

Sr²⁺ and Cd²⁺ coordination polymers: the effect of the different coordinating behaviour of a newly designed tricarboxylic acid†

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This article presents the investigation of the coordination behavior of a newly synthesized tricarboxylate ligand, obtained by joining imidazole dicarboxylic acid and 4-carboxybenzyl moieties [cbimdaH₃, 1-(4-carboxybenzyl)-1*H*-imidazole-4,5-dicarboxylic acid]. Two novel coordination polymers were obtained through solvothermal reactions under similar conditions namely [Sr(cbimdaH)(H₂O)]_n (**1**) and [Cd₂(cbimdaH)₂(H₂O)₆]_n·(DMF)_{3n}(H₂O)_{3n} (**2**), with the ligand behaving as a dianionic tricarboxylate linker. The single crystal X-ray structures show that while **1** forms a 3D coordination polymer, **2** forms a 1D polymer which is further assembled in three dimensions through supra-molecular interactions (H-bonding). Complex **1** consists of Sr²⁺ ions in a distorted dodecahedral coordination geometry, while **2** consists of Cd²⁺ ions in distorted pentagonal bipyramidal geometries. A topology study reveals that **1** has a new topology based on the 5,6-coordinated 3D net architecture. The luminescence properties of the complexes in the solid state and their thermal stabilities were studied.

Introduction

The interest in crystal engineering for constructing multidimensional metal ion based molecular complexes has progressively increased over the last two decades.^{1–3} While the main focus of this field of study has been to design organic linkers to control the geometry of the resulting coordination polymers; serendipitous assemblies still play a major role for providing intricate new topologies which are otherwise hard to pre-design.⁴ Polycarboxylates have been widely used for both designed and serendipitous assemblies.^{1–3,5–7}

Assemblies obtained from tricarboxylates and bivalent metal ions are particularly interesting, as the neutralisation of the charge requires either a foreign charged species that may or may not take part in the framework formation, or 2 : 3 complexes will result with complicated net architectures.^{5–7} 1,3,5-Bezenetricarboxylic acid has been extensively investigated for this purpose, especially for its symmetry properties. Still a few complexes are known where this versatile ligand acts as a dianion with bivalent metal ions with one of the carboxylates remaining protonated.⁷ The resulting complexes

however are still governed by a high degree of structural symmetry.

We were interested to see the effect of the coordination behaviour between the non-symmetrical tricarboxylates and the bivalent metal ions, as they can provide examples of new structural topologies. Imidazole dicarboxylic acid and its derivatives have been widely used with various types of metal ions for the construction of coordination polymers with interesting topologies.⁸ Here we report the synthesis and characterization of a new tricarboxylic acid [cbimdaH₃, 1-(4-carboxybenzyl)-1*H*-imidazole-4,5-dicarboxylic acid], obtained from the substitution of bromide on 4-bromomethylbenzoic acid by 1*H*-imidazole-4,5-dicarboxylic acid (imdaH₂) (Scheme 1). Two metal complexes of this ligand were then synthesized using solvothermal methods under similar conditions to obtain [Sr(cbimdaH)(H₂O)]_n (**1**) and [Cd₂(cbimdaH)₂(H₂O)₆]_n·(DMF)_{3n}(H₂O)_{3n} (**2**), with the ligand behaving as a dianionic linker giving 1 : 1 complexes. The complexes were thoroughly characterized by elemental analyses, FTIR, PXRD, single crystal X-ray structure determination and thermal analysis. The coordination polymer **1** forms an intricate 3D architecture, while **2** gives a 1D polymer which is further assembled in three dimensions through hydrogen bonding. Interestingly, in complex **1** the Sr²⁺ ions have distorted dodecahedral coordination geometries, while in **2** the Cd²⁺ ions possess distorted pentagonal bipyramidal geometries. **1** has a new topology based on a 5,6-coordinated 3D net. The photoluminescence of the free ligand and the complexes were also studied at room temperature.

