

Synthesis, Characterization and biological activity of Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) complexes of Butanamide 3-oxo-N-phenyl-2-(4-nitro phenyl hydrazono)

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Abstract

Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) complexes of Butanamide 3-oxo-N-phenyl-2-(4-nitro phenyl hydrazono) have been synthesized and characterized. Complexes were isolated in solid state and characterized from elemental analysis, magnetic studies, uv-visible, IR and NMR data. The elemental analysis confirms the assigned stoichiometries. The stereochemistry of the complexes was ascertained using magnetic studies, uv-visible diffuse reflectance, IR and ¹H NMR. In the complexes, the phenylazo group (C₆H₅N₂) exhibits bidentate character and co-ordinates with the metal through the phenylazo and methylketo groups. Metal:Ligand ratio is found to be 1:2. Presence of coordinated water was observed in some complexes. The complexes exhibited considerable activity against gram positive *S.Aureus*, gram negative *E.coli* and fungus *A.niger*.

KEYWORDS: Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) complexes, hydrazone complex.

Introduction:- β-diketones and anilides are found to be very good complexing agents especially for transition and inner transition metal ions. Their complexing ability is enhanced by introduction of active groups like hydrazones. The complexes are found to exhibit striking structural features and applications in diverse areas.

Since structure and reactivity are interdependent, studies on molecular structure of transition metal complexes are of paramount importance. Excellent modern theories on metal ligand bonding are available. These theories aid in interpreting the experimental data obtained using sophisticated instrumental techniques available to the research workers.

Hydrazone compounds exhibit biological activities as antifungal, antibacterial, anticonvulsant, anti-inflammatory, antimalarial, analgesic, antituberculosis, antiviral, antitumor diseases and as antidiabetic. The lone pair on trigonally hybridized nitrogen atom of the azomethine group is responsible for the chemical and biological activity¹.

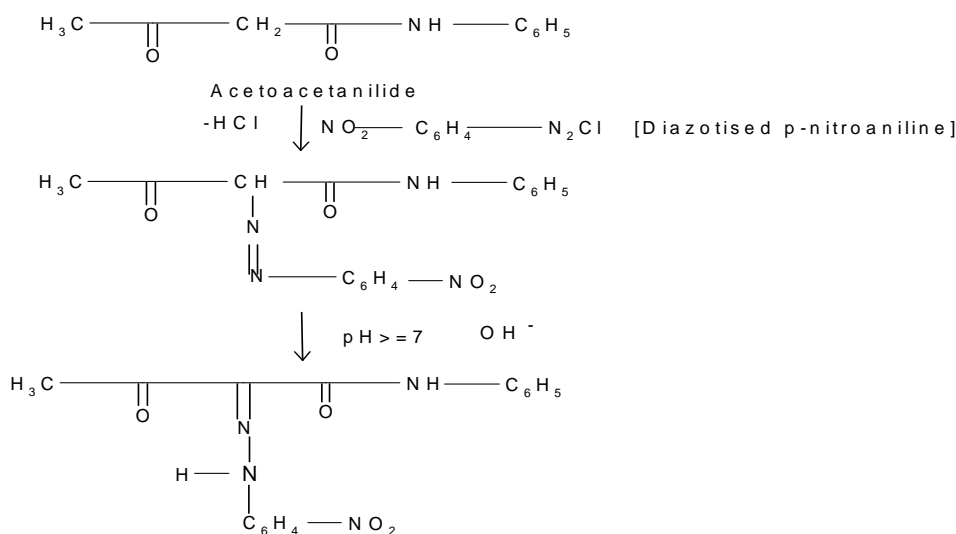
The present work deals with preparation and characterization of Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) complexes with ligand Butanamide 3-oxo-N-phenyl-2-(4-nitro phenyl hydrazono) i.e. nitro derivative of phenylazoacetoacetanilide (NO₂HPAAC) and to study their biological activity.

Experimental:-

All pH measurements, concerned with isolation of complexes and their related analysis were carried out on Equiptronics EQ-614A using glass electrode as indicator and calomel as reference electrode. Absorption measurements in the visible region

were carried out on digital spectrophotometer, Equiptronics model No EQ 820. For molar conductance measurements Equiptronics, Digital Conductivity Meter Model No. EQ-660A was used. Gouy's balance by PerkinElmer was used for measurement of magnetic susceptibility at room temperature. Jasco V-670 spectrophotometer and Shimadzu UV-2600 series with a attachment for a reflectance measurement was used for diffuse reflectance measurement. FTIR 84008 by M/s Shimadzu Corporation of Japan was used for IR spectra. NMR spectra for complexes and ligands were recorded on Bruker Avance 2 -300 MHz frequency.

