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# THE STRUCTURES OF NICKEL (II) COMPLEXES OF SOME O,O' DIHYDROXY SCHIFF BASES

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ABSTRACT

N–(2–hydroxyphenyl)–salicylaldimine and twelve derivatives were synthesised and their Ni(II) complexes isolated.

The composition and the structures of the complexes were investigated by elemental analysis, magnetic susceptibility measurements and electronic spectroscopy. All of the complexes were found to have a pseudo-octahedral structure.

## INTRODUCTION

The $Ni^{2+}$ complex of the of N–(2–hydroxyphenyl)-salicylaldimine, C–O, was first synthesized in 1937 (1). More recent studies have shown that the complex was dimeric in structure with two nickel ions bridged together by the phenolic oxygens of the ligands (2,3). Planar complexes are expected to be diamagnetic. The observed paramagnetic behaviour of this planar complex needs an explanation. Although there is no strong evidence it is assumed that the planar dimer units are converted into octahedral structure by axial polymerization through Ni–I–Ni bridges (4).

In this work twelve different derivatives of the Schiff base N–(2–hydroxyphenyl)-salicylaldimine were synthesized and their $Ni^{2+}$ complexes were prepared. The substituents were Cl, Br, $CH_3$ and $NO_2$ at different positions. The general structure of ligands is shown above.

The compositions and the structures of the complexes were elucidated on the basis of elemental analysis, magnetic properties and especially electronic spectra. The electronic spectra of all the complexes covered the range 1600–400 nm and their d-d transitions were examined.

| x | x′ | Symbol of the complex |
|---|---|---|
| H | H | C–O |
| Cl | H | C–1–Cl |
| Br | H | C–1–Br |
| $CH_3$ | H | C–1–$CH_3$ |
| $NO_3$ | H | C–1–$NO_2$ |
| H | Cl | C–2–Cl |
| H | Br | C–2–Br |
| H | $CH_3$ | C–2–$CH_3$ |
| H | $NO_2$ | C–2–$NO_2$ |
| Cl | Cl | C–3–Cl |
| Br | Br | C–3–Br |
| $CH_3$ | $CH_2$ | C–3–$CH_3$ |
| $NO_2$ | $NO_2$ | C–3–$NO_2$ |

## EXPERIMENTAL

### Preparation of Ligands

The Schiff base coded (L.O) was prepared by a procedure appeared in the literature (5,6) previously. The other Schiff bases were sythesized through a similar procedure using appropriate amines and aldehydes.

### Preparation of Complexes

All complexes were prepared from equimolar amounts of ligand and nickel-II-acetate as follows.

The Schiff base was dissolved in methanol, equimolar amount of $Ni(CH_2COO)_2 \cdot 2H_2O$ solution in methanol was added and refluxed for two hours. The mixture was kept for 24 hours and then filtered in vacuum, washed twice with hot water and hot methanol and dried at room temperature at 25 mm Hg.

All complexes have yellow-brown colour and are stable up to 360°C.

Elemental analyses were carried out in a Helvet Packard 185 C, H, N Analyzer. Nickel was analyzed by atomic absorbtion in a Hitachi 180–80 Zeeman AAS. Experimental values regarding the elemental anayses and the respective compositions of the complexes are listed in Table 1.

### Mangetic Measurements

Magnetic susceptibilities were measured at room temperature by the Gouy method. $Hg(Co(NCS)_4)$ was used as a calibrating agent. The $\mu_{eff}$ results of the complexes are listed in Table 1.

### Electronic Spectra

The electronic spectra of the complexes were run with a Cary -17 model recording spectrophotometer. The spectra were taken of solids in nujol, because the complexes were not sufficiently soluble in general organic solvents. The sample was mixed with unjol and sandwiched between two plates (7,8). Pure nujol squeezed between two plates was used as reference cell.

## RESULTS AND DISCUSSION

In general, the ligand-field spectra of octahedral $Ni^{2+}$ complexes consist of three spin-allowed transitions from $^3A_{2g}$ to $^3T_{2g}(\nu_1)$, $^3A_{2g}$ $(\nu_2)$ and $^3T_{1g}$ (P), $(\nu_3)$ generally fall within the ranges 7000–13000, 11000–20000 and 19000–27000 $cm^{-1}$ respectively (9). The frequencies and wave numbers of the d-d transitions of all the complexes were tabulated in Table 2. This method could be applied over the wavelength range between 1700–350 nm. Because there was a strong interference beyond 1700 nm possibly due to the nujol used (8) and a very strong absorbtion of glass plates at around 350 nm. Beside these there were small interference bands of nujol which approximate band widths of 5–25 nm appearing at about 980, 1260 and 1380 nm regions (8). The ligand-field spectra of $C-3-NoO_2$ and $C-2-CH_3$ were shown in Fig.1.

The ligand-field spectra of all complexes are in good agreement with those of expected for octahedral nickel (II) complexes. In view of the elemental and spectral analysis and paramagnetic properties of the complexes, the structures must be considered as pseudo-octahedral as shown in Fig. 2.

