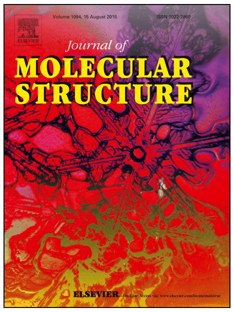

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Synthesis, characterization and spectroscopy studying of some metal complexes of a new Schiff base ligand; X-ray crystal structure, NMR and IR investigation of a new dodecahedron Cd(II) complex

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Abstract

Some new $[Cd(H_2L^1)(NO_3)]ClO_4$ (**1**), $[Mn(H_2L^1)](ClO_4)_2$ (**2**), $[Ni(H_2L^1)](ClO_4)_2$ (**3**) and $[Cu(H_2L^1)](ClO_4)_2$ (**4**) complexes were prepared by the reaction of a Schiff base ligand and M (II) metal ions in equimolar ratios (M = Cd, Mn, Ni and Cu). The ligand H_2L^1 was synthesized by reaction of 2-[2-(3-formyl phenoxy)propoxy]benzaldehyde and ethanol amine and characterized by IR, ^1H,^{13}C NMR spectroscopy and elemental analysis. The synthesized complexes were characterized with IR and elemental analysis in all cases and ^1H, ^{13}CNMR, and X-ray in the case of Cd(II) complex. The X-ray crystal structure of compound **1** showed that all nitrogen and oxygen atoms of Schiff base ligand (N_2O_4) and a molecule of nitrate with two donor oxygen atom have been coordinated to the metal ion and the Cd(II) ion is in an eight-coordinate environment that is best described as a distorted dodecahedron geometry

Keywords: Schiff base ligand, Complex, Ethanol amine, Crystal structure, X-ray, Dodecahedron

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1. Introduction

We are interested in the polydentate coordination chemistry of different metal ions and we have a number of publications of macrocyclic [1, 2] and macroacyclic [3-7] Schiff base complexes. Recently Schiff base compounds have been extensively employed as ligands for mono- or multinuclear macrocyclic or macroacyclic metal complexes, which are applicable to biomimetic catalysts, transporter agents, magnetic or electronic functional materials, building materials in nano-space construction and so on [8-10]. In addition, 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 [11-17]. Herein, we continue the study of the various complexes which show characteristic architecture and properties depending on the conformation of the Schiff base ligand. In addition, we are interested in the polydentate coordination chemistry of different metal ions specially Cd(II), Mn(II), Ni(II) and Cu(II) complexes and we have studied their complexes containing multidentate ligands [1-7]. In the current work, we report the synthesis and characterization of Cd(II), Mn(II), Ni(II) and Cu(II) complexes with a new macroacyclic Schiff base ligand derived from the 2-[2-(3-formyl phenoxy)propoxy] benzaldehyde. After synthesis the Schiff base ligand and preparation some new complexes, we tried to get appropriate crystals of them. Finally, the suitable crystals of Cd(II) complex were prepared and we successes to take its X-ray analysis data. The X-ray crystal structure shows distorted dodecahedron geometry for Cd(II) metal ion.

2. Experimental

2.1. General Information

Hydrated metal salts and ethanol amine were obtained from Aldrich and were used without further purification. 2-[2-(3-formyl phenoxy)propoxy]benzaldehyde (H_2L^1) was prepared via literature method [18]. IR and NMR spectra were measured on a Perkin Elmer FT-IRGX and a Bruker DPX 300 spectrometer, respectively.

2. 2. X-ray crystal structure determination

Single crystal X-ray data on complex **1** were collected at 120 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [19]. The data integration and reduction were carried out with SAINT [20] software. Empirical absorption correction was applied to the collected reflections with SADABS [21] and the space group was determined using XPREP [22]. The structure was solved by the direct methods using SHELXTL-97 [23] and refined on F^2 by full-matrix least-squares using the SHELXL-97 program [24] package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters.

2.3. Synthesis

2.3.1. Preparation of Aldehydes

1, 3-dibromo propane (0.1 mol) and NaOH (0.2 mol) were mixed and heated under reflux in 500 ml equas ethanol (300 ml H_2O and 200 ml EtOH). Salsylaldehyde (0.2 mol) in 30 ml EtOH was added and heated under reflux for 4 days. After cooling the resulting yellow crystals were filtered, washed and recrystallized [18].

