

View Article Online View Journal

CrystEngComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. Liao, C. W. Ingram, J. Bacsa, Z. J. Zhang and T. Dinadayalane, *CrystEngComm*, 2016, DOI: 10.1039/C6CE00360E.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/crystengcomm

A Hydrogen Bonded Co(II) Coordination Complex and a Triply Interpenetrating 3-D Manganese(II) Coordination Polymer from Diaza Crown Ether with Dibenzoate Sidearms

Liang Liao^{$\$ \perp$}, Conrad W. Ingram^{$\$ \perp *$}, John Bacsa[†], Z. John Zhang[‡], Tandabany Dinadayalane^{\perp}

[§] Center for Functional Nanoscale Materials, [⊥]Department of Chemistry, Clark Atlanta University, 223 James P. Brawley Drive, Atlanta, GA 30314, [†]Department of Chemistry, Emory University, Atlanta, GA 30332, [‡] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30322

*Corresponding author: Tel.: +1 404-880-6898; E-mail address: cingram@cau.edu

ABSTRACT

The diaza crown ether dicarboxylate ligand, 4,4'-((1,7-dioxa-4,10-diazacyclododecane-4,10-diyl)bis(methylene))dibenzoate), L, forms a monomeric coordination complex of Co(II) ions, $CoL(H_2O)_2 \cdot 2H_2O$, 1, and a coordination polymer (MnL \cdot H₂O)_n, 2, with Mn(II) ions under hydrothermal conditions. The monomeric coordination complex (Structure 1) is polar with mirror symmetry and crystallizes in the non-centrosymmetric space group Cm. The mirror plane bisects the complex at the six-coordinate Co(II) ion, the two oxygen atoms of the crown moiety and the two oxygen atoms from coordinated water molecules. The coordinated water molecules take part in strong, linear hydrogen bonds with carboxylate oxygens provided by neighboring Co(II)-crown complexes resulting in a three-dimensional $(1:1)_n$ polar network in which the topology of the underlying 8-coordinated net is sqc3. The structure of 2 crystallizes in the orthorhombic Fdd2 space group as an infinite, polar triply interpenetrating three-dimensional network. The eight-coordinate Mn(II) ion coordinates two oxygen and two nitrogen atoms of the crown moiety, as well as single carboxylate O atom from each of two neighboring ligands. In both structures, the ligand assumes a flexed-wing bird shape, with the two benzoate sidearms of the crown moiety locked in a syn orientation. The metal ion elevated above the plane of the diaza-crown oxygen and nitrogen atoms. The diaza-crown moiety with its two benzoate sidearms has the peculiar property of forming an oriented crystal structure where the metalcrown vectors are oriented parallel to each other in the crystal. However, the structures are achiral, but the rigid crystal lattice prevents re-orientation of the structure through inversion. The coordination polymer (MnL \cdot H₂O₂, **2**, is a 3-center uninodal net with **ths** (ThSi₂) topology. Density Functional Theory calculations explain why the flexed-wing bird shape is the preferred and most stable ligand conformation for metal ion binding. Both structures demonstrate

magnetic properties that are characteristic of the respective non-interacting isolated paramagnetic transition metal ions that are present.

INTRODUCTION

Published on 04 March 2016. Downloaded by test 3 on 04/03/2016 14:30:02.

Coordination polymers (CPs) and metal-organic frameworks (MOFs), whose 1-D, 2-D or 3-D structures are based on extended networks of coordinatively bonded metal ions and multidentate organic linkers, are of great interest for applications in heterogeneous catalysis,¹ adsorption,² and molecular separation³ among many others. The overwhelming approach to the assembly of the structures involves coordinating the extended functional groups of the organic linkers with individual metal ions or metal clusters. Much less explored is the positioning of additional metal ions within the center of the organic linkers, thus generating a metalloligand. This approach can lead to an increase in the number and types of metal coordination sites, and also to increased diversity in the resulting CP and MOF structures.

The use of metalloligand-based linkers to synthesize CPs and MOFs have been scarcely reported, ⁴ examples of which include, Ag-tris(dipyrrinato), ⁵ Mn metalloporphyrins, ⁶ Cu-pyridine-2,4-dicarboxylate and Cu-sulfosalicylideneglycylglycine,⁷ Fe, Ru, Os porphyrinato and phthalocyaninato macrocycles, ⁸ 4,4'-biphenyldicarboxylate–Mn(II) chiral Schiff base metalloligand, ⁹ Pt²⁺ bypyridyl carboxylate ¹⁰ and Pd organometallic complexes ¹¹. A macrocyclic polyamine tetraacetic acid was recently used to synthesize heterometallic MOFs.¹²

Ligands containing a crown ether core are potentially useful platforms for isolating the metal ions in center of the linker. Batten and coworkers synthesized 1-D and 2-D coordination polymers using N,N'-bis(4-pyridyl-methyl) diaza-18-crown-6 in which the 4-pyridyl-methyl side arms coordinates Co²⁺, Fe²⁺ and Ag⁺ metal ions, and with the crown moiety simultaneously coordinating the s-block metal ions, K⁺, Ba²⁺ or Ca^{2+,13} We have been investigating the use diaza crown ether polycarboxylates as platforms to coordinate and isolate transition metal ions within their crown moieties, while simultaneously directing the self-assembly of the CP and MOFs structures.¹⁴¹⁶ It was observed that the dimensionality and connectivity of the CP structures obtained were influenced by the number and position of carboxylate groups present. We observed that the presence of four carboxylates groups (two on each side of the diaza crown moiety and in *meta* positions on each benzene ring) resulted in a triply interpenetrating 3-D

Published on 04 March 2016. Downloaded by test 3 on 04/03/2016 14:30:02.

View Article Online DOI: 10.1039/C6CE00360E

structure when the ligand combines with Co (II) ions. With two carboxylates (one on each side of the diaza crown moiety and in *meta* position on each benzene ring), 2-D layered and 1-D chain structures were obtained when the ligand combines with Co (II) and Zn (II) ions.

