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Hydroxycoumarine Azodye, Thermal Stability, Harmonic Vibrational Spectra, Conductance, and pH Measurements

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Two metal complexes resulting from reaction of hydroxycoumarine azodye with Zn(II) and Cd(II) have been synthesized and characterized using elemental analyses, thermal analyses (TGA and DTG), IR, and conductance measurements. The results show that the ligand coordinates to Zn(II) and Cd(II) as a neutral bidentate through the carbonyl oxygen and the azo nitrogen. Semiempirical calculations using PM3 and ZINDO/1 have been employed to study the harmonic vibrational spectra of the ligand and its metal complexes with the purpose to assist in the experimental assignments of the bands. The thermodynamic parameters E, ΔH, ΔG, and ΔS have been calculated from the thermal analysis curves (TGA and DTG) using the Coats−Redfern, Horowitz−Metzger, and Freeman−Carroll methods. The dissociation constant of the ligand has been determined pH-metrically in 0.1 $\text{mol}\cdot\text{dm}^{-3}$ KCl at 298.15 K. Conductometric titrations showed that all the investigated metal ions have 1:1 and 1:2 (M:L) stoichiometric ratios.

Introduction

Azodyes find wide industrial and analytical applications as reagents in microdetermination of metal ions. Recently, chemically synthesized azo chromophores in compact, nanopore membrane discs, as chemical strips for visual detection of ultratrace ions, have been reported.[1,2] Coumarins constitute an important class of natural products, many of which exhibit useful drug activity. Moreover, coumarins are a group of compounds that play important roles as food constituents, antioxidants, stabilizers, and immunodualatory substances, such as fluorescent markers for use in analyses, in stains, and in clinical use.[3−6] Coumarine derivatives reduced the development of periodontitis.[7] The applicability of chemical compounds is associated with their chemical stability.

In this work, the metal complexes of 4-hydroxy-3-(*p*-methylphenylazo)-benzopyran-2-one with Zn(II) and Cd(II) have been synthesized and characterized to clarify their chemical stability, and the thermodynamic parameters and the formation constants have been calculated from thermal analyses and potentiometery, respectively. Semiempirical calculations using PM3 have been employed to study the harmonic vibrational spectra of the ligand and its metal complexes with the purpose to assist in the experimental assignment of the bands. Also, a conductometric titration has been carried out to determine the stoichiometric ratios of the formed complexes in solution.

Experimental Section

Reagents. All chemicals used were of analytical grade or purified with the recommended methods.[8]

Technique. Carbon and hydrogen contents were determined using the microanalytical unit of Mansoura University. The analyses for metals were carried out by standard methods.[9] Molar conductance measurements of the complexes (10^{-3} M) in DMSO and/or water were carried out with a conductivity bridge YSI model 32. Infrared spectra were measured using KBr discs on a Mattson 5000 FTIR spectrometer. Calibration with frequency reading was made with polystyrene film at Mansoura University.

The pH-metric titration was carried out at 298.15 K in 50 % (v/v) ethanol−water solvents using a pH-meter of type Mettler Toledo MP 220. Also, the conductometric titration was carried out at 298.15 K in 50 % (v/v) ethanol−water solvents using a conductivity bridge (Jenway). Both the pH-meter and conductivity bridge were connected with ultrathermostate of a type MLW prufgerate-werk to maintain the temperature at (298 ± 0.1) K.

Preparation of the Ligand. The ligand 4-hydroxy-3-(*p*-methyl-phenylazo)-benzopyran-2-one was prepared as reported earlier.[10]

Preparation of the Metal Complexes. Metal complexes were isolated by adding equimolar amounts (0.001 mol) of the metal acetate in 10 cm^3 ethanol to the ligand (0.001 mol (0.398 g)). The reaction mixture was refluxed on a hot plate for 2 h, and a yellow precipitate was isolated directly in the case of the Zn complex. The Cd complex was isolated after concentrating the reaction mixture and addition of a few drops of diethylether. The complexes were filtered off, washed successively with ethanol, and kept in a desiccator over calcium chloride.