2.3.1. Preparation of ligand H_2L_1

Aldehyde (0.284 g, 1mmol) and ethanol amine (0.122 g, 2 mmol) were mixed and heated in the 40 ºC for 30 min in EtOH (30ml). The solution was filtered and the filtrate was reduced to ca 10 cm^3. Yellow crystalline compound was obtained washed with cooled ethanol and dried. Yield: 54%. Anal. Calc. for $C_{21}H_{26}N_2O_4$: C, 67.85; H, 6.84; N, 7.91. Found: C, 67.44; H, 6.79; N, 17.81. IR (KBr, cm^{-1}): 1638 (νC=N Schiff base), 1490 (νC=C), 3365 (νOH). ^{1}HNMR (DMSO, ppm, 300 MHz): δ 2.36 (m, 2H), 3.71 (t, 4H), 3.82 (t, 4H), 4.25 (t, 4H), 6.99 (m, 2H), 7.40 (m, 2H) 7.96 (m, 2H), 7.99 (m, 2 H), 875 (s, 2H), ^{13}CNMR (DMSO, ppm, 300 MHz): δ 62.48 (C-1), 63.57 (C-2), 65.03 (C-3), 76.73(C-4), 77.05(C-5), 112.20, 121,09, 125.62, 125,74, 12684, 127.40, 132.16 (Aromatic Rings), 158.88 (Schiff base).

2.3.3. Preparation of complex $[CdH_2L^1(NO_3)]ClO_4$ (1)

This complex was prepared by reaction of ligand H_2L_1 and $Cd(NO_3)_2.4H_2O$. Ligand H_2L^1 (0.370 g, 1mmol) was solved in 10 ml methanol and the solution was stirred at 30-40 ºC. $Cd(NO_3)_2$. $4H_2O$ (0.308 g, 1mmol) dissolved in MeOH (5 ml) was subsequently added. The mixture was stirred at 50–60 ºC for24 h, then $NaClO_4$ (0.28 g, 2 mmol) was added. The solution was filtered and the filtrate was reduced to ca. 10 cm^3. A crystalline compound was obtained by slow diffusion of Et_2O vapor into this solution. Yield of the complex $[CdH_2L^1(NO_3)]ClO_4$ (**1**), 75%. Anal. Calc. for ($C_{21}H_{25}CdClN_3O_{11}$): C, 39.10; H, 4.10; N, 6.50. Found: C, 38.78; H, 3.89; N, 3.76%. IR (KBr, cm^{-1}): 1682 (νC=N Schiff base), 1456 (νC=C), 3445 (νOH), 1384 (νN-O), 1111 (νClO_4). ^{1}HNMR (DMSO, ppm, 300 MHz): δ 2.09 (m, 2H, 1-H), 2.55 (t, 4H, 2-H), 2.67(t, 4H, 3-H), 3.05 (t, 4H, 4-H), 6.97(2H), 7.14(4H), 7.41(2H), 8.63 (s, 2H, Schiff base). ^{13}CNMR (DMSO, ppm, 300 MHz): δ60.65 (C-1), 63.71 (C-2), 64.78 (C-3), 68.75(C-4). 112.69, 120.54, 126.66 and 131.94, (Aromatic Rings), 156.67 (Schiff base).

2.3.4. Preparation of complex $[Mn(H_2L^1)](ClO_4)_2$ (2)

Compound **2** was prepared in an analogous method to **1**. Yield of the complex $[Mn(H_2L^1)](ClO_4)_2$ (**2**), 66%. Anal. Calc. for ($C_{21}H_{26}MnCl_2N_2O_{12}$): C, 40.38; H, 4.16; N, 4.48. Found: C, 39.86; H, 4.03; N, 4.18%. IR (KBr, cm^{-1}): 1643 (νC=N Schiff base), 1604 (νC=C), 1106 (νClO_4), 3431 (νOH).

2.3.6. Preparation of complex $[Ni(H_2L^1)](ClO_4)$ (3)

Compound **3** was prepared in an analogous method to **1**. Yield of the complex $[Ni(H_2L^1)(NO_3)]ClO_4$ (**3**), 67%. Anal. Calc. for ($C_{21}H_{26}NiCl_2N_2O_{12}$): C, 40.12; H, 4.14; N, 4.45. Found: C, 39.79; H, 4.06; N, 4.29%. IR (KBr, cm^{-1}): 1652 (νC=N Schiff base), 1598 (νC=C), 1108 (νClO_4), 3420 (νOH).

