crystals

MDPI

Article

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

Franz A. Mautner [1,*], Roland C. Fischer [2], Mark Spell [3], Andres R. Acevedo [4], Diana H. Tran [4] and Salah S. Massoud [4,*]

[1] Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria
[2] Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9/V, A-8010 Graz, Austria; roland.fischer@tugraz.at
[3] Department of Chemistry, Louisiana State University, Choppin Hall, Baton Rouge, LA 70803, USA; mspell4@tigers.lsu.edu
[4] Department of Chemistry, University of Louisiana at Lafayette, P.O. Box 43700, Lafayette, LA 70504, USA; ara4921@louisiana.edu (A.R.A.); dht8287@louisiana.edu (D.H.T.)
* Correspondence: mautner@tugraz.at (F.A.M.); ssmassoud@louisiana.edu (S.S.M.); Tel.: +43-316-4873-8234 (F.A.M.); +1-337-482-5672 (S.S.M.)

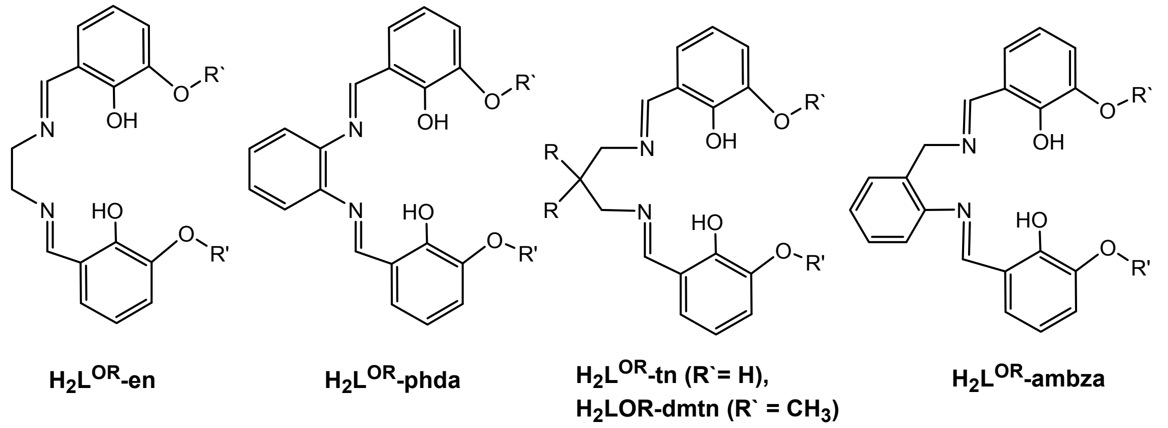
Academic Editors: Thomas Doert and Mathias Wickleder
Received: 6 July 2016; Accepted: 3 August 2016; Published: 9 August 2016

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 (H_2L^{OEt}-phda) and 2-ethoxy-6-({2-[(3-ethoxy-2-hydroxybenzylidene)amino]-benzyl}iminomethyl) phenol (H_2L^{OEt}-ambza): [Cu(L^{OEt}-phda)(H_2O)]·H_2O (**1**), [Ni(L^{OEt}-phda)]·H_2O (**2**), [Cu(L^{OEt}-ambza)]·H_2O·EtOH (**3**), [Cu(L^{OEt}-ambza)]·H_2O (**4**), [Ni(L^{OEt}-ambza)] (**5**) and [Zn_2(L^{OEt}-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 Zn^{2+} ion and a tetrahedral around the second ion, with one acetate is acting as a bridging ligand. In all cases, metal ions were incorporated into the N_2-O_2 binding site with no involvement of the alkoxy groups in the coordination. The L^{OEt}-ambza-complexes **3**–**6** revealed significant dihedral angles between the phenol rings and the plane containing the central benzene ring, and large O_2-O_2 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 (pK_a = 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: N_2-O_2 + O_2-O_2 for transition metal ions and lanthanides as well as for alkali metal ions, resulted in the formation of discrete mononuclear, homoand 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**-alkoxysalicylaldehyde.

The rich diversity of the Schiff base metal complexes constructed from 3-alkoxysalicylaldehyde 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 N_2-O_2 coordination sites at which *3d* metal(II) (Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and metal(III) (Mn^{3+}, Fe^{3+}) 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 (H_2L^{OEt}-phda) and particularly 2-ethoxy-6-({2-[(3-ethoxy-2-hydroxybenzylidene)amino]-benzyl}iminomethyl)phenol (H_2L^{OEt}-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 H_2L^{OEt}-phda and H_2L^{OEt}-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 ^{13}C NMR as well as ESI-MS.

In ethanol, the reaction of H_2L^{OEt}-phda with $Cu(OAc)_2{\cdot}H_2O$ in a 1:1 or 1:2 molar ratio afforded the long needles olive green compound $[Cu(L^{OEt}\text{-phda})(H_2O)]{\cdot}H_2O$ (**1**). Also, the same product was obtained when $Cu(OAc)_2{\cdot}H_2O$ was added to the ligand followed by the addition of $Zn(OAc)_2{\cdot}2H_2O$ (1:1:1) and heated for about 15 min on a steam-bath or when the order of addition was reversed. The $[Ni(L^{OEt}\text{-phda})]{\cdot}H_2O$ (**2**) complex was produced using a similar fashion as that described for **1**. It was isolated regardless the use of excess $Ni(OAc)_2{\cdot}4H_2O$ and/or upon the addition of $Zn(OAc)_2{\cdot}2H_2O$ first followed by nickel(II) acetate.