We herein modified the diaza crown ether dibenzoate ligand by placing the carboxylate groups in *para* position on each benzene ring to generate 4,4'-((1,7-dioxa-4,10-diazacyclododecane-4,10-diyl)bis(methylene))dibenzoate), LH₂.



 LH_2

The reaction of LH_2 with Co (II) ions yields a coordination complex, **1**, while the reaction of the ligand and Mn(II) ions yields a triply interpenetrating 3-D coordination polymer, **2**. Both **1** and **2** have their respective metal ions encapsulated within the ligand's diaza crown-4 moiety. Structure **1** is composed of CoL'H₂O units that are interconnected into a 3-D (1:1)n polymer-like network through hydrogen bonding. The ligand's carboxylate O atoms form strong hydrogen bonds with the H atoms of water molecules that are coordinated to Co(II) ions that are encapsulated in the center of neighboring ligands. For **2**, the 3-D connectivity is achieved as the encapsulated Mn(II) ion in one ligand unit is further coordinated by a single carboxylate O atom from each of two neighboring ligands. In both structures, the ligand assumes a flexed-wing bird shape configuration with the two benzoate side-arms of the crown moiety locked in syn orientation. DFT calculations show this to be the thermodynamically preferred conformation of this ligand.

EXPERIMENTAL SECTION

Materials: Chemicals and solvents are commercially available and were purchased and used without further purification.

Synthesis of dimethyl 4,4'-((1,7-dioxa-4,10-diazacyclododecane-4,10-diyl)bis(methylene)) dibenzoate (**A**)

Methyl 3-(bromomethyl)benzoate (0.378g, 2.17 mmol) and sodium carbonate (0.68 g, 6.42 mmol) were added to a solution of 1,7-diaza-12-crown-4 (0.189 g, 1.09 mmol) in acetonitrile (15 mL) and the mixture was refluxed with stirring for 1 d. The concentrated filtrate of the reaction mixture produced title product after crystallization in acetonitrile. Pale yellow crystals (0.435 g, yield 85 %). Chemical formula: $C_{24}H_{30}N_2O_6$ (FW: 442.51). ¹H NMR (400 MHz, CDCl₃) & 2.73 (8H, t, J = 4.0 Hz, OCH₂CH₂N), 3.57 (8H, t, J = 4.0 Hz, OCH₂CH₂N), 3.69(4H, s NCH₂Ar), 3.90(6H, s, OCH₃), 7.50 (4H, d, J = 7.5 Hz, ArH), 7.99 (4H, d, J = 7.5 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃) d: 52.1(OCH₃), 55.3 (NCH₂CH₂O), 60.8 (NCH₂Ar), 69.7(NCH₂CH₂O), 128.8(Ar-C), 128.9(Ar-CCO₂), 129.7(Ar-C), 145.5(Ar-CCH₂N), 167.2 (CO₂CH₃).

Synthesis of 4,4'-((1,7-dioxa-4,10-diazacyclododecane-4,10-diyl)bis(methylene)) dibenzoic acid, LH₂

Compound A (0.2303 g, 0.489 mmol) was reacted with HCl (aq. 6 N, 2.56 mL) at 90 °C for 6 h with stirring. The white crystals were collected and then recrystallized in water, filtered and dried in air at ambient temperature for 1 d to produce LH₂ as its chloride salt (0.193 g, yield 89 %) with chemical formula, $C_{24}H_{30}N_2O_6\cdot 2HCl\cdot nH_2O$. Elem. anal. calcd. %: C, 47.61; H, 6.99; N, 4.63. Found %: C, 47.44; H, 6.80; N, 4.57. ¹H NMR (400 MHz, D₂O): 3.35-3.55 (m, 4 H), 3.55-3.68 (m, 4 H), 3.68-3.77 (m, 4 H), 3.77-3.91 (m, 4 H), 4.58 (s, 4 H, ArCH₂-N), 7.71 (d, J=8.0 Hz, 4H, ArH_{3.5}), 8.12 (d, J=8.0 Hz, 4H, ArH_{2.6}); ¹H NMR (400 MHz, DMSO-d₆): 2.80-3.73 (multi, 16 H, N-CH₂CH₂-O), 4.53 (br., 4H, ArCH₂-N), 7.58-8.10 (multi, 8H, Ar-H), 10.35 (2H, COOH). ¹³C NMR (100 MHz, D₂O)): 55.5 (N-CH₂CH₂-O), 59.7 (N-CH₂-Ar), 64.1(N-CH₂CH₂-O), 130.2(C₃ and C₅ of Ar), 132.4(C₂ and C₆ of Ar), 132.0(C₁ of ArCOOH), 132.7(C₄ of ArCOOH), 170.0(COOH). ¹³C NMR (100 MHz, DMSO-d₆): 52.93 (N-CH₂CH₂-O), 59.05 (N-CH₂-Ar), 64. 35 (N-CH₂CH₂-O), 129.30 (C₃ and C₅ of Ar), 131.93 (C₂ and C₆ of Ar), 133.05 (C₂ and C₆ of Ar), 133.68 (C₁ of ArCOOH), 166.78 (COOH). FTIR (cm⁻¹): 426(w), 454(w), 498(m), 585(w), 636(w), 705(m), 727(m), 768(w), 784(m), 808(w), 857(w), 878(w), 902(w), 955(m), 969(w), 1021(w), 1054(m), 1079(m), 1109(s), 1131(s), 1159(w), 1183(m),

1227(m), 1273(m), 1322(w), 1355(w), 1374(m), 1418(m), 1452(w), 1513(w), 1577(w), 1615(w), 1641(w), 1702(s), 2500-3150(broad, COOH), 3305.

