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Original Research Article

Synthesis, characterization, and crystal structure determination of a new copper (II) complex: $[H_2en][Cu(pydc)_2] \cdot 2H_2O$

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ABSTRACT

The new complex of $[H_2en][Cu(pydc)_2] \cdot 2H_2O$ (1) (where H_2en and $pydc$ are ethylenediammonium and 2,6-pyridinedicarboxylate, respectively) was synthesized by the reaction of a mixture of ethylenediamine (en) and 2,6-pyridinedicarboxylic acid (H_2pydc) in a mixture of CH_3OH/H_2O as solvent. This complex was fully characterized by elemental analysis, IR, UV-Vis spectroscopy as well as single-crystal X-ray diffraction method. The crystallographic analysis revealed that the complex of 1 consists of discrete $[Cu(pydc)_2]^{2-}$ anion, one bis(protonated) ethylene diamine cation and two crystal water molecules. In the anionic part of this complex, the copper(II) cation is coordinated by two tridentate $pydc$ anionic ligands through the two oxygen atoms of two carboxylate groups and one nitrogen atom of pyridine ring. Also, in this complex, intermolecular C-H...O, N-H...O and O-H...O hydrogen bonds and the strong $\pi \dots \pi$ interactions between the pyridine rings are effective on the stabilization of the crystal packing.

Keywords: Cu (II) complex, Crystal structure, Ethylene diamine, 2,6-Pyridinedicarboxylic acid.

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Introduction

In recent years, considerable attention has been focused on the synthesis of copper(II) carboxylate complexes due to their applications such as anti-bacterial activities [1-3], anticancer activity [4, 5], catalytic activity [6, 7] and magnetic properties [8, 9]. The anionic form of 2,6-pyridinedicarboxylic acid (H_2pydc) or dipicolinic acid (H_2dipic) is a good chelated ligand and can be coordinated to metal by one nitrogen atoms from one pyridine ring and four oxygen atoms from two carboxylate groups. These multiple coordination modes of $pydc^{2-}$ may lead to discrete, self-assembled coordination polymers, porous coordination polymers (PCPs), and metal-organic frameworks (MOFs) with topologically interesting structures [10-27]. These complexes are of interest owing to their importance for application in catalysts [20, 21], electronics and optics [22, 23], CO_2 sorption [24] and magnetic properties [25, 26]. In continuation of these research works, herein I report the synthesis of a new complex of $[H_2en][Cu(pydc)_2] \cdot 2H_2O$ (**1**). This complex was studied by elemental analysis, X-ray crystallography, and also UV-Vis and IR spectroscopic techniques.

Experimental

Materials and Physical Measurements

All chemicals were purchased from Merck. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. Melting point was obtained on a Kofler Heizbank Rechart type 7841 melting point apparatus. Infrared spectrum ($4000-250\text{ cm}^{-1}$) was taken on a Shimadzu-470 spectrometer in CsI pellet. UV-Vis spectrum was recorded on a Perkin Elmer (Precisely P-T-P 1 Peltier System) spectrometer using a 1 cm path length cell in water at room temperature.

Synthesis of [H₂en][Cu(pydc)₂].2H₂O (1)

2,6-Pyridinedicarboxylic acid (0.27 g, 1.60 mmol) was dissolved in a mixture of 15 ml H₂O, 20 ml CH₃OH and 3.2 ml ethylenediamine (0.50 M in methanol solution, 1.60 mmol). Then this solution was stirred for 10 min at 50 °C and added gradually to a solution of 0.14 g CuCl₂.2H₂O (0.80 mmol) in 5 ml H₂O and the resulting blue solution was stirred for 20 min at 50 °C. The blue solution was then left to evaporate slowly at room temperature. After one week, blue prismatic crystals of **1** were isolated (yield: 0.28 g; 71.1 %; m.p.: 268 °C). IR (CsI): 3445br, 3105m, 3055w, 3022m, 2946w, 1643s, 1593s, 1434m, 1373s, 1281m, 1189m, 1081m, 914w, 805m, 771m, 741s, 686s, 605w, 540w, 438m, 319s. UV-Vis: λ_{max} (water, nm), 267 and 595. Elemental analysis: C₁₆H₂₀CuN₄O₁₀ (%) (491.91); Anal. Calcd (%): C, 39.06; H, 4.07; N, 11.38; O, 32.53. Found: C, 38.85; H, 4.05; N, 11.27; O, 32.65.

