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Study of Transition Metal Complexes of Some Oximic Ligands

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Oximic ligands were synthesized using 2-hydroxy-1-napthaldehyde and 2,4-dihydroxyacetophenone. Cobalt(II), nickel(II), copper(II) complexes of oximes were synthesized having metal to ligand stoichiometry 1 : 2. The ligands and complexes were diagnosed for their analytical parameters and various spectral features. The structures of the complexes were proposed on the basis of electronic absorption spectra and magnetic susceptibility data.

INTRODUCTION

The oximes act as excellent bidentate ligands with nitrogen and oxygen as donor atoms. The oximes can coordinate with transition metal elements with different structural geometry. The variance in the structural geometry can be related with different transitions on the ligand molecule. The structural diagnosis of different transition metal oximes can be evaluated from spectral properties.

Literature survey reveals that transition metal complexes generally crystallize with octahedral, tetrahedral or square-planar geometries. The ligands have important analytical applications in the determination of metal concentration in natural products[1,2]. Some of these oximic ligands are also reported to possess catalytic and biological activity. It is therefore interesting to diagnose structural chemistry of certain selected transition metal oximes. The oximic ligands are extensively used to investigate structural configuration of Co(II), Ni(II), and Cu(II). However, oximic complexes of these metals are not reported systematically. An attempt was made to synthesize the oximic ligands derived from 2-hydroxy-1-napthaldehyde and 2,4-dihydroxyacetophenone. Co(II), Ni(II), and Cu(II) complexes of these ligands were prepared and characterized for their spectral features.

EXPERIMENTAL

The oximic ligands L_1 and L_2 were synthesized from 2-hydroxy-1-napthaldehyde and 2,4-dihydroxyacetophenone respectively using oximation reaction[3]. The equimolar solution of aldehyde in alcohol was mixed with aqueous solution of hydroxylamine hydrochloride. The solution was buffered with sodium acetate and refluxed for 4–5 h on water bath. The solution was acidified with acetic acid after cooling and filtered to get oxime. The crude oximes were crystallized from their aqueous alcoholic solutions.

TABLE-1
ANALYTICAL AND PHYSICO-CHEMICAL PARAMETERS OF LIGANDS AND METAL COMPLEXES

Ligands/ Complexes	Colour	m.w.	Molar conductivity $\times 10^{-3}$ siemens	Elemental analysis % found (calcd.) C	H	N	M	$\mu_{eff.}$ (B.M.)
$C_{11}H_9O_2N$ (L_1)	Pale Brown	187.00	2.120	70.04 (70.59)	4.82 (4.81)	6.92 (7.49)	—	—
$Co(L_1)_2$	Brown	430.93	3.500	60.97 (61.30)	3.72 (3.71)	6.17 (6.50)	13.14 (13.61)	2.14
$Ni(L_1)_2$	Green	430.69	2.258	60.83 (61.30)	3.69 (3.71)	5.77 (6.50)	13.75 (13.63)	Dia-magnetic
$Cu(L_1)_2$	Buff	435.55	2.088	60.37 (60.61)	3.68 (3.67)	6.61 (6.43)	13.91 (14.59)	1.48
$C_8H_9O_3N$ (L_2)	Pale Brown	167.00	1.938	58.16 (57.49)	5.48 (5.39)	8.11 (8.38)	—	—
$Co(L_2)_2$	Reddish Brown	390.93	3.800	48.60 (49.11)	4.11 (4.09)	6.95 (7.16)	15.02 (15.07)	2.56
$Ni(L_2)_2$	Green	390.69	2.358	48.76 (49.14)	4.13 (4.10)	6.81 (7.17)	15.06 (15.02)	2.94
$Cu(L_2)_2$	Brown	395.55	2.260	47.60 (48.54)	3.98 (4.04)	6.78 (7.08)	15.48 (16.07)	1.78

TABLE-2
SALIENT FEATURES OF SPECTRAL DATA

Ligands/ Complexes	IR spectral Data (cm^{-1}) ν(—OH)	ν(C=N)	ν(M—O)	ν(M—N)	Electronic absorption spectral data (cm^{-1})
L_1	3335(s)	1633(s)	...	...	28288 29326 32015
$Co(L_1)_2$	3432(b)	1620(s)	419	567	36297
$Ni(L_1)_2$	3432(b)	1615(s)	426	570	24722 32000 38268
$Cu(L_1)_2$	3407(s)	1615(s)	422	535	27137 31546 38388
L_2	3372(b)	1646(s)	...	...	33333 37175
$Co(L_2)_2$	3437(b)	1617(s)	412	642	37878
$Ni(L_2)_2$	3446(b)	1624(s)	405	642	28694 32626
$Cu(L_2)_2$	3457(b)	1624(s)	458	643	30864 36563

Co(II), Ni(II) and Cu(II) complexes of 2-hydroxy-1-napthaldehyde and 2,4-dihydroxyacetophenone were prepared from their respective acetates. The pH of reaction mixture was mintained between 5 and 6 and refluxing was carried out for 2–3 h. After reflux, the solution was cooled whereby metal complexes precipitated out. Each of these complexes was crystallized and analyzed for various physico-chemical parameters. Each of these complexes was also diagnosed for various spectral and magnetic features. IR spectra were recorded on Jasco 410-IR spectrophotometer. The electronic spectra of these complexes as well as that of ligands were recorded on UV-VIS spectrophotometer supplied by Shimadzu Corporation. The magnetic susceptibilities of these complexes were established using Gouy balance method. The results of these experiments are illustrated in Tables 1 and 2.

