

Mixed Ligand Complexes of Cu(II) & Ni(II) with Salicylaldehyde & 2-Hydroxy-, 2-Hydroxy-4-methyl- & 2-Hydroxy-5-methyl-benzophenones & Their Reaction with Amines*

V. B. MOHAN KUMAR & P. K. BHATTACHARYA

Chemistry Department, M.S. University of Baroda, Baroda 390002

Received 7 February 1976; accepted 23 July 1976

Mixed ligand complexes of the type MLL' [where $M = \text{Cu(II)}$ or Ni(II) , $\text{LH} = \text{salicylaldehyde}$ and $\text{L'H} = 2\text{-hydroxybenzophenone}$ or its 4- or 5-methyl derivative] have been prepared. The mixed ligand complexes on treatment with ammonia afford imine complexes containing one molecule each of salicylaldehyde and 2-hydroxybenzophenoneimine. The above Schiff base complexes can also be prepared by treating metal ammine complexes with one equivalent each of salicylaldehyde and 2-hydroxybenzophenone or its methyl derivative. In the reaction of mixed imine Schiff base complexes with ethylenediamine or propylenediamine, amine exchange takes place and new Schiff base complexes are formed where the diamines have salicylaldehyde condensed at one end and 2-hydroxybenzophenone or its methyl derivative condensed at the other end. The Cu(II) complexes have a square planar structure while Ni(II) mixed ligand complexes probably have a distorted octahedral geometry due to polymerization. Ni(II) Schiff base complexes have a square planar structure. The spectral and magnetic moment data of the compounds have been discussed.

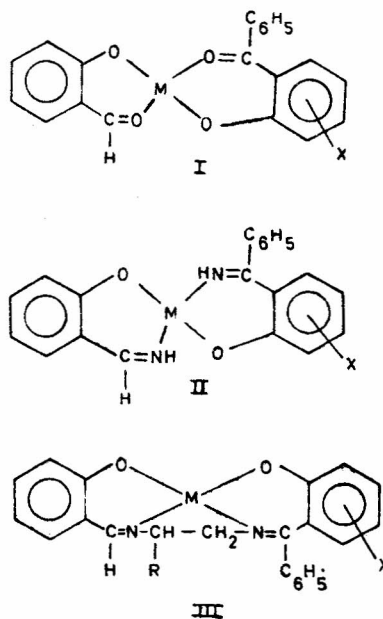
STUDY of the reactions of amine with 2-hydroxyacetophenone or bis-2-hydroxybenzophenone complexes of Cu(II) and Ni(II) has been recently reported from our laboratory. The possibility of the formation of mixed Schiff base complexes of Ni(II) with different N-substituted bis-salicylaldehyde ligands has been indicated by Chakravorty and Holm³ on the basis of NMR studies. Such complexes have, however, not been isolated in the solid state. Reactions of mixed ligand complexes of the type MLL' where $\text{LH} = \text{salicylaldehyde}$ and $\text{L'H} = 2\text{-hydroxyacetophenone}$ ⁴ or $\text{L'H} = 2\text{-hydroxy-1-naphthaldehyde}$ and $\text{L'H} = 2\text{-hydroxybenzophenone}$ ⁵ with amines have been reported recently by Bhattacharya and coworkers. The present paper deals with the preparation of mixed ligand complexes of the general formula MLL' , where $M = \text{Cu(II)}$ or Ni(II) , $\text{LH} = \text{salicylaldehyde}$ and $\text{L'H} = 2\text{-hydroxybenzophenone}$ or its methyl derivatives and their reaction with ammonia ethylenediamine (en) and propylenediamine (pn). The mixed ligand and mixed imine Schiff base complexes can be represented by the structures I, II and III.

Materials and Methods

2-Hydroxybenzophenone and its methyl derivatives were prepared and recrystallized from abs. ethanol. The complexes were prepared in non-aqueous medium. Nickel nitrate and cupric chloride used were of Analar grade.

