

Structural Investigation of Ni (II), Cu (II), Pd (II) and UO₂(II) Chelates with Some Hydroxynaphthoic Acid Azo Dyes

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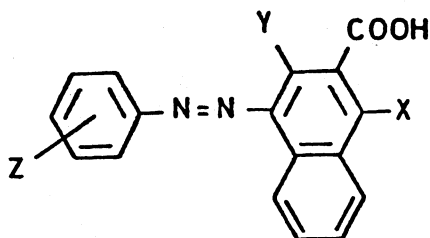
The chelates of divalent Ni, Cu, Pd and UO₂ with some azo derivatives of hydroxy-2-naphthoic acid were investigated using several experimental techniques. The potentiometric technique was utilized to determine the ionization constants of these ligands and the formation constants of their complexes. The conductimetric method was used to identify the complex species in solution, whereas the structure of the separated solid complexes was investigated using IR and NMR spectra and TGA analysis.

INTRODUCTION

Hydroxynaphthoic acids have been used as analytical reagents in some potentiometric and conductimetric studies. Values of stability constants of some transition and lanthanide complexes have been reviewed¹⁻⁴

The interest in the hydroxynaphthoic acid azo dyes is attributed to their antifungal and antitubercular activity^{5,6} and their uses as disperse dyes⁷. In a trial to locate the N=N band position, the IR spectra of 110 azo dyes were investigated⁸. The acid-base properties of some 1-hydroxy-2-naphthoic acid azo dyes were determined⁹. The formation constants of some trivalent lanthanide ion chelates with azo derivatives of 3-hydroxy-2-naphthoic acid were also determined¹⁰. The thermal stability of some hydroxynaphthoic acid azo dyes and their resonance and the inductive effect of the substituents were all correlated to each other by Necas *et. al.*¹¹

In the present work, the formation constants of Ni (II), Cu (II), Pd (II) and UO₂ (II) complexes with some hydroxynaphthoic acid azo dyes are determined potentiometrically in 50% ethanolic solution using Sarin and Munshi method¹². Conductimetric titrations are carried out to obtain information about the stoichiometry of the complex species in solution. The IR and NMR spectra and TGA analysis were performed to investigate their molecular structure. The azo derivatives under investigation have the general formula:



where X = OH, Y = H(I); X = H, Y = OH (II); Z = 2-OH (a); 2-COOH (b); 2-OH, 5-SO₃H (c); 2-OAs (OH)₂ (d); H (e); 3-NO₂ (f); 4-NO₂ (g); 3-Cl (h); 4-Cl (i); 4-I (j); 4-CH₃ (k); 2-OCH₃ (l).

EXPERIMENTAL

The 4-(aryloxy)-1-hydroxy-2-naphthoic acid derivatives (Ia-l) and 4-(aryloxy)-3-hydroxy-2-naphthoic acid derivatives (IIa-d) were prepared by coupling of hydroxynaphthoic acids with the corresponding diazonium salt in sodium hydroxide⁴. The elemental analysis of the resulting azo dyes were carried out in the microanalytical centre, Cairo University. Stock dye solutions (10⁻³ M) were prepared in spectroscopic pure ethanol.

Three mixtures (A), (B) and (C) of total volume 50 ml were prepared as follows:

(A) 3 ml 0.1 M HCl + 5 ml 1 M KCl + 25 ml ethanol and distilled water up to 50 ml.

(B) 3 ml 0.1 M HCl + 5 ml 1 M KCl + 20 ml ethanolic dye solution (10⁻³ M) + 5 ml ethanol and distilled water up to 50 ml.

(C) 3 ml 0.1 M HCl + 5 ml 1 M KCl + 20 ml ethanolic dye solution (10⁻³ M) + 5 ml ethanolic metal (Ni (II), Cu (II), Pd (II) or UO₂ (II)) solution (10⁻³ M) and distilled water up to 50 ml.

