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Nickel and copper complexes with few amide-based macrocyclic and open-chain ligands

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ABSTRACT

The present work shows three new amide-based ligands H_2L^1 , H_2L^2 and H_2L^3 and their nickel and copper complexes. The X-ray structural analysis substantiate that the ligands constitute a square-based basal plane around the metal center. The crystal structures also show interesting solid state packing due to hydrogen-bonding and various weak C···H interactions. The solution-based spectral studies support the solid-state geometry observed for these complexes. The electrochemical results show that the Ni^{3+/2+} and Cu^{3+/2+} redox couple primarily depends on the N₄ donors composed of N_{amide} and N_{amine} atoms. It was observed that the ligands H_2L^1 and H_2L^2 are better suited to stabilize the Cu(III) species whereas ligand H_2L^3 is ideal for the stabilization of Ni(III) species. On the basis of electrochemical findings, transient Ni³⁺ species were generated and characterized by the absorption spectroscopy.

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1. Introduction

Amide-based macrocyclic ligands as well as their open-chain analogues are important since they carve up the properties of oligopeptides and polyamine moieties. Such ligands have been explored extensively for preparing transition metal complexes with implications in the field of coordination, bioinorganic and oxidation chemistry [1–17]. The coordination chemistry of nickel and copper ions has received much attention due to their presence in the redox cycles of several metalloenzymes [18-29]. Thus, a large number of high-valent nickel and copper complexes with amidebased ligands are available in literature and constitute an important area of research [30-63]. Several such compounds are also important as biomimetic models in addition to their potential application as catalytic oxidants. Prominent among them are the $Ni^{2+/3+}$ and $Cu^{2+/3+}$ complexes of amidate containing ligands from the groups of Margerum [30-35], Collins [36-39], Ruiz-Garcia and Journaux [40-45], Holm and Kruger [46-50], Mukherjee [51-56], and Lampeka and Gavrish [57-63]. These examples have successfully demonstrated the stabilizing effect of $N_{\mbox{\scriptsize amidate}}$ donors in bringing out the high oxidation state of a metal ion. In addition, such studies also showcase that the ligand architecture plays a crucial role in the redox regulation of a metal center and subsequent stabilization and/or isolation of the product. The present study is in continuation of our earlier work on the coordination chemistry and redox investigation of nickel and copper ion with amide-based macrocyclic ligands [64,65] and their open-chain analogues (Scheme 1) [66-70]. The macrocyclic ligands and some of their open-chain analogues have been shown to stabilize 2+ as well as 3+ oxidation state of a metal ion in a somewhat rare square-planar geometry [64-66]. Recently, we have extended our work on 12membered macrocyclic chemistry and have expanded the ring size of the macrocycle to 13-membered macrocyclic ligands. The expansion of the ring size from 12-membered to 13-membered has helped in the optimal placement of the Ni(II) ion within the macrocyclic cavity of ligands (Scheme 1) [71]. In addition, several macrocyclic ligands carrying various electronic substituents (-CH₃, -Cl, and -OCH₃) have been shown to significantly alter the redox properties and subsequent generation/stability of the M³⁺ species [65,71]. In all aforementioned complexes, the basic coordination environment was kept identical with subtle differences in the ligand framework to evaluate their architectural effect on the structural and electrochemical properties of the metal ions.

The present work designs few amide-based ligands where the primary coordination framework has been kept identical while altering the peripheral parts (Scheme 2). In particular, ligands H_2L^1 , H_2L^2 , and H_2L^3 have been synthesized which differ by the placement of an arene ring between two amide donors. Notably, ligands H_2L^1 and H_2L^2 are macrocyclic whereas ligand H_2L^3 is an open-chain analogue. Interestingly, placement of an arene ring and/or inclusion of $-CH_2$ - group (with sp³ carbon center) that separates two amide functionalities; may alter the electronic communication between the deprotonated $N_{amidate}$ fragments with the *o*-phenylene ring. Further, inclusion of this methylene group will also induce asymmetrical coordination from both amide donors.





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Scheme 1. Metal complexes discussed in text.



Scheme 2. Ligands used in this work.

Finally, in continuation with our earlier work, the emphasis has been given to understand the effect of ligand architecture on the structure, properties and redox chemistry of the metal ion.

2. Experimental

2.1. Chemicals and reagents

All reagents were obtained from the commercial sources and used as received. The solvents were purified as reported earlier [64–70]. *N,N'*-Bis(chloroacetyl)propylenediamine was synthesized according to a literature report [72].

2.2. Physical methods

The microanalysis data were obtained from the Elementar Analysen Systeme GmbH Vario EL-III instrument. The NMR measurements were made using an Avance Bruker (300 MHz) and/or Jeol Delta (400 MHz) instruments. The infra-red spectra (either as KBr pellet or as a mull in mineral oil) were recorded with the Perkin-Elmer FT-IR-2000 spectrometer. The absorption spectra were recorded using the Perkin-Elmer Lambda-25 spectrophotometer. The X-band electron paramagnetic resonance spectra were recorded with a Jeol JES-FA 200 spectrometer (fitted with quartz Dewar for measurements at 120 K). Solution conductivity measurements were performed with the digital conductivity bridge from the Popular Traders, India (Model number: PT-825). Solution magnetic susceptibility measurements were made by the Evan's NMR spectral method [73]. The diamagnetic corrections were applied according to the standard text [74]. Cyclic voltammetric and coulometric experiments were performed using a CHI electrochemical analyzer (Model No: CHI 1120 A). The cell contained a glassy carbon or a platinum working electrode, a Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) or Ag/Ag⁺ as the reference electrode. A salt bridge (containing supporting electrolyte tetra-*n*-butylammonium perchlorate, TBAP) was used to connect the reference electrode with the electrochemistry solution [75]. The solutions were ca. 1 mM in complex and ca. 0.1 M in supporting electrolyte, TBAP. Under our experimental conditions, the $E_{1/2}$ value for the couple Fc⁺/Fc was found to be 0.40 V in CH₃CN versus SCE [76].

2.3. Crystallography

Single crystals suitable for the X-ray diffraction studies were grown by the vapor diffusion of diethyl ether to a DMF (complex **2**) or CH_2Cl_2 solution (complex **5**) of the compound. The intensity data for complexes 2 and 5 were collected on an Oxford XCalibur CCD diffractometer equipped with graphite monochromatic Mo K α radiation (λ = 0.71073 Å) at 150(2) K [77]. A multi-scan absorption correction was applied [77]. The structures were solved by the direct methods using SIR-92 and refined by full-matrix least-squares refinement techniques on F^2 using SHELXL97. The hydrogen atoms were placed into the calculated positions and included in the last cycles of the refinement. All calculations were done using the WinGX software package [78]. For complex 2, disorder was observed for the C7, C8, C9, and C10 atoms. These atoms were occupying two crystallographically independent positions which could be located from the additional residual electron density. The site occupancy factors were refined with the help of free variable PART instruction. Refinement of the site occupancy factors for the disordered atoms gave the value 0.52 and 0.48, respectively. A structure model based on statistically disordered carbon atoms improved the accuracy of C-C bonds of interest. The crystallographic data collection and structure refinement parameters are compiled in Table 1.

