RESEARCH PAPER

Physico-Chemical Study of Mixed Ligand Metal Complexes and their Biological Activity and Corrosion Studies

V. Palani[1], P. Shakila[1] and M. Santhana Raj Prabhu[1]

*[1]Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore - 632002, Tamil Nadu, India, Affiliated to Thiruvalluvar University. Corresponding Author: msrgcr@gmail.com.

ABSTRACT

The study presents the synthesis through characterization of three mixed ligand complexes, $[Cu(L)(Phen)]NO_3$, $[Zn(L)(phen)Cl_2]$ and $[Cu(L)(NCS)_2]$, where L is a Schiff base formulated from 3-nitrobenzaldehyde and 1,3-diaminopropan-2-ol. The complexes were characterized by Infrared (IR), Ultraviolet-Visible (UV-Vis), Electron paramagnetic resonance (EPR) spectroscopy and Mass spectrometry. The compounds were evaluated for antimicrobial activity, showing notable inhibition against *E. coli, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus subtilis, Candida albicans,* and *Candida tropicalis*. Anti-corrosion studies demonstrated that $[Cu(L)(NCS)_2]$ exhibits good corrosion inhibition efficiency than $[Cu(L)(Phen)]NO_3$ and $[Zn(L)(phen)Cl_2]$ due to effective surface adsorption and protective film formation. The integration of spectroscopic, electronic, biological, and corrosion investigations highlights the multifunctional nature of these complexes and provides insight into the design of metal based agents with enhanced antimicrobial and corrosion protective properties.

Keywords: Mixed ligand, Schiff base, Antimicrobial, Corrosion Inhibition

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INTRODUCTION

Schiff base metal complexes have evolved as a remarkable class of compounds with assorted applications in various fields, including medicine, catalysis, and materials science.[1] Parveez Gull *et al* showed the antimicrobial activity of the copper and zinc complexes was evaluated against various bacterial and fungal strains, revealing their potential as effective antimicrobial agents against the tested pathogens.[2] The introduction of co-ligands to these metal complexes can significantly alter their properties, leading to intensified biological activity and corrosion inhibition efficiency.[3,4] Copper and zinc are essential elements in biological systems, playing crucial roles in various enzymes and proteins.[5] Cu(II) and Zn(II) complexes with Schiff base ligands have been reported to exhibit antimicrobial, antifungal, and anticancer activities.[6] The co-ligand can impact the complex's stability, solubility, and lipophilicity, thereby affecting its biological activity.[7] Corrosion is a major concern in various industries, leading to significant economic losses and environmental damage.[8] Schiff base metal complexes have been investigated as corrosion inhibitors for metals like mild steel, copper, and aluminum. The presence of heteroatoms like nitrogen, oxygen, and sulfur in the Schiff base ligand can facilitate adsorption onto metal surfaces, reducing corrosion. Fungal and bacterial infections pose significant threats to human health, and the emergence of antibiotic-resistant strains has created an urgent need for new antimicrobial agents.[9,10] This study focuses on the synthesis, characterization, and biological evaluation of Cu(II) and Zn(II) complexes. The complexes are assessed for their corrosion inhibition efficiency on mild steel in acidic media. The results highlight the potential of these complexes as multifunctional agents, with applications in corrosion protection and biomedical fields. The complex structures are elucidated using spectroscopic techniques, and their properties are correlated with their biological activities. This study aims to contribute to the development of new materials with potential applications in medicine and in agriculture industry.

RESULT AND DISCUSSION

Methods and Materials

Three new complexes were synthesized using ethanol as a solvent. The starting materials $Cu(NO_3)_2.3H_2O$, anhydrous $ZnCl_2$, 1,3-diaminopropan-2-ol, 1,10-phenanthroline, ammonium thiocyanate, 3-nitrobenzaldehyde, CH_3CN, CH_3OH, DMF, DMSO and diethylether were purchased in good assay. The synthesized complexes were characterized by various spectroscopic analysis. FT-IR recorded on Shimadzu FT-IR (KBr pellet form) (4000-400 cm^{-1}). UV recorded on Specord 210 plus spectrometer. EPR was recorded using a JEOL JES-X320 X-band spectrometer. The scheme of this work is given below.

