

Coordination diversity of new mononucleating hydrazone in 3d metal complexes: Synthesis, characterization and structural studies

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Abstract: The mononucleating hydrazone ligand LH₃, a condensation product of salicyloylhydrazine and (2-formylphenoxy)acetic acid, was synthesized and its coordination behavior with first row transition metal(II) ions was investigated by isolating and elucidating the structure of the complexes using elemental analysis, conductivity and magnetic susceptibility measurements, as well as IR, ¹H-NMR, electronic and EPR spectral techniques. The ligand forms mononuclear metal(II) complexes of the type [CoLH(H₂O)₂], [NiLH(H₂O)₂], [CuLH] and [ZnLH]. The ligand field parameters, *Dq*, *B* and *β* values, in the case of the cobalt and nickel complexes support not only the octahedral geometry around the metal ion, but also imply the covalent nature of the bonding in the complexes. The EPR study revealed the presence of a spin exchange interaction in the solid copper complex and the covalent nature of the bonding. The ¹H-NMR study of the zinc(II) complex indicated the non-involvement of the COOH group in the coordination. The physico-chemical study supports for the presence of octahedral geometry around cobalt(II), nickel(II) and tetrahedral geometry around copper(II) and zinc(II) ions.

Keywords: coordination diversity, hydrazone complexes, ligand field parameters, copper(II) complex, nickel(II) complex, cobalt(II) complex, zinc(II) complex.

INTRODUCTION

In view of their applicability in various fields,^{1–8} hydrazones, a member of the Schiff base family with triatomic >C=N–N< linkage, takes the forefront position in the development of coordination chemistry. Reports on the synthesis, characterization and structural studies on hydrazone ligands derived from salicylaldehyde show the importance of hydrazone complexes in various fields, including analytical and biological fields. Arylhydrazones of *o*-hydroxybenzaldehyde and ketones possess a third potent coordination site, which makes them tridentate ligands, and these compounds have attracted most researchers due to their vital role in the bio-

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logical field.⁹ Due to the biological interest in such a type of ligand systems, various structural studies have been carried out.^{10–13}

In order to pursue the interesting coordination properties of hydrazones, hydrazone complexes with different types of ligand environments are essential. Studies of hydrazone complexes derived from salicylaldehyde^{14–22} shed light not only on the interesting coordination properties of these ligands in complexes, but also reveals the sparse study of these properties with modifications at the phenolic OH group of salicylaldehyde. Here, the purpose was to alter the metal ion coordination environment, which is primarily responsible for the properties exhibited by the complex. Hence, in order to achieve this aim and to broaden the perspective on hydrazone ligands, to explore potential transition metal aggregation as a function of flexibility in the ligands, the preparation of a ligand with (2-formylphenoxy)acetic acid as the starting precursor, which plays an important role in reducing the toxicity of the parent drug and acts as a pro-drug, called aconiazide,^{23,24} which will give a modification at the phenolic –OH group and make the ligand appear as a triprotic tetra- or pentadentate chelating agent, was undertaken. Such a ligand also gives the scope to scrutinize the effect of the amide, phenolic and carboxyl protonation state on the structural and physical properties of the complex.

Herein the synthesis and successful utilization of –O–CH₂–COOH to construct the potentially tetrafunctional ligand LH₃ (Fig. 1) is described. Also the metal-ion induced changes in the coordination sphere of the ligand in mononuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes are discussed.

EXPERIMENTAL

Materials, analytical methods and physical measurements

All employed chemicals were of reagent grade. Solvents were distilled prior to use in the synthetic part. The metal content of the complexes were estimated after decomposition with a mixture of HCl and HClO₄ by the gravimetric method (copper and nickel) and the EDTA titration method (cobalt and zinc). Elemental analysis for carbon, hydrogen and nitrogen were performed on a Vario-EL III CHNS instrument. The magnetic susceptibility of the complexes were measured at room temperature on a Gouy balance, using Hg[Co(SCN)₄] as the calibrant. The electronic spectra were recorded using a UV-160A UV-visible spectrophotometer (Shimadzu) in DMSO.

The IR spectra of the ligand and its complexes were recorded as KBr pellets in the region 4000–400 cm⁻¹ on a Nicolet 170 SX FT-IR spectrometer. The ¹H-NMR spectrum of the ligand and its zinc(II) complex, along with D₂O exchange, were recorded in DMSO-*d*₆ on a JEOL GSX 400 spectrometer using TMS as an internal standard. The EPR spectrum of the copper(II) complex was recorded at room temperature on a Varian E-4 X-band spectrometer using TCNE as the *g*-marker. Conductivity measurements were measured on 10⁻³ M solutions of the complexes in DMSO using a ELICO-CM82 Conductivity Bridge provided with a cell having a cell constant of 0.51.

