Facile Carboxylate Ligand Variation of Heterotrimetallic 12-Metallacrown-4 Complexes

Jordan R. Travis^a, Matthias Zeller^b, and Curtis M. Zaleski^{a*}

^aDepartment of Chemistry, Shippensburg University, Shippensburg, Pennsylvania 17257-2200, United States of America

^bDepartment of Chemistry, Youngstown State University, Youngstown, Ohio 44555-0001, United States of America

*Corresponding Author: Curtis M. Zaleski, Department of Chemistry, Shippensburg University, E-mail: cmzaleski@ship.edu, Phone: (717) 477-1522, Fax: (717) 477-4048

Abstract

Single crystal X-ray structures are presented for three 12-metallacrown-4 complexes, $\text{Er}^{\text{III}}\text{Na}(\text{L})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^-}4]$, where L is trimethylacetate (OTMA), benzoate (OBen), or salicylate (OSal), MC is metallacrown, and shi^{3-} is salicylhydroximate: $\text{Er}^{\text{III}}\text{Na}(\text{OTMA})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^-}4](\text{H}_2\text{O})_{3.73}(\text{DMF})_{0.27} \cdot 7.45\text{DMF} \cdot 1.47\text{H}_2\text{O}$, **1**, $\text{Er}^{\text{III}}\text{Na}(\text{OBen})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^-}4](\text{H}_2\text{O})_4 \cdot 4\text{DMF} \cdot 0.87\text{H}_2\text{O}$, **2**, and $\text{Er}^{\text{III}}\text{Na}(\text{OSal})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^-}4](\text{H}_2\text{O})_{3.54}(\text{DMF})_{0.73} \cdot 4\text{DMF} \cdot 0.24\text{H}_2\text{O}$, **3**, where DMF is *N,N*-dimethylformamide. Compounds **1** – **3** demonstrate the facile ligand variation of a self-assembled supramolecular coordination complex containing three different metal types. In all three structures, the monoanion carboxylate ligands serve as bridges between the central Er^{III} ion and the ring Mn^{III} ions. The structures of **1** – **3** are all domed towards the side of the central Na^+ ion, and the 12-MC-4 frameworks of **1** – **3** are very similar regardless of the monoanion carboxylate bridge, as the metallacrown cavity radii of **1** – **3** are 0.55 Å, 0.54 Å, and 0.55 Å, respectively. In addition, the cross cavity measurements indicate that the metallacrown frameworks are not significantly altered by the presence of different monoanion carboxylate ligands as the $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$ cross cavity distances for **1** – **3** are 6.52 Å, 6.51 Å, and 6.49 Å, respectively, and the oxime oxygen – oxime oxygen cross cavity distances for **1** – **3** are 3.71 Å, 3.68 Å, and 3.69 Å, respectively. The conservation of the 12-MC-4 framework among the different structures will be important when assessing the physical properties this class of molecules.

Keywords

metallacrown; heterotrimetallic; coordination complex; self-assembly; supramolecular

Introduction

The purposeful design of supramolecular coordination complexes is of particular interest to inorganic chemists. The labile nature of coordination bonds, flexibility of metal coordination geometry, and multiple binding modes of ligands can lead to a multitude of interesting structures with unique properties; thus, the ability to control the formation of specific metal – ligand bonds in a particular geometry can be elusive. Unlike organic chemistry with well understood reaction mechanisms, many inorganic molecules are the result of yet unpredictable interactions between the metal center and ligands [1]. Self-assembled coordination complexes though provide an opportunity to direct the synthetic route to a particular molecular target. The typical requirement is a rigid multidentate ligand that can pre-determine the orientation, number, and types of bonds that the metal center can obtain [2]. Using the self-assembly strategy, polymetallic grids, cages, cycles, calixarenes, helicates, wheels, polyhedra, two- and three-dimensional structures, and other polymetallic supramolecular coordination complexes can be designed [3]. Through self-assembly synthetic schemes, the properties of a molecule can be tailored as different metals and ligands can impart particular physical and chemical properties. Self-assembled polymetallic supramolecules have numerous applications including molecular magnetism, photophysical properties, host-guest chemistry, catalysis, and sensing [3].

Despite the success of the self-assembly strategy, the synthetic control of a system that contains multiple different metal types and ligand components still remains a difficult task. One particular class of macrocycles that has been very successful in this regard is metallacrowns (MCs) [4]. Considered the structural and functional inorganic analogues of crown ethers, the original version of these molecules self-assemble in solution to form molecules with a metal-nitrogen-oxygen ring repeat unit and a metal ion captured in a central cavity formed by the ligands [4]. Since 1989 metallacrowns have proven to be a versatile and robust class of molecules. Not only has the classic synthetic strategy of selecting ligands that place the metals at particular angles relative to each other to produce molecules with a predicted geometry generated a wide range of structures, but the strategy has also yielded metallahelicates, metallacryptands, host-guest metallacrown sandwich complexes, one- and two-dimensional coordination polymers, and metallacrowns that contain peptide components [5]. Furthermore, metallacrowns are capable of the self-assembly of homometallic, heterobimetallic, and heterotrimetallic supramolecular coordination complexes in the presence of multiple ligand types [4, 6]. Thus, this class of molecules provides an excellent opportunity to study molecular variation and the systematic substitution of individual components of a molecular system.

