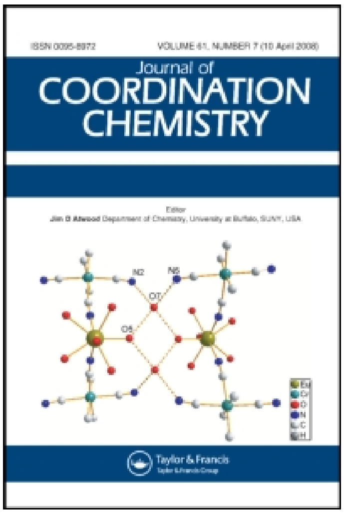

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Synthesis and crystal structure of potassium and manganese complexes of 1,2,3-triazole-4,5-dicarboxylic acid

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Synthesis and crystal structure of potassium and manganese complexes of 1,2,3-triazole-4,5-dicarboxylic acid

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Three coordination compounds $[K(H_2TDA)H_2O]_n$ (**1**), $[K(H_2TDA)(H_3TDA)2H_2O]_n$ (**2**), and $Mn_2(phen)_2(HTDA)_2(H_2O)_4$ (**3**) have been synthesized and characterized structurally by X-ray diffraction, where $H_3TDA = 1,2,3$-triazole-4,5-dicarboxylic acid and phen = 1, 10-phenanthroline. Their solid-state structures have been characterized by elemental analysis and IR spectroscopy. In **1**, a 3-D (4, 8)-connected metal-organic framework has been constructed using dinuclear potassium clusters as eight-connected nodes and the ligands as four-connected nodes; it represents the fluorite topology network. Compound **2** exhibits 1-D chains along *c*-axis, which are connected by strong hydrogen-bond interactions in 2-D layers; the layers are further stacked via hydrogen bonds in the *b*-direction. In **3**, two neighboring Mn(II) ions are bridged by two 1,2,3-triazole-4,5-dicarboxylic groups, forming a binuclear structure, with Mn(II)···Mn(II) distance of 4.356 Å, which is further linked to generate a 2-D layer structure via interdimer hydrogen bonds. The fluorescence for these compounds was investigated.

Keywords: Coordination compounds; Hydrogen bonds; 1,2,3-Triazole-4,5-dicarboxylic acid; Fluorescent properties

1. Introduction

Interest in coordination polymers is rapidly expanding because of their intriguing architectures and potential applications, such as magnetism [1–3], host–guest chemistry [4, 5], catalysis [6, 7], and functional porous materials [8, 9].

Heterocyclic dicarboxylic acids have been used to prepare metal coordination polymers because the heteroatoms may serve as potential coordinating sites, resulting in formation of the structures of higher dimensions [10–13]. 1,2, 3-Triazole-4,5-dicarboxylic acid (H_3TDA) is one such ligand. The three triazole nitrogens of this ligand may coordinate such that this ligand with various metals should produce intriguing poly-dimensional structures with complicated topologies. There have been several structurally determined examples of Rh(II), Cu(II), Mn(II), Gd(III), and Cd(II) complexes with coordination of this ligand [modes (e)–(i)

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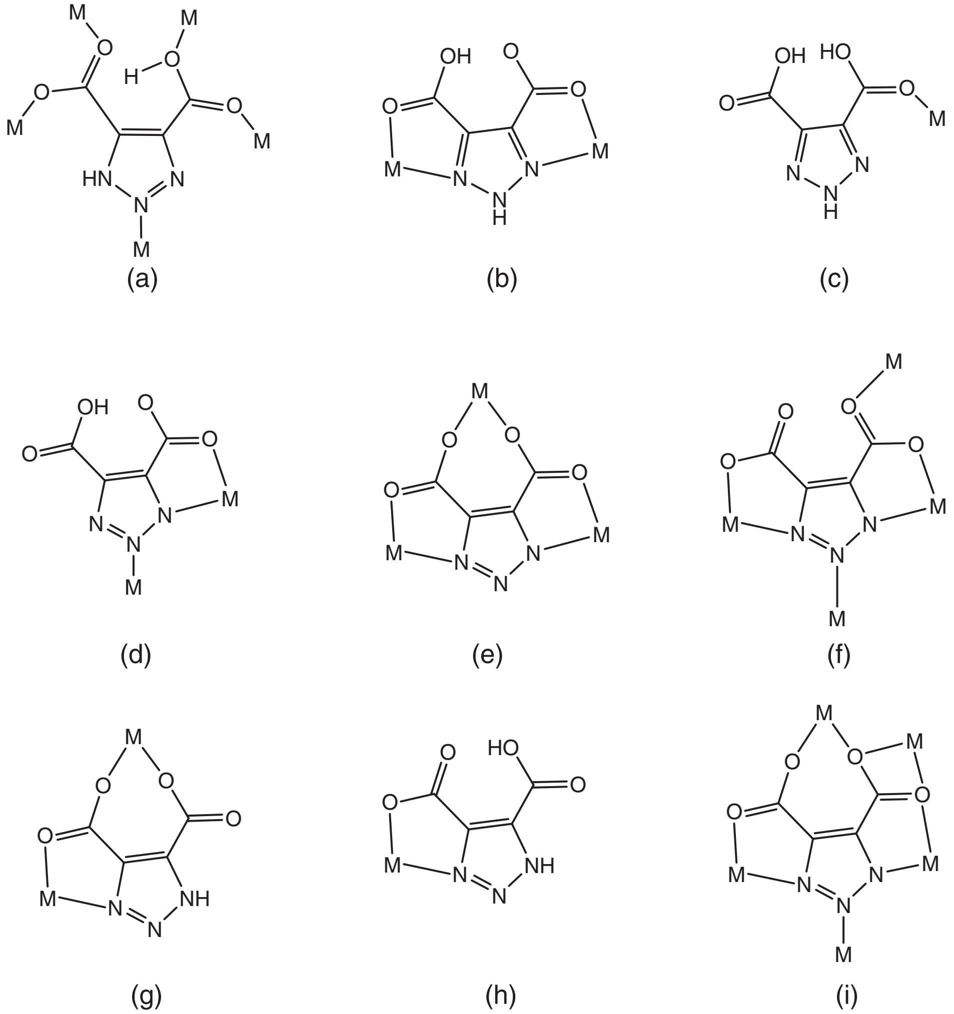

