Asian Journal of Chemistry Vol. 10, No. 2 (1998), 306–311

Synthesis, Characterization and Antimicrobial Activity of Cobalt(II), Nickel(II) and Copper(II) Complexes with 3-Phenyl-5-Substituted Indole-2-Carboxyhydrazones of Salicylaldehyde

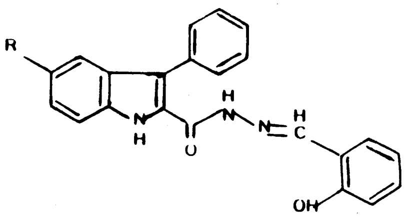
G. RAJSHEKHAR, B.K. SHANTHAVEERAPPA, S.D. ANGADI,
V.H. KULKARNI and B.H.M. MRUTHYUNJAYASWAMY*
Department of Chemistry
Gulbarga University, Gulbarga-585 106, India

Co(II), Ni(II) and Cu(II) complexes have been prepared by reacting metal chlorides with 3-phenyl-5-substituted indole-2-carboxyhydrazones of salicylaldehyde in alcohol medium. All the complexes are coloured solids and are non-electrolytes in DMF and DMSO. Elemental analyses conform to the 1:2 stoichiometry. Magnetic, electronic and IR spectral information suggest that divalent Co, Ni and Cu in these complexes exhibit co-ordination number six. The ligands and complexes have been tested for their biological activity.

INTRODUCTION

Hydrazides have been successfully tried for preparing the complexes with transition metals and it has been shown that both NH_2 and C=O groups are involved in the bond formation[1–5]. The hydrazones are the products of hydrazides and aldehydes or ketones. A good research work has been carried out from our laboratory on the synthesis of various substituted indole-2-carboxyhydrazides, which can serve as very good precursors for large number of novel heterocyclic systems. Some indole-2-carboxyhydrazides have shown good anti-inflammatory and antimicrobial activities[6, 7]. Mruthyunjayaswamy *et al.*[8] have synthesised 3-(3′,5′-disubstituted indole-2′-carboxamidyl)-7-substituted-1,3-benzoxazines by making use of 3,5-disubstituted indole-2-carboxyhydrazides as the starting materials.

The paucity of information on the complexes of the ligands (Fig. 1) has infused interest in us to undertake a systematic study of transition metal complexes with these ligands. In this paper we address ourselves to the synthesis, characterization and antimicrobial activity of Co(II), Ni(II) and Cu(II) complexes.



R = Br, OCH_3, Cl
Fig. 1 Ligands a, b, c

EXPERIMENTAL

Synthesis of ligands

All the chemicals used were of reagent grade, 3-phenyl-5-substituted indole-2-carboxyhydrazides were prepared according to the method reported earlier[9].

2-(3′,5′-disubstituted indole-2′-carboxamidyl)iminomethylphenols (a–c)

Salicylaldehyde (0.002 mol) and 3-phenyl-5-substituted indole-2-carboxyhydrazides (0.002 mol) were refluxed in presence of catalytic amount of concentrated hydrochloric acid in ethanol (10 mL) for 4 h on a water bath. Excess of ethanol was removed by distillation. Crystalline residue obtained was further purified by crystallisation to afford (**a–c**) in good yield.

Synthesis of complexes

To an ethanolic solution containing 2-(3′,5′-disubstituted indole-2′-carboxamidyl)iminomethylphenols (0.02 mol), the metal chlorides (0.01 mol) were added. The reaction mixture was refluxed for about 2 h and then was added 2 g sodium acetate. Again the reaction mixture was refluxed for 1 h. The reaction mixture was poured into distilled water, the precipitated complex filtered, washed with distilled water and dried *in vacuo* over fused calcium chloride.

