

Aggregate, Polymer and Cluster Formation from Metal-Imino Carboxylate Complexes

DAN M.J. DOBLE, RICHARD D. KAY, COLIN H. BENISON, ALEXANDER J. BLAKE, XIANG LIN, CLAIRE WILSON and MARTIN SCHRÖDER*

School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

(Received: 15 July 2001; in final form: 31 August 2001)

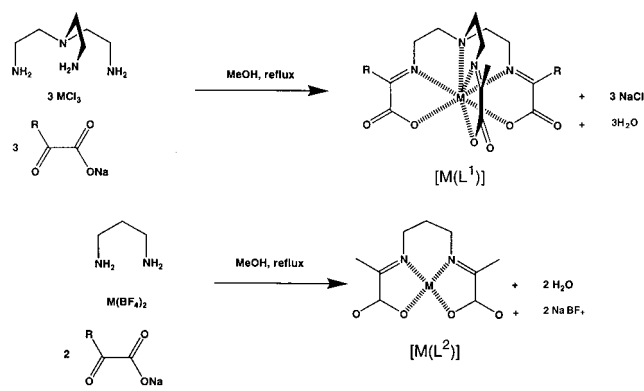
Key words: metal-imino carboxylate complexes, $[L^1]^{3-}$

Abstract

Reaction of tris-(2-aminoethyl)amine (tren) and the sodium salt of an α -keto carboxylic acid, typically sodium pyruvate, affords in the presence of a lanthanide ion a series of complexes and aggregates including mononuclear, cyclic tetranuclear and polymer species of $[L^1]^{3-}$ ($[L^1]^{3-} = N[CH_2CH_2N=C(CH_3)COO^-]^3$). The aggregation of these and related d-block element complexes with Na^+ ions leads to the formation of polymeric materials, and the factors influencing the formation and control of these various aggregation states are discussed. Metal cations also template the aggregation of the fragment $[Ni(L^2)]$ ($[L^2]^{2-} = CH_2[CH_2N=C(CH_3)COO^-]_2$) to give, in high yield, the polynuclear aggregates $\{[Ni(L^2)]_6M\}^{x+}$ ($M = Nd, Pr, Ce, La, x = 3$; $M = Sr, Ba, x = 2$). The structures of $[Ni(L^2)]_6M^{x+}$ show an interstitial twelve co-ordinate, icosahedral cation M^{x+} encapsulated by six $[Ni(L^2)]$ fragments. In the presence of Na^+ , aggregation of $[Ni(L^2)]$ fragments affords $\{[Ni(L^2)]_9Na_4(H_2O)(MeOH)(ClO_4)\}^{3+}$ the structure of which shows four Na^+ ions templating the formation of a distorted tricapped trigonal prismatic $[Ni(L^2)]_9$ cage. Thus, control over construction of various polynuclear cages *via* self-assembly at octahedral junctions can be achieved using main group, transition metal and lanthanide ion templates.

Introduction

There is currently considerable interest in the design of polydentate chelating ligands capable of forming stable complexes of lanthanides for the development of radiopharmaceuticals [1], and as contrast agents for magnetic resonance imaging (MRI) [2]. Much of the work on MRI agents has focussed on poly(aminocarboxylate) ligands [3], especially 1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane (DOTA) and its derivatives [4, 5]. As part of a study of the synthesis of new metal complexes with potential applications in therapy and imaging [6], we have investigated the synthesis and co-ordination properties of new tripodal and square-planar ligands derived from the Schiff-base condensation of tris-(2-aminoethyl)amine (tren) and 1,3-diaminopropane with α -keto carboxylates, respectively (Scheme 1). The ligands $[L^1]^{3-}$ and $[L^2]^{2-}$ are particularly interesting since they afford metal complexes that incorporate not only acceptor sites at the metal ion centre, for example at the apical sites of square-planar $[M(L^2)]$, but also have potential carboxylate donors that may bridge to external metal ions (Scheme 2). These systems are, therefore, designed and organised for the assembly to molecular aggregates, polynuclear clusters and related oligomers and polymers. This article reviews our work in this area [7, 8] and shows how ligand design can yield new metal cluster to-



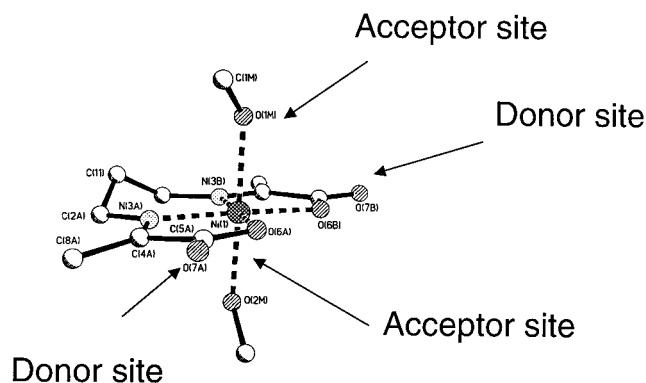
Scheme 1. Synthesis of Schiff-base ligand complexes.

pologies and aggregates. Related tripodal ligands formed by Schiff-base condensation of tris-(2-aminoethyl)amine with 2,6-diformyl-4-methylphenol [9], 2,6-diformylpyridyl [10], salicylaldehyde [11], and acetylacetonone [11] have been reported previously, as have related binuclear bismuth [12] and trinuclear gadolinium [4] complexes.

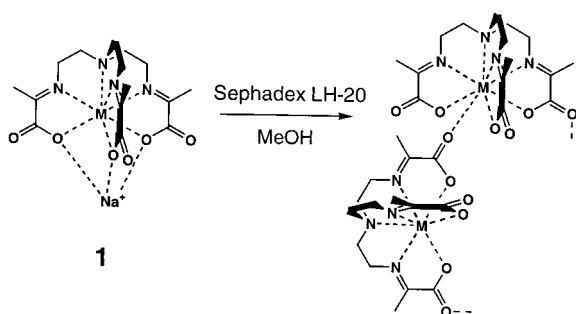
Complexes of the tripodal ligand $[L^1]^{3-}$

Reaction of tris-(2-aminoethyl)amine (tren) with 3 molar equivalents of the sodium salt of an α -keto carboxylic acid, typically sodium pyruvate ($R = Me$), in MeOH in the presence of a lanthanide(III) ion ($Ln = Y, Sm, Gd, Yb$) as

* Author for correspondence; E-mail: M. Schroder@nottingham.ac.uk



Scheme 2. Donor-acceptor sites in complexes of type $[M(L^2)]$ as illustrated by the structure of $[Ni(L^2)(MeOH)_2]$.