2.4. Synthesis of ligands

2.4.1. H_2L^1

LiBr (0.76 g, 9 mmol), Na₂CO₃ (5.0 g, 40 mmol) and *N*,*N*'-bis(chloroacetyl)propylenediamine (1.0 g, 5 mmol) were taken in MeCN (150 mL) and the mixture was refluxed with stirring for 1 h. To this mixture was added *N*,*N*'-dimethyl ethylenediamine (0.4 g, 5 mmol) dissolved in MeCN (50 mL). The resulting mixture was refluxed under stirring for an additional 48 h. The mixture was cooled, filtered and the solvent was removed under reduced pressure to afford a sticky solid. The crude product was recrystallized by layering the CHCl₃ solution with petroleum ether (boiling range 60–80 °C). Yield: 0.8 g (75%). Mp 195–197 °C. FT-IR spectrum (KBr, selected peaks, cm⁻¹): v = 3327 (v_{NH}), 1645 ($v_{C=0}$). ¹H NMR spectrum (300 MHz, CDCl₃, 25 °C): $\delta = 1.81$ (m, 2H, -CH₂-, H^a), 2.33 (s, 6H, CH₃), 2.59 (s, 4H, -CH₂-, H^c), 3.05 (s, 4H, -CH₂-(O)-, H^d), 3.48 (m, 4H, -CH₂-CH₂-, H^b), 7.85 (s(broad), 2H, NH). MS (EI⁺, *m/z*): Calc. for C₁₁H₂₂N₄O₂ 242.32. Found: 243.897 [(H₂L¹+H⁺)].

2.4.2. N,N'-Bis(chloroacetyl)-2-aminobenzylamine

2-Aminobenzylamine (1.07 g, 9 mmol) was dissolved in dichloromethane (130 mL) and kept under stirring on an ice-bath. A solution of chloroacetyl chloride (2.68 g, 18 mmol) dissolved in dichloromethane (10 mL) was added drop-wise followed by the addition of pyridine (0.75 g, 9.0 mmol). The resulting reaction mixture was stirred for 12 h at room temperature. A white product was obtained after removal of the solvent followed by washing with water. The product was filtered; washed with water followed with

Table 1

Crystallographic data collection and structural refinement parameters for complexes $[Cu(L^1)(H_2O)]$ (2) and $[Ni(L^3)]$ -CH₂Cl₂ (5).

Complex	$[Cu(L^1)(H_2O)](2)$	$[Ni(L^3)] \cdot CH_2 Cl_2 (5)$
Formula	$C_{11}H_{22}N_4O_3Cu$	C16H24N4O2Cl2Ni
Formula weight	321.87	434.00
T (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	Pbca	P21/c
Unit cell dimensions		
a (Å)	8.9522(4)	8.0386(5)
b (Å)	16.6759(7)	17.1921(11)
c (Å)	19.0465(9)	14.2759(9)
α (°)	90	90
β (°)	90	101.796(6)
γ (°)	90	90
V (Å ³)	2843.4(2)	1931.3(2)
Ζ	8	4
D_{calc} (g cm ⁻³)	1.504	1.493
Absorption coefficient (mm ⁻¹)	1.546	1.298
F(000)	1352	904
θ (°)	3.12 to 26.50	2.92 to 25.00
Index ranges	$-11\leqslant h\leqslant 6$,	$-9\leqslant h\leqslant 9$,
	$-13\leqslant k\leqslant 20$,	$-18\leqslant k\leqslant 20$,
	$-23 \leqslant l \leqslant 13$	$-15 \leqslant l \leqslant 16$
Reflections collected	7926	8532
Independent reflections (R_{int})	2945 (0.0660)	3405 (0.0445)
Data completeness	99.9%	99.9%
Refinement method	full-matrix least-	full-matrix least-
	squares on F ²	squares on F^2
Data/restraints/ parameters	2945/91/192	3405/0/230
Goodness-of-fit (GOF) on F^2	0.889	1.067
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0531$,	$R_1 = 0.0428$,
	$wR_2 = 0.0656$	$wR_2 = 0.1119$
R indices (all data)	$R_1 = 0.1454,$	$R_1 = 0.0545$,
· · · ·	$wR_2 = 0.0792$	$wR_2 = 0.1155$
Largest difference in	0.594 and 0.372	0.695 and 0.625
	0.334 and -0.372	0.035 and -0.025

diethyl ether and dried. Yield: 1.07 g (50%). Mp 125 °C. FT-IR spectrum (KBr, selected peaks, cm⁻¹): 3260 (ν_{NH}), 3076, (ν_{CH}), 1665 ($\nu_{C=0}$). ¹H NMR spectrum (CDCl₃, 300 MHz, 25 °C): δ = 4.27 (s, 2H, -CH₂C(O)-), 4.32 (s, 2H, -CH₂C(O)-), 4.55 (d, 2H, -CH₂-), 7.55 (m, 4H, Aromatic-H), 8.7 (s(broad), 2H, NH).

2.4.3. H_2L^2

LiBr (0.4 g, 4 mmol), Na₂CO₃ (2.0 g, 0.016 mmol) and N,N'bis(chloroacetyl)-2-aminobenzylamine (1.0 g, 5 mmol) were taken in MeCN (140 mL) and the mixture was refluxed with stirring for 1 h. To this was added N,N'-dimethylethylenediamine (0.18 g, 2 mmol) dissolved in MeCN (20 mL). The resulting mixture was further refluxed under stirring for an additional 48 h. The mixture was cooled, filtered and the solvent was removed under reduced pressure to afford the crude product. This product was further purified by the column chromatography using silica gel (100-200 mesh) with 10% MeOH–CHCl₃ ($R_f = 0.45$). A white product was obtained after the removal of solvent. Yield: 0.260 g (43%). Mp 138–140 °C. An analytically pure product (~82% vield) can also be obtained by layering CHCl₃ solution of the product with the hexanes. FT-IR spectrum (KBr, selected peaks, cm^{-1}): 3232 (v_{NH}), 3062, 2949, 2839, (v_{CH}), 1668 (v_{C=0}). ¹H NMR spectrum (CDCl₃, 300 MHz, 25 °C): $\delta = 2.40$ (s, 3H, -CH₃), 2.44 (s, 3H, -CH₃'), 2.58 (s, 4H, -CH₂-CH₂-, H^b), 3.06 (s, 2H, -CH₂C(0)-, H^c), 3.18 (s, 2H, -CH₂C(0)-, H^d), 4.49 (d, 2H, -CH₂-, H^e), 7.31 (m, 2H, Ar-H^g), 7.10 (m, 1H, Ar-H^h), 8.48 (d, 1H, Ar-H^f), 7.81 (s (broad), 1H, N-H), 9.84 (s (broad), 1H, N–H). MS (El⁺, m/z): Calc. for C₁₅H₂₂N₄O₂ 290.36. Found: 290.3207 [(H₂L²+H⁺)].

