The Effect of Ligand Architecture on the Structure and Properties of Nickel and Copper Complexes of Amide-Based Macrocycles^[‡]

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The present work demonstrates the influence of electron-donating and electron-withdrawing substituents on the structural, chemical and redox properties of nickel(II) and copper(II) complexes in a set of 12-membered macrocyclic ligands. Four macrocyclic ligands, H_2L^H , H_2L^{CI} , H_2L^{Me} , and H_2L^{OMe} , in their doubly deprotonated form, have been used to synthesize the Ni^{II} and Cu^{II} complexes. The crystallographic studies reveal that whereas the nickel ion is in an N₄ square-planar environment, the Cu^{II} complexes have a square-pyramidal geometry with an N₄ basal plane and the O_{amide} atom in the apical position. Furthermore, the Cu-N_{amide} bonds are shorter than the Ni–N_{amide} bonds. The Ni^{II} and Cu^{II} complexes are capable of undergoing one- and twoelectron oxidations that are most likely metal- and ligand-

Introduction

The importance of redox-active transition metal ions in metalloenzymes is an area of considerable research interest. The coordination chemistry of nickel and copper in variable oxidation states is particularly important in this context.^[1] The structure, spectroscopy and redox investigation of highvalent nickel and copper complexes has received much attention from inorganic chemists as biomimetic models or for potential use as catalytic oxidants.^[2] Interest in the redox chemistry of nickel and copper complexes has been further renewed due to the participation of such species in the redox catalytic cycle of several metalloenzymes.^[3,4] Thus, a good number of well-characterized high-valent nickel and copper complexes with diverse ligand types and coordination geometries are available,^[5,6] including the squareplanar nickel(III) and copper(III) complexes of amidatecontaining ligands from the groups of Margerum,^[7,8] Collins^[5,9] and Journaux.^[10] On the other hand, the participation of redox-active ligands adds a new dimension to the coordination and redox chemistry of the transition metal

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centered. The electrochemical results indicate that the Ni^{III/II} potentials are more positive than the Cu^{III/II} potentials. Electron-donating substituents on the ring shift the redox-potential value towards less positive values and better stabilize a higher oxidation state of the metal ion. The Ni^{III} and Cu^{III} species were generated in solution both electrochemically as well as chemically and are shown to have rich spectroscopic features. The absorption and anisotropic EPR spectra of the nickel complexes suggest that the Ni^{III} species is in a square-planar geometry. The spectroscopic data for the nickel(III) and copper(III) species bearing an OMe group on the ligand suggest a metal complex with a semiquinone-type ligand-based radical.

ion.^[11–13] In this category, the ligand system based on an ophenylenediamine skeleton containing additional nitrogen, oxygen and sulfur donors has shown quite interesting results.^[11–13] Thus, the redox non-innocence of the *o*-phenvlenediamine fragment $[NH(C_6H_4)NH]$ when coordinating to a metal ion has been a major focus of study.^[11-13] Extended conjugation of the *o*-phenylenediamidate fragment in a metal complex may alter its redox properties as it involves both metal- and ligand-based orbitals. In this regard, an investigation to assess the possible role of non-innocent ligands derived from o-phenylenediamine in the stabilization of the high-valent nickel complexes has been initiated by us recently.^[14,15] Our goal is to understand the factors that contribute towards the stability of metal ions in high oxidation states where both the metal center and the ligand can serve as electron reservoirs. The present study forms the basis of our earlier work on the coordination chemistry and redox investigation of nickel ions with amide-based macrocyclic ligands^[14] and their open-chain analogues^[15] (Scheme 1). These macrocyclic ligands and their open-chain analogues have been shown to stabilize +2 as well as +3(transiently) oxidation states of the nickel ion in a squareplanar geometry. Herein, we extend our earlier work on macrocyclic chemistry and present the synthesis of three new 12-membered macrocyclic ligands containing electronwithdrawing (Cl) and electron-donating groups (CH₃ and OCH₃). We then discuss the effect of such substituents on the structure, properties and redox chemistry of nickel and copper ions.

621

^[‡] Part 2: Electronic Effects. Part 1: Ref.^[14]

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Scheme 1. Ni^{II} complexes of macrocyclic and open-chain ligands reported by our laboratory.

Results and Discussion

Ligand Design: Emphasis on Electronic Effects

The ligands H_2L^H , H_2L^{Cl} , H_2L^{Me} and H_2L^{OMe} have been designed to subtly change the electronic character of the ophenylene ring directly attached to the amide groups. The design element originated from our earlier study,^[14] where we showed that out of four macrocyclic ligands used to synthesize Ni^{II} complexes A-D (Scheme 1), ligand H₂L^H stabilized the Ni^{III} state to a great extent. We reasoned that the proximity of the o-phenylenediamidate fragment to the nickel(III) ion in the complex C with H_2L^H helped to delocalize the unpaired electron density onto the ligand's π orbitals.^[14] This success with ligand H₂L^H prompted us to introduce electron-withdrawing (Cl) and -donating groups (CH₃ and OCH₃) onto the phenylene ring to gain a thorough understanding of the electronic effects on the relative stabilization of the M^{2+/3+} states. In addition, the present work compares the chemistry of nickel with that of copper to further delineate the effect of the ligand architecture on the physical and redox properties of the metal center. The ligands H_2L^H , H_2L^{Cl} , H_2L^{Me} , and H_2L^{OMe} were synthesized in a manner similar to that of the previously reported 12-membered macrocyclic ligands.^[14] The process involves two steps whereby the diamine is first converted into the respective bis(chloroacetamide) and then macrocyclized with a secondary amine to obtain the desired ligands. All new ligands were thoroughly characterized by various spectroscopic techniques and gave satisfactory microanalysis results.

Metal Complexes

 Ni^{II} complexes 1–3 and Cu^{II} complexes 4–7 were synthesized as follows: a dmf solution of the respective ligand was first deprotonated with NaH under N₂, and then the metal salt [NiCl₂ or Cu(OTf)₂] was added. Complexes 3 and 7 could be synthesized in better yield by treating an MeOH solution of the ligand H₂L^{OMe} with 2 equiv. of NaOH fol-

lowed by addition of the [M(H₂O)₆](ClO₄)₂ salt. The usual workup and recrystallization procedures afforded highly crystalline materials in moderate recrystallized yields (Scheme 2). All nickel complexes are deep yellow to orange in colour, whereas the copper complexes are blue, except for complex 7, which is dark green. The absence of a v_{N-H} stretching frequency in the FTIR spectra^[16] confirms the deprotonated nature of the amide ligands. Furthermore, the bathochromic shift in the $v_{C=O}$ stretching frequency observed for all complexes with respect to the free ligand further confirms that the deprotonated N_{amide} group is involved in coordination.^[14-16] Different shifts were noticed in the position of the $\nu_{C=O}$ stretches for the nickel (55 $\mbox{cm}^{-1})$ and copper complexes (70 cm⁻¹) with respect to the free ligand. This difference indicates different degrees of delocalization of the excess electron density on the deprotonated $N_{\mbox{amide}}$ atom into the NCO fragment for these complexes. Solution conductivity data^[17] confirmed the non-electrolytic nature of all metal complexes, and elemental analysis results authenticated the purity of the bulk samples. The solution-state magnetic moment was determined for copper complexes 4-7 by using Evans' NMR method.^[18] The room-temperature magnetic moments (μ_{eff}) in dmf were found to be 1.70, 1.80, 1.65 and 1.68 μ_B , respectively. These values are in the range for S = 1/2 in a magnetically dilute condition. A weak interaction between two copper(II) ions cannot, however, be ruled out if the solid-state 1D zig-zag chain structure (see below) is retained in solution.



Scheme 2. Synthesis of Ni^{II} and Cu^{II} complexes.

Crystal Structure Studies

Some representative nickel and copper complexes were structurally characterized. The coordination geometry around the nickel center is square-planar in complexes 1 and 2, whereas it is square-pyramidal for copper complexes 5 and 6. The metal ion is coordinated by two deprotonated N_{amide} atoms and two neutral N_{amine} atoms in the N_4 basal

plane in all cases, although the fifth coordination site in the copper complexes is occupied by an Oamide group from a neighboring molecule^[19] to form a 1D chain. The metal ion is surrounded by four five-membered chelate rings in all complexes.^[14] The bond angles formed by the lateral chelate rings about the metal center are close to the ideal value of 90° for a perfect square-planar complex. For nickel (copper) complexes, however, the bond angle involving two anionic N_{amide} atoms has a slightly smaller value of about 88° (84°), which is compensated by a slightly wider angle of 93° (approx. 90°) for the chelate ring involving the two N_{amine} atoms.^[14] For copper complexes, the bond angles involving the two N_{amide} and two N_{amine} atoms are around 4° narrower than in the nickel complexes. An interesting feature of all structures is the orientation of the CH₂CH₂ fragments of the amine part of the macrocyclic ligand, which adopts an envelope conformation similar to that in our earlier nickel complexes A-D (see Scheme 1).^[14] The lateral fivemembered chelate rings [C(O)CH2 fragment] in all complexes also adopt an envelope conformation.^[14] Both carbon atoms in these rings are present on the same side of the N_{amide}-Ni-N_{amine} plane, with a larger displacement of the carbon atoms connected to the amine nitrogen atoms. The methyl groups on the tertiary nitrogen centers are located on one side of the plane in all cases. This is in line with our earlier examples of Ni^{II} complexes A-D,^[14] although it is in contrast to a number of examples where the relative position of the N-H or N-R groups results in the presence of geometrical isomers.^[20]

Structure of [Ni(L^{Cl})] (1)

The molecular structure of complex 1 is shown in Figure 1. The average Ni-Namide bond length in this complex is 1.81 Å, and the average Ni–N $_{\rm amine}$ bond length is 1.90 Å.^[14] The difference of 0.1 Å between the two is due to the different coordination types (anionic for the deprotonated amide nitrogen atoms and neutral for the amine nitrogen donors).^[14] The phenyl ring, the two chlorine atoms and all four nitrogen atoms lie in a plane, with a maximum deviation from this plane of 0.06 Å for N4 and C2. Both carbonyl carbon atoms (C7 and C12) and the adjacent methylene carbon atoms (C8 and C11) also form a plane, which is almost parallel to the previously defined plane (dihedral angle 8°) and lies below it. The Ni atom lies 0.15 and 0.74 A above these two planes, respectively, thus giving the molecule a butterfly-like conformation. The Ni^{II} ion is thus exposed on one side and shows a weak coordination [3.319(1) Å] to Cl2ⁱ of a symmetry-related molecule (i = -x, -y + 1, -z + 1) to form a dimer in the bc plane (Figure S1) These Ni-Cl interactions are very weak, as can be seen from the Ni^{II}-Cl bond lengths of 2.053 Å in NiCl₂.^[21] The dimers are further strengthened by face-toface $\pi \cdots \pi$ interactions between the two phenyl rings, with a centre-to-centre distance of 3.715(2) Å. The phenyl ring, methyl, methylene and carbonyl carbon atoms together create a hydrophobic environment around the Ni^{II} ion and

keep the water molecule out of the coordination sphere of the metal atom, where it is maintained by various H-bonding interactions.



