

## Synthesis and characterization of novel M(II) (M= Co(II), Ni(II), Cu(II), Zn(II) or Cd(II)) complexes with N,O-donor ligand (*E*)-1-(1-(1*H*-pyrrol-2-yl)ethylidene)carbonohydrazide ( $H_5L$ ).

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**Abstract:** The Schiff bases ( $H_3L$ ), derived from 2-acetylpyrrole and carbonohydrazide, and its reactions with some transition metal ions (Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)) afforded complexes of formulae  $[M(H_3L)_2(H_2O)_x] \cdot 2(NO_3)_z \cdot (CH_3CN)_y \cdot (H_2O)_{y-x}$  (M= Co, Ni, Cu or Zn ;  $0 \leq x < y \leq 3$ ,  $z = 0$  or 1) and  $\{Cd(H_4L_A)(NO_3)\}_n$ . These compounds have been characterized by means of elemental analysis, UV-Vis spectroscopy, IR spectroscopy, <sup>1</sup>H and <sup>13</sup>C NMR, molar conductance and room temperature magnetic measurements. Single crystal X-ray analysis of the cadmium complex  $\{Cd(H_4L_A)(NO_3)\}_n$  has revealed the nature of the structure with the space group C2/c. The cadmium (II) ion is six-coordinated. The coordination polyhedron of the cadmium complex can be best described as a distorted trigonal antiprism.

**Keywords:** Cobalt, Nickel, Copper, Zinc, Cadmium, antiprism.

### I. Introduction

Organic ligand derived from carbonohydrazide and their transition metal complexes have been widely studied in the last years for several reasons, such as magnetic, electronic, catalytic or biological properties [1-6]. Metal transition complexes of these kind of ligand are specially reported as antimicrobial or anticonvulsant [7-9]. In order to study the coordination mode of ligand with a pyrrole carbon termination, we undertook to synthesize a 1/1 ligand between the thiocarbonohydrazone and the 1*H*-pyrrole-2-carbaldehyde. Our present work investigate the chelating properties of (*E*)-1-(1-(1*H*-pyrrol-2-yl)ethylidene)carbonohydrazide ( $H_5L$ ) towards metal transition ions (Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>), including structural elucidation by spectroscopy studies and X-ray diffraction of the cadmium complex.

### II. Experimental Section

#### 2.1. Starting materials and Instrumentations

Carbonohydrazide, 2-acetylpyrrole as well as Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) nitrate hydrate were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. Elemental analyses were performed in a Carlo-Erba EA microanalyser. Infrared spectra were recorded as KBr discs on a Bruker IFS-66V spectrophotometer. LSI-MS were recorded using a Micromass Autospec spectrometer with 3-nitrobenzyl alcohol as the matrix. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in DMSO-*d*<sub>6</sub> on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference. The UV-Vis spectra were run on a Shimadzu UV-2501 PC Recording spectrophotometer (1000–200 nm). The molar conductance of 10<sup>-3</sup> M solutions of the metal complexes in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance {calibrant Hg[Co(SCN)<sub>4</sub>]}. Melting points were recorded on a Büchi apparatus and are uncorrected.