Computational Details. Molecular geometries of all forms of complexes were optimized using molecular mechanics and the semiempirical PM3 method using the hyperchem series of programs.[11] The molecular mechanics technique was used to investigate rapidly the geometries of the suggested structures. The low-lying conformers obtained from this search were then optimized by PM3 and ZINDO/1 methods (Polak-Ribiere), and the criterion of root-mean-square (rms) gradient was selected

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Table 1. Analytical and Physical Data for the Complexes Derived From Hydroxycoumarine Azodye

			found (calcd) (%)		
compound	color	M.P. (°C)	C	H	M
$[\mathrm{Zn(HL)(OAc)_2}]$	yellow	>300	51.5 (51.8)	4.1 (3.9)	14.4 (14.1)
$[\mathrm{Cd(HL)(OAc)_2}]$	yellow	>300	47.3 (47.0)	3.9 (3.5)	22.3 (22.0)

Table 2. Experimental and Theoretically Calculated IR Spectra of the Ligand and Its Metal Complexes Geometry Optimized by ZINDO/1 and PM3 Semi-Empirical Calculations[a]

HL		Zn		Cd		
(exptl)	(theor.)	(exptl)	(theor.)	(exptl)	(theor.)	assignment
3439(br)	3828	3437(br)	3828	3333(br)	3840	ν(OH)
1702(s)	1729	1624(sh)	1633	1659(sh)	1632	ν(C=O)
1609(s)	1633	1610(s)	1608	1605(sh)	1617	ν(N=N)
1275(m)	1262	1272(s)	1261	1273(m)	1241	ν(C−N)
1422(m)	1434	1453(s)	1445	1424(sh)	1424	ν(C−O)
1311(s)	1320	1315(sh)	1315	1316(sh)	1313	δ(OH)
-	-	1529(s)	1529	1531(sh)	1510	ν_{as}(OAc)
-	-	1343(s)	1344	1345(m)	1365	ν_{s}(OAc)
-	-	463(w)	464	465(w)	473	ν(M−N)
-	-	560(w)	570	567(w)	568	ν(M−O)

[a] ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation; w, wagging; ρ, rocking; S, strong; m, medium; sh, shoulder; br, broad; w, weak.

for 0.01 kcal. Where applicable, these methods are commonly used for the calculations of energy states of transition metal complexes.

Results and Discussion

The Zn complex is stable in air, while the Cd complex is hygroscopic. The two complexes are soluble in most common organic solvents. The low molar conductivity values [(5.0 to 9.0) $\Omega^{-1}\cdot\mathrm{cm}^2\cdot\mathrm{mol}^{-1}$] in DMF of the Zn(II) and Cd(II) complexes indicate the nonconducting nature of these complexes.[12]

Elemental analyses and other physical data are presented in Table 1. Only one form of metal complex with the general formula $[\mathrm{M(HL)(OAc)_2}]$ (where M = Zn(II) or Cd(II)) was obtained.

IR Spectra. The most important experimental and theoretically calculated IR spectral bands of the ligand and its metal complexes are collected in Table 2. The IR spectrum of the ligand L, where L = 4-hydroxy-3-(*p*-methyl-phenylazo)-benzopyrane-2-one, exhibits bands at (1700, 1609, 1562, and 1275) cm^{-1} assigned, respectively, to ν(C=O), ν(N=N), ν(C=C), and ν(C−N).[13] The spectrum also shows two bands at (3439 and 1311) cm^{-1} assigned to νOH and δOH, respectively.[13] Furthermore, the bands centered at (2715 and 2575) cm^{-1} are due to O−H···N stretching vibrations and indicate the presence of intramolecular hydrogen bonding.[14] The ligand has neutral bidentate coordinating to the metal ions through the carbonyl oxygen and azo nitrogen (Figures 1 and 2).