Figure 1. Molecular structure of complex 1 (thermal ellipsoids are drawn at the 50% probability level). Hydrogen atoms and water molecule have been omitted for clarity.

Extensive H-bonding involving the water molecule, carbonyl oxygen atoms, chlorine atoms and various carbon atoms (Table S1) forms a 3D H-bonded network. The water molecule O1W donates hydrogen bonds to carbonyl oxygen atoms O1 and O2 and accepts hydrogen bonds from methylene and methyl carbon atoms. The H-bonding interactions O1W-H2W···O2, C13-H13B···O2 and C9-H9B···O1W give rise to linear chains running parallel to the *a* axis, whereas C2-H2···Cl1 H-bonding interactions extend the structure diagonally in the *ab* plane to form planar sheets. These parallel sheets interact with each other through the above-mentioned Ni···Cl2 and π ··· π interactions and O1W-H1W···O1, C11-H11A···O1, C8-H8B···O2 and C10-H10B···N4 Hbonds to form an extended 3D network (Figure S2).

Structure of [Ni(L^{Me})] (2)

The crystal structure of complex **2** (Figure 2) shows that there are two crystallographically independent molecules, henceforth referred to as molecule 1 (with Ni1) and molecule 2 (with Ni2), in the unit cell. The Ni^{II} ion is coordinated by two N_{amide} and two N_{amine} atoms in an N₄ basal plane, with maximum deviations of 0.05 and 0.04 Å, respectively. The Ni^{II} ion lies 0.12 and 0.14 Å above these planes in molecule 1 and molecule 2, respectively. These square planes are also coplanar with their respective phenyl rings in both molecules (dihedral angles of 5.6° and 2.7°, respectively). The two molecules are, however, rotated with respect to each other, with an angle of 58° between the two square planes. The average Ni–N_{amide} bond length is 1.80 Å, and the average Ni–N_{amine} bond length is 1.90 Å in both molecules.^[14]

The crystal structure shows the formation of a 3D network arising from weak C–H···O-type H-bonding interactions within and between molecules 1 and 2. In molecule 1,



Figure 2. Molecular structure of complex 2 (thermal ellipsoids are drawn at the 50% probability level) showing two crystallographically independent molecules. Hydrogen atoms have been omitted for clarity.

the intermolecular C–H···O H-bonding interactions between methyl carbon atoms C13 and C14 and amide oxygen atoms O2 and O1, respectively, form a double helical chain running parallel to the *b* axis. Figure 3 shows one such chain. On the other hand, C24–H24B···O4 and C26– H26B···O4 H-bonding interactions within molecule 2 generate centrosymmetric dimers which are further joined to each other through C32–H32A···N5 hydrogen bonds to form zig-zag chains running parallel to the *a* axis (Figure 4). These two chains are further connected to each other through various other C–H···O H-bonding interactions (Figure S3, Table S2) to constitute a 3D H-bonded network.



Figure 3. Space-filling models showing the double helical chain in molecule 1 of complex 2: front view along the *a* axis (left) and side view (right). Only atoms which form part of the helical chain are shown.

Structure of [Cu(L^{Cl})] (5)

A perspective view of **5** is shown in Figure 5, and selected bonding parameters are given in Table 1. Each copper atom is coordinated by the O_{amide} atom to form a one-dimensional polymeric chain with an intramolecular Cu...Cu dis-



Figure 4. Centrosymmetric dimers in complex 2 formed by C24–H24B····O4 and C26–H26B····O4 H-bonding interactions in molecule 2. These dimers are further joined to each other through C32–H32A····N5 hydrogen bonds to form zig-zag chains running parallel to the a axis.



tance of 6.153(4) Å^[19] (Figure 6a). The square-pyramidal Cu^{II} ion is coordinated by two N_{amide} and two N_{amine} atoms in the basal plane, with the apical position being filled by the amide O atom from a neighboring complex [Cu-O(2) 2.214(3) Å]. This distance is around 0.14 Å shorter than the Cu-O_{amide} distances in a closely related system containing an open-chain, amide-based ligand.^[19] The distortion parameter τ , which is 0 for a perfect square-planar and 1 for a perfect trigonal-bipyramidal geometry,^[22] is 0.029, thus indicating a slightly distorted square-pyramidal geometry. The copper atom is displaced by 0.5089 Å from the N₄ basal plane towards the O_{amide} atom O(2). The Cu–O(2) bond is slightly bent off the perpendicular to the CuN₄ plane by 8.753°. The average Cu-Namide bond length is 1.912 Å, whereas the average Cu-Namine bond length is 2.044 Å. The difference of 0.13 Å is due to the anionic coordination of the deprotonated amide nitrogen atoms compared to the neutral amine nitrogen donors. The average Cu-N_{amide} distance is around 0.1 Å longer than the average Ni-N_{amide} distance (in complexes 1 and 2), whereas the Cu-N_{amine} distance is around 0.16 Å longer than the Ni–N_{amine} bond lengths. The average Namide-Cu-Namide and Namine-Cu-N_{amine} angles are around 4° and 2°, respectively, smaller



Figure 5. Molecular structure of complex 5 (thermal ellipsoids are drawn at the 50% probability level). Hydrogen atoms have been omitted for clarity.

than in analogous Ni^{II} complexes. These comparative parameters indicate that the copper ion protrudes further out of the basal plane in this 12-membered complex than in analogous nickel complexes.

Structure of [Cu(L^{Me})] (6)

The molecular structure of 6 shows that the asymmetric unit contains two independent molecules. In contrast to the structure of 5. each dinuclear unit repeats rather than the mononuclear unit. One such dinuclear unit is shown in Figure 7. Each copper atom is coordinated by an O_{amide} atom to generate a one-dimensional polymeric chain with an intramolecular Cu···Cu distance of 5.610(9) Å (Figure 6b).^[19] The coordination environment around each Cu^{II} ion is distorted square-pyramidal, with an N4 basal plane and Oamide axial donor. The corresponding distortion value τ is 0.140 [0.110 for the Cu(2) atom].^[22] The average Cu-N_{amide} distance is 1.92 Å and is 0.13 Å shorter than the average Cu-N_{amine} bond (2.052 Å). The average Cu-N_{amide} distance is 0.1 Å longer than the average Ni-Namide distance, whereas the Cu-N_{amine} distance is 0.16 Å longer than the Ni-N_{amine} bond length. The average N_{amide}-Cu-N_{amide} angle is about 4° smaller than the average N_{amide}-Ni-N_{amide} bond angle, whereas the $N_{amine}\mathchar`-Cu\mathchar`-N_{amine}$ bond angle is about 2° smaller than the N_{amine}-Ni-N_{amine} angle. This trend indicates the larger displacement of the copper ion in 12-membered macrocyclic systems out of the N₄ basal plane compared to nickel complexes. The other bonding parameters are similar to those for 5 and comparable with a similar crystallographically characterized system.^[19]

The amide oxygen atoms O1 and O3 coordinate to Cu^{II} ions at the apical position to form spiral coordination polymers running parallel to the *b* axis and diagonally across the *ac* plane. One such spiral chain is shown in Figure S4. Intermolecular hydrogen bonding involving solvent water and methanol molecules and the coordination polymer results in a very interesting and intricate crystal structure (Table S3). Water molecule O1W lies on the twofold axis of rotation and joins a pair of the above-mentioned spiral chains through hydrogen bonding via two symmetry-related

Table 1. Selected bond lengths []	Å1	and angles [°	l for	[Ni(L ^{Cl})]•H ₂ O (]	D. I	[Ni(L ^{Me})]	(2).	$[Cu(L^{Cl})]$	(5)	and	[Cu(L ^{Me})	1.2H2O·CH2OF	I (6).
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	[Ni(L ^{Cl})] (1)	[Ni(L ^{Me})] (2) ^[a]	$[Cu(L^{Cl})]$ (5)		[Cu(L ^{Me})] (6)	[b]
M1-N1	1.814(2)	1.793(8), 1.804(7)	1.911(4)	1.926(6)	Cu2–N5	1.929(6) ^[c]
M1-N2	1.897(2)	1.913(7), 1.914(7)	2.056(4)	1.929(6)	Cu2–N6	1.931(6) ^[c]
M1-N3	1.904(2)	1.904(8), 1.916(7)	2.214(3)	2.057(5)	Cu2–N7	$2.048(6)^{[c]}$
M1-N4	1.810(2)	1.824(7), 1.802(7)	1.913(4)	2.029(5)	Cu2–N8	2.043(6) ^[c]
M1-O	_	_	2.214(3)	2.172(6)	Cu2–O1	$2.170(5)^{[c]}$
N1-M1-N2	88.7(1)	89.9(3), 89.8(3)	85.0(1)	84.1(2)	N5-Cu2-N6	83.9(3) ^[c]
N3-M1-N4	89.7(1)	89.2(3), 89.0(3)	85.3(2)	90.0(2)	N5-Cu2-N8	85.4(3) ^[c]
N1-M1-N3	169.8(1)	174.5(3), 172.8(3)	151.0(1)	146.8(2)	N6-Cu2-N8	150.3(3) ^[c]
N2-M1-N4	171.1(1)	168.7(3), 168.5(3)	149.1(1)	154.7(2)	N5-Cu2-N7	$148.6(3)^{[c]}$
N1-M1-N4	87.5(1)	87.1(3), 87.2(3)	83.8(2)	85.8(2)	N6-Cu2-N7	86.1(3) ^[c]
N2-M1-N3	92.8(1)	93.0(3), 92.8(3)	89.8(1)	85.9(2)	N8-Cu2-N7	88.8(2) ^[c]

[a] There are two independent molecules in the asymmetric unit cell. Bonding parameters are reported for both molecules. [b] The repeat unit is an O-amide-bridged dimer. [c] Distances/angles are for the Cu2 atom.