#### 2.2. Synthesis of (*E*)-1-(1-(1*H*-pyrrol-2-yl)ethylidene)carbonohydrazide ( $H_5L$ )

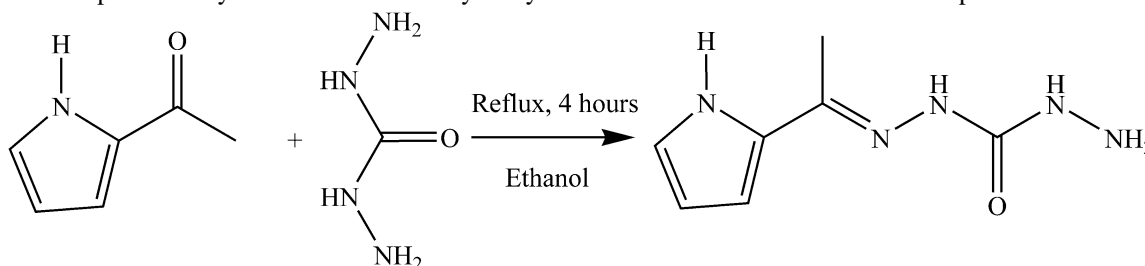
Carbonohydrazide (1 g, 11.11 mmol) and 2-acetylpyrrole 2.4 g (22.2 mmol) were refluxed during 4 hours in ethanol (50 mL) and stored overnight in a refrigerator. A gray solid was separated, filtered off and dried in a dessicator to yield monohydrated 1-(1-(1*H*-pyrrol-2-yl)ethylidene)carbonohydrazide ( $H_5L \cdot H_2O$ ) (1.3 g, 7.2 mmol). Yield: 64.6%. Anal. Calcd for C<sub>7</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 42.20; H, 6.58; N, 35.16 %. Found C, 42.25; H, 6.60; N, 35.22 %. MS (ESI-TOF, *m/z*): 222 [ $H_5L \cdot H_2O \cdot Na$ ]<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): 1650 (C=N+C=O); 1529; 1416 (Pyrrole); 3270 (N-H and O-H ( $H_2O$ )). <sup>1</sup>H-RMN (*dms*<sub>o</sub>-*d*<sub>6</sub>, δ en ppm) : 9.2 (1H, s, =N-NH-(CO)-); 8.4 (1H, s, -(CO)-NH-NH<sub>2</sub>); 6.8 (1H, m, H<sub>pyr</sub>); 6.3 (1H, m, H<sub>pyr</sub>); 6.0 (1H, m, H<sub>pyr</sub>); 4.0 (2H, s, NH-NH<sub>2</sub>); 2.0 (3H, s, H<sub>methyl</sub>). <sup>13</sup>C-

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RMN ( $dms\text{-}d_6$ ,  $\delta$  en ppm): 120.9 ( $C_{Ar}$ ) ; 108,6 ( $C_{Ar}$ ) ; 109.7 ( $C_{Ar}$ ) ; 131,2 ( $C_{Ar}$ ) ; 139.3 (C=N) ; 13.1 ( $-\text{CH}_3$ ) ; 158.4 (C=O). M.P. 241 °C.

### 2.3. Synthesis of the complexes of $H_5L$

Ligand  $H_5L \cdot H_2O$  (1.0 mmol, 199.1 mg) was dissolved under reflux in acetonitrile (5 mL) to give a clear solution. The appropriate nitrate salt (1 mmol) was added. The resulting mixture was stirred and refluxed for about three hours and the solution was filtered off. Allowing the solution to concentrate in air the complexes are isolated as powder. Crystals suitable for X-ray analysis were obtained for the cadmium complex.



**Scheme 1.** Synthetic scheme for preparation of  $H_5L$ .

#### $[Co(H_5L)_2] \cdot 2(NO_3) \cdot CH_3CN \cdot H_2O$

Yield: 58 %. Anal. Calc for  $CoC_{16}H_{27}N_{13}O_9$ : C, 31.80; H, 4.50; N, 30.13. Found: C, 31.75; H, 4.53; N, 30.25 %. IR (KBr,  $cm^{-1}$ ): 2400 ; 1650 ; 1606 ; 1544 ; 1457 ; 1374. UV-vis (solid, nm): 474; 1029.  $\mu_{eff} = 4.1$  MB.  $\Lambda$  ( $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ , DMF): fresh solution: 122.3; after 15 days: 138.9. SM (ESI-TOF) (m/z): 500 ( $[Co(H_4L_A)(H_5L_A) \cdot H_2O \cdot NO_3]^+$ ). M.P.: 212°C.

#### $[Ni(H_5L)_2(H_2O)_x] \cdot 2(NO_3) \cdot (H_2O)_{3-y}$

Yield: 70 %. Anal. Calc for  $NiC_{14}H_{28}N_{12}O_{11}$ : C, 28.07; H, 4.71; N, 28.05. Found: C, 28.00; H, 4.67; N, 28.15 %. IR (KBr,  $cm^{-1}$ ): 1650; 1603; 1544; 1448; 1367. UV-vis (solid, nm): 378; 589; 1030.  $\mu_{eff} = 2.93$  MB.  $\Lambda$  ( $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ , DMF): fresh solution: 120.1; after 15 days: 134.9. SM (ESI-TOF) (m/z): 419.13 ( $[Ni(H_4L_A)(H_5L_A)]^+$ ). M.P.: 222 °C.