Recently we reported the first synthetic strategy for heterotrimetallic metallacrowns (Scheme 1), which were also the first individual 12-MC-4 complexes to contain a central lanthanide metal ion [6]. The alkali metal-lanthanide-manganese complexes $\text{Ln}^{\text{III}}\text{M}(\text{OAc})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^3-4}]$, where Ln^{III} is Pr^{III} to Yb^{III} (except Pm^{III}) and Y^{III} , M is Na^+ or K^+ , OAc is acetate, and shi^{3-} is salicylhydroximate, demonstrated the ability to systemically alter the central lanthanide ions and the ability to incorporate either a sodium or a potassium ion as a second central metal ion [6]. This systematic substitution of the lanthanide ion has also been demonstrated for 15-MC-5 systems [7]. In the heterotrimetallic report [6], we proposed that in addition to the central metal ions substitutions there were other possible points of variation in the $[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^3-4}]$ system: the ring metal ion (Mn^{III} in the original structures), the MC framework ligand (shi^{3-}), and the

bridging ligand between the ring metal ion and the central lanthanide ion (acetate). Thus, we proposed that a multitude of different molecules are possible based on this particular 12-MC-4 system alone and that molecules could be designed and customized to particular desired chemical and physical properties. Herein we report the ability to substitute the bridging carboxylate monoanion between the ring metal ion and the central lanthanide ion. While carboxylate ligand variation has been studied for lanthanide-containing 15-MC-5 complexes, those investigations focused on the ability of the 15-MC-5 molecules to bind carboxylate anions as guest molecules as the carboxylate anions are not crucial to the formation and the structure of the metallacrown [8]. However, in the heterotrimetallic $[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ systems the bridging carboxylate anion is critical to the self-assembly of the metallacrown as four carboxylate anions serve to tether the central lanthanide ion to the metallacrown framework.

Scheme 1

The ability to selectively modify a supramolecular coordination complex is still a synthetic challenge, especially systems that contain multiple different types of metal centers. Herein we report the self-assembly and single crystal X-ray structures of three erbium(III) derivatives of the lanthanide-sodium-manganese $\text{Er}^{\text{III}}\text{Na}(\text{L})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ complexes, where L is trimethylacetate (OTMA), benzoate (OBen), or salicylate (OSal) (Schemes 1 and 2): $\text{Er}^{\text{III}}\text{Na}(\text{OTMA})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}](\text{H}_2\text{O})_{3.73}(\text{DMF})_{0.27} \cdot 7.45\text{DMF} \cdot 1.47\text{H}_2\text{O}$, **1**, $\text{Er}^{\text{III}}\text{Na}(\text{OBen})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}](\text{H}_2\text{O})_4 \cdot 4\text{DMF} \cdot 0.87\text{H}_2\text{O}$, **2**, and $\text{Er}^{\text{III}}\text{Na}(\text{OSal})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}](\text{H}_2\text{O})_{3.54}(\text{DMF})_{0.73} \cdot 4\text{DMF} \cdot 0.24\text{H}_2\text{O}$, **3**, where DMF is *N,N*-dimethylformamide. These structures demonstrate the flexibility of this class of molecules for structural design. Where the archetypical molecules [6] in this particular series possessed acetate anions to bridge the central lanthanide ion to the ring manganese ions, the derivatives presented herein utilize either trimethylacetate, benzoate, or salicylate as the bridging carboxylate monoanion. The facile syntheses of these molecules are a hallmark of metallacrown chemistry and exhibit the ability to tailor molecules for substitutions of specific ligands.

Scheme 2

Material and Methods

Synthetic Materials

Sodium trimethylacetate hydrate (99%) was purchased from Sigma-Aldrich. Salicylhydroxamic acid (H_3shi , 99 %) and sodium benzoate (99%) were purchased from Alfa Aesar. Manganese(II) acetate tetrahydrate (99+%) and erbium(III) nitrate pentahydrate (99.9%) were purchased from Acros Organics. Sodium salicylate (99.9%) was purchased from Fisher Scientific. *N,N*-dimethylformamide (DMF, Certified ACS grade) was purchased from BDH Chemicals. All reagents were used as received and without further purification.

Syntheses

General Preparation of $Er^{III}Na(L)_4[12-MC_{Mn^{III}(N)shi-4}]$ Compounds

Erbium(III) nitrate pentahydrate (0.125 mmol), the sodium carboxylate salt (4 mmol; **1**: trimethylacetate hydrate based on an assumption of three waters of hydration; **2**: sodium benzoate; **3**: sodium salicylate), and salicylhydroxamic acid (2 mmol) were mixed in 10 mL of DMF resulting in a cloudy, white mixture for **1** and **2** or a clear, colorless solution for **3**. In a separate beaker, manganese(II) acetate tetrahydrate (2 mmol) was dissolved in 10 mL of DMF resulting in an orange/red solution. The two solutions were mixed resulting in a dark brown solution and then allowed to stir overnight. The solution was then filtered to remove a dark brown precipitate, which was discarded. The filtrate was then prepared for crystal growth (details below).

$Er^{III}Na(OTMA)_4[12-MC_{Mn^{III}(N)shi-4}](H_2O)_{3.73}(DMF)_{0.27} \cdot 7.45DMF \cdot 1.47H_2O$, **1.** Slow evaporation of the dark brown filtrate yielded X-ray quality black/dark brown crystals after 12 days. The percent yield was 24% based on erbium(III) nitrate pentahydrate. Elemental analysis for $C_{71.16}H_{116.44}ErMn_4NaN_{11.72}O_{32.92}$ [FW = 2072.92 g/mol] found % (calculated): C = 40.90 (41.23), H = 5.13 (5.66), N = 7.44 (7.92). FT-IR bands (KBr pellet, cm^{-1}): 1659, 1600, 1573, 1549, 1516, 1484, 1435, 1427, 1394, 1319, 1257, 1229, 1157, 1147, 1100, 1062, 1032, 933, 896, 866, 791, 770, 756, 687, 666, 650, 612, 598, 539, 480, 449, 432, 412.

