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Na^+-Mediated aggregation of imino-carboxylate transition metal complexes †

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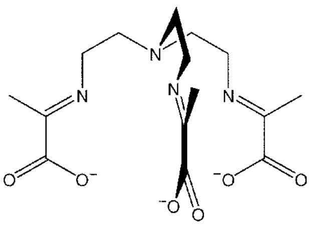
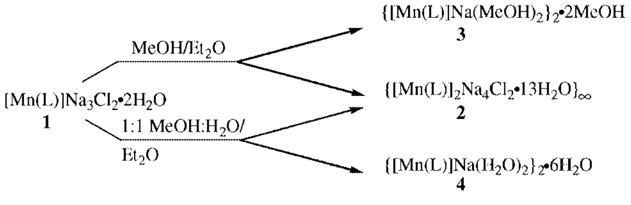
The imino-carboxylate complexes $[M(L)]^-$ (M = Mn, Ni) form the polymers $\{[Mn(L)]_2Na_4Cl_2\cdot13H_2O\}_\infty$ and $\{[Ni(L)]_2Na_4(BF_4)_2\}_\infty$ in the presence of Na^+; the degree of aggregation can be controlled by variation of the counter-anion and the amount of Na^+ present, the Na^+ ions forming sandwiched layers between aggregates of $[M(L)]^-$.

Aggregation of metal complexes of polychelate ligands through *exo* co-ordination of metal ions has resulted in the formation of a wide range of cluster and polymeric species.[1–4] In particular, carboxylate-based complexes are particularly effective in binding Group I and II metal ions.[2] For example, Na_2CO_3 can be encapsulated by [Gd(DO3A)] (DO3A = 1,4,7-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane) to form the complex cluster $[Gd(DO3A)]_3Na_2CO_3$,[3] while derivatives of *N*-hydroxyiminodiacetic acid (H_3hida) are able to adopt a variety of aggregation states in the presence of hard metal ions.[4] We were particularly interested in forming polymeric aggregates which feature channels or sheets of metal ions which may have potential as ionic conductors and charge-storage devices,[5,6] and as biomimetic models.[7] We report herein the controlled aggregation of Mn(II) and Ni(II) complexes of the imino-carboxylate ligand, L^{3-},[8] in the presence of Na^+ to give new polymeric sandwich materials.



L^{3-}

Reaction of tris(2-aminoethyl)amine (tren) with three equivalents of sodium pyruvate in the presence of $MnCl_2\cdot4H_2O$ followed by addition of excess Et_2O affords a white solid of stoichiometry $[Mn(L)]Na_3Cl_2\cdot2H_2O$, **1**. Although it is not known whether **1** is a single species or a mixture of products, dissolution of **1** in MeOH followed by slow diffusion of Et_2O affords pale yellow crystals of two distinct morphologies, acicular and hexagonal (Scheme 1).



