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Ultra Wave Assisted Tetra Aza-Macrocyclic Complexes of 4-Nitro O-Phenylene Diamine Complexes

*¹SN Ibatte and ²BS More¹Department of Chemistry, Dayanand Science College Latur, Maharashtra, India.²Department of Chemistry, Adarsh College Omerga, Maharashtra, India.

Abstract

Innovative tetraazamacrocyclic complexes of Cu(II), Co(II), Ni(II) and Zn(II) has been synthesized from the reaction of 4-Nitro O-phenylene diamine with acetyl acetone and divalent metal ions using solid-supported perchloric acid (HClO₄-SiO₂) as a catalyst. The complexes were characterized by IR, ¹HNMR, EPR spectra, magnetic moments, conductance, thermal analysis, and powder X-ray analysis (XRD). The antimicrobial studies of these complexes against *Staphylococcus typhi*, *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* species by Minimum Inhibitory Concentration (MIC) method revealed that these complexes possess potent antibacterial activity.

Keywords: IR, NMR, XRD, 4-Nitro O-phenylene diamine, metal salts

Introduction

The design and study of well-arranged metal containing macrocycles is an interesting field of chemistry. Some synthetic macrocyclic complexes have been investigated for accelerating the photodegradation of hazardous pollutants. One pot templet condensation reactions lie at the heart of macrocyclic chemistry. Hence, templet reactions have been widely used for the synthesis of macrocyclic complexes. There is continued interest in synthesis of macrocyclic complexes due to their potential application in fundamental and applied sciences. Synthetic macrocyclic complexes mimic some naturally occurring macrocycles because of their similarity with many natural macrocycles, like metalloproteins and metalloenzymes. Macrocyclic metal chelating agent, DOTA, is useful for detecting tumour lesion. Some macrocyclic complexes have special attention because of their mixed soft-hard donor character.

Result and Discussion

Typical Procedure

To a ethanolic solution (50ml) of 4-Nitro O-phenylene diamine (10 m mol) was added divalent copper, cobalt, nickel and zinc salts (5 m mol) of chloride, nitrate and acetate dissolved in ethanol and (10 m mol) of acetyl acetone along with 10 mol% solid supported perchloric acid. The mixture was then kept to ultrawave radiation at room temperature for ½ hour, a colored complexes formed, which were filtered washed with ethanol, and ether.

The complex was dissolved in DMF and then filtered. Filtrate was subjected to vacuum rota evaporator, a shiny colored complex was obtained which were dried in vacuo (yield 70-80%)



Chemistry

The obtained data suggest the formula of macrocyclic complexes as [M(C₂₂H₂₂N₄)X₂] where M = CO(II), Cu(II), Ni(II), Zn(II) and X = Cl⁻¹, NO₃⁻¹, CH₃COO⁻¹ test for anion gives positive after decomposing the complex with conc. HNO₃ indicating their presence inside the coordination sphere The molar conductivity values for all complexes in DMSO suggest that they have non electrolytic nature.⁵All complexes have high melting point >250°C. Complexes prepared are intensively colored. Magnetic movement values suggest octahedral environment around all metal complexes (table-1).

Infrared Spectra

The infrared spectra of complexes (table - 2) do not exhibit any bands characteristics for NH₂ and CO groups and the appearance of two new bands characteristics of C=N and C-N groups in the region 1590 – 1640cm⁻¹, 1540 – 1560 cm⁻¹

respectively, which supports the macrocyclic structure of the complex.

An important feature is the appearance of a new medium intensity band at $420 - 460\text{cm}^{-1}$ attributable to $\nu(\text{M-N})$ which provides strong evidence for the involvement of nitrogen in co-ordination.⁵⁰

¹H NMR Spectra

The ¹H NMR spectra doesn't show any signal corresponding to NH₂ protons. However Zinc complex shows (table) signals at 1.75ppm and 2.25ppm, assigned to -CH₃ protons and -CCH₂C- protons respectively. Other signals appeared in the region 6.50 to 7.60ppm assigned to multiplet of benzene ring.

EPR Spectra

EPR spectra of complexes were recorded in powder form at room temperature differ significantly g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} and G values of complexes are summarized in (table-4). Difference in values of line width suggests that they are independent of temperature.

Ni (II) complex exhibit sharp line width around 3346gauss reflecting isotropy. The $g_{\parallel} = 2.0005$ and $g_{\perp} = 1.9989$ and exchange interaction coupling constant $G = 0.6595$. Value of electron per gram found to be 1.5068×10^{21} .

