Iraqi Journal of Scientific and Industrial Research
Volume 4, Issue 2, April-June 2025, pp. 41-46

# A New Nanostructured Copper Schiff Base Complex: Structural and Thermal Observations

Ali S., Lateef R. Fairuz

*Department of Chemistry, College of Education, Al-Iraqia University, Baghdad, IRAQ*

**Abstract**

Producing and studying two new Cu (II) Schiff base complexes: $[Cu(L)_2] (ClO_4)_2$ and $[Cu(L)_2NO_3]NO_3$ of Schiff base ligand (L=4,5,9,13,14-pentaaza-benzo[b] triphenylen). Nanostructured compounds were made using different techniques such as X-ray powder diffraction, infrared spectroscopy, scanning electron microscopy, and elemental studies. Differential scanning calorimetry (DSC) and thermal gravimetric (TGA) analyses were used to examine the thermal stability of bulk complexes and nanoparticles. By calcining the nanostructure complexes at 450°C, CuO nanoparticles were produced. In $CH_3CN$ solution, the copper complexes provide a quasi-reversible reduction process, according to comparative electrochemical experiments.

***Keywords***: Nanoparticles; Metal complexes; Schiff base; Structural study; Thermal properties

**Received:** 5 January 2025; **Revised:** 7 February 2025; **Accepted:** 14 February 2025; **Published:** 1 April 2025

## 1. Introduction

The numerous ramifications of transition metal complexes containing Schiff bases as ligands make them of utmost scientific interest [1]. Coordination chemistry pertaining to catalysis and enzymatic reactions, magnetism, molecular structures, and liquid-crystal technology is developed in large part by these compounds [2,3]. A chelate ligand with an o-quinoid moiety, 1,10-phenanthroline-5,6-dione displays a number of intriguing properties. There have been numerous documented condensation reactions between a diamine group and the o-quinoid moiety of pdon [4]. The ability of 5,6-Diamino-1,10-phenanthroline (phen-diamine) can directly bridge two metal centers or condense with a range of ortho-quinones to produce addition derivatives makes it especially significant. Tetrapyrido[3,2-a:2',3",2"-h:2'",3'"-j] phenazine (tpphz), for instance, is a valuable bridging ligand that is easily produced when 1,10-phenanthroline-5,6-dione (phen-dione) condenses with phen-diamine [5,6]. For this reason, it is crucial to synthesize and characterize nanostructures with various particle sizes and shapes for both fundamental science and technological applications [7].

In recent years, nanoparticles have garnered a lot of attention due to their distinct physical and chemical characteristics that set them apart from single atoms or bulk materials. Applications for nanomaterials could be found in ceramics, optoelectronics, catalysis, and other fields [8]. Among these materials, metal oxide nanoparticles are technologically significant for liquid crystal displays, chemical sensors, and solar cells. Due to its significant features and numerous uses, CuO, a significant p-type semiconductor with a narrow band gap (1.4 eV), has drawn a lot of attention. In recent years, metal complexes composed of metal ions and polydentate organic ligands have expanded quickly due to their possible uses. Studies on the synthesis of nano- or microscale structures using metal complexes as precursors, however, have not been as widely publicized up to this point. The properties of CuO nanomaterials can be optimized by manipulating their purity and shape through the use of copper complexes as precursors [9].

## 2. Experimental Part

All reagents and olefins, which were utilized exactly as supplied and without additional purification, were supplied by Merck and Fluka. Using the traditional procedure, the solvents utilized for the reactions were dried and filtered. Aldrich supplied the copper (II) perchlorate hexahydrate. The method described was used to make 1, 10-phenanthroline-5, 6-dione [19]. The synthesis of the Schiff base ligand (4, 5, 9, 13, 14-pentaaza-benzo[b] triphenylen) followed the guidelines provided in the literature [10-12].