Scheme 3. Schematic representation of Na^+ aggregation with $[Ln(L^1)]$ and Na^+ removal by chromatography.

a template, affords a clear, pale yellow solution after 2h (Scheme 1). Addition of excess Et_2O affords a white precipitate of **1** and $NaCl$ in high yield. Although the FAB mass spectrum of **1** shows a peak for $\{[Ln(L^1)]_2Na\}^+$, the precise assignment of **1** remains tentative, with co-ordination of solvent molecules to $Ln(III)$ and Na^+ and association of Na^+ cations with the neutral complex $[Ln(L^1)]$ via interaction with the terminal carboxylate O-donors highly likely. $NaCl$ can be removed by elution of a $MeOH$ solution of **1** through a Sephadex LH-20 column to yield crystals of the Na^+ -free neutral complex (Scheme 3). Crystals suitable for X-ray diffraction were obtained for the Y(III) and Yb(III) complexes with $[L^1]^{3-}$ ($R = Me$) and the Y(III) complex with $[L^1]^{3-}$ ($R = Et$).

The Yb(III) (Figure 1) and Y(III) complexes of $[L^1]^{3-}$ were found to be iso-structural tetrameric structures $[Ln(L^1)]_4$ with one carboxylate group from each ligand bridging to the next metal centre. Since the two halves of the tetramer are related by an inversion centre, the four $Ln(III)$ centres are precisely planar to form a molecular parallelogram. The Yb(III) and Y(III) centres are eight co-ordinate, bound by the heptadentate tripodal ligand $[L^1]^{3-}$ and an additional carboxylate oxygen of an adjacent complexed ligand. There is a high degree of planarity in the fragments C(2)–C(8) (labelling scheme shown in Figure 3) within the pyruvate arms due to conjugation between the imine and carboxylate groups with mean deviations from the plane of only 0.024–0.132 Å. The tetrameric structure is surrounded by independent $MeOH$ and H_2O solvent molecules, which are involved in intermolecular hydrogen-bonding. These

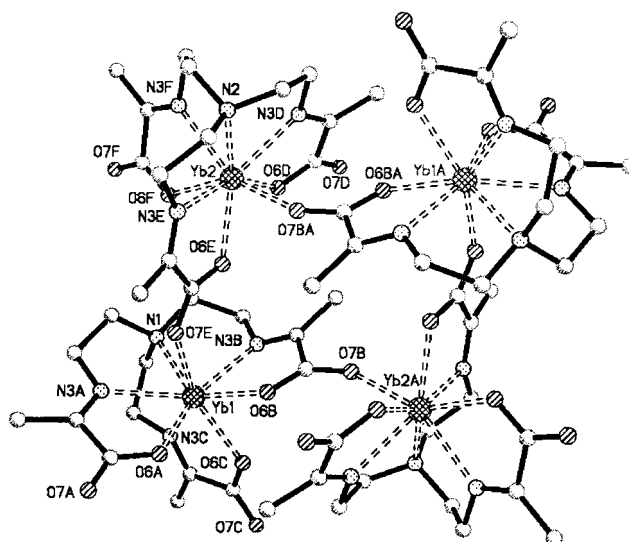


Figure 1. View of the structure of $[Yb(L^1)]$ ($R = Me$) with numbering scheme adopted.

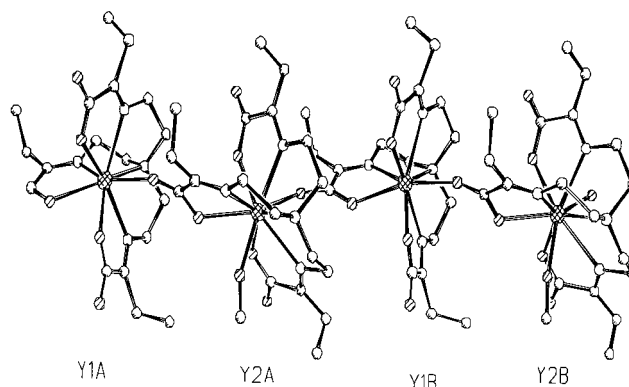


Figure 2. View of the structure of $\{[Y(L^1)]_2CH_3OH\}_\infty$.

Yb(III) and Y(III) complexes are, to our knowledge, the first structurally characterised cyclic tetramers of the lanthanides [13]. Interestingly, electrospray mass spectrometry suggests that a Y(III) tetramer does exist, at least in part, in aqueous solution.

In contrast, the Y(III) complex of $[L^1]^{3-}$ is a linear polymer $[Y_2(L^1)_2MeOH]_\infty$ ($R = Et$) (Figure 2) rather than a cyclic tetramer as observed above. The complex aggregates via a bridging carboxylate group linking metal centres. The Y(III) centres alternate between eight co-ordinate Y(1) and nine co-ordinate Y(2) respectively, with the ninth co-ordination site filled by a $MeOH$ molecule. The Y(III)-donor atom bond lengths are generally longer for the nine co-ordinate centres. These linear polymeric chains are hydrogen-bonded to each other and to $MeOH$ molecules. The remarkable differences in structure between $[Y_2(L^1)_2MeOH]_\infty$ ($R = Et$) and $[Y(L^1)]_4$ ($R = Me$) show how an apparently minor change of an organic substituent remote from the metal centres can have a dramatic effect on the observed solid-state structure.

Dissolution of the Sm(III) and Gd(III) complexes of **1** in H_2O results in the slow growth of X-ray quality crystals of the mononuclear species $[Ln(L^1)(OH_2)_2]$ [$Ln = Sm, Gd$

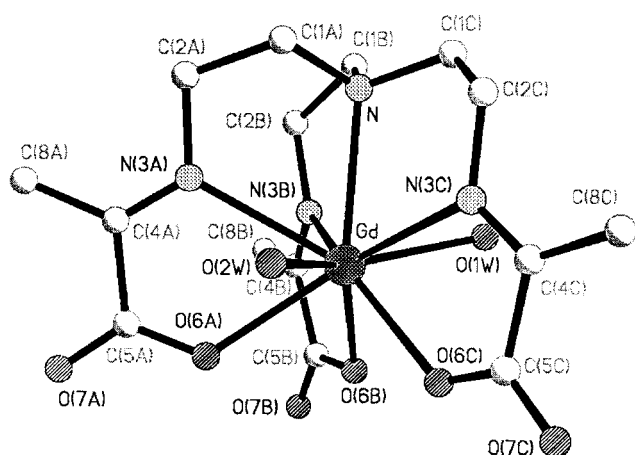


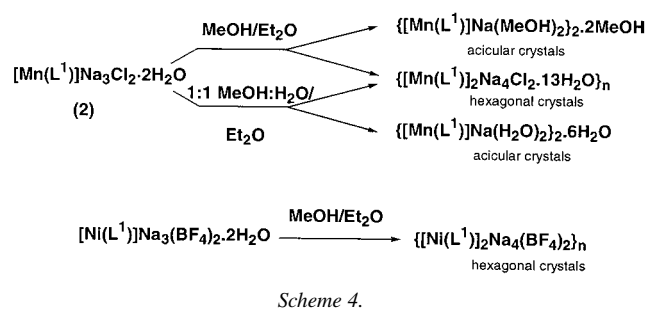
Figure 3. Structure of $[\text{Gd}(\text{L}^1)(\text{OH}_2)_2]$ ($\text{R} = \text{Me}$) with numbering scheme adopted.

