Alkali metal ion directed self-assembled Ni(II) molecular clusters†

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A series of Ni^{2+} complexes of *N*-(7-hydroxy-4-methyl-8-coumarinyl)-glycine (H_2mugly) and *N*-(7-hydroxy-4-methyl-8-coumarinyl)-L-alanine (H_2muala) has been prepared by self-assembly of $Ni(CH_3COO)_2{\cdot}4H_2O$ with ligands in the presence of alkali metal ions. The complexes have been characterized by elemental analysis, thermogravimetry, IR and ESI-MS studies, and several of these complexes have also been structurally characterized by X-ray crystallography. Interestingly, the alkali metal ions have been found to direct the self-assembly processes and facilitate the formation of oligonuclear structures. Structural investigations showed that the molecular clusters displayed intriguing architectures including heptanickel metallocrowns with highly symmetrical hexagonal shapes, a heterobimetallic molecular cage and a pentanickel cluster with a nanobasket shape. The diversity of the coordination geometries and the cluster structures are discussed in detail.

Introduction

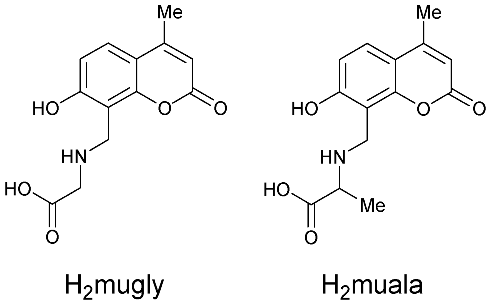
In the past decades, the chemistry of metal complexes with Schiff base ligands has been well studied. Rational design of ligand, metal selection and controlled experimental conditions have led to the creation of many polynuclear complexes with interesting structural and physico-chemical properties.[1] On the other hand, amino acids and their derivatives have been demonstrated to be ubiquitous ligands in the assembly of homo- and heterometallic clusters[2,3] which is attributed to the presence of both amino and carboxylate donor groups and various coordination modes. Nevertheless, relatively few polynuclear Schiff base complexes derived from salicaldehyde and amino acids have been reported. Our laboratory has been interested in the coordination chemistry of *N*-(2-hydroxybenzyl)-amino acids for some time.[4] In most cases, metal complexes were found to be dinuclear[5] while there are only a few examples of mononuclear[6] and multinuclear[7] complexes. Research by others also showed that the majority of the Schiff base and reduced Schiff base complexes exhibited mononuclear[8] and dinuclear[9] structures while limited literature on polynuclear complexes is available.[10]

As a part of our ongoing interest in the coordination chemistry of amino acid derivatives, we further explored the metal complexes of coumarin-derivatized amino acid ligands. Metal complexes of 4-methylumbelliferone-8-methyleneiminodiacetic acid exhibit interesting solid-state structures as mononuclear species, ion-pairs and coordination polymers. These complexes display extensive hydrogen bonding interactions owing to the presence of carboxylate, phenolate, solvents and solvated cations. It is worthwhile to note that the coumarin rings in the complexes are involved in π–π interactions which further facilitate the formation of ion-pair complexes.[11a,b] Recently, we have shown that Zn^{2+} and Mg^{2+} complexes of coumarin-derivatized amino acids, *N*-(7-hydroxy-4-methyl-8-coumarinyl)-amino acids, self-assemble into 1D coordination polymers and more interestingly form coordination polymeric gels.[11c,d] It is our interest to further study the complexation of this ligand system with other metal ions. It is anticipated that the cooperation of flexibility of the amino acid backbone, hydrogen bonding and π–π interactions will lead to interesting structural networks and polynuclear complexes. Herein, we report the synthesis, characterization and crystal structures of Ni^{2+} complexes of *N*-(7-hydroxy-4-methyl-8-coumarinyl)-amino acids.

Results and discussion

Synthesis

The Mannich base of the *N*-(7-hydroxy-4-methyl-8-coumarinyl)-amino acid ligands, namely H_2mugly and H_2muala, were synthesized by reacting 4-methylumbelliferone with the corresponding amino acid in the presence of formaldehyde, according to the reported literature method (Scheme 1).[11c] Complexes $[Ni_7(\mu_3\text{-}OH)_6(\text{mugly})_6][(\mu_3\text{-}OH)Li_3(H_2O)_3]_2{\cdot}7H_2O$ (**1**), $[Ni_7(\mu_3\text{-}OH)_6(\text{mugly})_6][(\mu_3\text{-}OH)Na_3(H_2O)_3]_2{\cdot}28H_2O$ (**2**), $[Ni_7(\mu_3\text{-}OH)_6(\text{mugly})_6][(\mu_3\text{-}OH)K_3(H_2O)_3]_2{\cdot}21H_2O$ (**3**), $[Ni_7(\mu_3\text{-}OH)_6(\text{muala})_6][(\mu_3\text{-}OH)Li_3(H_2O)_3]_2{\cdot}17H_2O$ (**4**),



Scheme 1 Structures of ligands used in this study.

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$[Ni_7(\mu_3\text{-}OH)_6(muala)_6][(\mu_3\text{-}OH)Na_3(H_2O)_3]_2\cdot 20H_2O$ (**5**), and $[Ni_7(\mu_3\text{-}OH)_6(muala)_6][(\mu_3\text{-}OH)K_3(H_2O)_3]\cdot 17H_2O$ (**6**) were prepared as bulk powdered samples by the reactions of $Ni(CH_3COO)_2\cdot 4H_2O$ with the corresponding ligands in the presence of two equivalents of MOH (M = Li, Na, K) in MeOH–Et_2O. Single crystals of **1** and $[Ni_7(mugly)_6(OH)_6][Na_6(OH)_2(H_2O)_6]\cdot 5H_2O$ (**2a**) were grown by slow evaporation in MeOH–DMF solvent systems. Complex $\{[Ni_4(mugly)_4(\mu_2\text{-}CH_3COO)_2(H_2O)_2][K_2(H_2O)_8(EtOH)_2]\}\cdot 3.6EtOH\cdot 2.4H_2O$ (**7**) was obtained by slow evaporation of the filtrate from the solvothermal reaction in H_2O–EtOH and KOH, while complex $[Ni_5(muala)_2(\mu_2\text{-}CH_3COO)_4(\mu_3\text{-}OH)_2(H_2O)_4]\cdot 2.75H_2O\cdot 0.5DMF$ (**8**) was isolated by slow evaporation in MeOH–DMF in the presence of LiOH. All the complexes were characterized by elemental analysis, thermogravimetry (TG) data, IR and ESI-MS studies, while complexes **1**, **2a**, **7** and **8** were structurally characterized by X-ray crystallography.

