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Spectroscopic and Solution Studies of Some Transition Metal Complexes of New 4-Hydroxy Coumarin Semi- and Thiosemicarbazone Complexes

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Abstract Two new ligands, 4-hydroxy coumarin-3-thiosemicarbazone (H_2L^1) and 4-hydroxy coumarin-3-semicarbazone (H_2L^2) were synthesized and used for the preparation of a series of transition metal complexes (Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+}), derived from these ligands. These complexes have the forms $[ML^1Cl_2]\cdot n$X (**1–5**) and $[ML^2Cl]\cdot n$X (**6–9**) (X = H_2O or ethanol). The structures of these complexes were elucidated by elemental analyses, IR, UV–Vis, and electrical conductivity, as well as magnetic susceptibility measurements and thermal analyses. IR spectral data indicates that in all complexes, the ligands act as monobasic tridentate, coordinated through keto oxygen or sulfur, azomethine nitrogen and deprotonated phenolic oxygen atom. On the basis of other physicochemical investigations, tetrahedral or square planar geometries are assigned for Cu^{2+} complexes in monomeric structures. In the case of the Co^{2+}, Ni^{2+} and Fe^{3+} complexes, octahedral stereochemistries in monomeric structures are suggested. The dissociation constants of the ligands and the stability constants of their Cu(II), Co(II), Ni(II), and Fe(III) complexes have been also determined using potentiometric pH-metric titration in mixed solvents of dioxane: H_2O and DMF: H_2O with different ratios and different temperatures.

Keywords Semicarbazone · Thiosemicarbazone · Transition metal complexes · Potentiometric titration · Thermodynamic parameters

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1 Introduction

A good deal of work has been reported on the preparation and structural investigation of semicarbazone, thiosemicarbazone, and their metal complexes [1–3]. This is due partially to their capability of acting as bi- and polydentate NO, NNO and NNS donors with the formation of either mono- or bi- or polynuclear complexes [4–7]. In addition to their interesting ligational properties, these carbazones and their complexes have important biological applications [8–11], primarily because of their bioinorganic relevance [12] and particularly because of their potentially beneficial biological activities (viz. antibacterial, antimalarial, antiviral, and antitumor) [13–15].

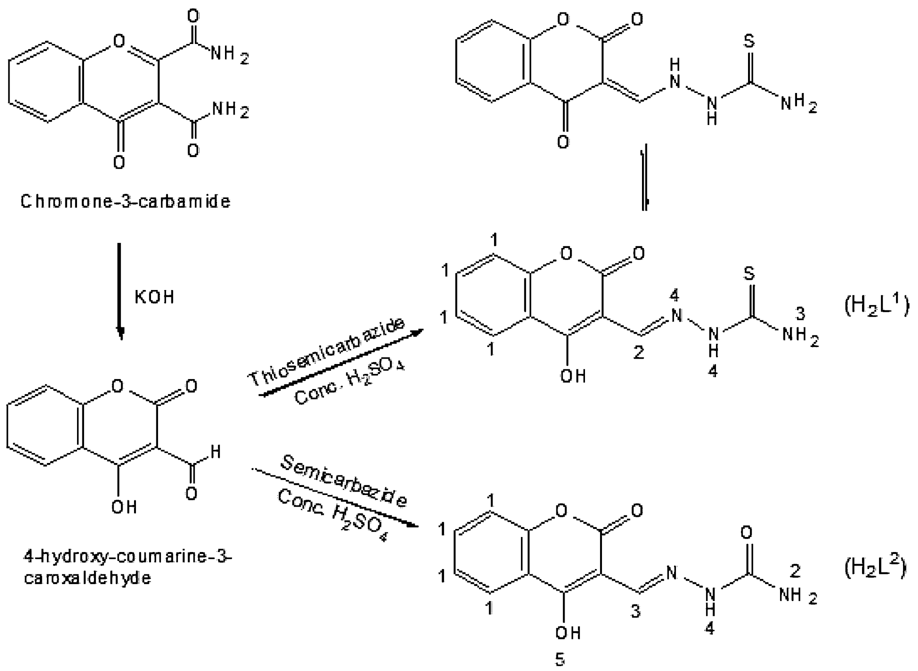
Several coumarin derivatives have pronounced medicinal values as antibacterial and antifungal agents; they have also important pharmaceutical value because of their anti-coagulant and antitumor activities [16–19]. The simple coumarin causes strong reduction of plasma, inhibits caspase-3 activation and prevents hepatocellular carcinoma (HCC) on oral administration in hepatitis C virus (HCV) infections.

Aromatic substituents on semicarbazone and thisemicarbazone skeletons can enhance the delocalization of electron charge density, which upon coordination to the metal center is further increased through the metal chelate rings. This inspired us to search for new derivatives of semicarbazone and thisemicarbazone-containing coumarin (Scheme 1) namely, namely 4-hydroxy coumarin-3-thiosemicarbazone (H_2L^1) and 4-hydroxy coumarin-3-semicarbazone (H_2L^2). These two potentially tridentate carbazones have been allowed to react with some transition metal ions of Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+}, and VO(II), affording complexes of the types $[ML^1Cl_2]\cdot nX$ (**1**–**5**) and $[ML^2Cl]\cdot nX$ (**6**–**9**) ($X = H_2O$ or ethanol). The chemistry of these complexes is reported with special reference to their formation and structure in the solid state and in solution. The acidity constants, K_a of the ligands and the stability constants, $\log_{10} K_{st}$, of their obtained metal complexes were determined using pH-metric titration in mixed solvents of dioxane: H_2O and DMF: H_2O with different ratios and at different temperatures.

2 Experimental

2.1 Materials and General Methods

All reagents were commercially available and were used as received. Chromone-3-carbamide, thisemicarbazide, and metal salts chloride and nitrates and were from Merk. The solvents used in the pH-metric titrations (1,4-dioxane, methanol, and DMF) were of HPC analytical grade. Reagents used for the physical measurements were of spectroscopic grade. The yields are reported with respect to the metal salts. The IR spectra were recorded as KBr disks in the range of 4,000–400 cm^{-1} on a Perkin Elmer FT-IR 1650 spectrophotometer. The electronic absorption spectra were obtained in DMF solution with a Shimadzu UV-1601 spectrophotometer UV-1601. The ^1H NMR measurements were recorded by using a Brucken 250 MH_2 spectrophotometer. Magnetic moments were measured using Johnson Matthey Alfa product Cambridge, UK, calibrated using $HgCo(CSN)_4$, the values using Bascol constants using $\mu_{eff} = 2.83\ (x^{corr}\cdot T)^{1/2}$. The specific conductances of the complexes were measured using freshly prepared (0.001 $mol\cdot dm^{-3}$) solutions in electrochemically pure DMF at room temperature, using a Weilhem WTWD-8120 conductivity meter fitted with a model LF42 cell. Thermogravimetric (TGA) analyses of metal complexes were performed on a Shimadzu thermogravimetric analyzer TA-50



Scheme 1 The synthesis of ligands H_2L^1 and H_2L^1

WSI program. All the samples were placed in alumina crucibles. Experiments were performed using sample sizes of 6.0 ± 0.3 mg. All the experiments were conducted under nitrogen as the purge gas with a flow rate of 50 $mL \cdot min^{-1}$. The range of the temperature studied was from 30 to 1,000 °C, at a heating rate of 10 $°C \cdot min^{-1}$.