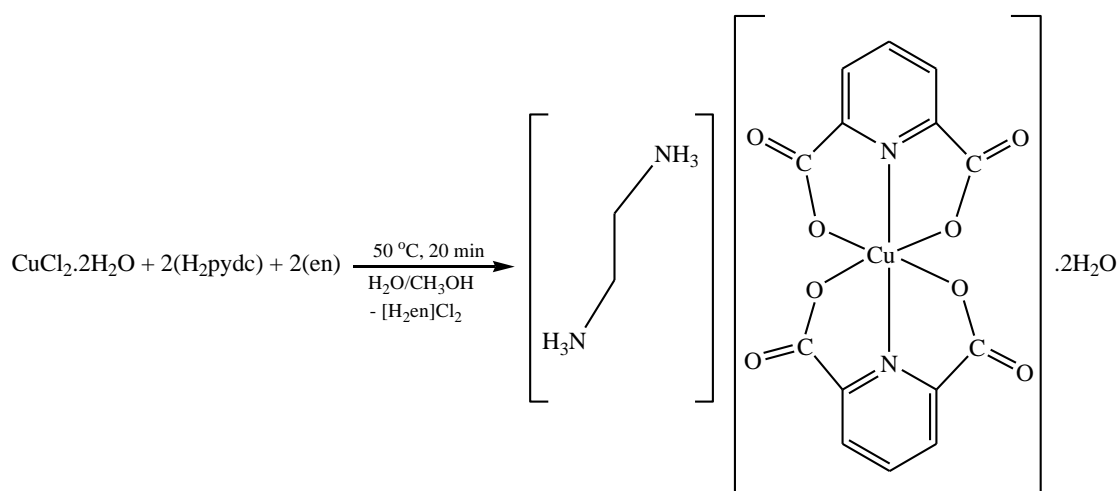
Crystal structure determination and refinement

The X-ray diffraction measurements for title complex was made on a Bruker APEX II CCD area detector diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å) at 298 K. The structure of **1** was solved by SHELX-97 and absorption corrections were done using the SADABS programs [28, 29]. Data collection, cell refinement, and data reduction were performed by APEX II, SAINT, SHELXTL and PLATON [29-32]. The molecular structure and packing diagram were generated by using PLATON and Mercury 2.4 [33] programs, respectively. Full crystallographic detail is deposited with the Cambridge Structural Database (CCDC No. 1908568).

Results and discussion

Synthesis of $[\text{H}_2\text{en}][\text{Cu}(\text{pydc})_2]\cdot 2\text{H}_2\text{O}$ (1)

Complex **1** was obtained from the reaction mixture of two equivalents of 2,6-pyridinedicarboxylic acid and two equivalents of ethylenediamine ligands with one equivalent of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ in mixture of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solvents. Suitable crystals of title complex for X-ray diffraction measurement were obtained by slow evaporation of the resulted blue solution at room temperature. The synthetic route of this complex is shown in Scheme 1.



Scheme 1. The preparation method of complex **1**.

Spectroscopic characterization of $[\text{H}_2\text{en}][\text{Cu}(\text{pydc})_2]\cdot 2\text{H}_2\text{O}$ (1)

Infrared spectrum absorption bands of the compound **1** are listed in experimental section. The broad absorption band at 3445 cm^{-1} and two medium absorption bands at 3105 and 3022 cm^{-1} are assigned to $\nu(\text{O-H})$ and $\nu(\text{N-H})$, respectively. The weak absorption bands which appeared at 3055 and 2946 cm^{-1} are due to the $\nu(\text{C-H})$ of pyridine rings and $-\text{CH}_2$ groups [34, 35]. The infrared spectra of carboxylate compounds are usually produced by two strong bands between 1350 and 1650 cm^{-1} , which is due to the vibrations of carbon-oxygen

