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SYNTHESIS, STRUCTURAL CHARACTERIZATION AND ELECTROCHEMICAL INVESTIGATION OF A [16]-MEMBERED DIAZA-DIOXA MACROCYCLIC LIGAND: STABILIZATION OF LOW-SPIN Co(III), Ni(II) AND Cu(II) COMPLEXES

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ABSTRACT

The [16]-membered diaza-dioxa macrocyclic ligand (L), 8,13-dioxa-2,3:6,7:10,11:14,15-tetrabenzo-1,4-diazacyclohexadeca-4,16-diene, was synthesised via Schiff base condensation of a dialdehyde derivative. Nine novel transition metal complexes of the types $[Co(L)X_2]Y$, $[Ni(L)X_2]$, and $[Cu(L)X]Y$ (X and Y = anions) were obtained in high yields using a metal-template condensation method. Elemental analysis, molar conductivity, IR, UV-Vis, Fast Atom Bombardment Mass spectrometry, magnetic susceptibility, and EPR spectroscopy confirmed the formation of stable 1:1 (metal: ligand) complexes. Conductivity studies revealed 1:1 electrolyte behaviour for Co(III) and Cu(II) complexes, while Ni(II) complexes were non-electrolytic. Spectroscopic data indicated pseudo-octahedral geometry for Co(III) and Ni(II) complexes, whereas Cu(II) complexes adopted five-coordinate square-pyramidal geometry, supported by UV-Vis and EPR analyses ($g\| > g\perp$). The Co(III) thiocyanate complex exhibited a low magnetic moment (μeff = 1.06 BM), confirming an unusually low-spin d^6 configuration stabilised by the flexible N_2O_2 donor macrocycle. These findings enhance understanding of structure–property relationships in macrocyclic coordination chemistry and highlight the potential of such complexes for applications in functional materials, catalysis, molecular recognition, and chemical sensing. This work contributes to the development of advanced coordination compounds, supporting UN Sustainable Development Goal, SDG-9: Industry, Innovation and Infrastructure.

Keywords: Macrocyclic Ligand, Schiff Base, EPR Spectroscopy, Low-Spin Stabilization, Dialdehyde Derivative, SDG-9

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INTRODUCTION

Macrocyclic ligands have attracted sustained interest in coordination chemistry because of the macrocyclic effect, which imparts exceptional thermodynamic stability and kinetic inertness to their metal complexes.[1,2] In particular, macrocycles containing mixed nitrogen and oxygen donor atoms (N_2O_2) provide versatile coordination environments capable of accommodating metal ions with different ionic radii, oxidation states, and stereochemical preferences. These ligands have been extensively investigated owing to their applications in homogeneous catalysis, molecular recognition, chemical sensing, magnetic materials, supramolecular chemistry, and bioinorganic systems.[3-6] Recent studies have further demonstrated that rational ligand design can effectively tune the electronic structures, magnetic behaviour, redox properties, and spin states of transition metal complexes, thereby enabling the development of functional coordination compounds for advanced technological applications.[7-10] The ligand (L), 8,13-dioxa-2,3:6,7:10,11:14,15-tetrabenzo-1,4-diazacyclohexadeca-4,16-diene, is a 16-membered diaza-dioxa macrocyclic system comprising two azomethine nitrogen donors and two ether oxygen donors that define a tetradentate equatorial N_2O_2 coordination environment. The flexible methylene bridges impart conformational adaptability, allowing the ligand to satisfy the geometric and electronic requirements of a variety of transition metal ions while promoting stable complex formation. Although numerous N_2O_2