Er^{III}Na(OBen)₄[12-MC_{Mn^{III}(N)_{shi}-4](H₂O)₄·4DMF·0.87H₂O, 2.} X-ray quality black/dark brown crystals were grown in 23 days by placing an open vial of the filtrate in a capped bottle, which was partially filled with water. The percent yield was 27% based on erbium(III) nitrate pentahydrate. Elemental analysis for C₆₈H_{73.74}ErMn₄NaN₈O_{28.87} [FW = 1875.01 g/mol] found % (calculated): C = 43.12 (43.56), H = 3.82 (3.96), N = 6.09 (5.98). FT-IR bands (KBr pellet, cm⁻¹): 1655, 1597, 1570, 1547, 1516, 1472, 1434, 1417, 1399, 1318, 1257, 1248, 1176, 1159, 1145, 1101, 1065, 1029, 934, 866, 844, 767, 760, 725, 689, 650, 611, 589, 537, 482, 445, 431, 414.

Er^{III}Na(OSal)₄[12-MC_{Mn^{III}(N)_{shi}-4](H₂O)_{3.54}(DMF)_{0.73}·4DMF·0.24H₂O, 3.} Slow evaporation of the dark brown filtrate yielded X-ray quality black/dark brown crystals after 10 days. The percent yield was 17% based on erbium(III) nitrate pentahydrate. Elemental analysis for C_{70.18}H_{76.66}ErMn₄NaN_{8.73}O_{32.51} [FW = 1972.61 g/mol] found % (calculated): C = 42.19 (42.73), H = 3.74 (3.92), N = 6.02 (6.20). FT-IR bands (KBr pellet, cm⁻¹): 1654, 1598, 1572, 1511, 1482, 1468, 1436, 1396, 1360, 1318, 1247, 1160, 1145, 1102, 1061, 1031, 933, 868, 821, 808, 760, 708, 690, 669, 651, 611, 553, 534, 482, 450, 414.

Physical Methods

FT-IR spectra were obtained on a Jasco FT-IR 460 Plus spectrometer. Elemental analyses were performed on a Carlo Erba 1108 elemental analyzer and a PerkinElmer 2400 elemental analyzer.

X-ray Crystallography

Crystals used for single crystal X-ray diffraction were taken from the mother liquor prior to analysis and were not dried. For compounds **1** – **3**, a mineral oil coated crystal was mounted on a MicroMesh MiTeGen micromount and transferred to the diffractometer. For **1** and **2**, data were collected on a Bruker AXS D8 Quest diffractometer equipped with a solid state CMOS area detector and an I- μ S microsource X-ray tube using Mo K α radiation (λ = 0.71073 Å) monochromated with a laterally graded multilayer (Goebel) mirror. For compound **3**, data was collected using a Bruker AXS SMART APEXII CCD X-ray diffractometer using graphite-monochromated Mo K α radiation. All data were collected at 100 K, and for all three compounds, data collection and cell refinement was performed using APEX2 (version 2013.4-1) and SAINT+ embedded in APEX2, respectively [9]. The data were scaled and corrected for absorption with SADABS as built into APEX2 [9, 10]. Space groups were assigned using the SHELXTL suite of programs [11]. The structures were solved using direct methods with SHELXS-97 and refined using least-squares refinements based on F^2 with SHELXL-2013 or 2014 [12] and the graphical interface SHELXLE [13]. All structures show substantial disorder of solvate molecules, and compound **3** also exhibits disorder of sections of the metallacrown molecule involving two Mn ions, one salicylhydroximate ligand, and two salicylate ligands. Compound **1** is twinned by 180° rotation around the reciprocal axis (1 1 0). Additional details are provided in Table 1 and in the individual CIFs of each compound.

Results

General Description of Er^{III}Na(L)₄[12-MC_{Mn^{III}(N)_{shi}-4] Structures.}

All three metallacrowns (**1** – **3**) possess the same general [12-MC_{Mn^{III}(N)_{shi}}-4] framework with a pseudo-C₄ axis through the central cavity of the molecule (Fig. 1 – 3). Due to the similarity of the structures, a general description will be given for the [12-MC_{Mn^{III}(N)_{shi}}-4] framework and additional details regarding each individual structure will be given in context. The pseudo-C₄ axis in each molecule generates the typical Mn-N-O repeat unit of the MC, which repeats four times to generate a molecule with square arrangement of the Mn ions. In the center of each molecule, an erbium ion and a sodium ion are bound on opposite faces of the MC. Each erbium ion is also bound to the MC through carboxylate monoanion bridges that connect the erbium ion to the ring manganese ions. In addition, each MC is slightly domed with the erbium ion on the convex side of the central cavity and the sodium ion captured on the underside of the metallacrown.

In structures **1** – **3**, the ring manganese ions and central erbium ion are assigned a 3+ oxidation state. These assignments are based on average bond lengths for each ion, the presence of elongated axial bond lengths expected for a high-spin *d*⁴ ion, and the calculated Bond Valence Sum values for each ion [14] (Table 2). Furthermore, charge considerations support the assigned oxidation states. The total positive charge (16+) of the four Mn^{III} ions, one Er^{III} ion, and one Na⁺ ion is balanced by the presence of four triply deprotonated salicylhydroximate ligands (shi³⁻) and four negative bridging carboxylate monoanions (trimethylacetate for **1**, benzoate for **2**, and singly-deprotonated salicylate for **3**).