stretching vibrations. The frequency difference $\Delta\nu[\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})]$ is correlated with the carboxylate ligand coordination [34, 36-39]. In the infrared spectrum of **1**, the difference $\Delta\nu [\Delta\nu = \nu_{\text{as}}(\text{COO})-\nu_{\text{s}}(\text{COO})]$ is 270 cm^{-1} which is almost similar to that found in $[\text{Cu}(\text{phen})(\text{tda})].2\text{H}_2\text{O}$ (268 cm^{-1} , where phen is 1,10-phenanthroline and tda^{2-} is thiodiacetate), as anticipated for a unidentate mode of carboxylate ligand [38]. Several medium and strong absorption bands appeared in the range of $1593\text{--}540 \text{ cm}^{-1}$ are related to the hetero aromatic ring mode vibrations for C=N, C=C, C-N and C-C [35, 36]. Furthermore, the medium and strong absorption bands appeared at 438 and 319 cm^{-1} are related to Cu-N and Cu-O stretching vibration, respectively [38, 39].

The electronic absorption spectrum of title complex in water solution display a broad band at 266 nm , which is assigned to the $\pi\rightarrow\pi^*$ transition [40], and a weak broad band at 595 nm , which is assigned to the ${}^2E_g\rightarrow{}^2T_{2g}$ transition [14].

Description of the molecular structure of $[\text{H}_2\text{en}][\text{Cu}(\text{pydc})_2].2\text{H}_2\text{O}$ (**1**)

Crystallographic data for title complex are given in Table 1 and selected bond lengths and angles are presented in Table 2. The molecular structure of title complex with the atomic labeling scheme is shown in Fig. 1. As shown in this figure, in the asymmetric unit of this complex, there are one 2,6-pyridinedicarboxylate anion, one half of ethylenediammonium cation, one half-occupied Cu(II) cation and two water solvents (according to high thermal motions of oxygen atom in the one of water solvent, one hydrogen atom refined in two positions with reduced occupancy). In the $[\text{Cu}(\text{pydc})_2]^{2-}$ anionic part, the coordination geometry around Cu(II) is six-coordinated in a distorted octahedral configuration by two N atoms in axial position and four O atoms in equatorial position from two 2,6-pyridinedicarboxylate anion ligands. In the $[\text{Cu}(\text{pydc})_2]^{2-}$ anionic part, the Cu-N distance is

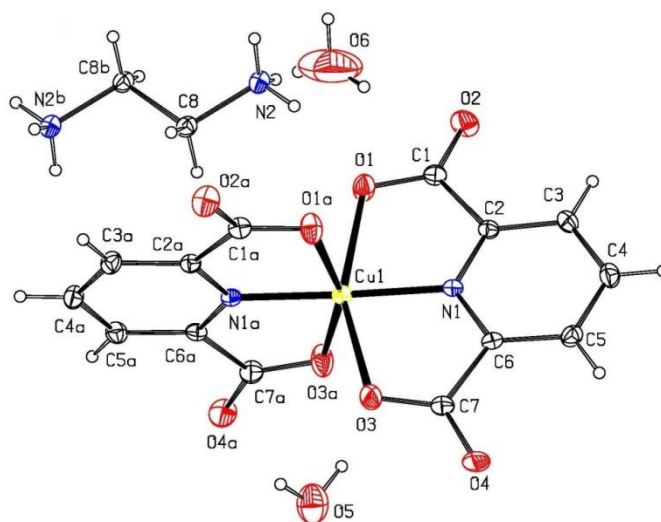
1.924(3)Å, which is slightly smaller than found in [H₂pen][Cu(pydc)₂].5H₂O, 1.945(2)Å [41] and in [H₂pn][Cu(pydc)₂].4H₂O, 1.949(2)Å [42], (H₂pen is pentane-1,5-diaminium and H₂pn is propane-1,2-diaminium). The Cu–O bond distances are 2.186(4) and 2.206(3)Å and almost are similar to in [H₂pen][Cu(pydc)₂].5H₂O [41] and [H₂pn][Cu(pydc)₂].4H₂O [42]. Also, in this anionic complex, the O–Cu–O, O–Cu–N and N–Cu–N bond angles (Table 2) are within normal range [41, 42].

Table 1. Crystallographic and structural refinement data for **1**.

