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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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Synthesis, IR, Magnetic, Solid Reflectance, and Thermal Characterization of Transition Metal Chelates with 2-(5-Acetylamino-2-hydroxyphenylazo)-benzoic Acid

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ABSTRACT

The azo ligand 2-(5-acetylamino-2-hydroxyphenylazo)benzoic acid (H_2L) is derived from the diazotization of 4-acetamidophenol with anthranilic acid. Metal(II) and (III) chelates were prepared and characterized by elemental and thermal analyses, conductance, IR, mass, magnetic, and diffuse reflectance spectra. The complexes were found to have the formulae $[Cr(HL)_2]Cl \cdot H_2O$; $[Cd(HL)_2] \cdot 2H_2O$; $[M(HL)(H_2O)_z]X \cdot nH_2O$ for $M = Co(II)$ $(X = Cl,\ z = 1,\ n = 2)$, $M = Ni(II)$ $(X = Cl,\ z = 1,$

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$n = 2.5$); M = Cu(II) (X = AcO, $z = 2$, $n = 2$), and M = Zn(II) (X = AcO, $z = 1$, $n = 2$); and $[Fe(HL)Cl_2(H_2O)] \cdot 2H_2O$. The molar conductance data reveal that the Cd(II) and Fe(III) chelates are non-electrolytes, while the Cr(III), Co(II), Ni(II), Cu(II), and Zn(II) chelates are 1 : 1 electrolytes. IR spectra show that the ligand is coordinated to the metal ions in a terdentate manner with ONO donor sites of the phenolic OH, azo–N, and carboxylic OH. Magnetic and solid reflectance spectra were used to infer the coordinating capacity of the ligand and the geometrical structure of these complexes. The mass spectra give the possible molecular ion fragments resulting from the fragmentation of the chelates. The thermal behavior of these chelates shows that water molecules (coordinated and uncoordinated) and anions are removed in two successive steps followed immediately by decomposition of the ligand molecule in the subsequent steps. The relative thermal stability of the anhydrous chelates is evaluated. The final decomposition products are found to be the corresponding metal oxides. The thermodynamic activation parameters, such as, E^*, ΔH^*, ΔS^*, and ΔG^* are calculated from the TG curves and discussed.

Key Words: 2-(5-Acetylamino-2-hydroxyphenylazo)benzoic acid complexes; IR; Conductance; Solid reflectance; Mass spectra; Thermal analyses.

INTRODUCTION

Azo compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA, and protein synthesis, carcinogenesis, and nitrogen fixation.[1,2] Furthermore, they were proved to have biological activity against bacteria and fungi.[3,4] Metal chelates of Schiff bases containing anthranilic acid have been prepared previously.[5–10] Anthranilic acid has been also involved in mixed-ligand complex formation with different ligands.[11–13] Macrocyclic aza complexes of anthranilic acid have been reported.[14–18] In continuation of our interest in azo ligands and their metal chelates,[19–23] the main target of the present study is to synthesize new azo-metal chelates and determine the coordination capacity of the highly colored 2-(5-acetylamino-2-hydroxyphenylazo)benzoic acid (H_2L) that incorporates several binding sites. The coordination behavior of H_2L towards transition metal ions is investigated by IR, molar conductance, magnetic moment, solid reflectance, and mass spectral measurements. The thermal decomposition of the complexes was also used to infer the structure and the various thermodynamic activation parameters are calculated. The structure of H_2L is shown in Fig. 1.

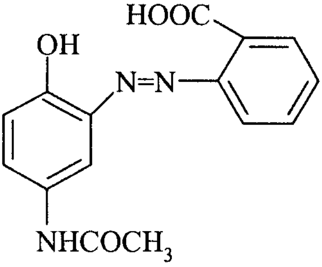

Figure 1. Structure of the ligand (H_2L).

EXPERIMENTAL

Material and Methods

All chemicals used were of analytical reagent grade. They include 4-acetamidophenol (Sigma), 2-aminobenzoic acid (Aldrich), sodium nitrite and hydroxide (BDH), ethyl alcohol (Adwic), and the disodium salt of ethylenediaminetetraacetic acid (Adwic). Cupric acetate dihydrate (Prolabo), cobalt, chromium, and nickel chloride hexahydrates (BDH), zinc and cadmium chlorides (Adwic), and ferric chloride hexadydrate (Riedel-de Haën) were used as received. The elemental analyses (C, H, N) were made at the Microanalytical Center at Cairo University. IR spectra were recorded on a Perkin–Elmer FT-IR type 1650 spectrophotometer. The solid reflectance spectra were measured on a Shimadzu 3101 PC spectrophotometer. The molar magnetic susceptibilities were measured on powdered samples using the Faraday method. The conductance measurements were carried out using a Sybron–Barnstead conductometer. A Shimadzu TGA-50H thermal analyzer was used to record simultaneously thermogravimetric (TG) and DTG curves. The experiments were carried out in a dynamic nitrogen atmosphere ($20\,\mathrm{mL\,min^{-1}}$) with a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ in the temperature range of 20–1000 °C using platinum crucibles. The sample sizes ranged in mass from 1.2 to 3.5 mg. Highly sintered α-Al_2O_3 was used as a reference. The mass spectra were recorded by the EI technique at 70 eV on a Hewlett–Packard Model MS-5988 GS–MS instrument in the Microanalytical Center of Cairo University. Metal contents were determined by titration against standard EDTA after complete decomposition of the complexes with aqua regia in a Kjeldahl flask several times.

