

## Crystal structure and characterization of new cadmium complex from 4-pyridin-carbohydrazide and 2-chlorobenzaldehyde

Saeedeh Hashemian \* and Mahbobah Mangeli

Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, 89195-155, Iran

\* Corresponding author at: Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, 89195-155, Iran  
 Tel.: +98.35.31872572. Fax: +98.35.37266065. E-mail address: [sa\\_hashemian@iauyzad.ac.ir](mailto:sa_hashemian@iauyzad.ac.ir) (S. Hashemian).

### ARTICLE INFORMATION



DOI: 10.5155/eurjchem.8.2.101-104.1544

Received: 15 January 2017  
 Received in revised form: 27 February 2017  
 Accepted: 02 March 2017  
 Published online: 30 June 2017  
 Printed: 30 June 2017

### KEYWORDS

Cd complex  
 Trans-complex  
 Octahedral geometry  
 2-Chlorobenzaldehyde  
 Single crystal structure  
 4-Pyridin-carbohydrazide

### ABSTRACT

Reaction of 4-pyridincarbohydrazide, 2-chlorobenzaldehyde and Cd(II) ion in ethanol resulted the complex *trans*-[Cd(H<sub>2</sub>O)<sub>4</sub>(C<sub>13</sub>H<sub>10</sub>N<sub>3</sub>ClO)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>. The title complex was characterized by elemental analyses, UV-Vis and IR spectroscopy. The structure of complex also was established by single crystal X-ray diffraction analysis. The [Cd(H<sub>2</sub>O)<sub>4</sub>(C<sub>13</sub>H<sub>10</sub>N<sub>3</sub>ClO)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> complex has monomeric structure with monoclinic crystal system and space group of *P*2<sub>1</sub>/*n*, *a* = 7.7720(16) Å, *b* = 17.594(4) Å, *c* = 11.823(2) Å, β = 97.29(3)° with *Z* = 2. The cadmium atom in the crystal structure has octahedral geometry by coordination of the two nitrogen atoms of ligand and four oxygen atoms of water molecules.

Cite this: *Eur. J. Chem.* 2017, 8(2), 101-104

### 1. Introduction

The hydrazone produced from isonicotinic acid hydrazide was initially synthesized in 1954 [1]. Hydrazones derived from condensation of isoniazid with pyridine-aldehydes and ketones have shown different medical, physiological and biological activity. There has been growing interest in the study of hydrazones for their physiological activity, coordinative capability, and applications in analytical chemistry [2,3].

Isonicotinyl hydrazine (INH) also known as isoniazid is an organic compound that is the first-line medication in prevention and treatment of tuberculosis. Hydrazones are used as intermediates in synthesis, as functional groups in metal carbonyls, in organic compounds [4,5] and in particular in hydrazone Schiff base ligands. It was proved that isoniazid has also has an anti-depressive effect, one of the first anti depressive drugs discovered. It is also used in a wide range of bacterial diseases [6-9]. Hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelate complexes with transition metals, which catalyze physiological processes [10,11]. In context to previous research a number of complexes of transition metals with isonicotinoyl hydrazone ligands were obtained and characterized [12,13]. The variety complexes such as mononuclear

[14], binuclear [15] and tetranuclear [16] with Cd(II) by different ligand were prepared and studied.

