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Dinuclear Copper(II) Complex with Intramolecular O–H···O Hydrogen Bonding: Magneto-Structural Correlation for Acylhydrazone-Based Phenoxido Bridged Copper(II) Complexes

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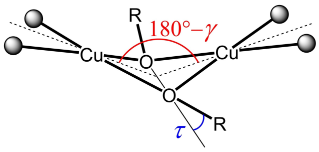
The μ-phenoxido-bridged dinuclear copper(II) complex, $[Cu_2(L^1)_2(dmso)(MeOH)]$ (**1**), has been synthesized using N'-(4-(diethylamino)-2-hydroxybenzylidene)-1-naphthohydrazide (H_2L^1) as ligand. The structural analysis of **1** reveals that the coordination geometry at the copper ions is best described as a square pyramidal with a Cu···Cu distance in the dinuclear complex of 303 pm which is supported by hydrogen bonding between the two apical oxygen donor ligands (O···O 277 pm). Magnetic studies indicate that **1** exhibits a strong antiferromagnetic interaction between the two copper(II) ions with a coupling constant of $J = -450\ \text{cm}^{-1}$ ($\hat{H} = -J\hat{S}_1\hat{S}_2$). The magnetic exchange is transmitted through the central $[Cu_2(OR)_2]^{2+}$ core, a fragment for which different magneto-structural correlations have been reported depending on the substituent at the bridging oxygen atom. However, the properties of complex **1** cannot be explained by any of the established correlations. Nevertheless, complex **1**, together with the series of compounds based on an acylhydrazone ligand framework reported so far, shows a magneto-structural correlation as a function of the Cu–O–Cu bridging angle that significantly differs from all previously reported.

Introduction

The continued interest in the magnetism of copper-based complexes has developed over the years because of their importance in biological systems,[1] hydrometallurgy,[2] sensing,[3] heterogeneous catalysis,[4] and more recently due to potential applications in topical fields such as molecular spintronics.[5] Moreover, hydrogen bonding at ligands coordinated to metal ions is known to have profound effects on the fundamental properties of the complexes in question, ranging from structural parameters such as the metal-ligand bond lengths to their reactivity and even magnetism.[6] As a matter of fact, the study of magnetic interaction in copper complexes has a long history, beginning with the observation by Bleaney and Bowers that the two metal ions in the dinuclear copper(II) acetate complex are antiferromagnetically coupled.[7] Since then, dinuclear copper(II) complexes have been a testing ground for a theoretical description of molecular magnetism.[8] This has led to reports of linear relationships between the Cu–O–Cu bond angle and the exchange coupling J obtained by fitting the experimental magnetic susceptibility data for bis(hydroxido)- and bis(alkoxido)-bridged complexes with a $[Cu_2(OR)_2]^{2+}$ core.[9] After a first theoretical explanation based on the orbital picture provided by Hoffmann and Kahn,[10] density functional theory (DFT) later even enabled a quantitative description of the magneto-structural correlations for such hydroxido- and alkoxido-bridged dinuclear copper(II) complexes.[11,12] It was found that besides the bridging angle Cu–O–Cu two additional parameters play a significant role (Scheme 1): (i) the out-of-plane angle τ of the substituent at the bridging oxygen atom, and (ii) the so-called hinge distortion (γ), i.e., the bending of the $[Cu_2(OR)_2]^{2+}$ core at the O···O hinge.

However, the situation is much less obvious in the case of phenoxido-bridged complexes with a $[Cu_2(OR)_2]^{2+}$ core.[13] After a first attempt for a magneto-structural correlation was reported by Thompson et al. covering a series of dinuclear complexes supported by macrocyclic ligands,[14] other examples showed that this correlation cannot generally be used for phenoxido-bridged complexes.[15] In fact, complexes with



Scheme 1. Structural distortions of a $[Cu_2(OR)_2]^{2+}$ core: Hinge distortion defined by the angle γ and the out-of-plane distortion given by the angle τ of the substituent at the bridging oxygen atom.

