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Physico-chemical Studies, Thermal Decomposition Kinetics and Anti-fungal Studies of Some Bivalent Metal Complexes of Camphor-2-aminophenol

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The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with camphor-2-aminophenol(HCAP) have been synthesized and characterized on the basis of elemental analysis, molar conductance, magnetic moment, UV-visible and IR spectra. Co(II), Ni(II) and Mn(II) complexes of HCAP were subjected to thermal analysis so as to understand their thermal stability and decomposition patterns. The kinetic parameters like activation energy (E), frequency factor (A), entropy of activation (ΔS) and order parameter (n) were calculated from the TG curves, using Coats-Redfern equation. The ligand HCAP and its Co(II), Ni(II), Cu(II) and Zn(II) complexes were tested against the mycelial growth of *Phytophthora capsici*, a soil borne pathogen that affects and destroys black pepper.

Key Words: Camphor-2-aminophenol, Kinetics and anti-fungal studies, Complexes, Thermal decomposition.

INTRODUCTION

In recent years, Schiff base ligands and their metal complexes have come to the forefront of interest in coordination chemistry because of their biological significance. Copper(II) complexes of Schiff bases derived from 5-nitrosalicylaldehyde, 2-aminophenol and 4-aminophenol are reported to have mild to moderate activity against common pathogenic organisms[1]. The Schiff base ligands derived from phenyl butanone and 2-aminophenol and their metal complexes were tested for their antibacterial behaviour using *E. coli* as a test organism[2]. The observation that many such Schiff base ligands, especially their metal complexes, have ample biological activities, demands a detailed investigation of the donor characteristics of these chelating agents. This study attempts to establish the nature of metal ligand bonding and stereochemistry of such complexes.

EXPERIMENTAL

The ligand camphor-2-aminophenol (HCAP) was prepared by refluxing a methanolic solution of camphor (1.52 g, 0.01 mol) with an ethanolic solution of 2-aminophenol (1.09 g, 0.01 mol) containing sodium acetate solution (0.5 g) for 4 h on a water bath. The resulting solution was kept overnight and concentrated

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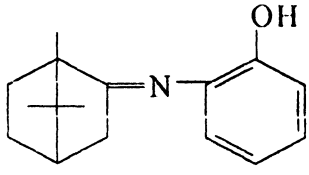
by evaporation. It was then poured into ice-cold water in a beaker with stirring. The yellowish black product thus separated was further purified by recrystallization from ethanol and dried over anhydrous $CaCl_2$. The melting point was found to be 150°C. The ligand was characterized on the basis of C, H, N analysis, UV and IR spectral data.



Camphor-2-aminophenol(HCAP)

Preparation of Complexes

Metal complexes of camphor-2-aminophenol were prepared by mixing an aqueous solution of metal(II) acetate (0.001 mol) with an ethanolic solution of 2-aminophenol (0.002 mol) and methanolic solution of camphor (0.002 mol) in the presence of sodium acetate solution. The resulting solution was refluxed, for about 5 h. The separated complexes were filtered and washed with water. It was finally washed with very dilute alcohol and was dried in a desiccator over anhydrous $CaCl_2$. In the preparation of Cu(II) complexes, sodium acetate was not used.

Analysis for the metal content of the complexes was performed by standard methods[3]. The complexes were characterized on the basis of elemental analysis, magnetic measurements, electronic and IR spectral data, conductance measurements and thermal data. TG curves were recorded in static air atmosphere with a constant heating rate of 10°C min^{-1} and sample masses of 5–10 mg were used for the entire study.

Antifungal activity

The fungus used was *Phytophthora capsici*, a soil borne pathogen that destroys black pepper causing 'foot rot' also known as 'quick wilt' causing severe crop loss. It is reported that contaminated soil is the main source of inoculum and the fungus survives in the infected plant for a period of nineteen months[4]. The culture was obtained from the National Repository of *Phytophthora.*

The metal complexes and the ligands were dissolved in ethyl alcohol to form a stock solution of 2000 ppm. These stock solutions were then autoclaved and kept aside to be added to the carrot agar medium[5]. For the study on the growth of mycelium, poisoned food technique was used. To the molten carrot agar medium, the autoclaved stock solutions of the complexes and ligands were added aseptically to form final concentrations of 50 and 100 ppm. The amended medium was poured into petriplates. Discs of inoculum of *phytophthora capsici*, 5 mm in diameter, were placed centrally on to the amended medium in petriplates. The plates with ethyl alcohol of concentration of 50 and 100 ppm served as control. Three plates were kept for 96 h at 24°C and the radial growth was measured at 24 h interval. The percentage inhibition was calculated using the formula

$$\text{inhibition } \% = (a - b)100/a$$

where 'a' is the radial growth in the control medium and 'b' is the radial growth in the test medium.

