

Synthesis and Characterization of Iron(III), Cobalt(II), Nickel(II) and Copper(II) Complexes of 4-Formylazohydrozoaniline Antipyrine

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4-Formylazohydrozoaniline antipyrine and its iron(III), cobalt(II), nickel(II) and copper(II) complexes have been synthesized and characterized by IR, electronic spectra, molar conductivities, magnetic susceptibilities and ESR. The ligand behaves as a neutral bidentate and tridentate ligand in the hydrazo form or monobasic tridentate ligand in the enol-azo form. Coordination takes place *via* the carbonyl oxygen of the side chain, azomethine nitrogen atom for bidentate coordination. The carbonyl oxygen of the pyrazolone ring is added for tridentate coordination and enolic oxygen appears in monobasic tridentate coordination.

Key words: complexes, IR, ESR spectra, magnetic properties, conductivity, synthesis

Antipyrine(2,3-dimethyl-1-phenyl-5-pyrazolone) and its derivatives have a diversity of applications including biological [1], clinical [2] and pharmacological [3] areas. Among the pharmaceutical application they are used as antipyretic, analgesic, antihistaminic, anti-rheumatic, and anti-inflammatory drugs. Antipyrines have also been used as analytical reagents in the determination of some metal ions [4]. Similarly, compounds containing azo group have demonstrated significant biological, antifungal, antibacterial activities and industrial achievements [5]. Considerable study has been devoted to ligands derived from either 4-amino- and 4-formyl-antipyrine [6]. Here, we report on the iron(III), cobalt(II), nickel(II) and copper(II) complexes of 4-formylazohydrozoaniline antipyrine (HL).

EXPERIMENTAL

Reagent grade chemicals were used without further purification. The ligand 4-formylazohydrozoaniline antipyrine was prepared by coupling the diazonium salt of aniline with 4-formylcyanoaceto-hydrazide antipyrine in sodium hydroxide solution [7]. The product was recrystallized several times from ethanol.

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The metal complexes were prepared by stirring magnetically at *ca.* 60°C the solution of 0.002 moles of a metal salt with 0.002, 0.004 or 0.001 moles of the 4-formylazohydrozoaniline antipyrine (HL) in *ca.* 50 ml EtOH for periods of 6 h or more. The resulting solids were filtered off, washed several times with EtOH and dried under vacuum over P₄O₁₀. Elemental analyses (C, H, Cl) were performed by the microanalytical unit of the University of Cairo. Metal analyses were carried out by standard methods. IR spectra were performed as KBr discs using a Perkin-Elmer 1430 recording spectrophotometer, ¹H NMR spectra were recorded in d⁶-DMSO using a 300 MHz Varian NMR spectrometer. The electronic spectra were carried out in N,N-dimethylformamide (DMF) solution using a Perkin-Elmer lambda 4B spectrophotometer. The molar conductivity measurements were made in DMF solutions (10⁻³ M) using a Tacussel conductimeter type CD6N. Magnetic susceptibilities were measured at 27°C by the modified Gouy method using Magnetic Susceptibility Johnson Matthey Balance. Diamagnetic corrections were effected by employing Pascal's constants. The magnetic moments were calculated from $\mu_{\text{eff}} = 2.84\sqrt{\chi_M^{\text{corr}} T}$. ESR spectra were recorded with a Varian E 104 spectrometer and calibrated with diphenylpicrylhydrazide.

RESULTS AND DISCUSSION

The ¹H NMR spectrum of 4-formylazohydrozoaniline antipyrine (HL) has been recorded in d⁶-DMSO at room temperature. The spectrum of the ligand shows strong signals at 2.413 and 3.260 ppm, due to C-CH₃ and N-CH₃ protons respectively. The spectrum also shows signals at 10.419, 8.349 and 6.954 ppm, assigned to intramolecular hydrogen bonding (NH...O), intermolecular hydrogen bonding to the solvent and CH=N protons respectively.

The IR spectrum of the ligand (Table 2) shows bands at 3190, 2180, 1655, 1635, 1608 and 1530 cm⁻¹ assigned to $\nu(\text{N-H})$, $\nu(\text{C}\equiv\text{N})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{O})$ of the pyrazolone ring, $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ respectively.