The above three mixtures were titrated potentiometrically using glass electrode against 0.208 M KOH solution. Correction of the pH meter readings for alcohol-water medium was made by subtraction of 0.2 from the measured pH values¹³. The average number of protons (\bar{n}_A) associated with the ligand at various pH values, the average number of ligand molecules (\bar{n}) attached to a metal ion and the free ligand exponent (pL) were calculated using the equations given by Irving and Rossotti¹⁴. The successive formation constants log K₁ and log K₂ were calculated by the interpolation at half \bar{n} value (method A) and by using the correction term (method B).

Conductimetric titrations of 10⁻⁴ M metal ion solution with 10⁻³ M dye solution were made using conductivity meter Myron L Model DC4 with platinum electrode.

The solid complexes were prepared by reacting 1:1 or 1:2 stoichiometric proportions of metal acetate with alcoholic dye solution. The mixture was heated on a water bath for 2 hrs, then cooled and the separated complex filtered, washed

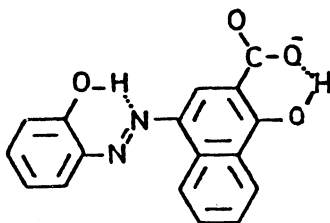
with ethanol, dried and subjected to elemental analysis. The spectral measurements of the complexes include IR (using Perkin Elmer spectrometer) and NMR (using Varian Em-390.90 MHz). The TG analysis of the complexes were made from the room temperature to 1000°C using STA 409 Netzsch firm thermal analyzer.

RESULTS AND DISCUSSION

Potentiometric Study

The protonation constants of the ligands Ia–l and IIa–d were calculated by two methods. In the first method, \bar{n}_A values were calculated at various pH values from the first two titration curves for mixture (A) and (B) then plotting a curve relating the pH as abscissa versus the corresponding \bar{n}_A values. The protonation constants $\log K_1, \log K_2, \log K_3$ and $\log K_4$ were then calculated by interpolation at $\bar{n}_A = 0.5, 1.5, 2.5$ and 3.5 respectively. In the second method, the plotting of pH values as abscissa versus $\log(\bar{n}_A/1 - \bar{n}_A), \log(\bar{n}_A - 1/2 - \bar{n}_A), \log(\bar{n}_A - 2/3 - \bar{n}_A)$ and $\log(\bar{n}_A - 3/4 - \bar{n}_A)$ as ordinates gives lines intersecting with the abscissa at $\log K_1, \log K_2, \log K_3$ and $\log K_4$ respectively (Table 1).

As would be expected, the more acidic COOH group exhibits a smaller $\log K^H$ value than that of the phenolic OH group. This is in accordance with the fact that the carboxylate ion is highly stabilized by resonance. For example, the $\log K^H$ values of the derivative Ia increase in the order $\log K_3 < \log K_2 < \log K_1$ as the acid strength decreases in the order COOH > OH (phenolic) > OH (naphthoic) respectively. Both OH groups are believed to be involved in an intramolecular hydrogen bonding; a reason why their acid strengths are smaller than would be expected. Moreover, the OH (phenolic) being involved in N...H bond is more acidic than the OH (naphthoic) being involved in a stable O...H bridge (Table 1), thus:



The formation constants of the azo dyes under investigation with Ni (II), Cu (II), Pd (II) and UO₂ (II) ions were calculated as follows. From the titration curves (A), (B) and (C), the values of \bar{n} and pL were calculated and plotted versus each other to produce the formation curves of the 1 : 1 and 1 : 2 complexes. The stepwise formation constants $\log K_1$ and $\log K_2$ (Table 2) were evaluated by the two methods described in the experimental section, *i.e.* interpolation at half \bar{n} value and correction term methods.

