

## Synthesis of mixed schiff base complexes of Cu(II) and Ni(II) and their spectral, magnetic and antifungal studies

V K Patel, (Miss) A M Vasanwala & C R Jejurkar\*

Applied Chemistry Department, Faculty of Technology and Engineering, M S University, Baroda 390 001

Received 19 May 1988; revised 29 August 1988; accepted 17 October 1988

Mixed ligand schiff base complexes of Cu(II) and Ni(II) derived from 7-formyl-8-hydroxyquinoline and 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxyacetophenone, 2-hydroxy-1-acetophenone or 1-hydroxy-2-acetophenone and ethylenediamine have been synthesised and their spectral, magnetic and antifungal studies carried out.

Some binary and mixed ligand schiff base complexes of hydroxy ketones and hydroxy aldehydes have been reported by Bhattacharya and coworkers<sup>1-4</sup>. The schiff base complexes are known to show antifungal activity<sup>5-7</sup>, which is increased by the presence of hydroxy group in the ligand. So, it was thought worthwhile to synthesise complexes of schiff bases with hydroxy substituents on the phenyl and heterocyclic rings. We report here new mixed ligand schiff base complexes derived from 7-formyl-8-hydroxyquinoline and 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxyacetophenone, 2-hydroxy-1-acetophenone or 1-hydroxy-2-acetophenone and ethylenediamine. Work on complexes of 7-formyl-8-hydroxyquinoline or its mixed schiff base has not been reported in the literature.

As schiff base complexes are known to have fungicidal activities, such isolated complexes have been tested against *Alternaria triticina* and *Puccinia recondita* as test organisms, which are found to affect the growth of potatoes, maize and wheat crops.

All the chemicals were AR grade reagents. 7-Formyl-8-hydroxyquinoline was prepared by the modified form of earlier reported method<sup>8</sup>.

### Experimental

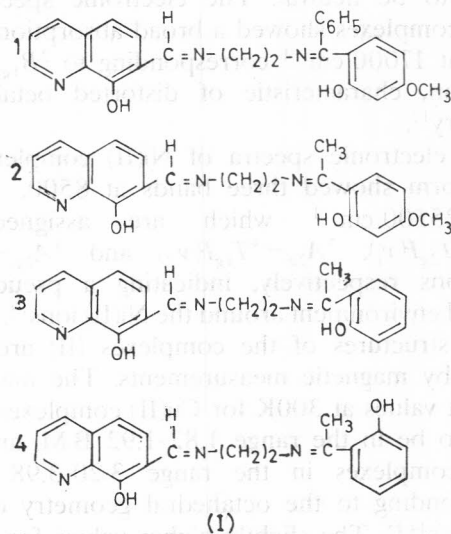
#### Preparation of 7-formyl-8-hydroxyquinoline

A solution of 8-hydroxyquinoline (8g) in 20ml of chloroform was mixed with a solution of sodi-

um hydroxide (16.5g) in 30 ml water and 60ml of ethanol were added. The contents were refluxed at 100°C for 12hr. Then the solution was acidified (pH 6.5-6.8) with dilute HCl when a brick-red solid was precipitated. On TLC analysis it was found to be a mixture of 5-formyl-8-hydroxyquinoline, 7-formyl-8-hydroxyquinoline and unreacted 8-hydroxyquinoline. The unreacted 8-hydroxyquinoline was removed by washing the brick-red solid with ether and then 7-formyl-8-hydroxyquinoline was extracted by chloroform. The residue left was 5-formyl-8-hydroxyquinoline which was discarded. 7-Formyl-8-hydroxyquinoline was recovered from chloroform by evaporation of chloroform. The yield was found to be 3.0g. The substance was crystallized repeatedly from chloroform (m.p. 263°C, lit. 264°C).

#### Preparation of ligands (schiff bases)

Schiff base ligands (I) were prepared by using the method reported by Dharkaray and Saxena<sup>9</sup>.