2.2 Syntheses of the Ligands and their Metal Complexes

2.2.1 Synthesis of 4-Hydroxycoumarine-3-carboxaldhyde, I

Compound I was synthesized according to previously reported method [20]. Chromone-3-carbamide (6.4 g, 20 mmol) was added gradually to a solution of KOH (200 mL, 1 $mol \cdot dm^{-3}$). The mixture was stirred for 15 min, then acidified with concentrated HCl until complete precipitation. The precipitate was filtered off, washed with 10 mL of distilled water, followed by 5 mL of ethanol, and finally by diethyl ether. The product was purified and recrystallized from petroleum ether. Yield (84 %) and m.p. 137 °C.

2.2.2 Synthesis of 4-Hydroxycoumarine-3-thiosemiecarbazone H_2L^1

4-Hydroxycoumarine-3-carboxaldehyde (1.0 mmol) in hot ethanol (20 mL) was added to thiosemicarbazide (1.0 mmol) in the least amount of water (10 mL), then a few drops of concentrated H_2SO_4 was added with constant stirring. The mixture was left to stand and then filtered. The solid obtained was re-crystalized from dilute acetic acid to give golden yellow needles. ^{1}H NMR (DMSO-d_6): 7.4–8.0 (m, 4H, Ar–H), 7.95 (s, 2H, NH_2), 8.4 (s, 1H, $CH_{azomethine}$), 11.53(s, 1H, NH_{imino}). Yield (80 %) and m.p. 210 °C.

2.2.3 *Synthesis of 4-Hydroxycoumarin-3-semicarbazone H_2L^2*

The ligand H_2L^2 was synthesized in a similar fashion to H_2L^1 and recrystalized from acetic acid to give canary yellow plate crystals. ^{1}H NMR (DMSO-d_6): 7.3–7.7 (m, 4H, Ar–H), 7.95 (s, 2H, NH_2), 8.3 (s, 1H, $CH_{azomethine}$), 9.94 (s, 1H, NH_{imino}), 15.27 (s, 1H, $OH_{phenolic}$).Yield (73 %) and m.p. 260 °C.

2.2.4 *Synthesis of the Solid Metal Complexes*

The complexes $[ML^1Cl_2]nX$ and $[ML^2Cl]nX$ (X = H_2O or ethanol) (Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+}) were prepared by mixing a hot ethanolic solution of the metal salt and the corresponding carbazone ligand in 1:1 molar ratio. After 3 h refluxing, the chelation reaction was completed and the complexes were completely formed and precipitated. In each case, the microcrystalline colored product formed was filtered off, washed several times with hot aqueous ethanol (50 %, v/v), then ether, and finally dried under vacuum over anhydrous $CaCl_2$. The complexes obtained were stable solids. They are insoluble in water and common organic solvents such as ethanol, methanol, chloroform or acetone. However, they are soluble in DMSO and DMF and decompose above 230 °C without melting.

2.3 Potentiometric pH Titration

Potentiometric titrations were carried out at 20, 30 and 40 ± 0.2 °C with a WTW-series unolab pH730 titrator with a combined glass electrode. All solutions were prepared in double distilled water. Metal solutions of 0.01 $mol{\cdot}dm^{-3}$ were prepared from reagent grade nitrates salts of Cu(II), Co(II), Ni(II), Zn(II), Mn(II), and Fe(III). The ligands were dissolved in HPLC 1,4-dioxane of Across Organic. Carbonate free 0.05 $mol{\cdot}dm^{-3}$ KOH solution was prepared and standardized against potassium hydrogen phthalate (BDH). pH-meter readings, B, were converted to hydrogen ion concentrations [H^+] using the relation:

$$-\log_{10}[H^+] = B + \log_{10}\mu_H \tag{1}$$

where μ_H is a correction factor [21, 22], which depends on the solvent's composition percentage and ionic strength; the value of μ for 75 % dioxane is +0.28. The association constants, K_a, of the ligands were determined by titrating solutions of the ligands (30 mL, 3×10^{-3} $mol{\cdot}dm^{-3}$) with 0.1 $mol{\cdot}dm^{-3}$ of KOH and the stability constants, $\log_{10}K_{st}$ of the metal complexes were determined by titrating a solution of the ligand (30 mL, 3×10^{-3} $mol{\cdot}dm^{-3}$) in the presence of 1×10^{-3} $mol{\cdot}dm^{-3}$ of the metal ions.

3 Results and Discussion

3.1 Characterization of the Ligands H_2L^1 and H_2L^2 and their Metal Complexes

The coumarin-containing carbazone ligands H_2L^1 and H_2L^2 were synthesized as shown in Scheme 1 by reacting equimolar amounts of 4-hydroxycoumarine-3-carboxaldhyde and the respective carbazide in water. These ligands act as monoprotic tridentate ONS and ONO donor sets, respectively. Spectral studies reveal the existence of these ligands in the keto form in the solid state.

The ^{1}H-NMR spectrum of the ligand H_2L^1 shows a singlet at 8.4 ppm for the proton of the active azomethine group (–CH=N–), whereas there are two doublets, at 7.95, 11.53 ppm, attributed to the (NH_2) of the amino group and 2NH imine group indicating that the OH proton transferred to –CH=N and the presence of both enolic thione and thiol forms. The spectrum also shows a multiplet at 7.4–8.0 ppm for the aromatic protons.

The ^{1}H-NMR spectrum of H_2L^2 shows singlets at 15.28, 8.30, 9.94 ppm for the phenolic OH, azomethin CH and imin NH; the spectra also shows a multiplet at 7.30–7.7 ppm for the aromatic protons.

The reactions with the transition metal salts of Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+}, which were carried out with both carbazones in refluxing ethanol, proceeded smoothly to yield a series of differently colored complexes in decent yields. Chemical analysis and some physical properties of their isolated pure complexes are listed in Table 1. The analytical results demonstrate that all the prepared complexes have 1:1 (metal:ligand) stoichiometry with the general formula $[MLX](Y)_n$ ($X = Cl$ or NO_3 and $Y = H_2O$, ethanol or dioxane, $n = 0$–7). They are freely soluble in DMF and DMSO. All compounds are stable at room temperature and insoluble in water. The molar electrical conductances were measured for 0.001 $mol\cdot dm^{-3}$ DMF solutions and the results show that the complexes have low molar conductances, indicating the non-ionic nature of these complexes and they are considered to be non-electrolytes. The magnetic moments of the complexes, calculated from the corrected magnetic susceptibilities determined at room temperature (Table 1), show that all complexes are diamagnetic except for the complexes $[NiL^1Cl(H_2O)_2]$ and $[FeL^2Cl]\cdot2$dioxane with μ_{eff} values of 3.3 and 5.07 B.M., respectively, indication high spin configurations. The structures and properties were also characterized by TGA analysis, FT-IR and UV–Vis spectroscopies.

3.1.1 Infrared Spectra

The most important bands in the IR spectra of the metal complexes are presented in Table 2. The IR spectra of the ligands H_2L^1 and H_2L^2 have very strong and sharp bands in the region 3,260–3,390 cm^{-1} which may be attributed to the ν(N–H) stretching vibration of the semicarbazones and thiosemicarbazones. A broadening in this band in the ligands indicates a probable association of ν(N–H) with the phenolic OH vibration. This band does not exist in all of the complexes, suggesting chelation through nitrogen of the azomethine group [23].

