

Syntheses and Characterization of Cu(II)/Ni(II) Metal Complexes of a Reduced Schiff Base Ligand Derived from L-Methionine

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Abstract

There is growing interest in the metal complexes of bio-active Schiff base ligands for their extensive use as catalysts, anti-oxidative/anti-inflammatory agents, anticancer drugs and also in industry for their anti-corrosion properties. Amino acid-based Schiff bases are very effective metal chelators and their metal complexes are models for a number of important biological systems. In this present report we have synthesis of an L-methionine based reduced schiff base ligand by condensation reaction with furfural aldehyde. The synthesized ligand, 2-((furan-2-ylmethyl)amino)-4-(methylthio)butanoic acid (**L**) was allowed to react with 3d metals like copper and nickel to synthesize complexes having general formula ML_2 ($M = Cu(I)/Ni(2)$).

The ligand and its complexes characterized by various spectroscopic (FT-IR, UV-Visible, ¹H-NMR) methods. The structure of synthesized metal complexes has been unambiguously determined by using single crystal X-ray structure determination. Complex **1** was crystallized in monoclinic crystal system with C2 space group while Complex **2** crystallized in triclinic crystal system with P-1 space group. These complexes will be tested for their biological efficacy as antimicrobial (antibacterial and antifungal) agents in future.

Keywords: Reduced Schiff Base, Metal Complexes, Single Crystal X-Ray Diffraction, Antimicrobial Agents.

Introduction

Chiral compounds play very important role in biochemical/biological processes occurring in pharmaceutical and agriculture industry due to their high selectivity. It became a general practice for the scientists to test every stereoisomer separately for their drug action in medicine.¹ As amino acids are naturally occurring chiral compounds, amino acids and their derivatives also perform number of biological functions and have variety of applications in the fields of biochemistry, pharmacology, drug delivery etc.²⁻⁴

L-methionine among all the amino acids has been considered as a special one due to its available binding sites and coordination diversity which are very useful in providing

synthetic model for metalloenzyme.⁵⁻⁷ Schiff base and reduced schiff base ligands based on amino acids are of interest due to their ease of functionalization, inherent chirality and flexibility towards metal binding.⁸ Reduced schiff base is particularly preferred for the study due to higher stability and flexibility as they do not have constraint to be planer during complexation.⁹⁻¹¹

Transition metal complexes of schiff bases and reduced schiff bases of amino acids show great applications as anti-microbial, antifungal, anti-inflammatory and anti-viral agents.¹²⁻¹⁴ They play important role in enzymatic reaction intermediates and also catalyze many organic reactions.¹⁵⁻¹⁷ Schiff base metal complexes are also extensively used in medicinal chemistry mainly in the cancer diagnosis and treatment of tumor.¹⁸⁻²⁰

In this work we have reported synthesis of a L-methionine based reduced schiff base ligand, 2-((furan-2-ylmethyl)amino)-4-(methylthio)butanoic acid (**L**) and its complexation with 3d metals such as copper (II) and nickel (II). All synthesized compounds are characterized by spectroscopic techniques such as ¹H NMR, FTIR and UV-Vis spectroscopy. Structural studies of metal complexes were successfully established by single crystal x-ray diffractometer. The potential application of these compounds in biological process will be studied.

Material and Methods

All the chemicals and solvents are commercially available and used without further purification. Methanol was purchased from Fisher Scientific, while glacial acetic acid, sodium hydroxide (NaOH), sodium borohydride (NaBH₄) and L-methionine were purchased from AVRA India. Copper(II)perchlorate hexahydrate, nickel(II)perchlorate hexahydrate and 2-furfural aldehyde were purchased from Sigma-Aldrich.

¹H NMR spectra were recorded on Bruker 400 MHz advance-II spectrometer respectively using TMS as internal reference at room temperature. Elemental analysis (CHN) was performed on a Thermo Scientific Flash 2000 Organic Elemental Analyzer instrument. IR spectra of all compounds were recorded using Thermo Scientific (NICOLET IS50) FT-IR spectrophotometer in the range 4000-400 cm⁻¹. UV-Vis spectra were obtained using JASCO V-530 UV/Vis spectrophotometer. Perchlorate salts used as starting materials are potentially dangerous as explosives and should only be handled in small quantities.

