A rare pentanuclear cadmium(II) complex and two new mononuclear zinc(II) complexes of pyrazole derived ditopic ligands – Synthesis, crystal structures and spectral studies

Saugata Konar a, Atanu Jana a, Kinsuk Das b, Sangita Ray a, James A. Golen c, Arnold L. Rheingold c, Susanta Kumar Kar a,⁎

a Department of Chemistry, University College of Science, University of Calcutta, 92 A.P.C. Road, Kolkata 700009, India
b Department of Chemistry, Haldia Government College, Debhog, Purba Midnapur 721657, India
c Department of Chemistry and Biochemistry, University of California, San Diego, CA 92093, USA

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A B S T R A C T

Pyrazole based ditopic ligand HL1 (\((Z)-N^\text{3}O-(5\text{-methyl-1H-pyrazole-3-carbonyl})\) picolinohydrazonamide) reacts with Cd(ClO4)2.6H2O and Zn(ClO4)2.6H2O to form a self assembled pentanuclear Cd(II) complex [Cd3(L1)6][ClO4]4 (1) and a mononuclear Zn(II) complex [Zn(HL1)2][ClO4]2 (2). On the other hand, HL2 (\((Z)-N^\text{3}O-(5\text{-methyl-1H-pyrazole-3-carbonyl})\) pyrazine-2-carbohydroxamide) also forms a mononuclear [Zn(HL2)][ClO4]2(MeOH)2 (3) with Zn(ClO4)2.6H2O. All these complexes have been characterized crystallographically and spectroscopically. The Cd(II) complex (1) has a pentanuclear core with trigonal bipyramidal arrangement of Cd(II) atoms, where, the axial metal centers (Cd2 and Cd5) have N3O3 chromophore and the equatorial centers (Cd1, Cd3 and Cd4) have N4O2 chromophore with distorted octahedral arrangement around the metal centres. In 2 and 3, the NNO donor ligand molecules in their ketoimine form produce distorted octahedral environment around the Zn(II) centre with N6O2 chromophore utilizing pyridine/pyrazine N, one azomethine N and one carbohydrazide O atoms. Here, the pyrazole ring N atoms remain silent in coordination process. On the other hand, in 1, the same ligand HL1 coordinates in its deprotonated imineel form and functions as N3O donor, while, the pyrazole N atoms take part in coordination process. Ligands HL1 and HL2 are fluorescence silent but complexes 1, 2 and 3 show considerable fluorescence. The fluorescence intensity of 1 is higher than that of 2 and 3.

1. Introduction

Ditopic ligands containing aromatic spacers have been shown to be useful reagents for the fabrication of supramolecular arrays [1–6]. These ligands promote the metal ion dependent self-assembly processes to produce homoleptic, pentanuclear alkoxo-bridged trigonal-bipyramidal metal clusters with Mn(II), Co(II), and Zn(II) salts of noncoordinating anions (e.g., ClO4−) where the metal centres are in octahedral coordination pockets [7,8]. The binding of transition metal ions with properly designed ditopic ligands has been continuously attracting scientific interest since the seminal reports on the metal-mediated self-assembly processes [9–11]. Self-assembly of transition metals with multifunctional organic ligands represents a successful paradigm for the single step synthesis of new clusters of aesthetical and appealing architectures with electronic, redox, magnetic, photo-physical and catalytic properties [12–15]. The spontaneous assembly of metal ion centers into homoleptic grids or clusters offers particularly an attractive method for the production of nanosized, supramolecular aggregates whose properties are direct consequences of the positioning and identity of the coordination pockets within the ligand and the ability of the metal ion to read these sites in terms of its own coordination algorithms. “Ditopic” ligands, e.g., HL1 and HL2, are coordinatively versatile, and can bridge metal ions via μ-O or μ–N–N connections [16–19]. Such types of ditopic hydrazone ligands have two coordination pockets. The configurational flexibility of the ligand in its tautomeristic form presents choices for metal ion coordination. Although, examples of grid-based complexes have been referred [17,19] other structural motifs result as the metal ions find more stable structural alternatives. The interesting part of this paper is the synthesis of a novel Cd5(II) cluster compound using this type of ditopic ligand which is an unprecedented one as per our knowledge. We choose zinc and cadmium because the d10 configuration in zinc permits a wide range of symmetries and various coordination numbers, i.e., 4, 5 or 6 in its complex relatively Easily [20–22], while cadmium shows 4, 6, 7 coordination. Moreover, luminescent compounds are attracting much current research

⁎ Corresponding author. Tel.: +91 033 23508386; fax: +91 033 23519755. E-mail address: skkar_cu@yahoo.co.in (S.K. Kar).