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Experimental section

Materials and physical measurements

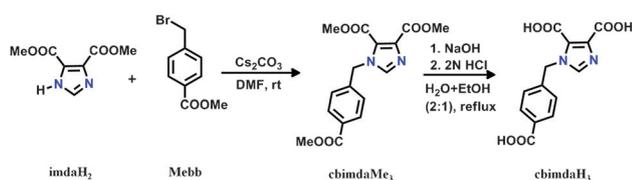
All chemicals and solvents used in the syntheses were obtained from commercial sources (analytical grade) and were used without further purification. Elemental analyses of C, H and N were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded as KBr pellets using a Magna 750 FT-IR spectrophotometer (Fig. S1–S3, ESI[†]). NMR spectra were recorded on Bruker 400 MHz spectrometer (Fig. S4 and S5, ESI[†]). The powder XRD data were collected using a D8 Advance X-Ray diffractometer to verify the phase purity of the complexes (Fig. S6 and S7, ESI[†]).

The synthesis of the ligand (cbimdaH₃)

184 mg (1 mmol) dimethyl 1*H*-imidazole-4,5-dicarboxylate (imdaMe₂) was dissolved in 10 mL DMF and 391 mg (1.2 mmol) Cs₂CO₃ was added to it. After 1 h stirring, to the suspension, 250 mg (1.09 mmol) methyl-4-(bromomethyl)benzoate (Mebb) was added and stirred at room temperature for 24 h. The solvent was evaporated completely under vacuum at 60 °C. 291 mg white solid (cbimdaMe₃) was isolated by column chromatography eluted with ethyl acetate. The product was refluxed with NaOH in a 2:1 (v/v) water and ethanol mixture for 24 h. The neutralization of the resulting solution by 2*N* HCl yielded 249 mg white solid product (cbimdaH₃, yield 86% with respect to imdaH₂). ¹H NMR (400 MHz, DMSO-*d*₆): 9.26 (H, s), 7.90 (2H, d), 7.36 (2H, d), 5.85 (2H, s). ¹³C NMR (100 MHz, DMSO-*d*₆): 167.0, 159.8, 158.8, 140.8, 138.8, 131.5, 130.3, 129.6, 127.3, 126.8, 50.75. Anal. calcd (%) for C₁₃H₁₀N₂O₆: C, 53.80; H, 3.47; N, 9.65. Found: C, 53.98; H, 3.32; N, 9.34. FT-IR (cm⁻¹): 3133(w), 2956(w), 2769(w), 2559(w), 1685(s), 1549(s), 1458(s), 1375(s), 1293(m), 1239(m), 1167(m), 1111(m), 1002(m), 943(m), 837(m), 757(s), 692(w), 686(s), 518(s).

The synthesis of complex [Sr(cbimdaH)(H₂O)]_{*n*} (1)

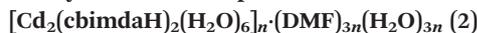
10 mg (0.034 mmol) cbimdaH₃ and 11 mg (0.052 mmol) Sr(NO₃)₂ was dissolved in 2 mL DMF:water (1:1, v/v). The solution was sealed in a 4 mL borosilicate screw vial and then heated at 95 °C for 12 h. Colorless rod shaped crystals, suitable for X-ray analysis were obtained after one day by the slow evaporation of the clear resulting solution. The crystals were washed with distilled water and dried under vacuum. Yield: ~55% based on Sr²⁺. Anal. calcd (%) for C₁₃H₁₀N₂O₇Sr: C, 39.64; H, 2.56; N, 7.11. Found: C, 39.36; H, 2.67; N, 7.02.



Scheme 1 The synthesis of the ligand.

FT-IR (cm⁻¹): 1694(w), 1595(m), 1513(s), 1390(s), 1273(m), 1143(m), 1013(m), 857(w), 776(w), 709(w), 622(w), 505(m).

The synthesis of complex



This complex was synthesized in a similar way to complex 1, using 10 mg (0.034 mmol) cbimdaH₃ and 16 mg (0.052 mmol) Cd(NO₃)₂·4H₂O. Colourless rectangular shaped crystals were obtained after one day by slow evaporation. Yield: ~42% based on Cd²⁺. Anal. calcd (%) for C₃₅H₅₅N₇O₂₄Cd₂: C, 35.54; H, 4.69; N, 8.29. Found: C, 35.28; H, 4.42; N, 8.12. FT-IR (cm⁻¹): 3246(m), 3189(m), 3124(m), 2357(w), 1657(m), 1582(m), 1527(s), 1391(s), 1282(m), 1154(w), 1099(w), 959(w), 860(w), 762(m), 641(m), 521(s).

