Asian Journal of Chemistry Vol. 12, No. 3 (2000), 629–632

Structural and Fungicidal Studies of Transition Metal Complexes of Substituted Thiadiazole

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Metal complexes of 3d series with 3-(4′-pyridyl)-6-phenyl amino-S-triazolo [3,4-b]-1,3,4-thiadiazole (PATAT) have been prepared and characterised on the basis of analytical data and spectral studies. Mass spectrum of the ligand was also recorded. I.R. data showed bidentate chelating behaviour of the ligand coordinating through S-atom of the thiadiazole ring and exocylic N of the amino group. Fungicidal activity of the ligand and metal complexes were also evaluated. The ligand as well as metal complexes showed significant activities.

INTRODUCTION

Compounds containing 1,3,4-thiadiazole nucleus have been reported to possess a wide spectrum of pharmacological activities[1,2]. By virtue of toxophoric $-N{=}\overset{|}{C}-S$ moiety in the thiadiazole compounds[3] their complexes may be expected to display better fungicidal activities. In continuation of our earlier work on complexes of 1,3,4-thiadiazole[4], we report here the synthesis and characterization of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with PATAT. So far there is no systematic study on fragmentation pattern of S-triazolo-[3,4,-b]-thiadiazoles; we also investigated MS spectrum of PATAT.

EXPERIMENTAL

The analytical data of the ligand and its metal complexes were obtained as reported earlier[4,5]. The mass spectra were recorded on a Jeol JMS spectrophotometer operating at 70 eV.

The ligand PATAT was synthesised in two steps:

(i) 3-(4′-Pyridyl)-4-amino-5-mercapto-1,2,4-triazole (AMT) was prepared by the method of Reid and Heindel[6]. It was confirmed by its m.p. (260°C), elemental analysis ($C_7H_7N_5S$: Calc.: C = 43.51, H = 3.65, N = 36.25. Found: C = 43.44, H = 3.60, N = 36.15%) and IR data [ν_{max}: 1610 ν(C=N), 2570 ν(SH), 3270, 3160 ν(NH) cm^{-1}].

(ii) 3-(4′-Pyridyl)-6-phenylamino-S-triazolo [3,4-b]-1,3,4-thiadiazole (PATAT) was synthesised according to the synthesis of 3-alkyl-6-aryl-amino-S-triazolo [3,4,-b]-1,3,4-thiadiazoles[7]. To a stirred solution of AMT in dry acetone-triethyl amine (3 : 1), an equimolar amount of phenyl isothiocyanate was added. Triethylamine acts probably via the complex isothiocyanate-triethylamine that improves the electrophilic activity of NCS group to enhance the addition of phenyl isothiocyanate with AMT. Furthermore, excess of triethylamine activates probably SH group in AMT and promotes the cyclisation of the intermediate to afford

PATAT. The above mixture was refluxed for 20 h, the product crystallised from DMF and analysed by elemental analysis ($C_{14}H_{10}N_6S$: Calc.: N = 43.30, S = 16.49. Found: N = 43.25, S = 16.44%) and m.p. 320°C.

General method for the preparation of metal complexes: A hot ethanolic solution of the ligand (0.01 mol, 20 mL) was refluxed for 2 h with hot ethanolic solution of respective metal chloride (0.01 mol, 15 mL). The Cu(II) complex separated immediately while solid sodium acetate was added with magnetic stirring to facilitate complexation in case of Co(II), Ni(II), Zn(II) and Cd(II) complexes. The separated complexes were filtered, washed with ethanol, dried, analysed and presented in Table-1.