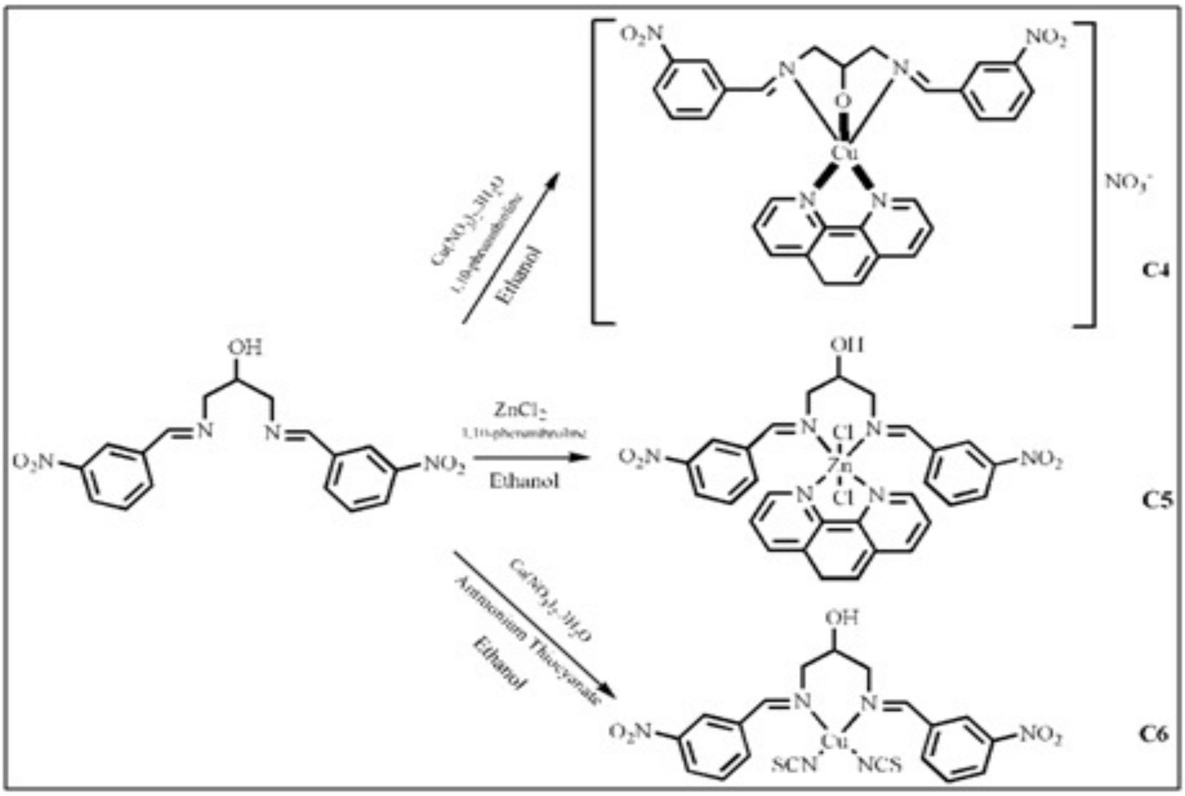
General Procedure

Complex-1[Cu(L)(phen)](NO_3) (C4): The formulated Schiff base ligand (0.3505 g, 0.98 mmol) from 1,3-diaminopropan-2-ol and 3-nitrobenzaldehyde and Copper(II)nitrate (0.2378 g, 0.98 mmol) is mixed with

*Author for Correspondence: msrgcr@gmail.com

equal mole ratio using ethanol as a solvent. The reaction mixture kept stirring in room temperature for one hour. Then an equi-molar amount of the co-ligand 1,10-phenanthroline (0.1783 g, 0.98 mmol) were added causing the solution changes to turn dark green. The reaction mixture is left stirring overnight. The resulting complex is precipitated, filtered, washed with ether and dried.Complex-2 [Zn(L)(phen)Cl_2] (C5): The formulated Schiff base ligand (0.2516 g, 0.70 mmol) from 1,3-diaminopropan-2-ol and 3-nitrobenzaldehyde is combined with an equal mole ratio of Zinc(II)chloride (0.0963 g, 0.70 mmol) in ethanol. The solution is stirred at room temperature for one hour. After that equi-molar co-ligand 1,10-phenanthroline (0.128 g, 0.70 mmol) is introduced. The mixture is stirred overnight. The complex is precipitated, filtered, washed with ether and dried.

