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Heterobimetallic Complexes

Crystal Structure and Magnetic Properties of an Oxamato-Bridged Heterobimetallic Tetranuclear [Ni^{II}Cu^{II}]₂ Complex of the Rack Type

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Dedicated to Professor Olivier Kahn in recognition of his invaluable contribution to molecular magnetism

Abstract: This work discusses a new heterobimetallic nickel(II)– copper(II) complex of the formula [Ni(tpa)Cu(opba)]₂·6H₂O (**1**) {H₄opba = *N*,*N*'-1,2-phenylenebis(oxamic acid) and tpa = tris(2pyridylmethyl)amine}. The molecular structure of **1** consists of neutral tetranuclear species with a ⁴R rack-type architecture featuring two Ni^{II}Cu^{II} dinuclear units connected through two outof-plane oxo(carboxylate-oxamate) atoms from the opba ligands. The crystal packing of **1** exhibits a supramolecular 1D arrangement of tetranuclear entities connected by hydrogen bonds and π - π stacking interactions. The dc magnetic proper-

Introduction

The first preparation of heterobimetallic Mn^{II}Cu^{II} magnetic chains containing oxamato as a ligand were carried out by Kahn and co-workers having in mind the rational preparation of molecule-based magnets.^[1] Kahn's approach consisted of using an organic ligand that can act as a molecular bridge connecting paramagnetic metal ions of different spin states. This will produce a system with a net spin resulting from the non-compensation of the antiferromagnetically interacting local spins being at the base of the obtention of heterobimetallic ferrimagnetic systems. The aim was to govern the crystal packing of the ferromagnetic chains in such a way to create spontaneous magnetization below a critical temperature.^[2,3]

Since then, many other systems containing functionalized oxamate/oxamidate bridging ligands have been described, with

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ties of **1** were interpreted according to its dimer-of-dimer structure; the spin Hamiltonian being defined as { $H = -J[S_{\text{Ni1}} \cdot S_{\text{Cu1}} + S_{\text{Ni1}} \cdot S_{\text{Cu1}'} - j_{\text{eff}}(S_{\text{Cu1}} \cdot S_{\text{Cu1}})]$ }. The analysis of the magnetic data shows the occurrence of a strong intradimer antiferromagnetic coupling between the Ni^{II} and Cu^{II} ions [$J = -115.2(4) \text{ cm}^{-1}$] and a weak interdimer antiferromagnetic coupling between the Cu^{II} ions [$j_{\text{eff}} = -1.12(7) \text{ cm}^{-1}$]. DFT-type calculations were performed to visualize the exchange pathway through the oxamate bridge and substantiate the value of J.

special attention paid to their multifunctional character.^[4] Some illustrative results are the achievement of magnetic sponges,^[5] molecular magnetic electroswitches,^[6] multielectron transfer systems,^[7] molecular switches for reversible biphasic processes,^[8] Single-Ion Magnets (SIMs),^[9] Chiral Single-Chain Magnets (CSCMs),^[10] chiral homo- and heterobimetallic wheels,^[11] dynamic,^[12] chiral^[13] and luminescent porous 3D magnets,^[14] three-dimensional (3D) proton-conducting chiral biological metal–organic frameworks (bioMOFs),^[15] SIM hosting into magnetic MOFs^[16] and palladium(II) compounds exhibiting cytotoxic activity against leukaemia cells^[17] or catalytic activity.^[18]

These compounds were synthesized by the "complex as ligand" strategy, which is a preparative route that requires the use of the notions of metallosupramolecular chemistry and some tools of crystal engineering.^[19] It allows the rational design of chemical objects of different dimensionality nD (n = 0-3).^[20] The objects display several molecular architectures such as metal grids, ladders, racks, polyhedral metal cages, metallodendrimers, interlocked networks, corrugated planes and so forth.^[21,22] The easy functionalization of the *N*-substituted oxamate ligands together with their good coordinating properties and remarkable ability to mediate magnetic interactions between the paramagnetic centres bridged by them is at the origin of the variety of multifunctional magnetic systems obtained during recent years.^[5–18]

In this work, we describe the synthesis, crystal structure and magnetic characterization, as well as theoretical calculations, of





the new heterobimetallic rack-type tetranuclear complex of the formula $[Ni(tpa)Cu(opba)]_2$ ·6H₂O (1), where tpa is tris(2-pyridylmethyl)amine and H₄opba is *N*,*N'*-1,2-phenylenebis(oxamic acid) (Scheme 1). The $[Cu(opba)]^{2-}$ complex is a well-known building block that presents high stability and versatility when coordinating to other metal ions. Furthermore, $[Cu(opba)]^{2-}$ acts as a bis(chelating) ligand and can efficiently transmit magnetic interactions between metal centres through oxamate bridges, allowing the preparation of interesting magnetic systems.



Scheme 1. Chemical structures of the ligands used in this work.

In order to control the dimensionality of chemical systems, researchers usually work with blocking ligands that can coordinate at the metal ions and preclude chain growth. The tpa ligand leaves two free coordination sites in the *cis* position at the metal centre available for oxamato binding. This will restrict the coordination capacity of building blocks with a metal centre, leading to better control of the dimensionality of the resulting compound.