Preparation of Ligand:- The Ligand NO₂HPAAC was prepared knowing that β-dicarbonyl compounds like acetoacetanilide undergo diazocoupling at the reactive methylene group. Diazotization was carried with p-nitroaniline at 0-5°C. The elemental analysis is agreeing well with the expected value. M.P of ligand=210°C



Preparation of Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) complexes of NO₂HPAAC:

The (0.005 moles) solutions of Cd(II), MoO₂(VI), Th(IV), ZrO(IV) with appropriate A.R.quality salts were prepared by dissolving in very minimum quantity of distilled water and equal amount of alcohol was added. To this, (0.01 moles) of ligand NO₂HPAAC dissolved in minimum quantity of nitrobenzene followed by addition of required amount of alcohol was added by constant stirring so that reaction mixture contained metal to ligand molar ratio of 1:2. and suitable pH was adjusted. Yellow to yellowish brown colour complexes were separated. Each of the complexes were filtered, washed with alcohol and dried. It was found to be almost insoluble in water and most of the common organic solvents. The thoroughly dried complex was analysed.

Analytical and physicochemical parameters of Cd(II), MoO₂(VI), Th(IV), ZrO(IV) complex of NO₂HPAAC

Formula of the Complex	Colour	pH	Molar conductance $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$	Carbon Hydrogen Nitrogen Metal %			
				Obs (Cal)	Obs (Cal)	Obs (Cal)	Obs (Cal)
NO ₂ HPAAC (Mol wt=326)	Yellowish brown	-----	2.52	59.32 (58.89)	4.52 (4.29)	16.81 (17.17)	-----
Cd(NO ₂ PAAC) ₂ . 2H ₂ O (Mol wt=798.4)	Yellowish brown	7.6	6.2	48.32 (48.09)	3.83 (3.76)	13.96 (14.02)	13.98 (14.07)
MoO ₂ (NO ₂ PAAC) ₂ (Mol wt=777.9)	Yellowish white	6.8	3.63	49.05 (49.36)	3.48 (3.60)	14.89 (14.40)	12.01 (12.33)
Th(NO ₂ PAAC) ₂ .2 H ₂ O (Mol wt=918)	Yellow	6.6	5.1	40.99 (41.83)	3.11 (3.27)	12.34 (12.20)	25.49 (25.27)
ZrO(NO ₂ PAAC) ₂ .1H ₂ (Mol wt=775)	Yellow	5.0	6.4	49.86 (49.55)	3.87 (3.61)	15.01 (14.45)	11.83 (11.74)

Result and Discussion:- Characterization of the ligand NO₂HPAAC: The ligand NO₂HPAAC under investigation is soluble in organic solvents like Dimethyl Sulphoxide (DMSO), Nitrobenzene etc. The conductivity measurements of $1 \times 10^{-3} \text{M}$ ligand in DMSO is $2.52 \text{ ohm}^{-1}\text{mol}^{-1}\text{cm}^2$. The values of molar conductance are extremely low hence it is beyond doubt to assign non ionic character to the ligand. The ligand possesses nitrogen and oxygen as the most potential donor atoms.

Characterization of Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) complexes of NO₂HPAAC

Elemental analysis reveals that all of the complexes bear 1:2 metal to ligand ratio. The elemental analysis of the complexes is in agreement with the general formula where L= NO₂HPAAC and M= Cd(II), MoO₂(VI), Th(IV) and ZrO(IV). The complexes are soluble in DMSO and nitrobenzene. The extremely low molar conductance values suggest non electrolytic nature of the complexes.

Structural investigation of the complex is done by using different physicochemical techniques. The coordination sites in the complexes are fixed on the basis of elemental analysis, magnetic studies, diffuse reflectance spectra, I.R. spectral studies, NMR studies, and supported by thermal studies. All the complexes were found to be diamagnetic as expected. The magnetic properties of the complexes are supported by diffuse reflectance spectra of the complexes.