Physico-chemical studies

In all of the complexes, the IR spectra displayed a broad absorption band in the range of 3800–2600 cm^{-1}, which can be assigned to the O–H stretching of the carboxylate groups. The bands *ca.* 3420 cm^{-1} correspond to the presence of water molecules and this is further supported by the weight loss observed in TG. The absorption bands for phenoxo C–O are observed *ca.* 1393 cm^{-1}. The asymmetric $[\upsilon_{as}COO^-]$ and symmetric $[\upsilon_{s}COO^-]$ bands of the carboxylate group respectively, were observed in the region *ca.* 1685 and 1580 cm^{-1}. The $\Delta\upsilon$ value of *ca.* 100 cm^{-1} observed in these complexes suggests that the carboxylate groups are in the bridging mode.[12] The same findings have also been reflected in solid-state structures of these complexes.

The structural behavior of the complexes **1–8** in methanolic solution has been studied by ESI-MS. The major peaks can be assigned to the metal–ligand species containing solvent molecules. Oligonuclear species including Ni_2L_2, Ni_3L_3 and Ni_4L_4 (L = ligand H_2mugly or H_2muala) also have been observed in solution.

Description of crystal structures

Structure of H_2mugly·H_2O. H_2mugly was crystallized in the zwitterionic form; Fig. 1 shows a perspective view of H_2mugly·H_2O. The coumarin ring constitutes a plane and the carboxylate group is found to be out of plane with the coumarin ring by 111.3° which seems to prevent the close-packing of H_2mugly in the solid-state.

H_2mugly forms two types of π–π interactions with the adjacent molecules in the solid-state as shown in Fig. 2. The slip-stacked π–π stacking occurs between the pyranone rings with the distance between C10 and C12 being 3.307 Å (A). Another type of π–π stacking was found between the displaced hydroxybenzyl rings, and the distance between C1 and C2 is 3.381 Å (B). A further C=O···π parallel interaction is also observed (noted as C in Fig. 2).[5g,13] with a distance of 3.282 Å between the carbonyl oxygen O1 and the ring centroid, and the dihedral angle of 7.37° between the planes defined by C2C=O and the aromatic system. In other words, the carbonyl group is roughly parallel to the ring plane. Such a π–π interaction between the carbonyl group and the phenyl ring has been found responsible for weakening of the neighbouring hydrogen bonding, thermal dehydration behavior and preventing formation of new Cu–O bonds in the crystal lattice of $[Cu_2(Sgly)_2(H_2O)]\cdot H_2O$ (H_2Sgly = *N*-(2-hydroxybenzyl)-glycine).[5g] Though the pyranone rings are close to each other in the solid-state, [2 + 2] photodimerization cannot occur, since the C=C bonds are not aligned parallel to each other.

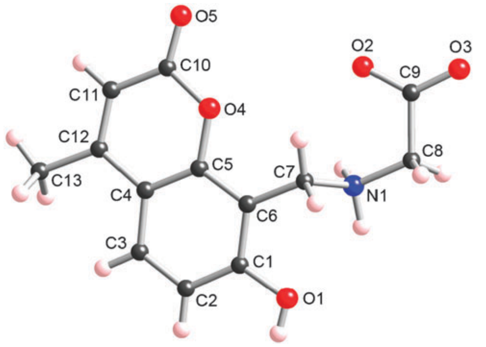


Fig. 1 A perspective view of H_2mugly·H_2O. The lattice water molecule is omitted for clarity.

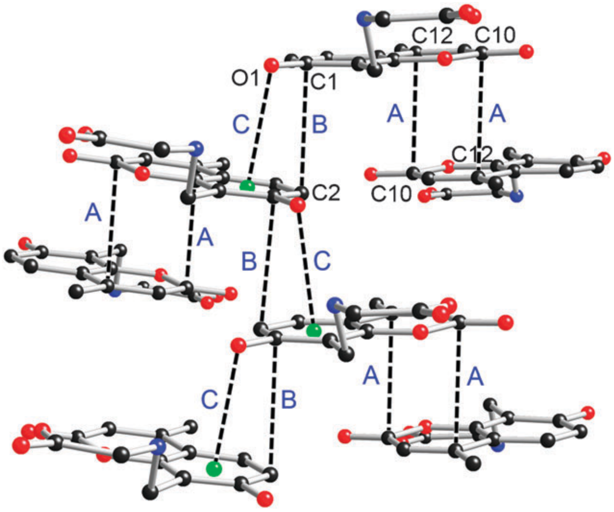


Fig. 2 A portion of H_2mugly showing the π–π interactions. Green atoms represent the centroids of the phenyl rings. All hydrogen atoms and water molecules have been omitted for clarity.

Extensive complementary O–H···O and N–H···O hydrogen bonding interactions have constructed the H_2mugly·H_2O into a 3D hydrogen-bonded polymer. As displayed in Fig. 3a, the hydrogen atoms of the amine groups are hydrogen-bonded to the lattice water, carboxylate O and phenol O atoms. Hydrogen-bonding interactions have also been observed between the phenolic hydrogen atom and both the carbonyl and carboxylate O atoms. Furthermore, pyranone carbonyl O atoms are hydrogen-bonded to the lattice water molecules. Interestingly, the packing of H_2mugly·H_2O viewed down from *c*-axis exhibits a porous channel as seen in Fig. 3b which also nicely exemplifies the segregation of the hydrophilic interactions and the hydrophobic interactions in the crystal packing. The total potential solvent area volume is 96 Å^3,

