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Three New Isostructural Coordination Polymers with Cd(II) Clusters as the SBU: Synthesis, Structural Characterization, and Luminescence Properties

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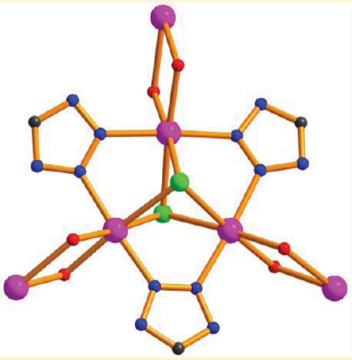
S Supporting Information

ABSTRACT: Three new isostructural coordination polymers, $\{Cd_{1.33}L(Cl)_{0.67}(H_2O)_{0.67}\}_n$ (**1**), $\{Cd_{1.33}L(Br)_{0.67}(H_2O)_{0.67}\}_n$ (**2**), and $\{Cd_{1.33}L(I)_{0.67}(H_2O)_{0.67}\}_n$ (**3**), have been synthesized using a semiflexible *in situ* generated tetrazole ligand. All the complexes crystallize in cubic space group $P4_132$. In complex **1**, three Cd^{2+} ions along with two N atoms each from three tetrazole units form a trinuclear unit where each metal ion is additionally bridged by carboxylate O and μ_3-Cl units. This Cd(II) cluster along with the ligand form a trigonal arrangement that extends to form a two-dimensional sheet that further undergoes extensive interpenetration to generate an overall three-dimensional coordination polymer. All complexes exhibit thermal stability up to ~330 °C losing coordinated water molecules at ~140 °C. Upon excitation at 340 nm, the complexes exhibit solid-state luminescence with an emission peak at ~415 nm that shows slight red shift with broadening of the band with changing the halide anion from chloride to bromide to iodide.



INTRODUCTION

Coordination polymers have attracted considerable attention in recent years because of their potential applications as functional materials as well as the intriguing nature of molecular connectivities and topologies.[1] The design possibilities of organic ligands and the coordination tendencies of metal ions besides crystallization conditions have led to a large number of coordination polymeric structures quite often endowed with novel structural features as well as unique properties.[2] Various nitrogen[3] and carboxylate[4] donating ligands have been used for this purpose. Heterocycles incorporating poly-nitrogen donors such as tetrazoles[5] and triazoles[6] have been demonstrated to be very good ligands for the construction of three-dimensional (3D) coordination polymers exhibiting a great structural diversity. So, our main aim was to prepare a ligand that contains both tetrazole as well as carboxylate groups as donors. The *in situ* hydrothermal synthesis to initiate [2 + 3] cycloaddition of azides with nitriles in presence of metal ions to form tetrazoles are known in the literature.[7] *In situ* ligand synthesis, first proposed by Champness and Schroder in 1997,[8] is regarded as a new and efficient approach for the synthesis of both organic compounds and coordination polymers. Recently, this technique has been developed rapidly in coordination polymers, as it usually generates unexpected structures, which cannot be obtained by the direct reaction of ligands with metal salts.[9] Using this approach, we have synthesized a new tetrazole-based semiflexible ligand that forms coordination polymers with Cd(II) metal ion (Scheme1).

Herein, we report the synthesis and crystal structural studies of three coordination polymers of Cd(II) having the formulas $\{Cd_{1.33}L(Cl)_{0.67}(H_2O)_{0.67}\}_n$ (**1**), $\{Cd_{1.33}L(Br)_{0.67}(H_2O)_{0.67}\}_n$ (**2**), and $\{Cd_{1.33}L(I)_{0.67}(H_2O)_{0.67}\}_n$ (**3**) using an *in situ* generated tetrazole ligand.

EXPERIMENTAL SECTION

Materials and Methods. 4-Fluorobenzonitrile, ethyl isonipecotate, sodium azide, and Cd(II) salts were acquired from Aldrich and used as received. All solvents and K_2CO_3 were procured from S. D. Fine Chemicals, India. All solvents were purified prior to use.

Infrared spectra were obtained (KBr disk, 400−4000 cm^{-1}) on a Perkin-Elmer model 1320 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL-ECX 500 FT (500 and 125 MHz, respectively) instrument in $CDCl_3$ and DMSO-d_6 with Me_4Si as the internal standard. ESI-mass spectra were recorded on a WATERS Q-TOF premier mass spectrometer. Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.) while thermogravimetric analyses (TGA) were obtained using a Mettler Toledo star system (heating rate of 5 °C/min). Solid-state photoexcitation and emission spectra were recorded on double UV−vis-NIR spectrophotometer (Varian model Cary 5000) and Jobin Yvon Horiba Fluorolog-3 spectrofluorimeter at room temperature.

Synthesis. The ligand was synthesized in several steps as described below.