#### Preparation of complexes

A solution of metal acetate in 95% ethanol (20 mmol) was mixed with the schiff base ligand in 95% ethanol (20 mmol) in 1:1 (M:L) ratio and contents were refluxed in 150 ml ethanol on a water-bath for 2-3hr. The refluxed solution was then poured into ice cold water when a coloured solid separated out which was isolated by filtration and washed with ether, recrystallised from chloroform and dried *in vacuo* at room temperature. The

complexes were analysed for metal contents using complexometric titration with EDTA. Carbon, hydrogen and nitrogen were determined by micro-analysis (Table 1) at the Chemistry Department, Faculty of Science, M.S. University of Baroda. Purity of the complexes was checked by TLC technique, using silica gel G (Si-Chem) with chloroform + ether (5:3) mixture as adsorbant and ultra-violet light as visualisation agent.

The IR spectral data were recorded in KBr on a Perkin-Elmer 427 grating spectrophotometer and electronic spectra in chloroform on a Beckman spectrophotometer. The magnetic measurements were carried out by Gouy's method. The fungicidal activity was studied by the Agar plate technique<sup>10-11</sup> using *Alternaria triticiniae* found in potatoes and *Puccinia recondita* found in wheat and maize as test organisms (Table 2).

### Results and Discussion

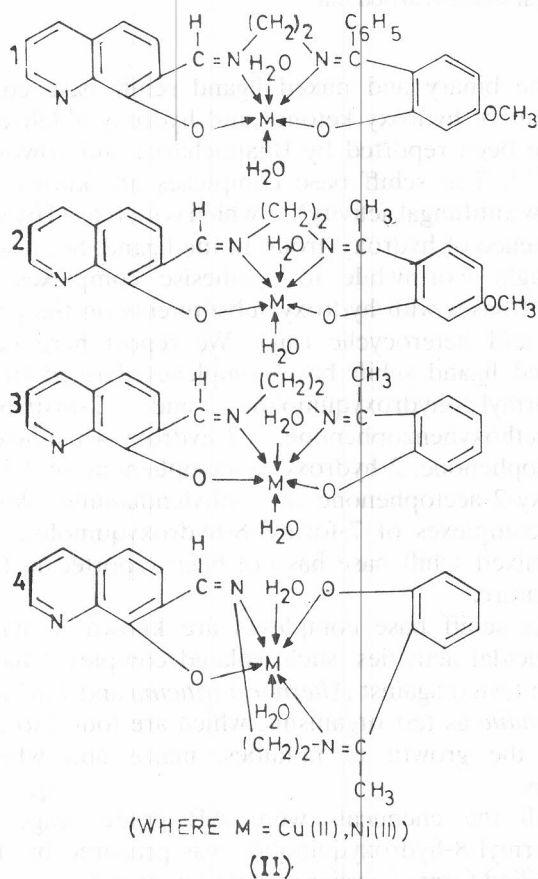
The analytical data (Table 1) show that the composition of the complexes is  $ML(H_2O)_2$  where  $M = Cu(II)$  or  $Ni(II)$  and  $L = schiff$  bases. The chloroform solutions of the complexes showed very poor molar conductivity ( $5.8-8.2 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) indicating the complexes to be neutral. The electronic spectra of  $Cu(II)$  complexes showed a broad absorption maximum at  $17000 \text{ cm}^{-1}$  corresponding to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transition, characteristic of distorted octahedral geometry<sup>12</sup>.

The electronic spectra of  $Ni(II)$  complexes in chloroform showed three bands at  $8500$ ,  $14500$  and  $25500 \text{ cm}^{-1}$  which are assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F\nu_1)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F\nu_2)$  and  ${}^3A_{2g} \rightarrow P(\nu_3)$  transitions respectively, indicating a pseudo-octahedral environment around the  $Ni(II)$  ions<sup>13</sup>.