Results and Discussion

Description of the Structure

The molecular structure of **1** is shown in Figure 1. It consists of two neutral oxamato-bridged dinuclear [Ni(tpa)Cu(opba)] units interconnected by the carboxylate-oxygen atoms from the adjacent [Cu(opba)]^{2–} subunits in a parallel-displaced out-of-plane disposition to give a centrosymmetric tetranuclear [Ni(tpa)-



Figure 1. Perspective view of the centrosymmetric tetranuclear unit of **1** showing the atom numbering of non-carbon atoms. Hydrogen atoms and solvent molecules were omitted for clarity [symmetry code: (i) = 1 - x, -y, 1 - z].

 $Cu(opba)]_2$ entity with an overall ⁴R rack-type architecture (Figure 1). A summary of the crystal data and refinement conditions for **1** are listed in Table 1, and the main bond lengths and angles are given in Table 2.

Table 1. Summary of the crystal data and refinement conditions for 1.

	1	
Formula	C ₅₆ H ₅₆ Cu ₂ Ni ₂ N ₁₂ O ₁₈	
FW	1429.63	
Temperature / K	150(2)	
λ / Å	1.5418	
Crystal system	monoclinic	
Space group	P2 ₁ /n	
a / Å	11.739(2)	
b / Å	12.807(3)	
c / Å 18.866(4)		
β/°	95.43(3)	
Volume / Å ³	2823.5(10)	
Ζ	2	
$\varrho / \text{mg m}^{-3}$	1.682	
μ / mm ⁻¹	2.343	
F(000)	1468	
Crystal size / mm ³	0.16 imes 0.09 imes 0.06	
heta / °	3.5-66.4	
h; k; l	$-13 \leq h \leq 13;$	
	$-15 \leq k \leq 15;$	
	<i>−</i> 22 ≤ <i>l</i> ≤ 22	
Reflections collected	33461	
GOF on F ²	1.047	
$R^{[a]}, wR^{[b]} [l > 2\sigma(l)]$	0.0396, 0.0908	
R ^[a] , wR ^[b] (all data) 0.0603, 0.1031		
Largest difference peak and hole / e Å ⁻³	0.36, -0.37	

[a] $R = \Sigma ||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}, w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where *a* and *b* are adjustable constants and $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths [Å] and angles [°] of 1.^[a]

Cu1-N1	1.905(3)	Ni1-O5	2.054(2)
Cu1–N2	1.928(3)	Ni1-06	2.076(2)
Cu1-02	1.976(3)	Ni1–N3	2.090(3)
Cu1-04	2.031(2)	Ni1-N4	2.083(3)
Cu1–O2 ⁱ	2.478(3)	Ni1–N5	2.052(3)
		Ni1-N6	2.102(3)
N1-Cu1-N2	82.87(11)	O5-Ni1-O6	81.59(8)
N1-Cu1-O2	84.42(10)	N3-Ni1-N4	82.00(11)
N1-Cu1-O4	161.95(10)	N4-Ni1-N5	82.44(10)
02-Cu1-O4	107.76(9)	N5-Ni1-N6	91.00(10)
N2-Cu1-O2	165.23(10)	O6-Ni1-N6	89.96(10)
N2-Cu1-O4	83.03(10)	N4-Ni1-N6	80.85(11)

[a] Symmetry code (i) = 1 - x, -y, 1 - z.

The copper(II) ion is five coordinate in a somewhat distorted CuN_2O_3 square-pyramidal environment, with the value of the trigonality parameter τ being 0.055 ($\tau = 0$ and 1 for square-pyramidal and trigonal-bipyramidal surroundings, respectively).^[23] The basal position around Cu1 is occupied by two amidate-nitrogen (N1 and N2) and two carboxylate-oxygen (O2 and O4) atoms from two oxamate ligands, whereas the apical site is filled by an oxygen atom (O2ⁱ) from a symmetry-related oxamate fragment. The copper atom is shifted by 0.18 Å from the mean basal plane towards the apical O2ⁱ atom. The geometrical constraints caused by the occurrence of three-fused five-membered chelate rings subtended by the opba ligand at the Cu1 account for the important distortion of the ideal basal







Figure 2. Crystal packing view of 1 showing the π - π stacking interactions between the tetranuclear entities.

square at the metal environment: an opening at the less constrained O2–Cu1–O4 angle [107.76(9)°], whereas the bite angles at the 5–5–5 fused chelate ring are smaller than 90° [values in the range of 82.87(11)–84.42(10)°]. The average Cu1–N and Cu1–O bond lengths in the basal plane (1.91 and 2.01 Å, respectively) agree with those previously reported for the [Cu(opba)]^{2–} unit in other structurally characterized compounds where this entity acts as a ligand;^[1k,1],24] the shorter value for the copper– nitrogen interaction arises from the stronger basicity of the amidate-nitrogen atoms compared with that of the carboxylate-oxygen atoms.^[25]

The nickel(II) ion in **1** is six coordinate in a distorted octahedral NiN₄O₂ environment. The equatorial plane at the nickel(II) ion is defined by one amidate-oxygen (O6) atom and one carboxylate-oxygen (O5) atom from the opba ligand plus the amine-nitrogen (N4) atom and one pyridyl-nitrogen (N5) atom from the tetradentate tpa ligand, while the two axial positions are filled by the remaining pyridyl-nitrogen atoms (N3 and N6). The values of the axial bond lengths [2.090(3) and 2.102(3) Å for Ni–N3 and Ni–N6, respectively] are somewhat longer than the equatorial bonds [values in the range of 2.052(3)– 2.083(3) Å]. The nickel atom practically lies in the mean equatorial plane.

