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Design, Synthesis And Characterization Of Macrocyclic Ligand And Study Of Its Complexes With Divalent Metal Salts

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Abstract: The present investigation describes the synthesis of a novel macrocyclic ligand obtained through the condensation of benzyl and oxalyldihydrazide in a methanolic medium under reflux conditions. The reaction yields a stable, crystalline macrocycle containing both nitrogen and oxygen donor centers capable of coordinating with transition metal ions. The ligand was subsequently allowed to react with divalent cobalt, nickel, and copper salts in the presence of chloride, nitrate, and acetate anions, resulting in a series of metal complexes of the general formula $[M(C_{32}H_{24}N_8O_4)X_2]$, where M = Co(II), Ni(II), Cu(II) and X = Cl^-, NO_3^-, or OAc^-.

Comprehensive analytical and physicochemical studies were carried out to confirm the composition and structural features of the synthesized ligand and its complexes. Elemental analysis and molecular weight determination verified the proposed stochiometry, while molar conductance measurements indicated their non-electrolytic or weakly electrolytic nature depending on the coordinating anion. The magnetic susceptibility data, together with electronic spectral transitions, provided valuable insight into the electronic environment of the metal ions and strongly suggested the formation of six-coordinate octahedral complexes.

Spectroscopic investigations—including infrared, far-infrared, UV–Visible, and proton NMR studies—revealed significant shifts in characteristic vibrational and electronic bands, confirming the coordination of metal ions through azomethine nitrogen and carbonyl oxygen atoms of the macrocyclic framework. Infrared spectra displayed lowering of C=N and C=O stretching frequencies upon complexation, supporting metal–ligand bond formation, while far-IR spectra provided additional evidence through metal–nitrogen and metal–oxygen vibrational bands. The UV–Vis spectra exhibited characteristic d–d transitions consistent with octahedral geometry for Co(II), Ni(II), and Cu(II) complexes.

Overall, the combined spectral, magnetic, and analytical data conclusively establish the formation of stable, six-coordinate octahedral complexes of the synthesized macrocyclic ligand with Co(II), Ni(II), and Cu(II) ions. The study highlights the strong chelating ability of the ligand, the influence of anions on coordination behavior, and the potential applications of such macrocyclic complexes in catalysis, bioinorganic modelling, and material science.

Keywords: Macrocyclic ligand, Template synthesis, Benzil, Oxalyldihydrazide, Co(II), Ni(II), Cu(II) complexes, Infrared spectroscopy, UV–Visible spectroscopy, NMR studies, Far-infrared spectra, Magnetic susceptibility, Molar conductance, Octahedral geometry

INTRODUCTION:

Macrocyclic ligands and their metal complexes constitute an important and rapidly expanding area of research in inorganic and bioinorganic chemistry.[1–3] Macrocycles possess preorganized, cyclic architectures capable of binding metal ions with exceptional selectivity and stability through the well-known macrocyclic effect, which enhances both thermodynamic and kinetic stability of their complexes compared to open-chain analogues.[4–6] This effect arises due to their rigid structure, entropic advantages, and the ability to encapsulate metal ions within a well-defined coordination cavity.[7–8] As a result, macrocyclic ligands have been extensively studied in relation to coordination chemistry, catalysis, molecular recognition, and biomedical systems.[9–11]

Nitrogen-containing macrocycles, including tetraaza and Schiff-base macrocyclic ligands, have attracted particular attention due to their strong donor ability toward transition metals and their relevance to biological systems.[12–14] These ligands mimic natural macrocycles such as heme, chlorophyll, porphyrins, and corrinoids, which are vital to enzymatic catalysis, oxygen transport, electron transfer, and vitamin B_{12}-dependent pathways.[15–18] The structural and functional resemblance between synthetic macrocyclic ligands and natural metalloproteins has inspired extensive efforts to design artificial metal-binding macrocycles with tailored cavity sizes, donor sets, and coordination geometries.[19–21]

In addition to their biological significance, macrocyclic complexes exhibit diverse physicochemical properties. Many macrocyclic metal complexes show strong electronic absorption in the UV-vis region, making them useful as dyes, pigments, and functional colorants for industrial and material applications.[22–24] Their capacity to stabilize unusual oxidation states and mediate electron transfer reactions also makes macrocycles important in redox catalysis, electrocatalysis, and photocatalysis.[25–28]