Single-Crystal XRD Studies: Crystal of the complex **1** and **2** was mounted on Hampton cryoloops. All geometric and intensity data for the crystals were collected using a Super-Nova (Mo) X-ray diffractometer equipped with a micro-focus sealed X-ray tube Mo-K α ($\lambda = 0.71073$ Å) X-ray source and HyPix3000 detector with increasing ω (width of 0.3 per frame) at a scan speed of either 5 or 10 s/frame. The CrysAlisPro software was used for data acquisition and data extraction. Using Olex2,²¹ the structure was solved with the SIR2004²² structure solution program using direct methods and refined with the ShelXL²³ refinement package using Least Squares Minimisation.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Detailed crystallographic data and structural refinement parameters are summarized in table 3 and 4. CCDC 2023506 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Syntheses

2-((furan-2-ylmethyl)amino)-4-(methylthio)butanoic acid (**L**) Ligand:

The ligand (**L**) (C₁₀H₁₅NO₃S) was synthesized by modified literature procedure⁸ (Scheme 1). Initially a mixture of L-methionine (1 g, 6.70 mmol) and NaOH (0.28 g, 6.70 mmol) was taken in methanol (MeOH) (100 ml) and stirred for 30 min to obtain a clear solution. To the solution furfuraldehyde (0.56 ml, 6.70 mmol) was added drop wise with stirring to produce a light-yellow colored mixture, which was stirred for 3 hrs at 50–60 °C. The resulting mixture was then reduced by adding NaBH₄ (0.25 g, 6.70 mmol) in portions at low temperature in ice bath and the stirring was further continued for additional 3–4 hrs. The final reaction mixture was acidified using dilute glacial acetic acid to bring the pH around 6–7 resulting white precipitate of the ligand. The compound was separated by filtration, thoroughly washed with water followed by methanol and dried in vacuum.

Anal. calcd for **L** (C₁₀H₁₅NO₃S): C, 52.38; H, 6.59; N, 6.11; found C, 51.92; H, 6.68; N, 6.64.

IR (cm⁻¹): (N–H) 2828 (symm), 3000 (asymm); (C=O) 1565 (symm), 1628 (asymm).

¹H NMR (*d*₆-DMSO, 400 MHz, ppm): –CH (aromatic) (8.1, d, 1H), –CH (aromatic) (7.95, t, 1H), –CH (aromatic) (7.88, d, 1H), –COOH (7.65 and 7.46, broad, 1H), –CH₂ (3.59, t, 2H), –CH (3.47, t, 1H) –CH₂ (3.29, m, 2H), –NH (3.2, broad, 1H), –CH₃ (3.1, s, 3H) mix with other, –CH₂ (3.1 and 2.5, m, 2H) (Figure 1).



To a methanolic solution (20 ml) of ligand (**L**) (0.25 g, 1.09 mmol) and NaOH (0.044 g, 1.09 mmol), methanolic solution (5 ml) of Cu(ClO₄)₂·6H₂O (0.21 g, 0.55 mmol) was added drop wise with continuous stirring to result a blue colored solution of the complex (Scheme 1). Thereafter, the resulting solution was refluxed at 40–50 °C for approximately 2 hrs and precipitate obtained was separated by filtration and dried in vacuum. Block shaped blue crystals of complex **1** were obtained through slow evaporation of the mother liquor used for the single crystal X-ray diffraction study. Yield (precipitate) 60%.

Anal. calcd for [Cu(C₁₀H₁₄NO₃S)₂]: C, 46.18; H, 5.43; N, 5.39; found C, 46.26; H, 5.51; N, 5.49.

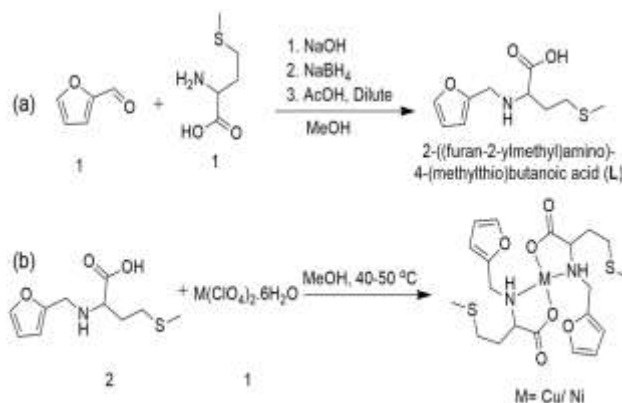
IR (cm⁻¹): (N–H) 3115 (symm), 3187 (asymm); (C=O) 1660.



To a methanolic solution (20 ml) of ligand (**L**) (0.25 g, 1.09 mmol) and NaOH (0.044 g, 1.09 mmol), methanolic solution (5 ml) of Ni(ClO₄)₂·6H₂O (0.20 g, 0.55 mmol) was added drop wise with stirring to result a clear solution (scheme 1). Thereafter, the resulting solution was refluxed at 40–50 °C for approximately 2 hrs and precipitate obtained was separated by filtration and dried in vacuum. Rod shaped light green crystals of complex **2** were obtained through slow evaporation of the mother liquor used for the single crystal X-ray diffraction study. Yield (precipitate) 55%.