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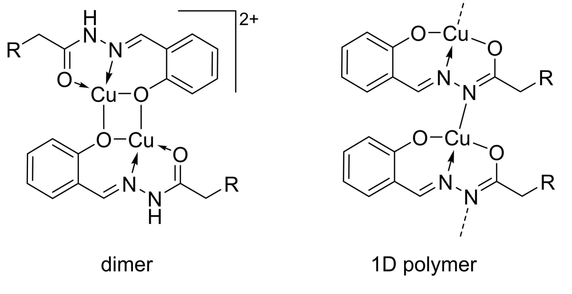
Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202400531 macrocyclic ligands tend to have much larger antiferromagnetic coupling constants and an extremely small crossover angle below which a ferromagnetic behavior would be expected. On the other hand, the numerous known dinuclear copper(II) complexes not supported by a macrocyclic ligand system exhibit a broad distribution of observed coupling constants as a function of the Cu–O–Cu bridging angle, as shown in Figure S1. Nevertheless, in the majority of cases, the fundamental trends can be explained utilizing the parameters defined in Scheme 1 and an additional structural feature given by the torsion angle of the aromatic plane of the bridging phenolate moiety with respect to the bridging plane between the copper ions.[13] Furthermore, an additional influence can be expected from electronic effects due to the substituents at the phenyl ring of the corresponding ligand system.[13]

A subgroup of dinuclear phenoxido-bridged complexes with a $[Cu_2(OR)_2]^{2+}$ core is supported by acylhydrazone-based ligands that provide a tridentate coordination pocket. For the alkyl derivatives in this subgroup, the protonation state of the acylhydrazone-based ligand was identified as a critical factor leading either to the formation of cationic dinuclear complexes with monoanionic ligands or to neutral 1D coordination polymers with a dianionic ligand, as illustrated in Scheme 2.[16] The two structures exhibit distinct magnetic properties, indicating that the magnetic exchange between neighboring copper(II) ions is markedly enhanced in the phenoxide-bridged dimer relative to the azine-bridged 1D polymer.

The general interest in acylhydrazone-based complexes has steadily increased in recent decades due to their biological and pharmacological importance.[17] In this context, it is worth noting that phenoxido-bridged dinuclear nickel(II) complexes with acylhydrazone ligands can support intramolecular hydrogen bonding between metal-bonded coligands.[18,19] In this work, a novel phenoxido-bridged dinuclear copper(II) complex with the Schiff-base ligand *N'*-(4-(diethylamino)-2-hydroxybenzylidene)-1-naphthohydrazide (H_2L^1) is presented. This acylhydrazone-based dinuclear copper(II) complex is additionally supported by an intramolecular hydrogen bond between the two different apical coligands coordinated at the two copper(II) ions.



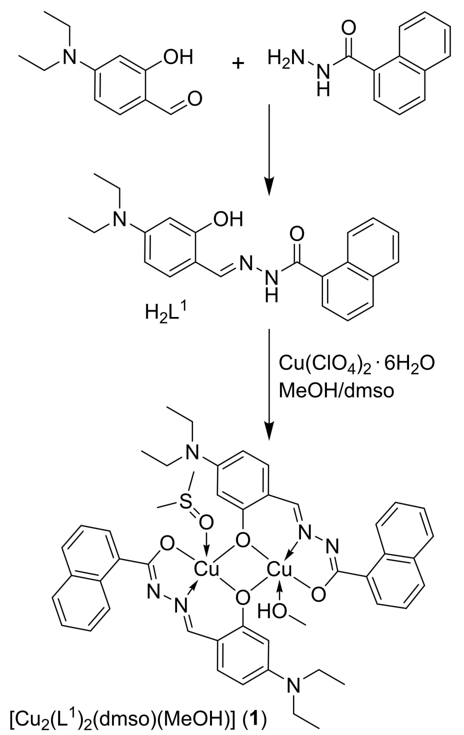
Scheme 2. Different bridging modes for copper(II) complexes with acylhydrazone-based ligands (R = alkyl) in cationic dinuclear complexes and neutral 1D coordination polymers, depending on the mono- (left) of dianionic (right) protonation state of the ligand.[16]

Results and Discussion

Synthesis and Characterization

The acylhydrazone ligand H_2L^1 was synthesized by Schiff-base condensation of 4-(diethylamino)salicylaldehyde and 1-naphthoic hydrazide in ethanolic solution (Scheme 3). The FT-IR spectrum of the ligand shows bands that can be assigned to characteristic stretching vibrations of OH, NH, C=O, and C=N groups. The ^1H NMR of the ligand shows resonances for the NH and OH proton at 11.75 and 11.43 ppm, respectively, while that for the CH proton of the methine group is found at 8.39 ppm.