#### $[Cu(H_5L)_2(H_2O)_x] \cdot 2(NO_3) \cdot CH_3CN \cdot (H_2O)_{2-x}$

Yield: 60 %. Anal. Calc for  $CuC_{16}H_{29}N_{13}O_{10}$ : C, 30.65; H, 4.66; N, 29.04. Found: C, 30.71; H, 4.63; N, 28.95 %. IR (KBr,  $cm^{-1}$ ): 2400; 1640; 1606; 1544; 1464; 1361. UV-vis (solid, nm): 631; 787; 443.  $\mu_{eff} = 1.53$  MB.  $\Lambda$  ( $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ , DMF): fresh solution: 176.9; after 15 days: 215. SM (ESI-TOF) (m/z): 242.12 ( $[Cu(H_4L_A)(H_5L_A)]^+$ ). M.P.: 189 °C.

#### $[Zn(H_5L)_2] \cdot 2(NO_3) \cdot CH_3CN \cdot H_2O$

Yield: 72 %. Anal. Calc for  $ZnC_{16}H_{27}N_{13}O_9$ : C, 31.46; H, 4.46; N, 29.81. Found: C, 31.54; H, 4.42; N, 29.76 %. IR (KBr,  $cm^{-1}$ ): 2400; 1654; 1613; 1541; 1455; 1371.  $^1H$ -RMN ( $dms\text{-}d_6$ ,  $\delta$ , ppm): 7.0-6.1 (3H-pyrrol, m); 2.0 (3H, s,  $-\text{CH}_3$ ); 4.0 (1H, s,  $H_4$ ); 8.4 (1H, s,  $H_3$ ); 9.2 (2H, s,  $-\text{NH}_2$ ). SM (ESI-TOF) (m/z): 425.12 ( $[Zn(H_4L_A)(H_5L_A)]^+$ ). M.P.: 239°C.

#### $\{Cd(H_5L_A)_2(NO_3)_2\}_n$

Yield: 52 %. Anal. Calc for  $CdC_{14}H_{22}N_{12}O_8$ : C, 28.18; H, 3.38; N, 28.16. Found: C, 28.25; H, 3.35; N, 28.29 %. IR (KBr,  $cm^{-1}$ ): 1674; 1642; 1536; 1455; 1420; 1303; 1000.  $^1H$ -RMN ( $dms\text{-}d_6$ ,  $\delta$ , ppm): 6.9-6.1 (3H, m, H-pyrrole), 2.0 (3H, s,  $-\text{CH}_3$ ), 4.0 (1H, s,  $H_4$ ), 8.3 (1H, s,  $H_3$ ), 9.2 (2H, s,  $-\text{NH}_2$ ).  $\Lambda$  ( $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ , DMF): fresh solution: 72.9; after 15 days: 76.0. M.P.: 204 °C.

### 2.4. X-ray data collection, structure determination and refinement

The details of the X-ray crystal data, and the structure solution and refinement are given in Table 1. Measurements were made on a Bruker Smart CCD area detector. All data were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. Complex scattering factors were taken from the program package *SHELXTL* [10]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters for all non hydrogen atoms [11]. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using *ORTEP-3* [12].

### III. Results And Discussion

#### 3.1. General study

The acyclic Schiff bases  $H_5L$  have been prepared following a method well known in the literature. The synthesis of the ligand was achieved in a one step procedure using the direct condensation of 2-acetylpyrrole and carbonohyrazide in a quantitative yield. The mass spectra of the ligand present an intense peak at 222 uma corresponding to the molecular ion of  $[H_5L \cdot H_2O \cdot Na]^+$ . The  $^1H$  and  $^{13}C$  NMR spectra of the ligand were recorded in deuterated dimethylsulfoxide. The  $^1H$  NMR spectrum of the compound revealed signals at 9.2 ppm, 8.4 ppm and 4.0 ppm assigned respectively to  $Me-C=N-HN-(CO)-$ ,  $-(CO)-HN-NH_2$  and  $-(CO)-HN-NH_2$ . These facts confirm that the reaction is a monocondensation one of the hydrazide groups while the other one remains free despite of the used stoichiometry. The  $^{13}C$  NMR corroborates this observation. Signals at 158.4 ppm and 139.3 ppm are assigned respectively to  $-C=O$  and  $-C=N$ .

The main IR bands are summarized in Table 2. The IR spectrum of the ligand shows moderate-intensity absorption at *ca.*  $1650\text{ cm}^{-1}$  which is attributable to the  $\nu(C=N)$ . The bands at  $3270\text{ cm}^{-1}$  assignable to  $\nu(N-H)$  indicating that uncompleted condensation has occurred. Bands in the region  $1530-1410\text{ cm}^{-1}$  are assigned to the aromatic pyrrole ring.