The magnetic susceptibilities of Cu(II) and Ni(II) complexes were determined at room temperature

*Part II of the series "Studies on some mixed Schiff base complexes".



by the Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. IR spectra of the complexes were recorded on a Perkin-Elmer 267 grating infrared spectrophotometer whereas electronic spectra in the region 300-1000 nm in chloroform were taken on a DU-2 Beckman spectrophotometer at room temperature using 1 cm quartz cell, where the compounds were insoluble in chloroform, their reflectance spectra were taken on a DU-Beckman spectrophotometer in LiF with dilution 2:1 in the region 400-1000 nm.

TABLE 1 — ANALYTICAL DATA OF Cu(II) AND Ni(II) MIXED LIGAND COMPLEXES AND MIXED SCHIFF BASE COMPLEXES

No.	Complexes	Metal (%)		N (%)		μ_{eff} BM
		Calc.	Found	Calc.	Found	
1	(Salicylaldehydato)(2-hydroxybenzophenonato)Cu(II)	16.65	16.40	—	—	1.93
2	(Salicylaldehydato)(2-hydroxybenzophenoniminato)Cu(II)	16.74	16.50	7.38	7.61	1.91
3	[N,N'-Ethylene(salicylaldehydato-2-hydroxybenzophenoniminato)]-Cu(II)	15.67	15.30	6.90	6.45	1.86
4	[N,N'-Propylene(salicylaldehydato-2-hydroxybenzophenoniminato)]-Cu(II)	15.15	14.90	6.67	6.19	1.88
5	(Salicylaldehydato)(2-hydroxybenzophenonato)Ni(II)	15.58	15.21	—	—	3.30
6	(Salicylaldehydato)(2-hydroxybenzophenoniminato)Ni(II)	15.67	15.41	7.47	7.84	0.89
7	[N,N'-Ethylene(salicylaldehydato-2-hydroxybenzophenoniminato)]-Ni(II)	14.65	14.31	6.99	7.40	0.89
8	[N,N'-Propylene(salicylaldehydato-2-hydroxybenzophenoniminato)]-Ni(II)	14.15	13.82	6.75	7.15	0.65
9	(Salicylaldehydato)(2-hydroxy-4-methylbenzophenonato)Cu(II)	16.06	15.80	—	—	1.77
10	(Salicylaldehydato)(2-hydroxy-4-methylbenzophenoniminato)Cu(II)	16.15	15.89	7.11	6.84	1.81
11	[N,N'-Ethylene(salicylaldehydato-2-hydroxy-4-methylbenzophenoniminato)]Cu(II)	15.15	14.90	6.67	6.40	1.94
12	[N,N'-Propylene(salicylaldehydato-2-hydroxy-4-methylbenzophenoniminato)]Cu(II)	14.66	14.42	6.46	5.93	1.91
13	(Salicylaldehydato)(2-hydroxy-4-methylbenzophenonato)Ni(II)	15.02	14.80	—	—	3.16
14	(Salicylaldehydato)(2-hydroxy-4-methylbenzophenoniminato)Ni(II)	15.10	14.90	7.20	6.96	1.10
15	[N,N'-Ethylene(salicylaldehydato-2-hydroxy-4-methylbenzophenoniminato)]Ni(II)	14.15	13.86	6.75	6.51	0.50
16	[N,N'-Propylene(salicylaldehydato-2-hydroxy-4-methylbenzophenoniminato)]Ni(II)	13.69	13.46	6.53	6.68	0.64
17	(Salicylaldehydato)(2-hydroxy-5-methylbenzophenonato)Cu(II)	16.06	15.89	—	—	1.95
18	(Salicylaldehydato)(2-hydroxy-5-methylbenzophenoniminato)Cu(II)	16.15	15.80	7.11	6.85	1.98
19	[N,N'-Ethylene(salicylaldehydato-2-hydroxy-5-methylbenzophenoniminato)]Cu(II)	15.15	14.91	6.67	6.93	2.10
20	[N,N'-Propylene(salicylaldehydato-2-hydroxy-5-methylbenzophenoniminato)]Cu(II)	14.66	14.31	6.46	5.91	2.06
21	(Salicylaldehydato)(2-hydroxy-5-methylbenzophenonato)Ni(II)	15.02	14.78	—	—	3.39
22	(Salicylaldehydato)(2-hydroxy-5-methylbenzophenoniminato)Ni(II)	15.10	15.15	7.20	7.10	1.10
23	[N,N'-Ethylene(salicylaldehydato-2-hydroxy-5-methylbenzophenoniminato)]Ni(II)	14.15	13.71	6.75	6.15	0.77
24	[N,N'-Propylene(salicylaldehydato-2-hydroxy-5-methylbenzophenoniminato)]Ni(II)	13.69	13.40	6.53	7.00	1.10