TABLE I
FORMATION CONSTANTS OF HYDROXYNAPHTHOIC ACID AZO DYES IN ETHANOL-WATER

Dye	Z	1st method				2nd method				mean pK			
		log K ₁	log K ₂	log K ₃	log K ₄	log K ₁	log K ₂	log K ₃	log K ₄	log K ₁	log K ₂	log K ₃	log K ₄
Ia	2-OH	11.90	11.25	3.55	—	11.90	11.25	3.70	—	11.90	11.25	3.60	—
Ib	2-COOH	12.30	7.20	3.00	—	12.30	7.20	3.70	—	12.30	7.20	3.35	—
Ic	2-OH, 5-SO ₃ H	12.45	12.15	9.00	3.75	12.45	12.15	9.00	4.15	12.45	12.15	9.00	3.83
Id	2-AsO(OH) ₂	12.45	10.20	5.80	3.05	12.45	10.70	5.80	3.15	12.45	10.45	5.80	3.10
Ie	H	12.30	2.73	—	—	12.30	2.73	—	—	12.30	2.73	—	—
If	3-NO ₂	12.05	6.60	—	—	12.05	6.80	—	—	12.05	6.70	—	—
Ig	4-NO ₂	12.45	7.85	—	—	12.35	7.85	—	—	12.40	7.85	—	—
Ih	3-Cl	12.10	6.63	—	—	12.10	6.65	—	—	12.10	6.64	—	—
Ii	4-Cl	9.95	3.10	—	—	9.70	3.10	—	—	9.83	3.10	—	—
Ij	4-I	10.80	3.05	—	—	10.80	3.05	—	—	10.80	3.05	—	—
Ik	4-CH ₃	11.50	5.31	—	—	11.50	5.30	—	—	11.50	5.31	—	—
Il	o-CH ₃ O	12.45	3.95	—	—	12.45	4.00	—	—	12.45	3.98	—	—
Ila	2-OH	12.10	9.55	6.25	—	12.00	9.00	6.15	—	12.05	9.53	6.20	—
Ilb	2-COOH	12.60	6.00	4.55	—	12.55	6.00	4.60	—	12.58	6.00	4.58	—
Ilc	2-OH, 5-SO ₃ H	12.73	12.29	7.15	3.08	12.73	12.30	7.30	3.15	12.73	12.30	7.23	3.12
Ild	2-AsO(OH) ₂	12.57	10.50	6.00	3.50	12.57	10.75	6.05	3.60	12.57	10.63	6.03	3.55

1st method: Proton-ligand formation curve method.

2nd method: $\log \bar{n}_A/1 - \bar{n}_A$, $\log \bar{n}_A - 1/2 - \bar{n}_A$, $\log \bar{n}_A - 2/3 - \bar{n}_A$, $\log \bar{n}_A - 3/4 - \bar{n}_A$ versus pH method.

TABLE 2
 Log K₁ AND Log K₂ VALUES OF THE CHELATES OF HYDROXYNAPHTHOIC
 ACIDS AZO DYES WITH Ni (II), Cu (II), Pd (II) AND UO₂ (II) IONS

Metal ion	log K ₁			log K ₂		
	A	B	Mean	A	B	Mean
<i>Complexes with Ia</i>						
Ni (II)	8.62	9.98	9.30	4.22	4.02	4.12
Cu (II)	14.35	14.98	14.65	8.20	7.32	7.76
Pd (II)	15.05	16.48	15.77	6.61	5.42	6.02
U (VI)	14.08	14.26	14.17	6.92	6.74	6.83
<i>Complexes with Ib</i>						
Cu (II)	9.05	9.48	9.27	3.75	3.52	3.64
Pd (II)	12.65	12.98	12.82	6.55	5.87	3.21
U (VI)	9.95	10.38	10.17	3.77	3.57	3.67
<i>Complexes with Ic</i>						
Cu (II)	14.68	15.48	15.08	5.23	5.02	5.13
Pd (II)	11.75	12.43	12.09	5.35	5.02	5.19
U (VI)	13.15	13.63	13.39	5.25	4.77	5.01
<i>Complexes with Id</i>						
Ni (II)	6.26	6.88	6.57	4.21	4.02	4.12
Cu (II)	10.72	11.08	10.90	5.49	4.72	5.11
Pd (II)	12.88	13.08	12.98	8.25	7.62	9.93
U (VI)	4.72	7.98	7.70	5.25	4.92	5.09
<i>Complexes with Ie</i>						
Ni (II)	7.00	9.53	8.27	4.65	4.27	4.46
Cu (II)	9.85	10.18	10.02	4.40	4.14	4.27
Pd (II)	10.18	10.20	10.19	5.78	5.07	5.43
U (VI)	9.67	10.20	9.94	7.03	6.82	6.93
<i>Complexes with If</i>						
Ni (II)	5.50	6.13	5.82	4.05	3.87	3.96
Cu (II)	8.53	9.44	8.98	6.68	6.46	6.57
Pd (II)	11.06	11.93	11.50	7.1	6.82	6.96
U (VI)	6.43	7.30	6.87	4.90	4.72	4.81
<i>Complexes with IIa</i>						
Ni (II)	14.19	14.43	14.31	11.17	10.47	10.82
Cu (II)	15.72	17.68	16.70	10.92	10.27	10.59
Pd (II)	12.98	14.28	13.63	10.85	10.52	10.68
U (VI)	13.63	14.08	13.85	7.75	5.22	6.48

