

Chelation activity of N'_1, N'_6 -bis((*E*)-3,4-dihydroxybenzylidene)adipohydrazide towards some transition metal ions

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ABSTRACT

New chelating agent, N'_1, N'_6 -bis((*E*)-3,4-dihydroxybenzylidene)adipohydrazide (DBAH) was synthesized and its crystal structure was analyzed by X-ray single crystal diffractometer. Homometallic complexes of Zr(IV), Co(II), Ni(II), Cu(II), Cd(II) and heterometallic complex of Co(II)/Zn(II) or Co(II)/Zn(II)/Cd(II) have been synthesized and characterized by spectroscopic and physicochemical methods. The data confirms the formation of bi- and tetra-metallic complexes. The ligand behaves as a neutral tetradentate in the Co(II) and Ni(II) complexes; tetranegative tetradentate in Zr(IV) and Cd(II) complexes and binegative octadentate in $[\text{Co}_2\text{Zn}_2(\text{DBAH})\text{Cl}_6]$ and $[\text{Co}_2\text{ZnCd}(\text{DBAH-4H})(\text{H}_2\text{O})_4\text{Cl}_4]\cdot\text{H}_2\text{O}$. A tetrahedral structure was proposed for the Ni(II), Zr(IV) and Co(II)/Zn(II) complexes; square-planar for the Cu(II) complex and octahedral geometry for the Co(II) complex. The ESR spectrum confirms the proposed structure of the Cu(II) complex. The thermal analyses confirm the stability of these complexes in the range 275-418 °C. The molecular modeling of $[\text{Co}_2\text{Zn}_2(\text{DBAH})\text{Cl}_6]$ was drawn and its parameters were calculated.

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1. Introduction

Presently, much effort was being devoted to the synthesis and screening for biological activities of different metal complexes in medicinal chemistry. Hydrazone complexes have pharmacological applications [1]. The complexes may bind and cleave the deoxyribose nucleic acid (DNA) strands via different mechanisms under different physiological conditions [2]. Tridentate hydrazones derived from heterocyclic aldehydes/ketones and of methyl pyruvate showed coordination ability towards metal ions [3]. The CT-DNA and bovine serum albumin binding ability of a series of isonicotinoyl hydrazones and their Cu(II) complexes indicated good binding to DNA and serum albumins (BSA). The compounds have cytotoxicity on A549 human lung cancer cell [4]. Moreover, series of pyridazinyl hydrazones inhibit *tyrosine hydroxylase* and *dopamine hydroxylase* in vivo and in vitro [5]. Some hydrazones have been evaluated as potential oral iron-chelating drugs for genetic disorders such as thalassemia [6]. The X-ray crystal structure of the ferric complex of pyridoxal isonicotinoyl hydrazone showed its acting as tridentate planar chelating agent with chloride ions or water molecules occupied the remaining sites [7]. On the other hand, salicylaldehyde benzoyl hydrazone has unusual potent inhibitor of DNA synthesis and cell growth in a variety of human and rodent cell lines [8].

Metal complexes of Co(II), Cu(II), Ni(II), Zn(II), Cd(II), Pd(II), UO₂(II) and Ce(III) with chromone-3-benzoylhydrazone and chromone-3-acetylhydrazone were prepared and characterized. Their IR spectra indicate the bidentate nature of the ligands. Electronic spectra and magnetic moments prove the octahedral structure for Co, Ni and Mn complexes and a distorted octahedral structure for Cu complex [9]. Binuclear complexes of oxalyl bis(diacetylmonoximehydrazone) have octahedral geometry for VO(II), tetrahedral for Zn(II) and square planar for Co(II), Ni(II) and Cu(II) complexes [10]. 2,5-Dihydroxyacetophenone isonicotinoylhydrazone and its Cr(III), Mn(III), Fe(III), VO(II), Zr(IV) and UO₂(II) complexes were synthesized. It behaves as a flexidentate ligand and commonly coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. Most of the compounds were screened for their antimicrobial activity by agar cup-plate method against various organisms and the results have been evaluated [11]. However, a series of mono and binuclear Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), La(III), Ru(III), Hf(IV), ZrO(II) and UO₂(II) complexes of phenylamino dibenzoyl hydrazone were synthesized and characterized [12]. Meanwhile, Cu(II) complexes of succinoyl salicylaldehyde and adipoyl salicylaldehyde dihydrazones have a square-planar geometry.

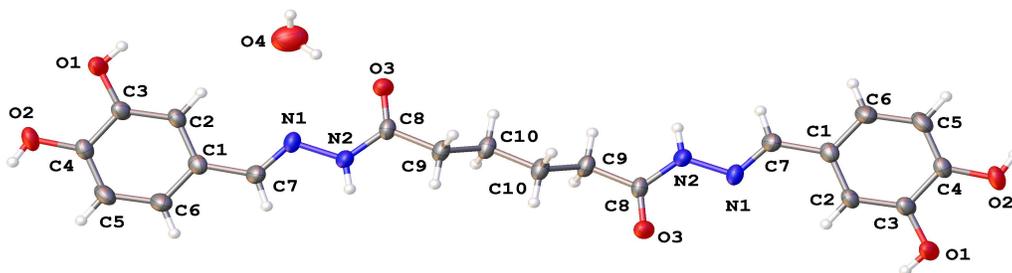


Figure 1. Structure of N',N' -bis((*E*)-3,4-dihydroxybenzylidene)adipohydrazide.

One electron reduction waves were observed at a glassy carbon electrode in DMSO solution [13].

In continuation of our ongoing studies on dihydrazide ligands [14-21], we have synthesized and characterized new metal complexes of Zr(IV), Co(II), Ni(II), Cu(II), and Cd(II) ions with N',N' -bis((*E*)-3,4-dihydroxybenzylidene)adipohydrazide.

2. Experimental

2.1. Materials

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, and ZrCl_4 , diethyl adipate, hydrazine hydrate, 3,4-dihydroxybenzaldehyde, ethanol, diethyl ether and DMSO were obtained from the BDH Chemicals and used as supplied.