(Salicylaldehydato)(2-hydroxybenzophenonato)Cu(II) or Ni(II) — Precooled ($^{\circ}\text{C}$) salicylaldehyde (1.05 ml) and 2-hydroxybenzophenone (1.98 g) solutions in abs. ethanol (30 ml) were added to a cold ($^{\circ}\text{C}$) ethanolic solution of CuCl_2 (1.70 g) or $\text{Ni}(\text{NO}_3)_2$ (2.90 g). The pH was raised to ~ 5 by adding ammonia solution and the reaction mixture stirred well until solid separated out. It was filtered, washed and dried. The complexes prepared (Table 1) were insoluble in organic solvents and have not been recrystallized.

(Salicylaldehydato)(2-hydroxybenzophenoniminato)-Cu(II) or Ni(II) — These complexes were prepared by the following two methods. In the first method the mixed imine Schiff base complexes were prepared by refluxing (4 hr) the preformed mixed ligand complexes (2 g) of Cu(II) or Ni(II) in ethanol (25 ml) with an excess of ammonia (50 ml).

In the second method ammonia (50 ml) was added to CuCl_2 (1.70 g) or $\text{Ni}(\text{NO}_3)_2$ (2.90 g) and to it was added an ethanolic solution of salicylaldehyde (1.05 ml) or 2-hydroxybenzophenone (1.98 g). The reaction mixture was refluxed for 3 hr when a solid separated out which was filtered, washed, dried and recrystallized from chloroform (Table 1).

[N,N'-Ethylene- or propylene-(salicylaldehydato-2-hydroxybenzophenoniminato)]Cu(II) or Ni(II) —

These above tetradentate Schiff base complexes were prepared directly and by the amine exchange methods.

In the first method the preformed mixed ligand complexes (2 g) of Cu(II) or Ni(II) were refluxed for 5 hr with en or pn (2 ml) in abs. ethanol (30 ml). The solid separated out was filtered, washed with hot water, 50% ethanol, dried and recrystallized from chloroform (Table 1).

The above complexes were also obtained by the transimination reaction. The preformed imine Schiff base complex of Cu(II) or Ni(II) (2 g) with ammonia was refluxed (5 hr) under stirring with en or pn (2 ml) in ethanol (30 ml). The complex formed was filtered, washed, dried and recrystallized from chloroform (Table 1).

Complexes of the substituted 2-hydroxybenzophenones were prepared by similar methods as described above.

Results and Discussion

The complexes listed in Table 1 are crystalline, stable and insoluble in water. However, the Schiff base complexes are soluble in chloroform. TLC of all the complexes was performed using chloroform-ether (5:3) as the solvent. When the above solvent was used for the mixture of the two corresponding bis-complexes two spots were

obtained indicating that the two components have distinct R_f values. The mixed ligand complexes, however, showed only one spot with R_f value being the intermediate of the two corresponding bis-complexes. This shows that the mixed complexes are homogeneous rather than mixtures of the bis-complexes of the two ligands.

Mixed ligand and amine complexes of Cu(II) — The Cu(II) complexes are paramagnetic showing the presence of one unpaired electron. The value of μ expected for an unpaired electron is 1.73 BM. The excess over this value found for the present complexes (Table 1) can be attributed to spin orbit coupling⁶. The visible absorption spectra of Cu(II) complexes (1, 9) and 17 (Table 1) are similar and show a peak around 650 nm. However, Cu(II) imine Schiff base complexes (2, 10 and 18) show a band around 560 nm ($\epsilon \sim 100$) and the en (3, 11, 19) and pn (4, 12, 20) Schiff base complexes exhibit a band at about 550 nm ($\epsilon \sim 375$). The shift of band to the lower wavelength in Schiff base⁷ complexes indicates formation of a stronger M-N bond⁸. The higher extinction coefficient obtained in the case of en or pn Schiff base complexes indicates that the nitrogen atoms are in *cis*-position resulting in structures without a centre of symmetry.