Metal ion	log K ₁			log K ₂		
	A	B	Mean	A	B	Mean
<i>Complexes with IIb</i>						
Ni (II)	12.85	13.28	13.07	8.05	7.47	7.76
Cu (II)	10.70	11.03	10.87	4.25	4.07	4.16
Pd (II)	8.26	9.03	8.64	4.72	4.47	4.60
U (VI)	10.90	11.43	11.17	6.75	6.62	6.69
<i>Complexes with IIc</i>						
Ni (II)	12.00	13.18	12.59	5.45	4.97	5.21
Cu (II)	13.85	14.38	14.12	5.45	4.97	5.21
Pd (II)	23.82	24.38	24.10	19.85	19.42	19.63
U (VI)	17.65	19.68	18.67	9.95	9.47	9.47
<i>Complexes with IId</i>						
Ni (II)	10.67	14.68	12.68	4.65	3.07	3.86
Cu (II)	10.72	11.28	11.00	4.65	4.42	4.53
Pd (II)	12.70	13.08	12.89	8.37	7.57	7.97
U (II)	7.94	9.46	8.70	5.31	4.94	5.12

Where A: interpolation at half \bar{n} values method; B: correction-term method.

The correlation between log K of the complexes formed by a series of ligands with their respective basic strength has been always of interest in the field of solution chemistry. Most of such correlations are linear and obey the equation:

$$\log K_{ML} = a \log K_{HL} + b$$

where HL and ML represent the ligand and its complex respectively; a and b are constants. Irving and Rossotti¹⁵ discussed the conditions under which the correlation is to be expected, and they attributed the deviation from linearity to steric effects. The graph shows a good linear relation between the pK (OH) of the azo dyes Ia–l and IIb–d and the log K₁ of their uranyl complexes.

The conductimetric titrations of Cu (II) acetate, Ni (II) acetate and Pd (II) chloride with the dyes Ic, g, i, j, l and IId, and UO₂ (II) acetate with Ie and IId were performed to give an insight to the stoichiometry of the complexes in solution. The change in conductivity occurring during the titration can be used to detect the complex species by plotting the measured conductance (corrected for dilution effect) against the volume of the azo dye as a titrant. The resulting titration curves are composed of straight lines intersecting at the molar ratios of the complexes. Most of the titration curves exhibit two inflections at molar ratios L/M = 1 and 2 indicating the formation of 1 : 1 and 1 : 2 complex species in solution, except for Cu (II)–Ij complex which forms only 1 : 1 species. The gradual increase of conductance during the titration may be attributed to the release of