(Figure 3)]. Both $[\text{Ln}(\text{L}^1)_4]$ and $[\text{Ln}(\text{L}^1)(\text{OH}_2)_2]$ are of lower solubility in H_2O and MeOH than **1**, and we believe that **1** and $[\text{Ln}(\text{L}^1)(\text{OH}_2)_2]$ are in equilibrium in H_2O , thereby explaining the slow crystallisation of $[\text{Ln}(\text{L}^1)(\text{OH}_2)_2]$ from a solution of **1**. The structure of $[\text{Sm}(\text{L}^1)(\text{OH}_2)_2]$ confirms the binding of the tripodal, heptadentate Schiff-base ligand to a nine co-ordinate $\text{Sm}(\text{III})$ centre. The two remaining co-ordination sites on the $\text{Sm}(\text{III})$ ion are occupied by two H_2O molecules, each of which is positioned between two tripod arms. Again, each arm of $[\text{L}^1]^{3-}$ shows a high degree of planarity allowing effective conjugation of the imine with the carboxylate groups and stabilising the imine moiety. $[\text{Sm}(\text{L}^1)(\text{OH}_2)_2]$ crystallises as a heptahydrate with extensive intermolecular hydrogen-bonding. The $\text{Gd}(\text{III})$ complex $[\text{Gd}(\text{L}^1)(\text{OH}_2)_2]$ (Figure 3) is isostructural.

The novel tripodal ligands reported here are heptadentate, whereas lanthanide metal ions usually prefer 8 or 9 co-ordination. It is, therefore, necessary for the $\text{Ln}(\text{III})$ centres to include additional donors in their co-ordination spheres. Both $[\text{Ln}_2(\text{L}^1)_2\text{MeOH}]_\infty$ ($\text{R} = \text{Et}$) and $[\text{Ln}(\text{L}^1)_4]$ ($\text{R} = \text{Me}$) are crystallised from MeOH , in which the best donors available are the carboxylate oxygens of neighbouring complexes, resulting in the observed oligomeric structures. However, $[\text{Ln}(\text{L}^1)(\text{OH}_2)_2]$ ($\text{R} = \text{Me}$) is crystallised from H_2O which is itself a good donor, resulting in the observed monomeric complex.

Formation of mixed-metal aggregates

Previous work has confirmed that aggregation of metal complexes by polychelate ligands through *exo* co-ordination of metal ions can afford a wide range of cluster and polymeric species [14–17]. In particular, carboxylate-based complexes are particularly effective in binding Group I and II metal ions [15]. For example, Na_2CO_3 can be encapsulated by $[\text{Gd}(\text{DO}_3\text{A})]$ ($\text{DO}_3\text{A} = 1,4,7$ -tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane) to form the complex cluster $[\text{Gd}(\text{DO}_3\text{A})_3\text{Na}_2\text{CO}_3]$ [16], while derivatives of *N*-hydroxyiminodiacetic acid (H_3hida) are able to adopt a variety of aggregation states in the presence of hard metal ions [17]. We were particularly interested



Scheme 4.

in forming polymeric aggregates which feature channels or sheets of metal ions which may have potential as ionic conductors and charge-storage devices [18, 19], and as bio-mimetic models [20]. We were also interested in developing these ideas further with specific focus upon aggregation of metal complex fragments *via exo* metal binding to $[\text{L}^1]^{3-}$ and $[\text{L}^2]^{2-}$. We have thus far been unable to confirm the connectivity and precise details of binding of Na^+ with the neutral fragments $[\text{Ln}(\text{L}^1)]$ by single crystal diffraction. We therefore investigated the complexation of anionic complexes of type $[\text{M}(\text{L}^1)]^-$ [$\text{M} = \text{Mn}(\text{II}), \text{Ni}(\text{II})$] in which the Na^+ cation would be carried over and be incorporated directly as the counter cation in the product.

Reaction of *tris*(2-aminoethyl)amine (*tren*) with three equivalents of sodium pyruvate in the presence of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ followed by addition of excess Et_2O affords a white solid of stoichiometry $[\text{Mn}(\text{L}^1)]\text{Na}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, **2**. Although it is not known whether **2** is a single species or a mixture of products, dissolution of **2** in MeOH followed by slow diffusion of Et_2O affords pale yellow crystals of two distinct morphologies, acicular and hexagonal (Scheme 4).

Single crystal X-ray diffraction on the hexagonal crystals reveals a co-ordination polymer of stoichiometry $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$ (Figure 4). The structure consists of complex anions $[\text{Mn}(\text{L}^1)]^-$ in which $\text{Mn}(\text{II})$ lies on a crystallographic three-fold axis and is bound to $[\text{L}^1]^{3-}$ *via* three carboxylate O-donors, $\text{Mn}-\text{O} = 2.257(2)$ Å, three imine N-donors, $\text{Mn}-\text{N} = 2.273(2)$ Å and, at longer range, the bridge-head tertiary N-donor, $\text{Mn}-\text{N} = 2.597(4)$ Å, to give overall seven co-ordination at the $\text{Mn}(\text{II})$ centre. The three arms of the tripodal ligand twist around the $\text{Mn}(\text{II})$ center with a pitch angle of 78.6° . Significantly, an infinite polymeric sheet of Na^+ ions bridge carboxylate O-donors of adjacent layers of $[\text{Mn}(\text{L}^1)]^-$ units with $\text{Na}-\text{O} = 2.374(2)-2.592(3)$ Å. The Na^+ centres bind additionally to solvent water molecules, $\text{Na}-\text{O} = 2.723(3)$ Å, to give five and six co-ordinate Na^+ ions. The Cl^- anions and remaining solvent water molecules are unco-ordinated and are themselves sandwiched between $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\}_\infty$ layers (Figure 5).

Slow diffusion of Et_2O into a solution of **2** in a 1:1 mixture of MeOH and H_2O results in crystals of both the polymer $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$ and the tetranuclear cluster, $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}$ (Scheme 4). The structure of $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}$ (Figure 6) is analogous to that of $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{MeOH})_2\}_2 \cdot 2\text{MeOH}$, formed by recrystallisation of $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$, **2**, from $\text{MeOH}/\text{Et}_2\text{O}$ only, but with solvation of Na^+ cations

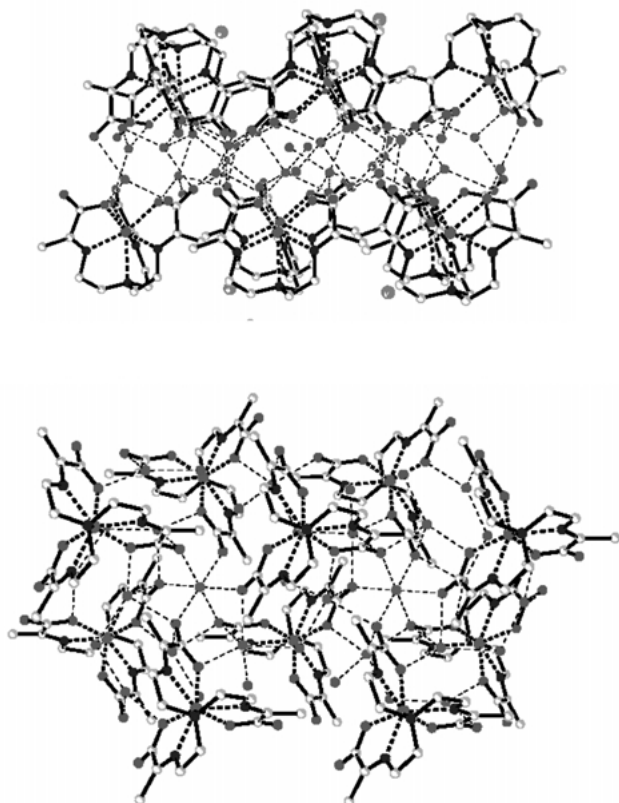


Figure 4. Two complementary views of the structure of $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$ viewed normal and incident to the plane of the Na^+ sheet.