Formula	C ₁₆ H ₂₀ CuN ₄ O ₁₀
Formula weight	491.91
Temperature /K	298(2)
Wavelength λ /Å	0.71073
Crystal system	Monoclinic
Space group	<i>P2/n</i>
Crystal size /mm	0.30×0.22×0.18
<i>a</i> /Å	8.3744(6)
<i>b</i> /Å	8.2026(5)
<i>c</i> /Å	14.6536(11)
β /°	101.548(6)
Volume /Å ³	986.21(12)
Z	2
Density (calc.)/g.cm ⁻³	1.656
θ ranges for data collection	2.48-27.00
<i>F</i> (000)	506
Absorption coefficient/mm ⁻¹	1.172
Index ranges	-10 ≤ <i>h</i> ≤ 10 -10 ≤ <i>k</i> ≤ 9 -17 ≤ <i>l</i> ≤ 18
Data collected	5589
Unique data (<i>R</i> _{int})	2145, 0.0379
Parameters, restraints	168, 0
Final <i>R</i> ₁ , <i>wR</i> ₂ (Obs. data)	0.0437, 0.1254
Final <i>R</i> ₁ , <i>wR</i> ₂ (All data)	0.0494, 0.1287
Goodness of fit on <i>F</i> ² (S)	1.105
Largest diff peak and hole/e.Å ⁻³	0.523, -0.531

Table 2. Selected bond distances/Å and bond angles/° for **1**.

Cu1-N1	1.924(3)	N1 ^a -Cu1-O1	100.13(12)
Cu1-O3	2.186(4)	N1-Cu1-O1	78.37(12)
Cu1-O1	2.206(3)	O3 ^a -Cu1-O1	92.28(16)
N1 ^a -Cu1-N1	177.89(17)	O3-Cu1-O1	156.93(12)
N1 ^a -Cu1-O3 ^a	78.57(12)	N1 ^a -Cu1-O1 ^a	78.37(12)
N1-Cu1-O3 ^a	102.92(12)	N1-Cu1-O1 ^a	100.13(12)
N1 ^a -Cu1-O3	102.92(13)	O3 ^a -Cu1-O1 ^a	156.93(12)
N1-Cu1-O3	78.57(12)	O3-Cu1-O1 ^a	92.28(16)
O3 ^a -Cu1-O3	93.4(3)	O1-Cu1-O1 ^a	91.2(2)

Symmetry code: (a) $-x+3/2, y, -z+3/2$ **Figure 1.** ORTEP drawing (30% probability displacement ellipsoids) of the complex **1** with the atom numbering scheme. Symmetry codes: (a) $-x+3/2, y, -z+3/2$ and (b) $-x+2, -y+2, -z+1$.

The crystal packing diagram for title complex is shown in Fig. 2. As show in this figure, intermolecular C-H...O, N-H...O and O-H...O hydrogen bonds (Table 3) and $\pi\cdots\pi$ interactions between the pyridine rings, Cg5...Cg5ⁱ [distance is 3.456(2)Å, symmetry code: $i = 2-x, 1-y, 2-z$, and Cg5 is centroid of the ring (N1/C2-C6)] are effective in the stabilization of the crystal structure and formation of a three-dimensional supramolecular structure.

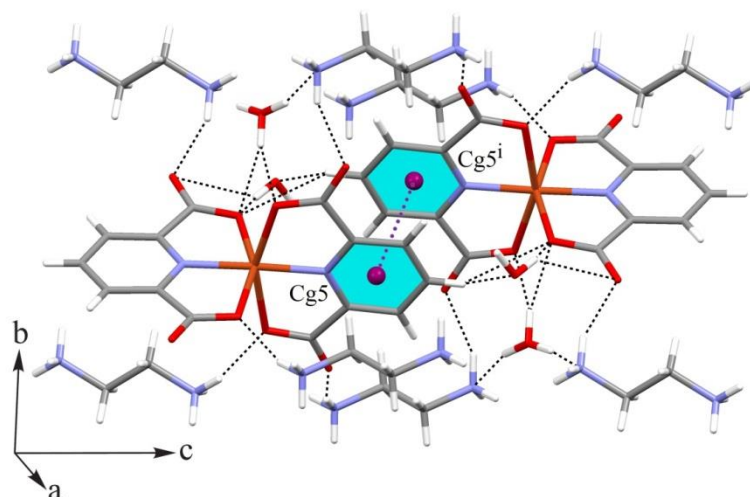


Figure 2. Crystal packing diagram for complex **1**. The $\pi \cdots \pi$ contacts and intermolecular C-H...O, N-H...O and O-H...O hydrogen bonds are shown as dashed lines. Symmetry code: (i) $2-x, 1-y, 2-z$.