Analysis of the Cu and Ni complexes

The Cu and Ni contents of the complexes were estimated by following standard methods.²⁵ The data of the elemental analysis is presented in Table I.

Estimation of copper as copper salicylaldoximate

An accurately weighed (≈ 0.1 g) amount of complex was taken and the organic matter was destroyed as above. The resulting clear solution was diluted with distilled water (100 ml) and then

treated dropwise with sodium hydroxide solution (2 M) to neutralize the mineral acid and then acidified with dilute acetic acid. Finally a 1 % aqueous solution of salicylaldehyde reagent was added slowly to it under constant stirring. The precipitate was allowed to stand for half an hour, filtered through a previously weighed sintered glass crucible (G-4) and washed thoroughly with water until washings were free from chloride. It was dried to constant weight at 373–378 K and weighed as $\text{Cu}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$.

Estimation of nickel as nickel dimethylglyoximate

About 0.150 g of complex was accurately weighed and the organic matter destroyed as described above. The solution was diluted to ≈ 150 ml with distilled water. The solution was heated to 343–353 K and to the hot solution a slight excess of a 1 % ethanolic solution of dimethylglyoxime was added, followed by the dropwise addition of ammonia solution until the precipitation was complete. The resulting precipitate was digested on a water bath for about 30 min. After cooling for 1 h, the solution was filtered through a dried and previously weighed sintered glass crucible (G-4). The precipitate was washed with water until free from chloride and dried to a constant weight at 383–393 K for 1 h. It was weighed as $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$.

Synthesis of salicyloylhydrazine

To an EtOH solution (100 ml) of methyl salicylate (0.5 mol), hydrazine hydrate (99 %, 0.5 mol) was added drop wise with stirring at room temperature. After complete addition of the hydrazine hydrate, the resulting clear solution was refluxed for 2–3 h on a water bath and then the volume was reduced and cooled to room temperature. The isolated white solid was filtered, washed with cold EtOH and then recrystallized from aqueous EtOH. M.p. 419–420 K (lit. 420 K).

Synthesis of the ligand, LH₃

The precursor (2-formylphenoxy)acetic acid was prepared by following the method described in the literature.²⁶ To a hot EtOH solution (30 ml) of salicyloylhydrazine (0.005 mol), warm EtOH solution (25 ml) of (2-formylphenoxy)acetic acid (0.005 mol) was added dropwise with stirring in the hot. After complete addition, the resulting very pale yellowish solution was stirred for 15 min in the hot and then refluxed for 3 h on a water bath. The separated crystalline product was filtered, washed with EtOH and dried. Yield: 70 %, m.p. 517–518 K.

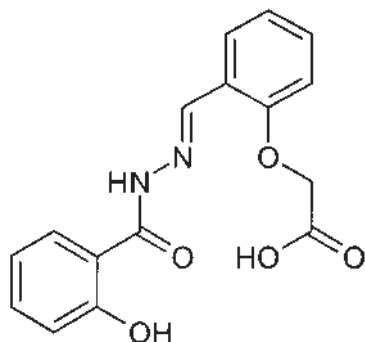


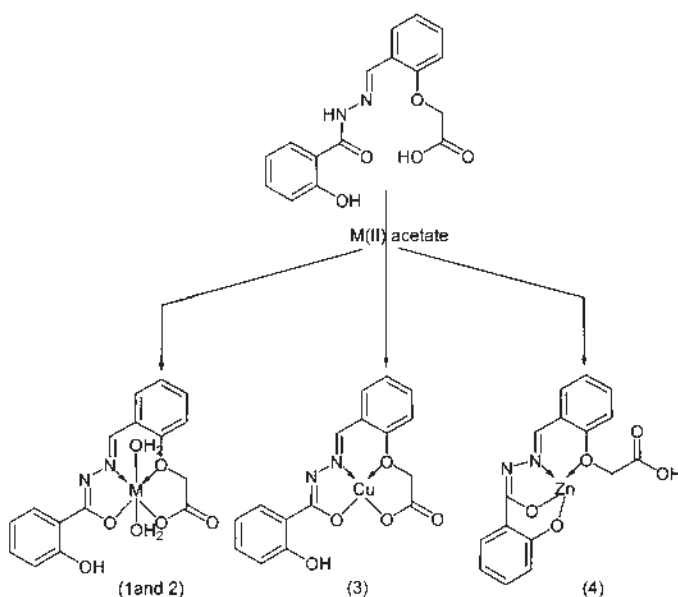
Fig. 1. Structural formula of the ligand LH₃.