The intradimer copper–nickel separation through the oxamato bridge (*d*) is 5.317(1) Å, while the interdimer copper---copper distance (*d'*) through the double oxo(carboxylate-oxamate) bridge is 3.395(1) Å. These values are much shorter than the shortest intermolecular copper---copper [10.517(2) Å for Cu1---Cu1ⁱⁱ; symmetry code: (ii) = 1/2 + x, 1/2 - y, -1/2 + z], nickel---nickel [8.083(2) Å for Ni1---Ni1ⁱⁱ] and copper---nickel [6.300(1) Å for Cu1---Ni1ⁱⁱ] separations.

The 3D structure is ruled by π ··· π interactions involving one pyridyl ring [set of C18–C22 and N5 atoms] of the tpa molecule and the phenylene group [C3–C8 atoms] of the opba ligand belonging to adjacent tetranuclear units (see Figure 2), which contribute to the stabilization of the structure of **1**. These supramolecular interactions occur mostly between an edged carbon atom from one aromatic ring and the whole nearest aromatic ring because the rings are separated from each other by 1.40(9) Å. The distances of the centroid to the mean plane are equal to 3.488(6) (from the opba phenylene centroid to the pyridyl plane) and 3.976(8) Å (from the tpa pyridyl centroid to the phenylene plane). This pattern leads to the formation of a supramolecular double chain of interlinked tetranuclear units. Additional hydrogen bonds involving one of the water molecules (O9 atom) and one free oxygen (O3) atom and one coordinated oxygen (O5) atom from the opba^{2–} ligand that occur along the crystallographic *a* axis also contribute to the stabilization of the structure of **1** (see Figure S3). Details of the hydrogen-bonding pattern are given in Table S1 (see Supporting Information).

Magnetic Properties

The study of the magnetic properties of **1** in the form of a $\chi_{\rm M}T$ versus *T* plot ($\chi_{\rm M}$ is the molar magnetic susceptibility per tetranuclear entity and *T* is the temperature) is shown in Figure 3. At room temperature, $\chi_{\rm M}T$ is equal to 2.70 cm³ mol⁻¹ K, a value which is well below the expected value for two copper(II) ($S_{\rm Cu} = 1/2$) and two nickel(II) ($S_{\rm Ni} = 1$) ions that are magnetically non-interacting ($\chi_{\rm M}T = 3.24$ cm³ mol⁻¹ K with $g_{\rm Cu} = 2.10$ and $g_{\rm Ni} = 2.20$). Upon cooling, $\chi_{\rm M}T$ continuously decreases to reach a plateau at 30 K (with $\chi_{\rm M}T$ about 0.93 cm³ mol⁻¹ K), and it further decreases below 15 K to attain a value of 0.83 cm³ mol⁻¹ K at 2.0 K. This magnetic behaviour is as expected for the dimer-of-dimer structure of **1**.



Figure 3. $\chi_{M}T$ vs. *T* plot for **1** (H_{dc} = 10 kOe for *T* > 25 K and 250 Oe for *T* ≤ 25 K): (\bigcirc) experimental; (–) best-fit curve by Equation (2) (see text).

At high temperature, the strong intradimer antiferromagnetic coupling between nickel(II) and copper(II) metal ions leads





to two low-lying spin states, a ground spin doublet and an excited spin quartet ($J = J_{NiACuA} = J_{NiBCuB}$). The plateau at low temperatures is consistent with a thermal population of the ground doublet state (S = 1/2) of each dinuclear Ni^{II}Cu^{II} unit [with $g_{1/2} = (4g_{Ni} - g_{Cu})/3 = 2.23$ with $g_{Ni} = 2.20$ and $g_{Cu} = 2.10$]. The decrease in $\chi_{M}T$ at very low temperatures is most likely a result of an effective interdimer antiferromagnetic coupling $(j_{eff} < 0)$ between the $S = 1/2 \text{ Ni}^{II} \text{Cu}^{II}$ units, leading to a singlet ground state (S = 0) for the tetranuclear entity. These features are confirmed by variable-temperature X-band EPR spectra of polycrystalline samples of 1 (see Figure S4), which show an isotropic signal centred at 3108 G for T = 50 K (q = 2.18) corresponding to the ground spin doublet of the oxamidato-bridged Cu^{II}Ni^{II} unit. The intensity of this signal significantly decreases upon cooling, and it tends to vanish as expected for a singlet ground spin state resulting from an antiferromagnetic interaction between the spin doublets. Other weak intermolecular antiferromagnetic interactions could be mediated by hydrogen bonds and π --- π -type interactions (see Figure S3 and Figure 2). However, bearing in mind the copper-copper separation through the double oxo(carboxylate-oxamate) bridge, which is about 3.40 Å (a value much less than the shortest intermolecular metal-metal distance of about 6.30 Å), the decrease in the $\chi_{\rm M}T$ values at very low temperatures would be mainly due to this intramolecular copper-copper pathway.