The reaction of the acylhydrazone ligand H_2L^1 with copper(II) perchlorate hexahydrate in methanol solution resulted in the dinuclear copper(II) complex $[Cu_2(L^1)_2(dmso)(MeOH)]$ (**1**). The synthetic procedure is illustrated in Scheme 3. Complex **1** could be isolated as dark green brownish crystals suitable for X-ray diffraction by recrystallizing the residue of the reaction mixture obtained after removal of all volatiles in dimethyl sulfoxide (dmso) as solvent. The purity of the bulk material of the compound was further confirmed by elemental analyses. The formation of a neutral complex, i.e., the twofold deprotonation of the acylhydrazone ligand, is evidenced by the FT-IR spectrum of complex **1**, indicating the disappearance of the characteristic stretching vibrations of the NH and OH groups observed for the free ligand and the absence of otherwise required additional bands of perchlorate anions. The coordination of the acylhydrazone moiety at the copper(II) ion is further confirmed by the appearance of two additional prominent peaks at 1507 and 1596 cm^{-1} probably



Scheme 3. Synthesis scheme for the ligand H_2L^1 and its copper(II) complex $[Cu_2(L^1)_2(dmso)(MeOH)]$ (**1**).

due to characteristic stretching vibrations of the –C=N–N=C– moiety in the complex formed.[16,20]

Crystal Structure

The structure of the dinuclear complex **1** has been determined by single-crystal X-ray diffraction using suitable crystals obtained from the recrystallized reaction product (for details see Experimental Section). The molecular structure is depicted in Figure 1 and the selected bond lengths and angles are listed in Table S1.

The dinuclear complex **1** contains two mononuclear fragments of square-pyramidally coordinated copper(II) ions where the ONO donor atoms of an acylhydrazone ligand occupy three positions in the basal plane, while the fourth position is occupied by the bridging μ_2-O-phenolate oxygen atom of the ligand of the other complex fragment (O1 at Cu2 and O3 at Cu1). The observed bond lengths and angles within the basal planes at the copper ions are comparable with those reported in a number of other related copper(II) compounds.[19,21]

The apical positions at the copper ions are occupied by the oxygen atoms of two different solvent molecules, i.e., MeOH at Cu1 and dmso at Cu2. These additional ligands are in a cisoid arrangement with respect to the bridging plane and forming a hydrogen bond at a distance of 277 pm (O5···O6). To our knowledge, this cisoid arrangement is unique for this class of complexes. This is slightly shorter than the Cu1···Cu2 distance in the dinuclear $[Cu_2(OR)_2]^{2+}$ core at about 303 pm, indicative for a rather strong hydrogen bonding interaction between the coordinated ligands. As expected, the bond lengths of the neutral oxygen donor ligands at the apical positions of the copper(II) ions are significantly larger than those within the basal plane. For the MeOH ligand at Cu1, a Cu1–O5 distance of 234 pm is observed, whereas for the coordinated dmso molecule at Cu2 the Cu2–O6 distance is even slightly larger with 243 pm.

It is interesting to note that complex **1** is a rare example within the series of acylhydrazone-based copper(II) complexes that exhibits a dinuclear molecular structure for the neutral complex, containing a fully deprotonated dianionic ligand system. This finding appears to contradict the trend observed for alkyl derivatives of the acyl group, where the dianionic form of the ligand typically leads to 1D polymeric structures (see Scheme 2). However, a dinuclear molecular structure has been reported for another complex with an acylhydrazone-based ligand in its dianionic form, which contains an aromatic acyl group (see Scheme S1). Thus, the preferred protonation state of acylhydrazone-based ligand systems in dinuclear copper(II) complexes seems to be correlated with the nature of the acyl group. Alkyl derivatives are typically monoanionic, whereas aryl derivatives tend to be fully deprotonated, forming the dianionic ligand.

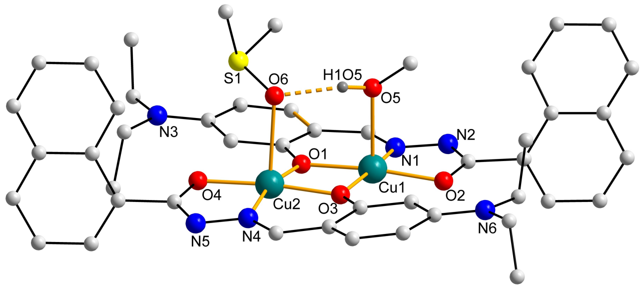


Figure 1. Molecular structure of **1** in ball and stick representation. The dinuclear $[Cu_2(OR)_2]^{2+}$ core is supported by the hydrogen bond O5···O6 at a distance of 277.0(3) pm. All remaining hydrogen atoms have been omitted for clarity.