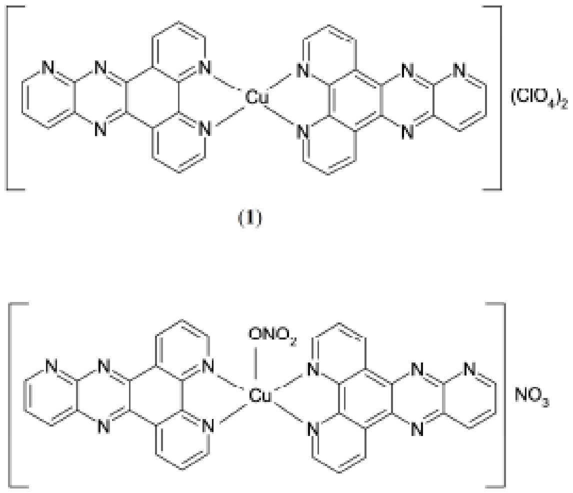
The perchlorate salts mentioned here should be handled carefully because they have the potential to explode. Using an Elemental CHN Analyzer Vario El III, the compounds' elemental analyses (carbon, hydrogen, and nitrogen) were identified. Using KBr discs, infrared (FTIR) spectra were captured using a Shimadzu FT-IR model Prestige 21 spectrometer. Uncorrected melting points were measured with an electrothermal device. Using a Perkin-Elmer Lambda 25 spectrophotometer, the UV-Vis spectra in the 200–900 nm region were acquired in $CH_3CN$. A Metrohm conductometer was used to measure the conductivity in room-temperature acetonitrile solution. TGA was performed in a nitrogen atmosphere using a Mettler-Toledo TGA 851e at a heating rate of 10°C/min.

A Mettler-Toledo DSC 822e module, calibrated with indium metal (T=156.6±0.3, ΔH=28.45±0.61 J/g), was used to acquire the compounds' DSC thermograms. Solid samples weighing between 2 and 5.8 mg were put into 40 µl aluminum pans with pierced lids, heated or cooled at a scan rate of 10°C/min under nitrogen flow, and powered by GPES (Ecochimie) in combination with a three-electrode system and a PC for data processing and storage. For the electrochemical investigations, a glassy carbon working electrode (Metrohm 0.0314 $cm^2$), a Pt wire (counter electrode), and an Ag/AgCl (Saturated KCl)/ 3M KCl reference electrode were used. At room temperature, voltametric tests were conducted using 0.1M tetrabutylammonium perchlorate in an acetonitrile solution as an auxiliary electrolyte. For the ultrasonic irradiation, an ultrasonic generator (Dr. Hirscher UP400 S ultrasonic processor) with a 22 mm diameter H22 sonotrode running at 24 kHz and 400 W of maximum power output was employed. The power level of the ultrasonic generator is automatically adjusted. A Philips diffractometer made by X'pert was used to measure X-ray powder diffraction (XRD) using monochromatized CuKα radiation. A scanning electron microscope (SEM) with a gold coating (Philips XL 30) was used to characterize the nano-sized complexes. Preparation of copper compounds.

The ligand (L) (0.283 g, 1 mmol) was added to an ethanol solution (10 mL) containing 5 mL of metal salt (copper perchlorate or nitrate) (0.5 mmol). Two hours were spent refluxing the resultant solution. At room temperature, the resulting-colored solution was allowed to settle. The product was filtered out, cleaned with chilled 100% ethanol, recrystallized from acetonitrile or methanol, and then vacuum-dried.

Making $[Cu(L)_2](ClO_4)_2$ (3) nanoparticles using the sonochemistry technique 0.1 M $Cu(ClO_4)$ solution in 10 ml. In a high-density ultrasonic probe that ran at 24 kHz and had a 400 W maximum power output, $6H_2O$ in EtOH were placed. Dropwise additions of 10 ml of a 0.2 M ligand L solution were made to this mixture. The resulting precipitates were removed by filtering, followed by a methanol wash and air drying.

The process of $[Cu(L)_2](ClO_4)$ using a solvothermal technique, two nanorods The ligand (L) (0.283 g, 1 mmol) and $Cu(ClO_4)_2.6H_2O$ (0.185 g, 0.5 mmol) were dissolved in 15 ml of EtOH. For 24 hours, the solution was heated to 150°C in a stainless-steel autoclave lined with Teflon. The autoclave was promptly cooled to room temperature, and the resulting substance was filtered, dried, and described.



(1)

(2)

**Fig. (1) Suggested structure of the Cu(II) complexes**

## 3. Results and Discussion

1,10-phenanthroline-5,6-dione and 2,3-diaminopyridine undergo [1+1] cyclocondensation to provide the ligand 4,5,9,13,14-pentaaza-benzo[b] triphenylen (L). The corresponding copper (II) complexes of (1) and (2) are easily produced by the ligand L reacting with $Cu(X)_2.nH_2O$ in ethanol (X = $ClO_4$, $NO_3$, n = 6 and 3, respectively) (Fig. 1). Molar conductivity, UV-Vis, FTIR spectroscopy, and elemental analysis (CHN) were used to characterize the complexes. These complexes showed high stability in the air at room temperature and were found to be reasonably soluble in methanol, acetonitrile, DMF, and DMSO.

