Metal(II) Complexes of Compartmental Polynuclear Schiff Bases Containing Phenolate and Alkoxy Groups

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Abstract: Five mono-nuclear Cu(II) and Ni(II) complexes and one dinuclear Zn(II) complex were synthesized from the Schiff bases N,N’-bis(3-ethoxy-2-hydroxybenzylidene)-1,2-phenylenediamine (H₂L₂OEt-phda) and 2-ethoxy-6-({2-[(3-ethoxy-2-hydroxybenzylidene)amino]-benzyl}iminomethyl) phenol (H₂L₂OEt-ambza): [Cu(L₂OEt-phda)(H₂O)]·H₂O (1), [Ni(L₂OEt-phda)]·H₂O (2), [Cu(L₂OEt-ambza)]·H₂O·EtOH (3), [Cu(L₂OEt-ambza)]·H₂O (4), [Ni(L₂OEt-ambza)] (5) and [Zn₂(L₂OEt-ambza)(µ-OAc)(OAc)] (6). The complexes were structurally characterized with elemental microanalyses, IR, UV-Vis and ESI-MS spectroscopic techniques as well as single crystal X-ray crystallography. The metal centers display distorted square planar geometries in 2–4 and 5 and distorted square pyramidal (SP) in 1, whereas in 6 an intermediate geometry between SP and TBP was observed around the first Zn²⁺ ion and a tetrahedral around the second ion, with one acetate acting as a bridging ligand. In all cases, metal ions were incorporated into the N₂O₂ binding site with no involvement of the alkoxy groups in the coordination. The L₂OEt-ambza-complexes 3–6 revealed significant dihedral angles between the phenol rings and the plane containing the central benzene ring, and large O₂–O₂ bond distances (5.1–5.9 Å). Results are discussed in relation to other related Schiff base complexes.

Keywords: coordination compounds; crystal structure; Schiff bases; nickel; copper; zinc

1. Introduction

Polynucleating ligands are a class of compounds that are able to simultaneously bind two or more metal ions leading to the formation of di- or polynuclear metal complexes. Among many of these compounds which are widely used are those emerged through the Schiff base condensation reactions of diamines (ethylenediamine, en; propylenediamine, tn; 2,2-dimethylpropylenediamine, dmtn; o-phenylenediamine, phda and o-aminobenzylamine, ambza) with 2-hydroxy-3-alkoxybenzaldehyde (Scheme 1) in ethanol or methanol [1–13]. This is most likely attributed to not only to their ease of preparation but also to the bridging capability of the deionized phenolic group (pKₐ = 8–12) to bind two metal ions in close proximity [1–6,14–17]. In addition, these compartmental Schiff base ligands utilize two bonding coordination sites: N₂–O₂ + O₂–O₂ for transition metal ions and lanthanides as well as for alkali metal ions, resulted in the formation of discrete mononuclear, homo-
and heteronuclear metal complexes (3d/3d, 3d/4f and 3d/M⁺: M⁺ = Na⁺, Li⁺, K⁺) [1–11,14–42]. Some of these complexes showed a wide variety of potential applications ranging from mimic of biologically important molecules [8,27], biomedical field [5,24], catalysis [9,11,17,23,28] to magnetic materials [14,19,26,29,30,33–39] and particularly in single molecular magnets (SMM) [26,35–37].

![Scheme 1. Some of the very common compartmental Schiff base ligands based on 3-alkoxysalicyaldehyde.](image)

The rich diversity of the Schiff base metal complexes constructed from 3-alkoxysalicyaldehyde led to the isolation of fascinating coordination compounds [14,29–32,36–39]. Moreover, aside from the existence of two coordination sites in these compounds, they showed some selectivity towards the N₂O₂ coordination sites at which 3d metal(II) (Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺) and metal(III) (Mn³⁺, Fe³⁺) are incorporated [6,14,18,20–22,36,37,41,42]. In this work, we like to shed the light onto such preference site by exploring the interaction of 3d metal(II) ions with some Schiff bases which have not been extensively studied such as N,N'-bis(3-ethoxy-2-hydroxybenzylidene)-1,2-phenylenediamine (H₂LOEt-phda) and particularly 2-ethoxy-6-((2-[3-ethoxy-2-hydroxybenzylidene]amino)-benzyl|iminomethyl)phenol (H₂LOEt-ambza). The structure formulas of these ligands are illustrated in Scheme 1.

2. Results and Discussion

2.1. Synthetic Aspects

The two crystalline yellowish-orange ligands H₂LOEt-phda and H₂LOEt-ambza were prepared in good yield (80%–90%) by the Schiff base condensation of an ethanolic solution containing 1,2-diaminobenzene or 2-aminobenzylamine with 3-ethoxy salicylaldehyde in a 1:2 molar ratio, respectively. These were characterized by elemental microanalysis, IR, ¹H and ¹³C NMR as well as ESI-MS.

In ethanol, the reaction of H₂LOEt-phda with Cu(OAc)₂·H₂O in a 1:1 or 1:2 molar ratio afforded the long needles olive green compound [Cu(L²OEt-phda)(H₂O)]·H₂O (I). Also, the same product was obtained when Cu(OAc)₂·H₂O was added to the ligand followed by the addition of Zn(OAc)₂·2H₂O (1:1:1) and heated for about 15 min on a steam-bath or when the order of addition was reversed. The [Ni(L²OEt-phda)]·H₂O (2) complex was produced using a similar fashion as that described for I. It was isolated regardless the use of excess Ni(OAc)₂·4H₂O and/or upon the addition of Zn(OAc)₂·2H₂O first followed by nickel(II) acetate.