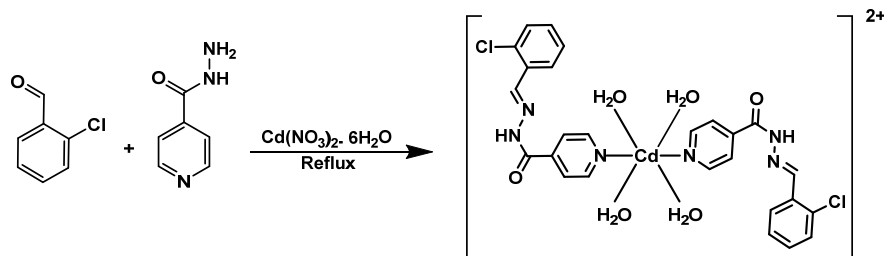
### 2. Experimental

#### 2.1. Instrumentation

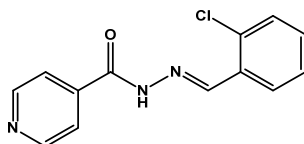
Melting points were determined on an Electrothermal 9100 apparatus. The elemental analyses (C, H, N) were realized with an elemental combustion system CHN, using a Costech device, type ECS 4010, and the metal contents were determined by atomic absorption spectroscopy. For study of electronic spectra, UV-Vis spectrophotometer 160 A Shimadzu was used. The IR spectra (4000-400 cm<sup>-1</sup>) were recorded in KBr pellets using a Shimadzu IR-470 spectrophotometer. Single crystal X-ray diffraction data for Cd(II) complex of *N'*-(2-chlorobenzylidene)isonicotino hydrazide was collected at 293(2) K on a STOE-IPDS II CCD diffractometer using MoKα radiation (λ = 0.71073 Å). The structure was solved by the direct method and refined by full-matrix least-squares fitting on *F*<sup>2</sup> by SHELX-97 [17].

#### 2.2. Synthesis

All chemicals were reagent grade and were used without further purification. 4-Pyridin-carbohydrazide, 2-chlorobenz-



Scheme 1

Figure 1. Chemical structure of *N'*-(2-chlorobenzylidene)isonicotino hydrazide.

aldehyde and all of other chemicals were purchased from Merck. Distilled water and ethanol were used as solvents.

*N'*-(2-Chlorobenzylidene)isonicotino hydrazide was obtained by refluxing of an aqueous solution of 1 mmol (0.14 g) of 4-pyridin-carbohydrazide and 0.5 mmol of NaOH (5%) and 1 mmol (0.14 g) of 2-chlorobenzaldehyde (Scheme 1). Ethanol and water (30 mL, 1:3, v:v) was used as solvents. After the completion of the reaction, as indicated by the TLC, the sample was filtered and washed with ethanol and then filter off. The product was purified by crystallization technique to afford the pure product. Title complex was synthesized as the same procedure but 1 mmol (0.24 or 0.30 g) Cd(II) nitrate was added. Single crystal of the title complex was formed. They were subjected to a single crystal X-ray diffraction study whereby their crystal structure was determined. Color: Light yellow. Yield: 85%. M.p.: 220-225 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3350-3054 ( $\text{NH}_{\text{as}}$ ,  $\text{NH}_{\text{sym}}$ ), 1670 and 1460 (amide group), 860 (N-N). Anal. calcd. for  $\text{C}_{26}\text{H}_{28}\text{CdCl}_2\text{N}_8\text{O}_{12}$ : C, 37.94; H, 3.26; N, 13.43. Found: C, 37.80; H, 3.42; N, 13.50%. UV/Vis ( $\text{CHCl}_3$ ,  $\lambda_{\text{max}}$ , nm): 232, 275.

### 3. Results and discussion

In the present paper, at single step, the new complex of Cd(II) with 4-pyridin-carbohydrazide, 2-chloro benzaldehyde was synthesized. *N'*-(2-Chlorobenzylidene)isonicotino hydrazide and its Cd complex were characterized by elemental analysis and IR spectroscopy methods. The results of elemental analysis confirmed formation of the title compound. The chemical structure of ligand is shown in Figure 1.

The IR spectra for the *N'*-(2-chlorobenzylidene)isonicotino hydrazide ligand and its Cd complex are recorded between 400-4000  $\text{cm}^{-1}$ . In the IR spectrum of *N'*-(2-chlorobenzylidene)isonicotino hydrazide, the average intensity bands appears at 3350 and 3080  $\text{cm}^{-1}$ , which were assigned to the  $\nu(\text{NH}_{\text{as}})$  and  $\nu(\text{NH}_{\text{sym}})$  vibrations, and bands at 1670 and 1460  $\text{cm}^{-1}$ , which were assigned to amide groups [2]. The average intensity band at 864  $\text{cm}^{-1}$  is due to the N-N vibration frequency. In the IR spectra of complex, a very intense band appears in 1383-1389  $\text{cm}^{-1}$  range, which is assigned to nitrate anion. The bands in the 3380-3420 and 1080  $\text{cm}^{-1}$  domain, from IR spectra of the Cd complex, suggest the existence of coordination of water molecule. The vibration frequencies  $\nu\text{N-H}$  are strongly displaced in complex (3054  $\text{cm}^{-1}$ ) suggesting the involvement of the amino nitrogen in coordination with Cd(II) ion. In accordance with this is the fact that the vibration frequency  $\nu\text{N-N}$  is displaced towards lower values as compared with the ligand spectrum in IR spectra of complex [18,19].