*Synthesis of 1-(4-Cyano-phenyl)-piperidine-4-carboxylic Acid Ethyl Ester (**L_1**).* Ethyl isonipecotate (2 mL, 12.9 mmol) and dry K_2CO_3 (1.9 g, 13.8 mmol) were taken in a 50 mL round-bottom flask under an inert atmosphere, and then, 10 mL of dry DMF was added to it. The mixture

Received: August 8, 2011
Revised: September 30, 2011
Published: October 07, 2011

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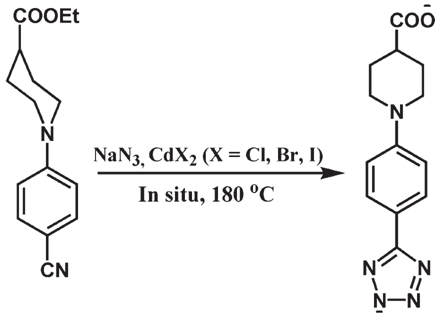
Scheme 1. Schematic Representation of an *in situ* Generated Tetrazole Ligand



L_1 **L^{2-}**

was stirred for a while at 80 °C followed by addition of 4-fluorobenzonitrile (1.6 g, 13.2 mmol), and the resulting mixture was stirred for 24 h in an oil bath at 80 °C. The resulting solution was poured into ice-cold water (100 mL) whereupon a solid crystalline compound (**L_1**) was obtained that was collected by filtration, washed several times with distilled water, and dried in air. Yield: 3.1 g (93%). Melting point: 67 °C. IR: sharp peaks were observed at 2211 and 1721 cm^{-1} corresponding to υ_{CN} and υ_{CO} (str), respectively. ^1H NMR ($CDCl_3$), δ (ppm): 1.26 (t, J = 7.1 Hz, 3H); 1.86−1.93 (m, 2H); 2.11−2.13 (m, 2H); 2.54−2.59 (m, 1H); 3.04 (t, J = 10.3 Hz, 2H); 3.75−3.79 (m, 2H); 4.16 (q, J = 7.3 Hz, 2H); 7.00−7.04 (m, 2H,); 7.52 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$), δ (ppm): 14.1, 27.2, 40.4, 47.1, 60.5, 100.0, 114.5, 119.9, 133.4, 152.8, 174.1. Elemental analysis: calcd. for $C_{15}H_{18}N_2O_2$ (258.13): C, 69.74%; H, 7.02%; N, 10.84%; found: C, 69.61%; H, 7.15%; N, 10.76%. ESI-MS m/z: calcd. for $C_{15}H_{18}N_2O_2$, 258.1368; found, 259.1368 $[M + 1]^+$.

*Synthesis of 1-(4-(2H-tetrazol-5-yl)phenyl)piperidine-4-carboxylic acid (**H_2L**).* Complex **1** (0.2 g), which was prepared *in situ*, was dissolved by adding 1 M HCl solution such that the final pH is maintained ∼3. To this solution, 1 M NaOH solution was added dropwise under ice-cold condition to give light brown compound at pH 7. The resulting solid compound (**H_2L**) obtained was collected by filtration, washed several times with distilled water, and dried in air. Yield: 0.09 g (75%). Melting point, 208 °C. IR: peaks around 1700 cm^{-1} corresponding to υ_{CO} (str) of carboxylic acid group. ^1H NMR (DMSO-d_6), δ (ppm): 1.54−1.62 (m, 2H); 1.85−1.88 (m, 2H); 2.45 (m, 1H); 2.88 (t, J = 10.9 Hz, 2H); 3.79 (d, J = 13.1 Hz, 2H); 7.07 (d, J = 8.9 Hz, 2H); 7.82 (d, J = 8.9 Hz, 2H); 12.22 (s, 1H). ^{13}C NMR (DMSO-d_6), δ (ppm): 27.7, 47.3, 47.4, 114.2, 115.4, 128.6, 129.4, 152.9, 176.4. Elemental analysis: calcd. for $C_{15}H_{18}N_2O_2$ (273.13): C, 57.13%; H, 5.5%3; N, 25.63%; found: C, 57.21%; H, 5.40%; N, 25.77%. ESI-MS m/z: calcd. for $C_{13}H_{15}N_5O_2$, 273.1226; found, 272.1226 $[M - 1]^+$.

*Synthesis of $\{Cd_{1.33}L(Cl)_{0.67}(H_2O)_{0.67}\}_n$ (**1**).* A mixture containing **L_1** (0.04 g, 0.15 mmol), NaN_3 (0.02 g, 0.30 mmol), and $CdCl_2 \cdot xH_2O$ (0.06 g, 0.30 mmol) in 3 mL of water was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 180 °C for three days and then allowed to cool to room temperature at the rate of 1 °C per minute. Truncated octahedron-shaped brown crystals of **1** were collected in 51% yield. The crystals were washed with water followed by acetone and air-dried. Anal. calcd. for $C_{13}H_{13.67}N_5O_{2.67}Cl_{0.67}Cd_{1.33}$: C, 34.23%; H, 3.02%; N, 15.35%; found: C, 34.35%; H, 3.11%; N, 15.26%. IR (cm^{-1}): 3366(w, br), 2924(s), 2854(s), 2812(s), 1615(m), 1565(m), 1446(m), 1386(m), 1351(m), 1281(s), 1251(s), 1216(m), 1197(m), 1149(s), 1103(s), 1045(s), 990(s), 956(s), 915(s), 858(s), 836(m), 764(m), 720(s), 653(m).