This behavior is supported by the following evidence: (i) A shift to lower frequency of the band assigned to the carbonyl group. (ii) The ν(N=N) band is shifted to a lower wavenumber. (iii) The presence of two new bands in the spectra of the two complexes at (≈1530 and ≈1345) cm^{-1} assigned to ν_{as} and ν_{s} stretching vibrations of the acetate group. The correlation between the positions of the antisymmetric and symmetric stretching vibrations of the acetate group and the type of coordination of this group was studied earlier.[15] It was concluded from these studies that the frequency difference between the two carboxyl stretchings in the case of ionic acetate groups is usually in the interval ~167 cm^{-1}; longer values were found for monodentate and lower values for bidentate groups. Correspondingly, the difference of 186 cm^{-1} in the case of Cd(II) and Zn(II) complexes may be evidence for the monodentate nature of the acetate group. (iv) The appearance of new bands in the spectra of the two complexes in the regions (567 to 560) cm^{-1} and (463 to 465) cm^{-1} assigned, respectively, to ν(M−O) and ν(M−N).[16]

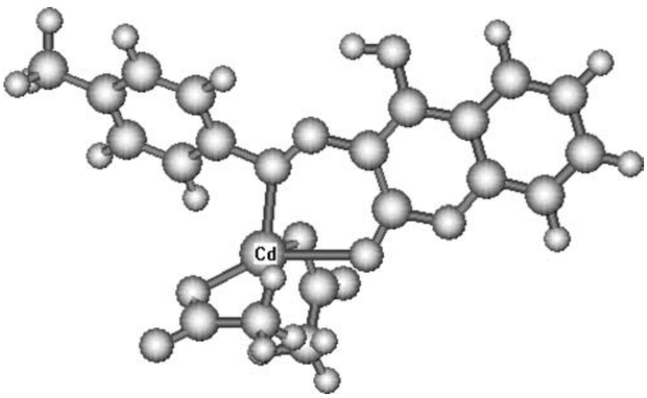

Figure 1. Geometry optimized structure of Cd complex by the ZINDO/1 method.

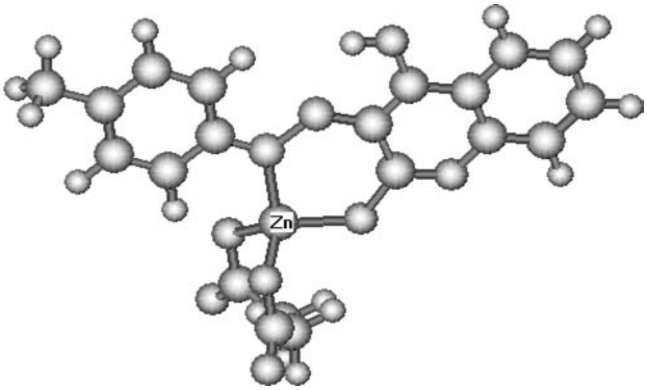

Figure 2. Geometry optimized structure of Zn complex by the ZINDO/1 method.

The bands at (3437 and 1315) cm^{-1} due to ν(OH) and δ(OH) remain more or less unaltered, indicating that this group does not take part in coordination.

The experimental and theoretically calculated frequencies by the semiempirical PM3 and ZINDO/1 methods are listed in Table 2. The cause of the difference between the calculated and observed frequencies may result from the hydrogen bond which has not been taken into consideration in the optimized molecules in the theoretical calculations. Also, the experimental data were obtained from the solid state, whereas the calculated harmonic frequencies are for the gas phase.

Thermogravimetric Analyses

The thermal analyses (thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG)) for prepared complexes were done to indicate the mode of fragmentation of the ligand and to shed more light about the thermal stability. The thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) for $[\mathrm{ZnHL\ (OAc)_2}]$ and $[\mathrm{CdHL(OAc)_2}]$ are represented in Figures 3a and 3b. The results of the thermal analyses are listed in Table 3.

Kinetic Study. The activation energy (E^*) of the decomposition processes of $[\mathrm{ZnHL(OAc)_2}]$ and $[\mathrm{CdHL(OAc)_2}]$ was evaluated graphically by employing three methods as follows.