Scheme 1

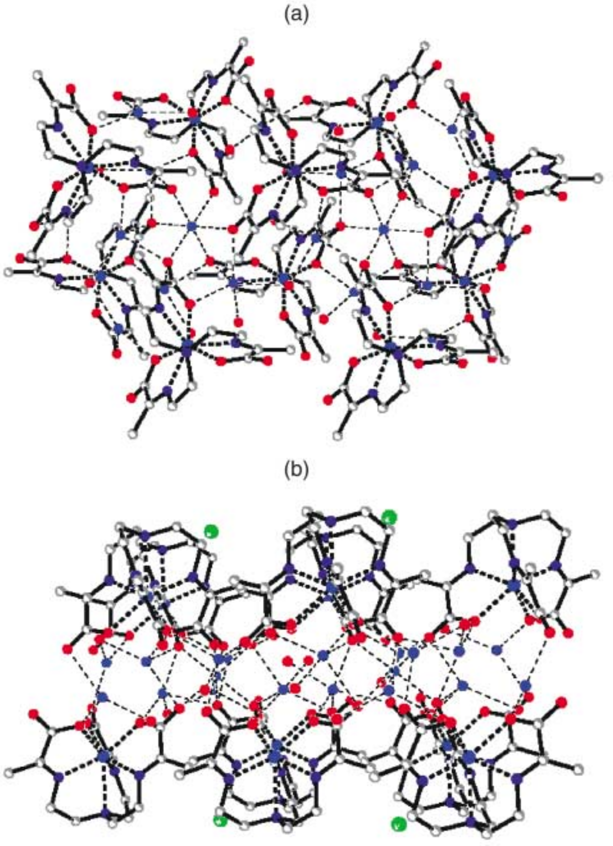


Fig. 1 Structure of **2** $\{[Mn(L)]_2Na_4Cl_2\cdot13H_2O\}_\infty$ viewed normal (a) and incident (b) to the plane of the structure. C—black open circles, N—dotted blue circles, O—red circles, Na—blue circles joined by thin dotted lines, Mn—blue circles joined by thick dotted lines. Cl—green circles (b only). All hydrogen atoms and the H_2O molecules which occupy the same layer as the chlorides have been omitted for clarity.

Single crystal X-ray diffraction on the hexagonal crystals reveals a co-ordination polymer of stoichiometry $\{[Mn(L)]_2Na_4Cl_2\cdot13H_2O\}_\infty$, **2**, (Fig. 1).[9] The structure consists of complex anions $[Mn(L)]^-$ in which Mn(II) lies on a crystallographic three-fold axis and is bound to L^{3-} *via* three carboxylate O-donors, Mn–O = 2.257(2) Å, three imine N-donors, Mn–N = 2.273(2) Å and, at longer range, the bridge-head tertiary N-donor, Mn–N = 2.597(4) Å, to give an overall seven co-ordinate Mn(II) centre. The three arms of the tripodal ligand twist about the Mn(II) centre with a pitch angle of 78.6°. Significantly, an infinite polymeric sheet of Na^+ ions bridge carboxylate O-donors of adjacent layers of $[Mn(L)]^-$ units with Na–O = 2.374(2)–2.592(3) Å. The Na^+ centres bind additionally to solvent water molecules, Na–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 $\{[Mn(L)]_2Na_4\}_\infty$ layers (Fig. 2).

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† Electronic supplementary information (ESI) available: further crystallographic details. See http://www.rsc.org/suppdata/dt/b1/b107873a/

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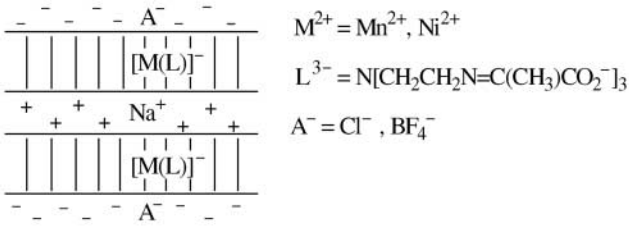

Fig. 2 Schematic of the layered structure of **2**.