2.4.4. H_2L^3

A mixture of dimethylamine (0.49 g, 10.9 mmol), K₂CO₃ (7.5 g, 5.4 mmol), and *N*,*N*'-bis(chloroacetyl)-2-aminobenzylamine (1 g, 3.6 mmol) were taken in MeCN (10 mL). The resulting mixture was refluxed for 12 h. The solvent was removed under reduced pressure to afford a colorless oil. Yield: 1.07 g (50%). FT-IR spectrum (Film, selected peaks, cm⁻¹): 3244 (ν_{NH}), 2948, (ν_{CH}), 1681, 1589 ($\nu_{C=0}$). ¹H NMR spectrum (CDCl₃, 300 MHz, 25 °C): δ = 2.4 (s, 6H, -CH₃), 2.5 (s, 6H, -CH₃'), 4.40 (s, 2H, -CH₂-, H^e), 4.45 (s, 4H, -CH₂C(O)-, H^{c/d}), 7.50 (m, 4H, Aromatic-H, H^{f/g/h}), 9.5 (s (broad), 2H, NH).

2.5. Synthesis of metal complexes

2.5.1. $[Ni(L^1)](\mathbf{1})$

The ligand H₂L¹ (0.10 g, 0.413 mmol) was dissolved in MeOH (5 mL) and treated with solid NaOH (0.036 g, 0.909 mmol) under magnetic stirring. A solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.15 g, 0.413 mmol) dissolved in MeOH (6 mL) was added drop-wise to the ligand solution. The resulting orange-yellow solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the crude compound was isolated after washing with diethyl ether. The recrystallization was achieved by dissolving the crude compound in MeCN and subjecting to the vapor diffusion of diethyl ether at room temperature. The orange crystalline product thus obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.07 g (56%). Anal. Calc. for C₁₁H₂₄N₄O₄Ni (including 2H₂O, 335.03): C, 39.44; H, 7.22; N, 16.72. Found: C, 39.59; H, 7.50; N, 17.02%. FT-IR spectrum (KBr, selected peaks, cm⁻¹): $v = 3369 (v_{OH})$, 2922 (v_{CH}), 1602 ($v_{C=0}$). Conductivity (DMF, \sim 1 mM solution, 298 K): $\Lambda_{\rm M}$ = 12 Ω^{-1} cm² mol⁻¹. UV–Vis spectrum [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)] (in CH₃CN): 213 (23480), 257 (15700), 470 (430). MS (EI⁺, m/z): Calc. for C₁₁H₂₀N₄O₂Ni 299.00. Found: 299.21 ([Ni(L¹)]+H⁺). ¹H NMR spectrum (300 MHz, DMSO- d_6 , 25 °C): δ = 1.16 (m, 2H, -CH₂-, H^a), 1.98 (m, 2H, -CH₂-, H^e), 2.30 (m, 2H, -CH₂-, H^b), 2.21 (s, 6H -CH₃), 2.34 (d, 2H, -CH₂-, H^{b'}), 2.48 (d, 2H, -CH₂C(0)-, H^c), 3.22 (m, 2H, $-CH_2CH_2-$, H^f), 3.65 (d, 2H, $-CH_2C(O)-$, H^d) ppm. ¹³C NMR spectrum (75 MHz, DMSO- d_6 , 25 °C]: δ = 32.38 (-CH₂-), 42.55 (-CH₃), 60.50 (-CH₂CH₂-), 49.09 (-NCH₂-), 67.67 (-C(O)CH₂-), 176.38 (C=O) ppm.

2.5.2. $[Cu(L^1)(H_2O)]$ (2)

The ligand H_2L^1 (0.10 g, 0.413 mmol) was dissolved in DMF (10 mL) under magnetic stirring and treated with solid NaH (0.021 g, 0.908 mmol) under dinitrogen atmosphere. The resulting mixture was stirred until H₂ evolution was ceased. To this mixture was added a solution of copper triflate (0.149 g, 0.413 mmol) dissolved in DMF (10 mL). The resulting deep purple solution was stirred for 3 h at room temperature. The solvent was evaporated under reduced pressure and the crude product was isolated after washing with diethyl ether. The recrystallization was achieved by diffusing vapors of diethyl ether to a DMF solution of the crude product. The crystalline product thus obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.034 g (26%). Anal. Calc. for C₁₁H₂₂N₄O₃Cu (321.86): C, 41.05; H, 6.89; N, 17.41. Found: C, 40.75; H, 7.22; N, 17.65%. FT-IR spectrum (KBr, selected peaks, cm⁻¹): v = 3461 (v_{OH}), 2927 (v_{CH}), 1586 ($v_{C=0}$). Conductivity (DMF, ~1 mM solution, 298 K): $\Lambda_{\rm M} = 12 \,\Omega^{-1} \,{\rm cm}^2 \,{\rm mol}^{-1}$. UV–Vis spectrum [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)] (in DMF): 454 (sh, 115), 505 (145), 568 (sh, 125). UV–Vis spectrum $[\lambda_{max}, nm (\varepsilon, M^{-1} cm^{-1})]$ (in CH₃CN): 484 (sh, 90), 570 (110). UV–Vis spectrum [λ_{max} , nm $(\varepsilon, M^{-1} \text{ cm}^{-1})]$ (in MeOH): 542 (495). MS (EI⁺, *m/z*): Calc. for C₁₁H₂₂N₄O₃Cu 321.86. Found: 322.14 ([Cu(L¹)(H₂O)]+H⁺). μ_{eff} (CH₃CN, 298 K) = 1.94 μ_{B} .

2.5.3. $[Ni(L^2)]$ (**3**)