Anal. calcd for [Ni(C₁₀H₁₄NO₃S)₂]: C, 46.02; H, 5.41; N, 5.37; found C, 46.11; H, 5.38; N, 5.45.

IR (cm⁻¹): (N–H) 3117 (symm), 3231 (asymm); (C=O) 1571.



Scheme 1: Schematic representation of (a) the synthesis of ligand **L and (b) its metal complexes **1** and **2****

Spectroscopic and analytical studies

NMR Spectroscopy: The ^1H NMR spectrum of ligand was recorded in d_6 -DMSO confirming the formation of reduced schiff base ligand (Figure 1). There are three protons in the aromatic region of the ligand of which two show doublet peak, while one shows multiplet splitting peaks. The protons in the region from 2.5 ppm to 3.7 ppm belong to alkane hydrogen atoms. Amine hydrogen peak is doublet and found around 3.22 ppm in the spectra. COOH peak and H adjacent to chiral carbon were divided in two halves due to different

electronic environment. The detail assignment of ^1H NMR peaks of the ligand is given in table 1.

FTIR Spectroscopy: The FTIR spectra (Figure 2) show two stretching peaks (symm. and asymm.) of C=O ($-\text{COOH}$) at 1565 and 1628 cm^{-1} in the ligand respectively. The absence of these peaks in the complexes (**1** and **2**) indicates deprotonation of acidic hydrogen during complexation process. Presence of N–H stretching bands in ligand **L** (2828 (asym) and 3000 (sym) cm^{-1}) is shifted towards higher wave number² in the complexes as depicted in table 2.

Table 1
 ^1H NMR Peaks assignment of L.

Assignment	^1H NMR Peak
(a) –CH (aromatic)	7.88, d, 1H
(b) –CH (aromatic)	7.95, t, 1H
(c) –CH (aromatic)	8.1, d, 1H
(d) –CH ₂	3.59, t, 2H
(e) –NH	3.2, broad, 1H
(f) –CH	3.47, t, 1H
(g) –COOH	7.65 & 7.46, broad, 1H
(h) –CH ₂	3.1 & 2.5, m, 2H
(i) –CH ₂	3.29, m, 2H
(j) –CH ₃	3.1, s, 3H

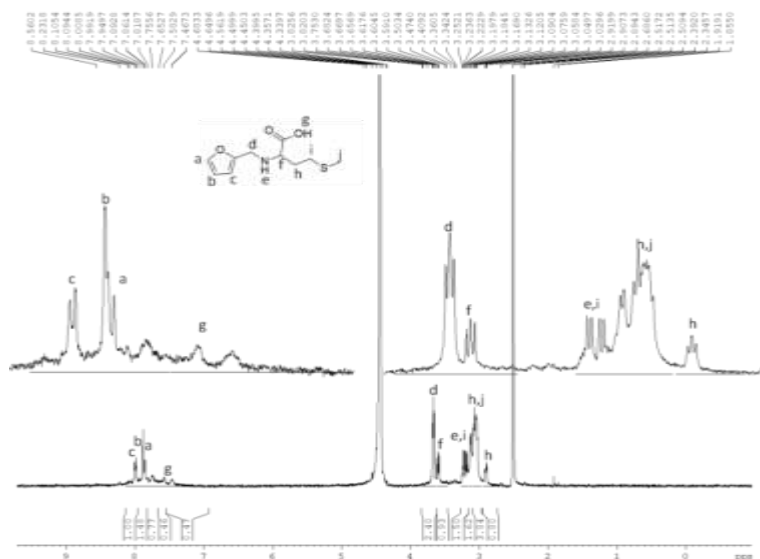


Figure 1: NMR spectra of Ligand (L).

Table 2
Comparison of FTIR frequencies data of L, 1 and 2.

Bond	Frequency (cm^{-1})		
	L	1	2
N–H (asymm)	3000	3187	3231
N–H (symm)	2828	3115	3117
COO (asymm)	1565	1660	1571
COO (symm)	1628	—	—
C=C (Ar)	1371	1364	1401
C–O (Furan)	1151	1140	1147

