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Metal Chelates of Benzimidazolylazo Derivatives

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Summary. The complexation of 2-(4-benzimidazolylazo)-*R*-acid and 5-(4-benzimidazolylazo)-8-hydroxy-quinoline with Mn(II), Co(II), Ni(II), and Cu(II) have been studied potentiometrically using the Calvin-Bjerrum titration technique as employed by Irving and Rossotti. Protonation constants of the ligands and stability constants of the metal complexes have been determined at constant temperature (25°C) and ionic strength (0.1 μ NaCl). The order of stability constants ($\log \beta_1$), Mn(II) < Co(II) < Ni(II) < Cu(II) is in conformity with the Irving-Williams order. The structures of the solid complexes have been assigned on the basis of elemental analysis and IR spectroscopy. Also conductimetric titrations have been made to characterize the composition of the complexes.

Keywords. Azo dyes; Benzimidazole; Mn(II), Co(II), Ni(II), and Cu(II) chelate; Stability constants.

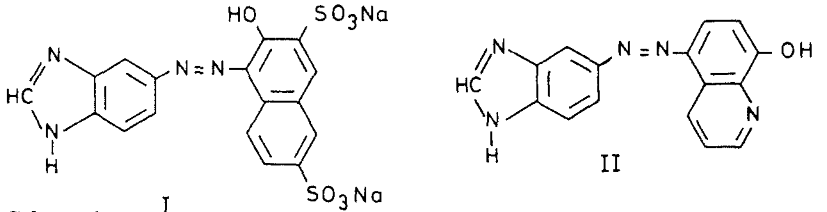
Metallchelate von Benzimidazolylazo-Derivaten

Zusammenfassung. Es wurde die Komplexierung von 2-(4-Benzimidazolylazo)-2-hydroxynaphthalin-3,6-disulfonsäure und 5-(4-Benzimidazolylazo)-8-hydroxychinolin mit Mn(II), Co(II), Ni(II) und Cu(II) potentiometrisch mittels der Calvin-Bjerrum-Titrationsmethode in der Modifikation von Irving-Rossotti untersucht. Die Protonierungskonstanten der Liganden und die Stabilitätskonstanten der Metallkomplexe wurden für eine Temperatur von 25 °C und eine Ionenstärke von 0.1 μ (NaCl) bestimmt. Die Reihung nach Stabilitätskonstanten ($\log \beta_1$), Mn(II) < Co(II) < Ni(II) < Cu(II), ist in Übereinstimmung mit der Irving-Williams-Ordnung. Die Strukturen wurden mittels Elementaranalyse und IR-Spektroskopie charakterisiert. Zur Ermittlung der Zusammensetzung der gebildeten Komplexe wurden auch Leitfähigkeitsmessungen durchgeführt.

Introduction

Azo dyes of the types 8-hydroxyquinoline and *R*-acid (2-hydroxy-naphthaline-3,6-disulphonic acid) are known as excellent analytical reagents in spectrophotometric [1–3] and chelatometric determination of metal ions [4]. They are of great pharmaceutical importance as they have diabetogenic, bacteriostatic and fungicidal properties [5–8]. They were used successfully as mordant dyes applicable to cotton, artificial textiles and propylene fibres [9, 10]. The coupling products of diazonium salts and 8-quinolinol exist entirely in the azo form. This was attributed to the presence of a weak intramolecular hydrogen bond between the heterocyclic nitrogen and the hydroxyl hydrogen [11, 12]. The acid dissociation constants of substituted phenylazo-8-quinolinol and *R*-acid were the subject of several investigations [13, 14].

The purpose of the present investigation is to study the stoichiometry and structure of the complexes formed when Mn(II), Co(II), Ni(II), and Cu(II) salts are allowed to react with 2-(4-benzimidazolylazo)-*R*-acid (**I**) and 5-(4-benzimidazolylazo)-8-hydroxyquinoline (**II**) (Scheme 1). The conditional formation constants are determined potentiometrically following the Bjerrum *pH*-titration technique as adopted by Irving and Rossotti [15]. The azocompounds used are found to form mono and binuclear metal complexes.