Synthesis of 2-(5-Acetylamino-2-hydroxyphenylazo)benzoic Acid

2-Aminobenzoic acid (4.11 g, 10 mmol) was mixed with HCl (11.5 M, 5 mL) and diazotized below 5 °C with $NaNO_2$ (2.07 g, 10 mmol). The resulting diazonium chloride was coupled with an alcoholic NaOH solution (3 g, 25 mL) of 4-acetamidophenol (4.53 g, 10 mmol) below 5 °C. The formed solid product was separated by filtration, purified by crystallization from diethyl ether and dried in a vacuum over anhydrous calcium chloride. The red azo product is produced in 80% yield (6.92 g). Anal. Calcd. for $C_{15}H_{13}N_3O_4$ (299 g/mol): C, 60.20; H, 4.35; N, 14.05%. Found: C, 60.45; H, 4.50; N, 14.35%, m.p., 165 ± 2 °C.

Synthesis of the Complexes

The metal complexes of H_2L were prepared by the addition of the appropriate metal chloride or acetate (1 mmol) in an ethanol–water mixture (1 : 1, 25 mL) to the solution of the azo compound (0.299 g, 2 mmol) in the same solvent (50 mL). The resulting mixture was stirred under reflux for one half hour whereupon the complexes precipitated. They were collected by filtration, washed with a 1 : 1 ethanol : water mixture and diethyl ether. The analytical data for C, H, and N were repeated twice.

RESULTS AND DISCUSSION

The general reaction for the preparation of the metal complexes of 2-(5-acetylamino-2-hydroxyphenylazo)benzoic acid is shown below

$$CrCl_3 + 2H_2L + H_2O \longrightarrow [Cr(HL)_2]Cl \cdot H_2O + 2HCl \qquad (1)$$

$$CdCl_2 + 2H_2L + 2H_2O \longrightarrow [Cd(HL)_2] \cdot H_2O + 2HCl \qquad (2)$$

$$FeCl_3 + H_2L + 3H_2O \longrightarrow [Fe(HL)Cl_2 \cdot H_2O)]_2 \cdot 2H_2O + HCl \qquad (3)$$

$$MX_2 + H_2L + zH_2O + nH_2O \longrightarrow [M(HL)(H_2O)_z]X \cdot nH_2O + HX \qquad (4)$$

(where M = Co(II) (X = Cl, $z = 1$, $n = 2$), Ni(II) (X = Cl, $z = 1$, $n = 2.5$); Cu(II) (X = AcO, $z = 2$, $n = 2$), and Zn(II) (X = AcO, $z = 1$, $n = 2$).

The results of the elemental analyses of the metal chelates of 2-(5-acetylamino-2-hydroxyphenylazo)benzoic acid, which are recorded in Table 1, are in good agreement with those required by the proposed formulae. In most cases 1 : 1 (M : L) solid complexes were isolated and found to have the general formulae $[M(HL)(H_2O)_z]X \cdot nH_2O$, where M = Co(II) (X = Cl,

Table 1. Analytical and physical data of H_2L and its metal chelates.

Compounds	Color (% yield)	F.wt[a] found (calcd)	M.p. (°C)	Found (Calcd) % C	H	N	M	μ_{eff} (BM)	Λ_m (Ω^2 mol^{-1} cm^{-1})
H_2L	Red (80)	—	165 ± 2	60.45	4.50	14.35	—	—	—
$C_{15}H_{13}N_3O_4$		(299)		(60.20)	(4.35)	(14.05)			
$[Cr(HL)2]Cl \cdot H_2O$	Light	692.5	>160	52.60	4.20	12.10	6.55	3.95	135
$C_{30}H_{26}ClCrN_6O_9$	brown (73)	(692.5)	(decom.)	(52.14)	(4.06)	(12.17)	(6.23)		
$[Fe(HL)Cl_2(H_2O)] \cdot 2H_2O$	Dark	481	>300	37.30	3.90	8.45	11.26	5.35	10
$C_{15}H_{18}Cl_2FeN_3O_7$	brown (78)	(479)		(37.58)	(3.76)	(8.77)	(11.69)		
$[Co(HL)(H_2O)]Cl \cdot 2H_2O$	Dark	449	>300	40.60	4.50	9.52	13.25	3.60	125
$C_{15}H_{18}ClCoN_3O_7$	grey (81)	(446.5)		(40.31)	(4.03)	(9.41)	(13.21)		
$[Ni(HL)(H_2O)]Cl \cdot 2.5H_2O$	Light	457	>300	39.70	4.40	8.99	12.89	Diam.	100
$C_{15}H_{19}ClN_3NiO_{7.5}$	brown (75)	(455.5)		(39.52)	(4.17)	(9.22)	(12.95)		
$[Cu(HL)(H_2O)_2](AcO) \cdot 2H_2O$	Dark	493.5	>300	41.50	4.50	8.20	12.60	2.10	150
$C_{17}H_{23}CuN_3O_{10}$	violet (82)	(492.5)		(41.42)	(4.67)	(8.53)	(12.89)		
$[Zn(HL)(H_2O)](AcO) \cdot 2H_2O$	Brown (70)	475	>300	42.70	4.30	8.68	13.60	Diam.	130
$C_{17}H_{21}N_3O_9Zn$		(476)		(42.86)	(4.41)	(8.82)	(13.66)		
$[Cd(HL)_2] \cdot 2H_2O$	Light	708	>150	48.40	3.50	11.56	15.43	Diam.	25
$C_{30}H_{28}CdN_6O_{10}$	brown (76)	(744)	(decom.)	(48.39)	(3.76)	(11.29)	(15.05)		