**Table 1.** Crystallographic data and refinement parameters for  $\{Cd(H_5L_A)_2(NO_3)_2\}_n$ .

Empirical formula	$\{Cd(H_5L)_2(NO_3)_2\}_n$
Formula mass	596.80
<i>T</i> (K)	298
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	15.673 (2)
<i>b</i> (Å)	18.398 (2)
<i>c</i> (Å)	8.4623 (11)
$\beta$ (°)	117.289 (2)
<i>V</i> (Å <sup>3</sup> )	2168.58 (5)
<i>Z</i>	4
<i>D</i> <sub>cal</sub> (g/cm <sup>3</sup> )	1.858
$\mu$ (mm <sup>-1</sup> )	1.056
$\lambda$ (Å)	0.71073
<i>F</i> (000)	1016
Crystal size	0.09 x 0.07 x 0.06
$2\theta$	1.83 to 25.03
Index ranges	16→18, -21→10, -10→10
Reflections collected	5714
Independant reflections ( <i>R</i> <sub>int</sub> )	1913
Data/restraints/parameters	1913/ 0/187
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.074
<i>R</i> Indices [ <i>I</i> >2σ( <i>I</i> ): <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	<i>R</i> <sub>1</sub> = 0.0434, <i>wR</i> <sub>2</sub> = 0.1058
<i>R</i> Indices (all data) <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	<i>R</i> <sub>1</sub> = 0.0518, <i>wR</i> <sub>2</sub> = 0.1122
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.53 and -1.19

The reactions of  $H_5L$  with nitrate metal salts in 1:1 molar ratios were investigated, and the complexation was performed by mixing acetonitrile solutions of both ligand and metal salt. The products isolated were mononuclear complexes. In all cases the complexes appear to be air stable and soluble in common organic solvents. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solution of  $\{Cd(H_5L_A)_2(NO_3)_2\}_n$ .

All the compound are characterized by elemental analysis (C, N, H), IR spectroscopy, molar conductivity, magnetic measurements and X-ray diffraction for  $\{Cd(H_5L_A)_2(NO_3)_2\}_n$ .

**Table 2.** Main IR bands of the H<sub>5</sub>L ligand and its complexes.

Compound	Pyrrole	$\nu(\text{N-C})$	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{NO}_3)$
<b>H<sub>5</sub>L<sub>A</sub></b>	1529, 1469	1200	1625	1668	-----
[Cu(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>x</sub> ]·2(NO <sub>3</sub> )·CH <sub>3</sub> CN·(H <sub>2</sub> O) <sub>2-x</sub>	1544, 1464	1203	1606	1640	1361
[Ni(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>y</sub> ]·2(NO <sub>3</sub> )·(H <sub>2</sub> O) <sub>3-y</sub>	1544, 1448	1203	1603	1650	1367
[Zn(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> ]·2(NO <sub>3</sub> )·CH <sub>3</sub> CN·H <sub>2</sub> O	1541, 1455	1191	1613	1654	1371
{Cd(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> } <sub>n</sub>	1536, 1455	1194	1674	1642	1420, 1303, 1000
[Co(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> ]·2(NO <sub>3</sub> )·CH <sub>3</sub> CN·H <sub>2</sub> O	1544, 1457	1200	1606	1650	1374

Upon complexation of H<sub>5</sub>L with M(II) ions (M= Co, Ni, Cu, Zn or Cd), no significant shift of the C=N band to lower frequency is observed on comparison to the corresponding band of the free ligand (Table 2). This fact is indicative of the no participation of the azomethine in the coordination. The bands of the C=O group, appearing in the range 1640-1655 cm<sup>-1</sup> in the IR spectra of the complexes are suggesting an interaction between the metal ion and the carbonyl oxygen atom. Information regarding the possible bonding modes of the nitrate group was obtained. The presence of band between 1360 and 1380 cm<sup>-1</sup> indicates that ionic nitrate groups are present [13] in the complexes of Cu(II), Ni(II), Zn(II) and Co(II). The spectrum of the Cd(II) complex shows band at 1420 (ν<sub>5</sub>), 1303 (ν<sub>1</sub>) and 1000 (ν<sub>2</sub>) cm<sup>-1</sup>. The magnitude Δν= ν<sub>5</sub>- ν<sub>2</sub> of 117 cm<sup>-1</sup> is characteristic of a nitrate group acting as unidentate fashion [14]. In the infrared spectrum of the complexes of Cu(II), Zn(II) and Co(II) a strong band near 2400 cm<sup>-1</sup> (ν<sub>C=N</sub>) appear and confirms the presence of acetonitrile molecule solvent in the compounds. Additional bands at ca. 3250-3310 cm<sup>-1</sup> were observed in the spectrum of both complexes and are assignable to coordinated -NH<sub>2</sub> stretching vibration. The water present in all the complexes is probably lattice and/or coordinated according to the broad band at 3460 cm<sup>-1</sup>.