The ligand H_2L^2 (0.10 g, 0.344 mmol) was dissolved in MeOH (5 mL) and treated with solid NaOH (0.03 g, 0.758 mmol) under magnetic stirring. A solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.125 g, 0.344 mmol) dissolved in MeOH (6 mL) was added drop-wise to the ligand solution. The resulting orange-yellow solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the crude compound was isolated after washing with diethyl ether. The recrystallization was achieved by dissolving the crude compound in MeCN and diffusing diethyl ether. This afforded orange crystalline product that was filtered, washed with diethyl ether and dried under vacuum. The compound **3** was found to co-crystallize with one equivalent of NaClO₄. The presence of NaClO₄ was established by the microanalysis results. FT-IR spectrum, and conductivity measurement. It may also be noted that several attempts gave the identical observation. Yield: 0.08 g (67%). Anal. Calc. for C₁₅H₂₆N₄O₉ClNiNa (including 3H₂O and 1NaClO₄, 523.52): C, 34.41; H, 5.01; N, 10.70. Found: C, 34.12; H, 4.96; N, 10.72%. FT-IR spectrum (KBr, selected peaks, cm^{-1}): v = 3425 (v_{OH}) , 2925 (v_{CH}) , 1618, 1581 $(v_{C=0})$, and 1091 (v_{CIO4}) . Conductivity (DMF, $\sim 1 \text{ mM}$ solution, 298 K): $\Lambda_{\rm M} = 38 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV–Vis spectrum [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)] (in CH₃CN): 450 (160), 238 (8900). UV–Vis spectrum [λ_{max} , nm (ε , M⁻¹ cm⁻¹)] (in DMF): 282 (7520), 306 (4020), 380 (160), 458 (140). MS (EI⁺, m/z): Calc. for C₁₅H₂₀N₄O₂Ni 347.04. Found: 347.22 ([Ni(L²)+H⁺]). ¹H NMR spectrum (400 MHz, DMSO- d_6 , 25 °C]: δ = 2.45 (s, 3H, -CH₃), 2.51 (s, 3H, --CH₃'), 2.63 (m, 2H, -CH₂, H^b), 2.91 (d, 1H, -CH₂C(O)-, H^d), 2.98 (d, 1H, -CH₂C(0)-, H^e), 3.41 (d, 1H, -CH₂-, H^f), 3.62 (m, 2H, -CH2-, H^c), 3.82 (d, 1H, -CH2C(O)-, H^{e'}), 3.90 (d, 1H, -CH2C(O)-, H^{d'}), 4.48 (d, 1H, -CH₂-, H^f), 6.74 (m, 1H, H^g), 6.96 (m, 2H, H^h), 7.77 (m, 2H, Hⁱ) ppm. ¹³C NMR spectrum (100 MHz, DMSO-d₆, 25 °C]: $\delta = 45.79$ (-CH₂-), 46.48 (-CH₃), 47.42 (-CH₃), 58.12 (-CH₂C(O)-), 58.84 (CH₂C(O)-), 66.06 (-NCH₂-), 121.10 (Ar-k), 123.37 (Ar-n), 125.95 (Ar-m), 128.65 (Ar-l), 132.59 (Ar-j), 142.18 (Ar-i), 173.19 (C=O), 175.36 (C=O) ppm.

2.5.4. $[Cu(L^2)]$ (4)

This compound was synthesized following the procedure for complex **2** with following reagents: H_2L^2 (0.10 g, 0.344 mmol), NaH (0.018 g, 0.758 mmol), CuCl₂ (0.046 g, 0.344 mmol). The product was isolated as blue colored powder. Recrystallization was achieved by diffusing diethyl ether to a DMF solution of the crude product at room temperature. Yield: 0.076 g (62%). *Anal.* Calc. for C₁₅H₂₅N₄O_{4.5}Cu (including 2.5H₂O): C, 45.39; H, 6.35; N, 14.12. Found: C, 45.47; H, 6.10; N, 14.31. FT-IR spectrum (KBr, selected peaks, cm⁻¹): ν = 3401 (ν _{OH}), 2923, 2860 (ν _{CH}), 1562 (ν _{C=0}). Conductivity (DMF, ~1 mM solution, 298 K): Λ _M = 8 Ω ⁻¹ cm² mol⁻¹. UV–Vis spectrum [λ _{max}, nm (ε , M⁻¹ cm⁻¹)] (in DMF): 570 (180), UV–Vis spectrum [λ _{max}, nm (ε , M⁻¹ cm⁻¹)] (in CH₃CN): 560 (280). μ _{eff} (CH₃CN, 298 K) = 1.97 μ B.

2.5.5. $[Ni(L^3)]$ (5)

This compound was synthesized following the procedure for complex **2** with following reagents: H_2L^3 (0.07 g, 0.23 mmol), NaH (0.013 g, 0.55 mmol), NiCl₂ (0.03 g, 0.24 mmol). The filtrate was concentrated under reduced pressure to one fourth of its original volume and diethyl ether was added to precipitate the crude product as orange red powder. Recrystallization was achieved by diffusing diethyl ether to a CH₂Cl₂ solution of the crude product at 5 °C. Yield: 0.058 g (69%). *Anal.* Calc. for C_{15.5}H₂₃N₄O₂ClNi (including 0.5CH₂Cl₂): C, 47.55; H, 5.92; N, 14.31. Found: C, 47.76; H, 6.09; N, 14.46%. FT-IR spectrum (KBr disk, selected peaks,

cm⁻¹): 2949, 2782 (ν_{CH}), 1618, 1587 ($\nu_{C=0}$). Conductivity (DMF, ~1 mM solution, 298 K): $\Lambda_{M} = 10 \ \Omega^{-1} \ cm^{2} \ mol^{-1}$. UV–Vis spectrum [λ_{max} , nm (ε , M⁻¹ cm⁻¹)] (in DCM): 558 (sh, 100), 470 (210), 350 (570). UV–Vis spectrum [λ_{max} , nm (ε , M⁻¹ cm⁻¹)] (in CH₃CN): 555 (sh, 790), 470 (170), 340 (450). UV–Vis spectrum [λ_{max} , nm (ε , M⁻¹ cm⁻¹)] (in DMF): 550 (sh, 730), 470 (140), 340 (420). ¹H NMR spectrum (400 MHz, DMSO- d_6): δ 2.65 (12H, d, – CH₃ and –CH₃'); δ 3.05 (2H, s, –CH₂C(O), H^c); δ 3.40 (2H, s, –CH₂C(O), H^d); δ 3.80 (2H, s, –CH₂–, H^e); δ 6.75 (1H, t, J = 6.6 H_z, H^h); δ 6.90 (1H, d, J = 6.9 H_z, H^g); δ 7.05 (1H, t, J = 7.8 H_z, H^g); δ 7.45 (1H, d, J = 7.8 H_z, H^f) ppm. ¹³C NMR spectrum (100 MHz, DMSO- d_6 , 25 °C): δ = 46.69 (C_e), 51.2 (C_{a'}), 46.69 (C_a), 73.58 (C_{b'}), 74.41 (C_b), 126.61 (C_h), 130.98 (C_{g'}), 131.66 (C_g and C_f), 139.41

2.5.6. $[Cu(L^3)]$ (**6**)

 $(C_{d'})$, 148.41 (C_{d}) , 176.40 $(C_{c'})$, 177.24 (C_{c}) ppm.

This compound was synthesized following the procedure for complex **2** with following reagents: H_2L^3 (0.15 g, 0.51 mmol), NaH (0.028 g, 1.1 mmol), CuCl₂ (0.06 g, 0.51 mmol). The product was isolated as blue colored powder. Recrystallization was achieved by diffusing diethyl ether to a CH₂Cl₂ solution of the crude product at 5 °C. Yield: 0.13 g (72%). *Anal.* Calc. for C_{15.5}H₂₃N₄O₂ClCu (including 0.5CH₂Cl₂): C, 46.97; H, 5.85; N, 14.13. Found: C, 47.14; H, 5.74; N, 14.37%. FT-IR spectrum (KBr disk, selected peaks, cm⁻¹): v = 2981, 2888 (v_{CH}), 1601, 1583 ($v_{C=0}$). Conductivity (DMF, ~1 mM solution, 298 K): $A_M = 14 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV–Vis spectrum [λ_{max} , nm (ε , M⁻¹ cm⁻¹)] (in CH₃CN): 540 (190), 400 (310). UV–Vis spectrum [λ_{max} , nm (ε , M⁻¹ cm⁻¹)] (in DMF): 550 (150), 410 (250). μ_{eff} (CH₃CN, 298 K) = 1.89 μ_{B} .