The electronic spectrum of ligand and complex were studied. The isoniazid presents in UV two bands at 225 and 260 nm, assigned to transitions of  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$ , respectively. The electronic spectra of complex showed that the same bands, displaced at higher wave number 232 and 275 nm, respectively. This suggests the coordination of ligand to the metallic ion.

The structure of Cd(II) complex of *N'*-(2-chlorobenzylidene)isonicotino hydrazide was determined in a single crystal X-ray diffraction study. Figure 2 shows the labelled structure and Figure 3 shows unit cell-packing diagram of  $[\text{Cd}(\text{H}_2\text{O})_4(\text{C}_{13}\text{H}_{10}\text{N}_3\text{ClO})_2](\text{NO}_3)_2$  complex. Details of crystal structure determination are summarized in Table 1, and the bond lengths and angles in Table 2 and hydrogen-bonding geometry at Table 3. The results show that the cadmium has six-coordinated by two pyridine N atoms of two *N'*-(2-chlorobenzylidene)isonicotino hydrazide and four coordinated water oxygen atoms. The equatorial plane is formed by oxygen atoms, while the axial positions are occupied by nitrogen atoms. The two hydrazone ligands are in *trans* configuration.

Table 1. Crystallographic data, details of data collection and structure refinement parameters for  $[\text{Cd}(\text{H}_2\text{O})_4(\text{C}_{13}\text{H}_{10}\text{N}_3\text{ClO})_2](\text{NO}_3)_2$ .

Empirical formula	$\text{C}_{26}\text{H}_{28}\text{CdCl}_2\text{N}_8\text{O}_{12}$
Formula weight	827.87
Temperature/K	120(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	7.7720(16)
b/Å	17.594(4)
c/Å	11.823(2)
$\alpha/^\circ$	90.00
$\beta/^\circ$	97.29(3)
$\gamma/^\circ$	90.00
Volume/Å <sup>3</sup>	1603.6(6)
Z	2
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.715
$\mu/\text{mm}^{-1}$	0.923
F(000)	836.0
Crystal size/mm <sup>3</sup>	0.20 × 0.20 × 0.17
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	5.78 to 50
Index ranges	-8 ≤ h ≤ 9 -20 ≤ k ≤ 18 -14 ≤ l ≤ 14
Reflections collected	7674
Independent reflections	2810 [R <sub>int</sub> = 0.0912]
Data/restraints/parameters	2810/3/238
Goodness-of-fit on F <sup>2</sup>	0.951
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0490, wR <sub>2</sub> = 0.0635
Final R indexes [all data]	R <sub>1</sub> = 0.0926, wR <sub>2</sub> = 0.0698
Largest diff. peak/hole / e Å <sup>-3</sup>	0.59/-0.51
Full-matrix least-squares on F <sup>2</sup>	Refinement

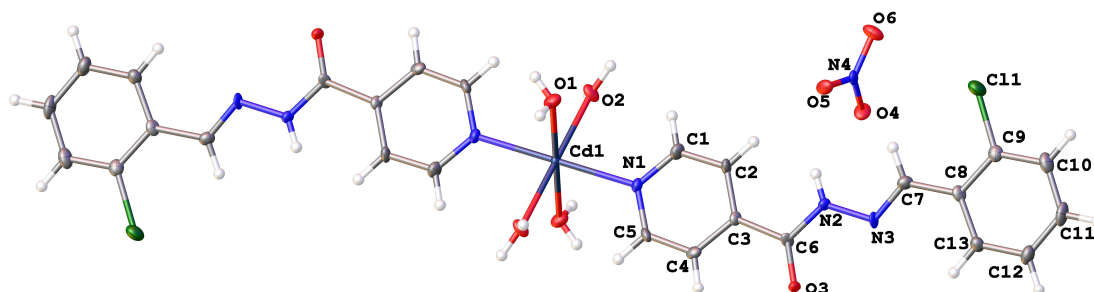


Figure 2. The labeled structure of complex  $[\text{Cd}(\text{H}_2\text{O})_4(\text{C}_{13}\text{H}_{10}\text{N}_3\text{ClO})_2](\text{NO}_3)_2$ .

