CROATICA CHEMICA ACTA CCACAA 54 (1) 149—155 (1981)

CCA-1270

YU ISSN 0011-1643
UDC 546.3:547.821
Original Scientific Paper

Synthesis and Molecular Structure of Cu(II) and Mn(II) 2-Hydroxynaphthalene-1-azo-2'-pyridine *N*-oxide Complexes

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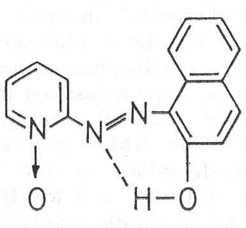
Received June 20, 1980

The purpose of this work was the preparation of Cu(II) and Mn(II) 2-hydroxynaphthalene-1-azo-2'-pyridine *N*-oxide complexes. By means of IR, UV/VIS, NMR, MS and electrophoresis the structure of the ligand itself, as well as its Cu(II) and Mn(II) complexes was studied in great detail. It was confirmed that the ligand behaves as a tridentate molecule. The Cu(II) complex forms a chelate molecule 1 : 1 with acetate as the anion, while the Mn(II) complex shows a 1 : 2 type of metal complex structure.

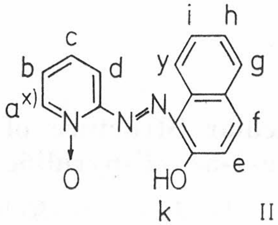
With regard to the importance of the certain types of metal complex compounds in the dye industry, the coordinative behaviour of 2-hydroxy-naphthalene-1-azo-2'-pyridine *N*-oxide complexes with (Cu(II) and Mn(II) ions whose ability at complexing was noted earlier[1,2,3] has been studied. The interactions of the ligand, 2-hydroxynaphthalene-1-azo-2'-pyridine *N*-oxide with Cu(II) and Mn(II) ions, and the results of the examination of the structures of these complexes as well as of the ligand itself, are shown in this paper. The nature of bonding was determined via IR, UV/VIS as well as by mass spectra. IR and NMR spectra confirm that the ligand is a molecule with an intramolecular hydrogen bond.

The IR spectrum shows a broad absorption band around 3400 cm^{-1} corresponding to the ν(OH) stretching vibrations, which is one of the confirmations of the hypothesis that the hydrogen bond probably forms a six membered ring involving in linkage the N atom of the azo group and the hydroxy H atom of the β naphthol nucleus.



I

The chemical shift of the proton of the hydroxy group of the β-naphthol nucleus toward the low field in NMR spectra also proved the existence of an intramolecular hydrogen bond in the ligand molecule. This phenomenon can be explained by the decrease in electron density around the proton, which is involved in the hydrogen bond, with oxygen from the N—O pyridine group.



II

The positions of protons in the ligand molecule are denoted by a, b, c . . . and an attempt is made to interpret the NMR spectrum without calculating the theoretical spectra. The data are given in Table I.

TABLE I

The Chemical Shift Data for Particular Protons in the Molecules of the Ligand (1)

Proton	Chemical Shift/ppm
a, d	5.6 — 6.00
j	5.39
e	5.07
b, c, i	4.60 — 5.10
g	4.78
h	4.30 — 4.60
f	4.10
k	9.85

The mass spectrum (MS) of the ligand shows a molecular ion M^+ m/Z 265, which is also the base peak.

EXPERIMENTAL

General

Melting points were taken on a Kofler hot stage apparatus and are uncorrected. All samples of substances for elemental analyses were dried for 6 hours in a vacuum of 0.04 mm Hg and 373 K, above phosphoric pentoxide. The IR spectra were recorded on Perkin-Elmer spectrophotometers, Models 257 and 457. The spectra in the 4000—400 cm^{-1} range were measured in KBr discs of chloroform. The UV/VIS spectra were taken in a 95% ethanol solution using a Beckman double-beam spectrophotometer, Model DK-2. The NMR spectra were recorded on a Varian HR-60 instrument using tetramethylsilans as the internal standard and chloroform-D as solvent. The samples of Cu(II) and Mn(II) complexes were not recorded because of their insolubility in all available solvents. The mass spectra (MS) were determined on a Hitachi-Perkin-Elmer Model RMU-6D. An electrophoresis study was made in an acetic acid medium with Na-acetate as buffer (pH-3.5; 4.0; 4.6; 5.3; 5.7; 6.7; and 8.7) at 30 V/cm and 2—3 mA. The presence of metals in complex compounds was confirmed by the JARELL-ASH type of atomic absorption apparatus.

