

Synthesis and Characterization of 1,2-bis[4-(pent-3-en-4yl-2-one)ethane], a Novel QuardidentateLigand and its TransitionMetal Complexes

¹ Muhammad Shabbir, ¹ Zareen Akhter*, ¹ Asghari Gul and ² Michael Bolte
¹Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan.
²Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt,
 Max-von-Laue-Strasse 7, 60438 Frankfurt / Main, Germany.
 zareenakhter@yahoo.com*

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Abstract. A novel crystalline enamino-ketone ligand was synthesized by reacting 1, 2-di (4-aminophenoxy) ethylene with acetyl acetone. After that it was complexed with different metal acetates to prepare chromium Cr (II), cobalt Co (II), copper Cu (II) and zinc Zn (II) complexes. Elemental analysis, magnetic susceptibility measurements, thermogravimetric analysis, x-rays crystallographic studies, UV-visible spectroscopy were carried out for structural elucidation and property exploration. The ligand exhibited quardidentate structure with two N-donor and two O-donor atoms with central methylene bridge in the gauche conformation which was stabilized by two intramolecular N-H–O hydrogen bonds. The dihedral angle between the two aromatic rings was 45.1°. All complexes were thermally stable and exhibit square planar or tetrahedral geometries.

Keywords: Crystal structure; Metal complexes; Quardidentate ligand (enaminoketone)

Introduction

Multidentate Schiff base ligands have been widely studied in coordination chemistry due to their facile synthesis and interesting properties like good solubility in common solvents, their ability to reversibly bind oxygen and complexing ability towards some toxic transition metals. Moreover, the electronic and steric properties of these can be partly altered by varying the substituent on N atom [1-7]. These can accommodate a wide variety of metals having different coordination numbers resulting in metal complexes having unusual configuration and sensitivity towards environment [4-15]. These complexes are expected to show catalytical activities like they can be used (1) for the copolymerization of cyclohexane and carbondioxide and (2) in the polymerization of lactides.[18-20]

We report here in the preparation of a quardidentate, crystalline, nitrogen and oxygen donor ligand derived from acetyl acetone and 1, 2-di (4-aminophenoxy) ethylene (DAPE) which is further used for complexation with acetates of chromium, cobalt, copper and zinc to prepare thermally stable Cr (II), Co (II), Cu (II) and Zn (II) complexes.

Results and Discussion

The ligand (L) was prepared in good yield following the reported method, scheme 1 [23]. The structure and properties of the L was studied by melting point, spectroscopic studies elemental and single crystal X-ray analysis. It was found that tautomeric forms were possible for the 'L'. Single

crystal analysis showed that the "ketoimines" existed almost exclusively in enaminone tautomeric form (Fig. 1). It was further confirmed by ¹H NMR spectroscopic studies which had a broad signal around 12.47 ppm suggesting the presence of a proton bound to heteroatoms. The synthesized ligand was complexed with different transition metal acetates (scheme 2). The resulting complexes were characterized by various analytical techniques like elemental analysis, magnetic susceptibility measurements, IR, UV-Vis spectroscopy and thermogravimetric analysis.

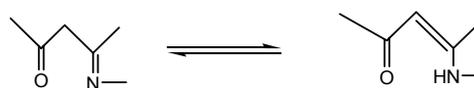


Fig. 1: Tautomeric forms of ligand L.

X-ray Structure Analysis of Ligand (L)

The L crystal, suitable for single crystal X-ray studies was grown from a saturated solution (in ethanol) at room temperature for three days. A crystal of size 0.33 x 0.27 x 0.14 was mounted on a glass fiber and intensity data was collected at 173K on a STOE IPDS-II diffractometer, using Mo K_α radiation. The direct methods were used to solve the structure and refinement was done with full-matrix least-squares techniques on F² [24]. The ORTEP diagram of the ligand is shown in Fig. 2. Crystal data, refinement details are tabulated in Table-1 and the selected bond lengths and angles for ligand L are

*To whom all correspondence should be addressed.

summarized in Table-2. It can be seen that the central methylene bridge is gauche in conformation and the molecular conformation is stabilized by two intramolecular N-H...O hydrogen bonds (Fig. 3). The dihedral angle between two aromatic rings is 45.1° . Single crystal analysis showed that the presence of enamino tautomeric form predominant in solid state

Analytical and Physical Measurements of Ligand and Complexes

The elemental analyses data for L and metal complexes, summarized in the Table-4, showed good agreement with the calculated values. It revealed that metal to ligand ratio in complexes was 2:1.