The structures of the complexes (II) are supported by magnetic measurements. The magnetic moment values at  $300\text{K}$  for  $Cu(II)$  complexes were found to be in the range  $1.82-1.92 \text{ B.M.}$  and for  $Ni(II)$  complexes in the range  $3.20-3.98 \text{ B.M.}$  corresponding to the octahedral geometry of the molecules<sup>14,15</sup>. The slightly higher values for  $Ni(II)$  complexes than the spin-only value may be due to orbital contribution. The IR spectra of the free schiff base ligands exhibited two bands at  $\sim 1600$  and  $\sim 1690 \text{ cm}^{-1}$  due to  $\nu C=N$  and  $\nu C=C$  frequencies respectively<sup>16</sup>. These bands show shifts to lower wavenumbers in the IR spectra of the metal complexes indicating the involvement of nitrogen of azomethine group in the metal complex formation<sup>17,18</sup>. The coordinated nature of water molecule was confirmed by a broad band in the region  $3300-3400 \text{ cm}^{-1}$  due to stretching mode and a

Table 1—Analytical and structural data of mixed schiff base complexes

Complexes	Found (Calc) %				$\mu_{\text{eff}}$ (B.M.)
	Metal	N	C	H	
$(CuC_{26}N_3O_3H_{21} \cdot 2H_2O)$	11.60 (12.15)	8.16 (8.03)	60.21 (59.11)	4.11 (4.01)	1.85
$(CuC_{21}N_3O_3H_{19} \cdot 2H_2O)$	15.11 (14.09)	9.08 (9.32)	54.01 (55.93)	5.21 (5.10)	1.82
$(CuC_{20}N_3O_2H_{17} \cdot 2H_2O)$	16.02 (15.73)	11.01 (10.48)	58.50 (59.47)	4.98 (5.20)	1.92
$(CuC_{20}N_3O_2H_{17} \cdot 2H_2O)$	16.52 (15.73)	11.08 (10.48)	59.03 (59.47)	5.72 (5.20)	1.85
$(NiC_{26}N_3O_3H_{21} \cdot 2H_2O)$	11.52 (11.33)	8.20 (8.11)	61.02 (60.26)	4.90 (4.82)	3.90
$(NiC_{21}N_3O_3H_{19} \cdot 2H_2O)$	13.01 (12.88)	9.10 (9.22)	55.80 (55.24)	5.13 (5.04)	3.28
$(NiC_{20}N_3O_3H_{17} \cdot 2H_2O)$	14.02 (14.36)	9.82 (10.27)	59.20 (58.73)	5.51 (5.13)	3.20
$(NiC_{20}N_3O_3H_{17} \cdot 2H_2O)$	13.85 (14.36)	10.35 (10.27)	57.8 (58.73)	5.40 (5.13)	3.80



band at  $\sim 800 \text{ cm}^{-1}$  due to rocking mode in the  $Cu(II)$  and  $Ni(II)$  complexes. The new bands observed in the far IR spectra of the metal complexes at  $450$  and  $380 \text{ cm}^{-1}$  are due to  $\nu M-O$  and  $\nu N-M$  respectively.

Table 2—Fungicidal activity data of mixed schiff base complexes in PDA medium

Complexes	Concentration of complexes	% inhibition	
		<i>A. triticina</i>	<i>P. recondita</i>
(CuC <sub>26</sub> N <sub>3</sub> O <sub>3</sub> H <sub>21</sub> ·2H <sub>2</sub> O)	10 µg/ml	(70-90)	(60.70)
(CuC <sub>21</sub> N <sub>3</sub> O <sub>3</sub> H <sub>19</sub> ·2H <sub>2</sub> O)	10 µg/ml	(75-90)	(50-75)
(CuC <sub>20</sub> N <sub>3</sub> O <sub>2</sub> H <sub>17</sub> ·2H <sub>2</sub> O)	10 µg/ml	(75-85)	(70-90)
(CuC <sub>20</sub> N <sub>3</sub> O <sub>2</sub> H <sub>17</sub> ·2H <sub>2</sub> O)	10 µg/ml	(70-90)	(70-90)
(NiC <sub>26</sub> N <sub>3</sub> O <sub>3</sub> H <sub>21</sub> ·2H <sub>2</sub> O)	10 µg/ml	(60.70)	(65-75)
(NiC <sub>21</sub> N <sub>3</sub> O <sub>3</sub> H <sub>19</sub> ·2H <sub>2</sub> O)	10 µg/ml	(65-70)	(60-70)
(NiC <sub>20</sub> N <sub>3</sub> O <sub>2</sub> H <sub>17</sub> ·2H <sub>2</sub> O)	10 µg/ml	(60-70)	(60-70)
(NiC <sub>20</sub> N <sub>3</sub> O <sub>2</sub> H <sub>17</sub> ·2H <sub>2</sub> O)	10 µg/ml	(60-70)	(60-75)