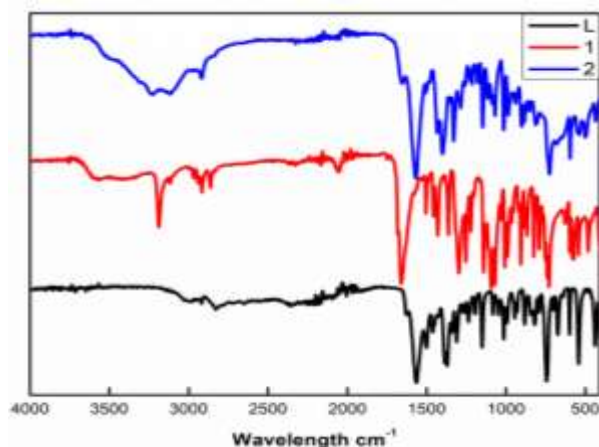


Figure 2: Comparative FTIR spectra of ligand L, complexes 1 and 2

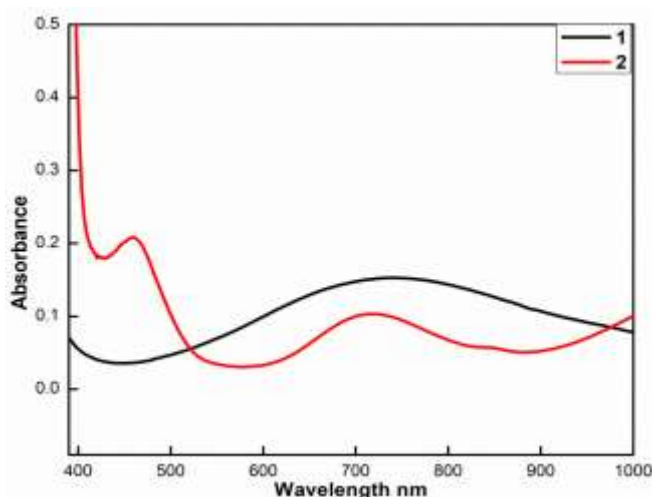


Figure 3: Comparative UV-Vis spectra of complexes 1 and 2.

UV-Vis Spectroscopy: The UV-Vis spectra of complex **1** and **2** were recorded in methanol solvent having 1.0×10^{-4} M concentration in the range 200–1000 nm (Figure 3). A broad peak having λ_{\max} at 742 nm was due to *d-d* transition in the complex **1** suggesting copper in +2 oxidation state (d^9 system). Similarly, two *d-d* transition peaks with λ_{\max} at 416 and 719 nm confirm the +2 oxidation state of nickel (d^8 system) in complex **2**.

Molecular structure (SCXRD)

Blue colored block shaped crystals of complex **1** (CuL_2) suitable for X-ray diffraction were obtained by slow evaporation of mother liquor at room temperature. Complex **1** was crystallized in monoclinic crystal system with $C2$ space group. The crystallographic data of the complexes along with selected bond lengths and bond angles are shown in table 3 and 4. The metal center is surrounded by N_2O_2 coordination environment in distorted square planer geometry. Two ligands are coordinated to one metal center in ML_2 fashion forming a charge neutral species without any solvent of crystallization. The +2 charge of copper is neutralized by two deprotonated carboxylic group present in the chelated ligands. The labeled molecular view of complex was shown in figure 4a.

The metal is coordinated to two nitrogen atoms (one from each ligand) and two carboxylic oxygen atoms (one from each ligand) in *cis* form forming a distorted square planer environment leaving one oxygen and sulphur of each ligand uncoordinated. The average Cu–N bond length is $2.0003(8) \text{ \AA}$ whereas the average Cu–O bond length is $1.909(7) \text{ \AA}$. The lower Cu–O bond distance can be attributed to the deprotonation of the carboxylic oxygen.^{11,24} The O–Cu–O bond angle is $90.56(4)^\circ$ and the N–Cu–N bond angle is $98.64(4)^\circ$ whereas both the N–Cu–O bond angles are $85.74(2)^\circ$. These bond length and bond angle values are in accordance with similar reported complexes.

The angles are deviated from the ideal value of 90° to extent of 8.64° . Each metal center forms stable five membered ring around itself through coordination with angles varying from $85.80(11)$ to $115.68(3)$. The packing diagram of complex **1** along *ab*-plane shows a planar brickbone π -stacking of 2D motive (figure 4b).

Light green colored rod-shaped crystals of complex **2** (NiL_2) were grown similarly to that of complex **1** by slow evaporation of mother liquor. Complex **2** crystallized in triclinic crystal system with $P-1$ space group. The molecular

figure of the complex is depicted in figure 5a, whereas the crystallographic data along with selected bond angles are given in table 3 and 4. The coordination environment around the metal center in the complex **2** is distorted square planar identical to complex **1**. The only deviation observed in case of complex **2** is that both the nitrogen and oxygen atoms (one from each ligand) are coordinated to the metal center in a trans fashion at angle exactly 180° to each other instead of cis as in complex **1**.

The average bond length between Ni–N atoms is $2.098(8)$ Å whereas the average bond length of Ni–O is $2.050(6)$ Å. Again, the shorter Ni–O bonds indicate the deprotonation of the carboxylic oxygen. The set of O–Ni–N bond angles is $94.0(4)^\circ$ and $86.0(4)^\circ$ respectively. The C–C, C–N and C–S bond lengths are in accordance to similar L-methionine based reduced Schiff base ligands reported in the literature in both the complexes.⁸ The packing diagram of complex **2** along *ac*-plane shows a Lamellar motif, 1D p -stacking (figure 5b).