The reaction of an ethanolic solution containing H₂LOEt-ambza and Cu(OAc)₂·H₂O (1:2) or Cu(NO₃)₂·3H₂O and in the presence of Et₃N (1:2:2 molar ratio) yielded the mononuclear olive green [Cu(L²OEt-ambza)]·H₂O·EtOH (3) complex. Also, the interaction of a mixture of H₂LOEt-ambza, Cu(OAc)₂·2H₂O and Ni(OAc)₂·4H₂O (1:1:1) did not produce the Cu-Ni complex and resulted in the isolation of 3. Attempts made to synthesize hetero-dinuclear 3d-4f complexes through reactions of 3 with Ln(NO₃)₃·6H₂O (Ln = Gd, Tb or Dy) were unsuccessful. On the other hand, the reaction of
the ligand with Cu(hfacac)2 and Dy(NO3)3·6H2O at pH ~9 (Et3N) afforded a complex that is similar to 3 except with different solvents of crystallization: [Cu(L\textsuperscript{OEt}-ambza)]·H2O (4). Probably, one of the reasons for not-isolating any dinuclear Cu\textsuperscript{II}/II complexes may be attributed to the existence of the ligand in [Cu(L\textsuperscript{OEt}-ambza)] in an E conformation with respect to each azomethine link, where the two phenol-substituted benzene rings are twisted away from the plane of the diimine central benzene ring, as this was the case in the free H2L\textsuperscript{OEt}-ambza complex \[12,13\]. The brownish yellow crystalline [Ni(L\textsuperscript{OEt}-ambza)] (5) complex, the analog of 4, was obtained from the reaction of the ligand with Ni(NO3)3·6H2O (1:1 molar ratio) in slightly basic ethanolic solution (Et3N, pH ~ 9). In the 1–5 compounds, Cu(II) or Ni(II) ions are bound to the N2-O2 coordination sites (see X-ray section) and many similar mononuclear \[6,20–22,32\] with (N2-O2 site) as well as polynuclear complexes (N2-O2 + O2-O2 sites, assembling ligands or through a bridging ligand) have been isolated and structurally characterized with H2L\textsuperscript{OR}-en H2L\textsuperscript{OR}-tn, H2L\textsuperscript{OR}-dmtm and other related Schiff bases which were constructed from linear flexible aliphatic diamines \[3–7,14–16,19,25–29,32–39,41,42\]. The rigidity associated with the Schiff bases derived from 1,2-diaminobenzene (H2L\textsuperscript{phda}) and 2-aminobenzylamine (H2L\textsuperscript{OEt}-ambza) make the two phenolate rings not coplanar with the central benzene ring and as a result the two alkoxy groups are pointing away. This may account for the limited number of dinuclear metal complexes, with N2-O2 + O2-O2 bonding sites, which are obtained from these ligands \[8–11,24,30–32,41,42\]. Although the reaction of H2L\textsuperscript{OEt}-ambza with Zn(OAc)\textsubscript{2}·H2O (1:2) produced the yellow crystalline dinuclear complex [Zn2(L\textsuperscript{OEt}-ambza)(μ-OAc)(OAc)]\textsuperscript{6} (6), the two Zn\textsuperscript{2+} ions were incorporated into the N2-O2 bonding site. The synthesized complexes were characterized by elemental microanalyses, IR, UV-Vis and ESI-MS Spectroscopy and by single crystal X-ray crystallography.

2.2. General Characteristic Properties of the Complexes

The purity of the isolated complexes 1–6 was confirmed by elemental microanalyses (see experimental section). The complexes were found to be soluble in most common organic solvents: EtOH, MeOH, propan-2-ol, acetone, CH2Cl2, CHCl3 and CH3CN and in some cases Et2O. This course reflects their non-electrolytic nature and may explain why the complexes were obtained in relatively low yields (40%–60%). The non-electrolyte behavior of the complexes was also supported by measuring their molar conductivities in CH3CN, \(\Lambda_M = 1–10 \ \Omega^{-1}\cdot cm^{2}\cdot mol^{-1}\). The ESI-MS which was performed in MeOH on the 1–3 complexes clearly revealed the m/z peak of each complex is consistent with its given mononuclear formula [M(L\textsuperscript{OEt-}X)] (M = Ni\textsuperscript{2+} or Cu\textsuperscript{2+} and X = phda\textsuperscript{2−} or ambza\textsuperscript{2−}). Also, in addition to the mononuclear m/z peak, complex [Cu(L\textsuperscript{OEt-phda})(H2O)]·H2O (1) showed its major m/z peak at 933.016 corresponding to the protonated dimeric species [Cu2(C24H22N2O4)2+H]\textsuperscript{+} (calcd m/z = 933.182). This peak was not observed in complexes 2 and 3 nor in the dinuclear complex [Zn2(L\textsuperscript{OEt-ambza})(μ-OAc)(OAc)]\textsuperscript{6} (6). In contrast, the ESI-MS of 6 did not show any m/z peak that corresponded to either the di- nor the mono-nuclear species, but instead the major peak was found to be for the ligand; [H2L\textsuperscript{OEt-ambza+H}]\textsuperscript{+} (calcd m/z = 419.54, Found: 419.197). This result may indicate the instability of the mononuclear [Zn(L\textsuperscript{OEt-ambza})] species compared to Cu(II) and Ni(II) complexes.

2.3. IR and UV-VIS Spectra of the Complexes

Although the IR spectra of the two ligands under investigation did not clearly reveal the stretching frequencies of the phenolic O-H and the C=N imine groups, the structures of the ligands were confirmed by \textsuperscript{1}H and \textsuperscript{13}C NMR as well as with ESI-MS (experimental section). In general, the structural features of the complexes were strongly dominated by the ligands and hence the IR did not provide conclusive evidence about the coordination modes of the O-H and C=N bonds. However, the IR spectra of the complexes show some general features for example, they display a weak band around 3050 cm\textsuperscript{-1} and a weak series over the frequency range 2980–2870 cm\textsuperscript{-1} attributable to ν(C-H) of the aromatic and aliphatic groups, respectively. Also, the complexes showed a strong band at
730 cm\(^{-1}\) due to the C-H out of plane bending. Complexes 1–4 displayed one or two weak band(s) over the 3520–3870 cm\(^{-1}\) region due to the stretching frequency, v(O-H) of H\(_2\)O/EtOH molecules of crystallization and/or coordinated H\(_2\)O in [Cu(LO\(_{\text{OEt}}\)-phda)(H\(_2\)O)]H\(_2\)O (1) where the two bands were located at 3099 and 3467 cm\(^{-1}\).

