Erzincan Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
2020, 13(1), 25-32
ISSN: 1307-9085, e-ISSN: 2149-4584
Araştırma Makalesi

Erzincan University
Journal of Science and Technology
2020, 13(1), 25-32
DOI: 10.18185/erzifbed.566231
Research Article

Cadmium(II) Chloride Complex Containing 1-Vinylimidazole Ligand: Structural, Spectroscopic and Thermal Properties

Zuhal YOLCU

Department of Chemistry, Faculty of Arts&Science, Giresun University, Giresun/Turkey

Geliş / Received: 16/05/2019, Kabul / Accepted: 20/02/2020

Abstract

In this work dichlorotetrakis(1-vinylimidazole)cadmium(II), [$CdCl_2$(vim)$_4$] complex was synthesized using 1-vinylimidazole (vim) ligand and $CdCl_2$. The structure of the complex was characterized by FT-IR spectroscopy, thermal analysis (TG, DTG, DTA) and X-ray single crystal studies. In the FT-IR spectrum of the complex, the characteristic peaks (C−H stretch, C=C and C=N vibration bands) of vim were observed. X-ray crystallographic data of the titled complex revealed that vim ligand coordinated to the metal atom via the heterocyclic ring nitrogen atom. The coordination geometry of the Cd(II) central atom is elongated octahedral. Compound crystallized in P21/n space group, and the mononuclear units were weakly linked to each other by C-H···Cl hydrogen bonds. It was determined by thermal analysis data that the complex degraded in four steps and total mass loss was 99%.

Keywords: 1-Vinylimidazole, Cadmium(II) Complex, Crystal Structure, Thermal Analysis

1-Vinilimidazol Ligantı İçeren Kadmiyum(II) Klorür Kompleksi: Yapısal, Spektroskopik ve Termal Özellikler

Öz

Bu çalışmada 1-vinilimidazol (vim) ve $CdCl_2$ kullanılarak; diklorotetrakis(1-vinilimidazol)kadmiyum(II), [$CdCl_2$(vim)$_4$] kompleksi sentezlendi. Kompleksin yapısı FT-IR spektroskopisi, termal analiz (TG, DTG, DTA) ve X-ışınları tek kristal çalışmaları ile karakterize edildi. Kompleksin IR spektrumunda vim ligandna ait karakteristik pikler (C−H gerilme, C=C ve C=N titreşim bandları) gözlendi. Kompleksin X-ışınları kristallografik verileri komplekste vim ligantlarının heterosiklik halka azotu üzerinden metal atomuna koordine olduğunu ortaya koymuştur. Cd(II) merkez atomunun koordinasyon geometrisi uzamış oktahedraldir. Kompleks P21/n uzay grubunda kristallenmiş ve mononükleer birimler, C-H···Cl hidrojen bağları ile birbirlerine zayıf şekilde bağlanmıştır. Termal analiz verilerinden kompleksin dört basamakta bozunduğu ve toplam kütle kaybının % 99 olduğu belirlenmiştir.

Anahtar Kelimeler: 1-Vinilimidazol, Kadmiyum(II) Kompleksi, Kristal Yapı, Termal Analiz

1. Introduction

Imidazole is of great significance as a ligand due to its presence in many biological systems (such as amino acids histidine and purines, enzymes) and providing a potential binding site for metal ions (Edsall et al., 1954; Brooks and Davidson 1960, Mighell and Santoro, 1971). Imidazole and its derivatives have become an important part of many pharmacological activities such as, analgesic, anti-inflammatory (Suzuki et al., 1992), anti-anthelmintic (Lunt et al., 1987), anti-fungal (Johnson et al., 1999), antitubercular (Pandey et al., 2009), antimicrobial (Vijesh et al., 2013), anticancer (Miyachi et al., 1998) and cardiovascular (Erhardt et al., 1989) activities.

Except their pharmacological effects, they also function as catalysts (Jencks, 1970) and polymerizing agents (Samdal and Møllendal, 2011) for example 1-vinylimidazole (vim) (Figure 1) is used as

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*Corresponding Author: zuhal.yolcu@giresun.edu.tr

a copolymerization agent in the production of cationic polymers (Ebel et al., 2000).

Imidazole and its derivatives are actively used in the synthesis of various coordination compounds. Vim is a unidentate simple heterocyclic ligand and forms complexes with metal ions through its tertiary nitrogen atom (Vijesh et al., 2013).

