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Synthesis and characterization of iron(III), manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of salicylidene-*N*-anilinoacetohydrazone (H_2L^1) and 2-hydroxy-1-naphthylidene-*N*-anilinoacetohydrazone (H_2L^2)

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Abstract

Salicylidene-*N*-anilinoacetohydrazone (H_2L^1) and 2-hydroxy-1-naphthylidene-*N*-anilinoacetohydrazone (H_2L^2) and their iron(III), manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes have been synthesized and characterized by IR, electronic spectra, molar conductivities, magnetic susceptibilities and ESR. Mononuclear complexes are formed with molar ratios of 1:1, 1:2 and 1:3 (M:L). The IR studies reveal various modes of chelation. The electronic absorption spectra and magnetic susceptibility measurements show that the iron(III), nickel(II) and cobalt(II) complexes of H_2L^1 have octahedral geometry. While the cobalt(II) complexes of H_2L^2 were separated as tetrahedral structure. The copper(II) complexes have square planar stereochemistry. The ESR parameters of the copper(II) complexes at room temperature were calculated. The *g* values for copper(II) complexes proved that the Cu—O and Cu—N bonds are of high covalency.

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Keywords: Mononuclear complexes; Magnetism; Spectra; Hydrazone shiff bases

1. Introduction

Acid hydrazides exhibit a broad spectrum of biological, bactericidal and fungicidal activities [1,2]. The complexes of hydrazide and other hydrazine derivatives have great interest due to their analytical, industrial and pharmacological importance [3,4]. The group 12 metal ions in concentration less than 10^{-8} M can be detected and determined using Ru(II) (di-2-pyridylketone-*p*-nitrophenyl hydrazone $[Ru(pby)_2(dpknph)]Cl_2$ [5]. The coordination chemistry of these ligands is also of interest because they behave differently toward transition metal ions depending on the reaction conditions and the anions [6]. In this paper, we report the syntheses as well as magnetic and spectral properties of Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of salicylidene-*N*-anilinoacetohydrazone (H_2L^1) and 2-hydroxy-1-naphthylidene-*N*-anilinoacetohydrazone (H_2L^2).

2. Experimental

Reagent grade chemicals were used without further purification. The hydrazone schiff bases H_2L^1 and H_2L^2 were prepared by adding equimolar amounts of salicylaldehyde or 2-hydroxy-1-naphthaldehyde to *N*-anilinoacetylhydrazide in 50 ml absolute ethanol. The mixture is magnetically stirred and heated for an hour. The formed solid product was filtered off, washed with ethanol, crystallized from ethanol and finally dried under vacuum over anhydrous $CaCl_2$. The metal complexes were prepared by stirring magnetically at ca 70 °C, the solution of 0.02 mol of metal salts with 0.02 or 0.04 mol of the appropriate ligand (H_2L^1 and H_2L^2) in ca. 50 ml EtOH for a period of hours. The resulting solid complexes were filtered off, washed several times with ethanol and dried under vacuum over P_4O_{10}. Elemental analyses (C, H, Cl) were estimated by the microanalytical unit in Cairo University. IR spectra were performed as KBr discs using a Perkin-Elmer 1430 recording spectrophotometer. The electronic spectra were carried out in *N*,N^1-dimethylformamide (DMF) solution using a Perkin-Elmer Lambda 4B spectrophotometer. The electron spin resonance spectra (ESR) were recorded using a varian E104 spectrophotometer and calibrated with

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Table 1
Colour, molar conductivities, molar ratios of preparation (M:L), magnetic moments and elemental analyses of ligands and their metal complexes