Table 1

Diffuse reflectance data of ligand NO₂HPAAC and its complexes

Ligand/ Complex	Wavelength (nm)	Wavenumber (cm ⁻¹)	Assignment
NO ₂ HPAAC	460.5	21715	Ligand charge transfer band n→π* π→π* π→π*
	321.5	31104	
	252.0	39682	
	233	42918	
Cd(NO ₂ PAAC) ₂ .2H ₂ O	433	23094	Charge transfer band n→π* π→π*
	331	30211	
	208	48076	
MoO ₂ (NO ₂ PAAC) ₂	480	20833	O→Mo Charge transfer band n→π* π→π*
	420	23809	
	320	31240	
	210	47619	
Th(NO ₂ PAAC) ₂ .2H ₂ O	456	21929	Charge transfer band n→π* π→π*
	327	30581	
	212	47169	
ZrO(NO ₂ PAAC) ₂ .1H ₂ O	437	22883	Charge transfer band n→π* π→π*
	315	31746	
	220	45454	

The data reveals that the ligand comprises four sets of bands. The first and second band of the shortest wavelength appeared at 233 and 252 nm may be assigned to the π→π* transition in the benzenoid moieties. The third band appears at 321.5 nm may be assigned to n→π* of the carbonyl group. These bands are shifted to higher or lower energy on complexation indicating the participation of these groups in coordination with metal ions. The charge transfer absorption band at 460.5 nm in the electronic spectra of the ligand may be assigned to the π→π* electronic transition of the conjugated π- system of the hydrazone moiety influenced by charge transfer throughout the molecule. This band provides additional evidence that the compound under study exist as azo-hydrazo tautomer and the hydrazone form is the most predominant one ².

The diffuse reflectance spectra of Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) complexes of NO₂HPAAC shows shifts of all the ligand bands to higher or lower energy on complexation indicating the participation of these groups in coordination with metal ions ^{3,4,5}. The bands observed in the 433-480 nm range may be due to ligand charge transfer transition and LMCT. The bands observed in the range 315 to 331 nm may be due to n→π* transition of the C=O group. The maintenance of the 321.5 nm ligand bands even in the coordinated state suggest that the double bond character of C=O in the acetyl group is not eliminated with the complex formation. The lone pair electrons of the carbonyl oxygen will coordinate with metal atom to form a σ (coordinate covalent) bond⁶. The bands observed in the range 208 to 252 nm may be due to π→π* transitions of the benzenoid moieties. The diamagnetic complexes of Cd(II), MoO₂(VI), Th(IV) and ZrO(IV) ion do not show d-d transition. The diffused reflectance spectra of dioxomolybdenum (VI) complexes exhibit one band in the range 450 to 480 nm due to charge transfer transition, O (π) →d (Mo).

Table 2

I.R. spectral studies of ligand NO₂HPAAC and its metal complexes

Ligand and complex	Wavenumbers ν (cm ⁻¹)											
	ν (C=O) acetyl	ν (C=O) anilide	ν (N-H) hydrazone	ν (N-H) anilide	ν (C=N)	ν (C-H) aromatic	ν (C-H) aliphatic	ν (H ₂ O) coordinated	ν (M-N)	ν (M-O)	ν (Mo=O) / ν (Zr=O)	ν (N-O ₂)
NO ₂ HPAAC	1666	1678	3178 to 3093	3230	1596	3093	2939	-	-	-	-	1338
Cd(NO ₂ PAAC) ₂ .2H ₂ O	1646	1678	-	3230	1594	3062	2920	3510	543	480	-	1338
MoO ₂ (NO ₂ PAAC) ₂	1649	1678	-	3228	1593	3093	2939	-	560	458	933	1338
Th(NO ₂ PAAC) ₂ .2H ₂ O	1650	1678	-	3226	1596	3093	2839	3556	530	480	-	1338
ZrO(NO ₂ PAAC) ₂ .1H ₂ O	1652	1678	-	3226	1596	3093	2933	3556	550	455	886	1338

In the ligand spectra the lower frequency of CH₃-C=O group compared to normal value suggests that this group is hydrogen bonded to N-H of hydrazone group⁷. The ligand spectra also indicates broad band at 3178-3093 cm⁻¹ corresponding to hydrogen bonded N-H group. These observations show that the ligand nitro derivative of phenylazoacetanilide (NO₂HPAAC) remains in hydrazone form. The azo compounds of reactive methylene ketones and esters are found to remain in hydrazone form.