TABLE-1
ANALYTICAL AND MOLAR CONDUCTANCE DATA OF THIADIAZOLE COMPLEXES

Compound	% Found/(Calcd.)				(Molar Conductance
	N	S	Cl	M	ohm^{-1} cm^2 mol^{-1})
$[Co(C_{14}H_{10}N_6S)Cl_2]$	32.38 (32.43)	12.30 (12.35)	13.65 (13.71)	11.32 (11.38)	11.8
$[Ni(C_{14}H_{10}N_6S)_2Cl_2]$	32.39 (32.45)	12.32 (12.36)	13.68 (13.71)	11.30 (11.34)	12.6
$[Cu(C_{14}H_{10}N_6S)_2Cl_2]$	32.10 (32.15)	12.20 (12.25)	13.60 (13.58)	12.20 (12.16)	11.2
$[Zn(C_{14}H_{10}H_6S)Cl_2]$	24.78 (24.81)	9.40 (9.45)	20.87 (20.97)	18.69 (18.77)	6.5
$[Cd(C_{14}H_{10}N_6S)Cl_2]$	22.23 (22.26)	8.45 (8.48)	18.78 (18.81)	29.68 (29.78)	8.3

RESULTS AND DISCUSSION

Synthesised complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The analytical results reveal 1 : 2 (M : L) stoichiometric ratio for Co(II), Ni(II) and Cu(II) complexes and 1 : 1 (M : L) for Zn(II) and Cd(II) complexes. Molar conductance in DMF (10^{-3} M) are in the range 6.5 to 12.6 ohm^{-1} cm^2 mol^{-1} indicating non-electrolytic nature of the complexes.

Infra-red Spectra: IR spectrum of the ligand exhibits broad medium intensity bands at 3300–3260 cm^{-1} assignable to ν_{asym} and ν_{sym} NH stretchings respectively. These bands shift to lower region by 50–100 cm^{-1} during complexation owing to the drainage of electrons towards metal atom through N atom of NH group resulting in the formation of metal-nitrogen bond[8]. The medium intensity bands at 710 cm^{-1} due to C—S—C (ring) stretching vibrations in the free ligand show a downward shift with splitting and decreased intensity on complexation suggesting involvement of ring sulphur in bonding with the metal ions[9]. The medium intensity bands at 1635 cm^{-1} due to (C=N cyclic) in ligand remained unchanged in the spectra of all the complexes indicating non-involvement of thiadiazole ring nitrogen in bonding due to steric hindrance. The bands at 1590, 1450 cm^{-1} are assigned to $\nu_{C=C}$ and $\nu_{C=N}$ skeletal frequencies while the bands at 990, 810, 610, 425 cm^{-1} may be assigned to ring breathing mode out-of-plane and in-plane C—C deformation mode of the pyridine ring.

The far-infrared spectral data reveal bands at 435, 455, 460, 410, and 415 cm^{-1} which may be assigned to ν(Co—N), ν(Ni—N), ν(Cu—N), ν(Zn—N) and ν(Cd—N) respectively[10]. The bands observed at 315–275 cm^{-1} may be due to ν(M—S) in all the complexes[10]. Metal-halogen stretching vibrations at 290, 285 and 275 cm^{-1} due to ν(Co—Cl), ν(Ni—Cl) and ν(Cu—Cl) respectively are in good agreement with six-coordinate halide bridged vibrations[10]. However, the weak bands at 210 and 215 cm^{-1} due to ν(Zn—Cl) and ν(Cd—Cl) are in consistent with the tetrahedral geometry[10].

