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X-Ray Diffraction Studies of Co(II) Complexes with Hydroxy Oximes

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Oximic ligands were synthesized using 2-hydroxy-1-naphthaldehyde and 2,4-dihydroxyacetophenone. Co(II) complexes of these oximes were synthesized having metal : ligand stoichiometry 1 : 2. The ligands and the complexes were diagnosed for their analytical parameters and various spectral features. The structures of these complexes were proposed on the basis on electronic absorption spectra, magnetic susceptibility. The lattice parameters were calculated using X-ray powder diffraction data.

INTRODUCTION

Hydroxy oximes act as excellent bidentate ligands with nitrogen and oxygen as donor atoms. A number of complexes of hydroxy oximes with transition metal ions are known.[1] 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 geometry.[2–4] The oximes have important analytical applications in the determination of metal concentration from natural products.[5] Some of these oximic ligands are also reported to possess catalytic and biological activity. Cobalt also plays an important role among biologically active ions.[6, 7] It is therefore interesting to diagnose the structural chemistry of Co(II) complexes with oximes. In the past, a number of attempts were made to investigate the structural configuration of Co(II) complexes. However, oximic complexes of this were not reported systematically. An attempt was made to synthesize the oximic ligands derived from 2-hydroxy-1-naphthaldehyde and 2,4-dihydroxyacetophenone. Cobalt(II) complexes of these ligands were prepared and characterized for their spectral features.

EXPERIMENTAL

The oximic ligands HL^1 and HL^2 were synthesized from 2-hydroxy-1-naphthaldehyde and 2,4-dihydroxyacetophenone respectively using oximation reaction. Around 16–17 g (0.2 mole) aldehyde or ketone in alcohol was mixed with (1 : 1.3 mole) excess of 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 10% acetic acid solution and ice was added to obtain oxime. The crude oxime was crystallized from aqueous alcoholic solutions.

Cobalt(II) complexes of 2-hydroxy-1-naphthaldehyde oxime and 2,4-dihydroxyacetophenone oxime were prepared from their respective acetates. The pH of reaction mixture was maintained between 5 and 6 and reflux 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 physicochemical 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 those of ligands were recorded on UV-visible 2100 spectrophotometer supplied by Shimadzu Corporation, Japan. The magnetic susceptibility of these complexes was established using Gouy balance method.

The powder diffraction data for both the complexes were obtained using X-ray diffractometer supplied by Shimadzu Corporation, Japan, Model No. XRD-6000. Cu-Kα_1 radiation (1.5404 Å) was used with nickel filter. The X-rays were generated at a voltage of 30 kV and 20 mA. The indexing was done using computer software (HCL Busy Bee AT$^+$) by least square method.

RESULTS AND DISCUSSION

Both the complexes of Co(II) are reddish brown in colour. The elemental analyses of these complexes are in good agreement with calculated values based on 1 : 2 metal to ligand stoichiometry. Both the complexes are anhydrous in nature and show appreciable stability at room temperature. Various polar and non-polar solvents were tried to find solubility of these complexes. The complexes were found to be insoluble in methanol, carbon tetrachloride, nitrobenzene, chloroform, but sufficiently soluble in DMSO. The molar conductivity of these complexes was determined from their solutions in DMSO, which was found to be 3.5 and 3.8×10^{-3} siemens. The extremely low values of molar conductivity indicate that these complexes are non-electrolytic in nature.[8] The room temperature magnetic moments were determined to investigate their magnetic behaviour. Both ligands were diamagnetic in nature, hence any magnetic moment exhibited by the complexes is due to electronic distribution around the central metal ion. Co(II) complexes of 2-hydroxy-1-naphthaldehyde oxime Co$(L^1)_2$ and 2,4-dihydroxyacetophenone oxime Co$(L^2)_2$ have the magnetic moments of 2.14 B.M. and 2.56 B.M. respectively. These magnetic moments are in good agreement with those reported for Co(II) salicylaldoxime by Jorgenson and Heathcock[9], which according to them are diagnostic of low spin square-planar Co(II) complexes. Analytical findings for both the complexes are reported in Table-1.