The magnetic susceptibility measurements were performed at room temperature and the data related to the complexes are presented in Table-4. It showed that except zinc, all other complexes were paramagnetic in nature. Low magnetic moment of copper complex indicated presence of an unpaired electron whereas greater values for chromium and cobalt complexes showed more number of unpaired electrons. Zinc complex showed no magnetic moment and was found diamagnetic in nature. The study showed that the geometry of copper, chromium and cobalt complexes was square planar while zinc complex was tetrahedral [25-28]. The magnetic moment data was in good agreement with the expected high spin configurations of the complexes.

IR Spectroscopy

The IR spectrum of the quardidentate ligand showed peak around 1720 cm^{-1} indicating presence of C=O group. An absorption band at 3284 cm^{-1} was assigned to the -NH group. The IR data of the complexes indicated the coordination of the ligand was through nitrogen and oxygen atoms. The IR spectra of all complexes showed shift of C=O band to the lower frequency coincident with the appearance of new peaks around $480\text{--}540\text{ cm}^{-1}$ and $450\text{--}400\text{ cm}^{-1}$, assigned to the M-N and M-O bond vibrations respectively, confirming the successful preparation of the complexes [29-30]

UV Visible Spectroscopy

UV visible spectral studies of the ligand and the complexes were performed in ethanol in 200-800

nm range. The bands in regions 261 and 303nm in the ligand corresponds to $\pi\text{-}\pi^*$ transitions (-C=C- and benzene) [31-32]. Copper (II), chromium (II) and cobalt (II) complexes display three bands each at 280, 355, 583, 288, 405, 53 and 321, 403, 529nm respectively indicating $\pi\text{-}\pi^*$, d-d and charge transfer transitions, suggesting square planar geometry [33]. The Zn (II) complex displays two bands at 305 and 560nm owing to $\pi\text{-}\pi^*$, and charge transfer transitions, however it does not exhibit d-d transition due to completely filled d-orbital. Generally zinc forms tetrahedral complexes.

The UV-visible spectra supplement the magnetic measurements suggesting the square planar and tetrahedral geometries for the metal complexes

Thermal Analysis

Thermal analysis of the complexes was carried out under inert atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ in a temperature range of $40\text{--}800^\circ\text{C}$. The weight loss for each complex was calculated within corresponding temperature range. The thermograms revealed the presence of four molecules of coordinated water per molecule of the complex in Cu (II), Cr (II), Co (II), and Zn (II). The proposed structure of all divalent complexes showed loss of coordinated water in a one step process at 141°C for Cu(II) complex, 134°C for Cr(II), 104°C for Co(II) complex and 152°C for Zn(II) complex. Thermogravimetric data of $\text{Cu}_2\text{L}4\text{H}_2\text{O}$ showed decomposition in three steps. The first step involved weight loss of 4.016% at 157°C owing to the removal of moisture. The second weight loss step of 63.15% (between 241°C and 457°C) corresponded to the loss of four coordinated water molecules (calculated 63.5) [34]. Third stage is removal of NO, CO₂ and organic moieties (between $550\text{--}663.5^\circ\text{C}$) accompanied by further loss of 14.94% weight (calculated 14.17%). The thermal decomposition plot reached at a constant mass of 22.53% zone near 675°C where almost all the volatile groups have been lost and a solid phase of metal oxide is left. The thermal decomposition of the other complexes showed similar behavior and final product in all the complexes is metal oxide [35-34]. A representative thermo gram is shown in Fig. 4. The data suggest the general formula $[\text{M}_2\text{L}4\text{H}_2\text{O}]$ where M=Cu (II), Co (II), Cr (II), Zn (II) for metal complexes. On the basis of these analytical and physical measurements the proposed structure of the complexes is shown in Fig. 5.