The UV-Vis spectral data of the complexes 2–5 were recorded in CH\(_3\)CN, whereas 1 was recorded in CH\(_2\)Cl\(_2\). The spectrum of copper(II) complex [Cu(LO\(_{\text{OEt}}\)-phda)(H\(_2\)O)]H\(_2\)O (1) revealed the presence of a broad band at 600 nm and a less intense low energy band at 976 nm. This feature often indicates a distorted square pyramidal (SP) environment around the central Cu\(^{2+}\) ion, which is characteristic with the appearance of a broad band in the 550–650 nm region (dx\(_z\)y, dy\(_z\)z → dx\(_z^2\)-y\(_z^2\) transition) and may be associated with a low energy shoulder at λ > 800 nm [43–46]. The very strong band observed at 500 nm can be assigned to ligand-metal charge transfer transition (CT M→L). The visible spectra of Cu(II) complexes 3 and 4 displayed single absorption bands at 613 and 619 nm, respectively. This band could be attributed to \(^2\)B\(_{1g}\) ← \(^2\)A\(_{1g}\) transition in square planar Cu(II) geometry [47–49].

The visible spectral data of Ni(II) compound 2 exhibited very strong band at 398 (ε = 1920 M\(^{-1}\)cm\(^{-1}\)) which can be assigned to LMCT transition as in the case of Cu(II) complex 1 for the same dianion ligand, LO\(_{\text{OEt}}\)-phda\(^{2-}\) and another band at 422 nm due \(^1\)A\(_{1g}\) ← \(^1\)B\(_{1g}\) transition [47]. On the other hand, complex 5 displayed only one band at a much lower energy (624 nm) compared to 2. The very strong red shift of this band is most likely attributed to the reduced ligand field strength of LO\(_{\text{OEt}}\)-ambza\(^{2-}\).  

2.4. Description of the Structures

2.4.1. [Cu(LO\(_{\text{OEt}}\)-phda)(H\(_2\)O)]H\(_2\)O (1)

Compound 1 consists of neutral and mononuclear [Cu(LO\(_{\text{OEt}}\)-phda)(H\(_2\)O)] units and twofold disordered lattice water molecules with split occupancy 0.5. It crystallizes in the tetragonal space group P-42\(_1\)m (no. 113) with Z = 4. The Cu\(^{II}\) center, aqua ligand (O3) and lattice water molecules (O4, O5) are located at special positions with site symmetry m. A perspective view together with a partial atom numbering scheme of 1 is depicted in Figure 1. The Cu1 center is penta-coordinated by N1, N1’, O1, O1’ donor atoms of the tetradeinate LO\(_{\text{OEt}}\)-phda\(^{2-}\) Schiff base dianion, and O3 of aqua ligand. The CuN\(_2\)O\(_3\) chromophore may be described as tetragonal pyramid (SP) (τ = 0.00) [48] with O3 in the apical site [Cu1-O3 = 2.360(3) Å] The basal Cu-O/N bond distances are 1.9337(14) and 1.9711(16) Å, and the O1-Cu1-N1’ bond angle is 170.15(7)°. Cu1 deviates by 0.160 Å from the basal O2N2 plane. The dihedral angle between the two N-Cu-O coordination planes is 13.7° and the dihedral angle of the two benzene rings of the phenolate moieties is 6.0°, whereas the dihedral angle of the phenolate ring with the central benzene ring is 4.1°. The N1⋯N1’ and O1⋯O1’ separations within the N\(_2\)O\(_2\) unit are 2.613 and 2.707 Å, the O2⋯O2’ separation of the O\(_2\)-O\(_2\) unit is 5.605 Å. The shortest metal-metal separation is 4.9513(5) Å. Along the c-axis of the unit cell a supramolecular 1D system is formed via bifurcated hydrogen bonds of type O–H⋯(O,O) from aqua donor ligands to neighboring O1 and O2 acceptor atoms of LO\(_{\text{OEt}}\)-phda\(^{2-}\) (Table S1, Figure S1, see supplementary material section).
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2.4.2. [Ni(L\textsuperscript{OEt}-phda)]·H\textsubscript{2}O (2)

Compound 2 crystallizes in the monoclinic space group P2\textsubscript{1}/c (no. 14) with Z = 4 and consists of neutral and mononuclear [Ni(L\textsuperscript{OEt}-phda)] units and lattice water molecules. A perspective view together with partial atom numbering scheme of 2 is presented in Figure 2. The Ni\textsuperscript{II} ion has a slightly distorted square planar geometry, ligated by the N\textsubscript{2}-O\textsubscript{2} unit of the tetradeutate Schiff base ligand L\textsuperscript{OEt}-phda\textsuperscript{2−} [Ni1-O: 1.8411(13) and 1.8442(12); Ni1-N: 1.8550(15) and 1.8624(14) Å; N1-Ni1-O2 and N2-Ni1-O1 bond angles: 175.70(6) and 176.37(6)°]. Ni1 deviates by 0.006 Å from the O\textsubscript{2}N\textsubscript{2} plane. The dihedral angle between the two N-Ni-O coordination planes is 5.1° and the dihedral angle of the two phenolate rings is 132.3°, whereas the dihedral angles of the phenolate rings with the central benzene ring are 118.2 (ring-O1) and 35.5° (ring-O2), respectively. The N1···N2 and O1···O2 separations within the N2-O2 unit are 2.858 and 2.653 Å, the O3···O4 separation of the O2-O2 unit is 5.088 Å. The shortest metal-metal separation is 5.6773(4) Å. The water H atoms form bifurcated O-H···(O,O) intermolecular hydrogen bonds with the O atoms of the phenolate and ethoxy groups (Table S1, Figure S2).

