Synthesis, structure and magnetic characterization of dinuclear copper(II) complexes bridged by bicompartamental phenolate†

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The reaction of Cu(II) salts with the bicompartamental 2,6-bis[2-pyridylmethyl]aminomethyl]-4-chlorophenol (LCl-OH) ligand afforded four new dinuclear bridged phenoxido Cu(II) complexes. Three doubly bridged complexes namely [Cu2(μ-Cl-O)(μ-X)][ClO4]2 (1: X = OH−, 3: X = O2P(OC6H5)2) and 2: [Cu2(μ-Cl-O)(μ-pz)]ClO4, ClO4 (2) where pz = pyrazolyl anion, and one singly bridged-phenoxido, [Cu2(μ-Cl-O)(dcac)]PF6 2CH3CN (4 2CH3CN) (dcac = dicyanamido anion). A complex similar to 4 was also obtained with 2,6-bis[2-pyridylmethyl]aminomethyl]-4-methylphenol (L Me-OH), [Cu2(μ-L-Me-O)(dcac)]PF6 2CH3CN (5 2CH3CN) where in both cases dcac are acting as terminal monodentate ligands. The complexes were structurally characterized by various spectroscopic techniques (IR, UV-VIS and ESI-MS) and by single crystal crystallography. Magnetic susceptibility measurements at variable temperature revealed strong to very strong antiferromagnetic coupling (AF) in the doubly bridged complexes 1–3 and very weak AF interaction in the dicyanamido compounds 4 and 5. The DFT calculations for the coupling constants, J were in agreement with the experimentally observed behavior. The trend in magnetic properties was attributed to the strength of overlap between the orbitals (dν−,y/dν−,z vs. dν/dχ−,y vs. dν/dχ−,z) resulting from trigonal bipyramidal (TBP) or square pyramidal (SP) geometries.

Introduction

A variety of compartmental ligands based on phenolic compounds which possess two symmetrical and asymmetrical pendant chelating arms attached to the 2- and 6-positions of the phenol ring have been synthesized.1–11 These ligands are known to accommodate two homo- or hetero-metallic 3d metal ions and hence producing dinuclear metal complexes bridged by the deprotonated phenolic group and in some cases by one or two other groups such as acetate, benzoate or hydroxide ions.11–25 In many of these compounds, the coordination environment around the central metal ions is “coordinatively unsaturated” and/or the metal ion(s) is coordinated to “weakly bound” ligand(s).1,2,4–6,10–13 This property made this class of compounds to serve as good candidates for mimicking biological systems and as a consequence they have been extensively employed to elucidate the structural spectroscopic parameters and to mimic the mechanism of metalloenzymes in catecholase oxidases, Mn catalases, metallo-β-lactamases (MβL)7,13,24–30 and particularly in the hydrolytic systems.8,21,31,32 These includes phosphodiester bonds of biomolecules such as DNA, purple acid phosphatasas and Zn phosphesterases.6,21,31–33

In addition to the advantages of the compartmental dinuclear metal(II) complexes which derived from phenolic compounds in enhancing our understanding for the role of metal ions in the active sides of metalloenzymes, the compounds could provide interesting magnetic properties as a result of the magnetic coupling between the two paramagnetic metal centers (3d7−9) bridged via the phenoxido group. The close proximity between the bridged metal ions, which is generally within the range of 2.9–4.0 Å provide an excellent pathway for strong antiferromagnetic interaction between the two metallic centers.1,2,4,26,30,34,35 Also, the magnetic coupling between the two metal ions could be
enhanced by inserting another bridging ligand which can further propagate the magnetic coupling.\textsuperscript{4,28,30,34,35}

Herein, we report a continuation of our previous studies on dinuclear metal\(\text{II}\) based phenolate ligands.\textsuperscript{14} Our discussion will be limited on symmetrical tetra-methyl pyridyl compounds namely bis[bis(2-pyridylmethyl)aminomethyl]-4-chlorophenol (L\(\text{Cl}^\text{–}\)), OH and bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (L\(\text{Me}^\text{–}\)) which are illustrated in Chart 1. We report the synthesis, structure and magnetic characterization of three doubly bridged copper\(\text{II}\)-phenoxido complexes with OH\(\text{–}\), pyrazolyl anion (pz\(\text{–}\)) and diphenyl phosphate, as well as two singly bridged complexes with dicyanamide ion N(CN)\(_2^\text{–}\) ([LClO)\(\text{–}\)]PF\(_6^\text{–}\) (1), [Cu\(_2\)(L\(\text{Cl}^\text{–}\))\(\mu\)-pz](ClO\(_4^\text{–}\))ClO\(_4^\text{–}\) (2) and [Cu\(_2\)(L\(\text{Me}^\text{–}\))\(\mu\)-O\(_2\)P(O\(_\text{OCMe}_3\))\(\text{H}_2\)](ClO\(_4^\text{–}\))\(_2^\text{–}\) (3) (see X-ray section).

In the complexes 1–3, the two Cu\(\text{II}\) ions are doubly bridged by the phenoxido group and a hydroxido group in 1, pyrazolyl and diphenylphosphate anions in 2 and 3, respectively. Bridged phenoxido complexes similar to 1 have been previously obtained in similar class of ligands.\textsuperscript{5,28,36} Interestingly, although doubly-bridged mono(diphenylphosphato) complex 3 was isolated here, only-doubly-bridged bis(diphenylphosphato) complex was reported with Co\(\text{II}\), [Co\(_2\)(L\(\text{Me}^\text{–}\))\(\mu\)-O\(_2\)P(O\(_\text{OCMe}_3\))\(\text{H}_2\)](ClO\(_4^\text{–}\))\(_2^\text{–}\) Attempts made to synthesize the corresponding bis-(4-nitrophosphonophosphato) (BNP) of 3 were unsuccessful, most likely due to the rapid hydrolysis of BNP under the reaction conditions. Similarly attempts made to synthesize the bridged-azido or bridged-dicyanamido complexes were completely failed and instead, only the bridged-phenoxido complexes [Cu\(_2\)(L\(\text{Me}^\text{–}\))\(\mu\)-N\(_3^\text{–}\)]ClO\(_4^\text{–}\) (ref. 2) and [Cu\(_2\)(L\(\text{Me}^\text{–}\))\(\mu\)-Cl](dca)\(_2^\text{–}\)PF\(_6^\text{–}\)·2CH\(_3\)CN (4, R = Cl; 5, R = Me) were produced in which N\(_3^\text{–}\) and dca were acting as simple monodentate ligands.