In complexes **1** – **3**, each Mn^{III} ion is six-coordinate and possesses a tetragonally distorted octahedral geometry with elongated axial bond lengths. The equatorial plane of each Mn^{III} ion is composed of the oxime nitrogen atom and phenolate oxygen atom of one shi³⁻ ligand to form a six-membered chelate ligand and a *trans* five-membered chelate ring that is formed from the oxime oxygen atom and carbonyl oxygen atom of a second shi³⁻ ligand. The elongated axial axis is comprised of a carboxylate oxygen atom of the bridging trimethylacetate (**1**), benzoate (**2**), or salicylate (**3**) and an oxygen atom of a solvent molecule, either water or DMF. In **1** Mn1, Mn2, and Mn4 are bound to water molecules, while for Mn3 the solvent axial coordination site is either occupied by a water molecule (73% occupancy) or a DMF molecule (27% occupancy). For **2** all of the Mn^{III} ions are bound to water molecules. For **3** Mn1, Mn2, the salicylhydroximate ligand (C1-C7, O1-O3, and N1) that bridges Mn1 and Mn2, the oxygen atom (O6) of an adjacent salicylhydroximate ligand, and the two salicylate ligands (O22-O24 and C50-C56; O13-O15 and C29-C35) attached to Mn1 and Mn2, respectively, are disordered over two sites with the occupancy rates of the major and minor moieties being 82% and 18%. For Mn1, Mn1B, Mn3, and Mn4 a water molecule occupies the axial coordination site opposite the carboxylate oxygen atom of the bridging salicylate. For Mn2 and Mn2B a water molecule and two DMF molecules with different orientations occupy the axial coordination site. The occupancy of the water molecule associated with O25C is 27%, the occupancy of the DMF associated with O25 is 31%, and the occupancy of the DMF associated with O25B is 42%. For **1** – **3** the Mn^{III}-O_{solvent} distances are particularly long (~2.4 – 2.5 Å), which is likely due to the fact that the O_{solvent} atoms are also coordinated to the central Na⁺ ion.

For **1** – **3** each Er^{III} ion is eight coordinate with a distorted square antiprismatic geometry (Fig. 4). The lower four atoms of the geometry are provided by the oxime oxygen atoms of the MC

central cavity, and the upper four atoms are supplied by the carboxylate oxygen atoms of the bridging carboxylate monoanions. The square antiprismatic geometry assignment is supported by the calculated average skew angles between the two different planes of oxygen atoms (carboxylate oxygen atom plane vs oxime oxygen atom plane), which are 49.95° for **1**, 46.85° for **2**, and 47.35° for **3** (Table 3). In an ideal square antiprismatic geometry the skew angle would be 45°, while for the ideal square prismatic geometry the skew angle would be 0° [15]. The skew angles were calculated with the program *Mercury* [16] and in the same manner as previously reported for the acetate versions of these molecules [6]. In **1** – **3** the Er^{III} ion does not lie in the center of the square antiprism, instead the Er^{III} ions lie closer to the mean plane of the carboxylate oxygen atoms (Table 4 and Fig. 4b).

For **1** and **2** each Na⁺ ion is eight coordinate with a geometry between that of an ideal square prism and square antiprism (Fig. 5). For **3** the Na⁺ ion is mainly eight coordinate with a similar geometry to the Na⁺ ions in **1** and **2**; however, for **3** the Na⁺ ion also has a partially occupied water molecule in a ninth coordination site (27% occupancy). The calculated skew angles of 28.78°, 28.74°, and 29.06° for **1**, **2**, and **3**, respectively (Table 3), reveal that the geometry is severely distorted from either ideal square antiprismatic or square prismatic geometry. The coordination environment of each Na⁺ ion is composed of a plane of four oxime oxygen atoms from the MC central cavity and another plane of solvent oxygen atoms, which derive either from water or DMF molecules. As discussed above for the Mn^{III} ions, these solvent molecules bridge between the Na⁺ and Mn^{III} ions. In **3** the partially occupied water molecule in the ninth coordination site is positioned in approximately the middle of the square face produced by the oxygen atoms of the four solvent molecules. As in the Er^{III} ion geometry, the Na⁺ ion is not centered in the polyhedron geometry. In **1** – **3** the Na⁺ ions lie closer to the mean plane generated by the solvent oxygen atoms (Table 4 and Fig. 5b).

For complexes **1** – **3** each metallacrown is domed towards the side of the Na⁺ ion. The degree of doming can be inferred from two different measurements. The first measurement is the angle of the elongated axial axis of each Mn^{III} ion relative to the MC. By measuring the angle about the axial coordination of the Mn^{III} ions with respect to the carboxylate oxygen atom, the Mn^{III} ion, and the calculated centroid of the oxime oxygen atoms (*Mercury*), the planarity of the [12-MC_{Mn^{III}(N)_{shi}-4}] framework can be evaluated. The angles were measured in the same manner as previously reported for the acetate versions of these molecules [6]. In a perfectly planar MC, this angle would be 90°. For the salicylate derivative of these molecules the average angle value indicates that **3** is slightly less domed than **1** and **2** (Table 4). Furthermore, the average distance of each Mn^{III} ion from the equatorial mean plane of its first coordination sphere ligand atoms can be an indication of planarity. As we previously reported [6], the domed feature of the [12-MC_{Mn^{III}(N)_{shi}-4}] molecules is not due to the presence of the Ln^{III} ions or the alkali metal ions. Instead the degree to which the MC is domed is due to how far the ring metal ion is raised above the individual equatorial mean plane of the ligand atoms [6]. Again the salicylate derivative is slightly less domed than **1** and **2**, as the Mn^{III} ions of **3** are raised the least distance above the mean plane of the equatorial atoms (Table 4).

In addition to the structural description thus far, several solvent molecules are located in the lattices for compounds **1** – **3**. In **1** there are several DMF molecules located in the lattice, some of which are only partially occupied. In addition, two water molecules are correlated with the

water and DMF molecules that are disordered over the binding site to Na1 and Mn3. In total there are 7.45 DMF molecules and 1.47 water molecules located in the lattice of **1**. For **2**, four DMF molecules are located in the lattice. One DMF molecule is flipped disordered over two sites, and a different DMF molecule is disordered over two sites with different orientations. In addition, a water molecule is partially occupied at 87%. In **3** four DMF molecules are located in the lattice. One DMF molecule is flipped disordered over two sites. A different lattice DMF molecule is disordered over a site with a DMF molecule and a water molecule. The occupancy of the water molecule is only 24%.