TABLE-1
ANALYTICAL AND PHYSICO-CHEMICAL PROPERTIES OF LIGANDS AND THEIR COBALT(II) COMPLEXES

Ligands/ complexes (colour)	m.w.	Molar conductivity ($\times 10^{-3}$ siemens)	Magnetic susceptibility (B.M.)	Elemential analysis % observed (calculated)			
				C	H	N	Co
$C_{11}H_9NO_2(L^1)$	187.00	2.120	–	70.04	4.82	6.92	–
(Pale brown)				(70.59)	(4.81)	(7.49)	
$Co(L^1)_2$	430.93	3.500	2.14	60.97	3.72	6.17	13.14
(Brown)				(61.30)	(3.71)	(6.50)	(13.61)
$C_8H_9NO_3(L^2)$	167.00	1.938	–	58.16	5.48	8.11	–
(Pale brown)				(57.49)	(5.39)	(8.38)	
$Co(L^2)_2$	390.93	3.800	2.56	48.60	4.11	6.95	15.02
(Reddish brown)				(49.11)	(4.09)	(7.16)	(15.07)

For the Co(II) complex of 2-hydroxy-1-naphthaldehyde oxime complex, the three absorption bands were observed at 23,809 cm^{-1}, 28,169 cm^{-1} and 36,300 cm^{-1}. The band appearing at 36,300 cm^{-1}can be assigned to intraligand $\pi \rightarrow \pi^*$ transition.

The two maxima at 28,169 cm^{-1} and 23,809 cm^{-1} can be assigned to metal → ligand charge transfer transitions $^2A_{1g} \rightarrow {}^2E_g$, $^2A_{1g} \rightarrow {}^2B_{2g}$ and $^2A_{1g} \rightarrow {}^2E_{2g}$ respectively.[10]

The d-d transitions in the absorption spectra could not be observed properly, may be due to the overlapping of charge-transfer transitions which are 1000 times stronger than d-d transitions.[11] It can be easily observed that $Co(L^2)_2$ complex exhibits similar type of pattern. The band observed around 37,383 cm^{-1} can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions. The bands observed at 28,571 cm^{-1} can be assigned to metal to ligand charge transfer transitions. The observed spectral pattern suggests square-planar geometry for Co(II) complexes.

For getting correct idea about the coordination behaviour, reflectance spectra of the complexes were recorded using $BaSO_4$ as diluting media. The reflectance spectra help in assigning some d-d transitions, which could not be observed in absorption spectra of the complexes; as the spectra are recorded in solid media, any effect of solvent, if taking place, is eliminated. The reflectance spectra of $Co(L^1)_2$ complex exhibits three transition bands around 11,217 cm^{-1}, 11,448 cm^{-1} and 16,722 cm^{-1} which can be assigned to d-d transitions. Furthermore the band at 19,084 cm^{-1} is characteristic band for Co(II) complexes in low-spin square environment.[12] The diffused reflectance spectra of $Co(L^2)_2$ similarly show the bands at 11,217 cm^{-1}, 11,428 cm^{-1} and 15,798 cm^{-1} which are due to d–d transitions. The broad band observed at 20,618 cm^{-1} is characteristic of square-planar configuration for Co(II) complexes.

