

## Simple inorganic complexes but intricate hydrogen bonding networks: Synthesis and crystal structures of $[M^{II}(\text{opda})_2(\text{NO}_3)_2]$ ( $M = \text{Zn}$ and $\text{Cd}$ ; opda = orthophenylenediamine)

SABBANI SUPRIYA

School of Chemistry, University of Hyderabad, Hyderabad 500 046  
e-mail: sabbani07@gmail.com

MS received 14 November 2006; revised 7 January 2009

**Abstract.** The compounds  $[\text{Zn}^{II}\{\text{C}_6\text{H}_4(\text{NH}_2)_2\}_2(\text{NO}_3)_2]$ , (**1**) and  $[\text{Cd}^{II}\{\text{C}_6\text{H}_4(\text{NH}_2)_2\}_2(\text{NO}_3)_2]$  (**2**) have been prepared ( $\text{C}_6\text{H}_4(\text{NH}_2)_2 = \text{orthophenylenediamine} = \text{opda}$ ) and characterized by routine spectroscopic methods and single crystal X-ray diffraction analysis. Compound **1** crystallizes in orthorhombic space group  $Pcab$ , where as compound **2** crystallizes in monoclinic space  $P2_1/n$ . In the crystal structure of **1** an extended hydrogen bonding network is formed involving zinc coordinated amines and nitrate ligands. The compound **2** consists of molecules in which the cadmium ion is eight coordinated, with two bidentate nitrate groups and two bidentate opda ligands. The geometry around the cadmium described as a distorted dodecahedron. The crystal structure of **2** shows an intricate hydrogen bonding network, formed by amine and nitro groups coordinated to cadmium.

**Keywords.** Orthophenylenediamine; metal complexes; crystal structures; intricate hydrogen bonding networks.

### 1. Introduction

The coordination chemistry of transition metal complexes with benzene-1,2-diamine (ortho-phenylenediamine = opda) as ligand is long known. In mid 60's more than a dozen metal complexes had been prepared using opda as a ligand.<sup>1</sup> However, only few of these were structurally characterized.<sup>2</sup> The synthesis of opda complexes is quite easy, but obtaining single crystals, suitable for crystal structure analysis, is a difficult and challenging task. We are interested in obtaining single crystals of metal-opda complexes because their crystal structures would show complex hydrogen bonding network due to the presence of  $-\text{NH}_2$  groups in the opda ligand (hydrogen bonding donor sites) and inorganic anions having mostly oxo groups (hydrogen bonding acceptor sites) that stabilize the metal-opda cationic complex.

The present contribution describes the synthesis and structural analysis of compounds  $[\text{Zn}(\text{opda})_2(\text{NO}_3)_2]$  (**1**) and  $[\text{Cd}(\text{opda})_2(\text{NO}_3)_2]$  (**2**) emphasizing intricate supramolecular hydrogen bonding networks in their crystal structures. Whereas, compound **1** has distorted octahedral coordination around  $\text{Zn}^{2+}$  ion with monodentate nitrate anions, the geometry around

$\text{Cd}^{2+}$  in compound **2** is distorted dodecahedron with different coordination mode of nitrate anions.

### 2. Experimental

#### 2.1 Materials and methods

Orthophenylene diamine was purchased from Lancaster, where as nitrate salts of zinc and cadmium were purchased from E. Merck and S.D. Fine Chemicals. Solvents were purified by standard methods. Distilled water was used as solvent in synthesis. All chemicals were of analytical grade and were used without further purification.

#### 2.2 Synthesis of $[\text{Zn}^{II}\{\text{C}_6\text{H}_4(\text{NH}_2)_2\}_2(\text{NO}_3)_2]$ (**1**)

A saturated solution of zinc(II) nitrate trihydrate in water (~20 mL) taken in a flask was treated with saturated aqueous solution of benzene-1,2-diamine until compound **1** separated as white microcrystalline product. This was separated by filtration and the filtrate was left undisturbed at room temperature for 24 h. The colourless crystals of **1**, suit-