Table 1. Crystallographic Details of the $\text{Er}^{\text{III}}\text{Na}(\text{L})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]\text{Compounds (1-3)}$

	1	2	3
Empirical Formula	$\text{C}_{71.16}\text{H}_{116.44}\text{ErMn}_4\text{NaN}_{11.72}\text{O}_{32.92}$	$\text{C}_{68}\text{H}_{73.74}\text{ErMn}_4\text{NaN}_8\text{O}_{28.87}$	$\text{C}_{70.18}\text{H}_{76.66}\text{ErMn}_4\text{NaN}_{8.73}\text{O}_{32.51}$
FW (g/mol)	2072.92	1875.01	1972.61
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$	Pn	Cc
a (Å)	14.8590(10)	14.0158(10)	23.580(4)
b (Å)	17.3185(14)	16.5416(12)	24.334(4)
c (Å)	19.2126(15)	16.7281(11)	14.329(2)
α (deg)	83.560(3)	90	90
β (deg)	82.533(4)	95.865(2)	91.670(2)
γ (deg)	72.894(3)	90	90
Volume (Å ³)	4671.0(6)	3858.0(5)	8218(2)
Z	2	2	4
Density (Mg/m ³) [calculated]	1.474	1.614	1.594
Abs coeff (mm ⁻¹)	1.502	1.805	1.702
$F(000)$	2135.6	1895.4	3991.7
Crystal Size (mm)	0.180 x 0.170 x 0.110	0.390 x 0.370 x 0.300	0.330 x 0.220 x 0.180
Crystal Habit	Block	Block	Block
Crystal Color	Brown	Brown	Brown
θ range for data collection (deg)	2.3921 to 30.5128	2.8635 to 30.5732	2.7243 to 27.5280
Limiting indices	$-20 \leq h \leq 21, -24 \leq k \leq 24, 0 \leq l \leq 26$	$-18 \leq h \leq 18, -22 \leq k \leq 22, -22 \leq l \leq 22$	$-31 \leq h \leq 31, -32 \leq k \leq 26, -19 \leq l \leq 19$
Reflections collected/unique	46373/23912 [R(int) = 0.0500]	114567/19019 [R(int) = 0.0472]	31207/19085 [R(int) = 0.0323]
Max. and min. transmission	0.746071 and 0.555081	0.7461 and 0.6280	0.7462 and 0.6064
Data/restraints/parameters	23912/361/1214	19019/172/1129	19085/521/1307
Goodness-of-fit of F^2	1.137	1.069	0.999
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0784, wR_2^b = 0.1738$	$R_1^a = 0.0306, wR_2^b = 0.0674$	$R_1^a = 0.0416, wR_2^b = 0.0919$
R indices (all data)	$R_1^a = 0.1271, wR_2^b = 0.1980$	$R_1^a = 0.0354, wR_2^b = 0.0694$	$R_1^a = 0.0587, wR_2^b = 0.0996$
Largest diff. peak and hole (e ⁻ Å ⁻³)	2.720 and -2.491	1.489 and -0.544	1.114 and -0.560

$${}^aR_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|, {}^bwR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}; w = 1/[\sigma^2(F_o^2) + (mp)^2 + np];$$

$$p = [\max(F_o^2, 0) + 2F_c^2]/3 \text{ (} m \text{ and } n \text{ are constants); } \sigma = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}.$$

Table 2. Bond Valence Sum (BVS) values and Average Bond Length Data for the Metal Ions in the $\text{Er}^{\text{III}}\text{Na}(\text{L})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ Compounds (**1–3**)

	Mn1		Mn2		Mn3		Mn4		Er	
	BVS	Avg. Bond Length (Å)	BVS	Avg. Bond Length (Å)	BVS	Avg. Bond Length (Å)	BVS	Avg. Bond Length (Å)	BVS	Avg. Bond Length (Å)
1	3.10	2.042	3.04	2.050	3.04	2.058	3.11	2.053	3.03	2.346
2	3.10	2.048	3.08	2.042	3.09	2.048	3.13	2.052	3.15	2.331
3	3.11 ^a 3.11 ^b	2.040 ^a 2.017 ^b	3.14 ^a 3.22 ^b	2.035 ^a 1.995 ^b	3.10	2.040	3.09	2.043	3.19	2.324

^aFor Mn1 and Mn2

^bFor Mn1B and Mn2B

Table 3. Average Skew Angles about the Er^{III} and Na^+ ions of the $\text{Er}^{\text{III}}\text{Na}(\text{L})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ Compounds (**1–3**)

Compound	Average Skew Angle about Er^{III} (°)	Average Skew Angle about Na^+ (°)
1	49.95	28.78
2	46.85	28.74
3	47.35	29.06

Table 4. Structural Feature Comparison of the $\text{Er}^{\text{III}}\text{Na}(\text{L})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ Compounds (**1–3**) and $\text{Er}^{\text{III}}\text{Na}(\text{OAc})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}](\text{H}_2\text{O})_4 \cdot 6\text{DMF}$ (**4**)[6]

Compound	Er^{III} Crystal Radius (Å) ^b	MC Cavity Radius (Å) ^c	Avg. Adjacent $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$ Distance (Å)	Avg. Cross Cavity $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$ Distances (Å)
1	1.05	0.55	4.61	6.52
2	1.03	0.54	4.60	6.51
3 ^a	1.02	0.55	4.59	6.49
4 [6]	1.04	0.55	4.61	6.51

a. For **3** distances and angles where determined for only the major moiety.

b. The Er^{III} crystal radii were calculated by determining the average M–O bond distance and then subtracting the estimated radius of an oxygen atom (1.30 Å).

c. The metallacrown cavity radius was calculated in the same manner as previously reported [6]. First the average oxime oxygen distance was determined about the MC ring, and then this distance was used to determine the distance from the oxime oxygen atom to the center of the MC ring. The MC cavity radius was calculated by subtracting 1.30 Å (estimated oxime oxygen atom radius) from the distance of the oxygen atom to the center of the MC ring.