Although there are numerous transition metal complexes with imidazole and its derivatives in the literature (Jian et al., 2002; Wu et al., 2013; Taş et al., 2014; Di Santo et al., 2017), the number of transition metal complexes with vim ligand have been limited (Baran and Linert, 1999; Pang et al., 2007; Yolcu et al., 2016; Li et al., 2007). In the early studies, cadmium complexes with vim ligand were described in literature (Liu et al., 2007; Yilmaz et al., 2018). Liu et al. have reported synthesis, structural characterization and electrochemical property of $[Cd(NCS)_2(Vim)_4]$ complex (Liu et al., 2007). Yilmaz and co-workers have studied surface areas and hydrogen storage capacities of polymeric squaric acid Co(II), Zn(II), and Cd(II) complexes containing vim ligand (Yilmaz et al., 2018). It is also known that the compounds assembled by d^{10} metal centre Cd(II) and imidazole or imidazole derivatives ligands are promising candidates for luminescent materials (Cheng et al., 2017).

In this contribution, a new coordination compound of Cd(II) ion containing vim ligand and ancillary Cl atom was synthesized. Spectroscopic (FTIR) and thermal (TG/DTG/DTA) properties of the complex were investigated. The molecular structure of the complex was determined by using X-ray single crystal diffractometry.

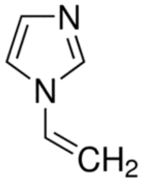

Figure 1. The structure of 1-vinylimidazole

2. Material and Method

All the chemicals for synthesis and analysis were commercially available and used as received. Elemental analysis for C, H, and N were performed using a Costech ECS 4010 CHNSO analyzer. Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1}) were recorded on a JASCO FT-IR 430 spectrophotometer, with samples prepared as KBr pellets. An SII-O Extar 6000 thermal analyzer (Japan) was used to record TG, DTG, and DTA curves in a static air atmosphere at a heating rate of 10 (ºC)min^{-1} from 30 to 700 ºC using platinum crucibles. Highly sintered α–Al_2O_3 was used as a reference.

2.1. X-ray Crystallography

Suitable crystals for single-crystal structure determination were carefully selected under an optical microscope. The diffraction data were collected on a STOE IPDS 2 diffractometer with graphite monochromatized (λ=0,71073 Å) at the temperature of 293(2) K. The structure was solved by direct methods (Altomare et. al., 1999) and refined with full-matrix least-squares method (Sheldrick, 2015). Mercury programs were used for molecular graphics (Macrae et. al., 2008). All non-hydrogen atoms were refined anisotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 1915988. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223- 336033 or e-mail: deposit@ccdc.cam.ac.uk).

2.2. Synthesis of [$CdCl_2$(vim)$_4$]

[$CdCl_2$(vim)$_4$] complex was prepared by the reaction of 1-vinlylimidazole (4 mmol) with $CdCl_2.0.5H_2O$ (1 mmol) in 20 mL ethanol by stirring at room temperature for 2 hours. Colourless stick-like tiny crystals suitable for X-ray measurements were obtained by slow evaporation of the solvent within 2 weeks in a 75% yield. Anal. Calc. for $C_{20}H_{24}N_8Cl_2Cd$: C, 42.91; H, 4.32; N, 20.02. Found: C, 42.56; H, 4.63; N, 19.85.

3. Results and Discussion

3.1. FT-IR Study

The infrared spectroscopic investigation was conducted to define the coordination environment of the cadmium atom in the [$CdCl_2$(vim)$_4$] complex. In the IR spectrum of the complex (Figure 2), the vinylic ν(C–H) stretching and aromatic ν(C–H) stretching vibrations of vim ligand occurred at 3111 cm^{-1} and 3040 cm^{-1}, respectively. The peaks at 1647 cm^{-1} and 1498 cm^{-1} in the complex belong to the ν(C=C) and ν(C=N) stretching vibrations of vim ligand. The presence of bands in this range indicates that vim coordinated to metal (Yolcu et al., 2016; Yilmaz et al., 2018).