Synthesis of coordination complex 1

A mixture of ligand, $LH_{2,}$ (7.1 mg, 0.016 mmol), $Co(AcO)_2 4H_2O(14.7 mg, 0.059 mmol)$, pyridine (16 µL, 0.19 mmol) and water (10 mL, 0.56 mol) was sealed in a Teflon lined autoclave, heated at 125 °C for 3 d in an oven and then cooled to ambient temperature. The red crystals were collected and washed with water to yield structure **1** (5.8 mg, 80.2 % yield based on LH₂) with formula $C_{24}H_{32}CoN_2O_8$. Elem. anal. $C_{24}H_{28}CoN_2O_6 \cdot 2(H_2O)$ (FW535.44). calcd. (wt %): C, 53.83; H, 6.02; N, 5.23; Found: C, 52.60; H, 5.85; N, 5.02. FTIR (cm⁻¹): 408(w), 458(w), 513(w), 566(w),591(w), 717(s), 741(m), 774(m), 797(m), 851(m), 944(m), 980(w), 1011(w), 1033(w),1046(w), 1075(w), 1092(m),1104(m), 1175(w), 1375(s), 1456(w), 1547(m), 1595(m),2356(w), 2908(w), 2949(w), 2993(w).

Synthesis of coordination polymer 2

A mixture of LH₂ chloride salt (9.8 mg, 0.018 mmol), Mn(AcO)₂·4H₂O (29.4 mg, 0.12 mmol), pyridine (80 μ L, 0.94 mmol) and H₂O (15 mL, 0.83 mol) was sealed in a Teflon lined autoclave, heated at 125 °C for 3 d in an oven and then cooled to ambient temperature. The yellowish crystals were collected and washed with water to give **2** (9.4 mg, 95 % yield based on LH₂) with formula C₂₄H₂₈MnN₂O₆•2(H₂O) (FW 531.45); Elem. anal. calcd. (wt %): C, 54.24; H, 6.07; N, 5.27; Found: C, 53.42; H,5.82; N, 5.21. FTIR (cm⁻¹): 401(m), 465(m), 513(m), 530(m), 587(m), 611(w), 720(m), 740(m), 783(s), 814(m), 838(w), 852(w), 887(w), 932(w), 959(m), 1017(w), 1027(m), 1051(w), 1081(s), 1076(s), 1104(w), 1137(w), 1156(w), 1182(w), 1257(w), 1286(w), 1394(w), 1380(s), 1441(w), 1470(w), 1481(w), 1554(m), 1598(s), 1667(m), 2600-3100, 3475(m, broad).

Characterization:

¹H and ¹³C NMR spectra were acquired on a Bruker AVANCE400 spectrometer at 400 MHz and 100 MHz, respectively (peak pattern: d-doublet, m-multilet, q-quartet, s-singlet, t-triplet). Infrared measurements were recorded on a Bruker Alpha-P FTIR spectrophotometer (intensive pattern: m-medium, s-strong, w-weak). Single crystal X-ray data were collected on a Bruker APEX2 diffractometer with 1.6 kW graphite monochromated Mo radiation (fine-focus

sealed tube, 45 kV, 35 mA).. The frames were integrated with the SAINT v7.68a.¹⁷ The structure was solved and refined with Olex2 ¹⁸ and SHELX.¹⁹ Structure refinement and other experimental details are presented in Table S1. Powder X-Ray diffraction pattern was recorded on a Panalytical Emperian Series II diffractometer with CuKα radiation source at 45kV and 40 mA, time per step 2s, and step size of 0.04. Thermogravimetric analysis was conducted on a TA Instrument Q50 thermal analyzer at heating rate of 5 °C/min from ambient temperature to 700 °C under air flow. Temperature dependent magnetization measurements were carried out on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). All samples for the magnetic measurements were prepared by fully dispersing an appropriate amount of dry powder nanocrystals in eicosane.

RESULTS AND DISCUSSION

Published on 04 March 2016. Downloaded by test 3 on 04/03/2016 14:30:02.

Ligand LH₂ was synthesized through reaction of 1,7-diaza-12-crown-4 with methyl 3-(bromomethyl)benzoate in the presence of sodium carbonate in acetonitrile under reflux, followed by treatment with aqueous hydrochloric acid. Upon HCl treatment, the ligand crystallized as the chloride salt in orthorhombic space group, Pca2₁, and with unit cell dimensions, a = 10.6102(10) Å, b = 21.855(2) Å, c = 22.183(2) Å. Other crystallographic and structure refinement data are presented in Table 1 (and Electronic Supplementary Information ESI Tables S12-S17). The ligand assumes a flexed-wing bird shape configuration, the orientation of which appears to be stabilized by the electrostatic bonding of the chloride ions to its diaza crown moiety (ESI Figure S1). The configuration of the ligand is further explored below in coordination complex **1** and coordination polymer **2**, which were formed from the thermal reaction of the ligand with cobalt (II) acetate and manganese (II) acetate respectively, in the presence of pyridine and water, and both of which have the ligand's crown moiety coordinating metal ions instead chloride.