Table-1: Crystal data and structure refinement for Ligand L

Formula weight	408.48
Empirical formula	C ₂₄ H ₂₈ N ₂ O ₄
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P ₂ /n
Unit cell dimensions	a = 10.6102(7) Å b = 14.8207(7) Å c = 13.8242(8) Å α = 90° β = 93.822(5)° γ = 90°
Volume	2169.0(2) Å ³ Z 4
Density (calculated)	1.251 Mg/m ³
Absorption coefficient	0.085 mm ⁻¹
F (000)	872
Crystal size	0.33 x 0.27 x 0.14 mm ³
Theta range for data collection	3.61 to 27.57°
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -17 ≤ l ≤ 17
Reflections collected	33043
Independent reflections	4980 [R (int) = 0.0510]
Completeness to theta = 25.00°	99.7 %
Absorption correction	None
Max. and min. transmission	0.9882 and 0.9724
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4980 / 0 / 284
Goodness-of-fit on F ²	1.020
Final R indices [I > 2σ(I)]	R ₁ = 0.0418, wR ₂ = 0.1026
R indices (all data)	R ₁ = 0.0566, wR ₂ = 0.1088
Extinction coefficient	0.0081(14)
Largest diff. peak and hole	0.257 and -0.171

Table-2: Selected Bond lengths [Å] and angles [°] for Ligand L.

N(1)-C(3)	1.3456(17)	N(1)-C(3)-C(4)	122.50(12)
N(1)-C(14)	1.4368(16)	N(1)-C(3)-C(31)	117.13(12)
N(1)-H(1)	0.883(18)	O(3)-C(5)-C(4)	123.11(12)
N(2)-C(6)	1.3458(18)	O(3)-C(5)-C(51)	118.81(13)
N(2)-C(24)	1.4365(16)	C(4)-C(5)-C(51)	118.08(12)
N(2)-H(2)	0.881(19)	N(2)-C(6)-C(7)	121.52(13)
O(1)-C(11)	1.3796(15)	N(2)-C(6)-C(61)	118.47(13)
O(1)-C(1)	1.4363(16)	O(4)-C(8)-C(7)	122.76(12)
O(2)-C(21)	1.3772(14)	O(4)-C(8)-C(81)	118.50(13)
O(2)-C(2)	1.4353(15)	C(7)-C(8)-C(81)	118.73(13)
O(3)-C(5)	1.2482(17)	O(1)-C(11)-C(12)	124.47(12)
O(4)-C(8)	1.2517(17)	O(1)-C(11)-C(16)	115.97(11)
C(3)-N(1)-C(14)	124.49(11)	O(2)-C(21)-C(22)	125.02(11)
C(3)-N(1)-H(1)	115.4(11)	O(2)-C(21)-C(26)	115.41(11)
C(14)-N(1)-H(1)	120.1(11)	C(24)-N(2)-H(2)	119.4(12)
C(6)-N(2)-C(24)	126.26(12)	O(1)-C(1)-C(2)	109.63(11)
C(6)-N(2)-H(2)	114.3(12)		

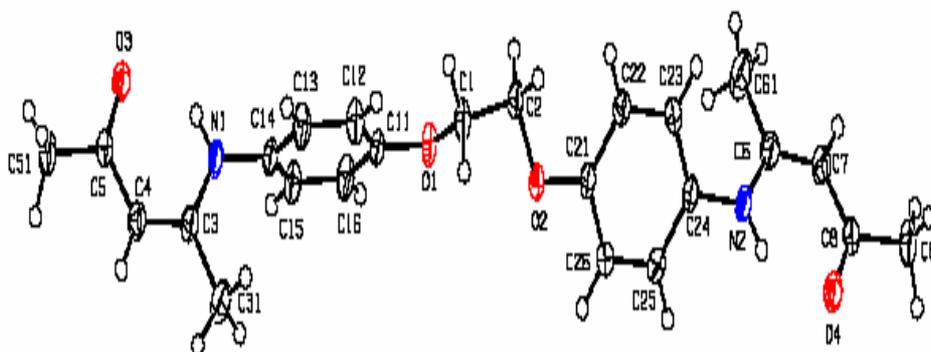


Fig. 2: ORTEP drawing of Ligand L.