The electronic spectral data of the complexes are recorded in solid state and the main bands are listed in Table 3. The assignments are made by comparison with literature data [15-18, 21, 22].

An intense band is observed in the spectra of the Cu, Ni and Co complexes near 250 nm and is assigned to π→π\* transition of the aromatic rings [17]. In the region 300–445 nm intense bands are observed and are assigned to n→π\* transition in carbonyl group. In the spectrum of the copper (II) complex two bands at 631 and 787 nm are observable and are assigned to d-d transition. This fact is indicative of a pentacoordinated environment around the copper ion [18]. The copper complex shows μ<sub>eff</sub> value of 1.51 μ<sub>B</sub>, which is lower than the spin only value of 1.73 μ<sub>B</sub>, expected for mononuclear copper complex [19]. This weak value is indicative of a square pyramidal environment as reported by Golobic [20].

In the spectrum of the nickel (II) complex three well resolved bands at 378, 589 and 1030 nm are observable. The band at 378 nm is assignable to the MLCT while the two other bands are respectively assigned to d-d transitions: <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub>, <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>2g</sub>(F). This fact is indicative of an octahedral environment around the nickel ion [21]. The nickel complex shows μ<sub>eff</sub> value of 2.93 μ<sub>B</sub> which is comparable to those reported by Rao [22] for an octahedral mononuclear nickel (II) complex.

The spectrum of the cobalt (II) complex reveals two bands at 474 and 1029 nm. These two bands are assignable respectively to <sup>4</sup>A<sub>2</sub> →<sup>4</sup>T<sub>1</sub>(P) and <sup>4</sup>A<sub>2</sub> →<sup>4</sup>T<sub>1</sub> transition [22] suggesting a tetrahedral environment around the cobalt ion. The complex shows μ<sub>eff</sub> value of 4.10 μ<sub>B</sub> which is comparable to the values reported in literature by tetrahedral cobalt (II) complexes [23, 24].

The <sup>1</sup>H NMR of the cadmium and the zinc complexes, which are paramagnetic in nature, are recorded in dmsO-d<sub>6</sub> solutions. On comparison with the spectrum of the free ligand, no significant difference is observed for the signal of the pyrrole moiety. For the hydrazone moiety a shift of ca. 1 ppm is observed for the signals of the protons. These observations are respectively indicative of the no participation of the nitrogen atom of the pyrrole moiety in the coordination and the implication of the hydrazone moiety in the coordination with the metal ions.

Molar conductivities were measured for freshly prepared DMF solutions and after standing for two weeks (Table 3). The conductivities increased with time in DMF for all the complexes. For copper, cobalt and nickel complexes, the conductance values lie in the range observed for 2:1 electrolytes (130-170 cm<sup>2</sup> Ω<sup>-1</sup> mol<sup>-1</sup>) [25]. The molar conductance value of the cadmium complex in DMF (73 cm<sup>2</sup> Ω<sup>-1</sup> mol<sup>-1</sup>) showed the compound to be 1:1 electrolyte indicating that the complex is partially ionized in DMF solution.

The mass spectra of Co, Ni, Cu and Zn complexes exhibit a characteristic peak of the ligand moiety and a fragment wherein a metal ion is associated with two organic ligand molecules (Table 4).