2.2. Synthesis of N',N' -bis((*E*)-3,4-dihydroxybenzylidene)adipohydrazide

The reaction between 8.7 g (0.05 mol) of adipic acid dihydrazide (30 mL, EtOH) and 13.8 g (0.1 mol) of 3,4-dihydroxybenzaldehyde, dissolved in 20 mL EtOH, was carried out on a hot plate for 3 h. The yellow precipitate was collected by filtration, recrystallized from ethanol and dried; the yield is 85%. The ligand was characterized by spectral studies and elemental analysis. Single crystals of DBAH was grown by slow evaporation method and solved. Color: Yellow. Yield: 85 %. M.p.: 240-242 °C. FT-IR (KBr, ν , cm^{-1}): 3267 (OH aromatic), 3201 (NH), 1644 (C=O), 1530 (amidic group). ^1H NMR (200 MHz, DMSO- d_6 , δ , ppm): 1.645 (m, 4H, CH_2CH_2), 2.632 (m, 4H, COCH_2CH_2), 4.393 (s, 2H, N=CH), 7.958-6.938 (m, 6H, Ar-H), 9.288 (s, 4H, OH), 10.983 (s, 1H, NH), 11.124 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO- d_6 , δ , ppm): 173.93, 168.27 (C=O), 147.82, 146.42 (C=N), 125.89 (C-O), 25.06 (CH_2). MS (EI, m/z (%)): 415.2 (M+1, 100). Anal. calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_6 \cdot \text{H}_2\text{O}$: C, 55.55; H, 5.59; N, 12.96. Found: C, 55.20; H, 5.74; N, 12.99%. UV/Vis (DMSO, λ , cm^{-1}): 33900 ($\pi \rightarrow \pi^*$), 31055 ($n \rightarrow \pi^*$). Λ_m ($\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$): 4.5.

2.3. Synthesis of complexes

The metal complexes were synthesized by the reaction of the calculated amounts (2:1 or 4:1 ratio; M:L) of the metal salt and DBAH in ethanol solution. The mixture was heated under reflux on a water bath for 6-8 h. In the preparation of Zr(IV) complex, the medium solution is $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ (1:1, v:v). The precipitate thus formed was filtered off, washed with hot water, hot ethanol and diethyl ether and finally dried in a vacuum desiccator over silica gel. The mixed metal (Co/Zn) complex was prepared by adding 0.255 g of the ligand (0.01 mol) in 30 mL ethanol, to a mixture of 0.75 g (0.02 mol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.33 g (0.02 mol) $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, in 30 mL ethanol and heating for 5 h.

2.4. Analysis and equipment

Elemental analysis of DBAH and its complexes was determined at the Microanalytical Unit (Varian Micro V1.5.8, CHNS Mode, 15073036) of Kuwait University, Kuwait. The metal content was determined using ICP-OES GBC Quantum Sequential at Kuwait University, Kuwait. The FT-IR spectra were recorded on a FT/IR-6300 type A (400-4000 cm^{-1}). The electronic spectra, in Nujol, were recorded on Cary 5 UV-Vis Spectrophotometer, Varian (200-900 nm). The NMR spectrum of the ligand was recorded in DMSO- d_6 , on a Bruker WP 200 SY spectrometer (200 MHz) at room temperature using tetramethylsilane (TMS) as an external standard. The mass spectra were recorded on a GC-MS Thermo-DFS (BG_FAB) mass spectrometer. The ESR spectrum of the Cu(II) complex was recorded on a Bruker EMX Spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW and the modulation amplitude at 4 Gauss. The low field signal was obtained after four scans with a 10-fold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature (25 °C). The magnetic measurements were carried out on a Johnson-Matthey magnetic balance, UK. Thermogravimetric analysis (10-850 °C) was measured on a Shimadzu TGA-60; the nitrogen flow and heating rate were 50 mL/min and 10 °C/min. The X-ray single crystal diffraction data of the ligand were collected on a Rigaku R-Axis or Bruker X8-Prospector Rapid diffractometer using filtered $\text{MoK}\alpha$ radiation. The structure was solved by the direct methods and expanded using Fourier techniques at Kuwait University, Kuwait.

The molecular geometry of the Co(II)/Zn(II) complex are first optimized at molecular mechanics (MM+) level using HyperChem 7.5 program. Semi empirical method PM3 is then used for optimizing the full geometry of the system using Polak-Ribiere (conjugate gradient) algorithm and Unrestricted Hartee-Fock (UHF) is employed keeping RMS gradient of 0.01 kcal/Å mol.

3. Results and discussion

3.1. Single crystal analysis of DBAH

Clear light colorless block crystals with formula $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_8$ of the title compound have $\text{P2}_1/\text{c}$ space group and monoclinic crystal system (Table 1-3 and Figure 1). The O2-C4 and O1-C3 bond distances, 1.349(4) and 1.365(4) Å, are in the range of single C-O bond while the O3-C8 (1.228(4) Å) is consistent with a formal double C=O bond. Also, the bond distance of C7-N1 is 1.453(5) Å due to the azomethine group. The distance of N1-N2 is 1.388(4) Å, consisting with single bond (Table 2).

Table 1. Crystal data and structure refinement for *N'*₁,*N'*₆-bis(*E*)-3,4-dihydroxybenzylidene)adipohydrazide.

Empirical formula	C ₂₀ H ₂₆ N ₄ O ₈
Formula weight	450.45
Temperature (K)	296.(2)
Crystal system	Monoclinic
Space group	P2 ₁ /c
a (Å)	11.4582(9)
b (Å)	6.4854(5)
c (Å)	14.0935(11)
β (°)	93.889(6)
Volume (Å ³)	1044.89(14)
Z	2
ρ _{calc} (g/cm ³)	1.432
μ (mm ⁻¹)	0.945
F(000)	476.0
Crystal size (mm ³)	0.180 × 0.140 × 0.040
Radiation	Cu-Kα (λ = 1.54178 Å)
2θ range for data collection (°)	7.74 to 133.28
Index ranges	-13 ≤ h ≤ 7, -6 ≤ k ≤ 7, -16 ≤ l ≤ 16
Reflections collected	5605
Independent reflections	1804 [R _{int} = 0.0567]
Data/restraints/parameters	1804/4/153
Goodness-of-fit on F ²	1.172
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0632, wR ₂ = 0.1649
Final R indexes [all data]	R ₁ = 0.1091, wR ₂ = 0.1862
Largest diff. peak/hole / e.Å ⁻³	0.26/-0.48