Complex-3 [Cu(L)$(NCS)_2$] (C6): The Schiff base ligand (0.3020 g, 0.84 mmol) formed from 1,3-diaminopropan-2-ol and 3-nitrobenzaldehyde and Copper(II)nitrate (0.2048 g, 0.84 mmol) mixed with equal mole ratio using ethanol as a solvent. The reaction mixture kept stirring in room temperature for one hour. After that 2 moles of ammonium thiocyanate (0.1289 g, 1.6 mmol) were added. The reaction mixture kept for overnight with stirring. The complex is precipitated out, filtered, washed with ether and dried.



Scheme:1

Molar conductance:

Molar conductance measurement reveals Complex(C4) was a 1:1 electrolyte (85 Ω^{-1} cm^2 mol^{-1}), complexes (C5) and (C6) were non electrolyte due to lower molar conductance (24 and 33 Ω^{-1} cm^2 mol^{-1} respectively).

Table – 1: Physical properties of the C4-C6

	[Cu(L)(phen)](NO_3)	[Zn(L)(phen)Cl_2]	[Cu(L)$(NCS)_2$]
Yield	24%	37%	29%
m.p	284ºC	>300ºC	178ºC
Solubility	DMF, DMSO	DMF, DMSO	DMF, DMSO
Color	Green	Colorless	Dark green

IR Spectra

Infrared Spectroscopy gives valuable information about the bonding modes of metal complexes. O-H bond in ligand is disappeared in complex C4 which suggesting deprotonation and formation of a metal-oxygen bond. The imine bond frequency for ligand is 1645 cm^{-1} this value is shifted in complexes whose values are 1602, 1606, 1587 cm^{-1} which indicates imines nitrogen involved to form metal complexes. New bands appear at 636 and 621 cm^{-1} for complexes C4 and C6 assigned to Cu-N respectively. In complex C6 the characteristic band at 2092 cm^{-1} indicates $Cu\text{-}NCS^-$.

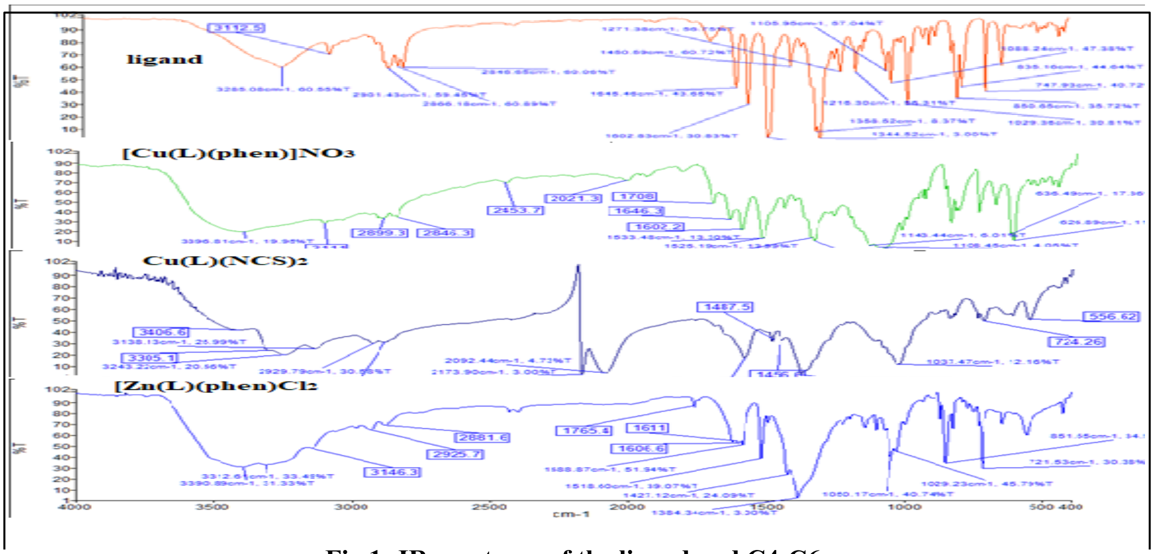


Fig.1- IR spectrum of the ligand and C4-C6

Electronic Spectra:

The electronic spectra showed two types of transition for the ligand and the complexes. The range 207-232 nm is responsible for $\pi\rightarrow\pi^*$ transition of benzene ring and the double bond present in the imine group. Non-bonding electron present on the nitrogen of the imine group is responsible for $n\rightarrow\pi^*$ which appeared in the region 241-344 nm. The Cu(II) complexes showed a d-d transition at 690 nm and 634 nm.