In the light of these considerations, the magnetic data of **1** were analyzed according to an effective isotropic spin Hamiltonian for a dimer-of-dimer model, derived from a perturbational model,^[26] given by Equation (1):

$$H = -J(S_{Ni1} \cdot S_{Cu1} + S_{Ni1^i} \cdot S_{Cu1^i}) - j_{eff}(S_{Cu1} \cdot S_{Cu1^i})$$
(1)

where *J* denotes the exchange coupling parameter within Cu1– Ni1 (dimer 1) and Cu1ⁱ–Ni1ⁱ (dimer 1ⁱ) ($S_{Ni1} = S_{Ni1}i = 1$; $S_{Cu1} = S_{Cu1}i = 1/2$), while j_{eff} represents the exchange coupling parameter within the Cu1–Cu1ⁱ unit. The next-nearest-neighbour interactions between the peripheral nickel(II) ions of the two heterodinuclear units are expected to be negligible, and they were not taken into account. The expression of the magnetic susceptibility derived through this Hamiltonian is given by Equation (2):

$$\chi_M = (N\beta^2/kT) (A/B) \tag{2}$$

$$\begin{split} A &= 2g_1^2 \exp\bigl(j_{eff}/4kT\bigr) + (10g_3^2 + 2g_4^2 + 10g_5^2 + 2g_6^2) \exp(3J/2kT) \\ &+ (28g_7^2 + 10g_8^2 + 2g_9^2) \exp(3J/kT) \end{split} \tag{2a}$$

$$B = 3 \exp(j_{eff}/4kT) + \exp(-j_{eff}/4kT) + 16 \exp(3J/2kT) + 16 \exp(3J/kT)$$
(2b)

where *N*, *k* and β have their usual meanings, and g_n is the average Landé factor associated with the pair state of spin S₁ and S₁i, which in turn is associated with the pair state of spin S_{Ni} and S_{Cu}. Each g_n factor was calculated as a function of g_{Ni} and g_{Cu} (see Table S3). Least-squares best-fit parameters for **1** are J = -115.2(4) cm⁻¹, $g_{Cu} = 2.106(7)$, $g_{Ni} = 2.203(2)$ and $j_{eff} = -1.12(7)$ cm⁻¹ for **1**. The calculated curve (solid line in Figure 3)

matches well with the experimental data in the whole temperature range investigated.

The magnetization isotherm at 2.0 K for 1, shown in Figure 4, fully agrees with this interpretation. The magnetization saturation (M_{sat}) at 7 T is 2.2 N β , a value which is close to the expected value for an antiparallel spin alignment of nickel(II) ($S_{Ni} = 1$) and copper(II) ($S_{Cu} = 1/2$) ions ($M_{sat} = 2.3 \text{ N}\beta$ with $g_{Cu} = 2.1$ and $q_{\rm Ni}$ = 2.2). It can be seen that the calculated curve for the ferromagnetically coupled dimer (Ni^{II}–Cu^{II})–(Cu^{II}–Ni^{II}) entity ($j_{eff} > 0$, dashed line) deviates from the magnetization data by using the above values of the best-fit parameters according to the Brillouin function.^[27] In contrast, the calculated values considering two magnetically isolated dinuclear Ni^{II}–Cu^{II} units ($j_{eff} = 0$, solid line) using the best-fit parameters arising from the $\chi_{M}T$ versus T plot according to the Brillouin function reproduces the magnetization data very well, thus being more consistent with a system with very weak antiferromagnetic interactions between the copper(II) ions within the tetranuclear entity.



Figure 4. *M* vs. *H* plot for **1** at 2.0 K: (\bigcirc) experimental; (---) calculated curve for the ferromagnetically coupled dimer (Ni^{II}–Cu^{II})–(Cu^{II}–Ni^{II}) entity ($j_{eff} > 0$); (–) calculated curve for the two magnetically isolated dinuclear Ni^{II}–Cu^{II} units ($j_{eff} = 0$).