Results and discussion

Synthesis of the complexes

The reaction of a methanolic solution of 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-chlorophenol (L\(\text{Cl}^\text{–}\)) with two equivalents of Cu(ClO\(_4^\text{–}\))\(_2^\text{–}\)·6H\(_2\)O in the presence Na\(_2\)CO\(_3\), pyrazole (Hpz) and diphenyl phosphate afforded the dinuclear Cu\(\text{II}\) complexes [Cu\(_2\)(L\(\text{Cl}^\text{–}\))\(\mu\)-OH][ClO\(_4^\text{–}\)]\(_2^\text{–}\) (1), [Cu\(_2\)(L\(\text{Cl}^\text{–}\))\(\mu\)-pz](ClO\(_4^\text{–}\))ClO\(_4^\text{–}\) (2) and [Cu\(_2\)(L\(\text{Me}^\text{–}\))\(\mu\)-O\(_2\)P(O\(_\text{OCMe}_3\))\(\text{H}_2\)](ClO\(_4^\text{–}\))\(_2^\text{–}\) (3), respectively whereas the corresponding reactions of Cu(NO\(_3^\text{–}\))\(_2^\text{–}\)·3H\(_2\)O and 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-chlorophenol (L\(\text{Cl}^\text{–}\)) or 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (L\(\text{Me}^\text{–}\)) with an aqueous solution of sodium dicyanamide (Nadca) resulted in the formation of [Cu\(_2\)(L\(\text{Cl}^\text{–}\))\(\mu\)-Cl](dca)\(_2^\text{–}\)PF\(_6^\text{–}\)·2CH\(_3\)CN (4–5, R = Cl; 6–7, R = Me) were produced in which N\(_3^\text{–}\) and dca were acting as simple monodentate ligands.

IR spectra of the complexes

The IR spectra of the perchlorate complexes 1–3 displayed the \(v(\text{Cl}\–\text{O})\) band as broad strong absorption around 1092 cm\(^{-1}\) as in complex 1 or split of the band into two or three bands over the range 1090–1120 cm\(^{-1}\) as observed in complexes 2 and 3, respectively. The broadening or split of the \(v(\text{Cl}\–\text{O})\) band is attributed to the reduction of the ClO\(_4^\text{–}\)\(\text{ion}\) symmetry from \(T_d\) to \(C_{\text{ip}}\) or \(C_{2v}\) symmetries as a result of the involvement of the counter ClO\(_4^\text{–}\)\(\text{ion}\) in H-bonding with the ligand or its presence in a distorted location. The dicyanamido hexafluorophosphate complexes 4 and 5 displayed strong absorption band around 840 cm\(^{-1}\), due to \(v(\text{P}\–\text{F})\). The latter two complexes showed two series of bands: a strong absorption in the 2160–2180 cm\(^{-1}\) region corresponding to \(v_s(\text{C}–\text{N})\) and two weak to medium absorption bands in the 2220–2290 cm\(^{-1}\) region corresponding to \(v_n(\text{C}–\text{N})\) and \(v_s + v_n(\text{C}–\text{N})\) and these were in agreement with those observed in other monodentate dicyanamido complexes.\textsuperscript{37} The frequencies of these peaks were shifted to higher values compared to the corresponding peaks observed in the free dca in its sodium salt (2129, 2232 and 2286 cm\(^{-1}\)) indicating its coordination. The bridged hydroxido complex 1, revealed the stretching frequency \(v(\text{O}\–\text{H})\) band at 3429 cm\(^{-1}\). The complexes also displayed a series of weak to medium

**Chart 1** Structural formula of bis[bis(2-pyridylmethyl)aminomethyl]-4-substitutedphenol (L\(\text{Me}^\text{–}\)).

\[ R = \text{Cl}([L\text{Cl}^\text{–}\]), \text{Br}([L\text{Br}^\text{–}\]), \text{CH}_3([L\text{Me}^\text{–}\]), \text{C(CH}_3)_2([L\text{Bu}^\text{–}\]), \text{OMe}([L\text{OMe}^\text{–}\]), F([L\text{F}^\text{–}\]). \]
intensity bands over the 1610–1440 cm\(^{-1}\) region which are characteristic of the bis(pyridyl) moieties\(^{49}\) and C=\(\equiv\)C of the phenolate group.

**Electronic spectra of complexes**

The acetonitrile spectra of copper complexes under investigation revealed the presence of two broad maxima over the wavelength regions 440–480 and 700–810 nm. The former band in the 440–480 nm region observed in complexes 2–4, most likely corresponds to L \(\rightarrow\) M CT transition between the bridged phenoxido and copper ions. The second observed broad band (710–810 nm region, \(\epsilon = 140–200\ \text{M}^{-1}\ \text{cm}^{-1}\)) is characteristic for Cu(\(\mu\)) d–d transition in five-coordinate complexes. The long wavelength position of this band suggests a distorted square pyramidal (SP) stereochemistry around the central Cu(\(\mu\)) ions. It is well established that five-coordinate SP Cu(\(\mu\)) complexes are most likely producing a broad band in the visible region which occasionally may or may not be associated with a low-energy shoulder at \(\lambda > 800\ \text{nm}\). This band results from \(d_{\pi} \rightarrow d_{\pi^*}\) transition.\(^{44,44}\) Similar UV-Vis spectral features have been previously reported in related \(\mu\)-phenoxido dicopper(II) complexes.\(^{1,3,28,44}\) Thus, based on the above criterion in CH\(_3\)CN solution, the complexes under investigation adopt distorted SP geometry around the central Cu(\(\mu\)) atoms. This assignment in solution was in agreement with those obtained by single crystal X-ray crystallography.

**Mass spectra of complexes**

ESI-MS spectra of the chlorophenate complexes 1–4 and the methylphenolate complex 5, recorded in acetonitrile and all are shown in Fig. S1–S5 (ESI†), displayed some general characteristic features which provide qualitative information about their compositions. The mass spectra of the complexes 1, 3 and 4 showed two major peaks at \(m/z = 835.059 \pm 0.001\) (this was observed at \(m/z = 821.020\) for complex 2) and 767.071 ± 0.002. The former peak may result from the formation of a species with additional coordination of OH/H\(_2\)O/MeCN to the Cu(\(\mu\)) centers such as \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{OH})/\text{H}_2\text{O}/\text{MeCN})]^{2+}\) (calcd \(m/z = 835.158\)) in complexes 1, 3 and 4, whereas the corresponding peak observed in complex 2 \(m/z = 821.020\) could be assigned to \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{pz})/\text{H}_2\text{O}/\text{MeCN})]^{2+}\) (calcd \(m/z = 821.317\)). The second major peak which was detected in complexes 1–4 at 767.071 ± 0.002 could be attributed to the fragments \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{H}_2\text{O})]^{2+} + 2\text{Cl}^{-} + \text{H}^+ \) (calcd \(m/z = 767.094\)) in complexes 1–3 and \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{OH})/\text{H}_2\text{O})]^{2+} + \text{F}^{-} + \text{H}^+ \) (calcd \(m/z = 767.031\)) in complex 4. Similar peaks were observed in complex 5 at \(m/z = 813.113\) and 747.125 corresponding to the species \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{OH})_2/\text{MeCN})]^{+}\) (calcd \(m/z = 813.917\)) and \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{OH})(\text{H}_2\text{O})]^{2+} + \text{F}^{-} \) (calcd \(m/z = 746.798\)), respectively. The spectra revealed a distinct peak at \(m/z = 361.035 \pm 0.001\) for complexes 1–4 and at 351.063 for complex 5 due to doubly charged ions. These were assigned to the fragment \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{H}_2\text{O})(\text{HCN})]^{2+}\) (calcd \(m/z = 361.103\) for R = Cl in complexes 1–4 and \(m/z = 350.894\) for R = Me in complex 5). In addition to these peaks, the perchlorate complexes 1–3 and the hexafluorophosphate complexes 4 and 5 displayed an \(m/z\) peak at 98.949 (100%) and 144.949 (100%) attributable to the \(\text{ClO}_4^{-}\) (calcd \(m/z = 99.451\)) and \(\text{PF}_6^{-}\) (calcd \(m/z = 144.642\)) ions, respectively.