For complexes were $g_{\parallel} > g_{\perp}$ and G value observed to be less than 4 which indicates that electron lies on $dx^2 - y^2$ orbital. According to Hathway, if exchange interaction coupling constant If G is larger than 4 the exchange interaction are negligible because local tetragonal axes are aligned parallel and slightly misaligned and if it is less than 4 the exchange interaction are considerable and local tetragonal axes are misaligned. For present complexes G value is very small suggests exchange interactions are considerable and local tetragonal axes are misaligned.

Powder X-ray Analysis

Powder XRD diffractogram of some selected complexes were recorded in 2θ range 20 to 80° cu-radiation source at wavelength 1.5447° A at room temperature are shown in figure. Major reflexes were used to determine corresponding interplaner distances. Diffractogram were then indexed independently. Miller indices were calculated and lattice parameters a, b, c and interfacial angles α, β, γ were determine by computer based powder programme. Unit cell volumes of complexes were determine.

Thermal Analysis

From TG analysis, presence of lattice water, coordinated water and breakdown pattern of complexes are evaluated.

In complex of Cu (II) three peaks are reflected, one is endothermic and other is exothermic. First endothermic mass loss corresponds to elimination of water and acetate below 200°C and second exothermic mass loss corresponds to elimination of acetyl acetone moiety at above 200°C remaining part ligand to be removed above 380°C and decomposition completed at 600°C , leading final product of cobalt oxide. Amount of cobalt oxide found in residue is close agreement with calculated.

The kinetic and thermodynamic parameters viz, order of reaction (n), energy of activation (E_a), three exponential factor (Z) etc. for non- isothermal decomposition of metal complexes were determined by the Horowitz Metzger approximation method. The data obtained are given in (table-6). The calculated values of the activation energy of the

complexes are relatively low, indicating the autocatalytic effect of the metal ion on the thermal decomposition of the complex. The negative activation entropy values suggest that the activated complex were more ordered than the reactants and that the reaction were slow. The more ordered nature may be due to polarization of bonds in activated state.

Antimicrobial Activity

For in vitro antimicrobial activity, the investigated compounds were tested against the bacteria salmonella typhi, staph aureus, Escherichia coli and Bacillus subtilis. The minimum inhibitory concentration values of compounds against the growth of microorganisms are summarized in table. From this it is observed that copper and zinc complexes are more active in salmonella typhi and Bacillus subtilis respectively compared to other bacterial organisms. Cobalt and nickel complexes are moderately active in all bacterial organisms. Moreover, all complexes are moderately active in above four bacterial organisms compared with standard cefadroxil.

A comparative study of metal complexes exhibit higher antimicrobial activity. Such increased activity of complexes can be explained with respect to Overtone's concept and Tweedy's chelation theory. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favour the passage of only lipid soluble material whose liposolubility is an important factor, which controls antimicrobial activity. On chelation, the polarity of metal ion is reduced to a great extent due to overlap of ligand orbital and partial sharing of positive charge of metal ion with donor groups. Further, it increases the delocalization of π electron over the hold chelate ring and enhance the lipophilicity of the complexes. This increased lipophilicity enhance the penetration of complexes in to lipid membranes and blocking the metal binding sites in the enzyme of microorganisms.

Table 1: Magnetic movements and molar conductivity of complexe.

Complexes of acetyl acetone	$\lambda \Omega^{-1}\text{cm}^2 \text{M}^{-1}$	Magnetic Moment μ_B
[CuL ₈ Cl ₂]	52	1.78
[Cu L ₈ (NO ₃) ₂]	50	1.77
[Cu L ₈ (CH ₃ COO) ₂]	49	1.78
[CO L ₈ Cl ₂]	53	4.83
[CO L ₈ (NO ₃) ₂]	52	4.83
[CO L ₈ (CH ₃ COO) ₂]	49	4.82
[Ni L ₈ Cl ₂]	42	2.80
[Ni L ₈ (NO ₃) ₂]	41	2.82
[Ni L ₈ (CH ₃ COO) ₂]	41	2.80
[Zn L ₈ Cl ₂]	59	-
[Zn L ₈ (NO ₃) ₂]	58	-
[Zn L ₈ (CH ₃ COO) ₂]	57	-

Table 2: IR spectra of complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{M}-\text{N})$
[CO L ₈ Cl ₂]	1639	1531	-

Table 3: ¹H NMR Spectroscopic data of the complexes

Complex	-CH ₃	-CCH ₂ CH ₂ C-	-CCH ₂ C-	Benzene Ring
ZnL ₈ (NO ₃) ₂	1.80	-	2.20	6.50 to 7.60