The reaction of an ethanolic solution containing H_2L^{OEt}-ambza and $Cu(OAc)_2{\cdot}H_2O$ (1:2) or $Cu(NO_3)_2{\cdot}3H_2O$ and in the presence of Et_3N (1:2:2 molar ratio) yielded the mononuclear olive green $[Cu(L^{OEt}\text{-ambza})]{\cdot}H_2O{\cdot}EtOH$ (**3**) complex. Also, the interaction of a mixture of H_2L^{OEt}-ambza, $Cu(OAc)_2{\cdot}H_2O$ and $Ni(OAc)_2{\cdot}4H_2O$ (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 $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Gd, Tb or Dy) were unsuccessful. On the other hand, the reaction of the ligand with Cu(hfacac)$_2$ and Dy(NO$_3$)$_3$·6H$_2$O at pH ~9 (Et$_3$N) afforded a complex that is similar to **3** except with different solvents of crystallization: [Cu(L^{OEt}-ambza)]·H$_2$O (**4**). Probably, one of the reasons for not-isolating any dinucear Cu^{II}-M$^{II/III}$ complexes may be attributed to the existence of the ligand in [Cu(L^{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 H$_2$L^{OEt}-ambza compound [12,13]. The brownish yellow crystalline [Ni(L^{OEt}-ambza)] (**5**) complex, the analog of **4**, was obtained from the reaction of the ligand with Ni(NO$_3$)$_2$.6H$_2$O (1:1 molar ratio) in slightly basic ethanolic solution (Et$_3$N, pH ~ 9). In the **1**–**5** compounds, Cu(II) or Ni(II) ions are bound to the N$_2$-O$_2$ coordination sites (see X-ray section) and many similar mononuclear [6,20–22,32] with (N$_2$-O$_2$ site) as well as polynuclear complexes (N$_2$-O$_2$ + O$_2$-O$_2$ sites, assembling ligands or through a bridging ligand) have been isolated and structurally characterized with H$_2$L^{OR}-en H$_2$L^{OR}-tn, H$_2$L^{OEt}-dmtn 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 (H$_2$L^{OR}-phda) and 2-aminobenzylamine (H$_2$L^{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 N$_2$-O$_2$ + O$_2$-O$_2$ bonding sites, which are obtained from these ligands [8–11,24,30–32,41,42]. Although the reaction of H$_2$L^{OEt}-ambza with Zn(OAc)$_2$·H$_2$O (1:2) produced the yellow crystalline dinuclear complex [Zn$_2$(L-^{OEt}-ambza)(μ-OAc)(OAc)] (**6**), the two Zn^{2+} ions were incorporated into the N$_2$-O$_2$ 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, CH$_2$Cl$_2$, CHCl$_3$ and CH$_3$CN and in some cases Et$_2$O. This of 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 CH$_3$CN; Λ_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^{OEt}-X)] (M = Ni^{2+} or Cu^{2+} and X = phda^{2-} or ambza^{2-}). Also, in addition to the mononuclear m/z peak, complex [Cu(L^{OEt}-phda)(H$_2$O)]·H$_2$O (**1**) showed its major m/z peak at 933.016 corresponding to the protonated dimeric species [Cu$_2$(C$_{24}$H$_{22}$N$_2$O$_4$)$_2$+H]$^+$ (calcd m/z = 933.182). This peak was not observed in complexes **2** and **3** nor in the dinuclear complex [Zn$_2$(L-^{OEt}-ambza)(μ-OAc)(OAc)] (**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; [H$_2$L^{OEt}-ambza+H]$^+$ (calcd m/z = 419.54, Found: 419.197). This result may indicate the instability of the mononuclear [Zn(L^{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 ^{1}H and ^{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^{-1} and a weak series over the frequency range 2980–2870 cm^{-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, ν(O-H) of H_2O/EtOH molecules of crystallization and/or coordinated H_2O in [Cu(L^{OEt}-phda)(H_2O)]·H_2O (**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_3CN, whereas **1** was recorded in CH_2Cl_2. The spectrum of copper(II) complex [Cu(L^{OEt}-phda)(H_2O)]·H_2O (**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 (dxz,dyz → dx^2-y^2 transition) and may be associated with a low energy shoulder at $\lambda > 800$ 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 $^2B_{1g} \leftarrow {}^2A_{1g}$ transition in square planar Cu(II) geometry [47–49].

The visible spectrum 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, L^{OEt}-phda^{2-} and another band at 422 nm due $^1A_{1g} \leftarrow {}^1B_{1g}$ 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 L^{OEt}-ambza^{2-}.

2.4. Description of the Structures

2.4.1. [Cu(L^{OEt}-phda)(H_2O)]·H_2O (**1**)

Compound **1** consists of neutral and mononuclear [Cu(L^{OEt}-phda)(H_2O)] 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 tetradentate L^{OEt}-phda^{2-} Schiff base dianion, and O3 of aqua ligand. The CuN_2O_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 O_2N_2 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 L^{OEt}-phda^{2-} (Table S1, Figure S1, see supplementary material section).

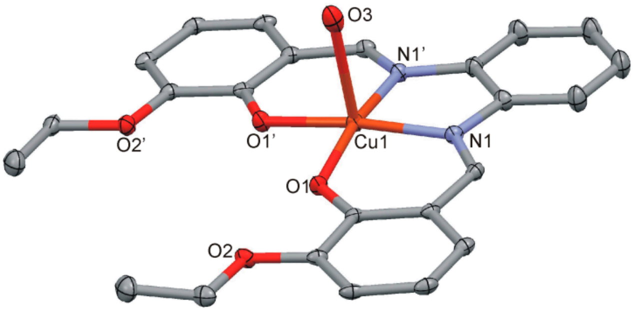


Figure 1. Perspective view of **1**. Disordered water molecule is omitted.

2.4.2. [Ni(L^{OEt}-phda)]·H_2O (**2**)

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with Z = 4 and consists of neutral and mononuclear [Ni(L^{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^{II} ion has a slightly distorted square planar geometry, ligated by the N_2-O_2 unit of the tetradentate Schiff base ligand L^{OEt}-$phda^{2-}$ [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_2N_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 1.5°, whereas the dihedral angle of the phenolate ring with the central benzene ring is 15.4°. The N1···N2 and O1···O2 separations within the N_2-O_2 unit are 2.540 and 2.461 Å, the O3···O4 separation of the O_2-O_2 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).

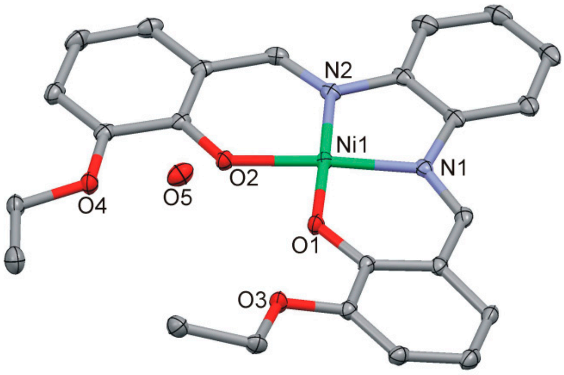


Figure 2. Perspective view of **2**.

2.4.3. [Cu(L^{OEt}-ambza)]·H_2O·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 $P2_1/n$ (no. 14) with Z = 4 and consists of neutral and mononuclear [Cu(L^{OEt}-ambza)] units and solvent ethanol and water molecules. The ambza moiety differs from the symmetric phda moiety where one –CH_2 is inserted between N1 donor atom and central benzene ring. As a consequence, the conformation of the [Cu(L^{OEt}-ambza)] unit is changed to a non-planar "saddle-like" arrangement. The Cu^{II} ion has a distorted square planar geometry, ligated by the N_2O_2 unit of the tetradentate Schiff base ligand L^{OEt}-$ambza^{2-}$ [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_2N_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 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 N_2-O_2 unit are 2.858 and 2.653 Å, the O3···O4 separation of the O_2-O_2 unit is 5.873 Å. The shortest metal-metal separation 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).

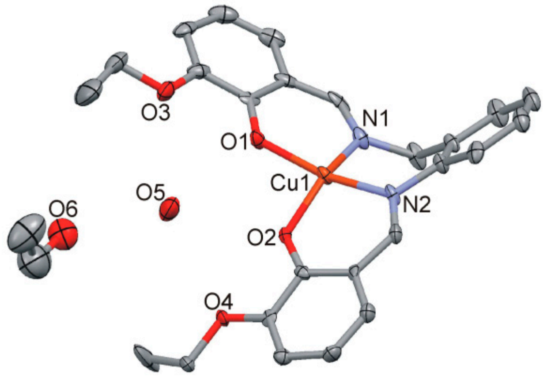


Figure 3. Perspective view of **3**.

2.4.4. [Cu(L^{OEt}-ambza)]·H_2O (**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) 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 N_2O_2 unit of the tetradentate Schiff base dianion L^{OEt}-ambza^{2-} [Cu1-O: 1.8979(10) and 1.9029(9); Cu1-N: 1.9325(12) and 1.9715(12) Å; N1-Cu1-O2 and N2-Cu1-O1 bond angles: 152.87(4) and 156.26(4)°]. Cu1 deviates by 0.025 Å from the O_2N_2 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 N_2-O_2 unit are 2.875 and 2.640 Å, the O3···O4 separation of the O_2-O_2 unit is 5.818 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).