*Synthesis of $\{Cd_{1.33}L(Br)_{0.67}(H_2O)_{0.67}\}_n$ (**2**).* A mixture containing **L_1** (0.04 g, 0.15 mmol), NaN_3 (0.02 g, 0.30 mmol), and $CdBr_2 \cdot 4H_2O$ (0.11 g, 0.3 mmol) in 3 mL of water were sealed in a Teflon-lined autoclave and heated under autogenous pressure to 180 °C for three days and then allowed to cool to room temperature at the rate of 1 °C per minute. Truncated octahedron-shaped brown crystals of **2** were collected in 55% yield. The crystals were washed with water followed by acetone and air-dried. Anal. calcd. for $C_{13}H_{13.67}N_5O_{2.67}Br_{0.67}Cd_{1.33}$: C, 32.14%; H, 2.83%; N, 14.41%; found: C, 32.25%; H, 2.76%; N, 14.32%. IR (cm^{-1}): 3363(w, br), 2924(s), 2814(s), 1614(m), 1566(m), 1446(m), 1387(m), 1353(m), 1281(s), 1251(s), 1216(m), 1198(m), 1150(s), 1104(s), 1045(s), 956(s), 915(s), 858(s), 836(m), 764(m), 720(s), 654(m).

*Synthesis of $\{Cd_{1.33}L(I)_{0.67}(H_2O)_{0.67}\}_n$ (**3**).* A mixture containing **L_1** (0.04 g, 0.15 mmol), NaN_3 (0.02 g, 0.30 mmol), and CdI_2 (0.12 g, 0.3 mmol) in 3 mL of water were sealed in a Teflon-lined autoclave and heated under autogenous pressure to 180 °C for three days and then allowed to cool to room temperature at the rate of 1 °C per minute. Truncated octahedron-shaped brown crystals of **3** were collected in 52% yield. The crystals were washed with water followed by acetone and air-dried. Anal. calcd. for $C_{14}H_{14.67}N_5O_{2.67}I_{0.67}Cd_{1.33}$: C, 31.72%; H, 2.78%; N, 13.21%; found: C, 31.65%; H, 2.86%; N, 13.30%. IR (cm^{-1}): 3362(w, br), 2923(s), 2853(s), 2817(s), 1612(m), 1556(m), 1446(m), 1385(m), 1354(m), 1281(s), 1252(s), 1213(m), 1151(s), 1103(s), 1040(s), 952(s), 913(s), 857(m), 834(m), 764(m), 721(s), 652(s).

All attempts to synthesize these complexes in single crystal form using the ligand **H_2L** with Cd(II) salts remained unsuccessful. Thus, it appears that the complexes can be synthesized via *in situ* generated tetrazole as well as carboxylate.

Single-Crystal X-ray Studies. Single-crystal X-ray data on **L_1** and complexes **1**−**3** were collected at 298 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[10] The data integration and reduction were carried out with SAINT[11] software. For each data set, empirical absorption correction was applied to the collected reflections with SADABS,[12] and the space group was determined using XPREP.[13] The structure was solved by the direct methods using SHELXTL-97[14] and refined on F^2 by full-matrix least-squares using the SHELXL-97[15] program package. In complexes **1**−**3**, all non-hydrogen atoms were refined anisotropically. The H atoms have been refined as follows: the hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. The one H atom of water molecule was located from difference Fourier maps but the other one could not be located even from difference Fourier maps. Several DFIX commands were used to fix the bond distances of ligand and water molecule. The higher R_1 values and low data of completeness in all Cd^{2+} complexes are due to the poor diffraction quality of crystals. Data collection, lattice parameters, and structure solution parameters are collected in Table 1 while selective bond distances and angles are given in Table S1 (Supporting Information).

■ RESULTS AND DISCUSSION

The semiflexible ligand **L_1** has been designed to provide some rotational freedom for the carboxylate and tetrazole moieties that can facilitate bridging of Cd(II) centers. Under hydrothermal reaction conditions applied, the ester group is hydrolyzed to carboxylic acid and the nitrile group reacts with added azide to form a tetrazole moiety (L^{2-}) both of which coordinate to metal ions. Once isolated, the coordination polymers are stable in air and insoluble in common organic solvents and water. The IR spectra of all the compounds show strong absorption bands between 1422 and 1616 cm^{-1} that are diagnostic[16] of coordinated

Table 1. Crystal and Structure Refinement Data for L_1 and 1−3

	L_1	1	2	3
empirical formula	$C_{15}H_{18}N_2O_2$	$C_{13}H_{13.67}Cl_{0.67}N_5O_{2.67}Cd_{1.33}$	$C_{13}H_{13.67}Br_{0.67}N_5O_{2.67}Cd_{1.33}$	$C_{13}H_{13.67}I_{0.67}N_5O_{2.67}Cd_{1.33}$
formula wt	258.31	456.13	485.76	517.09
crystal system	monoclinic	cubic	cubic	cubic
space group	$P2_1/c$	$P4_132$	$P4_132$	$P4_132$
a, Å	12.637(2)	16.499(5)	16.635(3)	16.614(5)
b, Å	13.230(5)	16.499(5)	16.635(3)	16.614(5)
c, Å	8.256(6)	16.499(5)	16.635(3)	16.614(5)
α (deg)	90.000	90.000	90.000	90.000
β (deg)	102.010(5)	90.000	90.000	90.000
γ deg)	90.000	90.000	90.000	90.000
U, Å^3	1350.1(11)	4491(2)	4603(2)	4586(2)
Z	4	12	12	12
ρ_{calc}, Mg/m^3	1.271	2.024	2.103	2.247
μ, mm^{-1}	0.085	2.058	3.628	3.245
$F(000)$	552	2680	2824	2968
refl. collected	8270	21403	20422	20782
independent refl.	3061	1358	1352	1199
GOOF	1.042	1.003	1.010	1.086
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0596$	$R1 = 0.0750$	$R1 = 0.0849$	$R1 = 0.0969$
	$wR2 = 0.1422$	$wR2 = 0.1723$	$wR2 = 0.2088$	$wR2 = 0.2144$
R indices (all data)	$R1 = 0.0892$	$R1 = 0.1561$	$R1 = 0.1488$	$R1 = 0.1236$
	$wR2 = 0.1708$	$wR2 = 0.2222$	$wR2 = 0.2538$	$wR2 = 0.2341$
Flack parameter	—	0.001(10)	0.06(8)	0.2(2)