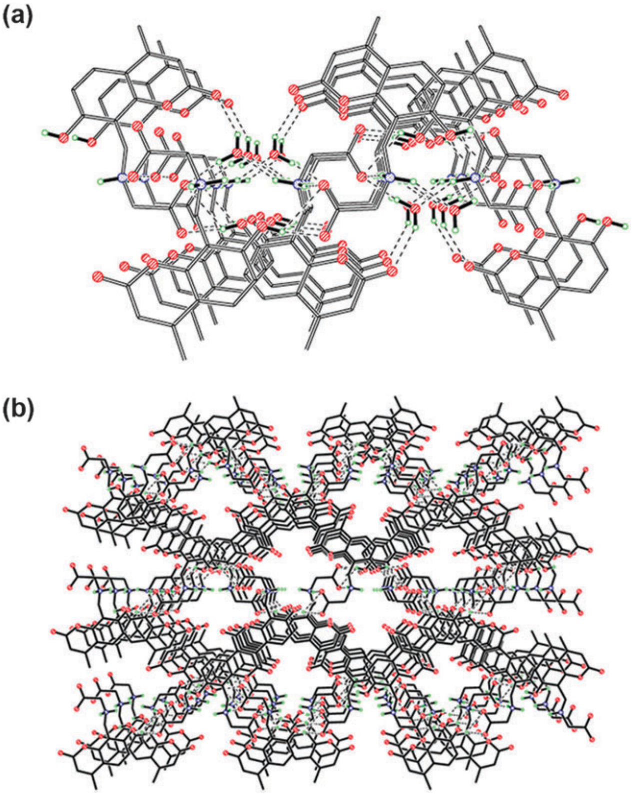


Fig. 3 (a) A portion of the 3D hydrogen-bonded network of H_2mugly; (b) Packing of H_2mugly viewed down the *c*-axis. All C–H hydrogen atoms are omitted for clarity.

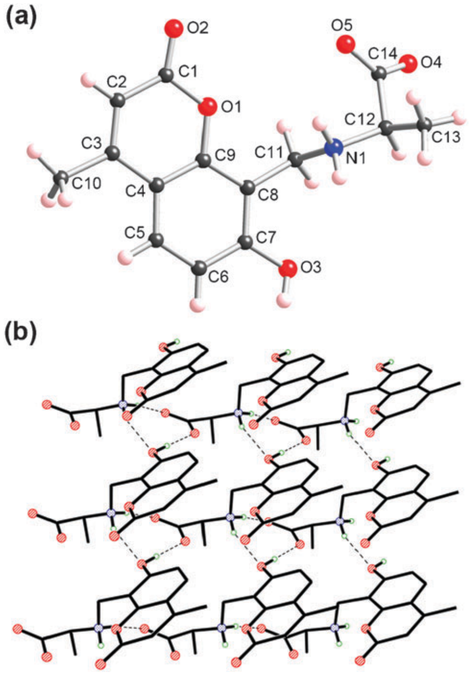


Fig. 4 (a) A perspective view of H_2muala; (b) Hydrogen-bonded 2D sheet structure of H_2muala. All C–H hydrogen atoms are omitted for clarity.

which is 7.5% per unit cell volume. Table 1 contains the selected hydrogen bond parameters of H_2mugly·H_2O.

Structure of H_2muala. H_2muala crystallized in the chiral space group *P*1 due to the chirality in the L-alanine side arm. A perspective view of H_2muala is displayed in Fig. 4a. Similar to H_2mugly, H_2muala also exists in the zwitterionic form, which is common in amino acid structures. The ligand H_2muala is packed in the solid-state to give a hydrogen-bonded 2D sheet as shown in Fig. 4b. The 2D sheet is constructed from the N–H···O and O–H···O hydrogen bonds between the amine N1, the carboxylate O4 and O5 and the phenol O3 with the $R_3^3(8)$ motif. The hydrogen bond parameters of H_2muala are given in Table 1.

Closer examination of the crystal structure of H_2muala reveals that a pair of C═C bonds in the pyrone rings are well aligned parallel to each other. However, the distance between the two C═C bonds is about 5.85 Å, which is too far for a photodimerization reaction to occur, based on the Schimidt criteria.[14] Though several exceptions to this rule have been noted before,[15] attempts to photodimerize H_2muala by irradiation under UV light for 60 h did not yield the dimerized products, as monitored by ^{1}H NMR spectroscopy.

Structures of 1 and 2a. Reactions of $Ni(CH_3COO)_2·4H_2O$ with H_2mugly in the presence of two equivalents of LiOH or NaOH in MeOH–DMF afforded crystals suitable for X-ray crystallographic studies. Although the preliminary crystallographic data shows that the structure of **1** is highly disordered, the existence of the $[Ni_7(\mu_3\text{-}OH)_6(\text{mugly})_6]^{4-}$ cation is confirmed beyond any doubt. Nonetheless, the positions of the Li^+ and the O atoms of the water molecules could not be resolved unambiguously. This is attributed to the disordered cations and solvents combined with the location of these atoms near crystallographically unique positions. In order to resolve this problem, complexes **2–6** were synthesized and

Table 1 Hydrogen bond parameters in H_2mugly and H_2muala

D–H	*d*(D···H)	*d*(H···A)	*d*(D···A)	∠DHA	A	Symmetry
H_2mugly						
N1–H1N	0.95	1.90	2.831	169	O2	$1 - x, -y, 2 - z$
O1–H1O	0.83	1.77	2.586	167	O3	$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$
O1S–H1S	0.89	1.93	2.800	167	O2	$1 - x, -y, 1 - z$
N1–H2N	0.96	2.06	2.935	151	O1S	$x, \frac{1}{2} - y, \frac{1}{2} + z$
O1S–H2S	0.90	2.49	3.321	154	O5	$1 - x, -y, 1 - z$
H_2muala						
N1–H1A	0.91	2.09	2.860	142	O3	$1 + x, y, z$
N1–H1B	0.91	1.84	2.744	171	O4	$x, -1 + y, z$
O3-H3	0.83	1.79	2.615	175	O5	$-1 + x, -1 + y, z$