I II

Scheme 1

Experimental

Doubly distilled water was used and the chemicals were all of the highest available purity.

The azo dyes **I** and **II** were prepared as previously recommended [1]. The dyes obtained were recrystallized from absolute ethanol and their purity was confirmed by elemental analysis. Ligand **I**: Calc. C 41.46, H 2.03, N 11.38, S 13.01; found C 41.39, H 1.98, N 11.41, S 12.99%. Ligand **II**: Calc. C 66.44, H 3.81, N 24.22; found C 66.49, H 3.92, N 24.26%.

Stock dye **I** solution (0.001 *M*) was prepared in water and dye **II** solution (0.001 *M*) was prepared in absolute ethanol. The solutions of Mn(II), Co(II), Ni(II), and Cu(II) (0.001 *M*) were prepared by diluting previously standardized [16] 0.05 *M* stock solutions. Solutions of 0.10 *N* hydrochloric acid, 0.237 *N* NaOH and 1 *M* sodium chloride were also prepared.

Three mixtures were prepared as follows:

(a) 3 ml 0.10 *N* HCl + 5 ml 1 *M* NaCl + 30 ml ethanol in case of dye **II** (no alcohol was added in case of dye **I**) and the volume was made up to 50 ml with distilled water.

(b) 3 ml 0.10 *N* HCl + 5 ml 1 *M* NaCl + 20 ml 0.001 *M* ethanolic solution of dye **II** (or 20 ml 0.001 *M* aqueous solution of dye **I**) + 10 ml ethanol (in case of dye **II**) and the total volume was made up to 50 ml.

(c) 3 ml 0.10 *N* HCl + 5 ml 1 *M* NaCl + 20 ml 0.001 *M* ethanolic solution of dye **II** (or 20 ml 0.001 *M* aqueous solution of dye **I**) + 10 ml ethanol (in case of dye **II**) + 5 ml 0.001 *M* of the metal ions and the volume was made up to 50 ml.

The above three mixtures were titrated potentiometrically [17] against 0.237 *N* NaOH using a *pH*-meter (Chemtrix Model 62 A) at 25 ± 0.1°C. The appropriate correction factor for converting the *pH*-meter reading in 60% ethanol-water to the *pH* value amounts to 0.20 [18]; the curves are plotted accordingly. The $\bar{n}_A$, $\bar{n}$ and *pL* values were calculated using the method describes by Irving [15]. The methods used for calculating successive stability constants were: interpolation at half $\bar{n}$ value, correction term and successive approximation [19].

Conductimetric titrations were carried out at 25°C in pure ethanolic solutions using a conductivity meter model CM-1K to confirm the molar ratio (*M* : *L*) obtained by potentiometric titration.

The solid metal chelates were prepared by mixing a hot ethanolic solution of the ligand **I** or **II** with a hot ethanolic solution containing an appropriate amount of the metal salt, such that the metal : ligand ratio was (1 : 1) or (1 : 2). The reaction mixture was then refluxed on a water bath for 2–3 hours. On cooling, the solid complexes separated as fine crystals. They were filtered off, dried and preserved in a desiccator over dried calcium chloride. They were subjected to elemental analysis or determination of their metal content by *EDTA* titration [16].

Results and Discussion

The protonation constants of **I** and **II** are calculated from the potentiometric titration curves of hydrochloric acid in presence and absence of the ligands. The formation curves for the proton-ligand system are extended between 0 and 1 on the $\bar{n}_A$ scale, thus indicating that the ligands have one dissociable proton. The values of log K_1^H are obtained directly from their formation curves. Also, log K_1^H is calculated by the average value method [20]. The protonation constant obtained, given in Table 1, is assumed to be of the naphthalenic OH group. In case of ligand **I** the two sulphonic acid groups were not detected, since the prepared compound was found to be the sodium salt.