The ligand H_2L^1 can exhibit thione-thiol tautomerism since it contains a thioamide-NH-C=S functional group. The ν(S–H) band at 2,565 cm^{-1} is absent in the IR spectrum of the ligand, indicating that in the solid state, the ligand remains as the thione tautomer. The presence of a stretching vibration at 1,480–1,491 cm^{-1}, assigned to –NH–C=S, indicates that the ligand bonded to the metal ion in the thione form. The sharp ν(C=N) band of the thiosemicarbazone appears at 1,608 cm^{-1}, but is shifted 20 cm^{-1} lower in the complexes indicating coordination via the azomethane nitrogen. This is also confirmed by the appearance of bands in the range of 459–485 cm^{-1}, which have been assigned to the ν(M–N). A strong band found at 1,106 cm^{-1} is due to the ν(N–N) of the thiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. This is due to the increase in the bond strength, which again confirms coordination via the azomethane nitrogen. The band appearing at ca. 837 cm^{-1} ν(C=S) in the IR spectrum of the ligand is shifted towards lower wave number. It also indicates that the thione sulfur coordinates to the metal ion. Thus, it may be concluded that the ligand behaves as a

Table 1 Molecular formulae, elemental analyses, and physical properties of metal complexes

Complex		Found (Calc.) %					Color	Yield (%)	Magnetic moment (BM)
		C %	H %	N %	MO %	M %			
[Cu L^1Cl]	(**1**)	(36.79) 36.57	(2.27) 2.23	(11.38) 11.63	(23.5) 22.02	(18.55) 17.59	Green	85	1.95
[Ni L^1Cl·2H_2O]	(**2**)	(33.72) 33.66	(2.89) 3.08	(10.53) 10.70	(18.51) 19.03	(14.61) 14.96	Brown	87	3.2
[CoL^1Cl_2·EtOH]· ½EtOH·2H_2O	(**3**)	(33.85) 33.82	(3.97) 4.26	(8.63) 8.45	(18.50) 16.68	(11.67) 11.85	Brown	85	Diamagnetic
[Cr L^1Cl_2]·½EtOH·4H_2O	(**4**)	(30.00) 30.01	(4.05) 3.99	(8.99) 8.75	(>18) 15.83	(10.57) 10.83	Green	82	3.88
[FeL^1Cl_2]·½EtOH	(**5**)	(34.78) 34.98	(2.49) 2.69	(10.34) 10.20	(17.87) 18.20	(13.37) 13.55	Brown	87	5.60
[CuL^2Cl]	(**6**)	(38.17) 38.27	(2.48) 2.34	(11.96) 12.17	(24.30) 23.03	(18.26) 18.41	Green	85	2.15
[NiL^2Cl]·7H_2O	(**7**)	(28.38) 28.32	(4.54) 4.75	(9.14) 9.00	(23.50) 23.30	(12.43) 12.58	Green yellow	89	3.18
[CoL^2Cl·2H_2O]·4H_2O	(**8**)	(29.46) 29.51	(4.29) 4.28	(9.36) 9.39	(>24) 17.78	(12.94) 13.16	Pink	94	4.90
[Fe L^2Cl]·2dioxane	(**9**)	(44.68) 44.51	(3.67) 4.52	(8.25) 8.20	(15.32) 15.58	(12.67) 12.89	Green	47	5.45

Table 2 IR spectra of the carbazone complexes

Complex	*v*(C=O)	*v*(NH)	*v*(NH_2)	*v*(C=N)	*v*(N–C=S)	*v*(C–O)	*v*(C–N)	*v*(C–S) or *v*(C–O)*	*v*(M–N)	*v*(M–O)	*v*(M–Cl)
H_2L^1	1,683	3,337	3,294 3,183	1,605 1,561	–	1,402	1,273	601	–	–	–
H_2L^2	1,685 1,659	3,431	3,305 3,182	1,616 1,548	–	1,406	1,277	899	–	–	–
(**1**)	1,687	3,340	3,291 3,185	1,608 1,568	–	1,409	1,279	606	506	438	900
(**2**)	1,674	3,355	3,259 3,168	1,620 1,594	1,498	1,336	1,289	609	505	438	900
(**3**)	1,700	3,388	3,388	1,607 1,572	1,496	1,340	1,287	621	500	450	901
(**4**)	1,675			1,608 1,675	1,498	1,421	1,286	620	497	437	901
(**5**)	1,671	3,423	3,317 3,202	1,606 1,503	1,480	1,338	1,284	615	489	436	900
(**6**)	1,691 1,661	3,434	3,307 3,178	1,621 1,549	–	1,409	1,279	903*	510	434	903
(**7**)	1,681 1,658	3,357	– 3,065	1,617 1,557		1,336	1,289	903*	510	454	903
(**8**)	1,682 1,658	3,364	3,222 3,064	1,616 1,556		1,340	1,287	895*	497	465	895
(**9**)	–	3,406		1,606 –		1,421	1,286	–	511	416	–

* *v*(C=O)

tridentate chelating agent, coordinating through phenolic oxygen, azomethane nitrogen, and thiolate sulfur.

The IR spectrum of the ligand H_2L^2 (Supplementary material, S2) shows characteristic bands in the range of 3,307–3,178 cm^{-1}, corresponding to symmetric ν_s and asymmetric stretching ν_{as} for the NH_2 group. It also shows a sharp strong band at 1,685 cm^{-1}, attributed to the ν(C=O) stretching vibration. The IR spectra of all the metal complexes of H_2L^2 show downshifts in ν(–N–C=O) from 1685 to 1661, 1666, and 1678 cm^{-1} for Cu^{2+}, Ni^{2+}, and Co^{2+} complexes, respectively. This clearly indicates involvement of the oxygen atom of the carbonyl group in coordination to metal ion. The next IR band of structural significance in the spectrum of the ligand appears at 1,610 cm^{-1}, assigned to the azomethin ν(C=N) group. This band has also downshifted (red shift) to 1,554–1,555 cm^{-1} upon coordination, which clearly indicates coordination of the nitrogen to the metal ion [24, 25]. The appearance of strong bands at 1,494 and 1,292 cm^{-1}, attributed to ν(C=N) and ν(O–C=N), supports the formation of the enolic structure. The broad stretching vibration at 3,229 cm^{-1}, corresponding to the phenolic ν(OH) which forms H-bonds with the azomethin nitrogen. This indicates the presence of the keto/enol equilibrium.

The IR spectral data of L^2-based metal complexes (Table 2) show the disappearance of the phenolic υ(OH) vibration, indicating that the phenolic OH group is involved in complex formation, as no solvent molecules are attached to the complex of CuL^2Cl. The symmetric and asymmetric stretching vibrations of NH_2 groups are not present in the spectra of complexes. This indicate that the NH_2 group does not participate in complex formation, except in complexes FeL^1Cl_2 and FeL^2Cl_2, in which the ν(N–C=O) at 1,465 cm^{-1} disappears indicating that the ligand bonds to metal ion in the enol form.