Free ligand and their complexes' infrared spectra were recorded in the 4000-400 $cm^{-1}$ region. The complexes' spectra data confirm that the ligands in their metal complexes are cyclic, with a band at 1646-1657 $cm^{-1}$ attributed to the imine groups and no bands from ν(C=O) vibrations. The spectra show medium bands at 1609–1612 $cm^{-1}$, which correspond to the coordinated phenanthroline's ring vibrations, and 1585–1588 $cm^{-1}$, which correspond to the pyridine vibrations. The ν(C=N) band at 1602 $cm^{-1}$ is shifted to a higher frequency by 7–10 $cm^{-1}$ in the complexes, according to the FT-IR spectra of all complexes when compared to the ligand. This suggests that the ligand is coordinated to the metal ions via the nitrogen atom of the phenanthroline group [13-16].

The perchlorate complexes' infrared spectra revealed absorptions at roughly 1085 and 625 cm$^{-1}$ that were attributed to the perchlorate ions [13]. It appears that the perchlorate anions are not coordinated based on the absence of band splitting [14]. Complex (2) exhibits bands in the 1494 cm$^{-1}$ (ν1), 1360 cm$^{-1}$ (ν5), 1112 cm$^{-1}$ (ν2), and 820 cm$^{-1}$ (ν6) areas, which demonstrate that the nitrate group is coordinated [15,16]. A distance of about 134 cm$^{-1}$ between ν1 and ν5 suggests that the nitrate group has an unknown coordinating character [15].

There is also a strong band at 1384 cm$^{-1}$ in complex (2) that is caused by ionic nitrate [26]. Complexes (1) and (2) exhibit 1:2 and 1:1 electrolytic nature, respectively, according to the molar conductivity data at ambient temperature.

Compounds (1) and (2) were examined for their absorption spectroscopic behavior in $CH_3CN$. Everybody of the complexes exhibit three absorption bands at 250–270 nm and 320–380 nm, due to the ligand centered π–π* transitions or charge transfer (CT) transitions [28]. The appearance of broad absorption band at 698 nm in the spectrum of the complex (1) which are assigned to d-d transitions, suggests that the coordination geometry at the metal ion could be distorted from square planer.

The square pyramidal structure surrounding the metal center of complex (2) can be attributed to the observed absorption band at 716 nm. Both ultrasonic irradiation (3) and solvothermal (4) in an ethanolic solution produced the nanostructures of (1), respectively. The nanostructures' infrared spectra are identical. According to the obtained XRD data, the bulk compound (1)'s XRD pattern is identical to that of the complexes (3) and (4) made using the sonochemical and solvothermal techniques, respectively. The information gathered suggests that the compounds produced as a bulk complex by hydrothermal and sonochemical methods are an amorphous phase. The particles' 48–56 nm size is consistent with what scanning electron microscopy (SEM) showed (Fig. 2).

CuO nanostructures were created when the nanoparticles of (1) thermally decomposed in air at 450°C. The CuO nanostructure's SEM picture is displayed in Fig. (3). The XRD pattern of the produced CuO nanostructures is displayed in Fig. (4). CuO nanostructures have demonstrated the highest levels of crystallinity due to the presence of distinct peaks in the XRD pattern. The CuO nanostructures' phase purity as manufactured is readily apparent and the lattice constants are similar to the published data (JCPDS 01-1117), and all diffraction peaks are precisely indexed to the monoclinic CuO phase. In the XRD pattern, no distinctive impurity peaks are found. The peaks' widening suggested that the particles were nanometer-sized.