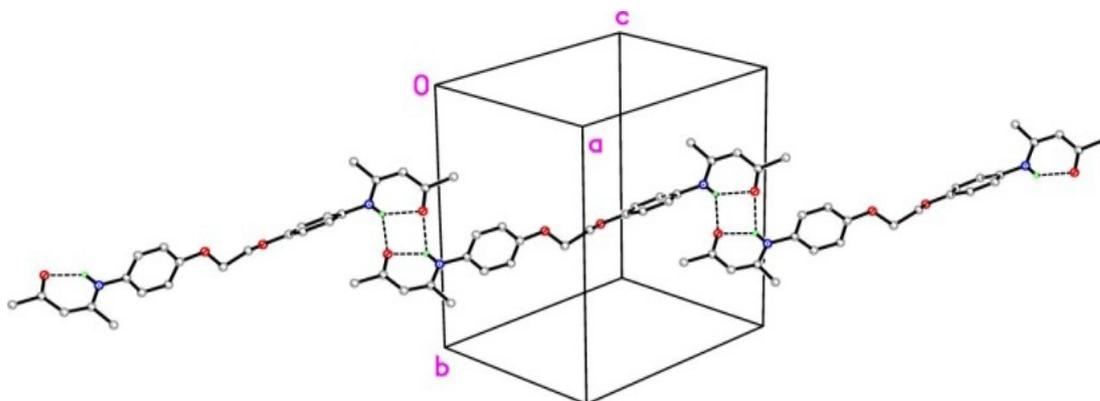


Fig.3: Intramolecular N-H...O hydrogen bonds in ligand L.

Table-3: N-H...O hydrogen bonds in ligand L.

H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N (1)-H (1)...O (3)	0.883(18)	2.009(18)	2.7055(15)	134.8(15)
N (1)-H (1)...O (4)	0.883(18)	2.327(18)	3.0412(16)	138.0(15)
N (2)-H (2)...O (3)	0.881(19)	2.462(19)	3.1712(15)	137.9(16)
N (2)-H (2)...O (4)	0.881(19)	1.956(19)	2.6712(15)	137.4(16)

Table 4: Analytical and magnetic moment data of Ligand and its transition metal complexes

compound	Color	% found (calc.)					magnetic moment (μ_{eff})BM	Magnetic behavior
		Metal	C	H	N			
L (C ₂₄ H ₂₈ N ₂ O ₄)	brown	158	-	70.72(70.72)	6.72(6.72)	7.17(7.18)	-	-
Cu ₂ L.4H ₂ O	chocolate	265	20.48(20.92)	47.51(47.44)	4.13(4.61)	5.13(5.93)	1.8	Para-magnetic
Cr ₂ L.4H ₂ O	dark brown	240	17.89(17.81)	49.28(49.31)	4.73(4.79)	6.20(6.16)	4.8	Para-magnetic
Co ₂ L.4H ₂ O	brown	270	19.48(19.46)	48.16(48.32)	4.65(4.71)	6.13(6.04)	2.9	Para-magnetic
Zn ₂ L.4H ₂ O	white	280	-	70.72(70.72)	6.72(6.72)	7.17(7.18)	-	Dia-magnetic

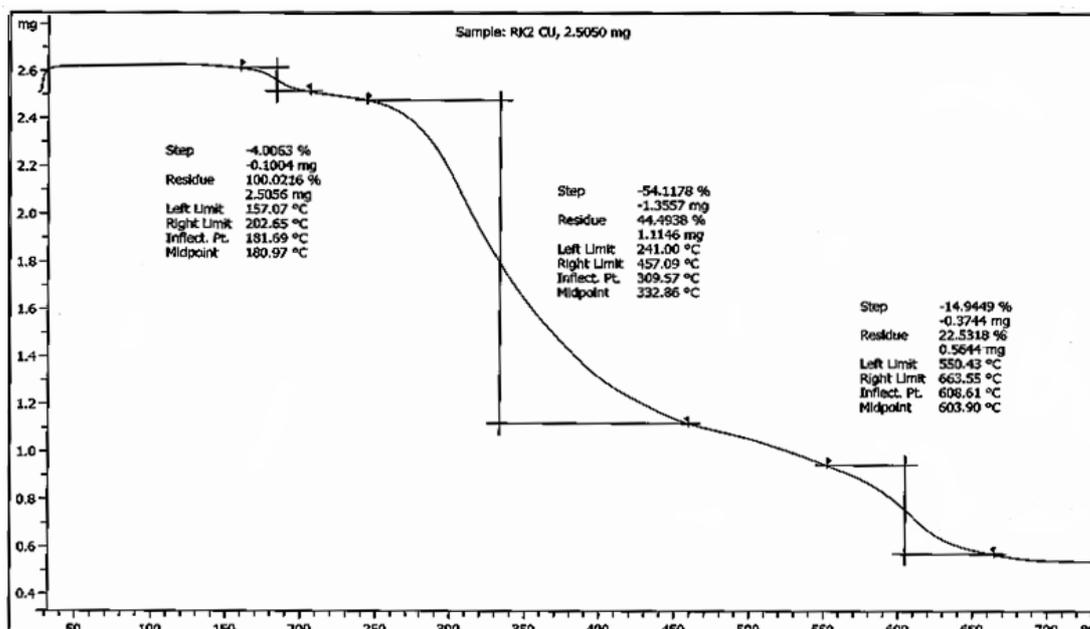


Fig. 4: TGA of copper complex.