X-Ray crystallographic data collection and refinements

Single crystal X-ray data for both the complexes were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software.⁹ The intensity data were collected using graphite-monochromatized Mo K α radiation (0.71073 Å) at 293 K for 1 and at 100 K for 2. The structures were solved by direct methods using the SHELX-97¹⁰ program incorporated into WinGX.¹¹ Empirical absorption corrections were applied with SADABS.¹² All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they were attached. Hydrogen atoms bonded to oxygen have been modeled directly from the diffraction data, except for one free water molecule [O(9W)] in the structure of 2, for which the hydrogen atoms could not be found. The value of *R*_{int} for 1 is slightly higher than the recommended value of 0.12, but the reported structure has the best value (0.134) among several times collected X-ray data for this complex. The crystallographic data and refinement parameters are given in Table 1, and important inter-atomic distances and angles are provided in Table 2.

Results and discussion

Synthesis and general characterization

Both complexes were obtained from the solvothermal reactions of the corresponding metal nitrate salts and the tricarboxylic acid ligand in the molar ratio of 3:2 under the same conditions, and we expected a complete neutralization of the charges. However, in both complexes the ligand retains one of the protonated carboxylic acid groups and forms 1:1 complexes. The formation of these complexes is strongly governed by the solvent mixture and the metal to ligand ratio. Optimum yields were obtained for both of the complexes under the stated conditions. Complex 1 was found to be stable at room temperature in the solid state upon extended exposure to air, however, 2 loses its crystalline

Table 1 Crystallographic data and refinement parameters for 1 and 2

	1	2
Empirical formula	C ₁₃ H ₁₀ N ₂ O ₇ Sr	C ₃₅ H ₅₅ N ₇ O ₂₄ Cd ₂
Fw	393.85	1182.67
T (K)	293(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /c
a/Å	5.8966(3)	18.775(4)
b/Å	26.4910(16)	11.423(2)
c/Å	9.3632(6)	22.206(5)
α/°	90.00	90.00
β/°	104.022(2)	90.663(6)
γ/°	90.00	90.00
V/Å ³	1419.01(14)	4762.1(17)
Z	4	4
ρ _{calcd} (g cm ⁻³)	1.844	1.647
μ (Mo Kα) (mm ⁻¹)	3.840	0.984
λ/Å	0.71073	0.71073
F(000)	784	2400
Collected reflns	53 951	135 468
Unique reflns	4366	9310
GOF (F ²)	1.167	1.062
R ₁ ^a	0.0486	0.0432
wR ₂ ^b	0.1159	0.0841

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^{2\alpha})^2\}]^{1/2}.$$

nature within 2–3 days, which is probably due to the loss of the free solvent molecules in the structure (DMF and water).

PXRD was used to check the phase purity of the bulk samples in the solid state (Fig. S6 and S7, ESI†). The PXRD patterns of the as synthesized complexes were found to closely match with the simulated patterns obtained from the single crystal X-ray data. However, for 2 the activated form (upon treatment with a DCM and MeOH mixture followed by the removal of the free solvent molecules by vacuum drying at

100 °C) shows that the crystal structure collapses on the removal of the non-coordinated solvent molecules.

In the IR spectra (Fig. S1–S3, ESI†) of the complexes the ν_s and ν_{as} bands are not well resolved which is probably due to the presence of three different types of carboxylate groups. However, multiple intense peaks are seen in the region 1400–1700 cm⁻¹, which are attributed to these carboxylate groups. Broad peaks close to 3200 cm⁻¹ can be attributed to the O–H stretch of the lattice or coordinated water molecules. For 2 the peaks in this region are more numerous and intense as expected from the crystal structure (1 has no lattice water molecules and has only one coordinated water molecule).

