

Stereochemistry of copper (II), nickel (II) and cobalt (II) 2'-hydroxy-5'-X-chalconeoxime complexes

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Abstract. Cu (II), Ni (II) and Co (II) complexes of the type $ML_2, 2B$ where L = 2'-hydroxy-5'-X-chalconeoxime (X = H, CH₃, Cl) and B = water or pyridine have been obtained from chalconeoximes and by reacting the preformed metal (II) chalcone complexes with hydroxylamine. They have been characterised on the basis of elemental and thermal analyses, conductivity and magnetic measurements and ligand field and IR spectra. All the complexes are high-spin octahedral species in contrast to the low-spin square planar Ni (II) and Co (II) salicylaldoxime complexes. IR spectral studies indicate that conjugation is relatively damped in chalconeoxime. The lower ligand field strength of the oxime is attributed to the weak M-N bonding and less extensive $d\pi - \pi^*$ back-bonding. Replacement of water by pyridine weakens metal-oximino bond in the complexes.

Keywords. Chalconeoxime complexes; high spin; ligand field spectra.

1. Introduction

Extensive conjugation of coordinated C=O in nickel (II) and cobalt (II) 2'-hydroxychalcone complexes (Palaniandavar and Natarajan 1980) leads to spin pairing. However, extensive conjugation of coordinated C=N in 2'-hydroxychalconeimine complexes (Natarajan and Palaniandavar 1982) leads only to a lower ligand field strength; nickel (II) complexes possess associated pseudo octahedral configuration while cobalt (II) complexes a tetrahedral one. It will therefore be interesting to investigate the effect of extensive conjugation of coordinated C=NOH in 2'-hydroxy-5'-X-chalconeoximes on the nature of bonding and stereochemistry of their metal (II) complexes. Here we report their isolation and characterisation.

2. Experimental

The metal salts and hydroxylamine hydrochloride were of analytical reagent grade. Solvents and pyridine were purified in the usual manner, distilled and stored. The complexes were physically measured as described earlier (Palaniandavar and Natarajan 1980).

2.1 Syntheses of ligands

2'-Hydroxychalcone, 2'-hydroxy-5'-methylchalcone and 5'-chloro-

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2'-hydroxychalcone were prepared as reported earlier (Palaniandavar and Natarajan 1980). The oximes were obtained by heating to reflux ethanolic solutions of the chalcones with excess of 1:1 mixture of hydroxylamine hydrochloride and sodium acetate in minimum amount of water.

2.2 Synthesis of bis(2'-hydroxy-5' X-chalconeoximato) diaquo metal(II) from the chalconeoximes

2.2a Copper (II) complexes: Copper(II) acetate monohydrate (5 mmol) was dissolved in water (400 ml) and dilute ammonia added till a clear blue solution was obtained. To this was added with stirring an ethanolic solution (50 ml) of the chalconeoxime (10 mmol). The precipitate obtained was collected on a filter, washed with water and aqueous ethanol (1:1 v/v) and dried over CaCl_2 (yield 90-95%).

2.2b Nickel (II) and cobalt (II) complexes: An ethanolic solution (50 ml) of the chalconeoxime (10 mmol) was added with stirring to an aqueous solution (100 ml) of the corresponding metal(II) acetate tetrahydrate (5 mmol) and the pH raised to 6-7 with dilute ammonia. The precipitated complex was filtered, washed with water followed by aqueous ethanol (1:1 v/v) and dried in a desiccator over CaCl_2 (yield 80-88%).

2.3 Synthesis from the preformed chalcone complexes

To a suspension of the metal(II) chalcone complex (2 mmol) in ethanol (30 ml) was added a solution of hydroxylamine hydrochloride (8 mmol) and anhydrous sodium acetate (8 mmol) in minimum amount of water (4 ml). This was heated to reflux on a water bath for 30 mins. The complex obtained on cooling was filtered, washed with aqueous ethanol (1:1 v/v) and dried *in vacuo* over CaCl_2 . The filtrate was diluted with water to precipitate more of the oxime complex (yield 50-70%).