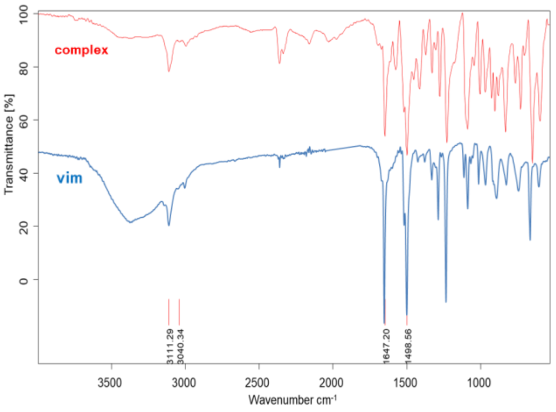

Figure 2. FT-IR spectra of [$CdCl_2$(vim)$_4$] and vim ligand

3.3. X-Ray Crystal Structure

The crystallographic data and details of structure-refinement parameters of title complex are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1. Crystal data of [$CdCl_2$(vim)$_4$] complex.

Chemical formula	$C_{20}H_{24}N_8CdCl_2$
M	559.77
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature(K)	293
λ (Å)	0.71073
a (Å)	7.4719(4)
b (Å)	15.3167(7)
c (Å)	11.4673(7)
β ( )	111.082(5)
V (Å^3)	1224.53(11)
Z	2
d (mg/m^3)	1.518
Absorption coefficient (mm^{-1})	1.133
F(000)	564
Crystal size (mm)	0.42 x 0.23 x 0.13
θ range for collection ( )	2.32-27.52
h, k, l range	$-9 \leq h \leq 9$ $-19 \leq k \leq 19$ $-14 \leq l \leq 14$
Collected reflection	9647
Independent reflection	2818 [R(int) = 0.0555]
Observed reflection (>2σ)	2160
Completed data	1.000
Refinement method	Least squares method
Absorption correction	Integration
T_{max}- T_{min}	0.7810-0.3898
Data/ restraints / parameters	2818/0/142
Compatibility (F^2)	1.058
Final R indices [I>2σ(I)]	R~1=0.0356 wR~2=0.0864
Final R indices (all data)	R~1=0.0509 wR~2 = 0.0914
Highest positive and negative electron density (e.Agst^{-3})	0,545 ve -0,724

The complex is crystallized in a monoclinic crystal system with the $P2_1/c$ space group The molecular structure of the complex is depicted in Figure 3. The results of X-ray diffraction analysis show that the molecular structure of the complex consists of one cadmium central atom, two chloro atoms, and four vim ligands. The coordination environment of the Cd(II) atom is an elongated octahedron occupied by two chloro atoms and four N atoms from vim ligands. The equatorial plane of the complex is constructed by four Cd−N bonds with lengths ranging from 2.340 (3) to 2.360 (2) Å, and the axial positions are occupied by two Cd−Cl bonds (2.6355(7) Å).

These data correspond with those observed in [$Cd(NCS)_2(Vim)_4$] (Liu et al., 2007) and [$CdCl_2(Im)_4$] (Cheng et al., 2017). The values of the bond angles around Cd(II) ion are close to those expected for a regular octahedral geometry (Table 2). The trans angles are all 180° as result of symmetry restrictions and the cis ones are all close 90° with ranges from 87.43(9)° to 92.57(9)°.

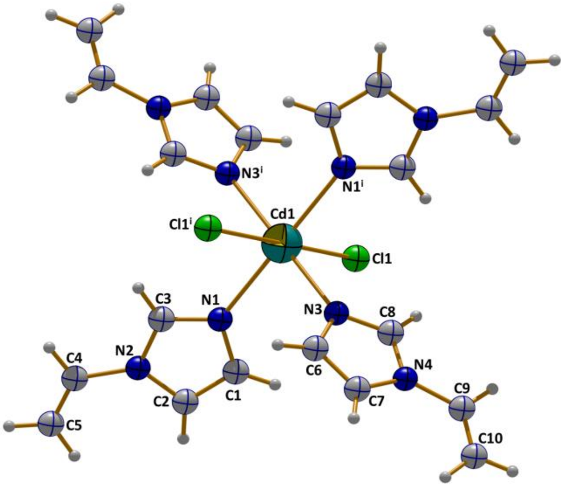

Figure 3. Molecular structure of [$CdCl_2(vim)_4$]. Symmetry code: i:-x+1,-y+1,-z+1