7

	Ligand-LH ₂ chloride	1	2				
Empirical formula	$C_{24}H_{34}Cl_2N_2O_7$	$C_{24}H_{32}CoN_2O_8$	$C_{24}H_{32}MnN_2O_8$				
Formula weight	533.22	535.44	531.45				
Temperature/K	100(2)	110(2)	173(2)				
Crystal system	orthorhombic	monoclinic	orthorhombic				
Space group	Pca2 ₁	Cm	Fdd2				
a/Å	10.6102(10)	9.7472(9)	33.046(4)				
b/Å	21.855(2)	22.777(2)	9.0309(10)				
c/Å	22.183(2)	7.0903(7)	16.4592(18)				
α/°	90	90	90				
β/°	90	131.453(6)	90				
$\gamma/^{\circ}$	90	90	90				
Vol/Å ³	5143.9(8)	1179.8(2)	4912.0(9)				
Ζ	8	2	8				
Z'	2		2				
Density(calcd)mg/mm ³	1.378	1.507	1.437				
Absorption coefficient(mm ⁻¹)	0.299	0.781	0.589				
F(000)	2256	562	2232				
Crystal size/mm ³	0.27 x 0.14 x 0.13	$0.427\times0.203\times0.062$	$0.888 \times 0.619 \times 0.318$				
Θ range for data collection	1.864 to 27.484°	2.465 to 29.569°	1.79 to 37.78°				
Index ranges	$-13 \le h \le 14, -29 \le k \le 29,$	$-8 \le h \le 14, -33 \le k \le 24, -$	$-56 \le h \le 40, -15 \le k \le 4$				
	$-30 \le l \le 30$	$10 \le l \le 10$	$13, -22 \le 1 \le 25$				
Reflections collected	36384	4866	15648				
Independent reflections	11495[R(int) = 0.0877]	2617[R(int) = 0.0368]	4964[R(int) = 0.0335]				
Data/restraints/parameters	8549/8/650	2617/5/173	4964/14/186				
Goodness-of-fit on F^2	1.028	1.020	1.060				
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0641, wR_2 = 0.1327$	$R_1 = 0.0462, wR_2 = 0.0940$	$R_1 = 0.0489, wR_2 = 0.1259$				
Final R indexes [all data]	$R_1 = 0.0970, wR_2 = 0.1515$	$R_1 = 0.0539, wR_2 = 0.0975$	$R_1 = 0.0523, wR_2 = 0.1299$				
Largest diff. peak/hole / e $Å^{-3}$	1.202/-0.348	1.01/-0.50	1.03/-0.33				
Flack parameter	0.28(9)	0.032(18)	0.01(2)				
			<u> </u>				
Crystal structure of 1							
Compound 1 crystallizes in the monoclinic space group <i>Cm</i> as a polymer-like (1:1)n							

Table 1.	Crystallogra	phic data	and structure	refinement f	or LH ₂ . 1	and 2 .
1 4010 1.	CI J Stullogit	pine auta	und buldetuie	rennement i	$or \mathbf{Lin}_2, \mathbf{I}$	

Crystal structure of 1

Compound 1 crystallizes in the monoclinic space group Cm as a polymer-like (1:1)n polar but achiral complex. Crystallography data are presented in Table 1. Bond angles, bond lengths and other crystallographic data are presented in ESI Tables S1-S6. The powdered X-Ray diffraction pattern of 1 matches that of its simulated pattern from single crystal diffraction analysis, indicating that the structure crystallizes as a pure phase (ESI Figure S2a). The coordination complex is comprised of the deprotonated ligand, L, and a single Co (II) ion that is

coordinated by the four donor atoms (two N and two O atoms) of the 1,7-diaza-12-crown-4 moiety (Figure 1). In order to satisfy its six coordinate octahedral environment, the Co(II) elevates above the crown to form two bonds to water molecules. The four ligating atoms of the crown distort the octahedral geometry. The Co-N(1) bond length is 2.242(3) Å and Co-O bond lengths ranged from 2.114 (3) to 2.118(3) Å. The crown based angle between oxygen atoms (O1-Co1-O2) is $87.1(2)^{\circ}$ The angle of the coordinated oxygen atom and the Co-N axis (O-Co-N) is $101.86(8)^{\circ}$ and $99.40(8)^{\circ}$ for the second water molecule.



Figure 1. Structure unit of 1.

The two benzoate sidearms of the L are tethered in a *syn* conformation, and therefore the overall metalloligand with the encapsulated metal ion, assumes a flexed-winged bird shape configuration, similar to that observed in the chloride salt of the pure ligand, described above. The angle between the benzene ring and the crown at the methylene group (angle N1-C5-C6) is $115.0(3)^{\circ}$. There are multiple conformers that can be accommodated by this angle as the molecular modelling studies below show. However, it is this ligand conformation that is observed here, in **2** discussed below, and in other 1-D, 2-D, and 3-D coordination polymers with a similar ligand L but containing different number and locations of the carboxylate groups that we previously reported.¹⁴⁻¹⁶ It is also observed in a K-diaza-18-crown-6-ether coordination complex containing partially-fluorinated benzyl sidearms,²⁰ and seems to suggest that this is thermodynamically the most preferred conformation of the ligand. However, further stabilization of this conformer by coordination to Co(II) ions is quite likely. The N(1)-Co(1)-N(1) angle is 147.17(17)° and the Co(II) ion, is elevated above the crown, presumably due to the small size of the crown. However the cobalt atom remains below the methylene carbons of the

CrystEngComm

sidearms. This is also observed in our prior reported 1-D, 2-D and 3-D coordination network structures with *meta* located carboxylates.

Structure **1** crystallizes as a coordination compound instead of a covalently bonded network for unclear reasons, but is most likely due to a delicate balance between the *para* location of the carboxylate groups and the size, electronic environment and elevation of Co(II) ion. However, the extended hydrogen bonded network, with its very strong and linear hydrogen bonds between the carboxylate groups and the coordinated water does resemble a coordination polymer. This arrangement makes sense from a steric and bond valence perspective. The coordinated water forms bonds of 0.5 v.u. to each Co(II) and two external hydrogen bonds of 0.25 v.u. to each oxygen of the carboxylate group. The bond valence sum of the two hydrogen bonds is what can be expected for a Co-O bond in an arrangement with bridging Co(II) atoms without intervening water molecules.

The structure **1** consists of infinite chains of hydrogen bonded $[CoL(H_2O)_2]$ units that lie on mirror planes perpendicular to the ab-plane. The ligand's carboxylate O atoms accept strong hydrogen bonds form water molecules that are coordinated to Co(II) ions encapsulated in the center of neighboring ligands. Each carboxylate oxygen atom accepts a hydrogen bond from a unique $[CoL(H_2O)_2]$ unit. There are four acceptor oxygen atoms and four donor hydrogen atoms in the $[CoL(H_2O)_2]$ unit which therefore behaves as 8-coordinate node in the underlying uni-nodal net. Thus the hydrogen bonding extends the $[CoL(H_2O)_2]$ units into a three dimensional (1:1)_n network via hydrogen bonding with H atoms of the coordinated water molecules and O atoms of the carboxylate groups. The position of coordinated water molecules in the midpoint of the ligand and to O atoms of the carboxylate groups at either end, has an interesting effect on the stacking of $CoL(H_2O)_2$ units and the overall topology of the network (Figures 2a and 2b). Visually, the structure appears like a flock of birds formation along the cdirection. The chains are not linear but instead we have a zig-zag arrangement in which the each $[CoL(H_2O)_2]$ unit is displaced 11.388(2) Å along the *b*-direction. In this arrangement, the H atoms of the water molecules are in ideal positions for donating strong hydrogen bonds to carboxylate O atoms. This repeat distance is exactly half the length of the *b*-axis (22.777(2) Å). The O...H bonds are very short (1.641(7) Å and 1.617(7) Å) and linear (as expected for strong hydrogen bonds), compared to 1.8 Å commonly reported for normal hydrogen bonds in water