Structure description of [Sr(cbimdaH)(H₂O)]_n (1)

This complex crystallizes in the monoclinic space group P2₁/n revealing a 3D arrangement consisting of chains of Sr²⁺ ions linked by bridging water and dianionic cbimdaH molecules. The asymmetric unit (Fig. 1) consists of one metal atom, one dianionic cbimdaH ligand and one water molecule. Each metal ion is octa-coordinated with a distorted dodecahedral coordination geometry. The free imidazole nitrogen atom [Sr(1)–N(2), 2.644(3) Å] and a carboxylate oxygen atom [Sr(1)–O(3), 2.734(2) Å] of the same ligand chelate the metal ion. The same oxygen atom also bridges the neighbouring metal ions, so a symmetry generated O(3) atom from a different ligand also occupies one of the coordination sites [Sr(1)^{#3}–O(3), 2.552(2) Å]. Similarly the coordinated water molecule also links two neighbouring metal ions, so two symmetry generated water molecules occupy adjacent coordination sites on the metal [Sr(1)–O(1W), 2.684(2) Å; Sr(1)^{#5}–O(1W), 2.651(3) Å]. One other coordination site is

Table 2 Selected bond distances (Å) and angles (°) for 1 and 2^a

1					
Sr(1) ^{#1} –O(1)	2.475(2)	Sr(1) ^{#2} –O(2)	2.530(2)	Sr(1)–O(3)	2.734(2)
Sr(1) ^{#3} –O(3)	2.552(2)	Sr(1) ^{#4} –O(6)	2.583(3)	Sr(1)–O(1W)	2.684(2)
Sr(1) ^{#5} –O(1W)	2.651(3)	Sr(1)–N(2)	2.644(3)		
N(2)–Sr(1)–O(3)	60.68(7)	O(3)–Sr(1)–O(3) ^{#3}	75.03(8)		
O(3) ^{#3} –Sr(1)–O(6) ^{#4}	84.13(8)	O(6) ^{#4} –Sr(1)–O(1) ^{#6}	80.27(10)		
O(1W)–Sr(1)–O(1W) ^{#5}	67.88(9)	O(2) ^{#7} –Sr(1)–N(2)	83.14(9)		
O(2) ^{#7} –Sr(1)–O(6) ^{#4}	73.88(9)	O(6) ^{#4} –Sr(1)–O(1W)	72.85(9)		
2					
Cd(1)–O(1)	2.673(3)	Cd(1)–O(2)	2.274(3)	Cd(1)–O(9)	2.543(3)
Cd(1)–O(1W)	2.300(4)	Cd(1)–O(2W)	2.252(4)	Cd(1)–O(3W)	2.319(3)
Cd(1)–N(4)	2.263(3)	Cd(2)–O(7) ^{#8}	2.542(3)	Cd(2)–O(8) ^{#8}	2.317(3)
Cd(2)–O(3)	2.559(3)	Cd(2)–O(4W)	2.284(4)	Cd(2)–O(5W)	2.279(4)
Cd(2)–O(6W)	2.252(4)	Cd(2)–N(2)	2.294(3)		
O(1)–Cd(1)–O(2)	52.19(9)	O(2)–Cd(1)–O(2W)	87.01(12)		
O(2W)–Cd(1)–O(9)	76.35(12)	O(9)–Cd(1)–N(4)	68.72(11)		
O(1)–Cd(1)–N(4)	80.51(10)	O(1W)–Cd(1)–O(2W)	82.94(16)		
O(2W)–Cd(1)–O(3W)	99.94(14)	O(1W)–Cd(1)–O(3W)	173.64(11)		
O(7) ^{#9} –Cd(2)–O(8) ^{#9}	53.73(9)	O(7) ^{#9} –Cd(2)–N(2)	83.36(10)		
O(3)–Cd(2)–N(2)	67.93(11)	O(3)–Cd(2)–O(5W)	72.68(11)		
O(5W)–Cd(2)–O(8) ^{#9}	88.41(11)	O(4W)–Cd(2)–O(5W)	80.95(16)		
O(5W)–Cd(2)–O(6W)	100.70(16)	O(4W)–Cd(2)–O(6W)	174.00(14)		

^a Symmetry transformations used to generate equivalent atoms: [#1], x + 1/2, -y + 1/2, z - 1/2; [#2], x - 1/2, -y + 1/2, z - 1/2; [#3], -x + 1, -y, -z + 1; [#4], x, y, z - 1; [#5], -x, -y, -z + 1; [#6], x - 1/2, -y + 1/2, z + 1/2; [#7], x + 1/2, -y + 1/2, z + 1/2; [#8], x - 1, +y, +z; [#9], x + 1, y, z.