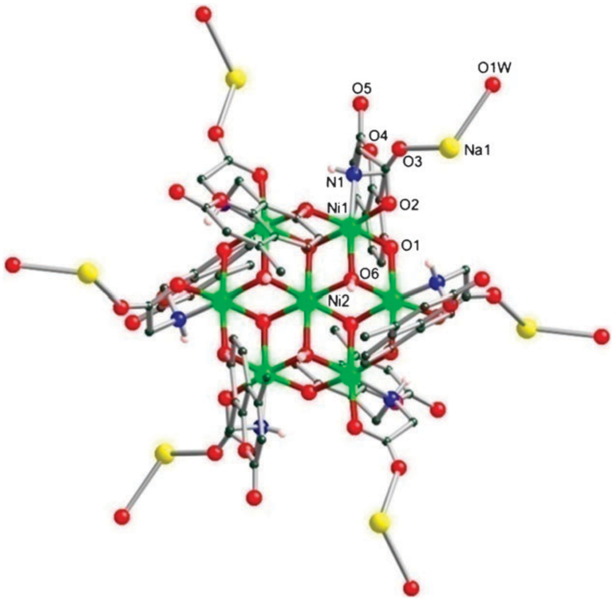


Fig. 5 A perspective view of the metallocrown ring in **2a**. All the hydrogen atoms and water molecules are omitted for clarity.

attempts were made to grow single crystals. We obtained single crystals of **2a** which is isostructural to **1**. Since the crystallographic data of **2a** is better resolved, we have only discussed the structure of **2a** in detail. Complexes **1–6** are expected to show structures analogous to **2a**.

A perspective view of **2a** is displayed in Fig. 5. The Ni atoms are arranged in a highly symmetrical hexagonal fashion, with six Ni atoms residing at the edges and the seventh Ni atom at the centre. The Ni1 centre has a distorted octahedral geometry in which amine N (Ni1–N1, 2.078(6) Å), carboxylate O (Ni1–O2, 2.085(5) Å) and two μ_3-hydroxo ligands (Ni1–O6, 2.023(5) Å and Ni1–O6a, 2.053(5) Å) occupy the equatorial plane and two phenoxo O (Ni1–O1, 2.130(5) Å and Ni1–O1a, 2.089(5) Å) fill the axial positions. Each phenoxo O atom bridges two Ni1 atoms and results in the formation of a hexanuclear Ni_6O_6 macrocycle ring. Six OH groups bridge the six peripheral Ni1 atoms and are further bonded to the central Ni2 (Ni2–O6, 2.077(4) Å), exhibiting μ_3-bonding.

Though there are many homo-[16,17] and mixed valance[18] heptanuclear complexes known in the literature, there are relatively few discrete homoheptanickel complexes.[16] Gatteschi *et al.* reported a distorted hexagon with the seventh Ni atom at the centre. The six Ni^{2+} atoms deviated from planarity by distances ranging from −0.026 to 0.999 Å, and the Ni7 was found to be 1.842 Å away from the plane.[16a] Herein, seven Ni^{2+} atoms of **2a** are coplanar with a RMS deviation of 0.0856 Å. Hence, **2a** is the first example of a homoheptanickel cluster in a highly symmetrical hexagonal shape. Of course, there are some disc-like heptanuclear clusters comprised of other metal ions[17d–f] and multinuclear Ni^{2+} clusters.[19]

The **2a** metallocrown ring has a crystallographic threefold rotational symmetry. In the cluster, the Ni–Ni distance from edge to edge is 3.126 Å and from the edge to centre is 3.121 Å. A closer examination at the Ni_7O_{12} cluster has revealed different types of Ni–O interactions as shown in Fig. 6. The distances between the Ni1 and phenoxo O are 2.130(5) Å (A) and 2.089(5) Å (B) and distances between Ni1 and μ_3-OH are 2.053(5) Å (C) and 2.023(5) Å (D). Interestingly, the Ni2 atom at the center displays an ideal octahedral geometry with a distance of 2.077(4) Å (E) between the Ni2 and the μ_3-OH.

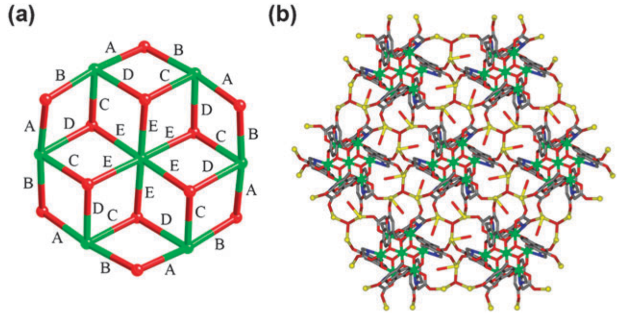


Fig. 6 (a) Simplified diagram of theNi$_7$O$_{12}$ cluster showing five types of Ni–O interactions; (b) A view of a two-dimensional sheet of **2a**.

It is noteworthy that the carboxylate groups of the six different mugly^{2-} ligands are bonded to six Na^+ atoms (Fig. 5). The six Na^+ ions are further bonded to the carbonyl O atoms of the coumarin rings of the neighbouring clusters, furnishing a 2D network as shown in Fig. 6b. Each Na^+ ion adopts a tetrahedral geometry which comprises a carboxylate O (Na1–O3, 2.677(8) Å), a carbonyl O (Na1–O5, 2.873(10) Å), a μ_3-hydroxide (Na1–O8, 2.86(3) Å) and a terminal aqua ligand (Na1–O7, 2.774(10) Å). $[Na_3(\mu_3\text{-}OH)(H_2O)_3]^{2+}$ units are present in this structure, where the μ_3-OH is disordered on both sides of the Na_3 plane. Due to the presence of the disordered atoms near the threefold rotation axis, the cations and guest molecules are not well-defined. Hence, they are not discussed in detail here.