Magnetic Measurements

The magnetic susceptibility of the dinuclear complex **1** was measured in the temperature range from 2 to 300 K, and the results are presented in Figure 2, which depicts the temperature dependence of $\chi_M T$. At 300 K, the observed $\chi_M T$ value of 0.32 $cm^3 K mol^{-1}$ is markedly smaller than the anticipated spin-only value ($g=2$) of 0.75 $cm^3 K mol^{-1}$ for a dinuclear complex with two independent $S=\frac{1}{2}$ spins. Upon lowering the temperature, the $\chi_M T$ value decreases to about 0.01 $cm^3 K mol^{-1}$ at 100 K and virtually vanishes below 75 K. The data clearly indicates the presence of a strong antiferromagnetic interaction between the two copper(II) ions in complex **1**.

The magnetic data can be fitted assuming an isotropic exchange interaction ($\hat{H} = -J\hat{S}_1\hat{S}_2$) between the two copper(II) ions of complex **1**. This leads to an antiferromagnetic exchange coupling constant J of -450 cm^{-1} and an isotropic g value of 2.23. This is well within the range of coupling constants reported for dinuclear copper(II) complexes with $[Cu_2(OR)_2]^{2+}$ core and phenoxido-bridges.[13] The reported values span a range from ferromagnetic interactions of about 100 cm^{-1} to antiferromagnetic interactions of about -700 cm^{-1} (cf. Figure S1). These variations depend on chemical and structural

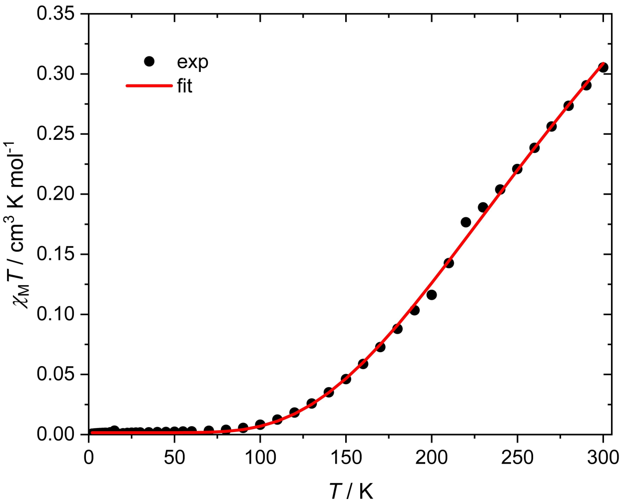


Figure 2. Temperature dependence of $\chi_M T$ for complex **1** measured at 2 kOe. The red line represents the calculated values for the best-fit parameters with $J=-450$ cm^{-1} and $g=2.23$.

differences in the ligands used, resulting in a complex mixture of possible geometrical and electronic effects that influence the nature and strength of the magnetic exchange coupling between the two copper(II) ions.[13] Nevertheless, the Cu–O–Cu bridging angle at the μ_2-oxygen donor of the $[Cu_2(OR)_2]^{2+}$ core is generally considered to be the most crucial factor in determining the magnitude and nature of the exchange interaction.

Computational Studies

To further investigate the magnetic properties of **1**, broken-symmetry DFT (BS-DFT) studies have been performed (for more details, see Experimental Section). A satisfactory agreement with the experimental exchange coupling constant J of $-450\ \mathrm{cm}^{-1}$ was obtained using the B3-LYP density functional, with a calculated value of $-500.7\ \mathrm{cm}^{-1}$. This is consistent with the established observation that the B3-LYP density functional, which includes a contribution of 20 % exact Hartree-Fock (HF) exchange, is an effective approach to calculate exchange interactions in multinuclear transition metal complexes.[22] However, the type of functional employed and the amount of incorporation of exact HF exchange is known to significantly affect the energy splitting between states of different multiplicity.[23,24] To further investigate this phenomenon in the context of complex **1**, two additional hybrid density functionals with varying exact HF exchange contributions were evaluated, namely TPSSh with 10 % and PBE0 with 25 %, resulting in values of -729.4 and $-380.7\ \mathrm{cm}^{-1}$, respectively. There is a notable discrepancy between the results with the three density functions, which can be primarily attributed to the influence of the HF exchange. This is due to the observation that the energy splitting is approximately linear to the proportion of exact exchange included.[23]