Sporangial production: The solutions of the ligand and the metal complexes that were found to inhibit mycelial growth of *Phytophthora capsici* were selected for further study. Different concentrations of 10, 25, 50 and 100 ppm of test solution as well as ethyl alcohol were poured into petriplates. These were kept under fluorescent light for 48–72 h. The number of sporangia produced per microscopic field (20x) was recorded and inhibition percentage was calculated.

Zoospore release: To study the effect of ligand and various metal complexes on zoosporogenesis, the discs kept for sporulation were taken after 48 h and solutions of different concentrations were placed over them and incubated at 4°C for 10 min. The number of sporangia, which released zoospores, was counted. Observations were taken for 5 microscopic fields per disc and five discs per plate. The inhibition percentage was calculated.

Zoospore germination: For the study of zoospore germination, sporulating discs were subjected to cold shock at 4°C for 10 min and zoospores released were collected in test tubes and vortexed. The zoospores settled at the bottom were collected. 500 μL of the water containing spores were placed on clean microscopic fields and 500 μL of the complexes were poured and mixed so that the final concentration ranged from 10 to 100 ppm. In control ethyl alcohol was used. The number of germinated zoospores was counted. Inhibition of zoospore germination was calculated by comparing with control. The results were presented in tables.

RESULTS AND DISCUSSION

The analytical data, molar conductance and magnetic moments of the complexes are summarized in Table-1.

TABLE-1
MICROANALYTICAL, MAGNETIC AND CONDUCTANCE DATA OF TRANSITION METAL CHELATES OF CAMPHOR-2-AMINOPHENOL

Complex	Colour	M %	C %	H %	N %	μ_{eff} (B.M.)	Ω_m (ohm^{-1} cm^{-2} mol^{-1})
$[Mn(CAP)_2(H_2O)_2]$	Brown	9.67 (9.56)	66.54 (66.78)	7.43 (7.65)	4.83 (4.87)	5.8	2.38
$[Co(CAP)_2(H_2O)_2]$	Coffee brown	10.46 (10.18)	66.45 (66.32)	7.41 (7.60)	4.71 (4.84)	5.0	1.92
$[Ni(CAP)_2(H_2O)_2]$	Black	10.51 (10.14)	66.39 (66.36)	7.55 (7.60)	4.61 (4.84)	3.4	8.63
$[Cu(CAP)_2(H_2O)_2]$	Brown	10.45 (10.89)	65.76 (65.80)	7.45 (7.54)	4.53 (4.80)	2.0	1.25
$[Zn(CAP)_2(H_2O)_2]$	Coffee brown	11.23 (11.17)	65.50 (65.60)	7.32 (7.53)	4.91 (4.78)	diamag.	1.65
$[Cd(CAP)_2]$	Pale yellow	17.68 (17.77)	60.35 (60.72)	6.80 (6.96)	4.52 (4.43)	diamag.	4.48

Calculated values are given in parentheses.

The very low molar conductance value of the complexes in ethanol indicates that these complexes are non-electrolytes in ethanol and neutral in nature[6]. The electronic spectrum of the ligand HCAP is characterized by two bands lying around 22831 and 32362 cm^{-1}. During complex formation, a red shift is detected for these bands, which indicates the involvement of the Schiff bases in coordination. The band appearing at 25000 cm^{-1} in the electronic spectrum of Mn(II) complex is a support for the assigned octahedral geometry[8]. The electronic spectrum of Co(II) complex of the ligand HCAP gives only one characteristic band at 17,400 cm^{-1} due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition. Ni(II) complex exhibits two *d-d* transitions in the electronic spectra at about 16,700 and 22,500 due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions. The electronic specta of Cu(II) complexes showed absorption maxima at about 15,380 cm^{-1} and 16,000 cm^{-1} which supported a distorted octahedral geometry[8]. The Zn(II) and Cd(II) complexes do not show any characteristic *d-d* transition bands.

The IR spectrum of the ligand shows a sharp band at 3200 cm^{-1}, which can be assigned to the hydrogen bonded —OH group. On complexation, this band disappears indicating that the hydrogen atom of the hydroxyl group is replaced by the metal. A broad feature at 3410–3250 cm^{-1} in the spectra of several complexes is attributed to the hydroxyl stretching mode of water molecules[9-12]. In addition, a medium band approximately at 950–870 cm^{-1} suggests that the water molecules are coordinated[13]. A strong intense band at 1550 cm^{-1} in the spectrum of the ligand HCAP may be assigned to ν(C=N) stretch. This band shows a downward shift about 40–30 cm^{-1} in the spectra of all the metal complexes[14] indicating the participation of the azomethine nitrogen in coordination with metal ions. Spectra of all the metal complexes prepared showed bands at 590–530 cm^{-1} and 550–430 cm^{-1} assignable to ν(M—N) and to ν(M—O) respectively.

