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Cobalt(II), Nickel(II) and Copper(II) Complexes of 1-Hydroxy-2-Naphthyl(4-X-Styryl) Ketoneoximes

P. THARMARAJ*, C.D. SHEELA† and C. NATARAJAN
Department of Chemistry,
Thiagarajan College (Autonomous), Madurai-625 009, India

Metal complexes of the type ML_2 [M = Co(II), Ni(II), Cu(II); L = 1-hydroxy-2-naphthyl(4-X-styryl)ketoneoximes (HNXSKOx), (X = H, Me, MeO)] have been synthesized. All the chelates are anhydrous. The copper complexes possess *trans*-square-planar geometry and the nickel and cobalt complexes have low-spin *trans*-square-planar configuration. As the conjugation of C═N with Ph—C═C is inhibited, the basic nature of oximino nitrogen is not affected. The strong M—N σ-bond leads to enhanced ligand field strength and spin-pairing.

Key Words: Co(II), Ni(II), Cu(II) Complexes, 1-Hydroxy-2-naphthyl(4-X-styryl)ketoneoximes.

INTRODUCTION

Organic chelating ligands containing the oxime functional group have been extensively used in analytical chemistry for the detection or separation of metals[1]. By involvement of oximino group in hydrogen bonding the stability of oxime complexes differs from that of Schiff base complexes and consequently the stereochemistry differs widely. Thus the salicylaldoxime complex of nickel(II) is square-planar[2] and weakly paramagnetic while N-R-salicylaldimine[3] complexes of nickel(II) possess structures depending on the nature of R group. Studies on the effect of extensive conjugation have shown that the nickel(II) and cobalt(II) complexes of 2′-hydroxychalconeoximes[4] are high-spin with octahedral structure. Thus in spite of conjugation spin-pairing does not occur. The nickel complexes of 1-hydroxy-2-acetonaphthoneoxime[5] are low-spin and possess planar configuration. However, the structure of N-R-1-hydroxy-2-acetonaphthone-imine nickel(II) complexes depend upon the R group. So it will be worth while to investigate the effect of extensive conjugation of C═N with C═C in 1-hydroxy-2-naphthyl(4-X-styryl)ketoneoxime on the nature of bonding and the stereochemistry of metal complexes. In this paper we report the synthesis and characterization of metal complexes of 1-hydroxy-2-naphthyl (4-X-styryl) ketoneoximes.

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†Department of Chemistry, The American College (Autonomous), Madurai- 625 002, India

EXPERIMENTAL

All the metal salts (BDH, AR) and hydroxylamine hydrochloride (BDH, LR) were used as such. Elemental analyses were performed at V.H.N.S.N. College, Virudhunagar, India. Metal contents determination and other physical measurements were performed as reported elsewhere[6].

1-Hydroxy-2-naphthyl(4-X-styryl)ketones (X = H, Me, MeO) were prepared by known method.

1-Hydroxyl-2-naphthyl(4-methylstyryl)ketoneoxime (HNMeSKOx)

To a solution of 1-hydroxy-2-naphthyl(4-methylstyryl)ketone (10 mmol) in EtOH (80 mL) was added an aqueous solution (25 mL) of $NH_2OH \cdot HCl$ (2.5 mmol) and CH_3COONa (5 g) and heated to reflux for 4 h. The solution was concentrated and refrigerated. The colourless solid obtained was recrystallised from ethanol. Yield, 54%; m.p. 155–157°C.

1-Hydroxy-2-naphthyl(4-methoxystyryl)ketoneoxime (HNMeOSKOx)

HNMeOSKOx was prepared and purified by the procedure as described above from 1-hydroxy-2-naphthyl(4-methoxystyryl)ketone, $NH_2OH \cdot HCl$ and CH_3COONa. Yield 52%; m.p. 164-166°C.

All attempts to isolate 1-hydroxy-1-naphthylstyryl ketoneoxime proved futile.

$Cu(NHSKOx)_2$, $Ni(NHSKOx)_2$, $Co(NHSKOx)_2$

A solution of 1-hydroxy-2-naphthylstyryl ketone (10 mmol in 50 mL ethanol) was treated with a mixture of $NH_2OH \cdot HCl$ (25 mmol) and CH_3COONa (5 g) in water and refluxed for 4 h. To the cooled solution was added with stirring the metal(II) acetate $M(OCOCH_3)_2 \cdot nH_2O$ (M = Cu(II), Ni(II) and Co(II) (5 mmol) in water (20 mL). The resulting solid complex was washed with water, aqueous ethanol in 1 : 1 ratio under reduced radical pressure over anhydrous $CaCl_2$.