Table 3. Hydrogen bond geometry for **1** in crystal packing

D-H...A	D-H/Å	H...A/Å	D...H/Å	D-H...A/ $^{\circ}$	Symmetry code
N2-H2A...O4	0.86(6)	1.96(6)	2.768(5)	156	$3/2-x, 1+y, 3/2-z$
N2-H2B...O1	0.88(5)	2.00(5)	2.849(5)	162	-
N2-H2C...O2	0.82(6)	1.96(6)	2.743(5)	160	$5/2-x, y, 3/2-z$
O5-H5B...O3	0.942(6)	2.215(5)	3.084(5)	152	-
O6-H6A...N2	0.95(10)	2.58(10)	3.481(4)	159	-
O6-H6B...O3	0.838(19)	2.393(13)	3.069(9)	138	$x, 1+y, z$
O6-H6B...O3	0.838(19)	2.393(13)	3.069(9)	138	$3/2-x, 1+y, 3/2-z$
C4-H4...O5	0.930	2.673(3)	3.2611(5)	122	$1-x, 1-y, 2-z$
C4-H4...O3	0.930	2.718(3)	3.531(5)	147	$-1/2+x, 1-y, -1/2+z$

Conclusion

In this work, new complex of $[\text{H}_2\text{en}][\text{Cu}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$ (**1**) has been synthesized. This complex was characterized by spectroscopic methods and its structure was determined by the single crystal X-ray diffraction method. In this complex, intermolecular C-H...O, N-H...O and O-H...O hydrogen bonds and the strong $\pi \cdots \pi$ interactions between the pyridine rings are effective on the stabilization of the crystal packing.

Acknowledgments

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References

- [1] M. Iqbal, S. Ali, M. N. Tahir, *J. Coord. Chem.*, 71, 991 (2018).
- [2] M. Premkumar, D. Kaleeswaran, G. Kaviyarasan, D. A. Prasanth, G. Venkatachalam, *ChemistrySelect*, 4, 7507 (2019).
- [3] A. Rauf, J. Ye, S. Zhang, L. Shi, M. A. Akram, G. Ning, *Polyhedron*, 166, 130 (2019).
- [4] Z. Zhang, H. Wang, Q. Wang, M. Yan, H. Wang, C. Bi, S. Sun, Y. Fan, *International Journal of Oncology*, 49, 691 (2016).
- [5] F. Xie, F. Peng, *Journal of Fluorescence*, 27, 1937 (2017).
- [6] S. E. H. Etaiw, M. M. El-bendary, *Appl. Organomet. Chem.*, 32, e4213 (2018).
- [7] X. S. Tai, P. F. Li, L. L. Liu, *Bull. Chem. React. Eng. & Catal.*, 13, 7 (2018).
- [8] M. Mikuriya, R. Indrawati, R. Hashido, S. Matsubara, C. Nakamura, D. Yoshioka, K. Yokota, M. Fukuzaki, M. Handa, *Magnetochemistry*, 4, 22 (2018).
- [9] E. A. Buvaylo, V. N. Kokozay, V. G. Makhankova, A. K. Melnyk, M. Korabik, M. Witwicki, B. W. Skelton, O. Y. Vassilyeva, *Eur. J. Inorg. Chem.*, 1603 (2018).
- [10] L. Wang, Z. Wang, E. Wang, *J. Coord. Chem.*, 57, 1353 (2004).
- [11] H. Aghabozorg, S. Ahmadvand, M. Mirzaei, H. R. Khavasi, *Acta Crystallogr.*, E66, m1318 (2010).
- [12] H. Aghabozorg, N. Firoozi, L. Roshan, J. Attar Gharamaleki, M. Ghadermazi, *Acta Crystallogr.*, E64, m743 (2008).
- [13] M. Mirzaei, H. Eshtiagh-Hosseini, A. Bauzá, S. Zarghami, P. Ballester, J. T. Maguee, A. Fronter, *CrystEngComm.*, 16, 6149 (2014).
- [14] O. Z. Yeşilel, I. Ilker, M. S. Refat, H. Ishida, *Polyhedron*, 29, 2345 (2010).
- [15] J. C. MacDonald, T. J. M. Luo, G. T. R. Palmore, *Crystal Growth & Design*, 4, 1203 (2004).
- [16] K. Ghasemi, A. R. Rezvani, A. Shokrollahi, I. A. Razak, M. Refahi, A. Moghimi, M. M. Rosli, *J. Mol. Struct.*, 1096, 102 (2015).
- [17] A. Moghimi, M. A. Sharif, A. Shokrollahi, M. Shamsipur, H. Aghabozorg, *Z. Anorg. Allg. Chem.*, 631, 902 (2005).
- [18] M. Rafizadeh, V. Amani, B. Neumüller, *Z. Anorg. Allg. Chem.*, 631, 1753 (2005).
- [19] M. Rafizadeh, V. Amani, B. Neumüller, *Z. Anorg. Allg. Chem.*, 632, 2383 (2006).
- [20] J. An, L. Duana, L. Sun, *Faraday Discuss.*, 155, 267 (2012).
- [21] M. Devereux, M. McCann, V. Leon, V. McKee, R. J. Ball, *Polyhedron*, 21, 1063 (2002).
- [22] K. L. Hou, F. Y. Bai, Y. H. Xing, Y. Z. Cao, D. M. Wei, S. Y. Niu, *J. Inorg. Organomet. Polym.*, 21, 213 (2011).
- [23] A. Fernandes, J. Jaud, J. Dexpert-Ghys, C. Brouca-Cabarrecq, *Polyhedron*, 20, 2385 (2001).
- [24] A. Thirumurugan, W. Li, A. K. Cheetham, *Dalton Trans.*, 41, 4126 (2012).