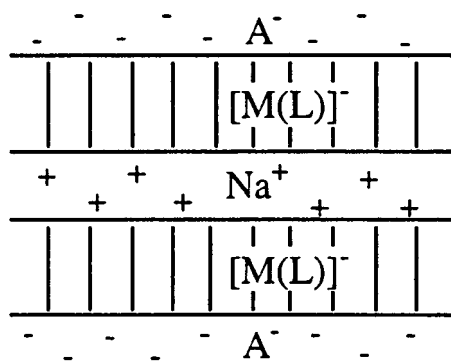


Figure 5. Schematic of layered structure of $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$.

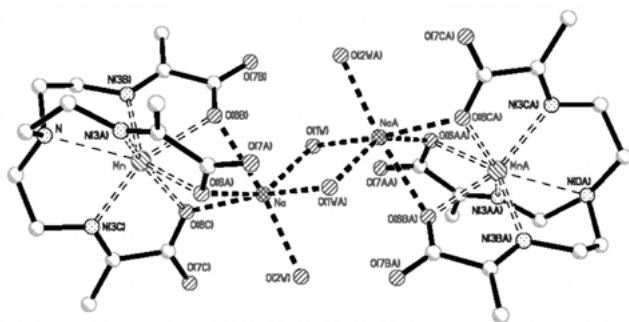


Figure 6. View of the structure of $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}$. The structure lies across a crystallographic inversion centre. All hydrogen atoms and uncoordinated solvent molecules are omitted for clarity.

in the former being by H_2O rather than MeOH . The structure of $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{MeOH})_2\}_2 \cdot 2\text{MeOH}$ confirms two Na^+ cations bound to the carboxylate oxygens, $\text{Na}-\text{O}(\text{carboxylate}) = 2.348(3)-2.686(3)$ Å, from two $[\text{Mn}(\text{L}^1)]^-$ anions, $\text{Mn}-\text{O} = 2.234(2)-2.258(2)$, $\text{Mn}-\text{N}(\text{imine}) = 2.260(2)-2.274(2)$, $\text{Mn}-\text{N}(\text{amine}) = 2.658(2)$ Å. The Na^+ cations also bind to two bridging and two terminal MeOH molecules, $\text{Na}-\text{O}(\text{MeOH}) = 2.385(3)-2.390(3)$ Å, giving overall six co-ordination at Na^+ , $\text{Na}-\text{O}(\text{carboxylate}) = 2.339(4)-2.451(3)$, $\text{Na}-\text{O}(\text{H}_2\text{O}) = 2.404(3)-2.457(5)$ Å. Significantly, bulk samples of the tetranuclear clusters $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}$ and $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{MeOH})_2\}_2 \cdot 2\text{MeOH}$ always contain the layered polymer $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$ (Scheme 4). The primary difference in stoichiometry between these two aggregation states is that the planar polymer $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$ contains two additional Na^+ and two additional Cl^- ions compared to the tetranuclear clusters $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}$ and $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{MeOH})_2\}_2 \cdot 2\text{MeOH}$. Thus, $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$ can be considered as being formed by the co-crystallisation of $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}$ and $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{MeOH})_2\}_2 \cdot 2\text{MeOH}$ with NaCl .

Atomic absorption measurements, elemental analytical data, and X-ray powder diffraction have been used to study the ratio of products formed in any given reaction. Thus, typically, the percentage of $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$ crystallised from a solution of **2** is 17–21% by mass, the remainder being $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}$ and $\{[\text{Mn}(\text{L}^1)]\text{Na}(\text{MeOH})_2\}_2 \cdot 2\text{MeOH}$. Elution of **2** in MeOH through a Sephadex LH-20 column followed by slow diffusion of Et_2O yields crystals which contain less than 2% of $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$. Thus, chromatography on Sephadex removes all the NaCl except for the one Na^+ per $[\text{Mn}(\text{L}^1)]^-$ unit required to maintain electroneutrality, resulting in the observed increase in tetranuclear clusters relative to layered polymer. This demonstrates how the aggregation state of $[\text{Mn}(\text{L}^1)]^-$ can be controlled. Addition of NaCl to a solution of **2** would be expected to result in preferential crystallisation of $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$, but quantitative analysis is complicated by crystallisation of cubic NaCl at higher NaCl concentrations.

Interestingly, when BF_4^- anion is used in place of Cl^- in the above reaction, a solid precipitates with a $\text{Na}^+:\text{Mn}^{2+}$ ratio corresponding to 95–98% planar polymer. It has not yet been possible to grow crystals of this product suitable for X-ray diffraction, but crystals of the $\text{Ni}(\text{II})$ analogue have been prepared. The complex $\{[\text{Ni}(\text{L}^1)]_2\text{Na}_4(\text{BF}_4)_2\}_\infty$ has been synthesised *via* reaction of tren with sodium pyruvate and $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in MeOH followed by recrystallisation from $\text{MeOH}/\text{Et}_2\text{O}$. The single crystal X-ray structure of $\{[\text{Ni}(\text{L}^1)]_2\text{Na}_4(\text{BF}_4)_2\}_\infty$ (Figure 7) shows a layered polymeric sandwich structure similar to $\{[\text{Mn}(\text{L}^1)]_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$, although the presence of BF_4^- in $\{[\text{Ni}(\text{L}^1)]_2\text{Na}_4(\text{BF}_4)_2\}_\infty$ leads to BF_4^- anions binding to three Na^+ cations within the Na^+ layer. The arms of $[\text{L}^1]^{3-}$ helicate about $\text{Ni}(\text{II})$ with a pitch angle of 56.1° , with the $\text{Ni}(\text{II})$ cations bound approximately octahedrally by three