TABLE-1
ANALYTICAL, MOLAR CONDUCTANCE, MAGNETIC MOMENT, MELTING POINT AND COLOUR OF THE COMPLEXES

Complex/Colour	Elemental analysis Found (Calcd.) %		Conductivity in ohm^{-1} cm^{2} mol^{-1}		μ_{eff} (B.M.)	mp (°C)
	M	N	DMF	DMSO		
$Co(C_{22}H_{15}N_3O_2Cl)_2$ (dark brown)	7.25 (7.04)	10.00 (10.04)	4.12	2.94	4.70	315
$Co(C_{22}H_{15}N_3O_2Br)_2$ (dark brown)	6.34 (6.36)	9.00 (9.08)	3.21	2.57	4.80	298
$Co(C_{23}H_{18}N_3O_2)_2$ (dark brown)	7.32 (7.40)	10.23 (10.56)	4.29	3.21	4.90	275
$Ni(C_{22}H_{15}N_3O_2Cl)_2$ (greenish yellow)	7.00 (7.04)	10.00 (10.04)	2.19	2.51	3.24	295
$Ni(C_{22}H_{15}N_3O_2Br)_2$ (greenish yellow)	6.30 (6.34)	9.01 (9.08)	2.51	2.64	3.20	297
$Ni(C_{23}H_{18}N_3O_2)_2$ (greenish yellow)	7.12 (7.37)	10.30 (10.56)	2.71	3.12	3.26	>315
$Cu(C_{22}H_{15}N_3O_2Cl)_2$ (parrot green)	7.55 (7.55)	9.78 (9.99)	2.14	2.71	1.90	310
$Cu(C_{22}H_{15}N_3O_2Br)_2$ (parrot green)	6.74 (6.83)	9.00 (9.03)	1.94	2.57	1.91	300
$Cu(C_{23}H_{18}N_3O_2)_2$ (parrot green)	7.70 (7.93)	10.23 (10.05)	2.39	2.86	1.92	295

*Calculated values

Co(II), Ni(II) and Cu(II) in the complexes were determined gravimetrically as oxinate, dimethyl glyoxinate and salicylaldoxinate respectively[10]. Nitrogen was determined by Kjeldahl method. The results of the elemental analysis are summarised in Table-1.

The IR spectra of the ligands and their complexes were recorded on a Hitachi 270–50 infrared spectrophotometer in the region 4000–250 cm^{-1} in nujol using KBr discs. The electronic spectra were taken with UV-160A, UV-visible recording Shimadzu spectrophotometer in the region 900–200 nm. The magnetic susceptibilities of the complexes at room temperature were obtained with a Guoy balance using $Hg[Co(NCS)_4]$ as a calibrant. Molar conductances were measured in DMF and DMSO using Elico model CM 82T conductivity bridge, with a cell of cell constant 1.1 cm^{-1}.

Antibacterial activity of test compounds was assessed against *S. aureus* and *E. coli* and the antifungal activity was assessed against *A. niger* by cup-plate diffusion method.

RESULTS AND DISCUSSION

The cobalt(II) complexes are dark brown, the nickel(II) complexes are greenish yellow and the copper(II) complexes are parrot green in colour. These complexes are soluble in DMF, DMSO and dioxane. All the complexes are amorphous and stable in air and have high melting points (*ca.* 300°C).

The elemental analyses (Table-1) show that these complexes have 1:2 stoichiometry of the type ML_2. The molar conductance values in DMF and DMSO at the concentration 10^{-3} M are in the range of 2–5 ohm^{-1} cm^2 mol^{-1}, indicating that all these complexes are non-electrolytes.

The hydrazones exhibit keto-enol tautomerism and as such they exist in one of the two forms in the complexes[11]. A medium intensity broad band observed around 3260 cm^{-1} and the other band of high intensity around 1650 cm^{-1} are assigned to ν(NH) and ν(C═O) respectively in view of the previous assignments[11]. It has been established that the formation of intramolecular hydrogen bonding results in weakening and broadening of the band attributable to —OH vibration and also shifts to lower frequency[12]. In view of this a broad band with fine structure observed in the region 2700–2650 cm^{-1} is attributed to the intramolecularly H-bonded OH stretch[12]. This band is absent in the complexes showing that the ligands have reacted with the metal ions *via* deprotonation. The band due to ν(NH)[13] in the region 3240–3222 cm^{-1} remains unperturbd in the complexes. NH group does not involve in bond formation with the metal ions. The bands in the region 1670–1640 cm^{-1} are assigned to C═O stretch[14]. A negative shift of about 45 cm^{-1} in the complexes indicates the bonding of C═O group to the metal ions through oxygen.

The band due to phenolic C—O[11] around 1280 cm^{-1} in ligands shows a considerably high frequency shift and observed in the complexes in the region 1330–1290 cm^{-1}. This suggests that the oxygen atom of the phenolic —OH group has participated in the coordination. The C═N stretch[15] for the ligand is observed in the region 1625–1610 cm^{-1}. The same stretch is observed in the region

1600–1550 cm^{-1} for the complexes suggesting that the coordination bond is formed between nitrogen of the azomethine group and metal, resulting in the decrease of the bond order of the C═N group.

In the light of previous assignments[16], we have assigned the bands in the region 490–400 cm^{-1} to ν(M—N) coupled with a ligand vibration and the band in the region 580–530 cm^{-1} may be attributed to ν(M—O). .

The magnetic moments at room temperature are listed in Table-1. The observed magnetic moment values for Co(II) complexes are in the range of 4.7–4.9 B.M. These values are within the expected range of 4.7–5.2 B.M.[17, 18] for octahedral complexes. Hence, the Co(II) complexes may be expected to have octahedral configuration. For Ni(II) complexes the observed magnetic moments lie in the range 3.24–3.26 B.M. These values are well within the range of reported values for hexa-coordinated nickel(II) complexes (2.9–3.4 B.M.)[17, 18]. For Cu(II) complexes the magnetic moments fall in the range of 1.90–1.92 B.M. These values agree well with the expected spin only values reported for the Cu(II) complexes (1.75–2.20 B.M.)[18]. This indicates the absence of spin-spin interaction.