3.1.2 Electronic Absorption Spectra and Magnetic Measurements

The electronic spectra of L^1-based metal complexes were measured and the results are shown in Table 3.

The electronic spectrum of CuL^1Cl (**1**) in DMF has an absorption maximum at 15,151 cm^{-1}, corresponding to the $^2E_{2g} \rightarrow {}^2T_{2g}$ transition belonging to O_h geometry around the Cu(II) ion (Supplementary material). The spectrum also shows a transition due to CT at 24,213 cm^{-1}. The magnetic moment value of 1.95 BM indicates the square planar geometry configuration. This means that DMF is coordinated in the axial position.

The electronic spectrum of the complex $[CuL^2Cl]$ (**6**) gives absorption maxima at 21,367 and 20,242 cm^{-1}, corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions. This is a characteristic of square planer geometry around Cu^{2+} ions. The spectrum also shows a transition due to CT at 23,693 cm^{-1}. The magnetic moment value of 2.15 BM also indicates the square planar geometry configuration.

The electronic spectrum of the complex $[NiL^1Cl\cdot 2H_2O]$ (**2**) has absorption bands at 19,762 and 16,400 cm^{-1}, corresponding to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions. The magnetic moment value is 3.20 BM, supporting the same geometry.

The electronic spectrum of complex $[NiL^2\cdot 2H_2O]\cdot 5H_2O$ (**7**) has absorption bands at 22,200 and 16,520 cm^{-1} and a magnetic moment of 3.50 BM, suggesting octahedral O_h geometry around the Ni(II) ion.

The electronic spectra of complexes $[CoL^1Cl_2\cdot(H_2O)_2]$ EtOH (**3**) and $[CoL^2Cl\cdot(H_2O)_2]$ $4H_2O$ (**8**) have absorption bands at 22,172, and 24,096 cm^{-1}, corresponding to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transitions. The band position indicates distorted octahedral O_h geometry, the diamagnetic character indicates oxidation of Co^{2+} to Co^{3+} in (**3**). Complex (**8**) has a magnetic moment value of 4 95 BM.˙ The electronic spectra of

Table 3 Thermogravimetric analysis of carbazone complexes

Complex	% Weight loss		Decomposition temp. (°C)	Assignments
	Found	Calc.		
(**1**)	42.80	43.50	319	Loss of coumarin
	24.12	24.67	390	Loss of thiosemicarbazone
	9.55	9.81	450	Loss of Cl_2 mol
	23.50	22.02	718	Residual oxide CuO
(**3**)	3.30	4.63	37	Loss of 1/2EtOH
	15.57	16.49	113	$2H_2O$ Loss of EtOH+
	43.52	45.80	148–318	Loss of coumarin + Cl_2
	16.61	17.92	476–579	Loss of thiosemicarbazon
	>19.50	17.30	>670	Residual oxide Co_2O_3
(**4**)	19.50	19.79	39–210	1/2EtOH and $4H_2O$
	45.13	45.84	210	Loss of coumarin + Cl_2
	18.08	18.55	555	Loss of thiosemi carbazone
	>18	15.83	800>	Residual oxide Cr_2O_3
(**6**)	54.33	55.80	292	Loss of coumarin then $1/2Cl_2$
	21.03	21.15	336	Loss of semicarbazon + 1/2 Cl_2
	24.30	23.03	800	Residual oxide CuO
(**7**)	52.76	53.42	145–290	Loss of coumarin + $6H_2O$
	22.85	23.27	360	Loss of semicarbazon + 1/2 Cl_2
	23.5	23.30	627	Residual oxide $NiO_2{\cdot}H_2O$
(**8**)	15.35	16.08	32–104	Loss of $4H_2O$
	37.96	39.80	284–376	Loss of coumarin + $2H_2O$
	23.48	24.25	583	Loss of semicarbazon + 1/2 Cl_2
	>24	18.53	650	Residual oxide Co_2O_3

complexes $FeL^1Cl_2{\cdot}1/2$ EtOH (**5**) and $FeL^1Cl_2{\cdot}2$ dioxane (**9**) have CT bands at 35,040 and 34,840 cm^{-1} only. The magnetic moment values of 5.6 and 5.45 BM indicate high spin O_h geometry around the Fe(III) ions [26].

3.1.3 Thermal Analysis

The TG–DTA thermogram of the ligand H_2L^1 shows decomposition of the ligand at temperatures lower than 120 °C, whereas the ligand H_2L^2 begins to decompose at 140 °C. This indicates that the ligand H_2L^2 is more thermally stable than H_2L^1. The thermograms of the two ligands are identical and decompose in two steps. With weigh loses in three exothermic steps, H_2L^1 show weigh loss at 126 °C, corresponding to loss of adducted CH_3COOH molecule, the second step corresponding to loss of coumarine followed by thiosemicarbazone. H_2L^2 show two steps whose weigh losses correspond to the coumarine part then semicarbazone.

The thermograms of complexes of H_2L^2 (Table 4) show they began to decompose at ~300 °C indicating their stability. The lattice water molecules dehydrated at 140 °C, while the coordinated ones are eliminated at 300 °C. Then, the complexes begin to decompose at temperatures higher than 340 °C. This is because the M–O bond is more

Table 4 Thermodynamic parameters of H_2L^1 with some transition metal ions in 75 % (v/v) dioxane–water and $I = 0.1$ at (313, 303, and 293 K)

Compd.	log β			$T = 313$ K			T = 303 K			$T = 293$ K		
	313 K	303 K	293 K	$\Delta H°$ (kJ·mol^{-1})	$\Delta G°$ (kJ·mol^{-1})	$\Delta S°$ (JK^{-1}·mol^{-1})	$\Delta H°$ (kJ·mol^{-1})	$\Delta G°$ (kJ·mol^{-1})	$\Delta S°$ (JK^{-1}·mol^{-1})	$\Delta H°$ (kJ·mol^{-1})	$\Delta G°$ (kJ·mol^{-1})	$\Delta S°$ (JK^{-1}·mol^{-1})
H_2L^1	18.24*	18.46*	18.75*	−80.58	−109.26	91.63	−80.58	−107.05	87.34	−80.58	−105.14	83.82
Cu(II)	25.27	25.64	26.06	−100.73	−151.37	161.81	−100.73	−148.68	158.27	−100.73	−146.13	154.96
Ni(II)	25.30	26.57	27.94	−229.66	−151.55	249.53	−229.66	−154.07	249.44	−229.66	−156.67	249.09
Co(II)	26.11	27.03	28.01	−191.38	−156.40	111.74	−191.38	−156.74	114.32	−191.38	−157.06	117.12
Mn(II)	24.16	25.30	25.50	−130.94	−144.72	44.02	−130.94	−146.71	52.03	−130.94	−142.99	41.11
Fe(III)	27.33	28.67	31.01	−239.22	−163.71	241.25	−239.22	−166.25	240.83	−239.22	−173.89	223.00