[a] Formula weight.

$z = 1$, $n = 2$), Ni(II) (X = Cl, $z = 1$, $n = 2.5$), Cu(II) (X = AcO, $z = 2$, $n = 2$) and Zn(II) (X = AcO, $z = 1$, $n = 2$). While the Cr(III) and Cd(II) chelates are of the type 1 : 2 (M : L) and have the formulae $[Cr(HL)_2]Cl \cdot H_2O$ and $[Cd(HL)_2] \cdot 2H_2O$. In addition, Fe(III) forms a 1 : 1 (M : L) chelate of the formula $[Fe(HL)Cl_2(H_2O)] \cdot 2H_2O$. The H_2L ligand offers several alternatives to coordination to metals. The results shown in Table 1 prove that H_2L is indeed monoanionic, where the carboxylate proton is lost when coordinated to the metal ions, and thus reducing the charge on the complex ion. The presence of chloride or acetate ions in the inner or outer sphere of the chelates neutralizes the charge on the complex. Thus H_2L is expected to fill three coordination positions and contribute a charge of -1. The non-involvement of chloride or acetate ions in the coordination to the metal ions is also confirmed by the conductance measurements.

IR Spectra and Mode of Bonding

A detailed interpretation of the IR spectra of H_2L and the effect of binding with Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions on the vibrational frequencies of the free H_2L ligand are discussed. The IR spectra of the free ligand and its metal chelates were carried out in the 4000–200 cm^{-1} range (Table 2). The IR spectrum of the ligand shows a broad band at 3500–3050 cm^{-1}, which can be attributed to the phenolic OH, acetamide NH, and carboxylic OH groups. This band is still broad in all complexes, which renders it difficult to attribute to the involvement of phenolic OH and carboxylic OH groups in coordination. The involvement of the phenolic OH group in chelation is confirmed by the blue-shift of the ν(C–O) stretching band, observed at 1266 cm^{-1} in the free ligand, to the extent of 3–29 cm^{-1} in the complexes.[21] However, the ν(N=N) stretching band in the free ligand is observed at 1506 cm^{-1}.[19,21] This band is shifted to higher or lower frequency values upon complexation suggesting coordination via the azo group (M ← N). If the diazo nitrogen bonded to the pohenol is coordinated to the metal ion, 7- and 5-membered chelate rings are formed, with 7-membered chelate rings not being favored. However, if the diazo nitrogen bonded to the benzoic acid coordinated to the metal ion, two 6-membered chelate rings, which, energetically, should be more favored.[24]

In addition, the IR spectrum of H_2L reveals bands at 1604 and 1374 cm^{-1} due to $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$.[25] These bands decrease in intensity and shift to lower frequency on complexation, suggesting coordination *via* the carboxylate OH group.[22] In the far-IR spectra of all the complexes, the non-ligand bands observed at the 435–414 cm^{-1} region can be assigned to the ν(M–N) stretching vibration.[22] Conclusive evidence regarding the bonding

Table 2. Characteristic IR bands (4000–400 cm^{-1}) of H_2L and its metal chelates.

Compounds	ν(COO) (asym)	ν(COO) (sym)	ν(C–O) (phenolic)	δ(OH) (phenolic)	δ(OH) (coord. H_2O)	ν(N═N)	ν(M–O)	ν(M–N)
H_2L	1,604 s	1,374 s	1,266 m	1,413 s	—	1,506 m	—	—
$[Cr(HL)_2]Cl \cdot H_2O$	1,600 s	1,330 m	1,278 s	1,400 s	—	1,512 m	505 w	419 w
$[Fe(HL)Cl_2(H_2O)] \cdot 2H_2O$	1,605 s	1,323 s	1,270 s	1,405 s	883 m, 769 m	1,500 s	496 w	422 m
$[Co(HL)(H_2O)]Cl \cdot 2H_2O$	1,605 s	1,322 m	1,275 s	1,401 s	880 m, 775 m	1,520 m	500 m	425 m
$[Ni(HL)(H_2O)]Cl \cdot 2.5H_2O$	1,605 m	1,322 m	1,275 m	1,401 s	880 m, 750 m	1,500 m	502 w	435 w
$[Cu(HL)(H_2O)_2](AcO) \cdot 2HO$	1,605 m	1,322 m	1,269 m	1,400 s	872 w, 767 m	1,500 m	469 w	423 m
$[Zn(HL)(H_2O)](AcO) \cdot 2H_2O$	1,600 br	1,340 m	1,287 s	1,388 s	898 s, 728 m	1,500 br	496 w	418 m
$[Cd(HL)_2] \cdot 2H_2O$	1,599 br	1,332 m	1,295 s	1,404 s	—	1,520 br	492 m	414 m

of oxygen to the metal ions is provided by the occurrence of bands at 505–496 cm^{-1} as the result of ν(M–O).[21,22]

Therefore, the IR spectra indicate that H_2L behaves as monobasic acid and the coordination sites being Ar–OH, –N=N– and the O atom of the carboxylic OH group.