**Table 1.** Crystal data and structure refinement for compounds **1** and **2**.

| Structure parameter  | <b>1</b>   | <b>2</b>  |
|--|--|---|
| Empirical formula  | C <sub>12</sub> H <sub>16</sub> N <sub>6</sub> O <sub>6</sub> Zn | C <sub>12</sub> H <sub>16</sub> CdN <sub>6</sub> O <sub>6</sub> |
| Formula weight   | 405.68   | 452.71  |
| <i>T</i> /K  | 293(2) K   | 293(2) K  |
| Wavelength (Å)   | 0.71073  | 0.71073   |
| Crystal system   | Orthorhombic   | Monoclinic  |
| Space group  | <i>Pcab</i>  | <i>P2<sub>1</sub>/n</i>   |
| <i>a</i> (Å)   | 7.8237(16)   | 11.161(5)   |
| <i>b</i> (Å)   | 10.041(5)  | 13.065(4)   |
| <i>c</i> (Å)   | 20.825(4)  | 23.007(10)  |
| $\alpha$ (°)   | 90   | 90  |
| $\beta$ (°)  | 90   | 94.90(4)  |
| $\gamma$ (°)   | 90   | 90  |
| Volume (Å <sup>3</sup> )                                     | 1636.0(9)  | 3343(2)   |
| <i>Z</i>   | 4  | 8   |
| <i>D</i> (mg/m <sup>3</sup> )                                | 1.647  | 1.799   |
| $\mu$ (mm <sup>-1</sup> )                                    | 1.545  | 1.350   |
| <i>F</i> (000)   | 832  | 1808  |
| 2 $\theta$ range (°)   | 1.96 to 27.43  | 1.79 to 24.98   |
| Reflections collected/unique                                 | 1785/1785  | 5578/5578   |
| Completeness to 2 $\theta$                                   | 95.7%  | 94.8%   |
| Data/restraints/parameters                                   | 1785/0/132   | 5578/0/451  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                     | 1.075  | 0.994   |
| Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | <i>R</i> 1 = 0.0485,<br><i>wR</i> 2 = 0.1158                     | <i>R</i> 1 = 0.0389,<br><i>wR</i> 2 = 0.0868                    |
| <i>R</i> indices (all data)                                  | <i>R</i> 1 = 0.0797,<br><i>wR</i> 2 = 0.1292                     | <i>R</i> 1 = 0.0641,<br><i>wR</i> 2 = 0.0995                    |
| Largest diff. peak/hole (Å <sup>-3</sup> )                   | 0.596 and -1.033   | 0.976 and -0.919  |

able for single crystal X-ray diffraction studies, were isolated. A single crystal was mounted from its mother liquor for X-ray data collection. Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>ZnN<sub>6</sub>O<sub>6</sub>: C, 35.53; H, 3.97; N, 20.71. Found: C, 35.43; H, 4.15; N, 20.79. IR (KBr pellet) [cm<sup>-1</sup>]: 3248 *s*, 1612 *m*, 1585 *m*, 1495 *w*, 1383 *vs*, 1321 *vs*, 1122 *w*, 1089 *w*, 1041 *m*, 1003 *m*, 860 *w*, 819 *w*, 750 *s*, 603 *m*, 441 *m*.

### 2.3 Synthesis of [Cd<sup>II</sup>{C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (**2**)

A solution of cadmium (II) nitrate tetrahydrate (1.0 g, 2.3 mmol) in 20 mL of water was added into a flask containing benzene-1,2-diamine (0.7 g, 6.4 mmol) dissolved in 30 mL of water. The crystalline precipitate of **2**, formed in time duration of 3–4 days, was isolated by filtration, washed with water and dried at room temperature. The crystals, obtained in this way, were suitable for crystal structure determination. Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>CdN<sub>6</sub>O<sub>6</sub>: C, 31.84; H, 3.56; N, 18.56. Found: C, 32.06; H, 3.79; N, 18.14. IR (KBr pellet) [cm<sup>-1</sup>]: 3329 *s*, 3261 *s*, 3103 *s*, 1620 *m*, 1587 *m*,

1502 *s*, 1363 *vs*, 1259 *m*, 999 *w*, 852 *w*, 814 *w*, 746 *s*, 623 *m*, 447 *w*, 422 *m*.