Figure 6. Perspective views of the 1D polymeric chain in complexes 5 (a) and 6 (b). All hydrogen atoms have been omitted for clarity.



Figure 7. Molecular structure of complex 6 (thermal ellipsoids are drawn at the 50% probability level). Water molecules, methanol and hydrogen atoms have been omitted for clarity.

O2W water molecules. Each O2W water molecule acts as an H-bond donor to the carbonyl oxygen atom O3 and to the water molecule O1W as shown in Figure S5. The intermolecular H-bonding interaction O2W···O1W forms water trimers that hold two spiral chains together. Thus, each such pair of chains has a hydrophilic interior that leads to the formation of channels filled with water molecules running parallel to the *b* axis (Figure S5b). Furthermore, each amide oxygen atom O2 accepts a hydrogen bond from the methanol oxygen atom O5 (Figure S5a). The water trimers are further stabilized in the channels by O2W···O2W and some C-H···O H-bonding interactions. Various C-H···Oand C-H···N-type H-bonding interactions between amide oxygen atoms, nitrogen atoms and methyl, methylene and phenylene carbon atoms are further responsible for holding these pairs of chains together (Table S3) and result in a packing structure along the *b* axis (Figure S6).

It should be noted that the Cu^{II} complex of a closely related macrocyclic ligand (L¹) has been reported,^[23,24] although the metal ion has a square-pyramidal geometry with an N₄ basal plane and an apical water molecule. Extensive hydrogen bonding between the Cu^{II} complex and water molecules most likely prevents coordination to the O_{amide} group of the neighboring complex, as observed in our case. The average Cu–N_{amide} bond length in this complex is 1.926 Å, whereas the average Cu–N_{amine} bond length is 2.026 Å. The Cu–O_{water} bond length is 2.165 Å. The square-planar copper(II) complex of the corresponding 13membered ligand (L²)^[23,24] has Cu–N_{amide} and Cu–N_{amine} distances of 1.905 and 1.992 Å, respectively. Furthermore, the copper(II) complex containing an analogous openchain ligand^[19] (reported by us previously) also has a similar structure to those of complexes **5** and **6**, including the O_{amide} -bridged 1D chain. The average Cu–N_{amide}, Cu– N_{amine} and Cu – O_{amide} bond lengths in this complex are 1.935, 2.075, and 2.354 Å, respectively.^[19]

Spectral Studies

The absorption spectra of complexes 1-3 in CH₃CN are displayed in Figure 8. The Ni^{II} complexes are deep yellow to orange in color, and their spectra display distinct features for the four-coordinate square-planar Ni^{II} ion. Three transitions from the four lower-lying fully occupied d orbitals to the upper empty d orbital are expected for a diamagnetic Ni^{II} ion with d⁸ electronic configuration in a square-planar environment.^[10a,10b] However, these lower four orbitals are often so close together in energy that individual transitions to the upper d orbital cannot be distinguished. This results in a single transition in the absorption spectrum,^[10a,10b] as noted for the present complexes. Complexes 1-3 have very similar λ_{max} values (442–450 nm), thus indicating a similar environment created by the ligand around the Ni ion. It is important to mention here that complexes A-D also displayed a narrow range of absorption maxima (436-444 nm).^[14] The similarity observed between the absorption features of the nickel complexes is also reflected in their solid-state crystal structures (see above) and solution-state NMR spectra (see below). The high-energy features observed below 310 nm could tentatively be assigned as intraligand transitions.



Figure 8. UV/Vis spectra of Ni^{II} complexes in CH₃CN: 1 (-----), 2 (-----), and 3 (-----). Complex C (-----) is shown here for comparison.

Copper complexes 4–7 display a single band in the region 573–593 nm (Figure 9), with extinction coefficients (ε) in the range of 100–300 m⁻¹ cm⁻¹. This low-energy band is the typical d–d transition band of a Cu^{II} ion in a square-planar environment and actually consists of three individual d–d transitions (i.e. ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$, ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, and ${}^{2}B_{1g} \rightarrow {}^{2}E_{1g}$ in D_{4h} symmetry).^[10a,10b] The only exception is complex 7, which shows a second band at 430 nm with an extinction coefficient of around 1000 m⁻¹ cm⁻¹ that we tentatively as-

sign to charge transfer from OCH_3 to Cu^{II} . High-energy features below 310 nm are tentatively assigned as intra-ligand transitions.



Figure 9. UV/Vis spectra of Cu^{II} complexes in CH₃CN: 4 (-----), 5 (-----), 6 (-----).

In order to analyze the binding affinity of some potential ligands towards the metal ion, all complexes were titrated with Cl⁻, pyridine, or 4-(dimethylamino)pyridine. No change in the absorbance maxima was observed for any of the complexes, thus ruling out the binding of these ligands to the metal center. The spectra for copper complexes 4–7 were also recorded in a better coordinating solvent, such as dmf, although they displayed similar features to those in CH₃CN. Strain in the ring system is indicated by the high value of the extinction coefficient and the redshift of the absorption maxima for copper complexes with respect to nickel complexes. The Cu^{II} complex of ligand H₂L^{OMe} (7: $\lambda_{max} = 593$ nm; $\varepsilon = 300 \text{ m}^{-1} \text{ cm}^{-1}$) exhibits the greatest strain, whereas the least strain is observed for complex 4.

The solid-state EPR spectra (Figure S7) of copper complexes 4–7 at liquid-nitrogen temperature exhibit the typical axial spectra with $g_{\parallel} > g_{\perp}$.^[25] The g_{\parallel} and g_{\perp} values for complexes 4–7 were found to be 2.18 and 2.08, 2.15 and 2.06, 2.19 and 2.07, and 2.13 and 2.08, respectively. The observation of axial EPR spectra suggests anisotropy^[26] around the copper centre, which most likely arises from coordination of the O_{amide} atom from a neighboring molecule, as observed structurally (cf. crystal structures of **5** and **6**). Ruiz et al.^[10a,10b] have reported similar EPR spectra for a series of Cu^{II} complexes supported with oxamide-based tetradentate ligands. The room-temperature EPR spectra also display similar features, as shown in Figure S7.

To investigate the solution-state structures of the nickel complexes, their ¹H and ¹³C NMR spectra were recorded in [D₆]dmso (Figures S8 and S9 and Tables 2 and S4). All nickel complexes are diamagnetic with an S = 0 ground state, as highlighted by their sharp NMR spectra, which show only minor chemical-shift differences with respect to the free ligands. A comparison of the spectrum of complex $C^{[14]}$ with that of complexes 1–3 shows an up-field shift of around 0.39 ppm for the protons labeled f in the order $1 \rightarrow C \rightarrow 2 \rightarrow 3$.^[27] This reveals a higher electron density on the benzene ring with more electron-donating groups in the order Cl < H < Me < OMe. Interestingly, twisting of the -CH₂CH₂- fragment of the *N*,*N*'-dimethylethylenediamine

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Table 2. ¹H NMR spectroscopic data for Ni^{II} complexes [Ni(L^{CI})] (1), [Ni(L^{Me})] (2), [Ni(L^{OMe})] (3), and [Ni(L^H)] (C).^[a]



[a] Spectra recorded in [D₆]dmso. [b] Geminal coupling constant in Hz. [c] Ref.^[14]

part results in a different chemical environment for the protons attached to these carbon centers. Thus, two sets of H signals (labeled as a and c) are observed as multiplets at δ = 2.85 and 3.99, 2.87 and 4.05, and 2.81 and 3.94 ppm for complexes 1-3, respectively. Our earlier nickel complexes A-D also display a similar NMR spectral feature for the -CH₂CH₂- fragment.^[14] Another interesting aspect of the spectra for complexes 1–3 is the observation of an AB-type or germinal coupling between the protons attached to the $-C(O)CH_2$ - fragment. The pair of protons from the -C(O)-CH₂- fragment (d and e) appear at δ = 3.27 and 4.27 ppm for 1, 3.32 and 4.28 for 2, and 3.21 and 4.20 ppm for complex 3. The geminal coupling constant, $J(H^{d}H^{e})$ for complexes 1, 2 and 3 was found to be 16.16, 15.30 and 16.0 Hz, respectively. Similar values were found for our earlier Ni^{II} complexes A-D (15.12-16.2 Hz).^[14] It can therefore be concluded that the conformational rigidity of the macrocycle results in complex ¹H NMR spectra for complexes 1–3.^[28] In contrast to the ¹H NMR spectra, the ¹³C NMR spectra of 1–3 are quite straightforward (Table S4 and Figure S9). Moreover, a close similarity in the ¹³C NMR chemical shifts of identical carbon centers was observed for all complexes. The observation of diamagnetic NMR spectra for these complexes corroborates the conclusion drawn from the absorption spectral studies, namely that the present nickel complexes do not interact with or bind additional axial ligands [Cl-, pyridine, 4-(dimethylamino)pyridine] and/or better coordinating solvents and retain their squareplanar geometry.