2.3.6. Preparation of complex $[Cu(H_2L^1)](ClO_4)_2$ (4)

Compound **4** was prepared in an analogous method to **1**. Yield of the complex $[Cu(H_2L^1)(NO_3)]ClO_4$ (**4**), 67%. Anal. Calc. for ($C_{21}H_{26}CuCl_2N_2O_{12}$): C, 39.84; H, 4.10; N, 4.42.

Found: C, 39.28; H, 4.02; N, 4.31%. IR (KBr, cm^{-1}): 1639 (νC=N Schiff base), 1599 (νC=C), 1068 (νClO_4), 3535 (νOH).

3. Result and discussion

3.1. Synthesis and characterization

All complexes **1-4** were synthesized by the reaction of Schiff base H_2L^1 Cd(II), Mn(II), Ni(II) and Cu(II) metal ions, respectively (Schemes 1). The Schiff base ligand was characterized by IR, elemental analysis and ^1H,^{13}CNMR and the resulting complexes were characterized by IR and elemental analysis in all cases and ^1H,^{13}CNMR and X-ray crystal structure in the case of Cd(II). The complexes are quite stable in air and can be stored in a desiccator for long periods of time without decomposition.

3.2. IR Study

Condensation of all the primary amino group is confirmed by the lack of N–H stretching bands in the IR reign (3150–3450 cm^{-1}) and the presence of strong C=N (Schiff base) stretching bands at 1638 cm^{-1} for Schiff base ligands H_2L^1. Also the stretching bands of C=N (imine) complexes **1-4** have been observed at 1649, 1643, 1652 and 1639 cm^{-1} respectively (Fig. 1). As it can be seen the bands related to the imine groups in Schiff bases have been shifted in the IR for all complexes and it can show that the donor atoms in ligands have been coordinated to the metal ions and the complexes have been formed. The bands observed at 1363 and 1674 cm^{-1} in the IR of complex **1** can be assigned to the asymmetric bidentate nitrate group. A broad intense band at ca. 1105 cm^{-1} due to ClO_4^- shows no splitting, indicating the absence of coordination of ClO_4^{-1}

for all complexes. The NMR studies of Schiff base ligands and synthesized complexes are completely consistent with their formulation.

3.3. X-ray crystal structure analysis

As mentioned previously, the Cd(II) complex of ligand H_2L^1 was prepared and the fine and suitable crystals of **1** were obtained by slow diffusion of diethyl ether vapor into a methanol-ethanol solution of the corresponding complex. A summary of the details of the crystal data, data collection and refinement details is given in Table 1. ORTEP diagram of the molecular structure of **1** is shown in Fig. 2. with the atomic numbering. Selected bond lengths and bond angles are listed in Table 2. The Cd–O (O aldehyde and hydroxy) and Cd–N bond lengths (N imine) are within the normal range. The crystal structure of **1** consists of a cadmium metal center coordinated to two nitrogen and four oxygen donor atoms from Schiff base ligand and two oxygens from the nitrate ion. Eight-coordinate systems are found to adopt a cube, a square antiprism or a triangulated dodecahedron (TD) arrangement [25]. On the basis of the observed angles, (N–Cd–N, N–Cd–O and O–Cd–O), complex **1** adopts a slightly distorted TD geometry [25]. The two Cd–O distances [2.430 and 2.402 Å] in the cadmium complex differ substantially, one being long and the other short. The Cd–O distance for the bidentate nitrate group (av. 2.531 Å) is comparable with the calculated mean value [2.416(144) Å] observed in 28 eight-coordinate Cd(II) complexes obtained from the Cambridge Structural Database [26], navigated using CONQUEST [27], thus both oxygen atoms are coordinated to the central cadmium ion. The Cd–N distances are in the normal range [from 2.246(3) to 2.262(3) Å]. Both $Cd–N_{imine}$ bond lengths are shorter (2.246(3) and 2.262(3) Å) than Cd–O bond lengths. The bond distance between the atom Cd(1) and the O(1), 2.499(3) Å and O(2), 2.647 (2) Å is longer than the bond distance between Cd(1) and O(3), 2.430(2) Å and O(4) 2.457 (2) Å. Also, The longest and shortest bond angles are related to O(6)–Cd–O(1), 153.82º and O(7)–Cd–N(1), 50.93 º respectively. In addition, the longest angles between the N_{imine} and oxygen atoms are related to theN(2)–Cd(1)–O(2) and N(1)– Cd(1)–O(6), 139.44 º and 126.75 º respectively. The X-ray crystal structure showed that there are five rings that three of them are six membered and both of them are five membered. The five membered rings almost are *ci*s together, there are no manly different between the bond angles in all rings. The bond angles in six membered rings are, 77.00º, 72.45º 68.23º for N(2)–Cd(1)–O(3), O(2)–Cd(1)–O(3) and O(2)–Cd(1)–N(1) respectively. As same as, the bond angles in five member rings are 71.82º and 73.53º for O(1)–Cd(1)–N(1) and O(4)–Cd(1)–N(2) respectively.