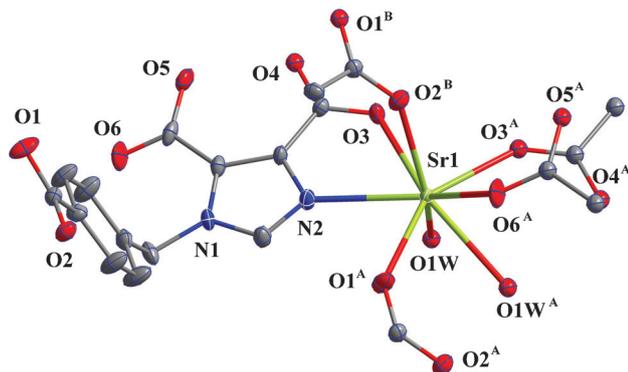


Fig. 1 The thermal ellipsoid probability plot of the basic unit of **1**. The hydrogen atoms have been removed for clarity. The thermal ellipsoids are at the 40% probability level.

taken up by an oxygen atom of a protonated carboxylate group on the imidazole ring [Sr(1)^{#4}-O(6), 2.583(2) Å] from a third ligand. The remaining two coordination sites are taken up by two carboxylate oxygen atoms (benzoate moiety) from another two different ligands [Sr(1)^{#1}-O(1), 2.475(2) Å; Sr(1)^{#2}-O(2), 2.530(2) Å]. So each Sr²⁺ ion is linked to five different ligands and two different water molecules. The adjacent metal ions are alternately joined [Sr(1)-Sr(1), 4.426(2) Å] through two bridging water molecules and two carboxylate oxygen atoms [Sr(1)-Sr(1), 4.194(2) Å] to form a zig-zag chain structure running along the crystallographic *a* axis. In addition, every third metal atom in the chain is joined [Sr(1)-Sr(1), 5.897(2) Å] by a μ_2 -carboxylate bridge (benzoate moiety), with the Sr(1)-O(1)-O(2)-Sr(1) torsion angle of 85.6°. The two carboxylate groups on the imidazole ring of the ligand link these chains along the crystallographic *c* axis, while the benzoate carboxylate helps them to link parallel to the *b* axis, forming the overall 3D structure of the complex (Fig. 2). To gain a better insight into the complicated 3D architecture, a topological analysis was carried out using the TOPOS program.¹³ The simplified 3D net structure of **1** can be described in the cluster representation as a

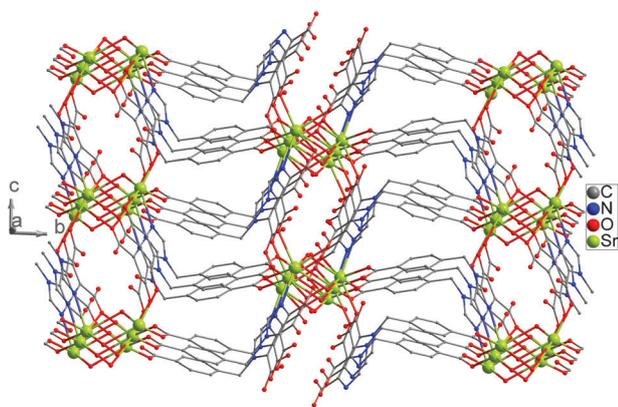


Fig. 2 The ball and stick representation showing the 3D arrangement of complex **1**. The hydrogen atoms have been removed for clarity.

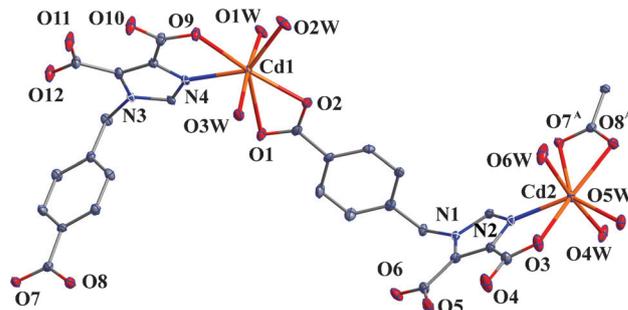
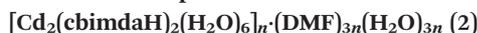


Fig. 3 The thermal ellipsoid probability plot of the basic unit of **2**. The hydrogen atoms and the free solvent molecules have been removed for clarity. The thermal ellipsoids are at the 40% probability level.

