

Co(II), Ni(II) and Cu(II) Complexes of Some Phenylazosalicicylaldehyde Derivatives

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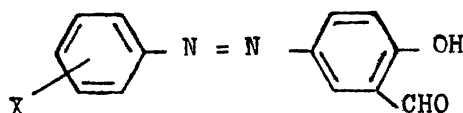
Complexes of some phenylazosalicicylaldehyde derivatives with Co(II), Ni(II) and Cu(II) are investigated using spectrophotometric and potentiometric methods in buffer solutions. The study revealed the formation of 1 : 1 and 1 : 2 (metal : ligand) complexes. The conditional stability constants K_f and ΔG° values are determined. The structure of the ligands in the solid chelates are studied by ir spectroscopy and shows that chelate formation takes place through proton displacement from the ligand.

COORDINATION of transition metal ions to chelating azodyes has been the subject of many interesting investigations¹⁻⁷. However, the study of metal chelates of phenylazosalicicylaldehyde derivatives has not been reported. The present article is devoted to a potentiometric and spectrophotometric study of Co(II), Ni(II) and Cu(II) chelates with phenylazosalicicylaldehydes. The structure of the chelates in the solid state is studied and their conditional stability constants are also determined.

Experimental

0.1 M solutions of Co²⁺, Ni²⁺ and Cu²⁺ were prepared by dissolving the appropriate amount of anhydrous metal chloride (B.D.H., A.R.) in absolute ethanol. The metal content was checked by recommended methods⁸.

The ligands used in the present investigation have the general formula



in which X = H ; *o*-, *m*-, *p*-OCH₃ ; *o*-, *m*-, *p*-CH₃ ; *o*-, *m*-, *p*-NO₂ ; *m*-, *p*-COOH ; *p*-Cl or *p*-Br.

The compounds were prepared according to reported method⁹.

The solid complexes :

The solid complexes were prepared by mixing a hot ethanolic solution of the ligands (1 or 2 mole) with a similar solution of the metal chloride containing the required amount. The mixture was refluxed for ~ 30 min on a water bath. On cooling, the solid complexes separated as fine crystals which were filtered, washed with ethanol and dried. The compounds obtained were analysed for their metal content by EDTA titration¹⁰. The chloride present was determined by Volhard's method. The water

content was determined by conventional dehydration. The results of analysis are recorded in Table 1.

Potentiometric measurement :

For the potentiometric titration, the following mixtures were prepared :

- (A) 5.0 ml 1.0 M NaClO₄ + 5.0 ml 0.1 M HClO₄.
- (B) 5.0 ml 1.0 M NaClO₄ + 5.0 ml 0.1 M HClO₄ + 25 ml 10⁻³ M ligand.
- (C) 5.0 ml 1.0 M NaClO₄ + 5.0 ml 0.1 M HClO₄ + 25 ml 10⁻³ M ligand + 2.0 ml 10⁻³ M metal ion solution.

The volume of each mixture was made up to 50 ml with double distilled water and ethanol such that the ethanol content was maintained at 75% by volume. The mixtures were then titrated with 0.01 M NaOH in 75% ethanol.

Spectrophotometric measurements :

The absorption spectra were recorded on a Beckman digital spectrophotometer, Model 25 using 1 cm matched silica cells. The blank was the same buffer solution as that of the test experiment. The solid ir spectra were obtained as KBr discs on a Beckman Infrared 4220 double beam spectrophotometer.

Results and Discussion

Reactions in solution :

Potentiometric titration :

The titration of mixtures A and B with NaOH was used to determine the proton-ligand stability constants, K^H , using the Calvin and Bjerrum^{12,13} pH technique as modified by Rossotti^{14,15}. The proton-ligand formation curves were constructed by plotting \bar{n}_A values against pH (Fig. 1). The method of interpolation at half \bar{n}_A values was used to evaluate K^H . The values for some of the ligands are given in Table 2.