In the spectra of most of the complexes splittings and shoulders have been observed in the bands corresponding to the transitions $\nu_2$ and $\nu_3$. They are thought to be originated either from spin forbidden transitions (11) or from distorted octahedral structures (10).

Table 1. Elemental Analysis. Compositions and Magnetic Moment of the Complexes.

| Complex | Formula | Found (%) | | | | Calc (%) | | | | Composition* | $\mu$ (BM) eff |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | Ni | C | H | N | Ni | | |
| C–O | $C_{12}H_{11}NO_2Ni$ | 54.7 | 3.9 | 5.6 | 19.6 | 54.2 | 3.8 | 4.9 | 20.4 | $NiL.H_2O$ | 2.72 |
| C–1–Cl | $C_{12}H_{12}NO_2ClNi$ | 48.5 | 2.9 | 4.0 | 18.0 | 48.4 | 3.1 | 4.3 | 18.2 | $NiL.H_2O$ | 2.72 |
| C–1–Br | $C_{12}H_{12}NO_2BrBi$ | 41.9 | 2.76 | 3.6 | 15.7 | 42.6 | 2.7 | 3.8 | 16.0 | $BiL.H_2O$ | 2.94 |
| C–1–$CH_2$ | $C_{12}H_{11}NO_2Ni$ | 58.1 | 4.0 | 4.8 | 19.6 | 58.8 | 3.9 | 4.9 | 20.6 | NiL.N | 2.99 |
| C–1–$NO_2$ | $C_{12}H_2N_2O_2Ni$ | 50.9 | 3.5 | 7.9 | 18.0 | 49.3 | 2.5 | 8.8 | 18.5 | NiL | 2.95 |
| C–2–Cl | $C_{12}H_2NO_2ClNi$ | 50.2 | 2.5 | 4.2 | 19.1 | 51.0 | 2.6 | 4.6 | 19.2 | NiL | 2.89 |
| C–2–Br | $C_{12}H_{12}NO_2BçNii$ | 42.0 | 2.5 | 3.6 | 16.7 | 42.6 | 2.7 | 3.8 | 16.0 | $NiL.H_2O$ | 2.70 |
| C–2–$CH_2$ | $C_{12}H_{12}NO_2Ni$ | 55.4 | 4.2 | 3.8 | 21.6 | 55.3 | 4.3 | 4.6 | 19.3 | $NiL.H_2O$ | 2.87 |
| C–2–$NO_2$ | $C_{12}H_2N_2O_2Ni$ | 48.0 | 2.8 | 8.8 | 19.0 | 49.3 | 2.5 | 8.8 | 18.5 | NiL | 2.97 |
| C–3–Cl | $C_{12}H_2NO_2Cl_2Ni$ | 45.5 | 2.3 | 4.0 | 17.3 | 45.8 | 2.1 | 4.1 | 17.2 | NiL | 3.02 |
| C–3–Br | $C_{12}H_2NO_2Br_2Ni$ | 35.5 | 1.8 | 3.1 | 12.5 | 34.9 | 2.0 | 3.1 | 13.1 | $NiL.H_2O$ | 3.11 |
| C–3–$CH_2$ | $C_{12}H_{12}NO_2Ni$ | 56.6 | 4.0 | 4.2 | 18.5 | 57.0 | 4.7 | 4.4 | 18.5 | $NiL.H_2O$ | 2.87 |
| C–3–$NO_2$ | $C_{12}H_2N_2O_2Ni$ | 39.7 | 2.8 | 10.9 | 15.3 | 41.1 | 2.4 | 11.1 | 15.5 | $NiL.H_2O$ | 2.96 |

* L reperesents the appropriate ligand.

Table 2. The electronic transitions of complexes.

| Complex | (cm$^{-1}$) $\nu_1$<br>(nm$^{-1}$) $\lambda_1$ | $\nu_2$<br>$\lambda_2$ | $\nu_2$<br>$\lambda_2$ |
|---|---|---|---|
| C–O | 7353–7042 | 12364 | 23381 |
| | 1360–1420 | 808.8 | 427.7 |
| C–I–Cl | 7576–7143 | 12231 | 23635 |
| | 1320–1400 | 817.6 | 423.1 |
| C–I–Br | 7326–7143 | 12241 | 23613 |
| | 1365–1400 | 819.6 | 423.5 |
| C–I–$CH_3$ | 7407–6944 | 12228 | 24355 |
| | 1350–1440 | 817.8 | 410.6 |
| C–I–$NO_2$ | 7843–7519 | 12302 | 21519 |
| | 1275–1330 | 812.9 | 464.7 |
| C–II–Cl | 7407–7042 | 12226 | 22821 |
| | 1350–1420 | 817.9 | 438.2 |
| C–II–Br | 7463–7042 | 12161 | 22722 |
| | 1340–1420 | 822.3 | 440.1 |
| C–II–$CH_3$ | 7463–7042 | 12136 | 22712 |
| | 1340–1420 | 824.0 | 440.3 |
| C–II–$NO_2$ | 7547–7453 | 12228 | 21377 |
| | 1325–1345 | 817.8 | 467.8 |
| C–III–Cl | 7353–7143 | 12231 | 23781 |
| | 1360–1400 | 817.6 | 420.5 |
| C–III–Br | 7407–7194 | 12194 | 23680 |
| | 1350–1390 | 820.1 | 422.3 |
| C–III–$CH_3$ | 7576–7353 | 12247 | 24284 |
| | 1320–1360 | 816.5 | 411.8 |
| C–III–$NO_2$ | 8130–8000 | 12143 | 19102 |
| | 1220–1260 | 823.5 | 523.5 |