Table 2. Bond lengths for *N'*₁,*N'*₆-bis(*E*)-3,4-dihydroxybenzylidene)adipohydrazide.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
C1	C6	1.390(5)	C8	N2	1.339(4)
C1	C2	1.397(5)	C8	C9	1.510(4)
C1	C7	1.453(5)	C4	O2	1.349(4)
C7	N1	1.272(4)	C4	C5	1.369(5)
C3	O1	1.365(4)	C6	C5	1.385(5)
C3	C2	1.376(5)	C10	C9	1.524(5)
C3	C4	1.409(5)	C10	C10 ¹	1.526(6)
C8	O3	1.228(4)	N2	N1	1.388(4)

¹ 2-x, -y, 1-z.**Table 3.** Bond angles for *N'*₁,*N'*₆-bis(*E*)-3,4-dihydroxybenzylidene)adipohydrazide.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C6	C1	C2	118.6(3)	O2	C4	C5	124.1(3)
C6	C1	C7	118.3(3)	O2	C4	C3	116.6(3)
C2	C1	C7	123.0(3)	C5	C4	C3	119.4(3)
N1	C7	C1	123.4(3)	C3	C2	C1	120.6(3)
O1	C3	C2	123.4(3)	C5	C6	C1	120.8(4)
O1	C3	C4	116.6(3)	C4	C5	C6	120.5(3)
C2	C3	C4	120.0(3)	C9	C10	C10 ¹	111.6(4)
O3	C8	N2	121.9(3)	C8	C9	C10	113.6(3)
O3	C8	C9	122.7(3)	C8	N2	N1	120.5(3)
N2	C8	C9	115.4(3)	C7	N1	N2	114.4(3)

¹ 2-x, -y, 1-z.

3.2. General information

The color, melting points and elemental analyses of DBAH and its complexes are compiled in Table 4. The data agree with the formation of bi- and tetra-nuclear complexes having the formulae [Co₂(DBAH)(H₂O)₄Cl₄].2H₂O, [Ni₂(DBAH)(H₂O)₄Cl₄].2H₂O, [Cu₄(DBAH-6H)(H₂O)₄(OAc)₂].2H₂O, [Cd₂(DBAH-4H)(H₂O)₄], [Zr₂(DBAH-4H)Cl₄].6H₂O, [Co₂ZnCd(DBAH-4H)(H₂O)₄Cl₄].H₂O and [Co₂Zn₂(DBAH)Cl₈]. The complexes, [Ni₂(DBAH)(H₂O)₄Cl₄].2H₂O and [Zr₂(DBAH-4H)Cl₄].6H₂O were found insoluble in KOH indicating the involvement of the four OH in coordination which prevent the formation of potassium salt. The other complexes were soluble in KOH due to the replacement of OH's by potassium.

All complexes have high melting points (> 330 °C), insoluble in most solvents and partially soluble in DMSO. The insolubility of all complexes in different solvents prevents the measurements of molar conductance or NMR and no growing for single crystals. The Cd(II) complex has light green color due to charge transfer. The thermal analyses indicate high stability for some complexes; a behavior consistent with polymeric nature of the complexes.

3.3. IR and NMR spectra

The FT-IR spectral bands of DBAH and its complexes with their assignments are presented in Table 5. The ligand spectrum showed bands at 3267, 3201, 1644 and 1530 cm⁻¹ attributed to the stretching vibrations of OH, NH, C=O and C=N, respectively [15,16]. Its ¹H NMR spectrum showed signals at δ 9.288 (s, 4H); 11.124, 10.983 (s, 1H); 7.958-6.938 (m, 6H); 2.632 (m, 4H); 1.645 (m, 4H); 4.393 (s, 2H) ppm due to the OH, NH, aromatic CH's, COH₂CH₂, CH₂CH₂ and NCH protons. ¹³C NMR spectrum showed peaks at 173.93, 173.88 ppm (C=O); 147.82, 146.42 (C=N); 125.89 (C-O) and 25.06 (CH₂). The mass spectrum of DBAH has m/z = 415.2 (Calcd. 432.444). The calculated molecular weight contains H₂O which confirmed from X-ray crystallography.

In [Co₂(DBAH)(H₂O)₄Cl₄].2H₂O and [Ni₂(DBAH)(H₂O)₄Cl₄].2H₂O, the ν(C=O) and ν(C=N) bands are shifted to 1636; 1621 cm⁻¹ and 1485; 1511 cm⁻¹ indicating chelation through O and N donors (they exist on opposite sides). Figure 2 indicates the chelation mode in [Co₂(DBAH)(H₂O)₄Cl₄].2H₂O. Also, evidence is the presence of new bands at 534 and 431 cm⁻¹ due to ν(M-O) and ν(M-N) [17].

Table 4. Elemental analysis and some properties of DBAH and its complexes.