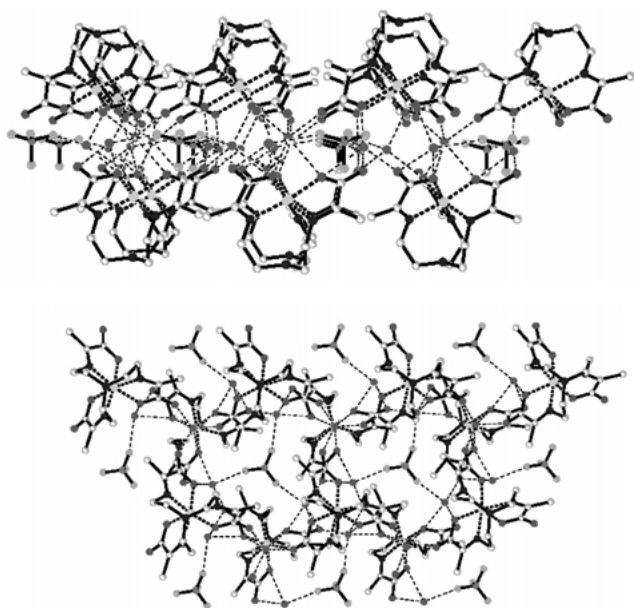


Figure 7. Single crystal X-ray structure of $\{[\text{Ni}(\text{L}^1)_2\text{Na}_4(\text{BF}_4)_2]\infty\}$ viewed normal and incident to the plane.

imine N-donors, Ni-N = 2.082(14)–2.098(15) Å, and three carboxylate O-donors, Ni-O = 1.95(3)–2.11(2) Å. In contrast to the Mn(II) centre in $\{[\text{Mn}(\text{L}^1)_2\text{Na}_4\text{Cl}_2 \cdot 13\text{H}_2\text{O}]\infty\}$, the Ni(II) centre in $\{[\text{Ni}(\text{L}^1)_2\text{Na}_4(\text{BF}_4)_2]\infty\}$ does not interact strongly with the bridgehead N-donor, Ni...N = 3.15(2)–3.16(2) Å. The Na⁺ cations in $\{[\text{Ni}(\text{L}^1)_2\text{Na}_4(\text{BF}_4)_2]\infty\}$ are extensively disordered and interact with the carboxylate O-centres, Na-O = 2.25(2)–2.78(2) Å and BF₄⁻ anions, Na-F = 2.18(3)–2.48(3) Å, with no co-ordinated solvent molecules. Within the Na⁺ layer, there are vacant sites surrounded by six carboxylate oxygens at 2.20(2)–2.70(2) Å. These vacancies are of considerable interest as they may allow the movement of Na⁺ cations through the structure as in the ionic conductor sodium β-alumina [19]. Future work will be concerned with studying the mobility of both anions and cations in these planar polymeric structures. Significantly, elemental analysis and atomic absorption measurements indicate that $\{[\text{Ni}(\text{L}^1)_2\text{Na}_4(\text{BF}_4)_2]\infty\}$ is the only species formed in the above reaction. The preference for the planar polymeric structure is attributed to the presence of BF₄⁻ anions, which, unlike Cl⁻, are directly involved in aggregation with the Na⁺ cations. Therefore, as for recently reported examples of anion-templated self-assembly of metal-ligand frameworks [21], the anion can be regarded as controlling the aggregation of complexes of [L¹]³⁻.

In order to study the interaction between [Ln(L¹)] and NaCl more fully, several attempts were made to crystallise [Ln(L¹)] (R = Me) in the presence of Na⁺ and other hard metal centres such as Li⁺, K⁺, Mg²⁺, Ca²⁺, Mn²⁺ or Y³⁺. Unfortunately, all of these attempts were unsuccessful in producing crystals of a quality suitable for X-ray diffraction. However, reaction of tren with one molar equivalent of Ca(ClO₄)₂ and three molar equivalents of sodium pyruvate in MeOH followed by slow diffusion of Et₂O resulted in the slow growth of colourless crystals.

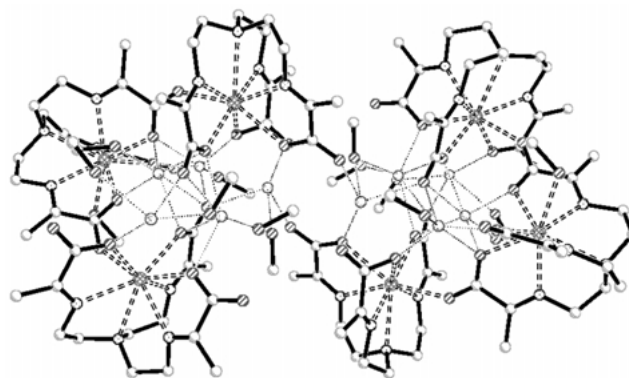


Figure 8. Structure of $\{[\text{Ca}(\text{L}^1)_3\text{Na}_5(\text{MeOH})_7]\{\text{ClO}_4\}_2\}\infty$.

The Ca(II) ion has a similar ionic radius and co-ordination number to Ln(III) $\{r(\text{Ca}^{2+})\} = 1.00$ Å, $r[\text{La}(\text{III})] = 1.16$, $r[\text{Lu}(\text{III})] = 0.85$ Å. Therefore, the $[\text{Ca}(\text{L}^1)]^-$ anion might be expected to interact with Na⁺ in a similar way to $[\text{Ln}(\text{L}^1)]^-$. Single crystal X-ray diffraction reveals the linear polymer $\{[\text{Ca}(\text{L}^1)_3\text{Na}_5(\text{MeOH})_7]\{\text{ClO}_4\}_2\}\infty$ in which three $[\text{Ca}(\text{L}^1)]^-$ anions are bound together by bridging carboxylate groups to form a $\{[\text{Ca}(\text{L}^1)_3\text{MeOH}]\}^{3-}$ moiety encapsulating five Na⁺ cations, which in turn are bound to six MeOH molecules (Figure 8). Each Ca(II) centre is bound by three carboxylate oxygens, three imine nitrogens and the bridgehead tertiary amine nitrogen of (L¹)³⁻. The two outer Ca(II) centres are also bound by carboxylate oxygens of the central $[\text{Ca}(\text{L}^1)]^-$ unit, whereas a MeOH molecule occupies the eighth co-ordination site on the central Ca(II) cation. The Na⁺ centres are five and six co-ordinate, binding to MeOH solvent molecules and the carboxylate oxygens of the $[\text{Ln}(\text{L}^1)]$ units. The $\{[\text{Ca}(\text{L}^1)_3\text{Na}_5(\text{MeOH})_7]\}^{2+}$ clusters bind together through Na⁺-carboxylate and Na⁺-MeOH interactions to produce a complex polymeric structure with a zigzag Na⁺ backbone surrounded by $\{[\text{Ca}(\text{L}^1)_3]\}^{3-}$ fragments.