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interest because of their many fold applications, including emitting materials for organic light emitting diodes, light harvesting materials for photo catalysis and fluorescent sensors for organic or inorganic analyses [23]. Hence it is important to understand the coordination chemistry and luminescence property of group 12 metal ions for developing new materials which can function as fluorescent sensors [23]. Thus, our goal is to observe the changes in luminescent behavior of the ligand with different metal ions as guests.

This present study (Scheme 1) is a continuation of our earlier work [17,19], one new pentanuclear Cd(II) complex (1) and a new mononuclear Zn(II) complex (2) have been synthesized using ditopic ligand HL1 (condensation product of 5-Methylpyrazole-3-carbohydrazide and the methyl ester of iminopicolinic acid prepared in situ, earlier symbolized as PzOAP) and another mononuclear Zn(II) complex (3) with HL2 (condensation product of 5-Methylpyrazole-3-carbohydrazide and the methyl ester of iminopyrazine-2-carboxylic acid prepared in situ, earlier symbolized as PzOAPyz) using zinc perchlorate and cadmium perchlorate as the metal precursors. We report the synthetic details, X-ray crystal structures and spectral studies of 1, 2 and 3. We have also studied the photoluminescence properties of the ligands HL1 and HL2 and its metal complexes. Interestingly, we have observed that the ligands HL1 and HL2 are fluorescence silent, whereas, the complexes show chelation enhanced fluorescence. Among all the complexes 1 has highest fluorescence intensity.

2. Experimental

2.1. Material

2-Cyanopyridine and 2-cyanopyrazine were purchased from Aldrich Chemical Company, USA. Other commercially available chemicals and solvents were used and purified by standard procedures [24].

Caution! Although we have not encountered any problem, it should be kept in mind that perchlorate compounds of metal ions are potentially explosive in the presence of organic ligands. Only a small amount of the material should be prepared and it should be handled with care.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) of the ligand and metal complexes were determined with a Perkin–Elmer CHN analyzer 2400 at the Indian Association for the Cultivation of Science, Kolkata. The electronic spectra of the complexes were recorded on a Hitachi model U-3501 spectrophotometer. IR spectra (KBr pellet, 500-4000 cm⁻¹) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. The fluorescence spectra were recorded on a Perkin Elmer LS 50B fluorimeter.

2.3. Synthesis of the ligands (HL1 and HL2)

The ligands HL1 and HL2 were synthesized by following reported methods [17,19].

2.4. Preparation of complexes

2.4.1. Preparation of [Cd₅(L₁)₆](ClO₄)₄ (1)

A methanolic solution (10 ml) of Cd(ClO₄)₂·6H₂O (1 mmol, 0.419 g) was added dropwise to a solution of HL₁ (1 mmol, 0.244 g) in the same solvent (15 ml) taken in 1:1 molar ratio with constant stirring for 2 h. The solution turned yellow. It was filtered and left for slow evaporation at room temperature. Single crystals of the compound suitable for X-ray crystallography were isolated from the filtrate after standing for one week (Yield: 58.5%). Anal. Calc. for C₅₈H₅₁N₂₁O₂₉Cd₅: C, 31.70; H, 2.98; N, 19.58. Found: C, 31.58; H, 2.74; N, 19.64%. IR (KBr, cm⁻¹): 1560 (νC=N).
2.4.2. Preparation of [Zn(HL1)2](ClO4)2(MeOH)2 (2)