Synthesis of the complexes

To a hot EtOH solution (40 ml) of ligand (0.003 mol), a hot aqueous EtOH solution (30 ml) of copper(II) acetate (0.003 mol) (a hot EtOH solution in the case of cobalt(II), nickel(II) and zinc(II) acetates) was added dropwise with stirring at 345–347 K. After complete addition of the metal salt solution, the reaction mixture was stirred for a further 30 min at the same temperature and then refluxed for 4 h on a water bath. The isolated complex was filtered in the hot, washed with hot aqueous EtOH, hot EtOH and dried. In the case of the cobalt(II), nickel(II) and zinc(II) complexes, the final product was washed with hot EtOH and dried. Yield: 67–70 %, m.p. > 523 K.

RESULTS AND DISCUSSION

The mononuclear Co(II), Ni(II), Cu(II) and Zn(II) (1–4) complexes were prepared by reacting the ligand with the corresponding metal(II) salts in a 1:1 ligand to metal ion ratio (Scheme 1). The analytical and some of the physical data of these complexes are depicted in Table I. From the presented data, the 1:1 ligand to metal stoichiometry of the complexes is confirmed. The prepared complexes are non-hygroscopic, soluble in dimethyl sulphoxide but insoluble in common organic solvents and are stable at room temperature.



Scheme 1. Synthesis of the complexes.

TABLE I. Analytical, conductivity and magnetic moment data of the ligand LH₃ and the complexes (1)–(4)

Compound	Empirical formula	Analysis Found (Calcd.)/%				Λ_M $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} μ_B
		C	H	M	N		
LH ₃	C ₁₆ H ₁₄ N ₂ O ₅	61.92(61.14)	4.92(4.45)	–	8.89(8.91)	–	–
(1)	[Co(LH)(H ₂ O) ₂] [Co(C ₁₆ H ₁₆ N ₂ O ₇)]	46.96(47.18)	4.23(3.98)	14.4(14.5)	6.7(6.9)	1.1	4.82
(2)	[Ni(LH)(H ₂ O) ₂] [Ni(C ₁₆ H ₁₆ N ₂ O ₇)]	47.92(47.21)	4.12(3.93)	14.6(14.4)	6.9(6.8)	1.2	3.1
(3)	[Cu(LH)] [Cu(C ₁₆ H ₁₂ N ₂ O ₅)]	50.65(51.13)	3.19(3.92)	16.8(16.9)	7.5(7.4)	1.6	1.63

TABLE I. Continued

Com- pound	Empirical formula	Analysis Found (Calcd.)/%				Λ_M $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} μ_B
		C	H	M	N		
(4)	Zn(LH)	51.21(50.87)	3.18(3.72)	17.5(17.3)	7.3(7.4)	1.2	–
	[Zn(C ₁₆ H ₁₂ N ₂ O ₅)]						