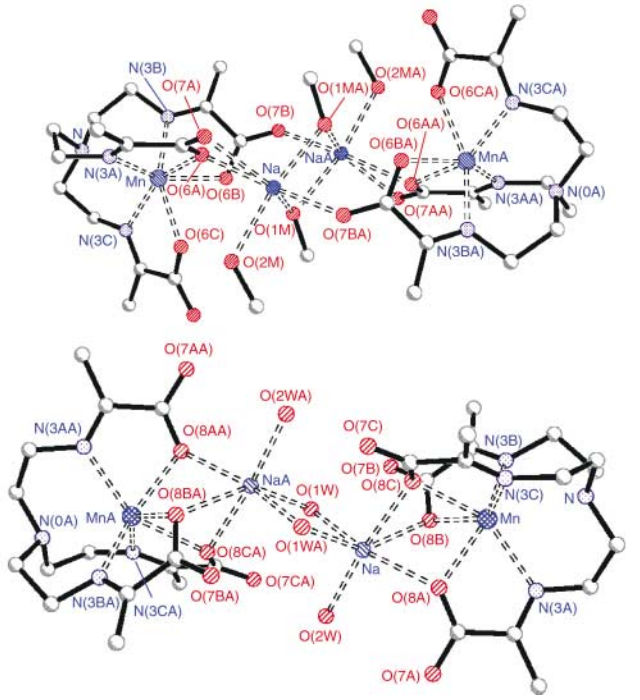

Fig. 3 Views of the structures of **3** $\{[Mn(L)]Na(MeOH)_2\}_2{\cdot}2MeOH$ and **4** $\{[Mn(L)]Na(H_2O)_2\}_2{\cdot}6H_2O$. Both structures lie across crystallographic inversion centres. All hydrogen atoms and unco-ordinated solvent molecules are omitted for clarity.

X-Ray diffraction studies on the acicular crystals reveal a tetranuclear cluster $\{[Mn(L)]Na(MeOH)_2\}_2{\cdot}2MeOH$, **3**,[9] in which two Na^+ cations are bound to carboxylate oxygens, Na–O(carboxylate) = 2.348(3)–2.686(3) Å, from two $[Mn(L)]^-$ anions, Mn–O = 2.234(2)–2.258(2), Mn–N(imine) = 2.260(2)–2.274(2), Mn–N(amine) = 2.658(2) Å (Fig. 3). The Na^+ cations also bind to two bridging and two terminal MeOH molecules, Na–O(MeOH) = 2.385(3)–2.390(3) Å, giving overall six co-ordination at Na^+.

Slow diffusion of Et_2O into a solution of **1** in a 1 : 1 mixture of MeOH and H_2O results in crystals of both the polymer **2** and the tetranuclear cluster, $\{[Mn(L)]Na(H_2O)_2\}_2{\cdot}6H_2O$, **4**. The structure of **4**[9] is analogous to that of **3** but with solvation of Na^+ cations in the former being by H_2O rather than MeOH, Na–O(carboxylate) = 2.339(4)–2.451(3), Na–O(H_2O) = 2.404(13)–2.457(5) Å, (Fig. 3). Significantly, bulk samples of the tetranuclear clusters **3** and **4** always contain the layered polymer **2** (Scheme 1). The primary difference in stoichiometry between these two aggregation states is that the planar polymer **2** contains two additional Na^+ and two additional Cl^- ions compared to the tetranuclear clusters **3** and **4**. Thus, **2** can be considered as being formed by the co-crystallisation of **3** or **4** 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 **2** crystallised from a solution of **1** is 17–21% by mass, the remainder being **3** or **4**. Elution of **1** in MeOH through a Sephadex LH-20 column followed by slow diffusion of Et_2O yields crystals which contain less than 2% of **2**. Thus, chromatography on Sephadex removes all the NaCl except for the one Na^+ per $[Mn(L)]^-$ unit required to maintain electroneutrality, resulting in the observed increase in tetranuclear clusters relative to layered polymer **2**. This demonstrates how the aggregation state of $[Mn(L)]^-$ can be controlled. Addition of NaCl to a solution of **1** would be expected to result in preferential crystallisation of **2**, but quantitative analysis is complicated by crystallisation of cubic NaCl at higher NaCl concentrations.