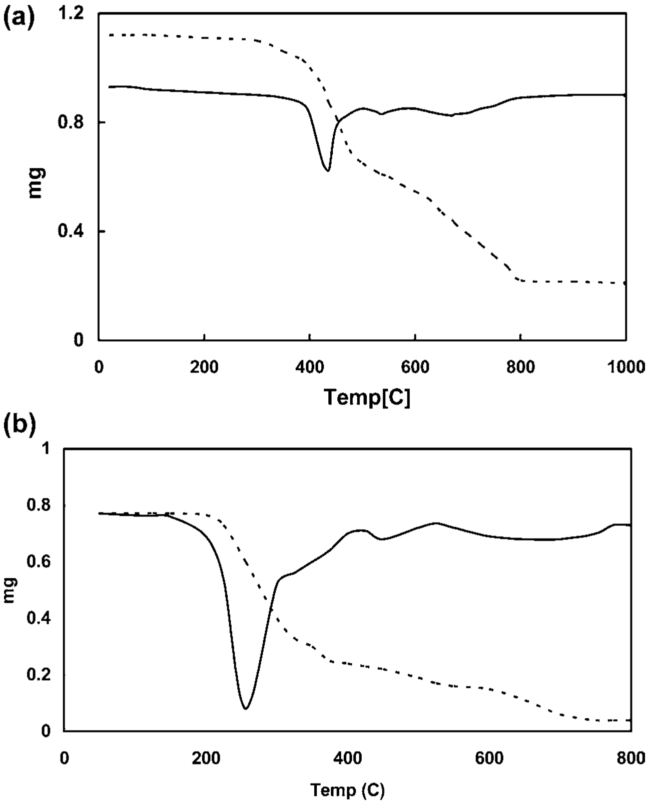

Figure 3. (a) TGA (- - -) and DTG (—) curves of [ZnHL(OAc)$_2$]. (b) TGA (- - -) and DTG (—) curves of [CdHL(Ac)$_2$].

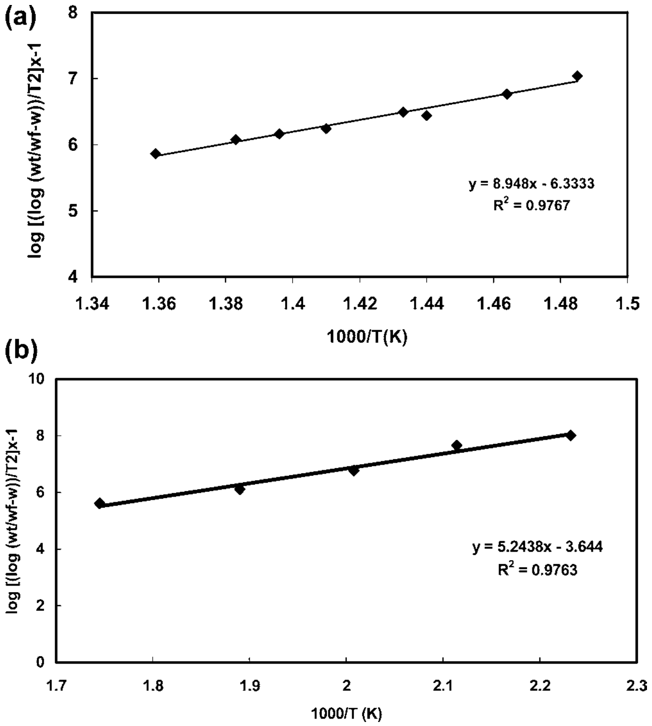

Figure 4. (a) Coats−Redfern plots for the first stage of the thermal decomposition of the [ZnHL(OAc)$_2$] complex. (b) Coats−Redfern plots for the first stage of the thermal decomposition of the [CdHL(OAc)$_2$] complex.

