J. Environ. Econ. Chem. Process.,: Vol. 1, No. 1, (2024) 15-18

Journal of Enviromental Economics
& Chemical Processes (JEECP)

Journal of Enviromental Economics & Chemical Processes (JEECP)

journal homepage: *WWW.JEECPJournal.com*

A New Example $^{111/113}$Cd–^{1}H Heteronuclear Coupling ^{1}HNMR of Cd(II) as a Toxic Trace Metal

Reza Golbedaghi [a*], Shirin Mohammadi [b]

[a] *Department of Chemistry, Payame Noor University, 19395-4697, Tehran, Iran.*

PAPER INFO

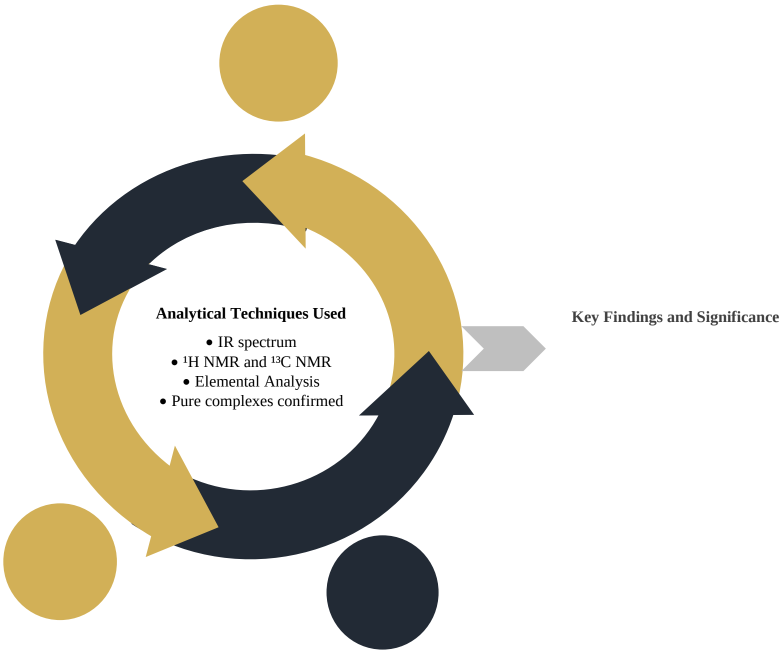
Paper history:
Received 06/01/2024
Accepted in revised form 09/01/2024

Keywords:
Schiff base
NMR studies
Salicylaldehyde
Complex

ABSTRACT

As we know spectroscopy studying is one the most important subjects in Chemistry. One of the most important types of spectroscopy measurements to indicate the structural properties such as type and number of atoms is NMR study. For this mean, we need to synthesis of new compounds and we should try for studying their spectroscopy properties. Herein, we report the synthesis of a new macroacyclic Schiff base ligand (H_3L) obtained from the condensation reaction of 2-[3-(formylphenoxy)-2-hydroxy propoxy] benzaldehydewith 2-aminophenol and characterized with IR, ^{1}H NMR and ^{13}C NMR spectrometry. The related metal complexes of Cd(II) and Zn(II) are prepared with above ligand and characterized by ^{13}C,^{1}HNMR, IR and elemental analysis spectroscopy methods. The spectroscopy studying of the prepared compounds in this paper shows that all of them are pure. In addition, the microanalysis results show that the phenolic groups coordinated to the metal ions as OH and the proton hasn't separated.In the^{1}H NMR spectrum of the cadmium complex signal of the imine proton has two satellite peaks with intensities in 1:6:1 due to the coupling with neighboring ^{113}Cd NMR spectroscopy.

https://doi.org/...



---

* golbedaghi82@gmail.com

URL:

Please cite this article as: : R., Golbedaghi, & S., Mohammadi., (2024). *Journal of Enviromental Economics & Chemical Processes (JEECP)*, ?(4), ??-??. https://doi.org/10.30501/................