Let us finish this part with a brief discussion about the values of j_{eff} and J in **1**. The first discussion concerns the magnetic interaction between Cu1 and Cu1ⁱ through the out-of-plane exchange pathway provided by the double oxo(carboxylateoxamate) bridge connecting one equatorial position at one copper(II) ion with the apical site at the adjacent copper(II) ion. The unpaired electron at each copper(II) ion is defined by a $d(x^2 - y^2)$ magnetic orbital which is delocalized in the equatorial plane (the x and y axes approximately correspond to the N_{amidate}-Cu-O_{carboxvlate} vectors). So, the spin density at the copper(II) ions is mostly located in their basal planes which are parallel to each other and connected in an equatorial-axial way. Under these conditions, a poor overlap between the two magnetic orbitals is predicted, and a weak magnetic coupling (either ferro- or antiferromagnetic) is expected. Its nature and magnitude depend on subtle structural factors such as the angle at the bridgehead atom (θ) and the axial Cu–X bond length (R_{ax}) . Previous magnetostructural studies of double oxo(carboxylate-oxamate)-bridged dicopper(II) complexes





showed that smaller values of θ led to weak antiferromagnetic interactions.^[28] In the present case, $\theta = 98.69(8)^\circ$; this value is in the region of θ values for which antiferromagnetic interactions in the range –2.36 [$\theta = 102.8(1)^\circ$] to –0.80 cm⁻¹ [$\theta = 95.4(1)^\circ$] were observed.^[29]

As far as the considerably strong antiferromagnetic coupling between the Cu^{II} and Ni^{II} ions through the oxamato bridge in 1 is concerned $[J = -115.2(4) \text{ cm}^{-1}]$, very strong antiferromagnetic interactions were observed for oxamato-bridged dicopper(II) complexes (-J values greater than 400 cm⁻¹), which were also substantiated by theoretical calculations.^[30,31] The value of J in 1 compares well to that found for the heterodinuclear compound $[Ni(cth)Cu(opba)] \cdot CH_3OH$ [cth = rac-5,7,7,12,14,14hexamethyl-1,4,8,11-tetraazacyclotetradecane] (2) (] = -108.0 cm⁻¹);^[24b] the structural parameters that determine the magnetic coupling in both cases are very close in 1 and 2, as shown in Table S4. The slightly stronger antiferromagnetic interaction in 1 than that in 2 is a result of the accentuated coplanarity between magnetic orbitals observed to 1 in comparison to that of 2; this is directly related to the dihedral angles between the equatorial NiN₂O₂ and CuN₂O₂ mean planes (see Table S4).

DFT-Type Calculations

The magnetic coupling constants for complex **1** were computed at the DFT level of theory,^[32] employing the broken symmetry (BS) approach that generates a wavefunction breaking the spatial and spin symmetry and introduces a multideterminantal character within a single determinant framework.^[32–36] The exchange coupling constant for **1** was obtained by calculating the energy difference between the high spin state (E_{hs}) and the broken symmetry state (E_{bs}), according to Equation (3), introduced by Yamaguchi and co-workers:^[37]

$$J = -\frac{E_{hs} - E_{bs}}{\langle S_{hs}^2 \rangle - \langle S_{bs}^2 \rangle}$$
(3)

where $\langle S_{hs}^2 \rangle$ and $\langle S_{bs}^2 \rangle$ are average-spin square values for the corresponding high spin (hs) and broken symmetry (bs) spin states. Single-point energy calculations at the TPSSh/Def2-TZVP level of theory were carried out on the X-ray crystal structure of the tetranuclear complex. The broken symmetry state is generated by flipping the spins of the Cu^{II} centres, after the SCF convergence of the high spin state, and reconverging the new wavefunction.

Table S5 shows the spin density (ϱ) values for the complexes in their hs and bs states. The positive and negative signs represent α and β spin densities, respectively. As can be seen, the spin densities at the Ni^{II} centres are 1.608 and 1.595 in the hs and bs spin states, respectively, and these values are consistent with the formal electron-counting value of 2.0. The α spin densities computed at the Cu^{II} centres are 0.584 and 0.573 in the hs spin state, values also consistent with a single unpaired electron, and in the bs spin state, the spin densities at the Cu^{II} centres are inverted, showing β spin densities of -0.575 and -0.573. It is worth noting that the spin densities are polarized over the oxamato bridge. The inversion of spin densities on the atoms of the ligands indicates the participation of the oxamate bridge in the magnetic-exchange mechanism within each dinuclear unit. This is consistent with a σ/π pathway involving the in-plane oxamate p orbitals and the metal d orbitals, as can be seen in the plot of the corresponding magnetic orbitals^[34] shown in Figure 5. The computed magnetic constant is -67.3 cm⁻¹ at the TPSSh/Def2-TZVP level of theory. On removal of the water molecules from the crystal structure, the computed antiferromagnetic coupling constant increases to -75.2 cm⁻¹, which is in line with the experimental value of -115 cm⁻¹, despite the absolute deviation of 36 %, which is higher than usually found (about 20 %) for bimetallic systems.^[38] This deviation can be attributed to limitations of the broken symmetry approach for this tetranuclear system, and further studies with multiconfigurational methods are needed to test this assumption, which is beyond the scope of the present work.



Figure 5. Views of the calculated magnetic orbitals containing the unpaired electrons of **1** at the TPSSh/Def2-TZVP level of theory. Orbital number and overlap integral (S) are quoted.