Electrochemical Studies

Cyclic voltammetric (CV) and controlled potential electrolysis studies were performed on all Ni^{II} and Cu^{II} complexes to investigate the extent of stabilization of the M^{III} state and the role of electronic substituents present on the ligand. In addition, the CV results should also help in understanding the accessibility of the higher oxidation states of the present systems. The electrochemical data for complexes 1-7 are summarized in Table 3, and the oxidation processes are displayed in Figures 10 and 11. All complexes display a reversible to quasi-reversible one-electron oxidative response with lower potentials for the complexes carrying electron-donating groups (Table 3). Each complex undergoes a one-electron oxidation in the potential range 0.49–0.80 V (vs. SCE). As anticipated, the E values for the Cu^{II} complexes (4-7) are less positive than those for the nickel complexes (1-3), thereby suggesting that the 12-membered ring is more suited for stabilization of the Cu^{III} oxidation state. A dramatic influence of the peripheral substituents in complexes 1-7 was observed in the CV analysis. Thus, it was noted that on going from 1 to 3 and from 4 to 7, a potential of 350 and 145 mV, respectively, separates the two extreme systems [Cl (1 and 4) and OCH₃ (3 and 7)], thus explaining the electronic effect on the relative accessibility of the Ni^{III} and Cu^{III} states.

Complexes 1–7 display oxidation waves corresponding to both metal- and ligand-based oxidations. Complex 1 displays oxidation waves at 0.80 and 1.24 V, which we tentatively assign to the Ni^{3+/2+} response and ligand oxidation, respectively. Complex 2 displays a reversible metal-based oxidation at 0.64 V and a ligand-based irreversible oxidation at 0.96 V (E_{na}), whereas complex 3 shows two reversible oxidative waves at 0.48 and 0.83 V for metal- and ligand-centered oxidation, respectively. The significant shift in the E_1 potentials of complexes 1–3 towards less positive values in the order [1] > [2] > [3] clearly suggests that the first oxidation is metal-centered and leads to an Ni^{III} species.^[14] Similarly, all copper complexes undergo a one-electron oxidation in the potential range 0.54–0.68 V (vs. SCE). The first redox responses were found to be reversible and are tentatively assigned as the metal-centered oxidation. The individual values for 4-7 were found to be 0.56, 0.68, 0.54, and 0.535 V, respectively. The shift in the E_1 potentials for complexes 4–7 ([5] > [4] > [6] \approx [7]) suggests that the first oxidation is metal-centered and generates a Cu^{III} speВ

С

D

Е

F

G

H

 $[M^{II}(dioxo[12]aneN_4)]^{[c]}$ [M^{II}(dioxo[13]aneN₄)]^[c]

[M^{II}(dioxo[14]aneN₄)]^[c] [M^{II}(dioxo[15]aneN₄)]^[c]



this work [14]

[14]

[14]

[14]

[15]

[15]

[15]

[15]

[29]

[29] [29]

[29]

		-	
Complex	E_1 [V] (ΔE_p) [mV]; $n^{[b]}$	E_2 or E_{pa} [V]; $n^{[b]}$	Ref.
$\overline{[Ni(L^{Cl})](1)}$	0.80 (70); 1.00	1.24; 1.91	this work
$[Ni(L^{Me})]$ (2)	0.64 (60); 1.00	0.96; 1.98	this work
$[Ni(L^{OMe})]$ (3)	0.48 (100); 0.90	0.83; 1.92	this work
$[Cu(L^H)]$ (4)	0.56 (60); 1.00	1.30; 1.92	this work
$[Cu(L^{Cl})]$ (5)	0.68 (90); 1.00	1.37; 1.96	this work
$[Cu(L^{Me})]$ (6)	0.54 (80); 1.00	_	this work
$\left[Cu(L^{OMe})\right]$ (7)	0.535(90); 0.71	_	this work

Table 3. Cyclic voltammetric data	^{a]} for nickel(II) and copper((I) complexes $1-7$ and c_{4}	omparison with literature.
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0.61 (90); 0.94

0.71 (70); 1.00

0.83 (73); 1.02

0.62^[d]; 0.42^[e]

0.90^[d]; 0.56^[e]

0.80^[d]; 0.64^[e]

0.62^[d]: 0.69^[e]

0.75

0.82

0.80

0.78

0.78 (100): 0.96

[a] Conditions: complex approx. 1 mm CH ₃ CN solution, TBAP supporting electrolyte approx	. 100 mM solution, potential vs. SCE, Pt as
the working electrode, Pt wire as auxiliary electrode, scan rate = 100 mV/s. [b] Coulombic r	<i>i</i> [number of electron(s) taking part in the
oxidation process]. [c] In water with Na ₂ SO ₄ as supporting electrolyte and glassy carbon as	s working electrode. [d] $M = Ni^{II}$. [e] $M =$
Cu ^{II} .	



Figure 10. Cyclic voltammograms of Ni^{II} and Cu^{II} complexes in CH_3CN at a platinum working electrode. Scan rate: 100 mV s⁻¹; supporting electrolyte: 0.1 M TBAP.

cies.^[10,14] The second oxidation potentials are irreversible and are most likely ligand-centered. The electron-donating substituents on the ring play an important role by shifting the redox potential to a less positive value.^[28]

The E_1 potential (the first oxidation process) for all nickel complexes (including complex C) falls within the potential range 0.49-0.80 V, whereas the potential range for the copper complexes is 0.54-0.68 V. A comparison of the $Ni^{3+/2+}$ redox potential of complex C (0.71 V) with that of the analogous copper complex 4 (0.56 V) shows that the Cu^{III} state is more easily accessible by 150 mV.^[29,30] Overall, we observe that the Cu^{III} state is more easily accessible by at least 60 to 150 mV than the Ni^{III} state. The incorporation



1.88: 1.91

1.10; 1.98

1.13; 1.96

1.10

1.00

1.14

Figure 11. Comparative cyclic voltammograms of nickel and copper complexes in CH₃CN: (A) complexes C and 4, (B) complexes 1 and 5, (C) complexes 2 and 6, (D) complexes 3 and 7.

of electron-donating groups such as OCH₃ stabilizes the Ni^{III} and Cu^{III} state by about 200 mV. It should also be noted that the corresponding Ni^{3+/2+} redox potentials for the nickel complexes with analogous open-chain ligands (E-H) are 0.75, 0.82, 0.80, and 0.78 V, respectively. In addition, the redox potential for the $[Ni/Cu(dioxo[12]aneN_4)]$ complexes are 0.62/0.42 V (vs. SCE in H₂O),^[29] whereas the potentials for the analogous 13-, 14-, and 15-membered macrocyclic systems are 0.90/0.56, 0.80/0.64, and 0.62/ 0.69 V, respectively.^[29]

FULL PAPER

Electrochemical Oxidation and Characterization of the Oxidized Species

Ni^{III} Species $[1^{O_x} to 3^{O_x}]^+$

The singly oxidized forms of complexes 1–3 were generated electrochemically in CH₃CN and characterized by absorption and EPR spectroscopy. Electrochemical oxidation of a solution containing the respective Ni^{II} complex generated a metastable green to greenish-brown species, which was stable enough to record its absorption (Figure 12) and EPR spectra (Figure 13). The absorption spectra of these oxidized complexes have rich features and are dominated by a string of charge-transfer bands with ε values in the range 500–1550 m⁻¹ cm⁻¹. The EPR studies clearly indicate the generation of an Ni^{III} species.



Figure 12. UV/Vis spectra of electrochemically generated Ni^{III} species in CH₃CN: $[1^{O_X}]^+$ (-----), $[2^{O_X}]^+$ (-----), $[3^{O_X}]^+$ (-----), and $[C^{O_X}]^+$ (-----). Species $[C^{O_X}]^+$ is shown here for comparison.

The oxidized species for complex 1 ($[1^{Ox}]^+$) was generated by oxidizing the solution at 1.0 V vs. SCE, which resulted in a dark-green solution. An intense peak with λ_{max} = 870 nm ($\varepsilon \approx 1000 \text{ M}^{-1} \text{ cm}^{-1}$) was observed along with two weak features at around 764 and 575 nm. Qualitatively, this oxidized species was also the most stable. We believe that the presence of an electron-withdrawing group (Cl) lowers the redox-active o-benezenediamidate orbitals in energy or deactivates the ring, which results in forceful ejection of electrons from the metal orbital.^[9b] In addition, the close proximity of the o-benezenediamidate fragment to the Ni^{III} center helps to better delocalize the unpaired spin onto the ligand's π orbitals.^[9b] This enhanced delocalization results in the higher stability of the green species as well as the occurrence of the intense and broad absorption features in the visible region.

