

Spectroscopic, thermal and magnetic properties of some transition metal complexes derived from 1-Phenyl-3-Substituted-4-Nitroso-5-Pyrazolones

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ABSTRACT

Complexes derived from some 1-Phenyl-3-methyl-4-nitroso-5-pyrazolone (L1), 1,3-diphenyl-4-nitroso-5-pyrazolone (L2) and 1-phenyl-3-anilino-4-nitroso-5-pyrazolone (L3) with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} metal ions have been prepared. Structural investigation of the ligands and their complexes has been made based on elemental analysis, infrared (FT-IR), ultraviolet and visible spectra (UV-Vis.), proton nuclear magnetic resonance (1H NMR), magnetic susceptibility (μ_{eff}) and thermal analysis (TG and DTG). The effect of solvents has been carried out in organic solvents of varying polarity. The observed transition energy and oscillator strengths were also calculated. The data obtained show that all of the prepared complexes contain water molecules in their coordination sphere. The investigated ligands acts as neutral bidentate ligands bonded to the metal ions through the two oxygen atoms of the carbonyl and nitroso groups. The isolated complexes behave as non-electrolyte in DMF solution. The Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} complexes show high spin configurations as the ground state. The high spin values of magnetic susceptibility may be due to the ligands being weak ligands. The Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes exhibit an octahedral or distorted octahedral coordination with the investigated ligands.

Keywords: Nitrosopyrazolones; Transition Metal Complexes; Spectroscopic; Thermal; Magnetic studies

1. INTRODUCTION

Pyrazolones and their pyrazol derivatives are formed by

the reaction between hydrazines and β -keto esters e.g. 3-methyl-1-phenylpyrazolone was prepared from phenylhydrazine and ethyl acetoacetate. This on methylation gives antipyrine which is used in medicine as an antipyretic [1]. Nitrosopyrazolones are used as analytical reagents. Pyrazolone derivatives are capable of forming complexes with a large number of transition metal ions [2-5]. The formed complexes are characterized by their high stability due to the formation of six-membered rings. 4-Nitroso-2-pyrazolin-5-one derivatives have significant activity against *Pyricularia oryzae* [6,7]. Complexation behaviour of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, oximido-benzotetronic acid and 4-nitroso-3-methyl-1-phenyl-2-pyrazoline-5-one each containing the same NO coordination group was complexed with some transition metal ions [8]. 1,3-Dimethyl-4-nitrosopyrazol-5-ol dissolved in methanol or DMSO together with small amount of H_2O_2 gives rise to nitroxide radicals when irradiated by UV light [9]. Nitrosation at C-4 of 1-n-alkyl-3-methyl-5-pyrazolone was achieved with sodium nitrite in hydrochloric acid medium. A tautomeric equilibrium in solution with a proton moving from OH at C-5 to nitrosated pyrazolones was proposed [10]. The structure and relative stabilities of the tautomers and isomers of 4-nitroso-pyrazolones were investigated at HF, DFT and MPn ($n = 2, 4$) quantum chemical levels. 1H , ^{13}C and ^{15}N NMR chemical shielding and coupling constants were calculated [11].

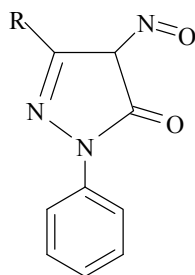
The present study deals with the preparation of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes with the investigated ligands (L1-L3). The complexes obtained were subjected to many analytical tools such as elemental analysis, infrared (FT-IR), thermogravimetric (TG) and derivative thermogravimetric analysis (DTG), molar conductance, magnetic susceptibility (μ_{eff}) and electronic spectra to throw some light on the bonds formed and on their structure.

2. EXPERIMENTAL

All chemicals used in this work were chemically pure, obtained from BDH chemicals. They include $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 , NH_4OH , sodium nitrite, ethyl acetoacetate, phenylhydrazine, ethyl benzoylacetate, 1-phenyl-3-amino-5-pyrazolone, aniline, sodium ethoxide, ethyl cyanoacetate. The solvents used were methanol, ethanol, dehydrated dimethyl sulfoxide (d_6 -DMSO), dimethyl formamide (DMF), chloroform, cyclohexane, isopropanol, dioxane, hydrochloric acid and sodium hydroxide.

2.1. Synthesis of the Ligands

The 1-phenyl-3-methyl-5-pyrazolone was prepared from ethyl acetoacetate and phenylhydrazine according to the method described by Vogel [12], m.p. 127°C . 1,3-Diphenyl-5-pyrazolone was prepared from ethyl benzoylacetate and phenylhydrazine [12]. 1-Phenyl-3-anilino-5-pyrazolone was obtained by the method described by Weissberger [13] from a mixture of 1-phenyl-3-amino-5-pyrazolone and aniline, m.p. 221°C . The investigated ligands were prepared [14] as follows, the nitrosation reactions were carried out by acidifying the cold aqueous solution of 1-phenyl-3-substituted-5-pyrazolone derivatives (0.1 mol) at 0°C in sodium hydroxide solution containing equivalent amount of sodium nitrite (0.1 mol) with hydrochloric acid. The precipitated ligands were filtered off, washed several times with water and recrystallized from ethanol. The purity of the compounds was determined from the results of elemental analysis and are summarized in **Table 1**, IR and ^1H NMR spectra. The resulting ligands have the following general formulae:



where $\text{R} = \text{CH}_3$ -, (1-phenyl-3-methyl-4-nitroso-5-pyrazolone), (L1)