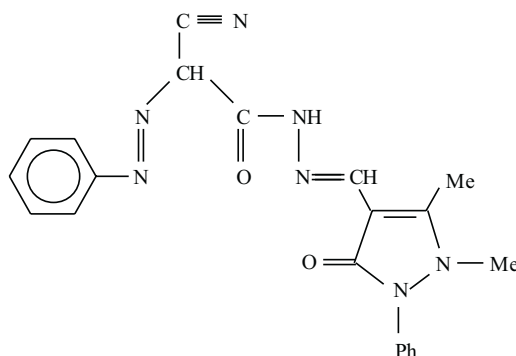


Figure 1. The chemical structure for HL.

The elemental analyses and spectral data for HL are consistent with the structure (Fig. 1):

The colours, magnetic susceptibilities and molar conductivities of the complexes are listed in Table 1. The reaction of the ligand (HL) with different salts of Cu(II), Ni(II) and Co(II) ions in different appropriate molar ratios gives different types of metal complexes of the general formulae $\text{MLX}\cdot n\text{H}_2\text{O}$, $\text{MLX}(\text{H}_2\text{O})_2$, $\text{M}(\text{L})_2\cdot n\text{H}_2\text{O}$ and $\text{M}(\text{HL})\text{X}_2(\text{H}_2\text{O})\cdot n\text{H}_2\text{O}$, where $n = 0-5$ and $\text{X} = \text{Cl}^-$, ClO_4^- , OAc^- and NO_3^- . The 1:1 and 1:2 molar ratio reactions of iron(III) chloride with the ligand produces the two com-

plexes $\text{FeLCl}_2(\text{H}_2\text{O})$ and $[\text{Fe}(\text{L})_2]\text{FeCl}_4 \cdot 3\text{H}_2\text{O}$ respectively. The reaction of $\text{Cu}(\text{OAc})_2 \cdot 5\text{H}_2\text{O}$ with HL in 2:1 molar ratio produces a binuclear complex $\text{Cu}_2\text{L}(\text{OAc})_3(\text{H}_2\text{O})_3$. 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 [8], indicating coordination of the anions. The data also show that $[\text{Fe}(\text{L})_2]\text{FeCl}_4 \cdot 3\text{H}_2\text{O}$ behaves as 1:1 electrolyte [9].

Table 1. Colours, molar conductivities and magnetic susceptibilities of 4-formylazohydrazoneaniline anti-pyridine (HL, $\text{C}_{21}\text{H}_{19}\text{N}_7\text{O}_2$) ligand and its metal complexes.

No.	Compound	Colour	Λ_{M} ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ_{eff} (B.M)
	HL	orange	—	—
1	$\text{CuLCl} \cdot \text{H}_2\text{O}$	green	20.0	1.71
2	$\text{Cu}(\text{HL})\text{Cl}(\text{OH})$	brown	20.0	1.85
3	$\text{CuL}(\text{ClO}_4) \cdot \text{H}_2\text{O}$	green	39.3	2.01
4	$\text{CuHL}(\text{H}_2\text{O})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	green	35.0	1.96
5	$\text{CuL}(\text{OAc}) \cdot 2\text{H}_2\text{O}$	green	23.6	2.03
6	$\text{Cu}_2\text{L}(\text{OAc})_3 \cdot (\text{H}_2\text{O})_3$	green	5.4	1.5 _{per metal atom}
7	$\text{NiHLCl}_2 \cdot 5\text{H}_2\text{O}$	red	43.2	2.75
8	$\text{Ni}(\text{L})_2 \cdot 4\text{H}_2\text{O}$	yellow	46.0	3.15
9	$\text{Ni}(\text{HL})_2(\text{ClO}_4)_2$	orange	63.0	3.2
10	$\text{Ni}(\text{L})_2$	greenish yellow	3.8	3.15
11	$\text{Ni}(\text{L})(\text{OAc}) \cdot 4\text{H}_2\text{O}$	green	9.1	3.4
12	$\text{Co}(\text{HL})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	brown	20.5	4.36
13	$\text{CoLCl}(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$	brown	16.7	4.44
14	$\text{Co}(\text{L})_2 \cdot 4\text{H}_2\text{O}$	dark red	13.0	4.95
15	$\text{CoL}(\text{NO}_3)(\text{H}_2\text{O})_2$	brown	14.5	3.7
16	$\text{FeLCl}_2(\text{H}_2\text{O})$	green	9.5	3.7
17	$[\text{Fe}(\text{L})_2]\text{FeCl}_4 \cdot 3\text{H}_2\text{O}$	brown	105	7.5