One particularly impactful area is the use of macrocyclic complexes in biomedical imaging, notably MRI contrast agents.[29–31] Macrocyclic gadolinium complexes (e.g., DOTA derivatives) display superior kinetic inertness and lower toxicity than acyclic analogues, making them safer for clinical applications. The role of macrocycles in PET imaging, drug delivery, and radiopharmaceuticals is expanding rapidly.[32–33] Furthermore, lanthanide macrocyclic complexes are widely employed as NMR shift reagents due to their paramagnetic anisotropy and ability to induce predictable chemical shifts.[34–36]

Macrocyclic complexes of Co(II), Ni(II), and Cu(II) have been intensely studied because of their wide range of structural possibilities and their importance in catalysis, magnetism, redox chemistry, and biological modeling.[37–39] Cobalt macrocycles have proven important in oxidation catalysis, molecular activation, and modeling of B_{12} cofactors,[40–42] while nickel macrocyclic complexes are relevant in hydrogenase mimics, urease models, and Ni-dependent metalloenzymes.[43–45] Copper macrocyclic complexes are extensively studied due to their participation in oxygen activation, superoxide dismutation, electron transfer, and oxidative catalysis.[46–48]

The synthesis of new macrocyclic ligands typically involves template condensation reactions, often aided by transition-metal ions that direct cyclization and promote the formation of stable macrocyclic frameworks.[49–51] Template synthesis is particularly valuable for generating tetraaza macrocycles, Schiff-base macrocyclic rings, and heterocyclic macrocyclic ligands.[52–53] These synthetic approaches allow fine-tuning of ligand properties, donor atoms, ring size, rigidity, and steric environment.

Characterization of macrocyclic complexes requires a combination of spectroscopic and analytical methods. Infrared spectroscopy provides insights into azomethine (C=N) coordination, ligand-metal bonding, and functional group behavior.[54] NMR spectroscopy is valuable for structural elucidation, though paramagnetic complexes require specialized interpretation.[55] UV-visible spectra reveal d–d transitions, charge-transfer bands, and geometry-dependent electronic features.[56] Magnetic susceptibility measurements help determine spin state and coordination geometry around metal ions.[57] Elemental analysis and conductance studies further support the stoichiometry and electrolytic nature of complexes.[58–59]

Given the broad applications and scientific importance of macrocyclic complexes, the present study focuses on the synthesis of a nitrogen-containing macrocyclic ligand and its Co(II), Ni(II), and Cu(II) complexes. The work includes comprehensive characterization using IR, NMR, magnetic susceptibility, elemental analysis, conductance, and electronic spectral studies, contributing valuable data on the coordination behavior, geometry, and physicochemical properties of these macrocyclic systems.

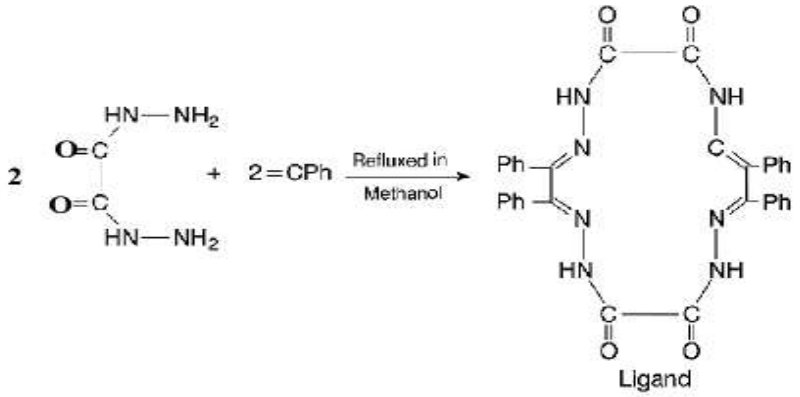
EXPERIMENTAL

Materials and Methods:

Oxalyldihydrazide and benzil were purchased from S.D. Fine Chem. Ltd. and CDH, Mumbai, respectively. All solvents were used without further purification.

Synthesis of the Ligand and Its Metal Complexes:

A hot, well-stirred methanolic solution of oxalyldihydrazide (10 mmol) was treated with benzil (10 mmol). The reaction mixture was refluxed for 4–5 hours. After completion of reflux, the solution was allowed to cool overnight, resulting in the formation of a light-yellow crystalline precipitate. The solid product was filtered, washed successively with methanol and acetone, and finally dried using diethyl ether. The yield obtained was approximately 60%. The synthetic route for the ligand is illustrated in Scheme 1.