Species $[2^{Ox}]^+$ was generated by oxidizing at a potential at 0.85 V vs. SCE, which gave a green solution with $\lambda_{max} =$ 851 and 595 nm. The absorption spectral features for $[\mathbf{C}^{Ox}]^+$ were observed at 855, 580, and 430 nm.^[14] The close similarity of the spectral features for $[\mathbf{C}^{Ox}]^+$,^[14] $[\mathbf{1}^{Ox}]^+$, and $[\mathbf{2}^{Ox}]^+$ suggests a similar electronic chromophore. The Ni^{III} species containing a tetradentate tetraamide ligand reported by Journaux and Ruiz-Garcia^[31] displays λ_{max} values at 863 and 993 nm for the ligand with OCH₃ substituents and 1014 nm for the ligand with CH₃ substituents.^[31c] The ob-



Figure 13. EPR spectra of electrochemically generated Ni^{III} species in CH₃CN at 100 K. Species $[C^{Ox}]^+$ is shown here for comparison.

served similarity between these Ni^{III} species and our systems suggests a similar electronic structure. These authors suggested ligand-to-metal charge transfer as the origin of such intense features in the visible region, and they attributed the low energy of these transitions to a small energy gap between the ground and excited states where MOs have mainly developed on the ligand compared to those mainly located on the metal center.^[31c]

The oxidized species for complex 3 ($[3^{Ox}]^+$) was generated by oxidizing the solution at 0.70 V vs. SCE, which gave a brown solution. This solution displays very broad features in the range 800–1000 nm. The absorption spectral features of $[3^{Ox}]^+$ are quite different to those of $[1^{Ox}]^+$, $[2^{Ox}]^+$, and $[C^{Ox}]^+$, thereby suggesting a different nature of the oxidized species (cf. EPR spectrum).

The oxidized species $[1^{O_X}]^+$ to $[3^{O_X}]^+$ generated in CH₃CN solution display anisotropic signals in their X-band EPR spectra. The EPR spectra of the singly oxidized complexes $[1^{O_X}]^+$, $[2^{O_X}]^+$ and $[3^{O_X}]^+$ in frozen CH₃CN solution at 100 K are shown in Figure 13. The spectra of $[1^{O_X}]^+$ and $[2^{O_X}]^+$ consist of a rhombic signal characteristic of a four-coordinate square-planar Ni^{III} ion (d⁷ low-spin system) with an S = 1/2 ground state.^[32,33] The individual g values for $[1^{O_X}]^+$ and $[2^{O_X}]^+$ are 2.28, 2.23, and 2.008 and 2.23, 2.197, and 2.008, respectively. The large rhombicity and the

high average g values $[g_{av} = (g_1 + g_2 + g_3)/3]$ of 2.173 and 2.145 for $[1^{Ox}]^+$ and $[2^{Ox}]^+$, respectively, unambiguously indicate that the oxidation is located at the Ni center.^[27,31] For comparison, the g values for $[\mathbf{C}^{\mathbf{Ox}}]^+$ are 2.300, 2.225, and 2.008 ($g_{av} = 2.178$).^[14] In a similar manner, the observed g values for $[\mathbf{E}^{\mathbf{Ox}}]^+$ and $[\mathbf{F}^{\mathbf{Ox}}]^+$ were 2.278, 2.232, and 2.009 and 2.300, 2.230, and 2.015, respectively.^[15] The observed g values for $[1^{O_X}]^+$ and $[2^{O_X}]^+$ are in good agreement with those for other nickel(III) complexes with a similar electronic ground state, [14,15,31] whereas $[3^{Ox}]^+$ displays g values of 2.140 and 2.008 and a g_{av} value of 2.074, which is quite close to that for a free electron.^[27,31c,33] In contrast to the higher intensity noted for the organic-based radical, the reason for the observed low intensity of the $[3^{O_X}]^+$ EPR signal is not clear. The observed EPR signal for $[3^{O_x}]^+$ suggests that the SOMO may have significantly developed on the ligand, although with some contribution from the metal center.^[28,31c] $[3^{Ox}]^+$ may therefore best be described as a nickel(II) complex with a semiquinone-type ligand-based radical. The different nature of these oxidized species is also reflected in the different absorption spectrum of species $[3^{Ox}]^+$ compared with those for $[1^{Ox}]^+$, $[2^{Ox}]^+$ and $[C^{Ox}]^+$.

Cu^{III} Species $[4^{Ox} to 7^{Ox}]^+$

The singly oxidized forms of complexes 4–7 were generated electrochemically in CH₃CN solution and characterized by absorption spectroscopy (Figure 14). The absorption spectra of these oxidized complexes display several charge-transfer bands,^[34] some of which are exceptionally intense (ε values up to 15500 m⁻¹ cm⁻¹). The oxidized species of complex 4 ([4^{Ox}]⁺) was generated by oxidizing the solution at 0.78 V vs. SCE, which gave a brown solution. This solution displays absorption features at $\lambda = 455$ ($\varepsilon =$ 1050 m⁻¹ cm⁻¹) and 372 nm ($\varepsilon = 1500$ m⁻¹ cm⁻¹).^[34] The new features are quite different from the original Cu^{II} complex ($\lambda_{max} = 573$ nm; $\varepsilon = 110$ m⁻¹ cm⁻¹), thus indicating that oxidation probably results in a change of geometry.^[10]



Figure 14. UV/Vis spectra of electrochemically generated Cu^{III} species in CH₃CN: $[4^{Ox}]^+$ (-----), $[5^{Ox}]^+$ (-----), $[6^{Ox}]^+$ (-----), and $[7^{Ox}]^+$ (-----).

The oxidized species $[5^{Ox}]^+$ was generated at a potential of 0.88 V vs. SCE and produced a brown-colored solution similar to that for $[4^{Ox}]^+$, with absorption bands at $\lambda = 466$ ($\varepsilon = 10200 \text{ m}^{-1} \text{ cm}^{-1}$) and 377 nm ($\varepsilon = 15500 \text{ m}^{-1} \text{ cm}^{-1}$).^[34] Qualitatively, this oxidized species was found to be the most stable, as was also the case for the analogous nickel system. The presence of electron-withdrawing groups (Cl) on the ring most likely lowers the redox-active benzene orbital in energy, which means that removal of electrons from the metal orbital is easier.^[14,28] In addition, the close proximity of the *o*-benezenediamidate fragment to the Cu^{III} center helps to delocalize the unpaired spin onto the ligand's π orbitals.^[14,31]

Complex 6 was oxidized in a similar fashion at 0.74 V to obtain a brown species ($[6^{Ox}]^+$) with $\lambda_{max} = 470$ ($\varepsilon = 1200 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 380 nm ($\varepsilon = 1900 \text{ M}^{-1} \text{ cm}^{-1}$).^[34] Finally, complex 7 was oxidized at 0.75 V to generate a brown-colored solution with $\lambda_{max} = 788 \text{ nm}$ ($\varepsilon = 270 \text{ M}^{-1} \text{ cm}^{-1}$) and a weak shoulder at 465 nm ($\varepsilon = 600 \text{ M}^{-1} \text{ cm}^{-1}$). As was the case for the MeO-substituted nickel complex $[3^{Ox}]^+$, the MeO-substituted copper complex $[7^{Ox}]^+$ also displays a different absorption spectrum, thus indicating a different chromophore than in $[4^{Ox}]^+$, $[5^{Ox}]^+$, or $[6^{Ox}]^+$.

The absorption spectra of the solution-generated Cu^{III} species with tetraanionic, tetradentate oxamide-based ligands reported by Journaux and co-workers have features at around 380, 435-460, and 540-600 nm.^[10] A similar situation has been observed for the Cu^{III} species $[4^{Ox}]^+$, $[5^{Ox}]^+$, and $[6^{O_x}]^+$. These authors suggested that three transitions (from four low-lying fully occupied d orbitals to the upper empty d orbital) would be expected for a diamagnetic Cu^{III} ion with a d⁸ electronic configuration in a square-planar environment. However, their closeness in energy may result in the overlap of these three transitions.^[10a,10b,34] This is the situation, for example, for the isoelectronic nickel(II) complexes 1-3, where a single absorption feature is observed in the range 442–450 nm. Interestingly, $[7^{Ox}]^+$ shows quite different spectra, as is also the case for the analogous nicke-1(III) species [3^{Ox}]⁺, thereby strongly suggesting the different nature of the oxidized species.

Our efforts to characterize the doubly oxidized species were unsuccessful, owing to their very unstable nature. It should be noted, however, that all these redox processes are one-electron in nature, as determined by the coulometric experiments.

Chemical Oxidation and Justification of Electrochemical Findings

The accessible redox potentials (cf. Table 3) of complexes 1–7 and the successful electrochemical generation of the singly oxidized forms $[1^{Ox}]^+$ to $[7^{Ox}]^+$ impelled us to attempt chemical oxidation with Cu(OTf)₂^[35] at the first oxidation potential ($E_{1/2} = 0.8$ V in CH₃CN vs. SCE). Thus, addition of 1.2 equiv. of Cu(OTf)₂ to a CH₃CN solution of the respective Ni^{II} and Cu^{II} complex resulted in a clean oneelectron oxidation.^[14,15] Chemical oxidation of solutions containing the respective Ni complexes generated green to greenish-brown species, as observed electrochemically. A brown-colored species was generated in a similar fashion in the case of copper complexes. The UV/Vis spectra of the chemically oxidized species were recorded and found to be identical to the electrochemically generated ones, as shown in Figures 12 and 14.

Conclusions

The present work has reported the synthesis and characterization of several square-planar Ni^{II} and square-pyramidal Cu^{II} complexes with amine/amide-based macrocyclic ligands. The important findings of the present study can be summarized as follows:

(1) To the best of our knowledge, this is the first systematic investigation aimed at understanding the structural, spectroscopic and redox properties of Ni^{II} and Cu^{II} ions bound to a set of 12-membered macrocyclic ligands containing electron-donating and -withdrawing substituents.

(2) The crystal structures of these complexes show that the Cu–N_{amide} bonds are shorter than the Ni–N_{amide} bonds. Furthermore, the Cu ion lies around 0.5 Å above the basal plane of the macrocyclic ligand, whereas the Ni ion is only about 0.17 Å above the basal plane.

(3) The Ni^{II} and Cu^{II} complexes are capable of undergoing one- and two-electron oxidations that are successively metal- and ligand-centered.

(4) The electrochemical results indicate that the Ni^{III/II} potentials are more positive than the Cu^{III/II} potentials.

(5) Electron-donating substituents on the ring shift the redox potentials towards less positive values or better stabilize the higher oxidation state of a metal ion; out of three substituents, OCH_3 was found to be the best.