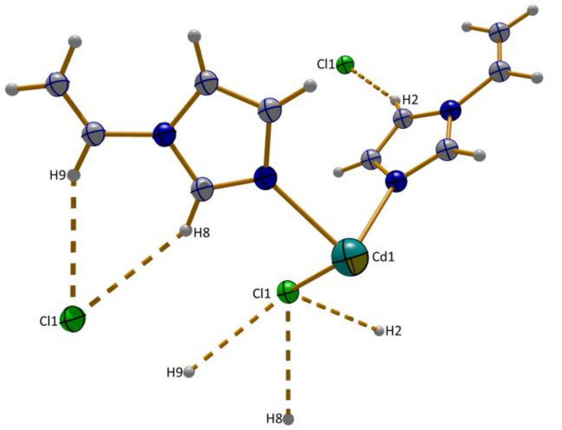

Figure 4. C−H···Cl H-bond interactions for the asymmetric unit of [$CdCl_2(vim)_4$]

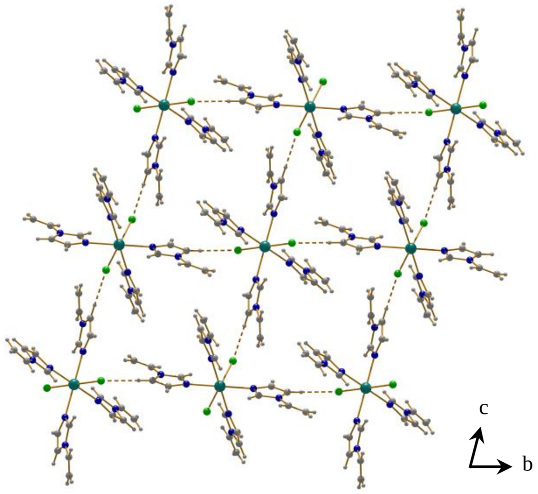

Figure 5. 2D supramolecular structure of [$CdCl_2(vim)_4$] along the *bc*-plane

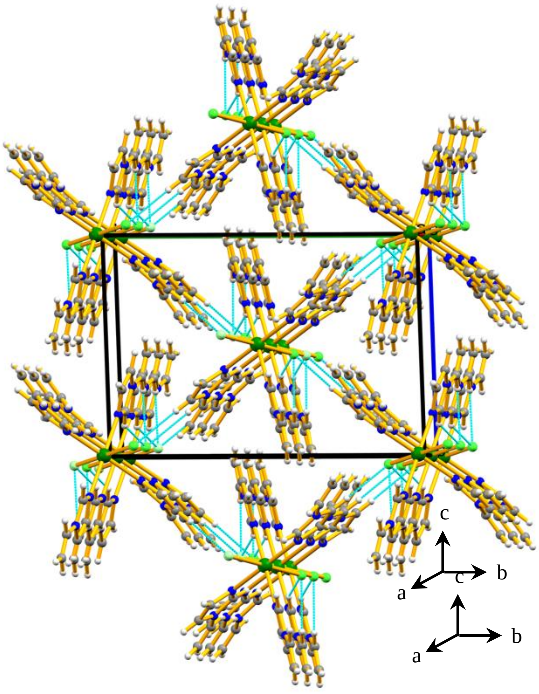

Figure 6. 3D supramolecular structure of [$CdCl_2(vim)_4$] along the *a*-axis

Table 2. Crystal data of [$CdCl_2(vim)_4$]

Selected Bond Lengths (Å)			
Cd1-N1	2.360(2)	Cd1-N3	2.340(3)
Cd1-Cl1	2.6355(7)		
Selected Bond Angles (°)			
N1-Cd1-Cl1	90.45(6)	N3-Cd1-Cl1	88.46(6)
N1-Cd1-N1ⁱ	180.00(1)	N3-Cd1-N1ⁱ	92.57(9)
N1-Cd1-Cl1ⁱ	89.55(6)	N3-Cd1-Cl1ⁱ	91.54(6)
N1-Cd1-N3	87.43(9)	N3-Cd1-N3ⁱ	180.00(1)
Cl1-Cd1-Cl1ⁱ	180.00(3)		

H Bond Interactions(Å, °)

D-H···A	D-H	H···A	D···A	D-H···A(°)

C2-H2···Cl1	0.93(4)	2.901(1)	3.794(4)	161.53
C8-H8···Cl1	0.93(4)	2.835(1)	3.652(4)	147.18
C9-H9···Cl1	0.93(6)	2.871(1)	3.717(6)	151.81

i:-x+1,-y+1,-z+1

The molecular structure is stabilized by weak van der Waals interactions and non-classical C−H···Cl hydrogen bonds. There are three intermolecular H-bonds: C2-H2···Cl1, C8-H8···Cl1 and C9-H9···Cl1, extending the structure into 3D supramolecular network (Figure 4, Table 2). The neighboring octahedral units are connected by the hydrogen bond C2−H2···Cl1, generating 2D supramolecular layers (Figure 5). The layers are assembled in *bc*-plane along the *a*-axis, extending the structure into 3D supramolecular network through the linkages of C8-H8···Cl1, and C9-H9···Cl1, as shown in Figure 6.