No.	Compound	Colour F.W	Salt and molar ratios of M:L preparation	Found, % (calculated)			Λ_M^a	μ_{eff}, per metal ion (BM)
				C	H	Cl		
	$H_2L^1C_{15}H_{15}N_3O_2$	Yellow 269.31	–	67.4 (67.2)	5.3 (5.2)	–	–	–
1	$[Fe(HL^1)_3]C_{45}H_{42}FeN_9O_6$	Brown 860.91	$FeCl_3$ (1:1) or (2:1)	63.3 (63.0)	3.7 (4.6)	–	23.50	5.60
2	$[Mn(HL^1)_2]C_{30}H_{28}MnN_6O_4$	Orange 591.60	$Mn(OAc)_2$ (1:1) or (2:1)	61.8 (61.1)	3.8 (4.4)	–	17.00	4.50
3	$[Co(HL^1)_2]C_{30}H_{28}CoN_6O_4$	Blue 595.54	$CoCl_2$ (1:1)	60.9 (60.7)	3.8 (4.4)		26.00	3.40
4	$[Co(HL^1)(H_2L^1)(NO_3)]C_{30}H_{29}CoN_7O_7$	Brown 658.55	$Co(NO_3)_2$ (1:1)	55.7 (54.9)	4.2 (4.1)		33.5	4.30
5	$[Co(HL^1)_2]C_{30}H_{28}CoN_6O_4$	Brown 595.54	$Co(OAc)_2$ (2:1)	60.4 (60.7)	4.5 (4.4)		17.80	4.60
6	$[Co(HL^1)(OAc)(H_2O)_2]C_{17}H_{22}CoN_3O_6$	Brown 422.19	$Co(OAc)_2$ (1:1)	49.2 (48.5)	4.4 (4.8)		13.20	4.60
7	$[Ni(HL^1)(H_2L^1)(NO_3)]C_{30}H_{29}NiN_7O_7$	Green 658.35	$Ni(NO_3)_2$ (1:1)	55.3 (54.9)	4.5 (4.1)	–	30.70	2.70
8	$[Ni(HL^1)(H_2L^1)Cl]C_{30}H_{29}ClNiN_6O_4$	Green 681.84	$NiCl_2$ (1:1)	57.1 (57.2)	4.8 (4.3)	5.5, 5.6	24.0	2.5
9	$[Ni(HL^1)_2]C_{30}H_{28}NiN_6O_4$	Green 595.33	$Ni(OAc)_2$ (2:1)	60.3 (60.7)	4.3 (4.4)	–	18.1	3.60
10	$[Cu(H_2L^1)Cl_2]C_{30}H_{30}Cl_2NiN_6O_4$	Brown 403.85	$CuCl_2$ (1:1)	44.7 (44.7)	3.5 (3.5)	16.7 (17.6)	24.00	1.63
11	$[Cu(HL^1)(OAc)]\cdot H_2OC_{17}H_{19}CuN_3O_5$	Green 408.84	$Cu(OAc)_2$ (1:1)	50.6 (50.1)	4.3 (4.4)	–	11.8	1.86
12	$[Cu(HL^1)_2]C_{30}H_{28}CuN_6O_4$	Green 600.14	$Cu(OAc)_2$ (2:1)	60.4 (60.3)	4.9 (4.4)	–	13.00	2.20
13	$[Cu(HL^1)NO_3]C_{15}H_{14}CuN_4O_5$	Green 393.85	$Cu(NO_3)_2$ (1:1)	44.1 (43.8)	3.9 (3.7)	–	24.00	1.60
14	$[Zn(HL^1)_2]C_{30}H_{28}ZnN_6O_4$	Yellow 601.97	$Zn(OAc)_2$ (2:1)	60.9 (60.1)	3.5 (4.3)		10.3	–
	$H_2L^2C_{19}H_{17}N_3O_2$	Yellow 319.37		72.3 (71.5)	5.3 (5.3)	–	–	
15	$[Fe\ (HL^2)_3]\cdot H_2OC_{57}H_{50}FeN_9O_7$	Brown 1029.08	$FeCl_3$ (2:1)	66.6 (66.5)	4.8 (4.9)	–	18.7	6.10
16	$[Mn(HL^2)_2]C_{38}H_{32}MnN_6O_4$	Yellow 691.72	$Mn(OAc)_2$ (1:1)	66.9 (66.0)	4.9 (4.7)	–	20.4	5.50
17	$[Co(HL^2)(H_2L^2)Cl]C_{38}H_{33}ClCoN_6O_4$	Green 732.16	$CoCl_2$ (1:1)	62.9 (62.3)	5.0 (4.5)	5.0 (4.8)	34.6	4.20
18	$[Co(HL^2)_2]C_{38}H_{32}CoN_6O_4$	Brown 695.65	$Co(NO_3)_2$ (1:1)	66.0 (65.6)	4.3 (4.6)	–	22.0	3.20
19	$[Co(HL^2)_2]\cdot H_2OC_{38}H_{34}CoN_6O_5$	Brown 713.65	$Co(OAc)_2$ (1:1)	63.9 (64.0)	4.4 (4.8)	–	21.74	3.80
20	$[Ni(HL^2)_2]\cdot 2H_2OC_{38}H_{36}NiN_6O_6$	Green 731.42	$NiCl_2$ (1:1)	62.1 (62.4)	5.3 (4.96)		24.52	2.90
21	$[Ni(HL^2)(H_2L^2)(NO_3)]\cdot H_2OC_{38}H_{35}NiN_7O_8$	Green 776.37	$Ni(NO_3)_2$ (1:1)	58.4 (58.8)	3.9 (4.5)		21.30	3.10
22	$[Ni(H_2L^2)(OAc)_2]\cdot H_2OC_{42}H_{42}NiN_6O_9$	Orange 833.44	$Ni(OAc)_2$ (2:1)	60.4 (60.5)	4.7 (5.08)		18.6	4.10
23	$[Cu(HL^2)_2]C_{38}H_{32}CuN_6O_4$	Brown 700.17	$CuCl_2$ (1:1)	65.3 (65.2)	4.7 (4.6)		13.00	2.20
24	$[Zn(HL^2)Cl(H_2O)]C_{19}H_{18}ClZnN_3O_3$	Brown 437.23	$ZnCl_2$ (1:1)	51.5 (52.2)	4.6 (4.1)		23.00	–
25	$[Zn(HL^2)_2]C_{38}H_{32}ZnN_3O_2$	Yellow 702.09	$Zn(OAc)_2$ (1:1)	64.4 (65.1)	4.9 (5.1)	–	15.00	–