![Figure 2. Perspective view of 2.](image)

2.4.3. [Cu(L\textsuperscript{OEt}-ambza)]·H\textsubscript{2}O·EtOH (3)

A perspective view together with partial atom numbering scheme of 3 is given in Figure 3. Compound 3 crystallizes in the monoclinic space group P2\textsubscript{1}/n (no. 14) with Z = 4 and consists of neutral and mononuclear [Cu(L\textsuperscript{OEt}-ambza)] units and solvent ethanol and water molecules. The ambza moiety differs from the symmetric phda moiety where one –CH\textsubscript{2} is inserted between N1 donor atom and central benzene ring. As a consequence, the conformation of the [Cu(L\textsuperscript{OEt}-ambza)] unit is changed to a non-planar “saddle-like” arrangement. The Cu\textsuperscript{II} ion has a distorted square planar geometry, ligated by the N\textsubscript{2}O\textsubscript{2} unit of the tetradeutate Schiff base ligand L\textsuperscript{OEt}-ambza\textsuperscript{2−} [Cu1-O: 1.899(4) and 1.904(4); Cu1-N: 1.937(6) and 1.978(6) Å; N1-Cu1-O2 and N2-Cu1-O1 bond angles: 151.0(2) and 158.2(2)°]. Cu1 deviates by 0.058 Å from the O\textsubscript{2}N\textsubscript{2} plane. The dihedral angle between the two N-Ni-O coordination planes is 144.9° and the dihedral angle of the two phenolate rings is 4.8273(11) Å. The water H atoms form bifurcated O-H···(O,O) intermolecular hydrogen bonds with the O atoms of the phenolate and ethoxy groups, and EtOH forms a hydrogen bond of type O-H···O to the water molecule (Table S1, Figure S3).
2.4.4. \([\text{Cu(L}\text{OEt-ambza)}] \cdot \text{H}_2\text{O} \) (4)

The monohydrate complex 4 differs from complex 3 by the lack of EtOH solvent molecule. It crystallizes in the monoclinic space group \(P2_1/c\) (no. 14) with \(Z = 4\). The unit cell volume of 4 differs by 13.21\% from that of complex 3 [2566.2(2) \(\text{Å}^3\)]. A perspective view together with partial atom numbering scheme of 4 is given in Figure 4. As in 3, the Cu1 center has a distorted square planar geometry, ligated by the N2O2 unit of the tetradentate Schiff base dianion \(L^{\text{OEt-ambza}}^{2-}\) \([\text{Cu1-O:} 1.8979(10) \text{ and } 1.9029(9); \text{Cu1-N:} 1.9325(12) \text{ and } 1.9715(12) \text{ Å}; \text{N1-Cu1-O2 and N2-Cu1-O1 bond angles:} 152.87(4) \text{ and } 156.26(4)°]\). Cu1 deviates by 0.025 Å from the O2N2 plane. The dihedral angle between the two N-Ni-O coordination planes is 34.7° and the dihedral angle of the two benzene rings of the phenolate moieties is 39.0°, whereas the dihedral angles of the phenolate rings with the central benzene ring are 64.2° (ring-O1) and 49.4° (ring-O2), respectively. The N1···N2 and O1···O2 separations within the N2-O2 unit are 2.875 and 2.640 Å, the O3···O4 separation of the O2-O2 unit is 5.873 Å. The shortest metal-metal separation is 4.1595(3) Å. The water H atoms form bifurcated O-H···(O,O) intermolecular hydrogen bonds with the O atoms of the phenolate and ethoxy groups (Table S1, Figure S4).

Figure 3. Perspective view of 3.

2.4.5. \([\text{Ni(L}\text{OEt-ambza)}]\) (5)

Complex 5 crystallizes without solvent molecules as neutral and mononuclear \([\text{Ni(L}\text{OEt-ambza)}]\) units in the monoclinic space group \(P2_1/c\) (no. 14) with \(Z = 4\). The unit cell volume of 5 differs by 42.5 \(\text{Å}^3\) from that of complex 4 [2227.13(12) \(\text{Å}^3\)]. A perspective view together with partial atom numbering scheme of 5 is given in Figure 5. The NiII ion has a slightly distorted square planar geometry, ligated by the N2O2 unit of the ligand \(L^{\text{OEt-ambza}}^{2-}\) \([\text{Ni1-O:} 1.8561(13) \text{ and } 1.8631(13); \text{Ni1-N:} 1.8731(16) \text{ and } 1.9082(16) \text{ Å}; \text{N1-Ni1-O2 and N2-Ni1-O1 bond angles:} 171.93(6) \text{ and } 172.61(6)°]\). Ni1 deviates by 0.001 Å from the O2N2 plane. The dihedral angle between the two N-Ni-O coordination planes is 8.1° and the dihedral angle of the two benzene rings of the phenolate moieties is 2.2°, whereas the dihedral angles of the phenolate rings with the central benzene ring are 128.0° (ring-O1) and 129.0°.
(ring-O2), respectively. The N1···N2 and O1···O2 separations within the N2-O2 unit are 2.735 and 2.457 Å, the O3···O4 separation of the O2-O2 unit is 5.177 Å. The shortest metal-metal separation is 3.4211(4) Å (Figure S5).

2.4.5. [Ni(LOEt-ambza)] (3)

The asymmetric unit consists of one LOEt-ambza2− dianionic ligand, two NiII metal centers and two acetate anionic ligands. The perspective view of the complex together with its partial atom numbering scheme is illustrated in Figure 6. The NiII ion has a slightly distorted square planar geometry, ligated by the N2O2 unit of the tetradentate Schiff base dianion LOEt-ambza2−. The Ni1-N1-O2 and Ni1-N2-O1 bond angles are 171.93(6) and 172.61(6)°. Ni1 deviates by 0.001 Å from the O2N2 plane. The dihedral angle between the two N-Ni-O coordination planes is 34.7° and the dihedral angle of the two benzene rings is 2.4°. The O2O2 separation of the O3·O4 atom is 5.177 Å. The shortest metal-metal separation is 3.4211(4) Å (Figure S5).

![Figure 6. Perspective view of 6.](image)

The Zn2 center has a distorted tetrahedral geometry formed by O1 and O2 of the LOEt-ambza Schiff base ligand, O6 of bridging acetate ligand and O7 of terminal acetate ligand. Their Zn-O bond distances are 2.002(3), 2.068(4), 2.002(3) and 1.918(4) Å, respectively. Thus, the two ZnII centers are triply bridged, with an intra-dinuclear distance of 2.9340(10) Å. The O1-Zn1-O2 and O1-Zn2-O2 bridging angles are 81.33(13) and 81.42(14)°. The O1-Zn2-O6 and O2-Zn2-O6 bond angles of 99.18(14) and 95.32(14)° are smaller than the O1-Zn2-O7, O2-Zn2-O7 and O6-Zn2-O7 bond angles of 124.25(14), 139.48(14) and
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108.64(15)°, respectively. The Zn2−O3, Zn−O4 and Zn2−O8 separations are 2.850(4), 2.786(4) and 2.713(4) Å, respectively. The shortest inter-dinuclear metal-metal separation is 6.3509(15) Å (Figure S6).