The respective metal ions with the ligands **I** and **II** were titrated against NaOH. A displacement was noticed in the metal titration curves with respect to the ligand titration curve indicating the release of protons due to complex formation.

Table 1. Formation constants of some bivalent metal ion chelates with ligands I and II

Metal ion	Computational method	Formation constants			$-\Delta G$ for **I, II** (kcal/mol)
		log K_1 for **I, II**	log K_2 for **I, II**	log β_n for **I, II**	
H^+	Half value	9.81, 8.26	–, –	9.81, 8.26	
	Average value	9.79, 8.20		9.79, 8.20	
	Mean	9.80, 8.23		9.80, 8.23	13.45, 11.30
Cu^{2+}	Half value	9.70, 9.83	9.75, 9.94	19.45, 19.77	
	Successive approximation	9.61, 9.72	9.62, 9.91	19.23, 19.63	
	Correction term	9.50, 9.92	9.73, 9.83	19.23, 19.75	
	Mean	9.60, 9.82	9.70, 9.89	19.30, 19.71	26.49, 27.05
Ni^{2+}	Half value	8.10, 8.32	5.00, 6.01	13.10, 14.33	
	Successive approximation	8.01, 8.22	5.21, 5.78	13.22, 14.00	
	Correction term	7.90, 8.11	5.12, 5.92	13.02, 14.03	
	Mean	8.00, 8.22	5.11, 5.90	13.11, 14.12	17.99, 19.38
Co^{2+}	Half value	7.53, 7.80	4.91, 5.31	12.44, 13.11	
	Successive approximation	7.43, 7.71	4.72, 5.11	12.15, 12.82	
	Correction term	7.32, 7.60	4.80, 5.21	12.12, 12.81	
	Mean	7.43, 7.70	4.81, 5.21	12.24, 12.91	16.80, 17.72
Mn^{2+}	Half value	6.58, 7.02	4.22, 4.70	10.80, 11.72	
	Successive approximation	6.40, 6.80	4.00, 4.61	10.40, 11.41	
	Correction term	6.50, 6.94	4.11, 4.58	10.61, 11.52	
	Mean	6.49, 6.92	4.11, 4.64	10.60, 11.56	14.55, 15.87

Values of $\bar{n}$ and pL were calculated as previously reported [15]. The values of $\bar{n}$ obtained in all metal ions were above 1.5, indicating the formation of 1 : 1 and 1 : 2 ($M:L$) complexes. The oxidation of Co^{2+} to give a complex of the type CoL_3 by the release of three protons or other Co^{3+} complexes seems unlikely in view of the similar nature of all formation curves. The results (Table 1) do not indicate any reversal of the stability order in the case of Co^{2+} complex. The values of $\log K_1$ and $\log K_2$ for all the complexes were either directly read from the formation curves or calculated using other methods [21] viz. successive approximation and correction term methods. The corresponding values are given in Table 1.

Values of $K_1 \leqslant K_2$ have been observed for some metal chelates studied with ligand **II**. This phenomenon has been found for the Cu^{2+} complex with 2,9-dimethyl-1,10-phenanthroline [22] and some transition metal complexes of 2-thienyl-8-hydroxy-quinoline [23]. These anomalous ratios of K_1/K_2 have been attributed to changes in the stereochemistry of the metal ion caused by steric interaction between the incoming first molecule of ligand and coordinated solvent resulting in a decrease in K_1 [24]. The second molecule of the ligand coordinates to the distored structure in the usual fashion without a decrease in K_2.

The free energy of formation (ΔG) accompanying the complexation reactions have been determined at 25°C using the standard equation: $-\Delta G = 2.303\,RT \log K$. The results are given in Table 1. The negative values of free energy change (ΔG) show that the driving tendency of the complexation reaction is from left to right and the reaction proceeds spontaneously.

The following is a discussion of relations between the properties of metal ions and ligands and the stability constants of the complexes.