Aggregation of complexes of [L²]³⁻

The aggregation of soft metal centres to form covalently-bonded clusters is well known [22–24], and there are well-established theories regarding the structure and bonding in these polynuclear complexes, for example Ru and Os carbonyl [23] and Au clusters [24]. In contrast, hard metal cations do not readily form metal–metal bonds, and usually require bridging ligands such as carboxylate [25], oxide [26] or hydroxide [26] ligands to induce aggregation. These ligands have enabled one-pot syntheses of some spectacular high nuclearity aggregates, often with interesting magnetic and electronic properties [25, 26]. However, such ligands can adopt a variety of co-ordination modes which, together with the often unpredictable co-ordination geometries of the metals concerned, makes it very difficult to rationalise the structures of the resulting aggregates. Recent developments in self-assembly have shown how metal-ligand frameworks can be successfully templated about a substrate anion or cation [21]. Our approach has been to use the tetradentate

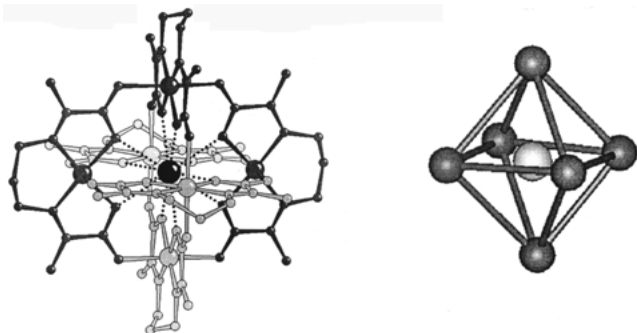


Figure 9. Structure of $\{[\text{Ni}(\text{L}^2)]_6\text{La}\}^{3+}$ with schematic of LaNi_6 polyhedron.

ligand, $[\text{L}^2]^{2-}$ [27], to chelate the four equatorial sites of a potentially octahedral metal ion $\text{M}(\text{II})$ leaving two free axial sites at the metal centre for aggregation by interaction with the carboxylate oxygen donors of neighbouring $[\text{M}(\text{L}^2)]$ units. Thus, each planar $[\text{M}(\text{L}^2)]$ moiety has available two acceptor sites on $\text{M}(\text{II})$ to form a 180° junction, and two carboxylates donors forming 90° junctions to the acceptor sites on $\text{M}(\text{II})$ (Scheme 2).

Slow co-diffusion of methanolic solutions of $[\text{Ni}(\text{L}^2)]$ and $\text{La}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ results in the growth of brown, columnar crystals of $\{[\text{Ni}(\text{L}^2)]_6\text{La}\}(\text{ClO}_4)_3$. A single crystal X-ray structure determination reveals a highly unusual [28] heptanuclear $\{[\text{Ni}(\text{L}^2)]_6\text{La}\}^{3+}$ cluster (Figure 9) in which a $\text{La}(\text{III})$ centre is located at the centre of the octahedral cage formed by six $[\text{Ni}(\text{L}^2)]$ moieties, and is bound by an icosahedron of twelve carboxylate O-donors. The $\text{La}(\text{III})$ centre lies on a crystallographic 3-fold axis so that all six $[\text{Ni}(\text{L}^2)]$ units are equivalent with the octahedral $\text{Ni}(\text{II})$ centres bound equatorially by $[\text{L}^2]^{2-}$ and axial sites occupied by the carboxylate O-centres of two neighbouring $[\text{Ni}(\text{L}^2)]$ units. Thus, each $[\text{Ni}(\text{L}^2)]$ unit is joined to four other $[\text{Ni}(\text{L}^2)]$ units such that the six $\text{Ni}(\text{II})$ centres lie at the vertices of a near-perfect octahedron with $\text{La}(\text{III})$ at its centre. A range of related heptanuclear clusters $\{[\text{Ni}(\text{L}^2)]_6\text{M}\}^{x+}$ ($\text{M} = \text{Ba}, \text{Sr}, x = 2$; $\text{M} = \text{Nd}, \text{Pr}, \text{Ce}, x = 3$) have been prepared and characterised. These complexes all show very similar structures with the intra polyhedral $\text{Ni} \dots \text{Ni}$ distances varying as a function of central template ion size and charge (Figure 10). Thus, as the ionic radius of the central template increases the outer Ni_6 polyhedron expands to accommodate the template. Likewise, the intra-cluster polyhedral $\text{Ni} \dots \text{Ni}$ distances decrease on going from a 2+ to a 3+ template ion. It is remarkable that the icosahedral cavity appears capable of binding to a wide range of metal centres. In particular, this cavity enables the encapsulation of an unprecedented 12-co-ordinate $\text{Sr}(\text{II})$ center.

Crystallisation of $[\text{Ni}(\text{L}^2)]$ from $\text{MeOH}/\text{Et}_2\text{O}$ in the presence of NaClO_4 yields purple crystals of $\{[\text{Ni}(\text{L}^2)]_9\text{Na}_4(\text{H}_2\text{O})(\text{MeOH})(\text{ClO}_4)\}(\text{ClO}_4)_3 \cdot \text{Et}_2\text{O} \cdot 6.5\text{MeOH} \cdot 0.15\text{H}_2\text{O}$ containing a highly novel Ni_9Na_4 cluster in which four Na^+ cations are encapsulated within a nine-membered $[\text{Ni}(\text{L}^2)]_9$ cage (Figure 11). The cage is comprised of $[\text{Ni}(\text{L}^2)]$ units which are related by an approximate, non-crystallographic, three-fold axis. All the

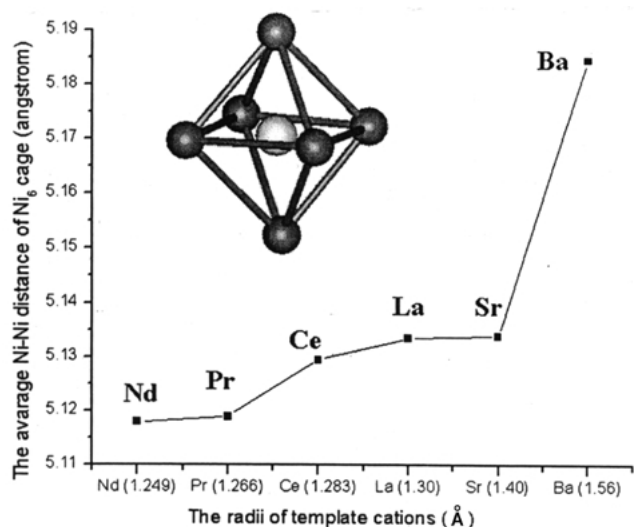


Figure 10. Variation of intra-cluster polyhedral $\text{Ni} \dots \text{Ni}$ distance with ionic radius of cation template.

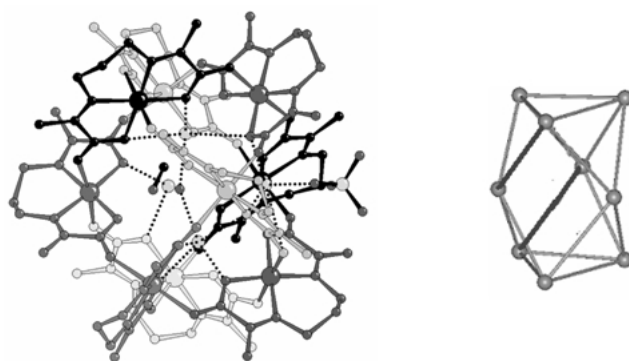


Figure 11. Structure of $\{[\text{Ni}(\text{L}^2)]_9\text{Na}_4(\text{H}_2\text{O})(\text{MeOH})(\text{ClO}_4)\}(\text{ClO}_4)_3 \cdot \text{Et}_2\text{O} \cdot 6.5\text{MeOH} \cdot 0.15\text{H}_2\text{O}$ with schematic of Ni_9 tricapped trigonal prism.