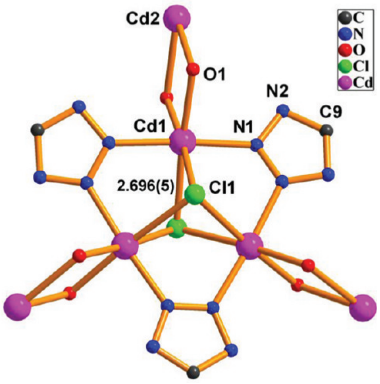


Figure 1. Trinuclear Cd^{2+} unit formed by the μ_3-chloride ion and tetrazole moiety of the ligand in complex **1**.

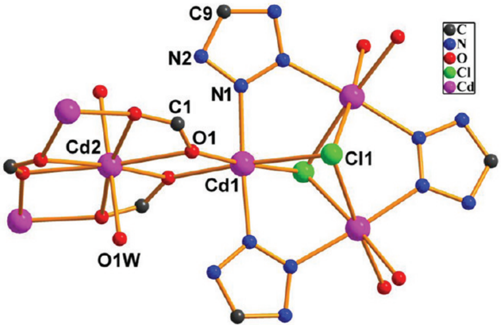


Figure 2. Section showing connection between two trinuclear units via bridging O atom in **1**.

carboxylate groups.[17] The IR spectra of **1**−**3** give broad peaks in the range of 3360−3370 cm^{-1} due to presence of coordinated water molecules.[16]

Since all the complexes are isostructural, the detail structural description of only complex **1** is discussed here. Complex **1** crystallizes in cubic space group $P4_132$ with two crystallographically independent Cd(II) ions (Cd1 with half occupancy and Cd2 with $^1/_6$ occupancy), half $\mathbf{L}^{2-}$, one chloride ion with $^1/_3$ occupancy, and one coordinated water molecule having $^1/_3$ occupancy in the asymmetric unit. Three Cd(1) ions form a trinuclear unit where each metal ion is coordinated to two O atoms from a bridging carboxylate ($Cd-O$ = 2.271(14) Å) and two Cl^- ions ($Cd-Cl$ = 2.696(5) Å) while the axial sites are occupied by two N atoms each from three tetrazole moiety ($Cd-N$ = 2.177(17) Å). Each of the Cl^- ions is triply bridged occupying the vertex of the pyramid where the base is formed by the three Cd^{2+} ions (Figure 1). All Cd−N, Cd−O, and Cd−Cl bond distances are normal[18] within statistical errors. The distance between the Cl^- ions is 3.372 Å; the covalent radius of chlorine is 1.75 Å while van der Waals radius[19] of Cl^- ion is 1.81 Å. The short distance suggests considerable interactions between the triply coordinated chloride ions. A similar situation is found in the case of coordination polymers with bromide and iodide (i.e., **2** and **3**, respectively). Such short distances between triply bridged halide ions have been reported[20] in case of discrete complexes of Cu(II) with the bis(diphenylphosphino)methane ligand. Each metal ion of this cluster is bridged via a carboxylate to another cluster containing three Cd^{2+} ions (Figure 2).

In the later cluster, each metal ion shows distorted hexagonal bipyramidal CdO_8 coordination from three chelating carboxylates ($Cd-O$ = 2.444(16) Å) and two water molecules ($Cd-O$ = 2.272(12) Å). A clear picture of the coordination geometry around each type of Cd^{2+} ion is shown in Figure 3.

The Cd^{2+} clusters form a unit, and three such units are connected to three **L**$^{2-}$ ligands to form a triangular unit that connects other triangular units to form a two-dimensional (2D) sheet structure (Figure 4a and b). The triangular units are interpenetrated (Figure 5a) to afford an overall 3D structure (Figure 5b). There are few examples of 3D self-penetrated structures reported in the literature.[21]

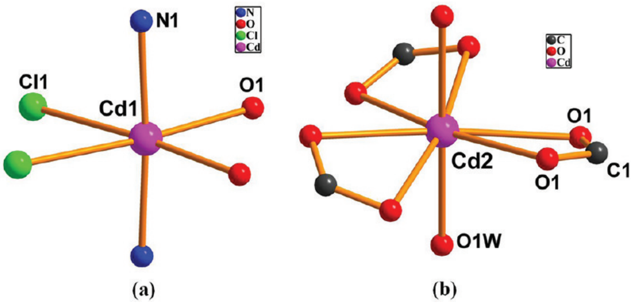


Figure 3. Coordination mode for (a) Cd1 and (b) Cd2 in **1**.