3. Experimental Section

3.1. Materials and Physical Measurements

2-Aminobenzylamine and 2-aminobenzene were purchased from TCI-America (Portland, OR, USA), whereas 3-ethoxy salicylaldehyde was purchased from Alfa Aesar (Ward Hill, MA, USA). All other chemicals were commercially available and used without further purification. Infrared spectra were recorded on a Cary 630 (ATR) spectrometer (Foster City, CA, USA). Electronic spectra were recorded using an Agilent 8453 HP diode array UV-Vis spectrophotometer (Santa Clara, CA, USA). $^1$H and $^{13}$C NMR spectra for the ligands were obtained at room temperature on a Varian 400 NMR spectrometer (Santa Clara, CA, USA) operating at 400 MHz ($^1$H) and 100 MHz ($^{13}$C). $^1$H and $^{13}$C NMR chemical shifts (δ) are reported in ppm and were referenced internally to residual solvent resonances (DMSO-d$_6$: δH = 2.49, δC = 39.4 ppm). ESI-MS were measured in MeOH on LC-MS Varian Saturn 2200 Spectrometer (Santa Clara, CA, USA). The conductivity measurements were performed using a Mettler Toledo Seven Easy conductivity meter (Columbus, OH, USA), calibrated by the aid of a 1413 µS/cm conductivity standard. Elemental analyses were carried out by the Atlantic Microlaboratory (Norcross, GA, USA).

3.2. Syntheses

3.2.1. Synthesis of the Ligands

$N,N'$-Bis(3-ethoxy-2-hydroxybenzylidene)-1,2-phenylenediamine ($H_2L_{OE}$-phda). 1,2-Diaminobenzene (1.082 g, 10 mmol) dissolved in warm ethanol (60 mL) was filtered on 3-ethoxy salicylaldehyde (3.324 g, 20 mmol) solution (40 mL ethanol) and the resulting solution was magnetically stirred at room temperature for 2 h, during which color turned orange. The solution was then allowed to evaporate at room temperature and the orange precipitate which separated, was collected by filtration and recrystallized from ethyl acetate and activated charcoal (overall yield: 3.64 g, 90%). Characterization: Anal. calcd for C$_{24}$H$_{24}$N$_2$O$_4$ (MM = 404.470 g/mol): C, 71.27; H, 5.98; N, 6.93%. Found: C, 71.38; H, 6.02; N, 6.78%. mp = 78–80 °C, IR (cm$^{-1}$): ~3300 (vw, br) ν(O-H); 3051 (w) (phenyl C-H stretching); 2978 (w), 2869 (w) (aliphatic C-H stretching), 1608 (s), 1584 (m), 1459 (s), 1389 (s) (C=C, C=N, C-N stretching); 1236 (s), 1188 (s) νas(C-O) (C-OEt stretching); 725 (vs) (C-H out of plane bending). ESI-MS (MeOH) m/z calcd for [M+H]$^+$ = 405.478, Found m/z = 405.181. $^1$H NMR (DMSO-d$_6$, 400 MHz, δ in ppm): δ = 12.98 (1H, s, OH); 8.91 (1H, s, HC=N); 7.44 (1H, m, -CH-phenol), 7.41 (1H, m, -CH-phenyl), 7.24 (1H, d, -CH-phenol), 7.11 (1H, d, CH-phenol), 6.88 (1H, t, CH-phenyl), 4.06 (2H, q, O-CH$_2$), 3.30 (s, 2H, HO-phenolic), 1.34 (3H, t, -CH$_3$). $^{13}$C NMR: (DMSO-d$_6$, 100 MHz) δ = 164.5 (C-OEt); 150.8 (C-OH); 147.0 (C=N); 142.1, 127.8, 124.0, 119.9 (C-phenol ring); 119.4, 118.5, 116.9 (C-phenyl ring); 64.0 (CH$_2$O); 14.7 (CH$_3$).

2-Ethoxy-6-({2-[3-ethoxy-2-hydroxybenzylidene)amino]-benzyl}iminomethyl)phenol ($H_2L_{OE}$-ambza). This ligand was synthesized using a similar procedure as that described for $H_2L_{OE}$-phda, except 2-aminobenzylamine was used instead of 1,2-diaminobenzene and the reaction mixture was refluxed for 2 h. The yellowish orange precipitate was recrystallized with CH$_2$Cl$_2$ and activated charcoal (overall yield: 80%). Characterization: Anal. calcd for C$_{25}$H$_{26}$N$_2$O$_4$ (MM = 418.53 g/mol): C, 71.75, H, 6.26, N, 6.69%. Found: C, 71.82, H, 6.62, N, 6.77%. mp = 115-117 °C. IR (cm$^{-1}$): 3056 (w) ν(C-H) (C-H stretching of phenyl and phenolate groups); 1628 (m) ν(C=N); 1614 (s), 1568 (m), 1460, 1394, 1339 (m) (C=C, C=N, C-N stretching); 1253 (vs), 1172 (s) νas(C-O) (C-OEt stretching); 728 (vs) (C-H out of plane bending). ESI-MS (MeOH) m/z calcd for [M+H]$^+$ = 405.478, Found m/z = 405.181. $^1$H NMR (DMSO-d$_6$, 400 MHz, δ in ppm): δ = 12.98 (1H, s, OH); 8.91 (1H, s, HC=N); 7.44 (1H, m, -CH phenol), 7.41 (1H, m, -CH phenyl), 7.24 (1H, d, -CH phenol), 7.11 (1H, d, CH phenol), 6.88 (1H, t, CH phenol), 4.06 (2H, q, O CH$_2$), 3.30 (s, 2H, HO phenolic), 1.34 (3H, t, -CH$_3$). $^{13}$C NMR: (DMSO-d$_6$, 100 MHz) δ = 164.5 (C-OEt); 150.8 (C-OH); 147.0 (C=N); 142.1, 127.8, 124.0, 119.9 (C-phenol ring); 119.4, 118.5, 116.9 (C-phenyl ring); 64.0 (CH$_2$O); 14.7 (CH$_3$).
3.2.2. Synthesis of the Complexes

A general method was used to synthesize the complexes 1-3 and 5 by heating an ethanolic solution (15 mL) containing a mixture of M(OAc)₂·nH₂O (M = Cu, n = 3; M = Ni, n = 4) or M(NO₃)₂·nH₂O (M = Cu, n = 3, M = Ni, n = 6) with pH adjusted to ~9 with Et₃N and the corresponding ligand (1:1 molar ratio and typically 0.25 mmol of each) for 5–10 min. The resulting solution was then filtered through celite and allowed to crystallize at room temperature for 1–3 days. The precipitate obtained was collected by filtration and dried in air.