1. Introduction

Compounds with the structure of —C=N— (azomethine group) are known as Schiff bases, which are synthesized from the condensation of primary amines and carbonyl groups [1, 2]. During the last few decades there has been great interest in synthesis of new Schiff base ligands and their coordination chemistry. This interest comes from the fact that Schiff base ligands and their complexes show remarkable biological activities including antibacterial, tumor, fungal, microbial, oxidant, cancer, diabetic, analgesic, and anti-HIV properties [3-21]. The azomethine linkage in Schiff base is responsible for the antimicrobial activity and several studies have shown that the presence of lone pair electrons in a sp^2-hybridized orbital of nitrogen atom of the azomethine group plays a significant chemical and biological role [22]. A very large number of coordination compounds with the diamine Schiff base ligand and its substituted derivatives have been reported [24, 25]. The chelating structures, moderate electron donation and easy tunable electronic and steric effects proved Schiff bases as versatile ligands capable of stabilizing different metals in various oxidation states with unusual structural features and controlling the performance of metals in variety of useful catalytic transformations [23, 26]. Schiff bases have been extensively employed in the understanding of molecular processes occurring in biochemistry, materials science, hydrometallurgy, catalysis and separation phenomena [23, 27, 28]. Schiff bases are considered as a very important class of organic compounds, having wide applications in many biological aspects, proteins, visual pigments, enzymicaldolization and decarboxylation reactions. In the recent years, there are some different reports about the macrocyclic, macroacyclic, cocrystals and other different complexes of Schiff base complexes. In addition to the biological, antitomoric, anticancer and other useful properties of Schiff base complexes, the studying of their structures is very interesting and there are some of good reviews in this field. In this paper we report the synthesis and characterization of a new macroacyclic Schiff base ligand and related complex of Cd(II) and Zn(II) metal ions. A new macroacyclic Schiff base ligand is characterized by IR, ^{1}H NMR and ^{13}C NMR spectrometry and their complexes are characterized by IR, conductivity measurements and elemental analysis in all cases. In the case of Cd(II) and Zn(II)complexes,^{1}H NMR and ^{13}C NMR spectroscopies are also used for identification in addition to the mentioned methods. Furthermore, we have been interested in the synthesis of Schiff base complexes [29-32] and 1H NMR spectra of Cd(II) Schiff base complexes and the 1H-111/113Cd coupling constants in these [33–35].

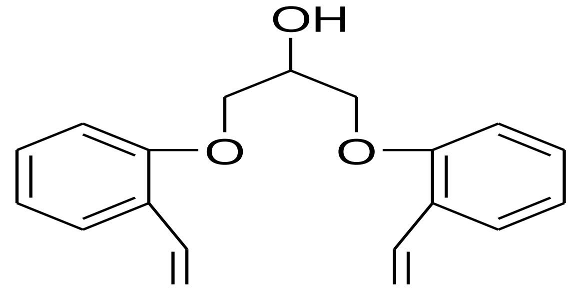
2. Experimental

2.1 Materials and measurements

All the reagents and solvents used in the synthesis were procured commercially and used without subsequent purification. The FT-IR spectra were recorded on a STOE IPDS-II spectrometer (400–4000 cm^{-1}) in KBr pellets. NMR spectra were measured on Bruker DPX 300 and 400 spectrometers.

2-2. Synthesis of Schiff-base ligand (H_3L)

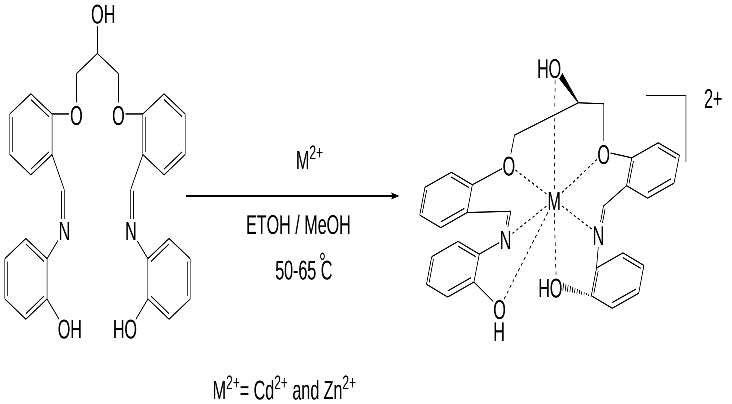
2-aminophenol (4 mmol) was dissolved in 20 ml of absolute ethanol and added slowly to a stirred solution of 2-[3-(formylphenoxy)-2-hydroxy propoxy] benzaldehyde(2mmol) in 30 ml of absolute ethanol at 65ºC temperature. The color immediately changed to red. The mixture was then stirred for 2h at 65ºC temperature before removal of solvent under vacuum.Yield: 81%, m.p. 74-76. Anal. Calc. for $C_{29}H_{26}N_2O_5$: C, 72.18; H, 5.43; N, 5.81. Found: C, 71.97; H, 5.38; N, 5.49%. IR (KBr, cm^{-1}): 1619, (νC=N Schiff base), 3391, (ν O-H).^{1}H NMR ($CDCl_3$, ppm, 300 MHz,): 9.09 (s, 2H, HC=N); 6.88–8.12 (m, 16H, ArH) ; 4.57 (m, 1H, CH); 4.34 (d, 4H, $2CH_2$). ^{13}C NMR ($CDCl_3$, ppm, 300 MHz,): 68.73, 69.76, 112.82, 115.06, 116.17, 120.15, 121.80, 124.80, 128.39, 130.40, 133.10, 136.35, 152.18, 153.25 and 158.40 (Scheme 1).