Spin-density plots for the high-spin and the broken-symmetry state of complex **1** are depicted in Figure S2. As expected, the spin density is found in the $3d_{x^2-y^2}$ orbitals of the two square-pyramidally coordinated copper(II) ions. Moreover, the spin density maps show a strong delocalization onto the donor atoms coordinating in the equatorial plane of the copper(II) ions. In particular, a distinct spin polarization of the oxygen atoms of the two phenoxido bridges is apparent, which mediate the strong antiferromagnetic exchange between the two spin centers. In contrast, no notable spin density is observed at the axially coordinated donor atoms of the copper(II) ions, indicating the absence of supplementary exchange contributions via the hydrogen bond between the solvent molecules. The presence of dominant superexchange interactions across the oxygen atoms of the phenoxido bridges emphasizes the importance of the geometrical parameters describing the bridging situation of the $[Cu_2(OR)_2]^{2+}$ core as introduced in Scheme 1.

While the hydrogen bonding interaction between the axial ligands at the copper ions does not contribute to the magnetic exchange, the shorter distance between the oxygen donor atoms of the ligands (O5···O6 277 pm) compared to the Cu···Cu distance (303 pm) suggests a significant contribution to the bonding. To investigate this further, the binding energies of the two apical ligands in **1** were analyzed by DFT–D3 calculations (for details see Experimental Section). The model structures used are depicted in Figure S3 and the results summarized in Tables S3–S5. The dmso ligand coordinated at Cu2 exhibits a bonding energy of −61.6 kJ/mol, whereas the MeOH ligand at Cu1 shows a slightly weaker bonding energy of −41.4 kJ/mol. Figure 3 illustrates the donor environment of the $[Cu_2(OR)_2]^{2+}$ core in **1** with the corresponding bonding energies. The formation of a hydrogen bond between the dmso and MeOH molecules serves to further reinforce the structural stability of the system with a binding energy of −43.4 kJ/mol. This, in turn, leads to an appreciable enhancement in the net bonding energy of the two apical ligands to a total of −146 kJ/mol.

Magneto-Structural Correlation

Dinuclear copper(II) complexes with a $[Cu_2(OR)_2]^{2+}$ core are among the best-studied exchange coupled transition metal systems. For the cases of bis(hydroxido)- ($J=-74.53\ \mathrm{cm}^{-1}/\mathrm{deg}\ \theta+7270\ \mathrm{cm}^{-1}$) and bis(alkoxido)-bridged ($J=-82.1\ \mathrm{cm}^{-1}/\mathrm{deg}\ \theta+7857\ \mathrm{cm}^{-1}$) complexes well-established magneto-structural correlations based on the Cu–O–Cu bridging angle θ have been reported.[11,12] A similar correlation was suggested for phenoxido-bridged complexes with a macrocyclic Robson-type backbone ($J=-31.95\ \mathrm{cm}^{-1}/\mathrm{deg}\ \theta+2462\ \mathrm{cm}^{-1}$).[14] However, this correlation cannot be extended to the entire family of phenoxido-bridged complexes,[15] as is evident from the scatterplot obtained for phenoxido-bridged complexes when their exchange coupling constant J is depicted as a function of the Cu–O–Cu bridging angle θ (see Figure S1).[13]

Consequently, describing magnetic exchange through geometrical parameters is not straightforward for phenoxido-bridged complexes. Even when including additional parameters (cf. Scheme 1) besides the well-known bond angle θ at the bridging oxygen donor atom, a quantitative description remains elusive. In addition, the magnetic coupling appears to be significantly affected by the characteristics of the ligand backbone. However, as was demonstrated by Thompson et al.,[14] a quantitative correlation can be established for specific ligand

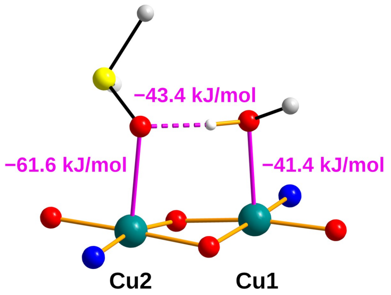


Figure 3. Donor environment of the $[Cu_2(OR)_2]^{2+}$ core of **1** with dmso and MeOH as axial ligands. The pink labels represent the calculated bonding energies (DFT–D3 level of theory). All energies have been corrected for the BSSE (for details see text and Experimental Section).

types, such as a series of dinuclear copper(II) supported by Robson-type macrocyclic ligands.