$\text{R} = \text{C}_6\text{H}_5$ -, (1,3-diphenyl-4-nitroso-5-pyrazolone), (L2)

$\text{R} = \text{C}_6\text{H}_5\text{-NH}$ -, (1-phenyl-3-anilino-4-nitroso-5-pyrazolone), (L3)

2.2. Synthesis of the Complexes

The 1:1 or 1:2 complexes were prepared by mixing a hot

alcoholic solution of the investigated ligands (0.001 or 0.002 mol) with the calculated (0.001 mol) of metal salt solution. The reaction mixture was refluxed for 4 h. The pH of the solution was maintained at a value of 5.0-6.0 by the addition of dilute ammonia solution (1:10). The solid complexes were dried on a steam bath with stirring, then filtered off and washed several times with ethanol-water mixture, (1:1 v/v) till a colorless filtrate was obtained. The solid complexes were dried by suction and finally kept in vacuum desiccators.

2.3. Physical Measurements

The FT-IR spectra were recorded in the range $4000\text{-}400\text{ cm}^{-1}$ on a Jasco FT-IR spectrophotometer as KBr discs. The NMR spectra were measured using Varian Gemini 200-200 MHz spectrometer and the spectra were recorded from 0-15 ppm using TMS as an internal standard in dimethylsulfoxide (d_6 -DMSO) as the solvent. Thermal analyses (TG and DTG) were obtained in a nitrogen atmosphere using a type TGA 50 of Shimadzu derivatograph thermal analyzer. The molar conductivities were carried out using a Jenway 4310 conductivity meter. Electronic spectra were recorded in the range 200-800 nm, on Jasco V-530 UV-Vis. spectrophotometer. Magnetic susceptibility values were obtained at room temperature using magnetic susceptibility balance (Sherwood scientific), Cambridge Science Park, Cambridge, England.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Ligands

The structures of the investigated ligands (L1-L3) were established by the use of elemental analysis in **Table 1**, IR, UV-Vis and ^1H NMR spectra.

3.1.1. Infrared Studies

The infrared spectra of the investigated ligands and the most important IR band assignments that affect the structural features are listed in **Table 2**. The νNH appears as a medium broad one at 3210 cm^{-1} for ligand L3. The band appearing at 1705, 1678 and 1688 cm^{-1} are ascribed to the stretching frequency of the $\text{C}=\text{O}$ group for ligands L1-L3, respectively. The band observed within the range $1410\text{-}1359\text{ cm}^{-1}$ assigned to $\nu\text{N}=\text{O}$ [14].

3.1.2. ^1H NMR Spectra

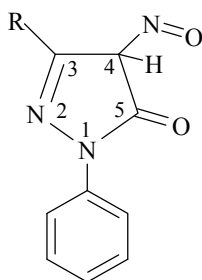
The different types of protons in DMSO of the investigated ligands (L1-L3) were obtained. The spectra of the ligands L1-L3 exhibit a sharp singlet signal at 2.23 ppm. This signal is assigned to the aliphatic proton at position number 4 [15,16] as shown in Figure:

Table 1. Elemental analyses and magnetic moments for Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ complexes with the investigated ligands (L1-L3).