Infrared spectra

The comparative IR spectral study of the ligand LH₃ and its complexes reveals the interesting coordination mode of the ligand during complex formation. The important IR bands with their possible assignment are depicted in Table II. The weak broad bands at 3434 and 2800 cm⁻¹ in the free ligand are attributed to the free OH stretching of the phenolic moiety and the hydrogen bonded –OH of the carboxylic moiety. In the complexes, except in the Zn(II) complex (4), the disappearance of the band at 2800 cm⁻¹, followed by a considerable blue shift in the acid carbonyl frequency, 1718 cm⁻¹ in the ligand, implies deprotonation and subsequent coordination of the oxygen of the carboxylic group to the metal ion. Furthermore, in all these complexes (1–4) the disappearance of the medium intensity broad band at 3284 cm⁻¹, due to $\nu(\text{NH})$ and 1640 cm⁻¹, due to amide-I ($>\text{C}=\text{O}$), support the deprotonation of –NH proton and subsequent coordination of the oxygen of the amide carbonyl to the metal ion *via* enolization. In the spectrum of the free ligand, the appearance of –NH and amide–I bands reveals the existence of the keto form of the ligand in the solid state, while the existence of the enol form of the ligand in the complexes is apparent from the present comparative study. In the case of Zn(II) complex (4), the band due to carboxylic –OH vibrations remained unaltered, suggesting the non-involvement of the carboxylic proton in the complex formation, whereas the band at 3434 cm⁻¹ due to phenolic –OH vibrations disappeared, indicating deprotonation of the phenolic OH group and subsequent coordination of the oxygen to the metal ion. This fact was further confirmed by the ¹H-NMR study. The blue shift in the azomethine band, 1603 cm⁻¹ in free ligand, is an indication of the coordination of the nitrogen of azomethine to the metal ion, which was further confirmed by observation of the red shift in the $\nu(\text{N}=\text{N})$ stretching frequency from 923 cm⁻¹ to 946–953 cm⁻¹ regions.^{27,28} Furthermore, in the Ni(II) and Cu(II) complexes (2 and 3), new bands observed at 1621 and 1625 cm⁻¹, respectively, are attributed to the $>\text{C}=\text{N}=\text{N}=\text{C}<$ group.²⁹ In addition, the coordination of the ethereal oxygen ($>\text{C}-\text{O}-\text{C}<$) to the metal ion was confirmed by the observed red shift of the 1226 cm⁻¹ band, which was assigned to the asymmetric stretching frequency of the $>\text{C}-\text{O}-\text{C}<$ group in the free ligand. In the complexes, this band appeared in the 1233–1252 cm⁻¹ region. The medium intensity broad bands at 3428 cm⁻¹, 3426 cm⁻¹ in the Co(II) and Ni(II) complexes, respectively, were attributed to the presence of coordinated water molecules.³⁰

TABLE II. IR spectral data (cm^{-1}) of the ligand and its complexes

Compound	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	Amide($\text{C}=\text{O}$)	$\text{N}(\text{C}=\text{N})$	$>\text{C}=\text{N}-\text{N}=\text{C}<$
LH_3	3284	1718	1640	1603	–
(1)	–	1647	–	1599	–
(2)	–	1641	–	1594	1621
(3)	–	1658	–	1601	1625
(4)	–	1632	–	1603	–

¹H-NMR spectral studies

The spectrum of the ligand shows the following signals (Table III) at 4.84 (*s*), 6.94–7.95(*m*), 8.87(*s*), 12.04–12.00 (*m*) and 13.12(*bs*) ppm which are assigned to $-\text{O}-\text{CH}_2-$, aromatic, azomethine, $-\text{OH}$ and $-\text{NH}$ together and carboxylic protons, respectively. The disappearance of signals due to $-\text{OH}$, $-\text{NH}$ and COOH protons on D_2O exchange confirms to the assignment of signals in the ligand spectrum. The signals due to $-\text{NH}$ and phenolic $-\text{OH}$ were overlapped at ≈ 12.0 ppm, but careful observation made it possible to assign the signals at 12.00 and 12.04 ppm to $-\text{NH}$ and phenolic $-\text{OH}$ protons, respectively. In addition, the presence of a signal due to $-\text{NH}$ protons in the spectrum of the ligand implies the ligand was present in the keto form in $\text{DMSO}-d_6$ solution.

TABLE III. ¹H-NMR spectral data (δ , ppm) of the ligand and its Zn(II) complex (4)

Comp.	$-\text{O}-\text{CH}_2-$	Ar-H	HC=N	$-\text{OH}$	$-\text{NH}$	COOH
LH_3	4.84	6.94–7.95	8.87	12.04	12.00	13.12
(4)	4.59	6.87–7.99	8.79	–	–	13.12

A comparative study of ¹H-NMR data of ligand and its Zn(II) complex (4) revealed the ligational behavior of this ligand. In the spectrum of the Zn(II) complex, the signal due to carboxylic protons, which appeared as a broad singlet, was present and confirms the non-involvement of this group in the coordination. However, two signals due to $-\text{NH}$ and $-\text{OH}$ (phenolic), overlapped with one another around ≈ 12.0 ppm, disappeared. This clearly indicates deprotonation of $-\text{NH}$ (*via* enolization) and $-\text{OH}$ (phenolic) protons and the subsequent coordination of the amide oxygen to the metal ion in the enolate form. The up-field shift in the signals assigned to azomethine protons and methylene protons, at 8.79 ppm and 4.59 ppm in complex is an indication of the coordination of the nitrogen of the azomethine linkage and the ethereal oxygen of the $-\text{O}-\text{CH}_2-$ linkage to the metal ion. No signal around 1.8–1.9 ppm was observed, which can be assigned to acetate resonance.³¹ This information clearly indicates that, during complex formation, two protons of free ligand are deprotonated and ligand behaves in a dibasic tetradentate fashion.

