_{max} = 0.02$, largest Fourier extrema: 0.87 and -0.88 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-104533 ($[Ni(L)(MeOH)_2] \cdot 2MeOH$), CCDC-104534 (**1**), CCDC-104535 (**2**), and CCDC-104536 (**3**). 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).

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Dendritically Cross-Linking Chiral Ligands: High Stability of a Polystyrene-Bound Ti-TADDOLate Catalyst with Diffusion Control**

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Polymer-bound reagents and catalysts[1] have received renewed attention in connection with combinatorial synthetic methods.[2] Besides the classical approach of grafting a functional group or ligand to a given polymer (e.g. the Merrifield resin), there have recently also been examples of incorporation of the groups of interest through copolymerization.[3] Both methods have already been applied to TADDOL, a versatile ligand or ligand precursor for EPC synthesis[4] (see **1** in Scheme 1).[5] Two years ago we incorporated for the first time a dendritically modified TADDOL (**2**) with copolymerizable groups at the periphery as cross-linker in polystyrene, and obtained an enantioselective catalytic efficiency with the resulting Ti complex which was similar to that of the homogeneous analogues.[6] Before starting to test this surprising effect with other ligands, we had to investigate its origin, and the stability of this new type of catalyst in multiple applications had to be analyzed.

By cross-linking suspension copolymerization with styrene of dendrimer **2** and—for comparison—of TADDOLs **3**–**5**, bearing shorter and longer, more or less flexible spacers, we have generated beads of p-**2**, p-**3**, p-**4**, and p-**5** (Scheme 1),[7] having a diameter of about 400 μm in the non-solvent-swollen state. Upon treatment with $Ti(OCHMe_2)_4$, polymer-bound diisopropoxy-Ti-TADDOLates were obtained, as illustrated in Scheme 2. Elementary analysis of the p-**2** derivative with a loading of 0.1 mmol g^{-1} showed that 85% of the chiral diol moieties within the polymer had been complexed with Ti ions.

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