and in ice. In other polymers the Co atoms are directly bridged by carboxylate O atoms (for example catena-poly[[diaquacobalt(II)]-l-oxalato]).²¹ However, in this arrangement, the hydrogen bonds are taking the role of bridging Co atoms, and the Co atoms are bridged indirectly *via* the water molecules. Thus the shortened bond is a reflection of the significant strength of the Co-O bond. This suggests that the O-H bonds are weakened considerably to compensate, and that these protons are acidic. Topological analysis of the underlying net shows that it is an 8-connected body centered cubic net with symbol **sqc**3.²²



Figure 2a. 3-D hydrogen bonded network of 1 (viewed along c)



Figure 2b. 3-D hydrogen bonded network of 1 (viewed a)

Crystal structure of 2

Compound 2 is stable in air and in common organic solvents such as methanol, ethanol, acetonitrile, acetone, tetrahydrofuran, and dimethylformamide. Single-crystal X-ray crystallography analysis reveals that it is an infinite, polar 3-D coordination network. The infinite chains lie on twofold symmetry axes parallel to the *c*-axis in the orthorhombic space group *Fdd2*. There are three interpenetrating nets present. Crystallography data for 2 are presented in Table 1. Bond angles, bond lengths and other crystallographic data are presented in ESI Table S1and Tables S7-S10. The powdered X-Ray diffraction pattern of 2 matches that of its simulated pattern from single crystal diffraction analysis, indicating that the structure crystallizes as a pure phase (ESI Figure S2b).



Figure 3. Representation of the partial structure unit of 2.

Mn(II) coordination environment: The Mn(II) ion is eight coordinate and forms a highly irregular polyhedron with surrounding atoms (Figure 3). Four bonds are with two N and two O atoms of the 1,7-diaza-12-crown-4 moiety. The remaining four bonds are with both carboxylate

O atoms from each of two neighboring ligands. The carboxylate binds asymmetrically; one Mn-O bond (2.816(3) Å) is significantly longer than the other (2.128(2) Å). It is not clear why this group forms such an irregular coordination environment but perhaps the resulting tilt is necessary to form a close packed network. Rather, it could be the result of steric crowding about the Mn(II) ion since the ideal coordination number is close to six. The Mn-O1, Mn-O3, Mn-N1 bond lengths are 2.1278(18), 2.3203(19) and 2.393(2) Å, respectively and within the range reported for Mn-O and Mn-N in coordination polymers.²³ The O1¹-Mn-O1, O3¹-Mn-O3, and N1¹-Mn-N1 bond angles are 99.63(11) °, 110.22(12) ° and 120.94(11) ° respectively.

Ligand coordination: The conformation of L with the encapsulated Mn(II) ions is shown in Figures 4. The ligand is octadentate and each ligand complexes three Mn(II) atoms, two through two terminal carboxylates, and one through four donor atoms from the crown. The deprotonated ligand encapsulates Mn(II) ions in its diaza-crown moiety and its two benzoate sidearms further coordinate Mn(II) ions in neighboring ligands. The ligand conformation is similar to 1, and to those we have reported for Co(II) and Zn(II) based 1-D, 2-D and 3-D structures in which the carboxylates were in *meta* positions on the ligand's benzene rings.¹⁴⁻¹⁶ In order to satisfy its eight coordinate environment the Mn(II) elevates above the crown to accommodate two carboxylate groups and the four ligating atoms of the crown distort the geometry. As in structure 1, the two benzoate sidearms of L are locked in a syn conformation, and therefore the overall metalloligand with the encapsulated metal ion in its crown, assumes the flexed-winged bird shape configuration (Figure 4). Each methylene group (C5) between the benzene ring and the crown shows a C-C-N angle of 115.4°, hence the degree of curvature of the benzoate sidearm in 2 is similar to that in 1. The C(8)-N(1)-Mn(1) angle of 108° is due to a higher elevation of the Mn(II) above the crown in comparison Co(II), and is consistent with the longer Mn-O and Mn-N bond lengths present.



Figure 4. Packing diagram of **2** viewed along *b*-axis showing ligand sidearms in syn configuration (blue-green Mn, red O, grey C, blue N, white H).

Figure 5. A portion from one of three 3-D networks of structure 2.

Three dimensional connectivity is achieved by the carboxylate oxygens of one ligand coordinating Mn(II) ions in crown of two adjacent ligands in *bis*-bidentate mode (Figures 4 and

5). Also, each Mn(II) is coordinated by carboxylate oxygens from each of the two neighboring ligands. A lattice water molecule is present and engages in hydrogen bonding with the uncoordinated oxygen atoms from the carboxylates of these neighboring ligands, thus further stabilizing the structure.

The Mn centers can be regarded a 3-connection nodes in the structure. Similarly, the ligands can be regarded as 3-connection nodes by connecting to one Mn atom through the crown, and to two Mn atoms through the carboxylate groups. This is a 3-center uninodal net with **ths** (ThSi₂) topology (Figure 6a). In the figure below the Mn are shown in blue and the 3-connection nodes of the ligands are shown in red. This net can be further simplified: each Mn(II) is linked to 4 other Mn(II) ions through the ligands. Thus each Mn can be considered to be a 4-coordinate node and the ligands as edges of the network. This simplification gives a 4-connected diamond net with **dia** topology and **4/6/c1**; **sqc6** code symbol. However, the 3-center uninodal net with **ths** topology is a better description because it contains the polar structure. The topological analysis with TOPOS²² indicates that structure **2** consist of three interpenetration vectors (Figure 6b). This is commonly observed in coordination polymers and MOFs.