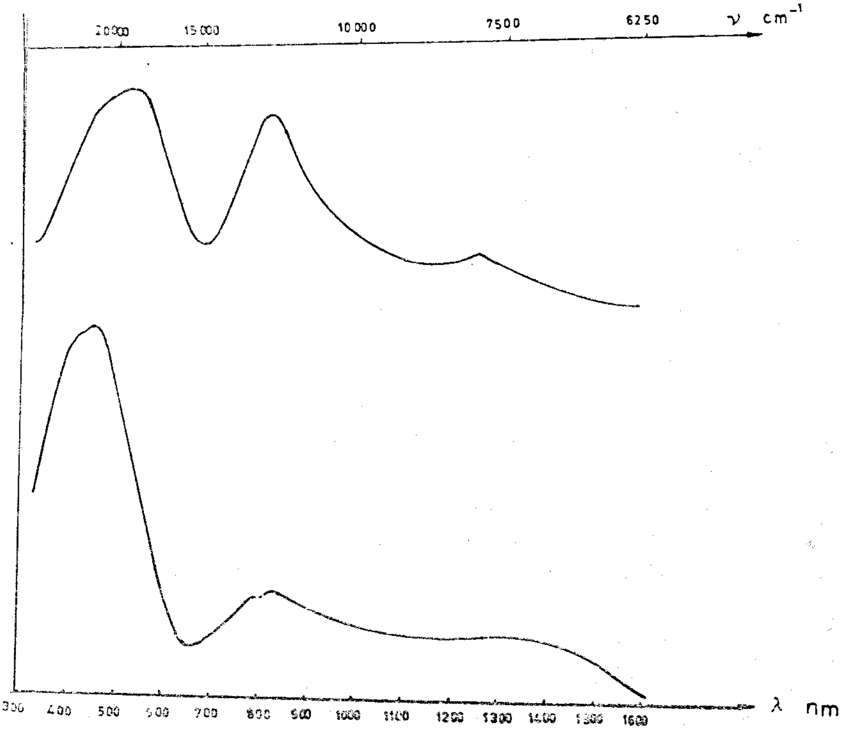

Fig. 1. The ligand-field spectra of C–3–$NO_2$ and C–2–$CH_3$.

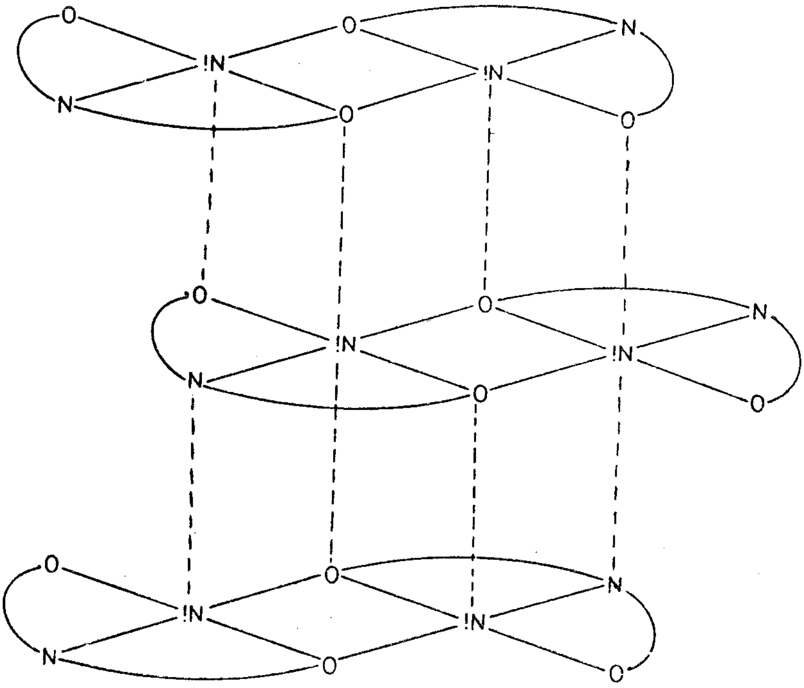

Fig. 2. The pseudo-octahedral structure of the complexes.

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