The Electronic Configuration of the Metal Ion

The complex forming abilities of the transitional metal ions are frequently characterized by stability orders. This is displayed graphically in Fig. 1. It can be seen that the $\log K_1$, $\log \beta_2$ ($\log K_1K_2$) order is Cu > Ni > Co > Mn in accordance with the Irving and Williams order [25] for divalent metal ions of the 3 d series.

The Ionic Radius

Assuming an electrostatic interaction of the metal ions and the ligands, the stability constants of complexes of metal ions of the same charge should be inversely pro-

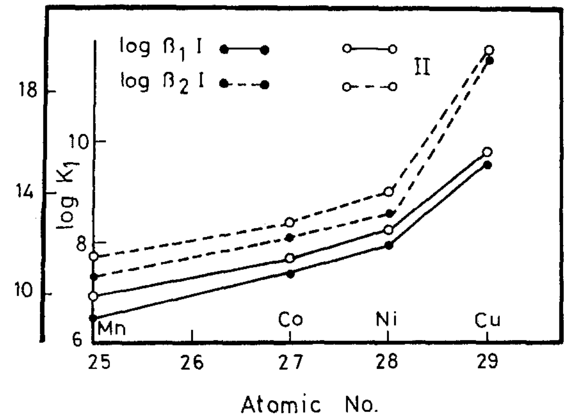


Fig. 1. Correlation between stability constants and atomic number

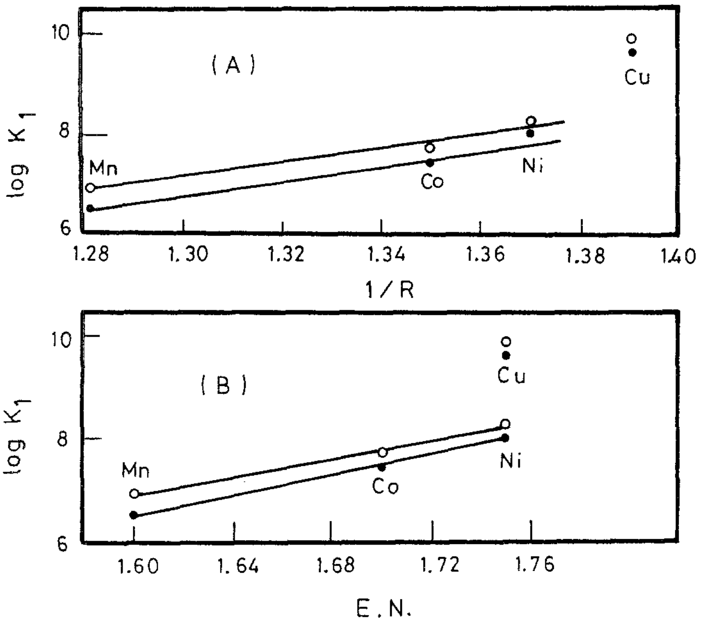


Fig. 2. (*A*) Relation between the stability constants and the ionic radius. (*B*) Relation between the stability constants and the electronegativity (E. N.)

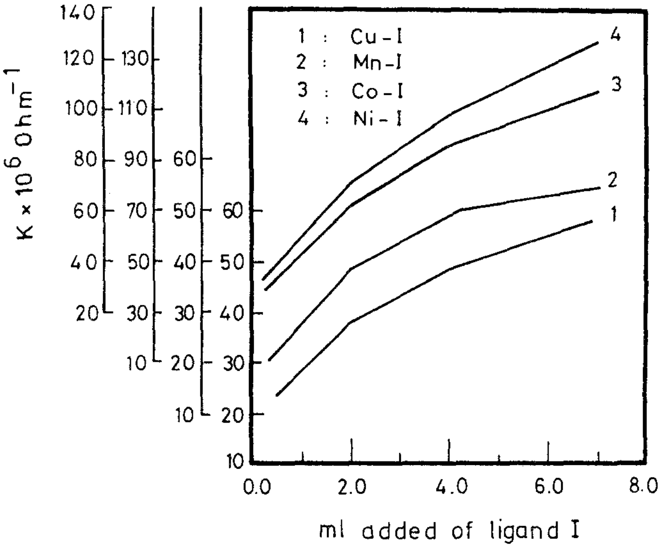


Fig. 3. Conductimetric titration of 50 ml ($4 \cdot 10^{-5} M$) metal ions with $10^{-3} M$ ligand I

portional to metal ions radii. For ions of similar electronic configuration this relationship may be approximately valid. The metal chelates of I and II show more or less linear behaviour when their $\log K_1$ values are plotted against the reciprocal ionic radii [26] ($1/R$) (see Fig. 2A).