Coats−Redfern Method (CR).[17] They derived the following relationship

$$\log[\log\{W_f/(W_f - W)\}/T^2] = \log[AR/\theta E^*\{1 - (2RT/E^*)\}] - (E^*/2.303RT)$$

where W_f is the mass loss at the completion of the reaction; W is the mass loss up to temperature T; A is the Arrhenius constant (s^{-1}); R is the gas constant (J·K^{-1}·mol^{-1}); θ is the rate of heating (°C/s); and E^* is the activation energy of the decomposition process (kJ·mol^{-1}). From the graphical application of this relationship for the three stages of decomposition, the activation energy of decomposition and the Arrhenius constant were calculated. The graphs of this relationship for the first stage of decomposition for [ZnHL(OAc)$_2$] and [CdHL(OAc)$_2$] are represented in Figures 4a and 4b, respectively. The linearity of the graphical relation with a higher coefficient of determination ($R^2 \sim 0.974$ to 0.976) indicates that this reaction is first order.

Horowitz−Metzger Method (HM).[18] By applying the following relation

$$\log[\log\{W_f/(W_f - W)\}] = (E^*\theta^*/2.303RT_s^2) - \log 2.303$$

where $\theta^* = T - T_s$; T_s is the DTG peak temperature; and T is the temperature at interval of decomposition. From the graphical application of this relationship, the activation energy of the decomposition processes of the [ZnHL(OAc)$_2$] and [CdHL(OAc)$_2$] complexes were calculated. The graph of this relationship for the decomposition of [ZnHL(OAc)$_2$] as an example is represented in Figure 5. The pre-exponential factor (Arrhenius constant) (A) was calculated from the following relation

$$(E^*/RT_s^2) = (A|/[\Phi \exp^{(-E^*/RT_s)}]$$

The entropy change of decomposition ΔS (in J·K^{-1}·mol^{-1}) can be calculated by applying the following equation[19]

$$\Delta S = R \ln(Ah/K_bT_s)$$

where (K_b) is the Boltzmann constant and h is the Plank constant. The linearity of the graphical relation with a higher coefficient of determination ($R^2 \sim 0.9846$) indicates that this reaction is first order. The enthalpy change ΔH and the Gibbs energy change ΔG of the decomposition process were also calculated.

Freeman−Carroll Method (FC).[20] From the following relation

$$[\{\Delta \log(d\alpha/dt)\}/\{\Delta \log(1 - \alpha)\}] = f\{\Delta T^{-1}/\Delta \log(1 - \alpha)\}$$

where α is the fraction decomposed at temperature T. The graphical application of this relationship enables calculation of

Table 3. Thermoanalytical Results TGA and DTG of Zn(II) and Cd(II) Complexes

complex	TG range °C	DTG range °C	number of stages	found (calcd) mass loss %	assignment (evolved moiety)
[ZnHL(OAc)$_2$]	385 to 497	436	1	33.58 (34.96)	4-OH-coumarine moiety ($C_9H_6O_3$)
	500 to 568	536	1	18.2 (18.1)	3CO
	566 to 781	671	1	29.0 (29.3)	$phCH_3 + N_2 + CH_4$
	>781	-	residue	18.1 (17.5)	ZnO
[CdHL(OAc)$_2$]	169 to 318	256	1	55.63 (54.60)	4-OH-coumarine moiety + 2Ac
	319 to 408	348	1	17.33 (18.01)	$PhCH_3$
	410 to 532	462	1	5.40 (5.50)	N_2
	>532	-	residue	23.22 (25.13)	CdO

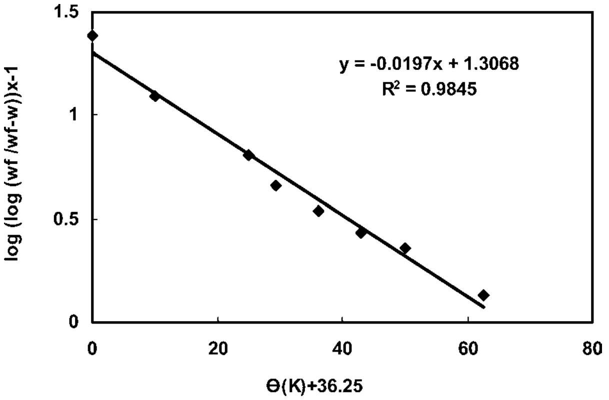

Figure 5. Horowitz−Metzger (HM) plots for the first stage of the thermal decomposition of the $[ZnHL(OAc)_2]$ complex.