Molar Conductivity Measurements

The solubility of the complexes in DMF permitted determination of the molar conductivity (Λ_m) of 10^{-3} M solutions at 25 °C[26] and, by comparison, the electrolytic nature for each complex (Table 1). The molar conductivity for the Cr(III) complex is 135 Ohm^{-1} cm^2 mol^{-1} indicating a 1 : 1 electrolyte and suggests under these circumstances the non-involvement of Cl in coordination to the Cr(III) ion. On the other hand, the low conductivity values of the Fe(III) and Cd(II) complexes prove their weak ionic nature (non-electrolytes). The conductance data in Table 1 also indicate that the Co(II), Ni(II), Cu(II), and Zn(II) complexes are 1 : 1 electrolytes indicating their ionic nature.

Magnetic Susceptibility and Electronic Spectral Measurements

The diffuse reflectance spectra of the Fe(III), Co(II), Ni(II), and Cu(II) chelates show two bands at 252–256 nm and 352–356 nm which are attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, within the H_2L ligand. For the hexa-coordinated Cr(III) complex there are three spin-allowed transitions in the electronic spectrum, ν_1: $^4A_{2g} \rightarrow {}^4T_{2g}$, ν_2: $^4A_{2g} \rightarrow {}^4T_{2g}(F)$, and ν_3: $^4A_{2g} \rightarrow {}^4T_{1g}(P)$.[27] The diffuse reflectance spectrum of the Cr(III) chelate shows three absorption bands at 19,050 (ν_1), 28,410 (ν_2), and 39,060 cm^{-1} (ν_3), where ν_1 corresponds to 10 Dq. The electronic spectrum of the chelate reported here is in reasonable agreement with those in the literature.[28] The magnetic moment at room temperature is 3.95 BM which corresponds to the expected value for Cr(III) compounds.[28] From the diffuse reflectance spectra, it is observed that the Fe(III)-chelate exhibits a band at 20,830 cm^{-1}, which may be assigned to the $^6A_{1g} \rightarrow {}^5T_{2g}(G)$ transition in octahedral geometry of the complex.[19] The $^6A_{1g} \rightarrow {}^5T_{1g}$ transition appears to be split into two bands at 11,110 and 8960 cm^{-1}. The observed magnetic moment of the Fe(III) complex is 5.37 BM. Thus, the complex formed has octahedral geometry involving d^2sp^3 hybridization for the Fe(III) ion.[19]

The reflectance spectrum of the Ni(II) chelate show two bands at 16,030 and 25,000 cm^{-1} which are assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively, in a square-planar geometry.[29] The diamagnetic nature of the complex lends support to the above geometry. The solid state electronic spectrum of the Co(II) chelate with H_2L shows three d–d transitions of the type expected for distorted tetrahedral Co(II) compounds,[27,30] centered at 23,810 (ν_3), 9520 (ν_2), and 5710 cm^{-1} (ν_1). The band in the visible region has been assigned to $^4A_2 \rightarrow {}^4T_1(P)$ transitions and the other two bands in the near-IR region to $^4A_2 \rightarrow {}^4T_1(F)$ $^4A_2 \rightarrow {}^4T_2$ transitions, respectively. The magnetic moment for the complex, 3.6 BM, is in the range expected for tetrahedral Co(II) compounds.[30] The Cu(II) chelate exhibits a broad band at 10,960 and 15,380 cm^{-1}. These peaks are generally consistent with a five-coordinate geometry for Cu(II) complexes.[31] The magnetic susceptibility measurements of 2.1 BM is indicative of the appearance of the copper complex in trigonal bipyramidal geometry.[31]

The Zn(II) chelate is diamagnetic and is likely to be tetrahedral. In analogy with described Zn(II) and Cd(II) complexes containing N–O donor Schiff bases[32,33] and according to the empirical formulae of these complexes, we propose an octahedral geometry for the Cd(II) chelate with the six axial positions occupied by two ligand molecules.

Mass Spectra

The electron impact mass spectra of H_2L and its chelates were recorded and investigated at 70 eV of electron energy. The important peaks and their relative intensities for the molecular ion fragments down to $m/z = 63$ (only predominant and important peaks are recorded for simplicity) are listed in Table 3. The mass spectra of the studied chelates are characterized by moderate to high relative intensity molecular ion peaks, except the Fe(III) chelate, which has a low abundance at 70 eV.