The Electronegativity

With respect to increasing electronegativity of the metals, the electronegativity difference between a metal atom and donor atom of the ligand will decrease, hence the metal-ligand would have more covalent character which may result in a greater stability of metal complexes. Plotting $\log K_1$ values against the electronegativity [26] of the metal atom gives more or less straight lines as shown in Fig. 2 B.

It is clear from Table 1 that the stability constants of the complexes of Cu^{2+} are considerably larger as compared to other metals of the 3 d deries. Under the influence of the ligand field Cu^{2+} ($3d^9$) will receive some extra stabilization [27] due to tetragonal distortion of the octahedral symmetry in their complexes. The Cu^{2+} complexes will be further stabilized due to the Jahn-Teller effect [27]; this also explains why $\log K_1$ values for copper do not fall on straight lines and are significantly above them when $\log K_1$ values of the metal chelates are plotted against the respective properties of the metal ions.

The conductimetric titration curves (Fig. 3) for the investigated complexes show two breaks at molar ratios 1 : 1 and 1 : 2 (metal ion : ligand), which is in accordance with the results obtained from *pH*-metric titrations. The titration curves indicate a gradual increase in the conductance values due to the displacement of protons from the ligand on complex formation.

The mode of bonding of the ligands **I** and **II** to Cu^{2+} was examined by elemental analysis (Table 2) and the IR spectra of the complexes by comparing them with those of the free ligands.

Infra Red Spectra of Cu^{2+}-**I** *Complexes*

The broad band observed at 3 450 cm^{-1} assigned to ν_{OH} in the spectra of the free ligand is shifted to lower wave numbers. This behaviour may be attributed to the participation of the OH group of the ligand in chelation with the metal ion. The presence of coordinated water molecules in the 1 : 1 complex is indicated by bands around 3 400 (sh), 860 – 870 (m) and 710 (w) cm^{-1}, assignable to OH stretching,

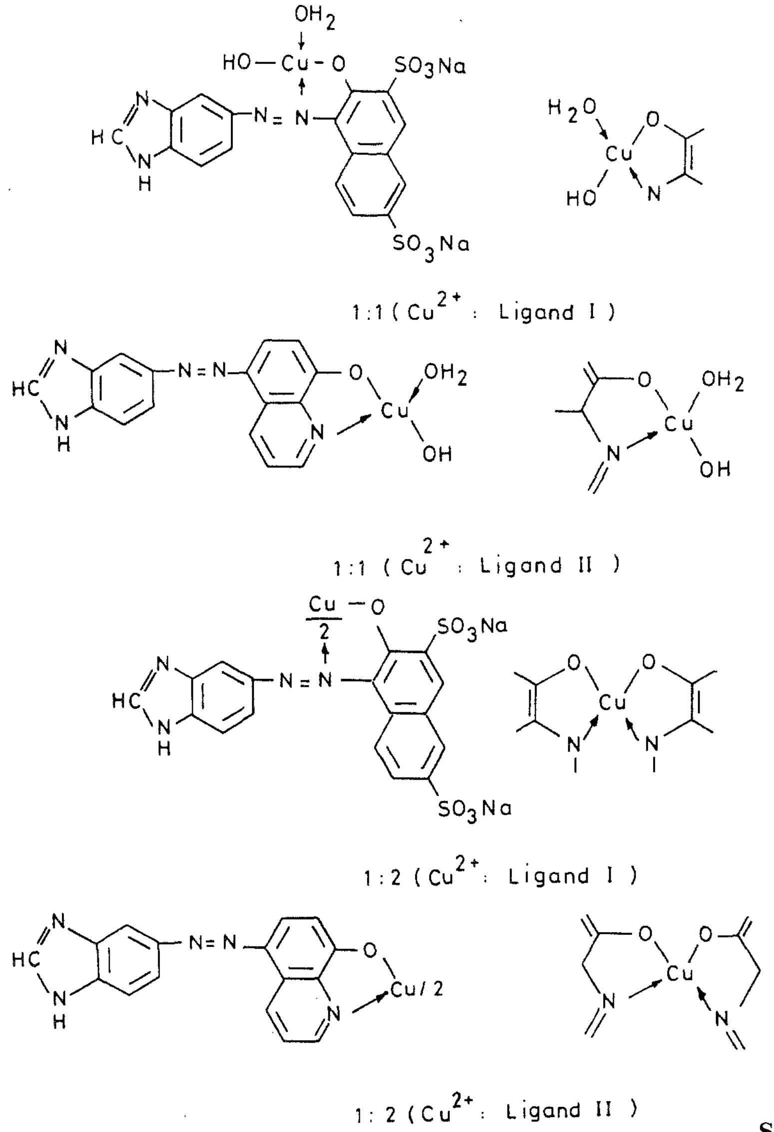
Table 2. Elemental Analysis of Cu^{2+}-**I**, **II** complexes