a in Ω^{-1} cm^2 mol^{-1}.

Table 2
Infrared spectral bands for the ligands and their metal complexes

No.	Compound	ν(O—H)	ν(N—H)	ν(C═O)	ν(C═N)	ν(C—OH)	δ(O—H)	ν(M—O)	ν(M—N)	ν(M—Cl)
	H_2L^1	3400(br)	3310, 3270	1680	1620	1275	1145	–	–	–
1	$[Fe(HL^1)_3]$	3300(s)	3130	–	1622, 1603	1275	1145	500	435	–
2	$[Mn(HL^1)_2]$	3420(s)	3150	–	1620, 1600	1290	1155	525	405	–
3	$[Co(HL^1)_2]$	3400	3200	–	1615, 1600	1275	1145	455	425	–
4	$[Co(HL^1)(H_2L^1)(NO_3)]$	3410, 3370(s)	3170	1620	1615, 1605	1275, 1265	1145, 1155	485	420	–
5	$[Co(HL^1)_2]$	3420	3200	–	1620, 1600	1285	1150	485	420	–
6	$[Co(HL^1)(OAc)(H_2O)_2]$	3400(br)	3220	–	1615, 1600	1285	1150	505	450	-
7	$[Ni(HL^1)(H_2L^1)(NO_3)]$	3410, 3370	3200(br)	1620	1615, 1605	1275, 1265	1145, 1155	450	420	–
8	$[Ni(HL^1)(H_2L^1)Cl]$	3410(sh), 3370(s)	3180	1620	1615, 1605	1275, 1265	1145, 1155	490	420	355
9	$[Ni(HL^1)_2]$	3410	3190	–	1620, 1605	1280	1155	495	420	–
10	$[Cu(H_2L^1)Cl_2]$	3340	3150	1680	1600	1280	1155	495	470	325
11	$[Cu(HL^1)(OAc)]\cdot H_2O$	3420[a]	3310, 3290	1615	1600	–	–	505	475	–
12	$[Cu(HL^1)_2]$	–	3310, 3250	1620	1600	–	–	520	400	–
13	$[Cu(HL^1)(NO_3)]$	3400	3200	–	1605, 1585	1280	1150	515	465	–
14	$[Zn(HL^1)_2]$	3420	–	–	1620, 1610	1280	1155	455	420	–
	H_2L^2	3460(br)	3330, 3290,	1680(s)	1620	1205	1050	–	–	–
15	$[Fe(HL^2)_3]\cdot H_2O$	3350	3150	–	1623, 1605	1205	1050	520	470	–
16	$[Mn(HL^2)_2]$	3410	3200	–	1620, 1605	1215	1090	505	450	–
17	$[Co(HL^2)(H_2L^2)Cl]$	3390	3330, 3290	1670	1625, 1605	1205	1080	525	425	350
18	$[Co(HL^2)_2]$	–	3330, 3290	1670	1605	–	–	505	425	–
19	$[Co(HL^2)_2]\cdot H_2O$	3350	3290	–	1620, 1605	1205	1080	505	410	–
20	$[Ni(HL^2)_2]\cdot 2H_2O$	3400, 3350[a]	3150	–	1620, 1605	1225	1090	510	425	–
21	$[Ni(HL^2)(H_2L^2)(NO_3)]\cdot H_2O$	3380	3200	1620	1620, 1605	1225, 1205	1185, 1080	480	420	–
22	$[Ni(H_2L^2)(OAc)_2]\cdot H_2O$	3420, 3350[a]	3200	1618	1605	1210	1145	455	425	–
23	$[Cu(HL^2)_2]$	–	3330, 3290	1680	1605	–	–	500	425	–
24	$[Zn(HL^2)Cl(H_2O)]$	3500[a]	3330, 3130	1680	1610	–	–	475	425	350
25	$[Zn(HL^2)_2]$	–	3330, 3290	1620	1605	–	–	455	425	–

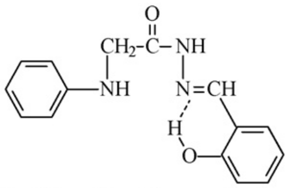
[a] $\nu(H_2O)$.

diphenyl-picrylhydrazide. The ^1H NMR spectra were recorded in deutrated chloroform ($CDCl_3$) using a 300 MHz Varian NMR spectrophotometer. Magnetic susceptibilities were measured at 27 °C using the modified Gouy method with a Jahnson Matthay balance. The molar conductivity measurements were made in DMF solution (10^{-3} M) using a type CD-6N Tacussel conductometer.