The precursor (**L**$_1$) has an ester group and a benzene ring bearing a nitrile group attached to a piperidine ring in *trans* arrangement to each other. The piperidine ring is in chair form in the structure (Figure 6a). Under hydrothermal conditions in the presence of sodium azide, the cyano group is converted to a tetrazole moiety while the ester group is hydrolyzed to a carboxylic acid. The chair conformation of the piperidine ring gets somewhat flattened making a dihedral angle of 27.7(5)° between the flattened ring and the phenyl moiety (Figure 6b) in **L**$^{2-}$ bound to metal ions.[17]

It has been observed that the tetrazole moiety can form different types of trinuclear and tetranuclear metal clusters in coordination polymers similar to that of carboxylate-based ligands.[22] In the present case, the tetrazole moiety and the carboxylate group along with Cd^{2+} ions form a triangular unit that propagate to form the coordination polymers. Each coordination polymer here provides an uncommon example of 6-connected self-penetrating 3D polymer with an *in situ* generated tetrazole moiety having $6^{12}\cdot 8^{3}$ topology. The 3D topological network of the complexes are analyzed by the OLEX program,[23] and the results show that the long topological vertex

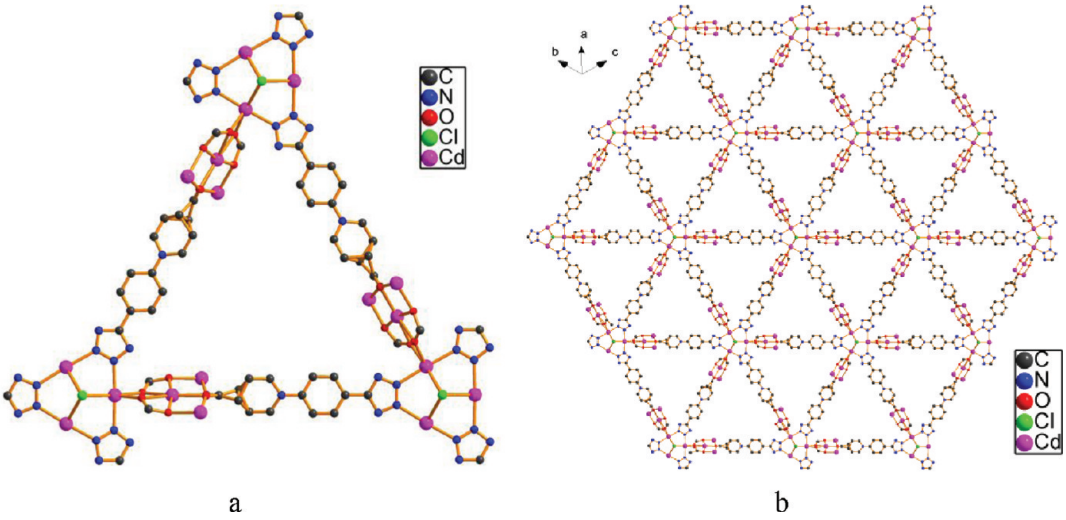


Figure 4. (a) Triangular unit present in **1** built using three **L**$^{2-}$, three trinuclear Cd(II) cluster units. (b) 2D layered network along the plane in **1**.

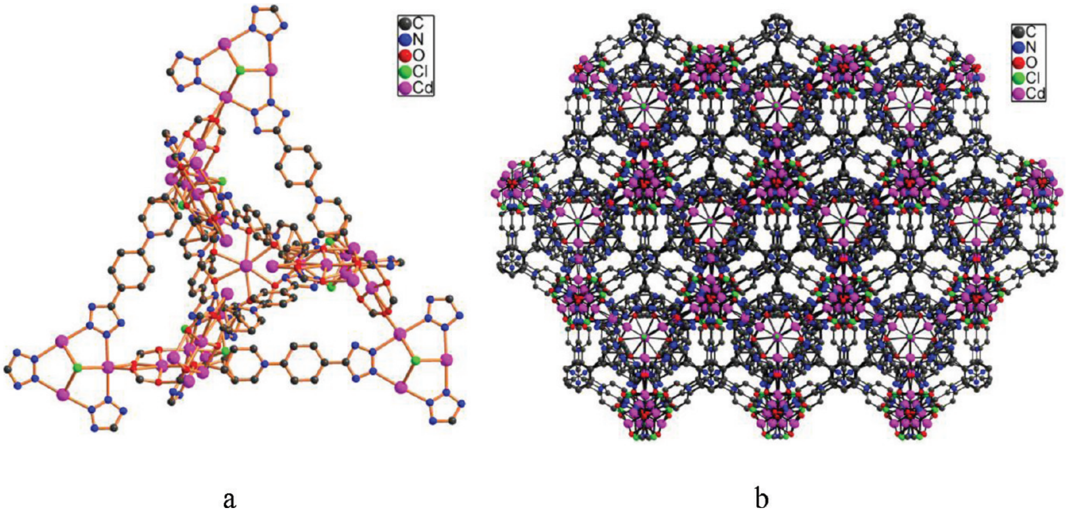


Figure 5. (a) View showing an interpenetration of ligand within a triangular unit. (b) 3D view of complex **1**.