2-Hydroxynaphthalene-1-azo-2'-pyridine N-*oxide (1)*

The compound was obtained by diazotization of 2-aminopyridine *N*-oxide and coupling the generated diazonium salt with 2-hydroxynaphthalene.[4,5] 2-aminopyridine *N*-oxide was prepared through 2-aminopyridine, which was initially acetylated (in order to protect) the amino group[6] and then oxidized with 40% peracetic acid[7] to obtain 2-acetylamino-pyridine *N*-oxide.

The separation of the latter from the reaction mixture was improved by use of cyclohexane for solvent extraction. Subsequently, 2-acetylaminopyridine *N*-oxide has been hydrolyzed with 10% sodium hydroxide[8] and the pure 2-aminopyridine *N*-oxide[9] was isolated. 2-hydroxynaphthalene was of p. a. purity (Merck).

Cu(II) *Complex of 2-Hydroxynaphthalene-1-azo-2'-pyridine* N-*oxide (2)*

According to Burger[10], 1.3 g (5 mmol) of 2-hydroxynaphthalene-1-azo-2'-pyridine *N*-oxide (1) were dissolved in 60 ml of methanol and 1.0 g (5 mmol) of Cu(II) acetatemonohydrate in 75 cm^3 of methanol. Both solutions were mixed and the mixture was refluxed for 45 minutes. 1.7 g (89.0%) of emerald-green crystals with a metallic shine were obtained.

Recrystallization from methanol was performed three times and the purity was examined by means of thin-layer chromatography (chloroform-methanol, 9 : 1 on silicagel G). M. p. = 525 K.

Anal. $C_{15}H_{10}N_3O_2CuCH_3COO$ (386.855) calc'd: C 52.78; H 3.38; N 10.86; Cu 16.45%
found: C 52.75; H 3.32; N 11.04; Cu 16.30%

The data of solubility, IR and UV/VIS spectra are given in Tables II, III and IV.

Mn(II) *Complex of 2-Hydroxynaphthalene-1-azo-2'-pyridine* N-*oxide (3)*

The mixture of 1.3 g (5 mmol) of 2-hydroxynaphthalene-1-azo-2'-pyridine *N*-oxide and 1.8 g (10 mmol) of Mn(II)-dichloride-tetrahydrate was dissolved in 30 ml of *N,N'*-dimethylformamide, heated for 1 hour at 323-333 K, then 1 hour at 363 K and finally 2 hours at 398—403 K.

1.2 g (55.5%) of dark brown-violet crystals characterised with intensive metallic glare were obtained.

Recrystallization was performed from the mixture of acetone-*N,N'*-dimethylformamide, 7 : 1. The purity was examined by means of thin-layer chromatography. A mixture of the following solvents was used: ethanol-methanol-chloroform-dioxan 3 : 3 : 3 : 1 on silicagel G.

M. p. = 633 K.

Anal. $C_{30}H_{20}N_6O_4Mn$ (583.478) calc'd: C 61.76; H 3.46; N 14.40; Mn 9.41%
found: C 61.21; H 3.62; N 14.35; Mn 9.91%

The data of solubility, the IR and UV/VIS spectra are given in Tables II, III and IV.

RESULTS AND DISCUSSION

Cu(II) and Mn(II) metal complexes of 2-hydroxynaphthalene-1-azo-2'-pyridine *N*-oxide[1] were obtained by interaction of the ligand with Cu/II acetate and Mn(II) chloride, respectively.

The ligand (1) was prepared by diazotization of 2-amino-pyridine *N*-oxide and coupling of the obtained diazonium salts with 2-hydroxynaphthalene[4]. The ligand solubility was investigated and the data are given in the Table II, together with the solubility of its Cu(II) and Mn(II) complexes.

