

Spectral and magnetic studies of complexes of Cu(II), Co(II), Mn(II) and Zn(II) with 2-hydroxy-1-naphthaldoxime

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Abstract. Cu(II), Co(II), Mn(II) and Zn(II) form 1 : 2 complexes with 2-hydroxy-1-naphthaldoxime. All the complexes are non-electrolytes in DMF and nitrobenzene. Square planar structures are assigned for Cu(II), Co(II) and Mn(II) complexes and tetrahedral structure for Zn(II) complex based upon electronic and room temperature magnetic measurements. IR studies reveal that the complexes are formed by the replacement of the hydrogen of the O-H group by the metal with the nitrogen atom of the oxime group coordinating to it.

Keywords. Spectral ; magnetic ; 2-hydroxy-1-naphthaldoxime.

1. Introduction

2-Hydroxy-1-naphthaldoxime has been extensively used for the determination of many metal ions (Mashima 1953 ; Gusev *et al* 1960 ; Raja Reddy 1969 ; Naidu and Naidu 1977, 1978). In view of its importance as an analytical reagent, it is desirable to study the physico-chemical aspects of the ligand and its metal complexes. The present communication deals with the preparation of copper(II), cobalt(II), manganese(II) and zinc(II) complexes of 2-hydroxy-1-naphthaldoxime and characterisation by analytical, molar conductance, spectral and magnetic studies.

2. Experimental

2.1. Preparation of complexes

Copper and cobalt complexes were prepared according to the procedure described by Mashima (1953). Manganese and zinc complexes were precipitated from an aliquot of the metal ion containing about 60 mg of the metal ion by adding a slight excess of the oxime solution (1% in rectified spirit) at pH 8.0-9.0 and 6.0-7.0 respectively, the precipitate is filtered, washed with hot water and dried *in vacuo*.

2.2. *Elemental analyses*

Microanalyses for carbon, hydrogen and nitrogen of the complexes were performed by the Australian Microanalytical Service, CSIRO, Melbourne, Australia.

2.3. *Determination of metal content in the complexes*

Known amounts of the metal complexes were decomposed with conc. HNO_3 , the excess nitric acid expelled by evaporation with conc. H_2SO_4 . The residue was cooled, dissolved in water and made up to a known volume in a volumetric flask. Copper was determined gravimetrically as cuprous thiocyanate and manganese, zinc and cobalt were determined by titration with EDTA using Erio-T as indicator for Mn and Zn and xylenol orange for Co (Vogel 1961).

2.4. *Physical measurements*

The molar conductance of the complexes in nitrobenzene and dimethyl formamide were measured with an Elico conductivity bridge using a dip type conductivity cell having a cell constant 0.482.

The IR spectra of the oxime and its chelates were recorded in the form of KBr pellet and in the range $4,000\text{--}400\text{ cm}^{-1}$ studied on Perkin-Elmer model 337 infrared spectrophotometer. Electronic spectra of the complexes in nujol mull were recorded using Unicam SP 700 spectrophotometer.

Magnetic susceptibility of the complexes at room temperature was determined by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Molar susceptibilities were corrected for diamagnetism of the constituent elements using Pascal's constants (Figgis and Lewis 1964).

3. Results and discussion

3.1. *Physical properties*

The copper, cobalt, manganese and zinc chelates are powders, the colours being light brown, orange red, dark green and white respectively. All are insoluble in water but soluble in nitrobenzene and dimethyl formamide. Copper and zinc complexes are insoluble in alcohols (methanol, ethanol, butanol and cyclohexanol), ketones (acetone, ethyl methyl ketone), chloroform, carbon tetrachloride, benzene, dioxane and tributyl phosphate. However, cobalt and manganese complexes are soluble in these solvents also. None of the complexes sublimed on heating. All the chelates are stable in air and non-hygroscopic.

All the chelates prepared exhibit 1:2 metal-ligand composition (table 1). Thermogravimetric, elemental analyses and IR studies revealed that copper and zinc complexes are anhydrous whereas manganese and cobalt complexes are hydrated.

Nitrobenzene and dimethyl formamide solutions of the complexes have low conductance values (table 1) in the range of 0.24–0.53 and 14.4–16.3 respectively indicating a non-electrolytic nature.

Table 1. Analytical, molar conductance and magnetic moment data of the complexes.

Complex	Colour	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Molar conductance (ν cm ²)		μ_{eff} (B.M.)
						DMF	Nitro-benzene	
$\text{Cu}(\text{C}_{11}\text{H}_8\text{O}_2\text{N})_2$	Light brown	14.5 (14.6)	60.8 (60.6)	3.7 (3.7)	6.4 (6.4)	14.4	0.38	1.74
$\text{Co}(\text{C}_{11}\text{H}_8\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$	Orange red	13.1 (13.1)	58.8 (58.8)	4.6 (4.5)	6.2 (6.2)	16.3	0.24	2.62
$\text{Mn}(\text{C}_{11}\text{H}_8\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$	Dark green	12.4 (12.3)	60.0 (59.3)	3.4 (4.5)	5.9 (6.3)	14.5	0.53	4.32
$\text{Zn}(\text{C}_{11}\text{H}_8\text{O}_2\text{N})_2$	White	15.1 (14.9)	60.1 (60.3)	3.7 (3.7)	6.4 (6.4)	14.4	0.34	Diamagnetic

Calculated values are given in parentheses.