Scheme 1. The coordination modes of H_3TDA.

in scheme 1] [14–19]. We present here the synthesis and crystal structure of $[K(H_2TDA)H_2O]_n$ (**1**), $[K(H_2TDA)(H_3TDA)2H_2O]_n$ (**2**), and $Mn_2(phen)_2(HTDA)_2(H_2O)_4$ (**3**) ($H_3TDA = 1,2,3$-triazole-4,5-dicarboxylic acid and phen = 1,10-phenanthroline).

2. Experimental

2.1. *Synthesis of $[K(H_2TDA)H_2O]_n$ and $[K((H_2TDA)(H_3TDA)2H_2O]_n$*

We synthesized H_3TDA according to the literature method [20] by $KMnO_4$ oxidation of benzotriazole. We used powdered $KMnO_4$ instead of saturated solution of $KMnO_4$. Interestingly, two potassium complexes containing 1,2,3-triazole-4,5-dicarboxylic acid ligand were found.

Powdered $KMnO_4$ (50.0 g, 317 mmol) was carefully added over 1 h to a vigorously stirred solution of 1,2,3-benzotriazole (6.7 g, 56 mmol) in water (400 mL), which was heated to 80°C. The resulting suspension was refluxed for 4 h. Then the reaction mixture was cooled to room temperature and the precipitated MnO_2 removed by filtration. Half of the filtrate was evaporated, then 30 mL 37% hydrochloric acid was added; the solution was allowed to stand overnight producing colorless acicular **1** in 52% yield. Elemental Anal. Calcd: C, 22.53; H, 1.89; N, 19.70%. Found: C, 22.50; H, 1.85; N, 19.76%. The IR spectrum exhibits a complicated pattern of bands in the range 4000–400 cm^{-1}: 3503 and 3426 ($\nu_{sO\text{–}H}$ and $\nu_{sN\text{–}H}$), 1644 and 1598 cm^{-1} ($\nu_{asC=O}$).

Colorless block crystals of **2** were obtained in 12% yield by slow evaporation of the filtrate over a period of 3 days. Elemental Anal. Calcd: C, 24.74; H, 2.34; N, 21.63%. Found: C, 24.70; H, 2.31; N, 21.68%. The IR spectrum exhibits a complicated pattern of bands in the range 4000–400 cm^{-1}: 3554 and 3232 ($\nu_{sO\text{–}H}$ and $\nu_{sN\text{–}H}$), 1742, 1634, and 1511 cm^{-1} ($\nu_{asC=O}$).

2.2. *Synthesis of $Mn_2(phen)_2(HTDA)_2(H_2O)_4$*

A mixture of $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.5 mmol), **2** (0.097 g, 0.25 mmol), and phen (0.103 g, 0.5 mmol) were dissolved in water (14 mL) and ethanol (1 mL); the mixed solution was stirred for 30 min at room temperature, transferred to and sealed in a 25-mL Teflon-lined stainless steel reactor, and then heated at 150°C for 24 h. Upon cooling to room temperature, light yellow crystals of **3** were obtained. Yield: 35% based on Mn. Elemental Anal. Calcd: C, 45.08; H, 3.07; N, 16.42%. Found: C, 45.17; H, 3.01; N, 16.35%. The IR spectrum exhibits a complicated pattern of bands from 4000 to 400 cm^{-1}: 3416 ($\nu_{sO\text{–}H}$), 1634 and 1573 cm^{-1} ($\nu_{asC=O}$).

2.3. *X-ray crystallography*

Diffraction data for crystals with dimensions $0.16 \times 0.10 \times 0.08$, $0.20 \times 0.18 \times 0.16$, and $0.18 \times 0.16 \times 0.12\ mm^3$ were performed with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker APEX area-detector. A semiempirical absorption correction was applied to the data. The structures were solved by direct methods using SHELXS-97 and refined against F^2 by full matrix least-squares using SHELXL-97. Hydrogens were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in table 1.