Figure 6a. The underlying 3-center uninodal net with **ths** (ThSi₂) topology in structure **2** viewed along the b-axis.

Figure 6b. Topological representation of the triply interpenetrating 3-D nets of **2** in (i) 2D and (ii) 3-D projection.

Computational investigation of Co-complex and ligand conformations

The shape of the ligand conformation observed in 1 and 2 as well as in the previously reported work encouraged us to conduct the computational investigation. Single unit of ligand

with Co metal ion was studied using the density functional theory (DFT) level. Truhlar's Minnesota density functional of M06-2X with the triple- ζ basis set of 6-311+G(d,p) was used for the geometry optimizations of the complex as well as the conformers of the neutral ligand.^{24, 25} All the calculations were carried out using Gaussian 09 program package.²⁶ Restricted open-shell (RO) formalism was used for optimization of the complex. The optimized structure of the complex with selected geometrical parameters is depicted in Figure 7. The computed bond distances are in close agreement with the experimental values except for Co–N distance. However, both computation and experiment show that two Co–N distances are identical.

Published on 04 March 2016. Downloaded by test 3 on 04/03/2016 14:30:02.

Figure 7. Selected bond distances (in Å) and bond angle (in degrees) obtained from the ROM06-2X/6-311+G(d,p) optimized geometry for the single-unit of cobalt complex **1**. The experimental values obtained by X-ray crystallography are given in parentheses with bold.

Seventeen (17) possible conformers were prepared for the neutral ligand structure (**LH**₂) and they were initially optimized using the M06-2X with 6-31G(d) basis set. The full geometry optimizations of the conformers were also carried out at the M06-2X/6-311+G(d,p) level in order to obtain very reliable results. The optimized structures of all the conformers are given in the ESI Figure S3 and Table S11. As depicted in Figure 8, the relative energies of the conformers show similar trend at the two levels and the difference in ΔE between these two levels is very small or negligible. The conformers of the neutral ligand structure (**LH**₂) contain two dicarboxylic acid groups that form hydrogen bond. We have also observed additional C-H…O and C-H…N hydrogen bonds in some of the conformers. Weak intramolecular C-H… π

interactions in addition to the above-mentioned hydrogen bonds were also observed in few cases.

Figure 8: The relative energy (ΔE , in kcal/mol) of different conformers computed at the M06-2X/6-31G(d) and M06-2X/6-311+G(d,p) levels.

Figure 9. Structures of selected conformers of the neutral ligand (LH_2) and the dicarboxylate anion optimized at the M06-2X/6-311+G(d,p) level.

Our computational investigation shows that LH_2 -C5 is the lowest energy structure among all the conformers explored and it is isoenergetic to LH_2 -C4. As shown in Figure 9, these two conformers possess multiple O–H···O, C–H···O and C–H···N hydrogen bonds along with intramolecular weak C–H··· π interactions because of the existence of two six-membered

CrystEngComm

rings in close contact to each other. However, the neutral conformer of ligand structure that resembles the shape in the complex, **LH₂-Comp** is around 7 kcal/mol less stable than the lowest energy conformer of **LH₂-C5**. It is important to note that the relative energy of the conformer **LH₂-C9**, in which the basic framework of diaza crown ether unit was altered and with no O–H···O hydrogen bond within COOH groups, is significantly higher (about 24 kcal/mol) compared to **LH₂-C5**. Computational results reveal that the low-energy conformers, which exhibit very similar shape of diaza crown ether framework of the complex, could be experimentally accessible. After thorough computational exploration of the conformer which looks the same in the complex to form dicarboxylate anions and run DFT calculations. In case of dianions, the ligand conformer in the complex (**L-Comp**) is more stable than **L-C5**, which is the optimized geometry by removing two hydrogens from the lowest energy **LH₂-C5**. This observed trend is reverse to the neutral conformers. Thus, the dicarboxylate anion prefers to be in the flexed-wing bird shape for metal ion binding.

Fourier Transform Infrared spectral analysis $(LH_2, and 2)(cm^{-1})$

The C=O stretching of LH₂ is observed at 1702 cm⁻¹ while that of **2** is split into 1598 and 1554 cm⁻¹ (α (CO₂)) due to the formation of the bonds between Mn(II) and CO₂¹⁻. The C-O stretching of LH₂ is observed at 1272 and 1227 cm⁻¹, and that of **2** shows a strong absorption at 1380 cm⁻¹. The stretching bands of CH₂-O-CH₂ and CH₂-N-CH₂ of the diaza crown moiety are observed at 1109 and 1131 cm⁻¹ for LH₂, respectively. The formation of coordination bonds with Mn(II) in **2** shift these bands to 1076 and 1081 cm⁻¹, respectively.

Thermal Analysis

The thermal properties of **1** and **2** were assessed from their respective TGA curves (Figure S4). For structure **1**, weight loss event between 170 °C to 235 °C of 7.4 % corresponds to the loss of two coordinated water molecules (calculated 6.7 wt %). Decomposition of the ligand corresponds to weight loss event between 240 °C and 443 C, leaving final residue of 13.6 wt % that is attributed to CoO (calculated 14.0 wt %). For structure **2**, weight loss event up to 125 °C of 6.5 wt. % is attributed to loss of hydrogen bonded lattice water molecules. Weight

loss event between 360 °C and 460 °C is attributed to the decomposition the ligand, and the final residue of 17.1 wt % (calc. 16.4 %) is attributed to manganese dioxide (MnO₂).

Magnetic properties

Published on 04 March 2016. Downloaded by test 3 on 04/03/2016 14:30:02.

