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Ni(II) and Cu(II) complexes of phenoxy-ketimine ligands: Synthesis, structures and their utility in bulk ring-opening polymerization (ROP) of L-lactide

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Abstract

Synthetic, structural and catalysis studies of Ni(II) and Cu(II) complexes of a series of phenoxy-ketimine ligands with controlled variations of sterics, namely 2-[1-(2,6-diethylphenylimino)ethyl]phenol (**1a**), 2-[1-(2,6-dimethylphenylimino)ethyl]phenol (**1b**) and 2-[1-(2-methylphenylimino)ethyl]phenol (**1c**), are reported. Specifically, the ligands **1a**, **1b** and **1c** were synthesized by the $TiCl_4$ mediated condensation reactions of the respective anilines with *o*-hydroxyacetophenone in 21–23% yield. The nickel complexes, {2-[1-(2,6-diethylphenylimino)ethyl]phenoxy}$_2$Ni(II) (**2a**) and {2-[1-(2,6-dimethylphenylimino)ethyl]phenoxy}$_2$Ni(II) (**2b**), were synthesized by the reaction of the respective ligands **1a** and **1b** with $Ni(OAc)_2 \cdot 4H_2O$ in the presence of NEt_3 as a base in 71–75% yield. The copper complexes, {2-[1-(2,6-diethylphenylimino)ethyl]phenoxy}$_2$Cu(II) (**3a**), {2-[1-(2,6-dimethylphenylimino)ethyl]phenoxy}$_2$Cu(II) (**3b**) and {2-[1-(2-methylphenylimino)ethyl]phenoxy}$_2$Cu(II) (**3c**) were synthesized analogously by the reactions of the ligands **1a**, **1b** and **1c** with $Cu(OAc)_2 \cdot H_2O$ in 70–87% yield. The molecular structures of the nickel and copper complexes **2a**, **2b**, **3a**, **3b** and **3c** have been determined by X-ray diffraction studies. Structural comparisons revealed that the nickel centers in **2a** and **2b** are in square planar geometries while the geometry around the copper varied from being square planar in **3a** and **3c** to distorted square planar in **3b**. The catalysis studies revealed that while the copper complexes **3a**, **3b** and **3c** efficiently catalyze ring-opening polymerization (ROP) of L-lactide at elevated temperatures under solvent-free melt conditions, producing polylactide polymers of moderate molecular weights with narrow molecular weight distributions, the nickel counterparts **2a** and **2b** failed to yield the polylactide polymer.

Keywords: Ring-opening polymerization; Phenoxy-ketimine; Copper complexes; Nickel complexes; L-Lactide

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1. Introduction

Phenoxy-imines are a versatile class of ligands that display a truly impressive range of diverse applications spanning from bioinorganic chemistry [1] to coordination chemistry [2], chemical catalysis [3–7], and materials related applications [8,9]. Equally impressive are their wide-ranging utility in chemical catalysis, namely in olefin polymerization [10–13], epoxidation reactions [14,15], Suzuki cross-coupling reactions [16], oxidation reactions [17], to name but a few. Of the various phenoxy-imine catalysts that exist, notable are the Fujita's fluorinated phenoxy-imine catalyst for olefin polymerization [18] and the Jacobsen's [19] Salen based catalyst for epoxidation reactions, both

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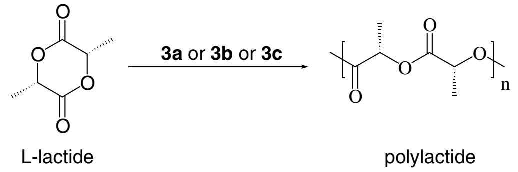
of which have contributed significantly to the development of the respective fields. The successes of phenoxy-imines are presumably due to the availability of scope for suitable tuning of the sterics and the electronics of the ligand ancillary and also due to their easy synthetic accessibility, as the phenoxy-imines are often prepared by Schiff base condensation reactions. Interestingly enough, despite extensive utility of phenoxy-imines in many important chemical transformations, their application in ring-opening polymerization (ROP) of L-lactide largely remains unexplored [20].

Our interest in the ring-opening polymerization (ROP) of L-lactide arises mainly because of its eco-friendly nature as the polylactide polymer (PLA) is biodegradable and also because the lactide monomer can be generated from renewable resources like the corn fermentation process or from agricultural starch wastes [21,22]. The PLAs are biocompatible and exhibit good mechanical properties and, hence, are long known for their use in medical and pharmaceutical related applications [23,24]. One of our core programs is centered around designing novel initiators for the bulk ring-opening polymerization of L-lactide, and in this regard we have recently reported Ag(I) [25] and Au(I) [26] complexes of N-heterocyclic carbenes (NHC) as initiators for the bulk polymerization of L-lactide under solvent-free melt conditions. It is noteworthy that the PLAs can be synthesized by both solution polymerization [27] and bulk polymerization [28], however, the solution polymerization suffers from certain disadvantages like being susceptible to the impurity levels and to various unwanted reactions namely racemization, transesterifications, etc. The bulk polymerization, which does not suffer from such limitations, is thus, often preferred for the large-scale production of PLAs [29].

With regard to designing new initiators for our ROP program we observed that the phenoxy-imine ligands, despite their proven successes in chemical catalysis, remain to be tried for ring-opening polymerization (ROP) of L-lactide [20] and so we became interested in exploring the scope of phenoxy-imine based transition metal complexes as catalysts for bulk polymerization of L-lactide. Furthermore, phenoxy-imine metal complexes, bearing a metal–alkoxide bond, are natural candidates for the catalysis, as the well accepted catalysts for the ring-opening polymerization (ROP) of L-lactide are often the metal–alkoxide complexes [21,30–33] (see Fig. 1).

Here in this contribution, we report the synthesis, structural characterizations and catalysis studies of a series of nickel (**2a** and **2b**) and copper (**3a**, **3b** and **3c**) complexes of phenoxy-ketimine ligands with varying steric demands, namely 2-[1-(2,6-diethylphenylimino)ethyl]phenol (**1a**), 2-[1-(2,6-dimethylphenylimino)ethyl]phenol (**1b**) and 2-[1-(2-methylphenylimino)ethyl]phenol (**1c**). Furthermore, we disclose that while the copper complexes (**3a**, **3b** and **3c**) were found to be efficient initiators for ring-opening polymerization of L-lactide at elevated temperatures under solvent-free melt conditions, producing polylactide polymers of moderate molecular weights with narrow molecular weight distributions (Eq. (1)), the nickel complexes (**2a** and **2b**) failed to yield a polylactide polymer.



Equation 1. Polymerization of L-lactide by **3a**, **3b** and **3c**.

2. Results and discussion

A series of monoanionic phenoxy-ketimine ligands, namely 2-[1-(2,6-diethylphenylimino)ethyl]phenol (**1a**), 2-[1-(2,6-dimethylphenylimino)ethyl]phenol (**1b**) and 2-[1-(2-methylphenylimino)ethyl]phenol (**1c**) were synthesized by a modification of a $TiCl_4$ catalyzed procedure reported in the literature for the condensation of α-haloketones with amines [34]. Specifically, the condensation reaction of *o*-hydroxyacetophenone with the respective anilines in presence of a catalytic amount of $TiCl_4$ gave the phenoxy-

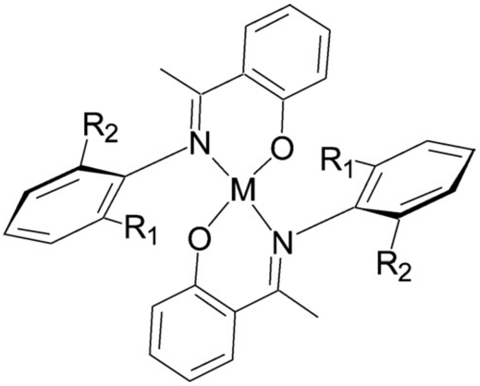
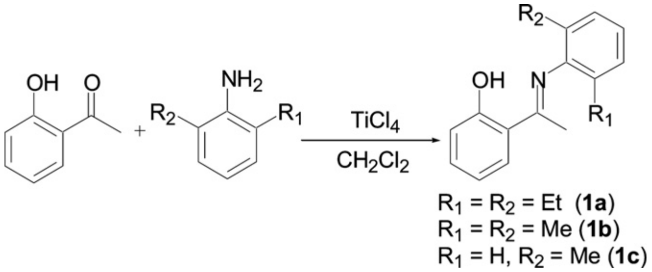


Fig. 1. Ni(II) and Cu(II) complexes of a series of phenoxy-ketimine ligands with controlled variation of sterics.