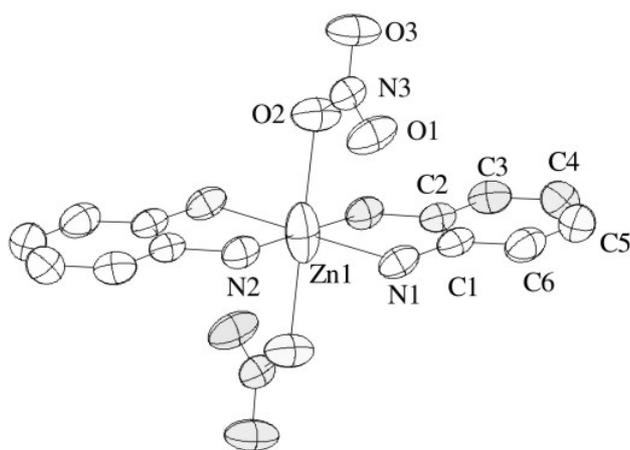
### 2.4 X-ray crystallography

The data were collected on an Enraf-Nonius CAD4 diffractometer by using graphite-monochromated Mo-K $\alpha$  (0.71073 Å) radiation at 20°C. The empirical absorption correction based on a series of  $\psi$  scans was applied. The structures were solved using SHELXS-97<sup>3</sup> and refined using SHELXL-97.<sup>4</sup> All non-hydrogen atoms were refined anisotropically. The ring hydrogens of benzene-1,2-diamine ligands were assigned positions on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. The hydrogen atoms of amine ligands (N(1) and N(2)) were located from difference Fourier maps, and their positions were refined for compound **1**. The hydrogen atoms of amine ligands (N(1), N(2), N(3), N(4), N(7), N(8), N(9) and N(10)) were assigned positions on the basis of geometrical considerations for compound **2**. The

**Table 2.** Selected bond lengths [Å] and angles [°] for **1**.

|                     |           |                     |           |
|---------------------|-----------|---------------------|-----------|
| Zn(1)–N(2)          | 2.071(3)  | Zn(1)–N(2)#1        | 2.071(3)  |
| Zn(1)–N(1)#1        | 2.106(3)  | Zn(1)–N(1)          | 2.106(3)  |
| Zn(1)–O(2)          | 2.375(3)  | Zn(1)–O(2)#1        | 2.375(3)  |
| N(1)–C(1)           | 1.447(5)  | N(2)–C(2)#1         | 1.451(4)  |
| N(3)–O(1)           | 1.231(4)  | N(3)–O(3)           | 1.232(3)  |
| N(3)–O(2)           | 1.258(3)  | C(1)–C(2)           | 1.382(4)  |
| C(2)–N(2)#1         | 1.451(4)  | C(3)–C(4)           | 1.388(6)  |
| N(2)–Zn(1)–N(2)#1   | 180.0     | N(2)–Zn(1)–N(1)#1   | 82.59(12) |
| N(2)#1–Zn(1)–N(1)#1 | 97.41(12) | N(2)–Zn(1)–N(1)     | 97.41(12) |
| N(2)#1–Zn(1)–N(1)   | 82.59(12) | N(1)#1–Zn(1)–N(1)   | 180.0     |
| N(2)–Zn(1)–O(2)     | 91.23(12) | N(2)#1–Zn(1)–O(2)   | 88.77(12) |
| N(1)#1–Zn(1)–O(2)   | 87.08(12) | N(1)–Zn(1)–O(2)     | 92.91(12) |
| N(2)–Zn(1)–O(2)#1   | 88.77(12) | N(2)#1–Zn(1)–O(2)#1 | 91.23(12) |
| N(1)#1–Zn(1)–O(2)#1 | 92.91(12) | N(1)–Zn(1)–O(2)#1   | 87.09(12) |
| O(2)–Zn(1)–O(2)#1   | 180.0     | C(1)–N(1)–Zn(1)     | 109.5(2)  |
| C(2)#1–N(2)–Zn(1)   | 110.0(2)  | O(1)–N(3)–O(2)      | 120.2(3)  |
| N(3)–O(2)–Zn(1)     | 125.9(2)  | C(2)–C(1)–C(6)      | 120.2(3)  |
| C(2)–C(1)–N(1)      | 117.9(3)  | C(6)–C(1)–N(1)      | 121.9(3)  |
| C(1)–C(2)–C(3)      | 119.9(3)  | C(1)–C(2)–N(2)#1    | 118.7(3)  |
| C(3)–C(2)–N(2)#1    | 121.4(3)  | C(2)–C(3)–C(4)      | 119.9(4)  |