Ligands and Complexes	Tentative Formula	M:L	m.p °C	C	H	% Calculated N	(found) Cl	M	μ_{eff}
L1	C ₁₀ H ₉ N ₃ O ₂	--	155	59.11 (59.3)	4.43(4.2)	20.68 (20.4)	--	--	--
L2	C ₁₅ H ₁₁ N ₃ O ₂	--	235	67.64 (67.8)	4.15 (4.5)	15.84 (15.6)	--	--	--
L3	C ₁₅ H ₁₂ N ₄ O ₂	--	241	64.28 (64.2)	4.24 (4.3)	20.00 (19.8)	--	--	--
Mn-L1	[MnC ₁₀ H ₂₁ N ₃ O ₈ Cl ₂]	1:1	325	27.52 (27.5)	4.81 (4.3)	9.63 (9.4)	16.05 (16.3)	12.59 (13.0)	5.94
Mn-(L1)2	[MnC ₂₀ H ₂₀ N ₆ O ₆]	1:2	330	48.49 (48.2)	4.04 (3.9)	16.97 (17.2)	--	11.09 (10.8)	5.86
Co-L1	[CoC ₁₀ H ₁₅ N ₃ O ₅ Cl ₂]	1:1	345	31.09 (30.9)	3.88 (3.7)	10.88 (11.1)	18.13 (18.5)	15.26 (14.9)	3.91
Co-(L1)2	[CoC ₂₀ H ₂₄ N ₆ O ₈]	1:2	344	44.86 (44.4)	4.48 (4.5)	15.70 (15.9)	--	11.01 (10.9)	3.98
Ni-L1	[NiC ₁₀ H ₂₉ N ₃ O ₁₂ Cl ₂]	1:1	343	23.45 (23.2)	5.66 (5.8)	8.20 (8.4)	13.67 (13.8)	11.47 (11.1)	3.12
Ni-(L1)2	[NiC ₂₀ H ₂₂ N ₆ O ₇]	1:2	335	46.44 (46.4)	4.25 (4.1)	16.25 (16.2)	--	11.36 (11.4)	3.10
Cu-L1	[CuC ₁₀ H ₁₇ N ₃ O ₆ Cl ₂]	1:1	305	29.37(28.9)	4.16 (4.3)	10.28 (10.4)	17.13 (16.9)	15.54 (15.8)	1.99
Cu-(L1)2	[CuC ₂₀ H ₂₆ N ₆ O ₉]	1:2	343	43.04 (43.2)	4.66 (4.2)	15.06 (15.2)	--	11.39 (11.5)	2.10
Zn-L1	[ZnC ₁₀ H ₁₅ N ₃ O ₅ Cl ₂]	1:1	335	30.58 (30.7)	3.82 (3.9)	10.70 (10.9)	17.83 (17.9)	16.66 (16.8)	--
Zn-(L1)2	[ZnC ₂₀ H ₂₂ N ₆ O ₇]	1:2	355	45.85 (45.9)	4.20 (4.1)	16.04 (16.3)	--	12.49 (12.8)	--
Mn-L2	[MnC ₁₅ H ₁₉ N ₃ O ₆ Cl ₂]	1:1	342	38.96 (38.5)	4.11(4.0)	9.09 (8.9)	15.15 (15.3)	11.88 (11.7)	5.84
Mn-(L2)2	[MnC ₃₀ H ₂₈ N ₆ O ₈]	1:2	320	54.97 (55.1)	4.27 (4.4)	12.82 (12.8)	--	8.38 (8.6)	5.66
Co-L2	[CoC ₁₅ H ₁₇ N ₃ O ₅ Cl ₂]	1:1	328	40.18 (40.4)	3.97 (3.6)	9.37 (9.2)	15.62 (15.4)	13.15 (12.8)	3.81
Co-(L2)2	[CoC ₃₀ H ₂₈ N ₆ O ₈]	1:2	335	54.63 (54.6)	4.24 (4.4)	12.74 (12.5)	--	8.93 (8.7)	3.78
Ni-L2	[NiC ₁₅ H ₁₇ N ₃ O ₅ Cl ₂]	1:1	350	40.20 (40.6)	3.79 (3.9)	9.38 (9.5)	15.63 (15.7)	13.11 (13.4)	2.99
Ni-(L2)2	[NiC ₃₀ H ₂₈ N ₆ O ₈]	1:2	337	54.65 (54.7)	4.25 (4.4)	12.75 (13.1)	--	8.91 (8.6)	3.00
Cu-L2	[CuC ₁₅ H ₁₇ N ₃ O ₅ Cl ₂]	1:1	281	39.77 (39.8)	3.75 (3.9)	9.28 (9.4)	15.46 (15.7)	14.03 (14.4)	2.05
Cu-(L2)2	[CuC ₃₀ H ₂₆ N ₆ O ₇]	1:2	290	55.77 (55.4)	4.02 (4.1)	13.01 (13.1)	--	9.83 (9.9)	1.98
Zn-L2	[ZnC ₁₅ H ₁₇ N ₃ O ₅ Cl ₂]	1:1	355	39.61 (39.4)	3.74 (3.8)	9.24 (9.4)	15.40 (15.6)	14.39 (14.5)	--
Zn-(L2)2	[ZnC ₃₀ H ₂₈ N ₆ O ₈]	1:2	334	54.10 (54.3)	4.20 (4.3)	12.62 (12.7)	--	9.82 (9.7)	--
Mn-L3	[MnC ₁₅ H ₂₈ N ₄ O ₁₀ Cl ₂]	1:1	341	32.79 (32.6)	5.10 (5.3)	10.20 (9.9)	12.75 (13.2)	10.00 (9.8)	5.74
Mn-(L3)2	[MnC ₃₀ H ₃₀ N ₈ O ₈]	1:2	327	52.56 (52.6)	4.38 (4.9)	16.35 (17.2)	--	8.01 (7.82)	5.86
Co-L3	[CoC ₁₅ H ₂₀ N ₄ O ₆ Cl ₂]	1:1	348	37.42 (37.7)	4.15 (4.3)	11.64 (11.9)	14.55 (14.8)	12.24 (12.4)	3.87
Co-(L3)2	[CoC ₃₀ H ₂₆ N ₈ O ₅ Cl ₂]	1:2	345	50.92 (50.6)	3.67 (3.4)	15.84 (15.9)	9.90 (9.8)	8.33 (8.1)	3.91
Ni-L3	[NiC ₁₅ H ₁₆ N ₄ O ₄ Cl ₂]	1:1	345	40.47 (40.3)	3.59 (3.3)	12.59 (13.4)	15.74 (16.3)	13.19 (12.7)	2.90
Ni-(L3)2	[NiC ₃₀ H ₃₆ N ₈ O ₁₀ Cl ₂]	1:2	335	45.18 (45.6)	4.51 (4.6)	14.05 (13.9)	8.78 (9.5)	7.36 (6.9)	2.88
Cu-L3	[CuC ₁₅ H ₁₆ N ₄ O ₄ Cl ₂]	1:1	295	40.04 (40.6)	3.55 (3.9)	12.45 (12.8)	15.57 (15.2)	14.12 (14.3)	1.99
Cu-(L3)2	[CuC ₃₀ H ₂₈ N ₈ O ₇]	1:2	306	53.29 (53.4)	4.14 (4.3)	16.58 (16.7)	--	9.40 (9.7)	1.84
Zn-L3	[ZnC ₁₅ H ₁₆ N ₄ O ₄ Cl ₂]	1:1	338	39.87 (40.3)	3.54 (3.6)	12.40 (11.9)	15.50 (15.3)	14.48 (15.0)	--
Zn-(L3)2	[ZnC ₃₀ H ₃₀ N ₈ O ₈]	1:2	357	51.76 (51.6)	4.31 (4.2)	16.10 (16.4)	--	9.40 (9.5)	--