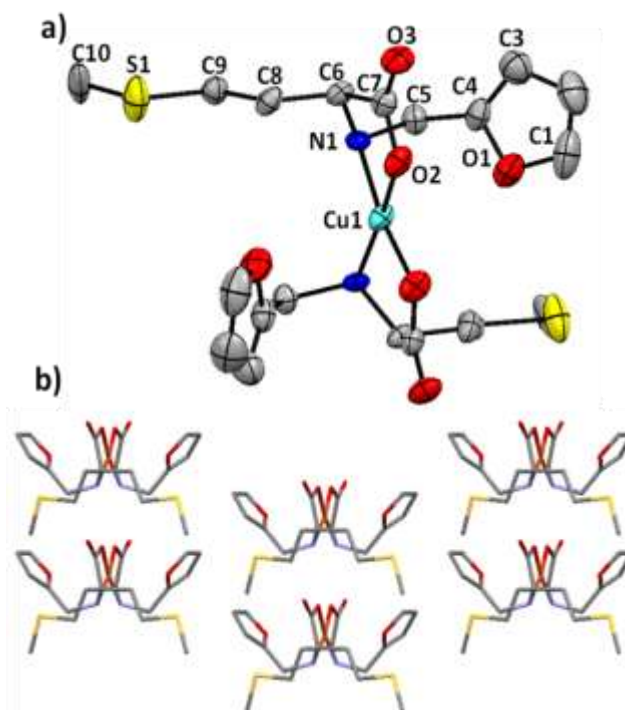


Figure 4: (a) ORTEP diagram and (b) Packing presentation of the complex 1.

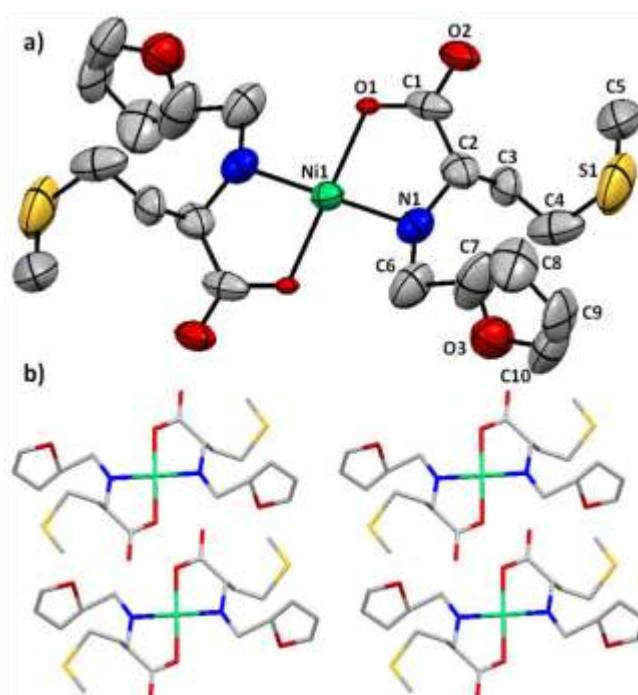


Figure 5: (a) ORTEP diagram and (b) Packing presentation of the complex 2.

Table 3
Crystallographic data and refinement parameters for the complex 1 and 2.

	1	2
Empirical Formula	CuC ₂₀ H ₂₈ N ₂ O ₆ S ₂	NiC ₂₀ H ₂₈ N ₂ O ₆ S ₂
<i>T</i> (K)	293	293
<i>M_r</i> [g mol ⁻¹]	520.13	190.22
Wavelength (Å°)	0.71073	0.71073
Crystal System	monoclinic	Triclinic
Space Group	C2	P-1
<i>a</i> [Å]	21.0934(18)	5.9096(2)
<i>b</i> [Å]	5.5580(4)	7.6872(5)
<i>c</i> [Å]	9.6837(9)	15.4141(8)
<i>α</i> [deg]	90	77.245(5)
<i>β</i> [deg]	90.066(9)	79.488(4)
<i>γ</i> [deg]	90	85.077(4)
<i>V</i> [Å ³]	1135.29(16)	670.74(6)
<i>ρ_{calc}</i> [g cm ⁻³]	1.5214	0.942
<i>Z</i>	2	1
<i>F</i> (000)	543.4	195.0
Reflection Collected	2333	7738
<i>μ</i> [mm ⁻¹]	1.185	0.816
Independent Reflections	1539	2845
Crystal Size [mm] ³	0.1 × 0.25 × 0.2	0.2 × 0.1 × 0.13
<i>θ_{min}/θ_{max}</i> [deg]	7.58 to 54.58	6.528 to 56.134
<i>R_{int}</i>	0.0775	0.1452
w <i>R</i> ₂	0.2030	0.4093
GOOF	0.991	1.682

Results and Discussion

A L-methionine based reduces Schiff base ligand 2-((furan-2-ylmethyl)amino)-4-(methylthio)butanoic acid (**L**) was synthesized and characterized by FTIR and ¹H NMR spectroscopy. The ligand was allowed to react with 3-d metal salts such as Cu(ClO₄)₂·6H₂O and Ni(ClO₄)₂·6H₂O in 2:1 ligand-metal stoichiometry at 50 °C temperature in the presence of NaOH yielding mononuclear charge neutral complexes **1** and **2** having general formula ML₂.