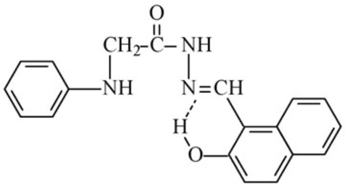
3. Results and discussion

The colours, the metal salts and molar ratios of preparation, molar conductivities, stoichiometries, and elemental analyses of the prepared complexes are listed in Table 1. The analytical data show that the reaction of ligands with different salts; Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions in different appropriate molar ratios give mononuclear complexes with different stoichiometries 1:1, 1:2 and 1:3 (M:L). The 1:1 and 1:2 molar ratio reactions of iron(III) chloride with the ligands separate the complex $[Fe(HL)_3]\cdot nH_2O$. The elemental analyses support the formation of metal complexes represented in Table 1. These air stable metal complexes are non-hygroscopic, partially soluble in most organic solvents but freely soluble in DMF and DMSO. The molar conductivities in DMF (10^{-3} M) solution show that the complexes behave as non-electrolytes, indicating coordination of anions [7]. The ^1H NMR spectra of H_2L^1 and H_2L^2 ligands have been carried out in deutrated chloroform ($CDCl_3$) at room temperature. The spectra of ligands show signals within 13.03–11.39, 9.67–8.71, 9.2–7.4 and 7.9–6.95 (multiple signals) ppm range assigned to OH proton in intramolecular hydrogen bonding OH···N, NH, =CH and aromatic protons, respectively. The spectra of H_2L^1 and H_2L^2 display signals at 3.99 and 4.33 ppm due to CH_2 protons.

The infrared spectra of ligands (Table 2) reveal bands at 3460–3400; 3330–3310, 3290–3270; 1680; 1620; 1275–1205 and 1145–1080 cm^{-1}, assigned to intramolecular hydrogen bonded hydroxy group ν(OH···H); ν(NH); ν(C=O); ν(C=N); ν(C–OH) and δ(O–H), respectively. The elemental analyses and



Salicylidene-N-anilinoacetohydrazone(H_2L^1)



2-hydroxy-1-naphthylidene-N-anilinoacetohydrazone (H_2L^2)

Fig. 1. The chemical structure for H_2L^1 and H_2L^2.

Table 3
Solution (DMF) electronic spectra (cm^{-1}) of the ligands and their metal complexes

Compound	Intraligand and charge transfer bands				d–d bands	
H_2L^1	35,020	29,410	27,240			
$[Fe(HL^1)_3]$	34,650	30,420	29,850	24,630	19,940	15,600
$[Mn(HL^1)_2]$				23,809	19,230	17,857
$[Co(HL^1)_2]$	34,910	31,060	29,940	25,000	20,200	15,480
$[Co(HL^1)(H_2L^1)(NO_3)]$	34,970	30,600	29,640	23,760	16,950	14,650
$[Co(HL^1)_2]$	34,840	29,720	28,780	23,620	17,100	14,920
$[Co(HL^1)(OAc)(H_2O)_2]$	34,960	30,100	29,650	24,210	17,240	14,870
$[Ni(HL^1)(H_2L^1)(NO_3)]$	33,740	29,870	28,800	23,940	16,420	
$[Ni(HL^1)(H_2L^1)Cl]$	34,150	30,200	28,750	24,100	16,540	
$[Ni(HL^1)_2]$	33,780	30,150	29,940	23,970	16,620	
$[Cu(H_2L^1)Cl_2]$	34,120	30,100	29,870	23,980	15,560	
$[Cu(HL^1)(OAc)]\cdot H_2O$	34,950	30,240	29,920	24,220	14,970	
$[Cu(HL^1)_2]$	33,740	30,760	29,740	23,950	15,950	
$[Cu(HL^1)(NO_3)]$	34,540	30,660	28,760	24,390	15,500	
H_2L^2	34,840	30,120	27,170			
$[Fe(HL^2)_3]\cdot H_2O$	34,620	29,850	29,410	22,730	20,000	15,390
$[Mn(HL^2)_2]$				23,809	20,325	16,325
$[Co(HL^2)(H_2L^2)Cl]$	33,970	31,220	30,400	23,420	19,940	14,980
$[Co(HL^2)_2]$	34,480	30,970	29,960	24,680	19,870	14,870
$[Co(HL^2)_2]\cdot H_2O$	34,200	31,420	30,650	23,950	20,420	15,200
$[Ni(HL^2)_2]\cdot 2H_2O$	33,500	30,790	29,870	23,750		16,430
$[Ni(HL^2)(H_2L^2)(NO_3)]\cdot H_2O$	34,220	29,920	30,140	23,780		16,520
$[Ni(H_2L^2)(OAc)_2]\cdot H_2O$	33,970	29,780	30,170	24,120		16,500
$[Cu(HL^2)_2]$	34,150	29,970	30,120	23,780		14,980