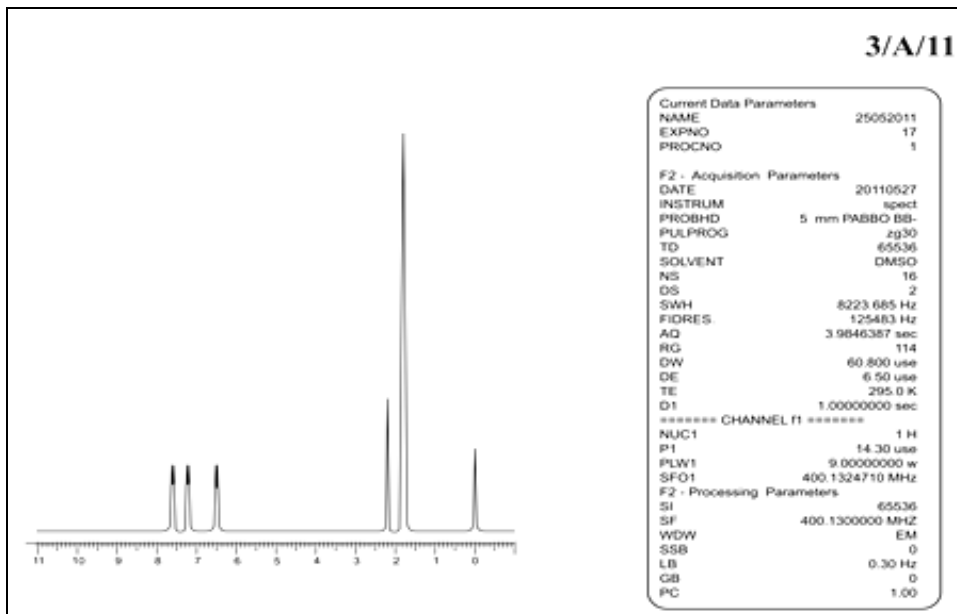


Fig 1: 1H NMR Spectroscopic data of the complexes

Table 4: EPR parameters for metal complexes.

Complex	Gyromatric ratio g	A gauss	G	e/gm*10 ²¹
NiL ₈ Cl ₂	g = 2.0005 g _⊥ = 1.9989 g _{av} = 1.9994	A = 4.09 A _⊥ = 8.19	0.6595	1.5078

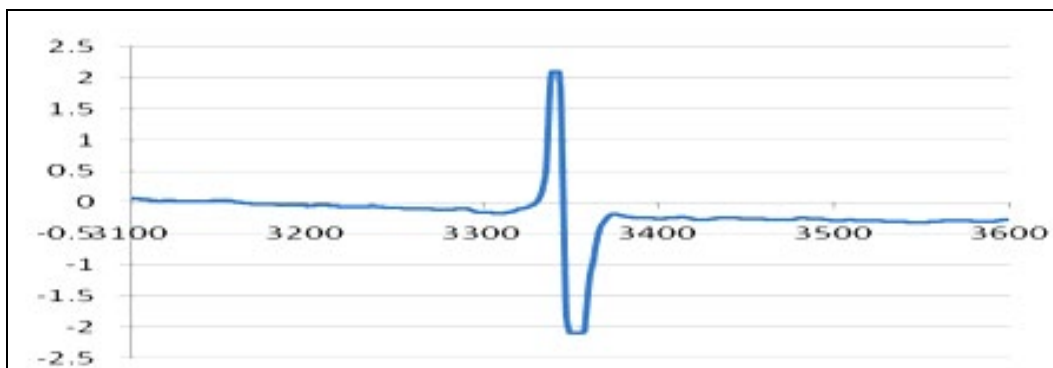
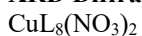


Fig 2: EPR parameters for metal complexes.

XRD Diffractogram



Crystal System: Monoclinic Lattice Type: P2/M

Lattice Parameter: a = 19.637068 b = 3.966733 c = 8.304183

Lattice Parameter: α = 90.00, β = 98.590157, γ = 90.00° Unit

cell volume = 639.60 cm³

Table 5: Milllar indices and interprener distances.