A methanolic solution (10 ml) of Zn(ClO4)2·6H2O (1 mmol, 0.372 g) was added dropwise to a solution of HL1 (1 mmol, 0.244 g) in the same solvent (15 ml) taken in 1:1 molar ratio with constant stirring for 2 h and filtered. The filtrate was left at room temperature. Diffraction quality single crystals were obtained by slow evaporation of the filtrate after standing for several days. (Yield: 63%). Anal. Calc. for C22H22Cl2N12O11Zn: C, 35.09; H, 3.69; N, 21.79%. Found: C, 34.09; H, 3.21; N, 21.87%. IR (KBr, cm−1): 1555 (υC=O), 1654 (υC=O), 3296 (υO–H). UV–Vis (DMF); λmax/νm = 352 and 470 nm.

2.4.3. Preparation of [Zn(HL2)2](ClO4)2(MeOH)2 (3)

A methanolic solution (10 ml) of Zn(ClO4)2·6H2O (1 mmol, 0.372 g) was added dropwise to a solution of HL2 (1 mmol, 0.245 g) in the same solvent (15 ml) taken in 1:1 molar ratio with constant stirring for 2 h. The resulting light yellow solution was filtered and left at room temperature. After standing for several days single crystals of the compound suitable for X-ray crystallography were obtained from mother liquor (Yield: 63%). Anal. Calc. for C22H22Cl2N12O11Zn: C, 34.10; H, 3.21; N, 21.87. Found: C, 34.09; H, 3.19; N, 21.87. IR (KBr, cm−1): 1555 (υC=O), 1654 (υC=O), 3296 (υO–H). UV–Vis (DMF); λmax/νm = 352 and 470 nm.

3. Crystallographic measurements

Selected crystal data for 1–3 are given in Table 1 and selected metrical parameters of these complexes are given in Table 2. For complexes 1–3 data collections were made using Bruker SMART APEX CCD area detector equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) source in φ and ω scan mode. Cell parameters refinement and data reduction were carried out using Bruker SMART [25] and Bruker SAINT software for all these complexes. All the structures were solved by conventional direct methods and refined by full-matrix least square methods using F2 data. SHELXS-97 and SHELXL-97 programs [26] were used for structure solution and refinement, respectively. In 1, one perchlorate anion was refined anisotropically while the three others were found to be disordered with respect to their O atoms. These O atoms were treated with fixed distances and angles, two PART disorder model and with a common EADP (51/49 and 60.5 39.5 ratio). Although hydrogen atoms were not located for solvent water they were included in the chemical unit cell along with residual electron density treated with PLATON program SQUEEZE (found 630 A3, 150 e) which was treated as 8 methanol molecules. These values added to unit card to adjust chemical formula, density, and F(000) value.

In 2, SQUEEZE (PLATON, A. Spek) was used to treat diffuse solvent and anion contributions. Total electron count found per unit cell is 222 indicating the possibility of two ClO4 ions and two water molecules which is well matched with elemental analyses and IR spectrum. The calculated for two ClO4 and two H2O is 216/unit cell. The intensive properties (density, F(000), etc.) reflect these contributions. In 3, hydrogen atoms on various nitrogen and oxygen atoms were found from a Fourier difference map and were allowed to refine while all other hydrogen atoms were placed in calculated positions with appropriate riding models.