The electronic spectra of Co(II), Ni(II) and Cu(II) complexes are recorded in DMF (10^{-3} M). The values of ligand field parameters such as Dq, B′, β, % have been calculated by using Underhill and Billing equation[22]. The results are presented in Table-2.

For the octahedral Co(II) complexes three spin allowed transitions are expected, in the region about 18,000–10,000 cm^{-1} .[19]

They are $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) (around 10,000 cm^{-1})

$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) (around 15,000 cm^{-1})

$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) (around 18,000 cm^{-1})

TABLE-2
ELECTRONIC SPECTRAL DATA OF COMPLEXES OF Co(II), Ni(II) AND Cu(II) WITH SCHIFF BASES

Complexes	Solvent % Conc. 10^{-3} M	Transitions (cm^{-1})			Dq cm^{-1}	B′ cm^{-1}	β	β%	LFSE kcal mol^{-1}	ν_2/ν_1
		1	2	3						
$Co(C_{22}H_{15}N_3O_2Cl)_2$	DMF	8380*	16670	21740	829	884	0.91	24.41	14.21	1.98
$Co(C_{22}H_{15}N_3O_2Br)_2$	DMF	8264*	17644	19230	938	805	0.83	16.75	16.08	2.13
$Co(C_{23}H_{18}N_3O_2)_2$	DMF	8333*	17803	20000	947	853	0.88	11.79	16.24	2.13
$Ni(C_{22}H_{15}N_3O_2Cl)_2$	DMF	8640*	13890	22730	864	713	0.67	32.44	29.62	1.60
$Ni(C_{22}H_{15}N_3O_2Br)_2$	DMF	8450*	15620	21740	845	800	0.75	24.24	28.97	1.85
$Ni(C_{23}H_{18}N_3O_2)_2$	DMF	8290*	13513	22727	829	758	0.71	28.20	28.40	1.63
$Cu(C_{22}H_{15}N_3O_2Cl)_2$	DMF	—	13700	16390	1538	—	—		26.36	—
$Cu(C_{22}H_{15}N_3O_2Br)_2$	DMF	—	14930	15870	1538	—	—		26.36	—
$Cu(C_{23}H_{18}N_3O_2)_2$	DMF	—	13160	16670	1471	—	—		25.22	—

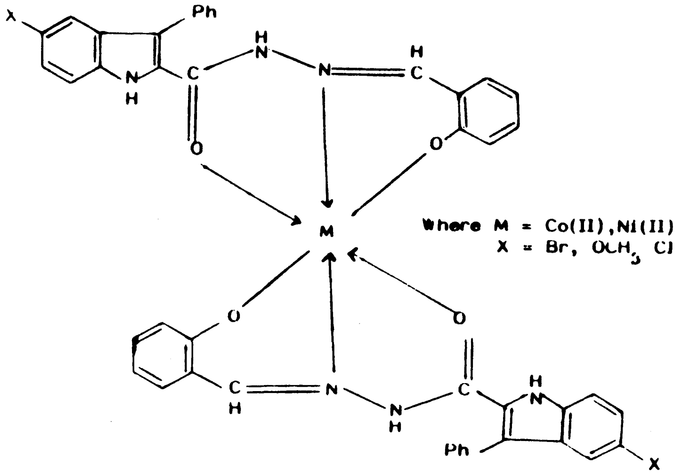
*Calculated values

The Co(II) complexes in the present investigation exhibit absorption bands in the region 21740–19230 cm^{-1} corresponding to ν_3 transition and in the region 17803–16670 cm^{-1} coresponding to ν_2 transitions. The band ν_1 could not be located due to instrument's limitation. The ratio $\nu_{2\,obs.}/\nu_{1\,cal.}$ was found to be in the range 1.98 to 2.13 as required for octahedral cobalt(II) complexes[23].

The octahedral and six coordinated nickel(II) complexes display simple spectra consisting of three transitions from $^3A_{2g}(F) \rightarrow {}^3T_{2g}$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ levels. These are reported to occur in the following regions: 13000–7000, 20000–11000 and 27000–19000 cm^{-1} respectively.[20] The ratio of $\nu_{2\,obs.}/\nu_{1\,cal.}$ lies in the range 1.60 to 1.85 expected for octahedral nickel(II) complexes[24], the usual range being 1.50 to 1.76 for octahedral symmetry. In the light of these assignments, the bands observed for these nickel(II) complexes in the region 22730–22740 cm^{-1} and in the region 15620–13513 cm^{-1} are assigned to ν_3 and ν_2 transitions respectively.