Scheme 1. Synthesis of phenoxy-ketimine ligands **1a**, **1b** and **1c**.

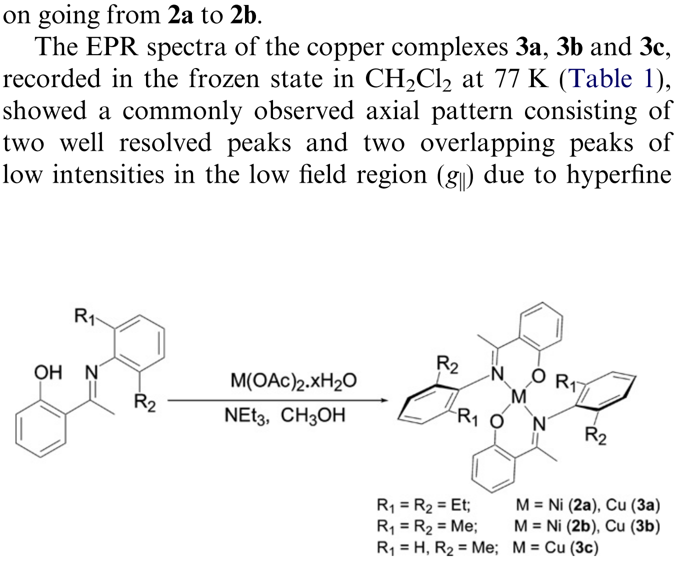
ketimine ligands, **1a**, **1b** and **1c** [35], in ca. 21–23% yield (Scheme 1). It is interesting to note that the ketimine ligands are often synthesized by two different methods, namely: (i) Schiff base condensation of ketones with amines in the presence of a catalytic amount of an acid like HCO_2H [36] or *p*-toluenesulfonic acid [16] and (ii) Friedel-Crafts acylation of the imidoyl chloride with the *ortho*-unsubstituted phenol [37]. The compounds **1a**, **1b** and **1c** have been characterized by ^1H NMR, ^{13}C NMR, IR, UV–Vis and mass spectrometry. The ^1H NMR spectra of **1a**, **1b** and **1c** showed the ketimine methyl (*Me*C=N) resonances as singlets at 2.09–2.17 ppm, while the phenolic –O*H* protons appeared as broad peaks at 14.7–14.8 ppm. The substantially high downfield shifts of the phenolic –O*H* protons in **1a**, **1b** and **1c** are attributed to an intramolecular hydrogen bonding interaction, [phenolic –OH··· N=C (imine N)]. A similar downfield shift of the phenolic –O*H* proton (16.8 ppm) due to an intramolecular hydrogen bonding interaction has been reported for the Schiff base ligand 1-(2-hydroxy-3,5-dichlorophenyl)-2,5-diaza-6-methylnona-1,6-diene-8-one [38]. Furthermore, the ketimine moieties (MeC=N) appeared at 171.1–171.9 ppm (Me*C*=N) in the ^{13}C NMR spectra and at 1609–1614 cm^{-1} ($\nu_{C=N\ str}$) in the infrared spectra. The electronic spectra of the phenoxy-ketimine ligands **1a**, **1b** and **1c** in $CHCl_3$ exhibited two distinct absorption bands in the UV region which have been identified as high energy π–π^* and low energy n–π^* transitions, based on the assignment made for a series of related phenoxy-imine ligands, namely 2-[1-(R)methyl]phenol (where R = $-CH_3$, $-C_6H_{11}$ and $-C_5H_4N$) [39]. The high energy bands due to the π–π^* transitions showed absorptions at 256 nm for **1a** (ε = 17263 L mol^{-1} cm^{-1}), 256 nm for **1b** (ε = 17933 L mol^{-1} cm^{-1}) and 257 nm for **1c** (ε = 21873 L mol^{-1} cm^{-1}), while the low energy n–π^* transition appeared at 323 nm for **1a** (ε = 5945 L mol^{-1} cm^{-1}), 322 nm for **1b** (ε = 5919 L mol^{-1} cm^{-1}) and 324 nm for **1c** (ε = 8776 L mol^{-1} cm^{-1}). Electrospray mass analysis gave peaks at m/z = 268 (**1a**), 240 (**1b**) and 226 (**1c**), corresponding to the respective M+1 ions in 100% abundances.

The nickel (**2a** and **2b**) and copper (**3a**, **3b** and **3c**) complexes were synthesized by the reaction of the ligands with $M(OAc)_2 \cdot xH_2O$ (M = Ni, Cu) in the presence of NEt_3 in methanol in 71–75% and 70–87% yields, respectively (see Scheme 2). Both of the nickel complexes, **2a** and **2b**, were diamagnetic in nature, consistent with a square planar geometry of the Ni(II) d^8 configuration. The ketimine methyl moieties (MeC=N) in **2a** and **2b** appeared as singlets at 1.87–1.94 ppm (*Me*C=N) in the ^1H NMR spectra and at 168.6–168.9 ppm (Me*C*=N) and 19.7–20.6 ppm (*Me*C=N) in the $^{13}C\{^1H\}$ NMR spectra. Comparison of infrared spectra for the $\nu_{C=N}$ stretching frequencies for **2a** (1574 cm^{-1}) and **2b** (1571 cm^{-1}) showed red shifts of ca. 35–43 cm^{-1} relative to the respective parent ligands **1a** (1609 cm^{-1}) and **1b** (1614 cm^{-1}). The $\nu_{C=N}$ stretching frequency values observed for **2a** and **2b** are similar to that of a related complex, {2-[1-(2,6-diisopropylphenylimino)-methyl]phenoxy}$_2$Ni(II) [36] (1602 cm^{-1}).

The paramagnetic copper complexes **3a**, **3b** and **3c** were characterized by IR, electronic spectroscopy, ESR, elemental analysis and X-ray diffraction studies. The $\nu_{C=N}$ stretching frequencies in the copper complexes, **3a** (1599 cm^{-1}), **3b** (1601 cm^{-1}) and **3c** (1599 cm^{-1}), are comparable to the closely related complex, {2-[1-(2-methoxyphenylimino)-methyl]phenoxy}$_2$Cu(II) [40], (1600 cm^{-1}) and, as was observed in the case of the nickel complexes **2a** and **2b**, the $\nu_{C=N}$ stretching frequencies are all red shifted by ca. 10–13 cm^{-1} relative to the ligands, **1a** (1609 cm^{-1}), **1b** (1614 cm^{-1}) and **1c** (1611 cm^{-1}).

The electronic spectra of the nickel complexes, **2a** and **2b**, in $CHCl_3$ showed absorption bands due to d–d transitions at 601 nm (ε = 118 L mol^{-1} cm^{-1}) and 592 nm (ε = 102 L mol^{-1} cm^{-1}), respectively, which are comparable to those reported for other square planar Ni(II) complexes. For example, square planar Ni(II) complexes of a series of $[N_2O_2]$ chelating salen type ligands with varying spacer lengths showed similar low intensity absorbances due to d–d transitions at 532–550 nm (ε = 240–260 L mol^{-1} cm^{-1}) [41]. The Cu complexes, **3a**, **3b** and **3c**, on the other hand showed the d–d transitions at 696 nm (ε = 89.4 L mol^{-1} cm^{-1}), 670 nm (ε = 130 L mol^{-1} cm^{-1}) and 630 nm (ε = 125 L mol^{-1} cm^{-1}), respectively, which are also similar to other square planar copper complexes, like *bis*-[(N2-(2-pyridylmethyl)-3-thenyl-carboxamido)copper(II)]perchlorate [42] (675 nm). Similar comparisons of the d–d transitions in **3a**, **3b** and **3c** can also be drawn with another set of Schiff base copper complexes, {3-methoxy -2-[1-(2-pyridylmethylimino)methyl]phenoxy}Cu(II)X [43] (X = Cl, Br), based on a phenolato-pyridine ligand, which showed weak broad bands in the 600–700 nm region which were attributed to d–d transitions. The differences in the absorption bands amongst the copper complexes **3a**, **3b** and **3c** is notable, showing marked shifts of ca. 30 nm with the decrease in steric bulk of the 2,6-*di*-substituted phenyl ring on going from **3a** to **3b** to **3c**. In contrast, the Ni complexes did not show any appreciable difference in the d–d transitions on going from **2a** to **2b**.

The EPR spectra of the copper complexes **3a**, **3b** and **3c**, recorded in the frozen state in CH_2Cl_2 at 77 K (Table 1), showed a commonly observed axial pattern consisting of two well resolved peaks and two overlapping peaks of low intensities in the low field region ($g_{\parallel}$) due to hyperfine



Scheme 2. Synthesis of the metal complexes.

