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Studies on Spectral Properties of Co(II), Ni(II) and Cu(II) Complexes with Bis-Acenaphthenequinonedioxime

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A series of complexes of the type $[M(HL)_2]$ [M = Co(II), Ni(II) and Cu(II) have been prepared by treating ethanolic metal salt solution with the solution of acenaphthenequinonedioxime in tetrahydrofuran. When solutions of these complexes were treated with ammonia or pyridine, another series of complexes of the type $[M(HL)_2X_2]$ were obtained. The complexes were characterised by elemental analysis, molar conductivity, electronic absorption spectra and infrared spectra. On the basis of experimental data former series was found to be square planar in geometry whereas the latter one to be octahedral.

INTRODUCTION

Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals[1–5]. A large number of these complexes containing both transition and non-transition metal ions and a variety of oxime ligand systems have been reported [6–9]. It is our intention here to study Co(II), Ni(II) and Cu(II) complexes with acenaphthenequinonedioxime.

EXPERIMENTAL

Chemicals used were mainly from BDH. First of all acenaphthenequinonedioxime was prepared from acenaphthene by the literature dioxime method described earlier[10].

Hydroxylamine hydrochloride (7.5 g) dissolved in minimum volume of water was neutralised with solid sodium bicarbonate by adding it portionwise. To this neutralised solution of hydroxylamine was added acenaphthenequinone (9 g) suspended in methanol portionwise in 15 min. The reaction mixture was then refluxed on water bath for 1 h when within 15 min a yellow crystalline precipitate was obtained. It was cooled, filtered, washed with methanol-water mixture (1 : 1), dried and crystallised from tetrahydrofuran, m.p. 223 ± 2°C (Fig. 1).

Bis-acenaphthenequinone dioximato Ni(II) Complex $[Ni(HL)_2]$

An ethanolic solution of Ni(II) dibromide hexahydrate (0.01 mol) was treated

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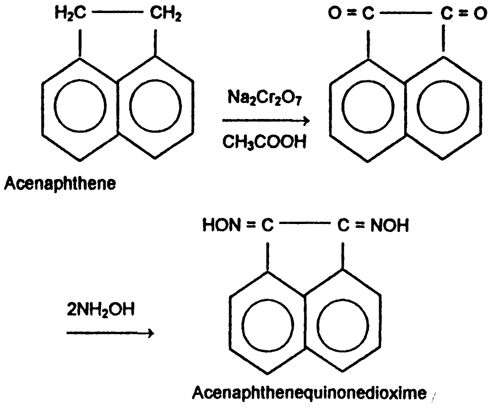


Fig. 1

with ligand (0.02 mol) dissolved in minimum volume of ethanol. The mixture was heated under reflux over a hot water bath for 3 h when a blue precipitate of Ni(II) complex was obtained. The precipitate was filtered and washed with cold water, followed by methanol and ether and dried in vacuum.

TABLE-1

SALIENT FEATURES OF INFRARED ABSORPTION SPECTRA (cm^{-1})

Sl. No.	Complexes	ν(O—H)	ν(C—N) acemethine	ν(N—O)	ν(M—N)
1.	Ligand	3250s	1700s	1120s	650 m
2.	$[Co(HL)_2]$	3240b	1610m	1110s	640 m
3.	$[Co(HL)_2(NH_3)_2]$	3235b	1605m	1115s	645 m
4.	$[Co(HL)_2(Py)_2]$	3240b	1600m	1110s	650 m
5.	$[Ni(HL)_2]$	3240b	1605m	1115s	650 m
6.	$[Ni(HL)_2(NH_3)_2]$	3235b	1610m	1110s	640 m
7.	$[Ni(HL)_2(Py)_2]$	3245b	1605m	1115s	645 m
8.	$[Cu(HL)_2]$	3245b	1605m	1110s	650 m
9.	$[Cu(HL)_2(NH_3)_2]$	3240b	1615m	1115s	640 m
10.	$[Cu(HL)_2(Py)_2]$	3245b	1610m	1110s	650 m

For the preparation of other complexes, metal salts dissolved in minimum volume of ethanol were treated with ligand solution dissolved in ethanol in the ratio 1 : 2. Standard procedures were adopted for obtaining physio-chemical data. Analysis agreed well with proposed formulations (Table-2).