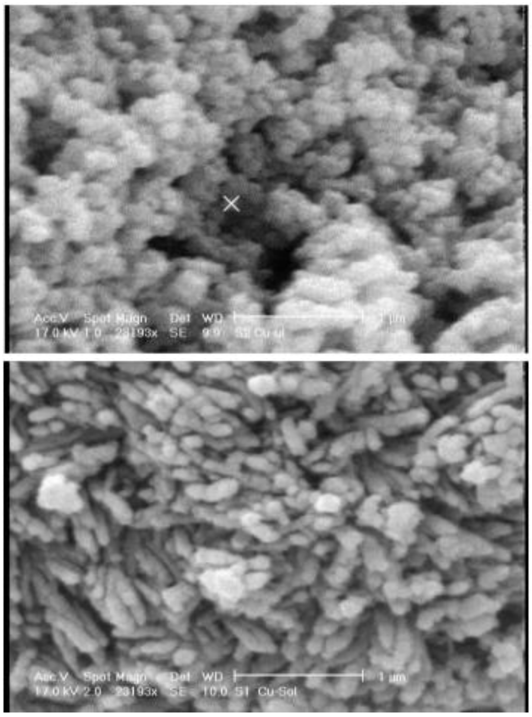


**Fig. (2) SEM images of nanoparticles (3) (top) and nanorods (4) (bottom) as produced by ultrasound irradiation and solvothermal methods, respectively**

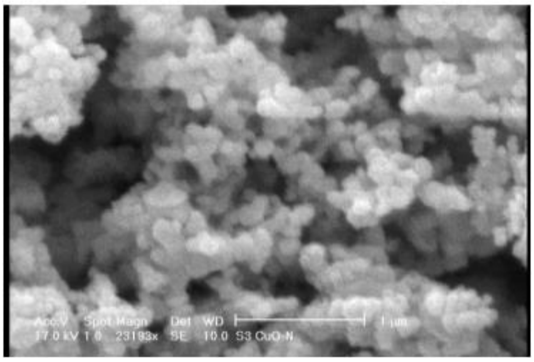


**Fig. (3) SEM image of CuO nanoparticles prepared by solvothermal method**

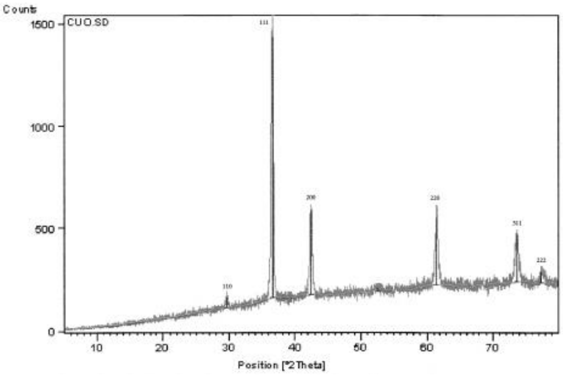


**Fig. (4) XRD pattern of CuO nanoparticles prepared by solvothermal method**

Using 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte, cyclic voltammograms (CVs) of complexes (1) and (2) were observed in the potential range of -2 to +0.1V in acetonitrile. In Fig. (5), typical CVs of (1) are displayed. The complex (1) experiences a one electron quasireversible ($\Delta E_p$ = 280 mV) redox process (table 1) when the voltage is swept to oxidizing potentials, which is attributed to the CuII/CuIII pair -0.45 V for $E_a$ and -0.73 V for $E_c$. $E_a$ = -0.71 V and $E_c$ = -0.95 V, the anodic and cathodic peaks, are seen at about the same potential value as the corresponding ligand and could be caused by irreversible reaction of the ligand.

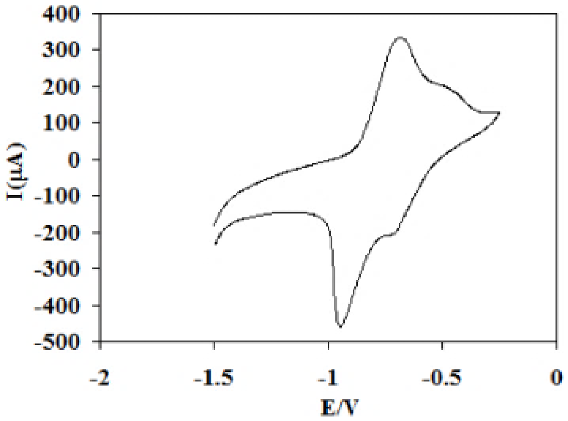


**Fig. (5) Cyclic voltammograms of a $10^{-3}$ M solution of (1) in acetonitrile, in presence of 0.1 M TBAP, using working electrode: glassy-carbon, reference electrode: Ag/AgCl; auxiliary electrode: Pt wire, scan rate 100 mV**