Table 1
EPR parameters of **3a**, **3b** and **3c** in CH_2Cl_2 at 77 K

Complex	$A_{\parallel}$	$A_{\perp}^{a}$	$g_{\parallel}$	$g_{\perp}$
3a	143	NR	2.2517	2.0399
3b	140	NR	2.2517	2.0463
3c	140	NR	2.2447	2.0465

[a] NR, not resolved.

splitting by the copper nucleus ($I = 3/2$) along with a high intensity peak in the high field region ($g_{\perp}$). In this context, it is worth mentioning that in square planar copper complexes, an unpaired electron when residing in the $d_{x^2-y^2}$ orbital ($^2B_{1g}$ ground state) exhibits $g_{\parallel} > g_{\perp}$ whereas the same when present in the other axial d_{z^2} orbital ($^2A_{1g}$ ground state) displays $g_{\perp} > g_{\parallel}$ [44–46]. Quite notably, in all the three copper complexes **3a**, **3b** and **3c**, the observed $g_{\parallel} > g_{\perp}$ is consistent with a square planar geometry at the metal center with the unpaired electron placed in the $d_{x^2-y^2}$ orbital [44–46]. Furthermore, the observed g and A values of **3a**, **3b** and **3c** are comparable to those of other reported copper complexes. For example, the average g and A values recorded at 77 K for the square planar complex {2-[1-(*N*,*N*-diethylethyleneimino)methyl]phenol)}$_2$Cu-(ClO_4)$_2$ [47] are $g_{\parallel}$ (2.225), $g_{\perp}$ (2.070) and $A_{\parallel}$ (179.7) and that of {4-[1-(4-methoxyphenylimino)-pent-2-ene-2-oxy]}$_2$-Cu(II) [45] are $g_{\parallel}$ (2.328), $g_{\perp}$ (2.067) and $A_{\parallel}$ (140).

The molecular structures of the nickel (**2a** and **2b**) (Figs. 2 and 3) and copper complexes (**3a**, **3b** and **3c**) (Figs. 4–6) have been determined by X-ray diffraction studies, which revealed the formation of metal complexes having 2:1 ligand to metal stoichiometries. The metal ions in these complexes reside at the center of a *trans*-N_2O_2 core which is perfectly square planar in case of the nickel (**2a** and **2b**) and two of the copper complexes (**3a** and **3c**), whereas it is distorted square planar in the other copper complex **3b**.

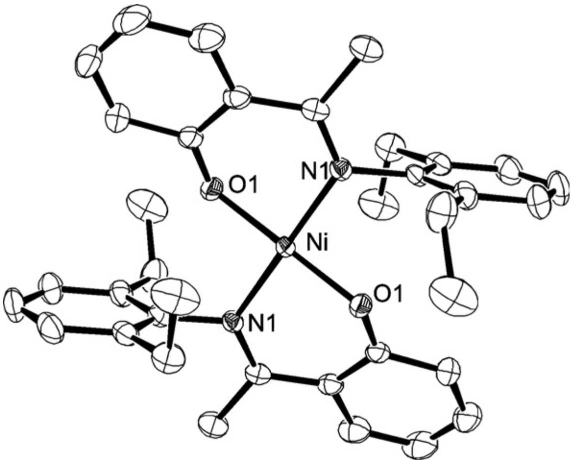


Fig. 2. ORTEP of **2a**. Thermal motion ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Ni1–N1 1.9085(14), Ni1–N1 1.9085(14), Ni1–O1 1.8258(11), Ni1–O1 1.8258(11), N1–Ni1–N1 180.00(13), O1–Ni1–O1 180.00(9), N1–Ni1–O1 91.10(6), N1–Ni1–O1 88.90(6).

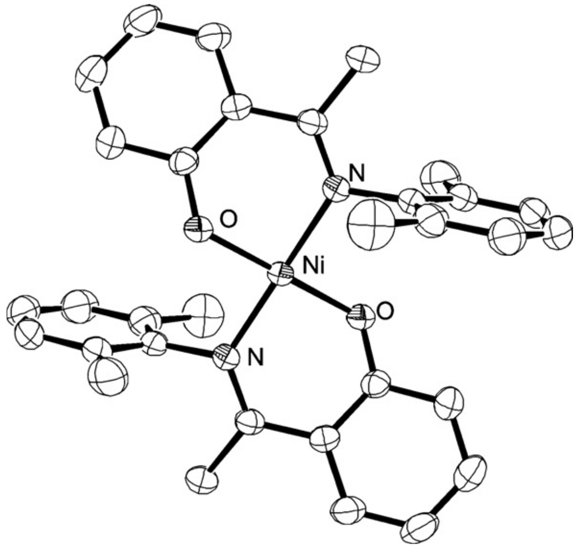


Fig. 3. ORTEP of **2b**. Thermal motion ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Ni–N 1.9199(11), Ni–N 1.9199(11), Ni–O 1.8248(10), Ni–O 1.8248(10), N–Ni–N 180.00(4), O–Ni–O 180.00(5), N–Ni–O 90.93(5), N–Ni–O 89.07(5).

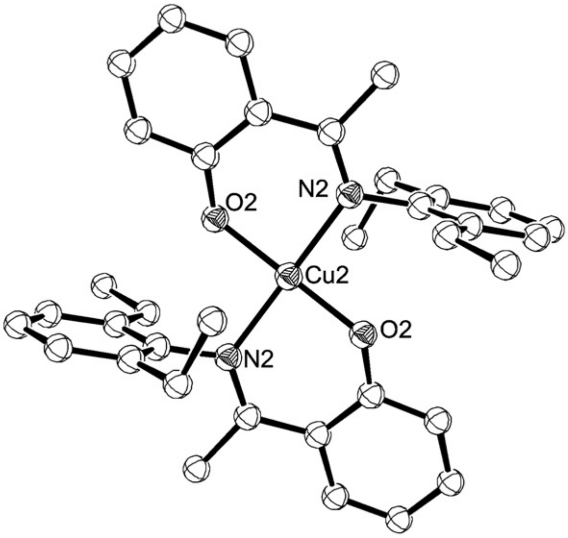


Fig. 4. ORTEP of **3a**. Thermal motion ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Cu2–N2 2.0161(14), Cu2–N2 2.0161(14), Cu2–O2 1.8631(11), Cu2–O2 1.8630(11), N2–Cu2–N2 180.00(12), O2–Cu2–O2 180.00(7), O2–Cu2–N2 90.50(5), O2–Cu2–N2 89.50(5).

Consistent with a square planar geometry, the Ni(II) centers in **2a** and **2b** are surrounded by two equidistant Ni–N [**2a**: 1.9085(14) Å (Fig. 2); **2b**: 1.9199(11) Å (Fig. 3)] and two equidistant Ni–O [**2a**: 1.8258(11) Å (Fig. 2); **2b**: 1.8248(10) Å (Fig. 3)] bond distances. The Ni–N and the Ni–O bond distances in **2a** and **2b** are, however, somewhat longer than the sum of the individual covalent radii of the respective atoms (Ni–N = 1.854 Å, Ni–O = 1.814 Å) [48]. Quite expectedly, the complementary ∠O–Ni–N and ∠N–Ni–O angles at the nickel centers in **2a** [91.10(6),

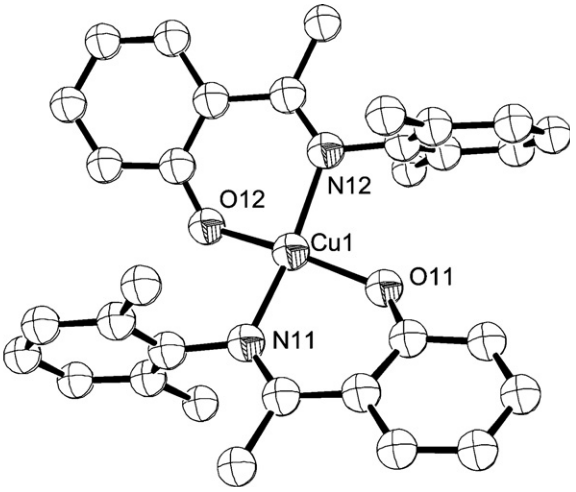


Fig. 5. ORTEP of **3b**. Thermal motion ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Cu1–N11 2.007(5), Cu1–N12 2.006(4), Cu1–O11 1.858(4), Cu1–O12 1.856(4), N11–Cu1–N12 161.58(19), O11–Cu1–O12 159.8(2), O12–Cu1–N12 89.36(17), O11–Cu1–N12 91.96(18).