### Fungicidal activity

The antifungal activity of the compounds was checked by Agar plate technique<sup>10-11</sup>. Seven-day old cultures of *Alternaria triticina* and *Puccinia recondita* were used as test organisms which were grown on potato agar medium prepared by dissolving 79g of dried potato powder, 20g of dextrose and 1.0g of agar in 150ml of water. The mixture was then heated till it became a jelly-like substance; it was then poured in a petri dish and cooled and then used as PDA medium.

For test solution a concentration of 10 µg/ml was used. The percentage inhibition was calculated as  $100X(C-T)/C$  where C is the diameter of fungus colony in test plate. All the complexes and ligands were found to be highly active against both the organisms tested. The metal complexes were more active than the corresponding ligands which is in accordance with the fact that chelation of metal to ligands increases the fungitoxicity of the molecule<sup>19</sup>.

### Acknowledgement

The authors are thankful to Prof J M Trivedi, Head, Applied Chemistry Department for providing necessary laboratory facilities. The authors are also thankful to Prof P K Bhattacharya, Head, Chemistry Department for permission to work in his laboratory.

### References

- 1 Thaker B T & Bhattacharya P K, *J inorg nucl Chem*, 37 (1975) 615.
- 2 Thaker B T & Bhattacharya P K, *Indian J Chem*, 14 (1976) 619.
- 3 Mohankumar V B & Bhattacharya P K, *J inorg nucl Chem*, 52 (1975) 1041.
- 4 Doraswami Uma & Bhattacharya P K, *J inorg nucl Chem*, 97 (1975) 1665.
- 5 Cyba H A, *US PAT* 3-398-170/1968; *Chem Abstr*, 69 (1968) 6363.
- 6 Snamt T & Umezari S, *Bull chem Soc (Japan)*, 29 (1956) 975.
- 7 Theiss H, Schomberger H & Borach K, *Arch Pharma*, 299 (1966) 1031.
- 8 Sen R N & Ray S K, *J chem Soc*, 9 (1932) 173.
- 9 Dharkarey R & Saxena G, *J chem Soc*, 32 (1985) 35.
- 10 Srivastav U, Khan R H & Bahel S C, *J Antibact Antifung Agents Japan*, 7 (1979) 8.
- 11 Harrigan W F & Margaret E, *Laboratory methods in microbiology* (Academic Press, Agriculture College Ayr Scotland) 1966, p 236.
- 12 Lever A B P, *Inorganic electronic spectroscopy* (Elsevier New York) 1968, p 236.
- 13 Yamada S, *Coord Chem Rev*, 1 (1963) 141.
- 14 Figgis B N & Lewis, *J Progr inorg Chem*, 12 (1964) 1954.
- 15 Flipen R B & Fridberg S A, *Phys Rev*, 121 (1961) 1541.
- 16 Nakamota K, *Infrared spectra of inorganic and coordination compounds*, 2nd edn (Wiley Interscience, New York) 1970, 163.
- 17 Daasch L M & Haninem U E, *J Am chem Soc*, 72 (1950) 3673.
- 18 Cox M, Clark R J H & Hilledge M J, *Nature London*, 212.
- 19 Cifferi R & Baldacci E, *Inst Bull Plant Project*, 19 (1945) 33.