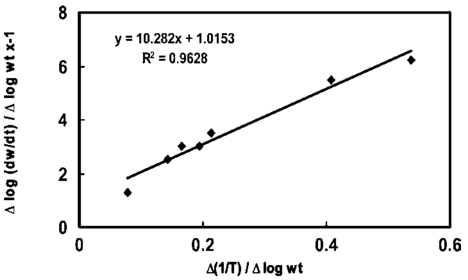

Figure 6. Freeman−Carroll plots for the first stage of the thermal decomposition of the $[ZnHL(OAc)_2]$ complex.

the activation energy and the order (n) of the decomposition reactions of the $[ZnHL(OAc)_2]$ and $[CdHL(OAc)_2]$ complexes. The graph of this relationship for the decomposition of $[ZnHL(OAc)_2]$ as an example is represented in Figure 6. The order of the reaction was found to equal 1.0153, i.e., ~1, which agrees well with that obtained from the previous two methods. The entropy change (ΔS), the enthalpy change (ΔH), and the free energy change of decomposition process were also calculated.

The calculated kinetic thermodynamic parameters by using the three graphical methods are listed in Table 4. According to these data, the complexes under study have a positive enthalpy, free energy change, and a negative entropy change, which shows the endothermic and nonspontaneous nature of the decomposition process. Negative values of the entropy change also indicate that the activated complex has a more ordered system than the reactants. The above finding clarifies the thermal stability of the investigated complexes.

From inspection of the results obtained by the three kinetic models, it was noticed that the results obtained from the CR model seem to be different from those of the other two models. This can lead to a conclusion that the data of the thermal analysis for the studied complexes achieve both the Horowitz−Metzger method (HM) and Freeman−Carroll method (FC) models more than that of the CR model, and therefore the average was given.

The obtained thermal analysis data show that the Cd complex is less stable than the Zn complex. This may be due to the larger size of Cd compared to Zn.

pH-Metric Study

The pH-metric titrations were carried out in 50 % (v/v) ethanol−water at 298.15 K as reported earlier[21] where the following mixtures were prepared and titrated potentiometrically against standard 0.004 M KOH in 50 % (v/v) ethanol−water at 298.15 K: (i) 1 mL (0.01 $mol \cdot dm^{-3}$) of HCl + 1 mL (0.1 $mol \cdot dm^{-3}$) of KCl; (ii) 1 mL (0.01 $mol \cdot dm^{-3}$) of HCl + 1 mL (0.1 $mol \cdot dm^{-3}$) of KCl + 1 mL (0.001 $mol \cdot dm^{-3}$) of ligand; (iii) 1 mL (0.01 $mol \cdot dm^{-3}$) of HCl + 1 mL (0.1 $mol \cdot dm^{-3}$) of KCl + 1 mL (0.001 $mol \cdot dm^{-3}$) of ligand + 0.2 mL (0.001 $mol \cdot dm^{-3}$) of metal ion.

For each mixture, the volume was made up to 10 mL with a suitable volume of water and ethanol to have 50 % (v/v) ethanol−water solvents. Figure 7 shows the plot of pH versus

Table 4. Kinetic Thermodynamic Parameters of the Thermal Decomposition of the Zn(II) and Cd(II) Complexes Calculated by Coats−Redfern (CR), Horowitz−Metzeger (HM), and Freeman−Carroll (FC) Methods