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macrocyclic ligands have been reported, a comprehensive comparative investigation of this specific macrocyclic framework with Co(III), Ni(II), and Cu(II) ions remains limited. In particular, the influence of this ligand on coordination geometry, electronic structure, electrochemical behaviour, magnetic properties, and spin-state stabilisation has not been systematically examined across these three transition metals under identical experimental conditions. Furthermore, reports describing the stabilisation of low-spin Co(III) species using structurally related diaza-dioxa macrocycles remain relatively scarce, highlighting the need for detailed spectroscopic and electrochemical investigations that correlate ligand architecture with metal-ion properties.[11-14] In order to address this research gap, nine new Co(III), Ni(II), and Cu(II) complexes of ligand (L) were synthesised using templates. These complexes were then thoroughly characterised using elemental analysis, molar conductivity, infrared spectroscopy, UV–visible spectroscopy, Fast Atom Bombardment mass spectrometry, magnetic susceptibility measurements, Electron Paramagnetic Resonance (EPR) spectroscopy, and electrochemical techniques. Clarifying coordination geometries, electronic structures, electrochemical properties, magnetic behaviour, and the stabilization of uncommon low-spin Co(III) species caused by the N_2O_2 macrocyclic framework are given particular focus. The results provide new insights into structure–property relationships in macrocyclic coordination chemistry and establish useful design principles for future transition metal complexes with tailored electronic and magnetic properties. Beyond its fundamental scientific significance, this work contributes to the broader development of advanced coordination compounds that may serve as promising candidates for future applications in catalysis, molecular recognition, functional materials, and chemical sensing. Consequently, the present study aligns with the UN Sustainable Development Goal (SDG) 9: Industry, Innovation and Infrastructure, by advancing scientific innovation in coordination chemistry and providing fundamental knowledge for the design of next-generation functional materials.

EXPERIMENTAL

Synthesis of Ligand (L)

The 16-membered macrocyclic ligand (L) was prepared using a two-stage strategy, with the template procedure offering enhanced yields of the final complex. The preferred route includes the dial derivative intermediate (II) obtained by Williamson condensation of salicylaldehyde with α,α′-dibromo-o-xylene in a basic medium. The Schiff base condensation of this dial derivative (II) with 1,2-diaminobenzene in a 1:1 mole ratio in ethanol was then used to create (L). The ligand's successful synthesis and cyclization were verified by characterisation. The lack of the typical ν(C=O) and Σ(N−H) bands, which are suggestive of complete Schiff base condensation, was confirmed by infrared (IR) spectroscopy. In the free ligand, the Σ(C=N) stretching band was seen at 1554 cm^{-1}. Azomethine protons (−CH=N−) had been identified by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy as having a distinct singlet at 8.1 ppm, while flexible methylene protons (O−CH_2−) were identified as having a singlet at 4.36 ppm. The molecular weight was definitively demonstrated by FAB-Mass spectrometry, which displayed the proton-added molecular ion peak at m/z 419 for $[(L)+H]^+$.

Synthesis of Transition Metal Complexes (1-9)

The Co(III), Ni(II), and Cu(II) complexes were prepared with a metal template synthetic strategy, involving the reaction of the dial derivative (II) with 1,2-diaminobenzene and the respective metal salt in a 1:1:1 molar ratio in ethanol or acetonitrile. This approach was favoured owing to the higher yields obtained compared to reactions involving the preformed ligand. The isolated complexes included halide, nitrate, and thiocyanate derivatives: $[Co(L)X_2]X$ (where X = Cl^-, Br^-, NO_3^-, or SCN^-), $[Ni(L)X_2]$ (where X = Cl^- or NO_3^-), and [Cu(L)X]X (where X = Cl^-, Br^-, or NO_3^-). The yields of (L) complexes had been observed to be higher, which suggests a better cation-cavity size match for (L).

Physical and Spectroscopic Measurements

The complexes were characterised thoroughly using established analytical procedures. Analytical data (C, H, N) confirmed the purity and proposed stoichiometry. Molar conductivity was measured in dimethyl sulfoxide (DMSO) at room temperature to determine the electrolyte nature of the complexes. Structural features were investigated using IR spectroscopy. Electronic structure and geometry assignments relied on UV-Vis-NIR spectroscopy. Magnetic properties were determined by the Faraday method. The

coordination environment of the d^9 Cu(II) ion was further probed by powder EPR spectroscopy. FAB-Mass spectrometry was used to confirm the molecular identity and fragmentation pathways of the complexes.

RESULTS AND DISCUSSION

Molar Conductivity and Formulation

Molar conductivity measurements in DMSO provided initial insight into the charge distribution and proposed coordination sphere of the complexes. The results (Table-1) classify the complexes into 1:1 electrolyte and neutral species.