Scheme 1. The synthetic route of macroacyclic H_3L.

2-3. Synthesis of complex [Cd (H_3L)(NO_3)] ClO_4, 1.

H_3L (0.97 g, 0.20mmol) and $Cd(NO_3)_2.4H_2O$ (0.046 g, 0.15 mmol) were mixed and heated under reflux for 30 min in ethanol (15 ml). After that $NaClO_4.H_2O$ (0.042 g, 0.30 mmol) was added and stirred for 10 min then cooled at 0 °C. The solution was filtered and the filtrate was reduced to ca 10 cm^3. A White-colored purified powder was obtained by slow diffusion of Et_2O vapor into this solution. Yield: 69%. Anal. Calc. for $C_{29}H_{26}CdClN_3O_{12}$: C, 46.05; H, 3.46; N, 5.56. Found: C, 45.87; H, 3.39; N, 5.61%. IR (KBr, cm^{-1}): 1644, (νC=N Schiff base), 3429, (ν O-H), 1245, (νC-O). ^{1}H NMR (DMSO-d$_6$, ppm, 300 MHz,): 4.30 (d, 4H, 2 CH_2); 4.47 (m, H, CH); 6.37–8.22 (m, 16H, ArH); 9.00; (s, 2H, HC=N) with two satellite peaks in the ratio 1:6:1 relative to the main signal ^{3}J ($^{111/113}$Cd- ^{1}H) for cation. ^{13}C NMR (DMSO-d$_6$, ppm, 300 MHz,): 67.29, 70.01, 112.89, 114.42, 116.44, 119.49, 120.78, 124.58, 127.52, 129.99, 132.85, 136.37, 154.51, 156.31 and 158.47 (Scheme 2).



Scheme 2. The synthetic rout of complexes of ligand H_3L

2-4 .Synthesis of complex [Zn H3L] (ClO4)2, 2.

H3L (0.97 g, 0.15 mmol) and ZnCl2.6H2O (0.037 g, 0.15 mmol) were mixed and heated under reflux for 30 min in ethanol (15 ml). After this, NaClO4.H2O (0.042 g, 0.30 mmol) was added and stirred for 10 min then cooled at 0 °C. The solution was filtered and the filtrate was reduced to ca 10 cm3. A yellow-colored purified powder was obtained by slow diffusion of Et2O vapor into this solution. Yield: 54%. Anal. Calc. for C29H26ZnCl2N2O13: C, 46.64; H, 3.51; N, 3.75. Found: C, 46.37; H, 3.16; N, 3.55%. IR (KBr, cm-1): 1646, (νC=N Schiff base), 3421, (ν O-H),1247, (νC-O). 1H NMR (DMSO-d6, ppm, 300 MHz,): 4.31 (d, 4H, 2 CH2); 4.43 (m, H, CH); 6.38–8.21 (m, 16H, ArH); 9.00; (s, 2H, HC=N) (Scheme 4).13C NMR (DMSO-d6, ppm, 300 MHz,): 67.23, 69.94, 112.90, 115.89, 118.18, 119.49, 120.78, 124.53, 127.09, 127.53, 132.87, 138.60, 154.50, 157.16 and 158.46 (Scheme 5).