4. Result and discussion

4.1. Syntheses

The ligands HL1 and HL2 were prepared following our previously reported methods [17,19]. Complex 1, 2 and 3 were obtained by mixing the ligands and the Cd(II) and Zn(II) perchlorate salts taken in a 1:1 molar ratio in methanol. An intractable mass was obtained in the reaction between H2CdCl2 and H2O is 216/unit cell. The intensive properties (density, F(000), etc.) reflect these contributions. In 3, hydrogen atoms on various nitrogen and oxygen atoms were found from a Fourier difference map and were allowed to refine while all other hydrogen atoms were placed in calculated positions with appropriate riding models.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C9H12Cl2O33</td>
<td>C2H6O4Cl2</td>
<td>C9H6Cl2Cd2N12O12</td>
</tr>
<tr>
<td>Formula weight</td>
<td>224.54</td>
<td>140.8</td>
<td>392.22</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2</td>
<td>P1</td>
<td>P1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>45.815(12)</td>
<td>11.4714(17)</td>
<td>11.7107(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.880(3)</td>
<td>12.0739(14)</td>
<td>12.0150(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.1097(6)</td>
<td>95.2900(10)</td>
<td>94.9240(10)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90.00</td>
<td>89.5090(10)</td>
<td>90.00</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.00</td>
<td>95.2900(10)</td>
<td>108.4850(10)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90.00</td>
<td>112.4850(10)</td>
<td>118.0774(10)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>9961(4)</td>
<td>1790.6(4)</td>
<td>1790.6(4)</td>
</tr>
<tr>
<td>z</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Density, calc (Mg cm⁻³)</td>
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<td>1.430</td>
<td>1.656</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>1.249</td>
<td>0.902</td>
<td>0.993</td>
</tr>
<tr>
<td>F(000)</td>
<td>5123</td>
<td>788</td>
<td>840</td>
</tr>
<tr>
<td>θ Range (°) for data collection</td>
<td>2.49–27.91</td>
<td>2.49–23.94</td>
<td>2.49–23.94</td>
</tr>
<tr>
<td>Index ranges</td>
<td>−55 ≤ h ≤ 59</td>
<td>−13 ≤ h ≤ 13</td>
<td>−14 ≤ h ≤ 15</td>
</tr>
<tr>
<td></td>
<td>−18 ≤ k ≤ 17</td>
<td>−14 ≤ k ≤ 14</td>
<td>−15 ≤ k ≤ 15</td>
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<tr>
<td></td>
<td>−21 ≤ l ≤ 21</td>
<td>−16 ≤ l ≤ 16</td>
<td>−15 ≤ l ≤ 13</td>
</tr>
<tr>
<td>Goodness-of-fit (GOF) on F²</td>
<td>1.113</td>
<td>1.068</td>
<td>1.050</td>
</tr>
<tr>
<td>Independent reflections (Rint)</td>
<td>22359 (0.051)</td>
<td>4674 (0.045)</td>
<td>4674 (0.045)</td>
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<tr>
<td>Absorption correction</td>
<td>multi-scan</td>
<td>multi-scan</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Refinement method</td>
<td>full-matrix least squares on F²</td>
<td>full-matrix least squares on F²</td>
<td>full-matrix least squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>22389/61/1220</td>
<td>4674(0)/334</td>
<td>4674(0)/334</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>73129</td>
<td>73129</td>
<td>73129</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R = 0.0658, wR² = 0.1865</td>
<td>R = 0.0567, wR² = 0.1624</td>
<td>R = 0.0416, wR² = 0.1080</td>
</tr>
<tr>
<td>Largest difference peak and hole (e Å⁻³)</td>
<td>−1.46, 3.39</td>
<td>−0.51, 1.00</td>
<td>−0.45, 0.55</td>
</tr>
</tbody>
</table>
of the suitable reaction mixtures at room temperature. These complexes were characterized by X-ray crystallography, elemental analyses and spectral studies.