3.4. Thermal Analysis

The thermal stability of the complex was investigated by TG, DTG and DTA techniques. The thermogram is shown in Figure 7, it is observed that the complex decomposes in four steps. The first and the second decomposition steps in the 121-222 °C thermal range, 2 mol vim ligands removed, with an experimental mass loss of 29.8% (calculated: 33.6%; DTA: 157,199 °C). In 222-347 °C range, the third step related to the removal of one mol vim ligand with a mass loss of 16.2 (calculated: 16.8%; DTA: 332 °C). The complex was stable at of 347-517 °C range, without any mass loss. The last step between 517 and 620 °C temperature range corresponds to the removal of 1 mol vim ligand and the volatilization of $CdCl_2$ (DTA: 554 and 598°C). The total experimental mass loss at 620 °C was 99.0%. This behavior can be explained by considering that $CdCl_2$ melts at 568 °C and then the compound vaporizes. (Di Santo et al., 2017).

4. Conclusions

In the present work, a novel coordination compound $[CdCl_2(vim)_4]$ was synthesized and characterized. The complex features a distorted octahedral $[CdCl_2N_4]$ coordination with chloro and vim ligands. vim bonded to the metal center via its ternary nitrogen atom as in a monodentate manner. The compound has 3D supramolecular structure constructed by weak van der Waals interactions and non-classical C−H···Cl hydrogen bonds in the solid state.

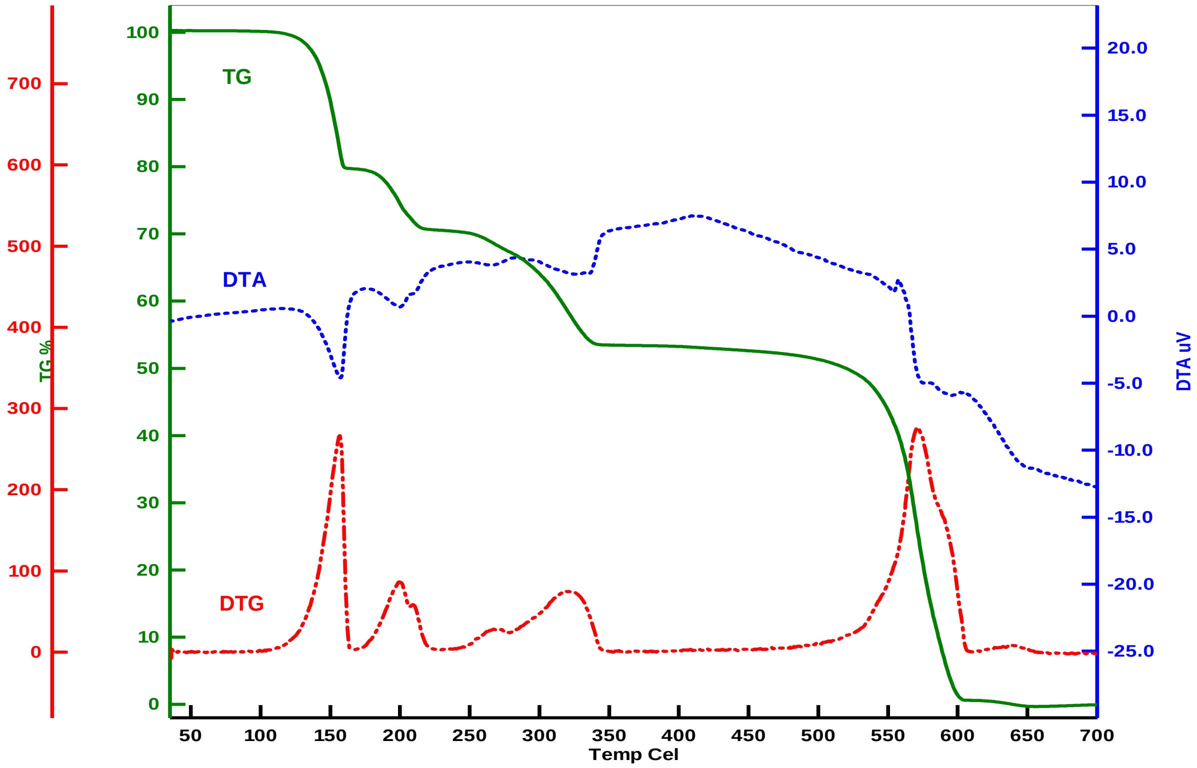

Figure 7. Simultaneous TG, DTG and DTA curves of [CdCl$_2$(vim)$_4$] (in the static air atmosphere)