spectral data for H_2L^1 and H_2L^2 verified the structure shown in Fig. 1.

The most important IR spectral bands of metal complexes are listed in Table 2. The IR spectra of complexes 1, 2, 3, 5, 6, 9, 13, 14, 15, 16, 19 and 20 reveal that, the ν(C=N) shows a shift to lower frequency ca.15 cm^{-1} compared to those of the free ligands, indicating that the azomethine nitrogen involved in coordination. The spectra of these metal complexes show also that the ν(C=O) disappears upon coordination and a new band appears at 1620 cm^{-1}, assigned to ν(N–N=C–O), indicating that the ligands in these complexes coordinate in their enol-form via the enolic oxygen atom. The ν(–OH), ν(C–OH) and δ(–O–H) bands in the spectra of this group of complexes except 1, 3, 15 and 19 display a shift to lower or higher frequencies, indicating that the O–H group coordinated without a deprotonation. The above arguments and elemental analyses indicate that the ligands behave as tridentate monobasic ligands and coordination occurs via the azomethine nitrogen, deprotonated enolic oxygen and the hydroxy oxygen atom. Whereas in case of complexes 1, 3, 15 and 19, the OH frequencies appear at the same positions as those of the free ligands, indicates that the OH group does not participate in coordination. The ligands in these complexes (1, 3, 15, 19) react with the metal ion as a monobasic bidentate ligands. The coordinations occur via the azomethine nitrogen and enolic oxygen atom. The IR spectra of complexes, 11, 12 and 25 show that the ν(C=O) and ν(C=N) bands shift to lower frequencies compared to those of the free ligands, indicates the involvement of the azomethine nitrogen and the carbonyl oxygen in coordination. The spectra also show that the frequencies of OH group disappear, indicating the deprotonation of the OH group upon coordination. The IR spectra of complexes 4, 7, 8 and 21 show bands corresponding to coordinated and uncoordinated hydroxy group, coordinated carbonyl oxygen, coordinated azomethine nitrogen and –HC=N–N=C–O. This can only achieved when the metal ion combines with a neutral and anionic ligands, the anionic one behaves as a monoanionic tridentate ligand and coordinates via the protonated phenolic oxygen, deprotonated enolic oxygen and the azomethine nitrogen. The neutral one behaves as a bidentate one and coordinates via the azomethine nitrogen and carbonyl oxygen atom. The IR spectra of complexes 18, 23 and 24 show that the bands corresponding to OH frequencies disappear upon coordination, the ν(C=N) appears at lower frequency compared to those of the free ligands and the νC=O) does not show any shift because it does not participate in coordination. This reveals that the ligands behave as a monoanionic bidentate one and coordinate via the azomethine nitrogen and deprotonated phenolic oxygen atom. The IR spectrum of complex 10 shows the band corresponding to ν(C=N) at lower frequency compared to that of the ligand. The frequencies of phenolic OH group display shift to lower or higher frequencies. The ν(C=O) appears at the same frequency compared to that of the free ligand. This may be considered as evidence that the ligand behaves as a neutral bidentate