TABLE II

Solubility of the Ligand (1), Cu(II) *and* Mn(II) *Complexes in Different Solvents*

Solvent	Ligand (1)			Cu(II)-complex (2)			Mn(II)-complex (3)		
	Solubility*		Color of Solution	Solubility		Color of Solution	Solubility		Color of Solution
	cold	warm		cold	warm		cold	warm	
Water	—	—+	orange	—	+	red	—	—	
Methanol	++		orange-red	—+	+	red	—	—+	red
Ethanol	++		orange-red	—+	+	red	—+	+	red
Chloroform	—+	+	orange	—+	+	red	—+	+	red
Benzene	—+	+	orange	—	—		—	—	
Pyridine	++		orange	—+	+	bluish-red	—+	—+	bluish-red
Acetone	++		orange	—	—	bluish-red	—+	+	red
Carbon tetrachloride	—+	+	orange	—	—		—	—+	red
Ether	—+	+	orange	—	—		—	—+	red
N,N'-Dimethyl--formamide	++		orange-red	++		red	+	++	violet-red
Ethanol+glac. acetic acid	++		orange	—+	+	red	—+	+	yellow-orange
Ethanol+ + 1/10 N HCl	++		orange	—+	+	red intensive	—+	+	yellow
conc. H_2SO_4	++		violet	++		violet	++		violet

* Note: — unsoluble —+ slightly soluble + soluble ++ very soluble

The positions of characteristic bands of ligand and its Cu(II) and Mn(II) complexes in IR spectra are given in Table III.

TABLE III

Characteristic Bands of Ligand Cu(II) *and* Mn(II) *Complexes in IR Spectra*

Compound	Absorption band wavenumbers/cm^{-1}
(1) $C_{15}H_{11}N_3O_2$	3400, 3095, 1445, 1325, 1260, 1220, 845
(2) $C_{15}H_{20}N_3O_2CuCH_3COO$	3100, 1745, 1450, 1285, 1255, 1220, 840, 455
(3) $C_{30}H_{20}N_6O_4Mn$	3075, 1445, 1250, 1210, 830, 455

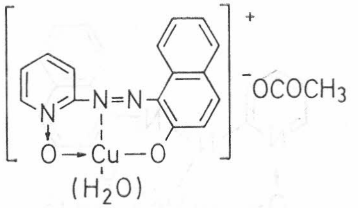
The data of UV/VIS spectra shown in Table IV also give an insight into the change of the structure as a consequence of chelation.

TABLE IV

Characteristic Bands of Ligand Cu(II) *and* Mn(II) *Complexes in UV/VIS Spectra*

Compound	*N,N'*-dimethylformamid	
	λ_{max}/nm	λ_{min}/nm
(1) $C_{15}H_{11}N_3O_2$	220, 265, *455*	242, 335
(2) $C_{15}H_{20}N_3O_2CuCH_3COO$	220, 265, 435, *520*	244, 348
(3) $C_{30}H_{20}N_6O_4Mn$	222, 246, *537*	275, 344, 432

From the data given in Table II and other analytical data, it was possible to deduce the ionic structure of the Cu(II) complex and the following structure was suggested:



III

In the literature[11,12,13] authors pointed out that the change in position of the stretching vibrations of the N—O group in pyridine *N*-oxide to the lower frequencies is a consequence of chelation.

The formation of the Me—O bond, that is the bond between metal and oxygen from the *N*-oxygen in the *N*-oxide group, weakens the N—O bond and the strength of the bond between metal and oxygen increases.

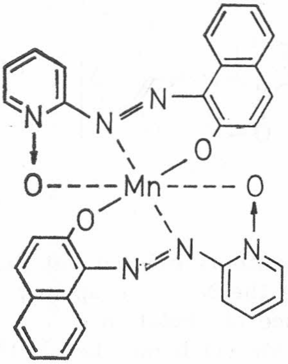
The position of the band at 1255 cm^{-1} in the IR spectrum of Cu(II) complex (N—O stretching vibrations) differs slightly from the same band in the spectrum of the ligand (1260 cm^{-1}). There is also a slight change in position of the band at 840 cm^{-1}, which is described as the N—O deformation vibrations[12]. This slight shift is a result of two opposite effects; one is caused by a change in the character of the band in the N—O group as a consequence of chelation, the other is similar to that which is manifested by the deformation vibrations of coordinated water. As both effects are almost equal, the result is a very slight shift in frequency.