(6) The Ni^{III} and Cu^{III} species can be generated in solution both electrochemically and chemically [after oxidizing with $Cu(OTf)_2$] and have been shown to have rich spectroscopic features.

(7) The metastable 1e⁻-oxidized species $[1^{Ox}]^+$, $[2^{Ox}]^+$, and $[4^{Ox}]^+$ to $[6^{Ox}]^+$ are concluded to be Ni^{III} and Cu^{III} species on the basis of their absorption spectral features.

(8) The anisotropic EPR spectra for nickel species indicate a Ni^{III} ion in a square-planar environment.

(9) The spectroscopic data for $[3^{O_x}]^+$ and $[7^{O_x}]^+$, both of which bear an MeO group on the phenylene ring, point towards a metal complex with a semiquinone-type ligand-based radical.

(10) It can therefore be concluded that changing the electronic substituent on the ligand shifts the locus of the oxidation.

Experimental Section

Materials and Reagents: All reagents were obtained from commercial sources and used as received unless otherwise stated. *N*,*N*-Dimethylformamide (dmf) was dried and distilled from molecular sieves (4 Å) and then stored over sieves. Acetonitrile was dried by distillation from anhydrous CaH₂. Diethyl ether was dried by refluxing in the presence of sodium wire under an inert gas. Ethanol and methanol were distilled from magnesium ethoxide and magnesium methoxide, respectively. Chloroform and dichloromethane were purified by washing with 5% sodium carbonate solution followed by water and finally drying with anhydrous CaCl₂, before final reflux and distillation. Petroleum ether (boiling range: 60– 80 °C) and hexanes (boiling range: 60–80 °C) were dried by refluxing and distilling from sodium wire. *N*,*N'*-Bis(chloroacetyl)-1,2phenylenediamine and *N*,*N'*-bis(chloroacetyl)-4,5-dimethoxy-1,2phenylenediamine were synthesized according to published procedures.^[36,37]

Physical Measurements: Conductivity measurements were performed in organic solvents by using a digital conductivity bridge from Popular Traders, India (model number: PT-825). Elemental analysis data were obtained by using an Elementar Analysen Systeme GmbH Vario EL-III instrument. NMR spectra were reocrded with an Avance Bruker (300 MHz) instrument. IR spectra (as either a KBr pellet or a mull in mineral oil) were recorded by using a Perkin-Elmer FTIR-2000 spectrometer. Absorption spectra were recorded by using a Perkin-Elmer Lambda-25 spectrophotometer. X-band EPR spectra were recorded by using either a Varian 109 C or a Bruker EMX 1444 spectrometer fitted with a quartz dewar vessel for measurements at 77 K and 120 K, respectively. The EPR spectra were calibrated with diphenylpicrylhydrazyl radical (DPPH, g = 2.0037). Solution-state magnetic susceptibilities were obtained by the Evans technique^[18] in dmf with a Hitachi R-600 FT NMR (60 MHz) spectrometer. Diamagnetic corrections were applied with the use of appropriate constants. ESI mass spectra were obtained by using an LC-TOF (KC-455) mass spectrometer.

Electrochemical Measurements: Cyclic voltammetric and coulometric experiments were performed by using a CH instruments electrochemical analyzer (Model No. 600B or 1100A Series). The cell contained a glassy-carbon or a Pt working electrode, a Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. A salt bridge [containing supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP) dissolved in either MeCN or dmf] was used to connect the SCE with the electrochemistry solution.^[38] For constant-potential electrolysis experiments a Pt mesh was used as the working electrode. The solutions were ca. 1 mM in complex and ca. 0.1 M in supporting electrolyte (TBAP). Under our experimental conditions, the $E_{1/2}$ values (in V) for the couple Fc⁺/ Fc was found to be 0.40 in MeCN vs. SCE.^[39]

N,N'-**Bis(chloroacetyl)-4,5-dimethyl-***o***-phenylenediamine:** 4,5-Dimethyl-*o*-phenylenediamine (1.0 g, 7.0 mmol) in toluene (60 mL) was stirred at 60–65 °C, then chloroacetyl chloride (1.8 g, 14 mmol) was added dropwise and the solution refluxed for 6 h. The solid thus obtained was filtered, washed with toluene and petroleum ether, and dried. Yield: 1.79 g (85%). M.p. 194–198 °C. FT-IR (KBr disk): $\tilde{v} = 3288$, 3048, 2943, 2921, 2863, 1703 cm⁻¹. ¹H NMR ([D₆]dmso, 60 MHz, 25 °C): $\delta = 2.30$ (s, 6 H, CH₃), 4.30 [s, 4 H, CH₂C(O)], 7.45 (s, 2 H, aromatic H), 9.70 (br. s., 2 H, NH) ppm. MS (EI⁺): calcd. for C₁₂H₁₄Cl₂N₂O₂ 289.16; found for [M⁺], [M⁺ + 2] 288.15, 290.14.

N,N'-Bis(chloroacetyl)-4,5-dichloro-*o*-phenylenediamine: This reagent was prepared in a similar manner to above from 4,5-dichloro*o*-phenylenediamine (1.0 g, 5.0 mmol) and chloroacetyl chloride (1.4 g, 10 mmol). Yield: 1.29 g (70%). M.p. 155–160 °C. FT-IR (KBr disk): $\tilde{v} = 3254$, 3111, 3039, 1688 cm⁻¹. ¹H NMR ([D₆]dmso, 60 MHz, 25 °C): $\delta = 4.30$ [s, 4 H, CH₂C(O)], 7.90 (s, 2 H, aromatic H), 9.89 (br. s., 2 H, NH) ppm. MS (EI⁺): calcd. for C₁₀H₈Cl₄N₂NaO₂ 352.98; found for [M⁺], [M + 2], [M + 4] 350.08, 352.07, 354.08.

N,N'-**Bis(chloroacetyl)-4,5-dimethoxy-***o***-phenylenediamine:** This compound was prepared according to a slightly modified literature procedure.^[35,36] Yield: 9.85 g (70%). FT-IR (KBr disk): $\tilde{v} = 3260$,



3072, 3006, 2961, 2835, 1749 cm⁻¹. ¹H NMR ([D₆]dmso, 60 MHz, 25 °C): δ = 4.0 (s, 6 H, OCH₃), 4.32 [s, 4 H, CH₂C(O)], 7.02 (s, 2 H, aromatic H), 8.30 (br. s., 2 H, NH) ppm. MS (EI⁺): calcd. for C₁₂H₁₄Cl₂N₂O₄ 321.15; found for [M + Na⁺] 344.00.

H₂L^{CI}: LiBr (0.57 g, 6 mmol), Na₂CO₃ (2.54 g, 24 mmol) and N,N'bis(chloroacetyl)-4,5-dichloro-o-phenylenediamine (1.0 g, 3 mmol) were mixed in MeCN (140 mL) and the mixture refluxed with stirring for 1 h. A solution of N,N'-dimethylethylenediamine (0.26 g, 3 mmol) in MeCN (20 mL) was then added. The resulting mixture was refluxed whilst stirring for an additional 48 h. The mixture was cooled, filtered, and the solvent removed under reduced pressure to afford a sticky material. The crude product was further purified by column chromatography on silica gel (100-200 mesh) with 3-4% MeOH/CHCl₃ ($R_f = 0.46$) to give a white solid. Yield: 0.230 g (22%). An analytically pure product (in ca. 75% yield) was obtained by recrystallizing the crude product by layering the CHCl₃ solution with hexane. M.p. 135–140 °C. FT-IR (KBr disk): \tilde{v} = 3344, 2947, 2840, 1673 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz, 25 °C): $\delta = 2.50$ (s, 6 H, CH₃), 2.70 (s, 4 H, CH₂CH₂), 3.23 [s, 4 H, CH₂C(O)], 7.79 (s, 2 H, aromatic H), 9.54 (br. s., 2 H, NH) ppm. MS (EI⁺): calcd. for $C_{14}H_{18}Cl_2N_4O_2$ 345.23; found for [M⁺], [M + 2], [M + 4] 344.6, 346.6, 348.6 (6:9:1) and for $[H_2L^{Cl} + Na^+]$ 366.5, 368.56, 370.58.

H₂**L**^{Me}: This ligand was synthesized in a similar manner to H₂L^{Cl} from LiBr (3.05 g, 35 mmol), Na₂CO₃ (15.0 g, 140 mmol), *N*,*N*'-bis(chloroacetyl)-4,5-dimethyl-*o*-phenylenediamine (5.09 g, 18 mmol), and *N*,*N*'-dimethylethylenediamine (1.55 g, 18 mmol). The crude product was further purified by column chromatography on silica gel (100–200 mesh) with 2–3% MeOH/CHCl₃ (*R*_f = 0.44) to give a white solid. Yield: 1.8 g (33%). An analytically pure product (in ca. 85% yield) was obtained by recrystallizing the crude product by layering the CHCl₃ solution with hexane. M.p. 120–130 °C. FT-IR (KBr disk): \tilde{v} = 3239, 2944, 2842, 1667 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ = 2.21 (s, 6 H, CH₃), 2.34 (s, 6 H, CH₃), 2.66 (s, 4 H, CH₂CH₂), 3.18 [s, 4 H, CH₂C(O)], 7.53 (s, 2 H, aromatic H), 9.45 (br. s, 2 H, NH) ppm. MS (EI⁺): calcd. for C₁₆H₂₄N₄O₂ 304.39; found for [H₂L^{Me} + H⁺] 304.10.