* ($pK_{a1} + pK_{a2}$) for H_2L^1

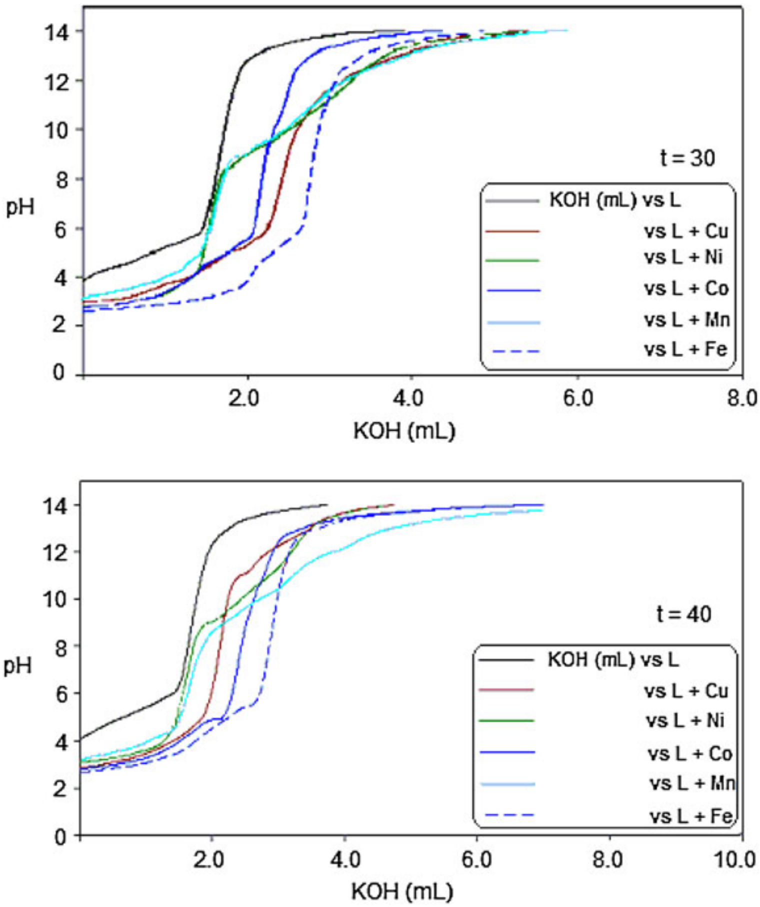


Fig. 1 Titration curves of the ligand H_2L^1 with M^{2+} and M^{3+} transition metals in 1,4-dioxane 75 % (v/v) and IS = 0.1 at (30 and 40 °C)

stable than the M–N bond. The thermal stability of L^2 based metal complexes may be arranged in the sequence of Co(II) > Cu(II) > Ni(II) and L^1 based metal complexes may be arranged in the sequence of Cu(II) $\simeq$ Ni(II) > Co(II). At the end of the thermogram, constant weights are obtained, indicating the formation of corresponding metal oxides [27–36].

3.2 Protonation Constants of the Ligands and their Complexation Constants

Protonation constants of the carbazones H_2L^1 and H_2L^2, which may considered to be diprotic acids, were determined by the pH-metric method. The ligands (3×10^{-3} mol·dm^{-3}) were titrated against standard solution of KOH (0.05 mol·dm^{-3}) at ionic strength (I) of 0.00, 0.05, 0.10 mol·dm^{-3} KNO_3 at temperatures of 20, 30 and 40 °C in mixed dioxane:water solvents [50, 60, and 75 % (v/v)]. The protonation constants were also determined in 75 % (v/v) DMF–water at $I = 0.1$ mol·dm^{-3} and 35 °C. The titration curves (Figs. 1, 2, 3, 4, 5, 6, 7) show two inflections at $a = 1$ and $a = 2$, where a is the

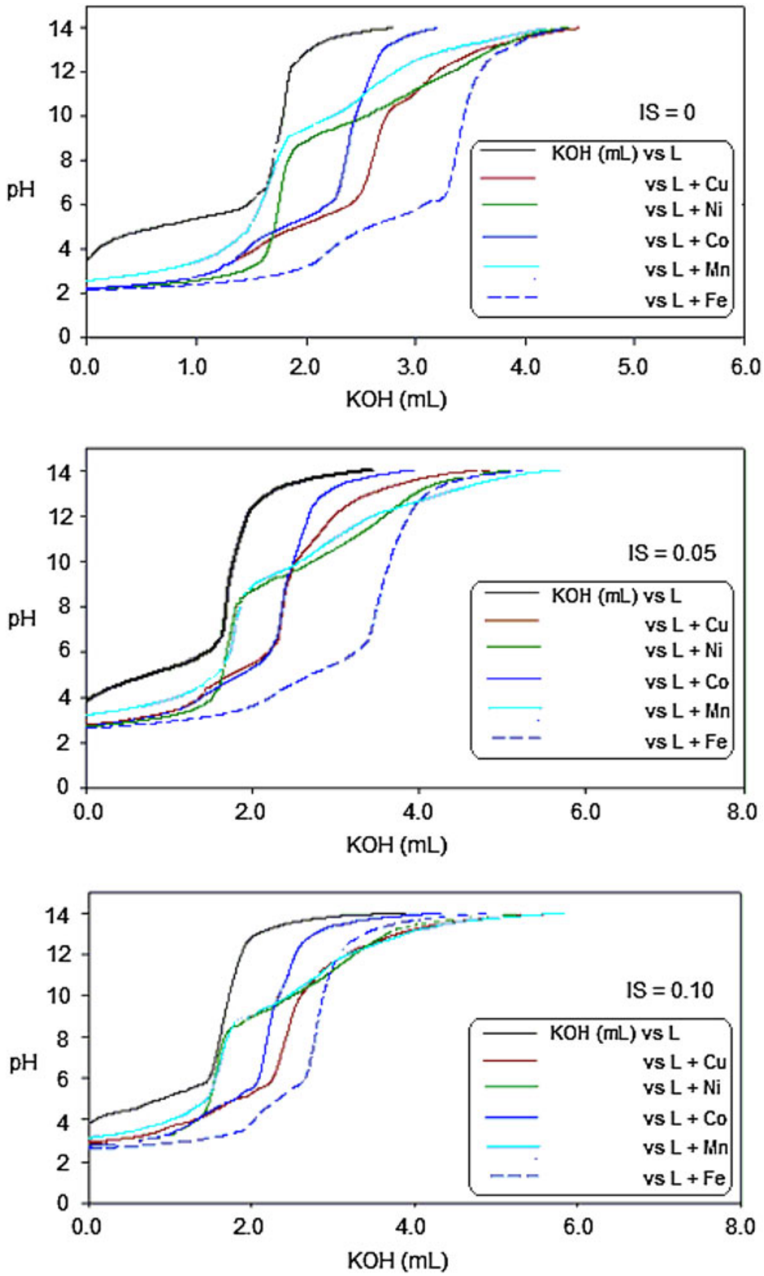


Fig. 2 Titration curves of the ligand H_2L^1 with M^{2+} and M^{3+} transition metals in 1,4-dioxane (75 %, v/v) and IS = 0.0, 0.05, and 0.1 at 30 and 40 °C

number of moles of base added per mole of ligand. This inflection indicates the formation of different deprotonated species due to one phenolic, amide or enolate, thiolate groups.