Table 4. (continued)

Compound	Avg. Cross Cavity O _{ox} -O _{ox} Distance (Å)	Er ^{III} -O _{car} MP Distance (Å)	Er ^{III} -O _{ox} MP Distance (Å)	Er ^{III} -MnMP Distance (Å)
1	3.71	1.07	1.57	1.91
2	3.68	1.06	1.56	1.88
3	3.69	1.13	1.51	1.87
4 ^[6]	3.69	1.04	1.57	1.91

Table 4. (continued)

Compound	Na ⁺ -O _{solvent} MP Distance (Å)	Na ⁺ -O _{ox} MP Distance (Å)	Avg. Distance of Mn ^{III} to Equatorial Ligand Atom Mean Plane (Å)	Avg. angle between the Carboxylate (car) Oxygen Atom, Mn ^{III} , and the Centroid of the Oxime (ox) Oxygen Atoms (O _{car} -Mn-O _{ox centroid}) (°)
1	0.69	1.97	0.15	101.61
2	0.67	1.95	0.14	102.01
3	0.54	2.07	0.10	100.61
4 ^[6]	0.79	1.91	0.17	102.03

Discussion

For supramolecular coordination complexes with multiple different types of metal centers and with multiple different ligand components, the selective modification of these self-assembled molecules can be a synthetic challenge. Metallacrowns have a proven track record of controllable formation; thus, this 12-MC-4 system provides an opportunity to explore the substitution ability of these molecules.

The syntheses of **1–3** in adequate yields (17 – 27%) attest to the generality of this class of molecules. For the previously reported parent Er^{III}Na(OAc)₄[12-MC_{Mn^{III}(N)_{shi}-4](H₂O)₄·6DMF (**4**) molecule, acetate anions serve as bridges between the ring Mn^{III} ions and the central Er^{III} ion. In molecules **1 – 3**, the acetate anions are replaced by the other monoanion carboxylate ligands trimethylacetate (**1**), benzoate (**2**), and salicylate (**3**). In general the use of different monoanion carboxylate ligands does not significantly alter the structural features of the [12-MC_{Mn^{III}(N)_{shi}-4] framework (Table 4). For all four compounds the key structural parameters of the [12-MC_{Mn^{III}(N)_{shi}-4] frameworks such as the MC cavity radius, adjacent Mn^{III}-Mn^{III} distances, cross cavity Mn^{III}-Mn^{III} distances, and cross cavity oxime oxygen (O_{ox}) – oxime oxygen distances are similar independent of the monoanion carboxylate bridge. Furthermore, the coordination properties of the central metal ions are similar. The Er^{III} crystal radii for **1 – 4** are similar as well as the distances of the Er^{III} ion from the ligand mean planes produced by the carboxylate oxygen atoms (O_{car}MP), oxime oxygen atoms (O_{ox}MP), and the ring Mn^{III} ions (MnMP). For the Na⁺ ion, again the distances of the Na⁺ ion from the ligand mean planes produced by the oxime}}}

oxygen atoms and the solvent oxygen atoms ($O_{\text{solventMP}}$) are similar. These latter measurements for **1** – **3** though have the greatest deviation from the parent compound **4**. However, in **4** only water molecules are bound to the Na^+ ion, while in structures **1** and **3** DMF molecules are also disordered over the binding sites to the Na^+ ions.

Not only are the individual metrics of the $[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ framework conserved among the monoanion carboxylate derivatives, but the domed feature of this class of metallacrowns is also conserved among all four compounds. The angles about the axial coordination of the Mn^{III} ions with respect to the carboxylate oxygen atom, the Mn^{III} , and the calculated centroid of the oxime oxygen atoms are similar, and the ring Mn^{III} ions are raised above the equatorial ligand mean plane in each compound to relatively the same extent (Table 4). The preservation of the domed feature is readily gauged by comparing overlay figures of the X-ray structures of compounds **1** – **3** with compound **4** (Fig.6).

Future work will focus on determining the magnetic properties, the solution lanthanide ion and carboxylate anion substitution capabilities and the possible interconversion of the different derivatives, and the photophysical properties of the presented molecules and of other lanthanide analogues. Conservation of the $[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ framework and structure is vital to the comparison of these properties. It is important when designing molecules for applications that the compound is amenable to ligand substitution with little deviation of the core structure. Thus, any properties such as magnetism should be predicated on the identity of the central metal ion and the identity of the bridging ligand, but not due to changes in the $[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ framework structure.

Conclusions

The recently reported $\text{Ln}^{\text{III}}\text{Na}(\text{OAc})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ compounds promised to be an opportunity to demonstrate how to selectively and easily modify self-assembled supramolecular coordination complexes. Compounds **1** – **3** deliver on that promise. The facile alteration of the bridging monoanion carboxylate ligands of the heterotrimetallic metallacrowns validate that the metallacrown class of compounds is an excellent example of self-assembled supramolecular chemistry. The variation in the carboxylate ligands does not affect the structural features of the $[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ framework. The conservation of this framework will be important when assessing the physical and chemical properties of this class of molecules.

Acknowledgements

CMZ and JRT thank the Undergraduate Research Grant Program and the CFEST Faculty Training and Continued Education program at Shippensburg University for financial support. MZ thanks NSF (grants CHE 0087210 and DMR 1337296) for funding for the X-ray diffractometer. CMZ thanks Laura Zaleski for useful discussions regarding the manuscript.