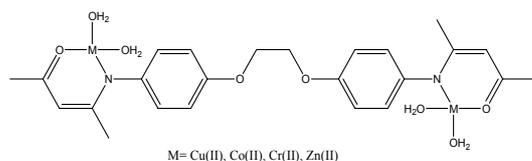


Fig. 5: Proposed structure of the complexes.

Experimental

Materials

Metal acetates were obtained commercially and used as received. All the chemicals and reagents used were of analytical grade. Solvents were purchased from Merck (A. R. grade) and were purified according to the standard procedures [21].

Measurements

Melting points were measured, using a MPD Mitamura Riken Kogyo (Japan) electro thermal melting point apparatus. Elemental analysis was carried out on a CHNS 932 (Leco-USA) elemental analyzer. FT-IR, model FTS 4800 MX spectrophotometer (USA) was used for FTIR analysis in the frequency range of 4000-400 cm^{-1} using KBr pellets. ^1H NMR spectral studies were performed on a Bruker 300MHz NMR Spectrophotometer in deuterated acetone using tetramethylsilane as internal reference. UV-Visible spectra of the ligand and the complexes were recorded in ethanol with a systronic double beam UV-Visible Spectrophotometer 2202 in the range 200-800 nm. Thermogravimetric analysis of the complexes was carried out on TGA/SDTA 851e Mettler Toledo Swiss at a heating rate of 10 $^{\circ}\text{C}$ /min over a temperature range of 40-800 $^{\circ}\text{C}$ under nitrogen flow. The metal contents of the complexes were determined by a Shimadzu model AA-670 in solutions using nitric acid as blank reference. Magnetic properties were evaluated by a Gouy method at room temperature using Hg [Co (NCS) $_4$] as calibrant.

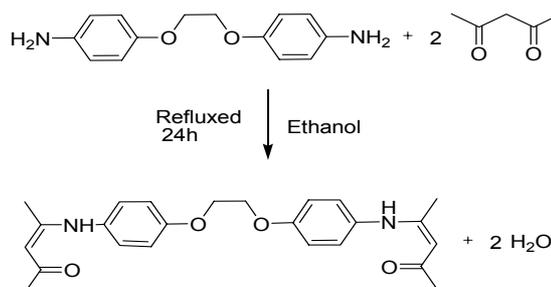
2-di (4-aminophenoxy) ethylene

1, 2-di (4-aminophenoxy) ethylene was prepared as reported earlier [22].

Synthesis of Ligand (L)

1, 2-di (4-aminophenoxy)ethylene (DAPE) (0.122g, 0.5 mmol) was dissolved in 20ml dried ethanol, at heating and continuous stirring in a 250ml round bottom flask fitted with a condenser, gas inlet, magnetic stirrer and hot plate. After that (0.1ml, 1.0 mmol) acetyl acetone was added dropwise to the flask under inert atmosphere. The mixture was refluxed for 24 hs till the color of the solution turned to light brown. Progress of the reactions and purity of

the products were checked by thin layer chromatography on pre-coated Kiesel gel 60HF TLC plates. The solution was concentrated and kept at room temperature for 24 hs. The crystalline product was filtered, washed with ethanol and dried in air. Good quality crystal was obtained by slow evaporation of ethanol solution for three days which was used for single crystal analysis, scheme 1.



Scheme-1: Synthesis of ligand L.