H₂**L**^{OMe}: This ligand was synthesized in a similar manner to H₂L^{Cl} from LiBr (0.57 g, 6 mmol), Na₂CO₃ (3.0 g, 24 mmol), *N*,*N*'-bis(chloroacetyl)-4,5-dimethoxy-*o*-phenylenediamine (1.0 g, 3 mmol), and *N*,*N*'-dimethylethylenediamine (0.26 g, 3 mmol). The crude product was purified by column chromatography on silica gel (100–200 mesh) with 1% MeOH/CHCl₃ (R_f = 0.53) to give a white solid after layering a CH₂Cl₂ solution with hexane. Yield: 0.33 g (30%). FT-IR (KBr disk): \tilde{v} = 3241, 2919, 2837, 2781, 1666, 1599, 1144 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ = 2.39 (s, 6 H, CH₃), 2.67 (s, 4 H, CH₂CH₂), 3.24 [s, 4 H, CH₂C(O)], 3.84 (s, 6 H, OCH₃), 7.46 (s, 2 H, aromatic H), 9.29 (br. s, 2 H, NH) ppm. MS (EI⁺): calcd. for C₁₆H₂₄N₄O₄ 336.39; found for [H₂ (L^{OMe}) + H⁺] 336.7 and for [H₂ (L^{OMe}) + Na⁺] 358.6.

[Ni^{II}(L^{CI})] (1): H_2L^{CI} (0.20 g, 0.579 mmol) was dissolved in dmf (15 mL) with stirring then treated with solid NaH (0.03 g, 1.275 mmol) under nitrogen. The resulting mixture was stirred until H_2 evolution ceased. A solution of NiCl₂ (0.075 g, 0.579 mmol) in dmf (10 mL) was then added. The resulting dark yellow solution was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure and the crude compound isolated after washing with diethyl ether. The crude compound thus obtained was dissolved in MeCN (15 mL) and passed through a pad of Celite on a medium-porosity frit. The filtrate was concentrated to one third of its original volume, and diffusion of diethyl ether resulted in a dark yellow crystalline product after 1 d. The product was

filtered and dried under vacuum. Yield: 0.082 g (45%). C₁₄H₁₆Cl₂N₄NiO₂ (401.92): calcd. C 41.82, H 3.98, N 13.94; found C 41.42, H 4.41, N 13.77. FT-IR (KBr disk): $\tilde{v} = 3400$, 2933, 1632 cm⁻¹. Conductivity (CH₃CN, ca. 1 mM solution, 298 K): $\Lambda_{\rm M}$ = 20 Ω^{-1} cm²mol⁻¹. UV/Vis (CH₃CN): $\lambda_{\rm max}$ (ε) = 275 nm (34200 m⁻¹ cm⁻¹), 298 (25400), 313 sh (18690), 329 (12400), 442 (460). MS (EI⁺): calcd. for C₁₄H₁₆Cl₂N₄NiO₂ 401.90; found for {[Ni(L^{C1})⁺], [Ni(L^{C1}) + 2], [Ni(L^{C1}) + 4]} 399.4, 402.4, 404.4. ¹H NMR ([D₆]dmso, 300 MHz, 25 °C): δ = 2.85 (m, 2 H, CH₂), 2.62 (s, 6 H, CH₃), 3.99 (m, 2 H, CH₂), 3.27 [d, 16.15 Hz, 2 H, CH₂C(O)], 4.27 [d, 16.18 Hz, 2 H, CH₂C(O)], 7.62 (s, 2 H, Ar-f) ppm. ¹³C NMR ([D₆]dmso, 75.46 MHz): δ = 47.78 (CH₃), 59.86 (CH₂CH₂), 69.50 [C(O)CH₂], 119.12 (Ar-j), 121.23 (Ar-k), 142.43 (Ar-i), 172.46 (C=O) ppm.

[Ni^{II}(L^{Me})] (2): This complex was synthesized according to a similar procedure to that for 1. The product was isolated as dark yellow blocks. Yield: 0.085 g (42%). C₁₆H₂₂N₄NiO₂ (361.09): calcd. C 53.23, H 6.09, N 15.53; found C 53.08, H 6.62, N 15.61. FT-IR (KBr disk): $\tilde{v} = 2990, 2953, 2921, 1627, 1585, 1485 \text{ cm}^{-1}$. Conductivity (CH₃CN, ca. 1 mM solution, 298 K): $\Lambda_{\rm M} = 30 \,\Omega^{-1} \,{\rm cm}^2 \,{\rm mol}^{-1}$. UV/Vis (CH₃CN): λ_{max} (ϵ) = 214 nm (40600 m⁻¹ cm⁻¹), 262 (15100), 270 (15270), 290 (12800), 318 sh (5900), 445 (245). UV/Vis (dmf): $\lambda_{\text{max}}(\varepsilon) = 270 \text{ nm} (13000 \text{ M}^{-1} \text{ cm}^{-1}), 292 (11140), 319 \text{ sh} (4750), 444$ (200). MS (EI⁺): calcd. for C₁₆H₂₂N₄NiO₂ 360.693; found for $[Ni(L^{Me}) + H^+]$ 362.57. ¹H NMR ($[D_6]$ dmso, 300 MHz, 25 °C): δ = 2.71 (s, 6 H, CH₃), 2.87 (m, 2 H, CH₂), 3.32 [d, 14.9 Hz, 2 H, CH₂C(O)], 4.05 (m, 2 H, CH₂), 4.28 [d, 15.7 Hz, 2 H, CH₂C(O)], 2.08 (s, 6 H, Ar-CH₃), 7.95 (s, 2 H, Ar-f) ppm. $^{13}\mathrm{C}$ NMR ([D₆]dmso, 75.46 MHz, 25 °C): δ = 18.82 (Ar-CH₃), 47.72 (CH₃), 59.74 (CH2CH2), 69.53 [C(O)CH2], 120.23 (Ar-k), 127.27 (Ar-i), 140.2 (Ar-i), 171.10 (C=O) ppm.

 $[Ni^{II}(L^{OMe})]$ (3): H_2L^{OMe} (0.10 g, 0.2979 mmol) was dissolved in MeOH (5 mL) then treated with solid NaOH (0.024 g, 0.595 mmol). A solution of [Ni(H₂O)₆](ClO₄)₂ (0.11 g, 0.2979 mmol) in MeOH (6 mL) was then added dropwise and the resulting orange-yellow solution stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the crude compound isolated after washing with diethyl ether. Recrystallization was performed by dissolving the crude compound in MeCN and diffusing diethyl ether. The orange crystalline product thus obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.02 g (18%). C16H22N4NiO4 (393.08): calcd. C 48.89, H 5.64, N 14.25; found C 49.08, H 5.92, N 14.61. FT-IR (KBr disk): $\tilde{v} = 3567, 2964, 2922, 1624, 1583, 1103 \text{ cm}^{-1}$. Conductivity (CH₃CN, ca. 1 mM solution, 298 K): $\Lambda_{\rm M} = 20 \ \Omega^{-1} \rm cm^2 mol^{-1}$. UV/Vis (CH₃CN): λ_{max} (ε) = 213 nm (23480 m⁻¹ cm⁻¹), 257 (15700), 292 (12520), 324 sh (6560), 450 (210). MS (EI⁺): calcd. for $C_{16}H_{22}N_4NiO_4$ 393.06; found for $[Ni(L^{OMe})$ + $H^+]$ 392.51. 1H NMR ([D₆]dmso, 300 MHz, 25 °C): δ = 2.60 (s, 6 H, CH₃), 2.81 (m, 2 H, CH₂), 3.21 [d, 16.1 Hz, 2 H, CH₂C(O)], 3.94 (m, 2 H, CH₂), 4.20 [d, 15.9 Hz, 2 H, CH₂C(O)], 3.58 (s, 6 H, OCH₃), 7.23 (s, 2 H, Ar-f) ppm. ¹³C NMR ([D₆]dmso, 75.46 MHz, 25 °C): δ = 55.91 (OCH₃), 47.91 (CH₃), 59.79 (CH₂CH₂), 69.58 [C(O)CH₂], 142.58 (Ar-k), 135.60 (Ar-i), 104.87 (Ar-j), 171.36 (C=O) ppm.

 $[Cu^{II}(L^{H})]$ (4): H_2L^H (0.15 g, 0.54 mmol) was dissolved in dmf (15 mL) with stirring, and solid NaH (0.03 g, 1.08 mmol) was added under nitrogen. The resulting mixture was stirred until H_2 evolution ceased. Solid Cu(OTf)₂ (0.20 g, 0.54 mmol) was added to this mixture, and the resulting dark blue solution was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure and the crude compound isolated after washing with diethyl ether. The crude compound was further dissolved in

MeOH (15 mL) and passed through a pad of Celite on a mediumporosity frit. The filtrate was concentrated to one third of its original volume, and diffusion of diethyl ether resulted in a dark blue crystalline product in 1 d. The product was filtered and dried under vacuum. Yield: 0.082 g (45%). C₁₄H₁₈CuN₄O₂ (337.87): calcd. C 49.77, H 5.37, N 16.58; found C 50.22, H 5.62, N 16.16. FT-IR (KBr disk): $\tilde{v} = 3424$, 2918, 1628, 1564 cm⁻¹. Conductivity (CH₃CN, ca. 1 mM solution, 298 K): $\Lambda_{\rm M} = 35 \,\Omega^{-1} {\rm cm}^2 {\rm mol}^{-1}$. UV/ Vis (CH₃CN): $\lambda_{\rm max}$ (ε) = 273 nm (4860 m⁻¹ cm⁻¹), 297 (12160), 573 (110). UV/Vis (dmf): $\lambda_{\rm max}$ (ε) = 275 nm (15540 m⁻¹ cm⁻¹), 298 (7450), 573 (240). MS (EI⁺): calcd. for C₁₄H₁₈CuN₄O₂ 337.87; found for [CuL^H + Na⁺] and [CuL^H)₂ + Na⁺] 360.27 and 697.60.