$$H_2L \rightleftharpoons HL^- + H^+ \rightarrow \text{phenolic OH}$$

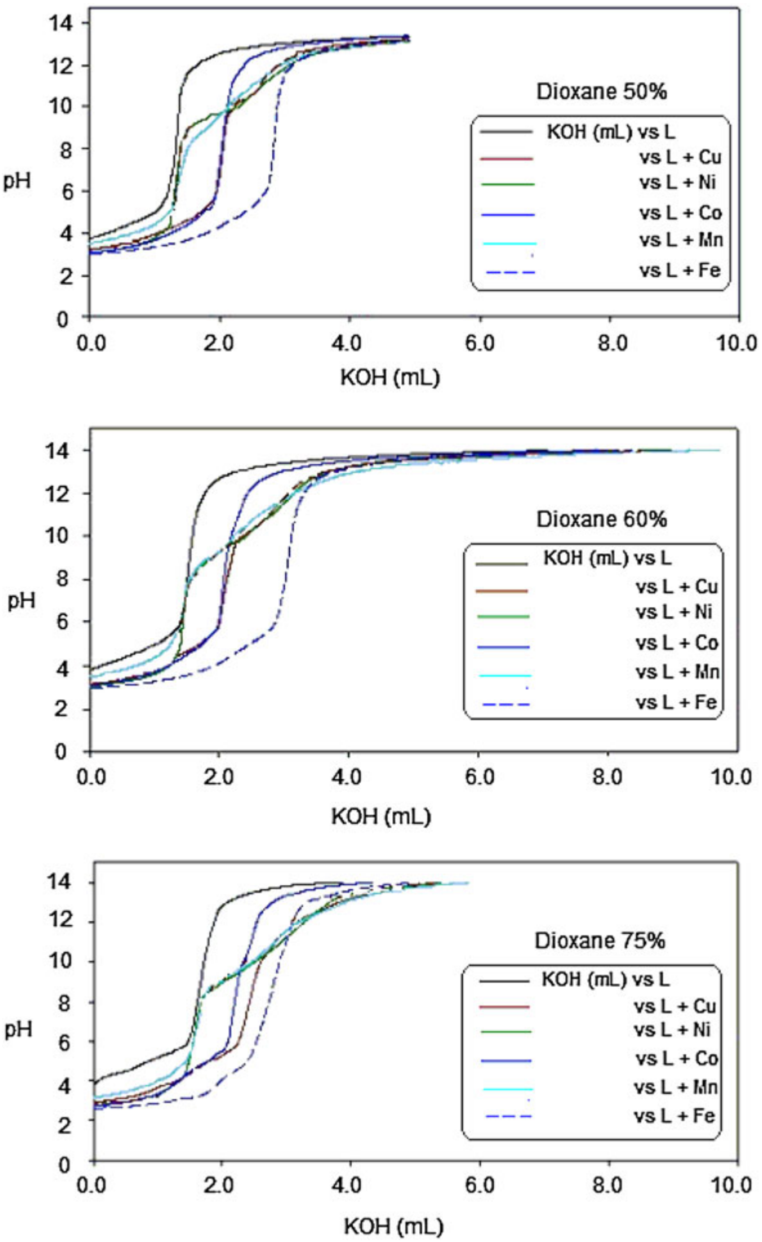


Fig. 3 Titration curves of the ligand H_2L^1 with M^{2+} and M^{3+} transition metals in 1,4-dioxane 50, 60, and 75 % (v/v) and IS = 0.1 at 30 °C

$$\mathrm{HL} \rightleftharpoons \mathrm{L}^- + \mathrm{H}^+ \rightarrow \text{ amide or enolate, thiolate}$$

The pK_a values were evaluated from the protonation ligand formation curves (Supplementary material using the following equation [30]:

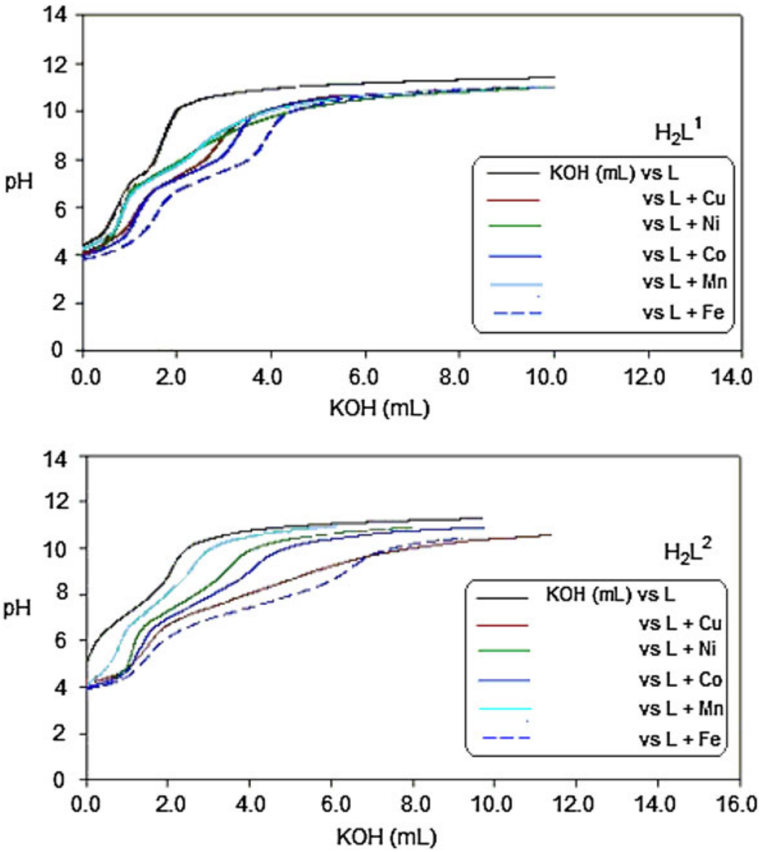
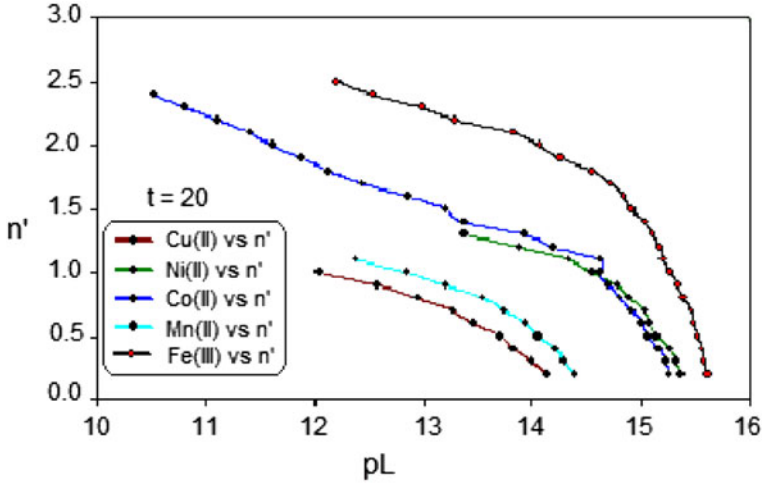