Structure of 7. Complex **7** was obtained from the filtrate produced from the solvothermal reaction of $Ni(CH_3COO)_2{\cdot}4H_2O$ and H_2mugly in the presence of KOH. The X-ray crystal structure of **7** reveals a heterometallocyclic ring structure which comprises of four Ni^{2+} ions, four mugly^{2-} ligands and two solvated K^+ cations. A ball-and-stick diagram of **7** is shown in Fig. 7. The Ni1 centres have a distorted octahedral geometry with the amine N (Ni1–N1, 2.079(2) Å), carboxylate O (Ni1–O2, 2.049(2) Å), bridging acetate O (Ni1–O11, 2.066(2) Å) and the phenoxo O (Ni1–O6, 2.021(2) Å) occupying the equatorial plane, while another phenoxo O (Ni1–O1, 2.055(2) Å) and aqua ligand (Ni1–O1W, 2.082(2) Å) decorate the axial positions. The Ni2 centres are also positioned in an octahedral geometry with different donor atoms. The equatorial plane is filled by two phenoxo O atoms (Ni2–O1, 2.031(2) Å and Ni2–O6, 2.039(2) Å), an amine N (Ni2–N2, 2.067(2) Å) and an aqua ligand (Ni2–O13, 2.050(2) Å), while the axial positions are occupied by a carboxylate O (Ni2–O7, 2.073(2) Å) and a bridging acetate O (Ni2–O12, 2.088(2) Å). In contrast, the potassium cations have a distorted pentagonal bipyramidal geometry with four aqua ligands (K1–O1W, 2.836(2) Å; K1–O2W, 2.672(2) Å; K1–O3W, 2.928(4) Å and K1–O4W, 2.777(3) Å) and an oxygen atom of the acetate anion (K1–O11, 2.908(2) Å) occupying the equatorial positions and a carbonyl O from the coumarin ring

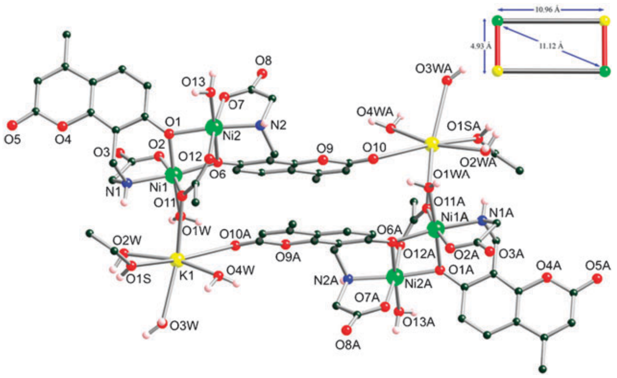


Fig. 7 A ball-and-stick diagram of **7**. All C–H hydrogen atoms and solvent molecules have been omitted for clarity. The atoms labeled with the suffix "A" are related by the symmetry $-x + 1, -y, -z + 1$. Inset shows a schematic representation of the heterobimetallic cage with dimensions.

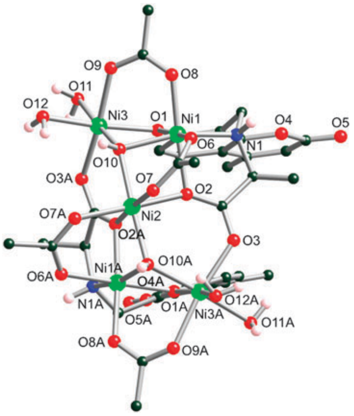


Fig. 8 A perspective view of **8** showing a pentanickel cluster. All C–H hydrogen atoms and solvent molecules have been omitted for clarity. The atoms with the extension "A" are related by the symmetry $-x + 2, y, -z + \frac{1}{2}$.

(K1–O10a, 3.256(2) Å) and an O from the ethanol molecule (K1–O1S, 2.861(3) Å), occupying the axial positions.

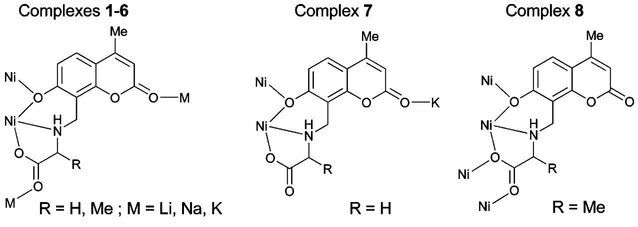
In this context, the phenoxo group bridges two Ni^{2+} ions to form a Ni_2O_2 ring. The dihedral angle between the two coumarin rings in the Ni_2 dimer is 83.4°, indicating they are approximately at right-angles to each other. More interestingly, the carbonyl O atoms in the pyranone rings are coordinated to the K^+ ions. It is rare that the carbonyl O in the pyranone ring is involved in coordination to a metal centre.[20] It is noted that this is the first example of a coordination of a carbonyl O in a pyranone ring to a main group metal. The coordination of both the phenoxo O and the carbonyl O have transformed the mugly^{2-} ligands into rigid spacer ligands. One of the aqua ligands of Ni1 and O of the bridging acetate is also coordinated to a K^+ centre. Interactions of the bridging carbonyl O atoms of the spacer ligand have transformed the dimeric Ni units and solvated K^+ species into a heterobimetallic metallocycle. The inset in Fig. 7 shows the metal connectivity of the metallocage **7**. This metallocycle has a rectangular shape with distances between the centres of Ni_2O_2 rings and potassium atoms being 4.93 Å and 10.96 Å. The diagonal distance between the two centres of the Ni_2O_2 rings is 11.12 Å. To date, there have been only two reported heterobimetallic cages comprising of Ni and K.[21]

Potassium cations act as a "template" to direct the coumarin rings with a parallel alignment. Here, the two coumarin rings are arranged roughly face-to-face with weak a π–π interaction. The distance between the centroids is 3.907 Å. While this interaction is not strong, the short distance is close enough for the [2 + 2] photodimerization of the coumarin moiety.[14] However, it is noted that the coumarin rings are related by the centre of inversion, thus preventing a cycloaddition reaction.