TABLE 3
ELEMENTAL ANALYSIS OF SOLID COMPLEXES

Complex	(M:L)	Formula	C%		H%		N%		M%	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Pd-Ia	(1:1)	$\text{PdNaC}_{17}\text{H}_9\text{N}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	43.38	42.62	2.78	2.37	5.95	6.27	22.60	22.15
Pd-Ia	(1:2)	$\text{PdNa}_2\text{C}_{34}\text{H}_{20}\text{N}_4\text{O}_8 \cdot 4\text{H}_2\text{O}$	48.77	48.59	3.30	2.46	6.69	6.66	12.72	12.82
UO ₂ -Ia	(1:1)	$\text{UO}_2\text{Na}_2\text{C}_{17}\text{H}_9\text{N}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$	29.66	30.97	2.77	1.79	4.06	3.79	34.58	34.85
UO ₂ -Ia	(1:2)	$\text{UO}_2\text{Na}_4\text{C}_{34}\text{H}_{18}\text{N}_4\text{O}_8 \cdot 4\text{H}_2\text{O}$	39.00	37.93	2.50	2.12	2.57	5.30	22.79	22.43
Cu-Ib	(1:1)	$\text{CuNaC}_{18}\text{H}_9\text{N}_2\text{O}_5$	51.50	52.43	2.16	2.95	6.67	6.71	15.13	14.98
Pd-Ib	(1:1)	$\text{PdNaC}_{18}\text{H}_9\text{N}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$	40.43	39.07	3.20	3.20	5.23	5.11	19.90	19.39
Pd-Ib	(1:2)	$\text{PdNa}_4\text{C}_{36}\text{H}_{18}\text{N}_4\text{O}_{10} \cdot 2\text{H}_2\text{O}$	47.99	47.19	2.46	2.45	6.22	6.09	11.81	11.71
UO ₂ -Ib	(1:2)	$\text{UO}_2\text{Na}_2\text{C}_{36}\text{H}_{18}\text{N}_4\text{O}_{10} \cdot 5\text{H}_2\text{O}$	42.45	42.23	1.97	1.79	5.50	4.98	23.37	23.09
Ni-IIc	(1:1)	$\text{NiNa}_2\text{C}_{17}\text{H}_9\text{N}_2\text{O}_7 \cdot \text{S} \cdot 4\text{H}_2\text{O}$	36.32	36.00	3.04	2.58	4.98	5.55	10.45	10.13
Cu-Ic	(1:1)	$\text{CuNa}_2\text{C}_{17}\text{H}_9\text{N}_2\text{O}_7 \cdot \text{S} \cdot 2\text{H}_2\text{O}$	38.46	38.00	2.46	2.48	5.27	5.74	11.97	12.14
Pd-IIb	(1:2)	$\text{PdNa}_2\text{C}_{36}\text{H}_{18}\text{N}_4\text{O}_{10} \cdot 2\text{H}_2\text{O}$	50.55	50.27	2.59	2.74	6.56	6.70	12.45	12.35
Cu-IIc	(1:1)	$\text{CuNa}_2\text{C}_{17}\text{H}_9\text{N}_2\text{O}_7 \cdot \text{S} \cdot 2\text{H}_2\text{O}$	38.46	37.59	2.46	2.52	5.27	5.33	11.97	12.07

H⁺ ions from the COOH and OH (naphthyl) groups of the ligand as a result of the complex formation.

Structure of Complexes

The high affinity for chelation of the hydroxynaphthoic acids azo dyes Ia, Ib, Ic, IIb and IIc was utilized to prepare their solid complexes. The formulation of these complexes as hydrated 1 : 1 and 1 : 2 species give a good agreement with the C, H, N and M analyses (Table 3). They have the general formula [ML_n]xH₂O where M = divalent Ni, Cu, Pd, UO₂; L = azo dye; n = 1 or 2; x = 0–5.

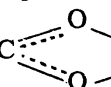
The IR spectral bands of some solid chelates together with their assignment are given in Table-4. The IR spectra of the ligands and their complexes have been recorded over the range 4000–600 cm⁻¹ to elucidate their molecular structure and to find the coordination sites involved in chelation.

TABLE 4
ASSIGNMENTS OF IR BANDS (cm⁻¹) OF SOME CHELATES

Complex	(M:L)	$\nu(\text{C}=\text{O})$	ν_{OH}	δ_{OH}	N=N
UO ₂ -Ia	(1 : 1)	—	3420b	1090, 1000w, sp	1430, 1450, 1475 w, sp
UO ₂ -Ia	(1 : 2)	1700sh	3430b	1090 m	1430m
Cu-Ib	(1 : 1)	—	3400b	1100w, 1140 m	1430s
Pd-Ib	(1 : 1)	—	3420b	1125, 1150 sh	1460s
Pd-Ib	(1 : 2)	1625m	3440b ^a	1090, 1120 w	1420m
UO ₂ -Ib	(1 : 1)	—	3440b	1100, 1140 w	1460s
UO ₂ -Ib	(1 : 2)	1610 m, 1650 s	3440b	1090, 1140 s	1445, 1470m, sp
Cu-Ic	(1 : 1)	—	3450b	1125 sh	1433, 1460, 1490w, sp
Ni-IIc	(1 : 1)	1610 m	3450b	1125s	1470m
Cu-IIc	(1 : 1)	1670 sh	3450b	1140s	1440s
Pd-IIb	(1 : 2)	1600 s, 1720 m	3440b	1100w	1430