2.4 Pyridine adducts

Bis(2'-hydroxychalconeoximato) diaquo metal(II) complexes were dissolved in pyridine from which the pyridine adducts crystallised out. They were collected and dried over CaCl_2 .

3. Results and discussion

All the complexes are insoluble in water but soluble in organic and coordinating solvents. TG and DSC studies indicate the loss of coordinated water in aquo complexes around 120° and pyridine in pyridine adducts around 80° . In the nickel adduct, loss of pyridine in two stages is shown by the doublet structure of the exothermic peak. In DSC traces of copper and cobalt complexes, a sharp exothermic peak is observed around 140° in dihydrates but around 190° in pyridinates. This may be due to the transition of the anhydrous chelate to a stable state or due to the exothermic combustion of the oximino group. The

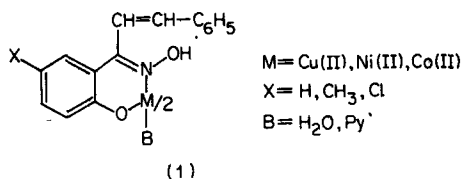
Table 1. Colour, analytical data and magnetic moments of metal(II) 2'-hydroxy-5'-X-chalconeoxime complex.

| X | Colour | Formula | % Found (required) | | | | μ_{eff} |
|---------------|----------------|--|--------------------|------------------|----------------|----------------|--------------------|
| | | | M | C | H | N | |
| H | dark green | $\text{CuL}_2 \cdot 2\text{H}_2\text{O}$ | 11.2 (11.00) | 63.12 (62.55) | 4.95 (4.87) | 4.85 (4.87) | 1.90 |
| H | light green | $\text{NiL}_2 \cdot 2\text{H}_2\text{O}$ | 10.02 (10.29) | 63.42 (63.07) | 5.21 (4.91) | 4.93 (4.91) | 3.10 |
| H | cream | $\text{CoL}_2 \cdot 2\text{H}_2\text{O}$ | 10.53 (10.30) | 62.36 (63.08) | 4.63 (4.91) | 4.85 (4.91) | 4.86 |
| CH_3 | dark green | $\text{CuL}_2 \cdot 2\text{H}_2\text{O}$ | 9.92 (10.53) | 62.83 (63.60) | 4.98 (5.30) | 4.82 (4.64) | 1.84 |
| CH_3 | light green | $\text{NiL}_2 \cdot 2\text{H}_2\text{O}$ | 10.21 (9.81) | 65.02 (64.14) | 5.5 (5.34) | 4.82 (4.68) | 3.21 |
| CH_3 | cream | $\text{CoL}_2 \cdot 2\text{H}_2\text{O}$ | 9.41 (9.83) | 63.42 (64.12) | 5.45 (5.34) | 4.81 (4.68) | 4.90 |
| Cl | dark green | $\text{CuL}_2 \cdot 2\text{H}_2\text{O}$ | 10.32 (9.86) | 55.37 (55.86) | 3.98 (4.03) | 4.53 (4.34) | 1.82 |
| Cl | light green | $\text{NiL}_2 \cdot 2\text{H}_2\text{O}$ | 8.74 (9.18) | 57.23 (56.29) | 3.79 (4.07) | 4.23 (4.38) | 3.22 |
| Cl | cream | $\text{CoL}_2 \cdot 2\text{H}_2\text{O}$ | 9.97 (9.21) | 55.72 (56.27) | 3.76 (4.06) | 4.40 (4.38) | 4.83 |
| H | greenish black | $\text{CuL}_2 \cdot \text{Py}_2$ | 8.72 (9.11) | 67.91 (68.81) | 4.62 (4.87) | 7.93 (8.03) | 1.83 |
| H | green | $\text{NiL}_2 \cdot \text{Py}_2$ | 8.06 (8.47) | 70.02 (69.29) | 4.82 (4.91) | 8.29 (8.08) | 3.02 |
| H | dark brown | $\text{CoL}_2 \cdot \text{Py}_2$ | 8.64 (8.50) | 70.02 (69.27) | 5.5 (4.91) | 8.33 (8.08) | 4.90 |

Note: Compounds obtained from the preformed oximes. The compounds obtained from the chalcone complexes also analysed satisfactorily.

latter seems to be probable because no such exothermic peak is observed in the DSC trace of bis(2'-hydroxychalconeiminato) copper(II).