Compound, empirical formula	M.W. (Found, m/e)	Color	M.p. (°C)	C % Calcd. (Found)	H % Calcd. (Found)	N % Calcd. (Found)	M % Calcd. (Found)
DBAH.H ₂ O*	432.44	Yellow	240-242	55.55	5.59	12.96	-
C ₂₀ H ₂₄ N ₄ O ₇	(415.20)			(55.20)	(5.74)	(12.99)	
[Ni ₂ (DBAH)(H ₂ O) ₄ Cl ₄].2H ₂ O	781.828	Brown	> 325	30.73	4.38	7.17	15.02
C ₂₀ H ₃₄ N ₄ O ₁₂ Cl ₄ Ni ₂	(786.0)			(30.31)	(4.18)	(7.16)	(15.27)
[Co ₂ (DBAH)(H ₂ O) ₄ Cl ₄].2H ₂ O	782.232	Brown	> 320	30.71	4.38	7.16	15.07
C ₂₀ H ₃₄ N ₄ O ₁₂ Co ₂ Cl ₄	(803.9)			(30.42)	(3.96)	(7.08)	(15.34)
[Zr ₂ (DBAH-4H)Cl ₄].6H ₂ O	865.096	Orange	> 320	28.51	3.59	6.65	-
C ₂₀ H ₃₀ N ₄ O ₁₂ Zr ₂ Cl ₄				(27.80)	(4.03)	(6.82)	
[Cd ₂ (DBAH-4H)(H ₂ O) ₄]	707.282	Pale green	> 340	33.96	3.71	7.92	31.79
C ₂₀ H ₂₆ N ₄ O ₁₀ Cd ₂				(33.81)	(3.88)	(8.05)	(31.90)
[Co ₂ Zn ₂ (DBAH)Cl ₆]	946.664	Pale brown	> 320	25.38	2.34	5.92	Co = 12.45
C ₂₀ H ₂₂ N ₄ O ₆ Co ₂ Zn ₂ Cl ₆				(25.70)	(2.48)	(6.23)	(12.82)
[Cu ₄ (DBAH-6H)(H ₂ O) ₄ (OAc) ₂].2H ₂ O	888.73	Dark brown	> 320	32.44	3.86	6.30	28.60
C ₂₄ H ₃₆ N ₄ O ₁₇ Cu ₄	(663.4)			(32.17)	(3.88)	(6.52)	(28.20)
[Co ₂ ZnCd(DBAH-4H)(H ₂ O) ₄ Cl ₄].H ₂ O	937.944	Dark brown	> 320	25.61	3.01	5.97	-
C ₂₀ H ₂₂ N ₄ O ₆ Co ₂ Zn ₂ Cl ₆	(803.6)			(25.62)	(3.06)	(5.62)	

* The values of CHN of DBAH containing the values of one water molecule.

Table 5. FT-IR spectral data of DBAH and its metal complexes.

Compound	v(OH)	v(N-H)	v(C=O)	v(C=N)	v(C=N)**	v(C-O)	v(M-O)	v(M-N)
DBAH	3267 (w)	3201 (w)	1644 (s)	1530	-	-	-	-
[Ni ₂ (DBAH)(H ₂ O) ₂ Cl ₄].4H ₂ O	3350 (br)*	3255 (br)	1636 (m)	1586 (m)	-	-	534 (br)	431
[Cu ₄ (DBAH-6H)(H ₂ O) ₄ (OAc) ₂].2H ₂ O	3420 (br)*	-	-	1573	1530 (sh)	1048 (w)	461 (w)	-
[Co ₂ (DBAH)(H ₂ O) ₄ Cl ₄].2H ₂ O	3550 (w)*, 3385 (br)*	3251 (br)	1621 (m)	1511 (m)	-	-	535 (w)	430
[Zr ₂ (DBAH-4H)Cl ₄].6H ₂ O	3395 (br)*	3233 (br)	1640 (m)	1586 (m)	-	-	501 (br)	-
[Cd ₂ (DBAH-4H)(H ₂ O) ₄]	3421 (br)*	3240 (br)	1644 (m)	1545	-	-	542 (w)	-
[Co ₂ Zn ₂ (DBAH)Cl ₆]	3420 (br)*	3267 (br)	1620 (m)	1581	-	-	538 (br)	-
[Co ₂ ZnCd(DBAH-H)(H ₂ O) ₄ Cl ₄].H ₂ O	3423 (br)*	3246 (br)	1645 (w)	1580 (s)	1490 (s)	1175 (w)	-	-

* Hydrated or coordinated water.

** New azomethine group due to enolization of NHC=O.

The v(OH) band appears broad due to overlapping between hydrated and coordinated water. DBAH coordinates through two C=O and two C=N groups as a neutral tetradentate.

The second mode is depicted in [Cu₄(DBAH-6H)(H₂O)₄(OAc)₂].2H₂O, [Zr₂(DBAH-4H)Cl₄].6H₂O (Figure 2) and [Cd₂(DBAH-4H)(H₂O)₄] by complete disappearance of the OH bands (stretching and bending vibrations) indicating the coordination of the four OH groups after deprotonation. The new band at 3350-3550 cm⁻¹ is due to hydrated or coordinated water. In [Cu₄(DBAH-6H)(H₂O)₄(OAc)₂].2H₂O, beside the absence of OH, the v(NH) and v(C=O) bands disappear indicating enolization of the carbonyl group. The v(C=N) band is shifted to lower wavenumber indicating its coordination. Also, the IR spectra of the complexes showed a new band at 461-542 and 420-450 cm⁻¹ due to v(M-O) and v(M-N) as well as a new one at 1338 cm⁻¹ due to δ(OH) of the coordinated water [18].

In [Co₂ZnCd(DBAH-4H)(H₂O)₄Cl₄].H₂O (Figure 2), DBAH acts also as a tetranegative octadentate but with the three metal ions. The coordination sites are two OH, two deprotonated OH, two C=N and two enolic C-O groups. The OH and C=N bands shifted to 3246 and 1580 cm⁻¹; the disappearance of v(NH) and v(C=O) bands with appearance of two new bands at 1490 and 1174 cm⁻¹ corresponding to v(C=N)* and v(C-O) bands [22] and appearance of new band at 3423 cm⁻¹ due to hydrated water. Another support for OH coordination is the appearance of its bending vibration, δ(OH), band at 1366 cm⁻¹ with low intensity and a band at 1338 cm⁻¹ duo to coordinated water.

In the last mode, the ligand acts as a neutral octadentate through 4 OH's, 2 C=N and 2 C=O in [Co₂Zn₂(DBAH)Cl₆]. The v(C=O) and v(C=N) appeared at 1620 and 1581 cm⁻¹ indicating chelation through these groups. Also, the shifts of OH band to 3225 and 3246 cm⁻¹ confirming its coordination. The IR spectra of the complexes showed a new band at 538 and 515 cm⁻¹ due to the v(M-O). The broad bands at ~3360, ~890 and ~540 cm⁻¹ in [Co₂(DBAH)(H₂O)₄Cl₄].2H₂O, [Ni₂(DBAH)(H₂O)₄Cl₄].2H₂O, [Cu₄(DBAH-6H)(H₂O)₄(OAc)₂].2H₂O and [Cd₂(DBAH-4H)(H₂O)₄] are attributed to v(OH), ρ_r(H₂O) and ρ_w(H₂O)

confirming water of coordination [23]; these bands are absent in the other complexes.