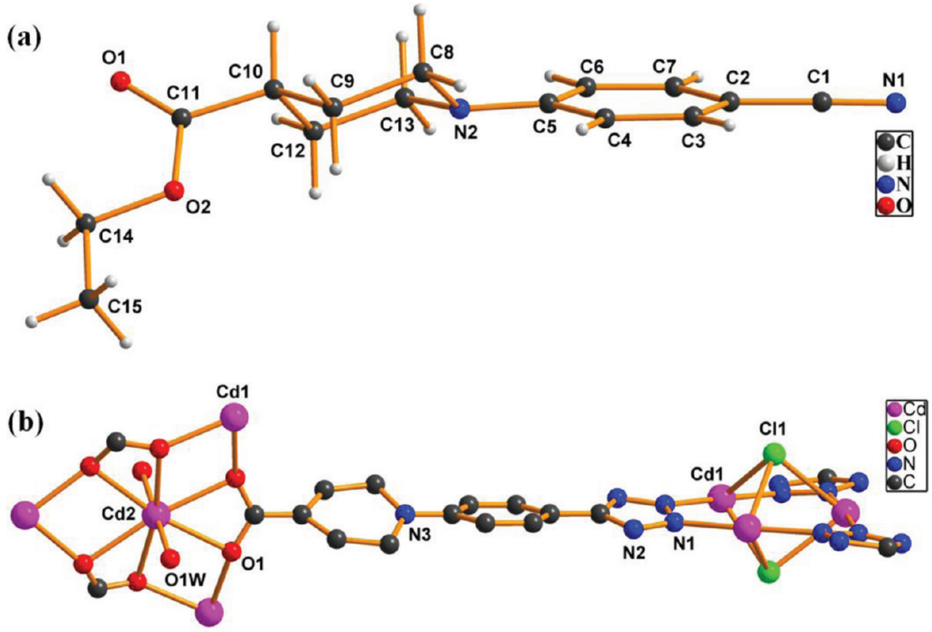


Figure 6. (a) Schematic view of ligand $\mathbf{L_1}$ in chair form. (b) View showing flattening of piperidine ring when the carboxylate and tetrazole moiety is bound to Cd^{2+} ions (H atoms are omitted for clarity).

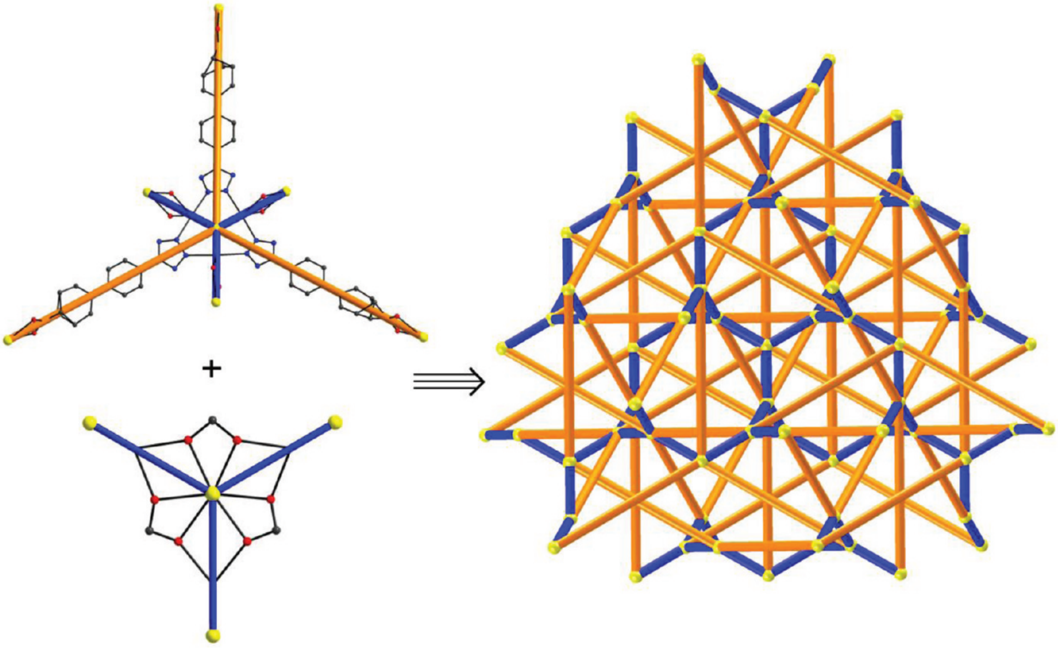


Figure 7. Topological view showing the interpenetration in complex **1**.

symbol is $6_6 \cdot 6_6 \cdot 6_4 \cdot 6_4 \cdot 6_2 \cdot 6_6 \cdot 6_2 \cdot 6_4 \cdot 6_4 \cdot 6_4 \cdot 6_2 \cdot 6_4 \cdot 8_{16} \cdot 8_{16} \cdot 8_{16}$ considering all Cd1 + halide as one node and $6_6 \cdot 6_6 \cdot 6_2 \cdot 6_4 \cdot 6_4 \cdot 6_6 \cdot 6_4 \cdot 6_2 \cdot 6_4 \cdot 6_4 \cdot 6_4 \cdot 6_2 \cdot 8_{16} \cdot 8_{16} \cdot 8_{16}$ for Cd2 + oxygen atoms, giving a short vertex symbol $6^{12} \cdot 8^3$ for both cases. Thus, the overall 3D framework can be abstracted into a 6-connected network (Figure 7).