3.2. Infrared spectra

In the infrared spectrum of 2-hydroxy-1-naphthaldoxime (table 2) there is no band at 3600 cm^{-1} indicating the absence of free $-\text{OH}$ group. The broad band with its centre at 3340 cm^{-1} present in the oxime may be attributed to the intramolecular hydrogen bonding of the type in which the phenolic OH group is bonded to the nitrogen of the $\text{C}=\text{NOH}$ group to give an average $\Delta\nu_{\text{O-N}}$ shift of about 260 cm^{-1} , suggesting that the hydrogen bonding in 2-hydroxy-1-naphthaldoxime is weaker than in salicylaldoxime and salicylideneanilines (Ramaswamy 1967; Ueno and Martell 1956).

The phenolic OH peak observed in the ligand at 3340 cm^{-1} was lowered to 3185 cm^{-1} in copper complex and shifted to higher frequency 3360 cm^{-1} in the zinc complex. This may be due to difference in geometry; copper forming a square planar complex and zinc a tetrahedral complex. The shift in the O-H peak frequency in the complexes compared to the ligand suggests that the chelation in complexes involves the participation of phenolic O-H. The elemental and thermogravimetric analyses showed that both manganese and cobalt complexes are hydrated. In the IR spectra of these complexes broad absorption vibrational modes in the range $3200\text{--}3500\text{ cm}^{-1}$ were observed indicating the presence of water in the complexes. A detailed examination of the IR spectra further showed that the cobalt and manganese complexes contain lattice water. In these complexes no new bands were observed at 800 cm^{-1} and $625\text{--}520\text{ cm}^{-1}$ region indicating the presence of lattice water (Nakamoto 1964; Speca *et al* 1973; Devoto *et al* 1975).

A strong band in the 1630 cm^{-1} region in the spectrum of the ligand appeared unchanged in almost all the complexes and is ascribed to the O-H deformation vibration. The $\nu_{\text{C-N}}$ band observed at 1590 cm^{-1} for the reagent appeared in the $1545\text{--}1530\text{ cm}^{-1}$ for the chelates. The shift of this band towards lower frequency in all the metal complexes suggests that coordination has taken place through the nitrogen of the oxime group. The large shift of $\nu_{\text{C-N}}$ frequency in the oxime from its normal value appears to be due to such factors as resonance, conjugation or coupling with $\text{C}=\text{C}$ vibrations and hydrogen bonding (Rao 1967; Ramaswamy *et al* 1967).

The absorption bands occurring at 1235 cm^{-1} and 930 cm^{-1} in the present oxime shifted to $1240\text{--}1250\text{ cm}^{-1}$ and $940\text{--}945\text{ cm}^{-1}$ regions in metal chelates may be attributed to the N-O stretching vibrations (Blinc and Hadzi 1958; Palm and Werbin 1953; Ramaswamy *et al* 1967; Hadzi 1956).

In view of the previous assignments and comparing the reagent spectrum with the spectra of the complexes, the intense bands observed in the $510\text{--}580\text{ cm}^{-1}$ and $470\text{--}490\text{ cm}^{-1}$ regions are assigned to M-N (Durig *et al* 1967; Prabhakaran and Patel 1969; Biradar *et al* 1975) and M-O (Djordjevic 1961; Behnke and Nakamoto 1967) vibrations respectively. There is little variance in the $\nu(\text{M-O})$ band in the case of 2-hydroxy-1-naphthaldoxime chelates suggesting that the same coordination number is prevailing in all the complexes (Clark 1965).

3.3. Electronic spectra

The electronic spectrum of copper-2-hydroxy-1-naphthaldoxime complex showed absorption peak at 15600 cm^{-1} . This band is assigned to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition

Table 2. Important IR absorption frequencies (cm^{-1}) of reagent and its metal chelates and their assignments.

Oxime	Copper chelate	Cobalt chelate	Manganese chelate	Zinc chelate	Assignments
3340 br	3185 br	3150-3250 br	3250-3500 br	3360 br	O-H stretching
1630 s	1635 s	1630 s	1630 s	1620 s	O-H deformation
1590 s	1545 s	1540 s	1540 s	1530 s	C=N stretch coupled with aromatic C=C stretching
1295 m	1295 m	1290 s	1290 m	1280 m	Phenolic C-O + N-O stretching
1235 s	1240 m	1242 s	1250 s	1240 s	N-O stretching
930 s	940 s	945 s	940 s, br	940 br s	
1095 s	1015 m	1029	1025 s br	1010 s	C-O stretching
	530 s	560 s		580 m	M-N stretching
	510 m	520 s	520 w	520 s	
	480 s	490 s	490 m	470 s	M-O stretching

s = strong; br = broad; m = medium; w = weak.

of square planar copper(II) by analogy with the spectra of other square planar copper(II) species (Sacconi and Ciampolini 1964; Fackler *et al* 1963; Lever 1968; Naidu and Naidu 1979). The band observed at 20000 cm^{-1} is attributed to ${}^2B_{1g} \rightarrow {}^2E_g$ transition. The electronic spectrum of manganese-oxime complex is of little value for identification of the stereochemistry, since it showed only very weak forbidden transitions due to masking by strong charge transfer bands.

3.4. Magnetic properties

The values of magnetic moments (μ_{eff}) for the complexes are given in table 1. The magnetic moment value of copper-oxime complex suggests square planar geometry and is supported by the electronic spectral data. The magnetic moment of 2.62 B.M. for cobalt(II) complex indicates its planarity (Lever *et al* 1963; Burger *et al* 1966; Graddon and Mockler 1968; Syamal and Ghanekar 1978). The manganese complex showed a magnetic moment of 4.32 B.M. suggestive of a square planar structure with partial spin pairing (Figgis and Nyholm 1959; Figgis 1976; Srivastava *et al* 1975). Zinc(II) ion has a d^{10} configuration and all the complexes are diamagnetic. The present complex was also found to be diamagnetic and hence a tetrahedral structure can be assigned for the complex.

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