In the IR spectra of $\mathrm{Co(L^1)_2}$ and $\mathrm{Co(L^2)_2}$ complexes the broad and strong bands observed at 3432 and 3420 cm^{-1} which can be assigned to intra-ligand hydrogen bonded —OH group. These bands were observed at 3335 and 3372 cm^{-1} in ligand due to intermolecular hydrogen bonding *via* oximino OH. These bands become broad and shift towards higher frequency as compared to their position in the spectrum of ligand. This may be due to weakening of the hydrogen bond in the complexes as compared to that of ligands.[1]

In the IR spectrum of oximes, the bands due to ν(C═N) were observed at 1633 and 1645 cm^{-1} which were found to be shifted to lower frequency (*ca.* 13 cm^{-1}) in the IR spectrum of complexes.[13] Furthermore, the band assigned to ν(N—O) at 937 cm^{-1} in the IR spectrum of oxime is shifted to higher frequency by about 15 cm^{-1} in the spectrum of complex. This indicates that ligand coordinates with central metal atom *via* oximino nitrogen.[14] The band observed due to intra-molecularly hydrogen bonded OH at 3049 cm^{-1}, in the IR spectrum of oxime, is absent in the spectrum of complex. This shows deprotonation of phenolic OH. The ν(C—O) band, observed at 1160 cm^{-1} in the spectrum of oxime, is found to be shifted to higher frequency by 30 cm^{-1} in the spectrum of the complex. This supports the bonding *via* phenolic oxygen. In addition to this two new bands at 566 cm^{-1} and 419 cm^{-1} appear in the spectrum of complex, which can be assigned to ν(Co—N) and ν(Co—O).[15] Above observation indicates that the ligand is coordinated to central metal atom through oximino nitrogen and phenolic oxygen atoms. Electronic absorption spectral data and salient features of IR spectra are reported in Table-2.

TABLE-2

UV-VIS AND IR SPECTRAL PROPERTIES OF LIGANDS AND COMPLEXES

Ligands/ complexes	Electronic absorption spectral data (cm^{-1})		IR spectral data (cm^{-1})			
	UV-VIS	Reflectance	ν(—OH)	ν(═C═N)	ν(Co—O)	ν(Co—N)
L^1	29,326	11,173	3335b	1633s	–	–
	32,015	28,248				
	38,610	40,000				
$\mathrm{Co(L^1)_2}$	36,300	11,217	3432b	1620s	419m	566m
	28,169	11,448				
	23,809	16,722				
		19,084				
L^2	33,333	11,364	3372b	1645s	–	–
	37,175	32.258				
		36,364				
$\mathrm{Co(L^2)_2}$	37,383	11,217	3420b	1605s	461m	640m
	33,333	15,798				
	28,571	20,618				
		26,990				

Both the complexes were examined for their powder diffraction data. The nature of the spectra indicates low crystallinity of the complexes. The major refluxes were used to calculate crystal lattice parameters. The observed values are reported in Tables 3 and 4. The system was found to be hexagonal with space group P_{mmm} and 24 molecules per unit cell for both the complexes. Very large volume of the order of $10,000 \times 10^{-24}$ $(Å)^3$ is consistent with the Z values calculated from densities. The observed values of densities of complexes are 1.5971 g cm^{-3} and 1.3568 g cm^{-3}, while the calculated values are 1.5934 g cm^{-3} and 1.3507 g cm^{-3} respectively. These values are in very well agreement with each other reflecting accuracy in assigning the correct crystal system and indexing it. The standard deviations observed for $Co(L^1)_2$ and $Co(L^2)_2$ complexes are 1.7% and 0.7% respectively which are within permissible limits.

TABLE-3

X-RAY POWDER DIFFRACTION DATA FOR $Co(L^1)_2$ COMPLEX

a (Å) = 22.3503 ± 0.1028
b (Å) = 22.3503 ± 0.0958
c (Å) = 25.0632 ± 0.1076
$\alpha = 90°$
$\beta = 90°$
$\gamma = 120°$

Volume = 10842.62×10^{-24} $(Å)^3$
$Density_{obs}$ = 1.5971 g/cm^3
$Density_{cal}$ = 1.5834 g/cm^3
Z = 24
Space group = P_{mmm}
Crystal system = Hexagonal