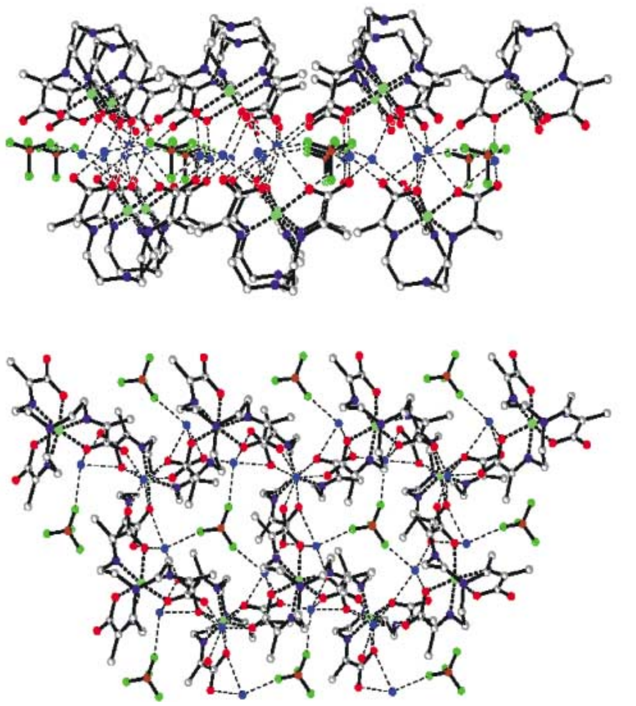

Fig. 4 Single crystal X-ray structure of **5**, $\{[Ni(L)]_2Na_4(BF_4)_2\}_\infty$ viewed normal and incident to the plane. Ni—light green circles, B—black circles, F—dark green circles. All hydrogen atoms and the unco-ordinated BF_4^- anions located between $\{[Ni(L)]_2Na_4(BF_4)\}_\infty$ layers are omitted for clarity.

Interestingly, when the BF_4^- anion is used in place of Cl^-, a solid precipitates with a $Na^+ : Mn^{2+}$ 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 Ni(II) analogue have been prepared. The complex $\{[Ni(L)]_2Na_4(BF_4)_2\}_\infty$, **5**, has been synthesised *via* reaction of tren with sodium pyruvate and $Ni(BF_4)_2{\cdot}6H_2O$ in MeOH followed by recrystallisation from MeOH–Et_2O. The single crystal X-ray structure of **5**[9] shows a layered polymeric sandwich structure (Fig. 4) similar to **2**, although the presence of BF_4^- in **5** leads to BF_4^- anions binding to three Na^+ cations within the Na^+ layer. The arms of L^{3-} helicate about Ni(II) with a pitch angle of 56.1° so that the Ni(II) cations are approximately octahedrally co-ordinated by three 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 **2**, Ni(II) in **5** does not interact strongly with the bridgehead amine N-donor, Ni···N = 3.15(2)–3.16(2) Å. The Na^+ cations in **5** are extensively disordered and interact with the carboxylate O-centres, Na–O = 2.25(2)–2.78(2) Å, and BF_4^- 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.[6] Future work will be concerned with studying the mobility of both anions and cations in the planar polymeric strucures **2** and **5**.

Significantly, elemental analysis and atomic absorption measurements indicate that **5** is the only species formed in the above reaction. The preference for the planar polymeric structure is attributed to the presence of BF_4^- 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,[10] the anion can be used to control the aggregation of complexes of L^{3-}.

Acknowledgements

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9 Crystal data for **2**: $C_{30}H_{68}N_8O_{25}Cl_2Na_4Mn_2$, yellow block, 0.51 × 0.51 × 0.33 mm, $M = 1213.66$, trigonal, space group $P\bar{3}$; $a = 9.004(5)$, $c = 18.119(12)$ Å, $U = 1272.0(14)$ Å^3, $T = 150(2)$ K, $D_c = 1.584$ g cm^{-3}, $Z = 1$. Of the 3090 reflections collected ($2\theta_{max} = 50°$, $-10 \le h \le 10$, $-9 \le k \le 10$, $0 \le l \le 21$), 1513 were unique ($R_{int} = 0.018$) and 1353 had $F \ge 4\sigma(F)$. The structure was solved using heavy atom and difference Fourier methods.[11] R_1 [$F \ge 4\sigma(F)$] = 0.0345, wR_2 [all data] = 0.0935 for 176 parameters, $(\Delta/\sigma)_{max} = 0.1$, largest difference peak and hole: 0.68 and −0.26 e Å^{-3}.