TABLE 1—ANALYSIS OF THE SOLID (1 : 1) METAL CHLORATES

Metal ion	Analysis % : Found/(Calcd.)			Formula
	Metal	Chlorine	Water	
Phenylazosalicylaldehyde complexes				
Co(II)	14.7 (16.57)	9.6 (9.97)	10.97 (10.12)	CoCl.L.2H ₂ O
Ni(II)	16.7 (16.52)	9.9 (9.98)	11.01 (10.13)	NiCl.L.2H ₂ O
Cu(II)	18.0 (17.64)	9.6 (9.84)	9.56 (9.99)	CuCl.L.2H ₂ O
<i>o</i> -Methoxyphenylazosalicylaldehyde complexes				
Co(II)	17.7 (15.28)	9.0 (9.19)	10.43 (9.33)	CoCl.L.2H ₂ O
Ni(II)	15.0 (15.23)	8.0 (9.2)	11.85 (9.33)	NiCl.L.2H ₂ O
Cu(II)	19.0 (16.28)	8.0 (9.08)	11.93 (9.22)	CuCl.L.2H ₂ O
<i>m</i> -Methoxyphenylazosalicylaldehyde complexes				
Co(II)	13.0 (15.28)	9.04 (9.19)	11.74 (9.33)	CoCl.L.2H ₂ O
Ni(II)	15.9 (15.23)	8.20 (9.2)	10.69 (9.33)	NiCl.L.2H ₂ O
Cu(II)	18.1 (16.28)	8.69 (9.08)	7.98 (9.22)	CuCl.L.2H ₂ O
<i>p</i> -Methoxyphenylazosalicylaldehyde complexes				
Co(II)	13.0 (15.28)	8.6 (9.19)	10.54 (9.33)	CoCl.L.2H ₂ O
Ni(II)	14.0 (15.23)	8.7 (9.2)	9.08 (9.33)	NiCl.L.2H ₂ O
Cu(II)	14.0 (16.28)	8.8 (9.2)	10.62 (9.22)	CuCl.L.2H ₂ O
<i>o</i> -Nitrophenylazosalicylaldehyde complexes				
Co(II)	15.6 (14.71)	8.69 (8.85)	7.45 (8.99)	CoCl.L.2H ₂ O
Ni(II)	14.4 (14.66)	9.02 (8.85)	8.63 (8.99)	NiCl.L.2H ₂ O
Cu(II)	15.0 (15.68)	8.2 (8.75)	6.12 (8.88)	CuCl.L.2H ₂ O
<i>m</i> -Nitrophenylazosalicylaldehyde complexes				
Co(II)	14.7 (14.71)	8.33 (8.85)	8.34 (8.99)	CoCl.L.2H ₂ O
Ni(II)	16.1 (14.66)	8.86 (8.85)	8.01 (8.99)	NiCl.L.2H ₂ O
Cu(II)	14.93 (15.68)	7.84 (8.75)	9.45 (8.88)	CuCl.L.2H ₂ O
<i>p</i> -Nitrophenylazosalicylaldehyde complexes				
Co(II)	15.32 (14.71)	8.17 (8.85)	5.99 (8.99)	CoCl.L.2H ₂ O
Ni(II)	14.68 (14.66)	8.59 (8.85)	7.95 (8.99)	NiCl.L.2H ₂ O
Cu(II)	15.57 (15.68)	8.33 (8.75)	5.34 (8.88)	CuCl.L.2H ₂ O

TABLE 2—PROTON STABILITY CONSTANT OF SOME PHENYLAZOSALICYLALDEHYDE DERIVATIVES AND THE CONDITIONAL STABILITY CONSTANTS OF THE COMPLEXES WITH METAL IONS