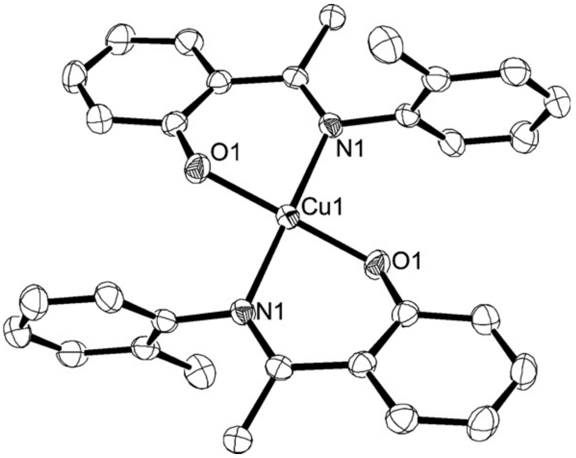


Fig. 6. ORTEP of **3c**. Thermal motion ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Cu1–N1 2.001(2), Cu1–N1 2.001(2), Cu1–O1 1.872(2), Cu1–O1 1.872(2), N1–Cu–N1 180.00(16), O1–Cu1–O1 180.00(12), O1–Cu1–N1 89.16(9), N1–Cu1–O1 90.84(9).

88.90(6)°] and **2b** [89.07(5), 90.93(5)°] are equal to ca. 90°. The *trans* disposition of the phenyl rings of the 2,6-disubstituted-phenyl moieties in both complexes **2a** and **2b** is a consequence of the reduction of steric strain.

The comparison of the molecular structures of **2a** and **2b** with the other reported nickel phenoxy-ketimine and phenoxy-aldimine complexes is important. For example, the Ni–O and Ni–N bond distances in the phenoxy-ketimine complex, {2-[1-(2,6-diisopropylphenylimino)ethyl]phenoxy}$_2$Ni(II) [36] [Ni–O = 1.8081(10) Å; Ni–N = 1.9262 (11) Å], and in the phenoxy-aldimine nickel complex, {3-*t*-butyl-5-methyl-2-[1-(ethylimino)methyl]phenoxy}$_2$Ni(II) [49], [Ni–O = 1.861(2), 1.852(2) Å; Ni–N = 1.905(2), 1.893(2) Å] are in good agreement with those in the complexes **2a** and **2b**.

The copper complexes **3a**, **3b** and **3c** are isostructural with their nickel counterparts, **2a** and **2b**, though certain variations were observed. The *di*-ethyl derivative **3a** and the *mono*-methyl derivative **3c** exhibit square planar geometries like the nickel complexes **2a** and **2b**, whilst a slightly distorted square planar geometry was observed in case of the *di*-methyl derivative **3b**. Thus, unlike the square planar nickel (**2a** and **2b**) and copper (**3a** and **3c**) complexes, in which two sets of equidistant M–O and M–N (M = Ni, Cu) bond lengths were observed, the Cu–N and Cu–O bond lengths of the *trans*-N_2O_2 core in **3b** are all marginally unequal, a consequence of the slight distortion of the square planar geometry around the copper center. For example, in **3b** the Cu1–N11 and Cu1–N12 bond lengths are 2.007(5) Å and 2.006(4) Å, while the Cu1–O11 and Cu1–O12 distances are 1.858(4) Å and 1.856(4) Å, respectively (Fig. 5). Owing to the presence of the distortion, the four ∠N–Cu–O bond angles at the copper center in **3b** are also marginally different from the ideal value of 90° [∠N12–Cu1–O12 = 89.36(17)° and ∠N12–Cu1–O11 = 91.96(18)°], while the diagonal angles [∠N11–Cu1–N12 = 161.58(19)° and ∠O11–Cu1–O12 = 159.8(2)°] at the copper in **3b** are significantly deviated from the expected value of 180°. The extent of the distortion of the square planar structure in **3b** becomes apparent upon comparison with the perfectly square planar nickel analog **2b** (Fig. 7b). It is interesting to note that although significant square planar distortion (as reflected in the angles, θ and ϕ, in Fig. 7b) is observed in the *di*-methyl derivative **3b** ($\theta = 21.4°$, $\phi = 17.7°$) relative to the square planar nickel counterpart **2b**, no such distortion was visible in case of the *di*-ethyl copper complex **3a** ($\theta = 1.0°$, $\phi = 1.8°$) relative to the nickel analog **2a** (Fig. 7a). The *mono*-methyl copper complex **3c** also showed no distortion and closely resembled the square planar copper complex **3a**.

The Cu–O and Cu–N bond distances in **3a**, **3b** and **3c** are comparable to those observed in other analogous copper phenoxy-ketimine complexes, {2-[1-(2-phenylethylimino)ethyl]phenoxy}$_2$Cu(II) [50] [Cu–O = 1.865(2) Å, Cu–N = 1.977(2) Å] and {2-[1-(2-methylpropylimino)ethyl]phenoxy}$_2$Cu(II) [51] [Cu–O = 1.891(2) Å, Cu–N = 2.003(2) Å], as well as in the related copper phenoxy-aldimine complexes, {5-bromo-2-[1-(3-methylphenylimino)methyl]phenoxy}$_2$Cu(II) [52] [Cu–O = 1.884(8) Å, Cu–N = 2.005(7) Å] and {2-[1-(phenylimino)methyl]phenoxy}$_2$Cu(II) [53] [Cu–O = 1.878(3) Å, Cu–N = 1.993(4) Å].

3. Polymerization studies

Quite significantly, the copper complexes **3a**, **3b** and **3c** efficiently catalyzed the ring-opening polymerization (ROP) of L-lactide at elevated temperatures under solvent-free melt conditions [28]. In stark contrast to the

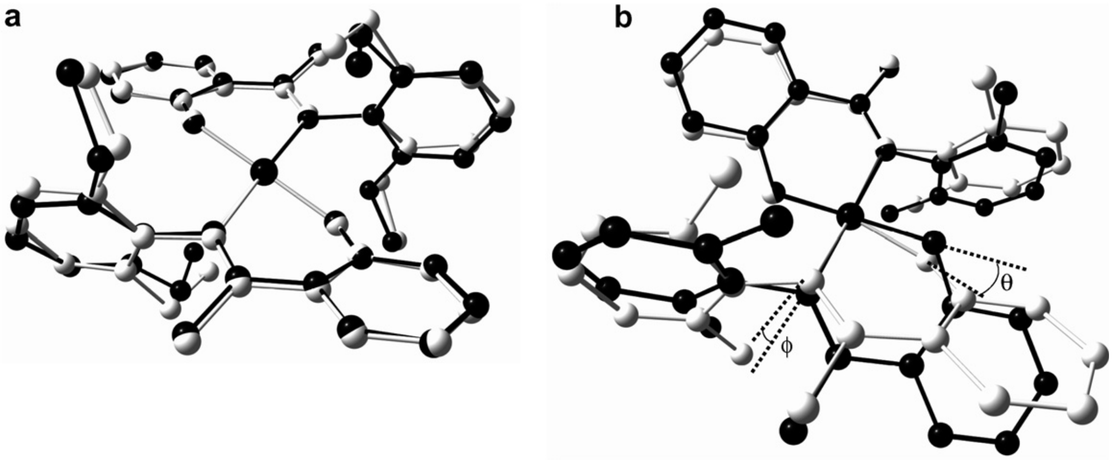


Fig. 7. (a). Overlaid structures of Ni (**2a**) (black) and Cu (**3a**) (grey) complexes. (b). Overlaid structures of Ni (**2b**) (black) and Cu (**3b**) (grey) complexes.

