Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1921–1924

Synthesis, Structural Properties and Biocidal Studies of 3*d*-Transition Metal Complexes with Diphenylamine Compounds and Schiff Bases

SAPNA TOMAR* and R.C. SHARMA
Department of Chemistry, Institute of Basic Sciences
Dr. B.R. Ambedkar University, Khandari Road, Agra-282 002, India

A number of new mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) containing diphenylamine-2-hydroxy-2-carboxylic acid (DPHC) and furfuralidine-2-amino thiazole (FAT) have been synthesized and characterized by elemental analysis, TLC, conductivity measurements and IR spectral data.

Key Words: Synthesis, Transition metals, Complexes, Diphenylamine, Schiff base.

Biological metal ions play a key role in structural organization. There are few reports on systematic investigations of mixed ligand complexes involving S, N containing ligands[1]. Mixed ligand complexes besides being academically important[2] have assumed analytical[3], industrial[4], pharmaceutical[3], medical[4], toxicological[5] and biochemical importance[6]. The metal complexes of nitrogen containing ligands have been found more biologically active[7] in comparison to the ligands having other donor sites.

The present paper describes the mixed-ligand complexes[8] of M^{2+} ions (M = Co(II), Ni(II), Cu(II), Zn(II) with diphenylamine-2-hydroxy-2′- carboxylic acid as primary ligand and furfuralidine-2-aminothiazole as secondary ligand.

(a) Synthesis of diphenylamine-2-hydroxy-2′-carboxylic acid (DPHC): Both *o*-chlorobenzoic acid (0.003 M) and *o*-aminophenol (0.003 M) were taken in 1 : 1 molar ratio in 100 mL distilled water in a flask fitted with a water condenser. This mixture was slightly alkaline with K_2CO_3 solution and a little copper oxide was added to it. The contents were refluxed on a water-bath for about 5 h. After decolorizing with charcoal, the contents were filtered, concentrated and cooled. The obtained solution was acidified with dilute HCl in excess till the precipitation of the resultant product was complete. It was filtered in cold, dried and recrystallized from alcohol to obtain a brown powder.

(b) Synthesis of furfuralidine-2-aminothiazole (FAT): A mixture of furan-2-aldehyde 1.70 mL (2×10^{-2} mole) and 2-aminothiazole 2.0 g (2×10^{-2} mole) in 50 mL dry ethanol was dissolved and refluxed for 12 h over a water-bath. The solution thus obtained was cooled at room temperature and the excess of ethanol

was almost distilled off under reduced pressure. On keeping the obtained viscous solution at room temperature for one week, a solid product was obtained. It was washed with acetone followed by ether and finally recrystallized from methanol and dried.

Synthesis of Metal Complexes

A mixture of ethanolic solution of metal acetates [0.10 g $(AcO)_2Cu\cdot H_2O$), 0.12 g $(AcO)_2Ni\cdot 4H_2O$, 0.13 g $(AcO)_2Co\cdot H_2O$, 0.11 g $(AcO)_2Zn\cdot 2H_2O$], DPHC (0.13 g, 5×10^{-4} mole) and FAT (0.98 g, 5×10^{-4} mole) was refluxed for 3 h after maintaining pH *ca.* 6. On cooling, the complex precipitated out, which was filtered, washed with ethanol and dried in a vacuum desiccator over anhydrous $CaCl_2$.

N, S and metals in complexes were determined by the standard method[9]. C and H analyses were performed in the Microanalytical Section (CDRI Lucknow) (Table-1). Molar conductance was measured in 10^{-3} M dry DMF solution using Toshniwal conductivity bridge, IR spectra were recorded on Perkin-Elmer Model-577 at Scientific Instrumentation Centre of the University of Delhi.

Analytical data of complexes (Table-1) suggest their 1 : 1 : 1 (MLL') stoichiometry and the conductivity measurements reveal their non-electrolytical nature.

The ligand DPHC revealed characteristic IR bands one at 3010 cm^{-1} (—NH stretching vibration), 3300 cm^{-1} and 1750 cm^{-1} (>OH and >C=O carboxylic stretching vibration) (Table-2). In the IR spectra of metal complexes, the band due to (—NH) is shifted to negative side by 30–40 cm^{-1} which indicates the involvement of this ligand in bonding with metal ions through nitrogen atom. The OH band of carboxylic group disappeared on complexation with metal ions due to the deprotonation from (M—OOC) bond. Another ligand FAT exhibits IR bands at 1650 cm^{-1} (>C=N azomethine stretching), 1485 cm^{-1} and 1525 cm^{-1}(breathing vibration of thiophene and furan ring) in the IR spectra of metal complexes; the band due to (>C=N) shifted to 10–30 cm^{-1} in the lower frequency region showing the coordination of metal with ligand. Some new bands corresponding to (M—O), (M—N), (M—S) also present in the IR spectra of the complexes respectively at 550, 445 and 335 cm^{-1} which further support the chelation the two ligands with the metal ions through the coordination site.