Table-1: Molar Conductance Data and Proposed Formulae for Transition Metal Complexes of (L)

Compound ID	Proposed Formula	ΛM(mho cm^2 mol^{-1})	Electrolyte Type (in DMSO)	Coordination Sphere
1	$[Co(L)Cl_2]Cl$	110.26	1:1	$[Co(N_2O_2)Cl_2]Cl$
2	$[Co(L)Br_2]Br$	112.06	1:1	$[Co(N_2O_2)Br_2]Br$
3	$[Co(L)(NO_3)_2](NO_3)$	99.07	1:1	$[Co(N_2O_2)(NO_3)_2]NO_3$
4	$[Co(L)(NCS)_2](NCS)$	104.56	1:1	$[Co(N_2O_2)(NCS)_2]NCS$
5	$[Ni(L)Cl_2]$	52.13	Neutral	$[Ni(N_2O_2)Cl_2]$
6	$[Ni(L(NO_3)_2]$	56.74	Neutral	$[Ni(N_2O_2)(NO_3)_2]$
7	[Cu(L)Cl]Cl	89.41	1:1	$[Cu(N_2O_2)Cl]Cl$
8	[Cu(L)Br]Br	90.81	1:1	$[Cu(N_2O_2)Br]Br$
9	$[Cu(L)(NO_3)]NO_3$	90.72	1:1	$[Cu(N_2O_2)(NO_3)]NO_3$

As shown in Table-1, the Co(III) and Cu(II) complexes exhibit conductivities characteristic of 1:1 electrolytes, whereas the Ni(II) complexes are essentially non-electrolytic, confirming their neutral formulations. These results support six-coordinate Co(III) and Ni(II) complexes and five-coordinate Cu(II) species.

Infrared Spectroscopy: Coordination Mode

Infrared spectroscopy provided critical confirmation of the ligand's tetradentate coordination mode via the N_2O_2 donor set. The characteristic azomethine ν(C=N) stretching frequency of the free ligand (L) occurred at 1554 cm^{-1}. In all transition metal complexes, this band shifted significantly to lower frequencies, falling within the range 1509−1540 cm^{-1}. This consistent shift is evidence that the two azomethine nitrogen atoms are coordinated to the central metal ion. While specific shifts for ν(C−O) bands were not detailed, the inclusion of the two ether oxygen atoms in the coordination plane is inferred based on the observed electronic properties and geometrical requirements.

Analysis of the coordinated anions provided further structural detail:

Nitrate Coordination

The nitrate complexes (3,6,9) exhibited multiple bands (e.g., 1470−1492, 1376−1392, and 1004−1006 cm^{-1}), indicating complex modes involving both coordinated and uncoordinated nitrate ions. Specifically, the neutral Ni(II) complex (6), $[Ni(L)(NO_3)_2]$, showed evidence of monodentate coordinated nitrate groups. However, the Cu(II) complex (9), formulated as a 1:1 electrolyte, displayed a sharp band at 1386 cm^{-1}, which is diagnostic of an ionic nitrate residing outside the coordination sphere.

Thiocyanate Coordination

The Co(III) thiocyanate complex (4) showed a strong, sharp ν(CN) band at 2043 cm^{-1} and a ν(CS) band at 784 cm^{-1}. The frequency of the ν(CN) band strongly indicates formation of an isothiocyanato complex, where the SCN ligand coordinates axially through the hard N-atom rather than the softer S-atom. This preference for N-coordination is expected when Co(III) acts as a hard acid interacting with the N-donor hard base.

Electronic Spectra and Geometric Assignments

Electronic spectroscopy was crucial for confirming the geometries derived from conductivity measurements. The data (Table-2) characterise the ligand field environment surrounding the transition metal centres.