3 .Results and discussion

3-1 Synthesis and characterization

The complexes 1 and 2 (see Scheme 2) are synthesized from the condensation reaction of 2-aminophenol with 2-[3-(formylphenoxy)-2-hydroxy propoxy]benzaldehyde in the presence of Cd(II) and Zn(II) metal ions. The resulting compounds are characterized by IR, elemental analysis and 13C,1HNMR. Condensation of all the primary amino groups is confirmed by the lack of N–H stretching bands in the IR spectra (3150–3450 cm-1) and the presence of strong C=N (Schiffbase) stretching bands at 1644–1646 cm-1 respectively. A broad intense band at ca. 1100 cm-1 for all complexes due to ClO-4 shows no splitting, indicating the absence of coordination of ClO-4 in all compounds.

3-2 NMR studies

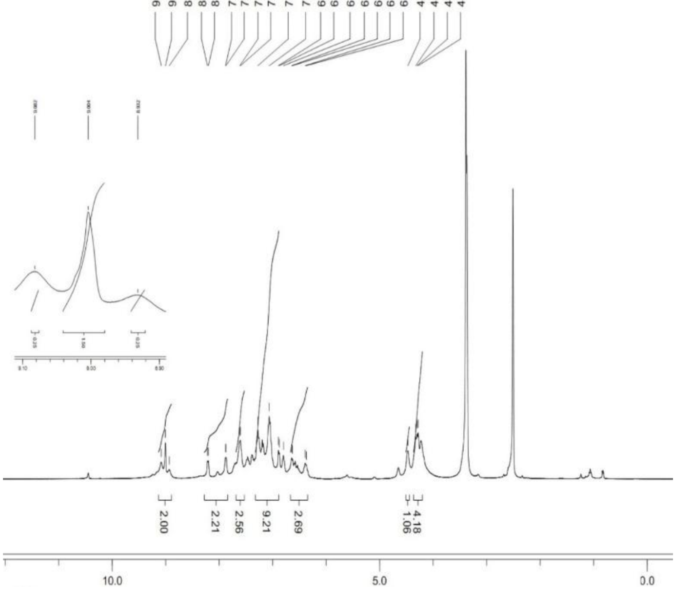
The structure of Schiff base ligand (H3L) obtained from the condensation reaction of 2-[3-(formylphenoxy)-2-hydroxy propoxy]benzaldehydewith 2-aminophenol and characterized and results of NMR measurement of ligand, cadmium and zinc complexes are presented in Schemes 1 and 2. The NMR study of Schiff base ligand is completely consistent with its formulation. The 1H-NMR spectra of the cadmium (Figure 1, a) and zinc (Figure 1, b) compounds 1 and 2 are consistent with formation of fully condensed Schiff base complexes. The 13C NMR spectra of complexes 1 (Figure 2, a) and 2 (Figure 2, b) show two distinct carbon peaks in the aliphatic region, respectively. The 1H NMR spectra of these complexes show two signals due to the aliphatic protons. Naturally occurring cadmium (48Cd) is composed of 8 isotopes. For two of them, natural radioactivity was observed, and three others are predicted to be radioactive but their decays were never observed, due to extremely long half-life times. The two natural radioactive isotopes are 113Cd (beta decay, half-life is 8.04 × 1015 years) and 116Cd (two-neutrino double beta decay, half-life is 2.8 × 1019 years). The other three are 106Cd, 108Cd (double electron capture), and 114Cd (double beta decay); only lower limits on their half-life times have been set. At least three isotopes 110Cd, 111Cd, and 112Cd are absolutely stable (except, theoretically, to spontaneous fission). Among the isotopes absent in the natural cadmium, the most long-lived are

109Cd with a half-life of 462.6 days, and 115Cd with a half-life of 53.46 hours. All of the remaining radioactive isotopes have half-lives that are less than 2.5 hours and the majority of these have half-lives that are less than 5 minutes. This element also has 8 known meta states with the most stable being 113mCd (t1/2 14.1 years), 115mCd (t1/2 44.6 days) and 117mCd (t1/2 3.36 hours).The known isotopes of cadmium range in atomic mass from 94.950 u (95Cd) to 131.946 u (132Cd). The primary decay mode before the second most abundant stable isotope, 112Cd, is electron capture and the primary modes after are beta emission and electron capture. The primary decay product before 112Cd is element 47 (silver) and the primary product after is element 49 (indium).In addition to the above observations the 1H NMR spectra of the cadmium complex show that the signal corresponding to the imine-proton displays two satellite peaks (3J = 41.2 Hz for the cation [CdH3L (NO3)] + in compound 1) with intensities in the ratio 1:6: Figure 1, a) due to coupling with the neighboring111/113Cd nucleus (111Cd, 12.50; 113Cd, 12.50%). The very similar magnetogyric ratios of 113Cd and 111Cd, -5.93303 and -5.6720 x 10-7rad/Ts, respectively, leads to satellite overlap at the collection frequency. As can be seen in (Figure 1, a), there is CH=N resonance appearing at 9.004 ppm, with expected satellites in this case.