Table 2 lists the most important IR spectral bands of the metal complexes. In the spectra of all complexes the $\nu(\text{C}=\text{N})$ shifts to lower frequency, due to its involvement in coordination. The bands corresponding to $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{O})$ of the side chain disappear in the spectra of complexes 1, 3, 5, 6, 8, 10, 11 and 13–17, indicating that the ligand reacts in the enol-hydrazo form and the oxygen atom coordinates in its enolic form. Whereas, in the spectra of the remaining complexes the $\nu(\text{N}-\text{H})$ bands almostly appear at the same frequency as that of the free ligand, and the $\nu(\text{C}=\text{O})$ of the side chain shifts towards lower frequency, indicating that the carbonyl oxygen involved in coordination and the ligand reacts in its keto-azo form. The spectra of all complexes, except 2, 9 and 12, show that the $\nu(\text{C}=\text{O})$ of the pyrazolone ring shifts to lower frequency as a result of its coordination, whereas in the spectra of the complexes 2, 9 and 12 this band remains at the same frequency as that of the free ligand, indicating that the carbonyl oxygen of the pyrazolone ring does not coordinate in complexes 2, 9 and 12. The IR spectra of all complexes reveal that the bands corresponding to $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{N}=\text{N})$ almostly appear at the same frequency as that of the free ligand, except

Table 2. Infrared spectral bands (cm^{-1}) for 4-formylazohydrozoamine antipyrine ligand and its metal complexes.

No.	Compound	$\nu(\text{H}_2\text{O})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{O})^a$	$\nu(\text{C}=\text{O})^b$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{O}_4)$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$
	HL	–	3190(w)	2210(w), 2180(s)	1655(s)	1635(sh)	1608(s)	1530(m)	–	–	–	–
1	CuLCl \cdot H $_2$ O	3410(br)	–	2210(s)	–	1620(s)	1590(s)	1530(sh)	–	500(m)	455(w)	335(m)
2	CuHLCI(OH)	–	3180(w)	2230(s)	1630(sh)	1635(s)	1595(s)	1530(s)	–	510(m)	450(m)	350(w)
3	CuL(ClO $_4$) \cdot H $_2$ O	3410(br)	–	2210(s)	–	1625(s)	1590(s)	1530(s)	1112(s), 1080(s), 625(s)	505(m)	460(m)	–
4	Cu(HL)(H $_2$ O)(ClO $_4$) $_2$ \cdot 2H $_2$ O	3460(br)	1190(sh)	2210(s)	1635(sh)	1625(s)	1590(m)	1530(s)	1112(s), 1085(s), 625(s)	510(w)	460(m)	–
5	CuL(OAc) \cdot 2H $_2$ O	3410(br)	–	2210(s)	–	1625(s)	1590(m)	1530(w)	–	510(s)	470(w)	–
6	Cu $_2$ L(OAc) $_3$ \cdot 3H $_2$ O	3410(br,s)	–	2195(s)	–	1625(s)	1585(s)	1545(s)	–	470(s)	405(w)	–
7	NiHLCI $_2$ \cdot 5H $_2$ O	3400(br)	3180(sh)	2210(s)	1635(s)	1625(s)	1595(sh)	1525(s)	–	500(m)	440(m)	–
8	Ni(L) $_2$ \cdot 4H $_2$ O	3400(br)	–	2210(s)	–	1625(s)	1595(sh)	1525(s)	–	500(br)	435(m)	–
9	Ni(HL) $_2$ (ClO $_4$) $_2$	–	3200(sh)	2210(m)	1623(s)	1635(sh)	1595(w)	1525(m)	1080, 1110(s)	500(m)	–	–
10	Ni(L) $_2$	–	–	2210(s)	–	1632(s)	1595(s), 1580(s)	1525(s)	–	500(m)	425(m)	–
11	Ni(L)(OAc) \cdot 4H $_2$ O	3410(s)	–	2210(s)	–	1625(s)	1585(s)	1530(s)	–	500(m)	440(m)	–
12	Co(HL) $_2$ Cl $_2$ \cdot 4H $_2$ O	3410(br)	3220(w)	2230(s)	1632(s)	1635(sh)	1620(m)	1540(m)	–	505(br)	435(m)	345(sh)
13	CoLCl(H $_2$ O) $_2$ \cdot 2H $_2$ O	3400(br)	–	2220(s)	–	1625(s)	1595(br)	1535(m)	–	500(br), 430(m)	460(m)	345(sh)
14	Co(L) $_2$ \cdot 4H $_2$ O	3410(br)	–	2218(s)	–	1630(s)	1600(m)	1530(s)	–	500(m)	435(w)	–
15	CoL(NO $_3$)(H $_2$ O) $_2$	3410(sh,br)	–	2215(s)	–	1625(s)	1595(m,br)	1528(s)	–	500(w)	430(w)	–
16	FeLCl $_3$ (H $_2$ O)	3420(br)	–	2210(s)	–	1620(s)	1590(m)	1520(s)	–	500(m)	440(w)	–
17	[Fe(L) $_2$][FeCl $_4$] \cdot 3H $_2$ O	3400(br)	–	2210(s)	–	1615(s)	1585(sh)	1525(sh)	–	500(w)	440(br)	380(sp)