Symmetry transformations used to generate equivalent atoms: #1  $-x, -y, -z + 1$



**Figure 1.** Thermal ellipsoid plot for complex **1**. Hydrogen atoms are not shown for clarity.

crystallographic data and the parameters of structure refinement for compounds **1** and **2** are summarized in table 1. Crystallographic data (excluding structure factors) for compounds **1** and **2** described in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary materials (CCDC number for **1** – 298278 and CCDC number for **2** – 298279). The crystal structure of cadmium compound **2** was solved in monoclinic system with two independent molecules in its asymmetric unit. The coordinates for these two molecules give the impression that there may be a symmetry relation-

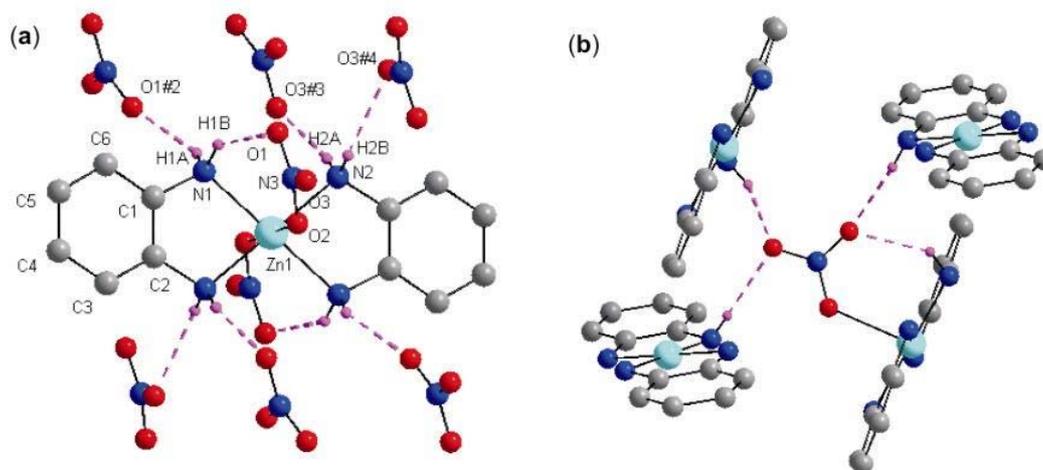
ship between these molecules indicating a higher symmetry space group. However, when we attempted to solve this in orthorhombic system starting from relevant raw data, we could not solve the structure. Platon suggested monoclinic space group and we could solve the structure accurately in  $P2_1/n$  space group. Finally, the checkcif results for the crystal structure of compound **2** did not give any alert on space group selection (checkcif reports for both compounds have been given as Supporting materials).

Infrared (IR) spectra were recorded on KBr pellets with a JASCO FT/IR-5300 spectrometer in the region of 400–4000  $\text{cm}^{-1}$ . Microanalytical (C, H, N) data were obtained with a Flash EA 1112 Series CHNS Analyzer.

### 3. Results and discussion

#### 3.1 Synthesis

Metal complexes of Zn(II) and Cd(II) with 2 : 1 stoichiometries were prepared by reaction of opda ligand with hydrated metal nitrate salts in water. The complexes were synthesized in a one-step procedure and the reactions gave crystals, suitable for single crystal X-ray structure analysis. The complexes appear to be air stable in solid state; however, their solutions (especially, the solution of Zn complex) are unstable at aerial conditions resulting in the