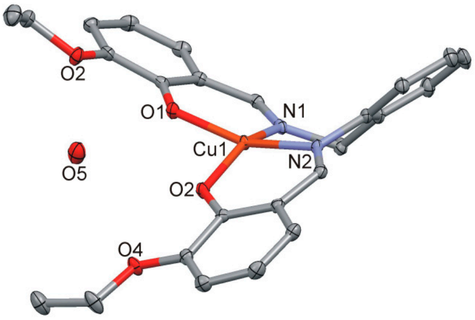


Figure 4. Perspective view of **4**.

2.4.5. [Ni(L^{OEt}-ambza)] (**5**)

Complex **5** crystallizes without solvent molecules as neutral and mononuclear [Ni(L^{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 Å^3 from that of complex **4** [2227.13(12) Å^3]. A perspective view together with partial atom numbering scheme of **5** is given in Figure 5. The Ni^{II} ion has a slightly distorted square planar geometry, ligated by the N_2O_2 unit of the ligand L^{OEt}-ambza^{2-} [Ni1-O: 1.8561(13) and 1.8631(13); Ni1-N: 1.8731(16) and 1.9082(16) Å; N1-Ni1-O2 and N2-Ni1-O1 bond angles: 171.93(6) and 172.61(6)°]. Ni1 deviates by 0.001 Å from the O_2N_2 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 N_2-O_2 unit are 2.735 and 2.457 Å, the O3···O4 separation of the O_2O_2 unit is 5.177 Å. The shortest metal-metal separation is 3.4211(4) Å (Figure S5).

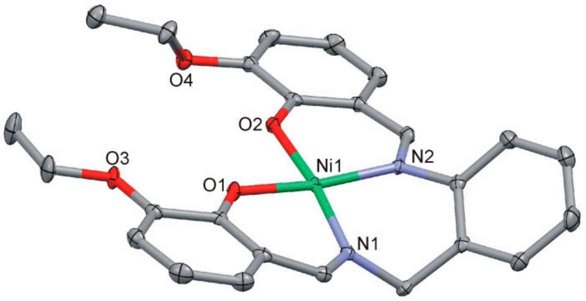


Figure 5. Perspective view of **5**.

2.4.6. [$Zn_2(L^{OEt}$-ambza)(μ-OAc)(OAc)] (**6**)

The dinuclear complex **6** crystallizes in the triclinic space group P-1 (no. 2) with Z = 2. The asymmetric unit consists of one L^{OEt}-ambza^{2-} dianionic ligand, two Zn^{II} 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 Zn1 center is penta-coordinated by N1, N2, O1, O2 donor atoms of L^{OEt}-ambza^{2-} Schiff base dianion and O5 atom of acetate bridging ligand. The ZnN_2O_3 chromophore may be described as intermediate geometry between SP and trigonal bipyramid (TBP) but more close to TBP (τ = 0.55) [50] with O1 and N2 in the axial sites [Zn1-O1 = 2.053(3), Zn1-N2 = 2.062(4) Å; O1-Zn1-N2 = 169.43(14)°]. The equatorial Zn-O/N bond distances are 2.021(3) to O2, 2.033(3) to O5 and 2.034(4) Å to N1, respectively. Zn1 deviates by 0.459 Å from the O_2N_2 plane of L^{OEt}-ambza^{2-} ligand. The dihedral angle between the N1-Zn1-O1 and N2-Zn1-O2 coordination planes is 43.9° and the dihedral angle of the two rings of the phenolate moieties is 38.5°, whereas the dihedral angles of the phenolate rings with the central benzene ring are 69.7 (ring-O1) and 31.8° (ring-O2), respectively. The N1···N2 and O1···O2 separations within the N_2-O_2 unit are 2.933 and 2.655 Å, the O3···O4 separation of the O_2-O_2 unit is 5.468 Å.

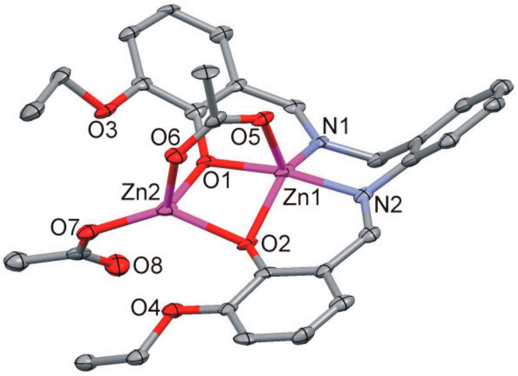


Figure 6. Perspective view of **6**.

The Zn2 center has a distorted tetrahedral geometry formed by O1 and O2 of L^{OEt}-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 Zn^{II} 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

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^{OEt}-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 $C_{24}H_{24}N_2O_4$ (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) ν_{as}(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_2O); 14.7 (CH_3).

2-Ethoxy-6-({2-[(3-ethoxy-2-hydroxybenzylidene)amino]-benzyl}iminomethyl)phenol (H_2L^{OEt}-ambza). This ligand was synthesized using a similar procedure as that described for H_2L^{OEt}-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_2Cl_2 and activated charcoal (overall yield: 80%). Characterization: Anal. calcd for $C_{25}H_{26}N_2O_4$ (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 (s), 1394, 1339 (m) (C=C, C=N, C-N stretching); 1253 (vs), 1172 (s) ν_{as}(C-O) (C-OEt stretching); 728 (vs) (C-H out of plane bending). ESI-MS (MeOH) calcd m/z for $[M+H]^+$ = 419.54, Found m/z = 419.198. ^{1}H NMR (DMSO-d_6, 400 MHz, δ in ppm): δ = 13.54, 13.10 (1H, s, OH); 8.91, 8.65 (1H, s, HC=N); 7.41 (2H, m), 7.31 (1H, d), 7.24 (1H, d) (-CH-phenol group); 7.10 (1H,d), 6.96 (m, 1H), 6.88 (1H, m), 6.74 (1H, m)

(-CH-phenyl group); 4.92 (2H, s, CH_2); 4.05, 3.97(2H, q, O-CH_2); 1.34, 1.27 (3H, t, -CH_3). ^{13}C NMR: (DMSO-d_6, 100 MHz) δ = 167.5, 164.4 (C-OEt); 151.6, 151.0 (C-OH); 147.4, 147.0 (C=N); 132.7, 126.3, 124.1, 119.9 (C-phenol ring); 119.8, 119.1, 119.0, 118.4, 116.8, 105.0 (C-phenyl ring); 64.4, 64.3 CH_2O); 58.8 (CH_2); 15.25, 15.1 (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 $M(OAc)_2{\cdot}nH_2O$ (M = Cu, n = 3; M = Ni, n = 4) or $M(NO_3)_2{\cdot}nH_2O$ (M = Cu, n = 3, M = Ni, n = 6) with pH adjusted to ~9 with Et_3N 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(L^{OEt}-phda)(H_2O)]·H_2O (**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 $C_{24}H_{26}CuN_2O_6$ (MM = 502.036): C, 57.42; H, 5.22; N, 5.56%. Found: C, 57.93; H, 5.60; N, 5.47%: IR: 3499 (w), 3467 (w), 3050 (w), 2972 (w), 2920 (w), 2866 (w); 1641 (m), 1607 (s), 1581 (s), 1535 (s), 1462 (s), 1442 (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 {λ_{max}, nm (ε, $M^{-1}cm^{-1}$)} in CH_2Cl_2: 500 (1820), ~600 (275), 976 (100); Λ_M (CH_3CN) = 8.7 $\Omega^{-1}{\cdot}cm^2{\cdot}mol^{-1}$. ESI-MS (MeOH): calcd m/z for [Cu($C_{24}H_{22}N_2O_4$)]: 466.004, found 466.094; calcd for $[Cu_2(C_{24}H_{22}N_2O_4)_2+H]^+$: 933.016, found: 933.182 (major peak for protonated dimer).