a = $\nu(\text{C}=\text{O})$ of hydrazide moiety b = $\nu(\text{C}=\text{O})$ of pyrazolone moiety.

the binuclear complex 6, while $\nu(\text{N}=\text{N})$ shifts to a higher frequency, indicating that the azo nitrogen atoms involved in coordination. The above arguments indicate that the ligand behaves as a monovalent or neutral tridentate ligand and coordination takes place *via* the carbonyl oxygen of the pyrazolone ring, azomethine nitrogen and the enolic oxygen or carbonyl oxygen atom, *i.e.* the ligand reacts in the enol-hydrazo or keto-azo form. The ligand in complexes 2, 9 and 12 behaves also as a neutral bidentate ligand. Coordination takes place *via* the azomethine nitrogen and the carbonyl oxygen of the side chain.

The IR spectra of all the complexes reveal new bands at 510–470 and 460–425 cm^{-1} , assigned to $\nu(\text{M}-\text{O})$ [10] and $\nu(\text{M}-\text{N})$ [10] respectively. The chloro complexes show an additional band at 350–320 cm^{-1} , assigned to $\nu(\text{M}-\text{Cl})$ [11]. The IR spectrum of the complex 17 shows a strong band at 380 cm^{-1} , assigned to $\nu_3(\text{FeCl}_4^-)$ [12].

The acetato ligand may coordinate to a metal center in either a monodentate, bidentate or bridging manner. The $\nu_a(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ of the free acetate ions are at 1560 and 1416 cm^{-1} , respectively. In monodentate coordination $\nu_a(\text{CO}_2)$ is found at higher energy than 1560 cm^{-1} and $\nu_s(\text{CO}_2)$ is lower than 1416 cm^{-1} [13]. As a result, the separation between the $\nu(\text{CO}_2)$ bands is much larger in monodentate complexes than the free ion, as found for $\text{CuL}(\text{OAc})\cdot 2\text{H}_2\text{O}$, $\text{Cu}_2\text{L}(\text{OAc})_3(\text{H}_2\text{O})_3$ and $\text{NiL}(\text{OAc})\cdot 4\text{H}_2\text{O}$ (*i.e.*, $\nu_a(\text{CO}_2) = 1585 \text{ cm}^{-1}$, $\nu_s(\text{CO}_2) = 1370\text{--}1340 \text{ cm}^{-1}$). The opposite trend is observed in bidentate acetato coordination; the separation between $\nu(\text{CO}_2)$ bands is smaller than for the free ion. For bridging acetato as in Cu(II) acetate, however, the two $\nu(\text{CO}_2)$ bands are close to the free ion [13], as found for $\text{Cu}_2\text{L}(\text{OAc})_3(\text{H}_2\text{O})_3$ shows additional two bands at 1560 and 1410 cm^{-1} , of a bridging acetato group [14]. The IR spectra of $\text{CuL}(\text{ClO}_4)\cdot \text{H}_2\text{O}$, $\text{CuHL}(\text{H}_2\text{O})(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$, and $\text{Ni}(\text{HL})_2(\text{ClO}_4)_2$ show a very strong split band (ν_3) at 1110 and 1085 cm^{-1} and a strong band at 625 cm^{-1} (ν_4), which are indicative of a monodentate coordinated perchlorate [15]. The IR spectrum of $\text{CoL}(\text{NO}_3)(\text{H}_2\text{O})_2$ shows a strong band at *ca.* 1380 cm^{-1} and a weak band at 1290 cm^{-1} , assigned to $\nu_a(\text{NO}_3)$ and $\nu_s(\text{NO}_3)$ respectively, indicating that this group coordinates as a monodentate ligand. The IR spectrum of the $\text{Cu}(\text{HL})\text{Cl}(\text{OH})$ shows a strong band at 3410 cm^{-1} , assigned to $\nu(\text{OH})$ of a coordinated hydroxo-ligand [16]. The inclusion of water molecules in the coordination sphere of the metal complexes, $\text{CuHL}(\text{H}_2\text{O})(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$, $\text{CoLCl}(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}$, $\text{CoL}(\text{NO}_3)(\text{H}_2\text{O})_2$ and $\text{FeLCl}_2(\text{H}_2\text{O})$ is supported by the appearance of bands at 3440, 1610(sh), 960 and 635 cm^{-1} , owing to $\nu(\text{OH})$, $\delta(\text{H}_2\text{O})$, $\rho_{\text{rock}}(\text{H}_2\text{O})$ and $\rho_{\text{wagg}}(\text{H}_2\text{O})$, respectively [17]. The latter two modes are missing from the spectra of the remainder of the complexes isolated with water molecules, indicating hydrate rather than coordinated water [18].