2.4. *Physical measurements*

Elemental analyses (C, H, and N) were determined on an Elementar Vario EL elemental analyzer. Infrared spectroscopy on KBr pellets was performed on a Nexus 912 AO446 FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Fluorescence spectroscopy was performed on a Perkin–Elmer LS 55 luminescence spectrometer.

Table 1. Crystal data and structure refinement for **1**–**3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_4H_4KN_3O_5$	$C_8H_9KN_6O_{10}$	$C_{32}H_{26}Mn_2N_{10}O_{12}$
Formula weight	213.2	388.31	852.51
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*P2(1)/c*	*Pna2(1)*	$P\bar{1}$
Units of dimensions (Å, °)			
a	6.622(3)	6.6718(4)	9.1702(18)
b	17.514(7)	14.1511(8)	9.5403(19)
c	6.707(3)	15.4806(9)	10.462(2)
α	90	90	82.23(3)
β	96.514(6)	90	80.54(3)
γ	90	90	78.10(3)
Z	4	4	1
D_{Calcd} ($\mathrm{Mg\,m^{-3}}$)	1.832	1.765	1.611
F(000)	432	792	434
µ ($\mathrm{mm^{-1}}$)	0.683	0.435	0.798
Crystal size ($\mathrm{mm^3}$)	0.16 × 0.10 × 0.08	0.20 × 0.18 × 0.16	0.18 × 0.16 × 0.12
θ Range (°)	2.33–25.04	1.95–25.05	1.98–25.05
Index ranges	$-3 \le h \le 7$; $-20 \le k \le 20$; $-7 \le l \le 7$	$-6 \le h \le 7$; $-10 \le k \le 16$; $-16 \le l \le 18$	$-10 \le h \le 10$; $-9 \le k \le 11$; $-7 \le l \le 12$
Reflections collected	3993	7225	4428
Unique reflections	1358 ($R_{\mathrm{int}} = 0.0392$)	2409 ($R_{\mathrm{int}} = 0.0159$)	3032 ($R_{\mathrm{int}} = 0.0221$)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-equivalents on F^2	Full-matrix least-equivalents on F^2	Full-matrix least-equivalents on F^2
Data/restraints/parameters	1358/0/118	2409/1/229	3032/0/253
Goodness-of-fit on F^2	0.998	1.026	1.110
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$, $wR_2 = 0.0919$	$R_1 = 0.0236$, $R_2 = 0.0584$	$R_1 = 0.0597$, $wR_2 = 0.1787$
R indices (all data)	$R_1 = 0.0557$, $wR_2 = 0.1025$	$R_1 = 0.0249$, $wR_2 = 0.0595$	$R_1 = 0.0711$, $wR_2 = 0.1874$

3. Results and discussion

3.1. *Description of the crystal structure for [K(H_2TDA)H_2O]*$_n$

[K(H_2TDA)H_2O]$_n$ crystallizes in the monoclinic system, with space group *P2(1)/c*. Figure 1 shows the coordination geometry and atom labeling. The central potassium is seven-coordinate, with four oxygens and one nitrogen from five bridged H_2TDA groups (O2, O1A, O3A, O4A, and N2A), and two oxygens from water (O5 and O5A), to form a distorted capped trigonal prism. One of the triangular faces is defined by two carboxylate oxygens and one nitrogen (O1A, O4A, and N2A); the other one is defined by three oxygens from H_2TDA and one coordinated water (O5, O5A, and O3A), the dihedral angle between the two trigonal faces is 13.5°, the carboxylate oxygen (O2) occupies the capped position. Each pair of K ions is bridged by two coordinated waters and two H_2TDA ligands to form a $K_2O_{10}N_2$ unit with a K(I)–K(I) distance of 4.1570 Å (figure 2). The dinuclear potassium clusters are further connected by H_2TDA ligands to form a 3-D network [figure 3(a)]. If H_2TDA ligands are considered as four-connected nodes, and dinuclear potassium clusters are considered as eight-connected nodes, then the overall structure of **1** is a 3-D (4, 8)-connected framework [figure 3(b)]. The Schläfli symbol for **1** is $(4^{12}, 6^{12}, 8^4)(4^6)_2$, which is different to that found in [K_2Cd(HTDA)$_2$], where a 3-D (4, 4, 6)-connected network was found [17].

Examples of (4, 8)-connected frameworks are rare [21–26], and it is reminiscent of fluorite (CaF_2), one of the most important and preferred structures for AB_2 type compounds. In the simplified structure of **1**, the H_2TDA ligands replace F^- ions as four-connected nodes, and the dinuclear potassium clusters replace Ca^{2+} ions as eight-connected nodes. Compared with the fluorite net, the eight-connected node of **1** is not a single atom but dinuclear, and this structure of **1** can be regarded as a decorated fluorite net. The (4, 8)-connected framework of **1** is similar to the Cd(II) complex with tetrakis(4-carboxyphenyl)methane [21], where (4, 8)-connected nodes are simplified by