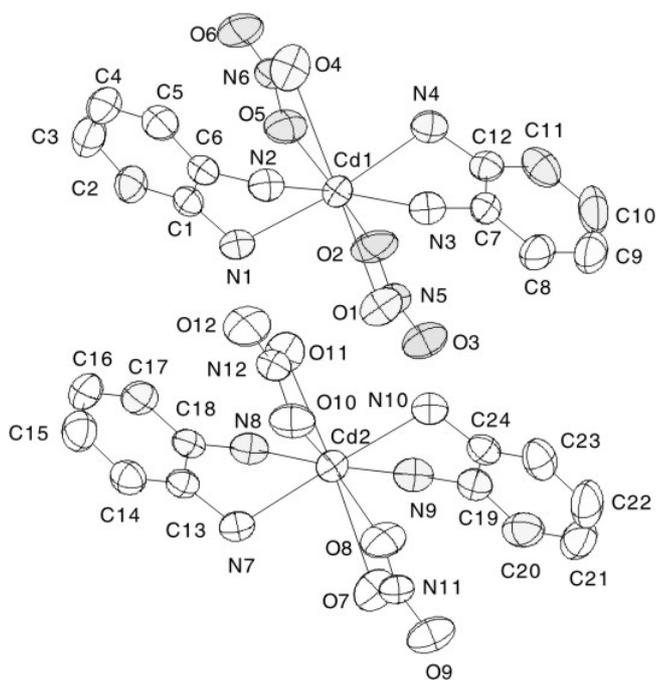


**Figure 2.** (a) N–H...O hydrogen bonding interactions around a zinc complex in compound **1** showing four types of N–H...O hydrogen bonds (see table 3). (b) Supramolecular interactions around a nitrate anion in compound **1**. Colour code: Zn, cyan; O, red; N, blue; C, gray; H, purple.

**Table 3.** Hydrogen bonding parameters in **1** (Å and °) (see figure 2).

| D–H...A       | $d(\text{D}\cdots\text{H})$ | $d(\text{H}\cdots\text{A})$ | $d(\text{D}\cdots\text{A})$ | $\angle\text{DHA}$ |
|---------------|-----------------------------|-----------------------------|-----------------------------|--------------------|
| N1–H1B...O1   | 0.85(6)                     | 2.25(6)                     | 2.985(4)                    | 144(4)             |
| N1–H1A...O1#2 | 0.80(5)                     | 2.37(5)                     | 3.093(4)                    | 151(4)             |
| N2–H2A...O3#3 | 0.85(4)                     | 2.22(4)                     | 3.057(4)                    | 169(3)             |
| N2–H2B...O3#4 | 0.84(5)                     | 2.26(5)                     | 3.041(4)                    | 154(4)             |

Symmetry transformations used to generate equivalent atoms: #2:  $-0.5 + x, 0.5 - y, z$ ; #3:  $0.5 - x, 0.5 + y, 1 - z$ ; #4:  $1 - x, -y, 1 - z$



**Figure 3.** Thermal ellipsoid plots for crystallographically independent cadmium complexes in **2**. Hydrogen atoms are not shown for clarity.

formation of the oxidation product (phenazine) of opda as shown in (1).



### 3.2 Crystal structures

The molecular structure of  $[\text{Zn}^{\text{II}}\{\text{C}_6\text{H}_4(\text{NH}_2)_2\}_2(\text{NO}_3)_2]$  (**1**) is shown in figure 1. Table 2 lists the selected bond lengths and angles for compound **1**. The Zn(II) center is characterized by  $\{\text{N}_4\text{O}_2\}$  coordination with a distorted octahedral geometry. Two nitrate anions act as monodentate ligands and coordinate the metal ion in axial positions. Two opda ligands coordinate the zinc ion in bidentate fashion (figure 1). The Zn–O bond lengths [2.379(3) Å] are in the range observed for other zinc complexes with N and O donor ligands.<sup>5</sup> The zinc(II)–opda–N distances are 2.074 and 2.104 Å which are comparable with those reported for other Zn(II) complexes containing the