Magnetic and electronic spectral studies: Iron(III) complexes: The complexes $\text{FeLCl}_2(\text{H}_2\text{O})$ and $[\text{Fe}(\text{L})_2]\text{FeCl}_4$ exhibit magnetic moments 3.7 and 7.5 B.M. respectively. The first one indicates an equilibrium between high and low spin states, ${}^6\text{A}_1$ and ${}^2\text{T}_2$, as has been observed for a number of iron(III) complexes [19]. The latter one is consistent with a low spin iron(III) cation $[\text{Fe}(\text{L})_2]^+$ and a high spin FeCl_4^- .

The absorption spectra of the iron(III) complexes show two bands around 17390 and 22220 cm^{-1} , being assigned to ${}^6\text{A}_{1g} \rightarrow \text{T}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ transitions, respectively, for the high spin iron(III), but the lower values for the magnetic susceptibility indicate that this solid may be a spin cross-over complex or a mixture of high and low spin iron(III) species [20].

Cobalt(II) complexes: Magnetic measurements of the complexes of cobalt(II) ($\mu_{\text{eff}} = 3.7\text{--}4.4$ B.M.) reported herein show that all are paramagnetic and have three unpaired electrons indicating a high spin octahedral configuration [21]. The electronic spectra of all the complexes recorded herein are very similar to each other and consist of two bands – one of the 15380–16130 cm^{-1} and the other band in the 19050–19610 cm^{-1} regions, which clearly indicate the octahedral stereochemistry of the complexes. In Table 3, the band maxima and their assignments and the calculated ligand field parameters are listed. The ligand field parameters, Dq and B are, in principle, calculated using first order perturbation theory [22] and the transition energies are given by the equations of Lever [23]. Dq has been calculated from the transition energy diagram using the relation ν_3/ν_2 ratio. The nephelauxetic parameter, β , is readily obtained using the relation $\beta = B(\text{complex})/B(\text{free ion})$, where B (free ion) is 971 cm^{-1} . β for these complexes indicate that the covalent character of the metal-ligand σ -bond is low.

Nickel complexes: Nickel complexes were found to be paramagnetic, what excludes a square planar configuration. The calculated magnetic moments for all nickel(II) complexes, 2.8–3.4 B.M., fall in the range reported for four-coordinate tetrahedral, five-coordinate square pyramidal or trigonal bipyramidal; and six-coordinate octahedral configurations. The possible geometry for the complexes had been assigned from their electronic spectral studies.

The electronic spectrum of the complex $[\text{Ni}(\text{HL})\text{Cl}_2] \cdot 5\text{H}_2\text{O}$ suggests five-coordinate trigonal bipyramidal geometry. The complex displays three well defined bands at 14810, 21280 and 24630 cm^{-1} . The electronic spectral features of this complex are similar to other five-coordinated nickel(II) complexes [24].

The rest of the nickel(II) complexes, except for the green complex $[\text{Ni}(\text{L})(\text{OAc}) \cdot 4\text{H}_2\text{O}]$, exhibit electronic spectra typical of an octahedral system. The spectra of the complexes show two bands in the range 16660–17540 cm^{-1} and 26320–27390 cm^{-1} , which may be assigned to the transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{P})$ (ν_3), respectively, in octahedral symmetry [25]. The transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_1)$ is expected to be at *ca.* 11000 cm^{-1} and the theoretical calculation of this band for the nickel complexes are shown in Table 4. The calculated value of ν_2/ν_1 (*ca.* 1.5) is consistent with an octahedral configuration [26]. Various ligand field parameters were calculated for the complexes and are listed in Table 4. Dq has been calculated from the transition energy diagram, using the relation ν_3/ν_2 ratio. The nephelauxetic parameter, β , is readily obtained using the relation $\beta = B(\text{complex})/B(\text{free ion})$; where B (free ion) is 1041 cm^{-1} . The values of β for these complexes indicate that the covalent character of the metal-ligand σ -bond is low. The green nickel(II) complex, $[\text{Ni}(\text{L})(\text{OAc}) \cdot 4\text{H}_2\text{O}]$, has an electronic spectrum typical of a tet-