$Cu(NXSKOx)_2$, $Ni(NXSKOx)_2$, $Co(NXSKOx)_2$ (X = Me, MeO)

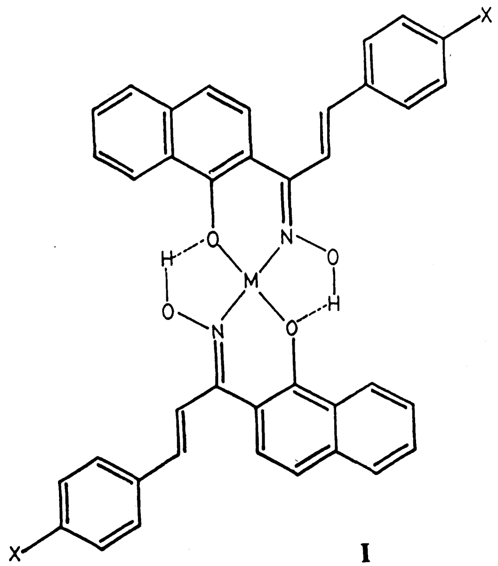
From the ketone oxime (HNXSKOx): 1-Hydroxy-2-naphthyl(4-X-styryl)-ketoneoxime (HNXSKOx) (X = Me, MeO) (10 mmol) in ethanol 20 mL was mixed with a solution of appropriate metal salt $M(OCOCH_3)_2 \cdot nH_2O$ in water (20 mL) with stirring. The solid that separated was washed successively with water, aqueous ethanol (1 : 1, v/v), ethanol 20 mL and dried under reduced pressure over $CaCl_2$.

RESULTS AND DISCUSSION

All the complexes are amorphous powders and insoluble in water. Except the cobalt complexes others are sparingly soluble in organic solvents such as $CHCl_3$, C_6H_6, CH_3COCH_3 and fairly soluble in coordinating solvents such as pyridine. The molar conductance of cobalt complexes in CH_3CN shows them to be nonelectrolytes. The elemental analysis and molar conductance data are in agreement with the assigned molecular formula **(Structure-I)**.

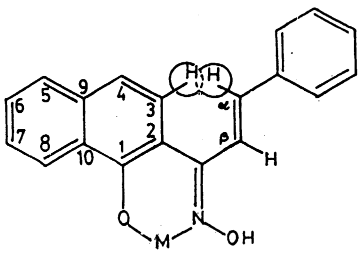
Magnetic properties and ligand field spectra: The copper(II) bischelates show magnetic moments (Table-1) in the range 1.98–2.03 BM typical of square-planar environment for copper(II). Their electronic absorption spectra show broad band centred in the 14705–15625 cm^{-1} region arising from a combination of $^2B_{1g} \longrightarrow {}^2A_{1g}$ and $^1A_{1g} \longrightarrow {}^1B_{2g}$ transitions, consistent with planar structure.

Nickel(II) bis-chelates are diamagnetic and square-planar in contrast to 2′-hydroxychalcone oxime[4] complexes which are high-spin and octahedral. This behaviour is similar to that of bis(salicylaldoximato)nickel(II)[2] and bis(1-hydroxy-2-acetonaphthoneoximato nickel(II). The electron density at the oximino-nitrogen stabilizes the MN_2O chromophore *via* strong M—N σ-bonding. The nickel complexes in $CHCl_3$ exhibit absorption bands around 16000 and 20000 cm^{-1} regions corresponding respectively to the transitions $^1A_{1g} \longrightarrow {}^1A_{2g}$ ($b_{1g} \longrightarrow b_{1g}$) and $^2B_{1g} \longrightarrow {}^2B_{2g}$ ($a_{1g} \longrightarrow b_{1g}$) characteristic of square planar[8] structure.



I

M = Cu(II), Ni(II), Co(II)
X = H, Me, MeO



II

TABLE-1
ANALYTICAL, MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF METAL(II) COMPLEXES

Complex (Colour)	% Found (Calcd.) M	C	H	N	μ_{eff} (B.M.)	λ_{max} (cm^{-1})
Cu(NHSKOx)$_2$ (grey green)	10.22 (9.94)	71.21 (71.30)	4,12 (4.38)	4.81 (4.38)	1.98	15265
Cu(NMeSKOx)$_2$ (grey green)	9.80 (9.52)	72.54 (71.91)	4.72 (4.79)	4.24 (4.00)	2.03	14705
Cu(NMeOSKOx)$_2$ (grey green)	9.51 (9.08)	68.43 (68.62)	4.00 (4.57)	3.95 (4.19)	1.98	15155
Ni(NHSKOx)$_2$ (yellow green)	9.30 (9.25)	71.54 (71.84)	3.84 (4.41)	4.72 (4.41)	diamag.	16130 20000
Ni(NMeSKOx)$_2$ (yellow green)	9.14 (8.86)	72.83 (72.43)	4.45 (4.83)	3.72 (4.23)	diamag.	16260 20200
Ni(NMeOSKOx)$_2$ (green)	8.33 (8.45)	68.92 (69.09)	4.80 (4.61)	4.32 (4.03)	diamag.	16660 20000
Co(NHSKOx)$_2$ (brown)	9.75 (9.28)	71.27 (71.82)	3.92 (4.41)	4.14 (4.41	2.90	17240
Co(NMeSKOx)$_2$ (brown)	8.74 (8.89)	72.12 (72.41)	4.61 (4.83)	3.62 (4.22)	3.12	17700
Co(NMeOSKOx)$_2$ (brown)	8.71 (8.48)	69.25 (69.07)	4.21 (4.60)	4.05 (4.03)	3.08	17390