b = Broad; w = Weak; s = Strong; sh = Shoulder; m = Medium; sp = Splitted

The band which appear at 3500 cm⁻¹ in the spectra of ligands may be assigned to the ν_{OH} of the H₂O molecules in the hydrated complexes. The appearance of the carboxylic C=O band at low frequency (near 1650 cm⁻¹ for free ligands) may be attributed to its conjugation with the neighbouring aromatic ring^{10,16}. Upon chelation, this band is either shifted to higher frequency or disappeared indicating the participation of the COOH group as a monodentate (COO–M) or a bidentate

ligand (C  M) respectively^{17,18}.

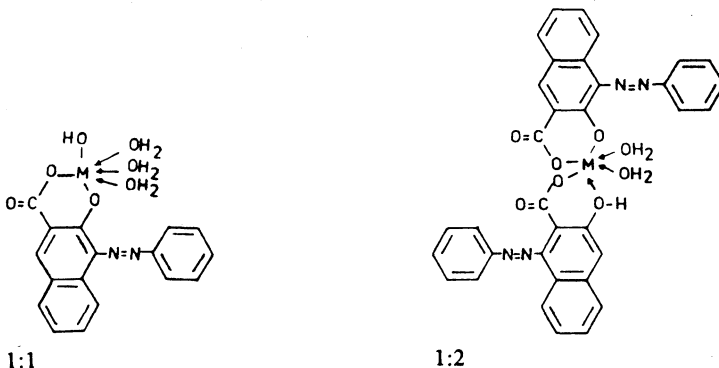
On the other hand, the appearance of the N=N stretching band unshifted upon chelation indicates that this group is not involved in coordination to the metal ion. However, the slight changes of the N=N band upon chelation may be

attributed to the change in its electronic charge distribution influenced by the participation of the neighbouring OH group in chelation.

The NMR is a complementary technique to the IR approach for elucidating the molecular structure of an organic ligand and its complexes. The NMR spectrum of the azo dye Ia shows a broad signal at 5 ppm which is assignable to the COOH proton. The aromatic protons of the phenyl and naphthyl rings display a multiplet signal at 7.2–8.9 ppm which obscures partially the signal of OH groups near 9 ppm. In the spectrum of 1 : 1 complex, the signal at 5 ppm disappears indicating the participation of COOH group in chelation while in the 1 : 2 complex, a small signal remains at 4 ppm which is assignable to the COOH group of the second molecule of azo dye. The new signal at 3.5 ppm is assignable to the H₂O in the complexes whereas the multiplet signal of the aromatic protons remain unshifted but with reduced splitting.

TG of the azo dye Ia complexes with Pd (II) and UO₂ (II) were performed from the ambient temperature up to 1000°C at a rate of 10°C min⁻¹. The initial weight loss in UO₂-Ia complex occurs at a temperature higher than 100°C indicating that all the H₂O molecules in this UO₂-Ia (H₂O)₅ complex are not hydrated but coordinated to the metal ion. On the other hand, the 4H₂O molecules in the Pd-Ia complex were all removed near 100°C indicating that all of them are hydrated thus, [Pd-Ia] 4H₂O. However, further heating above 200°C results in small continuing weight loss until the complex is decomposed producing the corresponding metal oxide as a final product at 500°C.

Based on the above results, it can be concluded that in the 1 : 1 chelates, two coordination sites are occupied by the replacement of hydroxy and carboxy protons of the naphthalene ring. The remaining sites are occupied by H₂O molecules. For the 1 : 2 chelates, two coordination sites are occupied by two COOH groups and the two OH groups remain undissociated in the complex. From these findings, the structures of the 1 : 1 and 1 : 2 chelates may be represented by the following formulae:



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AJC-570