**Table (1) Electrochemical data for Cu(II) complexes in $CH_3CN$ solution**

| Complex | $E_{pa}$ (V) | $E_{pc}$ (V) | $\Delta E_p$ $^a$(mV) | $i_{pa}/i_{pc}$ | $E_{1/2}{}^b$ |
|---|---|---|---|---|---|
| (1) | -0.453 | -0.733 | 280 | 0.89 | -0.59 |
| (2) | - | -0.660 | - | - | - |
| (3) | -0.447 | -0.725 | 278 | 0.89 | -0.59 |
| (4) | -0.450 | -0.729 | 279 | 0.89 | -0.59 |

*$^a\Delta E_p = E_{pc}$-$E_{pa}$ at scan rate 100 mV*

*$^b$Data from cyclic voltammetric measurements; $E_{1/2}$ is calculated as average of anodic ($E_{pa}$) and cathodic ($E_{pc}$) peak potentials = E1/2= 1/2 ($E_{pa}$+$E_{pc}$)*

It is evident that when the scan rate rises, the gap between Ep widens, which is typical of a system that is quasi-reversible. The cathodic and anodic peak currents and the square root of the scan rate ($v^{1/2}$) in the 100–450 mV/s range have a linear connection (Fig. 6). This is the usual behavior of a diffusion-controlled electron transfer mechanism. Combining the ligand peaks with one irreversible reduction peak associated with CuII/CuI reduction ($E_c$=-0.66 V) was demonstrated by complex (2) [17-19].

Thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses were performed between 25 and 850 °C in a static nitrogen environment to investigate the thermal stability of the nano-sized complexes and the corresponding bulk complex. According to the TGA data, complex (1) begins to decompose at 285 °C. Up to 200°C, there is no mass loss, suggesting that this combination lacks solvent or water molecules.

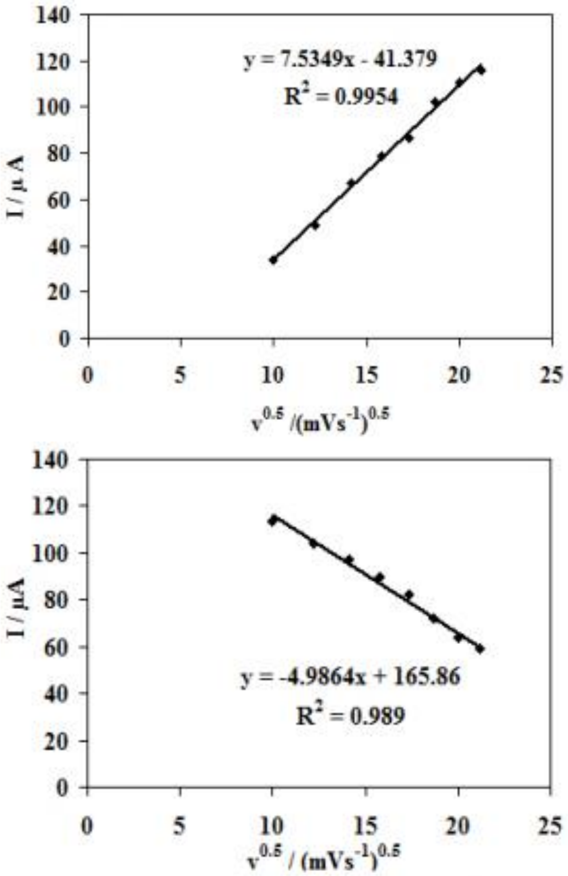


**Fig. (6) Plot of anodic and cathodic vs. the square root of sweep rate ($v^{1/2}$) for (1) complex**

According to the data from the DSC, the nano-sized complex (3) begins to break down around 232.48 °C. Since more heat is required to destroy the bulk compounds' lattices, the nano-complex of $[Cu(L)_2](ClO_4)_2$ begins to decompose detectably around 45° earlier than its bulk counterpart. This is most likely because the nano-sized particles have a much higher surface to volume ratio [19-21].