The separated macrocyclic ligand (10 mmol) was dissolved in ~40 mL of methanol. A well-stirred hot methanolic solution of metal salts (5 mmol) was added followed by refluxing of resultant solution for about 6–8 hours. The different coloured precipitates were formed by adding different divalent metal salts. After refluxing, the precipitate was kept for overnight for cooling. The precipitate was filtered and then washed with methanol, acetone and diethyl ether. Yield ~30%. The complexes show decomposition in the range of 250–300°C. The scheme of synthesis of complexes may be shown as below:

$C_{32}H_{24}N_8O_4 + MX_2 \rightarrow [M(C_{32}H_{24}N_8O_4)X_2]$

Ligand Complexes

Analytical and Physical Measurements

Microanalyses of C, H, and N were performed at the Sophisticated Analytical Instrument Facility (SAIF), CDRI, Lucknow. Metal contents were determined using standard EDTA titration methods. Electronic spectra (in DME) were recorded on a Cary 14 spectrophotometer. Magnetic susceptibility measurements were carried out at IIT Roorkee. IR spectra were recorded on an infrared spectrophotometer in the range 4000–667 cm^{-1} using KBr pellets.

NMR spectra were obtained on a Bruker 300 MHz NMR spectrometer. Molar conductivity measurements were carried out using a digital conductivity meter (HPG System, G-3001).

Table 1. Analytical data of divalent cobalt, nickel and copper complexes; found (calcd.) %

Sr. No.	Complexes	M	C	H	N	Colour	Mol.wt.
1.	$[Co(ODZ)Cl_2]$	8.82 (8.87)	53.31 (53.93)	3.33 (3.36)	15.57 (15.68)	Light Orange	714
2.	[Co(ODZ)(NO3)2]	7.56 (7.49)	49.89 (50.29)	3.59 (3.38)	14.49 (14.72)	Light Orange	767
3.	[Co(ODZ)(OAc)2]	7.91 (7.96)	52.19 (52.63)	3.27 (3.42)	14.94 (15.01)	Brown	761
4.	[Ni(ODZ)Cl2]	8.19 (8.25)	53.25 (53.56)	3.17 (3.36)	15.42 (15.68)	Light Pink	713
5.	[Ni(ODZ)(NO3)2]	7.45 (7.57)	50.11 (50.13)	3.11 (3.13)	18.18 (18.27)	Light Grey	766
6.	[Ni(ODZ)(OAc)2]	7.34 (7.63)	56.70 (56.84)	3.87 (3.94)	14.67 (14.73)	Brown	760
7.	[Cu(ODZ)Cl2]	8.61 (8.77)	53.78 (53.48)	3.30 (3.34)	15.50 (15.59)	Yellow	718
8.	[Cu(ODZ)(NO3)2]	7.96 (8.17)	53.67 (53.40)	3.22 (3.38)	14.73 (14.94)	Brown	771
9.	[Cu(ODZ)(OAc)2]	8.18 (8.23)	56.23 (56.47)	3.35 (3.92)	14.38 (14.64)	Dark Green	765

Where ODZ is oxalyl dihydrazone (Ligand)

IR Spectra

The presence of a single sharp band in the region ~3285–3309 cm⁻¹ in all complexes indicates that the amino groups of oxalyldihydrazide have condensed with the carbonyl groups of the benzil molecule[51-52]. The bands observed at ~3179–3183 cm⁻¹ are attributed to ν(C–H) vibrations of the benzil moiety. The absorption bands appearing in the region ~1531–1590 cm⁻¹ correspond to ν(C=N) stretching vibrations, and their comparatively lower frequencies suggest coordination through the azomethine nitrogen[53-54].

A band in the region 1685–1699 cm⁻¹ may be assigned to the C=O stretching of the CONH moiety[55], indicating that the carbonyl oxygen is not coordinated to the metal. Additional bands occurring in the ~1350–1000 cm⁻¹ range are attributed to C–N vibrations. These spectral features collectively support the formation of a quadridentate macrocycle, coordinating through all azomethine nitrogen atoms in the presence of metal salts.

Far-IR Spectra

The far-IR spectra exhibit bands in the region ~425–460 cm⁻¹, corresponding to ν(M–N) vibrations[56]. The consistent presence of these bands in all complexes indicates coordination through azomethine nitrogen atoms[57]. Bands observed at 300–320 cm⁻¹ are assigned to ν(M–Cl) vibrations, confirming the coordination of chloride in the respective complexes[58].

NMR Spectra

The ¹H NMR spectrum displays a broad signal at 9.95 ppm, corresponding to the amide hydrogen[59], confirming the presence of the NH group in the complexes. Multiplet signals in the region 7.30–7.94 ppm are assigned to the aromatic protons of the benzil moiety[60-61].