Structure of 8. A perspective view of **8** is shown in Fig. 8. The molecular structure of **8** consists of five Ni^{2+} atoms in a closed, cage-like arrangement. All the Ni^{2+} atoms are in distorted octahedral geometries and held together by muala^{2-}, acetate and hydroxide ligands. The Ni1 centres contain a amine N (Ni1–N1, 2.057(4) Å), phenoxo O (Ni1–O1, 2.039(3) Å), carboxylate O (Ni1–O2, 2.025(3) Å), μ_3-hydroxo O (Ni1–O10, 2.027(3) Å) and two μ_2-acetato O (Ni1–O6, 2.102(3) Å and Ni1–O8, 2.016(3) Å) donor atoms. The coordination geometry around the Ni3 center is comprised of phenoxo O (Ni3–O1, 2.047(3) Å), carboxylate O (Ni3–O3, 2.081(3) Å), μ_2-acetate O (Ni3–O9, 2.096(3) Å), μ_3-hydroxo O (Ni3–O10, 2.036(3) Å) and two aqua ligands (Ni3–O11, 2.045(3) Å and Ni3–O12, 2.057(3) Å). The Ni2 resides on the crystallographic twofold rotational axis. The octahedral geometry at the Ni2 atom is defined by the carboxylate O (Ni2–O2a, 2.045(3) Å), the μ_2-acetate O (Ni2–O7a, 2.053(3) Å) and the μ_3-hydroxide O (Ni2–O10a, 2.024(3) Å) donor atoms.

In this compound the Li^+ ion is not present; however, the hydroxide ion is believed to originate from the base. The phenoxo O atoms of the two ligands facilitated the bridging of the Ni^{2+} ions to form a rigid Ni_2O_2 ring. It may be noted that the hydroxo O bridges the Ni^{2+} centres in a μ_3-fashion. Furthermore, the carboxylate donor groups in muala^{2-} are also coordinated in a μ_3-fashion. The presence of the acetate anions has facilitated the bridging of the Ni^{2+} ions and formed a rigid and stable metal cluster. Scheme 2 illustrates the binding modes of mugly^{2-} and muala^{2-} in complexes **1–8**.

The phenolate, carboxylate, acetate and hydroxide groups have self-assembled with Ni^{2+} atoms into a novel and interesting pentanickel cage. Discrete homopentanuclear Ni^{2+} clusters[22] and linear chains[23] are relatively uncommon. More interestingly, all the Ni^{2+} and bridging O atoms are positioned on one side of the molecule to form a cage with width 5.3 Å and depth 9.1 Å, while two muala^{2-} ligands are directed outwards from the cage as shown in Fig. 9. This structure resembles a "basket", in which the pentanickel cluster acts as the base of the basket and the muala^{2-} ligands function as its handle. Hence, **8** can be described as a molecular basket.



Scheme 2 Binding modes of mugly^{2-} and muala^{2-} in complexes **1–8**.

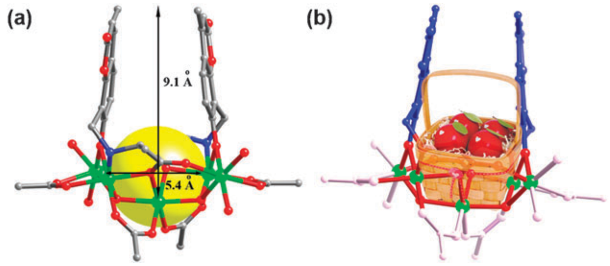


Fig. 9 (a) Molecular structure of **8** showing (a) the cavity; (b) the molecular basket shape.

Conclusions

Ni^{2+} complexes containing *N*-(7-hydroxy-4-methyl-8-coumarinyl)-amino acid ligands, H_2mugly and H_2muala have been demonstrated to form polynuclear clusters directed by alkali metal ions. The structures of these Ni^{2+} clusters display diverse and unprecedented architectures including the hepta-nickel hexagonal clusters, a nickel–potassium heterobimetallic metallocrown and a pentanickel cage. Such polymetallic clusters are of emerging research interest in view of structural and magnetic investigations. The isolation of these novel aggregates is an elegant example of an alkali-metal-templated self-assembly process.

Experimental

Materials and physical measurements

All reagents were commercially available and were used as received. The yields are reported with respect to the metal salts. The elemental analyses were performed in the micro-analytical laboratory, Department of Chemistry, National University of Singapore. The infrared spectra (KBr pellet) were recorded using an FTS165 Bio-Rad FTIR spectrophotometer in the range of 4000–400 cm^{-1}. ESI mass spectra were recorded on a Finnigan MAT LCQ mass spectrometer using the syringe pump method. Solvent presence in the compounds was determined using an SDT 2960 TGA thermal analyzer with a heating rate of 5 °C min^{-1} from room temperature to 500 °C in a N_2 atmosphere using a 5–10 mg sample per run.

Synthesis

$[Ni_7(\mu_3\text{-}OH)_6(mugly)_6][(\mu_3\text{-}OH)Li_3(H_2O)_3]_2\cdot 7H_2O$ (1). To a solution of H_2mugly (53.4 mg, 0.2 mmol) and LiOH (9.6 mg, 0.4 mmol) in MeOH (4 mL), was added $Ni(CH_3COO)_2\cdot 4H_2O$ (50 mg, 0.2 mmol) in MeOH (4 mL). The mixture was layered with excess Et_2O. After 1 day a green precipitate was obtained and filtered off, washed with Et_2O and then dried under vacuum. Yield: 72 mg, (15%). Anal. Calcd. for $C_{78}H_{100}N_6O_{51}Li_6Ni_7$ (2390.16): C, 39.20; H, 4.22; N, 3.52; found: C, 39.77; H, 4.58; N, 2.65; IR (KBr)/cm^{-1}: 3413, 1686, 1583, 1392; *m*/*z* (ESI)/(I_{rel} (%), ion): 326.1 (96, $[Ni(mugly)Li]^+$), 392.7 (84, $[Ni(mugly)(H_2O)_4H]^+$), 428.9 (68, $[Ni(mugly)(H_2O)_6H]^+$), 772.9 (38, $[Ni_2(mugly)_2(H_2O)_2\ (CH_3OH)_3H]^+$), 980.9 (48, $[Ni_3(mugly)_3(H_2O)Li]^+$), 1210.6 (48, $[Ni_2(Hmugly)_4(CH_3OH)Li]^+$), 1340.4 (40, $[Ni_4(mugly)_4\ (CH_3OH)_2H]^+$), 1693.9 (70, $[Ni_6(mugly)_6(H_2O)(CH_3OH)H]^+$). Calcd. TG weight loss for $13H_2O$ 9.8%; found 10.7%.

X-ray-quality green cubic crystals of **1** were obtained by slow evaporation, over three weeks, of the reaction mixture containing H_2mugly in MeOH (3 mL) and $Ni(CH_3COO)_2\cdot 4H_2O$ in DMF (1 mL).

