



SYNTHESIS, CHARACTERIZATIONS AND ANTI MICROBIAL ACTIVITY OF NOVEL METAL COMPLEXES

Nishant H. Yadav^{1*}, Rakesh Patel², Piyush Vyas³, Harsh Patel⁴

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Abstract:

The ligand, 6-(phenylcarbamoyl) cyclohex-3-enecarboxylic acid (PPAA) and its transition metal ions viz; Cu²⁺, Co²⁺, Ni²⁺, Mn²⁺, and Zn²⁺ complexes have been synthesized and characterized by elemental analysis, Spectral studies, magnetic moments and thermal studies. The antifungal activity of all the samples was monitored against common fungi.

Keywords: - Tetrahydrophthalic acid, Metal Chelates, IR, NMR & Spectral Studies, Thermogravimetric analysis.

^{1, 2, 3, 4}Department of Chemistry, Sheth M.N. Science College, Patan - 384265, Gujarat, India

*Corresponding author: - Nishant H. Yadav

*Department of Chemistry, Sheth M.N. Science College, Patan - 384265, Gujarat, India,

Email: ynishant577@gmail.com

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Introduction

The phthalamic acid derivative containing amide group. The derivatives of phthalamic acid and bisphthalamic acid are reported as metal complexing agents reported recently¹⁻⁵. The amide derivatives of similar type of ligands are also reported recently for their metal complexing study⁶⁻¹⁴. With this context the present work in light of complexation of 6-(phenylcarbamoyl) cyclohex-3-enecarboxylic acid (PPAA). Thus the present communication comprises the synthesis, characterization and microbial study of PPAA and its metal complexes. The research work is shown in scheme-1.

Experimental

Materials: All the chemical used were of laboratory grade.

Synthesis of ligand 6-(phenylcarbamoyl) cyclohex-3-enecarboxylic acid (PPAA):

Tetrahydrophthalic anhydride (0.05 mole) and aniline (0.052 mole) were dissolved separately in diethyl ether (50 ml). Both these solutions were mixed and stirred on a magnetic stirrer till the complete formation of 6-(phenylcarbamoyl) cyclohex-3-enecarboxylic acid (PPAA) takes place. The compound was filtered, washed with ether, dried and recrystallised from ethanol. Yield was 84%, m.p. 136-137⁰ C Uncorrected (Capillary method).

Analysis:	C ₁₄ H ₁₅ NO ₃ (245)		
	%C	%H	%N
Calcd:	68.56	6.16	5.71
Found:	68.5	6.1	5.6

IR:	3200 - 3600cm ⁻¹ (OH of COOH)
	3030 cm ⁻¹ (Aromatic C-H)
	28500, 2920, 1430cm ⁻¹ (-CH ₂)
	1690 cm ⁻¹ (CO of COOH)
	1680, 1580, 1610 cm ⁻¹ (-CONH)
	1630-1685 cm ⁻¹ (-C=C)

¹H NMR:	10.6ppm (1H,s,-COOH)
	6.6 - 7.8ppm (5H,m,aromatic-H)
	5.62-5.78(2H,q,=CH)
	2.70-2.76(2H,q,-CH)
	2.02-2.35(4H,t,-CH ₂)
	NH of CONH (not shown discernibly)

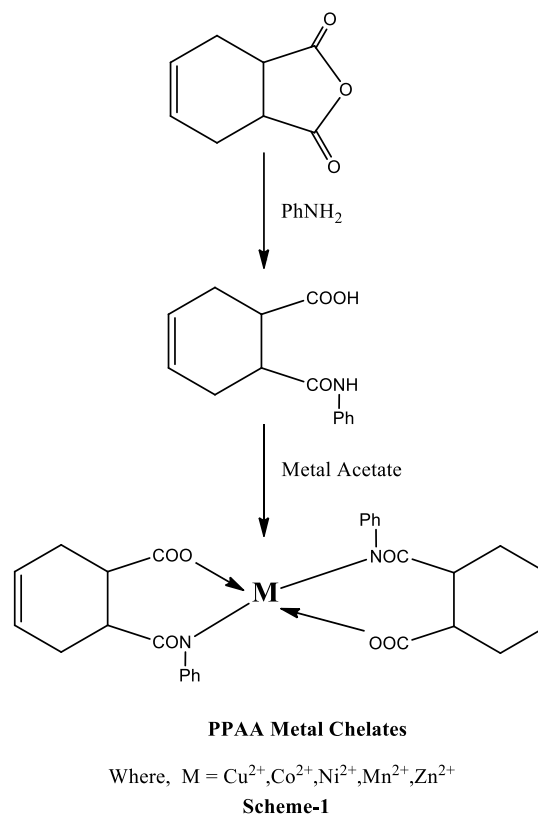
Acid value: 230 mg/1g of acid.