Compound	X	-log K ^H	log K _f (1 : 1)			log K _f Cu(II)				-ΔG°	
			Co(II)	Ni(II)	Cu(II)	1 : 1		1 : 2		1 : 1	1 : 2
						C.V.	M.R.	C.V.	M.R.		
I	H	7.5	3.3	4.4	4.3	4.68	4.55	8.87	8.79	6.293	12.041
II	<i>o</i> -OCH ₃	6.75	2.0	3.15	3.9						
III	<i>m</i> -OCH ₃	7.0	1.35	4.0	4.38						
IV	<i>p</i> -OCH ₃	7.05	1.58	3.05	4.1	4.88	4.51	8.99	9.05	6.675	12.300
VIII	<i>o</i> -NO ₂	8.05	2.5	3.6	5.9						
IX	<i>m</i> -NO ₂	9.0	4.4	3.35	6.13						
X	<i>p</i> -NO ₂	7.9	2.8	5.0	5.3	5.02	4.51	9.18	8.58	6.368	12.109
X	<i>p</i> -NO ₂					4.79*	4.87*	9.17*	9.08*	6.729*	12.709*

* Co(II)-complexes of ligand X.

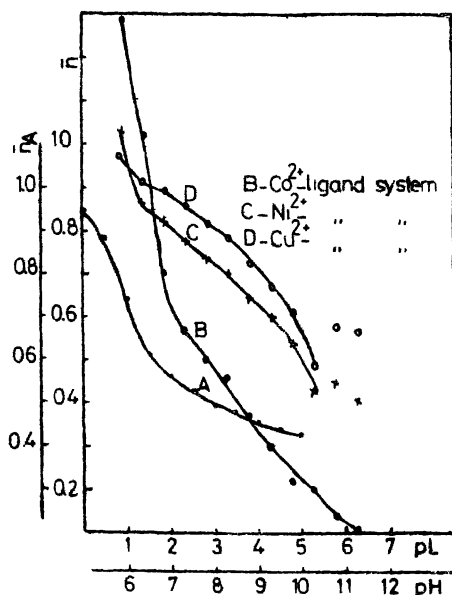


Fig. 1. Formations curves of proton *p*-nitrophenylazosalicylaldehyde system (A) and metal-ligand system.

The formation constants, K_f , of the complexes formed with ratio 1 : 1 and 1 : 2 ($M^{2+} : L$) were also determined by the method of half \bar{n} values. The results given in Table 2 indicate that for the complexes formed with one and the same ligand (IV or X), the formation constant runs in the order $Cu > Ni > Co$. The order reveals that the stability increases with the number of 3-d electron. Also, the K_f are higher for ligands with electron acceptor groups than those with donor substituents. It, thus, seems that the stability of the complex is related to the acid dissociation constant (K_a) which in turn is dependent on the strength of the intramolecular hydrogen bonding between the phenolic and aldehydic groups. Accordingly, the effect of substituent is explained by the transfer of its mesomeric action through the molecule over the N=N linkage as a bridge.

Spectrophotometric measurements :

Spectra in buffer solutions : These measurements were carried out in the thiel buffers¹¹ containing 30% ethanol. The suitable buffer solution for Cu^{2+} , Co^{2+} and Ni^{2+} is of pH 6.5.

The spectra of the solutions containing a constant metal ion concentration ($5 \times 10^{-5} M$) and varied ligand concentrations ($1 \times 10^{-5} - 1 \times 10^{-4} M$) are characterised by a red shift of λ_{max} on increasing the ligand concentration and a steady increase of absorbance. (Fig. 2.) Identical changes are observed when the ligand concentration is kept constant $3 \times 10^{-5} M$ while that of the metal ion is varied. This behaviour reveals the formation of complexes with varied metal : ligand ratio.