*[Ni(L^{OEt}-phda)]·H_2O (**2**).* The complex was separated as shiny brick-red crystals of X-ray quality (overall yield: 53%). Characterization: Anal. calcd for $C_{24}H_{24}N_2O_5Ni$ (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 (s), 736 (vs). UV-VIS {λ_{max}, nm (ε, $M^{-1}cm^{-1}$)} in CH_3CN: 398 (1920), 422 (62.5). Λ_M (CH_3CN) = 9.2 $\Omega^{-1}{\cdot}cm^2{\cdot}mol^{-1}$. ESI-MS (MeOH): Calcd m/z for [Ni($C_{24}H_{22}N_2O_4$)]: 461.124, found 461.100.

*[Cu(L^{OEt}-ambza)]·H_2O·EtOH (**3**).* Green long needles of X-ray quality were obtained from dilute ethanolic solution or upon recrystallization from CH_2Cl_2 (overall yield 48%). Characterization: Anal. calcd for $C_{27}H_{32}CuN_2O_6$ (MM = 544.12): 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), 1542 (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 {λ_{max}, nm (ε, $M^{-1}cm^{-1}$)} in CH_3CN: 613 (352), Λ_M (CH_3CN) = 9.5 $\Omega^{-1}{\cdot}cm^2{\cdot}mol^{-1}$. ESI-MS (MeOH): calcd m/z for [Cu($C_{25}H_{24}N_2O_4$)]: 480.06, found 480.110.

*[Cu(L^{OEt}-ambza)]·H_2O (**4**).* A mixture of the ligand H_2L^{OEt}-ambza (0.085 g, 0.20 mmol) and $Cu(hfacac)_2$ (0.096, 0.20 mmol) dissolved in EtOH (15 mL) and pH of the solution was adjusted to ~9 by Et_3N. 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 CH_3CN, 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 $C_{25}H_{26}CuN_2O_5$ (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 {λ_{max}, nm (ε, $M^{-1}cm^{-1}$)} in CH_3CN: 619 (304). Λ_M (CH_3CN) = 3.8 $\Omega^{-1}{\cdot}cm^2{\cdot}mol^{-1}$.

*[Ni(L^{OEt}-ambza)] (**5**).* This complex was isolated as a brownish-yellow crystalline compound upon further crystallization from EtOH (overall yield: 44%). Characterization: Anal. calcd for $C_{25}H_{24}N_2O_4Ni$ (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 {λ_{max}, nm (ε, $M^{-1}cm^{-1}$)} in CH_3CN: 624 (179). Λ_M (CH_3CN) = 1.6 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

*[$Zn_2(L^{OEt}$-ambza)(μ-OAc)(OAc)] (**6**).* A mixture of H_2L^{OEt}-ambza (0.085 g, 0.20 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (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_3CN to afford tiny yellow single crystals of suitable for X-ray structure determination (overall yield: 64%). Characterization: Anal. calcd for $C_{29}H_{30}N_2O_8Zn_2$ (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. Λ_M (CH_3CN) = 1.1 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

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 intensities were collected with Mo-Kα radiation (λ = 0.71073 Å). Data processing, Lorentz-polarization and absorption corrections were performed using SAINT, APEX and the SADABS computer programs [51–53]. The structures 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 > 2σ(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**.

Compound	1	2	3
Empirical formula	$C_{24}H_{24}CuN_2O_6$	$C_{24}H_{24}N_2NiO_5$	$C_{27}H_{32}CuN_2O_6$
Formula mass	500.00	479.14	544.10
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	$P\text{-}42_1m$	$P2_1/c$	$P2_1/n$
a/Å	21.9174(6)	12.9329(6)	10.7944(6)
b/Å	21.9174(6)	14.5517(7)	20.286(1)
c/Å	4.9513(2)	11.7485(6)	11.7600(6)
α/°	90	90	90
β/°	90	109.983(3)	94.767(2)
γ/°	90	90	90
$V/Å^3$	2378.47(16)	2077.74(18)	2566.2(2)
Z	4	4	4
T/K	100(2)	100(2)	100(2)
μ/mm^{-1}	0.959	0.975	0.895
$Dcalc/Mg\cdot m^{-3}$	1.396	1.532	1.408
Crystal size/mm	0.24 × 0.15 × 0.11	0.24 × 0.18 × 0.13	0.16 × 0.15 × 0.11
θ max/°	30.27	30.02	26.00
Data collected	72696	32859	5073
Unique refl./Rint	3594/0.0381	6067/0.0600	5044/——
Parameters/Restraints	164/1	297/2	339/3
Goodness-of-Fit on F^2	1.082	0.843	1.155
(I > 2σ(I))/wR2 (all data)	0.0332/0.0975	0.0343/0.0894	0.0818/0.2113
Residual extrema/$e\cdot Å^{-3}$	1.11/−0.59	0.56/−0.51	0.94/−0.73

Table 2. Crystallographic Data and Processing Parameters for Compounds **4**–**6**.

Compound	4	5	6
Empirical formula	$C_{25}H_{26}CuN_2O_5$	$C_{25}H_{24}N_2NiO_4$	$C_{29}H_{30}N_2O_8Zn_2$
Formula mass	498.03	475.15	665.33
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a/Å	12.0486(4)	12.0351(9)	8.1702(15)
b/Å	16.5021(5)	11.7906(8)	12.476(2)
c/Å	11.2905(3)	15.4288(11)	14.531(3)
$\alpha/^\circ$	90	90	70.908(8)
$\beta/^\circ$	97.206(2)	93.783(2)	78.161(8)
$\gamma/^\circ$	90	90	79.352(7)
$V/Å^3$	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
$Dcalc/Mg \cdot m^{-3}$	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 F^2	1.056	1.047	1.122
$(I > 2\sigma(I))$/wR2 (all data)	0.0287/0.0919	0.0375/0.0885	0.0934/0.2488
Residual extrema/$e \cdot Å^{-3}$	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 H_2L^{OEt}-phda and H_2L^{OEt}-ambza were synthesized and structurally characterized where the metal ions are bound through the N_2-O_2 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 [7,10,17,18,20–24,30–32,40–42,56–60]. Mononuclear complexes with O_2-O_2 bonding site mode are very rare but they have been observed in a few cases with H_2L^{OR}-en Schiff bases with K^+ [61] and especially with $Ln(NO_3)_3$ (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 N_2-O_2 and O_2-O_2 including the two alkoxy groups, especially with the bi-compartmental Schiff bases (H_2L^{OR}-en, H_2L^{OR}-tn, H_2L^{OR}-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 H_2L^{OEt}-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 in-appropriate position to coordinate to a second metal into the O_2-O_2 bonding site and (2) the large bite angle (bond distances in O_2-O_2 are within the range 5.2–5.9 Åin these complexes). This data is summarized in Table 3 for L^{OEt}-ambza-metal(II) complexes. As a result, no complexes with N_2-O_2 + O_2-O_2 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 O_2-O_2 Bond Distances and the Dihedral Angle(s) between the Phenolate Rings and Benzene Ring in the Complexes **3**–**6**.

Complex	Dihedral angle(s) (°)	O_2-O_2 bond distance (Å)
3	118.2, 35.5	5.873
4	64.2, 49.4	5.818
5	128.0, 129.0	5.177
6	69.7, 31.8	5.468

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.

Acknowledgments: Salah S. Massoud acknowledges the financial support of this research by the Department of Chemistry-University of Louisiana at Lafayette. Franz A. Mautner acknowledges the support by NAWI Graz Natural Sciences.