This prompted us to investigate the series of dinuclear copper(II) complexes with *N*-salicylidene-functionalized acylhydrazone ligands known in the literature (see Scheme S1). The corresponding structural and magnetic data for these complexes are summarized in Table 1. The graphical representation of the coupling constant *J* as a function of the Cu–O–Cu bridging angle θ is shown in Figure 4, which can be approximated by linear regression.

It is worth noting that a relatively broad range for the coupling constant *J* is accompanied by a comparatively small variation of the bridging angle θ at the oxygen atom (Cu–O–Cu), indicating a significant influence of the latter. The deviations observed for this linear correlation may be attributed to specific structural and electronic features, such as the large hinge angle γ of complex **3** or the electron-withdrawing nitro substituent in complex **5**. Moreover, although comparatively small for the complexes given in Table 1, also the τ values associated with the out-of-plane distortion of the substituents on the bridging oxygen donors of the $[Cu_2(OR)_2]^{2+}$ core unit are known to affect the exchange coupling in such systems.[11] In general, the coupling constants within this series are considerably lower than those observed for Robson-type complexes.[14] Interestingly, the magneto-structural correlation found here shows greater similarity to those reported for the hydroxido and alkoxido bridges than to those reported for the phenoxido bridged Robson-type complexes. This is also evident from the comparison of the crossover angle associated with $J = 0$, which is predicted to be around 95–97° for the former cases and around 77° for the Robson-type complexes.

Table 1. Comparison of the magnetic data and structural parameters for bis(μ-phenolate)-bridged dicopper(II) complexes with a Cu_2O_2 core based on *N*- salicylidene-functionalized acylhydrazone ligands (see Scheme S1).

Complex	Ligand	J/ cm^{-1}	θ/°	τ /°	γ /°	Ref.
1	$(L^1)^{2-}$	−450	101.0 (1.5)[a]	4.4 (1.5)[a]	2.5	this work
2	$(HL^2)^-$	−399	100.2[b]	3.0–11.2	0	[16]
3	$(HL^3)^-$	−410	99.9 (1.3)[a]	8.9 (4.2)[a]	16.4	[16]
4	$(HL^4)^-$	−311	99.1	11.3	0	[16]
5	$(L^5)^{2-}$	−372	100.4	5.6	0	[25]
6	$(HL^6)^-$	−349	99.5	4.0	0	[26]
7	$(HL^7)^-$	−477	100.8	2.6	0	[27]

[a] Mean value for the non-centrosymmetric core and the corresponding difference in parentheses. [b] Mean value for four symmetry independent complexes in the crystal structure.

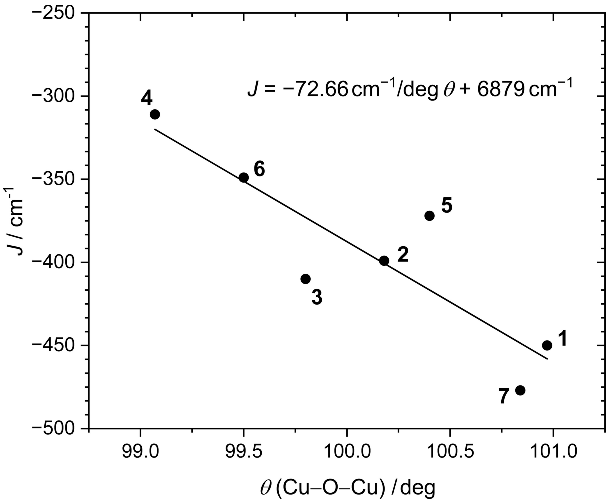


Figure 4. Magnetic coupling constant *J* as a function of the Cu–O–Cu bridging angle θ for bis(μ-phenoxido)-bridged dicopper(II) complexes with a $[Cu_2(OR)_2]^{2+}$ core based on *N*-salicylidene-functionalized acylhydrazone ligands (see Table 1). The black line represents the linear correlation according to the equation given in the diagram.