Thermal stabilities of the complexes are examined.[17] Complex **1** is thermally stable up to ~330 °C. It shows a weight loss of 2.5% (expected = 2.6%) in the temperature range 90−150 °C that corresponds to loss of coordinated water molecules. Decomposition of this compound is accomplished only above 330 °C. Similarly, both **2** and **3** exhibit weight loss corresponding to removal of coordinated water in the temperature range 80−130 °C and thereafter stable up to at least 300 °C.

Luminescence Properties. Luminescent compounds are of immense current interest because of their diverse applications in chemical sensors, photochemistry, as well as electroluminescent display.[24] The luminescence properties of carboxylate containing systems with a d^{10} metal have been reported in the literature.[25] The solid-state luminescence of compounds **1**−**3** are

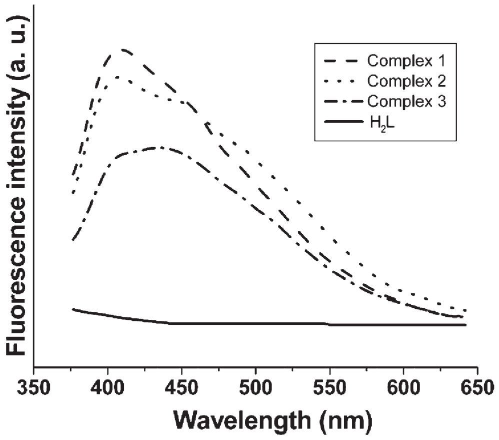


Figure 8. Solid-state emission at room temperature.

investigated at room temperature and are shown in Figure 8. Upon excitation at 340 nm, solid **1** exhibits strong luminescence in the visible region centered at λ_{max} = 415 nm. Compared with the ligands, which have no luminescence, the greatly enhanced photoluminescence intensities are attributed to the charge-transfer transition between ligands and metal centers[26] or intraligand fluorescence emission because ligand coordination to the metal center effectively increases the rigidity of the ligand and reducing the loss of energy by radiation-less decay.[27] Interestingly, the complexes show anion-dependent variation in luminescence property and are thus attributable to metal—ligand charge transfer transition. The Cd···Cd distances are long enough (more than 3.6 Å) to explain cluster-centered transition caused by Cd···Cd interaction in all the complexes. Therefore, in addition to charge-transfer transition between ligands and metal centers, there exists some mixing of halide-to-metal charged transfer characters.

■ CONCLUSION

In summary, we have synthesized three isostructural 3D coordination polymers with Cd^{2+} ions under hydrothermal conditions using a new semiflexible *in situ* generated tetrazole ligand. All the complexes display a rare μ_3-halide bridging that is extended in all dimensions to generate highly interpenetrated 3D coordination polymers. They show interesting anion-dependent luminescence property. Such type of cluster containing coordination polymers with other transition metal ions are under investigation with this and other ligands containing both carboxylate and nitrogen donor groups in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic data for L_1 and **1**−**3** in CIF format, table for selected bonds and distances for complexes **1**−**3**, IR, TG analysis, ESI-MS, and NMR and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We gratefully acknowledge the financial support received from the Department of Science and Technology, New Delhi, India (to P.K.B.) and SRFs from the CSIR to P.L. We also would like to thank Prof. Oleg Dolomanov for his help in finding the topology and Prof. R. Butcher for giving his valuable suggestion while solving crystal structures.

■ REFERENCES

(1) (a) Perry, J. J., IV; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400. (b) Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294. (c) Farha, O. K.; Yazaydm, A. O.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatazidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nat. Chem.* **2010**, *2*, 944. (d) Bradshaw, D.; Warren, J. E.; Rosseinsky, M. J. *Science* **2007**, *315*, 977. (e) Sharma, M. K.; Senkovska, I.; Kaskel, S.; Bharadwaj, P. K. *Inorg. Chem.* **2011**, *50*, 539. (f) Rajput, L.; Biradha, K. *Cryst. Growth Des.* **2009**, *9*, 40. (g) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2948. (h) Janiak, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 1431. (i) Jiang, H.-L.; Xu, Q. *Chem. Commun.* **2011**, 3351. (j) Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115.

(2) (a) Das, M. C.; Bharadwaj, P. K. *J. Am. Chem. Soc.* **2009**, *131*, 10942. (b) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. *Nat. Chem.* **2010**, *2*, 838. (c) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762. (d) Hurd, J. A.; Vaidhyanathan, R. Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, I. L.; Shimizu, G. K. H. *Nat. Chem.* **2009**, *1*, 705. (e) Sadakiyo, M.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 9906. (f) Navarro, J. A. R.; Barea, E.; Rodriguez-Dieguez, A.; Salas, J. M.; Ania, C. O.; Parra, J. B.; Masciocchi, N.; Galli, S.; Sironi, A. *J. Am. Chem. Soc.* **2008**, *130*, 3978. (g) Kim, H.; Das, S.; Kim, M. G.; Dybtsev, D. N.; Kim, Y.; Kim, K. *Inorg. Chem.* **2011**, *50*, 3691.

(3) (a) Aijaz, A.; Lama, P.; Bharadwaj, P. K. *Inorg. Chem.* **2010**, *49*, 5883. (b) Ohmori, O.; Fujita, M. *Chem. Commun.* **2004**, 1586.