3.4. Mass spectra

The FAB-MS of DBAH and some of its complexes showed molecular ion peaks confirming the proposed formulae (Table 4). The mass spectra of DBAH showed molecular ion peak at m/z = 415.2 (base peak) corresponding to C₂₀H₂₂N₄O₆. Another peak at m/z 263.1 with intensity of 13% is due to C₁₄H₁₂O₄N₂.

[Co₂(DBAH)(H₂O)₄Cl₄].2H₂O has molecular weight of m/z 782.3; there is a peak at m/z 803.9 corresponds to its formula with more water molecule. Its base peak is found at m/z 176.1 after several peaks at m/z 566.5, 482.3, 413.3 and 329.3. The mass spectra of [Ni₂(DBAH)(H₂O)₄Cl₄].2H₂O exhibits the molecular ion peak at m/z 786.0 (Mol. wt. = 782.23) and different peaks containing the base peak at m/z 176.1. These stoichiometries are further supported by the elemental data which are in close agreement with the value calculated from molecular formula.

3.5. Electronic and magnetic studies

The magnetic moment values and the electronic spectral bands of the complexes, in Nujol, are presented in Table 6. The absorption spectrum of DBAH showed the π → π* and n → π* bands at 33900 and 31055 cm⁻¹.

The electronic spectrum of [Ni₂(DBAH)(H₂O)₄Cl₄].2H₂O showed a band at 22220 cm⁻¹ attributed to the ³A_{2g} → ³T_{2g} transition in an octahedral geometry [24]. An additional broad band centered at 27855 cm⁻¹ is due to a charge transfer. The ligand field parameters (Dq = 1805 cm⁻¹, B = 429.8 cm⁻¹ and β = 0.46) are further support for the proposed geometry. The lower value of β indicates more covalency.

The electronic spectrum of [Co₂(DBAH)(H₂O)₄Cl₄].2H₂O showed bands at 16340 and 14790 cm⁻¹ attributed to ⁴T_{1g} → ⁴A_{2g} (v₂) and ⁴T_{1g} → ⁴T_{1g} (P) (v₃). The bands are similar to those reported for octahedral complexes [25]. The ligand field parameters (B, β and Dq) are calculated and are listed in Table 6.

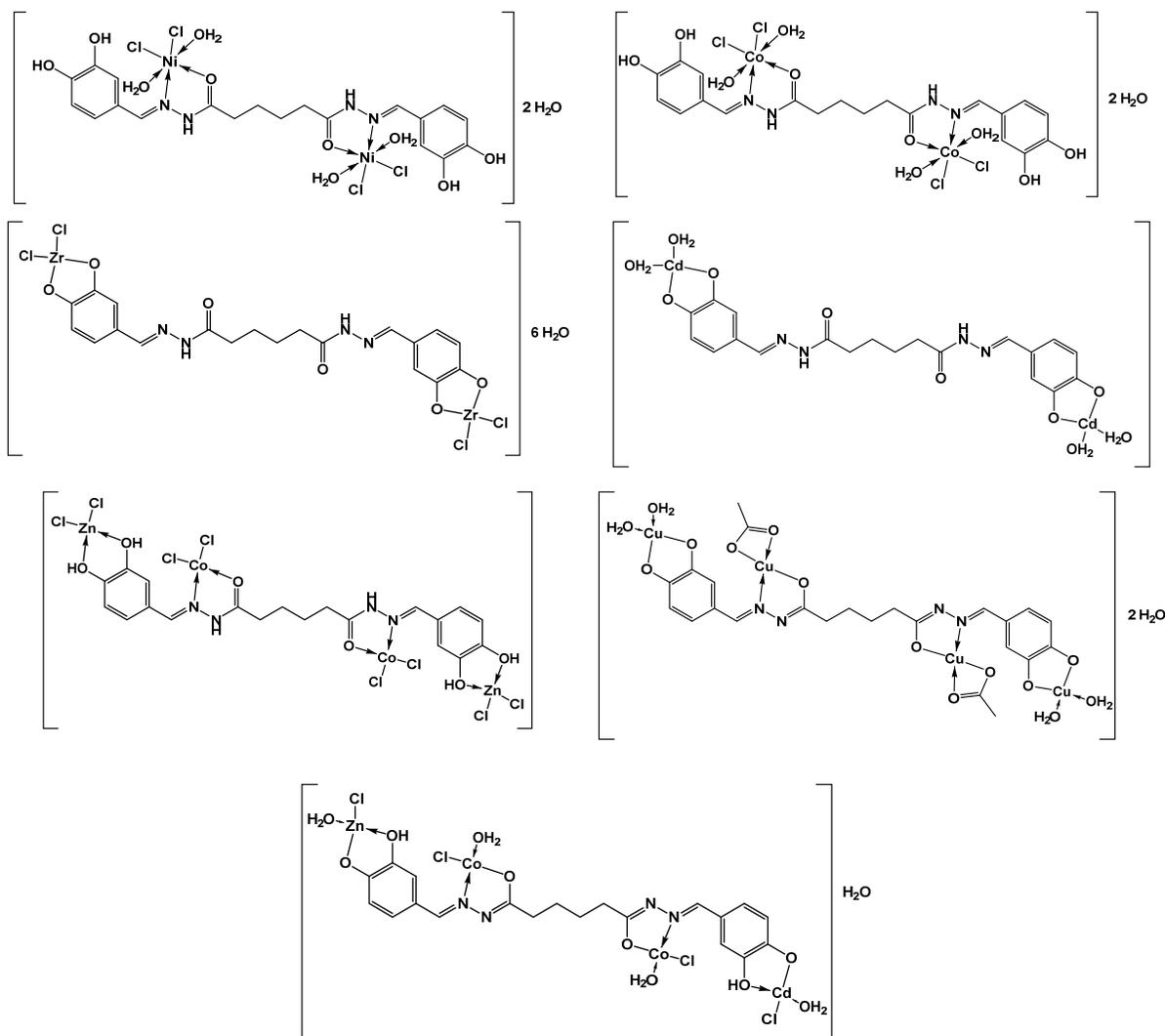


Figure 2. Suggested molecular structure for the prepared compounds.