**Table 4.** Selected bond lengths (Å) and angle (°) in compound **2**.

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| Cd(1)–N(1)        | 2.306(4)   | Cd(1)–N(4)        | 2.335(4)   |
| Cd(1)–N(3)        | 2.407(4)   | Cd(1)–N(2)        | 2.477(4)   |
| Cd(1)–O(1)        | 2.553(3)   | Cd(1)–O(5)        | 2.566(4)   |
| Cd(1)–O(2)        | 2.672(4)   | Cd(1)–O(4)        | 2.681(4)   |
| Cd(2)–N(7)        | 2.302(3)   | Cd(2)–N(10)       | 2.330(4)   |
| Cd(2)–N(9)        | 2.420(4)   | Cd(2)–N(8)        | 2.455(4)   |
| Cd(2)–O(11)       | 2.586(4)   | Cd(2)–O(10)       | 2.625(4)   |
| Cd(2)–O(8)        | 2.627(4)   | Cd(2)–O(7)        | 2.647(4)   |
| C(1)–C(6)         | 1.405(6)   | C(1)–N(1)         | 1.431(5)   |
| C(6)–N(2)         | 1.420(5)   | C(12)–N(4)        | 1.430(5)   |
| C(7)–N(3)         | 1.420(6)   | C(13)–C(18)       | 1.396(6)   |
| C(13)–N(7)        | 1.433(5)   | C(19)–C(24)       | 1.387(6)   |
| C(19)–N(9)        | 1.430(6)   | C(24)–N(10)       | 1.429(5)   |
| N(5)–O(2)         | 1.233(5)   | N(5)–O(1)         | 1.249(4)   |
| N(6)–O(4)         | 1.215(5)   | N(6)–O(5)         | 1.247(5)   |
| N(11)–O(8)        | 1.233(4)   | N(11)–O(7)        | 1.244(4)   |
| N(12)–O(10)       | 1.252(5)   | N(12)–O(11)       | 1.231(5)   |
|                   |            |                   |            |
| N(1)–Cd(1)–N(4)   | 157.16(14) | N(1)–Cd(1)–N(3)   | 132.62(12) |
| N(4)–Cd(1)–N(3)   | 68.87(13)  | N(4)–Cd(1)–N(2)   | 128.76(13) |
| N(3)–Cd(1)–N(2)   | 85.50(13)  | N(1)–Cd(1)–O(1)   | 81.01(12)  |
| N(4)–Cd(1)–O(1)   | 100.54(12) | N(3)–Cd(1)–O(5)   | 150.01(12) |
| N(2)–Cd(1)–O(5)   | 110.38(12) | O(1)–Cd(1)–O(5)   | 115.86(10) |
| N(7)–Cd(2)–O(11)  | 96.40(12)  | N(9)–Cd(2)–O(11)  | 121.56(12) |
| N(8)–Cd(2)–O(11)  | 79.80(12)  | N(9)–Cd(2)–O(10)  | 152.10(12) |
| N(8)–Cd(2)–O(10)  | 112.33(12) | O(11)–Cd(2)–O(10) | 47.82(10)  |
| N(7)–Cd(2)–O(8)   | 84.04(13)  | N(10)–Cd(2)–O(8)  | 78.33(13)  |
| N(9)–Cd(2)–O(8)   | 103.23(13) | N(8)–Cd(2)–O(8)   | 150.16(12) |
| O(10)–Cd(2)–O(8)  | 71.06(11)  | C(2)–C(1)–N(1)    | 123.2(4)   |
| C(6)–C(1)–N(1)    | 116.5(4)   | C(12)–C(7)–C(8)   | 119.5(5)   |
| C(8)–C(7)–N(3)    | 122.6(4)   | C(14)–C(13)–C(18) | 120.6(4)   |
| C(18)–C(13)–N(7)  | 117.2(4)   | C(24)–C(19)–C(20) | 118.5(6)   |
| C(20)–C(19)–N(9)  | 124.1(4)   | C(23)–C(24)–N(10) | 122.7(4)   |
| C(1)–N(1)–Cd(1)   | 105.5(3)   | C(6)–N(2)–Cd(1)   | 101.7(2)   |
| C(7)–N(3)–Cd(1)   | 105.0(3)   | O(3)–N(5)–O(2)    | 122.9(4)   |
| O(2)–N(5)–O(1)    | 116.7(4)   | C(13)–N(7)–Cd(2)  | 106.0(2)   |
| O(11)–N(12)–O(10) | 116.6(4)   | N(5)–O(1)–Cd(1)   | 100.2(2)   |

similar type of coordination environment. Both benzene-1,2-diamine ligands in **1** are planar within experimental error and their internal bonding parameters are comparable to other relevant published data.<sup>2a-c</sup> Interestingly, the simple complex  $[\text{Zn}^{\text{II}}\{\text{C}_6\text{H}_4(\text{NH}_2)_2\}_2(\text{NO}_3)_2]$  (**1**) undergoes a complex hydrogen bonding network in its solid state. This involves the coordinated amine groups (as hydrogen bond donor sites) and nitrate oxygen atoms (as hydrogen bond acceptor sites). As shown in figure 2(a), each complex unit undergoes eight hydrogen bonding interactions using its four amine groups (all amine hydrogens are engaged in forming H-bonds!). Among these eight H-bonds, six are inter- and two are intra-molecular types. Each nitrate anion is surrounded by four complex units by the use of four hydrogen bonds (figure 2b). The relevant hydrogen bonding parameters are presented in table 3.