The ligands and their metal complexes were screened for antibacterial and antifungal activities against two bacteria, *Staphylococus aureus* and *Escherichia coli* and two common fungi, *Aspergillus nidulans* and *Candida albicans*, by serial dilution method.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF SYNTHESIZED COMPOUNDS

Compound (m.f.)	Colour	m.w. Found (Calcd.)	m.p./ d.p. (°C)	% Analysis Found (Calcd.)				
				C	H	N	S	M
DPHC ($C_2H_{11}NO_3$)	Brown	245 (229)	144	69.23 (68.12)	4.97 (4.80)	5.90 (6.11)	—	—
FAT ($C_8H_6N_2OS$)	Brown	196 (178)	126	54.56 (53.93)	3.86 (3.37)	15.26 (15.73)	17.72 (17.91)	—
Co(II)-DPHC-FAT ($C_{21}H_{16}O_4N_3SCo$)	Blackish brown	396 (376)	270	38.60 (38.32)	5.55 (5.05)	10.57 (11.97)	8.11 (8.51)	0.644 (0.156)
Ni (II)-DPHC-FAT ($C_{21}H_{16}N_3O_4SNi$)	Brown	400 (376)	250	38.64 (37.32)	5.58 (5.07)	10.67 (11.17)	8.08 (8.51)	0.648 (0.156)
Cu(II)-DPHC-FAT ($C_{21}H_{16}N_3O_4SCu$)	Brownish black	410 (381)	260	38.09 (37.79)	5.40 (4.98)	10.52 (11.02)	7.89 (8.39)	15.99 (16.79)
Zn(II)-DPHC-FAT ($C_{21}H_{16}N_3O_4SZn$)	Brown	405 (381)	230	38.10 (37.89)	5.38 (5.00)	11.73 (11.03)	7.92 (8.42)	15.67 (16.57)

TABLE-2
KEY INFRARED SPECTRAL BANDS (cm^{-1}) OF
METAL COORDINATION COMPOUNDS

DPHC	FAT	Co(II)-DPHC-FAT	Ni(II)-DPHC-FAT	Cu(II)-DPHC-FAT	Zn(II)-DPHC-FAT	Probable assignments
3350	—	—	—	—	—	ν(OH) (phenolic)
3300	—	—	—	—	—	ν(OH) (carboxylic)
3010	—	2990	2995	2990	2995	ν(NH)
1750	—	1720	1725	1725	1730	>C=O (carboxylic)
—	1625	1615	1610	1615	1610	>C=N (azomethine stretching)
—	1525	1510	1510	1515	1505	Breathing vibration of furan ring
—	1485	1475	1470	1465	1460	Breathing vibration of thiophene ring
—	—	545	540	540	535	ν(M—O)
—	—	440	445	435	440	ν(M—N)
—	—	335	340	335	340	ν(M—S)

TABLE-3
ANTIMICROBIAL ACTIVITY DATA (MIC VALUES) IN MOLAR CONCENTRATION ($\times 10^{-5}$) OF SYNTHESIZED COMPOUNDS

S.No.	Compound	Bacteria		Fungi	
		S. aureus	*E.coli*	*A.nidulans*	*C. albicans*
1.	DPHC	20.80	20.80	41.60	41.60
2.	FAT	7.20	7.20	14.40	14.40
3.	Co(II)-DPHC-FAT	4.82	4.82	9.64	9.64
4.	Ni(II)-DPHC-FAT	4.80	4.80	9.60	9.60
5.	Cu(II)-DPHC-FAT	4.70	4.70	9.40	9.40
6.	Zn(II)-DPHC-FAT	4.81	4.81	9.62	9.62
7.	Standard	4.36	4.36	8.30	8.30

Abbreviations: *S. aureus* — *Staphylococcus aureus*, *E. coli* — *Escherichia coli*
A. nidulans — *Aspergillus nidulans*, *C. albicans* — *Candida albicans*

ACKNOWLEDGEMENTS

The authors are thankful to Central Drug Research Institute, Lucknow for elemental analysis and STC, Delhi for recording IR spectra.

REFERENCES

1. M Srivaskaran Nair and M.A. Neelakantan, *J. Indian Chem. Soc.*, **77**, 374 (2000).
2. B.E. Fisher and H. Siegal, *J. Am. Chem. Soc.*, **102**, 2998 (1980).
3. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry: A Comprehensive Text, 4th Edn., John Wiley & Sons, New York (1980).
4. G.R. Choppin, Eur. *J. Solid State Inorg. Chem.*, **28**, 319 (1991).
5. T.V.R.K. Rao and B.N. Das, *J. Inst. Chemists*, **70**, 5 (1998).
6. Firoz Khan and Farid Khan, *J. Indian Chem. Soc.*, **74**, 171 (1997).
7. S.S. Massud and H. Siegal, *Inorg. Chem.*, **110**, 6857 (1998).
8. Maria Pleniceanu, Loan Burnea, Maria Isvoranu, Cezar Spinu and Elena Glodeanu, *J. Indian Chem. Soc.*, **76**, 308 (1999).
9. B. Singh and H. Mishra *J. Indian Chem. Soc.*, **63**, 1069 (1986).
10. N.K. Gaur, R. Sharma and R.S. Sindhu, *J. Indian Chem. Soc.*, **78**, 26 (2001).
11. K. Nakamato, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley & Sons.

(*Received*: 9 July 2003; *Accepted*: 10 June 2004) AJC-3467