Species with additional coordination such as those observed in the above complexes when MeCN was used as a solvent in measuring the mass spectra, have been recently reported in some dinuclear metal(II) complexes based phenolate.\(^{2,44}\)

**Crystal structures of the complexes**

\([\text{Cu}_2(\mu-\text{L}^{\text{II}}\text{O})(\mu-\text{OH})]\text{ClO}_4 \ (1)\). The molecular structure of 1 consists of dinuclear \([\text{Cu}_2(\text{L}^{\text{II}}\text{O})(\text{OH})]^2+\) complex cations and \(\text{ClO}_4^{-}\) counter ions. A perspective view of the complex cation together with partial atom numbering schemes is given in Fig. 1, and selected bond parameters are summarized in Table S1 (ESI†). Each Cu(\(\mu\)) center within the dinuclear complex cation is penta-coordinated by three N-donor atoms of one bis-pyridylamino group, the bridging O(1) atom of central 4-chlorophenate moiety and O(10) oxygen atom of bridging hydroxy group. Both CuN\(_2\)O\(_2\) chromophores adopt distorted SP geometry \(\tau\)-values: 0.15 and 0.14, for Cu(1) and Cu(2), respectively\(^{44}\) with N(3) and O(1) atoms in apical sites [Cu(1)–N(3) = 2.205(5), Cu(2)–O(1) = 2.200(4) Å]. The basal Cu–N/O bond distances are in the range from 1.932(3) to 2.044(5) Å. The Cu(1)–Cu(2) intra-dimeric distance is 3.0297(13) Å, and the shortest inter-dimer metal–metal separation is 7.166(2) Å. The Cu(1)–O(1)–Cu(2), Cu(1)–O(10)–Cu(2), O(1)–Cu(1)–O(10) and O(1)–Cu(2)–O(10) bond angles are 93.36(15), 103.29(18), 84.49(15) and 78.27(14)°, respectively, Cu(2) forms an additional semi-coordinative bond to O(6A) atom of partially disordered perchlorato anion [Cu(2)–O(6A) (\(x, 1/2 – y, 1/2 + z\) = 2.719(8) Å] (Fig. S6†).

![Perspective view and atom numbering scheme of the complex cation, [Cu₂(L²O)(µ-OH)]²⁺ of complex 1. H-atoms are omitted for clarity.](image-url)
single deprotonated pyrazole, the bridging O(1) atom of central 4-chlorophenolate moiety and O(2) oxygen atom of a terminal perchlorate group. The four short Cu(1)–N bond lengths are in the range from 1.957(5) to 2.020(6) Å. The axial Cu(1)–O(1), Cu(1)–O(2) and O(1)–Cu(1)–O(2) bond parameters are 2.227(4) Å, 2.769(7) Å and 157.87(17)°, respectively. Cu(2) is penta-coordinated by three N donor atoms of second disordered bis-pyridylamino group, N(8) of a bridging single pyrazolyl anion, and the bridging O(1) atom of central 4-chlorophenolate moiety. The CuN₃O₂ chromophore adopts a distorted TBP geometry \([r\text{-value: 0.73 (for N5A) or 0.78 (for N5B)}].\) The axial sites are occupied by N(4) and N(8) atoms \([\text{Cu(2)}-\text{N(4)} = 2.020(6) \text{ Å}, \text{Cu(2)}-\text{N(8)} = 1.994(7) \text{ Å}, \text{N(4)}-\text{Cu(2)}-\text{N(8)} = 174.1(2)^\circ]\). The equatorial Cu(2) N/O bond distances are in the range from 1.979(10) to 2.186(11) Å. The Cu(1)–Cu(2) intra-dimeric distance is 3.463(5) Å, and the shortest inter-dimer metal–metal separation is 8.088(11) Å. The Cu(1)–O(1)–Cu(2) bond angles are 108.85(18)°. Packing plot of the compound is shown in Fig. S7.† 

The molecular structure of 3 consists of dinuclear \([\text{Cu}_{2}^{(II)}\text{L}^{(II)}\text{ClO}]^{2+}\) complex cations and ClO₄⁻ counter ions. A perspective view of the complex cation together with partial atom numbering scheme is given in Fig. 3 and selected bond parameters are summarized in Table S3.† Each Cu(n) center within the dinuclear complex cation is penta-coordinated by three N-donor atoms of one bis-pyridylamino group, the bridging O(1) atom of central 4-chlorophenolate moiety and an oxygen atom of bridging (PO₂)(OC₆H₅)₂ group. Both CuN₃O₂ chromophores adopt distorted SP geometry \([r\text{-values: 0.09 and 0.16, for Cu(1) and Cu(2), respectively}].\) The Cu(1)···Cu(2) intra-dimeric distance is 3.588(10) Å, and the shortest inter-dimer metal–metal separation is 6.762(12) Å. The Cu(1)–O(1)–Cu(2), Cu(1)–O(1)–P(1), and Cu(2)–O(11)–P(1) bond angles are 126.90(17), 124.1(2) and 120.1(2)°, respectively. Packing plot of compound 3 is shown in Fig. S8.†

\[
\begin{align*}
[\text{Cu}_{2}^{(II)}\text{L}^{(II)}\text{ClO}](\mu\text{-pz})\text{PF}_{6} & \quad \text{2MeCN (4 ·2MeCN) and [Cu}_{2}^{(II)}\text{L}^{(II)}\text{MeO}^{-} & \quad \text{(dca)}_{2}]\text{PF}_{6} \quad \text{2MeCN (3 ·2MeCN).} \\
\end{align*}
\]