3.4. NMR spectra

The NMR spectra of the cadmium complex confirm the formation of a fully condensed Schiff base ligand and cadmium complex. The appeared peaks in ^{1}H and ^{13}CNMR of Schiff base ligand show that the ligand has been synthesized and is pure and the comparison of shifted peaks in Cd(II) complex spectrum (^{1}H and ^{13}CNMR) with appeared peaks in the HMR spectrum of ligand show the donor atoms (N_2O_4) have been coordinated to the Cd(II) metal ion. The ^{13}CNMR of the ligand and complex shows five distinct methylene carbons in the aliphatic region. It is interesting that the ^{1}HNMR spectrum of this complex shows two kinds of protons for the methylene group.

4. Conclusion

The synthesis and characterization of a new Schiff base ligand and a number of M(II) complexes (M= Cd, Mn, Ni, Cu) are reported. The NMR of ligand and Cd(II) complex were studied; also the molecular structure of complex **1** has been determined by single crystal X-ray diffraction and has been shown dodecahedron coordinated Cd(II) ion.

Acknowledgment

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Appendix A. Supplementary data

CCDC 1463846 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ contains/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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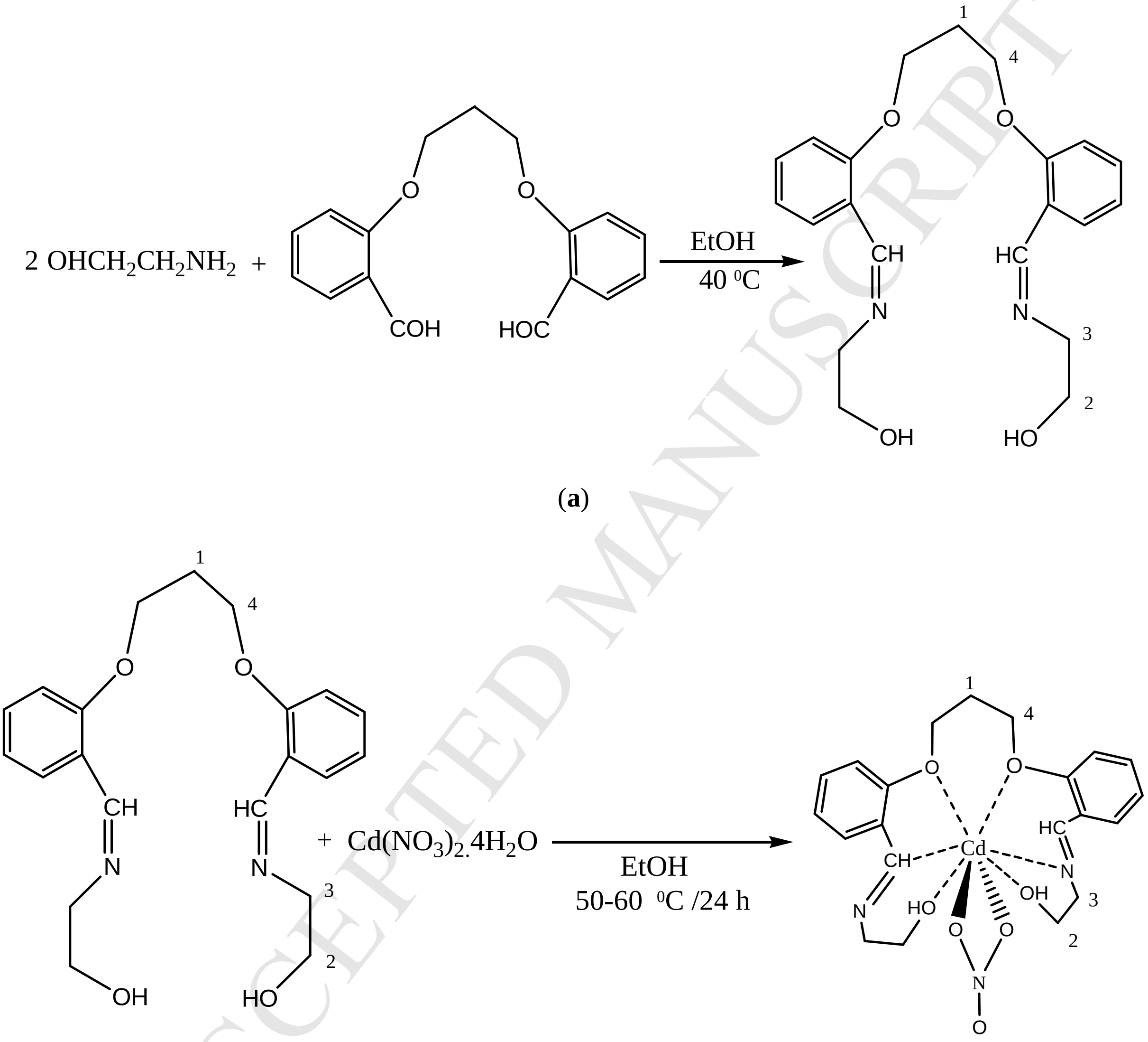
Table 1. Crystal data and structure refinement for compound **1**