The results of thermal and elemental analyses (table 1) are consistent with the general formula $\text{ML}_2 \cdot 2\text{B}$ for all complexes (Scheme 1). Conductivity



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

X = H, CH_3 , Cl

B = H_2O , Py

measurements in dimethylformamide show that they are non-ionic species.

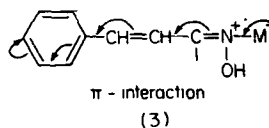
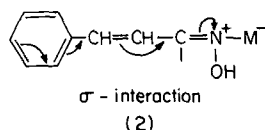
3.1 Magnetic properties and ligand field spectra

The magnetic moments of ~ 1.8 BM (table 1) and the electronic spectra with a broad shoulder in the $17200 - 15400 \text{ cm}^{-1}$ region of the copper(II) complexes are indicative of octahedral geometry (Ferguson 1970). All the nickel complexes have moments ~ 3.2 BM and their ligand field spectra show ν_1 near 11000 ν_2 around 16000 and ν_3 around 21000 as a shoulder on the ligand absorption. These are characteristic of octahedral environment for nickel(II). The ν_2/ν_1 ratio of 1.5 (Lever 1968) for the dihydrates indicates no tetragonal distortion. The pyridine adduct is tetragonally distorted (ν_2/ν_1 1.67). β for the dihydrate is of the order of 35%. The magnetic moments of ~ 4.9 BM and the ν_1, ν_2 and ν_3 around 9400 , 15600 sh and 18000 cm^{-1} respectively of the cobalt(II) complexes are consistent with an octahedral geometry. These absorptions of the dihydrates are shifted in pyridine solution showing adduct formation.

The CFSE's calculated (Figgis 1967) are 5180 , 13330 and 9230 cm^{-1} respectively for Co(II), Ni(II) and Cu(II) complexes. Including the additional Jahn-Teller stabilisation the order of stability will be $\text{Cu} > \text{Ni} > \text{Co}$ which is also Irving-Williams order.

3.2 Infrared spectra

Important IR frequencies are given in table 2. The σ and π interactions (schemes 2, 3) in the complexes should lead to the lowering of $\nu(\text{C}=\text{C})$, $\nu(\text{PhC}=\text{C})$ and $\nu(\text{C}=\text{N})$ of the ligands on coordination. It is seen that only the former two are lowered ($5-14$, $7-40 \text{ cm}^{-1}$ respectively) while the latter remains unaffected. However, $\nu(\text{NO})$ registers a lowering ($5-27 \text{ cm}^{-1}$); so any change in $\text{C}=\text{N}$ bond order on coordination is compensated by change in $\text{N}-\text{O}$ bond order. Since the coordinated nitrogen is attached to the polar OH group and also to the electron-withdrawing phenyl group through $\text{C}=\text{C}$, the $\text{M}-\text{N}$ σ -interaction is weak. So, despite the favourable but not extensive $d\pi - \pi^*_3$ back-bonding (Palaniandavar and Natarajan 1980), the chalcone oxime has weak ligand field strength. The presence of coordinated water and hydrogen bonding are shown by bands around 3200 and 2900 cm^{-1} respectively.



Due to involvement of phenolic oxygen in hydrogen bonding, nickel(II) and cobalt(II) complexes are isolated as octahedral diaquates while the 2'-hydroxychalconeimine complexes (Natarajan and Palaniandavar 1982) of nickel(II) and cobalt(II) are obtained as pseudo-octahedral and tetrahedral complexes respectively even though the conjugated system present in both is the same.