Table-2: UV data of the C4-C6

Wavelength (nm)	Ligand	$[Cu(L)(phen)](NO_3)$	$[Zn(L)(phen)Cl_2]$	$[Cu(L)(NCS)_2]$
$\pi\rightarrow\pi^*$	207	232	232	232
$n\rightarrow\pi^*$	241	344	324	343
d-d transition		690		634

Mass spectra

Mass spectrometry confirms the molecular compositions with experimental data closely matched with calculated m/z values. C4 M^+ = 662.10 (Cal. 662.14), C5 $[ZnL(phen)Cl_2]$ = 676.50 $[M+2]^+$ (Cal. 672.83) and C6 M^+ = 536.04 (Cal. 536.40) are good agreement with calculated value.

Table-3: Mass spectral studies

Complexes	Experimental	Calculated
$[Cu(L)(phen)](NO_3)$	662.10	662.14
$[Zn(L)(phen)Cl_2]$	676.50*	672.83
$[Cu(L)(NCS)_2]$	536.40	536.04

*Value include isotopic peak for Cl_2

EPR spectra

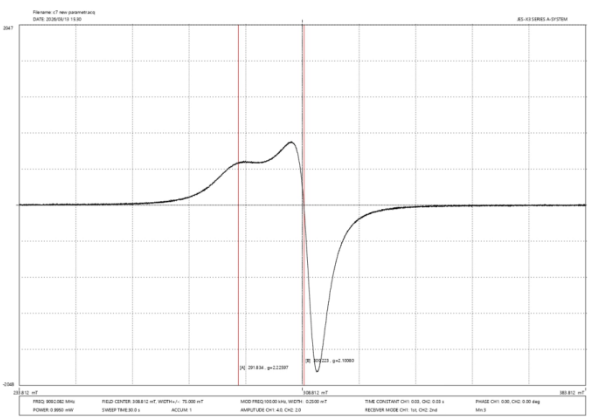


Fig.2–EPR spectrum for [Cu(L)(phen)](NO3)

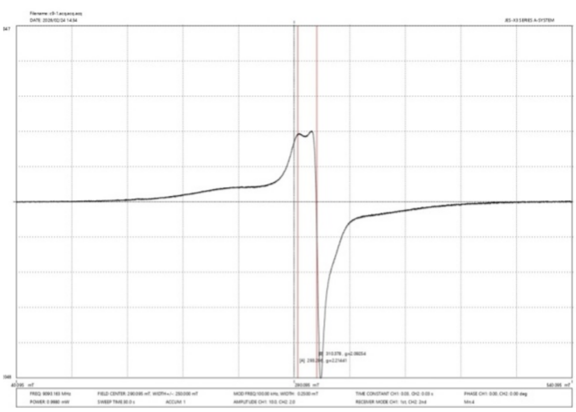


Fig.3–EPR spectrum for [Cu(L)(NCS)2]

ESR for complex C4 and C6 was carried out at room temperature. Single ESR signal reveals that both the complexes having one unpaired electron. EPR spectra for $[Cu(L)(phen)](NO_3)$ and $[Cu(L)(NCS)_2]$ indicates both the complexes are paramagnetic in nature. The observed g values for Complex C6 characteristic for square planar geometry whose unpaired electron in the ground state is dx^2-y^2 orbital. The complex C6 is likely square planar with an N coordination sphere (two N from L, two N from NCS^-)

Corrosion inhibition activities

The corrosion inhibition studies were done using standard weight loss method using mineral acids. 0.1M Nitric acid and well defined metal specimen were used to determine corrosion rate and inhibition efficiency.

Corrosion rate (C_R) = $\Delta W/(A \times t)$, where ΔW – weight loss of the metal coupon after corrosion, A – area of the metal coupon, t – required time for employing corrosion.