Table 2
X-ray crystallographic data for **2a**, **2b**, **3a**, **3b** and **3c**

Compound	**2a**	**2b**	**3a**	**3b**	**3c**
Lattice	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Formula	$C_{36}H_{40}NiN_2O_2$	$C_{32}H_{32}NiN_2O_2$	$C_{36}H_{40}CuN_2O_2$	$C_{32}H_{32}CuN_2O_2$	$C_{30}H_{28}CuN_2O_2$
Formula weight	591.41	535.31	596.24	540.14	512.08
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$	$P2_12_12_1$	$P2_1/n$
a (Å)	7.5871(9)	9.3513(6)	8.8749(18)	12.0618(8)	6.010 (3)
b (Å)	9.878(3)	7.8591(5)	20.702(5)	12.0625(7)	14.886 (3)
c (Å)	11.720(3)	18.2914(12)	16.6067(11)	37.054(3)	13.368 (3)
α (°)	64.95(3)	90.00	90.00	90.00	90.00
β (°)	74.013(15)	93.3590(10)	97.281(10)	90.00	91.90 (3)
γ (°)	87.642(15)	90.00	90.00	90.00	90.00
V (Å^3)	762.1(3)	1341.98(15)	3026.6(10)	5391.2(6)	1195.2 (6)
Z	1	2	4	8	2
Temperature (K)	150(2)	243(2)	293(2)	243(2)	150 (2)
Radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ(calcd.) (g cm^{-3})	1.289	1.325	1.309	1.331	1.423
μ(Mo Kα) (mm^{-1})	0.671	0.754	0.756	0.842	0.945
θ max (°)	32.1953	28.32	32.1670	27.893	29.9988
Number of data	2674	2452	10077	9875	2095
Number of parameters	190	172	379	681	162
R_1	0.0273	0.0266	0.0396	0.0651	0.0388
wR_2	0.0619	0.0737	0.0989	0.1231	0.0971
Goodness-of-fit	1.099	1.058	0.924	1.123	0.930

copper complexes **3a**, **3b** and **3c**, the nickel complexes **2a** and **2b**, however, failed to yield the polylactide polymer.

Specifically, a typical polymerization experiment involved heating L-lactide with any of the copper initiators **3a** or **3b** or **3c**, taken in the desired ratio, in a sealed vessel under vacuum at designated temperatures for stipulated periods of time. Under these conditions the reaction mixture would form a monomer melt in which the polymerization would occur. A study of the variation of monomer to initiator ratio [M]:[I] ratio (M = monomer, I = initiator) at 160 °C showed that the maximum molecular weights for **3a** ($M_w = 18.5 \times 10^3$ entry 1, Table 3), **3b** ($M_w = 10.4 \times 10^3$ entry 1, Table 4) and **3c** ($M_w = 15.9 \times 10^3$ entry 1, Table 5) were obtained at ratios of 50:1 in each case. The observed polydispersity indices (PDIs) were in the range 1.05–1.46 (**3a**), 1.08–1.43 (**3b**) and 1.10–1.58 (**3c**). An interesting correlation between the initiator structure and the polymer molecular weight that emerges is the structurally similar square planar complexes **3a** and **3c**, which differ significantly from the distorted square planar complex **3b**, also exhibit a similar resemblance in their polymer molecular weights [**3a** ($M_w = 18.5 \times 10^3$ entry 1, Table 3); **3c** ($M_w = 15.9 \times 10^3$ entry 1, Table 5)] that are significantly greater than that observed in the case of **3b** ($M_w = 10.4 \times 10^3$ entry 1, Table 4) obtained at the 50:1 [M]:[I] ratio. Consistent with the observed molecular weight distributions, no correlation of the polymer molecular weight with time was seen in the time dependency studies (**3a**: entries 1 and 9–12, Table 3, **3b**: entries 1 and 9–12, Table 4, **3c**: entries 1 and 9–12, Table 5). The temper-

Table 3
Melt polymerization of L-lactide by **3a**

Entry	L-Lactide/(**3a**) ratio	Temperature (°C)	Time (h)	M_w	M_w/M_n	Conversion (%)
1	50	160	4	18.5×10^3	1.28	66
2	100	160	4	6.2×10^3	1.08	51
3	150	160	4	3.2×10^3	1.09	54
4	200	160	4	2.2×10^3	1.09	58
5	250	160	4	2.3×10^3	1.08	52
6	50	120	4	9.9×10^3	1.07	27
7	50	140	4	16.5×10^3	1.27	62
8	50	180	4	26.3×10^3	1.46	57
9	50	160	1	7.6×10^3	1.05	71
10	50	160	2	9.8×10^3	1.18	67
11	50	160	3	11.3×10^3	1.1	80
12	50	160	6	14.6×10^3	1.3	86

Table 4
Melt polymerization of L-lactide by **3b**

Entry	L-Lactide/(**3b**) ratio	Temperature (°C)	Time (h)	M_w	M_w/M_n	Conversion (%)
1	50	160	4	10.4×10^3	1.32	70
2	100	160	4	8.2×10^3	1.17	72
3	150	160	4	4.7×10^3	1.3	74
4	200	160	4	4.5×10^3	1.43	76
5	250	160	4	4.5×10^3	1.08	33
6	50	120	4	5.3×10^3	1.22	39
7	50	140	4	8.2×10^3	1.21	54
8	50	180	4	12.0×10^3	1.23	64
9	50	160	1	7.1×10^3	1.19	53
10	50	160	2	8.5×10^3	1.21	59
11	50	160	3	8.5×10^3	1.2	58
12	50	160	6	11.2×10^3	1.24	72

Table 5
Melt polymerization of L-lactide by **3c**

Entry	L-Lactide/(**3c**) ratio	Temperature (°C)	Time (h)	M_w	M_w/M_n	Conversion (%)
1	50	160	4	15.9×10^3	1.36	55
2	100	160	4	14.1×10^3	1.14	25
3	150	160	4	6.4×10^3	1.58	33
4	200	160	4	6.5×10^3	1.29	28
5	250	160	4	2.9×10^3	1.1	20
6	50	120	4	8.6×10^3	1.18	54
7	50	140	4	11.1×10^3	1.11	60
8	50	180	4	13.8×10^3	1.21	61.5
9	50	160	1	8.0×10^3	1.16	45.2
10	50	160	2	8.1×10^3	1.16	48
11	50	160	3	13.4×10^3	1.31	48
12	50	160	6	10.2×10^3	1.24	72

ature dependence study carried out at the 50:1 [M]:[I] ratio in the range (100–180 °C)[1] showed that the molecular weight of the polymer increased with temperature for the initiators **3a** (Table 3: M_w: 9.9×10^3, 16.5×10^3, 18.5×10^3, 26.3×10^3) and **3b** (Table 4: M_w: 5.3×10^3, 8.2×10^3, 10.4×10^3, 12.0×10^3) whereas a slight decrease in molecular weight was observed in the case of **3c** at higher temperatures (Table 5: M_w: 8.6×10^3, 11.1×10^3, 15.9×10^3 and 13.8×10^3) at 120, 140, 160 and 180 °C, respectively.

Worth comparing are the copper initiators **3a**, **3b** and **3c** with other known catalysts for the ring-opening polymerization of L-lactide under solvent-free melt conditions, particularly the copper ones. Interestingly enough, even though very many metals like Mg [54,27a,31c], Ti [55], Zn [56,20a,33b,30a,30b,30d,32a], Al [57,20b,20d], Sn [58,30c], etc. have been reported for lactide polymerization, we are aware of only a single report of lactide polymerization by a Cu catalyst, K[LCu(II)].nH_2O (H_3L = L-aspartic acid–salicylidene Schiff base) [20c]. The viscosity average molecular weight ($M_v = 4.86 \times 10^3$) obtained at a 200:1 [M]:[I] ratio after 24 h at 130 °C for $K[LCu(II)] \cdot nH_2O$ (H_3L = L-aspartic acid–salicylidene Schiff base [20c] is slightly smaller than that observed for **3a** (M_w: 18.5×10^3), **3b** (M_w: 10.4×10^3), **3c** (M_w: 15.9×10^3) obtained at a 50:1 [M]:[I] ratio after 4 h at 160 °C. Similar comparisons of **3a**, **3b** and **3c** can also be extended to other metal catalysts. For example, the polymer molecular weights and the polydispersity indices observed at a 50:1 [M]:[I] ratio for **3a** (M_w: 18.5×10^3, PDI = 1.28), **3b** (M_w: 10.4×10^3, PDI = 1.32), **3c** (M_w: 15.9×10^3, PDI = 1.36), obtained after 4 h at 160 °C, are also comparable to several other melt polymerization catalysts, such as [3-mesityl-1-picolylimidazol-2-ylidene]Zn(Et)I [30a] (M_w: 29.4×10^3, PDI = 2.45, 100:1 [M]:[I] ratio, 140 °C, 5 min), {[3-mesityl-1-picolylimidazol-2-ylidene]$_2$ZnI}I [30a] (M_w: 15.3×10^3, PDI = 2.51, 50:1 [M]:[I] ratio, 140 °C, 5 min), [(1-*i*-propyl-3-{*N*-phenylacetamido}imidazol-2-ylidene)$_2$Ag]$^+$Cl$^-$ [25] (M_w: 12.2×10^3, PDI = 1.40, 100:1 [M]:[I] ratio, 160 °C, 4 h), [1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]AgCl [26] (M_w: 6.27×10^3, PDI = 1.23, 100:1 [M]:[I] ratio, 160 °C, 4 h) and [1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]AuCl [26] (M_w: 6.31×10^3, PDI = 1.17, 100:1 [M]:[I] ratio, 160 °C, 4 h). Furthermore, comparable viscosity-average molecular weights (M_v) were also reported for a series of late-transition metal based initiators of the type $K[LM(II)] \cdot nH_2O$ (H_3L = L-aspartic acid–salicylidene Schiff base) [20c] where M = Co (5.15×10^3), Ni (11.1×10^3) and Zn (5.23×10^3), obtained at a 200:1 [M]:[I] ratio after 24 h at 130 °C. However, several other initiators have also been reported, which produced higher molecular weight polymers, e.g., anhydrous $Fe(OAc)_2$ [59] (M_w: 65.9×10^3, PDI = 5.25, 0.24 weight % of catalyst, 170 °C, 10 h), iron isobutyrate [59] (M_w: 148×10^3, PDI = 1.60, 0.12 weight % of catalyst, 190 °C, 2 h) and [L]TiO(2,6-*i*-$Pr_2C_6H_3$) [28c] (H_3L = triethanolamine) (M_w: 66.1×10^3, PDI = 1.97, 300:1 [M]:[I] ratio, 130 °C, 24 h). Thus, the detailed comparison with other known catalysts revealed that the copper initiators **3a**, **3b** and **3c** are moderately active for lactide polymerization.