Table 2. IR band assignments for the investigated ligands (L1-L3).

L1	L2	L3	Band assignment
--	--	3210 m	ν NH
3050 m	3048 m	3070 m	ν CH
1705 w	1678 w	1688 w	ν C=O
1652 m	1595 m	1629 m	ν C=N
1499 m	1493 m	1494 m	ν C=C
1410 s	1414 s	1395 s	ν N=O



For ligand L1, a singlet observed at 2.40 ppm is assigned to CH_3 protons (the integration curve shows three protons). The signals observed at 7.23-7.84, 7.20-8.17 and 7.03-7.87 ppm are assigned to the aromatic hydrogen protons (the integration curve shows five and ten protons for the investigated ligands L1-L3, respectively). The spectrum of ligand L3 exhibits a singlet signal observed at 6.43 ppm is assigned to NH proton (the integration curve shows one proton).

3.1.3. Electronic Spectral Studies

The electronic spectral band of the investigated ligands scanned in different organic solvents are depicted in **Table 3**. In methanol solution, ligands L1 and L2 show three bands, the first one at 253-268 nm referred to π - π^* transition within the phenyl rings. The second band observed at 317-321 nm is ascribed to n - π^* transition of the carbonyl group. The third band at 385-400 nm arises from a transition involving electron migration along the entire conjugate system of the ligand *i.e.* comprises charge transfer (CT) from phenyl ring to the carbonyl group by resonance and from hetero ring by induction [17]. In case of chloroform, cyclohexane, isopropanol and dioxane, the spectra show two bands within the range 260-423 nm. The first band at 260-263 nm is assigned to π - π^* transition within the phenyl rings. The second band at 403-423 nm is ascribed to charge transfer interaction from the phenyl ring to the carbonyl group. For ligand L3 only one absorption band observed at 248-259 nm which may be ascribed to the high energy

π - π^* transition within the phenyl rings.

The ionization potential (Ip) of the investigated ligands (L1-L3) is calculated from their electronic spectral data applying the relationships previously applied [18-20]. The value of the experimental transition energies (E_{CT}) and oscillator strengths (f) were calculated from λ_{max} of the electronic spectra applying the equations previously reported [18-20].

The calculated E_{CT} values, as well as, the corresponding ionization potential (Ip) of the investigated ligands L1-L3 in different organic solvents are listed in **Table 3**. The variation in Ip values was found to follow the same order as λ_{max} of the CT band.

3.2. Characterization of the Complexes

The solid complexes were subjected to elemental analysis and metal content, infrared (FT-IR), ultraviolet and visible spectra (UV-Vis.), magnetic susceptibility (μ_{eff}) and thermal analysis. The results of elemental analysis are given in **Table 1** and are in good agreement with those calculated by the proposed formulae for 1:1 and 1:2 (M:L) solid complexes.

3.2.1. Conductimetric Measurements

Conductimetric titrations of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} metal ions with the investigated nitrosopyrazolone derivatives (L1-L3) were obtained by plotting the calculated molar ratio $[\text{L}]/[\text{M}]$ against the corrected molar conductance values. The results indicate that the conductance increases with the addition of the metal ion solution due to the release of the highly conducting hydrogen ions which may be present in nitroso-oxime tautomers as a result of chelation [10,16]. The titration curves show the presence of two distinctive breaks at metal to ligand 1:1 and 1:2 (M:L), respectively.

The prepared solid complexes of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} metal ions with the investigated ligands (L1-L3) were subjected to elemental analysis for their C, H, N, Cl and metal content [21], infrared (FT-IR), ultraviolet and visible spectra (UV-Vis.), magnetic susceptibility (μ_{eff}) and thermal analysis.

3.2.2. Infrared Studies

Infrared spectral data of the investigated complexes display interesting changes which may give a reasonable idea about these complexes. However, if these changes were interpreted in relation to elemental analysis in **Table 1**, also the thermogravimetric analysis, molar conductance, electronic spectra and magnetic susceptibility measurements, the structure of the solid complexes may be clarified.

In the spectra of the complexes (**Table 4**) the band observed within the range 1410-1395 cm^{-1} [14] assigned to ν N=O in the free ligands shifts to lower wave num-

Table 3. The transition energy (E_{CT}), ionization potential (I_p), oscillator strengths (f) and molar absorptivity (ϵ) derived from the electronic spectra of ligands L1 and L2 in different organic solvents.