$\text{Ni}(\text{II})$ centres are octahedral with the equatorial sites bound by $[\text{L}^2]^{2-}$ and the axial sites bound by the carboxylate oxygens of neighbouring complexes. The $\text{Ni}(\text{II})$ centres are set in a tricapped trigonal prismatic arrangement although connection of the $\text{Ni}(\text{II})$ centres of adjoining $[\text{Ni}(\text{L}^2)]$ units gives a polyhedron with three square faces and eight triangular faces, with each $[\text{Ni}(\text{L}^2)]$ moiety connected to four other $[\text{Ni}(\text{L}^2)]$ fragments (Figure 11). All the carboxylate oxygens are orientated inwards, encapsulating a core of four Na^+ cations of which two are five co-ordinate and two are four co-ordinate. A water molecule is bound within the Na_4 core with a ClO_4^- anion and a MeOH molecule protruding through two of the square faces of the $[\text{Ni}(\text{L}^2)]_9$ cage to bind to the Na^+ core. The cation in $\{[\text{Ni}(\text{L}^2)]_9\text{Na}_4\}^{4+}$ is, to our knowledge, the first complex cage to have been assembled around a template of four metal centres.

Therefore, $[\text{Ni}(\text{L}^2)]$ units aggregate into an octahedral cage in the presence of $\text{La}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ and 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 by Saalfrank and co-workers

in which Group 1 metal ions were found to template the formation of a surrounding cage of [Fe(triethanolamine)] complexes [29]. 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, $[\text{Ni}(\text{L}^2)]$ forms a larger aggregate in the presence of Na^+ than in the presence of the larger La(III) cation. We believe that the $[\text{Ni}(\text{L}^2)]$ 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 $[\text{Ni}(\text{L}^2)]_6$ octahedron accommodates a La(III) centre, it is too large for occupation by a single Na^+ centre, but too small to accommodate two Na^+ centres. Thus, the $[\text{Ni}(\text{L}^2)]$ units assemble into a larger, nine-membered cage around, in this case, four Na^+ centres.

In conclusion, aggregation in the above tripodal and square-planar systems can be controlled by template cations and anions, by solvent, and by variation in the tripodal polychelate as illustrated by the formation of mononuclear, cyclic tetranuclear and polymeric complexes.

Acknowledgements

We thank Nycomed-Amersham for a CASE award (to D.M.J.D.), the CVCP for an ORS Award (to XL), the EPSRC National Mass Spectrometry Service at Swansea University, and the EPSRC and the University of Nottingham for support.