Single crystals of both the complexes suitable for X-ray diffraction study were grown by the slow evaporation of mother liquor and used for structure elucidation. FTIR and UV-Vis spectra of these complexes were recorded which confirm the complex formation as well as their solution stability. The structural study provided the information about the coordination environment, geometry and all geometric parameters. Both the complexes have distorted square planer geometry having N₂O₂ coordination environment and the metal is coordinated to two ligands in bi-dentate fashion leaving one oxygen and one sulphur of the ligand uncoordinated. The +2 oxidation state of metals present in both the complexes is neutralized by deprotonated carboxylic oxygen atom.

The uncoordinated sulphur of the L-methionine can be used as chelating precursor for the capture of expensive metals

such as Pt, Au and Ag present in printed circuit board (PCB) of electronic waste or heavy metals like mercury (Hg) and lead (Pb).²⁵⁻²⁹ As L-methionine amino acid based ligands have high biological activity, these complexes will be studied for their potential usefulness in medicinal chemistry as antimicrobial agent also in agrochemical industry.³⁰⁻³² The potential of these complexes for the self-assembly to produce higher nuclear complexes will also be tested.

Conclusion

In this report, two new mononuclear complexes of copper and nickel from chiral reduced schiff base ligand (**L**) derived from L-methionine have been synthesized and structurally elucidated. The single crystal X-ray diffraction confirms the formation of metal complexes having the metal centers in N₂O₂ coordination environment with distorted square planar arrangement. One oxygen atom and one sulphur atom of the ligand remain free in the complexes which will be exploited to use them for precious metal recovery from the PCBs of electronic waste as well as for the capture of heavy metals like mercury and lead. Antimicrobial (antibacterial and antifungal) properties of the synthesized complexes will be studied to evaluate its potential biological efficacy.

In future this work will also be expanded for the synthesis of supramolecular assemblies by using this type of mononuclear complexes.

Table 4
Selected bond lengths (Å) and bond angles (°) for the complex 1 and 2.

Complex 1					
Atoms	Bond Lengths(Å)	Atoms	Bond Lengths(Å)	Atoms	Bond Lengths(Å)
Cu1 O2	1.909(7)	S1 C9	1.802(8)	N1 C6	1.482(11)
Cu1 O2 ¹	1.909(7)	S1 C10	1.780(11)	N1 C5	1.486(10)
Cu1 N1	2.003(8)	O2 C7	1.310(13)	O1 C4	1.378(11)
Cu1 N1 ¹	2.003(8)	O3 C7	1.206(12)		
¹ 1-X,+Y,1-Z					
Atoms	Angles(°)	Atoms	Angles(°)	Atoms	Angles(°)
O2 ¹ Cu1 O2	90.6(4)	N1 ¹ Cu1 O2 ¹	85.7(2)	N1 Cu1 O2 ¹	172.5(4)
N1 ¹ Cu1 N1	98.8(4)	N1 Cu1 O2	85.7(2)	N1 ¹ Cu1 O2	172.5(4)
¹ 1-X,+Y,1-Z					
Complex 2					
Atoms	Bond Lengths(Å)	Atoms	Bond Lengths(Å)	Atoms	Bond Lengths(Å)
Ni1 O1 ¹	2.046(6)	Ni1 O1A ¹	2.053(8)	O1 C1	1.32(2)
Ni1 O1	2.046(6)	Ni1 O1A	2.053(8)	N1 C6	1.42(2)
Ni1 N1	2.098(8)	C1 C2	1.52(3)	S1 C4	1.85(3)
Ni1 N1 ¹	2.098(8)	O3 C10	1.44(4)		
¹ 1-X,1-Y,1-Z					
Atoms	Angles(°)	Atoms	Angles(°)	Atoms	Angles(°)
O1 ¹ Ni1 O1	180.0	O1 Ni1 N1 ¹	94.0(4)	O1 ¹ Ni1 N1 ¹	86.0(4)
N1 ¹ Ni1 N1	180.0	O1 ¹ Ni1 N1	94.0(4)	O1 Ni1 N1	86.0(4)
¹ 1-X,1-Y,1-Z					