Ligand	Solvent	Absorbance	$\lambda_{max, nm}$	E_{CT}	I_p	f	$\epsilon_{max} \times 10^{-4}$
L1	Chloroform	0.06	403	3.07	7.30	0.02	0.12
	Cyclohexane	0.06	403	3.07	7.30	0.02	0.13
	Isopropanol	0.08	403	3.07	7.23	0.03	0.16
	Dioxane	0.06	414	2.99	7.21	0.02	0.12
	Methanol	0.12	385	3.22	7.39	0.04	0.24
L2	Chloroform	0.07	423	2.93	7.16	0.06	0.28
	Isopropanol	0.30	326	3.80	7.84	0.12	1.20
	Dioxane	0.07	411	3.01	7.23	0.05	0.28
	Methanol	0.10	400	3.09	7.29	0.06	0.40

ber indicating the involvement of the N=O group in chelation. Also, the shift of N=O group indicated that it is a center of chelation as it loses its double bond character. The band observed within the range 1705-1678 cm^{-1} assigned to $\nu C=O$ in the free ligands shifts to lower wave number (1610-1650 cm^{-1}) indicating the involvement of the C=O group in chelation as it also loses its double bond character [14]. The OH stretching frequency appears within the range 3336-3447 cm^{-1} for 1:1 and 1:2 complexes as broad band. This is due to the presence of water of hydration and/or coordinated water molecules. In some complexes, a sharp band appears within the range 3423-3640 cm^{-1} ascribed to chelated OH^- , which replace the Cl^- ion in coordination sphere. The OH frequency will be masked under the previously detected broad band [16]. The spectra of the metal complexes exhibit bands in the range 478-550 cm^{-1} that may be assigned to $\nu M-O$ stretching frequency [22,23]. These bands are not observed in the spectra of the free ligands and are possibly due to the formation of coordinated bond ($M \leftarrow O$) or ($M-O$).

3.2.3. Thermal Analysis

TG analyses are very useful method for investigating the thermal decomposition of solid substances involving simple metal salts [24], as well as for complex compounds [25,26]. The thermogram follows the decrease in sample weight with the linear increase in heat treatment temperature ($10^\circ C \text{ min}^{-1}$) up to $800^\circ C$. The aim of the thermal analysis is to obtain information concerning the thermal stability of the investigated complexes as seen in **Table 5** and **Figure 1**, to decide whether water molecules are inside or outside the coordination sphere.

For Mn-L3 (1:1) complex, a mass loss occurred within the temperature range 34-106 $^\circ C$ corresponding to the loss of 3.25% (Calcd 3.27%) for one molecule of water

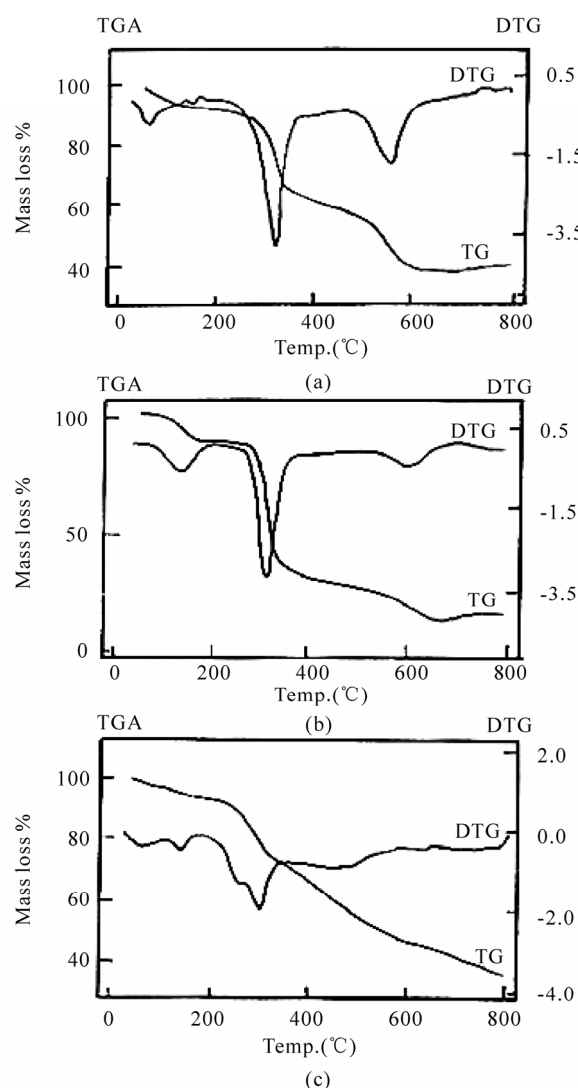
**Figure 1.** Thermogravimetric and derivative thermal analyses curves of Ni-L1 (a), Co-L2 (b) and Mn-L3 (c) 1:1 complex.

Table 4. IR band assignment of Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ complexes with the investigated ligands (L1-L3).