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.

References

1. Costes, J.-P.; Laussac, J.-P.; Nicodeme, F. Complexation of a Schiff base ligand having two coordination sites (N_2O_2 and O_2O_2) with lanthanide ions (Ln = La, Pr): An NMR study. *Dalton Trans.* **2002**, *13*, 2731–2736. [CrossRef]
2. Yao, H.H.; Huang, W.T.; Lo, J.M.; Liao, F.L.; Chattopadhyay, P. Copper(II) complexes with tetradentate imine-phenols: Synthesis, characterization and molecular structures. *J. Coord. Chem.* **2005**, *58*, 975–984. [CrossRef]
3. Angeles, V.-F.M.; Isabel, F.-G.M.; Gonzalez-Noya, A.M.; Maneiro, M.; Bermejo, M.R.; Jesus, R.-D.M. Supramolecular networks of Mn(III)-Schiff base complexes assembled by nitrate counterions: X-ray crystal structures of 1D chains and 2D networks. *Polyhedron* **2012**, *31*, 379–385. [CrossRef]
4. Maiti, M.; Thakurta, S.; Sadhukhan, D.; Pilet, G.; Rosair, G.M.; Nonat, A.; Charbonniére, L.J.; Mitra, D. Thermally stable luminescent zinc-Schiff base complexes: A thiocyanato bridged 1D coordination polymer and a supramolecular 1D polymer. *Polyhedron* **2013**, *65*, 6–15. [CrossRef]
5. You, Z.-L.; lu, Y.; Zhang, N.; Ding, B.-W.; Sun, H.; Hou, P.; Wang, C. Preparation and structural characterization of hetero-dinuclear Schiff base copper(II)-zinc(II) complexes and their inhibition studies on *Helicobacter pylori* urease. *Polyhedron* **2011**, *30*, 2186–2194. [CrossRef]
6. Thakurta, S.; Rizzoli, C.; Butcher, R.J.; Gomez-Garcia, C.J.; Garribba, E.; Mitra, S. Sterically-controlled nuclearity in new copper(II) complexes with di-compartmental ligands: Formation of antiferromagnetically coupled angular trimer and mononuclear inclusion complex. *Inorg. Chim. Acta* **2010**, *363*, 1395–1403. [CrossRef]
7. Chakraborty, P.; Mohanta, S. Mononuclear and heterometallic dinuclear, trinuclear and dimer-of-dinuclear complexes derived from single- and double- compartment Schiff base ligands having a less utilized diamine. *Polyhedron* **2015**, *87*, 98–108. [CrossRef]
8. Bermejo, M.R.; Fernandez, M.I.; Gonzalez-Noya, A.M.; Maneiro, M.; Pedrido, R.; Rodriguez, M.J.; Garcia-Monteagudo, J.C.; Donnadieu, B. Novel peroxidase mimics: μ-Aqua manganese-Schiff base dimers. *J. Inorg. Biochem.* **2006**, *100*, 1470–1478. [CrossRef] [PubMed]
9. Alsalim, T.A.; Hadi, J.S.; Al-Nasir, E.A.; Abbo, H.S.; Titinchi, S.J.J. Hydroxylation of phenol catalyzed by oxovanadium(IV) of salen-type Schiff base complexes with hydrogen peroxide. *Catal. Lett.* **2010**, *136*, 228–233. [CrossRef]

10. Majumder, S.; Dutta, S.; Carrella, L.M.; Rentschler, E.; Mohanta, S. Syntheses, structures, electrochemical measurements and magnetic properties of two iron(III) complexes derived from N,N'-o-phenylenebis(3-ethoxysalicylaldimine). *J. Mol. Struct.* **2011**, *1006*, 216–222. [CrossRef]
11. Majumder, S.; Hazra, S.; Dutta, S.; Biswas, P.; Mohanta, S. Syntheses, structures and electrochemistry of manganese(III) complexes derived from N,N'-*o*-phenylenebis(3-ethoxysalicylaldimine): Efficient catalyst for styrene epoxidation. *Polyhedron* **2009**, *28*, 2473–2479. [CrossRef]
12. Ambili, K.U.; Sreejith, S.S.; Jacob, J.M.; Sithambaresan, M.; Kurup, M.R.P. 2-Ethoxy-6-({2-[(3-ethoxy-2-hydroxybenzylidene)amino]benzyl}iminomethyl)phenol. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2012**, *E68*, o2482. [CrossRef] [PubMed]
13. Dey, D.K.; Dey, S.P.; Elmali, A.; Elerman, Y. Molecular structure and conformation of N-2-[3'-(methoxy salicylideneimino)benzyl]-3''-methoxysalicylideneimine. *J. Mol. Struct.* **2001**, *562*, 177–184. [CrossRef]
14. Saha, S.; Biswas, D.; Chakrabarty, P.P.; Schollmeyer, D.; Jana, A.D.; Sakiyama, H.; Mikuriya, M. Quantitative estimation of the antiferromagnetic interaction between Cu(II) and Sm(II) in two dimensional heterometallic coordination polymer with isonicotinic acid and tectons. *Inorg. Chem. Commun.* **2013**, *36*, 212–215. [CrossRef]
15. Bermejo, M.R.; Fernandez, M.I.; Gomez-Forneas, E.; Gonzalez-Noya, A.; Maneiro, M.; Pedrido, R.; Rodriguez, M.J. Self-assembly of dimeric Mn^{III}-Schiff-base complexes tuned by perchlorate anions. *Eur. J. Inorg. Chem.* **2007**, *24*, 3789–3797. [CrossRef]
16. Bhattacharyya, A.; Roy, S.; Chakraborty, J.; Chattopadhyay, S. Two new hetero-dinuclear nickel(II)/zinc(II) complexes with compartmental Schiff bases: Synthesis, characterization and self assembly. *Polyhedron* **2016**, *112*, 109–117. [CrossRef]
17. Kargar, H. Synthesis, characterization and crystal structure of a manganese(III) Schiff base complex and investigation of its catalytic activity in the oxidation of benzylic alcohols. *Transiti. Met. Chem.* **2014**, *39*, 811–817. [CrossRef]
18. Kia, R.; Kargar, H.; Zare, K.; Khan, I.U. {6,6'-Diethoxy-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethylidyne)] diphenolato}(2-ethoxy-6-formylphenolato)cobalt(III)-ethanol-water(1/1/1). *Acta Crystallogr. Sect. E Struct. Rep. Online* **2010**, *66*, m366–m367. [CrossRef] [PubMed]
19. Sarwar, M.; Madalan, A.M.; Maxim, C.; Andruh, M. A dinuclear iron(III) complex bridged by the dianion of trimesic acid $[\{Fe(3\text{-}MeOsaldmpn)(H_2O)\}_2Htrim]\cdot H_2O$. Synthesis, crystal structure and magnetic properties. *Revue Roumaine de Chimie* **2012**, *57*, 687–691.
20. Kargar, H.; Kia, R.; Fun, H.-K.; Jamshidvand, A. {6,6'-Diethoxy-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilom ethylidyne)]diphenolato}copper(II) monohydrate. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2009**, *65*, m515–m516. [CrossRef] [PubMed]
21. Kargar, H.; Jamshidvand, A.; Fun, H.-K.; Kia, R. {6,6'-Diethoxy-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilom ethylidyne)]diphenolato}nickel(II) monohydrate. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2009**, *65*, m403–m404. [CrossRef] [PubMed]
22. Yeap, C.S.; Kia, R.; Kargar, H.; Fun, H.-K. {6,6'-Dimethoxy-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilom ethylidyne)]diphenolato}nickel(II) 1.78-hydrate. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2009**, *65*, m570–m571. [CrossRef] [PubMed]
23. Rayati, S.; Rafiee, N.; Wojtczak, A. *cis*-Dioxo-molybdenum(VI) Schiff base complexes: Synthesis, crystal structure and catalytic performance for homogeneous oxidation of olefins. *Inorg. Chim. Acta* **2012**, *386*, 27–35. [CrossRef]
24. Nejo, A.A.; Kolawole, G.A.; Nejo, A.O.; Segapelo, T.V.; Muller, C.J. Synthesis, structural, and insulin-enhancing studies of oxovanadium(IV) complexes. *Aust. J. Chem.* **2011**, *64*, 1574–1579. [CrossRef]
25. Arnaiz, F.J.; Costes, J.-P.; Garcia-Tojal, J. Heteronuclear d-f complexes containing binucleating ligands. In *Inorganic Experiments*, 3rd ed.; Woollins, J.D., Ed.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2010; pp. 283–286.
26. Ishida, T.; Watanabe, R.; Fujiwara, K.; Okazawa, A.; Kojima, N.; Tanaka, G.; Yoshii, S.; Nojiri, H. Exchange coupling in TbCu and DyCu single-molecule magnets and related lanthanide and vanadium analogs. *Dalton Trans.* **2012**, *41*, 13609–13619. [CrossRef] [PubMed]
27. Thevenon, A.; Garden, J.A.; White, A.J.P.; Williams, C.K. Dinuclear zinc salen catalysts for the ring opening copolymerization of epoxides and carbon dioxide or anhydrides. *Inorg. Chem.* **2015**, *54*, 11906–11915. [CrossRef] [PubMed]