Empirical formula	$C_{21}H_{25}CdClN_3O_{11}$
Formula weight	643.30
Temperature (K)	120
Wavelength(A)	0.71073
Crystal system	Triclinic
Space group	p-1
Unit cell dimensions	
a (Å)	9.829(2)
b (Å)	11.411 (2)
c (Å)	13.489 (3)
α	95.15 (3)
β	102.24 (3)
γ	113.62 (3)
V (A^3)	1328.6(6)
Z	2
D_{calc} (Mg/m^3)	1.608
F(000)	650
Crystal size (mm^3)	0.3x 0.25 x 0.17
θ range for data collection (°)	2.33–29.17°
Index ranges	-13<=h<=12, -15<=k<=15, 0<=l<=18
Reflections collected	7109
Independent reflections	4300
R_i	0.016
Absorption correction	Numerical
Max. and min. transmission	0.410 and 0.223
Refinement method	Least-squares matrix: full on F^2
restraints	0
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.0942
R indices (all data)	R1 = 0.0501, wR2 = 0.0972
Largest diff. peak and hole (e.$Å^{-3}$)	1.785 and -1.045

Table 2. Selected bond lengths *(Å)* and bond angles *(°)* for compound **1**

Bond lenghts (Å)	**1**
N1—Cd1	2.262 (3)
N2—Cd1	2.246 (3)
O1—Cd1	2.499 (3)
O2—Cd1	2.647 (2)
O3—Cd1	2.430 (2)
O4—Cd1	2.457 (2)
O5—Cd1	2.402 (2)
O6—Cd1	2.607 (3)
Bond angle (°)	
N1—Cd1—N2	152.24 (10)
N1—Cd1—O5	92.79(10)
N2—Cd1—O5	92.53(11)
N1—Cd1—O3	120.44(9)
N2—Cd1—O3	77.00(9)
O5—Cd1—O3	126.05(8)
N1—Cd1—O4	80.90(9)
N2—Cd1—O4	73.53(10)
O5—Cd1—O4	78.43(9)
O3—Cd1—O4	142.41(8)
N1—Cd1—O2	68.23(8)
N2—Cd1—O2	139.44(9)
O5—Cd1—O2	84.62(8)
O3—Cd1—O2	72.45(7)
O4—Cd1—O2	143.89(8)
N1—Cd1—O1	71.82(9)
N2—Cd1—O1	92.72(11)
O5—Cd1—O1	154.84(8)
O3—Cd1—O1	79.09(8)
O4—Cd1—O1	79.52(10)
O2—Cd1—O1	106.74(8)
O6—Cd1—O1	153.82(8)
O6—Cd1 —O2	70.54(8)
O6—Cd1—N1	126.75(9)
O6—Cd1—O4	118.66(9)
N2—Cd1—O6	76.42(11)
O5—Cd1—O6	50.93 (8)
O3—Cd1—O6	75.30(8)