complex	method	decomposition range (°C)	E ($kJ \cdot mol^{-1}$)	A (s^{-1})	$-\Delta S$ ($J \cdot K^{-1} \cdot mol^{-1}$)	ΔH ($kJ \cdot mol^{-1}$)	ΔG ($kJ \cdot mol^{-1}$)
$[ZnHL(OAc)_2]$	CR	385 to 497	171 ± 2	$2.13 \cdot 10^{8}$	93 ± 1	165 ± 1	231 ± 1
	HM		189 ± 2	$2.10 \cdot 10^{-4}$	322 ± 1	186 ± 1	415 ± 1
	FC		196 ± 2	$2.19 \cdot 10^{-4}$	322 ± 1	191 ± 1	419 ± 1
	average		185 ± 2	-	246 ± 1	181 ± 1	355 ± 1
	CR	500 to 568	114 ± 1	$6.61 \cdot 10^{2}$	199 ± 1	107 ± 1	268 ± 1
	HM		133 ± 1	$1.19 \cdot 10^{-4}$	328 ± 1	126 ± 1	392 ± 1
	FC		142 ± 2	$1.23 \cdot 10^{-4}$	328 ± 1	135 ± 1	401 ± 1
	average		130 ± 1	-	285 ± 1	123 ± 1	354 ± 1
	CR	568 to 781	137 ± 1	$7.46 \cdot 10^{2}$	199 ± 1	129 ± 1	317 ± 1
	HM		155 ± 1	$1.34 \cdot 10^{-4}$	328 ± 1	147 ± 1	457 ± 1
	FC		167 ± 2	$0.94 \cdot 10^{-4}$	331 ± 1	159 ± 1	472 ± 1
	average		153 ± 1	-	286 ± 1	145 ± 1	415 ± 1
$[CdHL(OAc)_2]$	CR	169 to 318	100 ± 1	$7.9 \cdot 10^{5}$	137 ± 1	96 ± 1	169 ± 1
	HM		119 ± 1	$7.7 \cdot 10^{-4}$	309 ± 1	115 ± 1	278 ± 1
	FC		116 ± 1	$7.6 \cdot 10^{-4}$	308 ± 1	112 ± 1	275 ± 1
	average		112 ± 1	-	251 ± 1	108 ± 1	241 ± 1
	CR	319 to 408	108 ± 1	$1.2 \cdot 10^{5}$	155 ± 1	103 ± 1	199 ± 1
	HM		127 ± 1	$7.8 \cdot 10^{-4}$	309 ± 1	122 ± 1	314 ± 1
	FC		122 ± 2	$7.7 \cdot 10^{-4}$	308± 1	117 ± 1	308 ± 1
	average		119 ± 1	-	257 ± 1	114 ± 1	274 ± 1
	CR	410 to 532	122 ± 2	$2.3 \cdot 10^{4}$	169 ± 1	116 ± 1	240 ± 1
	HM		132 ± 1	$7.9 \cdot 10^{-4}$	310 ± 1	126 ± 1	354 ± 1
	FC		133 ± 1	$7.9 \cdot 10^{-4}$	311 ± 1	127 ± 1	356 ± 1
	average		129 ± 1	-	263 ± 1	123 ± 1	317 ± 1
	CR	532 to 750	133 ± 1	$2.9 \cdot 10^{3}$	188 ± 1	125 ± 1	296 ±
	HM						
	FC						
	average						

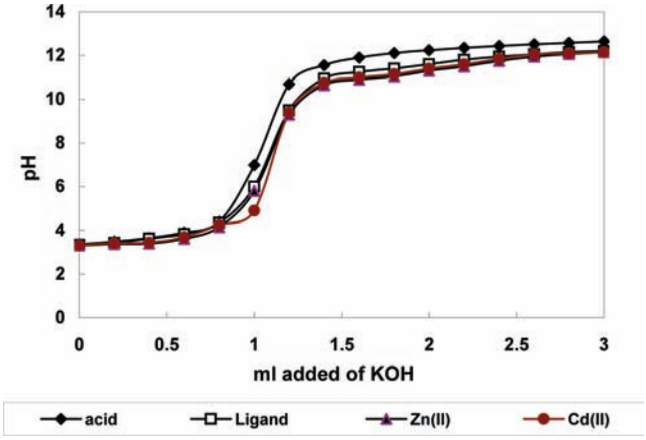

Figure 7. Potentiometric titration curves of the ligand and its complexes.