The values agree fairly well with those reported for octahedral Co(II) complexes. Considerable reduction in the B value from 971 to 700 cm^{-1} and β (from unity to 0.72) indicates the covalent character of L-M bond.

The magnetic moment of the mixed metal complex, $[\text{Co}_2\text{Zn}_2(\text{DBAH})\text{Cl}_8]$ measured as 4.15 B.M.; the value lies within those reported for tetrahedral Co(II) complexes [26]. Evidence is its electronic spectrum which showed one band at 15625 cm^{-1} due to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ in a tetrahedral structure [26]. Its ligand field parameters are given in Table 6.

The spectra of square-planar Cu(II) complexes have three spin allowed transitions [27]. The electronic spectrum of $[\text{Cu}_4(\text{DBAH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$ exhibits one band with maximum at 18500 cm^{-1} assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ in a square-planar geometry [28,29]. The band position and the magnetic moment (2.04 B.M.) are consistent with this geometry.

3.6. ESR spectrum of $[\text{Cu}_4(\text{DBAH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$

The ESR spectrum of $[\text{Cu}_4(\text{DBAH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$ showed axial symmetric g-tensor parameters with $g_{\parallel} > g_{\perp} > 2.0023$ indicating the ground state is $d_{x^2-y^2}$ characteristic of square-planar or octahedral stereochemistry [30]. Its G value is 3.50 suggesting a Cu-Cu exchange interaction (Table 7).

The tendency of A_{\parallel} to decrease with increasing g_{\parallel} is an index of an increase of the tetrahedral distortion in the coordination sphere of copper. In order to quantify the degree of distortion, the f factor ($g_{\parallel}/A_{\parallel}$) obtained from the ESR spectrum was evaluated. The value is 142 (Table 7) indicating a tetrahedral distortion from square-planar geometry. The existence of water molecules or acetate ions may give this distortion. No superhyperfine structure at higher fields excluding any interaction of the nuclear spins of nitrogen ($I = 1$) with the unpaired electron density on Cu(II). The absence of ${}^{14}\text{N}$ hyperfine coupling may be due to a relatively higher tetrahedral distortion [31].

3.7. Thermal analysis

Investigation of the data in Table 8, clearly showed that the complexes are found stable than the ligand. They have stability temperature at 275-418 $^{\circ}\text{C}$. The thermogram of DBAH showed one water molecule in the first step at 72 $^{\circ}\text{C}$ with purity of 98.16%.

The stability temperature of $[\text{Co}_2\text{Zn}_2(\text{DBAH})\text{Cl}_8]$ (358 $^{\circ}\text{C}$) is more than $[\text{Co}_2(\text{DBAH})(\text{H}_2\text{O})_2\text{Cl}_4] \cdot 2\text{H}_2\text{O}$ (310 $^{\circ}\text{C}$) indicating that tetranuclear complex is more stable than dinuclear.

Table 6. Magnetic moments and electronic spectral bands of the compounds.

Compound	μ_{eff} (BM)	Intra ligand and charge transfer, (cm ⁻¹)	d-d transition (cm ⁻¹)	Suggested Structure	Ligand field parameters		
					Dq	B	β
DBAH	-	33900; 31055	-	-	-	-	-
[Ni ₂ (DBAH)(H ₂ O) ₂ Cl ₄].4H ₂ O	1.73*	39060; 33900; 31150; 27855	22220	Octahedral	1805	430	0.46
[Cu ₄ (DBAH-6H)(H ₂ O) ₄ (OAc) ₂].2H ₂ O	2.04*	-	18500	Square-planar	-	-	-
[Co ₂ (DBAH)(H ₂ O) ₄ Cl ₄].2H ₂ O	3.65*	38460; 34000; 31250	16340; 14790	Octahedral	770	700	0.72
[Zr ₂ (DBAH-4H)Cl ₄].6H ₂ O	-	33900; 29150	-	Tetrahedral	-	-	-
[Cd ₂ (DBAH-4H)(H ₂ O) ₄]	-	31900; 30100	-	Tetrahedral	-	-	-
[Co ₂ Zn ₂ (DBAH)Cl ₆]	4.15*	36460; 32000; 30250	15625	Tetrahedral	603	406	0.817
[Co ₂ ZnCd(DBAH-H)(H ₂ O) ₄ Cl ₄].H ₂ O	2.15*	36460; 33500; 29050	16050	Tetrahedral	573	346	0.718

* Value for only one metal ion.

Table 7. ESR parameters of [Cu₄(DBAH-6H)(H₂O)₄(OAc)₂].2H₂O.

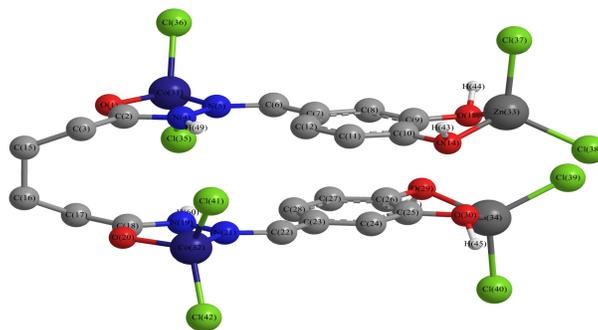
g_{\parallel}	g_{\perp}	$A_{\parallel} \times 10^{-4}$ (cm ⁻¹)	$g_{\parallel} / A_{\parallel}$	G	α^2	β^2
2.28	2.08	160	142	3.50	0.79	0.86

Table 8. Decomposition steps of the complexes based on the thermogravimetric data.