(**a**)

(**b**)

Scheme 1. Syntheses of the Schiff base ligand H_2L^1 (**a**) and related complex **1** and NMR numbering (**b**)

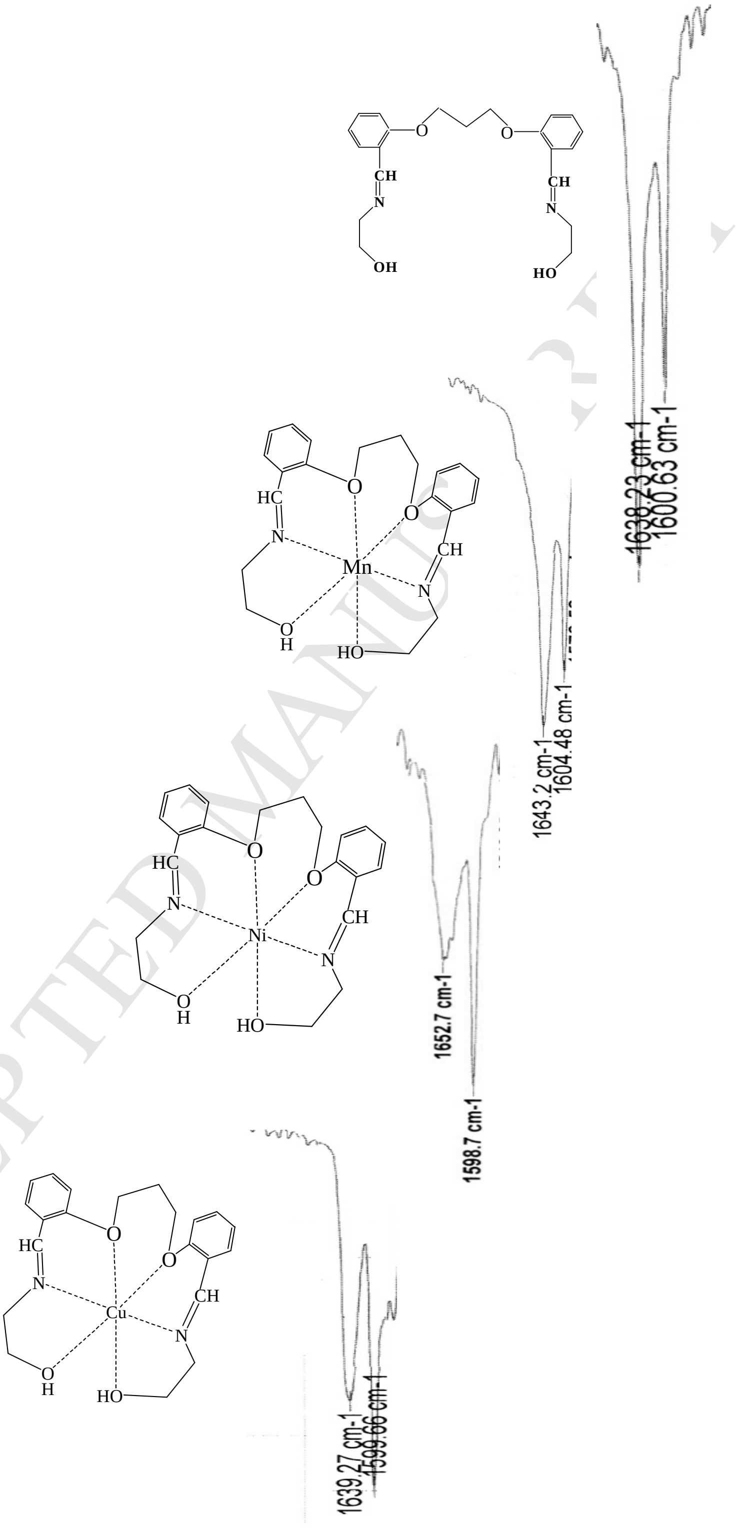
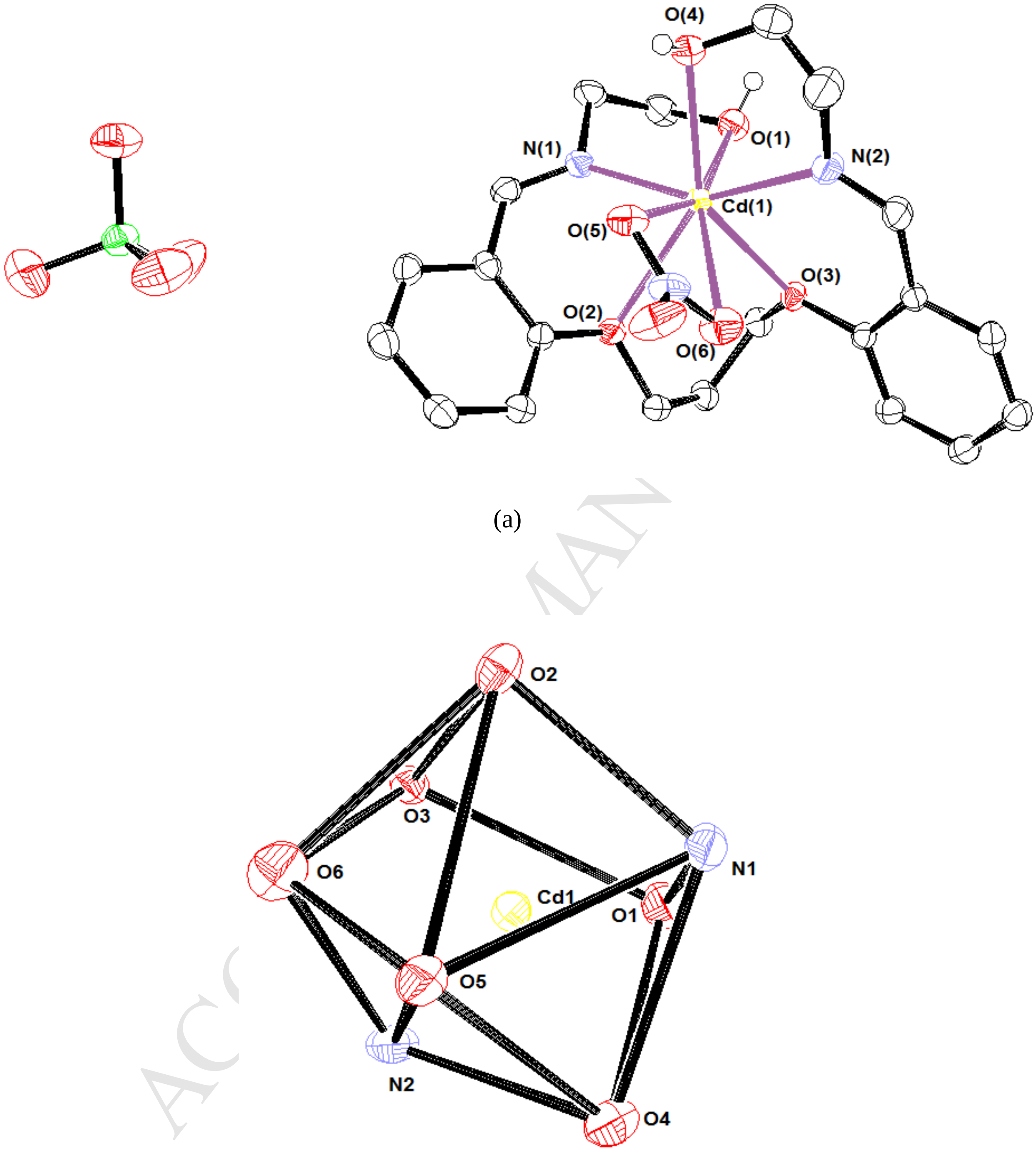


Fig. 1. The comparison of the appeared CH=N band of ligand and synthesized complexes in IR spectra



(a)

(b)

Fig. 2. X-ray crystal structure of complex **1**, (a), and its view of the dodecahedron coordination polyhedron (b).

Highlights

1- Synthesis and characterization a new Schiff base ligand
2- Synthesis and characterization of some new complexes
3- Synthesis and X-ray analysis data of a new dodecahedron Cd(II) complex
4- NMR and IR study of a new Schiff base complex