Table 4
Solid state ESR spectral parameters of the copper(II) complexes

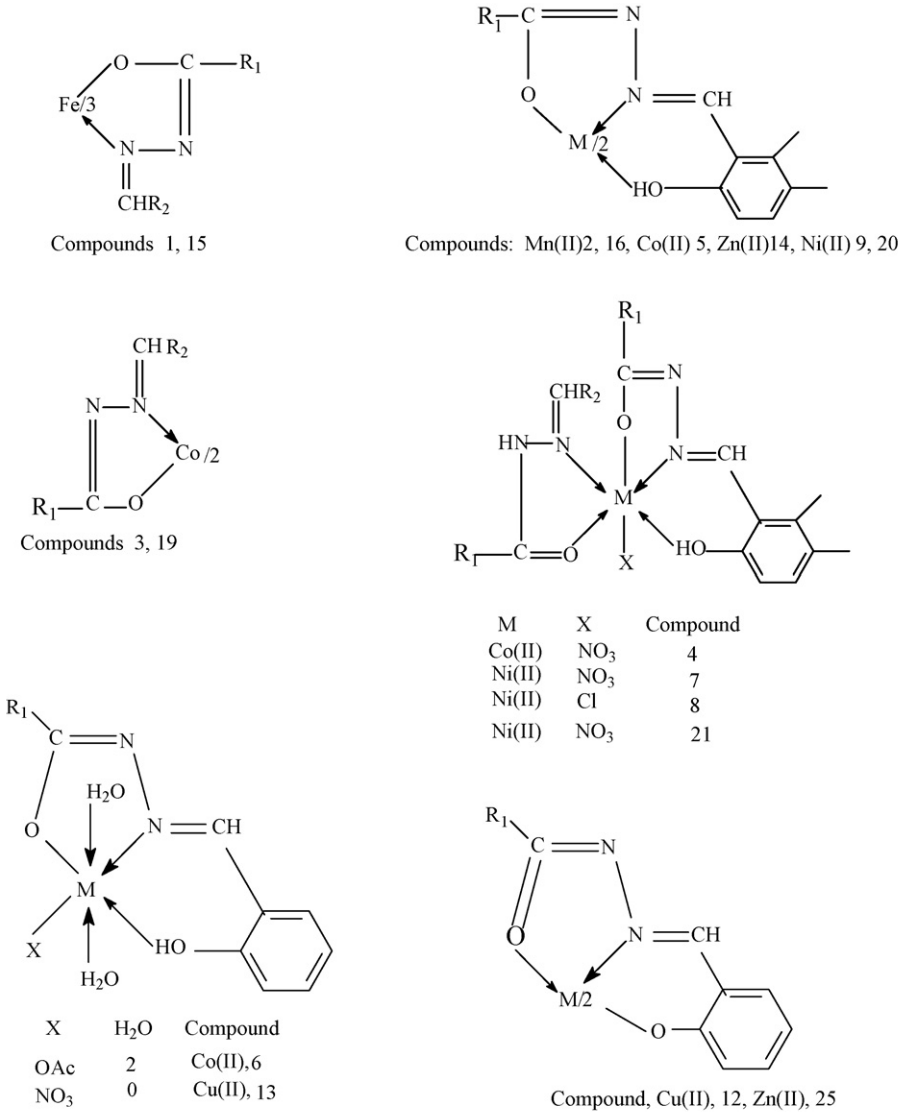
Compound	g_{11}	g_{1}	g_{av} or g_{iso}
$[Cu(H_2L^1)Cl_2]$			2.125
$[Cu(HL^1)(OAc)]\cdot H_2O$			2.116
$[Cu(HL^1)(NO_3)]$	2.223	2.059	2.114
$[Cu(HL^2)_2]$			2.113

one and coordinates via the azomethine nitrogen and protonated phenolic oxygen atom. The IR spectrum of complex 17 shows bands corresponding to ν(C=O), ν(OH), ν(C–OH) and δ(OH) at the same frequencies as that of the free ligand. The spectrum also shows two bands at 1625 and 1602 cm^{-1}, assigned to ν(–N–N=C–O) and ν(C=N), respectively. This would be fulfilled if Co(II) bonded with two ligand molecules one of them behaves as a monoanionic bidentate and coordinates via the azomethine nitrogen and deprotonated enolic oxygen atom and the second molecule of ligand behaves as a neutral monodentate coordinating through the azomethine nitrogen. The fourth coordination site is achieved by a chloride atom. The IR spectrum of complex 22 shows that the ligand in this complex behaves as a neutral bidentate ligand and coordination takes place via the azomethine nitrogen and the carbonyl oxygen atom. This is evidenced by the appearance of ν(C=O) and ν(C=N) at lower frequencies compared to that of the free ligand and the bands due to hydroxy group appear at the same positions as that of the free ligand.

The IR spectra of all metal complexes show two new bands at 525–450 and 475–400 cm^{-1}, assigned to ν(M–O) [8] and ν(M–N) [8,9], respectively. The IR spectra of chloro complexes display an additional new band at 355–325 cm^{-1}, assigned to ν(M–Cl) [10,11]. The IR spectra of the acetato complexes exhibit the ν_{asym}(COO$^-$) and ν_{sym}(COO$^-$) near 1570 and 1390 cm^{-1}, respectively, which is consistent with monodentate acetate coordination [12]. The IR spectra of nitrate-complexes show two strong bands at 1385 and 1285 cm^{-1} assigned to ν_{asym}(NO_3^-) and ν_{sym}(NO_3^-), respectively, indicate the presence of a terminally bonded monodentate nitrate group [13,14].