5. References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G., Spagna. R. 1999. “SIR97: a new tool for crystal structure determination and refinement”, *Journal of Applied Crystallography*, 32, 115-119.

Baran, Y. and Linert, W. 1999. “Hexa(1-vinylimidazole)Co(II) perchlorate”, *Journal of Chemical Crystallography*, 29(10), 1077-1079.

Brooks, P. and Davidson, N. 1960. “Mercury(II) Complexes of Imidazole and Histidine”, *Journal of the American Chemical Society*, 82(9), 2118-2123.

Cheng, C. C., Shen, N. N., Du, C. F., Wang, Z., Li, J. R., Huang, X. Y. 2017. “Cadmium(II) chloride complexes of imidazole-based ligands: Solvothermal syntheses, crystal structures and luminescent properties”, *Inorganic Chemistry Communications*, 85, 21-25.

Di Santo, A., Echeverria, G. A., Gustavo A., Piro, O. E., Perez, H., Ben Altabef, A., Gil, D. M. 2017. “Supramolecular architectures in luminescent Zn(II) and Cd(II) complexes containing imidazole derivatives: Crystal structures, vibrational and thermal properties, Hirshfeld surface analysis and electrostatic potentials”, *Journal Of Molecular Structure*, 1134, 492-503.

Ebel, K., Koehler, H., Gamer, A. O., Jäckh, R. (2000). “Ullmann’s Encyclopedia of Industrial Chemistry”, *Wiley-VCH*, Verlag GmbH & Co. KGaA, 637-645.

Edsall, J. T., Felsenfeld, G., Goodman, D. S., Gurd, F. R. N. 1954. “The Association of Imidazole with the Ions of Zinc and Cupric Copper” *Journal of the American Chemical Society*, 76(11), 3054-3061.

Erhardt, P. W., Hagdon, A. A., Davey, D., Pease, C. A., Venepalli, B. R., Griffin C. W., Gomez, R. P., Wiggins J. R., Ingebretsen W.R., Pang D. 1989. "Cardiotonic Agents. 5. Fragments From The Heterocycle-Phenyl-Imidazole Pharmacophore", *Journal of Medicinal Chemistry*, 32(6), 1173-1176.

Jencks, P. 1970. "Imidazole and proton transfer in catalysis" *Biochemical Journal*, 117(3), 50-50.

Jian, F., Zhao, P., Wang, S. and Zhang, S. 2002. "Structure of hexakis(imidazole) cadmium(II) carbonate trihydrate: $[Cd(Im)_6]CO_3.3H_2O$", *Journal of Chemical Crystallography*, 32(10), 395-398.

Johnson, R. A., Huong, S. M., Huang, E. S. 1999. "Inhibitory effect of 4-(4-fluorophenyl)-2-(4-hydroxyphenyl)-5-(4-pyridyl)1H-imidazole on HCMV DNA replication and permissive infection", *Antiviral Research*, 41(3), 101-111.

Li, R. X., Li, S. X., Wu, Q. Y., Liu, G. Y. Liu, F. Q. 2007. "Catena-Poly[[bis(1-vinylimidazole-kappa N-3)-zinc(II)]-mu-phthalato-kappa O-2(1): O-2]", *Acta Crystallographica Section E*, 63, M2874-U146.

Liu, F. Q., Li, R. X., Li, S. X., Li, C. Q., Liu, G. Y. 2007. "Dibromidotetrakis(1-vinyl-1H-imidazole-kappa N-3)copper(II)", *Acta Crystallographica Section E*, 63, M2437-U1691.

Liu, G. Y., Chen, H. N., Liu, F. Q., Li, S. X., Li, R. X., Huang, S. Y. 2007. "Crystal and Electrochemical Property of tetrakis(1-vinyl-1H-imidazole-kN(3))diisothiocyanatocadmium(II)", *Chinese Journal Of Inorganic Chemistry*, 23, 1085-1088.