The cadmium complex **2** crystallizes in the monoclinic system (space group  $P2_1/n$ ). Two crystallographically independent cadmium complexes appear in the asymmetric unit (figure 3). The cadmium atom is eight coordinated with four nitrogen donors from two bidentate opda ligands and four oxygen atoms of two nitrate anions as bidentate ligands. Selected geometrical data for compound **2** are given in table 4. The shape of the coordination polyhedron can be described as a distorted dodecahedron<sup>6</sup> of eight vertices, described by four nitrogen atoms and four oxygen atoms. The two oxygen atoms of a bidentate nitrate anion ligand occupy two adjacent vertices of the dodecahedron, in which one vertex has four neighbours and other has five neighbours. This is true for each of other pairs of vertices occupied by oxygens of second bidentate nitrate ligands, nitro-

gens of opda ligands. The features of this distorted dodecahedron are comparable to those of a regular dodecahedron.

The average cadmium–oxygen bond distances of 2.621 Å (Cd1 complex) and 2.624 Å (Cd2 complex) are similar to those observed for other eight coordinated Cd(II) complexes with N,O donors.<sup>7</sup> The cadmium–nitrogen (average) distances of 2.377 Å (Cd1 complex) and 2.378 Å (Cd2 complex) are, in general, slightly longer than those found in literature.<sup>7</sup> This lengthening of cadmium–nitrogen bond distances could be due to the fact that all hydrogen atoms on these nitrogens are exclusively hydrogen bonded to oxygen atoms of the coordinated nitrate anions through both intra- and inter-molecular interactions (*vide infra*). The dodecahedral geometry around cadmium centers in Complex **2** is a rare example in opda systems. In the crystal structure of **2** an intricate hydrogen bonding network, that involves coordinated –NH<sub>2</sub> and nitrate groups, is observed. Both crystallographically independent cadmium complexes, located in the asymmetric unit, are involved in hydrogen bonding interactions (figure 4). There are total 16 hydrogen bonds (figure 4): four of which are engaged in connecting these two crystallographically independent cadmium complexes (namely Cd(1) and Cd(2) complexes) and rest twelve H-bonds attach these Cd(1) and Cd(2) complexes with other surrounding complex units. This results in a complex supramolecular hydrogen bonding network. The formation of these hydrogen bonds accounts for the slight lengthening of the concerned Cd–N

bonds compared to other Cd–N bonds present in similar compounds known from literature.

#### 4. Conclusions

Even though opda (orthophenylenediammine) complexes are long known in literature, only a few opda complexes are structurally characterized. This is because of the difficulty in obtaining single crystals of this class of compounds. We have succeeded to obtain single crystals of opda-compounds [Zn<sup>II</sup>{C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (**1**) and [Cd<sup>II</sup>{C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (**2**). In the crystal structures of both compounds **1** and **2**, complex hydrogen bonding networks are encountered. The molecular formulae of **1** and **2** are similar, but the geometry around the central metal ions are octahedral and dodecahedral respectively. This results in two different types of supramolecular networks in **1** and **2** respectively.