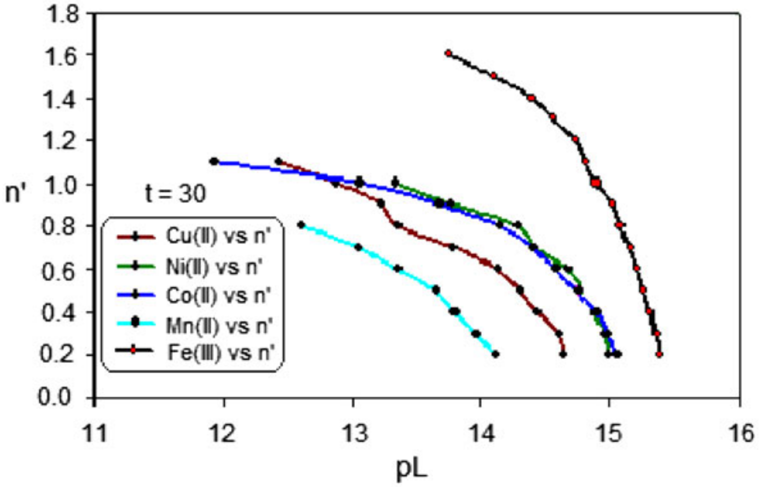
Fig. 4 Titration curves of the ligands H_2L^1 and H_2L^2 with M^{+2} and M^{+3} transition metal ions in 75 % (v/v) DMF–Water and IS = 0.1 at 30 °C

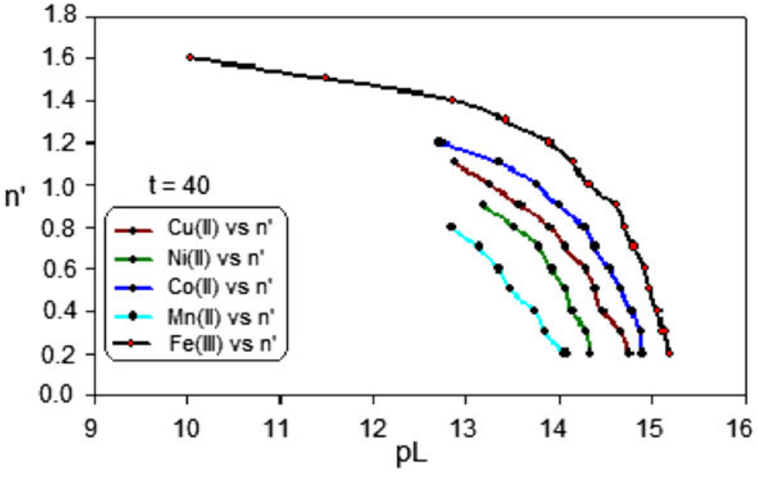
$$\mathrm{p}K_{\mathrm{a}} = \log_{10}\frac{a_{\mathrm{Cl}} - [\mathrm{H}^+] + [\mathrm{OH}^-]}{(1-a) + [\mathrm{H}^+] - [\mathrm{OH}^-]} + \mathrm{pH} + 0.28 \tag{2}$$

The determination of formation constants of the ligands H_2L^1 and H_2L^2 with different metal ions: Cu(II), Co(II), Ni(II), and Fe(III) were carried out by titrating the ligand (3×10^{-3} mol·dm^{-3}) using the same conditions, in the presence of metal ions (1×10^{-3} mol·dm^{-3}) in a molar ratio of 1:3. The deviations in metal–ligand titration curves occur after pH = 4 in the case of Cu(II) and after pH = 6 for other metal ions, indicating complex formation. The observed precipitation at pH = 7–8 may be due to the insolubility of the complexes in aqueous media. Calculations were carried out at pHs where no turbidity or solid phase appears. Titration curves and $\log_{10} K$, $\log_{10} \beta$ values prove the formation of ML and ML_2 complexes. The formation constants can be calculated using the following equations:

$$\log_{10}\frac{\bar{n}}{1-\bar{n}} = \log_{10} K_1 + \mathrm{pL} \tag{3}$$


3.0
2.5
2.0
1.5
1.0
0.5
0.0
n'
10
11
12
13
14
15
16
pL
t = 20
Cu(II) vs n'
Ni(II) vs n'
Co(II) vs n'
Mn(II) vs n'
Fe(III) vs n'


1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
n'
11
12
13
14
15
16
pL
t = 30
Cu(II) vs n'
Ni(II) vs n'
Co(II) vs n'
Mn(II) vs n'
Fe(III) vs n'


1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
n'
9
10
11
12
13
14
15
16
pL
t = 40
Cu(II) vs n'
Ni(II) vs n'
Co(II) vs n'
Mn(II) vs n'
Fe(III) vs n'

◀**Fig. 5** Relation between n' and pL of H_2L^1 with some M^{2+} and M^{3+} transition metals in 1,4-dioxane 75 % (v/v) and IS = 0.1 at 20, 30, and 40 °C

$$\log_{10}\frac{\bar{n}-1}{2-\bar{n}} = \log_{10}K_2 + \mathrm{pL} \qquad (4)$$

The values measured at different temperature 20, 30 and 40 ± 0.1 °C and ionic strength (I) of 0.0, 0.05, and 0.1 mol·dm^{-3} KNO_3 in mixed dioxane : water solvents (75:25, 50:50, 60:40) and DMF: water solvents (75:25).

The deviations in metal–ligand titration curves, after pH = 3–5 in 1,4-dioxane and pH = 6–7 in DMF, from the titration curve of ligand indicate complex formation. Dissociation constants of the ligand in 75/25 % (v/v) dioxane–water, $I = 0.1$ mol·dm^{-3} at 30 °C increase as the temperature decreases; also, the stability constants increase as the temperature decreases indicating exothermic reactions. It has been shown that stability of Cu(II) complex is less than that of Ni(II); this can be considered in terms of formation of a Ni(II) complex with higher coordination number or change in geometry.

Also, the Co(II) complexes have stability constants near to those of Ni(II). The calculated dissociation constants of the ligands and stability constants of the complexes show that the values increase as the ionic strength (I) and dielectric constant (ε) decrease. This means that both metal and ligand ions are affected by the increasing dielectric constant of the solvent. The formation constants of Fe(III) with the ligand H_2L^1 usually have values higher than the other metals due to the higher oxidation state.

The results also show that the formation constants of H_2L^1 complexes increase as the solvent ratio increase 75 > 60 > 50 % (dioxane–water); these values are higher than that in 75/25 % DMF. This is due to the ε values DMF (47) > dioxane (35). The ε values decrease as the ratio of dioxane increase and the electrostatic forces between ions increase thus facilitating complex formation; on the other hand, increasing water content leads to increasing hydration of the M ions, and formation of intermolecular hydrogen-bonding between dioxane and H_2O which tends to oppose complex formation.

The stability constant values of L^1-based Mn(II) and Fe(III) at 303 K and $I = 0.1$ mol·dm^{-3} show higher values than those of the L^2-based metal complexes this is due to the activity of thiolate (–NH=C–S$^-$) ion rather than enolate (–NH=C–O$^-$) ion [31–36].

The Gibbs energy change ΔG and the entropy change ΔS were calculated from the well known relationships:

$$\Delta G^{\circ} = -RT\ln K \qquad (5)$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \qquad (6)$$

The $-\Delta H^{\circ}$ values indicate exothermic reactions. Increasing temperature leads to a decrease in ΔG°.

