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NOTE

Synthesis and Fungicidal Screening of 2-Amino-4-(*p*-bromophenyl)thiazole and Its Metal Complexes

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> The metal complexes of Mn(II), Ni(II), Co(II), Cu(II), Zn(II) and Fe(III) with 2-amino-4-*p*-(bromophenyl)thiazole are synthesized and characterized. The structures of the synthesized complexes were established by IR, UV, magnetic moment and elemental analysis. The ligand and the complexes were also screened for their fungicidal activity against different fungi *viz.*, *Phoma exigua*, *Macrophomina phaseoli* and *Collectotrichum capsici*.

> Key Words: Synthesis, 2-Amino-4-(*p*-bromophenyl)thiazole, Metal complexes, Fungicidal activity.

The complexing behaviour of thiazoles with metal ions are well known¹⁻⁵. Few workers^{6.7} reported that 2-amino-4-aryl thiazole and their derivatives possess bactericidal and fungicidal activity. The fungicidal activities are due to -N=C-S group in thiazole nucleus⁸. Introduction of the halo group in the moiety of thiazole nucleus increases the fungicidal activity. Keeping the above fact in mind, the present paper reported the synthesis and fungicidal activity of 2-amino-4-*p*-(bromophenyl)thiazole and its complexes.

All the chemicals used were of BDH (AR) grade. *p*-Bromo acetophenone was purchased from Sisco Chemical Laboratories, Mumbai.

Synthesis of 2-Amino-4-(*p*-bromophenyl)thiazole: Iodine (0.2 mol) was added to a mixture consisting of bromocetophenone (0.2 mol) and thiourea (0.4 mol) and heated for 14 h on water bath. The reaction mixture was cooled and made alkaline with NH₄OH. The precipitated 2-amino-4-*p*-(bromophenyl)thiazole was filtered and crystallized from ethyl alcohol. The thiazole was obtained in yellow crystals and dried m.p. 165 °C, (yield 90 %).

Preparation of metal complexes: The complexes have been synthesized by mixing ethanolic solution of metal acetates to ethanolic solution of ligand in the ratio of (1:2) (metal:ligand). The contents were refluxed on water bath for 1 h. After refluxing, the obtained solution were concentrated

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to half of its volume and then kept overnight. Solid complexes was separated out, filtered, washed with ethanol and finally with dry ether and then dried in vacuum (yield 85-80 %). In all cases the metal ligand ratio was 1:2 except in case of Fe where it was 1:3 Analytical data of the ligand and its metal complexes are given in Table-1.

TABLE-1 ELEMENTAL ANALYSIS DATA OF 2-AMINO-4-(p-BROMOPHENYL)THIAZOLE AND ITS METAL COMPLEXES

Compound	Elemental analysis (%): Found (Calcd.)								
Compound	С	Н	S	Ν	М	Br			
ABPT	42.54 (42.35)	2.81 (2.74)	11.10 (10.98)	12.38 (12.54)	-	31.50 (31.37)			
[Mn(C ₉ H ₇ N ₂ SBr) ₂ (CH ₃ COO) ₂]	42.51	2.84	9.53	9.02	8.18	23.18			
	(42.32)	(2.70)	(9.37)	(8.91)	(8.05)	(23.42)			
$[\mathrm{Ni}(\mathrm{C}_{9}\mathrm{H}_{7}\mathrm{N}_{2}\mathrm{SBr})_{2}(\mathrm{CH}_{3}\mathrm{COO})_{2}]$	44.51	2.98	9.44	8.03	8.41	23.56			
	(44.40)	(3.01)	(9.32)	(8.15)	(8.54)	(23.30)			
$[\mathrm{Co}(\mathrm{C}_{9}\mathrm{H}_{7}\mathrm{N}_{2}\mathrm{SBr})_{2}(\mathrm{CH}_{3}\mathrm{COO})_{2}]$	45.06	3.02	9.53	8.28	8.68	23.50			
	(45.04)	(2.99)	(9.31)	(8.15)	(8.58)	(23.28)			
$[Cu(C_9H_7N_2SBr)_2(CH_3COO)_2]$	41.08	2.73	9.11	8.25	9.03	23.21			
	(41.01)	(2.75)	(9.25)	(8.09)	(9.18)	(23.13)			
$[Zn(C_9H_7N_2SBr)_2(CH_3COO)_2]$	43.08	2.88	9.16	8.18	9.54	23.25			
	(43.00)	(2.86)	(9.23)	(8.07)	(9.42)	(23.07)			
[Fe(C ₉ H ₇ N ₂ SBr) ₃ (CH ₃ COO) ₃]	42.09	2.79	9.55	8.54	5.68	24.18			
	(43.05)	(2.70)	(9.62)	(8.41)	(5.59)	(24.05)			

The fungicidal screening of ligand and metal complexes were recorded in Table-2. The activity was determined by using growth method. The fungi toxicity also varies from fungus to fungus as well as on the change of concentration. At higher concentration the ligand as well as metal complexes are more toxic.

TABLE-2 FUNGICIDAL SCREENING OF 2-AMINO-4-(p-BROMOPHENYL)THIAZOLE (ABPT) AND ITS METAL COMPLEXES

	Average percentage inhibition after 168 h								
Complex	Phoma exigua			Macrophomina phaseali			Collectotrichum capsici		
	Concentration in ppm								
	100	50	20	100	50	20	100	50	20
ABPT	55.60	46.40	38.20	45.60	40.00	36.20	48.00	42.28	37.90
$[Mn(C_9H_7N_2SBr)_2(CH_3COO)_2]$	38.79	34.40	30.00	27.95	22.79	18.80	35.48	30.00	25.56
$[Ni(C_9H_7N_2SBr)_2(CH_3COO)_2]$	40.68	35.50	31.35	30.48	25.68	20.90	38.59	32.65	30.54
$[Co(C_9H_7N_2SBr)_2(CH_3COO)_2]$	35.67	30.05	28.55	26.87	21.48	17.92	30.55	27.67	22.44
$[Cu(C_9H_7N_2SBr)_2(CH_3COO)_2]$	33.98	28.55	24.67	23.90	18.52	15.42	29.40	25.68	20.45
$[Zn(C_9H_7N_2SBr)_2(CH_3COO)_2]$	32.10	27.54	24.58	22.40	17.51	13.79	28.90	24.94	20.00
[Fe(C ₉ H ₇ N ₂ SBr) ₃ (CH ₃ COO) ₃]	28.00	23.55	20.00	20.00	15.57	12.50	25.75	20.00	15.50

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