5,6-coordinated 2-nodal net (each metal-ion being linked to six different cbimdaH ligands forms the 6-connected nodes and each cbimdaH ligand being connected to five different metal-ions forms the 5-connected nodes) with the point symbol of $\{4^6.5^2.6^2\}\{4^6.5^5.6^4\}$ (Fig. S10, ESI[†]). This simplified net defines a new topology, which to the best of our knowledge, is unprecedented in MOFs.

Structure description of



This complex crystallizes in the monoclinic space group $P2_1/c$ and the single crystal structure shows that it contains 1D chains formed by the coordination of the Cd²⁺ ions by the dianionic ligand which are further extended to three dimensions by inter-chain hydrogen bonding (Fig. 4). The asymmetric unit consists of two metal atoms [both Cd(1) and Cd(2) have similar hepta-coordinated geometries], two dianionic cbimdaH ligands, six coordinated water molecules, three non-coordinated water molecules and three non-coordinated DMF molecules (Fig. 3). The geometry of the metal ions can be described as distorted pentagonal bipyramidal. One nitrogen atom [Cd(1)-N(4), 2.263(3) Å; Cd(2)-N(2), 2.294(3) Å] from the imidazole ring and an oxygen atom [Cd(1)-O(9), 2.543(3) Å; Cd(2)-O(3), 2.559(3) Å] from the neighbouring carboxylate group on the ring forms a chelate and occupies two equatorial positions on both metal atoms. Two more oxygen atoms on the equatorial plane come from the same

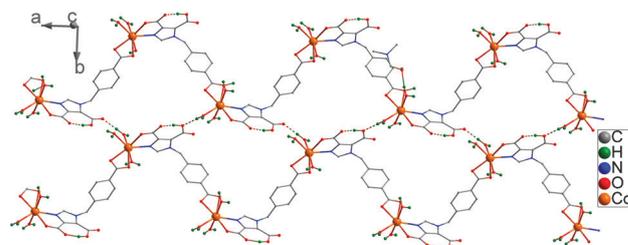


Fig. 4 The ball and stick representation, showing the partial hydrogen bonding arrangements in complex **2**. The hydrogen atoms linked to carbon atoms and free solvent molecules are removed for clarity.

carboxylato group on the benzene ring of another ligand [Cd(1)–O(1), 2.673(3) Å; Cd(1)–O(2), 2.274(3) Å; Cd(2)–O(7)^{#8}, 2.542(3) Å; Cd(2)–O(8)^{#8}, 2.317(3) Å], and the fifth equatorial site is occupied by a water molecule [Cd(1)–O(2W), 2.252(4) Å; Cd(2)–O(5W), 2.279(4) Å]. Both the axial coordination sites are occupied by two water molecules [Cd(1)–O(1W), 2.300(4) Å; Cd(1)–O(3W), 2.319(3) Å; Cd(2)–O(4W), 2.284(4) Å; Cd(2)–O(6W), 2.252(4) Å]. The axial bonds are nearly linear [angles created at the metal centers are 173.64(11) and 174.00(14)°] and almost perpendicular to the equatorial planes of the two metal atoms.

Unlike complex **1**, the second protonated carboxylate group in the imidazole ring does not coordinate to the metal atoms in **2**. Also the other two carboxylate groups do not bridge the neighboring metal atoms. As a result the overall coordination behavior of the ligand extends the complex in one dimension (chains running parallel to the crystallographic *a* axis, Fig. 4). However, these chains are linked together through hydrogen bonds involving the coordinated water molecules and the carboxylate oxygen atoms to form a 3D supramolecular framework structure (Fig. 4 and S11, ESI[†]). The hydrogen bonds parallel to the crystallographic *b* axis (Fig. 4) join the neighboring chains through the linkages O(2W)–H(3W)⋯O(5) and O(4W)–H(8W)⋯O(12). The architecture grows parallel to the crystallographic *c* axis (Fig. S11, ESI[†]) through the linkages O(1W)–H(1W)⋯O(7) and O(6W)–H(11W)⋯O(3W) [Table S1, ESI[†]].