4.2. Description of structures

4.2.1. Structural description of $[\text{Cd}_{5}L_{6}]^{2+}|\text{ClO}_{4}^{-} (1)$

The molecular structure of 1 is shown in Fig. 1a. Crystallographic details are listed in Table 1 and important bond distances and angles are listed in Table 1. Complex 1 crystallizes in space group $C21/c$ and the unit cell contains four molecules. The overall structural arrangement shows a pentanuclear cation, with four well defined perchlorate anions. The pentanuclear homoletic cluster involves five six-coordinate pseudo-octahedral cadmium(II) centers arranged at the five apices of a trigonal bipyramid. Each of the apical cadmium centers (Cd2 and Cd5) have N3O3 chromophore, while the cadmium centers (Cd1, Cd3 and Cd4) via alkoxy bridges from tetradentate ligands. Each ligand actually satisfies five metal coordination positions because of the bridging nature of the deprotonated oxygen. Each ligand bridges a pair of cadmium centers via the μ-O alkoxy oxygen atom, and the six ligands behave similarly, with an azomethine nitrogen, pyridine nitrogen and pyrazole nitrogen filling other coordination sites for each pair of metal ions. In the case, where the anions are poor donors, co-ligand competition is reduced, and other oligomeric cluster combinations are possible. The pentanuclear TBP core structure is illustrated in Fig. 1b. The apical cadmium centers (Cd2 and Cd5) have $N_{2}O_{5}$ chromophore, while the equatorial cadmium centers (Cd1, Cd3 and Cd4) have $N_{2}O_{4}$ chromophore. Cd–O–Cd bond angles fall in the range 123.94–128.19° and cadmium–ligand bond distances fall in the range 2.226–2.527 Å. Packing diagram is shown in Fig. 2 along ‘c’ axis.
4.2.2. Structural description of \([\text{Zn}(\text{HL}_1)_2]\)(\text{ClO}_4)_2 (2) and \([\text{Zn}(\text{HL}_2)_2]\)(\text{ClO}_4)_2(\text{MeOH})_2 (3)

The molecular structures of 2 and 3 are shown in Figs. 3 and 6 respectively, crystallographic details are listed in Table 1 and important bond distances and angles are listed in Table 2. Both the complexes 2 and 3 crystallize in space group \(P\bar{1}\). The unit cell of each complex comprises of two molecules. Each Zn(II) centre in these molecules has a distorted octahedral geometry with \(N_4O_2\) chromophore bis-mer \(ZnN_4O_2\) arrangement of two ligands around the metal ion. In 2, the equatorial positions are occupied by two pyridine nitrogen atoms (N6 and N12) in cis fashion [N6–Zn1–N12 = 97.12(10)\(^\circ\)] and two carbohydrazide carbonyl oxygen atoms (O9 and O10) also in cis orientation [O9–Zn1–O10 = 87.16(9)\(^\circ\)]. The axial positions are occupied by the two remaining azomethine nitrogen atoms (N4 and N10) which is evident from the N4–Zn1–N10 angle [162.75(10)\(^\circ\)]. Here, the two ligand moieties approach towards the metal centers orthogonally which is quite evident from the observed corresponding dihedral angle between the two planes [angle between Zn1–N6–N4–O9 and Zn1–N12–N10–O10 = 89.46\(^\circ\)].

In 3, the equatorial positions are occupied by two pyridine nitrogen atoms (N1 and N8) in cis fashion [N1–Zn1–N8 = 94.03(8)\(^\circ\)] and two carbohydrazide carbonyl oxygen atoms (O2 and O1) also in cis orientation [O2–Zn1–O1 = 90.47(7)\(^\circ\)]. The axial positions are occupied by the two remaining azomethine nitrogen atoms (N3 and N10) and the N3–Zn1–N10 angle [162.73(9)\(^\circ\)]. In 3, the two ligand moieties approach towards the metal centers orthogonally is quite evident from the observed corresponding dihedral angle between the two planes [angle between Zn1–N8–N10–O2 and Zn1–N1–N3–O1 = 89.22\(^\circ\)]. The pyrazole functions remain dangling, metal–ligand bond distances fall in the range 2.057–2.189 Å for 2 and 2.032–2.258 Å for 3. The chelate bite angles are in between 73.43\(^\circ\) and 74.59\(^\circ\) for 2 and 74.01–76.12\(^\circ\) for 3. Both the complexes are stabilized through a network of intermolecular H-bonding detailed in Table 3. The H-bonding interaction of 2 is shown in Fig. 4. The crystal structure of complex 3 contains two MeOH molecules in its constitution which are involved in imparting additional stability. In 2, \(\pi-\pi\) stacking (Fig. 5) is observed in between the two pyridyl parts from two different neighbouring complex molecules. Fig. 7 shows that the perchlorate molecules are involved in forming an ion channel throughout the lattice structure in 3.