## 4. Conclusion

Complexes of composition $[Cu(L)_2](ClO_4)_2$ (1) and $[Cu(L)_2NO_3]NO_3$ (2) are formed by Cu(II), where L is the Schiff base ligand of 4,5,9,13,14-pentaaza-benzo[b] triphenylen. Complexes (3) and (4) were produced at the nanoscale using solvothermal and ultrasonic irradiation, respectively, and were described using standard physicochemical methods in addition to XRD and SEM. Complex (1)'s calcination in an air atmosphere yields CuO nanoparticles. Cu(II) forms complexes of composition $[Cu(L)_2](ClO_4)_2$ (1) and $[Cu(L)_2NO_3]NO_3$ (2), where L is the Schiff base ligand of 4,5,9,13,14-pentaaza-benzo[b] triphenylen. In addition to XRD and SEM, complexes (3) and (4) were described using conventional physicochemical techniques. They were created at the nanoscale by solvothermal and ultrasonic irradiation, respectively. CuO nanoparticles are produced through the calcination of Complex (1) in an air atmosphere.

## References

[1] A. Pui, C. Policar, and J.P. Mahy, "Electronic and steric effects in cobalt Schiff bases complexes: Synthesis, characterization and catalytic activity of some cobalt(II) tetra-halogens-dimethyl salen complexes", Inorg. Chem. Acta., 360 (2007) 2139-2144.

[2] P. Panneerselvam, R.R. Nair, G. Vijayalakshmi, E.H. Subramanian, S.K. Sridhar", Synthesis of Schiff bases of 4-(4-aminophenyl)-morpholine as potential antimicrobial agents", Eur. J Med. Chem., 40 (2005) 225-229.

[3](a) M. Amirnasr, A.H. Mahmoudkhani, A. Gorji, S. Dehghanpour, H.R. Bijanzadeh, "Cobalt(II), nickel(II), and zinc(II) complexes with bidentate N,N′-bis(β-phenyl cinnamaldehyde)-1,2-diiminoethane Schiff base: Synthesis and structures", Polyhedron, 21 (2002) 2733-2742. (b) T. Shamsipur, M.H. Mashhadizadeh, I. Shaeikhshoaie, "Flame atomic absorption spectrometric determination of silver ion after preconcentration on octadecyl silica membrane disk modified with bis[5-((4-nitrophenyl) azosalicylaldehyde)] as a new Schiff base ligand", J. Anal. At. Spectrom., 18 (2003) 1407-1410.

[4] K. Larsson, L. Öhrström, "X-ray and NMR study of the fate of the Co(1,10-phenanthroline-5,6-diketone)$_3{}^{3+}$ ion in aqueous solution: supramolecular motifs in the packing of 1,10-phenanthroline-5,6-diketone and 1,10-phenanthroline-5,6-diol complexes", Inorg. Chim. Acta., 357 (2004) 657-664.

[5] (a) K. Yokoyama, T. Asakura, N. Nakamura, H. Ohno, "Chemical modification of cytochrome c by a ruthenium complex containing phenanthroline quinone", Inorg. Chem. Comm., 9 (2006) 281- 283. (b) N.J. Lundin, P.J. Walsh, S.L. Howell, J.J. McGarvey, A.G. Blackman, K.C. Gordon, "Complexes of Functionalized Dipyrido[3,2-a:2′,3′-c]-phenazine: A Synthetic, Spectroscopic, Structural, and Density Functional Theory Study", Inorg. Chem., 44 (2005) 3551-3560.

[6] D.M. Boghaei and F. Behzadian-Asl, "Synthesis, characterization and fluorescence spectra of mixed ligand Zn(II), Cd(II) and Hg(II) complexes with 1,10-phenanthroline-5,6-dione ligand", J Coord. Chem., 60 (2007) 1629–1635.

[7] A. Morsali, H. Hossieni Monfared, and A. Morsali, "Sonochemical synthesis and characterization of new one-dimensional manganese(II) coordination polymer nanostructures", Inorg. Chim. Acta., 24 (2015) 140-145.

[8] A. Askarinezhad and A. Morsali, "Syntheses and characterization of $CdCO_3$ and CdO nanoparticles by using a sonochemical method", Mater. Lett., 62 (2008) 478-482.

[9] (a) A. Askarinezhad and A. Morsali, "Syntheses and characterization of $CdCO_3$ and CdO nanoparticles by using a sonochemical method", Mater. Lett., 62 (2008) 478-482. (b) Y. Mu, J. Yang, S. Han, H. Hou, and Y. Fan, Mater. Lett., 64 (2010) 1287-1290. (c) K. Liu, H.P. You, G. Jia, Y.H. Zheng, Y.H. Song, M. Yang, Y.J. Huang, and H.J. Zhang, Cryst. Growth. Des., 9 (2009) 3519-3524.