I.R. spectra of the solid complexes of NO₂HPAAC recorded in KBR show no much structural alteration of ligand in formation of complex. The important I.R. frequencies are listed in (Table 2). The band at 1666 cm⁻¹ in (NO₂HPAAC) ligand spectra due to CH₃-C=O group is shifted to lower frequency at around 1640 cm⁻¹ in Cd(II) complex, whereas in MoO₂(VI) complex it was at 1649 cm⁻¹, in Th(IV) complex at 1650 cm⁻¹, in Zn(II) complex at 1635 cm⁻¹ and in ZrO(IV) complex at 1652 cm⁻¹ which indicates involvement of CH₃-C=O group of the ligand in coordination with metal ion⁸. Co-ordination of carbonyl oxygen to the metal atom reduces the electron density in the C=O bond causing a shift in the ν (C=O) band.

Spectra of ligand (NO₂HPAAC) also shows broad band at 3178-3093 cm⁻¹ due to N-H bond of hydrazone group of ligand which is found to be absent in all the complexes spectra indicating that proton of N-H group of hydrazone is replaced by metal atom during formation of all these complexes. The band at 1678 cm⁻¹ due to anilide C=O group in ligand spectra (NO₂HPAAC) is found to be present in same position in spectra of all the complexes indicating C=O of anilide group is not involved in the formation of complex. Weak band due to N-H of anilide is found to remain around 3230 cm⁻¹ in spectra of all the complexes⁹. The metal complexes also show weak band at 1596cm⁻¹ due to C=N stretching frequencies. Also weak bands at 3093 cm⁻¹ and 2939 cm⁻¹ are attributed to aromatic C-H and aliphatic C-H stretching frequencies respectively. The absence of 1420 cm⁻¹ and 1210 cm⁻¹ bands in I.R. of complexes corresponding to N=N stretching frequency suggests that ligand remains in hydrazone form during formation of complex⁷. Therefore it is reasonable to conclude that proton of hydrazino N-H group is replaced by metal atom during complex formation and oxygen atom of CH₃-C=O group forms coordinate bond with metal atom. Although the ligand NO₂HPAAC contains CO-NH-C₆H₅ (anilide) group, the coordination does not takes place by bonding through phenylamino proton of CONHC₆H₅ group of the ligand. This may be attributed to the electron withdrawing nature of phenyl ring and C=O group, attached to N-H group, reducing its basicity and also due to double character of C-NH bond arising from enolisation. Expected coordination sites, therefore are phenylamino nitrogen of hydrazone group and CH₃C=O group which also sterically favour orientation of metal atom near the position of hydrogen bonding, in ligand NO₂HPAAC. Experimental results support this fact because band around 3230 cm⁻¹ is found to persists in the spectra of metal complexes showing that CONH from anilide is not involved in coordination whereas band due to hydrogen bonded N-H of hydrazone group at 3178-3093 cm⁻¹ is found to disappear indicating that N-H proton from hydrazone is replaced by metal atom during complex formation. Band at 1380 cm⁻¹ is due to the presence of nitro group in the ligand which is found at almost the same position in the complexes^{10,11}. A broad band around 3500-3550 cm⁻¹ in the I.R. spectra of complexes indicates coordinated water molecules in the complexes⁷. The I.R. spectra of ligand (NO₂HPAAC) does not have any band at 400 to 600 cm⁻¹, but two new bands around 530 to 560 cm⁻¹ and 425 to 480 cm⁻¹ in the spectra of all the complexes are attributed to M-N and M-O vibrations respectively. M-N and M-O bondings¹².

¹H NMR spectral studies of ligand NO₂HPAAC and its complexes:

Functional group δppm / Ligand/ complex	N-H of hydrazone	N-H of anilide	Aryl – H	Water (DMSO)	DMSO	CH ₃ of acetyl group
NO ₂ HPAAC	12.856	10.831	7.111- 8.257	3.463	2.470- 2.496	2.012
Cd(NO ₂ PAAC) ₂ .2H ₂ O	-	10.835	7.109- 8.219	3.464	2.477- 2.516	2.175
MoO ₂ (NO ₂ PAAC) ₂	-	10.832	7.135- 8.256	3.456	2.470- 2.482	2.190
Th(NO ₂ PAAC) ₂ . 2H ₂ O	-	10.840	6.943- 8.209	3.448	2.512	2.185
ZrO(NO ₂ PAAC) ₂ . 1H ₂ O	-	10.895	7.119- 8.232	3.447	2.476	2.170

NMR spectrum of the ligand NO₂HPAAC in d₆-DMSO showed broad down field signals at δ 10.831 ppm due to CONH proton of anilide and broad signal at δ 12.856 ppm due to N-H of hydrazone group. NMR of diamagnetic Cd(II), MoO₂(VI), Th(IV), ZrO(IV) complexes of NO₂HPAAC in d₆-DMSO showed that signal at δ 10.831 ppm was remaining almost unchanged but signal at δ 12.856 ppm was absent, indicating proton from hydrazone group of ligand NO₂HPAAC was replaced by metal atom during complexation leaving CONH group free. Intensities of other signals were remaining almost unchanged^{13,14}.