3: $C_{36}H_{66}N_8O_{18}Mn_2Na_2$, pale yellow trigonal prism, 0.78 × 0.62 × 0.46 mm, $M = 1054.82$, triclinic, space group $P\bar{1}$, $a = 10.094(3)$, $b = 11.423(5)$, $c = 12.613(3)$ Å, $\alpha = 104.16(4)$, $\beta = 107.27(3)$, $\gamma = 106.27(3)°$, $U = 1245.0(6)$ Å^3, $T = 150(2)$ K, $D_c = 1.407$ g cm^{-3}, $Z = 1$. Of the 4402 data collected ($2\theta_{max} = 50°$, $-12 \le h \le 11$, $-13 \le k \le 13$, $0 \le l \le 15$), 4381 were unique ($R_{int} = 0.012$) and 4058 had $F \ge 4\sigma(F)$. The structure was solved using direct methods and difference Fourier syntheses.[11] R_1 [$F \ge 4\sigma(F)$] = 0.0494, and wR_2 [all data] = 0.1366 for 312 parameters, $(\Delta/\sigma)_{max} = 0.002$, largest difference peak and hole: 0.85 and −0.53 e Å^{-3}.

4: $C_{30}H_{62}N_8O_{22}Mn_2Na_2$, colourless irregular block, 0.67 × 0.54 × 0.43 mm, $M = 1024.74$, triclinic, space group $P\bar{1}$, $a = 10.062(4)$, $b = 11.572(4)$, $c = 12.334(10)$ Å, $\alpha = 65.02(4)$, $\beta = 66.08(4)$, $\gamma = 71.21(3)°$, $U = 1170.1(9)$ Å^3, $T = 150(2)$ K, $D_c = 1.480$ g cm^{-3}, $Z = 1$. Of the 4704 data collected ($2\theta_{max} = 50°$, $-10 \le h \le 11$, $-12 \le k \le 13$, $-9 \le l \le 14$), 4001 were unique ($R_{int} = 0.033$) and 3589 had $F \ge 4\sigma(F)$. The structure solution employed direct methods and difference Fourier syntheses.[11] R_1 [$F \ge 4\sigma(F)$] = 0.0605, and wR_2 [all data] = 0.1697 for 321 parameters, $(\Delta/\sigma)_{max} = 0.07$, largest difference peak and hole: 1.00 and −0.73 e Å^{-3}.

5: $C_{30}H_{42}N_8O_{12}B_2F_8Na_4Ni_2$, blue hexagonal plate, 0.58 × 0.44 × 0.29 mm, $M = 1089.72$, trigonal, space group $P31c$, $a = 9.369(3)$, $c = 28.603(7)$ Å, $U = 2174.5(5)$ Å^3, $T = 150(2)$ K, $D_c = 1.664$ g cm^{-3}, $Z = 2$. Of the 4749 reflections collected ($2\theta_{max} = 50°$, $-11 \le h \le 11$, $-9 \le k \le 11$, $0 \le l \le 34$), 1284 were unique ($R_{int} = 0.111$) and 1111 had $F \ge 4\sigma(F)$. The structure solution was carried out using direct methods and difference Fourier syntheses.[11] The crystal was found to have two twin components related by the twin law (0 1 0/1 0 0/0 0 −1). R_1 [$F \ge 4\sigma(F)$] = 0.0694, and wR_2 [all data] = 0.1885 for 198 parameters, $(\Delta/\sigma)_{max} = 0.007$, largest difference peak and hole: +1.16 and −0.47 e Å^{-3}. CCDC reference numbers 171265–171268. See http://www.rsc.org/suppdata/dt/b1/b107873a/ for crystallographic data in CIF or other electronic format.

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