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[1] The bulk polymerization temperatures were chosen higher than the melting point of the lactide monomer (96 °C).

4. Experimental

4.1. General procedures

All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. 2,6-Dimethylaniline and 2,6-diethylaniline were purchased from Sigma–Aldrich, Germany and o-hydroxyacetophenone was purchased from SD-fine Chemicals (India), and they were used without any further purification. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. ^{1}H NMR peaks are labelled as singlet (s), doublet (d), triplet (t) and multiplet (m). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. The electronic spectra were recorded in chloroform by using a Perkin–Elmer Lamda 35 UV-Visible spectrophotometer and JASCO V-570 UV/Vis/NIR spectrophotometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer. The EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K. The spectra were calibrated by using tetracyanoethylene (tcne) ($g = 2.0037$). The polymer molecular weights were determined using a Waters GPC (Waters 2414 RI Detector) with PL-gel, 5μ Mixed-D (2×300 mm) Column, with polystyrene standards in chloroform, covering molecular weight ranging from 140 to 4×10^5.

4.2. Synthesis of the ligands

4.2.1. Synthesis of 2-[1-(2,6-diethylphenylimino)ethyl]-phe- nol (**1a**)

o-Hydroxyacetophenone (4.31 g, 31.7 mmol) and 2,6-diethylaniline (14.3 g, 96.0 mmol) were taken in $\mathrm{CH_2Cl_2}$ (ca. 75 mL) maintained at 0 °C and a solution of $\mathrm{TiCl_4}$ (3 mL, 27.3 mmol) in $\mathrm{CH_2Cl_2}$ (ca. 10 mL) was added. The reaction mixture was stirred in an ice bath for 1 h, after which it was allowed to warm up to room temperature over a period of 3 h. An aqueous NaOH solution (20 mL, 2 M) was added to the reaction mixture and washed thoroughly. The organic layer was separated, dried over anhydrous $\mathrm{MgSO_4}$ and the solvent removed under vacuum to get the crude product as a yellow oil. The crude compound was purified by the removal of excess 2,6-diethylaniline and *o*-hydroxyacetophenone by vacuum distillation (180 °C, 0.2 mbar) to obtain the product as a yellow solid (1.83 g, 22%). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz, 25 °C) δ 14.8 (s, 1H, OH), 7.64 (d, 1H, $^3J_{\mathrm{HH}} = 8$ Hz, o-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.40 (t, 1H, $^3J_{\mathrm{HH}} = 8$ Hz, p-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.16–7.11 (m, 3H, m/p-$\mathrm{C_6}H_3\mathrm{(CH_2CH_3)_2}$), 7.04 (d, 1H, $^3J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 6.91 (t, 1H, $^3J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 2.48–2.32 (m, 4H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.17 (s, 3H, $\mathrm{C}H_3\mathrm{(C{=}N)}$), 1.13 (t, 6H, $^3J_{\mathrm{HH}} = 8$ Hz, $\mathrm{CH_2C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz, 25 °C) δ 171.9 ($C{=}\mathrm{N}$), 162.4 ($C_6\mathrm{H_4(OH)}$, 143.8 ($ipso$-$C_6\mathrm{H_3(CH_2CH_3)_2}$), 133.0 ($o$-$\mathrm{C_6H_4(OH)}$), 133.1 ($o$-$C_6\mathrm{H_3(CH_2CH_3)_2}$), 128.9 ($p$-$\mathrm{C_6H_4(OH)}$), 126.1 ($m$-$C_6\mathrm{H_3(CH_2CH_3)_2}$), 124.8 ($p$-$C_6\mathrm{H_3(CH_2CH_3)_2}$), 119.1 ($ipso$-$C_6\mathrm{H_4(OH)}$), 118.3 ($m$-$C_6\mathrm{H_4(OH)}$), 118.0 ($m$-($C_6\mathrm{H_4}$-(OH)), 24.7 ($\mathrm{C_6H_3(}C\mathrm{H_2CH_3)_2}$), 17.3 ((C=N)$C\mathrm{H_3}$), 14.0 ($\mathrm{C_6H_3(CH_2}C\mathrm{H_3)_2}$). LRMS (ES): m/z 268 $\mathrm{(M{+}H)^+}$ 100%. HRMS (ES): calcd. for $\mathrm{[M{+}H]^+}$ 268.1701, found m/z 268.1696. IR data cm^{-1} KBr pellet: 1609 (s) ($\nu_{\mathrm{C=N}}$). $\lambda_{\max}$ (ε) $\mathrm{CHCl_3}$: 256 nm ($\varepsilon = 17263$ L mol^{-1} cm^{-1}), 323 nm ($\varepsilon = 5945$ L mol^{-1} cm^{-1}).

4.2.2. Synthesis of 2-[1-(2,6-dimethylphenylimino)ethyl]-phenol (**1b**)

o-Hydroxyacetophenone (8.51 g, 62.5 mmol) and 2,6-dimethylaniline (12.4 g, 102 mmol) were taken in $\mathrm{CH_2Cl_2}$ (ca. 75 mL) maintained at 0 °C and a solution of $\mathrm{TiCl_4}$ (2 mL, 18.2 mmol) in $\mathrm{CH_2Cl_2}$ (ca. 10 mL) was added. The reaction mixture was stirred in an ice bath for 1 h, after which it was allowed to warm up to room temperature over a period of 3 h. An aqueous NaOH solution (20 mL, 2 M) was added to the reaction mixture and washed thoroughly. The organic layer was separated, dried over anhydrous $\mathrm{MgSO_4}$ and the solvent removed under vacuum to get the crude product as a yellow oil. The crude compound was purified by column chromatography (4% EtOAc–hexane mixture) followed by the removal of excess 2,6-dimethylaniline by vacuum distillation (180 °C, 0.2 mbar) to obtain the product as a yellow solid (3.09 g, 21%). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz, 25 °C) δ 14.7 (s, 1H, OH), 7.57 (d, 1H, $^3J_{\mathrm{HH}} = 8$ Hz, o-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.32 (t, 1H, $^3J_{\mathrm{HH}} = 8$ Hz, p-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.03 (d, 2H, $^3J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_3\mathrm{(CH_3)_2}$), 6.98–6.92 (m, 2H, p-$\mathrm{C_6}H_3\mathrm{(CH_3)_2}$and m-$\mathrm{C_6}H_4\mathrm{(OH)}$ overlapped), 6.83 (t, 1H, $^3J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 2.09 (s, 3H, $\mathrm{C}H_3\mathrm{(C{=}N)}$), 1.99 (s, 6H, $\mathrm{C_6H_3(C}H_3\mathrm{)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz, 25 °C) δ 171.7 ($C{=}\mathrm{N}$), 162.2 ($C_6\mathrm{H_4}$-(OH), 145.0 ($ipso$-$C_6\mathrm{H_3(CH_3)_2}$), 132.9 (o-$C_6\mathrm{H_4(OH)}$), 128.8 (p-$C_6\mathrm{H_4(OH)}$), 127.9 (m-$C_6\mathrm{H_3(CH_3)_2}$), 127.5 (p-$C_6\mathrm{H_3(CH_3)_2}$), 124.3 ($ipso$-$C_6\mathrm{H_4(OH)}$, 119.1 (m-$C_6\mathrm{H_4}$-(OH)), 118.1 (m-$C_6\mathrm{H_4(OH)}$), 117.9 (o-$C_6\mathrm{H_3(CH_3)_2}$), 18.1 ($C\mathrm{H_3(C{=}N)}$), 16.8 ($\mathrm{C_6H_3(}C\mathrm{H_3)_2}$). LRMS (ES): m/z 240 $\mathrm{(M{+}H)^+}$ 100%. HRMS (ES): calcd. for $\mathrm{[M{+}H]^+}$ 240.1388, found m/z 240.1380. IR data cm^{-1} KBr pellet: 1614 (s) ($\nu_{\mathrm{C=N}}$). $\lambda_{\max}$ (ε) $\mathrm{CHCl_3}$: 256 nm ($\varepsilon = 17933$ L mol^{-1} cm^{-1}), 322 nm ($\varepsilon = 5919$ L mol^{-1} cm^{-1}).