The molecular structures of these molecules consist of dinuclear complex cations \([\text{Cu}_{2}^{(II)}\text{L}^{(II)}\text{ClO}]^{2+}\) or \([\text{Cu}_{2}^{(II)}\text{L}^{(II)}\text{MeO}^{-}(\text{dca})_{2}]^{2+}\)]PF₆⁻ counter ions and MeCN lattice solvent molecules. Perspective views of the crystal structures together with partial atom numbering schemes are depicted in Fig. 4, and selected bond parameters are presented in Tables S4 and S5,† respectively. Each Cu(n) center within a dinuclear complex cation is penta-coordinated by three N donor atoms of one bis-pyridylamino group, a terminal dicyanamido anion in basal sites, and the bridging O(1) atom of central 4-substituted-phenolate moiety, which occupies the axial position of the distorted square pyramids \([r\text{-values: 0.05 and 0.07 for 4 and 0.05 and 0.04 for 5}].\) The corresponding axial Cu-O(1) bond distances are 2.190(5), 2.190(5), 2.170(2) and 2.172(2) Å, respectively. The basal Cu-N bond distances are in the range from 1.961(5) to 2.058(6) Å. The Cu(1)–O(1)–Cu(2) bridging bond angles are 136.82(17) and 137.65(8)°, respectively. The intra-dimeric metal–metal distances are 4.072(7) and 4.049(5) Å, and the shortest inter-dimer metal–metal separations are 8.364(16) and 8.368(6) Å, for 4 and 5, respectively (Fig. S9 and S10). The terminal dicyanamido ligands have the following bond parameters: C–N(nitrile): 1.142(4)–1.174(8) Å, C–N(amide): 1.288(8)–1.342(11) Å, N–C–N: 173.5(3)–175.0(9)°, C–N–C: 117.8(7)–119.9(3)°, Cu–N–C: 160.8(3)–164.7(3)°.

**Magnetic properties of complexes**

The analysis of the magnetic data was based on the spin Hamiltonian for dinuclear system of the form

\[
\hat{H} = -J \left( \mathbf{S}_1 \cdot \mathbf{S}_2 \right) + \sum_{i=1}^{N} \mu_{B} g_{i} \mathbf{S}_i \cdot \mathbf{B} \tag{1}
\]

where the isotropic exchange \((J)\) and Zeeman term \((g)\) are included. Then, the molar magnetization can be easily calculated using the following analytical formula

\[
M_{molar} = \frac{\mu_{B} N_{A} e^{(J \cdot x)/kT} - e^{(J \cdot x)/kT}}{1 + e^{(J \cdot x)/kT} + e^{J/kT} + e^{(J \cdot x)/kT}} \tag{2}
\]

where \(x = \mu_{B} g \mathbf{B}\).

Moreover, the small amount of monomeric paramagnetic impurity (Pi) which accounts for increase of molar...
magnetization (mean susceptibility) at low temperatures was taken into consideration by eqn (3)

\[ M_{\text{sample}} = (1 - \chi_{\text{PI}})M_{\text{mol}} + 2\chi_{\text{PI}}M_{\text{PI}} \]  

(3)

where \( M_{\text{PI}} \) was calculated using the Brillouin function. Both temperature and field dependent magnetic data of the studied compounds were included into fitting procedures.

The experimental magnetic data of 1 are depicted in Fig. 5. The theoretical effective magnetic moment \( \mu_{\text{eff}} \) for two uncoupled \( S_1 = S_2 = 1/2 \) and \( g = 2.0 \) is 2.45 \( \mu_B \) or for more typical value of \( g \)-factor for copper(II) compounds equaled to 2.2 is \( \mu_{\text{eff}} / \mu_B = 2.69 \). The room temperature value of \( \mu_{\text{eff}} \) is 2.06 \( \mu_B \) and is decreasing on lowering the temperature. The presence of two maxima of \( M_{\text{mol}} \) vs. \( T \) curve located at \( T_{\text{max,1}} = 52.3 \) K and \( T_{\text{max,2}} = 213.3 \) K suggests that most likely the sample was contaminated by unidentified impurity, which was not detected by standard physico-chemical methods. Probably, it should be mentioned that several independently prepared batches of the complex were tested and same result was obtained. However, there is a simple formula derived for dinuclear species which can be used to estimate \( J \)-value as

\[ |J|/kT_{\text{max}} = 1.599 \]  

(4)

Then, the first maximum corresponds to \( J_1 = -58.2 \) cm\(^{-1}\), while the second one to \( J_2 = -237 \) cm\(^{-1}\). The \( J_1 \) spans the interval between DFT calculated values (see next section) \( J_{\text{Ruiz}} = -43.1 \) cm\(^{-1}\) and \( J_{\text{Yam}} = -85.5 \) cm\(^{-1}\), so it can be suggested that \( J_1 \) matches the predicted magnetism of compound 1, while the \( J_2 \) may be assigned to the unknown impurity.

Contrary to the case described above, the experimental magnetic data for 2 (Fig. 6) matches well with the expectations where the effective magnetic moment is close to 2.7 \( \mu_B \) at 300 K and continuously decreases to 0.24 \( \mu_B \) at 1.9 K. The maximum of \( M_{\text{mol}} \) vs. \( T \) curve is located at \( T_{\text{max}} = 55.1 \) K, which corresponds to \( J = -61.2 \) cm\(^{-1}\). Fitting procedure, which was done according to eqn (1)–(3), resulted in \( J = -61.5 \) cm\(^{-1}\), \( g = 2.14 \), \( \chi_{\text{PI}} = 3.9 \times 10^{-9} \) m\(^3\) mol\(^{-1}\), \( \chi_{\text{PI}} = 0.85\% \).
DFT calculations

Our previous study on dinuclear singly bridged-phenoxydo metal(II) complexes showed that in the case of copper(II) complex of the type \( \left[ \text{Cu}_{2}(\mu-L^\text{S}-O)-(dca)_2]PF_6 \times 2\text{CH}_3\text{CN} \right. \): \( \text{R} = \text{Cl}; \: \text{R} = \text{CH}_3 \), DFT calculations predicted almost negligible antiferromagnetic exchange (see next section). Indeed, the effective magnetic moment is almost constant over the whole temperature range (the gradual increase of \( \mu_{\text{eff}}/\mu_\text{HS} \) on heating in the case of 5 can be attributed to small amount of para/ferromagnetic impurity and due to temperature-independent magnetism). There is no maximum of \( M_{\text{mol}} \) vs. \( T \) curve, which suggests that the value of \( |J| \) should be less than 2 cm\(^{-1}\). This agrees well with the fitted values: \( J = -0.26 \text{ cm}^{-1} \), \( g = 2.15 \), \( \chi_{\text{TIP}} = 1.0 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1} \) for 4 and \( J = -0.11 \text{ cm}^{-1} \), \( g = 2.08 \), \( \chi_{\text{TIP}} = 1.9 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1} \) for 5 (Fig. 8 and 9).