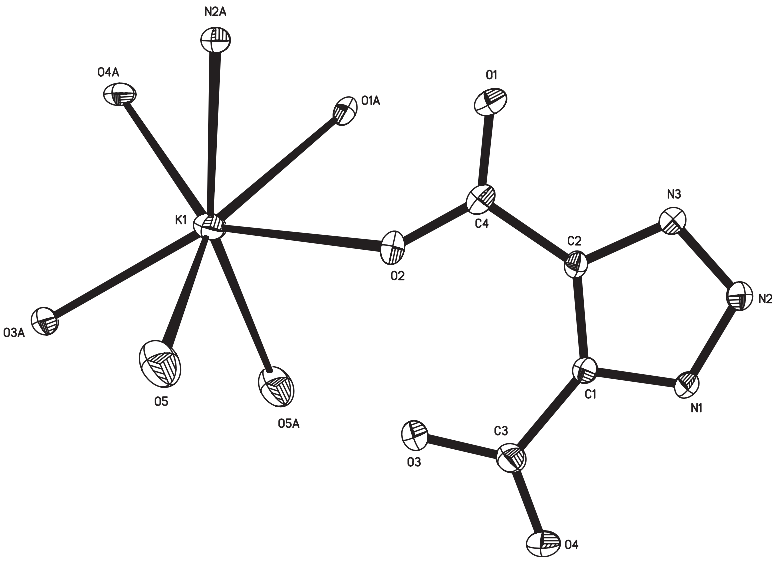

Figure 1. ORTEP drawing (50% thermal ellipsoids) of **1**.

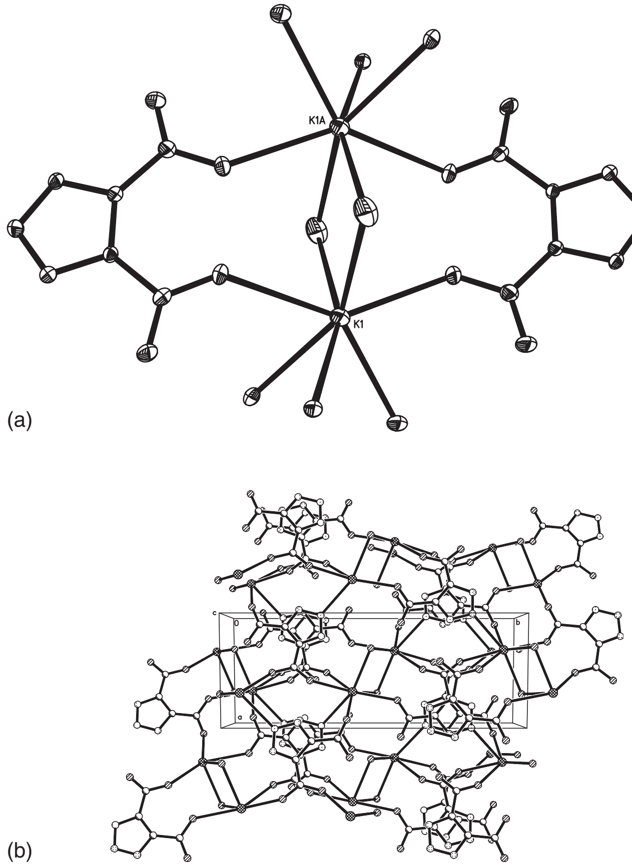

Figure 2. View of the dinuclear potassium cluster of **1**.

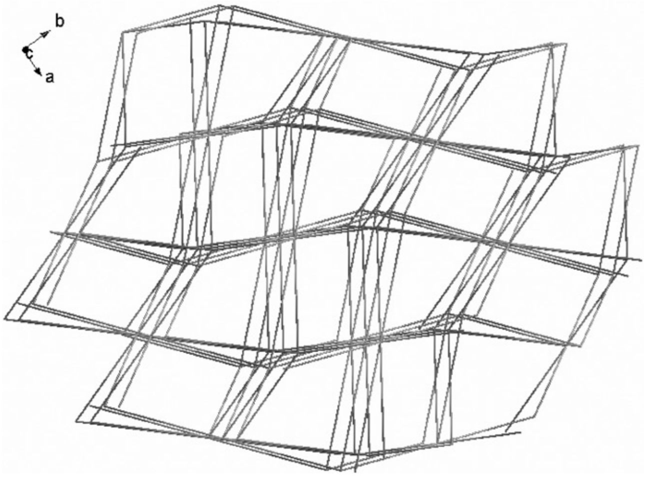

Figure 3. View of the (a) 3-D network structure and (b) (4, 8)-connected framework of **1**.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths			
K1–O3	2.759(2)	K1–O5^c	2.855(3)
K1–O4^a	2.788(2)	K1–N2^d	2.911(3)
K1–O5	2.804(3)	K1–O2^c	2.952(2)
K1–O1^b	2.814(2)	K1–K1^c	4.1570(16)
Bond angles			
O3–K1–O4^a	78.44(7)	O4^a–K1–N2^d	77.62(7)
O3–K1–O5	76.56(7)	O5–K1–N2^d	157.31(7)
O4^a–K1–O5	118.46(8)	O1^b–K1–N2^d	74.95(7)
O3–K1–O1^b	139.52(8)	O5^c–K1–N2^d	92.24(8)
O4^a–K1–O1^b	71.60(6)	O3–K1–O2^c	140.74(7)
O5–K1–O1^b	94.27(7)	O4^a–K1–O2^c	140.11(7)
O3–K1–O5^c	74.18(8)	O5–K1–O2^c	85.88(7)
O4^a–K1–O5^c	137.90(8)	O1^b–K1–O2^c	75.75(7)
O5–K1–O5^c	85.46(8)	O5^c–K1–O2^c	69.59(7)
O1^b–K1–O5^c	145.27(7)		

Symmetry transformations used to generate equivalent atoms: $^a -x+2, -y+1, -z+2$; $^b -x+1, y-1/2, -z+3/2$; $^c -x+1, -y+1, -z+1$; $^d -x+2, y-1/2, -z+3/2$.