Table 2. Infrared spectral data of bis(2'-hydroxy-5'-X-chalconeoximate) diaquometal(II) and bis(2'-hydroxychalconeoximate) dipyridinometal(II) complexes. Frequencies in cm^{-1}

| X | M | $\nu(\text{C}=\text{C})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{Ph}-\text{C}=\text{C})$ | $\nu(\text{N}-\text{O})$ | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{O}-\text{H})$ |
|---------------|----|--------------------------|--------------------------|------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Ligand | | | | | | | | |
| H | H | 1644 | 1603 | 1580 | 997 | - | - | 3230, 2900 |
| dihydrates | | | | | | | | |
| H | Cu | 1630 | 1600 | 1550 | 970 | 585 | 440 | 3350, 3150, 3040, 2900 |
| | Ni | 1630 | 1600 | 1570 | 975 | 577 | 422 | 3280, 3040, 2900 |
| | Co | 1630 | 1600 | 1572 | 980 | 563 | 422 | 3230, 3060, 2900 |
| dipyridinates | | | | | | | | |
| H | Cu | 1634 | 1600 | 1557 | 960 | 582 | 433 | 2900 |
| | Ni | 1632 | 1600 | 1574 | 958 | 575 | 400 | 2910 |
| | Co | 1633 | 1600 | 1577 | 956 | 563 | 400 | 2900 |
| CH_3 | H | 1646 | 1617 | 1595 | 1037 | - | - | 3240, 2800 |
| | Cu | 1640 | 1615 | 1571 | 1017 | - | - | 3150, 3040, 2920 |
| | Ni | 1635 | 1613 | 1575 | 1024 | - | - | 3225, 3040, 2920 |
| | Co | 1640 | 1615 | 1576 | 1023 | - | - | 3230, 3040, 2910 |
| Cl | H | 1640 | 1600 | 1572 | 977 | - | - | 3290, 2900 |
| | Cu | 1628 | 1595 | 1530 | 955 | - | - | 3500, 3150, 3060, 2940 |
| | Ni | 1630 | 1600 | 1560 | 970 | - | - | 3250, 3040, 2910 |
| | Co | 1630 | 1600 | 1565 | 972 | - | - | 3400, 3240, 3060, 2920 |

3.3 Effect of metal ion and ligand substitutions

The metal ion sensitive $\nu(\text{PhC}=\text{C})$ and $\nu(\text{NO})$ vary as $\text{Cu} < \text{Ni} \sim \text{Co}$, copper exhibiting maximum σ and π interaction in accordance with Irving-William's order of stability. The sequence of $\nu(\text{M}-\text{O})$ around 595 cm^{-1} and $\nu(\text{M}-\text{N})$ around 400 cm^{-1} (Trivedi and Haldar 1973) also follow the same order. Compared to the parent compound 5-methyl substituted complex shows positive shift in $\nu(\text{PhC}=\text{C})$ and $\nu(\text{N}-\text{O})$ whereas 5-chloro substituted complex shown as negative shift in the same. These would suggest that the stability of the substituted complexes follows the sequence $\text{Cl} > \text{H} > \text{CH}_3$. This indicates that the inductive effect of the substituent is important. The replacement of water by pyridine results in a considerable decrease in $\nu(\text{M}-\text{N})$ and slight decrease in $\nu(\text{M}-\text{O})$. This indicates that $\text{M}-\text{N}$ σ -bond in the complexes is further weakened by the newly formed $\text{M}-\text{N}$ σ -bond with pyridine.

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References

- Ferguson J 1970 *Prog. Inorg. Chem.* **12** 273
Figgis B N 1967 *Introduction to Ligand fields* (New York: Interscience)
Lever A B P 1968 *Coord. Chem. Rev.* **3** 119
Natarajan C and Palaniandavar M 1982 *Indian J. Chem.* **A21** 670
Palaniandavar M and Natarajan C 1980 *Aust. J. Chem.* **33** 737
Trivedi P C and Haldar B C 1973 *J. Indian Chem. Soc.* **50** 81