Conclusions

In summary, we describe here the synthesis, structural and magnetic characterization and DFT calculations of a tetranuclear copper(II)–nickel(II) system containing *ortho*-phenylenebis(oxamate) as bridging ligands and aromatic aminotris(pyridine) as terminal ligands. The fairly strong antiferromagnetic coupling between the copper(II) and nickel(II) ions through the oxamate bridge [$J = -115.2(4) \text{ cm}^{-1}$] illustrates the remarkable ability of the oxamate group to mediate electronic effects between different paramagnetic metal ions separated from each other by more than 5.3 Å. The weak antiferromagnetic interaction between the copper(II) ions through the double oxo-(carboxylate-oxamate) bridge [$j_{eff} = -1.12(7) \text{ cm}^{-1}$] is as expected for the out-of-plane exchange pathway involved, and it is within the range of previous reports concerning the parent dicopper(II) complexes.



Experimental Section

Materials: All chemicals used in this work were purchased from commercial sources and used as received. The tpa ligand and the building block ($Bu_4N)_2[Cu(opba)]$ (NBu_4^+ = tetra-*n*-butylammonium cation) were synthesized according to literature procedures.^[39,40]

Synthesis of [Ni(tpa)Cu(opba)]₂·6H₂O (1): An acetonitrile solution (7.0 cm³) of tpa (200.0 mg, 0.69 mmol) was added dropwise to an acetonitrile solution (7.0 cm³) containing Ni(ClO₄)₂•6H₂O (180.8 mg, 0.49 mmol) under continuous magnetic stirring. A pale-blue solid separated when the resulting green solution was poured into an acetonitrile solution (14.0 cm³) of (Bu₄N)₂[Cu(opba)] (270.8 mg, 0.37 mmol) whilst stirring at room temperature. After 30 min of continuous stirring, the mixture was centrifuged, and the solid product was dissolved in a mixture of dmso (10.0 cm³) and acetonitrile (20.0 cm³). This solution was allowed to evaporate in the dark at room temperature. X-ray-suitable blue crystals were grown after two weeks. Yield: 50 %. C₅₆H₅₆Cu₂Ni₂N₁₂O₁₈ (**1**, 1429.67 g mol⁻¹): calcd. C 47.16, H 3.96, N 11.69, Ni 8.32, Cu 8.92; found C 46.92, H 4.22, N 11.72, Ni 8.19, Cu 8.87. IR (KBr): v = 3595 [(vO-H)], 1670, 1624, 1604, 1574 [(vC=O)], 1589 [v(C=C) and v(C=N)], 1438 [(vC=C) and v(C=N)], 1276 [(vC=O)], 770 [(δ C-H)], 735 [(δ C-H)] cm⁻¹.

Physical Techniques: Elemental analysis (C, H, N) was carried out with a Perkin-Elmer PE2400 analyzer. Atomic absorption for Ni and Cu were performed with a Hitachi Z8200 polarized atomic absorption spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer FTIR Spectrum GX spectrometer in the range of 4000-4000 cm⁻¹ (resolution of 4 cm⁻¹) using KBr pellets. Thermogravimetric analysis (TG, DTG and DTA) data were collected with a Shimadzu-DTG60H Thermobalance by using the samples (approximately 2.0 mg) packed into an alumina crucible. Samples were heated at 10 °C min⁻¹ from room temp. to 901.5 °C in a dynamic air flow (flow rate of 200 cm³ min⁻¹). X-ray powder diffraction pattern was obtained by using a Rigaku/Geigerflex diffractometer at room temp. Data were collected in the Brag/Brentano mode (4° s⁻¹) by using monochromatic Cu- K_{α} radiation. The dc magnetic measurements were performed with a Quantum Design MPMS-XL7 SQUID Magnetometer. The diamagnetic correction for the constituent atoms of 1 was estimated from Pascal's constants as $715 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.^[41] Experimental susceptibilities were also corrected for the temperature-independent paramagnetism $[60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ per mol of}$ copper(II) ions] and the sample holder. X-band ($\nu = 9.3$ GHz) EPR spectra of polycrystalline samples of 1 were recorded in the 300-4 K temperature range with a Bruker-ELEXSYS 500 spectrometer using a helium continuous-flow cryostat.

X-ray Data Collection and Structure Refinement

X-ray diffraction data collection was performed with an Oxford GEMINI-Ultra Diffractometer by using Cu- K_{α} radiation ($\lambda = 1.5418$ Å). Measurements were carried out at 150 K, as shown in Table 1. Data integration and scaling of reflections were performed by using the CrysAlis suite.^[42] Final unit-cell parameters were based on the fitting of all reflections positions. Analytical absorption corrections were executed with the CrysAlis suite,^[42] and the space-group identification was achieved with XPREP.^[43] The crystal structure of the compound was solved by direct methods using the SUPERFLIP program.^[44] Refinement was performed using SHELXL.^[45] All nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in different in difference maps and included as fixed contributions according to the riding model.^[46] $U_{iso}(H) = 1.5 U_{eq}(O)$ for the water molecules, and C-H = 0.97 Å and $U_{iso}(H) = 1.2 U_{eq}(C)$ for the methylene groups. Selected bond lengths and angles for 1 are given in Table 2, and a more



complete list of bond lengths and angles is contained in Table S2 in the Supporting Information.

