SHORT COMMUNICATIONS

EFFECT OF AMIDE GROUP LIGANDS AND THEIR METAL COMPLEXES ON PATHOGENIC FUNGI

V. RAVINDAR and P. LINGAIAH
Department of Chemistry, Kakatiya University, Warangal 506 009, India.

AMIDE group ligands are important in biological systems and these are endowed with various types of biological activity. 2-[(2-phenylamino)carbonyl] benzoic acid and its derivatives possess antitubercular activity in addition to other pharmacological uses[1,2]. Further, these compounds act as herbicides, fungicides, insecticides, bactericides, plant growth regulators etc[3-6]. Golyshin and Abelentsev[7] reported synergistic herbicidal activity, associated with a mixture containing metal ion and 2-hydroxy benzamide. Though a large number of amide group ligands have been assayed for various types of biological activity, there is paucity of literature concerning the corresponding studies made on their metal complexes. In the present study, the ligands maleanilic acid (MA), malea-1-naphthalanilic acid (MNA), 2-(aminocarbonyl) benzoic acid (ACBA), 2-[(2-phenylamino)carbonyl] benzoic acid (PACBA), 2-[(1-naphthalenylamino)carbonyl] benzoic acid (NACBA), 2-[(2 aminophenylamino)carbonyl]benzoic acid (APACBA), 2-amino-benzanilide (ABn) and 2-(amino benzoyl)benzoic acid (ABBA) and their Pd(II) complexes as well as APACBA complexes of Co(II), Ni(II) and Cu(II) have been assayed for their fungicidal activity against *Drechslera rostrata, Curvularia lunata* and *Aspergillus niger*.

The ligands and the complexes were prepared as given elsewhere[8,9]. The fungitoxicity was assayed by agar plate technique[10]. Each compound (30 mg) was dissolved in 10 ml of acetone and the solution was added aseptically to the sterilized medium at 45°C, so as to give two concentrations (0.1 and 0.01%). The plates were inoculated with the spores of test fungi after cooling and were incubated at 28 ± 2°C. After the incubation period (8 days), the diameter of the colony was measured. The acetone alone was used as the control. Percentage inhibition was determined as the difference in growth between the control plates containing untreated medium and the treated plates of a given inhibitor concentration. The growth rates were determined in the linear phase and the percentage inhibition of fungal growth has been expressed as:

$$\% = [100 \times (C-T)/C],$$

where C = diameter of the fungus colony in the control plates after 8 days, and T = diameter of the fungus colony in the treated plates after 8 days.

The fungicidal activity of the compounds has been compared with agricultural fungicide, Dithane-M-45, screened under similar conditions. The activity of the metal salts from which the corresponding complexes of APACBA were prepared has also been determined for comparison.

The results presented in table 1 indicate that the Pd(II) complexes exhibit more fungistatic activity when compared to free ligands and Dithane M-45, a commercial fungicide. This may be due to the synergistic effect of the coordinated metal ion with the ligands. It is found that with increase in concentration, the percentage of growth inhibition is increased. Further, Pd(II) complexes at 0.1% are most effective against *D. rostrata* while *C. lunata* is comparatively less sensitive. The fungistatic activity of the Pd(II) chelates is found to be in the order APACBA > ABBA > ABn > ACBA > PACBA > NACBA > MA > MNA. According to Baichwal *et al*[5] 2-hydroxybenzamide derivatives show pronounced antifungal activity due to the involvement of hydrogen bonding of anilide hydrogen atom and chelation by the phenolic and amino oxygen atoms with an enzyme system of the fungus. The present investigation reveals that all the ligands are capable of forming stable complexes with the metal ions which are found in conjugation with an enzyme system of the fungus where these chelates may establish 'some sort of equilibrium', resulting in the formation of a more stable system. As a result, the biological activity of the fungus is inhibited thus reflecting the more effective nature of Pd(II) complexes.

A look at the data on the activity of free ligand APACBA, its Fe(III), Co(II), Ni(II), Cu(II) and Pd(II) complexes and the corresponding metal salts (table 2) reveals that the complexes show higher inhibition compared to the free ligand and the corresponding metal salt. Further, the fungitoxicity of the compounds varies with metal ion where Pd(II) complex exhibits maximum fungal inhibition and Co(II) complex minimum. The toxicity of the metal complexes follows

Table 1 *Average percentage inhibition of fungal growth induced by amide group ligands and their Pd(II) complexes*