Conclusions

In the present study, the μ-phenoxido-bridged dinuclear copper(II) complex $[Cu_2(L^1)_2(dmso)(MeOH)]$ (**1**), which contains a tridentate acylhydrazone-based ligand system, has been synthesized and characterized. The acylhydrazone ligand in complex **1** is fully deprotonated, which is a rare example and solely observed for aromatic derivatives of the acyl group. Notably, the molecular structure of the dinuclear complex is further supported by a hydrogen bonding between the axial coligands at the two square-pyramidally coordinated copper(II) ions, a feature that is not commonly observed in similar complexes. In fact, the observed hydrogen bonding distance between the oxygen donor atoms (O···O 277 pm) is considerably shorter than the distance between the two copper(II) ions at about 303 pm.

The magnetic studies revealed the presence of a strong antiferromagnetic interaction between the two copper(II) ions, characterized by a coupling constant of $J = -450\,cm^{-1}$. This magnetic exchange is mediated through the central $[Cu_2(OR)_2]^{2+}$ core. However, the coupling constant of complex **1** cannot be explained by previously established magneto-structural correlations for dinuclear copper(II) complexes. Instead, complex **1**, along with a series of phenoxido-bridged copper(II) complexes based on an acylhydrazone ligand scaffold, provides a novel magneto-structural correlation as a function of the Cu–O–Cu bridging angle. While this newly found correlation differs considerably from all previous magneto-structural correlations for dinuclear copper(II) complexes with a $[Cu_2(OR)_2]^{2+}$ core associated with different types of substituents at the bridging oxygen donor, they nonetheless correspond to a comparable critical angle of about 95–97° for the crossing between ferro- and antiferromagnetic behavior for all cases not involving steric strain by a macrocyclic scaffold.

Experimental Section

General Methods and Materials

Reagent grade solvents were dried and distilled before use whenever necessary. Other chemicals were available commercially and used as received. Elemental analyses were performed on a vario EL cube CHNS Elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 400 MHz spectrometer at 298 K using $SiMe_4$ as an internal reference. IR spectra were recorded with a Perkin-Elmer Spectrum RXI spectrometer. UV spectra were measured on a Lamda25, PerkinElmer spectrophotometer. **Caution**: Although no problems were encountered during the course of this work, attention is drawn to the potentially explosive nature of perchlorates.

Syntheses

***N′*-(4-(diethylamino)-2-hydroxybenzylidene)-1-naphthohydrazide (H_2L^1)**. 4-Diethyl amino salicylaldehyde and 1-naphthoic hydrazide were dissolved in ethanol (15 mL) and heated under stirring for 2 h at 60 °C. The resulting yellowish white compound was filtered, washed with ethanol, and dried over fused $CaCl_2$. Yield: 0.25 g (76 %). Anal. Calcd for $C_{22}H_{23}N_3O_2$: C, 73.11; H, 6.41; N, 11.63. Found: C, 73.59; H, 6.33; N, 11.20 %. FTIR (KBr, ν_{max}/cm^{-1}): ν(O–H) 3204, ν(N–H), 2980, ν(C=O) 1647, ν(C=N) 1584. ^{1}H NMR (400 MHz, dmso-d_6): δ (ppm) = 11.75 (s, 1H, –NH), 11.43 (s, 1H, –OH), 8.39 (s, 1H, –CH), 8.33–6.16 (m, 10H, aromatic), 3.34 (m, 4H, CH_2–N), 1.06 (m, 6H, CH_3). ^{13}C NMR (100 MHz, dmso-d_6): δ (ppm) = 164.95, 164.05, 152.29, 148.41, 148.09, 147.64, 144.33, 136.34, 135.19, 133.39, 130.79, 129.14, 128.79, 128.51, 128.37, 127.50, 123.78, 120.91, 119.61, 119.5, 44.80, 12.88.