Confirmation of the position of the stretching vibration band Cu—O at 455 cm^{-1} is found in the literature[10].

Table IV shows the bathochromic shift of complexing $\Delta \lambda = 65$ nm for Cu(II) related to λ_{max} UV/VIS spectra of the ligand (1). These data are in agreement with the data from the literature[14] and also suggest the possible 1 : 1 structure of this complex molecule.

The MS spectrum of the compound (2) does not show the molecular ion. The signal in the MS spectrum at *m/Z* 327 corresponds to the mass of the ligand and Cu, without the acetate ion. Because the elementary analysis, as well as IR spectrum, pointed to the existence of the acetate ion in the molecule (bands at 1745 cm^{-1} and 1285 cm^{-1}) the sample of Cu(II) complex was treated with KH_2PO_4 and after that, the mass spectrogram was recorded again at 513—523 K.

The signals at *m/Z* 60 and *m/Z* 45 confirm that the molecule of the complex contains the acetate ion. Other fragments in the spectrum are very similar to the fragments of the ligand itself. Although the molecular ion in the MS spectrum is not present, all mass spectral data confirm the proposed structure[2]. We could not determine whether the fourth coordination bond of Cu is vacant or occupied by a molecule of water. In the literature it has been found, with regard to similar complex molecules, that both cases can be applicable. The elemental analysis of the sample of Mn(II) complex and its greater solubility in unpolar solvents in relation to the solubility of the Cu(II) complex in the same solvents, points at the 1 : 2 structure of chelate molecule. On the basis of the most probable coordination number of Mn(6), a neutral structure of the molecule of Mn(II) complex of ligand (I) was suggested.



IV

The shifts of both bands in the IR spectrum of the sample; stretching vibration of N—O bond ν — 10 cm^{-1}, deformation vibration of N—O bond for ν — 15 cm^{-1} toward the lower frequencies in relation to the same bonds in IR spectrum of the ligand, can be explained in the same way as for the Cu(II) complex, i. e., by a change in the character of the π bond *N*-oxidic group as a result of chelation.

The presence of metal in the molecule confirms the bond at 455 cm^{-1}. It is evident from Table IV that the UV/VIS spectrum of the sample of the Mn(II) complex shows a bathochromic shift for $\Delta\lambda = 72$ nm in relation to λ_{max} of the ligand (1). Although the shift is slightly greater than that of the Cu(II) complex, it is still not a sufficient proof that two or more chelate rings were formed in the new molecule.

Mass spectrometry (MS) confirmed that this is a type of 1 : 2 complex molecule. The signal of the molecular ion is not present. However, at m/Z 551 there is an intensive signal which corresponds to the molecular ion minus two oxygen ($M^+ — O_2$) and the protonated signal of this fragment at m/Z 552. According to this, the suggested structure of the Mn(II) complex was proved to be correct.

By forming both complex molecules, the ligand 2-hydroxynaphthalene-1--azo-2'-pyridine *N*-oxide behaves as a threefunctional molecule.

Electrophoretic mobility measurements, carried out by means of a silicagel column and paper in different pH of NaAc/HAc buffer solutions (3.5—8.7), confirmed the formerly discussed molecular structures of the Cu(II) and Mn(II) metal chelates[15].

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SAŽETAK

Sinteza i molekulska struktura Cu(II) i Mn(II) kompleksa 2-hidroksinaftalen-1-azo-2'-piridin *N*-oksida

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U radu je prezentirana priprava kompleksa 2-hidroksi-naftalen-1-azo-2'-piridin *N*-oksida s Cu(II) i Mn(II) kationima. Primjenjujući analitičko-instrumentalne analize: IR, UV/VIS, NMR i MS detaljno je proučena struktura samog liganda kao i njegovih Cu(II) i Mn(II) kompleksa. Ustanovljeno je da se ligand ponaša kao tridentatna molekula.

Cu(II) kompleks stvara 1 : 1 helatnu molekulu s acetatnom skupinom kao anionom, dok Mn(II) kompleks pokazuje 1 : 2 tip strukture metal kompleksa.

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Prispjelo 20. lipnja 1980.