The formula weight of these chelates appear in their mass spectra at $m/z = 692.5$ [M^+ (9%)], 481 [MH_2^+ (1%)], 449 [$MH_{2.5}^+$ (33%)], 457 [$MH_{1.5}^+$ (15%)], 493 [M^+ (17%)], and 475 [M^- (6%)] for the Cr(III), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) chelates, respectively, whereas the peak of the Cd(II)-complex molecular ion at $m/z = 708$ is significantly lower than the calculated value, $m/z = 744$, which is attributed to the loss of two hydrated water molecules as it is subjected to ionization.

Mass spectra of the Cr(III), Fe(III), Co(II), and Cd(II), chelates show a fragment with $m/z = 299$ (1–42%) that corresponds to the $C_{15}H_{13}N_3O_4$ ion which is the molecular ion of the ligand, indicating that the H_2L molecule binds to the metal ions in the same manner. The mass spectra of the Cr(III),

Table 3. Mass spectral data of H_2L chelates.

Chelates	m/e Found (calcd)	RI[a] (%)	Fragment
$[Cr(HL)_2]Cl \cdot H_2O$	692.5 (692.5)	9	$C_{30}H_{26}ClCrN_6O_9$
	593 (592)	25	$C_{28}H_{20}CrN_6O_7$
	474 (474)	27	$C_{22}H_{17}CrN_4O_6$
	368 (368)	100	$C_{16}H_{13}CrN_3O_5$
	300 (299)	17	$C_{15}H_{13}N_3O_4$
	235 (236)	82	$C_8H_5CrN_2O_4$
	207 (207)	70	$C_8H_5CrO_4$
	70 (70)	62	$C_3H_2O_2$
$[Fe(HL)Cl_2(H_2O)] \cdot 2H_2O$	481 (479)	1	$C_{15}H_{18}Cl_2FeN_3O_7$
	426 (425)	1	$C_{15}H_{12}Cl_2FeN_3O_4$
	313 (311)	100	$C_{13}H_9FeN_3O_3$
	300 (299)	1	$C_{15}H_{13}N_3O_4$
	256 (254)	10	$C_{14}H_{12}N_3O_2$
	149 (147)	9	$C_8H_7N_2O$
	105 (104)	9	$C_6H_4N_2$
	70 (70)	8	$C_3H_2O_2$
$[Co(HL)(H_2O)]Cl \cdot 2H_2O$	449 (446.5)	33	$C_{15}H_{18}ClCoN_3O_7$
	367 (366)	31	$C_{15}H_{13}CoN_3O_{4.5}$
	299 (299)	42	$C_{13}H_8CoN_2O_3$
	299 (299)	42	$C_{15}H_{13}N_3O_4$
	236 (236)	75	$C_8H_5CoN_2O_3$
	163 (161)	16	$C_8H_5N_2O_2$
	135 (134)	77	$C_7H_4NO_2$
	121 (120)	100	$C_7H_4O_2$
	69 (70)	16	$C_3H_2O_2$
$[Ni(HL)(H_2O)]Cl \cdot 2.5H_2O$	457 (455.5)	15	$C_{15}H_{19}ClNiN_3O_{7.5}$
	376 (375)	12	$C_{15}H_{14}NiN_3O_5$
	313 (313)	30	$C_{13}H_8NiN_3O_3$
	239 (238)	48	$C_{13}H_8N_3O_2$
	194 (194)	100	$C_{12}H_8N_3$
	135 (134)	11	$C_7H_4NO_2$
	109 (108)	22	$C_6H_4O_2$
	71 (70)	19	$C_3H_2O_2$
$[Cu(HL)(H_2O)_2](AcO) \cdot 2H_2O$	493 (492.5)	17	$C_{17}H_{23}CuN_3O_{10}$
	459 (457)	6	$C_{17}H_{19}CuN_3O_8$
	406 (405)	47	$C_{17}H_{15}CuN_3O_5$
	359 (362)	29	$C_{15}H_{12}CuN_3O_4$

(*continued*)

Table 3. Continued.

Chelates	*m*/*e* Found (calcd)	RI[a] (%)	Fragment
	207 (209)	40	$C_8H_3CuNO_2$
	117 (117.5)	100	C_7H_3NO
	72 (70)	12	$C_3H_2O_2$
	68 (68)	19	C_3H_2NO
$[Zn(HL)(H_2O)](AcO) \cdot 2H_2O$	475 (476)	6	$C_{17}H_{21}N_3O_9Zn$
	362 (363)	8	$C_{15}H_{12}N_3O_4Zn$
	305 (305)	10	$C_{13}H_8N_2O_3Zn$
	207 (208)	19	$C_{13}H_8N_2O$
	154 (154)	28	$C_{10}H_7N_2$
	84 (84)	100	$C_3H_4N_2O$
	72 (70)	5	$C_3H_2O_2$
	63 (63)	24	C_5H_3
$[Cd(HL)_2] \cdot 2H_2O$	711 (744)	6	$C_{30}H_{28}CdN_6O_{10}$
	663 (664)	7	$C_{28}H_{20}CdN_6O_7$
	620 (620)	11	$C_{26}H_{17}CdN_6O_6$
	567 (568)	24	$C_{24}H_{17}CdN_4O_6$
	441 (440)	15	$C_{24}H_{17}N_4O_5$
	476 (474)	22	$C_{19}H_{13}N_3O_4$
	384 (384)	40	$C_{13}H_9N_2O_4$
	298 (299)	4	$C_{15}H_{13}N_3O_4$
	258 (256)	100	$C_{11}H_{10}N_3O_3$
	83 (82)	70	C_3NO_2

[a] Relative intensity.

Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) chelates show a fragment at $m/z = 70$ that may corresponds to the $[HO{-}C{\equiv}C{-}CHO]^+$ ion, with relative intensity values in the range 5–62%.

TG Analysis

The importance of this study of the H_2L ligand and its complexes stems from their possible biological activities. Therefore, they were subjected to thermal analyses and other physico-chemical methods. Thermal data of the complexes are given in Table 4, and the thermodynamic activation data associated with the loss of water of crystallization (dehydration process) and ligand molecules are listed in Table 5.

Table 4. Thermoanalytical results (TGA) of H_2L metal chelates.

			Found (Calcd %)			
Complexes	TG range (°C)	DTG_{max} (°C)	Mass loss	Total mass loss	Assignment	Metallic residue
$[Cr(HL)_2]Cl \cdot H_2O$	25–160	56	7.48 (7.73)		Loss of H_2O and HCl	CrO_2
	160–750	490	81.09 (81.44)	88.57 (89.17)	Loss of 2HL	
$[Fe(HL)Cl_2(H_2O)] \cdot 2H_2O$	25–150	82	7.79 (7.52)		Loss of $2H_2O$	(1/2) Fe_2O_3
	150–300	290	18.75 (18.58)		Loss of H_2O and 2HCl	
	300–600	410	57.37 (57.20)	83.91 (83.30)	Loss of HL	
$[Co(HL)(H_2O)]Cl \cdot 2H_2O$	30–150	65	8.16 (8.06)		Loss of $2H_2O$	CoO
	150–300	280	11.58 (11.98)		Loss of H_2O and HCl	
	300–700	400	63.39 (63.16)	83.16 (83.20)	Loss of 2HL	
$[Ni(HL)(H_2O)]Cl \cdot 2.5H_2O$	25–180	60	9.82 (9.88)		Loss of $2.5H_2O$	NiO
	180–350	300	11.50 (11.75)		Loss of H_2O and HCl	
	350–550	420	61.91 (62.30)	83.62 (83.54)	Loss of HL	
$[Cu(HL)(H_2O)_2](AcO) \cdot 2H_2O$	25–170	86	7.26 (7.36)		Loss of $2H_2O$	CuO
	170–320	279	19.70 (19.29)		Loss of $2H_2O$ and AcO	
	320–750	553	57.55 (57.26)	84.51 (83.91)	Loss of HL	
$[Zn(HL)(H_2O)](AcO) \cdot 2H_2O$	30–150	75	7.30 (7.56)		Loss of $2H_2O$	ZnO
	150–320	290	16.70 (16.18)		Loss of H_2O and AcO	
	320–850	630	59.05 (59.24)	83.05 (82.98)	Loss of HL	
$[Cd(HL)_2] \cdot 2H_2O$	30–150	50	4.83 (4.84)		Loss of $2H_2O$	CdO
	150–1000	350, 650	77.64 (77.96)	82.47 (82.80)	Loss of 2HL	

Table 5. Thermodynamic data of the thermal decomposition of H_2L metal chelates.

Complexes	Decomposition range (°C)	E^* (kJ mol^{-1})	A^a (S^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
$[Cr(HL)_2]Cl \cdot H_2O$	25–160	66.80	1.24×10^4	−20.54	56.28	48.75
	160–750	92.87	2.50×10^6	−22.81	83.30	96.42
$[Fe(HL)(Cl)_2(H_2O)] \cdot 2H_2O$	25–150	64.56	6.73×10^7	−18.29	45.64	46.37
	150–300	85.42	1.63×10^6	−20.16	75.23	65.75
	300–600	189.4	5.21×10^8	−34.86	185.3	180.7
$[Co(HL)(H_2O)]Cl \cdot 2H_2O$	30–150	34.54	7.60×10^5	−24.36	43.73	47.46
	150–300	64.98	3.06×10^7	−22.74	50.35	79.11
	300–700	153.0	3.85×10^8	−32.64	179.6	184.3
$[Ni(HL)(H_2O)]Cl \cdot 2.5H_2O$	25–180	49.84	2.97×10^6	−24.63	48.98	62.59
	180–350	227.3	2.68×10^{10}	−73.57	236.0	267.0
	350–550	286.0	6.97×10^5	−80.30	266.0	287.3
$[Cu(HL)(H_2O)_2](AcO) \cdot 2H_2O$	25–170	50.40	3.62×10^8	−14.80	68.35	49.40
	170–320	82.75	1.91×10^6	−11.48	87.93	83.50
	320–750	167.0	4.43×10^{11}	−16.75	162.7	185.3
$[Zn(HL)(H_2O)](AcO) \cdot 2H_2O$	30–150	55.43	3.52×10^6	−12.89	66.32	65.66
	150–320	85.24	3.08×10^6	−26.49	50.75	79.36
	320–850	177.3	5.65×10^9	−18.95	112.3	144.0
$[Cd(HL)_2] \cdot 2H_2O$	30–150	65.10	3.03×10^7	−14.56	49.37	52.83
	150–450	96.20	3.49×10^8	−12.67	80.60	86.12
	450–1000	210.0	2.04×10^{10}	−25.95	178.1	184.3

[a] Arrhenius constant.