4.2.3. Synthesis of 2-[1-(2-methylphenylimino)ethyl]phenol (**1c**)

o-Hydroxyacetophenone (7.25 g, 53.2 mmol) and 2-methylaniline (8.62 g, 80.5 mmol) were taken in $\mathrm{CH_2Cl_2}$ (ca. 60 mL) maintained at 0 °C and a solution of $\mathrm{TiCl_4}$ (2 mL, 18.2 mmol) in $\mathrm{CH_2Cl_2}$ (ca. 10 mL) was added. The reaction mixture was stirred in an ice bath for 2 h, after which it was allowed to warm up to room temperature over a period of 3 h. An aqueous NaOH solution (40 mL, 2 M) was added to the reaction mixture and washed thoroughly. The organic layer was separated, dried over anhydrous $\mathrm{MgSO_4}$ and the solvent removed under vacuum to get the crude product as a yellow oil. The crude compound was purified by the removal of excess 2-methylaniline and *o*-hydroxyacetophenone by vacuum distillation (180 °C, 0.2 mbar) to obtain the product as a yellow oil (2.72 g, 23%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 14.7 (s, 1H, O*H*), 7.63 (d, 1H, $^{3}J_{\mathrm{HH}} = 7$ Hz, o-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.37 (t, 1H, $^{3}J_{\mathrm{HH}} = 9$ Hz, p-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.25 (d, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(CH_3)}$), 7.21 (t, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(CH_3)}$), 7.10 (t, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.02 (d, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 6.89 (t, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, p-$\mathrm{C_6}H_4\mathrm{(CH_3)}$), 6.76 (d, 1H, o-$\mathrm{C_6}H_4\mathrm{(CH_3)}$), 2.26 (s, 3H, $\mathrm{C_6H_4(C}H_3)$), 2.15 (s, 3H, $\mathrm{C}H_3\mathrm{(C{=}N)}$). ^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C) δ 171.1 ($C{=}\mathrm{N}$), 162.0 ($C_6\mathrm{H_4(OH)}$, 145.8 ($ipso$-$C_6\mathrm{H_4(CH_3)}$), 133.0 (o-$C_6\mathrm{H_4(OH)}$), 130.5 (o-$C_6\mathrm{H_4(CH_3)}$), 128.8 (p-$C_6\mathrm{H_4(OH)}$), 126.4 (m-$C_6\mathrm{H_4(CH_3)}$), 124.8 (p-$C_6\mathrm{H_4(CH_3)}$), 120.5 (o-$C_6\mathrm{H_4(CH_3)}$), 119.5 ($ipso$-$C_6\mathrm{H_4(OH)}$, 118.1 (m-$C_6\mathrm{H_4(OH)}$), 118.0 (m-($C_6\mathrm{H_4(OH)}$), 17.9 ($\mathrm{(C{=}N)}C\mathrm{H_3}$), 17.0 ($\mathrm{C_6H_4(}C\mathrm{H_3)}$). LRMS (ES): m/z 226 $(\mathrm{M{+}H})^{+}$ 100%. HRMS (ES): calcd. for $[\mathrm{M{+}H}]^{+}$ 226.1232, found m/z 226.1234. IR data cm^{-1} KBr pellet: 1611 (s) ($\nu_{\mathrm{C=N}}$). $\lambda_{\max}$ (ε) CHCl$_3$: 257 nm ($\varepsilon = 21873$ L mol^{-1} cm^{-1}), 324 nm ($\varepsilon = 8776$ L mol^{-1} cm^{-1}).

4.3. Synthesis of the Ni complexes

4.3.1. Synthesis of {2-[1-(2,6-diethylphenylimino)ethyl]-phenoxy}$_2$Ni(II) (**2a**)

$\mathrm{Ni(OAc)_2 \cdot 4H_2O}$ (0.449 g, 1.81 mmol) and 2-[1-(2,6-diethylphenylimino)ethyl]phenol (**1a**) (0.478 g, 1.79 mmol) were taken in methanol (ca. 30 mL) and stirred at room temperature until a clear solution was obtained. To the solution was added NEt$_3$ (0.274 g, 2.70 mmol) with constant stirring. The reaction mixture was refluxed for 12 h and then allowed to cool to room temperature, when the product precipitated out as a green solid and was isolated by filtration and air dried (0.493 g, 71%). Crystals suitable for X-ray structure determination were obtained by slow evaporation from a saturated methanol solution. ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 7.31 (d, 1 H, $^{3}J_{\mathrm{HH}} = 8$ Hz, o-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.21 (t, 1H, p-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.11 (d, 2H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_3\mathrm{(CH_2CH_3)_2}$), 6.84 (t, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, p-$\mathrm{C_6}H_3\mathrm{(CH_2CH_3)_2}$), 6.38 (t, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 5.50 (d, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 3.29–3.19 (m, 2H, $\mathrm{C}H_2\mathrm{CH_3}$), 2.90–2.80 (m, 2H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.94 (s, 3H, $\mathrm{C}H_3\mathrm{(C{=}N)}$), 1.45 (t, 6H, $^{3}J_{\mathrm{HH}} = 8$ Hz, $\mathrm{CH_2C}H_3$). ^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C) δ 168.9 ($C{=}\mathrm{N}$), 163.6 ($C_6\mathrm{H_4(OH)}$, 145.8 ($ipso$-$C_6\mathrm{H_3(CH_2CH_3)_2}$)), 136.1 ($o$-$C_6\mathrm{H_4(OH)}$), 132.2 ($p$-$C_6\mathrm{H_4(OH)}$), 129.0 ($p$-$C_6\mathrm{H_3(CH_2CH_3)_2}$), 125.0 ($m$-$C_6\mathrm{H_3(CH_2CH_3)_2}$ and $ipso$-($C_6\mathrm{H_4(OH)}$), 123.2 (m-$C_6\mathrm{H_4}$-(OH), 122.1 (o-$C_6\mathrm{H_3(CH_2CH_3)_2}$), 113.9 ($m$-$C_6\mathrm{H_4(OH)}$), 24.6 ($\mathrm{C_6H_3(}C\mathrm{H_2CH_3)_2}$), 20.6 ($C\mathrm{H_3(C{=}N)}$), 13.7 ($\mathrm{C_6H_3(CH_2}C\mathrm{H_3)_2}$). IR data cm^{-1} KBr pellet: 1574 (s) ($\nu_{\mathrm{C=N}}$). $\lambda_{\max}$ (ε) CHCl$_3$: 601 nm ($\varepsilon = 118$ L mol^{-1} cm^{-1}). *Anal.* Calc. for $\mathrm{C_{36}H_{40}NiO_2N_2}$: C, 73.11; H, 6.82; N, 4.74. Found: C, 72.78; H, 7.06; N, 3.87%.