Complex	M:L	$\nu(\text{OH}^-)$	$\nu(\text{OH}) (\text{H}_2\text{O})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{O})$	$\nu(\text{M}-\text{O})$
[Mn(L1)(Cl) ₂ (H ₂ O) ₂]. 4H ₂ O	1:1	--	3430 s	--	1636 w	1593 m	1335 s	500 m
[Mn(L1) ₂ (OH) ₂]	1:2	3465 s	3435 s	--	1637 w	1523 m	1340 s	508 m
[Co(L1)(Cl) ₂ (H ₂ O) ₂]. H ₂ O	1:1	--	3400 s	--	1630 w	--	1350 s	505 m
[Co(L1) ₂ (OH) ₂]. 2H ₂ O	1:2	3552 s	3398 s	--	1635 w	1499 w	1340 s	509 m
[Ni(L1)(Cl) ₂ (H ₂ O) ₂]. 8H ₂ O	1:1	--	3425 s	--	1631 w	--	1353 s	550 m
[Ni(L1) ₂ (OH) ₂]. H ₂ O	1:2	3463 s	3418 s	--	1631 w	--	1340 s	510 m
[Cu(L1)(Cl) ₂ (H ₂ O) ₂]. 2H ₂ O	1:1	--	3352 s	--	1623 w	1488 w	1375 s	530 m
[Cu(L1) ₂ (OH) ₂]. 3H ₂ O	1:2	3435 s	3358 s	--	1646 w	--	1408 s	509 m
[Zn(L1)(Cl) ₂ (H ₂ O) ₂]. H ₂ O	1:1	--	3362 s	--	1637 w	1527 m	1365 s	509 m
[Zn(L1) ₂ (OH) ₂]. H ₂ O	1:2	3444 s	3396 s	--	1637 w	1535 m	1340 s	510 m
[Mn(L2)(Cl) ₂ (H ₂ O) ₂]. 2H ₂ O	1:1	--	3360 s	--	1632 w	1580 m	1356 s	509 m
[Mn(L2) ₂ (OH) ₂]. 2H ₂ O	1:2	3500 s	3397 s	--	1632 w	1595 m	1356 s	500 m
[Co(L2)(Cl) ₂ (H ₂ O) ₂]. H ₂ O	1:1	--	3405 s	--	1627 m	1595 m	1358 s	488 m
[Co(L2) ₂ (OH) ₂]. 2H ₂ O	1:2	3630 s	3360 s	--	1627 m	1595 w	1357 s	500 m
[Ni(L2)(Cl) ₂ (H ₂ O) ₂]. H ₂ O	1:1	--	3433 s	--	1632 w	1596 w	1359 s	478 w
[Ni(L2) ₂ (OH) ₂]. 2H ₂ O	1:2	3640 s	3405 s	--	1632 w	1596 w	1359 s	487 w
[Cu(L2)(Cl) ₂ (H ₂ O) ₂]. H ₂ O	1:1	--	3369 s	--	1620 w	1532 m	1421 s	486 m
[Cu(L2) ₂ (OH) ₂]. H ₂ O	1:2	3610 s	3289 s	--	1624 w	1610 m	1419 s	486 m
[Zn(L2)(Cl) ₂ (H ₂ O) ₂]. H ₂ O	1:1	--	3402 s	--	1635 m	1612 m	1378 s	507 w
[Zn(L2) ₂ (OH) ₂]. 2H ₂ O	1:2	3630 s	3388 s	--	1615 m	1614 m	1380 s	497 w
[Mn(L3)(Cl) ₂ (H ₂ O) ₂]. 6H ₂ O	1:1	--	3445 s	3350 m	1619 w	1570 m	1377 s	505 w
[Mn(L3) ₂ (OH) ₂]. 2H ₂ O	1:2	3423 s	3340 s	3220 m	1650 w	1631 m	1361 s	504 w
[Co(L3)(Cl) ₂ (H ₂ O) ₂]. 2H ₂ O	1:1	--	3447 s	3335 m	1620 w	1575 w	1378 s	510 w
[Co(L3) ₂ (Cl) ₂]. H ₂ O	1:2	--	3336 s	3210 m	1627 w	1570 w	1362 s	508 w
[Ni(L3)(Cl) ₂]. 2H ₂ O	1:1	--	3344 s	3200 m	1621 w	1600 m	1390 s	510 m
[Ni(L3) ₂ (Cl) ₂]. 6H ₂ O	1:2	--	3344 s	3200 m	1621 w	1563 m	1390 s	510 m
[Cu(L3)(Cl) ₂]. 2H ₂ O	1:1	--	3348 s	3220 m	1610 w	1580 m	1365 s	510 m
[Cu(L3) ₂ (OH) ₂]. H ₂ O	1:2	3446 s	3348 s	3230 m	1612 w	1550 m	1360 s	511 m
[Zn(L3)(Cl) ₂ (H ₂ O) ₂]	1:1	--	3354 s	3227 m	1624 w	1567 w	1394 s	494 w
[Zn(L3) ₂ (OH) ₂]. 2H ₂ O	1:2	3552 s	3364 s	3245 m	1618 w	1615 w	1401 s	497 w

s: strong, m: medium, w: weak

and at the temperature range 108-170°C another loss of 2.88% (Calcd. 3.20%) for another one water molecule. In the temperature range 170-256°C a mass loss of 14.44% (Calcd. 14.03%) corresponding to four water molecules. At the temperature 256-351°C a loss of 8.10% (Calcd. 8.16%) for two coordinated water molecules. At higher

temperature range 353-585°C a loss of 23.40% (Calcd. 23.78) and at the temperature range 585-797°C a loss of 11.68% (Calcd. 11.88%) corresponding to a loss of the organic moiety as an intermediate species. At the end of the thermogram at higher temperature the metal oxide and chloride residues MnO and MnCl₂ are formed as final

Table 5. Thermogravimetric results of Mn²⁺, Co²⁺ and Ni²⁺ complexes with the investigated ligands (L1-L3).