Inhibition efficiency (η %) = $(C_{R,0} - C_{R,inh}) \times 100 / C_{R,0}$, where $C_{R,0}$ – corrosion rate of blank and $C_{R,inh}$ – corrosion rate with inhibitor.

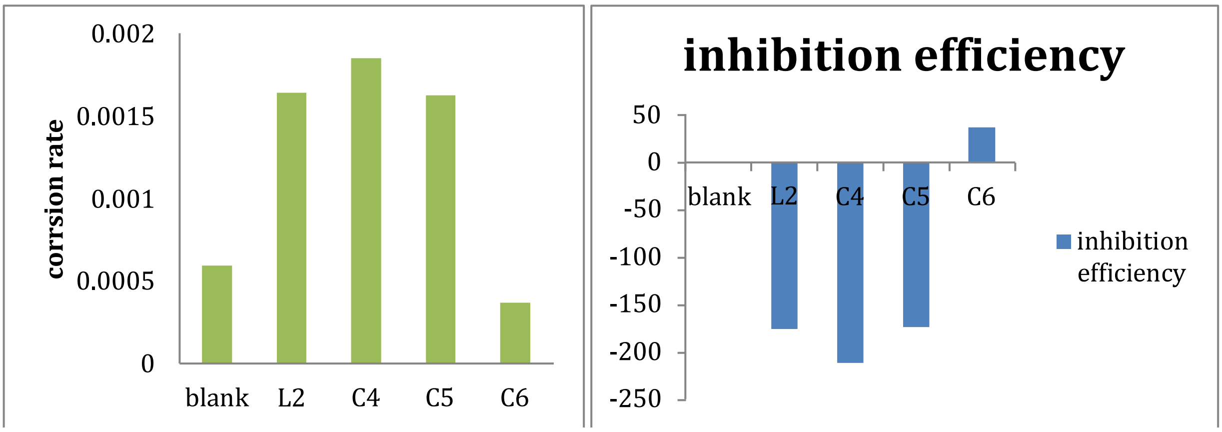


Fig. 4: Corrosion rate and inhibition efficiency

The above data reveals that the C6 complex having least corrosion rate and greater inhibition efficiency. So, the $[Cu(L)(NCS)_2]$ provides the greatest protection and reducing the corrosion rate more efficient among the tested ligand and complexes.

Anti-Bacterial and Anti-Fungal activities

The bacterial cultures were spread on freshly prepared Nutrient Agar (NA) plates using sterile cotton swabs. Wells (5mm diameter) were created in the inoculated plates, and extract was added in varying volumes (25 µL, 50 µL, 75 µL, 100 µL). Chloramphenicol (5 µL) served as a positive control. The bacterial plates were incubated at 37°C for 24 hours, while fungal plates were kept at room temperature for 4-5 days. The resulting zone of inhibition was measured (in mm) (Mohanraj *et al.*, 2011).[12] Stock cultures were stored at 4°C on potato dextrose agar slants. To prepare active cultures, cells from the stock were transferred to 50 mL potato dextrose broth and incubated under different conditions: fungal cultures were agitated at 37°C for 48 hours or kept at 27°C for 3-5 days. Test organisms were streaked on potato dextrose agar, and single colonies were isolated on slants, and then incubated at 37°C for 24 hours or 27°C for 3-5 days. Cultures were stored at 4°C.The antifungal activity was assessed using the agar diffusion method (Bauer et al., 1996).[11] Candida albicans stock culture was grown in nutrient broth at 37°C for 18 hours. Agar plates were inoculated with 18-hour-old cultures, and 5 wells were created. Extracts (25 µL, 50 µL, 75 µL, 100 µL) and Fluconazole (5 µL, standard) were added. Plates were incubated at 37°C for 24 hours, and inhibition zones (mm) were measured.