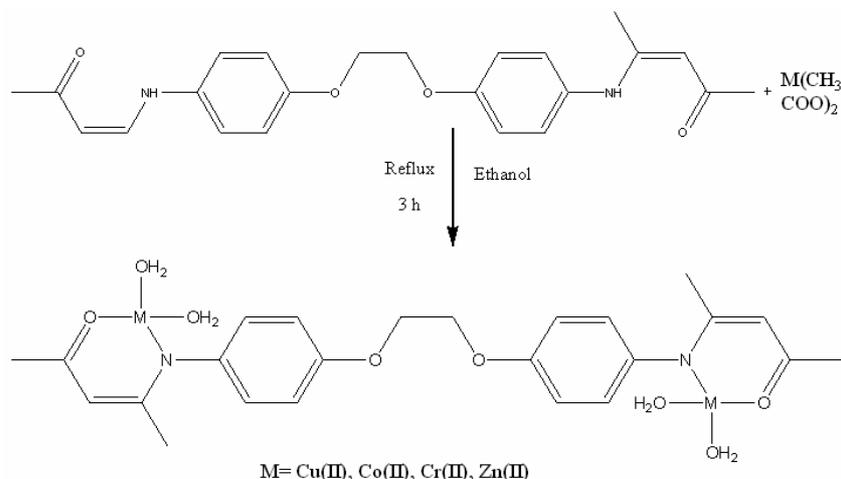
$\text{C}_{24}\text{H}_{28}\text{O}_4\text{N}_2$ (408); C, 70.72 (calc 70.59); H, 7.17 (6.86); N, 6.72 (6.86)%. IR (KBr) (ν cm^{-1}) 1720 (ketonic, C=O), 1628 (C=C), 3284 (N-H). UV-Vis (ethanol) $\lambda_{\text{max}} = 261.33 \text{ nm}$. ^1H NMR (300MHz, $[\text{D}_6]$ Acetone, 25 $^{\circ}\text{C}$): $\delta = 7.00-7.18$ (m, 8H, aromatic), 5.19 (s, 2H, olefinic), 1.95 (s, 6 H, 2CH $_3$). 1.98 (s, 6H, 2CH $_3$), 12.47 (s, 2H, NH), 4.40 (s, 4H, 2CH $_2$).

Synthesis of Cr (II), Co (II), Cu (II) and Zn (II) Complexes

The ligand (L) was dissolved in 20ml dried ethanol in a 250 ml round bottom flask fitted with magnetic stirrer, gas inlet and condenser. 20 ml solution of metal acetate (chromium, cobalt, copper and zinc) in ethanol was added slowly to the flask under inert atmosphere. The molar ratio of the reactant was 2:1. The mixture was refluxed for 3 hs. The progress of the reaction was checked by TLC. Different colored products obtained were filtered in hot, washed with ethanol, dried and stored under vacuum, scheme 2.

$\text{Cr}_2\text{L}\cdot 4\text{H}_2\text{O}$: Yield = 64 %, m. p. 240 $^{\circ}\text{C}$. Color dark brown, Elemental analysis %Found (calc.) Cr17.89 (17.81) C49.28 (49.31), H6.20 (6.16), and N4.73 (4.79), Magnetic moment (μ_{eff}): 4.8 BMIR (KBr) (ν cm^{-1}) = 1702 (ketonic, C=O), 1630 (C=C), 510 (M-N), 421 (M-O).

$\text{Co}_2\text{L}\cdot 4\text{H}_2\text{O}$: Yield (62%), m.p 270 $^{\circ}\text{C}$. Color brown, Elemental analysis %Found (calc.) Co19.48 (19.46), C48.16 (48.32), H6.13 (6.04), N4.65 (4.71), Magnetic moment (μ_{eff}): 2.9 BMIR (KBr) (ν cm^{-1}) = 1705 (ketonic, C=O), 1625 (C=C), 480 (M-N), 410 (M-O).



Scheme-2: Synthesis of metal complexes.

$\text{Cu}_2\text{L}\cdot 4\text{H}_2\text{O}$: Yield (72 %), m.p. 265 °C, Colour chocolate. Elemental analysis %Found(calc.) Cu.20.48(20.92), C 47.51 (47.44), H47.51 (47.44), N4.13(4.61), Magnetic moment(μ_{eff}): 1.8BM IR (KBr), ($\nu \text{ cm}^{-1}$) = 1699 (ketonic, C=O), 1620 (C = C), 488 (M-N), 440 (M-O).

$\text{Zn}_2\text{L}\cdot 4\text{H}_2\text{O}$: Yield (54%), m.p.280°C, Colour offwhite. Elemental analysis %Found(calc.) Zn 21.28(21.31), C47.30 (47.21), H5.11 (5.90), and N4.91 (4.59), Magnetic moment (μ_{eff}): zero IR (KBr), ($\nu \text{ cm}^{-1}$) = 1708 (ketonic, C=O), 1622 (C = C), 534(M-N), 432(M-O).

Conclusions

A new crystalline, quardidentate ligand having two N-donor and two O-donor atoms was synthesized and characterized successfully. The complexation of ligand with metal acetates resulted in the square planar and tetrahedral Cr (II), Co (II), Cu (II) and Zn (II)-complexes which were stable at room.

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