Synthesis of Complexes

The metal chelates of PPAA (i.e. of Cu²⁺, Mn²⁺, Zn²⁺, Co²⁺, Ni²⁺ ions) were prepared in similar

manner. The general method for synthesis of metal Complexes is as follow.

The metal salt (0.01 mole) solution in ethanol-dioxane (1:1V/V) mixture (25 ml) was added to 50 ml of solution of PPAA (0.02 mole) ethanol-dioxane (1:1 v/v) mixture with constant stirring. The reaction mixture was adjusted by the pH 4-5 by addition of sodium acetate. Then refluxed in water bath until solid separated out. The solid was filtered, washed with solvent and then air dried.



Measurements

The Elemental contents of C, H, N were determined by Thermofinigan Flash 1101 EA (Italy). The metals were determined volumetrically by Vogel's method¹⁵. To a 100 mg chelate sample, each 1ml of conc. HCl, H₂SO₄ and HClO₄ were added and then 1 gm of NaClO₄ were added. The mixture was evaporated to dryness and the resulting salt was dissolved in double distilled water and diluted to 100ml. From this Solution the metal content was determined by titration with standard EDTA solution. Infrared Spectra of the synthesized compounds were recorded on Nicolet. 760 FT - IR Spectrometers, NMR Spectrum of PPAA was recorded on 60 MHz Bruker NMR Spectrophotometer. Magnetic susceptibility measurement of the complexes was carried out on Gouy balance at room temperature. The electronic spectra of complexes in solid were recorded at room

temperature. MgO was used as reference. Thermogravimetric analyses of PPAA sample was carried out and antifungal activity of all the samples was monitored against various fungi, following the method reported in literature¹⁶.

Results and Discussion

The elemental content and IR - NMR spectral data of PPAA ligand are almost consistent with the predicted structure. The thermogram of PPAA indicate that the initial wt. loss is due to decarboxylation of PPAA in Air. The Value is quite consistent with the calculated Value. All these facts confirm the structure of PPAA.

Table-1 Analysis Of Ppaa Ligand And Its Metal Complex

METAL COMPLEX	Elemental analysis (%)									
	mol.wt	Yield %	C%		H%		N%		M%	
			Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
C ₂₈ H ₂₈ N ₂ O ₆ Cu ²⁺ ·2H ₂ O	557.54	76	60.28	60.2	5.74	5.7	5.02	5.0	11.73	11.7
C ₂₈ H ₂₈ N ₂ O ₆ Ni ²⁺ ·2H ₂ O	551.71	74	61.01	61.0	5.81	5.7	5.08	5.0	10.66	10.6
C ₂₈ H ₂₈ N ₂ O ₆ Co ²⁺ ·2H ₂ O	551.94	78	60.99	60.9	5.81	5.8	5.08	5.0	10.70	10.6
C ₂₈ H ₂₈ N ₂ O ₆ Zn ²⁺ ·2H ₂ O	557.38	76	60.28	60.2	5.74	5.7	5.02	5.0	11.73	11.7
C ₂₈ H ₂₈ N ₂ O ₆ Mn ²⁺ ·2H ₂ O	546.94	75	61.43	61.4	5.85	5.8	5.12	5.1	10.04	10.0

The acid value and TG data of PPAA are agree with the structure. The TG data indicate the decarboxylation step which is consistent with the theoretical value (~17.95). Thus the ligand containing one COOH group.

The metal complexes are stable at room temperature in humid atmosphere. The analytical data of all the complexes are shown in Table - 1. The elemental contents of complexes are consistent with the predicted structure.

The metal complexes showed the band between 3600 - 3200 cm⁻¹. This might be due to presence of coordinate water molecule. The bands due to amide $\nu_{C=O}$ mode around 1680 cm⁻¹ for the free ligands are shifted to higher frequency in all the complexes indicating involvement of the carbonyl oxygen of the amide group in coordination and non involvement of the amide nitrogen^{17, 18}. The

absorption band around 1690 cm⁻¹ and 1300 cm⁻¹ in the free ligands attributed to $\nu_{C=O}$ and ν_{C-OH} of the carbonyl group¹⁹. They are replaced by two bands in the region of 1540 - 1590 cm⁻¹ and 1340 - 1380 cm⁻¹ corresponding to $\nu_{C=O}$ (assymm.) and ν_{C-O} (symm.) in all the complexes.