rahedral system [27]. The spectrum of this complex shows two bands at 11360 and 14810 cm^{-1} , which may be assigned to the transitions ${}^3T_1(F) \rightarrow {}^3A_2(v_2)$ and ${}^3T_1(F) \rightarrow {}^3T_1(P)(v_3)$, respectively. The transition ${}^3T_1(F) \rightarrow {}^3T_2(v_1)$ is expected to be in the range of 3000 to 5000 cm^{-1} and the theoretical calculation of this band for the complex is 4940 cm^{-1} . Calculations of Dq, B and β , based on this assignment, yield 593 cm^{-1} , 698 cm^{-1} and 0.67, respectively. The value of β for this complex indicates a low covalent character of metal–ligand bonds.

The copper(II) complexes exhibit magnetic moments close to spin-only value for one unpaired spin (~ 1.73 B.M.), except for the complex $[\text{Cu}_2(\text{L})(\text{OAc})_3] \cdot 3\text{H}_2\text{O}$, which shows a magnetic moment of 1.5 B.M. This value indicates some sort of molecular association that could be achieved through a direct copper–copper interaction and/or magnetic exchange interaction through a bridging ligand [28]. Since the electronic spectrum of this complex, which will be discussed later, shows no absorption in the region 26000–27000 cm^{-1} due to Cu–Cu bonding, one should conclude that the observed magnetic moment is most probably due to magnetic exchange interaction through a bridging ligand [29].

Table 3. Electronic spectral bands (cm^{-1}) and ligand field parameters for Co(II) complexes with 4-formyl-azohydrozoaniline antipyrine.

Complex	v_2 ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$	v_3 $\rightarrow {}^4T_{1g}(P)$	v_1 $\rightarrow {}^4T_{2g}(F)$	Dq	B	β
$\text{Co}(\text{HL})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	15870	19610	7624	828	872	0.89
$\text{Co}(\text{L})\text{Cl}(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$	16130	19050	7620	800	848	0.87
$\text{CoL}(\text{NO}_3)(\text{H}_2\text{O})_2$	15380	19610	736	846	891	0.91

Table 4. Electronic spectral bands (cm^{-1}) and ligand field parameters for Ni(II) complexes with 4-formyl-azohydrozoaniline antipyrine.

Complex	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	$\rightarrow {}^3T_{1g}(F)$	$\rightarrow {}^3T_{1g}(F)$	Dq	B	β
$\text{Ni}(\text{L})_2 \cdot 4\text{H}_2\text{O}$	10730	16660	26320	1075	717	0.69
$\text{Ni}(\text{L})_2$	11070	17240	26740	1172	589	0.58
$\text{Ni}(\text{HL})_2(\text{ClO}_4)_2$	11560	17540	27390	1158	681	0.65

The electronic spectra of the copper(II) complexes show one broad absorption band between 13700–14800 cm^{-1} , suggesting a square-planar configuration [30] of these compounds. Although three d-d transitions are expected for a square-planar Cu(II) complexes, unfortunately, all of these bands could not be recognised by us. Similar difficulties have already been reported elsewhere [31].

The electronic spectrum of $[\text{Cu}_2(\text{L})(\text{OAc})_3(\text{H}_2\text{O})_3]$ displays a band at 12900 cm^{-1} and a well-defined shoulder at 15870 cm^{-1} , similar to those reported for six-coordinate copper(II) complexes in D_4 or C_{4v} symmetry, where three spin-allowed transitions in the visible and near-IR regions, due to ${}^2B_{1g} \rightarrow {}^2A_{2g}(d_{x^2-y^2} \rightarrow d_{x^2})$, ${}^2B_{1g} \rightarrow {}^2B_{2g}(d_{x^2-y^2} \rightarrow d_{xy})$ and ${}^2B_{1g} \rightarrow {}^2E_g(d_{x^2-y^2} \rightarrow d_{xz}, d_{yz})$ transitions in order of in-

creasing energy, appear. The energy level sequence will depend upon the distortion due to the ligand field and the Jahn-Teller effect [32]. Accordingly, the main bands in the spectrum can be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively. The third band, due to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition, could not be observed, perhaps due to its very low intensity and/or the distortion from the ideal symmetry.