For an octahedral Cu(II) complex the expected $^2E_g \rightarrow {}^2T_{2g}$ band is around 12500 cm^{-1}.[21] The Cu(II) complexes under study exhibit a single broad band in the region 16670–13000 cm^{-1} which implies that the complexes have tetragonally distorted octahedral structure. The broadness of the band may be due to dynamic John-Teller distortion.

The analytical results show that the complexes have 1:2 stoichiometry. The electronic spectral results and magnetic moment values obtained for these complexes indicate distorted octahedral configurations. The IR results show that these hydrazones exist in the keto form in the complexes and coordinate through C=O, C=N groups and react through OH group. All these facts taken together prompted us to propose the following structure for these complexes (Fig. 2).



where M = Co(II), Ni(II) and Cu(II)
X = Br, OCH_3, Cl
Fig. 2

The ligands and their complexes described in this work have been screened for antimicrobial activity against *E. coli, S. Aureus* and *A. niger.* It is evident from the results that complexes containing chloro and bromo substituents at 5′ position of indole moiety showed activity against all the organisms tested.

REFERENCES

1. P.V. Gaogorishvilli, M.V. Karkarashvilli and D.Z. Kalandrishvilli, Z. *Neorg. Khim.*, **14**, 1516 (1969); *Chem. Abstr.*, **71**, 66805p (1969).
2. K. Nagano, H. Kinoshita and A. Hirakawa, *Chem. Pharm. Bull.*, **12**, 1198 (1964).
3. R.C. Aggarwal and A. Bahadur, *Indian J. Chem.*, **7**, 1038 (1969).
4. J.F. Alcock, R.J. Baker and A.A. Daimantis, *Aust. J. Chem.*, **25**, 289 (1972).
5. R.M. Issa, M.F. Iskander and M.F. El-Shazly, Z. *Anorg. Allg. Chem.*, **354**, 98 (1967).
6. S.P. Hiremath, B.H.M. Mruthyunjayaswamy, N.J. Kalaskar and R.H. Kakkeri, *Gulbarga University Journal (Science & Technology)*, **112**, 38 (1990).
7. S.P. Hiremath, B.H.M. Mruthyunjayaswamy, M.G. Purohit, R.C. Kanta and R. Seshayyan, *J. Karn. Univ. Science* (1978).
8. B.H.M. Mruthyunjayaswamy, B.K. Shanthaveerappa and G. Rajashekhar (unpublished work).
9. S.P. Hiremath, B.H.M. Mruthyunjayaswamy and M.G. Purohit, *Indian J. Chem.*, **16B**, 789 (1978).
10. A.I. Vogel, A Text book of Quantitative Inorganic Analysis, ELBS, 3rd Edn., Longman Green, London.
11. N.S. Biradar and B.R. Havinale, *Inorg. Chem. Acta*, **17**, 157 (1976).
12. H.H. Freedman, *J. Am. Chem. Soc.*, **83**, 2900 (1961).
13. K.M. Ibrahim, T.H. Rakha, A.M. Abdallah and M.M. Hassanian, *Indian J. Chem.*, **32A**, 361 (1993).
14. A.C. Hiremath, M.B. Halli and N.V. Huggi, *J. Indian Chem. Soc.*, **61**, 191 (1984); **59**, 1017 (1982).
15. N.S. Biradar and V.H. Kulkarni, *J. Inorg. Nucl. Chem.*, **33**, 2451 (1971).
16. C. Noboru and K. Nakamoto, *Inorg. Chem.*, **10**, 798 (1975); K. Nakamoto, Infrared and Raman Spectra of Inorganic and Co-ordination Compounds, 3rd Edn., Wiley-Interscience, New York (1978).
17. B.N. Figgis, Introduction to Ligand Fields, Interscience, New York, p. 220 (1966).
18. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th Edn., Wiley, New York (1988).
19. (a) D.W. Meck and S.A. Bhradt, *Inorg. Chem.*, **4**, 584 (1968).
    (b) C.H. Krishna, C.M. Mahapatra and K.C. Dash, *J. Inorg. Nucl. Chem.*, **39**, 1253 (1977).
20. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Company, Amsterdam (1968).
21. T.M. Dunn, in: J. Lewis and R.G. Wilkins (Eds.), The Visible and Ultraviolet Spectra of Complex Compounds in Modern Co-ordination Chemistry, Interscience, New York (1960).
22. A.E. Underhill and D.E. Billing, *Nature*, **210**, 834 (1966).
23. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, New York (1984).
24. R.L. Carlin, Transition Metal Complexes, 4th Edn., Marcel-Dekker, New York (1968).

(*Received*: 26 September 1997; *Accepted*: 3 November 1997) AJC-1383