Molar conductance measurements

The molar conductance values obtained for the complexes lie in the 1.1–1.6 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ range (Table I), which suggests the non-electrolytic nature of the complexes.³²

Magnetic moments

The room temperature μ_{eff} values for the Co(II) and Ni(II) complexes (**1** and **2**) are $4.83 \mu_{\text{B}}$ and $3.1 \mu_{\text{B}}$, respectively, which implies the presence of octahedral geometry around the metal ion.^{33,34}

For the Cu(II) complex (**3**), the obtained room temperature μ_{eff} value is $1.63 \mu_{\text{B}}$, which is less than the spin only value. The lowering of the magnetic moment value is attributed to metal–metal interaction in the solid complex, which is further evident from their EPR study. The magnetic moment data are summarized in Table I.

Electronic spectra

The spectrum of the ligand exhibits bands with shoulders at 37878 and 32786, 29585, 28169 cm^{-1} region, probably due to $\pi \rightarrow \pi^*$ transitions and also at 26954 cm^{-1} due to $n \rightarrow \pi^*$ transitions of the imine function. In the complexes, the bands due to $n \rightarrow \pi^*$ transitions are shifted to higher or lower values. In the complexes, charge transfer bands were observed in the range of 38314–28011 cm^{-1} .

The electronic spectrum of the Co(II) complex (**1**) shows two bands at 19120 and 20366 cm^{-1} , which can be assigned, respectively, for ${}^4\text{T}_{2\text{g}}(\nu_2) \rightarrow {}^4\text{T}_{1\text{g}}$ and ${}^4\text{T}_{2\text{g}}(\text{p})(\nu_3) \rightarrow {}^4\text{T}_{1\text{g}}$ transitions.³⁵ The ligand field parameters, $Dq = 1012 \text{ cm}^{-1}$, $B = 832$, $\beta = 0.857$, further support the presence of octahedral geometry around the metal ion.³⁶

In the electronic spectrum of Ni(II) complex (**2**), the band at 27100 cm^{-1} is attributed to the ν_3 transition, ${}^3\text{T}_{1\text{g}}(\text{P}) \rightarrow {}^3\text{A}_{2\text{g}}(\text{F})$ and the low energy band at 10384 cm^{-1} is ascribed to the ν_1 , ${}^3\text{T}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{A}_{2\text{g}}(\text{F})$ transition. The low energy band was taken as a $10 Dq$ band in the calculation of ligand field parameters. In this case, the ν_2 band (16638 cm^{-1}) was calculated using the procedure given by Drago.³⁷ These two bands are characteristic for octahedral symmetry.³⁸ The calculated values of ν_2/ν_1 (1.6), Dq (1038.4 cm^{-1}), B (839.1 cm^{-1}), β (0.777), β^0 (22.3 %) lie in the range reported for an octahedral environment around a Ni(II) ion.^{22,39} The obtained β value, being less than unity, suggests the presence of a considerable amount of covalent character of the metal ligand bonds. The ligand field stabilization energy obtained for this complex is 35.60 kcal mol^{-1} .

In addition to the ligand bands, the Cu(II) complex (**3**) shows a distinct d-d band at 14224 cm^{-1} . The spectrum of the Zn(II) complex (**4**) exhibits a strong intense charge transfer transition (LMCT) band at 26737 cm^{-1} .

Electron paramagnetic resonance study

The room temperature EPR spectra of the polycrystalline Cu(II) complex (**3**) exhibit an isotropic signal, without any hyperfine splitting, with $g_{\text{iso}} = 2.1496$. In

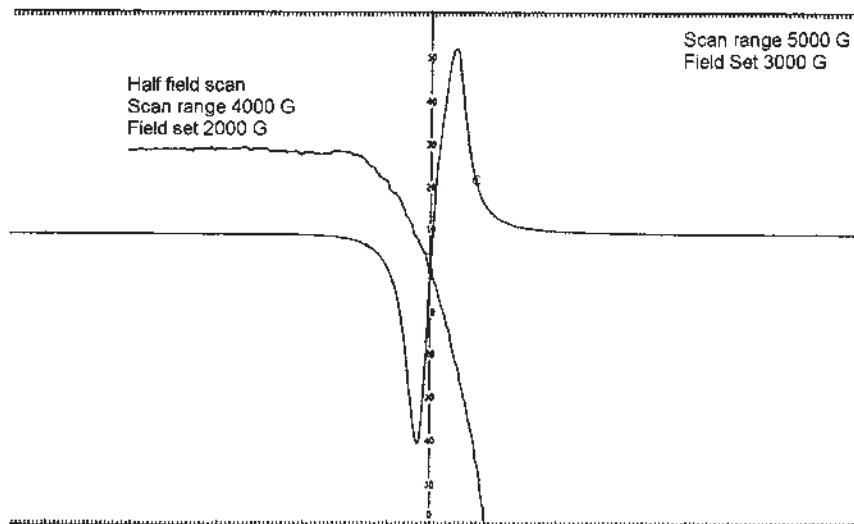


Fig. 2. Room temperature X-band EPR spectrum of the [Cu(LH)] complex.