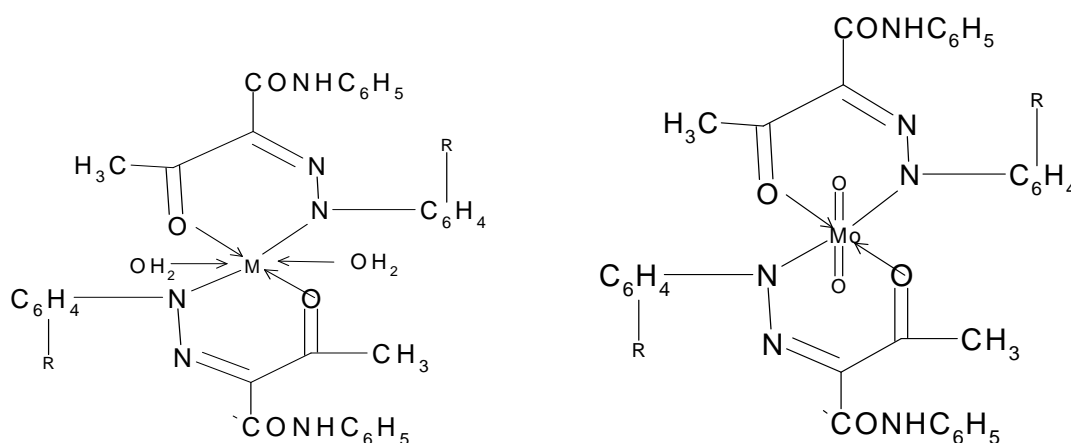
Signals around δ 2.012 ppm (s) in ligand (NO₂HPAAC) spectra were due to CH₃-C=O protons. Slight downfield shift of CH₃-C=O signals in the range δ 2.170 to 2.190 ppm in the complexes indicated involvement of acetyl group (CH₃-C=O) in coordination.^{13,14}

Signals due to DMSO in the ligand and complexes is observed at around 2.495 ppm.

Phenyl ring protons in the ligand NO₂HPAAC and its complexes were obtained in the range at δ 7.109 to 8.257 ppm. Intensities of integrated signals were obtained as expected¹⁰. Signal around 3.45 ppm in ligand NO₂HPAAC and its complexes was observed due to water present in DMSO/ coordinated water¹³.

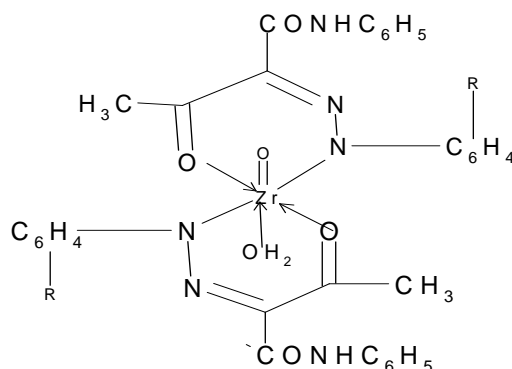
Thus on this experimental evidence it is reasonable to conclude that ligand acts as bidentate and complexation takes place through nitrogen of hydrazone group and supported by coordination through CH₃-C=O group.

Conclusion of structural study: In the light of these experimental data and observations Cd(II),Th(IV)complex of NO₂HPAAC, may be assigned tetrahedral structure



Octahedral Structure(I) M=Cd(II),Th(IV); Octahedral Structure (II) R=NO₂

R=NO₂



Octahedral Structure (IV) R=NO₂

Acknowledgement:- I express my thanks to Prof. Dr Deepa Khuslani and Mr Chandanshiva B, TIFR, Mumbai., Dr Ajit Dattar and Mr Amit, Shimadzu Ltd for services rendered in sample analysis of diffuse reflectance. I express my thanks to Mr Praveen Padalwar, Chemistry department, Mumbai University for helping me to record NMR of my samples. I express my thanks to Prof. Dr Raju Patil and Mr Sagar, Institute of Science for extending the facility to carry out magnetic susceptibility measurements. I acknowledge Chemo test lab for extending their facilities in carrying out I.R. analysis and SAIF, I.I.T Bombay for carrying out elemental analysis.

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