Structural correlations

In both complexes (**1** and **2**) the ligand behaves as a dianion (with one protonated carboxylate group on the imidazole ring). This is surprising, as the initial metal to ligand ratio of 3:2, was used for complete neutralization. It might be argued that the protonated carboxylate forms a strong hydrogen bond with the adjacent anionic carboxylic group in the imidazole ring, hence the deprotonation process for the third carboxylic acid group is energy demanding. However, in the case of 1,2,4-benzenetricarboxylic acid a similar situation may arise as the two carboxylic groups in the 1 and 2 positions of the benzene ring can form a strong hydrogen bonded structure. But, in the Ni²⁺ complex of this ligand, the metal to ligand ratio is 3:2 with the ligand behaving as a tri-anionic moiety.¹⁴ So the cbimdaH₃ ligand can be expected as well to form such complexes, especially when the 4,5-imidazoledicarboxylic acid deprotonates completely in almost all of its known complexes. This makes the behaviour of the cbimdaH₃ ligand so interesting, and it shows the advantage of serendipity rooted in the unsymmetrical bridging ligand.

The overall structure of the two complexes are entirely different. While the Sr²⁺ ion in **1** behaves as a 6-connected (coordinatively) metal ion, Cd²⁺ in **2** is only 2-connected. In both complexes the metal ions have rare coordination geometries. The eight coordinated dodecahedral geometry of the Sr²⁺ ions compared to the seven coordinated pentagonal bipyramidal geometry of the Cd²⁺ ions may be explained by

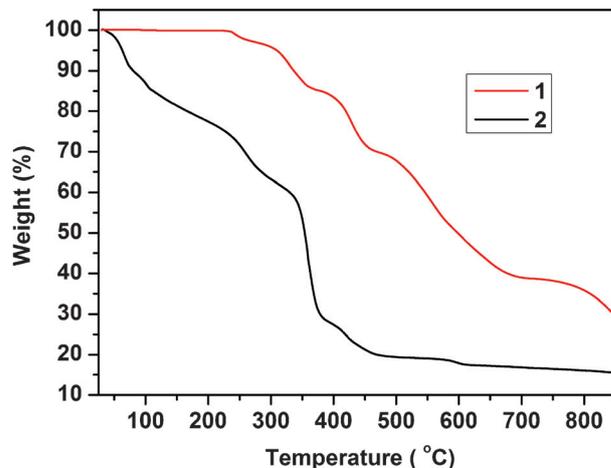


Fig. 5 The TGA curves for **1** and **2**.

the positions of these elements in the periodic table. Strontium lies just left of the 4d series (4d⁰), while cadmium rests at the end of the series (4d¹⁰). Therefore, the ionic radius of Sr²⁺ is much higher than that of Cd²⁺, due to the incomplete shielding of the filled 4d orbitals (increasing the effective nuclear charge) in the latter ion. Thus, strontium can accommodate more ligands in its coordination sphere. However, this small difference in coordination number cannot explain the structural differences. It is interesting to notice that one of the oxygen atoms of the protonated carboxylate group is coordinating with the metal in **1**, while it is functioning only as hydrogen bond acceptor in complex **2**. Also the two oxygen atoms of the carboxylato group on the benzene ring of the ligand link to different metal atoms (thus acting as a three atom bridge) in **1**, while they link to the same metal atom in **2** (acting as chelate). There are two and three coordinated water molecules in **1** and **2** per metal atom, respectively, however, in **1** they act as coordinating bridges while in **2** they form supramolecular interactions with neighbouring hydrogen bonding partners. It is quite unusual to find a divalent ion connected to five symmetry generated (different) ligands and thus the resulting topology for **1** is unprecedented in the literature. It is also very rare to obtain 1D coordination networks using cadmium with dicarboxylate or tricarboxylate ligands.¹⁵ Hence, both complexes are novel and interesting from a structural point of view, and this fact illustrates the point that while building new structures serendipity has an advantage over design, especially for unsymmetrical bridging ligands like the one used here with many possible binding-modes.