The thermal analysis of the chelates under study results in the following weight losses:

(1) 4.83–9.82%: loss of water molecules of hydration over the range 25–180 °C interval (calculated 4.84–9.88%), except the Cr(III) chelate, where the loss of water is accompanied by a loss of HCl.
(2) 11.5–19.29%: elimination of coordinated water and anions (Cl or AcO) molecules over the 150–350 °C interval (calculated 11.75–19.29%).
(3) 57.37–81.09%: elimination of the ligand molecules over the temperature range 150–1000 °C (calculated 57.20–81.44%).
(4) 11.43–17.53%: residues of metal oxides remain over the 550–1000 °C interval (calculated 10.83–17.20%).

Water loss at low temperature (25–150 °C) indicated that these H_2O molecules are in the lattice network, while water loss at higher temperatures up to 350 °C indicated that H_2O is coordinated to the metal ions.[34] The thermal stability of the chelates, after removal of hydrated and coordinated water and anions, follows the order Cd(II) > Cr(II) > Fe(III)=Co(II) > Cu(II)= Zn(II) > Ni(II).

In general, the stages of thermal decomposition of the complexes may be written as shown below.

For Co(II), Ni(II), Cu(II), and Zn(II) chelates:

$$[\mathrm{M(HL)(H_2O)}_z]\mathrm{X}\cdot n\mathrm{H_2O} \xrightarrow[\text{dehydration}]{25-150\,^\circ\mathrm{C}} [\mathrm{M(HL)(H_2O)}_z]\mathrm{X} + n\mathrm{H_2O} \tag{5}$$

$$[\mathrm{M(HL)(H_2O)}_z]\mathrm{X} \xrightarrow{150-350\,^\circ\mathrm{C}} [\mathrm{M(HL)}] + z\mathrm{H_2O} + \mathrm{HX} \tag{6}$$

$$[\mathrm{M(HL)}] \xrightarrow[\text{final decomposition}]{150-350\,^\circ\mathrm{C}} \text{Metal oxides} + \mathrm{HL} \tag{7}$$

where X = Cl or AcO, $z = 1$ or 2, $n = 2$ or 2.5.

For Cr(III) and Cd(II) chelates:

$$[\mathrm{Cr(HL)_2}]\mathrm{Cl}\cdot\mathrm{H_2O} \xrightarrow[\text{dehydration}]{25-160\,^\circ\mathrm{C}} [\mathrm{Cr(HL)_2}] + \mathrm{HCl} + \mathrm{H_2O} \tag{8}$$

$$[\mathrm{Cd[(HL)_2]}\cdot 2\mathrm{H_2O} \xrightarrow[\text{dehydration}]{30-150\,^\circ\mathrm{C}} [\mathrm{Cd(HL)_2}] + 2\mathrm{H_2O} \tag{9}$$

$$[\mathrm{M(HL)_2}] \xrightarrow[\text{final decomposition}]{160-1000\,^\circ\mathrm{C}} \text{Metal oxide} + 2\mathrm{HL} \tag{10}$$

For Fe(III) chelate:

$$[\mathrm{Fe(HL)(Cl)_2(H_2O)}]\cdot 2\mathrm{H_2O} \xrightarrow[\text{dehydration}]{25-150\,^\circ\mathrm{C}} [\mathrm{Fe(HL)(Cl)_2(H_2O)}] + 2\mathrm{H_2O} \quad (11)$$

$$[\mathrm{Fe(HL)(Cl)_2(H_2O)}] \xrightarrow{150-300\,^\circ\mathrm{C}} [\mathrm{Fe(HL)}] + 2\mathrm{HCl} + \mathrm{H_2O} \quad (12)$$

$$[\mathrm{Fe(HL)}] \xrightarrow[\text{final decomposition}]{300-600\,^\circ\mathrm{C}} \frac{1}{2}\mathrm{Fe_2O_3} + \mathrm{HL} \quad (13)$$

Kinetic Analysis

The first stage of dehydration of the complexes was studied in more detail. The kinetic parameters such as activation energy (ΔE^*), enthalpy (ΔH^*), entropy (ΔS^*) and free energy change of decomposition (ΔG^*) were evaluated graphically by employing the Coats–Redfern relation:[35]

$$\log\left[\frac{\log\{W_\mathrm{f}/(W_\mathrm{f}-W)\}}{T^2}\right] = \log\left[\frac{AR}{\theta E^*}\left(1-\frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \quad (14)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to the temperature T; R is the gas constant, E is the activation energy in kJ mol^{-1}, θ is the heating rate and $(1-(2RT/E^*)) \cong 1$. A plot of the left-hand side of Eq. (14) against $1/T$ gives a slope from which E^* was calculated and A (Arrhenius constant) was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated using the following equations:

$$\Delta S^* = 2.303\left[\log\left(\frac{Ah}{kT}\right)\right]R \quad (15)$$

$$\Delta H^* = E^* - RT \quad (16)$$

$$\Delta G^* = H^* - TS^* \quad (17)$$

where k and h are the Boltzmann and Plank constants, respectively. The calculated values of E^*, A, ΔS^*, ΔH^*, and ΔG^* for the decomposition steps are given in Table 5.