[Cu(L⁰-Etpha)(H₂O)]H₂O (1). Tiny long olive green crystals suitable for X-ray structure determination were obtained from dilute ethanolic solution (overall yield 48%). Characterization: Anal. calcd for C₂₄H₂₆CuN₂O₆ (MM = 502.036): C, 57.42; H, 5.22; N, 5.56%. Found: C, 57.93; H, 5.60; N, 5.47%. IR: 3518 (w, br), 3377 (w, br), 3053 (w), 2970 (w), 2876 (w); 1621 (m), 1603 (s), 1580 (s), 1542 (s), 1447 (s), 1386 (m), 1367 (m), 1342 (m), 1239 (vs), 1193 (vs), 1145 (m), 1099 (m), 1075 (m), 1015 (m), 956 (m), 910 (m), 845 (m), 732 (vs). UV-VIS (λmax, nm (ε, M⁻¹ cm⁻¹)) in CH₂Cl₂: 500 (1820), ~600 (275), 976 (100). ΛM (CH₃CN) = 8.7 Ω⁻¹ cm² mol⁻¹. ESI-MS (MeOH): calcd m/z for [Cu(C₂₄H₂₆N₂O₆)₂+H⁺]: 933.016, found: 933.182 (major peak for protonated dimer).

[Ni(L⁰-Etpha)]H₂O (2). The complex was separated as shiny brick-red crystals of X-ray quality (overall yield: 53%). Characterization: Anal. calcd for C₂₄H₂₆NiN₂O₆ (MM = 479.16): C, 60.16; H, 5.05; N, 5.85%. Found: C, 59.95; H, 5.31; N, 5.90%. IR: 3490 (m, br), 3057 (w), 2975 (w), 2931 (w), 2882 (w); 1605 (s), 1578 (s), 1541 (s), 1493 (m), 1462 (s), 1444 (s), 1383 (m), 1366 (m), 1335 (m), 1242 (vs), 1200 (vs), 1178 (s), 1101 (m), 1078 (m), 1021 (m), 919 (m), 849 (m), 760 (m), 736 (vs). UV-VIS (λmax, nm (ε, M⁻¹ cm⁻¹)) in CH₃CN: 398 (1920), 422 (62.5). ΛM (CH₃CN) = 9.2 Ω⁻¹ cm² mol⁻¹. ESI-MS (MeOH): calcd m/z for [Ni(C₂₄H₂₆N₂O₆)₂]: 461.124, found: 461.100.

[Cu(L⁰-ambza)]H₂O·EtOH (3). Green long needles of X-ray quality were obtained from dilute ethanolic solution or upon recrystallization from CH₂Cl₂ (overall yield 48%). Characterization: Anal. calcd for C₂₂H₂₆CuN₂O₅Ni (MM = 502.036): C, 59.60; H, 5.93; N, 5.15%. Found: C, 59.45; H, 5.63; N, 5.53. IR: 3518 (w, br), 3377 (w, br), 3053 (w), 2970 (w), 2876 (w); 1621 (m), 1603 (s), 1580 (s), 1447 (s), 1356 (s), 1320 (s), 1235 (s), 1213 (vs), 1181 (s), 1181 (s), 1134 (m), 1077 (s), 1038 (s), 1015 (m), 740 (vs). UV-VIS (λmax, nm (ε, M⁻¹ cm⁻¹)) in CH₃CN: 613 (352), ΛM (CH₃CN) = 9.5 Ω⁻¹ cm² mol⁻¹. ESI-MS (MeOH): calcd m/z for [Cu(C₂₂H₂₆N₂O₅Ni)]: 480.06, found: 480.110.

[Cu(L⁰-ambza)]H₂O (4). A mixture of the ligand H₂L⁰-ambza (0.085 g, 0.20 mmol) and Cu(fhfacac)₂ (0.096, 0.20 mmol) dissolved in EtOH (15 mL) and pH of the solution was adjusted to ~9 by Et₃N. This was followed by heating on a water-bath for 5 min, then filtered through celite and allowed to stand at room temperature. The resulting brownish green crude precipitate was collected by filtration and recrystallized from CH₃CN, where green plates of the complex of X-ray quality were isolated after 3 days. These were collected by filtration and dried in air (overall yield: 47%). Characterization: Anal. calcd for C₂₅H₂₆CuN₂O₅ (MM = 498.05): C, 60.30; H, 5.26; N, 5.62%. Found: C, 59.95; H, 5.37; N, 5.49%. IR: 3578 (m), 3525 (m); 3049 (w), 2974 (w), 2927 (w), 2924 (w) 2880 (w); 1633 (m), 1600 (vs), 1585 (vs), 1542 (s), 1445 (vs), 1384 (s), 1322 (s), 1236 (s), 1232 (vs), 1211 (vs), 1180 (vs), 1113 (m), 1076 (s), 1019 (m), 913 (m), 899 (m), 765 (m), 739 (vs). UV-VIS (λmax, nm (ε, M⁻¹ cm⁻¹)) in CH₃CN: 619 (304). ΛM (CH₃CN) = 3.8 Ω⁻¹ cm² mol⁻¹.