#### Supplementary material

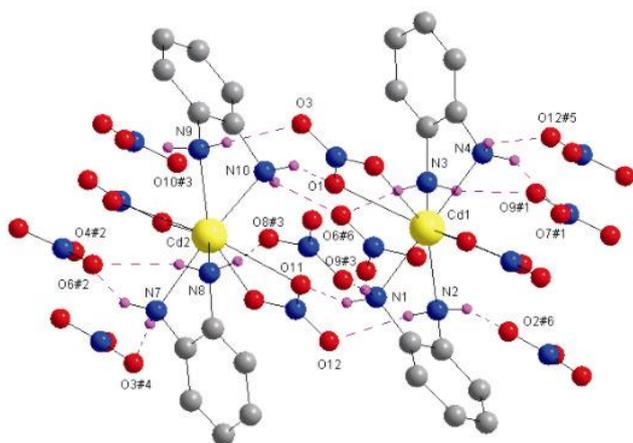
Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC number for **1** – 298278 and CCDC number for **2** – 298279. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

#### Acknowledgements

I am grateful to my Ph.D. supervisor, Dr Samar K Das for his helpful suggestions. I acknowledge Department of Science and Technology, New Delhi, India for single crystal X-ray diffraction facility at University of Hyderabad. I thank University Grants Commission (UGC), Government of India for infrastructure facility at University of Hyderabad under UPE and for a fellowship.

#### References

- (a) Marks D R, Philips D J and Redfern J P 1967 *J. Chem. Soc. (A)* 1464; (b) Marks D R, Philips D J and Redfern J P 1968 *J. Chem. Soc. (A)* 2013; (c) Duff E J 1968 *J. Chem. Soc. (A)* 434
- (a) Edler R C, Koren D and Mark H B 1974 *Inorg. Chem.* **13** 1644; (b) Jubb J, Larkworthy L F, Olivier L F, Povey D C and Smith G W 1991 *J. Chem. Soc., Dal-*



**Figure 4.** N–H...O hydrogen bonding interactions around crystallographically independent cadmium complexes in **2** showing 16 types of N–H...O hydrogen bonds. Colour code: Cd, yellow; O, red; N, blue; C, gray; H, purple.

- ton *Trans.* 2045; (c) Radshaw C, Wilkinson G, Bates B H and Hursthouse M B 1992 *J. Chem. Soc., Dalton Trans.* 1803; (d) Radshaw C, Wilkinson G, Bates B H and Hursthouse M B 1992 *J. Chem. Soc., Dalton Trans.* 555
- Sheldrick G M 1997 SHELXS-97, Program for solution of crystal structures, Germany, University of Göttingen
  - Sheldrick G M 1997 SHELXL-97, Program for refinement of crystal structures, Germany, University of Göttingen
  - (a) Long L S, Zheng L S, Chen X M and Ng S W 2001 *Main Group Metal Chemistry* **24** 461; (b) Muller B, Schneider A, Tesmer M and Vahrenkamp, H. 1999 *Inorg. Chem.* **38** 1900; (c) Muller B and Vahrenkamp H. 1999 *Eur. J. Inorg. Chem.* 137; (d) Barszcz B, Hodorowicz S, Jablonska-Wawrzycka A and Stadnicka K 2005 *Polyhedron* **24** 627
  - Huheey J E, Keiter E A and Keiter R L 2000 *Inorganic chemistry, principles of structure and reactivity* 4th edn (Addison-Wesley Publishing Company: New York) p 508
  - (a) Romero M A, Moreno M N, Ruiz J, Sanchez M P and Nieto F 1986 *Inorg. Chem.* **25** 1498; (b) Acuna-Cueva E R, Faure R, Illan-Cabeza N A, Jimenez-Pulido S B, Moreno-Carretero M N and Quiros-lozabal M 2003 *Inorg. Chim. Acta* **342** 209; (c) Grevy J M, Tellez F, Bernes S, Noth H, Contreras R and Barba-Behrens N 2002 *Inorg. Chim. Acta* **339** 209; (d) Hueso-Urena F, Jimenez-Pulido S B, Moreno-Carretero M N, Quiros-Olozabal M and Salas-Peregrin J M 1998 *Inorg. Chim. Acta* **277** 103; (e) Niklas N, Hampel F, Liehr G, Zahl A and Alsfasser R 2001 *Chem. Eur. J.* **7** 5135; (f) Barros-Garcia F J, Bernalte-Garcia A, Luna-Giles F, Maldonado-Rogado M A and Vinuelas-Zahinos E 2006 *Polyhedron* **25** 52; (g) Ferná'ndez-Ferná'ndez M C, Bastida R, Macias A, Valencia L and Pérez- Lourido P 2006 *Polyhedron* **25** 783