Table 5. Logarithm of the Ionization Constants and the Free Energy Change (ΔG, kJ·mol^{-1}) of the Ligand and Its Complexes with Zn(II) and Cd(II)[a]

compound	(−log *K*) or (+log *K*)	ΔG
ligand	$-\log K = 102(0.04)$	+56.98(0.2)
Zn complex	1:1 $+\log K_1 = 4.21(0.01)$	−23.52(0.1)
	1:2 $+\log K_2 = 3.71(0.01)$	−20.73(0.1)
Cd complex	1:1 $+\log K_1 = 3.95(0.02)$	−22.07(0.1)
	1:2 $+\log K_2 = 3.21(0.01)$	−17.93(0.1)

[a] Standard deviations are given in parentheses.

the milliliters added of KOH. The pK_1 of the ligand has been calculated by applying the interpolation at half $\acute{n}_a$ value method[22] and then refined with the ESAB2M computer program.[23] The ligand has one dissociable proton as revealed by the maximum $\acute{n}_a$ value ∼1.

The pK_1 of the ligand L is 10.2 which can be related to the hydroxyl group in position 4. This value is comparable with that obtained for similar compounds (10.30, 10.50, 10.54).[24,25] The stability constants of the stoichiometric 1:1 and 1:2 (M:L) complexes formed in solution between the ligand and the studied cations Zn(II) and Cd(II) have been determined as reported earlier.[27]

The free energy change of ionization and complexation was calculated using eq 1

$$\Delta G = -RT \ln K \qquad (1)$$

The ionization constant, stability constant, and free energy change values for the ligand and its complexes with Zn(II) and Cd(II) are listed in Table 5. The ionization process of the ligand is a nonspontaneous process as revealed from the positive value of the ionization free energy change, while the formation of the complexes is a spontaneous one as revealed from the negative value of the formation free energy change. The difficulty of liberation of the phenolate proton may result from its stabilization through hydrogen bonding. The titration curves also support this assumption, where the stronger the metal−ligand interaction the larger the difference between the titration curves. However, these curves all run together. Accordingly, there is no proton liberation on complexation between the ligand and the metal ions. Thus, complexation may occur through the oxo group, and the extra proton consumption at the basic pH range should indicate dissociation of the phenolic−OH without a pH effect. These observations support the suggested structure in the solid state.

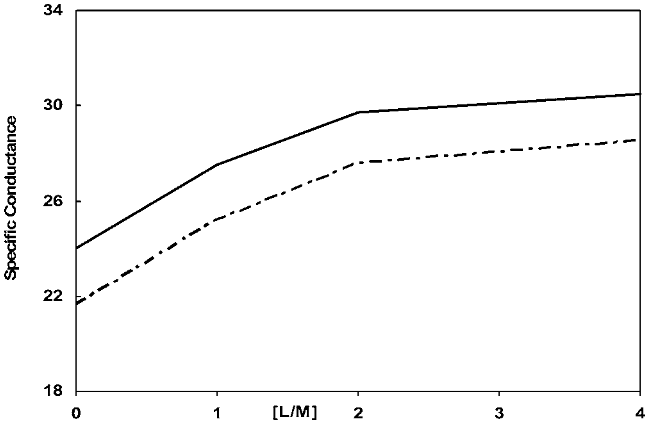

Figure 8. Conductometric titration curves for the ligand with the studied metal cations; solid line for Cd(II) and dotted line for Zn(II).

Conductometric Study

Many conductometric studies[28,29] have been used to decide the formation of different stoichiometric complexes in aqueous and nonaqueous solutions. The method of conductometric measurements was carried out at 298.15 K in water in 5 % (v/v) ethanol−water solvents as explained earlier[21] where 0.001 mol·dm^{-3} solution of the ligand was added to a 10 mL (0.0001 mol·dm^{-3}) solution of the metal cation. The specific conductance of the metal ion solution was measured (± 0.1 μS·cm^{-1}) before and after each addition of 0.2 mL of the ligand solution. The specific conductance (K_S, μS·cm^{-1}) was plotted versus the ratio of ligand to metal ion concentrations [L]/[M] (Figure 8).

As shown in Figure 8, straight lines with two breaks of the [L]/[M] ratio of 1 and 2 indicate the formation of 1:1 and 1:2 (M:L) stoichiometric complexes between the metal ion and the ligand under investigation.[26−29] These results agree with that obtained from the pH-metric study.

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