4.3.2. Synthesis of {2-[1-(2,6-dimethylphenylimino)ethyl]-phenoxy}$_2$Ni(II) (**2b**)

$\mathrm{Ni(OAc)_2 \cdot 4H_2O}$ (0.543 g, 2.19 mmol) and 2-[1-(2,6-dimethylphenylimino)ethyl]phenol (**1b**) (0.508 g, 2.12 mmol) were taken in methanol (ca. 30 mL) and stirred at room temperature until a clear solution was obtained. To the solution was added NEt$_3$ (0.324 g, 3.20 mmol) with constant stirring. The reaction mixture was stirred at room temperature for another 6 h when the product precipitated out as a green solid and was isolated by filtration and air dried (0.459 g, 75%). Crystals suitable for X-ray structure determination were obtained by slow evaporation from a saturated benzene solution. ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 7.26 (d, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, o-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.19 (br, 1H, p-$\mathrm{C_6}H_4\mathrm{(OH)}$), 7.02 (br, 2H, m-$\mathrm{C_6}H_3\mathrm{(CH_3)_2}$), 6.83 (t, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, p-$\mathrm{C_6}H_3\mathrm{(CH_3)_2}$), 6.35 (t, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 5.66 (d, 1H, $^{3}J_{\mathrm{HH}} = 8$ Hz, m-$\mathrm{C_6}H_4\mathrm{(OH)}$), 2.53 (s, 6H, $\mathrm{C_6H_3(C}H_3)_2$), 1.87 (s, 3H, $\mathrm{C}H_3\mathrm{(C{=}N)}$). ^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C) δ 168.6 ($C{=}\mathrm{N}$), 163.7 ($C_6\mathrm{H_4(OH)}$, 146.4 ($ipso$-$C_6\mathrm{H_3(CH_3)_2}$)), 132.3 (o-$C_6\mathrm{H_4(OH)}$), 130.9 (p-$C_6\mathrm{H_4(OH)}$), 129.0 (p-$C_6\mathrm{H_3(CH_3)_2}$), 127.6 (m-$C_6\mathrm{H_3(CH_3)_2}$), 124.9 ($ipso$-$C_6\mathrm{H_4(OH)}$, 122.0 (m-$C_6\mathrm{H_4(OH)}$), 118.2 (m-($C_6\mathrm{H_4(OH)}$), 114.1 (o-$C_6\mathrm{H_3(CH_3)_2}$), 19.7 ($C\mathrm{H_3(C{=}N)}$), 19.2 ($\mathrm{C_6H_3}$-$(C\mathrm{H_3})_2$). IR data cm^{-1} KBr pellet: 1571 (s) ($\nu_{\mathrm{C=N}}$). $\lambda_{\max}$ (ε) CHCl$_3$: 592 nm ($\varepsilon = 102$ L mol^{-1} cm^{-1}). *Anal.* Calc. for $\mathrm{C_{32}H_{32}NiO_2N_2}$: C, 71.80; H, 6.03; N, 5.23. Found: C, 71.14; H, 6.21; N, 4.88%.

4.4. Synthesis of the Cu complexes

4.4.1. Synthesis of {2-[1-(2,6-diethylphenylimino)ethyl]-phenoxy}$_2$Cu(II) (**3a**)

$\mathrm{Cu(OAc)_2 \cdot H_2O}$ (0.266 g, 1.33 mmol) and 2-[1-(2,6-diethylphenylimino)ethyl]phenol (**1a**) (0.709 g, 2.62 mmol) were taken in methanol (ca. 40 mL) and stirred at room temperature until a clear solution was obtained. To the solution was added NEt$_3$ (0.298 g, 2.94 mmol) with constant stirring. The reaction mixture was stirred at reflux for 24 h and then allowed to cool to room temperature when the product was obtained as dark brown crystals which were isolated by filtration and vacuum dried (0.542 g, 70%). Crystals suitable for X-ray structure determination were obtained by slow evaporation from a saturated benzene solution. IR data cm^{-1} KBr pellet: 1599 (s) ($\nu_{\mathrm{C=N}}$). $\lambda_{\max}$ (ε) CHCl$_3$: 696 nm ($\varepsilon = 89.4$ L mol^{-1} cm^{-1}). *Anal.* Calc. for $\mathrm{C_{36}H_{40}CuO_2N_2}$: C, 72.52; H, 6.76; N, 4.70. Found: C, 72.07; H, 7.06; N, 4.39%.

4.4.2. Synthesis of {2-[1-(2,6-dimethylphenylimino)-ethyl]phenoxy}$_2$Cu(II) (**3b**)

$\mathrm{Cu(OAc)_2 \cdot H_2O}$ (0.418 g, 2.14 mmol) and 2-[1-(2,6-dimethylphenylimino)ethyl]phenol (**1b**) (0.512 g, 2.14 mmol) were taken in methanol (ca. 30 mL) and stirred at room temperature until a clear solution was obtained. To the solution was added NEt$_3$ (0.282 g, 2.78 mmol) with constant stirring. The reaction mixture was stirred at room temperature for another 6 h when the product precipitated out as a dark brown solid and was isolated by filtration and vacuum dried (0.505 g, 87%). Crystals suitable for X-ray structure determination were obtained by slow evaporation from a saturated benzene solution. IR data cm^{-1} KBr pellet: 1601 (s) ($\nu_{C=N}$). λ_{max} (ε) $CHCl_3$: 670 nm ($\varepsilon = 130$ L mol^{-1} cm^{-1}). *Anal.* Calc. for $C_{32}H_{32}CuO_2N_2$: C, 71.15; H, 5.97; N, 5.19. Found: C, 71.18; H, 6.41; N, 5.34%.

4.4.3. Synthesis of {2-[1-(2-methylphenylimino)ethyl]-phenoxy}$_2$Cu(II) (3c)

$Cu(OAc)_2 \cdot H_2O$ (0.582 g, 2.92 mmol) and 2-[1-(2-methylphenylimino)ethyl]phenol (**1c**) (0.677 g, 3.00 mmol) were taken in methanol (ca. 40 mL) and stirred at room temperature until a clear solution was obtained. To the solution was added NEt_3 (0.314 g, 3.10 mmol) with constant stirring. The reaction mixture was stirred at reflux for 12 h and then allowed to cool to room temperature when the product was obtained as reddish-brown solid which was isolated by filtration and vacuum dried (0.573 g, 75%). Crystals suitable for X-ray structure determination were obtained by slow evaporation from a saturated benzene solution. IR data cm^{-1} KBr pellet: 1599 (s) ($\nu_{C=N}$). λ_{max} (ε) $CHCl_3$: 630 nm ($\varepsilon = 125$ L mol^{-1} cm^{-1}). *Anal.* Calc. for $C_{30}H_{28}CuO_2N_2$: C, 70.36; H, 5.51; N, 5.47. Found: C, 69.84; H, 5.55; N, 5.40%.

4.5. Polymerization experiments

Typical polymerization experiments: L-lactide (1.000 g, 6.94 mmol) and **3a**, **3b** and **3c**, in a stipulated molar ratio, were charged in an ampoule inside a glove box. The ampoule was taken out and put under vacuum at 50 °C for 30 min, after which the ampoule was sealed under vacuum and heated at 160 °C for 4 h. Under these conditions the reaction mixture turned into a monomer melt in which polymerization occurred. Subsequently, the molten reactive polymer mixture was cooled by immersing the sealed ampoule in liquid nitrogen to stop the polymerization. Conversion of L-lactide monomer was determined using the size exclusion chromatography method. The analyses were performed on the crude reaction mixture and no precipitation was executed to avoid fractionation of the sample in order to not influence the results.

4.6. X-ray analyses

X-ray diffraction data were collected either on a Bruker P4 diffractometer equipped with a SMART CCD detector or on an Oxford Diffraction XCalibur-S, and crystal data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).

5. Conclusion

In summary, a series of new nickel (**2a**, **2b**) and copper (**3a**, **3b**, **3c**) complexes, bearing a 2:1 ligand:metal stoichiometry, has been synthesized from the respective ligands, 2-[1-(2,6-diethylphenylimino)ethyl]phenol (**1a**), 2-[1-(2,6-dimethylphenylimino)ethyl]phenol (**1b**) and 2-[1-(2-methylphenylimino)ethyl]phenol (**1c**), by the reactions with the corresponding $M(OAc)_2 \cdot xH_2O$ (M = Ni, Cu) in the presence of NEt_3 as a base in moderate to high yields. The complexes **2a**, **2b**, **3a**, **3b** and **3c** have been structurally characterized by X-ray diffraction studies, which revealed that the geometry around the metal center is square planar in the nickel (**2a**, **2b**) and copper (**3a**, **3c**) complexes whilst it is distorted square planar in the copper **3b** complex. The catalysis studies revealed that while the copper complexes **3a**, **3b** and **3c**, efficiently catalyzed the ring-opening polymerization of L-lactide under solvent-free melt conditions, producing polylactide polymers of moderate molecular weights and having narrow molecular weight distributions, the nickel counterparts **2a** and **2b** failed to yield any polylactide polymer.

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Appendix A. Supplementary material

CCDC 609004, 605462, 607766, 605461 and 609526 contain the supplementary crystallographic data for **2a**, **2b**, **3a**, **3b** and **3c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.04.039.

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