Table 3. Hydrogen bonds in **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O3–H2···O2	0.82	1.64	2.457(3)	175.3
O5–H3···N3^a	0.85	2.17	2.992(3)	161.1
O5–H4···O4^b	0.85	2.12	2.963(3)	169.5
N1–H1···O1^c	0.86	1.89	2.735(3)	168.1

Symmetry transformations used to generate equivalent atoms: $^a -x+1, y-1/2, -z+3/2$; $^b x-1, y, z$; $^c x+1, -y+3/2, z+1/2$.

tetrakis(4-carboxyphenyl)methane and tetranuclear cadmium carboxylate clusters, respectively.

In **1**, the ligand exhibits an unusual pentadentate binding mode [mode (a) in scheme 1], chelating five potassium ions. The K–O bond distances fall in the range 2.756(2)–2.952(2) Å (table 2), the average K–O distance is 2.829(2) Å, slightly longer than that of [$K_2Cd(HTDA)_2$] [2.806(2) Å], while the K–N bond length [2.911(3) Å] is shorter than that of [$K_2Cd(HTDA)_2$] [2.972(2) Å] [17]. In addition, the coordination waters are connected with H_2TDA groups through multiple strong hydrogen bonds (table 3), which further stabilize the 3-D framework.

3.2. *Description of the crystal structure for [$K(H_2TDA)(H_3TDA)2H_2O]_n$*

Figure 4 shows the molecular structure of **2**, which contains one potassium cation, one 1,2,3-triazole-4,5-dicarboxylate anion, one 1,2,3-triazole-4,5-dicarboxylic acid molecule, and two coordination waters; the anion is tetradentate [mode (b) in scheme 1], chelating two potassium ions. The acid molecule is coordinated to potassium through one carbonyl oxygen [mode (c) in scheme 1]. The distances between the potassium cation and the oxygens range from 2.7013(15) to 2.8983(15) Å (table 4). The mean K–O

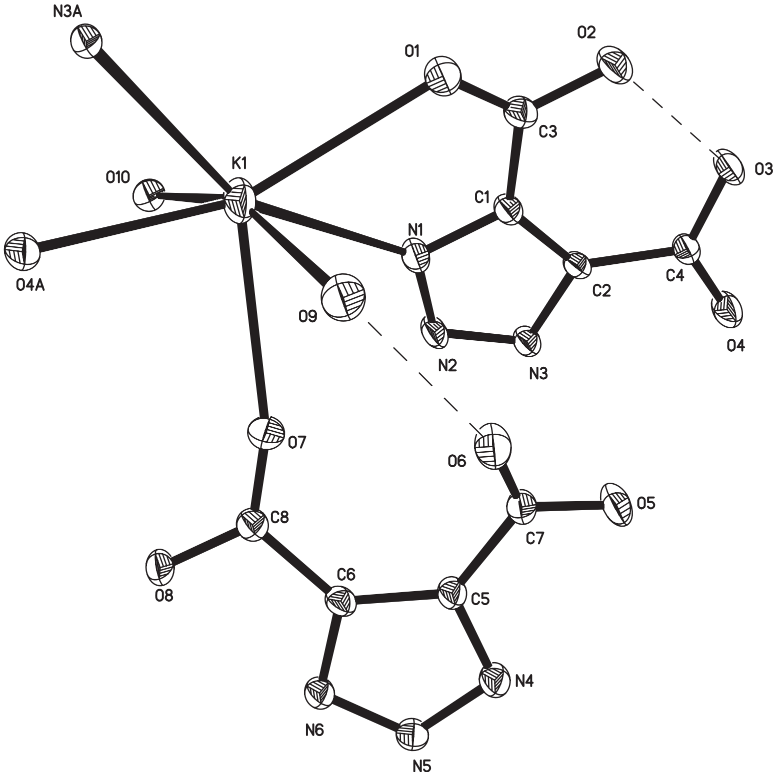

Figure 4. ORTEP drawing (50% thermal) of molecular structure of **2**.

Table 4. Selected bond lengths (Å) and angles (°) for **2**.