28. Rayati, S.; Zakavi, S.; Koliaei, M.; Wojtczak, A.; Kozakiewicz, A. Electron-rich salen-type Schiff base complexes of Cu(II) as catalysts for oxidation of cyclooctene and styrene with tert-butylhydroperoxide: A comparison with electron-deficient ones. *Inorg. Chem. Commun.* **2010**, *13*, 203–207. [CrossRef]
29. Costes, J.-P.; Garcia-Tojal, J.; Tuchagues, J.-P.; Vendier, L. Structural and magnetic study of a trinuclear Mn^{II}-Gd^{III}-Mn^{II} complex. *Eur. J. Inorg. Chem.* **2009**, *25*, 3801–3806. [CrossRef]
30. Nayak, M.; Hazra, S.; Lemoine, P.; Koner, R.; Lucas, C.R.; Mohanta, S. Self-assembled [2 × 1 + 1 × 2] heterotetranuclear $Cu^{II}{}_3Mn^{II}$/$Cu^{II}{}_3Co^{II}$ and [2 × 2 + 1 × 3] heptanuclear $Cu^{II}{}_7$ compounds derived from N,N'-*o*-phenylenebis(3-ethoxysalicylaldimine): Structures and magnetic properties. *Polyhedron* **2008**, *27*, 1201–1213. [CrossRef]
31. Salmon, L.; Thuery, P.; Ephritikhine, M. Synthesis and crystal structure of tetra- and hexanuclear uranium(IV) complexes with hexadentate compartmental Schiff-base ligands. *Dalton Trans.* **2004**, *24*, 4139–4145. [CrossRef] [PubMed]
32. Salmon, L.; Thuery, P.; Ephritikhine, M. Synthesis and crystal structure of uranium(IV) complexes with compartmental Schiff bases: From mononuclear species to tri- and tetranuclear clusters. *Dalton Trans.* **2004**, *10*, 1635–1643. [CrossRef] [PubMed]
33. Costes, J.-P.; Dahan, F.; Donnadieu, B.; Fernandez-Garcia, M.-I.; Rodriguez-Douton, M.-J. Reaction of a manganese(III)-Schiff base complex with gadolinium nitrate: Synthesis, structure and magnetic properties of an ionic species $[LMn(H_2O)_2]_2[Gd(NO_3)_5(MeOH)]$ (H_2L=1,3-bis((3-methoxysalicylidene)amino)-2,2-dimethylpropane). *Dalton Trans.* **2003**, *19*, 3776–3779. [CrossRef]
34. Costes, J.-P.; Dahan, F.; Garcia-Tojal, J. Dinuclear Co^{II}/Gd^{III} and Co^{III}/Gd^{III} complexes derived from hexadentate schiff bases: Synthesis, structure, and magnetic properties. *Chem. A Eur. J.* **2002**, *8*, 5430–5434. [CrossRef]
35. Liu, K.; Shi, W.; Cheng, P. Toward heterometallic single-molecule magnets: Synthetic strategy, structures and properties of 3d-4f discrete complexes. *Coord. Chem. Rev.* **2015**, *289*, 74–122. [CrossRef]
36. Sakamoto, S.; Fujinami, T.; Koshiro Nishi, K.; Matsumoto, N.; Mochida, N.; Ishida, T.; Sunatsuki, Y.; Re, N. Carbonato-bridged $Ni^{II}{}_2Ln^{III}{}_2$ (Ln^{III}=Gd^{III}, Tb^{III}, Dy^{III}) complexes generated by atmospheric CO_2 fixation and their single-molecule-magnet behavior: $[(\mu_4\text{-}CO_3)_2\{Ni^{II}(\text{3-MeOsaltn})(\text{MeOH or } H_2O)Ln^{III}(NO_3)\}_2]\cdot$solvent [3-MeOsaltn=N,N′-bis(3-methoxy-2-oxybenzylidene)-1,3-propanediaminato]. *Inorg. Chem.* **2013**, *52*, 7218–7229. [PubMed]
37. Ehama, K.; Ohmichi, Y.; Sakamoto, S.; Fujinami, T.; Matsumoto, N.; Mochida, N.; Ishida, T.; Sunatsuki, Y.; Tsuchimoto, M.; Re, N. Synthesis, structure, luminescent, and magnetic properties of carbonato-bridged $Zn^{II}{}_2Ln^{III}{}_2$ complexes $[(\mu_4\text{-}CO_3)_2\{Zn^{III}L^nLn^{III}(NO_3)\}_2]$ (Ln^{III}=Gd^{III}, Tb^{III}, Dy^{III}; L^1=N,N′-bis(3-methoxy-2-oxybenzylidene)-1,3-propanediaminato, L^2=N,N′-bis(3-ethoxy-2-oxybenzylidene)-1,3-propanediaminato). *Inorg. Chem.* **2013**, *52*, 12828–12841. [PubMed]
38. Yang, X.; Chan, C.; Lam, D.; Schipper, D.; Stanley, J.M.; Chen, X.; Jones, R.A.; Holliday, B. J.; Wong, W.-K.; Chen, S.; et al. Anion-dependent construction of two hexanuclear 3d–4f complexes with a flexible Schiff base ligand. *Dalton Trans.* **2012**, *41*, 11449–11453. [CrossRef] [PubMed]
39. Yang, X.; Lam, D.; Chan, C.; Stanley, J.M.; Jones, R.A.; Holliday, B.J.; Wong, W.-K. Construction of 1-D 4f and 3d–4f coordination polymers with flexible Schiff base ligands. *Dalton Trans.* **2011**, *40*, 9795–9801. [CrossRef] [PubMed]
40. Kurzak, K.; Ejsmont, K.; Koprek, K. X-ray and DFT-calculated structures of a vanadyl Schiff base complex: (methanol-κO)[2-methoxy-6-({2-[(2-oxido-3-methoxybenzylidene)-amino]benzyl}iminomethyl)phenolato-κ4O1, N,N,O1']oxido-vanadium(IV) monohydrate. *Acta Crystallog. Sect. C Crystal Struct. Commun.* **2012**, *68*, m161–m165. [CrossRef] [PubMed]
41. Orita, S.; Akitsu, T. Variety of crystal structures of chiral Schiff base Lu(III)-Ni(II)/ Cu(II)/Zn(II) and the related complexes. *Open Chem. J.* **2014**, *1*, 1–14.
42. Hayashi, T.; Shibata, H.; Orita, S.; Akitsu, T. Variety of structure of binuclear chiral Schiff base Ce(III)/Pr(III)/Lu(III)-Ni(II)/Cu(II)/Zn(II) complexes. *Eur. Chem. Bull.* **2013**, *2*, 49–57.
43. Hathaway, B.J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R.D., McCleverty, J.A., Eds.; Pergamon Press: Oxford, UK, 1987; Volume 5, p. 533.