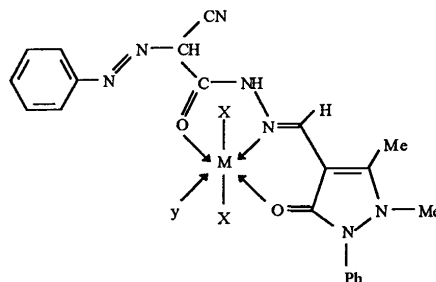
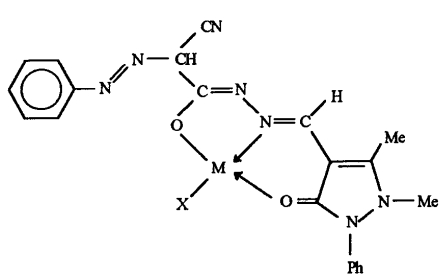
Information about the stereochemistry of different copper(II) complexes was obtained from the powder and solution ESR spectra. Copper(II) complexes generally exhibit three different types of ESR spectra, isotropic, anisotropic and rhombic [33]. Two of the copper(II) complexes studied have an anisotropic spectra with a $d_{x^2-y^2}$ ground state where $g_{||} > g_{\perp} > 2.0$. Complexes exhibiting rhombic spectra have three features, g_1 , g_2 and g_3 , and a lower symmetry.

Table 5. ESR spectral parameters of the copper(II) complexes of ligand HL.

Compound	Temp.	$g_{ }$ or g_{\perp}	g_2	g_1 or g_3	g_{av} or g_{iso}
CuLCl·H ₂ O	RT	2.094	2.080	2.076	2.083
	77 K	2.155	2.083	2.045	2.094
Cu(HL)Cl(OH)	RT	2.216	2.081	2.051	2.116
	77 K	2.224	2.075	2.045	2.115
CuL(ClO ₄)·H ₂ O	RT	2.176	2.072	2.046	2.098
	77 K	2.172	2.068	2.044	2.095
CuHL(H ₂ O)(ClO ₄) ₂ ·2H ₂ O	RT				2.060
	77 K				2.044
CuL(OAc)·2H ₂ O	RT			2.053	2.100
	77 K	2.249			2.118
Cu ₂ L(OAc) ₃ (H ₂ O) ₃	RT			2.051	2.082
	77 K	2.251			2.118

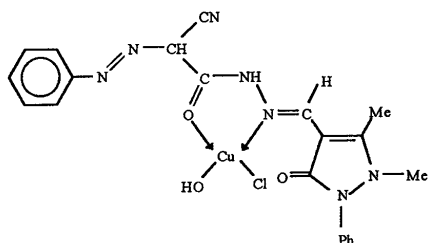
The powder ESR parameters of the copper(II) complexes measured at room and liquid nitrogen temperature are shown in Table 5. Temperature change causes no significant change in the g-values of the complexes, indicating no change in the axial interaction.

Hathaway and coworkers have defined an empirical parameter $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measures the exchange interactions between copper centers in a polycrystalline solid. According to [34], G larger than four means a negligible exchange interaction. On the other hand, G values less than four indicates the presence of an exchange interaction in the solid complex. As expected, G is less than four for the copper(II) complexes, indicating that the exchange interaction between the copper(II) centers is considerable in the polycrystalline solid. This is consistent with a weak bridging by the coordinated oxygen atoms to neighboring copper(II) centers. Based on the above arguments the suggested chemical structures are shown in Figure 2.

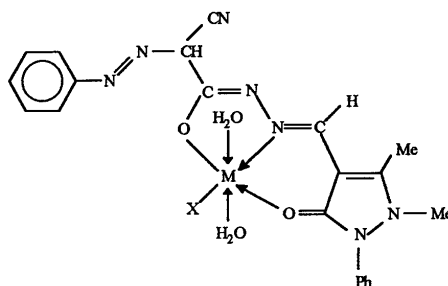


X	M	Compound	
Cl	Cu(II)	CuLCl·H ₂ O	(1)
ClO ₄	Cu(II)	CuL(ClO ₄)·H ₂ O	(3)
OAc	Cu(II)	CuL(OAc)·2H ₂ O	(5)
OAc	Ni(II)	NiL(OAc)·4H ₂ O	(11)