Bond lengths			
K1–O4^{a}	2.7011(15)	K1–N1	2.8826(17)
K1–O9	2.7376(18)	K1–O1	2.8983(15)
K1–O10	2.8433(17)	K1–N3^{a}	3.0195(16)
K1–O7	2.8596(15)		
Bond angles			
O4^{a}–K1–O9	97.57(5)	O9–K1–O1	81.30(5)
O4^{a}–K1–O10	79.20(5)	O10–K1–O1	109.77(5)
O9–K1–O10	157.97(5)	O7–K1–O1	115.01(5)
O4^{a}–K1–O7	83.88(5)	N1–K1–O1	56.75(4)
O9–K1–O7	66.24(5)	O4^{a}–K1–N3^{a}	57.64(4)
O10–K1–O7	91.73(5)	O9–K1–N3^{a}	90.47(5)
O4^{a}–K1–N1	145.02(5)	O10–K1–N3^{a}	105.55(5)
O9–K1–N1	91.89(5)	O7–K1–N3^{a}	132.49(5)
O10–K1–N1	79.57(5)	N1–K1–N3^{a}	156.25(5)
O7–K1–N1	69.31(5)		

Symmetry transformations used to generate equivalent atoms: $^{a}-x, -y+1, z+1/2$.

bond distance [2.808(2) Å] is slightly shorter than that of **1** while similar to the potassium complex of 1,2,3-tri(ethoxycarbonylpropyl)-*p*-*t*-butylcalix[6]arene [2.809(3) Å] [27]. The K–N bond distances [K–N1 = 2.8826(17) Å, K–N3A = 3.0195 (16) Å] are comparable to those of **1**.

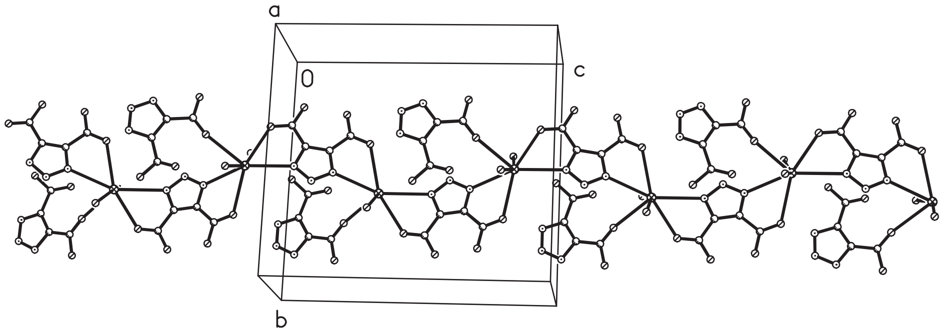

Figure 5. View of the 1-D polymeric chain of **2**.

Table 5. Hydrogen bonds in **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O9–H10···O6	0.85	2.05	2.857(2)	157.9
O2–H2···O3	0.82	1.67	2.491(2)	176.6
O5–H5···O3^a	0.82	1.81	2.6179(18)	169.0
O8–H8···O10^b	0.82	1.68	2.4831(19)	167.4
O9–H9···N4^c	0.85	2.14	2.963(2)	163.1
O10–H11···O9^d	0.85	1.93	2.738(2)	157.3
O10–H12···O4^e	0.85	1.88	2.7160(19)	166.1
N2–H2A···O8^f	0.86	2.18	2.845(2)	133.8
N2–H2A···N6^f	0.86	2.43	3.229(2)	155.7
N5–H5A···O1^g	0.86	1.89	2.747(2)	171.8

Symmetry transformations used to generate equivalent atoms: $^{a}x+1/2, -y+3/2, z, -z+1/2$; $^{b}x+1/2, -y+1/2, z$; $^{c}-x+1, -y+1, z+1/2$; $^{d}x-1, y, z$; $^{e}-x-1/2, y-1/2, z+1/2$; $^{f}x-1/2, -y+1/2, z$; $^{g}-x+1/2, y-1/2, z-1/2$.

The potassium of **2** is seven-coordinate with five O atoms and two N atoms from ligands and waters, but the coordination geometry is different than **1** and similar to [$K_2Cd(HTDA)_2$], a distorted monocapped octahedral coordination geometry in which the basal plane is formed by two nitrogen atoms (N1 and N3) and two oxygen atoms (O1 and O4) from two H_2TDA anions with a mean deviation of 0.0684 Å from the least-squares plane. The corresponding axial position is taken by two oxygen atoms (O9 and O10) from two water molecules with an O9–K1–O10 angle of 157.97(5)°; one carbonyl oxygen from H_3TDA (O7) occupies the capped position. The potassium ions are linked by H_2TDA anions into 1-D chains along *c*-axis (figure 5), which are connected by strong hydrogen bonds (table 5) to result in 2-D layers (figure 6). The layers further stack via hydrogen bonds in the *b*-direction into a 3-D supramolecular network, similar to $[\{Gd(H_2O)_4(Htda)\}\cdot(H_2tda)\cdot H_2O]_n$. In that complex, every $HTDA^{2-}$ ligand links two Gd(III) ions to form a 1-D zigzag chain [14]. The chains are linked by intermolecular hydrogen bonds between the nitrogen atoms in the triazole ring and the oxygen atoms of the carboxylate groups to form 2-D layers. These layers are further linked through the counterions of H_2tda^- and lattice water molecules into a 3-D supramolecular network. However, the tetradentate binding mode [mode (g) in scheme 1] of this ligand is different than **2**.