Name of the compound	Concentration	Name of the fungi		
		D. rostrata	*C. lunata*	*A. niger*
MA	0.01	23.0	10.9	18.2
	0.1	36.8	24.3	36.4
Pd(II)-MA	0.01	53.9	32.5	41.8
	0.1	76.1	48.4	63.5
MNA	0.01	26.4	12.7	24.0
	0.1	40.2	22.0	38.9
Pd(II)-MNA	0.01	50.0	30.6	43.2
	0.1	71.3	52.8	67.8
ACBA	0.01	31.5	25.2	31.0
	0.1	45.8	39.9	43.7
Pd(II)-ACBA	0.01	67.4	37.3	56.3
	0.1	86.1	59.7	74.5
PACBA	0.01	30.3	19.6	30.2
	0.1	52.5	32.4	50.6
Pd(II)-PACBA	0.01	60.8	36.5	58.1
	0.1	79.7	53.0	79.0
NACBA	0.01	29.4	21.7	26.5
	0.1	43.2	36.4	41.8
Pd(II)-NACBA	0.01	57.6	38.7	52.3
	0.1	80.5	56.9	76.0
APACBA	0.01	41.8	27.4	40.6
	0.1	60.3	50.0	58.0
Pd(II)-APACBA	0.01	76.7	41.8	71.3
	0.1	94.3	67.5	86.1
ABn	0.01	30.6	21.6	28.2
	0.1	54.0	46.5	54.5
Pd(II)-ABn	0.01	69.2	38.0	47.3
	0.1	87.5	65.5	82.0
ABBA	0.01	32.0	24.4	31.0
	0.1	58.8	48.4	56.3
Pd(II)-ABBA	0.01	71.5	40.6	67.5
	0.1	92.3	63.2	85.4
Dithane-M-45	0.01	47.6	38.7	44.0
	0.1	90.8	61.4	80.7

the order Pd > Cu > Ni > Fe > Co which parallels the stability order of the metal complexes.

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Table 2 *Percentage inhibition of fungal growth induced by free metal salts, ligand and its metal complexes*

Name of the compound	Concentration	Name of the fungi		
		D. rostrata	*C. lunata*	*A. niger*
APACBA	0 01	41 8	27.4	40 6
	0.1	60.3	50.0	58.0
$Fe(NO_3)_39H_2O$	0 01	12.3	11 6	12.8
	0.1	31 9	30.0	28.3
Fe(III)-APACBA	0.01	45.2	40.7	43.5
	0 1	70.5	68.0	68.8
$Co(NO_3)_26H_2O$	0.01	10.7	19.1	15.7
	0.1	36.4	34.8	33.4
Co(II)-APACBA	0.01	42.0	38.2	40.1
	0.1	64.8	60.0	61.3
$Ni(No_3)_36H_2O$	0.01	15.2	9.4	12.5
	0.1	50.1	46.8	50.0
Ni(II)-APACBA	0.01	45.6	42.3	40.8
	0.1	79.0	70.8	73.5
$Cu(CH_3COO)_2H_2O$	0.01	12.4	10.6	12.0
	0.1	32.8	25.9	33.8
Cu(II)-APACBA	0.01	52.1	45.0	49.2
	0.1	85.3	78 0	78.5
$PdCl_2$	0.01	20.6	18.3	20.1
	0.1	58.4	52.5	56.0
Pd(II)-APACBA	0.01	76.7	41.8	71.3
	0.1	94.3	67.5	86.1

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CHEMICAL EXAMINATION OF THE BARK OF *FICUS HISPIDA* LINN

B. M. ACHARYA and K. AKSHAYA KUMAR

Department of Chemistry, Osmania University, Hyderabad 500 007, India.

FICUS HISPIDA Linn. (N. O. Urtricaceae) is used in indigenous medicine—the total extract is effective against jaundice, leprosy and anemia[1, 2]. Since the chemical examination of this plant seems to be not well investigated, the bark of this plant was worked out and the results are, now, reported.

The crude petroleum ether (60–80°) extract of the dried bark powder of *Ficus hispida* linn was chromotographed over neutral alumina using solvent systems of increasing polarity. Three compounds were isolated and designated as compound I, II and III. Elutions from pet. ether–benzene (1 : 1) yielded compound I, mp. 70° (Lit[3] mp. 69–70°) $C_{32}H_{64}O_2$, $M^{+\cdot}$ (m/z) 480 ν_{max} 1735 cm^{-1} (acetate carbonyl) while elutions from benzene–chloroform (10 : 1) yielded compound II, mp. 238–39° (Lit.[4] mp. 238–40°) $C_{32}H_{52}O_2$ $M^{+\cdot}$ (m/z) 468 ν_{max} 1730 cm^{-1} (acetate carbonyl). Compounds I and II were separately hydrolysed with 1 % alcoholic KOH to yield alcohols which were identified as *n*-triacontanol and *β*-amyrin by comparison[5] (mp, mmp, Co-tlc and superimposable IR) with authentic samples. Thus compounds I and II were found to be the acetates of *n*-triacontanol and *β*-amyrin respectively.