Complex	M. Wt.	Temp. °C	Calcd.	Found	Assignment
			loss %	loss %	
[Mn(C ₁₅ H ₁₂ N ₄ O ₂)(Cl) ₂ (H ₂ O) ₂]. 6H ₂ O	548.9	34-105	3.27	3.25	H ₂ O
[Mn(C ₁₅ H ₁₂ N ₄ O ₂)(Cl) ₂ (H ₂ O) ₂]. 5H ₂ O	530.9	105-170	3.39	2.88	H ₂ O
[Mn(C ₁₅ H ₁₂ N ₄ O ₂)(Cl) ₂ (H ₂ O) ₂]. 4H ₂ O	512.9	170-256	14.03	14.44	4 H ₂ O
[Mn(C ₁₅ H ₁₂ N ₄ O ₂)(Cl) ₂ (H ₂ O) ₂]	440.9	256-351	8.16	8.10	2 coordinated H ₂ O
[Mn(C ₁₅ H ₁₂ N ₄ O ₂)(Cl) ₂]	404.9	353-585	23.78	23.40	-NHPPh, NO
[Mn(C ₁₂ H ₆ O)(Cl) ₂]	282.9	585-797	11.88	11.68	3 C, H, N ₂
		800	35.66	35.71	MnCl ₂ + MnO
[Co(C ₁₅ H ₁₁ N ₃ O ₂)(Cl) ₂ (H ₂ O) ₂]. H ₂ O	447.9	79-213	12.05	11.90	H ₂ O, 2 coordinated H ₂ O
[Co(C ₁₅ H ₁₁ N ₃ O ₂)(Cl) ₂]	393.9	213-460	61.84	61.00	2Ph, Cl ₂ , C-CH, CO
[Co(N ₃ O)]	116.9	461-721	12.94	13.00	NO, N ₂
		721-800	16.72	16.50	CoO
[Ni(C ₁₀ H ₉ N ₃ O ₂)(Cl) ₂ (H ₂ O) ₂]. 8H ₂ O	511.7	37-144	7.03	6.50	2 H ₂ O
[Ni(C ₁₀ H ₉ N ₃ O ₂)(Cl) ₂ (H ₂ O) ₂]. 6H ₂ O	475.7	146-370	28.14	28.90	6 H ₂ O, 2 coordinated H ₂ O
[Ni(C ₁₀ H ₉ N ₃ O ₂)(Cl) ₂]	331.7	372-607	24.62	24.60	N ₂ , C-CH, NO, CH ₃ , CO
		607-800	39.71	39.99	NiCl ₂ +NiO

product, the remainder is 35.71% (Calcd. 35.66%).

For Ni-L1 (1:1) complex, a mass loss occurred within the temperature range 36-144°C corresponding to the loss of 6.5% (Calcd. 7.03%) for two hydrated water molecules and at the temperature range 146-370°C corresponding to a loss of 28.90% (Calcd. 28.14%) for hydrated and two coordinated water molecules. In the temperature range 372-607°C a mass loss of 24.60% (Calcd. 24.62%) corresponding to the formation of intermediate species through the decomposition of the organic moiety of the complex [15] and this continues till a constant weight is obtained where a mixture of nickel chloride and nickel oxide residue are formed, the remainder is 39.99% (Calcd. 39.71%).

For Co-L2 (1:1) complex, a mass loss occurred within the temperature range 79-213°C corresponding to a loss of 11.90% (Calcd. 12.05%) for three water molecules. At the temperature range 213-460°C a loss of 61.00% (Calcd. 61.84%) and at the temperature range 461-721°C a loss of 13.00% (Calcd. 12.94%) corresponding to the formation of intermediate species. At higher temperature more than 721°C and at the end of the process a metallic oxide residue CoO is formed, the remainder is 16.50% (Calcd. 16.72%).

3.2.4. Molar Conductance Measurements

The molar conductivities of 1 mM in DMF (10⁻³ M) of some of the given complexes show that the investigated complexes are neutral in nature since the values obtained

are 7.45-37.7 ohm⁻¹ cm² mol⁻¹. These values were small to account for ionic complexes of the investigated metal ions.

For Mn-L1 (1:2), Co-L1 (1:1), Ni-L1 (1:1) and (1:2), Cu-L1 (1:2) and Zn-L1 (1:2), the values were 20.30, 17.29, 7.45, 13.88, 19.46 and 17.20 ohm⁻¹ cm² mol⁻¹, respectively.