RESULTS AND DISCUSSION

The analytical data in Table-1 indicate that the ligands are pale brown in colour, while Co(II) complexes are reddish brown in colour. Similarly Ni(II) complexes are green in colour and Cu(II) complexes are either buff or brown in colour. The chemical compositions of these complexes suggest metal to ligand ratio 1 : 2. Each of these complexes is anhydrous in nature. Various polar and non-polar solvents were tried to find the solubility of these complexes. The complexes were freely soluble in DMSO while sparingly soluble in methanol, carbon tetrachloride, nitrobenzene, chloroform, etc. The molar conductivity of these complexes was determined from their DMSO solutions, which ranges between 1.94 and 3.5×10^{-3} Siemens. The extremely low values of molar conductivities indicate that these complexes are non-electrolyte in nature[4].

The room temperature magnetic moments were determined to investigate their magnetic behaviour. Both the ligands were diamagnetic in nature, hence any magnetic moment exhibited by the complexes is due to electronic distribution in central metal ion. Cobalt complexes of L_1 and L_2 have magnetic moment of 2.14 B.M. and 2.56 B.M. These magnetic moments are in good agreement with those reported for Co(II) salicylaldoxime by Nishikawa and Yamada, which according to them are diagnostic of low spin square-planar Co(II).[5] $Ni(L_1)_2$ complex is diamagnetic in nature while $Ni(L_2)_2$ complex has 2.94 B.M. magnetic moment. Literature survey reveals that tetrahedral or pseudo-tetrahedral orientation in Ni atom may lie between 2.90 to 3.21 B.M. This suggest the presence of two unpaired electron in Ni atom.[6] The diamagnetic $Ni(L_1)_2$ is having square-planar orientation.[7] The copper complexes of these ligands have magnetic moment 1.48 B.M. and 1.78 B.M. respectively. The subnormal values of magnetic moment for $Cu(L_1)_2$ may be due to the large separation between ground state component of $^2B_{1g}$ and T_{2g} terms.[7]

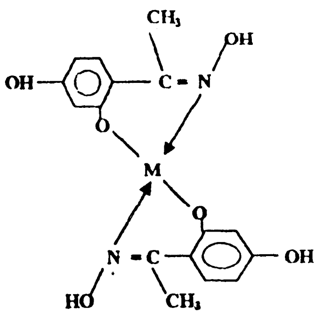
The complexes with subnormal values were assigned square-planar geometry. Similarly $Cu(L_2)_2$ exhibits magnetic moment characteristic of spin only value for square-planar configuration.[8]

The salient features of electronic absorption spectra for these complexes are summarized in Table-2. The spectra of Co(II) complexes exhibit one single band pointed in the region of 37000 cm^{-1}. This also can be assigned to charge transfer transition. The d–d transitions of these complexes could not be observed with certainty and probably broadness of charge transfer transition overlaps with these weak d–d transitions. Malcolm and Gerloch[9] have reported that d–d transitions in divalent complexes are 1000 times weaker than charge transfer transitions. The Ni complexes exhibit intra-ligand $\pi \rightarrow \pi^*$ transitions at 32000 and 32626 cm^{-1} respectively. The charge transfer transitions can also be assigned to weak absorption bands pointed at 24,722 and 28,694 cm^{-1} respectively. Lever *et. al.*[10] assigned square-planar geometry to Ni complexes with such absorption pattern.

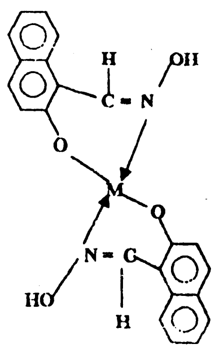
The Cu(II) complexes of ligands L_1 and L_2 show typical intra-ligand $\pi \rightarrow \pi^*$ transitions in the range 36,000 cm^{-1} and 38,400 cm^{-1}. The charge transfer transition for $Cu(L_1)_2$ is marked at 27,137 cm^{-1} while that for $Cu(L_2)_2$ at 30,864 cm^{-1} respectively. Agarwal *et. al.*[7] assigned square-planar geometry to these complexes.

The salient features of IR spectrum of ligands and complexes are summarized in Table-2. Ligands show characteristic broad band in the range 3,400 to 3,300 cm^{-1} due to free phenolic —OH group. A sharp band due to ν(>C—O) was observed in the range 1300–1200 cm^{-1}. The strong and sharp band between 1650 and 1630 cm^{-1} can be assigned to ν(C=N). In the IR spectra of the complexes nature of the —OH band is found to be considerably changed. It broadens and shifts to higher frequency. This may be because the phenolic oxygen is involved in bonding with central metal ion. And the band observed may be due to free oximino —OH.[11] Further shifting of ν(C=N) to lower frequency around 1615 cm^{-1} indicates coordination of oximino nitrogen with central metal ion. The strong bands around 1270 cm^{-1} and 880 cm^{-1} assigned to ν(>N—O) in ligands shifted to lower side (*ca.* 30 cm^{-1}) in the complexes support the above statement[11]. Two new frequencies in the range 650–550 cm^{-1} and 450–400 cm^{-1} were observed in IR spectra of complexes, which can be assigned to ν(M—N) and ν(M—O)[12] respectively.

On the basis of above discussions the following structures can be assigned for the complexes.



STRUCTURE (I)



STRUCTURE (II)

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