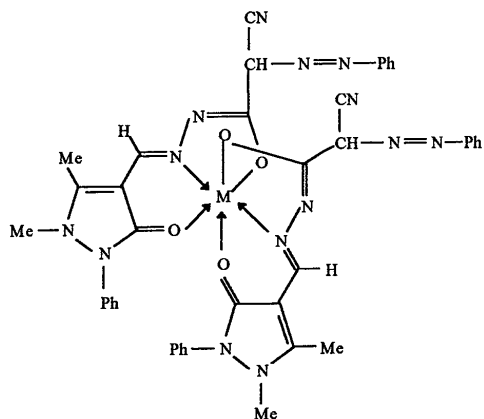
X	M	y	Compound
ClO ₄	Cu(II)	(H ₂ O)	CuHL(H ₂ O)(ClO ₄) ₂ ·2H ₂ O (4)
Cl	Ni(II)	O	NiHLCl ₂ ·5H ₂ O (7)



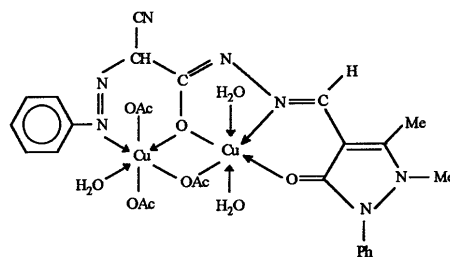
CuHLCl(OH) (2)



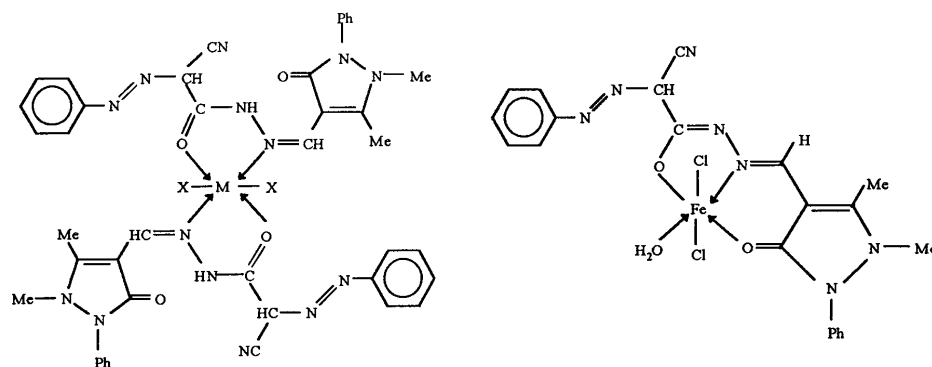
M	X	Compound
Co(II)	Cl	CoLCl(H ₂ O) ₂ ·2H ₂ O (13)
Co(II)	NO ₃	CoL(NO ₃)(H ₂ O) ₂ (15)



M	Compound
Ni(II)	Ni(L) ₂ ·4H ₂ O (8), Ni(L) ₂ (10)
Co(II)	Co(L) ₂ ·4H ₂ O (14)



Cu₂L(OAc)₃(H₂O)₃ (6)



X	M	Compound
ClO ₄	Ni(II)	Ni(HL) ₂ ·(ClO ₄) ₂ (9)
Cl	Co(II)	Co(HL) ₂ Cl ₂ ·4H ₂ O (12)

FeLCl₂(H₂O) (16)

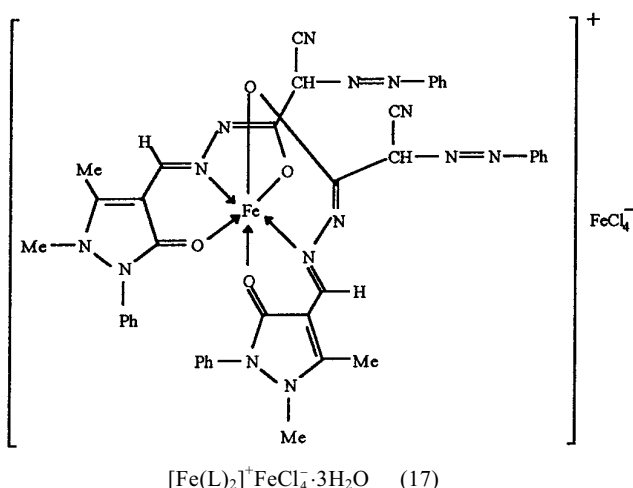


Figure 2. Suggested chemical structures for the complexes.

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