$[Cu_2(L^1)_2$(dmso)(MeOH)] (1). $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) was added to a hot methanolic solution (15 mL) of the ligand H_2L^1 (1 mmol) at 60 °C. The resulting solution was stirred for a further 5 h under reflux. After removal of all volatiles a dark brown residue was obtained. Crystallization of this residue from dmso solution over 5 days produced green crystals suitable for X-ray analysis. Yield: 0.23 g (37 %). Anal. Calcd for $C_{47}H_{52}Cu_2N_6O_6S$: C, 59.04; H, 5.48; N, 8.79; S, 3.35. Found: C, 59.30; H, 5.34; N, 9.13; S, 3.34 %. FTIR (KBr, ν_{max}/cm^{-1}): ν(C=H) 2915, ν(–C=N–N=C–) 1596 and 1507. UV-Vis (dmso): λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 637 (300), 406 (5522), 337 (1608), 285 (2319).

X-ray Crystallography

A single crystal of **1** was mounted on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-*K*α radiation. Lorentz and polarization effects as well as absorption were taken into account on a semi-empirical basis using multiple-scans.[28] The structure was solved by direct methods (SHELXS[29]) and refined by full-matrix least squares techniques against F^2 (SHELXL-2018[29]). The hydrogen atom bonded to the methanol molecule O5 was located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[29]

Crystallographic and Refinement Parameters for Complex 1. Formula $C_{47}H_{52}Cu_2N_6O_6S$, $M = 956.08$, Monoclinic, $P2_1/n$, $a = 11.14670(10)$, $b = 23.3042(4)$, $c = 16.6355(3)$ Å, $\beta = 97.775(1)^\circ$, $V = 4281.59(11)$ Å^3, $T = 133$ K, $Z = 4$, $\rho_{calc} = 1.483$ g/cm^3, $\mu = 1.100$ mm^{-1}, multi-scan, trans$_{min}$: 0.6753, trans$_{max}$: 0.7456, $F(000) = 1992$, 33102 reflections in h (−14/14), k (−30/30), l (−21/21), measured in the range $1.51^\circ \le 2\Theta \le 27.48^\circ$, completeness $\Theta_{max} = 99{,}8\,\%$, 9805 independent reflections, $R_{int} = 0.0460$, 8513 reflections with $F_o > 4\sigma(F_o)$, 570 parameters, no restraints, $R_1(\text{obs}) = 0.0418$, $wR_2(\text{obs}) = 0.0944$, $R_1(\text{all}) = 0.0516$, $wR_2(\text{all}) = 0.0997$, GOOF = 1.047, largest difference peak and hole: 0.40/−0.67 e Å^{-3}. Crystallographic data (excluding structure factors) for complex **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. A copy of the data can be obtained free of charge on quoting the depository number CCDC 1981838 (E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Magnetic Measurements

Magnetic susceptibility data were obtained from powdered samples in gelatin capsules at 1 and 2 kOe using a Quantum Design MPMS-5 SQUID magnetometer equipped with a 5 T magnet in the temperature range from 2 to 300 K. The data were corrected for the sample holder and the diamagnetic moment of the sample. Fitting of the data was performed using the MagProp package of the program DAVE.[30]

Computational Details

The structural model for the theoretical studies of **1** is based on the atomic positions derived from the single-crystal structure. Starting from these atomic positions the structure has been optimized with the TURBOMOLE 7.6 package of programs[31] at RI-DFT–D3[32,33]/PBE[34,35]/def2-TZVPP[36] level of theory in the high-spin state ($S = 1$). The intramolecular magnetic exchange was studied by calculations utilizing the DFT-optimized structure and the broken-symmetry DFT (BS-DFT) approach. BS-DFT results are based on three different hybrid functionals (B3-LYP,[37–39] PBE0,[34,35,40] and TPSSh[41]) with different amount of exact Hartree-Fock exchange (B3-LYP: 20 %; PBE0: 25 %; TPSSh: 10 %) in combination with the triple-ζ def2-TZVPP basis sets and a tight SCF convergence criterion (10^{-8} Hartree). The magnetic exchange constant J was obtained by Yamaguchi's approach[42] for an isotropic Heisenberg Hamiltonian ($\widehat{H} = -J\widehat{S}_1\widehat{S}_2$) with $J = 2(E_{BS} - E_{HS})/(\langle S^2_{HS}\rangle - \langle S^2_{BS}\rangle)$. The binding energies were calculated at the DFT–D3[32]/B3-LYP[37–39]/def2-TZVPP[36] level of theory and the final binding energies were corrected with the counterpoise method of Boys and Bernardi to minimize the basis set superposition error (BSSE).[43]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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