4. Magnetic and electronic spectral studies

Solution spectral data (DMF) of H_2L^1 and H_2L^2 ligands and their metal complexes as well as d–d bands in solution are represented in Table 3. H_2L^1 and H_2L^2 exhibit, a band at 35,020 and 43,840 cm^{-1}, respectively, assignable to phenyl ring transition π–π* which remain nearly unchanged in the spectra



Compounds 1, 15

Compounds: Mn(II)2, 16, Co(II) 5, Zn(II)14, Ni(II) 9, 20

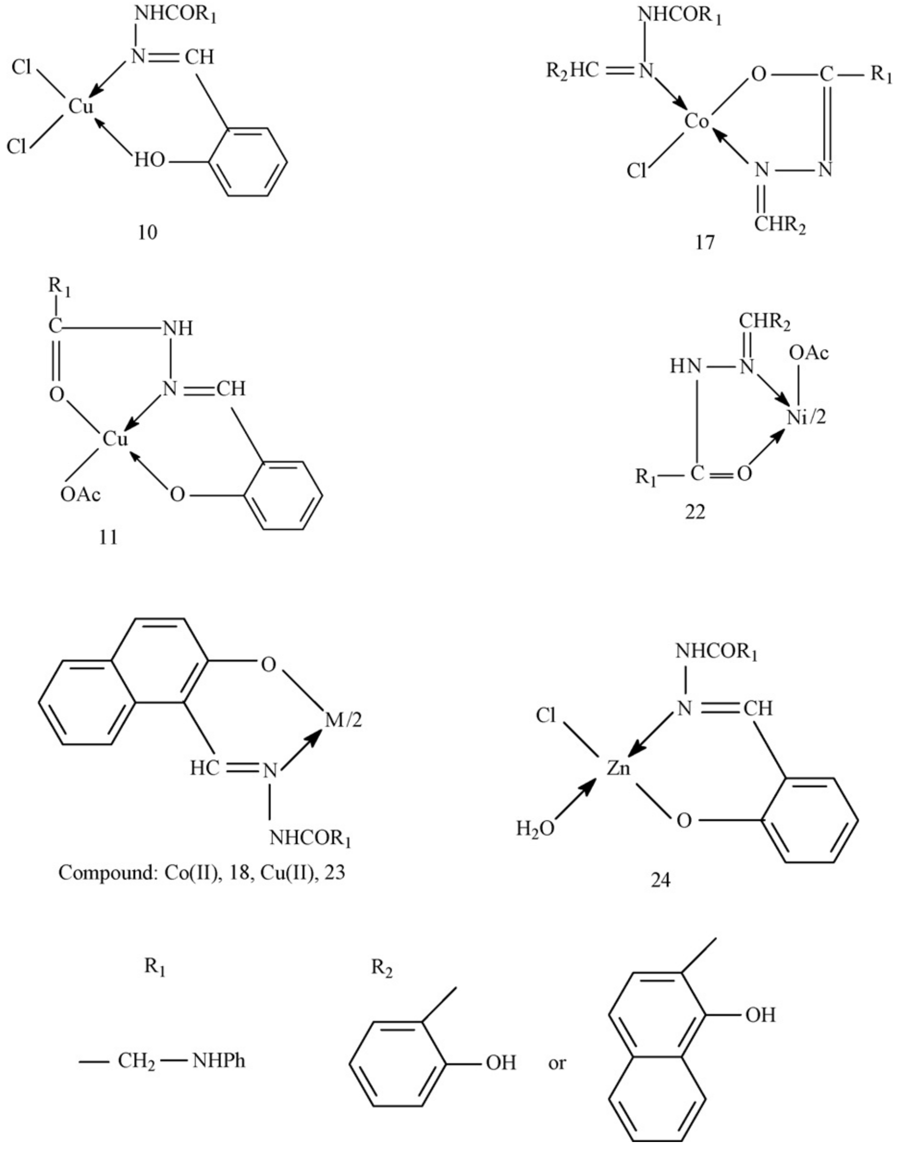
Compounds 3, 19

M	X	Compound
Co(II)	NO_3	4
Ni(II)	NO_3	7
Ni(II)	Cl	8
Ni(II)	NO_3	21

X	H_2O	Compound
OAc	2	Co(II),6
NO_3	0	Cu(II), 13

Compound, Cu(II), 12, Zn(II), 25

Scheme 1. Chemical formulae of the solid complexes.



Scheme 1. (*Continued*).

of their metal complexes. The ligands show bands in range 24,410–30,120 and 27,170–27,240 cm^{-1}, due to n–π* transition which shifted to higher energy on complexation.