3. Results and discussion

3.1. Ligand design and synthesis

All three ligands H_2L^1 , H_2L^2 and H_2L^3 have been designed to provide two N_{amide} and two N_{amine} coordinations to the metal center in an identical donor environment (Scheme 2). While ligands H_2L^1 and H_2L^2 are macrocyclic in nature, the ligand H_2L^3 is an openchain analogue. Interestingly, ligands H₂L² and H₂L³ are originated from 2-aminobenzyl amine and thus a flexible -CH₂- group (with sp³ carbon center) separates two amide functionalities. Inclusion of this group will induce asymmetric coordinations from both amide donors and may also interrupt the electronic communication between the N_{amidate} fragment and o-phenylene ring. All three ligands were synthesized in two steps in good overall yield. The FT-IR spectra of the ligands show the v_{N-H} stretching frequency in the range of 3230–3250 cm⁻¹ and the $v_{C=0}$ frequency is in the range of 1665–1685 cm⁻¹ [79]. The asymmetry in ligands H_2L^2 and H₂L³ is clearly visible by the observation of different chemical shifts for the methyl and methylene groups in the NMR spectra.

3.2. Synthesis and characterization of metal complexes

The nickel and copper complexes (Scheme 3) were synthesized by treating the deprotonated form of ligand with the necessary metal salt. The usual work up and recrystallization (vapor diffusion of diethyl ether to CH₃CN or DCM solution of the crude product) afforded highly crystalline product in moderate yield. The solution conductivity [80] confirms the non-electrolytic nature for all complexes, whereas the elemental analysis results authenticate the purity of the bulk samples. In the FT-IR spectra, the absence of v_{N-H} stretching and the observed bathochromic shift for $v_{C=0}$ (compared to free ligand) validate the involvement of



Scheme 3. Synthesized metal complexes.

deprotonated N_{amidate} group in the bonding [79]. In case of complex **2**, coordinated water molecule clearly shows the v_{O-H} stretching at 3461 cm⁻¹; whereas few complexes also have water as the solvent of crystallization which absorbs in the region of 3369–3425 cm⁻¹. The solution magnetic moment [73,74] for the complexes **2** (1.94 μ_B), **4** (1.97 μ_B), and **6** (1.89 μ_B) clearly support the monomeric nature of the complexes as the magnetic moment values were falling in the range typically observed for the Cu(II) ion in a magnetically dilute environment [65,70].

3.3. Molecular structures

3.3.1. Crystal structure of complex 2

The molecular structure of complex **2** is shown in Fig. 1 whereas the selected bond lengths and angles are provided in Table 2. The Cu(II) ion adopts a distorted square-pyramidal geometry where ligand constitute a N₄ basal plane and a water molecule serves as the fifth ligand. The Cu(II) ion is coordinated by two deprotonated N_{amide} (average: 1.931 Å) and two neutral N_{amine} atoms (average: 2.064 Å). The Cu-N_{amide} bond distances are shorter by ca. 0.13 Å than the Cu-N_{amine} bond distances (Table 2). This difference of 0.13 Å may be attributed to the anionic coordination from the deprotonated amidate nitrogen atoms compared to the neutral



Fig. 1. Thermal ellipsoidal (40% probability) representation of complex $[Cu(L^1)(H_2O)]$ (2). The atoms C7, C8, C9, and C10 were occupying two crystallographically independent positions and only the atoms with site occupancy factor higher than 0.5 are shown for clarity. The hydrogen atoms are omitted for clarity.

Table 2

Selected bond lengths and bond angles for complexes $[Cu(L^1)(H_2O)]$ (2) and $[Ni(L^3)]\text{-}CH_2Cl_2$ (5).

$[Cu(L^1)(H_2O)]$ (2)		$[Ni(L^3)] \cdot CH_2Cl_2$ (5)	
Bond lengths (Å)			
Cu-N1	1.921(3)	Ni-N1	1.862(2)
Cu-N2	1.941(3)	Ni-N2	1.888(2)
Cu-N3	2.071(3)	Ni-N3	1.993(2)
Cu-N4	2.057(4)	Ni-N4	1.998(2)
Cu-03	2.243(3)		
Bond angles (°)			
N1-Cu-N2	94.01(1)	N1-Ni-N2	91.03(10)
N1-Cu-N3	151.2(1)	N1-Ni-N3	84.01(10)
N1-Cu-N4	84.4(1)	N1-Ni-N4	169.70(11)
N2-Cu-N3	84.4(1)	N2-Ni-N3	170.56(10)
N2-Cu-N4	158.2(1)	N2-Ni-N4	83.87(10)
N3-Cu-N4	86.7(1)	N3-Ni-N4	102.24(10)
03-Cu-N1	110.64(13)		
03-Cu-N2	102.45(12)		
O3-Cu-N3	97.72(13)		
03-Cu-N4	98.46(12)		

amine nitrogen donors. The N_{amine}–Cu–N_{amine} bond angle (86.70°) is ca. 7° smaller than the N_{amide}–Cu–N_{amide} angle (94.00°) which is most likely due to the involvement of five- and six-membered chelate rings, respectively. The coordinated water molecule forms a Cu–O_{water} bond length of 2.243 Å. The Cu(II) ion is displaced by 0.431 Å from the N₄ equatorial plane towards the coordinated water molecule. The geometry around the Cu(II) ion is distorted square-pyramidal as the τ value [81], which is an indication of the distortion of the five-coordinate geometry towards square-pyramidal (τ = 0) or trigonal bipyramidal (τ = 1), is 0.116.

The solid-state packing of complex **2** is quite interesting where hydrogen atoms of the coordinated water molecule are engaged in connecting individual molecules together. The first hydrogen atom (H3A) of the coordinated water molecule (O3) makes a hydrogenbond with the O_{amide} (O1) group of the neighbor molecule resulting in the generation of a chain (Fig. 2a). The second hydrogen atom (H3B) of the coordinated water forms a hydrogen-bond with the O_{amide} (O2) group from the adjacent chain thus connecting two chains together (Fig. 2b). The heteroatom separations, O3…O1 and O3…O2 were found to be 2.720 and 2.713 Å, respectively.