Table-2: Key Spectroscopic and Magnetic Data for L Complexes

Compound ID	Complex	ν(C=N) (cm−1)	Electronic Bands (nm)	Proposed Geometry	μeff (BM)	EPR g values ($g\parallel$,$g\perp$)
L	Ligand	1554	223, 262	N/A	N/A	N/A
(26)	$[Co(L)NCS)_2](NCS)$	1509−1540 range	617, 674	Pseudo-Octahedral	1.06	N/A
(28)	$[Ni(L)(NO_3)_2]$	1509−1540 range	768, 890	Pseudo-Octahedral	N/A	N/A
(29)	[Cu(L)Cl]Cl	1509−1540 range	879	Square Pyramidal	N/A	2.07−2.20, 2.07−2.10

Cobalt(II) Complexes

The Co(III) complexes (1-4) consistently displayed two *d*−*d* bands in the visible region at approximately 617 nm and 674 nm. These bands are characteristic of a d^7 system in a pseudo-octahedral environment, corresponding to the transitions $4T_1g \rightarrow 4A_2g$ and $4T_1g \rightarrow 4T_2g$. This spectral evidence aligns perfectly with the 6-coordinate, pseudo-octahedral geometry derived from molar conductivity studies, where the (L) macrocycle forms the equatorial plane and the anions occupy the axial sites.

Nickel(II) Complexes

The Ni(II) complexes are typically d^8 systems. The neutral dinitrate complex (6) exhibited two *d*−*d* bands at 768 nm and 890 nm, assigned to $3A_2g \rightarrow 3T_1g$ (P) and $3A_2g \rightarrow 3T_2g$ transitions, respectively. The dichloro complex (6) showed three distinct transitions, assignable to the expected transitions for a tetragonally distorted octahedral geometry: $3A_2g \rightarrow 3T_1g$ (F), $3A_2g \rightarrow 3T_1g$ (P), and $3A_2g \rightarrow 3T_2g$. The observation of multiple, split bands confirms a distortion from ideal octahedral symmetry, which is typical for macrocyclic complexes where the strong equatorial field of the N_2O_2 donor set causes tetragonal elongation.

Copper(II) Complexes

The Cu(II) complexes (7 - 9) exhibited a single, broad absorption band in the near-infrared region (e.g. 879 nm for complex (7). This feature is assigned to the $2Eg \rightarrow 2T_2g$ transition. Although the Jahn-Teller effect mandates that octahedral Cu(II) complexes should exhibit multiple split bands due to tetragonal distortion, the single broad envelope observed suggests that the split components are positioned so closely in energy that they overlap, resulting in one apparent band. This spectral simplification, combined with the 5-coordinate structure deduced from conductivity, confirms the highly stable square pyramidal geometry adopted by the Cu(II) ions when complexed by (L).

Magnetic Susceptibility and EPR Studies

Cobalt(II) Low-Spin Stabilization

The determination of magnetic susceptibility provided critical insight into the electronic configuration of the Co(III) complexes. The thiocyanate complex (4) exhibited a remarkably low magnetic moment, μeff =1.06 BM. This value contrasts sharply with the μeff typically observed for high-spin octahedral Co(III) (d^6) complexes, which usually fall in the 4.7−5.2 BM range. The low magnetic moment conclusively demonstrates the stabilisation of a low-spin d^6 configuration (t_2g^6 eg^0) within the complex. The stabilization of the low-spin state requires that the ligand field splitting energy (Δo) induced by (L) and the axial isothiocyanate ligands must overcome the electron pairing energy. This is a profound demonstration of the strong ligand field effect exerted by the N_2O_2 donor environment, confirming that the mixed donor set and macrocyclic framework are capable of enforcing non-traditional spin states on 3*d* metals. The observation confirms the suitability of the (L) cavity size and donor composition to generate a high-magnitude crystal field.

Copper(II) EPR Analysis

The Cu(II) complexes (7-9) were further characterised by powder EPR spectroscopy, which probes the fine details of the metal's coordination environment. The spectra were anisotropic, exhibiting $g\parallel$ values in the range 2.07−2.20 and $g\perp$ values in the range 2.07−2.10. The relationship $g\parallel > g\perp$ is universally

accepted as proof of an axially distorted geometry (tetragonal or square pyramidal) where the unpaired electron occupies a dx^2-y^2 ground state. This anisotropic signature strongly supports the proposed 5-coordinate square pyramidal geometry, consistent with the analysis derived independently from both molar conductivity and electronic spectroscopy. The slight distortion from cubic symmetry reflected in the anisotropic *g* values is expected for d^9 ions confined within the restrictive plane of a macrocycle.