Complex	Middle Temp. °C	Removed species	Weight loss, % Found (Calcd.)
DBAH	72	- H ₂ O	6.69 (4.16)
	268	- 4 OH	18.65 (15.74)
	571	- C ₁₉ H ₁₈ N ₄ O ₂	72.43 (77.32)
	>650	Residue (Purity %)	1.84 (2.78) (98.16%)
[Ni ₂ (DBAH)(H ₂ O) ₄ Cl ₄].2H ₂ O	73	- 4 H ₂ O	9.15 (9.21)
	342	- 2 H ₂ O + 2 Cl ₂	21.91 (22.74)
	518	- C ₆ H ₁₀ N ₂ O ₂	17.28 (18.16)
	>600	2 C ₇ H ₄ NO ₂ Ni	51.66 (49.31)
[Co ₂ (DBAH)(H ₂ O) ₄ Cl ₄].2H ₂ O	67	- 2 H ₂ O	3.83 (4.60)
	285	- 2Cl ₂ + 4H ₂ O	20.57 (22.81)
	547	- C ₆ H ₁₀ N ₂ O ₂	20.02 (18.05)
	>800	2 C ₇ H ₄ NO ₂ Co	55.58 (53.89)
[Zr ₂ (DBAH-4H)Cl ₄].6H ₂ O	75	- 6 H ₂ O	13.90 (12.50)
	343	- 2 Cl ₂	15.35 (16.39)
	574	- 2 CO	6.47 (6.48)
	700	- C ₄ H ₈	6.25 (5.70)
[Cd ₂ (DBAH-4H)(H ₂ O) ₄]	> 800	2 C ₇ H ₆ N ₂ O ₂ Zr	56.03 (57.32)
	82	- 4 H ₂ O	9.42 (10.13)
	344	- C ₇ H ₆ NO ₂	20.16 (19.14)
	511	- C ₁₃ H ₁₂ N ₃ O ₂	35.41 (34.06)
>750	2 CdO	35.40 (36.10)	

Table 9. Molecular parameters data of [Co₂Zn₂(DBAH)Cl₆].

Molecular parameters	[Co ₂ Zn ₂ (DBAH)Cl ₆]
Total energy (kcal/mol)	-214046.35
Total energy (a.u)	-341.10
Binding energy (kcal/mol)	-6261.21
Isolated atomic energy (kcal/mol)	-207785.14
Electronic energy (kcal/mol)	-1835385.30
Electronic energy (kcal/mol)	1621338.94
Heat of formation (kcal/mol)	-388.75
Gradient (kcal/mol/Ang)	45.19
Dipole (Debyes)	40.24

**Figure 3.** Molecular modeling of [Co₂Zn₂(DBAH)Cl₆].

In [Co₂(DBAH)(H₂O)₄Cl₄].2H₂O and [Ni₂(DBAH)(H₂O)₄Cl₄].2H₂O, the steps are due to loss of water of crystallization, 2Cl₂ + 4H₂O and C₆H₁₀N₂O₂ at mid-points of (67; 73), (285; 342) and (518; 547) °C, respectively. The residues are 2 C₇H₄NO₂Co and 2 C₇H₄NO₂Ni. Both of the Co(II) and Ni(II) complexes have high residual % and the same steps of decomposition indicating similar structure. The TG curve of [Zr₂(DBAH-

4H)Cl₄].6H₂O displayed four thermal steps after which it left 2 C₇H₆N₂O₂Zr. The degradation steps were observed at 75, 343, 574 and 700 °C due to removal of 6H₂O with 13.90 (Calcd. 12.5%); 2Cl₂ [15.35 (Calcd. 16.39)]; 2CO [6.42 (6.48)] and C₄H₈ [6.25 (Calcd. 5.70)]. Three decomposition steps are depicted in the TGA of [Cd₂(DBAH-4H)-(H₂O)₄] at 82, 344 and 511 °C due to 4H₂O, C₇H₆NO₂ and C₁₃H₁₂N₃O₂ ending with 2CdO.

Table 10. Bond lengths and bond angles for [Co₂Zn₂(DBAH)Cl₈].

Bond length (Å)		Bond angle (°)	
Zn(34)-Cl(40)	2.240	Cl(40)-Zn(34)-Cl(39)	113.161
Zn(34)-Cl(39)	2.240	Cl(40)-Zn(34)-O(30)	111.485
Zn(33)-Cl(38)	2.240	Cl(40)-Zn(34)-O(29)	111.539
Zn(33)-Cl(37)	2.240	Cl(39)-Zn(34)-O(30)	112.629
Co(32)-Cl(42)	2.150	Cl(39)-Zn(34)-O(29)	112.917
Co(32)-Cl(41)	2.150	O(30)-Zn(34)-O(29)	93.620
Co(31)-Cl(36)	2.150	Cl(38)-Zn(33)-Cl(37)	113.157
Co(31)-Cl(35)	2.150	Cl(38)-Zn(33)-O(14)	112.912
O(30)-H(45)	0.970	Cl(38)-Zn(33)-O(13)	112.629
O(30)-Zn(34)	1.897	Cl(37)-Zn(33)-O(14)	111.540
C(27)-C(28)	1.341	Cl(42)-Co(32)-Cl(41)	113.666
C(26)-O(29)	1.369	Cl(42)-Co(32)-N(21)	112.607
N(21)-Co(32)	1.825	Cl(42)-Co(32)-O(20)	112.617
N(21)-C(22)	1.347	Cl(41)-Co(32)-N(21)	113.030
O(20)-Co(32)	1.774	Cl(41)-Co(32)-O(20)	112.314
N(19)-H(60)	1.017	N(21)-Co(32)-O(20)	90.552
N(19)-N(21)	1.363	Cl(36)-Co(31)-Cl(35)	113.664
C(18)-O(20)	1.217	Cl(36)-Co(31)-N(5)	112.604
C(18)-N(19)	1.396	Cl(36)-Co(31)-O(1)	112.613
		Cl(35)-Co(31)-N(5)	113.039
		Cl(35)-Co(31)-O(1)	112.312
		N(5)-Co(31)-O(1)	90.554
		H(45)-O(30)-Zn(34)	107.107

3.8. Molecular modeling

The molecular parameters of [Co₂Zn₂(DBAH)Cl₈] (Figure 3) are calculated and presented in Table 9. The bond lengths and angles are presented in Table 10. In [Co₂Zn₂(DBAH)Cl₈] all Zn-Cl distances (2.24 Å) are comparable with the average corresponding distances reported for related metal complexes with distorted ZnO₂Cl₂ tetrahedral environments, cf. 2.261(1) Å in *bis*(2-benzyl-1*H*-benzimidazole-*N*³)dichloro zinc(II), 2.224(1) Å in ZnCl₂ (5,7-dimethyl-1,2,4-triazole[1,5- α]pyrimidine)₂. The Co-Cl distances are 2.15 Å smaller than that of Zn-Cl. The Co-Cl distance is 2.15 Å less than Zn-Cl indicating more covalent for Co-Cl. Also, the Zn-O (1.897 Å) distance is more than Co-O (1.774 Å) [30].