**Table 3.** Main UV bands of the complexes of the H<sub>5</sub>L ligand.

Compound	$\mu_{\text{eff}}$ ( $\mu_B$ )	$\pi \rightarrow \pi^*$ , MLCT	$n \rightarrow \pi^*$	d-d (nm)	$\Lambda$ ( $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	
					Freshly	15 days
[Co(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ CH <sub>3</sub> CN $\cdot$ H <sub>2</sub> O	4,1	240, 295		474, 1029	122.3	138.9
[Ni(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>y</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ (H <sub>2</sub> O) <sub>3-y</sub>	2,93	307		378, 589, 1030	120.1	134.9
[Cu(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>x</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ CH <sub>3</sub> CN $\cdot$ (H <sub>2</sub> O) <sub>2-x</sub>	1,51	251, 313, 443		631, 787	176.9	215
[Zn(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ CH <sub>3</sub> CN $\cdot$ H <sub>2</sub> O	-	-		-		
{Cd(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> } <sub>n</sub>	-	-		-	72.9	76

**Table 4.** Main fragment peaks of the complexes.

Compound	m/z	Fragment correspondent
[Co(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ CH <sub>3</sub> CN $\cdot$ H <sub>2</sub> O	222.14 500.19	[(H <sub>5</sub> L <sub>A</sub> ) $\cdot$ H <sub>2</sub> O $\cdot$ Na] <sup>+</sup> [Co(H <sub>4</sub> L <sub>A</sub> )(H <sub>5</sub> L <sub>A</sub> ) $\cdot$ H <sub>2</sub> O $\cdot$ NO <sub>3</sub> ] <sup>+</sup>
[Ni(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>y</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ (H <sub>2</sub> O) <sub>3-y</sub>	222.15 419.13	[(H <sub>5</sub> L <sub>A</sub> ) $\cdot$ H <sub>2</sub> O $\cdot$ Na] <sup>+</sup> [Ni(H <sub>4</sub> L <sub>A</sub> )(H <sub>5</sub> L <sub>A</sub> )] <sup>+</sup>
[Cu(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>x</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ CH <sub>3</sub> CN $\cdot$ (H <sub>2</sub> O) <sub>2-x</sub>	222.15 424.12	[(H <sub>5</sub> L <sub>A</sub> ) $\cdot$ H <sub>2</sub> O $\cdot$ Na] <sup>+</sup> [Cu(H <sub>4</sub> L <sub>A</sub> )(H <sub>5</sub> L <sub>A</sub> )] <sup>+</sup>
[Zn(H <sub>5</sub> L <sub>A</sub> ) <sub>2</sub> ] $\cdot$ 2(NO <sub>3</sub> ) $\cdot$ CH <sub>3</sub> CN $\cdot$ H <sub>2</sub> O	222.15 425.12	[(H <sub>5</sub> L <sub>A</sub> ) $\cdot$ H <sub>2</sub> O $\cdot$ Na] <sup>+</sup> [Zn(H <sub>4</sub> L <sub>A</sub> )(H <sub>5</sub> L <sub>A</sub> )] <sup>+</sup>

### 3.2. Crystal structure of the {Cd(H<sub>5</sub>L<sub>A</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>}<sub>n</sub>