TABLE-2
COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRAL AND CONDUCTIVITY DATA OF METAL COMPLEXES OF ACENAPHTHENONEQUINONE DIOXIME

Complexes (Colour)	% Analysis found (Calcd.)				μ_{eff} (B.M.)	λ_{max} (electronic) cm^{-1}	Λ_m ohm^{-1} cm^{-1} mol^{-1}
	M	N	H	C			
$[Co(HL)_2]$ (Green)	12.22 (12.27)	11.59 (11.64)	2.89 (2.91)	59.81 (59.88)	2.10	21000	11
$[Co(HL)_2(NH_3)_2]$ (Red)	11.39 (11.46)	16.27 (16.31)	3.83 (3.88)	55.86 (55.92)	4.70	15500	14
$[Co(HL)_2(Py)_2]$ (Black green)	9.18 (9.23)	13.10 (13.15)	3.69 (3.76)	63.78 (63.85)	4.90	15300	17
$[Ni(HL)_2]$ (Blue)	12.19 (12.21)	11.60 (11.65)	2.88 (2.91)	59.86 (59.91)	2.95	24000	16
$[Ni(HL)_2(NH_3)_2]$ (Yellow)	11.36 (11.41)	16.28 (16.32)	3.84 (3.89)	55.91 (55.96)	2.85	23500	15
$[Ni(HL)_2(Py)_2]$ (Red yellow)	9.14 (9.19)	13.10 (13.15)	3.71 (3.76)	63.74 (63.81)	2.86	23500	13
$[Cu(HL)_2]$ (Dark green)	12.97 (13.08)	11.48 (11.53)	2.82 (2.88)	59.28 (59.32)	1.79	19900	12
$[Cu(HL)_2(NH_3)_2]$ (Green)	12.19 (12.22)	16.09 (16.17)	3.81 (3.85)	55.39 (55.44)	1.90	15100	18
$[Cu(HL)_2(Py)_2]$ (Green)	9.81 (9.87)	12.98 (13.05)	3.69 (3.73)	63.34 (63.40)	2.00	15000	20

RESULTS AND DISCUSSION

Infrared Spectra

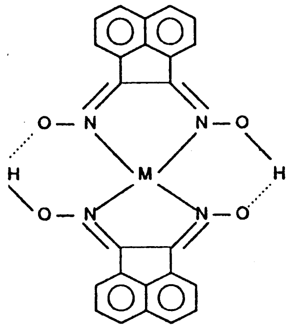
Infrared spectra of the complexes of the type $[M(HL)_2]$, M = Co(II), Ni(II) and Cu(II), H_2L = acenaphthenequinone dioxime, H = dissociable oximato proton and $[M(HL)_2X_2]$ [X = NH_3 or pyridine] have been recorded in the frequency region 4000–600 cm^{-1} and vibrational bands of structural significance are recorded in Table-1. The spectra have been analysed for elucidation of their structure and bonding. Although the infrared spectra of the complexes are quite complex, structurally important vibrational bands such as O—H stretching, N—O stretching and C—N stretching are quite distinguishable and provide unequivocal evidences concerning the nature of bonding of the ligands with the metal ions. Apart from this, there has been found similarity in spectra indicating similarity in structures and mode of coordination in the complexes.

The salient features of absorption frequencies of ligand and complexes are summarised in Table-1. The data indicate that the spectra of the complexes indicate the lowering of ν(C═N) from 1700 cm^{-1} to 1610 cm^{-1}. The ν(O—H) in the ligand appears at 3250 cm^{-1} as sharp and intense band but in the spectra of the complexes it has broadened with reduced intensity indicating intramolecular hydrogen bonding. The ν(N—O) band remains almost unperturbed indicating non involvement of oxygen atom of N—O group of oxime in coordination to the metal atom. A sharp band at 650 cm^{-1} in the spectra of the complexes which is not present in the spectrum of the ligand is assigned to ν(M—N).

The salient features of electronic spectra as well as magnetic moment data are summarised in Table-2. The data indicate complexes of the type $M(HL)_2$ to be square planar whereas those of the type $[M(HL)_2X_2]$ are expected to be octahedral.

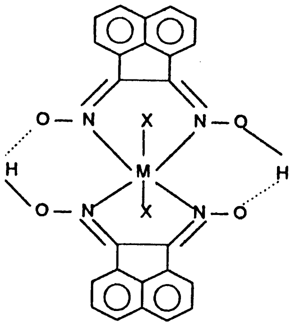
Conductivity of the complexes was measured in the slovent DMSO and all the complexes were found to be non-electrolytic in nature giving conductivity values in the range 10–20 ohm^{-1} cm^2 mol^{-1}. The conductivity data also support the structural assignment on the basis of magnetic and spectral studies.

The result of the investigation of spectral features so far discussed strongly supports the complex as shown in Figs. 2 and 3.



M = Co(II), Ni(II) and Cu(II)

Fig. 2



X = NH_3 or Pyridine
M = Co(II), Ni(II) and Cu(II)

Fig. 3

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