3.3.2. Crystal structure of complex 5

The unit cell of complex 5 contains a monomeric unit and a CH₂Cl₂ as the solvent of crystallization. The molecular structure of complex 5 is presented in Fig. 3 whereas Table 2 contains the bond distances and angles. The crystal structure shows that the deprotonated ligand, $[L^3]^{2-}$ is holding the Ni(II) ion in a somewhat distorted square-planar environment. The Ni(II) ion is coordinated by two deprotonated N_{amide} and two neutral N_{amine} atoms. The average Ni–N_{amide} distance (1.870 Å) is shorter than the average Ni-N_{amine} distance (1.996 Å) by 0.13 Å. A similar observation has been noted for complex 2 as well as several structurally characterized complexes from our laboratory as shown in Scheme 1 [64-71]. Further, the Ni-N_{amide} distances for complex 5 are bit longer than that of similar nickel complexes as shown in Scheme 1. This observation suggests that the inclusion of the flexible methylene group leads to weaker donor capacity of the amidate fragments. For comparison, structurally characterized Ni(II) complexes D and P (Scheme 1) show the Ni-Namide distances in the range of 1.801-1.845 Å [64,66]. The Ni(II) ion is optimally placed within the N₄ basal plane with the deviation of only 0.008 Å. Notably, the displacement of Ni(II) ion from the N₄ basal plane is 0.126 and 0.072 Å for complexes **D** and **P**, respectively [64,66]. This comparison suggests that the inclusion of methylene group in the ligand caused the expansion of chelate ring and resulted in



Fig. 2. (a) Linear 1D chain formation in complex **2** via hydrogen bonding of O_{amide} atom with hydrogen atoms of H_2O molecule attached to the metal center. (b) Chain structure extended along two-dimension via hydrogen bonding; view along *b*-axis.



Fig. 3. Thermal ellipsoidal (50% probability) representation of complex $[Ni(L^3)]$ -CH₂Cl₂ (5). The solvent molecule and hydrogen atoms are omitted for clarity.

the optimal placement of metal ion within the N₄ basal plane. Around Ni(II) center, theN_{amide}–Ni–N_{amide} bond angle is 91.03° whereas theN_{amine}–Ni–N_{amine} bond angle is 102.24°. Two lateral five-membered chelate planes NiN₁C₄C₃N₃ and NiN₂C₁₂C₁₃N₄ make an angle of ca. 16° with each other and suggest the relative twisting of these two planes. In addition, the methylene fragment (atom C5) is displaced by 0.706 Å out of the N₂C₁₁C₆N₁Ni plane that is part of six-membered chelate ring.

The CH_2Cl_2 molecules present in the unit cell stitch together the mononuclear units resulting in the formation of a chain running along the *bc* plane (Fig. 4). The O_{amide} atoms O1 and O2 interact

with the hydrogen atoms of the CH_2Cl_2 molecule via hydrogen bonding. Further, one of the Cl atoms of the CH_2Cl_2 molecule interacts with the hydrogen atom of the methylene group of the complex. In addition, there are several weak $CH \cdots O$ interactions between the hydrogen atoms of the methyl groups and O_{amide} atoms. Several such interactions connect two individual chains in the *bc* plane if viewed along the *a* axis (Fig. S1, Supporting Information).

3.4. NMR spectral studies for nickel complexes

To investigate the solution state structure of Ni(II) complexes **1**, **3**, and **5**, their ¹H and ¹³C NMR spectral studies were performed (Figs. S2–S6, Supporting Information). In these complexes, the Ni(II) ion is in square-planar geometry leading to a diamagnetic ground state. Assignment of the peaks has been made through consideration of the relative peak area and comparison to that of free ligand. The NMR spectra also prove that the metallation occurred with the fully deprotonated form of the ligand as the peaks corresponding to N–H_{amide} group of the ligand were absent.

For complex **1**, the twisting of $-CH_2CH_2-$ fragment of the *N*,*N*'-dimethylethylenediamine resulted in different chemical environment of the protons attached which were observed as multiplets at 1.98 and 3.22, respectively (labeled as *e* and *f*). The multiplet observed in the up-field region is characteristic of the $-CH_2-$ group (*a* and *a'* protons) of the trimethylene part in a chair conformation [63,82,83]. In the present case, their relative order ($\delta_{ax} < \delta_{eq}$) and separation are similar to those of other macrocyclic complexes [84,85] and six-membered organic rings [86]. Further, the trimethylenediamine fragment of the ligand is forming a six-membered chelate ring and is in a chair conformation and the axial protons (*b'*) are slightly de-shielded as compared to the equatorial protons (*b*). Two sets of signals (labeled as *b* and *b'*) were observed



Fig. 4. Linear 1D chain formation in complex 5 via hydrogen bonding of (a) O_{amide} atom with hydrogen atoms of CH₂Cl₂ molecule and (b) chlorine atom of CH₂Cl₂ molecule with hydrogen atoms of methylene fragment of the complex; view along the *a*-axis.

as doublet and triplet at 2.30 and 2.34 with the geminal coupling constant $I(H^bH^{b'})$ of ca. 12.3 Hz. Another interesting aspect of the proton spectrum was the observation of the AB-type geminal coupling between the protons attached to the $-C(O)CH_2$ - fragment [63-65,82,83]. The signals for the pair of protons from the - $C(O)CH_2$ - fragment (*c* and *d*) were found to appear at 2.48 and 3.65 ppm with the geminal coupling constant, $I(H^dH^e)$ of 14.85 Hz. The observation of the AB-type coupling suggests the rigid nature of the macrocyclic ligands that places protons *c* and *d* in different chemical environment. In general, the proton NMR spectra of the transition metal complexes of aza-macrocyclic ligands are complicated due to the *frozen* conformation of the chelate rings and the spectrum of the present complex is no exception [63-65,82,83]. Interestingly, in contrast to complex proton NMR spectrum, the ¹³C NMR spectrum of this complex was simple and displayed the signals at their respective positions.

The proton NMR spectrum of complex **3** is quite complicated since the complex as a whole is asymmetrical in nature (Fig. S3, Supporting Information). In this case a number of coupling between various protons is clearly observable. The $-C(O)CH_2$ - fragments labeled as (d/d' and e/e') and the $-CH_2$ - group labeled as f and f display AB-type coupling [63–65,82,83]. Thus, three sets of doublet at 2.98 and 3.82 ppm for e/e'; 2.91 and 3.90 ppm for d/d'; 3.41 and 4.48 ppm for f/f were observed with coupling constant $J(H^eH^{e'})$, $J(H^dH_{d'})$ and $J(H^fH^{f'})$ of ca. 15.90, 15.45 and 16.05 Hz, respectively. Further, the N–CH₃ groups were observed at two different positions (2.45 and 2.51 ppm) due to the asymmetric nature of complex. Similarly, the –CH₂CH₂- fragment of *N*,*N'*-dimethyleth-ylenediamine, displays two sets of signals at 2.63 and 3.62 ppm as multiplets (labeled as *b* and *c*). The proton NMR spectrum could only be interpreted after carrying out the 2D-correlation,

DEPT-135 and APT spectra along with the ¹³C NMR spectra. All these spectra are shown in Figs. S3, S5, and S6 (Supporting Information). APT was used to differentiate CH₂ signals from the CH and CH₃ signals where methine (CH) and methyl (CH₃) signals appear in negative mode and the quaternary (C) and methylene (CH₂) signals in positive mode [86]. The APT spectrum shows that the carbon atoms labeled as a, a' l, m, n and k resonate in the negative mode for CH_3 and CH, while the carbon atoms labeled as b, c, d, g, i, j, e and f for CH_2 and C resonate in the positive mode. Similarly, DEPT-135 yielded the CH and CH₃ signals in positive mode and CH₂ in negative mode whereas the carbons labeled as *i*, *j*, *e* and *f* are absent due to quaternary nature. In the ¹³C NMR spectrum of the complex **3**, 14 carbon signals corresponding to each carbon in the complex are clearly visible except for the -CH₂CH₂- fragment which coincidently resonate at the same position (Fig. S3).