Magnetic and electronic spectral studies: The magnetic moment values 2.90 and 3.15 B.M. observed for Co(II) and Ni(II) complexes respectively indicate six-coordinate, high-spin and octahedral geometries around the metal ions[11]. Electronic spectrum of Co(II) complex show three bands at *ca.* 8330, 18000 and 19500 cm^{-1} attributable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively suggesting an octaheral cofiguration[11]. The ligand field parameters (Dq = 935 cm^{-1}, B = 726 cm^{-1}, $\nu_2/\nu_1 = 2.12$, LFSE = 18.45 kcal mol^{-1}) calculated using Underhill and Billing equation[12] are also suggestive of octahedral structure[11]. The spectrum of Ni(II) complex consists of bands at 8550, 15500 and 25150 cm^{-1} which may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively, supporting an octahedral geometry. The ligand field parameters such as Dq (870 cm^{-1}), B′ (690 cm^{-1}), B (815 cm^{-1}), β% (33.92), ν_2/ν_1 (1.75) and LFSE (29.86 kcal mol^{-1}) further support the octahedral geometry of the complex[11]. The low value of nephelauxetic ratio β (0.75) is fairly characteristic of 6-coordination of the ligand[13] in the Ni(II) complex. The electronic spectrum of Cu(II) complex exhibits a broad band at 11800–17150 cm^{-1} with a shoulder towards lower energy side at 14500 cm^{-1}. The calculated values of Dq (1400 cm^{-1}) and LFSE (28.86 kcal mol^{-1}) are in accord with the distorted octahedral configuration[11]. The Zn(II) and Cd(II) complexes are found to be diamagnetic. Based on analytical, conductance and IR spectral studies, a tetrahedral geometry is proposed for these complexes.

Mass spectrum of PATAT: The mass spectrum of 3-(4′-pyridyl)-6-phenylamino-S-triazolo [3,4,-b]-1,3,4-thiadiazole showed weak molecular ion peak with relative intensity of about 18%. The molecular ion underwent cleavage[14] to show the following fragmentation pattern (Fig. 1). The base peak due to $C_6H_5^+$ occurs at m/z 77. Other important ion peaks due to triazole ions and $ArNCS^+$ were observed at m/z 115 and 135 respectively.

Fungicidal Screening: Fungicidal activities of the ligand and its metal complexes were evaluated against *Drechslera tetramera, Alternaria alternata* and *Fusarium oxysporum* by Growth method[15] at 100 ppm concentration. The ligand displayed higher fungitoxicity (zone of inhibition 29–32 mm) as compared to the metal complexes probably due to the presence of pyridine ring, $-N{=}\overset{|}{C}-S$ grouping and penetration in fungal hyphae. Among metal complexes, Cu(II) complex exhibits maximum inhibitory action (28 mm) due to denaturation of

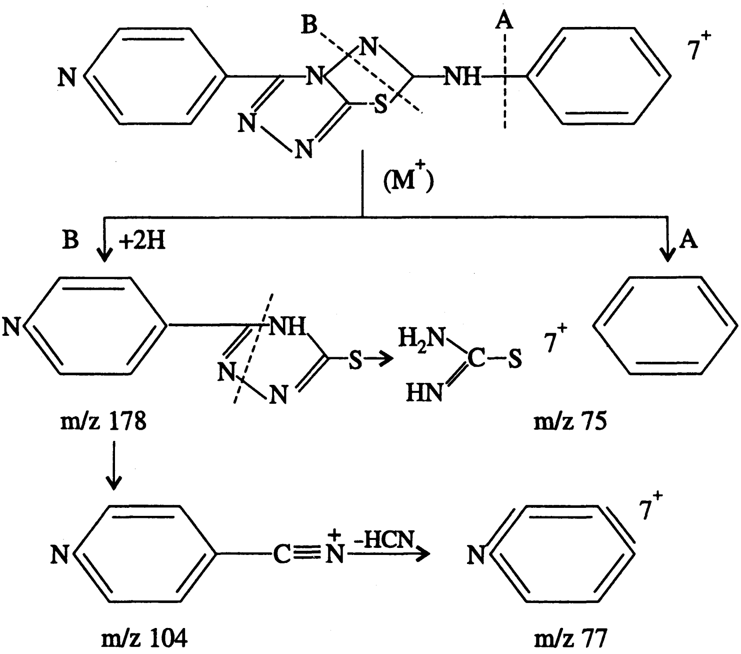

Fig. 1. Mass Spectrum of PATAT

proteins and DNA in fungus species. Co(II) and Ni(II) complexes are moderately active (20 and 22 mm) while Zn(II) and Cd(II) complex are least active (18 and 15 mm). Generally higher the concentration, greater the inhibitory effect.

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(*Received*: 26 June 1999; *Accepted*: 27 December 1999) AJC-1970