Complex	h k l	2θ Observed	2θ Calculated	d
CuL ₈ (NO ₃) ₂	0 1 0	22.404	22.394	3.9651
	2 0 2	24.776	24.754	3.5905
	-2 1 2	31.734	31.736	2.8173
	5 1 1	35.213	35.197	2.5465
	6 1 0	35.767	35.780	2.5084
	-4 1 1	30.074	30.058	2.9690

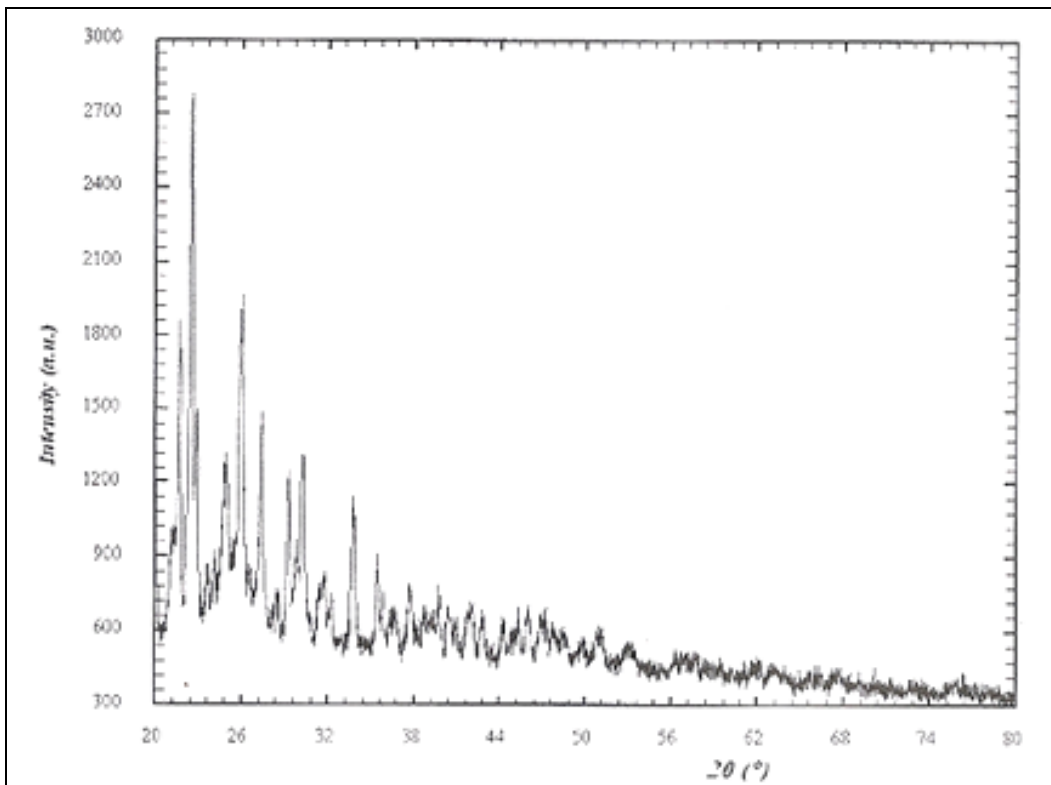


Fig 3: Milllar indices and interprener distances.

Table 6: Thermal decomposition and kinetic parameters

Complex	DTA peak °C	Temperature range °C	Mass loss (%) Observed (Calculated)	Nature of decomposition	Order of reactions n	Activation energy E _a kg/mole	Endropy change ΔS J/k/mole	Free energy of activation G KJ/mole	Frequency factor Z
CuL ₈ (CH ₃ COO) ₂	60	0-200	34.19(34.03)	Acetate+water	1.9	49.627	-179.406	61.206	4.777 X 10 ³
	200	200-410	22.23(22.04)	Acetyl	0.9	7.983	-273.263	29.204	7.211X 10 ⁻²
	550	410-600	35.91(36.22)	Acetone moiety 4-NOPDA moiety	0.5	31.985	-244.478	58.857	3.251