The magnetic moments for the cobalt(II) bis-chelates lying in the 2.90–3.12 BM range are characteristic of low-spin cobalt(II) complexes[9]. Mixing of the higher ligand field term $^2A_{2g}$ into the $^2A_{1g}$ ground term by spin-orbit coupling[7] enhances the moment considerably above the spin-only value (1.8 BM). Their ligand field spectra show a feature in the 17240–17700 cm^{-1} range consistent with square-planar cobalt(II)[8]. This band may be assigned to the transition from a lower filled orbital to the upper a_{1g} (dz^2) orbital.

Infrared spectra: In the ligands and metal complexes, the medium intensity band in the 1635–1585 cm^{-1} region is assigned as ν(C=N) vibration. The ν(C=C) appearing as a separate band in the 1605–1575 cm^{-1} region is assigned as phenylalkene vibration. The phenolic C—O and N—O streches occur at 1393–1370 and 1010–968 cm^{-1} (OH stretch of N—OH group) and it gets broadened in the complexes.

In relation to the ligands the metal chelates register a lower ν(C=N) (10–45) and ν(Ph—C=C) (3–15 cm^{-1}) frequencies, suggesting both σ and π-interaction between (C=N) and the metal as in the case of 1-hydroxyl-2-naphthyl(4-X-styryl) ketone complexes[6]. The magnitude of lowering indicates that the mesomeric interaction of the phenyl group with the metal is not as effective as in 1-hydroxyl-2-naphthyl-(4-X-styryl)ketone complexes. An examination of molecular model reveals lack of planarity in the molecule due to steric repulsion between C_3-hydrogen of naphthalene group and α-hydrogen of styryl group. Compared to the ligands, the phenolic C—O stretching vibration manifests a positive shift, the complexes indicating coordination of phenolic oxygen to the metal.

TABLE-2
INFRARED SPECTRAL DATA (cm^{-1}) OF 1-HYDROXY-2-NAPHTHYL (4-X-STYRYL) KETONEOXIMES AND THEIR METAL COMPLEXES

Compound	ν(OH)	ν(C=N)	ν(C=C)	ν(Ph–C=C)	ν(C–O)	ν(N–O)	ν(M–O)
HNMeSKOx	3320	1635	1600	1560	1375	1010	—
Cu(NMeSKOx)$_2$	3400, 3060	1610	1590	1550	1380	980	580
Ni(NMeSKOx)$_2$	3220	1608	1675	1557	1392, 1378	980	570
Co(NMeSKOx)$_2$	3340	1610	1590	1550	1375	968	570
HNMeOSKOx	3330	1630	1500	1555	1370	1000	—
Cu(NMeOSKOx)$_2$	3340, 3040	1620	1505	1540	1375	974	605
Ni(NMeOSKOx)$_2$	3320, 2890	1600	1580	1540	1378	980	580
Co(NMeOSKOx)$_2$	3300, 2980	1585	—	1540	1378	972	565
Cu(NHSKOx)$_2$	3320, 3020	1595	1575	1535	1385	970	600
Ni(NHSKOx)$_2$	3320, 2880	1620	1580	1540	1393	988	370
Co(NHSKOx)$_2$	3040	1620	1580	1540	1392	972	565

Conclusion

In relation to 2′-hydroxychalcone oxime[4] one would expect 1-hydroxy-2-naphthyl(4-X-styryl)ketoneoxime to be a weak field ligand, but it behaves as a strong field ligand.

In 2-hydroxychalconeoxime complexes the conjugation of electron-withdrawing phenyl group with (C═N) reduces its basic nature[4]. But in 1-hydroxy-2-naphthyl(4-X-styryl)ketoneoxime the conjugation of phenyl group with (C═N) is inhibited due to steric repulsion thereby not affecting the basic nature of nitrogen. Thus the strong M—N σ-bond supplements the poor d_{π}-p_{π}* interaction leading to enhanced ligand field strength and spin pairing. Additional stability is achieved from hydrogen bonding between the oximino hydrogen and phenolic oxygen which is reflected in the broadening of the OH stretching mode and also the lowering of the NO stretching mode.

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