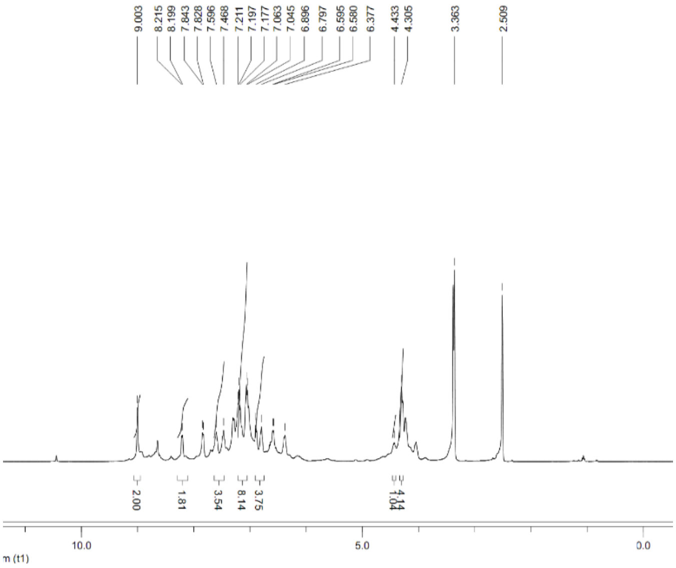
The carbon signals in DMSO solution have been assigned. The scalar coupling constants of cadmium atoms with proton and carbon atoms were measured from satellite lines observed in standard spectra. The most valuable spectral parameters in terms of hydrogen bond structure elucidation are chemical shifts of imine nitrogen atom and carbon atom in the assigned position. To state the presence of intramolecular H-bond the significant low field shift of potentially OH proton signal is e very good evidence, but to define the structure of H-bridge it is necessary to check the other spectral parameters. Analyzing those parameters we can state that the H3L in DMSO solution exist as OH form with intramolecular hydrogen.

Electronic effect seems to bethe minor one since the methyl group is considered as weak electro-donor substituent. Quite different structure of methyl derivative in the solid state suggests the presence of strong steric effect, which twists the imine group out of naphthalene ring plane making proton transfer impossible . As we know, in this type of ligands there is proton transfer, in that, proton transfer will be taken between imine group and hydroxyl .

The first evidence that some interaction with Cd2+ salt takes place is disappearance of low field OH signals in proton spectrum. The structure of cadmium complexes in solution can be determined by analysis of carbon, nitrogen and cadmium-111 chemical shifts and some heteronuclear couplings with cadmium atoms. The comparison of NMR data of Cd(H3L) and other previous synthesized Cd(II) complexes leads to the conclusion that complexation of cadmium ion is weaker in Cd(H3L) compound [33, 34]. The cadmium ion position in the complex can be confirmed by analysis of cadmium couplings observed in the spectra. In proton spectra we have measured cadmium coupling constants only some poroton atoms (three bond couplings). It is in good agreement with literature data [33-35], where 3-bond couplings usually are bigger then 2-bond interactions. It is also very interesting that we were able to record two couplings on C-1 atom, they are derived from two cadmium isotopes 111Cd and 113Cd present in natural cadmium. The abundances of both isotopes are almost equal so we can assign their coupling by satellite line intensity. The bigger value should be assigned to 113Cd isotope which has bigger giromagnetic moment. On the other positions we do not observe double splitting, probably due to bigger line widths and smaller differences in couplings values. The analysis of cadmium couplings confirms very clearly the mentioned earlier position of metal atom in the molecule.