- [25] H. L. Gao, L. Yi, B. Zhao, X. Q. Zhao, P. Cheng, D. Z. Liao, S. P. Yan, *Inorg. Chem.*, 45, 5980 (2006).
- [26] B. Zhao, L. Yi, Y. Dai, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang, *Inorg. Chem.*, 44, 911 (2005).
- [27] Y. R. Liu, T. Yang, L. Li, J. M. Liu, C. Y. Su, *Aust. J. Chem.*, 62, 1667 (2009).
- [28] Bruker APEX2 Software Package (Version 20-1), Bruker AXS Inc Madison, WI, USA, (2005).
- [29] G. M. Sheldrick, SHELXTL (Version 51), Structure Determination Software Suite, Bruker AXS, Madison, WI, USA, (1998).
- [30] G. M. Sheldrick, *Acta Crystallogr.*, A64, 112 (2008).
- [31] L. J. Farrugia, *J. Appl. Crystallogr.*, 32, 837 (1999).
- [32] L. J. Farrugia, *J. Appl. Crystallogr.*, 30, 565 (1997).
- [33] Mercury 141, Copyright Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, 2001-2005.
- [34] M. Rafizadeh, V. Amani, E. Iravani, Bernhard Neumüller, *Z. Anorg. Allg. Chem.*, 631, 952 (2005).
- [35] M. Taheriha, M. Ghadermazi, V. Amani, *J. Mol. Struct.*, 1107, 57 (2016).
- [36] F. Pirsiavash, V. Amani, A. Abedi, *Research on Chemical Intermediates*, 44, 7411 (2018).
- [37] V. Amani, N. Safari, H. R. Khavasi, *Spectrochim. Acta, Part A*, 85, 17 (2012).
- [38] A. Abbaszadeh, N. Safari, V. Amani, B. Notash, F. Raei, F. Eftekhari, *Iran. J. Chem. Chem. Eng.*, 33, 1(2014).
- [39] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York (2009).
- [40] A.P. Arumugam, G. Elango, S. Guhanathan, *Int. J. New. Chem.*, 6, No. 1, 1 (2019).
- [41] B. Das, J. B. Baruah, *Inorg. Chim. Acta*, 363, 1479 (2010).
- [42] H. Aghabozorg, A. A. Agah, B. Notash, M. Mirzaei, *Acta Crystallogr.*, E67, m992 (2011).

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