DFT Calculations

The results of DFT calculations are summarized in Table 1 and illustrated in Fig. 10. All the \( J \)-values were found negative and suggesting the presence of antiferromagnetic coupling ranging from very weak (5) to very strong (3). In case of square-pyramidal geometry (SP) the unpaired electron resides in d\(_{xy}\)-y\(^2\) orbitals, while the corresponding trigonal-bipyramidal (TBP) geometry resulted in magnetic orbital based on d\(_{xz}\) (Cu2 in compound 2). The smallest overlap \( S_{ab} \) between the non-
orthogonal orbitals was found for 5 and the largest for 3, which is in agreement with strength of antiferromagnetic exchange. Careful inspection of literature showed that there are only four other examples similar to ours where the magnetic properties were studied for copper(n) dimers containing both L\textsubscript{R}-OH and X ligands (Chart 1), namely [Cu\textsubscript{2}(μ-L\textsubscript{MeO})(μ-OH)][ClO\textsubscript{4}]\textsubscript{2}·THF (6), [Cu\textsubscript{2}(μ-L\textsubscript{MeO})(μ-OCH\textsubscript{3})][ClO\textsubscript{4}]\textsubscript{2}·H\textsubscript{2}O (7), \textsuperscript{34} [Cu\textsubscript{2}(μ-L\textsuperscript{MeO})(μ-CH\textsubscript{3}-COO)][PF\textsubscript{6}]\textsubscript{2} (8), \textsuperscript{34} and [Cu\textsubscript{2}(μ-L\textsuperscript{MeO})(μ-CH\textsubscript{3}COO)][PF\textsubscript{6}]\textsubscript{2} (9)\textsuperscript{a} with \(f_{\text{mag}} = -224, -312, -80, +308 \text{ cm}^{-1}\), respectively. The reported \(f_{\text{mag}}\) values were scaled according to the spin Hamiltonian definition in eqn (1). Interestingly, compounds 1, 6 and 7 have the same hydroxo/alkoxo-bridging groups (X = OH/CH\textsubscript{3}O\textsuperscript{-}) and despite the fact that structural parameters defining the bridges, like Cu-O\textsubscript{Ph}-Cu (93.45–95.66°) and Cu-O\textsubscript{Me}-Cu (102.1–103.29°) angles or Cu···Cu distances (2.966–3.030 Å) are almost the same (Table 1), the \(f_{\text{mag}}\) values vary significantly. More interesting is also the comparison of the \(f_{\text{mag}}\) values for acetato-bridged complexes 8 and 9, which are structurally almost identical (Table 1), their reported magnetic exchanges are either antiferromagnetic or ferromagnetic. Therefore, we utilized the above described DFT procedure to calculate the magnetic exchange parameters also for compounds 6–9 in order to elucidate the observed large variations of the isotropic exchange parameters within this family of coordination compounds. The main results are listed in Table 1 and illustrated in Fig. 10 and 11. Within the structurally similar first group of compounds 1, 6 and 7, it is obvious that the calculated strength of the antiferromagnetic exchange (\(J_{\text{ant}}/J_{\text{ex}}\)) increases with increasing the overlap of magnetic orbitals (\(S_{\text{ab}}\)): \(d_{x^2-z^2}/d_{x^2-y^2} < d_{y^2}/d_{y^2} < d_{x^2-y^2}/d_{x^2}\). Thus, we may conclude that the main source of variation of magnetic properties in 1, 6 and 7 is due to the different geometry around the central copper ions (SP vs. TB). The large difference in \(f_{\text{mag}}\) for compounds 2 (\(f_{\text{mag}} = -61.5 \text{ cm}^{-1}\)) and 3 (\(f_{\text{mag}} = -279 \text{ cm}^{-1}\)) with the bridging ligands X (X = the pyrazolyl anion for 2 and diphenylphosphate anion for 3) can be explained by the fact that in the case of the diphenylphosphate ligand, there is efficient overlap of orbitals (\(d_{x^2-y^2}/d_{x^2}\)) through both bridging ligands, whereas in compound 3, the μ-phenoxydi

Table 1. The DFT-calculated net Mulliken spin densities (\(\rho\)), expected values (\(S_\text{iso}\)), overlap \(S_{\text{ab}}\) between the corresponding orbitals and isotropic exchange parameters (\(J\)) from high-spin (HS) and broken symmtry spin (BS) states of the dinuclear molecular fragments based on X-ray structures of 1–9 completed with selected structural parameters

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| \(\rho_{\text{iso}}^{\text{Cu1}}/\rho_{\text{iso}}^{\text{Cu1}}\) | 0.63/0.64 | 0.61/0.62 | 0.64/0.63 | 0.61/0.61 | 0.63/0.63 | 0.63/0.63 | 0.61/0.61 | 0.61/0.61 |
| \(\rho_{\text{iso}}^{\text{Cu2}}/\rho_{\text{iso}}^{\text{Cu2}}\) | 0.63/0.63 | 0.60/0.62 | 0.63/0.62 | 0.61/0.61 | 0.61/0.61 | 0.63/0.62 | 0.62/0.62 | 0.61/0.61 | 0.60/0.61 |
| \(S_{\text{iso}}^{\text{Cu1}}\) | 2.00 | 2.01 | 2.01 | 2.01 | 2.01 | 2.00 | 2.01 | 2.01 | 2.01 |
| \(S_{\text{iso}}^{\text{Cu2}}\) | 1.00 | 1.00 | 0.99 | 1.01 | 1.01 | 0.99 | 0.97 | 1.00 | 1.01 |
| \(S_{\text{ab}}\) | 0.09278 | 0.07118 | 0.13903 | 0.00258 | 0.00272 | 0.13427 | 0.18057 | 0.02449 | 0.00894 |
| \(d_{\text{ex}}/\text{cm}^{-1}\) | -43.150 | -46.816 | -194.931 | -0.031 | -0.067 | -142.538 | -310.304 | 15.762 | 26.894 |
| \(f_{\text{mag}}/\text{cm}^{-1}\) | -43.1 | -46.8 | -194.9 | -0.03 | -0.06 | -142.5 | -310.3 | 15.8 | 26.9 |
| \(\alpha/\text{cm}^{-1}\) | -85.5 | -93.2 | -382.3 | -0.06 | -0.14 | -279.9 | -600.8 | 31.5 | 53.8 |
| \(\beta/\text{cm}^{-1}\) | -58.2/ -237\(^\text{a}\) | -61.5 | -279 | -0.26 | -0.09 | -224\(^\text{b}\) | -312\(^\text{c}\) | -80 | 30.8 |

\(\text{a} J\)-values are estimated from maxima of molar susceptibility. \(\text{b} J\)-values were reported in ref. 28 and 34 and scaled according to eqn (1). \(\text{c} See\ Chart\ 1.\)
The calculated isodensity surfaces of the broken symmetry spin states for molecular fragments of 6 and 7 and high spin states for molecular fragments of 8 and 9 using B3LYP/def2-TZVP(-f). Positive and negative spin densities are represented by dark blue, and dark red surfaces, respectively. Hydrogen atoms were omitted for clarity.