Appendix A. SupplementaryData

CCDC 1416768, 1416769, and 1416770 contain the supplementary crystallographic data for compounds **1**, **2**, and **3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] (a) R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.* (2002) 1–10. (b) R.W. Saalfrank, H. Maid, A. Scheurer, *Angew. Chem. Int. Ed.* 47 (2008) 8794–8824.
- [2] L.N. Dawe, T.S.M. Abedin, L.K. Thompson, *Dalton Trans.* (2008) 1661–1675.
- [3] (a) S.R. Seidel, P.J. Stang, *Accounts Chem. Res.* 35 (2002) 972–983. (b) B.H. Northrop, Y.-R. Zheng, K.-W. Chi, P.J. Stang, *Accounts Chem. Res.* 42 (2009) 1554–1563. (c) R. Chakrabarty, P.S. Mukherjee, P.J. Stang, *Chem. Rev.* 111 (2011) 6810–6918. (d) T.R. Cook, Y.-R. Zheng, P.J. Stang, *Chem. Rev.* 113 (2013) 734–777. (e) G. A. Timco, E. J. L. McInnes, R. E. P. Winpenny, *Chem. Soc. Rev.* 42 (2013) 1796–1806. (f) A.M. Castilla, W.J. Ramsay, J.R. Nitschke, *Accounts Chem. Res.* 47 (2014) 2063–2073. (g) A. Mishra, R. Gupta, *Dalton Trans.* 43 (2014) 7668–7682. (h) T.R. Cook, P.J. Stang, *Chem. Rev.* (2015).
- [4] (a) C. Y. Chow, E. R. Trivedi, V. L. Pecoraro, C. M. Zaleski, *Comments Inorg. Chem.* 25 (2015) 214–253. (b) G. Mezei, C. M. Zaleski, V. L. Pecoraro, *Chem. Rev.* 107 (2007) 4933–5003. (c) V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf, A. Barwinski, in K. D. Karlin, (Ed.), *Progress in Inorganic Chemistry*, John Wiley and Sons, Inc., New York, 1997, Vol. 45, pp 83–177.
- [5] (a) J.A. Johnson, J.W. Kampf, V.L. Pecoraro, *Angew. Chem. Int. Ed.* 42 (2003) 546–549. (b) C. Dendrinou-Samara, M. Alexiou, C. M. Zaleski, J. W. Kampf, M. L. Kirk, D. P. Kessissoglou, V. L. Pecoraro, *Angew. Chem. Int. Ed.* 42 (2003) 3763–3766. (c) C. M. Zaleski, A. D. Cutland-Van Noord, J. W. Kampf, V. L. Pecoraro, *Cryst. Growth Des.* 7 (2007), 1098–1105. (d) K. A. Mengle, E. J. Longenecker, M. Zeller, C. M. Zaleski, *J. Chem. Crystallogr.* 45 (2015) 36–43. (e) J. J. Bodwin, V. L. Pecoraro, *Inorg. Chem.* 39 (2000) 3434–3435. (f) M. Cal, Ł. Jaremko, M. Jaremko, P. Stefanowicz, *New J Chem* 37 (2013) 3770–3777. (g) M. Cal, A. Kotynia, Łukasz Jaremko, M. Jaremko, M. Lisowski, M. Cebo, J. Brasuń, P. Stefanowicz, *Dalton Trans.* 44 (2015) 11172–11181. (h) J. Jankolovits, C. M. Andolina, J. W. Kampf, K. N. Raymond, V. L. Pecoraro, *Angew. Chem. Int. Ed.* 50 (2011) 9660–9664.
- [6] M. R. Azar, T. T. Boron, III, J. C. Lutter, C. I. Daly, K. A. Zegalia, R. Nimthong, G. M. Ferrence, M. Zeller, J. W. Kampf, V. L. Pecoraro, C. M. Zaleski, *Inorg. Chem.* 53 (2014) 1729–1742.
- [7] (a) C. M. Zaleski, C.-S. Lim, A. D. Cutland-Van Noord, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* 50 (2011) 7707–7717. (b) A. V. Pavlishchuk, S. V. Kolotilov, I. O. Fritsky, M. Zeller, A. W. Addison, A. D. Hunter, *Acta Cryst. C* 67 (2011) m255–m265.

[8] (a) A.D. Cutland, J.A. Halfen, J.W. Kampf, V.L. Pecoraro, *J. Am. Chem. Soc.* 123 (2001) 6211–6212. (b) G. Mezei, J.W. Kampf, S. Pan, K.R. Poeppelmeier, B. Watkins, V.L. Pecoraro, *Chem. Commun.* (2007) 1148 – 1150. (c) C.-S. Lim, A. Cutland Van Noord, J.W. Kampf, V.L. Pecoraro, *Eur. J. Inorg. Chem.* (2007) 1347–1350. (d) M. Tegoni, M. Tropiano, L. Marchiò, *Dalton Trans.* (2009) 6705–6708. (e) C.-S. Lim, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* 48 (2009) 5224–5233. (f) J. Jankolovits, J.W. Kampf, S. Maldonado, V.L. Pecoraro, *Chem. Eur. J.* 16 (2010) 6786–6796. (g) C.-S. Lim, J. Jankolovits, J.W. Kampf, V.L. Pecoraro, *Chem. Asian J.* 5 (2010) 46–49. (h) J. Jankolovits, C.-S. Lim, G. Mezei, Jeff. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* 51 (2012) 4527–4538. (i) J. Jankolovits, A.D. Cutland Van-Noord, J.W. Kampf, V.L. Pecoraro, *Dalton Trans.* 42 (2013) 9803–9808. (j) A.V. Pavlishchuk, S.V. Kolotilov, M. Zeller, L.K. Thompson, A.W. Addison, *Inorg. Chem.* 53 (2014) 1320–1330.