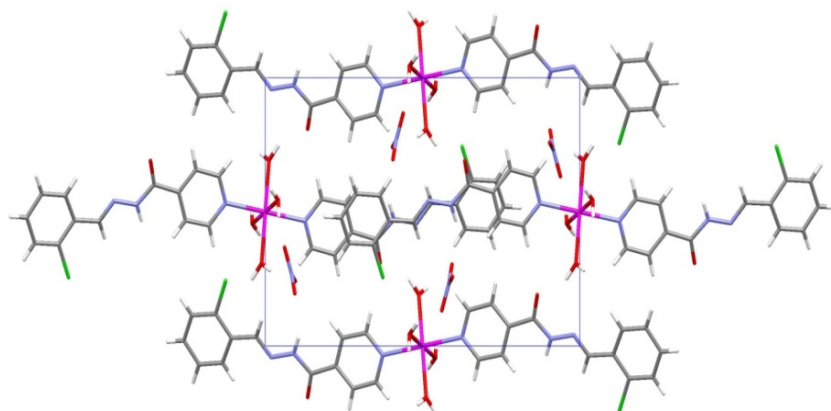


Figure 3. Unit cell-packing diagram of  $[\text{Cd}(\text{H}_2\text{O})_4(\text{C}_{13}\text{H}_{10}\text{N}_3\text{ClO})_2](\text{NO}_3)_2$ .

Table 2. Selected bond lengths and angles for the complex of  $[\text{Cd}(\text{H}_2\text{O})_4(\text{C}_{13}\text{H}_{10}\text{N}_3\text{ClO})_2](\text{NO}_3)_2$ .

Bond	Bond lengths, Å	Bond	Bond angles, °
Cd(1)-O(1)	2.281(4)	O(1)-Cd(1)-O(1)	180.0
Cd(1)-O(1)	2.281(4)	O(1)-Cd(1)-O(2)	84.83(13)
Cd(1)-O(2)	2.303(3)	O(1)-Cd(1)-O(2)	95.17(13)
Cd(1)-O(2)	2.303(3)	O(1)-Cd(1)-O(2)	95.17(13)
Cd(1)-N(1)	2.324(4)	O(1)-Cd(1)-O(2)	84.83(13)
Cd(1)-N(1)	2.324(4)	O(2)-Cd(1)-O(2)	180.0
Cl(1)-C(9)	1.755(5)	O(1)-Cd(1)-N(1)	92.50(14)
O(1)-H(1A)	0.805(19)	O(1)-Cd(1)-N(1)	87.50(14)
O(1)-H(1B)	0.76(5)	O(2)-Cd(1)-N(1)	87.50(14)
O(2)-H(2A)	0.87(5)	O(2)-Cd(1)-N(1)	92.09(12)
O(2)-H(2B)	0.807(19)	O(1)-Cd(1)-N(1)	87.50(14)
O(3)-C(6)	1.218(6)	O(1)-Cd(1)-N(1)	92.50(14)
O(4)-N(4)	1.238(5)	O(2)-Cd(1)-N(1)	92.09(12)
O(5)-N(4)	1.254(5)	O(2)-Cd(1)-N(1)	87.91(12)
O(6)-N(4)	1.265(5)	N(1)-Cd(1)-N(1)	180.000(1)
N(1)-C(5)	1.334(6)	Cd(1)-O(1)-H(1A)	107(4)
N(1)-C(1)	1.350(6)	Cd(1)-O(1)-H(1B)	122(4)
N(2)-C(6)	1.356(6)	H(1A)-O(1)-H(1B)	101(5)
N(2)-N(3)	1.368(5)	Cd(1)-O(2)-H(2A)	135(3)
N(2)-H(2C)	0.82(2)	Cd(1)-O(2)-H(2B)	115(3)
N(3)-C(7)	1.279(6)	H(2A)-O(2)-H(2B)	109(4)
C(1)-C(2)	1.384(7)	C(5)-N(1)-C(1)	117.3(4)

Table 3. Hydrogen-bonding geometry for  $[\text{Cd}(\text{H}_2\text{O})_4(\text{C}_{13}\text{H}_{10}\text{N}_3\text{ClO})_2](\text{NO}_3)_2$ .