4 Conclusion

It may be concluded that the new ligands 4-hydroxy coumarin-3-thiosemicarbazone (H_2L^1) and 4-hydroxy coumarin-3-semicarbazone (H_2L^2) behave as tridentate chelating agents, coordinating through phenolic oxygen, azomethane nitrogen, and thiolate sulfur, or carbonyl oxygen. These ligands were used for the synthesis of a series of transition metal

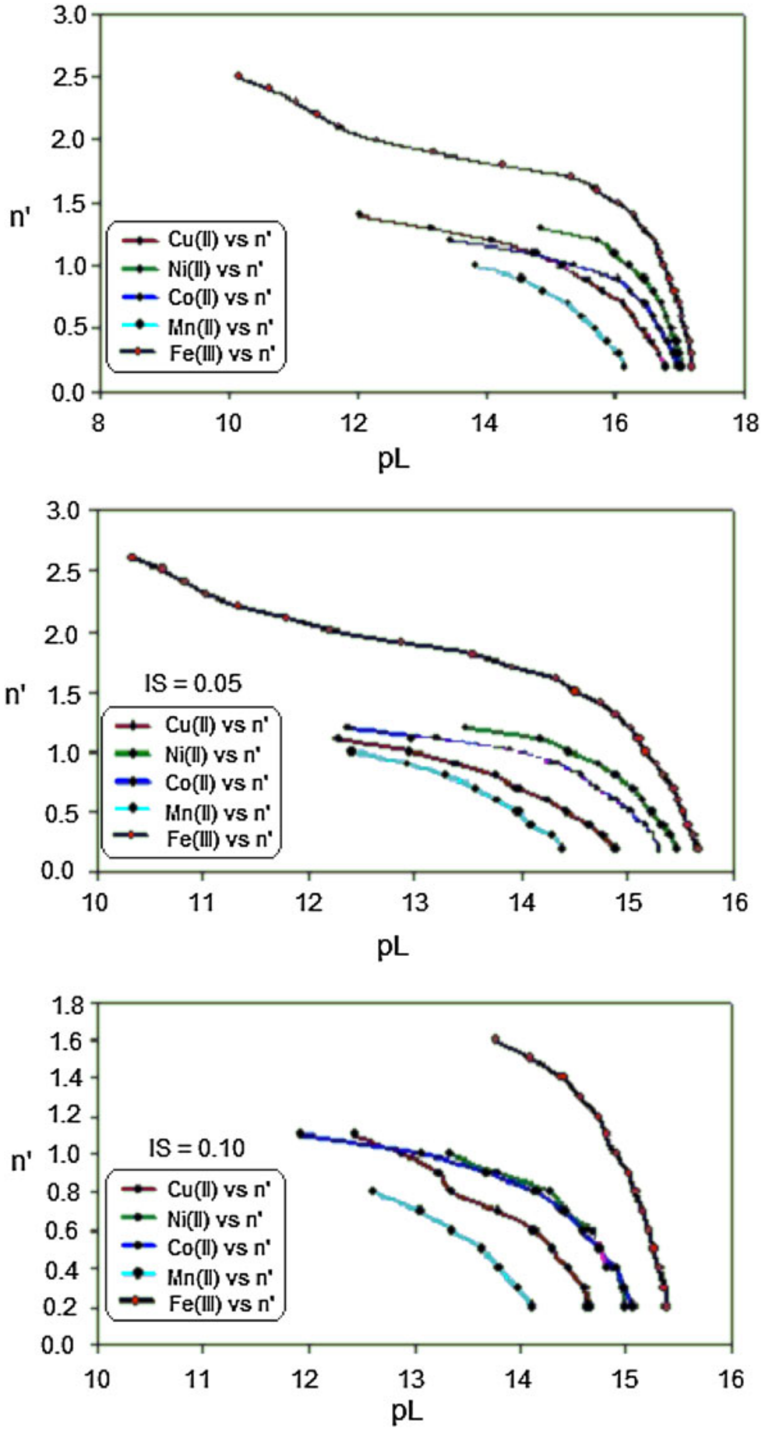
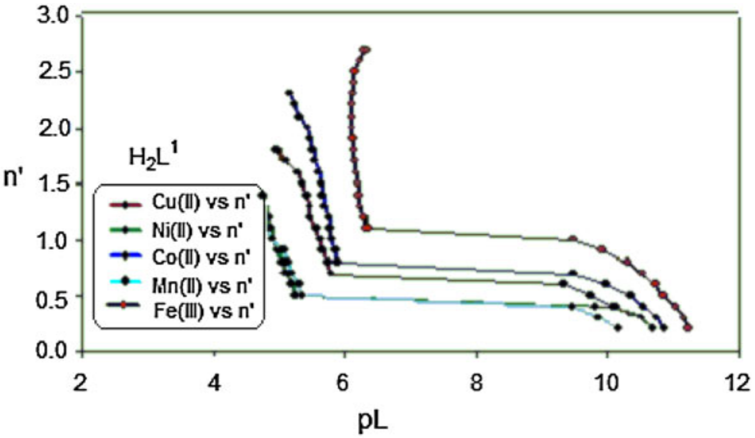


Fig. 6 Relation between *n*′ and pL of H_2L^1 with some M^{2+} and M^{3+} transition metals in 1,4-dioxane 50, 60, 75 % (v/v) and IS = 0.0, 0.05, and 0.1 at 30 °C



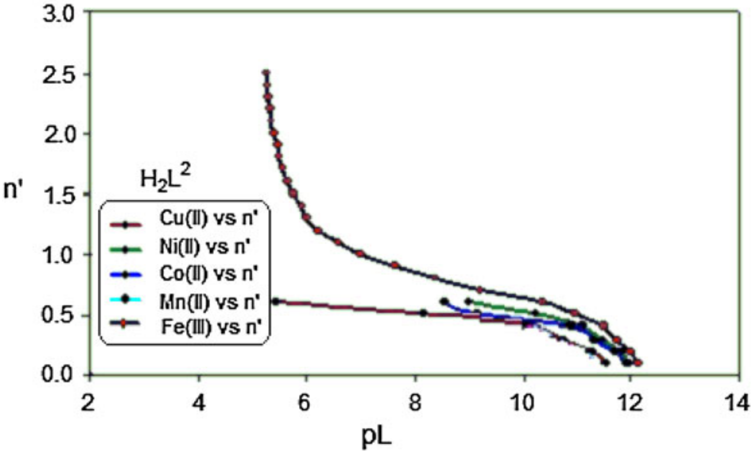


Fig. 7 Relation between *n*′ and pL of the ligands H_2L^1 and H_2L^2 with some M^{2+} and M^{3+} transition metals in 1,4-dioxane 75 % (v/v) and IS = 0.1 at 30 °C

complexes with the formula $[ML^1Cl_2]\cdot nX$ (**1**–**5**) and $[ML^2Cl]\cdot nX$ (**6**–**9**) ($X = H_2O$ or ethanol). On the basis of physicochemical measurements, tetrahedral or square planar geometries are assigned for the Cu(II) complexes in monomeric structures. In the case of Co(II), Ni(II) and Fe(III) complexes, octahedral stereochemistries in monomeric structures are suggested. The dissociation constants of the ligands and the stability constants of their Cu(II), Co(II), Ni(II), and Fe(III) complexes have been also determined using potentiometric pH-metric titrations in mixed solvents of dioxane: H_2O and DMF: H_2O with different ratios and at different temperatures.

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