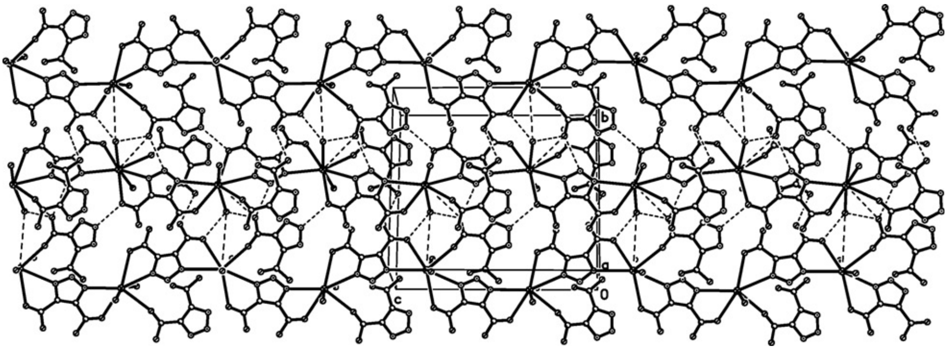

Figure 6. View of the 2-D layer structure of **2** formed by hydrogen bonds.

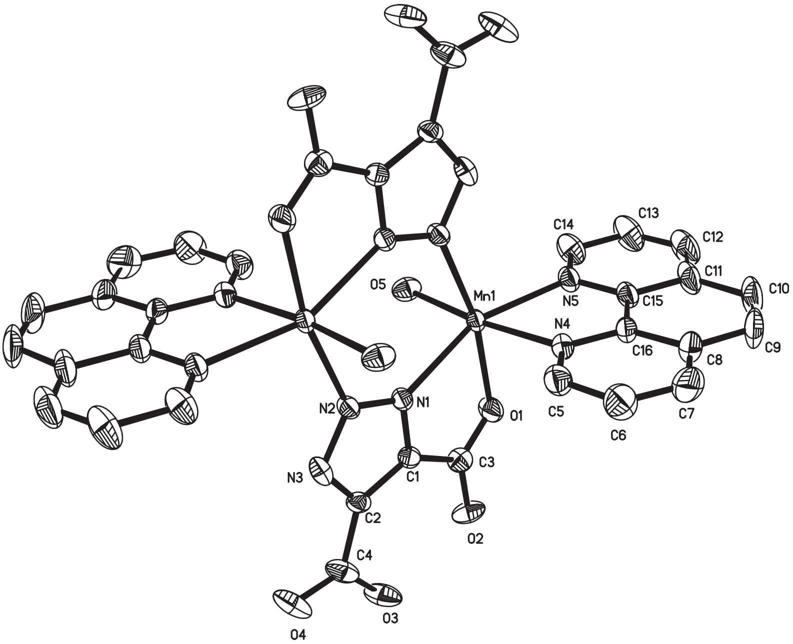

Figure 7. View of the dinuclear structure of **3**.

3.3. *Description of the crystal structure for* $Mn_2(phen)_2(HTDA)_2(H_2O)_4$

As shown in figure 7, two neighboring Mn(II) ions are bridged by two 1,2,3-triazole-4,5-dicarboxylic acid groups, forming a binuclear structure with the distance between Mn1 and Mn1A being 4.356 Å. Each Mn(II) coordinates with two nitrogens from one phen, one oxygen and two nitrogens from two 1,2,3-triazole-4,5-dicarboxylic acids, and one oxygen from water, to give a six-coordinate distorted octahedral structure, in which the basal plane is formed by N2A, N4, O5, and O1 with a mean deviation of 0.1680 Å from the least-squares plane. The axial positions are occupied by N1 and N5 with an N1–Mn1–N5 angle of 158.71(17)°.

Table 6. Selected bond lengths (Å) and angles (°) for **3**.

Bond lengths			
Mn1–O5	2.167(4)	Mn1–N4	2.255(5)
Mn1–O1	2.203(4)	Mn1–N5	2.261(4)
Mn1–N2[a]	2.209(4)	Mn1–N1	2.272(4)
Bond angles			
O5–Mn1–O1	88.13(17)	N2[a]–Mn1–N5	102.95(17)
O5–Mn1–N2[a]	87.58(16)	N4–Mn1–N5	73.83(18)
O1–Mn1–N2[a]	168.25(15)	O5–Mn1–N1	92.64(16)
O5–Mn1–N4	173.11(17)	O1–Mn1–N1	74.35(15)
O1–Mn1–N4	93.33(18)	N2[a]–Mn1–N1	94.92(15)
N2[a]–Mn1–N4	92.22(18)	N4–Mn1–N1	94.23(16)
O5–Mn1–N5	99.49(18)	N5–Mn1–N1	158.71(17)
O1–Mn1–N5	88.55(16)		

Symmetry transformations used to generate equivalent atoms: [a] $-x+1, -y+2, -z+1$.

Table 7. Hydrogen bonds in **3**.