4.3. IR and electronic spectra

The IR spectra of all the complexes (1-3) were recorded and compared with those of the ligands (HL\(_1\) and HL\(_2\)) to study the structural changes in the ligands upon complexation. The free
ligands display a pyridyl C=\text=N stretching frequency at 1584 and
1588 cm\(^{-1}\), upon complexation this band shifted to a lower wave
number 1565–1555 cm\(^{-1}\) in all the complexes. The observation
of strong bands at 1664 and 1660 cm\(^{-1}\) in the free ligands was
attributed to carbonyl group (\(\text{C}=\text{O}\)) and around 3200 cm\(^{-1}\) indi-
cates \(\text{(NH)}\) stretch of –CONH group. In 1, H L1 do not show the
\(\text{C}=\text{O}\) IR frequency of the free ligand at 1664 cm\(^{-1}\). It is also supported by
the absence of \(\text{NH}\) frequency around 3200 cm\(^{-1}\) in metal com-
plexes which supports its enolisation. This is further substantiated
by the presence of new non ligand band in the spectra of the com-
plexes around 1298 cm\(^{-1}\), which is due to the enolisation of
\(\text{C}=\text{O}\) and subsequent deprotonation of enolic OH and the participation
of \(\text{C}=\text{O}\) enolic in complexation [27] but in 2 and 3, stretching fre-
quencies of carbonyl group appear at 1654 cm\(^{-1}\) and 1649 cm\(^{-1}\),
respectively compared to free ligands indicating that >C=O is coor-
dinated to central atom in its ketoimine form. The band around
974 cm\(^{-1}\) is assigned to \(\text{(N–N)}\) stretching vibration of hydrazine
residue. This band in the complexes shift slightly to higher wave
number side confirming involvement of one of the nitrogens of –
N–N– in bonding with the metal ions. A broad band in the region
3500–3200 cm\(^{-1}\) indicates the presence of lattice held water mol-
ecules in all the complexes. The strong broad band around
1093 cm\(^{-1}\) for the complexes indicates the presence of an anionic
perchlorate group.

The electronic absorption spectra of ditopic ligands (HL\(_1\) and
HL\(_2\)) as well as their complexes (1–3) were measured in DMF solu-
tion. The electronic spectrum of the free ligands shows a band at
345 nm attributed to the \(n \rightarrow \pi^*\) transition of the azomethine
group. There is a strong band at 280 nm due to a \(n \rightarrow n^*\) transition.
The electronic spectra of the Zn(II) and Cd(II) complexes exhibit in-
tense bands at 350–380 nm range. These transitions are presum-
ably due to the intra ligand \(\pi \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions and
also a weak band at 450–480 nm is assigned to a MLCT band [28].

### Table 3
Details of hydrogen bond distances (Å) and angles (°) for complexes 2 and 3.

<table>
<thead>
<tr>
<th>D–H</th>
<th>A</th>
<th>d(D–H)</th>
<th>d(H–A)</th>
<th>d(D–A)</th>
<th>(&lt;\text{DHA})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N5–H5B</td>
<td>O10</td>
<td>0.8800</td>
<td>2.1100</td>
<td>2.875(4)</td>
<td>144.00</td>
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<tr>
<td>N9–H9A</td>
<td>O9</td>
<td>0.8800</td>
<td>2.1600</td>
<td>2.961(3)</td>
<td>150.00</td>
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<tr>
<td>N11–H11A</td>
<td>N2</td>
<td>0.8800</td>
<td>2.1800</td>
<td>2.972(5)</td>
<td>149.00</td>
</tr>
<tr>
<td>N7–H7NA</td>
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<td>0.78(4)</td>
<td>2.12(4)</td>
<td>2.826(3)</td>
<td>151(4)</td>
</tr>
<tr>
<td>N7–H7NB</td>
<td>N12</td>
<td>0.84(4)</td>
<td>2.14(4)</td>
<td>2.959(3)</td>
<td>167(3)</td>
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<td>N4–H4A</td>
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<td>0.84(3)</td>
<td>2.23(3)</td>
<td>3.017(3)</td>
<td>156(2)</td>
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<tr>
<td>N6–H6A.</td>
<td>O9</td>
<td>0.73(3)</td>
<td>2.15(4)</td>
<td>2.872(3)</td>
<td>171(4)</td>
</tr>
<tr>
<td>N11–H11B</td>
<td>O11</td>
<td>0.81(4)</td>
<td>1.98(4)</td>
<td>2.785(3)</td>
<td>172(3)</td>
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<tr>
<td>O11–H11C</td>
<td>O7</td>
<td>0.70(4)</td>
<td>2.48(4)</td>
<td>3.041(3)</td>
<td>163(4)</td>
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<tr>
<td>N11–H11B</td>
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<td>1.72(4)</td>
<td>2.697(3)</td>
<td>171(3)</td>
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<tr>
<td>N14–H14A</td>
<td>O11</td>
<td>0.90(4)</td>
<td>1.72(4)</td>
<td>2.862(3)</td>
<td>144(4)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