Thermal analysis

The results of the thermogravimetric analyses (TGA) carried out for the synthesized complexes are shown in Fig. 5. Complex **1** does not have any free solvent molecules in its structure and accordingly shows no weight loss up to 230 °C. The only coordinated water molecule in the molecular formula is

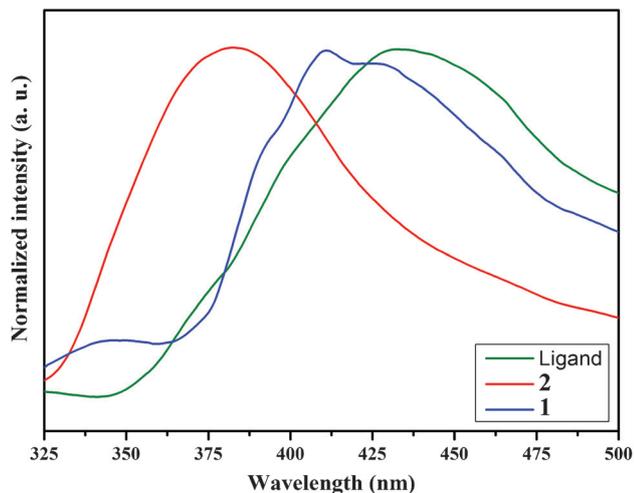


Fig. 6 The emission spectra for the free ligand and the complexes in the solid state.

lost between 235 and 310 °C, evidenced by a 4.9% loss in weight (calcd. 4.6%). Above this temperature the organic ligand starts to decompose and the weight cascades down with the increasing temperature. For 2 there are three DMF molecules and three water molecules, which are non-coordinated, amounting to 23.1% of the molecular weight. Accordingly a ~23% loss of weight is seen from the TGA curve below 200 °C. There are six coordinated water molecules in the structure of 2. These are lost below 280 °C, at which point there is a total decrease of weight of ~35% (calcd. 32.3%). Above 300 °C the ligand starts to decompose rapidly.

Photoluminescence properties

The extended coordination complexes have been investigated for photoluminescence properties due to their potential applications in photoactive materials.¹⁶ Thus, the emission spectra of the two complexes, together with the free ligand were measured in the solid state at room temperature (Fig. 6). The free *cblmdaH₃* ligand displays photoluminescence with an emission maxima at 433 nm ($\lambda_{\text{ex}} = 285$ nm). The emission spectra exhibit maximum emission peaks at 411 nm with a shoulder peak at 426 nm for 1 ($\lambda_{\text{ex}} = 287$ nm) and 382 nm for 2 ($\lambda_{\text{ex}} = 282$ nm) respectively. Compared with the free ligand, a blue shift of emission occurs in these complexes, which is probably due the coordination environment around the metal ions as the photoluminescence behaviour is intimately associated with the metal ions and the coordinated ligands around them.¹⁷

Metal ions with d^0 and d^{10} configurations are particularly difficult to oxidize or reduce. So, the emissions of these complexes cannot be assigned as metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT).¹⁸ Thus, they probably result from a combined effect of intra-ligand and ligand-to-ligand charge transition (LLCT), as reported for other similar complexes.¹⁹ The high intensity of luminescence in these complexes can be

attributed to the ligand chelation to the metal center causing the increased rigidity of the ligand and the reduction of energy loss by radiation-less decay.²⁰ The difference of the emission behaviours for the two complexes may result from the differences in the rigidity of the crystal packing in the solid state.

Concluding remarks

We have described the synthesis and coordination behavior of a new tricarboxylate ligand by joining an imidazole-dicarboxylate moiety and a 4-carboxybenzyl moiety. Two divalent metal ions from the extreme ends of the 4d-transition series were used for the complex formation, and the structural analyses showed novel structural features in both complexes. Both complexes feature metal ions in geometries with a high coordination number (dodecahedral for Sr^{2+} and pentagonal bipyramidal for Cd^{2+}). In terms of the coordination mode of the ligand in the strontium complex all three of the carboxylate groups take part in the coordination (although one of the carboxylates is protonated), while in the cadmium complex the protonated carboxylate remains free. The strontium complex was found to have an intricate connectivity with five different symmetry generated ligand molecules and two bridging water molecules in the metal atom's coordination sphere, and resulted in a novel 5,6-coordinated 2-nodal 3D net topology. The cadmium complex, although coordinatively 1D in nature, was found to possess supramolecular interactions (H-bonding) with neighboring chains resulting in a 3D network. In the field of MOFs and coordination polymers pre-design has taken center stage, but only through such examples as discussed in this article, which are fundamentally serendipitous in their formation approach, we can obtain new and interesting framework topologies that would otherwise be difficult to design.

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