The electronic spectra of Mn(II) complexes 2 and 16 in DMF solution display bands 16,949–17,857 and 19,230–20,325 cm^{-1}. These bands assigned to octahedral geometry around Mn(II). The lower magnetic moment value 4.5–5.5 BM may be due to the presence of equilibrium between high and low spin state together with metal–metal interaction [2,9].

The electronic spectral data of [Fe(HL^1)$_3$] and [Fe(HL^2)$_3$]·H$_2$O in DMF solution show bands at 19,940 and 15,600 cm^{-1} which arises from $^6A_{1g}$ to $^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ transitions in octahedral structures. The values of μ_{eff} per iron(III) atom 5.6 and 6.1 BM, respectively, are compatible with high-spin octahedral iron(III) complexes [2,15].

The electronic spectra of cobalt(II) complexes derived from H$_2$L^1 show two broad bands in the 14,500–15,000 and 16,600–17,300 cm^{-1} regions assignable to $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g} \rightarrow {}^4T_{1g}$ (p) (ν_3) transition, indicated to an octahedral stereochemistry around cobalt [12]. The calculated values of Dq, B, β and ν_2/ν_1 lie in the same range reported for an octahedral structure. Also, the values of magnetic moments (4.3–4.6 BM) are in good agreement with those reported for the octahedral structure [6]. However, the cobalt(II) separated from H$_2$L^2 ligand exhibit one main band at ca 15,500 cm^{-1} due to $^4A_2 \rightarrow {}^4T_1$ (P) transition (ν_3) in tetrahedral ligand field, there is also a shoulder at about 20,000 cm^{-1} due to spin–orbital coupling. Also, the values of μ_{eff} (4.2–3.2 BM) is an additional evidence for tetrahedral geometry [8].

The nickel complexes were found to be paramagnetic which excludes the possibility of square planar configuration. The measured magnetic moment values for all nickel(II) complexes, 2.5–4.1 BM, fall in the range reported for both octahedral and/or tetrahedral structures. The spectra of the nickel(II) complexes, Table 3, show one absorption band at ca. 16,500 cm^{-1} which is considered to be due to $^3A_{2g}$ (F) → $^3T_{1g}$ (F) transition of six coordinated nickel(II) complexes [16,17]. The $\nu_3\{^3A_{2g}\ (F) \rightarrow {}^3T_{1g}\ (P)\}$ band expected in the range of 26,000–28,000 cm^{-1}. The calculated value of ν_2/ν_1 at about 1.7 which is consistent with an octahedral configuration [18]. These assigned energies were used to calculate the spectral parameters Dq = ca. 1015, B = ca. 920 and $\beta = 0.82$ [18]. These values agree well with those reported for octahedral nickel(II) complexes. The value of the nephelauxetic parameter, B, indicate the covalent character of the metal–ligand bond is low.

The magnetic moment values of the copper(II) complexes under study (Table 3), lie in the range observed for Cu(II) complexes with one unpaired spin (∼1.73 BM). The electronic spectra of copper(II) complexes give one broad band with a maximum in the 15,000–16,000 cm^{-1} range due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in a square planar geometry [8].

5. Electron spin resonance spectroscopy (ESR)

The powder ESR parameters of the copper(II) complexes measured at room temperature are collected in Table 4. The ESR spectra of $[Cu(H_2L^1)Cl_2]$ and $[Cu(HL^1)(OAc)]\cdot H_2O$ and $[Cu(HL^2)_2]$ complexes display only one broad signal with no appearance of hyperfine structure. The broad universal spectral signal could be attributed to super exchange interaction between copper centers in the solid state [19]. The inhomogeneity of the signals is due to the anisotropic exchange interaction. These spectral features are consistent with the magnetic data for these complexes. The spectrum of $[Cu(HL^1)(NO_3)]$ is anisotropic with a parallel and perpendicular spin being assignable. The low g-value of complex $[Cu\ (HL^2)_2]$, indicating more covalent planar bonding and two ligands are likely bidentate, N, O, donor. From the observed g-values, it is clear that the unpaired electron lies predominantly in the $dx^2–y^2$ and implying a $^2B_{1g}$ as a ground state. The g-value for copper(II) complexes is greater than 2 indicating to the presence of Cu–O and Cu–N bonds in these chelates.

Kivelson and Neiman [20] have suggested that the g_{11} value in the Cu(II) complex can be used as a measure of covalent character of the metal–ligand bond. For the ionic environment, the g_{11} value is normally 2.3 or higher and for the covalent environment, it is less than 2.3. Using this criterion, the data show considerable covalent character of the metal–ligand bond in the present complexes.

Based on the above arguments the chemical structures of the complexes are shown in Scheme 1.

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