CCDC 1558468 (for 1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

DFT-Type Calculations: The calculations were carried out with the hybrid *meta*-GGA functional TPSSh^[47] and using the Ahlrichs full electron Def2-TZVP basis set^[48] for all atoms. Scalar relativistic effects were treated using the Zeroth Order Regular Approximation (ZORA) formalism.^[49–51] This combination of exchange correlation functional and basis set has been shown to produce coupling constants of bimetallic complexes in very good agreement with experimental measurements.^[38] All quantum mechanical calculations were performed with the ORCA program.^[52]

Supporting Information (see footnote on the first page of this article): TG and DTA curves, X-band EPR spectra, experimental and calculated X-ray diffraction patterns and crystallographic files of **1**.

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- [1] a) Y. Pei, M. Verdaguer, O. Kahn, J. Sletten, J. P. Renard, Inorg. Chem. 1987, 26, 138–143; b) O. Kahn, Y. Pei, M. Verdaguer, J. P. Renard, J. Sletten, J. Am. Chem. Soc. 1988, 110, 782-789; c) Y. Pei, O. Kahn, J. Sletten, J. P. Renard, R. Georges, J. C. Gianduzzo, J. Curely, Q. Xu, Inorg. Chem. 1988, 27, 47-53; d) Y. Pei, K. Nakatani, O. Kahn, J. Sletten, J. P. Renard, Inorg. Chem. 1989, 28, 3170-3175; e) K. Nakatani, J. Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J. P. Renard, Y. Pei, J. Sletten, M. Verdaguer, J. Am. Chem. Soc. 1989, 111, 5739-5748; f) K. Nakatani, J. Sletten, S. Halut-Desporte, S. Jeannin, Y. Jeannin, O. Kahn, Inorg. Chem. 1991, 30, 164-171; g) K. Nakatani, P. Bergerat, E. Codjovi, C. Mathonière, Y. Pei, O. Kahn, Inorg. Chem. 1991, 30, 3978-3980; h) Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Mathonière, J. Sletten, J. Am. Chem. Soc. 1991, 113, 6558-6564; i) O. Kahn, H. Stumpf, Y. Pei, J. Sletten, Mol. Cryst. Lig. Cryst. Sci. Technol. Sect. A 1993, 233, 231-246; j) F. Lloret, M. Julve, R. Ruiz, Y. Journaux, K. Nakatani, O. Kahn, J. Sletten, Inorg. Chem. 1993, 32, 27-31; k) H. O. Stumpf, Y. Pei, L. Ouahab, F. Le Berre, E. Codjovi, O. Kahn, Inorg. Chem. 1993, 32, 5687–5691; I) H. O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat, O. Kahn, J. Am. Chem. Soc. 1994, 116, 3866-3874; m) V. Baron, B. Guillon, J. Sletten, C. Mathonière, E. Codjovi, O. Kahn, Inorg. Chim. Acta 1995, 235, 69-76.
- [2] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.
- [3] V. Laget, C. Hornick, P. Rabu, M. Drillon, Z. Ziessel, Coord. Chem. Rev. 1998, 178–180, 1533–1553.
- [4] a) M. G. F. Vaz, M. Knobel, N. L. Speziali, A. M. Moreira, A. F. C. Alcantara, H. O. Stumpf, J. Braz. Chem. Soc. 2002, 13, 183–189; b) E. Pardo, R. Ruiz-

Eur. J. Inorg. Chem. 2018, 477–484 www.eurjic.org



García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y. Journaux, F. Lloret, M. Julve, *Dalton Trans.* **2008**, *21*, 2780–2805; c) M. C. Dul, E. Pardo, R. Lescouëzec, Y. Journaux, J. Ferrando-Soria, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, D. Cangussu, C. L. M. Pereira, H. O. Stumpf, J. Pasán, C. Ruiz-Pérez, *Coord. Chem. Rev.* **2010**, *254*, 2281–2296; d) M. Castellano, R. Ruiz-García, J. Cano, J. Ferrando-Soria, E. Pardo, F. R. Fortea-Pérez, S.-E. Stiriba, M. Julve, F. Lloret, *Acc. Chem. Res.* **2015**, *48*, 510–520; e) M. Castellano, R. Ruiz-García, J. Cano, J. Ferrando-Soria, E. Pardo, F. R. Fortea-Pérez, S.-E. Stiriba, M. Julve, F. Lloret, *Acc. Chem. Res.* **2015**, *48*, 510–520; e) M. Castellano, R. Ruiz-García, J. Cano, J. Ferrando-Soria, E. Pardo, J. Pardo, J. Pasán, C. Ruiz-Pérez, G. De Munno, D. Armentano, Y. Journaux, F. Lloret, M. Julve, *Coord. Chem. Rev.* **2015**, *303*, 110–138.