[Ni(L⁰-ambza)] (5). This complex was isolated as a brownish-yellow crystalline compound upon further crystallization from EtOH (overall yield: 44%). Characterization: Anal. calcd for C₂₅H₂₆NiN₂O₅Ni (MM = 475.20): C, 63.19; H, 5.09; N, 5.90%. Found: C, 63.07; H, 5.21; N, 5.71. IR: 3052 (w), 2973 (w), 2927 (w), 2878 (w); 1643 (w), 1604 (vs), 1579 (s), 1541 (s), 1439 (vs), 1395 (m), 1323 (s),
1218 (vs), 1213 (vs), 1182 (vs), 1099 (s), 1136 (m), 1019 (m), 913 (m), 851 (m), 727 (vs). UV-VIS [\( \lambda_{\text{max}}, \text{nm} \) (\( \varepsilon, \text{M}^{-1} \cdot \text{cm}^{-1} \))] in CH\(_3\)CN: 624 (179). \( \Lambda_{\text{M}} \) (CH\(_3\)CN) = 1.6 \( \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \).

\[ [\text{Zn}_{2}(\text{L}^{\text{OEt}}-\text{ambza})(\mu-\text{OAc})(\text{OAc})] \] (6). A mixture of H\(_2\)L\(^{\text{OEt}}\)-ambza (0.085 g, 0.20 mmol) and Zn(OAc)\(_2\)·2H\(_2\)O (0.088, 0.40 mmol) dissolved in EtOH (15 mL) was heated for 5 min, followed by filtration through celite and then allowed to stand at room temperature. After 3 days, the resulting crude precipitate was collected by filtration and recrystallized from CH\(_3\)CN to afford tiny yellow single crystals of suitable for X-ray structure determination (overall yield: 64%). Characterization: Anal. calcd for C\(_{29}\)H\(_{30}\)N\(_2\)O\(_8\)Zn\(_2\) (MM = 665.39): C, 52.35; H, 4.54; N, 4.21%. Found: C, 52.65; H, 4.68; N, 4.32. IR: 3060 (w), 2984 (w), 2932 (w), 2900 (w); 1634 (m), 1605 (s), 1558 (s), 1542 (s), 1439 (s), 1390 (s), 1328 (m), 1290 (m), 1236 (vs), 1183 (s), 1114 (m), 1076 (s), 1014 (s), 897 (s), 840 (m), 735 (vs). ESI-MS (MeOH): calcd m/z for [M+H]\(^{+}\): 419.54, found: 419.197. \( \Lambda_{\text{M}} \) (CH\(_3\)CN) = 1.1 \( \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \).

### 3.3. X-Ray Crystal Structure Analysis

The X-ray single-crystal data of the six compounds were collected on a Bruker-AXS APEX CCD diffractometer at 100(2) K (Madison, WI, USA). The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Tables 1 and 2. The structure refinements were solved by direct methods and refined by full-matrix least-squares methods on F\(^2\), using the SHELXTL [54] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use HFIX (parent C atoms) or DFIX (i.e., O-H distance restraints for parent O atoms) utility of the SHELXTL program package. In case of 1, split occupancy of 0.5 was applied for O4 and O5 atoms of disordered water molecule, and their H atoms were omitted. High R1 (I > 2\( \sigma(I) \)) values of 0.0818 (for 3) and 0.0934 (for 6) are caused by low crystal quality of samples. Molecular plots were performed with the Mercury program [55].

#### Table 1. Crystallographic Data and Processing Parameters for Compounds 1–3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{C}<em>{24}\text{H}</em>{24}\text{CuN}<em>{2}\text{O}</em>{6} )</td>
<td>( \text{C}<em>{24}\text{H}</em>{24}\text{N}<em>{2}\text{NiO}</em>{5} )</td>
<td>( \text{C}<em>{27}\text{H}</em>{32}\text{CuN}<em>{2}\text{O}</em>{6} )</td>
</tr>
<tr>
<td>Formula mass</td>
<td>500.00</td>
<td>479.14</td>
<td>544.10</td>
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<td>Crystal system</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-42( \text{m} )</td>
<td>P(_2)(_1)/c</td>
<td>P(_2)(_1)/n</td>
</tr>
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<td>( a/\text{Å} )</td>
<td>21.9174(6)</td>
<td>12.9329(6)</td>
<td>10.7944(6)</td>
</tr>
<tr>
<td>( b/\text{Å} )</td>
<td>21.9174(6)</td>
<td>14.5517(7)</td>
<td>20.286(1)</td>
</tr>
<tr>
<td>( c/\text{Å} )</td>
<td>4.9513(2)</td>
<td>11.7485(6)</td>
<td>11.7600(6)</td>
</tr>
<tr>
<td>( \alpha/\circ )</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>( \beta/\circ )</td>
<td>90</td>
<td>109.983(3)</td>
<td>94.767(2)</td>
</tr>
<tr>
<td>( \gamma/\circ )</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>( V/\text{Å}^3 )</td>
<td>2378.47(16)</td>
<td>2077.74(18)</td>
<td>2566.2(2)</td>
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<td>( Z )</td>
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<td>4</td>
<td>4</td>
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<tr>
<td>( T/\text{K} )</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>( \mu/\text{mm}^{-1} )</td>
<td>0.959</td>
<td>0.975</td>
<td>0.895</td>
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<tr>
<td>Dcalc/Mg ( \text{m}^{-3} )</td>
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<td>1.532</td>
<td>1.408</td>
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<tr>
<td>Crystal size/mm</td>
<td>0.24 ( \times ) 0.15 ( \times ) 0.11</td>
<td>0.24 ( \times ) 0.18 ( \times ) 0.13</td>
<td>0.16 ( \times ) 0.15 ( \times ) 0.11</td>
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<tr>
<td>( \theta ) max/\circ</td>
<td>30.27</td>
<td>30.02</td>
<td>26.00</td>
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<tr>
<td>Data collected</td>
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<td>32859</td>
<td>5073</td>
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<tr>
<td>Unique refl./Rint</td>
<td>3594/0.0381</td>
<td>6067/0.0600</td>
<td>5044/—</td>
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<td>Parameters/Restraints</td>
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<td>297/2</td>
<td>339/3</td>
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<td>Goodness-of-Fit on F(^2)</td>
<td>1.082</td>
<td>0.843</td>
<td>1.155</td>
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<tr>
<td>(I &gt; 2( \sigma(I) ))/( wR2 ) (all data)</td>
<td>0.0332/0.0975</td>
<td>0.0343/0.0894</td>
<td>0.0818/0.2113</td>
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<tr>
<td>Residual extrema/e/\text{Å}^3</td>
<td>1.11/−0.59</td>
<td>0.56/−0.51</td>
<td>0.94/−0.73</td>
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Table 2. Crystallographic Data and Processing Parameters for Compounds 4–6.