According to the kinetic data obtained from the DTG curves, all the complexes have a negative entropy, which indicates that the complexes are formed spontaneously. From Table 5 it is obvious that, the nickel complex shows a higher thermal stability than that of copper. This can be interpreted in terms of repulsion among electron pairs in the valence shell of the central ion. The higher electronegativity of copper compared with that of nickel leads to a higher repulsion between bonding pairs in the valence shell of copper ion giving lower stability.[36] Based on the activation energy values, the Zn(II) complex shows a lower thermal stability than the Cd(II) complex. This can be explained in terms of repulsion among electron pairs in the valence shell of the central ion. Both zinc and cadmium ions in the investigated complexes have multiple bonds (four bonds) in their valence shells. But due to the smaller ionic size of zinc compared with that of cadmium, this leads to a higher repulsion between the bonding pairs in the valence shell of zinc which in turn alters

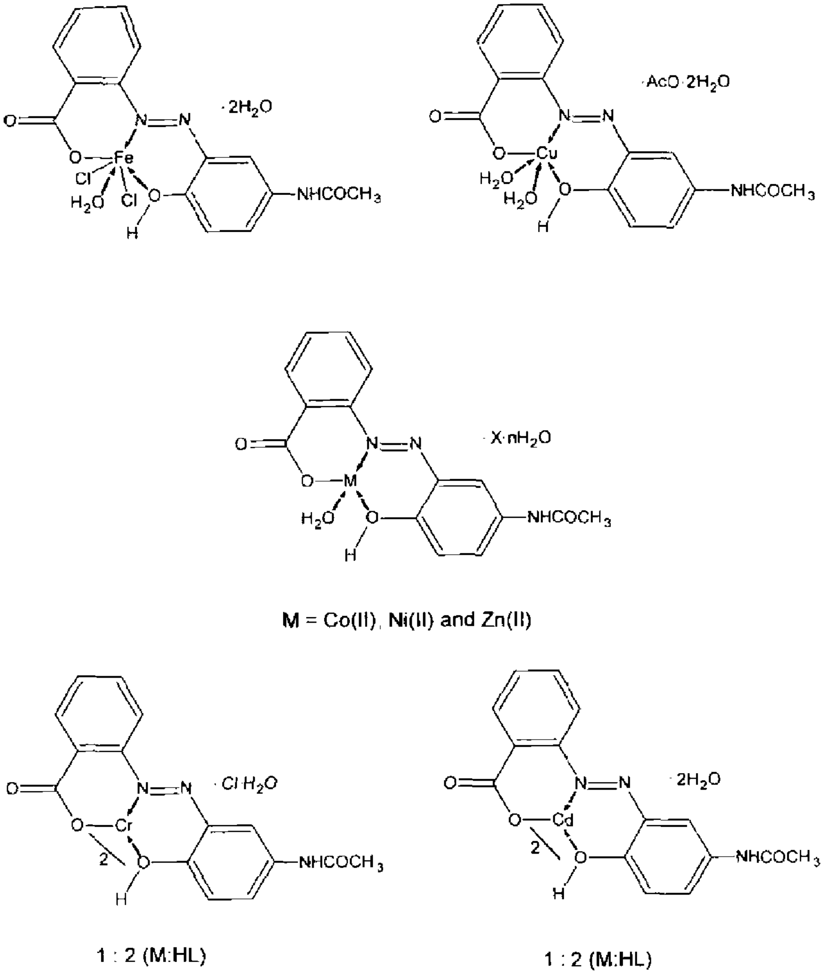

Figure 2. Suggested structural formulae of H_2L complexes.

the bond angles from those of ideal tetrahedral, giving a lower stability.[36,37] The lower thermal stability of the cobalt complex may be attributed to the higher repulsion between the multiple-bonding electron pairs (six bonds) in the valence shell of cobalt, as well as to the higher repulsion obtained by the non-bonded pairs of electrons on the axial donating oxygen of the water molecule and the bonded electrons.[36]

Structural Interpretation

The design and synthesis of a new tridentate azo ligand derived from 4-acetamidophenol and anthranilic acid for use in tetrahedral, square-planar, trigonal-bipyramidal or octahedral molecular templates have been successfully demonstrated. The synthesis of the ligand and its complexes proved to be as straightforward as expected, giving high yields of either the free ligand and its complexes in simple, one-pot reactions. As anticipated, the ligand coordinates equatorially to four- or six-coordinate transition metal ions to give square-planar [Ni(II)], tetrahedral [Co(II) and Zn(II)], octahedral [Cr(III), Fe(III), and Cd(II)] and trigonal-bipyramidal [Cu(II)] environments, around the metal ion anchor. The proposed general structures of the complexes are shown in Fig. 2.

There are additional factors which might affect the structure of these chelates such as the possibility of various isomeric structures and intermolecular hydrogen bonds, however, due to instrumental limitations, we are not able to explore this further.

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