[Cu^{II}(L^{C1})] (5): This complex was synthesized according to a similar procedure to that for **4**. The product was isolated as royal blue blocks. Yield: 0.075 g (45%). C₁₄H₂₃Cl₂CuN₄O_{5.5} (including 3.5H₂O): calcd. C 35.79, H 4.93, N 11.90; found C 35.77, H 4.89, N 11.92. FT-IR (KBr disk): $\tilde{v} = 3426$, 2925, 1613 cm⁻¹. Conductivity (CH₃CN, ca. 1 mM solution, 298 K): $\Lambda_{\rm M} = 30 \,\Omega^{-1} \,\rm cm^{2} \,\rm mol^{-1}$. UV/ Vis (CH₃CN): $\lambda_{\rm max}$ (ε) = 575 nm (210 m⁻¹ cm⁻¹). UV/Vis (CH₃OH): $\lambda_{\rm max}$ (ε) = 269 nm (22400 m⁻¹ cm⁻¹), 307 sh (7440), 587 (240). UV/ Vis (dmf): $\lambda_{\rm max}$ (ε) = 280 nm (20110 m⁻¹ cm⁻¹), 320 (7690), 578 (200).

[Cu^{II}(L^{Me})] (6): This complex was synthesized according to a similar procedure to that for **4**. The product was isolated as royal blue blocks. Yield: 0.078 g (45%). C₁₆H₂₅CuN₄O_{3.5} (including 1.5H₂O): calcd. C 48.91, H 6.41, N 14.26; found C 48.91, H 6.36, N 14.26. FT-IR (KBr disk): $\tilde{v} = 3434$, 2916, 1604 cm⁻¹. Conductivity (dmf, ca. 1 mM solution, 298 K): $\Lambda_{\rm M} = 10 \,\Omega^{-1} \,\rm cm^2 mol^{-1}$. UV/Vis (CH₃CN): $\lambda_{\rm max} (\varepsilon) = 575 \,(220 \,\,{\rm M^{-1} cm^{-1}})$. UV/Vis (dmf): $\lambda_{\rm max} (\varepsilon) = 274 \,(21590 \,\,{\rm M^{-1} cm^{-1}})$, 307 (8420), 573 (220). MS (EI⁺, *m/z*): calcd. for C₁₆H₂₂CuN₄O₂ 365.92; found for [CuL^{Me} + H⁺] and [CuL^{Me} + Na⁺] 366.583 and 388.547.

[Cu^{II}(L^{OMe})] (7): H₂L^{OMe} (0.10 g, 0.2979 mmol) was dissolved in MeOH (5 mL) and treated with solid NaOH (0.03 g, 0.60 mmol) whilst stirring. A solution of $[Cu(H_2O)_6](ClO_4)_2$ (0.11 g, 0.2979 mmol) in MeOH (6 mL) was then added dropwise and the resulting green solution stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the crude compound was isolated after washing with diethyl ether. Recrystallization was achieved by dissolving the crude compound in MeCN and diffusing diethyl ether. The green product thus obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.06 g (55%). C17H26CuN4O5 (including 1CH3OH): calcd. C 47.49, H 6.10, N 13.03; found C 47.10, H 6.44, N 13.26. FT-IR (KBr disk): $\tilde{v} = 3433$, 2926, 1562, 1511, 1132 cm⁻¹. Conductivity (CH₃CN, ca. 1 mM solution, 298 K): $\Lambda_{\rm M} = 20 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$. UV/ Vis (CH₃CN): λ_{max} (ϵ) = 430 nm (1000 $\text{M}^{-1}\text{cm}^{-1}$), 593 (300). UV/ Vis (CH₃OH): λ_{max} (ϵ) = 294 nm (5230 m⁻¹ cm⁻¹), 326 (2460), 424 (830), 593 (270).

Crystallography: Single crystals suitable for X-ray diffraction studies were grown by vapor diffusion of diethyl ether into a CH₃CN (for 1 and 2) or MeOH solution (for 5 and 6) of the complexes (Table 4). Intensity data for complexes 1 and 2 were collected at 295 K by using a Siemens P4 X-ray diffractometer in θ -2 θ scan mode with graphite-monochromated Mo- K_{α} radiation. A total of 13300 reflections were measured for complex 2, of which 5922 were unique and 3977 were considered observed [$I > 2\sigma$ (I)]. For complex 1, a total of 3242 reflections were measured, of which 3041 were unique and 2742 were considered observed. The data were corrected for Lorentz and polarization effects and a ψ -scan absorption correction was also applied. The structures were solved by di-

rect methods and refined by full-matrix least-squares refinement techniques on F^2 . All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were attached with U_{iso} values of 1.2 times (for methylene and phenylene carbon atoms) and 1.5 times (methyl carbon atoms) the U_{iso} values of their respective carrier atoms. Intensity data for complexes 5 and 6 were collected by using a Bruker SMART APEX CCD diffractometer at 100(2) K with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å).^[40,41] Intensity data were corrected for Lorentz polarization effects, and an empirical absorption correction (SADABS) was applied.^[42] The structures were solved with SIR-97, expanded by Fourier-difference syntheses and refined with SHELXL-97, incorporated in the WinGX 1.64 crystallographic software package.^[43] Hydrogen atoms were placed in idealized positions and treated by using a riding-model approximation with displacement parameters derived from those of the atoms to which they are bonded. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures on F^2 . Convergence was measured by the factors R and R_w where $R = \sum(||F_0| - |F_c||)/\sum |F_0|$ and R_w = $\{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$. The crystal quality of complex 2 was not very good, and a number of crystals were tried before measuring the present data set. This poor crystal quality is reflected in the rather high value of R_{int} (0.4898) and an A-evel error in the CIF file. For complex 6, a total of 22908 reflections were collected, of which 16450 were unique and 11453 were considered observed. An empirical absorption correction was applied by using SAD-ABS.^[41] The structure was initially solved in the triclinic space group $P\bar{1}$ with an R factor of 0.12 for observed reflections, although the Addsym command in Platon showed additional symmetry in the lattice. The data were then transformed to the monoclinic space group C2/c and the structure solved by the heavy-atom method with Patterson maps in SHELX-86. It was refined by the SHELXL-97 package in the WinGX program.^[43] The structure has two crystallographically independent units, one of which shows high disorder in four atoms of one of the phenyl groups, two methyl groups C29 and C30 attached to this group, one methylene group C26 and two lattice water molecules O1W and O2W. This disorder in the phenyl ring C17-C22 could be resolved for four of the atoms (C18-C21) and methyl groups C29 and C30 by splitting each of these atoms into two, but not for the water molecules, which had higher U_{iso} values. Treatment of this disorder did not help to improve the model to any significant extent, therefore the final model omitted this treatment, and the phenyl group C17-C22 was refined as a rigid group. All non-hydrogen atoms were refined anisotropically, except for the two water molecules, which were refined isotropically with a fixed U_{iso} value of 0.25. The hydrogen atoms of these two water molecules were located from the difference-Fourier map, not refined and assigned a U_{iso} value of 1.2 times that of the oxygen atoms. They were fixed at a distance of 0.926(3) Å from their respective oxygen atoms. All other hydrogen atoms were fixed geometrically and were not refined. The CIF file shows a few "A"level errors, which are due to the above-mentioned disorder and are explainable. Intermolecular C-H···Cl and C-H···O contacts were examined with the DIAMOND 2.0 package.[44] C-H distances were normalized along the same vectors to the neutron-derived values of 1.083 Å. CCDC-735978 (5), -735979 (6), -735980 (1), and -735981 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charges from The Cambridge Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figures showing crystal structures, packing diagrams, and weak interactions; NMR spectra; EPR spectra; tables of H-bond-ing interactions and NMR spectroscopic data.



Table 4. Crystallographic data for Ni^{II} complexes [Ni(L^{Cl})]·H₂O (1) and [Ni(L^{Me})] (2) and Cu^{II} complexes [Cu(L^{Cl})] (5) and [Cu(L^{Me})]· 2H₂O·CH₃OH (6).

	$[Ni(L^{Cl})] (1 \cdot H_2O)$	[Ni(L ^{Me})] (2)	$[Cu(L^{Cl})]$ (5)	$[Cu(L^{Me})] (\textbf{6} \cdot 2H_2O \cdot CH_3OH)$
Empirical formula	C ₁₄ H ₁₈ Cl ₂ N ₄ NiO ₃	C ₁₆ H ₂₂ N ₄ NiO ₂	C ₁₄ H ₁₆ Cl ₂ CuN ₄ O ₂	C ₆₆ H ₁₀₂ N ₁₆ O ₁₃ Cu ₄
Formula mass	419.93	361.07	406.75	1581.82
<i>T</i> [K]	295(2)	295(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	PĪ	$P2_1/c$	$P2_1/c$	C2/c
Color, shape	yellow, prism	yellow, prism	blue, block	blue, block
<i>a</i> [Å]	9.5602(10)	8.719(8)	11.9992(10)	47.699(10)
<i>b</i> [Å]	9.6891(12)	12.465(6)	14.1922(11)	9.018(5)
c [Å]	10.5312(13)	29.922(13)	10.0039(8)	17.330(5)
	84.869(7)	90	90	90
β [°]	69.457(8)	95.03	114.224(10)	111.024(5)
γ [°]	63.919(6)	90	90	90
$V[Å^3]$	818.01(17)	3239(4)	1553.6(2)	6958(5)
Z	2	8	4	4
$D_{\text{calcd.}} [\text{g cm}^{-3}]$	1.705	1.481	1.739	1.510
Absorption coefficient [mm ⁻¹]	1.534	1.213	1.764	1.281
<i>R</i> ^[a]	0.0368	0.0802	0.0504	0.0982
$R_w^{[b]}$	0.0914	0.2245	0.1311	0.2319
GOF on F^2	1.090	1.067	1.129	1.087

[a] $R = \Sigma ||F_o| - |F_c|| \Sigma ||F_o||$. [b] $R_w = \{ [\Sigma(|F_o|^2 ||F_c|^2)^2] \}^{1/2}$.

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FULL PAPER

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