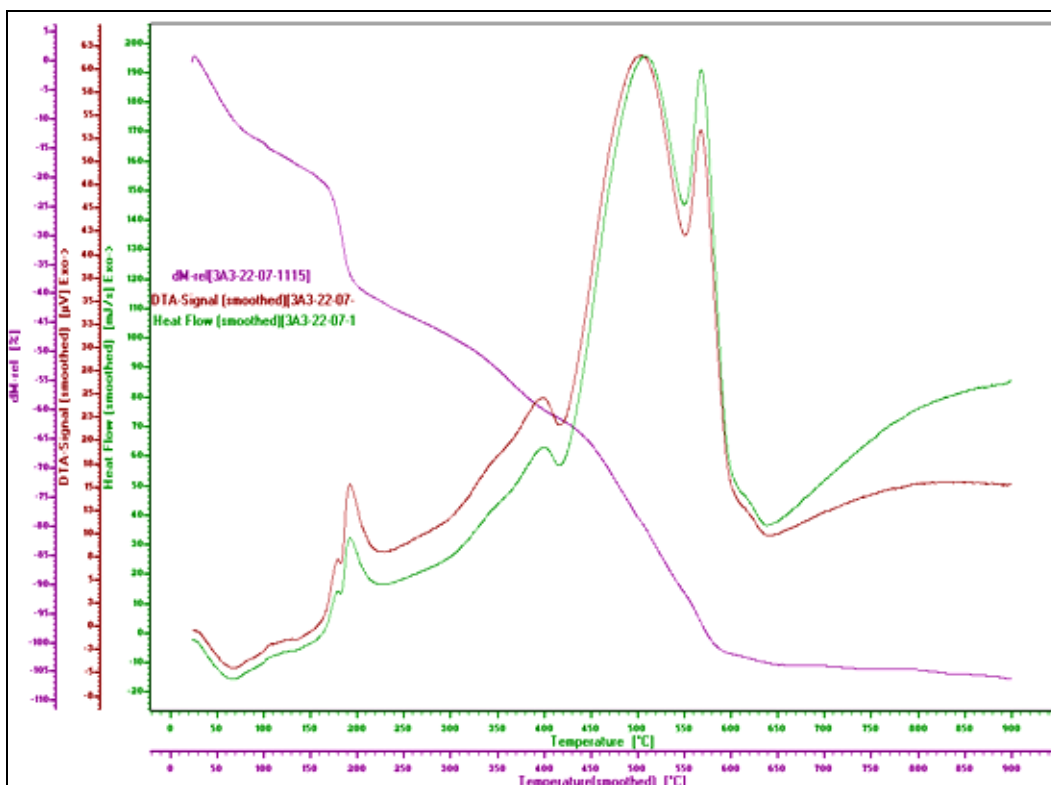


Fig 4: Thermal decomposition and kinetic parameters

Table 7: Antibacterial activity of complexes from Acetyl Acetone

Compound	S-typhi	S-aureous s	E-coli	B-subtilis
[CuL ₈ Cl ₂]	18	11	15	8
[Cu L ₈ (NO ₃) ₂]	20	9	19	9
[Cu L ₈ (CH ₃ COO) ₂]	18	10	14	8
[CO L ₈ Cl ₂]	17	8	9	12
[CO L ₈ (NO ₃) ₂]	15	11	11	10
[CO L ₈ (CH ₃ COO) ₂]	8	13	8	8
[Ni L ₈ Cl ₂]	12	15	14	13
[Ni L ₈ (NO ₃) ₂]	14	12	15	14
[Ni L ₈ (CH ₃ COO) ₂]	15	14	17	16
[Zn L ₈ Cl ₂]	25	14	18	14
[Zn L ₈ (NO ₃) ₂]	23	11	23	8
[Zn L ₈ (CH ₃ COO) ₂]	25	13	21	12
Cefodox	10	-	-	-
Linazoid	14	-	-	-

Conclusion

- Macrocyclic ligand complexes of transition metal ions are observed as tetradentate in nature.
- Macrocyclic ligand complexes decompose above an average 250°C suggesting good thermal stability.
- Macrocyclic ligand complexes are insoluble in organic solvents, freely soluble in DMSO/DMF. Molar conductivity of complexes in DMSO suggests non electrolytic nature.
- Magnetic moment suggest octahedral environment around metal ion.
- Infrared spectra suggest involvement of nitrogen in coordination.
- Solid state EPR spectral studies indicate anisotropic behavior, suggesting the line width is independent of temperature. Cu (II) complexes shows broad peaks indicating distortion and g value indicate sufficient covalent nature of metal ligand bond. Small G value of exchange interaction coupling constant suggest strong exchange interaction and local tetragonal axes are misaligned.
- Thermal analysis of complexes gives information regarding decomposition pattern of metal ligand ratio and also suggests presence of coordinated water molecules. Decomposition of complexes at higher temperature suggests thermal stability. Non isothermal kinetic parameter suggests decomposition process follow second order kinetics and activated complex has more ordered.
- Powder X-ray diffraction studies of complexes reveal monoclinic and orthorhombic system having lattice type P/2 and PMMM.

From above observations it is concluded that macrocyclic ligand complexes has undergone structural rearrangement to acquire stability and coordinated to metal through free donor atoms.

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