44. Massoud, S.S.; Louka, F.R.; David, R.N.; Dartez, M.J.; Nguyn, Q.L.; Labry, N.J.; Fischer, R.C.; Mautner, F.A. Five-coordinate thiocyanato- and azido-metal(II) complexes based pyrazolyl ligands. *Polyhedron* **2015**, *90*, 258–265. [CrossRef]
45. Massoud, S.S.; Louka, F.R.; Obaid, Y.K.; Vicente, R.; Ribas, J.; Fischer, R.C.; Mautner, F.A. Metal ions directing the geometry and nuclearity of azido-metal(II) complexes derived from bis(2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl)amine. *Dalton Trans.* **2013**, *42*, 3968–3978. [CrossRef] [PubMed]
46. Mautner, F.A.; Louka, F.R.; Le Guet, T.; Massoud, S.S. Pseudohalide copper(II) complexes derived from polypyridyl ligands. Synthesis and characterization. *J. Mol. Struct.* **2009**, *919*, 196–203. [CrossRef]
47. Lever, A.B.P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, The Netherlands, 1984.
48. Matović, Z.D.; Miletić, V.D.; Samardzˇić, G.; Pelosi, G.; Ianelli, S.; Snežana Trifunović, S. Square-planar copper(II) complexes with tetradentate amido-carboxylate ligands. Crystal structure of $Na_2[Cu(obap)]_2 \cdot 2H_2O$. Strain analysis and spectral assignments of complexes. *Inorg. Chim. Acta* **2005**, *358*, 3135–3144. [CrossRef]
49. Tharmaraj, P.; Kodimunthiri, D.; Sheela, C.D.; Shanmuga Priya, C.S. Synthesis, spectral characterization, and antimicrobial activity of copper(II), cobalt(II), and nickel(II) complexes of 3-formylchromonimino propylsilatrane. *J. Coord. Chem.* **2009**, *62*, 2220–2228. [CrossRef]
50. Addison, A.W.; Rao, T.N.; Reedijk, J.; Rijin, J.V.; Verschoor, G.C. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2′-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J. Chem. Soc. Dalton Trans.* **1984**, *7*, 1349–1356. [CrossRef]
51. Bruker. *SAINT v. 7.23*; Bruker AXS Inc.: Madison, WI, USA, 2005.
52. Bruker. *APEX 2, v. 2.0-2*; Bruker AXS Inc.: Madison, WI, USA, 2006.
53. Sheldrick, G.M. *SADABS v. 2*; University of Goettingen: Wilhelmsplatz, Germany, 2001.
54. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122. [CrossRef] [PubMed]
55. Macrae, C.F.; Edington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, T.; van de Streek, J. Mercury: Visualization and analysis of crystal structures. *J. Appl. Cryst.* **2006**, *39*, 453–457. [CrossRef]
56. Bhattacharya, S.; Mondal, S.; Sasmal, S.; Sparkes, H.A.; Howard, J.A.K.; Nayak, M.; Mohanta, S. Bis(nitrate)diaquauranyl(VI) synthon to generate $[1 \times 2 + 1 \times 1]$ and $[1 \times 1 + 1 \times 1]$ co-crystalized $3d \cdots 5f$ self-assemblies. *CrystEngComm.* **2011**, *13*, 1029–1036. [CrossRef]
57. Shao, H.; Muduli, S.K.; Tran, P.D.; Soo., H.S. Enhancing electrocatalytic hydrogen evolution by nickel salicylaldimine complexes with alkali metal cations in aqueous media. *Chem.Commun.* **2016**, *52*, 2948–2951. [CrossRef] [PubMed]
58. Biswas, A.; Mandal, L.; Mondal, S.; Lucas, C.R.; Mohanta, S. More surprising differences between two closely similar compartmental ligand families and another dinuclear synthon to stabilize dinuclear–mononuclear cocrystals. *CrystEngComm.* **2013**, *15*, 5888–5897. [CrossRef]
59. Bhowmik, P.; Nayek, H.P.; Corbella, M.; Aliaga-Alcalde, N.; Chattopadhyay, S. Control of molecular architecture by steric factors: mononuclear *vs* polynuclear manganese(III) compounds with tetradentate N_2O_2 donor Schiff bases. *Dalton Trans.* **2011**, *40*, 7916–7926. [CrossRef] [PubMed]
60. Mousavi, M.; Bereau, V.; Costes, J.-P.; Duhayon, C.; Sutter, J.-P. Oligomeric and polymeric organizations of potassium salts with compartmental Schiff-base complexes as ligands. *CrystEngComm.* **2011**, *13*, 5908–5914. [CrossRef]
61. Correia, I.; Pessoa, J.C.; Duarte, M.T.; da Piedade, M.F.M.; Jackush, T.; Kiss, T.; Castro, M.M.C.A.; Geraldes, C.F.G.C.; Avecilla, A. Vanadium(IV and V) complexes of Schiff bases and reduced Schiff bases derived from the reaction of aromatic *o*-hydroxyaldehydes and diamines: Synthesis, characterization and solution studies. *Eur. J. Inorg. Chem.* **2005**, *4*, 732–744. [CrossRef]
62. Yang, Y.; Yan, P.-F.; Gao, P.; Gao, T.; Hou, G.-F.; Li., G.-M. Salen-type lanthanide complexes with luminescence and near-infrared (NIR) properties. *J. Inorg. Organomet. Polym. Mater.* **2013**, *23*, 1211–1218. [CrossRef]
63. Gao, T.; Yan, P.-F.; Li, G.-M.; Hou, G.F.; Gao, J.-S. *N*,*N*′-Ethylene-bis(3-methoxysalicylideneimine) mononuclear (4f) and heterodinuclear (3d–4f) metal complexes: Synthesis, crystal structure and luminescent properties. *Inorg. Chim. Acta* **2008**, *361*, 2051–2058. [CrossRef]
64. Hazra, S.; Sasmal, S.; Nayak, M.; Sparkes, H.A.; Howard, J.A.K.; Mohanta, S. Syntheses and crystal structures of $Cu^{II}Bi^{III}$, $Cu^{II}Ba^{II}Cu^{II}$, $[Cu^{II}Pb^{II}]_2$ and cocrystallized $(U^{VI}O_2)_2.4Cu^{II}$ complexes: Structural diversity of the coordination compounds derived from *N*,*N*′-ethylenebis(3-ethoxysalicylaldiimine). *CrystEngComm.* **2010**, *12*, 470–477. [CrossRef]