Temperature dependent magnetic susceptibilities were measured between 5 K to 320 K for **1** and **2**. The χ and χT values versus temperature are both plotted, where χ is the molar magnetic susceptibility per molecular unit (Figure 10a). The $\chi_M T$ remains constant (inset) at ~ 0.25 cm³ mol⁻¹K over the temperature range measured.²⁷ The curve obeys the Curie-Weiss law with a Curie constant of 2.8 for translating into three unpaired electrons. The smaller value of $\chi_M T$ at room temperature is larger than the expected spin only value of 3.75 cm³ mol⁻¹K for single independent Co (II) ions with spin S =3/2, and is attributed to spin orbit coupling.

The temperature dependent magnetic susceptibility graph profile of structure **2** is similar to **1** (Figure 10b). The flat line of the $\chi_M T$ vs temperature plot (inset) indicates that the sample obeys the Curie-Weiss law, and with a Curie-Weiss constant of 0.4 cm³ mol⁻¹K over the temperature range investigated. This behavior is typical of isolated paramagnetic Mn (II) ions with five unpaired d electrons.^{21, 28}

a) Structure 1

b) Structure 2

Figure 10. Magnetic susceptibility vs temperature plots for 1 (a) and 2 (b).

Conclusions

Diaza-12-crown-4 with carboxylate groups located at para positions on its dibenzoate sidearms, forms a polymer-like (1:1)n polar coordination complex with Co(II) ions, and a 3-D coordination polymer with Mn(II) ions. The 6-coordinate Co(II) ions are coordinated by the four ligating atoms of the crown and by the O atoms from water molecules for 1, whereas the 8-coordinate Mn(II) utilizes carboxylate groups of neighboring ligands, instead of water molecules for 2. In both structures, the metal ion positioned above the plane of the crown moiety and the metalloligand assumes a flexed-wing bird shape, with the two benzoate sidearms of the crown moiety locked in syn conformation. DFT calculations showed this to be the most preferred and most stable ligand conformation of the deprotonated ligand, even in the absence of the metal ion, and therefore, the ligand will assume this predictable conformation in its role as a secondary building unit in synthesis of coordination complex, CPs and MOFs with a transition metal ion located in its center. Though the ligand conformation is common to both structures, it remains unclear why 1 crystallizes as a hydrogen bonded coordination compound,

while 2 is an infinite polar triply interpenetrating 3-D coordination network. Both structures demonstrate magnetic properties that are characteristic of the respective non-interacting isolated paramagnetic transition metal ions present.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as follows: CCDC 1452096 for LH₂ chloride salt, CCDC 1419712 for structure 1 and CCDC 1419711 for structure 2. These data can be obtained online free of charge via http://www.ccdc.cam.ac.uk/pages/Home.aspx (or from Cambridge Crystallographic Centre. 12 Union Road, Cambridge CB21EZ, Data UK. or www.deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by United States National Science Foundation Grants Nos. HRD-0630456 and HRD-1305041, United States National Nuclear Security Administration Grant No. NA0000979, and, United States Department of Energy Grant No. DE-FE0022952. We thank Daniel Sabo at Georgia Institute of Technology for conducting the magnetic susceptibility measurements.

References

 ⁽a) Marco Ranocchiari and Jeroen Anton van Bokhoven, *Phys. Chem. Chem. Phys.*, 2011,13, 6388-639, (b) Jiewei Liu, Lianfen Chen, Hao Cui, Jianyong Zhang, Li Zhang and Cheng-Yong Su, *Chem. Soc. Rev.*, 2014,43, 6011-6061; (c) Jorge Gascon , Avelino Corma , Freek Kapteijn , and Francesc X. Llabrés i Xamena, *ACS Catal.*, 2014, 4 (2), 361–378; (d) Corma, A.; Gracia, H.; Llabres I Xamena, F. X. *Chem. Rev.* 2010, 110, 4606-4655. (e) Vermoortele, F.; Ameloot, R.; <u>Vinmont</u>, A.; Serre, C.; DeVos, D. E. *Chem. Commun.* 2011, 47, 1521-1523. (f) Cirujano, F.G.; Llabres i Xamena, F. X.; Corma, A. *Dalton Trans.* 2012, 41, 4249-4254. (g) Liao, L.; Ingram, C.W.; Vandeveer, D.; Hardcastle, K.; Solntsev, K.; Sabo, M. D.; Zhang Z. J.; Weber, R. T. *Inorg. Chim. Acta.* 2012, 391, 1-9.

 ⁽a) Stylianou, K. C.; Warren, J. E.; Chong, S. Y.; Rabone, J.; Bacsa, J.; Bradshaw, D.;. Rosseinsky, M. J. *Chem. Commun.* 2011, 47, 3389-3391. (b) Suh, M. P.; Park, H. J.; Prasad, T. K. Lim, D.-W. *Chem. Rev.*, 2012, 112, 782-835. (c) Li, J.-R.; (c) Férey, G.;

Mellot-Draznieks, C.; Serre, C.; Millange, F.; Detour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, 309, 2040-2042. (d) Latroche, M.; Surble, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J. H.; Chang, J. S.; Jhung, S. H.; Férey, G.; *Angew. Chem. Int. Ed.* **2006**, 45, 8227-8231. (e) Gao, W.-Y.; Niu, Y.; Chen, Y.; Wojtas, L.; Cai, J.; Chen, Y. -S.; Ma, S. *CrystEngComm*, **2012**, 14, 6115-6117.