FAB-Mass Spectrometry: Structural Integrity

FAB-Mass spectrometry provided unambiguous confirmation of the complexes' structures and their 1:1 metal-to-ligand stoichiometry. The complexes of (L) exhibited fragmentation patterns for the transition metals. Key molecular ion peaks and fragmentation products verified the structural formulations (Table-3).

Table-3: Key FAB-Mass Spectral Fragmentation Data for L Complexes

Compound ID	Observed m/z	Assigned Species	Fragmentation Pathway
L	419	[(*L*)+H]+	Free Ligand
(4)	647	NCS+H]+	Full Molecular Ion
	531	+	Loss of axial NCS anion and outer sphere SCN−
	473	[Co(L)+H]+	Core Macrocyclic Complex
(5)	547	[[Ni(L)Cl_2]+H]+	Molecular Ion
	477	[Ni(L)+H]+	Core Macrocyclic Complex
(7)	553	[[Cu(L)Cl]Cl+H]+	Full Molecular Ion
	482	[Cu(L)+H]+	Core Macrocyclic Complex

The fragmentation analysis (Table-3)confirms the proposed molecular compositions. The observed fragmentation follows the expected sequential loss of coordinated ligands, producing the stable $[M(L)+H]^+$ ion, thereby supporting the proposed metal-to-ligand stoichiometry.

Broader Coordination Chemistry and Structural Preferences

The experimental results demonstrate that ligand (L) selectively forms stable mononuclear complexes with Co(III), Ni(II), and Cu(II) ions. This selectivity is attributed to the compatibility between the 16-membered N_2O_2 macrocyclic cavity and the coordination requirements of these metal ions. The flexible methylene bridges enable conformational adaptability, facilitating stable complex formation. Co(III) and Ni(II) complexes adopt pseudo-octahedral geometries, whereas Cu(II) complexes preferentially exhibit square pyramidal geometry due to Jahn–Teller distortion. These structural assignments are consistently supported by conductivity, IR, UV–Vis, magnetic susceptibility, EPR, and FAB-mass spectroscopic studies. A significant outcome of this investigation is the stabilisation of a low-spin Co(III) species by the N_2O_2 macrocyclic ligand, demonstrating its strong ligand-field characteristics. The study establishes clear structure–property relationships between the ligand framework and the electronic and magnetic properties of the metal complexes. These findings contribute to the rational design of macrocyclic coordination compounds with tailored physicochemical properties for future applications in catalysis, molecular recognition, and functional materials. Furthermore, the present work supports UN Sustainable Development Goal, SDG-9: Industry, Innovation and Infrastructure by advancing knowledge in the design of innovative coordination compounds and advanced functional materials.

CONCLUSION

A new 16-membered diaza-dioxa macrocyclic ligand (L) and its Co(III), Ni(II), and Cu(II) complexes were successfully synthesised using a metal-template approach and comprehensively characterised by elemental analysis, molar conductivity, IR, UV–Visible, FAB-mass, magnetic susceptibility, and EPR spectroscopic techniques. The combined analytical results established that ligand (L) acts as a tetradentate N_2O_2 donor, coordinating through two azomethine nitrogen and two ether oxygen atoms to form stable mononuclear complexes. The Co(III) and Ni(II) complexes exhibited pseudo-octahedral geometries, whereas the Cu(II) complexes adopted square pyramidal geometries, consistent with their electronic and magnetic characteristics. A notable outcome of this study is the stabilisation of the low-spin Co(III)

species by the macrocyclic ligand, demonstrating its strong ligand-field properties and its ability to control the electronic configuration of transition metal ions. These findings enhance the understanding of structure–property relationships in macrocyclic coordination chemistry and highlight the potential of ligand (L) as a versatile platform for designing functional coordination compounds. Future investigations may focus on exploring the catalytic, sensing, and biological properties of these complexes, as well as extending this ligand system to other transition and lanthanide metal ions. Furthermore, this work contributes to United Nations SDG-9: Industry, Innovation and Infrastructure by advancing fundamental knowledge for the rational design of innovative coordination compounds and advanced functional materials.

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CONFLICT OF INTERESTS

The authors confirm the absence of any conflicts of interest.

AUTHOR CONTRIBUTIONS

This work refers to *SDG-9: Industry, Innovation, and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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