References

- Teo S.K., Colburn W.A., Tracewell W.G., Kook K.A., Stirling D.I., Jaworsky M.S., Scheffler M.A., Thomas S.D. and Laskin O.L., Clinical Pharmacokinetics of Thalidomide, *Clin. Pharmacokinet.*, **43**(5), 311 (2004)
- Chen Z., Morimoto H., Matsunaga S. and Shibasaki M.A., Bench-Stable Homodinuclear Ni²⁺-Schiff Base Complex for Catalytic Asymmetric Synthesis of α -Tetrasubstituted anti- α,β -Diamino Acid Surrogates, *J. Am. Chem. Soc.*, **130**(7), 2170 (2008)
- Mouri S., Chen Z., Mitsunuma H., Furutachi M., Matsunaga S. and Shibasaki M., Catalytic Asymmetric Synthesis of 3-Aminooxindoles: Enantiofacial Selectivity Switch in Bimetallic vs Monometallic Schiff Base Catalysis, *J. Am. Chem. Soc.*, **132**(4), 1255 (2010)
- O'Donnell M.J., The Enantioselective Synthesis of α -Amino Acids by Phase-Transfer Catalysis with Achiral Schiff Base Esters, *Acc. Chem. Res.*, **37**(8), 506 (2004)
- Ngan N.K., Lo K.M. and Wong C.S.R., Dinuclear and polynuclear dioxomolybdenum(VI) Schiff base complexes: Synthesis, structural elucidation, spectroscopic characterization, electrochemistry and catalytic property, *Polyhedron*, **33**(1), 235 (2012)
- Saghatforoush L.A., Aminkhani A. and Chalabian F., Iron(III) Schiff base complexes with asymmetric tetradentate ligands: synthesis, spectroscopy and antimicrobial properties, *Transition Met. Chem.*, **34**, 899 (2009)
- Dhayabaran V.V. and Prakash T.D., Synthesis and multi-spectroscopic study on DNA-binding, cleavage and biological properties of M(II) complexes based on N₂O₂ donor Schiff base ligand, *Luminescence*, **32**(7), 1339 (2017)
- Kumar R., Mutreja V., Sharma G., Kumar S., Ali A., Mehta S.K., Venugopalan P., Kataria R. and Sahoo S.C., The role of a weakly coordinating thioether group in ligation controlled molecular self-assemblies and their inter-conversions in Ni(II) complexes of l-methionine derived ligand, *New J. Chem.*, **43**(28), 11222 (2019)
- Sarkar S., Mondal A., El Fallah M.S., Ribas J., Chopra D., Stoeckli-Evans H. and Rajak K.K., Synthesis, structure and magnetic properties of two end-on double azido bridged nickel(II) dinuclear entities incorporating N,N,N-coordinating tridentate reduced Schiff base ligands, *Polyhedron*, **25**(1), 25 (2006)
- Alghool S., Mononuclear complexes based on reduced Schiff base derived from l-methionine, synthesis, characterization, thermal and in vitro antimicrobial studies, *J. Therm. Anal. Calorim.*, **121**(3), 1309 (2015)
- Sreenivasulu B. and Vittal J.J., Hydrogen-bonded copper(II) and nickel(II) complexes and coordination polymeric structures containing reduced Schiff base ligands, *Inorg. Chim. Acta*, **362**(8), 2735 (2009)
- Abdel-Rahman L.H., El-Khatib R.M., Nasser L.A., Abu-Dief A.M. and Lashin Fel D., Design, characterization, teratogenicity testing, antibacterial, antifungal and DNA interaction of few high spin Fe(II) Schiff base amino acid complexes, *Spectrochim Acta A*, **111**, 266 (2013)