[9] Bruker (2007) Apex2, Bruker AXS Inc, Madison, Wisconsin, USA.

[10] Bruker (2001) SADABS, Bruker AXS Inc, Madison, Wisconsin, USA.

[11] G. M. Sheldrick, *Acta Cryst. A* 64 (2008) 112–122.

[12] G. M. Sheldrick (2013) SHELXL2013; University of Göttingen, Germany.

[13] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* 44 (2011) 1281–1284.

[14] (a) W. Liu, H. H. Thorp, *Inorg. Chem.* 32 (1993) 4102–4105. (b) A. Trzesowska, R. Kruszynski, T. J. Bartczak, *Acta Crystallogr. B* 60 (2004) 174–178.

[15] M. A. AlDamen, J. M. Clemente-Juan, E. Coronado, C. Martí-Gastaldo, A. Gaita-Ariño, *J. Am. Chem. Soc.* 130 (2008) 8874 – 8875. (b) M. A. AlDamen, S. Cardona-Serra, S. J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, C. Martí-Gastaldo, F. Luis, O. Montero, *Inorg. Chem.* 48 (2009) 3467 – 3479.

[16] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Cryst.* 39 (2006) 453 – 457.

Figures and Figure Captions

Fig. 1. Single-crystal X-ray structure of $\text{Er}^{\text{III}}\text{Na}(\text{OTMA})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^-}4](\text{H}_2\text{O})_{3.73}(\text{DMF})_{0.27}\cdot 7.45\text{DMF}\cdot 1.47\text{H}_2\text{O}$, **1**, (a) top view and (b) side view. The thermal ellipsoid plot of **1** is at the 50% probability level. The crystal structure features disorder of the solvent molecule bridging Mn3 and Na1. The axial coordinate site is either occupied by a water molecule (73% occupancy) or a DMF molecule (27% occupancy). Only the major moiety atoms are displayed in the figure. For clarity only the atoms composing the MC ring are labeled in (a), and only the metal atoms are labeled in (b). Hydrogen atoms and the lattice solvent molecules have been omitted for clarity. Color scheme: aqua – Er^{III} , green – Mn^{III} , yellow – Na^+ , red – oxygen, blue – nitrogen, and gray – carbon.

Fig. 2. Side view of the single-crystal X-ray structure of $\text{Er}^{\text{III}}\text{Na}(\text{OBen})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^-}4](\text{H}_2\text{O})_4 \cdot 4\text{DMF} \cdot 0.87\text{H}_2\text{O}$, **2**. The thermal ellipsoid plot of **2** is at the 50% probability level, and for clarity only the metal atoms are labeled. Hydrogen atoms and the lattice solvent molecules have been omitted for clarity. Color scheme: aqua – Er^{III} , green – Mn^{III} , yellow – Na^+ , red – oxygen, blue – nitrogen, and gray – carbon.

Fig. 3. Side view of the single-crystal X-ray structure of $\text{Er}^{\text{III}}\text{Na}(\text{OSal})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}^-}4](\text{H}_2\text{O})_{3.54}(\text{DMF})_{0.73} \cdot 4\text{DMF} \cdot 0.24\text{H}_2\text{O}$, **3**. The thermal ellipsoid plot of **3** is at the 50% probability level, and for clarity only the metal atoms are labeled. The crystal structure features disorder of portions of the MC framework and of the solvent molecule bridging Mn2 and Na1. Please see the Results section for a complete description of the disorder. Only the major moiety atoms are displayed in the figure. Hydrogen atoms and the lattice solvent molecules have been omitted for clarity.

omitted for clarity. Color scheme: aqua – Er^{III} , green – Mn^{III} , yellow – Na^+ , red – oxygen, blue – nitrogen, and gray – carbon.

Fig. 4. a) View of the first coordination sphere of the Er^{III} (aqua) ion in **1** along the pseudo- C_4 axis illustrating the square antiprismatic geometry of the 8-coordinate lanthanide ion. b) Side view of the first coordination sphere of the Er^{III} ion in **1** demonstrating the displacement of the Er^{III} ion from the center of the polyhedron surrounding the ion. The Er^{III} ion lies closer to the mean plane generated by the carboxylate oxygen atoms from the bridging trimethylacetate anions (O13, O15, O17, and O19). The thermal ellipsoid plot is at the 50% probability level.

Fig. 5.a) View of the first coordination sphere of the Na⁺ (yellow) ion in **1** along the pseudo-C₄ axis illustrating the significant distortion from square antiprismatic geometry of the 8-coordinate alkali metal ion. b) Side view of the first coordination sphere of the Na⁺ ion in **1** demonstrating the displacement of the Na⁺ ion from the center of the polyhedron surrounding the ion. The Na⁺ ion lies closer to the mean plane generated by the water oxygen atoms (O21, O22, O23, and O24). The thermal ellipsoid plot is at the 50% probability level.

Fig. 6. Overlay of the X-ray structures of (a) **1** (blue) and **4** (gray), (b) **2** (red) and **4** (gray), and (c) **3** (green) and **4** (gray). The overlay figures demonstrate that the replacement of the original acetate anion (**4**) with trimethylacetate (**1**), benzoate (**2**), or salicylate (**3**) does not significantly alter the domed feature of the [12-MC_{Mn}^{III}(N)_{shi}-4] framework. In each overlay the difference of the four atom oxime oxygen planes have been minimized between the two structures.

Graphical Abstract

Three single-crystal X-ray structures of a series of $\text{Er}^{\text{III}}\text{Na}(\text{L})_4[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{N})\text{shi}}\text{-4}]$ complexes, where L is either trimethylacetate, benzoate, or salicylate and shi^{3-} is salicylhydroximate, are presented. The self-assembled supramolecular coordination complexes demonstrate the ability to vary the bridging carboxylate monoanion in this heterotrimetallic family of compounds.