Fig. 11 The calculated isodensity surfaces of the broken symmetry spin states for molecular fragments of 6 and 7 and high spin states for molecular fragments of 8 and 9 using B3LYP/def2-TZVP(-f). Positive and negative spin densities are represented by dark blue, and dark red surfaces, respectively. Hydrogen atoms were omitted for clarity.

The compound bis(2-pyridylmethyl)amine (DPA) was purchased from TCI-America. All other chemicals were commercially available and used without further purification. The ligands 2,6-bis-[bis(2-pyridylmethyl)aminomethyl]-4-chlorophenol (LCl-OH) and 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (1M6-OH) [Chart 1] were prepared and characterized according to the published procedure.1-2 Infrared spectra of all complexes and ligands were recorded on a JASCO FTIR-480 plus spectrometer as KBr pellets, except complex 4 was measured using Nexus 670 spectrometer (ATR) (Thermo Nicolet, USA). Electronic spectra were recorded using an Agilent 8453 HP diode array UV-Vis spectrophotometer.1H and 13C NMR spectra were obtained at room temperature on a Varian 400 NMR spectrometer operating at 400 MHz (1H) and 100 MHz (13C). 1H and 13C NMR chemical shifts (δ) are reported in ppm and were referenced internally to residual solvent resonances (DMSO-d6: δH = 2.49, δC = 39.4 ppm). ESI-MS spectra were measured on an LC-MS Varian Saturn 2200 spectrometer. The conductivity measurements were performed using a Mettler Toledo Seven Easy conductivity meter and the cell constant was determined by the aid of 1413 μS cm⁻¹ conductivity standard. The molar conductivity of the complexes were determined from $\Lambda_M = (1.0 \times 10^5 \kappa)/M$, where $\kappa = $ cell constant and $M$ is the molar concentration of the complex. Magnetic measurements were performed with an MPMS XL7 SQUID magnetometer (Quantum Design, Inc.) ($T = 1.9-300$ K at $B = 1$ T; $B = 0-5$ T at $T = 2$ and $5$ K). The magnetic data were corrected for diamagnetic susceptibilities. Elemental analyses were carried out by the Atlantic Microlaboratory, Norcross, Georgia U.S.A.

Theoretical DFT calculations

The ab initio theoretical calculations were done with the ORCA 3.0 computational packages using the B3LYP functional and polarized triple-$\zeta$ quality basis set def2-TZVP(-f) for all the complexes (including all the atoms). The single-point energy

Experimental and physical measurements

Materials and physical measurements

$J^{\mu\nu}$ and $J^{\rho\sigma}$ determined isotropic exchange parameters vs. calculated energy difference $\Delta$, ($D = E_{\text{BS}} - E_{\text{HS}}$).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig12.png}
\caption{Comparison of the experimentally ($J^{\mu\nu}$) and theoretically ($J^{\mu\nu}$) determined isotropic exchange parameters vs. calculated energy difference $\Delta$, ($D = E_{\text{BS}} - E_{\text{HS}}$).}
\end{figure}
calculations were done on molecular fragments based on the experimental X-ray geometries: \([\text{Cu}_2(\mu-L^{1,3}-\text{O})(\mu-\text{OH})(\text{ClO}_4)]\) of 1, \([\text{Cu}_2(\mu-L^{1}-\text{O})(\mu-\text{pz})(\text{ClO}_4)]\) of 2, \([\text{Cu}_2(\mu-L^{1}-\text{O})(\mu-\text{O}(\text{Py})(\text{H}_{2}))(\text{ClO}_4)]\) of 3, \([\text{Cu}_2(\mu-L^{1,3}-\text{O})(\text{dca})_2]\) of 4, \([\text{Cu}_2(\mu-L^{1}-\text{M}_{4}\text{O})(\text{dca})_2]\) of 5, \([\text{Cu}_2(\mu-L^{1,3}-\text{M}_{4}\text{O})(\mu-\text{OH})]\) of 6, \([\text{Cu}_2(\mu-L^{1,3}-\text{M}_{4}\text{O})(\mu-\text{CH}_2O)]\) of 7, \([\text{Cu}_2(\mu-L^{1,3}-\text{M}_{4}\text{O})(\mu-\text{CH}_2\text{COO})]\) of 8 and \([\text{Cu}_2(\mu-L^{1,3}-\text{M}_{4}\text{O})(\mu-\text{CH}_2\text{COO})]\) of 9. All the calculations utilized the RI approximation with the decontracted auxiliary def2-TZV/J Coulomb fitting basis set and the chain-of-spheres (RJI/COSX) approximation to exact exchange.25 Also, increased integration grids (Grid5 and GridX5 in ORCA convention) and tight SCF convergence criteria were used. The isotropic exchange parameters \(\gamma\) were calculated by comparing the energies of high-spin (HS) and broken-symmetry (BS) spin states utilizing both Ruiz’s approach23 and Yamaguchi’s approach.24 Plots of spin densities were done by means of the VESTA 3 software.25

X-ray crystal structure analysis

The X-ray single-crystal data of compounds 1–5 were collected on a Bruker-AXS APEX CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 2. The intensities were collected with Mo-K\(\alpha\) radiation \((\lambda = 0.71073 \text{ Å})\). Data processing, Lorentz-polarization and absorption corrections were performed using APEX, and the SADABS computer programs.26 The structures were solved by direct methods and refined by full-matrix least-squares methods on \(F^2\), using the SHELXL27 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 of HFIX (parent C atom) or DFIX (parent O atom) utility of the SHELXTL program. Molecular plots were performed with the Mercury program.28 In case of 2, split occupancy of 0.508(7) and 0.492(7) were applied to disordered atoms of one pyridyl moiety.

Caution: Salts of perchlorate and their metal complexes are potentially explosive and should be handled with great care and in small quantities.