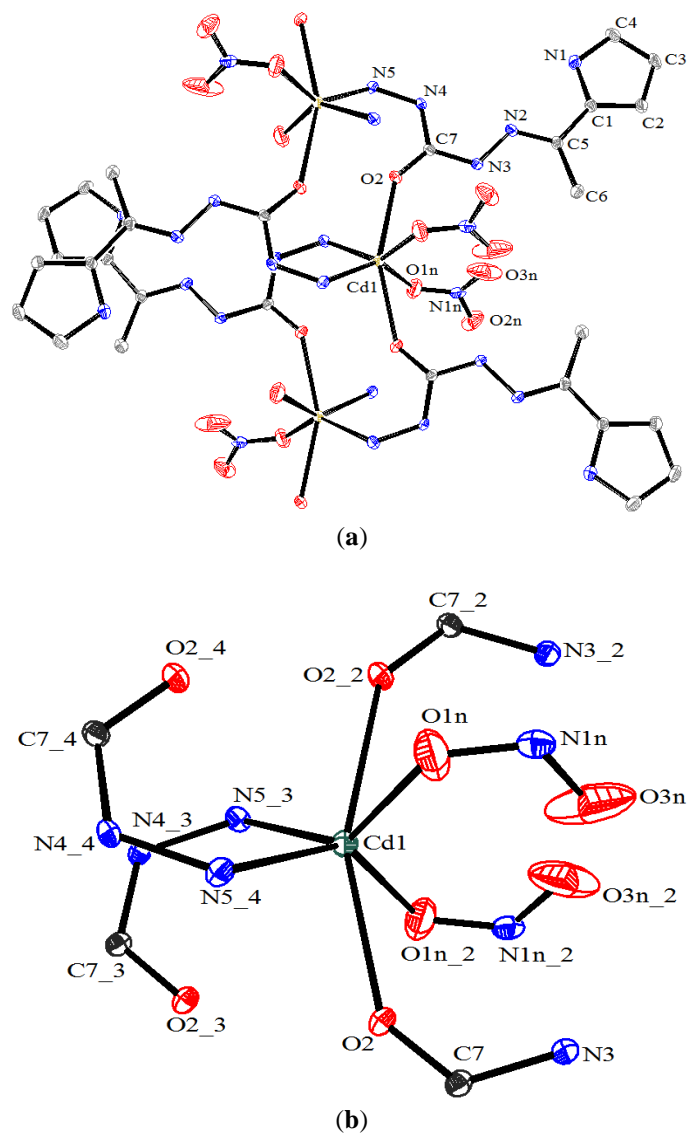
The cadmium complex crystallizes in the monoclinic space group C2/c. The asymmetric unit consists of one cadmium(II) center in N<sub>2</sub>O<sub>4</sub> coordination sphere. Four ligands act as unidentate and coordinate the metal ion via amino nitrogen atoms for two ligands and via hydrazone oxygen atoms for the two other molecules of ligand. Two nitrate groups acting as unidentate complete the coordination sphere via an oxygen atom. Each organic ligand acts as bridge between two cadmium(II) ions. One arm of the ligand is linked to a cadmium atom by its carbonyl oxygen atom while the other arm binds another cadmium atom through its amino nitrogen atom leading to a one-dimensional chain, as shown in figure: 1. Selected bond distances and angles are listed in Table 5. The cadmium (II) to amino nitrogen atom distance (Cd1–N5<sup>i</sup> and Cd1–N5<sup>ii</sup>) is 2.319(5) Å while the length of cadmium (II) to oxygen hydrazone atom (Cd1–O2 and Cd1–O2<sup>iii</sup>) is 2.355(3) Å. These values are comparable to those reported for other analogous Cd (II) complexes [26–28]. The cadmium (II) to oxygen nitrate (Cd1–O1N and Cd1–O1N<sup>iii</sup>) is 2.497 (6) Å and is longest than those found for nitrate cadmium complexes reported in literature [29,30]. The coordination polyhedron can be best described as a distorted trigonal antiprism (figure: 2) which is not common for six-coordinated complexes. Two oxygen atoms and one amino nitrogen atom [O2, O1N, N5<sup>i</sup>] occupy one trigonal face while the opposite trigonal face is defined by the remaining three coordinated atoms [N5<sup>ii</sup>, O2<sup>iii</sup>, O1N<sup>iii</sup>].

**Table 5.** Selected bond (Å) and angles (°) for the {Cd(H<sub>5</sub>L<sub>A</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>}<sub>n</sub>.

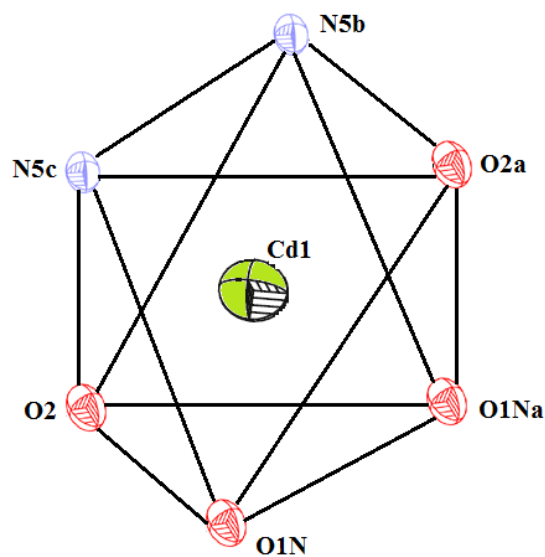
O2—Cd1	2.355 (3)	Cd1—N5 <sup>i</sup>	2.319 (5)
O1N—Cd1	2.497 (6)	N5 <sup>ii</sup> —Cd1—O1N	145.17 (18)
N5 <sup>i</sup> —Cd1—N5 <sup>ii</sup>	101.5 (2)	O2 <sup>iii</sup> —Cd1—O1N <sup>iii</sup>	92.75 (15)
N5 <sup>ii</sup> —Cd1—O2	119.69 (15)	O2—Cd1—O1N <sup>iii</sup>	77.75 (15)
N5 <sup>ii</sup> —Cd1—O2 <sup>iii</sup>	75.85 (14)	O2 <sup>iii</sup> —Cd1—O2	157.12 (17)
N5 <sup>ii</sup> —Cd1—O1N <sup>iii</sup>	72.69 (17)	O1N <sup>iii</sup> —Cd1—O1N	131.1 (2)