$[Ni_7(\mu_3\text{-}OH)_6(mugly)_6][(\mu_3\text{-}OH)Na_3(H_2O)_3]_2\cdot 28H_2O$ (2). Complex **2** was prepared as described for **1** but by using NaOH. Yield: 90 mg, (16%). Anal. Calcd. for $C_{78}H_{142}N_6O_{72}Na_6Ni_7$ (2864.78): C, 32.7; H, 5.00; N, 2.93; found: C, 33.42; H, 4.69; N, 2.14; IR (KBr)/cm^{-1}: 3437, 1685, 1580, 1393; *m*/*z* (ESI)/(I_{rel} (%), ion): 429 (100, $[Ni(mugly)(H_2O)_6H]^+$), 650.1 (18, $[Ni(mugly)_2(H_2O)_2(CH_3OH)]^+$). Calcd. TG weight loss for 34 H_2O 21.4%; found 21.9%.

X-ray-quality green cubic crystals of **2a** were obtained as described for **1**.

$[Ni_7(\mu_3\text{-}OH)_6(mugly)_6][(\mu_3\text{-}OH)K_3(H_2O)_3]_2\cdot 21H_2O$ (3). Complex **3** was prepared as described for **1** but by using KOH. Yield: 108 mg, (19%). Anal. Calcd. for $C_{78}H_{128}N_6O_{65}K_6Ni_7$ (2835.32): C, 33.04; H, 4.55; N, 2.96; found: C, 33.99; H, 4.47; N, 2.20; IR (KBr)/cm^{-1}: 3420, 1681, 1582, 1393; *m*/*z* (ESI)/(I_{rel} (%), ion): 1116.0 (26, $[Ni_3(mugly)_3(CH_3OH)_5H]^+$), 1314.6 (60, $[Ni_4(mugly)_4(H_2O)_2H]^+$), 1336.5 (76, $[Ni_4(mugly)_4(H_2O)K]^+$), 1650.8 (46, $[Ni_5(mugly)_5(CH_3OH)(H_2O)H]^+$); Calcd. TG weight loss for 27 H_2O 17.7%; found 17.3%.

$[Ni_7(\mu_3\text{-}OH)_6(muala)_6][(\mu_3\text{-}OH)Li_3(H_2O)_3]_2\cdot 17H_2O$ (4). Complex **4** was prepared as described for **1** but by using H_2muala. Yield: 68 mg, (13%). Anal. Calcd. for $C_{84}H_{132}N_6O_{61}Li_6Ni_7$ (2654.48): C, 38.01; H, 5.01; N, 3.17; found: C, 38.62; H, 4.95; N, 2.49; IR (KBr)/cm^{-1}: 3415, 1685, 1583, 1393; *m*/*z* (ESI)/(I_{rel} (%), ion): 352.7 (70, $[Ni(muala)(H_2O)H]^+$, 431.8 (100, $[Ni(muala)(CH_3OH)_3H]^+$), 769.2 (22, $[Ni_2(muala)_2(H_2O)_2(CH_3OH)_2H]^+$), 1080.7 (32, $[Ni_3(muala)_3(H_2O)(CH_3OH)_2H]^+$), 1407.1 (44, $[Ni_4(muala)_4(H_2O)_4H]^+$); Calcd. TG weight loss for 23 H_2O 15.6%; found 16.0%.

$[Ni_7(\mu_3\text{-}OH)_6(muala)_6][(\mu_3\text{-}OH)Na_3(H_2O)_3]_2\cdot 20H_2O$ (5). Complex **5** was prepared as described for **1** but by using H_2muala and NaOH. Yield: 112 mg, (20%). Anal. Calcd. for $C_{84}H_{138}N_6O_{64}Na_6Ni_7$ (2804.81): C, 35.97; H, 4.96; N, 3.00; found: C, 35.98; H, 4.68; N, 2.49; IR (KBr)/cm^{-1}: 3433, 1686, 1579, 1393; *m*/*z* (ESI)/(I_{rel} (%), ion): 309.8 (100, $[(H_2muala)(CH_3OH)H]^+$), 448.9 (10, $[Ni(muala)(H_2O)(CH_3OH)_3H]^+$), 612.7 (14, $[Ni(muala)(H_2muala)H^+$), 728.1 (28, $[Ni_2(muala)_2(H_2O)_2Na]^+$, 1349.2 (12, $[Ni_4(muala)_4(H_2O)H]^+$); Calcd. TG weight loss for 26 H_2O 16.7%; found 16.7%.

$[Ni_7(\mu_3\text{-}OH)_6(muala)_6][(\mu_3\text{-}OH)K_3(H_2O)_3]\cdot 17H_2O$ (6). Complex **6** was prepared as described for **1** but by using H_2muala and KOH. Yield: 70 mg, (25%). Anal. Calcd. for $C_{84}H_{132}N_6O_{60}K_6Ni_7$ (2847.39): C, 35.43; H, 4.67; N, 2.95; found: C, 36.05; H, 5.06; N, 2.62; IR (KBr)/cm^{-1}: 3422, 1684, 1579, 1396; *m*/*z* (ESI)/(I_{rel} (%), ion): 409.3 (18, $[Ni(muala)(H_2O)_3Na]^+$), 1121.9 (88, $[Ni_3(muala)_3)(H_2O)_2(CH_3OH)_2Na]^+$), 1431.6 (76, $[Ni_4(muala)_4(CH_3OH)_3H]^+$), 2030.7 (98, $[Ni_6(muala)_6(CH_3OH)H]^+$); Calcd. TG weight loss for 23 H_2O 9.8%; found 10.8%.