<table>
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<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>Crystallographic Data</th>
<th>Processing Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C_{25}H_{26}CuN_{2}O_{5}</td>
<td>Crystal system: Monoclinic</td>
<td>Space group: P2_1/c</td>
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<td></td>
<td></td>
<td>a/Å: 12.0486(4)</td>
<td>498.03</td>
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<tr>
<td>5</td>
<td>C_{25}H_{24}N_{2}O_{4}</td>
<td>Crystal system: Monoclinic</td>
<td>Space group: P2_1/c</td>
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<td></td>
<td></td>
<td>b/Å: 16.5021(5)</td>
<td>475.15</td>
</tr>
<tr>
<td>6</td>
<td>C_{29}H_{30}N_{2}O_{8}Zn_2</td>
<td>Crystal system: Triclinic</td>
<td>Space group: P-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c/Å: 11.2905(3)</td>
<td>665.33</td>
</tr>
</tbody>
</table>

| α(°)     | 90                | 90                    | 70.908(8)             |
| β(°)     | 97.206(2)         | 93.783(2)             | 78.161(8)             |
| γ(°)     | 90                | 90                    | 79.352(7)             |
| V/Å³     | 2227.13(12)       | 2184.6(3)             | 1358.8(4)             |
| Z        | 4                 | 4                     | 2                     |
| T/K      | 100(2)            | 100(2)                | 100(2)                |
| µ/mm⁻¹   | 1.021             | 0.923                 | 1.821                 |
| Dcalc/Mg m⁻³ | 1.485 | 1.445 | 1.626 |
| Crystal size/mm | 0.21 × 0.18 × 0.12 | 0.26 × 0.21 × 0.13 | 0.26 × 0.20 × 0.14 |
| θ max/°  | 30.52             | 28.00                 | 25.00                 |
| Data collected | 86525 | 20418 | 8896 |
| Unique refl./Rint | 6786/0.0241 | 5272/0.0389 | 4772/0.0803 |
| Parameters/Restraints | 306/2 | 291/0 | 374/0 |
| Goodness-of-Fit on F² | 1.056 | 1.047 | 1.122 |
| (I > 2σ(I))/wR² (all data) | 0.0287/0.0919 | 0.0375/0.0885 | 0.0934/0.2488 |
| Residual extrema/e.Å⁻³ | 0.54/−0.34 | 0.96/−0.59 | 1.89/−1.44 |

4. Conclusions

Five mononuclear Cu(II) and Ni(II) (1–5) as well as a dinuclear Zn(II) (6) derived from the Schiff bases H₂L⁰⁰E⁻phda and H₂L⁰⁰E⁻ambza were synthesized and structurally characterized where the metal ions are bound through the N₂-O₂ bonding site without the involvement of the alkoxy groups into the coordination. Many of such Schiff base complexes have been isolated with 3d, 4f and alkali metal ions [7,10,17,18,20–24,30–42,56–60]. Mononuclear complexes with O₂-O₂ bonding site mode are very rare but they have been observed in a few cases with H₂L⁰⁰R⁻en Schiff bases with K⁺ [61] and especially with Ln(NO₃)₃ (Ln = Ho, Sm, Nd) when the imino groups are protonated [62,63].

Large number of dinuclear metal complexes were formed through the incorporation of metal ions into the two coordination sites N₂-O₂ and O₂-O₂ including the two alkoxy groups, especially with the bi-compartmental Schiff bases (H₂L⁰⁰R⁻en, H₂L⁰⁰R⁻tn, H₂L⁰⁰R⁻dmtn) derived from aliphatic diamines [5,6,26,27,33,34,39,41,42,64–78]. Other di- and poly-nuclear complexes were obtained through assembly of the Schiff bases or through bridging ligands [29,32,34,36–38,41,64,67,68,78–84].

The unsuccessful isolation of dinuclear complexes with H₂L⁰⁰E⁻ambza where the alkoxy groups are not participating in the coordination with a second metal ion is most likely attributed to: (1) the large dihedral angles (32–129° in complexes 3–6, see X-ray section) between the phenolate rings and the plane containing the central benzene ring which make the alkoxy groups pointing away and coming in an inappropriate position to coordinate to a second metal into the O₂-O₂ bonding site and (2) the large bite angle (bond distances in O₂-O₂ are within the range 5.2–5.9 Å in these complexes). This data is summarized in Table 3 for L⁰⁰E⁻ambza-metal(II) complexes. As a result, no complexes with N₂-O₂ + O₂-O₂ were isolated. An alternative approach to synthesize such dinuclear complexes is to use large 4d or 5d transition metal ions and alkali/alkaline earth metal ions by incorporating them into the precursor synthesized mononuclear Cu(II) and Ni(II) complexes (3–5).
Table 3. The O₂-O₂ Bond Distances and the Dihedral Angle(s) between the Phenolate Rings and Benzene Ring in the Complexes 3–6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Dihedral angle(s) (°)</th>
<th>O₂-O₂ bond distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>118.2, 35.5</td>
<td>5.873</td>
</tr>
<tr>
<td>4</td>
<td>64.2, 49.4</td>
<td>5.818</td>
</tr>
<tr>
<td>5</td>
<td>128.0, 129.0</td>
<td>5.177</td>
</tr>
<tr>
<td>6</td>
<td>69.7, 31.8</td>
<td>5.468</td>
</tr>
</tbody>
</table>

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/6/8/91/s1. CCDC 1489003–1489008 contain the supplementary crystallographic data for 1–6, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Hydrogen bonds are listed in Table S1, packing views for crystal structures 1–6 are given in Figures S1–S6, respectively.

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Author Contributions: Franz A. Mauter and Roland C. Fisher were responsible for the single crystal structures determination. Mark Spell was responsible for the NMR and ESI-MS measurements. Andres R. Acevedo and Diana H. Tran were in charge of the synthesis, spectroscopic characterization of the compounds as well as molar conductivity measurements. Salah S. Massoud was responsible for part of the syntheses. Franz A. Mautner and Salah S. Massoud were in charge of interpretation of data and writing process of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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