Lunt, E., Newton, C. G., Smith, C., Stevens, G. P., Stevens, M. F., Straw, C. G., Walsh, R. J., Warren, P. J., Fizames, C., Lavelle, F., 1987. "Antitumor imidazotetrazines. 14. Synthesis and antitumor activity of 6- and 8-substituted imidazo[5,1-d]-1,2,3,5-tetrazinones and 8-substituted pyrazolo[5,1-d]-1,2,3,5-tetrazinones", *Journal of Medicinal Chemistry*, 30(2), 357-366.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J., Wood, P. A. 2008. "Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures", *Journal Of Applied Crystallography*, 41, 466-470.

,Mighell, A. D. and Santoro, A. 1971. "The crystal and molecular structures of hexakis(imidazole)cadmium(II) nitrate, $[Cd(C_3H_4N_2)_6](NO_3)_2$ and hexakis(imidazole)cadmium-(II) hydroxide nitrate tetrahydrate, $[Cd(C_3H_4N_2)_6](OH)(NO_3).4H_2O$", *Acta Crystallographica Section B*, B27, 2089-2097.

Miyachi, H., Kiyota, H., Segawa, M. 1998. "Novel imidazole derivatives with subtype-selective antimuscarinic activity", *Bioorganic & Medicinal Chemistry Letters*, 8(14), 1807–1812.

Pandey, J., Tiwari, V. K., Verma, S. S., Chaturvedi, V., Bhatnagar, S., Sinha, S., Gaikwad, A. N., Tripathi, R. P. 2009. "Synthesis and antitubercular screening of imidazole derivatives", *European Journal of Medicinal Chemistry,* 44(8), 3350-3355.
Pang, S. J., Su, J., Lin, Q. 2007. "Bis(thiocyanato-kappa N)tetrakis(1-vinyl-

1H-imidazole-kappa N-3)nickel(II)”, *Acta Crystallographica Section E,* 63, M2369-U1120.

Samdal, S. and Møllendal, H. 2011. “Microwave Spectrum and Conformational Composition of 1-Vinylimidazole”, *The Journal of Physical Chemistry A*, 115(26), 7559-7565.

Sheldrick, G. M. 2015. “Crystal structure refinement with SHELXL” *Acta Crystallographica C*, 71, 3-8.

Suzuki, F., Kuroda, T., Tamura, T., Sato, S., Ohmori, K., Ichikawa, S. 1992. “New antiinflammatory agents. 2. 5-Phenyl-3H-imidazo[4,5-c][1,8]naphthyridin-4(5H)-ones: a new class of nonsteroidal antiinflammatory agents with potent activity like glucocorticoids”, *Journal of Medicinal Chemistry,* 35(15), 2863-2870.

Tas, M., Topal, S., Camur, S., Yolcu, Z., Celik, O. 2014. “Structural elucidation of novel mixed ligand complexes of 2-thiophene carboxylic acid [$M(TCA)_2(H_2O)(x)(im)_2$] [x=2 M: Mn(II), Co(II) or Cd(II), x=0 Cu(II)]”, *Main Group Metal Chemistry,* 37(1-2), 39-47.

Wu, B., Bi, Y., Zhou, Z., Yang, L., Zhang, J. and Zhang, T. 2013. “Preparation, crystal structure, and thermal decomposition of an azide energetic compound [$Cd(IMI)_2(N_3)_2$]n (IMI = imidazole)”, *Journal of Coordination Chemistry*, 66(17), 3014–3024,

Vijesh, A. M., Isloor, A. M., Telkar, S., Arulmoli, T., Fun, H. K. 2013. “Molecular docking studies of some new imidazole derivatives for antimicrobial properties”, *Arabian Journal Of Chemistry*, 6(2), 197-204.

Yilmaz, H., Andac, O. 2018. “A novel zinc(II) complex containing square pyramidal, octahedral and tetrahedral geometries on the same polymeric chain constructed from pyrazine-2,3-dicarboxylic acid and 1-vinylimidazole”, *Journal Of Chemical Sciences*, 130(4), 1-11.

Yolcu, Z., Demir S., Andac O., Büyükgüngör O. 2016. “Synthesis, Characterization and DFT-Based Investigation of a Novel Trinuclear Singly-Chloro-Bridged Copper(II)-1-Vinylimidazole Complex”, *Acta Chimica Slovenica*, 63, 646–653.