Asian Journal of Chemsitry Vol. 8, No. 3 (1996), 353-356

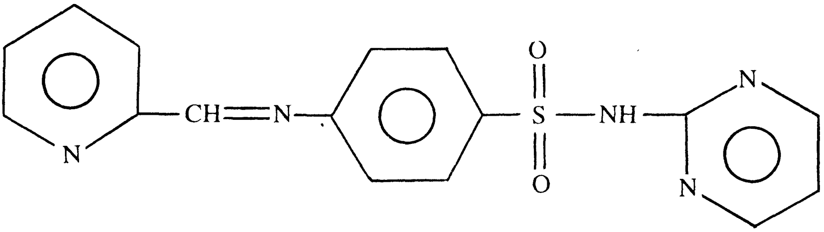
Synthesis and Structural Characterization of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of Schiff Base derived from Sulphadiazine and Pyridine-2-Carboxaldehyde

ASHOK K. PANDEY*, LALLAN MISHRA† and V.K. SINGH
Department of Chemistry
S.C. (Post-Graduate) College, Ballia-277 001, India

The chelation behaviour of Schiff base derived from sulphadiazine *i.e.*, 4-(2′-pyridomethyl)-imino-N-(2′-pyrimidyl)-benzene sulphonamide (L) with cobalt(II), nickel(II), copper(II) and zinc(II) salts has been studied. The complexes have been characterized by spectral (IR, NMR UV/visible), magnetic and powder X-ray diffraction studies as well as elemental analysis. All of the complexes except for copper(II) have octahedral coordination arrangement of ligand arount it.

INTRODUCTION

Sulphadiazine is a well known potential bactericide compound[1]. This drug acts as donor base and forms stable complexes with various metal ions[2, 3]. The coordination behaviour of sulpha-drugs has been reported earlier[4]. Gluko[5] and coworkers have studied the structure of solid crystalline palladium sulphaguanidine complexes and have reported the coordination of sulphaguanidine through NH_2 (aniline) group. It has therefore been thought that it would be worthwhile to investigate the coordinating behaviour of analogus sulphadiazine ligand (L) towards the biologically active trace metal ions.



EXPERIMENTAL

All the reagents used were of chemically pure grade. The ligand was prepared by refluxing sulphadiazine (4-amino-N-(2-pyrimidyl) benzene sulphonamide) (2.50 g, 0.01 mole) and pyridine-2-carboxaldehyde (1.06 g, 0.01 mole) in ethanol for 6 h. The excess solvent was reduced up to 15 cm^3 on water bath. After cooling

---

†Chemistry Department, Banaras Hindu University, Varanasi-221 005, India.

the content, a colourless precipitate was obtained. The crystalline solid thus obtained was filtered and washed several times with water followed by ethanol. The crude product was then recrystallized in water-ethanol (1 : 1) mixture. The complexes were prepared (except for cobalt(II)) by adding 25 mL of an aqueous ethanolic solution of respective metal chlorides (2 mmol) to that of ligand (2 mmol) in about 10 cm^3 ethanol with vigorous stirring. The whole content was further digested on a water bath for 1 h. The crystalline complex thus obtained was separated by filtration, washed by water and ethanol, and dried in vacuum.

The cobalt(II) complex was prepared by refluxing equimolar amounts of ligand and metal chloride in 30 cm^3 ethanol for 1 h. After cooling the reaction mixture the pink coloured cobalt(II) complex was precipated out.

The metals were estimated gravimetrically by standard procedure[6] after decomposing the complexes with HNO_3 whereas chlorine and sulphur were estimated as silver chloride and barium sulphate respectively, after decomposing the complexes with fusion mixture and Na_2O_2 (1:2:1) together in a nickel crucible. Carbon, hydrogen and nitrogen were determined microanalytically. The molar conductance was measured on a WTW conductivity bridge using concentration 10^{-3} M. The diamagnetic corrections were made using Pascal's constant[7].

All the complexes were found stable at room temperature and showed non-electrolytic behaviour in DMSO. The empirical composition of the complexes along with their physical and analytical data are represented in Table-1.

TABLE-1
PHYSICAL DATA FOR METAL COMPLEXES

Complexes (Colour)	m.p. (°C)	% Analysis Found (Calcd.)			
		M	C	H	N
($Co(L)Cl_2 \cdot 2H_2O$) (light pink)	180 (decomposed)	12.25 (11.68)	38.64 (38.02)	3.95 (3.36)	13.24 (13.86)
($Ni(L)Cl_2 \cdot 3H_2O$) (light green)	260–62	11.70 (11.23)	36.45 (36.73)	3.46 (3.63)	13.62 (13.39)
($Cu(L)Cl_2 \cdot 2H_2O$) (violet)	200 (decomposed)	13.41 (12.91)	39.29 (39.06)	2..32 (3.05)	14.56 (14.24)
($Zn(L)Cl_2 \cdot 3H_2O$) (colourless)	242–43	12.79 (12.33)	36.42 (36.27)	3.54 (3.58)	13.54 (13.22)

RESULTS AND DISCUSSION

Infrared spectra of the ligand showed bands in the region 3800 to 3140 cm^{-1} due to ν(NH) group. This peak was found unaltered in all metal complexes, indicating its non-participation during coordination with metal ions.

The peak due to CH=N group of ligand observed at *ca.* 1540 cm^{-1} is shifted towards lower region at *ca.* 1500 cm^{-1} indicating the coordination of CH=N group. Peak position observed at *ca.* 860 cm^{-1} and 580–570 cm^{-1} in ligand due to pyridyi group was shifted by 40 cm^{-1} in cobalt(II) thus showing the coordination of pyridyl nitrogen to the cobalt(II), whereas in the spectra of nickel(II), copper(II) and zinc(II) complexes, it remained constant. The spectra of the complexes showed a broad peak between 3400–3300 cm^{-1} due to $\nu(H_2O)$ which were further estimated quantitatively by the method reported earlier[8].