Mixed ligand complexes and amine complexes of Ni(II) — The mixed ligand Ni(II) complexes (5, 13 and 21) are also paramagnetic. Their reflectance spectra show bands around 620, 670 and 730 nm but no band in the higher wavelength region thereby eliminating a tetrahedral structure for the Ni(II) complexes.

It has been reported earlier^{9,10} that bis-salicylaldehyde and bis-ketone complexes of Ni(II) have distorted octahedral structure due to polymerization. By analogy with this, the present compounds 5, 13 and 21 (Table 1) can be expected to have distorted octahedral structure due to polymerization.

The Schiff base Ni(II) complexes are weakly paramagnetic, and were recrystallized until constant magnetic susceptibility was obtained. Anomalous magnetic behaviour of Ni(II) Schiff base complexes have been studied and interpreted in detail earlier¹¹⁻¹³. On the basis of earlier studies the paramagnetism observed in the present Schiff base complexes may be attributed to the partial polymerization. Due to low solubility of the complexes, their molecular weights could not be determined.

Visible spectra of the imine Schiff base complexes (6, 14, 22) in chloroform show a band at ~ 500 nm ($\epsilon \sim 90$). This is probably due to breakdown of the complexes resulting in square planar geometry. The absence of bands beyond 600 nm further confirms square planar structure for the complexes. In the case of (7, 15, 23) en or pn (8, 16, 24) Schiff base complexes similar spectra were obtained with a band around 550 nm but the extinction coefficient was high ($\epsilon \sim 140$). The higher extinction coefficient for these complexes may be due to the *cis*-structure with lower symmetry. That the coordination in mixed ligand complexes is through aldehydic and ketonic CO group of the ligand is evident for the shift in ν_{CO} to lower frequency region (1650 cm^{-1}) in the IR spectra of the mixed ligand complexes as compared with the free ligands. This band disappears and a new band at 1620 cm^{-1} assignable to $\nu_{C=N}$ appears in the Schiff base complexes. In the imine Schiff base complexes, the band at 3210 cm^{-1} corresponds to ν_{NH} which is absent in the case of en and pn Schiff base complexes.

Acknowledgement

The authors express their thanks to Prof. S. M. Sethna, Head, Department of Chemistry, for providing the necessary facilities. One of them (V.B.M.) is thankful to the M.S. University, Baroda, for the award of a research fellowship.

References

1. THAKER, B. T. & BHATTACHARYA, P. K., *J. Indian chem. Soc.*, **52** (1975), 454.
2. MOHAN KUMAR, V. B. & BHATTACHARYA, P. K., *Indian J. Chem.*, **13** (1975), 928.
3. CHAKRAVORTY, A. & HOLM, R. H., *J. Am. chem. Soc.*, **86** (1964), 3999.
4. THAKER, B. T. & BHATTACHARYA, P. K., *J. inorg. nucl. Chem.*, **37** (1975), 615.
5. MOHAN KUMAR, V. B. & BHATTACHARYA, P. K., *J. Indian chem. Soc.*, **52** (1975), 1041.
6. EARNSHAW, A., *Introduction to magnetochemistry* (Academic Press, New York), 1969, 35.
7. HIGSON, B. M., LEWTON, D. A. & MEKENZIE, E. D., *J. chem. Soc., Dalton*, (1974), 1690.
8. FRENCH, H. S., MAGGE, M. Z. & SHEFFIELD, E., *J. Am. chem. Soc.*, **64** (1942), 1924.
9. GRADDON, D. P. & MOCKLER, K. M., *Aust. J. Chem.*, **20** (1967), 21-23.
10. SACCONI, L., PAOLETTI, P. & CINI, R., *J. Am. chem. Soc.*, **80** (1958), 3583.
11. HOLM, R. H. & O'CONNOR, M. J., *Progr. inorg. Chem.*, **14** (1971), 252.
12. SACCONI, L., *Transition Metal Chem.*, **4** (1968), 269.
13. HOLM, R. H., *J. Am. chem. Soc.*, **83** (1961), 4683.