13. Abdel-Rahman L.H., El-Khatib R.M., Nasser L.A., Abu-Dief A.M., Ismael M. and Seleem A.A., Metal based pharmacologically active agents: synthesis, structural characterization, molecular modeling, CT-DNA binding studies and in vitro antimicrobial screening of iron(II) bromosalicylidene amino acid chelates, *Spectrochim Acta A*, **117**, 366 (2014)
14. Abu-Dief A.M. and Nasser L.A.E., Tailoring, physicochemical characterization, antibacterial and DNA binding mode studies of Cu(II) Schiff bases amino acid bioactive agents incorporating 5-bromo-2-hydroxybenzaldehyde, *J Iran Chem Soc*, **12(6)**, 943 (2014)
15. Corriu R.J.P., Lancelle-Beltran E., Mehdi A., Reyé C., Brandès S. and Guilard R., Ordered mesoporous hybrid materials containing cobalt(II) Schiff base complex, *J. Mater. Chem.*, **12(5)**, 1355 (2002)
16. He Y. and Cai C., Polymer-supported macrocyclic Schiff base palladium complex: An efficient and reusable catalyst for Suzuki cross-coupling reaction under ambient condition, *Catal. Commun.*, **12(7)**, 678 (2011)
17. He Y. and Cai C., Polymer-supported macrocyclic Schiff base palladium complex as an efficient catalyst for the Heck reaction, *Appl. Organomet. Chem.*, **25(11)**, 799 (2011)
18. Adsule S., Barve V., Chen D., Ahmed F., Dou Q.P., Padhye S. and Sarkar F.H., Novel Schiff Base Copper Complexes of Quinoline-2 Carboxaldehyde as Proteasome Inhibitors in Human Prostate Cancer Cells, *J. Med. Chem.*, **49(24)**, 7242 (2006)
19. Kulkarni A., Patil S.A. and Badami P.S., Synthesis, characterization, DNA cleavage and in vitro antimicrobial studies of La(III), Th(IV) and VO(IV) complexes with Schiff bases of coumarin derivatives, *Eur. J. Med. Chem.*, **44(7)**, 2904 (2009)
20. Patil S.A., Unki S.N., Kulkarni A.D., Naik V.H., Kamble U. and Badami P.S., Spectroscopic, in vitro antibacterial and antifungal studies of Co(II), Ni(II) and Cu(II) complexes with 4-chloro-3-coumarinaldehyde Schiff bases, *J. Coord. Chem.*, **64(2)**, 323 (2011)
21. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K. and Puschmann H., OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, **42(2)**, 339 (2009)
22. Burla M.C., Caliandro R., Camalli M., Carrozzini B., Cascarano G.L., De Caro L., Giacovazzo C., Polidori G., Siliqi D. and Spagna R., IL MILIONE: a suite of computer programs for crystal structure solution of proteins, *J. Appl. Crystallogr.*, **40(3)**, 609 (2007)
23. Sheldrick G., Crystal structure refinement with SHELXL, *Acta Crystallogr C*, **71(1)**, 3 (2015)
24. Maheswari P.U., Ster M.V.D., Smulders S., Barends S., Wezel G.P.V., Massera C., Roy S., Dulk H.D., Gamez P. and Reedijk J., Structure, Cytotoxicity and DNA-Cleavage Properties of the Complex [CuII(pbt)Br₂], *Inorg. Chem.*, **47(9)**, 3719 (2008)
25. Maxim C., Muntean D. and Andruh M., On the role played by the chirality of ligands on the aggregation of heterometallic Cu(II)-Hg(II) complexes, *Chirality*, **31(9)**, 621 (2019)
26. Mirdya S., Roy S., Chatterjee S., Bauzá A., Frontera A. and Chattopadhyay S., Importance of π -Interactions Involving Chelate Rings in Addition to the Tetrel Bonds in Crystal Engineering: A Combined Experimental and Theoretical Study on a Series of Hemi- and Holodirected Nickel(II)/Lead(II) Complexes, *Cryst. Growth Des.*, **19(10)**, 5869 (2019)
27. Hu C., Xu W., Li H., Zhou S., Mo X., Zhang P. and Tang K., Highly Efficient Adsorption of Au(III) from Water by a Novel Metal–Organic Framework Constructed with Sulfur-Containing Ligands and Zn(II), *Ind. Eng. Chem. Res.*, **58(38)**, 17972 (2019)
28. Choudhary B.C., Paul D., Borse A.U. and Garole D.J., Surface functionalized biomass for adsorption and recovery of gold from electronic scrap and refinery wastewater, *Sep. Purif. Technol.*, **195**, 260 (2018)
29. Monier M. and Abdel-Latif D.A., Fabrication of Au(III) ion-imprinted polymer based on thiol-modified chitosan, *Int. J. Biol. Macromol.*, **105(1)**, 777 (2017)
30. Khan N.U.H., Pandya N., Prathap K.J., Kureshy R.I., Abdi S.H.R., Mishra S. and Bajaj H.C., Chiral discrimination asserted by enantiomers of Ni (II), Cu (II) and Zn (II) Schiff base complexes in DNA binding, antioxidant and antibacterial activities, *Spectrochim Acta A*, **81(1)**, 199 (2011)
31. Nyawade E.A., Onani M.O., Meyer S. and Dube P., Synthesis, characterization and antibacterial activity studies of new 2-pyrral-L-amino acid Schiff base palladium (II) complexes, *Chem Pap*, **74**, 3705 (2020)
32. Adhikari S., Bhattacharjee T., Butcher R.J., Porchia M., De Franco M., Marzano C., Gandin V. and Tisato F., Synthesis and characterization of mixed-ligand Zn(II) and Cu(II) complexes including polyamines and dicyano-dithiolate(2-): In vitro cytotoxic activity of Cu(II) compounds, *Inorg. Chim. Acta*, **498**, 119098 (2019).

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