The proton NMR spectrum of complex **5** is simple due to nonmacrocyclic nature of the complex (Fig. S4, Supporting Information). For this complex, the methyl groups (CH₃ and CH₃') are coincidentally resonating at 2.65 ppm. The methylene group proton *e* appeared at 3.8 ppm while the methylene protons of $-CH_2C(O)$ group (protons *c* and *d*) were observed at 3.05 and 3.40 ppm due to non-equivalent nature. The ¹³C NMR spectrum of this complex is quite straightforward and supports the suggested asymmetric structure of the compound.

3.5. EPR spectral studies for copper complexes

To further understand the geometry around the metal ion in copper complexes, X-band EPR spectra were recorded as polycrystalline solid and in frozen DMF solution at 120 K (Figs. 5 and S7–S9, Supporting Information). The powder EPR spectrum of complex 2 strongly justifies the square-pyramidal geometry observed crystallographically as an axial signal was noted (Fig. 5a). The g_{\parallel} and g_{\perp} values were obtained at 2.185 and 2.085, respectively. This spectrum is typical of a square-pyramidal Cu(II) ion with the unpaired electron in the $dx^2 - y^2$ orbital [87]. It is well documented in the literature that the tetragonally coordinated Cu(II) complexes show features with $g_{\parallel} > 2.1 > g_{\perp} > 2.0$ [87,88]. In the DMF solution, a similar axial spectrum was observed; however, superimposed hyperfine coupling was clearly observable (Fig. S7). The lowtemperature powder spectra for complexes 4 and 6 displayed isotropic signal with large ΔH_{p-p} values (90–115 G). The isotropic g values were found to be 2.106 and 2.120 for complexes 4 and 6, respectively. In contrast, frozen solution EPR spectra were clearly anisotropic with the superimposition of hyperfine coupling from the copper nucleus (Fig. 5b, S8 and S9).

3.6. Absorption spectral studies

The Ni(II) complexes **1**, **3** and **5** are deep yellow to orange in color whereas Cu(II) complexes **2**, **4** and **6** were purplish-blue to deep blue. The absorption spectra of all complexes were studied in different solvents such as DMF, DCM and CH₃CN. The λ_{max} as well as other prominent features were found to remain invariant to change in solvent polarity or the coordinating ability. In addition, there is no change in the spectral features of the complexes (except complex **2**) on addition of potential axial ligands such as Cl⁻, pyridine, and 4-dimethylaminopyridine. These results strongly suggest that most complexes retain their four-coordinate



Fig. 5. EPR spectra of (a) complex **2** in the polycrystalline state at 120 K and (b) complex **6** in DMF at 120 K.



Fig. 6. UV-Vis spectra of Ni^{II} complexes 1 (--), 3 (---) and 5 (...) in CH₃CN.

square-planar geometry in the presence of various potential ligands. The representative spectra in CH_3CN for Ni(II) and Cu(II) complexes are shown in Figs. 6 and 7, respectively.

For nickel complexes, an absorption maximum was obtained between 450 and 470 nm with low extinction coefficient value. For complex **5**, however, the absorption maximum is accompanied with a low-energy shoulder at ca. 555 nm. These absorption bands clearly point towards the square-planar geometry in the solution as also seen for our earlier Ni(II) complexes [64–67,69,70] as well as literature examples [89–91]. For a diamagnetic Ni(II) ion with d^8 electronic configuration in a square-planar environment, three transitions are expected: from four lower-lying fully occupied d orbitals to the upper empty *d* orbital [41,42]. However, the lower orbitals are often so close in energy that individual transitions to the upper *d* orbital is indistinguishable and that results in a single band [41,42] as noted for the present complexes. Comparison of the λ_{max} values for nickel complexes shows almost identical ligand field strength in all cases albeit a somewhat distorted donor environment in case of complex 5. The reason can be well understood in terms of higher flexibility in complex 5 as compared to rigid macrocyclic complexes 1 and 3.

For copper complexes, the λ_{max} was observed as a broad feature between 540 and 570 nm with ε values in the range of 100–280 M^{-1} cm⁻¹. These low-energy bands are typical *d*–*d* transition for a



Fig. 7. UV-Vis spectra of Cu^{II} complexes 2 (-), 4 (---) and 6 (...) in CH_3CN .

Cu(II) ion in a tetragonal environment and actually consists of three individual transitions $({}^{2}B_{1g} \rightarrow {}^{2}A_{1g}; {}^{2}B_{1g} \rightarrow {}^{2}B_{2g};$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{1g}$ in D_{4h} symmetry) [41,42]. The complex **2** being square-pyramidal (cf. crystal structure of complex **2**) showed a broad peak and underlying features are clearly noticeable. Interestingly for this complex, a shift in the λ_{max} was noticed when the spectra were recorded in different solvents; for example, the λ_{max} changed from 570 nm in CH₃CN to 542 nm in MeOH to 505 nm in DMF. These experiments point out that the axial position occupied by the coordinated water molecule (cf. crystal structure of complex **2**) is displaced by the solvent molecule.

3.7. Electrochemical studies

The cyclic voltammetric (CV) and controlled potential electrolysis (coulometry) studies were performed for all complexes to investigate the extent of stabilization of M^{3+} state as well as the possible ligand oxidation. In addition, these results may also help in understanding the accessibility of higher oxidation states and the effect of ligand architecture on the redox potential. Reversible, quasi-reversible and irreversible responses were observed when the CV studies were performed in CH₃CN on the glassy carbon or platinum working electrode in the potential range of 0.2–2.0 V (Figs. 8–10).

3.7.1. Nickel complexes

The complex **1** showed only one quasi-reversible oxidative response at 0.79 V with peak-to-peak separation (ΔEp) of 120 mV. A single oxidative response is expected for this complex as the ligand, being redox innocent, is not involved in electron transfer process [64]. The coulometric experiment confirmed the one-electron nature of this response. For this complex, the oxidized species $[1^{ox}]^+$ was generated after oxidation at 1.0 V that resulted in the formation of a green species. This species displayed new absorption spectral features at 595, 475, and 385 nm (Fig. S10a, Supporting Information). For reference, complex **1** showed only single transition at 470 nm. Notably, the spectral features for the oxidized species $[1^{ox}]^+$ are similar to that of species $[A^{ox}]^+$ supported with 12-membered aliphatic-based macrocyclic ligand (Scheme 1) [64].