Table 2 Crystallographic data and structure refinement details

	H_2mugly	H_2muala	**2a**	**7**	**8**
Formula	$C_{13}H_{15}NO_6$	$C_{14}H_{15}NO_5$	$C_{78}H_{96}N_6Na_6Ni_7O_{49}$	$C_{67.2}H_{108.2}K_2N_4Ni_4O_{42}$	$C_{39}H_{59}N_3Ni_5O_{30.5}$
FW/g mol^{-1}	281.26	277.27	2450.52	1957.22	1351.44
Crystal system	Monoclinic	Triclinic	Trigonal	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P1$	$R\bar{3}$	$P2_1/c$	$C222_1$
a/Å	11.6019(13)	5.3583(5)	15.4367(9)	22.5549(16)	13.9467(5)
b/Å	15.159(2)	5.8497(6)	15.4367(9)	12.9601(9)	26.2945(10)
c/Å	7.5024(9)	10.4352(10)	35.721(4)	15.0085(10)	16.3610(6)
α (°)	90	88.144(2)	90	90	90
β (°)	103.930(3)	75.461(2)	90	105.823(2)	90
γ (°)	90	82.331(2)	120	90	90
V/Å^3	1280.7(3)	313.78(5)	7371.6(10)	4221.0(5)	5999.9(4)
Z	4	1	3	2	4
μ/mm^{-1}	0.117	0.112	1.439	1.074	1.496
D_{calc}/Mg m^{-3}	1.459	1.467	1.656	1.540	1.496
Reflections collected	8861	3256	13 252	29 384	21 518
Independent reflections	2927	1669	3003	9687	6891
R_{int}	0.0492	0.0066	0.0871	0.0444	0.0548
Data/restraints/parameters	2927/2/197	1669/3/184	3003/0/222	9687/12/617	6891/17/379
Goodness-of-fit on F^2	1.026	1.070	1.032	1.038	1.030
Final R [$I > 2\sigma(I)$], R_1 [a]	0.0846	0.0389	0.0795	0.0487	0.0473
wR_2 [b]	0.2103	0.1007	0.1900	0.1208	0.1172
Absolute structure parameter	—	—	—	—	0.020(17)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

{[Ni_4(mugly)$_4$(μ_2-CH_3COO)$_2$(H_2O)$_2$][K_2(H_2O)$_8$(EtOH)$_2$]}·3.6EtOH·2.4H_2O (7). A solution of H_2mugly (52.6 mg, 0.2 mmol), KOH (22.4 mg, 0.4 mmol) and Ni(CH_3COO)$_2$·4H_2O (50.0 mg, 0.2 mmol) in H_2O (1 mL) and EtOH (3 mL) was heated at 70 °C in a Teflon-capped 20 mL scintillation vial for 1 day. Green cubic crystals were obtained after the solution mixture was cooled down and left undisturbed for two days. Yield: 60 mg, (34%). Anal. Calcd. for the desolvated compound $C_{64}H_{86}N_4O_{38}K_2Ni_4$ (1832.36): C, 41.95; H, 4.73; N, 3.06; found: C, 41.11; H, 4.35; N, 3.34; IR (KBr)/cm^{-1}: 3409, 3237, 1688, 1580, 1393; m/z (ESI)/(I_{rel} (%), ion): 352.0 (78, [Ni(mugly)(CH_3OH)]$^+$), 383.8 (100, [Ni(mugly)(CH_3OH)$_2$]$^+$), 389.8 (80, [Ni(mugly)(CH_3OH)(H_2O)$_2$]$^+$); 417.9 (46, [Ni(mugly)(CH_3OH)$_3$]$^+$), 670.7 (60, [Ni_2(mugly)$_2$(CH_3OH)]$^+$), 670.7 (60, [Ni_2(mugly)$_2$(CH_3OH)]$^+$), 774.9 (36, [Ni_2(mugly)$_2$(CH_3OH)(H_2O)$_2$]$^+$), 997.9 (32, [Ni_3(mugly)$_3$(H_2O)$_2$]$^+$), 1095.8 (30, [Ni_3(mugly)$_3$(CH_3OH)(H_2O)$_4$]$^+$); Calcd. TG weight loss for 12 H_2O and 2 EtOH 16.8%; found 16.0%.

[Ni_5(muala)$_2$(μ_3-CH_3COO)$_4$(μ_3-OH)$_2$(H_2O)$_4$]·2.75H_2O·0.5DMF (8). To a solution of H_2muala (55.4 mg, 0.2 mmol) and LiOH (9.6 mg, 0.4 mmol) in methanol (2 mL), was added Ni(CH_3COO)$_2$·4H_2O (50 mg, 0.2 mmol) in DMF (10 mL). The reaction was stirred for 30 min and filtered. X-ray-quality green cubic crystals were obtained after one month. Yield: 49 mg, (41%). Anal. Calcd. for $C_{39}H_{47}N_3O_{21}Ni_5$ (1187.28): C, 39.45; H, 3.99; N, 3.54; found: C, 40.82; H, 4.60; N, 3.95; IR (KBr)/cm^{-1}: 3406, 1686, 1585, 1392; m/z (ESI)/(I_{rel} (%), ion): 387.0 (40, [Ni(muala)(H_2O)$_3$]), 474 (32, [Ni(muala)(H_2O)$_6$(CH_3OH)]$^-$), 556.1 (30, [Ni(muala) (CH_3OH)$_7$(H_2O)$_3$]$^-$); Calcd. TG weight loss for DMF 5.8%; found 6.1%.

X-ray crystallography

The diffraction experiments were carried out on a Bruker AXS SMART CCD diffractometer. The program SMART[24] was used for collecting frames of data, indexing reflections and determining lattice parameters. SAINT[24] was used for integration of the intensity of reflections and scaling, SADABS[25] for absorption correction and SHELXTL[26] for least-squares refinements on F^2, space group and structure determination. Selected crystallographic data and refinement details are displayed in Table 2. Complexes **1** and **2a** cannot be resolved unambiguously due to the disordered cations and solvents. Complex **1** is presented as a preliminary structure only, hence no crystallographic data has been provided. Although the connectivity in the [Ni_7(mugly)$_6$(OH)$_6$]$^{4-}$ cation is confirmed beyond any doubt, the positions of the Li^+ and Na^+, the O atoms of the water molecules and hydroxide anions could not be resolved unambiguously. This is attributed to disordered cations and solvents combined with the location of these atoms near crystallographically unique positions. Furthermore, the amount of lattice water molecules could not be determined by TG with certainty, as the crystal loses solvent molecules in air. These problems have hindered detailed understanding of the supramolecular interactions. Lattice solvent molecules in complexes **7** and **8** were disordered and resolved in partial occupancy.

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