addition, the spectrum also shows a signal for half field scans at 1540 G with a g value of 4.1876 (Fig. 2). This can be assigned to the $M_s = \pm 2$ transitions, indicating a spin exchange interaction in the complex.^{40,41} The higher g value obtained in the present study when compared to the g value of a free electron, 2.0023, indicates an increase of the covalent nature of the bonding between the metal ion and the ligand molecule.⁴²

CONCLUSION

The ligand was prepared by condensation of (2-formylphenoxy)acetic acid with salicylic hydrazide in ethanol in a 1:1 molar ratio. From the present investigation on the hydrazone complexes, it is evident that the $-\text{O}-\text{CH}_2-\text{COOH}$ group of (2-formylphenoxy)acetic acid functions as a side arm in the construction of a potentially tetradentate coordination sphere to arrest the metal(II) ion in the ONOO coordination sphere, giving neutral complexes of the type $[\text{M}(\text{ONOO}) \cdot n\text{H}_2\text{O}]$ or $[\text{M}(\text{ONOO})]$.

The fascinating aspect of this ligand is its coordinating and subtle behavior of the acidic protons. Under these aspects, it is evident that the ligand in the present investigation functions as a ONOO tetradentate dibasic donor, with the phenolic $-\text{OH}$ group remaining intact in the cobalt, nickel and copper(II) complexes. However, in the case of the zinc(II) complex, instead of the phenolic $-\text{OH}$, the carboxylic $-\text{OH}$ group remains intact and the complex is four-coordinated with the phenolic oxygen, amide oxygen (enolization), azomethine nitrogen and ethereal oxygen. This behavior may be attributed to the phenolic $-\text{OH}$ becoming more acidic with respect to the carboxylic proton in the presence of zinc(II) acetate salt.

Based on the above investigation, octahedral geometry for the Co(II) and Ni(II) (1 and 2) complexes and tetrahedral geometry for the Cu(II) and Zn(II) (3

and **4**) complexes is predicted (Scheme 1). In addition, it seems that the utilization of the $-O-CH_2-COOH$ group in the edifice of the desired coordination sphere, by anchoring the parent aldehyde moiety on various amines, will undeniably shed light on the interesting stereochemistry of the complexes. Further investigations are in progress.

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ИЗВОД

КООРДИНАЦИОНА РАЗНОВРСНОСТ НОВОГ ХИДРАЗОНА КОЈИ ГРАДИ
МОНОНУКЛЕАРНЕ КОМПЛЕКСЕ СА 3d МЕТАЛИМА: СИНТЕЗА,
КАРАКТЕРИЗАЦИЈА И СТРУКТУРНА ПРОУЧАВАЊА

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Синтетисан је хидразонски мононуклеазирајући агенс, лиганд LH_3 , кондензацијом салицилоилхидразина и (2-формилфеноксид)сирћетне киселине и изучавано његово координационо понашање са јонима првог реда прелазних метала(II), грађењем и разјашњавањем структуре комплекса применом елементарне анализе, мерењем проводљивости и магнетне суцептибилности, као и IR, ^1H-NMR , електронском и EPR спектралним техникама. Лиганд гради мононуклеарне метал(II) комплексе типа $[CoLH(H_2O)_2]$, $[NiLH(H_2O)_2]$, $[CuLH]$ и $[ZnLH]$. Вредности параметара лигандног поља Dq , B и β у случају кобалт и никал комплекса не само да подржавају октаедарску геометрију око металног јона већ наводе и на присуство ковалентне природе везивања у њима. EPR студија потврдила је присуство интеракције спинске измене бакар-комплекса у чврстом стању и ковалентну природу везе. ^1H-NMR проучавање цинк(II) комплекса указује да $COOH$ група није укључена у координацију. Физичко-хемијска студија потврђује присуство октаедарске геометрије око бакар(II) и цинк(II) јона.

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