Zone of Inhibition (mm)

Table-4: Inhibition zone of C4, C5 and C6

	25 µl	50 µl	75 µl	100 µl	Standard
			E.Coli		
Ligand	3.5	4.5	6.0	6.5	3.0
$[Cu(L)(phen)](NO_3)$	2.5	4.0	5.0	**7.0**	3.0

$[Zn(L)(phen)Cl_2]$	1.0	2.0	3.0	4.0	3.0
$[Cu(L)(NCS)_2]$	2.0	2.5	3.0	4.0	3.0
Pseudomonas aeruginosa					
Ligand	4.0	4.5	5.0	**6.0**	3.0
$[Cu(L)(phen)](NO_3)$	2.0	2.5	3.0	3.5	3.0
$[Zn(L)(phen)Cl_2]$	1.0	2.5	2.8	3.5	3.0
$[Cu(L)(NCS)_2]$	1.5	2.0	3.0	5.5	3.0
Staphylococcus aureus					
Ligand	0.4	0.5	0.8	1.5	3.0
$[Cu(L)(phen)](NO_3)$	1.0	1.5	2.0	2.5	3.0
$[Zn(L)(phen)Cl_2]$	0.5	1.0	2.5	**3.5**	3.0
$[Cu(L)(NCS)_2]$	1.0	1.5	1.8	2.0	3.0
Bacillus subtilis					
Ligand	3.0	5.0	5.5	6.5	3.0
$[Cu(L)(phen)](NO_3)$	3.0	3.5	5.0	**7.5**	3.0
$[Zn(L)(phen)Cl_2]$	2.0	3.0	3.5	5.0	3.0
$[Cu(L)(NCS)_2]$	2.5	3.0	3.5	3.8	3.0
Candida albicans					
Ligand	3.0	4.5	5.0	5.5	3.0
$[Cu(L)(phen)](NO_3)$	**4.0**	**5.0**	**7.0**	**10.0**	3.0
$[Zn(L)(phen)Cl_2]$	0.3	0.4	0.5	1.0	3.0
$[Cu(L)(NCS)_2]$	0.3	0.4	0.8	1.0	3.0
Candida tropicalis					
Ligand	2.0	2.5	3.0	4.0	3.0
$[Cu(L)(phen)](NO_3)$	**3.0**	**4.0**	**5.0**	**5.5**	3.0
$[Zn(L)(phen)Cl_2]$	0.5	0.7	0.8	1.0	3.0
$[Cu(L)(NCS)_2]$	1.0	1.4	1.5	1.7	3.0

Antimicrobial activity for the ligand and complexes were studied and ligand shows higher activity for *E.coli* and *Bacillus subtilis* when compared to Complexes. Complex C4 at 100 μl concentration the zone of inhibition value for *E.Coli* (7.0) and *Bacillus subtilis* (7.5) show higher inhibition activity than ligand and complexes (C5 and C6). In case of *Pseudomonas aeruginosa,* ligand shows higher activity than complexes in the chosen concentration for this study. On the other hand, antifungal activity for Complex C4 shows higher inhibition activity than ligand and complexes (C5 and C6) for both *Candida albicans* and *Candida tropicalis* for the chosen concentration. $[Cu(L)(phen)](NO_3)$ shows significantly boosts reactivity, making it the most reactive compound for fungal inhibition.

CONCLUSION

The investigation of the three mixed ligand complexes $[Cu(L)(phen)]NO_3^-$, $[Zn(L)(phen)Cl_2]$, and $[Cu(L)(NCS)_2]$ were synthesized and characterized by IR, UV-Vis, EPR spectroscopy, Mass Spectrometry. An anti-microbial study reveals distinct structure property relationships. IR and UV-Vis data confirm the formation of metal complexes through Schiff base (L), 1,10-phenanthroline (phen), and ancillary ligands (Cl^-& NCS^-). Mass spectrometry analysis reveals that the complexes are stable in solution state too. In the light of mass spectral studies and molar conductivity studies the proposed geometry for C4 is Trigonal bipyramidal and C5 is Octahedral. EPR analysis for Complex C4 and C6 reveals that both are paramagnetic in nature. For Complex C6 the g values shows $g_{\parallel}>g_{\perp}>2.0023$ which reveals its square planar geometry. Zn(II) complex is diamagnetic due to d^{10} configuration, which is EPR silent. Anti-microbial studies demonstrate notable antimicrobial efficacy, especially for the Cu(II) species, suggesting that the chelation environment enhances biological activity. A corrosion study shows that Complex C6 inhibition efficiency is better than ligand is due to NCS^- ligand. The novelty lies in integrating spectroscopic characterization with biological screening to establish a correlation between coordination geometry, electronic structure, and antimicrobial potency, providing a framework for designing metal based agents with optimized therapeutic potential.

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