The stoichiometry of the complexes liable to exist in solution was determined by the conventional spectrophotometric methods¹⁶⁻²⁰ which revealed the possible formation of two types of complexes

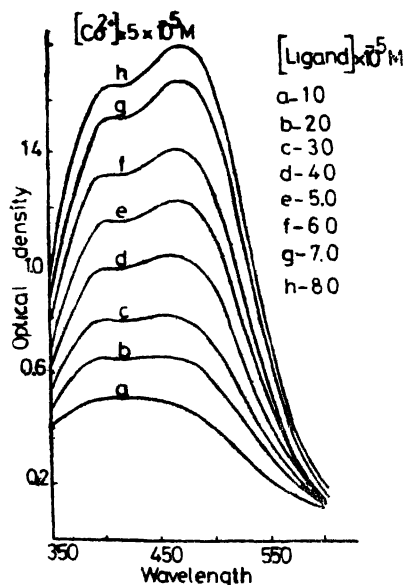


Fig. 2. Absorption spectra cobalt-*p*-nitrophenylazosalicylaldehyde complexes.

with stoichiometric ratios 1 : 1 and 1 : 2 (metal : ligand) which is in accordance with the results of analysis of the solid complexes.

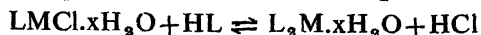
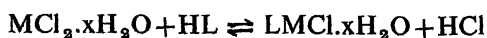
The conditional formation constants of the Cu^{2+} complexes were also evaluated from the results of the continuous variation¹⁶ and molar ratio¹⁷ methods. The values obtained as well as the free energy change $-\Delta G^\circ$ given in Table 2 are quite concordant with those of the potentiometric measurements.

Spectra of the solid complexes in DMF :

The electronic absorption spectra of the ligands and their solid complexes with Co^{2+} , Ni^{2+} and Cu^{2+} were recorded in DMF. The visible spectra indicate that the CT bands of the free ligands suffer a red shift in the spectra of the metal complexes. This behaviour recalls the ionisation of the ligands and hence can be explained on the basis that such ligands interact with the metal ions through proton displacement from the OH group.

Investigation of the solids :

The results of analysis of the solid complexes reveal the presence of one chloride ion per metal ion in the 1 : 1 complexes while the 1 : 2 complexes are deprived of chloride ion. This denotes that the reaction of the metal chlorides with the ligands takes place through proton displacement from the latter.



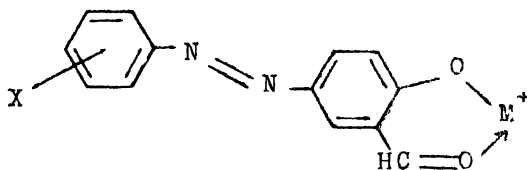
leading to the liberation of the chloride ions as HCl in the reaction medium. This confirms the conclusions derived from the potentiometric and spectrophotometric measurements.

Infrared spectra of the solid complexes :

Useful information about the structure of the complexes and the groups of the ligands involved in chelation can be obtained by comparing the ir spectra of the solid complexes with those of the organic ligands.

The ir spectra of the complexes exhibit broad intense bands near 3400 cm^{-1} due to $\nu(\text{OH})$ of water molecules. These bands disappear more or less completely on dehydration of the complexes. The presence of these bands in the spectra of the complexes masks the behaviour of the $\nu(\text{OH})$ bands of the phenolic groups. However, the $\delta(\text{OH})$ and $\nu(\text{C-OH})$ bands at $1395\text{-}1390$ and $1190\text{-}1170\text{ cm}^{-1}$ of the ligands are no more observed in those of the complexes. This indicates the displacement of the OH-proton from the ligand on reaction with the metal ion. The C=O bands at $1670\text{-}1660\text{ cm}^{-1}$ become broadened and shifted to lower wave numbers when the ligand is bonded to the metal ions.

The spectral shifts in the ir region reveal that the chelation of the metal ions to the ligands under investigation takes place through coordination to the C=O group and covalent linkage to the phenolic oxygen after displacement of the proton. Thus the bonding of the ligand to the metal ion can be formulated as shown below.



Based on these facts, the ligands under study function as bidentate monobasic groups.

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