Syntheses of the complexes

\([\text{Cu}_2(\mu-L^{1,3}-\text{O})(\mu-\text{OH})]\text{ClO}_4\)_2 (1). To a mixture of Cu(ClO)_4·6H_2O (0.152 g, 0.40 mmol) and 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-chlorophenol (0.110 g, 0.20 mmol) dissolved in MeOH (20 mL), an aqueous solution of Na_2CO_3 (21 mg, 0.20 mmol dissolved in 3 mL H_2O) was added. The resulting green solution was heated on a steam-bath for 10 min, filtered while hot through celite and then allowed to stand at room temperature. The precipitate which was obtained was collected by filtration, washed with propan-2-ol and Et_2O and then dried at room temperature (overall yield: 105 mg, 59%). Recrystallization of the product from H_2O afforded green crystals suitable for X-ray structure determination. Characterization for 1: calc’d for Cu_2H_6Cl_2Cu_2N_4O_10 (MM = 892.07 g mol\(^{-1}\)): C, 43.04; H, 3.50; N, 9.41%. Found: C, 42.96; H, 3.46; N, 9.27%. Selected IR bands (cm\(^{-1}\)): 3429 (m, b) \(\nu(C-O)\); UV-VIS spectrum \(\lambda_{\text{max}}\) (nm, \(\epsilon\) M\(^{-1}\) cm\(^{-1}\)) (Cu atom) in CH_2Cl_2: 805 (137, b). ESI-MS in CH_2Cl_2: m/z = 835.056, 767.069, 316.037 (major peaks) and for negative ion: m/z = 98.949 (100%). Molar conductivity, \(\Lambda_m\) (CH_2Cl_2) = 267 \(\Omega^{-1} \text{cm}^2\text{mol}^{-1}\) – 1.

\([\text{Cu}_2(\mu-L^{1,3}-\text{O})(\mu-\text{pz})]\text{ClO}_4\)\(_2\) (2). To a hot solution containing 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-chlorophenol (0.110

| Compound | 1 | 2 | 3 | 4·2MeCN | 5·2MeCN |
|----------|---|---|---|--------|--------|
| Empirical formula | \(\text{Cu}_2\text{H}_6\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{10}\) | \(\text{Cu}_2\text{H}_6\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_9\) | \(\text{Cu}_{11+}\text{H}_2\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{11}\) | \(\text{Cu}_{11+}\text{H}_2\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{11}\) | \(\text{Cu}_{11+}\text{H}_2\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{11}\) |
| Formula mass | 892.07 | 943.14 | 1125.24 | 1036.35 | 1015.93 |
| Space group | \(\text{P}2_1/\text{c}\) | \(\text{P}2_1/\text{c}\) | \(\text{P}2_1/\text{c}\) | Monoclinic | Monoclinic |
| \(a\) (Å) | 14.958(3) | 16.336(10) | 1149(10) | 16.262(7) | 16.323(5) |
| \(b\) (Å) | 10.770(2) | 10.326(7) | 10.835(10) | 12.001(8) | 12.027(7) |
| \(c\) (Å) | 23.043(7) | 23.924(15) | 21.776(9) | 21.832(7) | 4 |
| \(\beta\) (°) | 90 | 90 | 90 | 90 | 90 |
| \(\gamma\) (°) | 90 | 90 | 90 | 90 | 90 |
| \(V\) (Å\(^3\)) | 3611.3(15) | 3863.7(4) | 4520.3(3) | 4262.5(2) | 4 |
| \(Z\) | 4 | 4 | 4 | 4 | 4 |
| \(T\) (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| \(\mu\) (mm\(^{-1}\)) | 1.465 | 1.373 | 1.256 | 1.181 | 1.115 |
| \(\Delta_{\text{elek}}\) (Mg m\(^{-3}\)) | 1.641 | 1.621 | 1.691 | 1.620 | 1.583 |
| Crystal size (mm) | 0.22 × 0.19 × 0.13 | 0.28 × 0.23 × 0.17 | 0.28 × 0.23 × 0.17 | 0.27 × 0.23 × 0.12 | 0.24 × 0.19 × 0.17 |
| \(\theta\) max (°) | 25.50 | 26.80 | 25.30 | 26.500 | 29.030 |
| Data collected | 6771 | 40 785 | 69 771 | 70 106 | 55 430 |
| Unique refl./\(R_{\text{int}}\) | 6771/15 | 8253/0.0435 | 7989/0.0994 | 8660/0.0863 | 11 115/0.0652 |
| Parameters/rastrums | 505/6 | 579/0 | 622/0 | 589/1 | 589/1 |
| Goodness-of-Fit on \(F^2\) | 1.172 | 1.204 | 1.348 | 1.115 | 0.920 |
| \(R_p/W(R)\) (all data) | 0.0661/0.1957 | 0.0986/0.2343 | 0.0764/0.2165 | 0.0653/0.1893 | 0.0373/0.0775 |
| Residual extrema (eÅ\(^3\)) | 1.67/–0.93 | 1.23/–1.27 | 1.46/–0.78 | 0.81/–1.13 | 0.50/–0.48 |
g, 0.20 mmol) and Cu(ClO$_2$)$_2$-6H$_2$O (0.152 g, 0.40 mmol) dissolved in MeOH (30 mL) pyrazole, Hpz (14 mg, 0.20 mmol) was added. The resulting green solution was heated on a steam-bath for 10 min, filtered while hot through celite and then allowed to stand at room temperature. The greenish-blue precipitate which was obtained after few hours was collected by filtration, washed with propan-2-ol and Et$_2$O and then dried at room temperature (overall yield: 160 mg, 85%). Shiny greenish-blue crystals suitable for X-ray structure determination were obtained from dilute solution.

Characterization for 2: celd for C$_{42}$H$_{38}$Cl$_2$Cu$_2$Ni$_2$O$_8$ (MM = 943.144 g mol$^{-1}$): C, 44.57; H, 3.53; N, 11.88%. Found: C, 44.38; H, 3.59; N, 11.92%. Selected IR bands (cm$^{-1}$): 1609 (s), 1485 (w), 1460 (m), 1447 (m), (pyridyl groups); 1120, 1093 (vs. r$_{as}$ (Cl-O)).

UV-VIS spectrum ($\lambda_{max}$ nm ($\epsilon$, M$^{-1}$ cm$^{-1}$/Cu atom) in CH$_3$CN: 456 (sh), 799 (194). ESI-MS in CH$_3$CN: m/z = 821.012, 767.069, 361.035 (major peaks) and for negative ion: m/z = 98.950 (100%) [ClO$_4$]$^{-}$ = 99.453. Molar conductivity, $\Lambda_m$ (CH$_3$CN) = 298 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

$\left[\text{Cu}_2(\mu-\text{LClO})\left(\mu-O_2\text{P}(\text{OC}_6\text{H}_5)\text{H}_3\right)\right]^{2+}$ (3). Diphenyl phosphinate (50 mg, 0.20 mmol) which was neutralized with NaOH (0.2 mmol dissolved in 2 mL H$_2$O) was added dropwise to a warm solution containing 2,6-bis[2-pyridylmethyl]aminomethyl]-4-chlorophenol (0.110 g, 0.20 mmol) and Cu(ClO$_2$)$_2$.6H$_2$O (0.152 g, 0.40 mmol) in MeOH (20 mL).