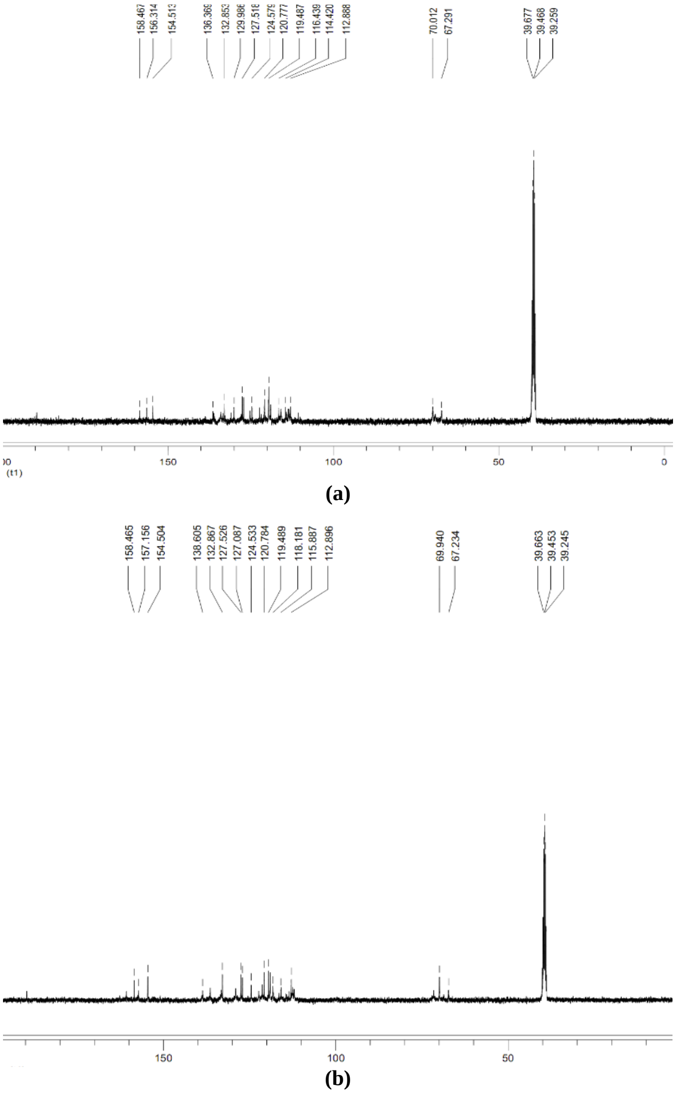


(a)



(b)

Figure 1. ^{1}H NMR of cadmium complex (a) and zinc Complex (b)



(a)

(b)

Figure 2. ^{13}C NMR of cadmium (a) and zinc complexes (b)

4. Conclusion

A new Schiff base ligand, H_3L derived from 2-[3-(formylphenoxy)-2-hydroxy propoxy]benzaldehyde have been synthesized and characterized.The related metal complexes of Cd(II) and Zn(II) are prepared with above ligand and characterized by ^{13}C,^{1}HNMR, IR and elemental analysis spectroscopy methods. In the ^{1}H NMR spectrum of the cadmium complex signal of the imine proton has two satellite peaks with intensities in 1:6:1 due to the coupling with neighboring ^{113}Cd NMR spectroscopy.

5. Acknowledgment

We are grateful to the Payame Noor University for financial support.

Reference

1. H. AmiriRudbari, A. VarastehMoradi, Synthesis,205 (2010).

2. H. AmiriRudbari, A. VarastehMoradi, R. Azadbakht,Synth. Commun.**41**, 528 (2011).

3. M. M. Abo-Aly, A. M. Salem, M. A. Sayed, A. A. Abdel Aziz,Spectrochim.Acta. A.Mol. Biomol.Spectrosc.**136**,993 (2015).

4. E. M. Zayed, M. A. Zayed,Spectrochim. Acta. A. Mol. Biomol. Spectrosc.**143**,81 (2015).

5. S. D. Gupta, D. Snigdha, G. I. Mazaira, M. D. Galigniana, C.V.S. Subrahmanyam, N. L. Gowrishankar, N. M. Raghavendra,Biomed. Pharmacother**68**,369 (2014).

6. A. M.A. Alaghaz, M. E. Zayed, S. A. Alharbi,J. Mol. Struct.**1083**, 430 (2015).

7. A. Avila-Sorrosa, J. I. Hernández-González, A. Reyes-Arellano, R. A. Toscano, R. Reyes-Martínez, J. R Pioquinto-Mendoza, D. Morales-Morales, J. Mol. Struct.**1085**, 249 (2015).