The Infrared spectra of all the complexes are identical and suggest the formation of all the metalocyclic compound by the absence of band characteristic of free - OH group of parent PPAA. The other bands are almost at their respectable positions as appeared in the spectrum of parent - PPAA ligand. However, the band due to (M-O) band could not be detected as if may appeared below the range of instrument used. The important IR spectral data are shown in Table - 2.

Table - 2 Spectral Features And Magnetic Moment Of Ppaa - Metal Chelates

Metal Chelates	μ_{eff} (BM)	Electronic spectral data(cm ⁻¹)	Transition
PPAA-Cu ²⁺	2.56	23530 14953	Charge Transfer ${}^2B_{1g} - {}^2A_{1g}$
PPAA-Ni ²⁺	3.68	24092 14922 9018	${}^3A_{2g}(\text{F}) - {}^3T_{2g}(\text{F})$ ${}^3A_{1g}(\text{F}) - {}^3T_{1g}(\text{F})$ ${}^3A_{2g}(\text{F}) - {}^3T_{1g}(\text{P})$
PPAA-Co ²⁺	4.72	22477 19929 9546	${}^4T_{1g}(\text{F}) - {}^4T_{2g}(\text{F})$ ${}^4T_{1g}(\text{F}) - {}^4T_{2g}(\text{F})$ ${}^4T_{1g}(\text{F}) - {}^4T_{2g}(\text{P})$
PPAA-Mn ²⁺	5.51	23863 18351 16827	${}^6A_{1g} - {}^6A_{2g}$ 4E_g ${}^6A_{1g} - {}^4T_{2g}$ $(4G) {}^6A_{1g} - {}^4T_{1g}(\text{PG})$
PPAA-Zn ²⁺	D	-	-

D*=Diamagnetic

Magnetic moments of metal chelates are given in Table-2. The diffuse electronic spectrum of Cu²⁺ Eur. Chem. Bull. 2023, 12(Special Issue 5), 1633 – 1636

chelates shows two broad bands around 14953 and 23530 cm⁻¹. The first band may be due to a

${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition. While the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{2+} metal chelates^{20,21}. The higher value of the magnetic moment of the Cu^{2+} chelate supports the same. The Co^{2+} metal chelate gives rise to three absorption bands at 22477 and 19929 and 9546 cm^{-1} , which can be assigned ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions, respectively. These absorption bands and the μ_{eff} value indicate an octahedral configuration of the Co^{2+} metal chelate^{19, 20}. The spectrum of Mn^{2+} polymeric chelate comprised three bands at 23863 cm^{-1} , 18351 cm^{-1} and 16827 cm^{-1} . The latter does not have a very long tail. These bands may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$

and ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transitions, respectively. The high intensity of the bands suggests that they may have some charge transfer character. The magnetic moment is found to be lower than normal range. In the absence of low temperature measurement of magnetic moment it is difficult to attach any significance to this. As the spectrum of the metal chelate of Ni^{2+} show three bands at 24092, 14922 and 9018 cm^{-1} are assigned as ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{1g} \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, respectively suggested the octahedral environment for Ni^{2+} ion. The observed μ_{eff} values in the range 3.00 - 3.28 moiety^{21,22}.

Table – 3 Antifungal Activity Of Ppaa Ligand And Its Metal Celates

Sample	Zone of Inhibition of Fungal at 1000 ppm(%)			
	<i>Penicillium Expansum</i>	<i>Alternaria solani.</i>	<i>Trichoderma sp</i>	<i>Nigrospra sp</i>
PPAA	53	47	62	61
PPAA-Cu ²⁺	86	86	81	83
PPAA-Zn ²⁺	72	61	79	68
PPAA-Ni ²⁺	81	71	73	67
PPAA-Co ²⁺	62	63	79	65
PPAA-Mn ²⁺	71	72	76	75

The examination of antifungal activity of PPAA ligand and its all complexes (Table - 3) reveals that the ligand is moderately toxic against fungi, while all the chelates are more toxic than ligand. Among all the chelates the Cu^{2+} complex is more toxic against fungi.

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