Magnetic measurements and electronic spectra Cobalt complexes

The magnetic moment was measured at room temperature and lie in the range 4.92–5.03 B.M. which corresponds to three unpaired electrons. The solution spectra of cobalt (II) complexes exhibit absorption in the region ~8710–9120 cm^{-1} (ν_1), 13500–15720 cm^{-1} (ν_2) and 18670–20210 cm^{-1} (ν_3), respectively. The spectra resemble to those reported as octahedral[62]. The spectra of complexes show a band in the visible region, which show a structure and is split due to the presence of low symmetry fields. Thus, assuming the effective symmetry to be D_4h, the various bands can be assigned to $^4T_1g \rightarrow {}^4T_2g$ (F), (ν_1), $^4T_1g \rightarrow {}^4A_2g$ (F), (ν_2) and $^4T_1g \rightarrow {}^4T_1g$ (P), (ν_3), respectively. It appears that the symmetry of these complexes is not idealized O_h, but is D_4h. The assignment of the first spin–allowed band seems plausible since the first band appears approximately at half the energy of the visible band[63].

Nickel complexes

The magnetic moment of nickel complexes at room temperature lie in the range 2.90–2.97 B.M. These values correspond to high spin configuration and show the octahedral environment around the Ni (II) ion in all complexes. The solution spectra of Ni (II) complexes exhibit a well discernable band which at higher order of the energy. The other two bands generally observed in the region at ~16,420–17,020 cm^{-1} (ν_2), and 27,950–28,275 cm^{-1} (ν_3), are assigned to $^3A_2g \rightarrow {}^3T_1g$(F) ($\nu_2$), and $^3A_2g \rightarrow {}^3T_1g$ (P) (ν_3), respectively. The first two bands result from the splitting of one band, ν1 and are in the range at ~9640–10,230 and 11,710–12,240 cm^{-1}, which can be assigned to $^3B_1g \rightarrow {}^3E$ g and $^3B_1g \rightarrow {}^3B_2g$, assuming the effective symmetry to be D_4h (component of ^3T_2g in O_h symmetry)[21]. The intense higher energy band at ~34,450 cm^{-1} may be due to a π–π* transition of the (C=N) group. Various bands do not follow any regular pattern and seem to be anion independent. The spectra are consistent with distorted octahedral nature of these complexes.

Copper Complexes

The magnetic moments of the copper complexes lie in the range **1.87–2.02 B.M.**, corresponding to one unpaired electron. The electronic absorption spectra of these complexes display bands in the region **~17,680–19,640 cm^{-1}**, along with a shoulder on the lower-energy side at **~14,520–16,020 cm^{-1}**. These spectral features indicate that the complexes possess a d-orbital energy level pattern typical of a distorted octahedral geometry[62-63].

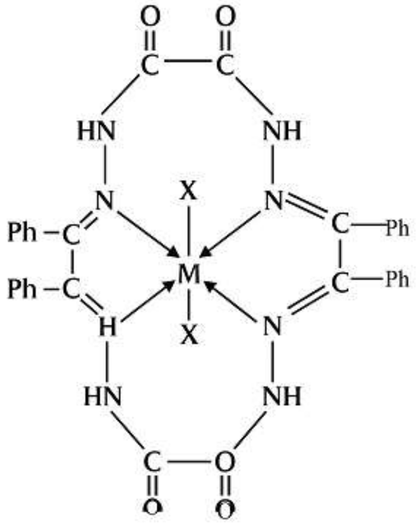
Assuming tetragonal distortion, the expected electronic configuration sequence is:

$x^2–y^2 > z^2 > xy > xz > yz$.

The shoulder observed in the spectra can be assigned to the **$z^2 \rightarrow x^2–y^2$ ($2B_{1g} \rightarrow 2B_{2g}$)** transition, while the broad band encompasses the **$xy \rightarrow x^2–y^2$ ($^2B_{1g} \rightarrow {}^2Eg$)** and **$xz, yz \rightarrow x^2–y^2$ ($^2B_{1g} \rightarrow {}^2A_{2g}$)** transitions.[22] The band separation, approximately **2500 cm^{-1}**, further supports the proposed distorted octahedral geometry[64].

Thus, it may be concluded that all copper(II) complexes formed with these macrocycles exhibit **distorted octahedral coordination**.

Based on elemental analyses, conductivity measurements, magnetic studies, electronic spectra, NMR, and IR spectral data, the following structure is proposed for the complexes:



Where,

M = Co(II), Ni(II), Cu(II) and

X = Cl^{-1}, NO_3^-, CH_3COO^-

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