- (a) Getman, R. B.; Bae, Y.-S.; Wilmer, C. E.; Snurr, R. Q. *Chem. Rev.* 2012, *112*, 703-723;
 (b) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* 2012, *112*, 724-781; (c) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* 2012, *112*, 782-835; (d) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* 2012, *112*, 869-932.
- (a) Robson, R. *Dalton Trans.* 2000, 3735-3744. (b) Janiek, C. *Dalton Trans.* 2003, 2781-2894. (c) James, S. L. *Chem. Soc. Rev.* 2003, 32, 276-278. (d) Garibay, S. J.; Stork, J. R.; Cohen, S. M. *Prog. Inorg. Chem.* 2009, *56*, 335-378. (e) Kitagawa, S.; Noro, S.-I.; Nakamura, T. *Chem. Commun.* 2006, 701-707.
- 5. Halper, S. R.; Do, Loi; Stork, J. R.; Cohen, S. M. J. Am. Chem. Soc. **2006**, 128, 15255-15268.
- (a) Suslick, K. S.; Bhyrppa, P.; Chou, J. H.; Kosal, M. E.; Nakagaki, S.; Smithenry, D. W.; Wilson, S. R. Acc. Chem. Res. 2005, 38, 283-291. (b) Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. J. Am. Chem. Soc., 2011, 133 (15), 5652-5655. (c) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. J. Am. Chem. Soc. 2009, 131 (12), 4204-4205. (d) Zou, C.; Zhang, Z.; Xu, X.; Gong, Q.; Li, J.; Wu, C.-D. J. Am. Chem. Soc., 2012, 134 (1), 87-90.
- (a) Noro, S; Kitagawa, S; Yamashita, M; Wada T. *Chem. Commun.*, 2002, 222-223. (b) Zhang, J. Cheng, S.; Wang, X.; Yuan, L.; Xue, M.; Y; Liu, W.; CrystEngComm, 2013, 15, 6074-6082.
- 8. Preparative Inorganic Reactions, W.L. Jolly, ed. Interscience, New York, **1964**, Vol. 1, pp1-25.
- 9. Cho, S. H.; Ma, B .Q.; Nguygen, S. T.; Hupp J. T. and Albrecht-Schmitt, T. E.*Chem. Commun.* **2006**, 2563-2565.
- 10. Szeto, K. C.; Prestipino, C.; Lamberti, C.; Zecchina, C. A.; Bordiga, S.; Bjorgen, M.; Tilset, M.; Lillerud, K. P. *Chem. Mater.*, **2007**, 19, 211-214.
- 11. Oisaki, K.; Li, Q.; Furukawa, H.; Czaija, A. U.; Yaghi, O. M. J. Am. Chem. Soc., **2010**, 132 9262-9264.

- 12. Zhu, X-D.; Lin, Z.-J.; Liu, T. Fu; Xu, B.; Cao, R.; *Cryst. Growth. Des.* **2012**, 12, 4708-4711.
- 13. Duriska, M. B; .Neville, S. M; Batten, S. R.; Chem. Commun, 2009, 37, 5579-5581.
- 14. Ingram, C. W.; Liao, L.; Bacsa, J.; Acta Cryst. 2012. E68, ml 410.
- 15. L. Liao, C. W. Ingram, J. Bacsa and C. Parker, Acta Cryst. 2014 70,1 M24.
- 16. Liao, L. Bacsa, J., Harruna, I., Sabo, D., Zhang, Z. J., Ingram, C.W., *Cryst. Growth & Design* **2013**,3,1131–1139.
- 17. Bruker SAINT V7.68a, B. A. I. M. W. U. 2. 2009.

- (a) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Crystallogr. 2009, 42, 339-341; (b) Barbour, L. J. X-seed a software tool for supramolecular crystallography. J. Supramol. Chem. 2003, 1, 189-191.
- 19. Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr.*, *Sect. A: Found. Crystallogr.* **2008**, *64*, 112-122.
- 20. Ki-Whan Chi, Kwang Taeg Shim, Hwang Huh, Uk Lee, and Young Ja Park, *Bull. Korean Chem. Soc.* **2005**, 26, (3), 393-398.
- 21. Bacsa, J.; Eve, D.; Dunbar, K. R.; Acta Cryst. (2005). C: Crystal Struct. Commun. 61, m58-m60.
- 22 Blatov, V.A.; Shevchenko, A. P.; Proserpio, D. M.; Cryst. Growth Des., 2014, 14, 3576– 3586
- 23. Peng Liang, Wen-Xiu Xia, Wei-Man Tian and Xian-Hong Yin, *Molecules* **2013**, *18*, 14826-14839.
- 24. Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry. J. Chem. Phys. 2006, 125, 194101.
- 25. Zhao, Y.; Truhlar, D. G. Theor. Chem. Acc. 2008, 120, 215-241.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Revision A.1 ed.; Gaussian, Inc.: Wallingford, CT, 2009; Gaussian 09.

- (a) K. G. Alley, R. Bircher, O. Waldmann, S. T. Ochsenbein, H. U. Güdel, B. Moubaraki, K. S. Murray, F. Fernandez-Alonso, B. F. Abrahams and C. Boskovic, *Inorg. Chem.*, 2006,45, 8950. (b) T. Duangthongyou, S. Jirakulpattana, C. Phakawathai and M. Kurmoo, *Polyhedron*, 2010, 29, 1156. (c) W. Xue, B.-Y. Wang, J. Zhu, W.-X. Zhang, Y.-B. Zhang, H.-X. Zhao and X.-M. Chen, *Chem. Commun.*, 2011, 47, 10233. (d) H.-L. Sun, Z.-M. Wang and S. Gao, *Inorg. Chem.*, 2005, 44, 2169.
- (a) Jia, H.; Luo,X.; Ma, B.; Liu, Y.; Li, G.; *Syn. React. Inorg., Metal-Organic, and Nano-Metal Chem.*, **2015**, 45, (11), 2015, 1627-1631, (b) Hazari, D.; Jana, S. K.; Puschmann, H.; Zangrando, E.; Dala, S.; *Trans. Met. Chem.* 2015 DOI:10.1007/s11243-015-9952-z; (c) Liu, C.-Y.; Lee, G.-H.; Wang, H.-T.; *J. Chinese Chem. Soc.* **2009**, 56, 709-717.

Graphical Abstract

Hydrogen bonded (top) and coordination polymeric (bottom) 3-D structures from diaza 12 crown 4 ether based dicarboxylate ligand and a transition metal ion. The ligand assumes a flexed-winged bird shape with the benzoate sidearms of the crown moiety locked in a *syn* orientation.