The resulting green solution was heated on a steam-bath for 10 min, filtered while hot through celite and then allowed to stand at room temperature. The golden single crystals, which separated in the following day, were collected by filtration, washed with propan-2-ol and Et$_2$O and then dried at room temperature (overall yield: 203 mg, 90%). Characterization for 3: celd for C$_{44}$H$_{44}$Cl$_3$Cu$_2$Ni$_2$O$_3$ (MM = 1129.272 g mol$^{-1}$): C, 46.97; H, 3.58; N, 7.47%. Found: C, 47.07; H, 3.73; N, 7.58%. Selected IR bands (cm$^{-1}$): 1611 (m), 1488 (m), 1448 (m) (pyridyl groups); 1121, 1108, 1092 (vs) r$_{as}$ (Cl-O). UV-VIS spectrum ($\lambda_{max}$ nm ($\epsilon$, M$^{-1}$ cm$^{-1}$/Cu atom) in CH$_3$CN: 440 (542, b). ESI-MS in CH$_3$CN: m/z = 835.060, 767.074, 361.037 (major peaks) and for negative ion: m/z = 98.949 (100%) [ClO$_4$]$^{-}$ = 99.453. Molar conductivity, $\Lambda_m$ (CH$_3$CN) = 294 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

$\left[\text{Cu}_2(\mu-\text{LClO})(\text{dca})\right]^{2+}$ (4-2CH$_3$CN). To a hot solution containing 2,6-bis[2-pyridylmethyl]aminomethyl]-4-chlorophenol (0.111 g, 0.20 mmol) and Cu(NO$_3$)$_2$.3H$_2$O (97 mg, 0.40 mmol) in MeOH (40 mL) sodium dicyanamide (36 mg, 0.40 mmol) dissolved in H$_2$O (3 mL) was added dropwise and this was followed by the addition of NH$_4$PF$_6$ (100 mg, 0.6 mmol). The resulting greenish-blue solution was heated on a steam-bath for 10 min, filtered while hot through celite and then allowed to stand at room temperature. The crude precipitate which separated in the following day was collected by filtration and recrystallized from acetonitrile to afford shiny greenish-blue single crystals. These were filtered, washed with propan-2-ol and Et$_2$O and then dried at room temperature (overall yield: 122 mg, 59%). Characterization for 4-2CH$_3$CN: celd for C$_{44}$H$_{44}$Cl$_3$Cu$_2$F$_6$N$_{14}$OP (MM = 1036.341 g mol$^{-1}$): C, 44.04; H, 3.50; N, 18.92%. Found: C, 44.48; H, 3.53; N, 18.76%. Selected IR bands (cm$^{-1}$): 2283 (m), 2227 (m), 2161 (vs); 1610 (m) 1574 (w), 1483 (w), 1445 (m), (pyridyl groups); 837 (s) r(P-F). UV-VIS spectrum ($\lambda_{max}$ nm ($\epsilon$, M$^{-1}$ cm$^{-1}$/Cu atom) in CH$_3$CN: 457 (117), 656 (155, b).}

**Conclusions**

The reaction of copper(II) salts with 2,6-bis[2-pyridylmethyl]aminomethyl]-4-substituted-phenol (L$^8$-OH) affords two categories of dinuclear complexes in which the phenolate ligand is bridging the two Cu(II) atoms via the deprotonated phenol group. The first category is the singly bridged μ-phenoxido complexes of the general formula $\left[\text{Cu}_2(\mu-L^8$-O$)[X]\right]^{2+}$ ($R = \text{Cl}, \ X = \text{dca (complex 4)}$; $R = \text{X} = \text{Cl}^{-}, \ X = \text{dca (complex 5)}$, $R = \text{CH}_3, \ X = \text{OAc}^{-}, \ X = \text{N}_3$, $\text{H}_2$O and CH$_3$CN)$^{24,25,26}$ This class of compounds mediates very weak antiferromagnetic coupling through the bridged phenoxido group.$^{15}$ The second category of the bicompartamental phenolate ligands is the doubly bridged complexes where in addition to the bridged phenoxido group, an extra bridge exists and this was observed here in this study in complexes $\left[\text{Cu}_2(\mu-L^8$-O$)[\mu-X]\right]^{2+}$ ($X = \text{OH}^{-}, \ X = \text{py}^{-2}$, $X = \text{O}(\text{OC}_6\text{H}_5)_2^{-}$) and in some other related complexes $6-9$ ($R = \text{CH}_3$, $\text{Bu}$, $X = \text{OH}^{-}, \ X = \text{OAc}^{-}, \ X = \text{H}_2$O, $X = \text{N}_3$)$^{4,26,34,47}$ In this case moderate ferromagnetic to very strong antiferromagnetic coupling was observed.

The DFT supported analysis of magnetic properties showed that in the case of the doubly bridged complexes $1-3$ and $6-9$, the key factor determining the nature and strength of the isotropic exchange is the geometry of copper(n) chromophores (SP-SP, SP-TBP or TBP-TBP), thus mutual orientation of magnetic orbitals based on d$_{x^2-y^2}$, d$_{xy}$, d$_{xz}$ or d$_{d_2}$ or d$_{d_2}$ orbitals and efficiency of their magnetic orbital overlaps mediated by both μ-L$^8$-O$_{ph}$ and μ-X bridging ligands. Therefore, the strongest antiferromagnetic exchange within the studied compounds was found in complexes $3$ ($X = \text{O}(\text{OC}_6\text{H}_5)_2^{-}$) and $7$ ($X = \text{CH}_3$O), where either d$_{xy}$ or d$_{xy}$-d$_{xz}$ or d$_{d_2}$ orbitals resulting from SP-SP or TBP-TBP copper geometries are efficiently overlapping, whereas the strongest ferromagnetic coupling was induced in the aceto-bridged complex 9. Moreover, the herein the DFT method used based on the B3LYP functional and def2-TZVP(f) basis set seems to predict properly the nature and strength of the magnetic exchange almost for all the studied complexes, thus enabling us to utilize it also for
other structurally similar compounds in future. The data in Table 1 revealed that magnetic exchange in the family of doubly hetero-bridged pentacoordinate copper[II] complexes cannot be simply predicted by analyzing the basic structural parameters like $\angle (\text{Cu-O}_{\text{P}}-\text{Cu})$ and $\angle (\text{Cu-X-Cu})$ angles but the efficiency of magnetic orbitals overlap is more critical in evaluating the variation of copper chromophores geometries (SP vs. TBP) and their mutual orientation.

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