(4) (a) Lama, P.; Aijaz, A.; Sañudo, E. C.; Bharadwaj, P. K. *Cryst. Growth Des.* **2010**, *10*, 283. (b) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 677. (c) Devic, T.; Serre, C.; Audebrand, N.; Marrot, J.; Férey, G. *J. Am. Chem. Soc.* **2005**, *127*, 12788. (d) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.

(5) (a) Zhang, S.-M.; Chang, Z.; Hu, T.-L.; Bu, X.-H. *Inorg. Chem.* **2010**, *49*, 11581. (b) Zou, Y.; Hong, S.; Park, M.; Chun, H.; Lah, M. S. *Chem. Commun.* **2007**, 5182. (c) Dinca, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876.

(6) (a) Wei, G.; Shen, Y.-F.; Li, Y.-R.; Huang, X.-C. *Inorg. Chem.* **2010**, *49*, 9191. (b) Su, C.-Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2004**, *126*, 3576.

(7) (a) Qiu, Y.; Deng, H.; Mou, J.; Yang, S.; Zeller, M.; Batten, S. R.; Wu, H.; Li, J. *Chem. Commun.* **2009**, 5415. (b) Zhao, H.; Qu, Z.-R.; Ye, H.-Y.; Xiong, R.-G. *Chem. Soc. Rev.* **2008**, *37*, 84.

(8) Blake, J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schroder, M. *Chem. Commun.* **1997**, 1675.

(9) (a) Chen, X.-M.; Tong, M.-L. *Acc. Chem. Res.* **2007**, *40*, 162. (b) Zhang, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 1201. (c) Tong, M.-L.; Li, L.-J.; Mochizuki, K.; Chang, H.-C.; Chen, X.-M.; Li, Y.; Kitagawa, S. *Chem. Commun.* **2003**, 428.

(10) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1952; Vol. III.

(11) *SAINT*, version 6.02; Bruker AXS: Madison, WI, 1999.

(12) Sheldrick, G. M. *SADABS: Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(13) *XPREP*, version 5.1; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(14) Sheldrick, G. M. *SHELXTL Reference Manual*, version 5.1; Bruker AXS: Madison, WI, 1997.

(15) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(16) (a) Luo, J.; Zhao, Y.; Xu, H.; Kinnibrugh, T. L.; Yang, D.; Timofeeva, T. V.; Daemen, L. L.; Zhang, J.; Bao, W.; Thompson, J. D.; Currier, R. P. *Inorg. Chem.* **2007**, *46*, 9021. (b) Lisnard, L.; Mialane, P.; Dolbecq, A.; Marrot, J.; Clemente-Juan, J. M.; Coronado, E.; Keita, B.; de Oliveira, P.; Nadjo, L.; Sécheresse, F. *Chem.—Eur. J.* **2007**, *13*, 3525.

(17) See Supporting Information.

(18) (a) Wei, G.; Shen, Y.-F.; Li, Y.-R.; Huang, X.-C. *Inorg. Chem.* **2010**, *49*, 9191. (b) Aijaz, A.; Barea, E.; Bharadwaj, P. K. *Cryst. Growth Des.* **2009**, *9*, 4480.

(19) Chauvin, R. *J. Phys. Chem.* **1992**, *96*, 9194.

(20) Bera, J. K.; Nethaji, M.; Samuelson, A. G. *Inorg. Chem.* **1999**, *38*, 218.

(21) (a) Wang, X.-L.; Lin, H.-Y.; Mu, B.; Tian, A.-X.; Liu, G.-C.; Hu, N.-H. *CrystEngComm* **2011**, *13*, 1990–1997. (b) Qi, Y.; Che, Y.-X.; Zheng, J.-M. *Cryst. Growth Des.* **2008**, *8*, 3602–3608. (c) Liu, B.; Hou, L.; Wang, Y.-Y.; Zhang, Y.-N.; Cui, L.; Shi, Q.-Z. *Inorg. Chem. Commun.* **2011**, *14*, 822–825. (d) Mu, Y.; Fu, J.; Song, Y.; Li, Z.; Hou, H.; Fan, Y. *Cryst. Growth Des.* **2011**, *11*, 2183–2193.

(22) Dinca, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6766.

(23) Dolomanov, O. V.; Blake, A. J.; Champness, N. R.; Schroder, M. *J. Appl. Crystallogr.* **2003**, *36*, 1283.

(24) (a) McGarrah, J. E.; Kim, Y. J.; Hissler, M.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 4510. (b) Wu, Q.; Esteghamatian, M.; Hu, N. X.; Popovic, Z.; Enright, G.; Tao, Y.; D'Iorio, M.; Wang, S. *Chem. Mater.* **2000**, *12*, 79.

(25) Lee, E. Y.; Jang, S. Y.; Suh, M. P. *J. Am. Chem. Soc.* **2005**, *127*, 6374.

(26) Li, S. L.; Lan, Y. Q.; Ma, J. F.; Yang, J.; Wei, G. H.; Zhang, L. P.; Su, Z. M. *Cryst. Growth Des.* **2008**, *8*, 675.

(27) (a) Zheng, S. L.; Yang, J. H.; Yu, X. L.; Chen, X. M.; Wong, W. T. *Inorg. Chem.* **2004**, *43*, 830.(b) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2002.