Powder pattern	d_{obs}	d_{cal}	Relative intensity	h	k	l
1.	12.2980	12.5316	93.70	0	0	2
2.	7.2759	7.4859	100.00	3	–1	0
3.	6.0689	5.9612	35.00	1	0	4
4.	4.5842	4.5736	14.80	2	–1	5
5.	4.1229	4.1351	18.40	3	–1	5
6.	3.6838	3.6846	18.60	6	–3	1
7.	3.4425	3.4435	42.30	6	–1	1
8.	3.3542	3.3499	61.00	6	–1	2
9.	3.0451	3.0399	28.50	6	–1	4
10.	2.5066	2.5063	6.10	0	0	10
11	2.3451	2.3409	32.00	9	–3	3
12.	2.0300	2.0291	12.70	10	–1	0

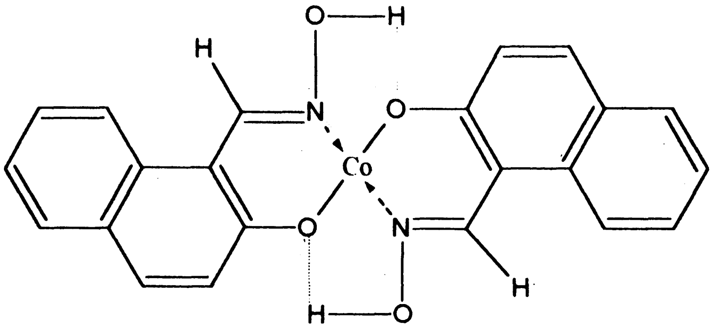
TABLE-4

X-RAY POWDER DIFFRACTION DATA FOR $Co(L^2)_2$ COMPLES

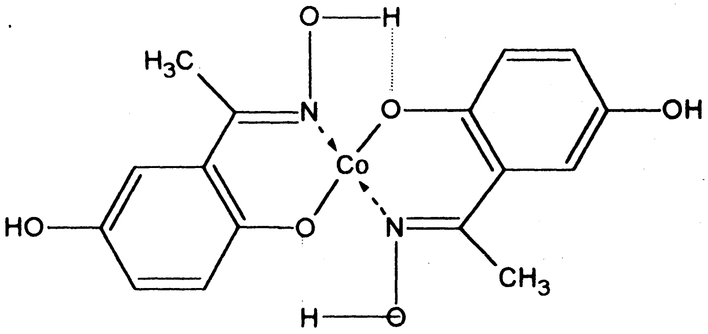
a (Å) = 22.2635 ± 0.0567	Volume = $11{,}530.62 \times 10^{-24}$ (Å)^3
b (Å) = 22.2635 ± 0.0528	Density$_{obs}$ = 1.3568 g/cm^3
c (Å) = 26.8619 ± 0.0898	Density$_{cal}$ = 1.3507 g/cm^3
$\alpha = 90°$	Z = 24
$\beta = 90°$	Space group = P_{mmm}
$\gamma = 120°$	Crystal system = Hexagonal

Powder pattern	d_{obs}	d_{cal}	Relative intensity	h	k	l
1.	10.3517	10.2837	9.7	1	1	1
2.	9.1060	9.0737	100.0	2	0	1
3.	8.5645	8.5707	47.8	2	–1	2
4.	5.2293	5.2446	20.5	3	1	1
5.	5.1260	5.1418	23.9	4	–2	2
6.	4.3436	3.3243	10.2	3	–1	5
7.	3.5085	3.5166	9.5	2	4	2
8.	3.3682	3.3750	6.2	2	4	3
9.	2.9660	2.9760	19.8	3	0	8
10.	2.2018	2.2041	11.3	5	0	10

On the basis of above discussions it can be suggested that cobalt(II) complexes are having low spin square planar geometry. The bonding in the complexes can be shown as.



Structure 1: $Co[L^1]_2$



Structure 2: Co$[L^2]_2$

Fig. 1 Structures of Co(II) Complexes

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