References

- S.E. Order, J.L. Klein, P. K. Leicher, J. Frinke, C. Lollo, and D. J. Carlo: *Int. J. Radiat. Oncol. Biol. Phys.* **12**, 277 (1986); J.P.L. Cox, K.J. Jakowski, R. Katakay, R.A. Beely, B.A. Boyce, M.A.W. Eaton, K. Miller, A.T. Millican, S. Harrison, C. Walker, and D. Parker: *J. Chem. Soc., Chem. Commun.* 797 (1989); T.J. Norman, D. Parker, L. Royle, A. Harrison, P. Antoniwi, and D.J. King: *J. Chem. Soc., Chem. Commun.* 1877 (1995); D. Parker: *Chem. in Britain* **30**, 818 (1994).
- R.B. Laufer: *Chem. Rev.* **87**, 901 (1987).
- P.J. Wong and G.R. Choppin: *ACS Symposium Series*, vol. 565 pp. 346–360; V. Alexander: *Chem. Rev.* **95**, 273 (1995); S.L. Wu, S.J. Franklin, K.N. Raymond, and W. DeW. Horrocks Jr.: *Inorg. Chem.* **35**, 162 (1996).
- C.A. Chang, L.C. Francesconi, M.F. Malley, K. Kumar, J.Z. Gougoustras, M.F., Tweedle, D.W. Lee, and L.J. Wilson: *Inorg. Chem.* **32**, 3501 (1993).
- S. Aime, M. Botta, D. Parker, and J.A.G. Williams: *J. Chem. Soc., Dalton Trans.* 2259 (1995); S. Aime, M. Botta, G. Ermondi, E. Terreno, P.L. Anelli, F. Fedeli, and F. Uggeri: *Inorg. Chem.* **35**, 2726 (1996) and references therein.
- D.M.J. Doble and M. Schröder: International Patent EP 97301548.0, WO 98/39288.
- A.J. Blake, D.M.J. Doble, W.-S. Li, and M. Schröder: *J. Chem. Soc., Dalton Trans.* 3655 (1997).
- D.M.J. Doble, C.H. Benison, A.J. Blake, D. Fenske, M.S. Jackson, R.D. Kay, W.S. Li, and M. Schröder: *Angew. Chem. Int. Ed. Engl.* **38**, 1915 (1999).
- S.J. Archibald, A.J. Blake, M. Schröder, and R.E.P. Winpenny: *J. Chem. Soc., Chem. Commun.* 1669 (1994); S.J. Archibald, A.J. Blake, M. Schröder, and R.E.P. Winpenny: *J. Chem. Soc., Dalton Trans.* 173 (1997). See also: A.J. Amoroso, A.M. Cargill Thompson, J.C. Jeffrey, P.L. Jones, J.A. McCleverty, and M.D. Ward: *J. Chem. Soc., Chem. Comm.* 2751 (1994).
- V. McKee, M.R.J. Dorrity, J.F. Malone, D. Marrs, and J. Nelson: *J. Chem. Soc., Chem. Commun.* 383 (1992).
- D.J. Berg, S.J. Rettig, and C. Orvig: *J. Am. Chem. Soc.* **113**, 2528 (1991); P. Caravan, T. Hedlund, S. Liu, S. Sjöberg, and C. Orvig: *J. Am. Chem. Soc.* **117**, 11230 (1995).
- H. Wullens, M. Devillers, J.P. Declercq, and D. Tinant: *J. Chem. Soc., Dalton Trans.* 2023 (1996).
- See also G.B. Deacon, T. Feng, D.C.R. Hockless, P.C. Junk, B.W. Skelton, and A.H. White: *J. Chem. Soc., Chem. Commun.* 341 (1997).
- For example see: G. Musie, P.J. Farmer, T. Tuntulani, J.H. Reibenspies, and M.Y. Darensbourg: *Inorg. Chem.* **35**, 2176 (1996); A.J. Blake, I.A. Fallis, R.O. Gould, S. Parsons, S.A. Ross, and M. Schröder: *J. Chem. Soc., Chem. Commun.* 2467 (1994); *J. Chem. Soc., Dalton Trans.* 173 (1997); T. Konno, K. Yonenobo, J. Hidaka, and K. Okamoto: *Inorg. Chem.* **33**, 861 (1994).
- For example see: Y. Yukawa, S. Igarishi, A. Yamano, and S. Sato: *J. Chem. Soc., Chem. Commun.* 711 (1997); A.K. Powell, S.L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo, and F. Pieralli: *J. Am. Chem. Soc.* **117**, 2491 (1995).
- C.A. Chang, L.C. Francesconi, M.F. Malley, K. Kumar, J.Z. Gougoustras, M.F. Tweedle, D.W. Lee, and L.J. Wilson: *Inorg. Chem.* **32**, 3501 (1993).
- S.M. Harben, P.D. Smith, R.L. Beddoes, D. Collison, and C.D. Garner: *Angew. Chem., Int. Ed. Engl.* **36**, 1897 (1997); P.D. Smith, R.E. Berry, S.M. Harben, R.L. Beddoes, M. Helliwell, D. Collison, and C.D. Garner: *J. Chem. Soc., Dalton Trans.* 4509 (1997); S.M. Harben, P.D. Smith, M. Helliwell, D. Collison, and C.D. Garner: *J. Chem. Soc., Dalton Trans.* 4517 (1997).
- P.G. Bruce: *Solid State Electrochemistry*, Cambridge University Press, Cambridge (1993); P.G. Bruce and C.A. Vincent: *J. Chem. Soc., Faraday Trans.* **89**, 3187 (1993); T. Nakamura, T. Akutagawa, K. Honda, A.E. Underhill, A.T. Coomber, and R.H. Friend: *Nature* **394**, 159 (1998).
- W. Hayes: *Contemp. Phys.* **19**, 469 (1978); P. Vashishta, J.N. Mundy, and G.K. Shenoy (eds.), *Fast Ion Transport in Solids: Electrodes and Electrolytes*, North-Holland, 1979 and references therein. See also: D. O'Connor, P. Barnes, D.R. Bates, and D.F. Lauder: *Chem. Comm.* 2527 (1998).
- M.J. Pregel, L. Jullien, and J.-M. Lehn: *Angew. Chem., Int. Ed. Engl.* **31**, 1637 (1992).
- For example: B. Hasenknopf, J.-M. Lehn, B.O. Kneisel, G. Baum, and D. Fenske: *Angew. Chem., Int. Ed. Engl.* **35**, 1838 (1996); J.S. Fleming, K.L.V. Mann, C.-A. Carraz, E. Psillakis, J.C. Jeffery, J.A. McCleverty, and M.D. Ward: *Angew. Chem., Int. Ed. Engl.* **37**, 1279 (1998); R. Vilar, D.M.P. Mingos, A.J.P. White, and D.J. Williams: *Angew. Chem., Int. Ed. Engl.* **37**, 1258 (1998); B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van-Dorsselaer, B. Kniessel, and D. Fenske: *J. Am. Chem. Soc.* **119**, 10956 (1997); B. Olenyuk, A. Fechtenkötter, and P.J. Stang: *J. Chem. Soc., Dalton Trans.* 1707 (1998); M. Withersby, A.J. Blake, N.R. Champness, P. Hubberstey, W.-S. Li, and M. Schröder: *Angew. Chem., Int. Ed. Engl.* **36**, 2327 (1997); M. Ziegler, J.J. Miranda, U.N. Anderson, D.W. Johnson, J.A. Leay, and K.N. Raymond: *Angew. Chem. Int. Ed. Engl.* **40**, 733 (2001) and references therein.
- M.D. Vargas and J.N. Nicholls: *Adv. Inorg. Chem. Radiochem.* **30**, 123 (1985); A. Simon: *Angew. Chem., Int. Ed. Engl.* **27**, 159 (1988); Early Transition Metal Clusters with π -Donor Ligands, M.H. Chisholm (ed.), VCH, New York (1995).
- S.M. Owen: *Polyhedron* **7**, 253 (1988); D.M.P. Mingos: *Nature Phys. Sci. (London)* **236**, 99 (1972); K. Wade: *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976).
- D.M.P. Mingos and M.J. Watson: *Adv. in Inorg. Chem.* **39**, 327 (1992).
- For example see: S.P. Watton, P. Fuhrmann, L.E. Pence, A. Caneschi, A. Cornea, G.L. Abbati, and S.J. Lippard: *Angew. Chem., Int. Ed. Engl.* **36**, 2774 (1997); R.A. Reynolds III and D. Coucouvanis: *J. Am. Chem. Soc.* **120**, 209 (1988); M. Murrie, S. Parsons, and R.E.P. Winpenny: *J. Chem. Soc., Dalton Trans.* 1423 (1988); E.K. Brechin, A. Graham, S.G. Harris, S. Parsons, and R.E.P. Winpenny: *J. Chem. Soc., Dalton Trans.* 3405 (1997); H.O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat, and O. Kahn: *J. Am. Chem. Soc.* **116**, 3866 (1994); C. Benelli, S. Parsons, G.A. Solan, and R.E.P. Winpenny: *Angew. Chem., Int. Ed. Engl.* **35**, 1825 (1996).

26. For example see: Y. Zhang, P.J. Zapf, L.M. Meyer, R.C. Haushalter, and J. Zubieta: *Inorg. Chem.* **36**, 2159 (1997); L. Suber, M. Bonamico, and V. Fares; *Inorg. Chem.* **36**, 2030 (1997); A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, C. Beugholt, P. Kögerler, and C. Lu: *Angew. Chem., Int. Ed. Engl.* **37**, 1220 (1998); A.K. Powell, S.L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo, and F. Pieralli: *J. Am. Chem. Soc.* **117**, 2491 (1995); A. Müller, F. Peters, M. J. Pope, and D. Gatteschi, *Chem. Rev.* **98**, 239 (1998).
27. A. Pajunen and S. Pajunen: *Acta. Crystallogr., Sect. B* **38**, 3093 (1982); A. Nakahara, H. Yamamoto, and H. Matsumoto: *Bull. Chem. Soc. Jpn.* **37**, 1137 (1964).
28. Y. Yukawa, S. Igarashi, A. Yamano, and S. Sato: *Chem. Commun.* 711 (1997).
29. R.W. Saalfank, I. Bernt, E. Uller, and F. Hampel: *Angew. Chem. Int. Ed. Engl.* **36**, 2482 (1997); R.W. Saalfank, N. Löw, S. Kareth, V. Seitz, F. Hampel, D. Stalke, and M. Teichert: *Angew. Chem. Int. Ed. Engl.* **37**, 173 (1998); R.W. Saalfank, N. Löw, F. Hampel, and H.-D. Stachel: *Angew. Chem. Int. Ed. Engl.* **35**, 2209 (1996); see also D.L. Caulder, R.E. Powers, T.N. Parac, and K.N. Raymond: *Angew. Chem. Int. Ed. Engl.* **37**, 1840 (1998).