D-H...A	d(D-H), Å	d(H...A), Å	d(D...A), Å	∠(D-H...A), °
O(1)-H(1A)...O(6)	0.805(19)	1.97(2)	2.752(5)	166(5)
O(1)-H(1B)...O(6)	0.76(5)	2.04(5)	2.763(5)	161(5)
O(2)-H(2A)...O(3)	0.87(5)	1.94(5)	2.752(5)	155(4)
O(2)-H(2B)...O(4)	0.807(19)	2.04(2)	2.835(5)	168(5)
N(2)-H(2C)...O(5)	0.82(2)	2.23(3)	2.999(5)	156(5)
C(1)-H(1)...O(3)	0.95	2.39	3.341(6)	156(5)
C(2)-H(2)...O(5)	0.95	2.47	3.386(6)	161.2
C(7)-H(7)...O(5)	0.95	2.44	3.275(6)	147.2

#### 4. Conclusion

The Cd(II) complex of *N'*-(2-chlorobenzylidene)isonicotino hydrazide was prepared and characterized by elemental analysis, IR, UV-Vis and single crystal X-ray diffraction analysis. Cd(II) coordinated with two of *N'*-(2-chlorobenzylidene)isonicotino hydrazide ligand and four aqua molecules. Results showed the prepared complex had octahedral geometry, monoclinic and space group  $P2_1/n$ .

#### Acknowledgements

The authors wish to thank Islamic Azad University of Yazd (IAUY) for the financial support of this work. Also, thank co-workers and technical staff in the chemical department help during various stages of this work.

#### Supplementary material

CCDC-1515372 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

#### References

- [1]. Sah, P. P.; Peoples, S. A. *J. Am. Pharm. Assoc. Am. Pharm. Assoc.* **1954**, *43*(9), 513-524.
- [2]. Singh, B.; Narang, K. K.; Srivastava, R. *Synth. React. Inorg. Met. Org. Chem.* **2002**, *32*(9), 1419-1577.
- [3]. Naran, K. K.; Singh, V. P. *Syn. React. Inorg. Met. Org. Chem.* **1997**, *27*, 721-725.
- [4]. Cesur, Z.; Buyuktimkin, S.; Buyuktimkin, N.; Derbentli, S. *Archiv der Pharmazie* **1990**, *323*, 141-144.
- [5]. Bottari, B.; Maccari, R.; Monforte, F.; Ottana, R.; Rotondo, E.; Vigorita, M. G. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 657-660.
- [6]. Pahlavani, L.; Kargar, H.; Sepehri, R.; Zahedan, N. *J. Res. Med. Sci.* **2015**, *17*(7), 7-10.
- [7]. Rodrigues, F. A. R.; Oliveira-Augusto, C. A.; Cavalcanti, B. C.; Pessoa, C.; Pinheiro, A. C.; Souza, M. V. N. *Sci. Pharm.* **2014**, *82*(1), 21-28.
- [8]. Khan, M. S. Y.; Chawla, M. A. *Indian J. Chem. B* **2004**, *43*, 1302-1305.
- [9]. Liu, L.; Alam, M. S.; Lee, D. U. *Bull. Korean Chem. Soc.* **2012**, *33*(10), 3361-3367.
- [10]. Mohan, M. G.; Chandra, M. P.; Jha, L. N. K. *Inorg. Chim. Acta* **1988**, *151*, 61-68.
- [11]. Sinh, R. B.; Jain, P. *Talanta* **1982**, *29*, 77-84.
- [12]. Kriza, I.; Oprea, O.; Stanica, N. *Revista de Chimie Bucharest Orig. Edi.* **2010**, *61*(8), 733-739.
- [13]. Mitu, L.; Ilis, M.; Raman, N.; Imran, M.; Ravichandran, S. *E-J. Chem.* **2012**, *9*(1), 365-372.
- [14]. Fu, Z.; Gao, S.; Liu, S. *Acta Crystallog. C* **2007**, *63*, m459-m461.
- [15]. Jian, G.; Xian-Hui, A.; Tong-Tao, X.; Yi-Cui, J.; Da-Qi, W. *Syn. React. Inorg. Met. Org. Chem.* **2006**, *36*(10), 753-757.
- [16]. Ming-Liang, L.; Qiong, Y. *Acta Crystallog. C.* **2013**, *69*, 17-20.
- [17]. Sheldrick, G. M. SHELX-97, Program for the Solution and Refinement of Crystal Structures; University of Göttingen: Germany, 1997.
- [18]. Kriza, A.; Ababei, L.; Stanica, N.; Rau, I. *Rev. Chim. (Bucuresti)* **2009**, *60*(8), 774-777.
- [19]. Kriza, A.; Pricop, L.; Meghean, A. *J. Indian Chem. Soc.* **2001**, *78*, 448-452.