65. Moroz, O.V.; Trush, V.A.; Sliva, T.Y.; Konovalova, I.S.; Amirkhanov, V.M. Crystal structure of {μ-6,6′-dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethanylylidene)]diphenolato}(meth-anol)(nitrato)nickel(II) sodium. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2014**, *70*, 305–308. [CrossRef] [PubMed]
66. Long, J.; Vallat, R.; Ferreira, R.A.S.; Carlos, L.D.; Paz, F.A.A.; Guari, Y.; Larionova, J. A bifunctional luminescent single-ion magnet: Towards correlation between luminescence studies and magnetic slow relaxation processes. *Chem. Commun.* **2012**, *48*, 9974–9976. [CrossRef] [PubMed]
67. Nayak, M.; Jana, A.; Fleck, M.; Hazra, S.; Mohanta, S. A unique example of a three component cocrystal of metal complexes. *CrystEngComm* **2010**, *12*, 1416–1421. [CrossRef]
68. Sarkar, S.; Mohanta, S. Syntheses, crystal structures and supramolecular topologies of nickel(II)–s/p/d^{10}/NH_4^+ complexes derived from a compartmental ligand. *RSC Adv.* **2011**, *1*, 640–650. [CrossRef]
69. Gao, T.; Yan, P.-F.; Li, G.-M.; Zhang, J.-W.; Sun, W.-B.; Suda, M.; Einaga, Y. Correlations between structure and magnetism of three *N*,*N*′-ethylene-bis(3-methoxysalicylideneimine) gadolinium complexes. *Solid State Sci.* **2010**, *12*, 597–604. [CrossRef]
70. Amirkhanov, O.V.; Moroz, O.V.; Znovjyak, K.O.; Sliva, T.Y.; Penkova, L.V.; Yushchenko, T.; Szyrwiel, L.; Konovalova, I.S.; Dyakonenko, V.V.; Shishkin, O.V.; et al. Heterobinuclear Zn–Ln and Ni–Ln complexes with Schiff-base and carbacylamidophosphate ligands: synthesis, crystal Structures, and catalytic activity. *Eur. J. Inorg. Chem.* **2014**, *23*, 3720–3730. [CrossRef]
71. Sasmal, S.; Majumder, S.; Hazra, S.; Sparkes, H.A.; Howard, J.A.K.; Nayak, M.; Mohanta, S. Tetrametallic [2 × 1 + 1 × 2], octametallic double-decker–triple-decker [5 × 1 + 3 × 1], hexametallic quadruple-decker and dimetallic-based one-dimensional complexes of copper(II) and s block metal ions derived from *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine). *CrystEngComm.* **2010**, *12*, 4131–4140.
72. Kajiwara, T.; Nakano, M.; Takahashi, K.; Takaishi, S.; Yamashita, M. Structural design of easy-axis magnetic anisotropy and determination of anisotropic parameters of Ln^{III}-Cu^{II} single-molecule magnets. *Chem. Eur. J.* **2011**, *17*, 196–205. [CrossRef] [PubMed]
73. Cimpoesu, F.; Dahan, F.; Ladeira, S.; Ferbinteanu, M.; Costes, J.-P. Chiral crystallization of a heterodinuclear Ni-Ln series: comprehensive analysis of the magnetic properties. *Inorg. Chem.* **2012**, *51*, 11279–11293. [CrossRef] [PubMed]
74. Costes, J.-P.; Clemente-Juan, J.M.; Dahan, F.; Dumestre, F.; Tuchagues, J.-P. Dinuclear (Fe^{II}, Gd^{III}) complexes deriving from hexadentate Schiff bases: Synthesis, structure, and mössbauer and magnetic properties. *Inorg. Chem.* **2002**, *41*, 2886–2891. [CrossRef] [PubMed]
75. Liu, T.-Q.; Yan, P.-F.; Luan, F.; Li, Y.-X.; Sun, J.-W.; Chen, C.; Yang, F.; Chen, H.; Zou, X.-W.; Li, G.-M. Near-IR Luminescence and Field-Induced Single Molecule Magnet of Four Salen-type Ytterbium Complexes. *Inorg.Chem.* **2015**, *54*, 221–228. [CrossRef] [PubMed]
76. Biswas, A.; Mondal, S.; Mohanta, S. Syntheses, characterizations, and crystal structures of 3d–s/d^{10} metal complexes derived from two compartmental Schiff base ligands. *J. Coord. Chem.* **2013**, *66*, 152–170. [CrossRef]
77. Mondal, S.; Hazra, S.; Sarkar, S.; Sasmal, S.; Mohanta, S. Syntheses, crystal structures and supramolecular topologies of copper(II)–main group metal complexes derived from *N*,*N*′-*o*-phenylenebis(3-ethoxysalicylaldi mine). *J. Mol. Struct.* **2011**, *1004*, 204–214. [CrossRef]
78. Koner, R.; Lee, G.-H.; Wang, Y.; Wei, H.H.; Mohanta, S. Two new diphenoxo-bridged discrete dinuclear $Cu^{II}Gd^{III}$ compounds with cyclic diimino moieties: Syntheses, structures, and nagnetic properties. *Eur. J. Inorg. Chem.* **2005**, *8*, 1500–1505. [CrossRef]
79. Sun, W.-B.; Yan, P.-F.; Jiang, S.-D.; Wang, B.-W.; Zhang, Y.-Q.; Hong-Feng, L.; Chen, P.; Wang, Z.-M.; Gao, S. High symmetry or low symmetry, that is the question–high performance Dy(III) single-ion magnets by electrostatic potential design. *Chem. Sci.* **2016**, *7*, 684–691. [CrossRef]
80. Visinescu, D.; Jeon, I.-R.; Madalan, A.M.; Alexandru, M.-G.; Jurca, B.; Mathoniere, C.; Clerac, R.; Andruh, M. Self-assembly of $[Cu^{II}Tb^{III}]^{3+}$ and $[W(CN)_8]^{3-}$ tectons: A case study of a mixture containing two complexes showing slow-relaxation of the magnetization. *Dalton Trans.* **2012**, *41*, 13578–13581. [CrossRef] [PubMed]
81. Maeda, M.; Hino, S.; Yamashita, K.; Kataoka, Y.; Nakano, M.; Yamamura, T.; Kajiwara, T. Correlation between slow magnetic relaxation and the coordination structures of a family of linear trinuclear Zn(II)–Ln(III)–Zn(II) complexes (Ln = Tb, Dy, Ho, Er, Tm and Yb). *Dalton Trans.* **2012**, *41*, 13640–13648. [CrossRef] [PubMed]
82. Costes, J.-P.; Donnadieu, B.; Gheorghe, R.; Novitchi, G.; Tuchagues, J.-P.; Vendier, L. Di- or trinuclear 3d–4f Schiff base complexes: The Role of anions. *Eur. J. Inorg. Chem.* **2008**, *33*, 5235–5244. [CrossRef]

83. Hu, K.-Q.; Jiang, X.; Wu, S.-Q.; Liu, C.-M.; Cui, A.-L.; Kou, H.Z. A trimetallic strategy towards $Zn^{II}_4Dy^{III}_2Cr^{III}_2$ and $Zn^{II}_4Dy^{III}_2Co^{III}_2$ single-ion magnets. *Dalton Trans.* **2015**, *44*, 15413–15416. [CrossRef] [PubMed]
84. Dhers, S.; Costes, J.-P.; Guionneau, P.; Paulsen, C.; Vendier, L.; Sutter, J.-P. On the importance of ferromagnetic exchange between transition metals in field-free SMMs: examples of ring-shaped hetero-trimetallic $[(LnNi_2)\{W(CN)_8\}]_2$ compounds. *Chem. Commun.* **2015**, *51*, 7875–7878. [CrossRef] [PubMed]