From all the above studies, it is clear that the ligand acts as monovalent bidentate towards transition metal ions. Based on the above observations, the structure of complexes can be confirmed to be octahedral for Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes. The Cd(II) complex may have tetrahedral geometry.

The results of the studies on the thermal decomposition of Mn(II), Co(II) and Ni(II) complexes of camphor-2-aminophenol are given in Table-2. Metal percentage from independent pyrolytic experiments and from thermal studies was found to be agreeable with the calculated values in the case of metal complexes of camphor-2-aminophenol. The thermal data have supported the structure of complexes as $[M(CAP)_2(H_2O)_2]$ where M = Mn(II), Co(II) and Ni(II).

A four-stage decomposition pattern was observed for all the three complexes of camphor-2-aminophenol. The first stage of decomposition stands for the removal of two-coordinated water molecules and the third stage stands for the removal of two-camphor molecules, which is the main decomposition stage.

TABLE-2
THERMAL DECOMPOSITION DATA OF Mn(II), Co(II) AND Ni(II) COMPLEXES OF CAMPHOR-2AMINOPHENOL(HCAP)

Complex	Stage	Temp. range in TG (°C)	Peak temp. in TG (°C)	Loss of mass (%)			Probable assignment
				From TG	Theoretical	From pyrolysis	
$[Mn(CAP)_2(H_2O)_2]$	I	90–120	110	6	6.2	—	Loss of $2H_2O$
	II	120–280		16	18.4	—	Loss of aminophenol part
	III	280–410	400	49	47.3	—	Loss of 2 camphor part
	IV	410–610		15	15.6	—	Loss of 1 aminophenol part
				86	87.5	86.5	$[Mn(CAP)_2(H_2O)_2] \rightarrow Mn_3O_4$
$[Co(CAP)_2(H_2O)_2]$	I	90–150	100	6	6.2	—	Loss of $2H_2O$
	II	150–250		8	9.0	—	Loss of 0.5 aminophenol part
	III	250–410	350	57	56.3	—	Loss of 2 camphor part +0.5 aminophenol part
	IV	410–710		15	15.6	—	Loss of 1 aminophenol part
				86	87.1	86.7	$[Co(CAP)_2(H_2O)_2] \rightarrow Co_3O_4$
$[Ni(CAP)_2(H_2O)_2]$	I	60–150	80	6	6.2	—	Loss of $2H_2O$
	II	150–290		15	18.3	—	Loss of 1 aminophenol part
	III	290–410	370	49	46.9	—	Loss of 2 camphor part
	IV	410–710		17	15.5	—	Loss of 1 aminophenol part
				87	86.9	86.5	$[Ni(CAP)_2(H_2O)_2] \rightarrow NiO$

The kinetic parameters calculated for the decomposition of Mn(II), Co(II) and N(II) complexes of camphor-2-aminophenol on the basis of Coats-Redfern equation are given in Table-3. It can be seen that the values of E and A for these complexes, for different stages, are fairly comparable. It is also found that the greater the thermal stability of the complex the larger the activation energy for the decomposition. The negative ΔS values of the two decomposition stages of the three complexes show that the complexes are more ordered in the activated state than the reactants and that the reactions are slower than normal. On the basis of the observations, the relative thermal stabilities of metal chelates can be given as

$$[Ni(CAP)_2(H_2O)_2] < [Co(CAP)_2(H_2O)_2] \approx [Mn(CAP)_2(H_2O)_2]$$

TABLE-3
KINETIC PARAMETERS FOR THE DECOMPOSITION OF Mn(II), Co(II) AND Ni(II) COMPLEXES OF CAMPHOR-2-AMINOPHENOL FROM COATS-REDFERN EQUATION

Complex	Stage	E (kcal/mol)	A (sec^{-1})	ΔS (e.u.)	γ	Order (n)
	I	5.086	5.08×10^{-2}	-137.393	0.9727	0.333
$[Mn(CAP)_2(H_2O)_2]$	II		Too rapid to carry out the kinetic study			
	III	7.868	4.471×10^{-1}	-131.95	0.9985	0.5
	I	3.199	6.36×10^{-1}	-141.57	0.9378	0.333
$[Co(CAP)_2(H_2O)_2]$	II		Too rapid to carry out the kinetic study			
	III	7.455	3.780×10^{-1}	-131.438	0.9991	0.5
	I	1.1987	1.62×10^{-1}	-148.97	0.9766	0.5
$[Ni(CAP)_2(H_2O)_2]$	II		Too rapid to carry out the kinetic study			
	III	14.691	7.57×10^{-1}	-130.996	0.9955	0.5