D–H···A	d(D–H)	d(H···A)	d(D··A)	∠DHA
O(3)–H(3)···O(2)	0.82	1.72	2.533(7)	172.9(2)
O(5)–H(15)···O(3)[a]	0.85	2.05	2.873(6)	163.9(2)
O(5)–H(15)···O(4)[a]	0.85	2.56	3.251(7)	139.8(2)
O(5)–H(16)···O(3)[b]	0.85	1.88	2.700(6)	161.9(2)
O(6)–H(17)···N(3)[c]	0.85	2.51	3.185(8)	137.4(2)
O(6)–H(17)···O(4)[c]	0.85	2.28	3.026(9)	147.4(2)

Symmetry codes: [a] $-x, -y+1, -z$; [b] $-x+1/2, -y+3/2, -z$; [c] $x, y, z-1$.

In **3**, the ligand exhibits an unusual tridentate binding mode [mode (d) in scheme 1], different than that found in $\{[Mn_3(TDA)_2(H_2O)_6]\cdot 6H_2O\}_n$ [14] and $[Mn_3(TDA)_2(phen)_3]\cdot 2H_2O$ [19]. In those compounds, the TDA^{3-} exhibits a hexadentate binding mode [mode (e) in scheme 1], chelating three Mn(II) ions. The Mn–O and Mn–N bond distances fall in range 2.167(4) –2.272(4) Å (table 6), similar to those of Mn(II) complexes with 1,2,3-triazole-4,5-dicarboxylic acid [19]. In addition, the coordination waters are connected with HTDA groups through multiple strong hydrogen bonds (table 7), generating a 2-D layer structure (figure 8).

3.4. *Photoluminescence*

The emission spectra of **1**–**3** in the solid state are investigated at room temperature under same conditions. As depicted in figure 9, excitation at 357 nm leads to a strong blue-fluorescent emission band at 447 nm for **2**. For **1** and **3**, the emission intensity is relatively weaker than that of **2**. The emission peak at 447 nm for **2** is tentatively assigned to ligand-to-metal charge transfer (LMCT) where the electron is transferred from the H_3TDA ligands to the potassium(I) [28]. Furthermore, the emission peak at 387 nm for **3** may be attributed to the π^*–π transition of phen [29].

In summary, the syntheses and crystal structures of two potassium complexes and one manganese complex containing 1,2,3-triazole-4,5-dicarboxylic acid

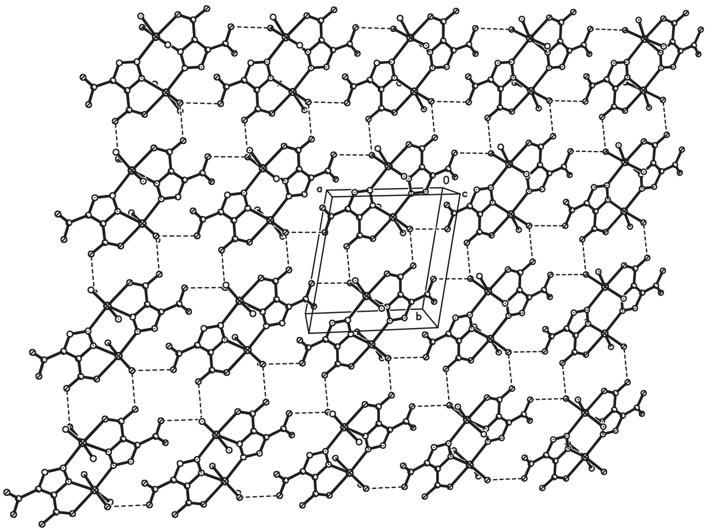

Figure 8. View of the 2-D supramolecular layer of **3**; the C atoms of phen and H atoms were removed for clarity.

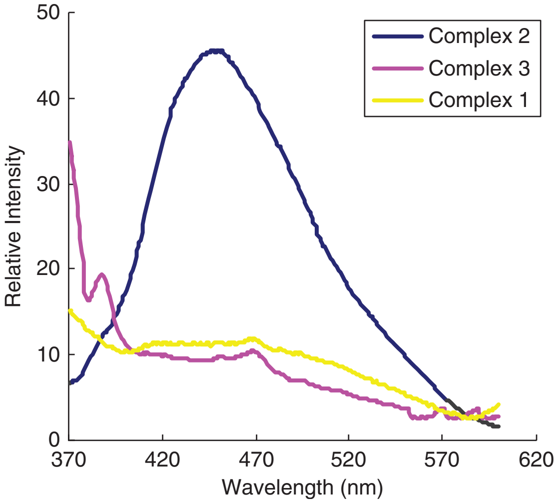

Figure 9. Emission spectra of **1**–**3** in the solid state at room temperature (excited at 357 nm).

have been reported. The potassium ions in **1** interlink by pentadentate bridging H_2TDA anions giving a 3-D (4, 8)-connected metal–organic framework, while the potassium ions in **2** were interlinked by tetradentate bridging H_2TDA anions into 1-D chains, which are connected by strong hydrogen bonds resulting in 2-D layers. In **3**, the neighboring Mn(II) ions are bridged by two 1,2,3-triazole-4,5-dicarboxylic acid groups, forming a binuclear structure, further linked to generate a 2-D layer structure via interdimeric hydrogen bonds.

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Supplementary materials

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC – 690414, 690415, and 701766. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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