8. M. Sönmez, M. Çelebi, İ. Berber,Eur. J. Med. Chem.,**45**, 1935 (2010).

9. D. Sinha, A. K. Tiwari, S. Singh, G. Shukla, P. Mishra, H. Chandra, A. K. Mishra,Eur. J. Med. Chem.**43**, 160 (2008).

10. J. McGinley, M. McCann, K. Ni, T. Tallon, K. Kavanagh, M. Devereux, X. Ma, V. McKee, Polyhedron**55**, 169 (2013).

11. N. A. Negm, M. F. Zaki,Colloids Surf. B. **64**, 179(2008).

12. S. Yadav, R. V. Singh, Spectrochim. Acta. A. Mol. Biomol. Spectrosc.,**78**, 298 (2011).

13. A. M. Alafeefy, M. A. Bakht, M. A. Ganaie, M. N. Ansarie, N. N. El-Sayed, A. S. Awaad, Bioorg. Med. Chem. Lett.**25**, 179(2015).

14. A. González, E. Gómez, A. Cortés-Lozada, S. Hernández, T. Ramírez-Apan, A. Nieto-Camacho, Chem. Pharm. Bull.**57**, 5 (2009).

15 G. Kumar, S. Devi, R. Johari, D. Kumar, Eur. J. Med. Chem., **52**, 269 (2010).

16. A. N. Kursunlu, E. Guler, F. Sevgi, B. Ozkalp,J. Mol. Struct.**1048**, 476 (2013).

17 J. Vanco, J. Marek, Z. Travnicek, E. Racanska, J. Muselik, O. Svajlenova, J. Inorg. Biochem.**102**, 595 (2008).

18. S. Y. Ebrahimipour, I. Sheikhshoaie, A. C. Kautz, M. Ameri, H. Pasban, H. AmiriRudbari, G. Bruno, C. Janiak,Polyhedron **93**, 99(2015).

19. S. Sathiyaraj, K. Sampath, R. J. Butcher, R. Pallepogu, C. Jayabalakrishnan,Eur. J. Med. Chem.64, 81 (2013).

20. H. Keypour, A. Shooshtari, M. Rezaeivala, F. OzturkKup, H. AmiriRudbari,Polyhedron 97, 75 (2015).

21.Ö. Güngör, P. Gürkan,J. Mol. Struct.**1074**, 62 (2014).

22. Y. Mohini, R. B. N. Prasad, M. S. L. Karuna, Y. Poornachandra, C. Ganesh Kumar,*Bioorg.* Med. Chem. Lett.**24**, 5224 (2014).

23. M. Shakir, N. Shahid, N. Sami, M. Azam, A.U. Khan,Spectrochim. Acta Part A**82**, 31 (2011).

24. A. Carey, Organic Chemistry, fifth ed., McGraw-Hill, New York, 2003.

25. H.H. Sabah, Der. Phar. Chem.**6 (2),** 38 (2014).

26. S. Chandra, L.K. Gupta, S. Agrawal, Trans. Met.Chem.**32**, 558 (2007).

27. (a) B. Singh, U. Srivastava, Synth. Reac.Inorg.Met.-Org. Chem.,**18**, 515 (1988);(b) A. Castineiras, R. Carballo, T. Perez, Polyhedron**20**, 441 (2001).

28. A. Hanaa, E. Boraeya, R.M. Abdel-Rahman, E.M. Atia, K.H. Hilmy, Cent. Eur. J.Chem.**8**, 820 (2010).

29. R. Golbedaghi, E. Alavipour, M. Shahsavari, Russian J. Inorg. Chem. 63, 414 (2018).

30. R. Golbedaghi, M. Rezaeivala, M. Khalili, B. Notash , J. Karimi, J. Mol. Struc. **1125**, 1442016).

31. R. Golbedaghi, S. Azimi, A. Molaei, M. Hatami, B.Notash, J. Mol. Struc. **1146**, 309 (2017).

32. R. Golbedaghi, E. Alavipour, J. Mol. Struc. **1099**, 286 (2015).

33. S. Salehzadeh, R. Golbedaghi, J. Chem. Res.**2**, 86 (2007).

34. R. Golbedaghi, S. Salehzadeh, H. Keypour, A. G. Blackman,Polyhedron **29**, 850 (2010).

35. S. Salehzadeh, R. Golbedaghi, I. S. Tidmarsh, N. K. Al-Rasbi, H. Adams, M. D. Ward, Polyhedron **27**, 3549 (2008).