Preliminary studies of antifungal activity using HCAP and its Co(II), Ni(II), Cu(II) and Zn(II) complexes revealed that they are active against the mycelial growth of *Phytophthora opsici.* Based on the leads from the preliminary study, a detailed study was undertaken to find out the inhibitory effect of this ligand and metal complexes on the various stages of growth of *Phylophthora capsiici, viz.*, sporangial production, zoospore liberation and zoospore germination. The results are given in Tables 4, 5, 6 and 7. The Co(II) complex showed the maximum inhibition of 81.9% followed by the ligand HCAP 73.6% and Ni(II) complex 72.2% on the radial growth of *Phytophthora capsici.* The ligand and the Co(II), Ni(II) and Cu(II) complexes which showed inhibitory effect on mycelial growth were then subjected to further study. In those studies, the Cu(II) complexes were found to be the most effective in inhibiting the sporangial production, sporangial liberation and zoospore germination of *Phytophthora capsici.* The study indicates that not only Cu(II) complexes but Co(II) and Ni(II) complexes also possess sufficient antifungal activity for tackling the problem of 'foot rot', a devastating disease that affects black pepper.

TABLE-4
INHIBITORY EFFECT OF METAL COMPLEXES OF HCAP ON RADIAL GROWTH OF *PHYTOPHTHORA CAPSICI*

Ligand/ Complexes	Radial growth in mm	% Inhibition over control	Radial growth in mm	% Inhibition over control
	50 ppm		100 ppm	
HCAP	9.3	74.2	9.5	73.6
$[Co(CAP)_2(H_2O)_2]$	7.5	79.2	6.5	81.9
$[Ni(CAP)_2(H_2O)_2]$	13.5	62.5	10.0	72.2
$[Cu(CAP)_2(H_2O)_2]$	13.6	62.0	11.2	69.0
$[Zn(CAP)_2(H_2O)_2]$	16.2	32.9	17.5	51.3
Control	36.0			

LSD (p-0.05)

TABLE-5
INHIBITORY EFFECT OF HCAP AND ITS METAL COMPLEXES ON SPORANGIAL PRODUCTION OF *PHYTOPHTHORA CAPSICI*

Ligand/Complex	No. of Sporangia/ field	% Inh.	No. of Sporangia/ field	% Inh.	No. of Sporangia/ field	% Inh.	No. of Sporangia/ field	% Inh.
	10 ppm		25 ppm		50 ppm		100 ppm	
HCAP	68.8	0.86	67.6	2.6	64.2	7.5	58	16.4
$[Co(CAP)_2(H_2O)_2]$	58.6	15.60	58.0	16.4	56.4	18.7	20.2	70.9
$[Ni(CAP)_2(H_2O)_2]$	59.6	14.12	58.6	15.6	55.8	19.6	54.6	21.3
$[Cu(CAP)_2(H_2O)_2]$	53.2	23.30	50.0	27.9	0.8	98.8	0.6	99.1
Control	69.4							

Field: Microscopic field (magnification 20X); LSD (P-0.05); Inh. = Inhibition

TABLE-6
INHIBITORY EFFECT OF HCAP AND ITS METAL COMPLEXES ON SPORANGIAL LIBERATION OF *PHYTOPHTHORA CAPSICI*

Ligand/Complex	Zoospore release (%)	% Inh.	Zoospore release (%)	% Inh.	Zoospore release (%)	% Inh.	Zoospore release (%)	% Inh.
	10 ppm		25 ppm		50 ppm		100 ppm	
HCAP	46.5	3.5	45.8	5.0	45.2	6.2	44.6	7.3
$[Co(CAP)_2(H_2O)_2]$	46.7	33.08	46.8	2.7	45.8	5.01	44.3	8.11
$[Ni(CAP)_2(H_2O)_2]$	48.2	0.0	46.5	3.47	46.2	4.24	45.2	6.2
$[Cu(CAP)_2(H_2O)_2]$	42.2	12.4	0.0	100	0.0	100	0.0	100
Control	48.4							

LSD (P-0.05); Inh. = Inhibition.

TABLE-7
INHIBITORY EFFECT OF HCAP AND ITS METAL COMPLEXES ON ZOOSPORE GERMINATION OF *PHYTOPHIHORA CAPSICI*

Ligand/Complex	% Ger.	% Inh.	% Ger.	% Inh.	% Ger.	% Inh.	% Ger.	% Inh.
	10 ppm		25 ppm		50 ppm		100 ppm	
HCAP	48.0	33.5	30.14	58.33	36.72	49.23	24.21	66.53
$[Co(CAP)_2(H_2O)_2]$	47.5	34.2	34.81	51.86	26.11	63.89	13.33	81.56
$[Ni(CAP)_2(H_2O)_2]$	45.0	37.7	40.50	43.92	28.89	60.05	27.78	61.59
$[Cu(CAP)_2(H_2O)_2]$	16.2	77.4	8.12	88.77	4.65	93.57	0.00	100.00
Control	72.3							

Ger. = Germination; Inh. = Inhibition.

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