- a = [2666.00] = 1 \(x\), 1 \(y\), 1 \(z\)
- b = [2656.00] = 1 \(x\), 1 \(y\), 1 \(z\)
- c = [2666.00] = 1 \(x\), 1 \(y\), 1 \(z\) for 2,
- a = [2665.00] = 1 \(x\), 1 \(y\), 1 \(z\), b = [2655.00] = 1 \(x\), 1 \(y\), 1 \(z\)
- c = [2666.00] = 1 \(x\), 1 \(y\), 1 \(z\) for 3.
4.4. Emission behavior

The emission properties of the ligands (HL₁ and HL₂) and its complexes were studied at room temperature (298 K) in 1 × 10⁻⁵ (M) DMF solution (Fig. 8). In general, quenching of fluorescence of a ligand by the transition metal ions during complexation is a rather common phenomenon which is explained by the process, such as magnetic perturbation, redox activity, electronic energy transfer etc. [29,30]. Enhancement of fluorescence through complexation is, however, of much interest as it opens up the opportunity for photochemical application of these complexes. In the absence of metal ions the fluorescence of a ligand is probably quenched by the occurrence of a photoinduced electron transfer (PET) process due to the presence of lone pair of electrons of the donor atom in the ligand. Such a PET process is prevented by the complexation of ligand with metal ions, thus the fluorescence intensity may be enhanced by the coordination of metal ions [31,32]. The ligands show no considerable fluorescence at λₑₓ = 315 nm while its cadmium(II) and zinc(II) complexes 1, 2 and 3 show emission at 513, 522 and 515 nm, respectively. For Zn(II) and Cd(II) complexes no emission arising from metal centred excited states of LMCT or MLCT are expected since they are difficult to oxidize or reduce due to their d¹⁰ configuration. However, the factor of chelation induced rigidity also plays an important role in causing a change of fluorescence behavior of free ligand on complexation with metal ions. The rigidity induced in the complexes is in turn dependent on the coordination geometry that the ligand assumes around the metal centre.

5. Conclusion

In summary, we have reported here the coordination behavior of two ditopic ligands HL₁ and HL₂ towards Cd(II) and Zn(II) ions. The ligand HL₁ reacts with Cd(ClO₄)₂·6H₂O to form a pentanuclear Cd₅(II) cluster with trigonal bipyramidal arrangement of Cd(II) centres, whereas, the same ligand (HL₁) and another ligand, HL₂, negate our expectation of cluster or grid formation with Zn(II) perchlorate and produce only mononuclear Zn(II) complexes. This is because of the topological complexity of the ligand and the fact that the individual coordinating component of the ligands do not always behave in a manner similar to their single ligand counterpart. In photoluminescence study, it has been observed that ligands (HL₁ and HL₂) are fluorescent silent, but the Cd(II) complex shows a strong chelation induced enhanced fluorescence compared to its Zn(II) analogue. The fluorescence silent behavior of the ligands may probably be due to the presence of several non-bonding electron pairs on the nitrogen donors. These electrons are involved in coordinate bond formation with metal ions during complexation. During the metal binding process, non-radiative channels and flexible bonds are inactive due to strong binding.

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Appendix A. Supplementary material

CCDC 864760, 864759 and 864761 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.12.003.

Fig. 7. Two dimensional structural representations of complex 3 with trapped perchlorate ions within the layers along ‘c’ axis.

Fig. 8. Fluorescence emission properties of the free ligands (HL₁ and HL₂) and its complexes (1–3).
References