4. Conclusions

A new chelating agent, DBAH, chelates with Zr(IV), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Co(II)/Zn(II). It coordinates as a neutral tetradentate in Co(II) and Ni(II) complexes; tetranegative tetradentate in Zr(IV) and Cd(II); binate negative octadentate in [Co₂Zn₂(DBAH-2H)Cl₆].4H₂O. The complexes have high stability with large residue.

Supplementary material

CCDC-1007321 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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References

- [1]. Golcu, A.; Tumer, M.; Demirelli, H.; Wheatley, R. A. *Inorg. Chim. Acta*, **2005**, *358*, 1797-1804.
- [2]. Ranford, J. D.; Vittal, J. J.; Wang, Y. M. *Inorg. Chem.* **1988**, *37*, 1226-1231.
- [3]. Monfareda, H. H.; Lalami, N. A.; Pazio, A.; Wozniak, K.; Janiak, C. *Inorg. Chim. Acta*. **2013**, *406*, 241-250.

- [4]. Ramadevi, P.; Singh, R.; Prajapati, A.; Gupta, S.; Chakraborty, D. *Advances Chem.* **2014**, *2014*, Article ID: 175384, 1-7.
- [5]. Huszti, Z.; Szihigyi, G.; Kasztreiner, E. *Biochem. Pharmacol.* **1983**, *32*, 627-636.
- [6]. Weinberg, E. D. *Adv. Appl. Microbiol.* **2003**, *52*, 187-208.
- [7]. Murphy, T. B.; Rose, N. J.; Schomaker, V.; Aruffo, A. *Inorg. Chim. Acta* **1985**, *108*, 183-194.
- [8]. Chetana, P. R.; Somashekar, M. N.; Srinatha, B. S.; Policegoudra, R. S.; Aradhya, S. M. *Int. J. Pharm. Sci. Rev. Res.* **2014**, *26*, 284-290.
- [9]. Khattab, M. A.; Soliman, M. S.; El-Enany, G. *Bull. Soc. Chim. Belg.* **1982**, *91*, 265-275.
- [10]. El-Metwally, N. M.; El-Asmy, A. A.; Abu-Hussen, A. A. *Int. J. Pure Appl. Chem.* **2006**, *1*, 75-62.
- [11]. Mandlik, P. R.; Aswar, A. S. *Polish J. Chem.* **2003**, *77*, 129-136.
- [12]. El-Tabl, A. S.; El-Saied, F. A.; Plass, W.; Al-Hakimi, A. N. *Spectrochim. Acta A* **2008**, *71*, 90-99.
- [13]. Ahmed, A.; Lal, R. A. *Arabian J. Chem.* doi: 10.1016/j.arabj.2012.12.026
- [14]. El-Asmy, A. A.; Al-Gammal, O. A.; Radwan, H. A.; Ghazy, S. E. *Spectrochim. Acta A* **2010**, *70*, 293-303.
- [15]. Jeragh, B.; El-Asmy, A. A. *Spectrochim. Acta A* **2014**, *129*, 307-313.
- [16]. El-Asmy, A. A.; Jeragh, B.; Ali, M. *Spectrochim. Acta A* **2015**, *150*, 504-513.
- [17]. El-Sayed, A. E. M.; Al-Fulaij, O. A.; Elaasar, A.; El-Defrawy, M. M.; El-Asmy, A. A. *Spectrochim. Acta A* **2015**, *135*, 211-218.
- [18]. El-Asmy, A. A.; Jeragh, B.; Ali, M. S. *Eur. J. Chem.* **2016**, *7*, 81-90.
- [19]. El-Asmy, A. A.; Jeragh, B.; Ali, M. S. *Chem. Central J.* **2015**, *9*, 69-80.
- [20]. Jeragh, B.; Ali, M. S.; El-Asmy, A. A. *Spectrochim. Acta A* **2015**, *145*, 295-301.
- [21]. Hassanien, M. M.; Abdel-Rhman, M. H.; El-Asmy, A. A. *J. Chem. Eng. Data* **2009**, *54*, 1277-1283.
- [22]. Amer, S.; El-Wakiel, N.; El-Ghamry, H. *J. Mol. Struct.* **2013**, *1049*, 326-335.
- [23]. Iqbal, M. S.; Bukhari, L. H.; Arif, M. *Appl. Organometal. Chem.* **2005**, *19*, 864-869.
- [24]. Bei, F.; Jian, F.; Yang, X.; Lu, L.; Wang, X.; Razak, A.; Shanmuga, S.; Raj, S.; Fun, H. K. *Acta Crystallog.* **2001**, *57*, 45-46.
- [25]. Rahaman, F.; Aswamy, B. H. M. *Complex Met.* **2014**, *1*, 88-102.
- [26]. Aly, A. A.; El-Meligy, M. S.; Zidan, A. S.; El-Shabasy, M. *An. Quim.* **1990**, *86*, 19-26.
- [27]. Jeragh, B.; El-Asmy, A. A. *Spectrochim. Acta A* **2014**, *125*, 25-35.
- [28]. Keypour, H.; Shayesteh, M.; Golbedaghi, R. *Trans. Met. Chem.* **2013**, *38*, 611-616.
- [29]. Nejo, A. A.; Kolawole, G. A.; Dumbele, M. C.; Opoku, A. R. *J. Coord. Chem.* **2010**, *63*, 4367-4379.
- [30]. Kucukbay, H.; Yilmaz, U.; Akkurt, M.; Buyukgungor, O. *Turk. J. Chem.* **2015**, *39*, 108-120.
- [31]. Alves, W. A.; Bagatin, I. A.; Ferreira, A. M. D. C. *Inorg. Chim. Acta* **2001**, *321*, 11-21.