[10] D.D. Perrin and W.L.F. Armarego, **"Purification of Laboratory Chemicals"**, 3rd ed., Pergamon, Oxford, 1980, p. 68, 174, 217.

[11] L.A. Saghatforoush, R. Mehdizadeh, and F. Chalabian, "Hydrothermal and sonochemical synthesis of a nano-sized nickel(II) Schiff base complex as a precursor for nano-sized nickel(II) oxide; Spectroscopic, catalytic and antibacterial properties", Transition. Met. Chem., 35 (2010) 903- 911.

[12] (a) P.K. Sasmal, A.K. Patra, and A.R. Chakravarty, "Synthesis, structure, DNA binding and DNA cleavage activity of oxovanadium (IV) N-salicylidene-S-methyldithiocarbazate complexes of phenanthroline bases", J. Inorg. Biochem., 102 (2008) 1463-1472. (b) H. Keypour, H. Goudarziafshar, A.K. Brisdon, R.G. Pritchard, and M. Rezaeivala, "New macrocyclic Schiff-base complexes incorporating a phenanthroline unit. Part 2: Template synthesis of some manganese(II) complexes and crystal structure studies", Inorg. Chim. Acta., 361 (2008) 1415-1420.

[14] H. Keypour, A.A. Dehghani-Firouzabadi, and H.R. Khavasi, "Synthesis and characterization of three novel manganese(II) octaaza macrocyclic Schiff base complexes containing a phenanthroline and two pyridyl units as pendant arms. X-ray crystal structure determination of one manganese(II) complex", Polyhedron, 28 (2009) 1546-1550.

[15] (a) M. Ghosh, P. Biswas, and U. Flörke, "Structural, spectroscopic and redox properties of transition metal complexes of dipyrido[3,2-*f*:2′,3′-*h*]-quinoxaline (dpq)", Polyhedron, 26 (2007) 3750-3762. (b) M. Shakir, M. Azam, S. Parveen, A.U. Khan, F. Firdaus," Synthesis and spectroscopic studies on complexes of N,N'-bis-(2-pyridinecarboxaldimine)-1,8-diaminonaphthalene (L); DNA binding studies on Cu(II) complex", Spectrochimica. Acta. Part A, 2009, 71, 1851-1856. (b) F. Firdaus, K. Fatma, M. Azam, S.N. Khan, A.U. Khan, M Shakir, "Template synthesis and physico-chemical characterization of 14-membered tetraimine macrocyclic complexes, $[MLX_2]$ [M = Co(II), Ni(II), Cu(II) and Zn(II)]. DNA

binding study on [CoLCl$_2$] complex”, Spectrochimica. Acta. A, 72 (2009) 591-596.

[16] K. Nakamoto, **“Infrared and Raman spectra of inorganic and coordination compounds”**, 3rd ed., Wiley, New York, 1978, p. 256.

[17] (a) S. Chandra, R. Kumar, and R. Singh, “Nickel(II) complexes with different chromospheres containing macrocyclic ligands: Spectroscopic and electrochemical studies”, Spectrochim. Acta. A, 65 (2006) 215-220. (b) S. Ilhan, H. Temel, I. Yilmaz, and M. Sekerci, “Synthesis and characterization of new macrocyclic Schiff base derived from 2,6-diaminopyridine and 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and its Cu(II), Ni(II), Pb(II), Co(III) and La(III) complexes”, Polyhedron, 26 (2007) 2795-2802.

[18] Z, Szafran, R.M. Pike, and M.M. Singh, **“Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience Microscale Inorganic Chemistry”**, Wiley, New York, 1991, p. 104.

[19] S. Ilhan, H. Temel, I. Yilmaz, and M. Sekerci, “Synthesis, structural characterization and electrochemical studies of new macrocyclic Schiff base containing pyridine head and its metal complexes”, J. Organomet. Chem., 692 (2007) 3855-3865.

[20] M.S. Nair and R.S. Joseyphus, “Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes of tridentate Schiff base derived from vanillin and DL-α-aminobutyric acid”, Spectrochimica. Acta. A, 70 (2008) 749-754.

[21] T.N. Mandal, S. Roy, A.K. Barik, S. Gupta, R.J. Butcher, and S.K. Kar, “Synthesis and structural characterization of copper(II) and vanadium(V) complexes of pyridyl/pyrimidyl–pyrazole derived Schiff base ligands – Metal specific adjustment of ligand binding mode”, Polyhedron, 27 (2008) 3267-3274.