For Mn-L2 (1:2), Co-L2 (1:2), Ni-L2 (1:2) and Cu-L2 (1:2) the values were 16.74, 10.25, 13.85 and 11.17 ohm⁻¹ cm² mol⁻¹, respectively.

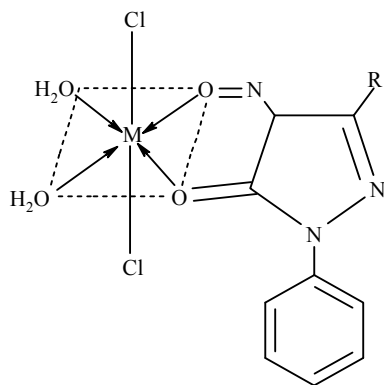
For Mn-L3 (1:1), Co-L3 (1:2), Ni-L3 (1:1) and (1:2), Cu-L3 (1:1) and Zn-L3 (1:1), the values were 25.30, 37.70, 20.90, 24.30, 32.7 and 13.25 ohm⁻¹ cm² mol⁻¹, respectively. These low conductivity values may be ascribed to the coordination of chloride ions, if present, rather than the ionic association to the metal ions during complex formation. This directly supports the fact that all of the investigated complexes are non-ionic in nature.

3.2.5. Electronic Spectral and Magnetic Studies

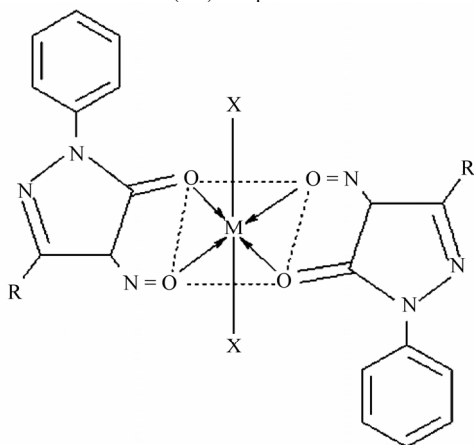
The Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ complexes (Table 1) show a high spin value d⁵, d³, d² and d¹ configurations as the ground state, the magnetic susceptibility (μ_{eff.} = 5.66-5.94 B. M.), (μ_{eff.} = 3.78-3.98 B. M.), (μ_{eff.} = 2.88-3.12 B. M.) and (μ_{eff.} = 1.84-2.10 B. M.) with the ligands (L1-L3), respectively, indicating (t_{2g}³e_g²), (t_{2g}³e_g), (t_{2g}²e_g) and (t_{2g}¹e_g). The high spin values of magnetic susceptibility may be due to the ligands being weak ligands [27].

Electronic absorption spectra of the free ligands and some of their chelates were recorded in DMF. In the free ligands the CT band appears in the range 385-400 nm for the ligands L1-L3. A shift to longer wavelength is observed on complex formation. This may be attributed to the M→L charge transfer CT spectra. A band of low intensity is observed at 460 nm for Co-L1 (1:1), and 458 nm for Co-L3 (1:2) which is typical for six-coordinate high-spin Co²⁺ complexes. The corresponding bands in the octahedral [Co(H₂O)₆]²⁺ ion have been assigned to ⁴T_{1g}→⁴T_{2g} (F), ⁴T_{1g}→²A_{1g} (F) and ⁴T_{1g}→⁴T_{1g} (P) transitions, respectively [28]. The absorption spectral bands of Ni-L3 (1:1) at 458 nm and 450 for Ni-L2 (1:2) are assigned to the ³A_{2g}→³T_{1g} (F) and ³A_{2g}→³T_{1g} (P) transitions, respectively, in an octahedral geometry [29] and is almost identical with that of the octahedral [Ni(H₂O)₆]²⁺ ion [30]. It is difficult to relate spectra with the structure of Cu²⁺ complexes, especially in view of the distorted geometry observed for its complexes [28].

Based on the above results the suggested structures of the 1:1 and 1:2 (M:L) complexes between the metal ions and the ligands can be represented as follows:



(1:1) complexes



(1:2) complexes

X = OH in all cases except for Co²⁺ and Ni²⁺ with ligand L3
R = CH₃-, Ph- and PhNH-, (1:2) complexes

4. CONCLUSIONS

In the present paper, the data obtained from elemental analysis, FT-IR, electronic absorption spectra, thermal analyses, molar conductivities and magnetic susceptibility measurements show that the complexes of Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ metal ions with the investigated ligands L1-L3 may be formulated, where bonding in case of 1:1 and 1:2 complexes are formed through coordination with oxygen of the carbonyl group and nitroso group. The complexes obtained contain water of coordination in their sphere. The investigated ligands act as neutral bidentate ligands. The solid complexes prepared behave as non-electrolytes in DMF solution. The electronic spectra of the investigated ligands exhibits a CT band appears in the range 385-400 nm for the ligands L1-L3. A shift to higher wavelength is observed on complex formation which may be attributed to M→L charge transfer spectra. The bands observed at higher wavelengths which are not observed in the spectra of the free ligands may be ascribed to d-d electronic transition within the metal ions. The complexes exhibit an octahedral or distorted octahedral (Cu²⁺ complexes) coordination with the investigated ligands.

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