M : *L*	Formula	C%	H%	N%	S%	Cu%
		Calc. (found)	Calc. (found)	Calc. (found)	Calc. (found)	Calc. (found)
(a) Ligand **I**:						
1 : 1	$C_{17}H_{12}N_4O_9S_2Na_2Cu$	34.60 (35.01)	2.04 (2.10)	9.50 (9.91)	10.86 (10.91)	10.77 (10.75)
1 : 2	$C_{34}H_{18}N_8O_{14}S_4Na_4Cu$	39.02 (38.89)	1.72 (1.90)	10.71 (10.82)	12.24 (12.20)	6.07 (6.12)
(b) Ligand **II**:						
1 : 1	$C_{16}H_{13}N_5O_3Cu$	49.68 (49.72)	3.36 (3.41)	18.11 (18.21)	–	16.43 (16.50)
1 : 2	$C_{32}H_{20}N_{10}O_2Cu$	60.05 (60.20)	3.13 (3.08)	21.89 (20.99)	–	9.93 (9.98)

rocking and wagging vibrations. The $\nu_{N=N}$ band at 1460 cm^{-1} exhibits a shift of 30 – 35 cm^{-1} to lower wave number values on complexation which may be taken as evidence for the participation of the N = N group in coordination.

Infra Red Spectra of Cu^{2+}-**II** *Complexes*

The broad weak band observed at 3400 cm^{-1} assigned as ν_{OH} in the spectra of the free ligand is changed to a broad band with its position shifted to lower wave numbers (3300 cm^{-1}) in the spectra of the complexes. This behaviour may be attributed to the deprotonation of the phenolic OH group and coordination through the oxygen atom. The presence of coordinated water molecules in the 1 : 1 complex is indicated by bands around 3410 (sh), 865 – 870 (m) and 720 (w) cm^{-1}, assignable to OH stretching, rocking and wagging vibrations. Participation of the quinolinic nitrogen atom in chelate formation is indicated by the presence of a strong band



Scheme 2

at about $450\,cm^{-1}$ which may be assigned to M-N stretching vibration [28]. The symmetrical N = N stretch observed at $1\,380\,cm^{-1}$ for free the ligand exhibits no shift in the spectra of the complexes. This indicated that the azo group is not involved in chelate formation, thus the reaction of dye **II** with Cu^{2+} is proposed to occur by the displacement of one proton from each ligand molecule in addition to coordination through the quinolinic nitrogen atom.

In the light of these findings, the structures shown in Scheme 2 may be assigned to the 1 : 1 and 1 : 2 complexes of Cu^{2+} with ligands **I** and **II**.

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