Symmetry codes: (i)  $x, -y+1, z-1/2$ ; (ii)  $-x+2, -y+1, -z+2$ ; (iii)  $-x+2, y, -z+3/2$ .

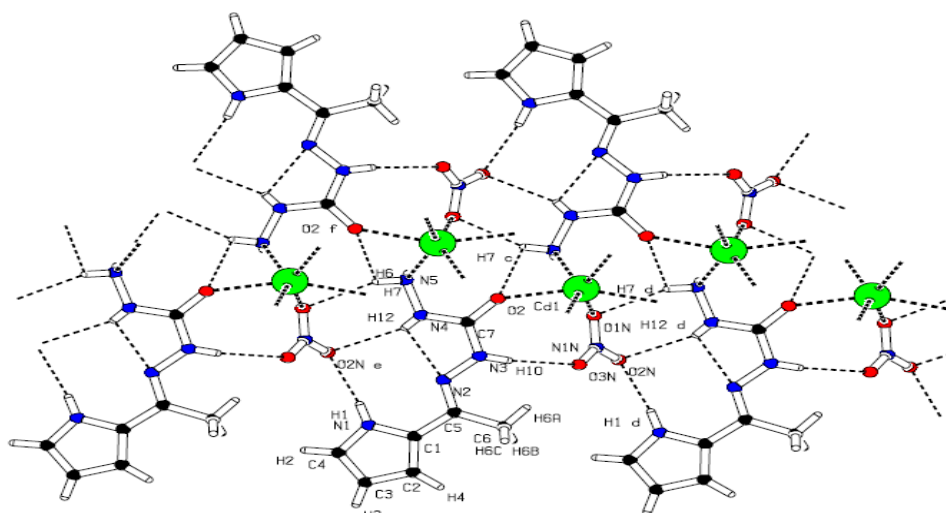
An interesting feature of this complex is the joining of neighboring chains via hydrogen bonds. The oxygen atoms of the monodentate nitrate groups, the oxygen atoms of the hydrazone and the amino groups of the ligands have a crucial role in the formation of sheet structure. These moieties are involved in hydrogen bonding connecting polymer chains. Hydrogen bonds of the O<sub>2</sub>N–O $\cdots$ H–N<sub>hydrazone</sub>, O<sub>2</sub>N–O $\cdots$ H–N<sub>pyrrole</sub>, –HN–H $\cdots$ O<sub>hydrazone</sub>, C=N $\cdots$ H–N<sub>hydrazone</sub> link the components into a sheet (figure: 3).



**Figure 1.** (a) ORTEP view of  $\{Cd(H_5L_A)_2(NO_3)_2\}_n$  complex with atom labels (thermal ellipsoids are drawn at 30% probability level); (b) the coordination polyhedron around Cd.



**Figure 2.** Plot showing the coordination sphere of Cd.



**Figure: 3.** Chains of hydrogen bonding in the crystal lattice  $\{Cd(H_5L_A)_2(NO_3)_2\}_n$ .

#### IV. Conclusion

The synthesis and characterization of complexes from 1-(1-(1*H*-pyrrol-2-yl)ethylidene)carbonohydrazide as chelating ligands have been described in this present paper. Metal ions (Co, Ni, Cu, Zn and Cd) are used for synthesizing molecular compounds. The structures of the complexes are described using the spectroscopic data and the physical measurements. Crystal structure of the cadmium (II) complex shows a polymeric chain where each metal ion is six-coordinated. The environment of the Cd(II) metal center is best described as a distorted trigonal antiprism which is not common for coordination number of six. Hydrogen bonding interactions among the neighboring chains of complex of the cadmium form a three-dimensional network.

#### V. Supplemental Data

CCDC 1012705 contains the supplementary crystallographic data for  $\{Cd(H_5L)_2(NO_3)_2\}_n$ . These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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