Complexes **3** and **5** exhibited two consecutive oxidative processes as both metal and the attached ligand take part in the redox process. In case of complex **3**, the first oxidative response was irreversible with E_{pa} of 0.84 V while the second response is reversible in nature with $E_{1/2}$ value of 1.34 V ($\Delta Ep = 70$ mV). In case of complex **5**, the first oxidative response is reversible ($E_{1/2} = 0.85$ V) with



Fig. 8. Cyclic voltammograms of Ni(II) **1** (-) and Cu(II) **2** (\cdots) complexes in CH₃CN. Complex \sim 1 mM solution; TBAP as supporting electrolyte \sim 100 mM; platinum working electrode, Pt wire auxiliary electrode; scan rate = 100 mV/s.



Fig. 9. Cyclic voltammograms of Ni(II) **3** (–) and Cu(II) **4** (…) complexes in CH₃CN. Complex ~1 mM solution; TBAP as supporting electrolyte ~100 mM; platinum working electrode, Pt wire auxiliary electrode; scan rate = 100 mV/s.



Fig. 10. Cyclic voltammograms of Ni(II) **5** (-) and Cu(II) **6** (\cdots) complexes in CH₃CN. Complex \sim 1 mM solution; TBAP as supporting electrolyte \sim 100 mM; platinum working electrode, Pt wire auxiliary electrode; scan rate = 100 mV/s.

peak to peak separation (ΔEp) of 100 mV whereas the second response is irreversible with E_{pa} value of 1.51 V. All these responses were one-electron in nature as confirmed by the controlled potential electrolysis experiments. For complexes 3 and 5, the first redox response (E_1) is suggested to be metal-centered leading to a Ni(III) state [64–66]. The second response, E_2 for both complexes **3** and **5** has been tentatively assigned as the ligand-based oxidation generating a cation radical [64–66]. The species [3^{ox}]⁺ was generated after setting the potential at 0.95 V that produced a brick-red solution. The absorption spectrum of this species shows two absorption maxima at 380 and 513 nm in addition to several weak features (Fig. S10b). The spectral features for this species are somewhat similar to our earlier Ni3+ species with macrocyclic ligands [64,65,71] as well as to that of Ni³⁺ species reported by Journaux and Ruiz-Garcia [89–91]. For complex 5, the electrochemical oxidation at the first oxidative response resulted in the generation of a reddish-brown solution of $[5^{ox}]^+$. This species displayed the absorption maximum at 780 nm and a shoulder at ca. 480 nm (Fig. S10c). Importantly, the absorption spectrum of species $[5^{ox}]^+$ is similar to that of $[\mathbf{P}^{\mathbf{ox}}]^+$ supported with an open-chain ligand (Scheme 1) [66]. Qualitatively, the oxidized species $[3^{ox}]^+$ was most stable compared to either $[1^{ox}]^+$ or $[5^{ox}]^+$. We postulate that the extra flexibility induced by the methylene spacer in $[5^{ox}]^+$ may have increased the distortion at the nickel center and diminished the possible delocalization of the unpaired spin accumulated on the Ni(III) ion; whereas in case of $[3^{ox}]^+$ the rigid macrocyclic nature of the ligand may have resisted the distortion introduced by the methylene fragment [64,65,71]. Moreover, such delocalization of the unpaired spin to the attached ligand is least feasible in $[1^{ox}]^+$ due to non-aromatic nature of the ligand.

3.7.2. Copper complexes

Complex 2 showed only one quasi-reversible oxidative response at 0.56 V with peak to peak separation (ΔEp) of 90 mV. As expected for a perfect innocent system, the single oxidative response is metal-based [64] as also noted for the nickel complex 1. In case of complexes 4 and 6, two quasi-reversible to irreversible electrochemical responses were observed. For complex 4, the first oxidative response is irreversible in nature with an E_{pa} value of 0.64 V while the second quasi-reversible response was noted at $E_{1/2}$ value of 1.24 V ($\Delta Ep = 110$ mV). For complex **6**, two irreversible responses (E_1 and E_2) appeared at 0.97 and 1.64 V, respectively. For complexes **5** and **6**, the first (E_1) and second (E_2) oxidative responses are tentatively assigned to be metal- and ligand-centered, respectively [64–66]. Both E_1 and E_2 redox processes were oneelectron changes as concluded by the coulometric studies. In case of copper complexes, the electrochemical oxidation at E_1 potential did not result in appreciable change in the absorption spectrum when compared to that of original Cu(II) complexes. This observation suggests that either these complexes are reluctant to oxidation or oxidation was accompanied with significant structural or geometrical changes that were not fully supported with the present ligand system.

It is worth mentioning here that the observed chemical irreversibility (during CV measurements) for some of the nickel and copper complexes suggests a possible chemical follow-up process centered on the complex. Such a process may lead to the decomposition of the complex as elegantly shown by Collins and co-workers [36–39] in several of their high-valent metal complexes supported with amide-based macrocyclic ligands. It would be interesting to explore the decomposition pathways of the metal complexes after electrochemical and/or chemical oxidation; however, is a matter of future studies.

3.7.3. Comparative redox chemistry

A comparative analysis of E_1 potentials for nickel complexes suggests that the Ni³⁺ state is evenly stabilized in all three cases. It could be concluded that the $Ni^{3+/2+}$ redox potentials primarily depend on the donor type and donor environment as in all three cases the Ni(II) ion is surrounded by two deprotonated Namide and two neutral Namine donors in a somewhat similar ligand framework. A further comparison of E_1 potentials for all complexes shows that the dianionic ligand framework is more suited to stabilize Cu^{3+} as compared to Ni³⁺ state since the E_1 potentials for copper complexes are ca. 200 mV less positive than the nickel complexes. However, a comparison of complexes 5 and 6 suggests that the potential for Cu(II) complex 6 is 120 mV more positive than the analogous Ni(II) complex 5. We believe that the flexible nature of open-chain ligand in these two complexes could support the geometrical change after oxidation to the M(III) state. Such a geometrical change is more prominent in case of copper complex and thus a large shift in the redox potential.

4. Conclusions

This work shows the synthesis and characterization of few mononuclear nickel(II) and copper(II) complexes with three

amide-based ligands H_2L^1 , H_2L^2 and H_2L^3 . The crystal structure analysis for representative complexes **2** and **5** substantiate that the ligand constitute a square-based basal plane around the metal center. The structural studies show that the Ni(II) complex **5** remains square-planar whereas the geometry in Cu(II) complex **2** is square-pyramidal with water molecule serving as the fifth ligand. The spectral studies support that the solid-state geometry for these complexes is retained in the solution. The electrochemical results suggest that the Ni^{3+/2+} and Cu^{3+/2+} redox couple primarily depends on the N₄ donors composed of two N_{amide} and two N_{amine} atoms. It was observed that the ligands H₂L¹ and H₂L² are better suited to stabilize the Cu(III) species whereas ligand H₂L³ is ideal for the stabilization of Ni(III) species. On the basis of electrochemical findings, transient Ni³⁺ species were generated *in situ* and characterized by the absorption spectroscopy.

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Appendix A. Supplementary material

CCDC 814925 and 814926 contain the supplementary crystallographic data for complexes **2** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.017.

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