The ν(M—N pyridyl) and ν(M—N=CH) were observed at *ca.* 420 cm^{-1} and *ca.* 330 cm^{-1} respectively in the lower region of the IR spectra of the cobalt(II) complexes whereas nickel(II), copper(II) and zinc(II) complexes showed only one peak at 340–330 cm^{-1} range. The weak peaks observed at *ca.* 280–270 cm^{-1} in all complexes were assigned to ν(M—Cl).

It was thus inferred that in all complexes (except cobalt(II) complex) ligand acted as monodentate. The coordination of pyrimidyl group was discarded on the basis of peak positions observed at *ca.* 620 cm^{-1} and 540 cm^{-1} in ligand which were found unaltered in the complexes. However, it is tentative, since it seems difficult to distinguish between ν(pyridyl) and ν(pyrimidyl) possible on the basis of IR spectra only.

The peak appearing at δ 8.4 due to CH=N protons is thought to be mixed with pyridyl proteins. Aryl, pyridyl and pyrimidyl group protons remained constant. NH group proton was observed at δ 5.63 in sulphadiazine and Schiff base both. From ^1H NMR spectra of zinc(II) complex, it was observed that CH=N proton was slightly shifted to higher field by δ 0.3. Signal observed at δ 3.49 arises due to water molecules. The identification of NH and H_2O proton was further made by deuteration with D_2O.

From the ^{13}C NMR spectrum of the ligand, it was found that signal observed due to CH=N carbon at δ 161.9 shifted to 161.2 in Zn(II) complex, showing the coordination of CH=N group to the metal atom. Pyridyl carbon of the ligand remained same alongwith other ligand signals.

Thus on the basis of ^1H and ^{13}C NMR spectra it could be concluded that ligand coordinated to zinc(II) only through nitrogen atom of the CH=N group.

NMR spectra of other complexes could not be determined due to their poor solubility in deuterated solvents.

Magnetic moment values for nickel(II) and cobalt(II) complexes were found to be 2.78 B.M. and 4.52 B.M. respectively, which lie in the range for high spin octahedral complexes. The copper(II) complex gave magnetic moment value as 2.12 B.M. which lies in the range reported for square planar complexes[9]. The zinc(II) complex is diamagnetic in nature.

The elecronic spectra of the ligand and metal complexes showed very similar band at *ca.* 43000 cm^{-1} which was assigned to intraligand and M-L(II) transitions respectively.

The nickel(II) complex showed three d-d bands at *ca.* 9700, *ca.* 15400 and *ca.* 25000 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)\ (\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)\ (\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)\ (\nu_3)$ transitions respectively. The observation is found to be consistent with the octahedral[10] environment. The band at *ca.* 9600, *ca.* 15300 and *ca.* 18000 cm^{-1} observed for cobalt(II) complex were assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)\ (\nu_1)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\ (\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)\ (\nu_3)$ transitions respectively which suggested octahedral geometry for the cobalt(II) complex. Copper(II) complex showed band lying at higher energy side at *ca.* 18500 cm^{-1} which may arise due to $^1B_{1g} \rightarrow {}^2E_g$ transition as reported for other square-planar complexes[11]. Ligand field parameters for the Co(II), Ni(II) and Cu(II) complexes were calculated using literature method[12] and their respective values were found to be 10 Dq = *ca.* 9600, *ca.* 9230 cm^{-1} as well as B^1 = 540.13 and 762.2 cm^{-1} for Co(II) and Ni(II) complexes respectively.

Powder X-ray diffraction studies

The X-ray powder diffraction of ($Zn(L)Cl_2 \cdot 3H_2O$) complex was calculated by the reported procedure[13]. The X-ray diffraction pattern of the complex has been successfully indexed. The indexing of the pattern yields a lattice ~~constant~~ as a = 8.02, b = 7.65 and c = 6.92 Å indicating that crystal system of the complex is orthorhmbic.

ACKNOWLEDGEMENT

Authors are thankful tc the authorities of Council of Scientific and Industrial Research for providing financial assistance.

REFERENCES

1. A. Burger, Medicinal Chemistry, Interscience, New York, p. 801 (1960).
2. K.K. Narang and J.K. Gupta, *Indian J. Chem.*, **13**, 705 (1975).
3. ________, *J. Inorg. Nucl. Chem.*, **38**, 589 (1979).
4. L. Wangkyu and Y. Hoe, *Jiv*, **13** (1969); *Chem. Abstr.*, **73**, 804794 (1970).
5. A. Gluko, W.F. Ritner, G. Ren., A. Weissman and G. Schmukler, *J. Inorg. Nucl. Chem.*, **74**, 761 (1971).
6. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, pp. 441, 462, 489 (1978).
7. J. Lewis and R.G. Wilkins, Modern Coordination Chemistry, Interscience, p. 403 (1960).
8. G.R. Burns, *Inorg. Chem.*, **7**, 277 (1968).
9. L. Sacconi and M. Campilini, *J. Chem. Soc.*, 276 (1964).
10. M.N. Nandi, R. Ray and J. Chaudhary, *Indian J. Chem.*, **27A**, 687 (1988).
11. K.K. Narang and J.K Gupta, *Curr. Sci. (India)*, **45**, 536 (1976).
12. B.N. Figgis, Introduction to Ligand Fields, Wiley Eastern Ltd., New Delhi (1976).
13. L.V. Azaroff and M.J. Burger, Power Method in X-ray Crystallography, McGraw-Hill, p. 103 (1958).

(*Received*: 2 June 1995; *Accepted*: 29 December 1995) AJC-1054