- [5] a) O. Kahn, J. Larionova, J. V. Yakhmi, Chem. Eur. J. **1999**, *5*, 3443–3449; b) J. Ferrando-Soria, R. Ruiz-García, J. Cano, S.-E. Stiriba, J. Vallejo, I. Castro, M. Julve, F. Lloret, P. Amorós, J. Pasán, C. Ruiz-Pérez, Y. Journaux, E. Pardo, Chem. Eur. J. **2012**, *18*, 1608–1617.
- [6] J. Ferrando-Soria, M. Castellano, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, C. Ruiz-Pérez, J. Pasán, D. Armentano, Y. Journaux, E. Pardo, *Chem. Eur. J.* 2013, 19, 12124–12137.
- M. Castellano, W. P. Barros, A. Acosta, M. Julve, F. Lloret, Y. Li, Y. Journaux, G. De Munno, D. Armentano, R. Ruiz-García, J. Cano, *Chem. Eur. J.* 2014, 20, 13965–13975.
- [8] W. D. do Pim, W. X. C. Oliveira, M. A. Ribeiro, E. N. de Faria, I. F. Teixeira, H. O. Stumpf, R. M. Lago, C. L. M. Pereira, C. B. Pinheiro, J. C. D. Figueiredo-Júnior, W. C. Nunes, P. P. de Souza, E. F. Pedroso, M. Castellano, J. Cano, M. Julve, *Chem. Commun.* **2013**, *49*, 10778–10780.
- [9] J. Vallejo, A. Pascual-Alvarez, J. Cano, I. Castro, M. Julve, F. Lloret, J. Krzystek, G. De Munno, D. Armentano, W. Wernsdorfer, R. Ruiz-García, E. Pardo, *Angew. Chem. Int. Ed.* **2013**, *52*, 14075–14079; *Angew. Chem.* **2013**, *125*, 14325.
- [10] J. Ferrando-Soria, D. Cangussu, M. Eslava, Y. Journaux, R. Lescouëzec, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, E. Lhotel, C. Paulsen, E. Pardo, *Chem. Eur. J.* 2011, *17*, 12482–12494.
- [11] a) T. Grancha, J. Ferrando-Soria, J. Cano, F. Lloret, M. Julve, G. De Munno, D. Armentano, E. Pardo, *Chem. Commun.* **2013**, *49*, 5942–5944; b) W. D. do Pim, E. N. de Faria, W. X. C. Oliveira, C. B. Pinheiro, W. C. Nunes, J. Cano, F. Lloret, M. Julve, H. O. Stumpf, C. L. M. Pereira, *Dalton Trans.* **2015**, *44*, 10939–10942.
- [12] J. Ferrando-Soria, P. Serra-Crespo, M. de Lange, J. Gascon, F. Kapteijn, M. Julve, J. Cano, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux, E. Pardo, J. Am. Chem. Soc. 2012, 134, 15301–15304.
- [13] T. Grancha, M. Mon, F. Lloret, J. Ferrando-Soria, Y. Journaux, J. Pasán, E. Pardo, *Inorg. Chem.* **2015**, *54*, 8890–8892.
- [14] J. Ferrando-Soria, H. Khajavi, P. Serra-Crespo, J. Gascon, F. Kapteijn, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux, E. Pardo, *Adv. Mater.* 2012, *24*, 5625–5629.
- [15] T. Grancha, J. Ferrando-Soria, J. Cano, P. Amorós, B. Seoane, J. Gascon, M. Bazaga-García, E. R. Losilla, A. Cabeza, D. Armentano, E. Pardo, *Chem. Mater.* 2016, 28, 4608–4615.
- [16] M. Mon, A. Pascual-Alvarez, T. Grancha, J. Cano, J. Ferrando-Soria, F. Lloret, J. Gascon, J. Pasán, D. Armentano, E. Pardo, *Chem. Eur. J.* **2016**, *22*, 539–545.
- [17] W. X. C. Oliveira, M. M. da Costa, A. P. S. Fontes, C. B. Pinheiro, F. C. S. de Paula, E. H. L. Jaimes, E. F. Pedroso, P. P. de Souza, E. C. Pereira-Maia, C. L. M. Pereira, *Polyhedron* **2014**, *76*, 16–21.
- [18] a) F. R. Fortea-Pérez, I. Schlegel, M. Julve, D. Armentano, G. De Munno, S.-E. Stiriba, *J. Organomet. Chem.* **2013**, *743*, 102–108; b) F. R. Fortea-Pérez, D. Armentano, M. Julve, G. De Munno, S.-E. Stiriba, *J. Coord. Chem.* **2014**, *67*, 4003–4015; c) F. R. Fortea-Pérez, B. L. Rothenpieler, N. Marino, D. Armentano, G. De Munno, M. Julve, S.-E. Stiriba, *Inorg. Chem. Front.* **2015**, *2*, 1029–1039.
- [19] a) D. Braga, Chem. Commun. 2003, 2751–2754; b) L. Carlucci, G. Ciani,
 D. M. Proserpio, Coord. Chem. Rev. 2003, 246, 247–289; c) S. Dhers, H. L. C.
 Feltham, S. Brooker, Coord. Chem. Rev. 2015, 296, 24–44.
- [20] a) O. Kahn, Acc. Chem. Res. 2000, 33, 647–657; b) M. Verdaguer, Polyhedron 2001, 20, 1115–1128; c) M. Kurmoo, Chem. Soc. Rev. 2009, 38, 1353–1379.
- [21] a) E. Pardo, D. Cangussu, R. Lescouëzec, Y. Journaux, J. Pasán, F. S. Delgado, C. Ruiz-Pérez, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, *Inorg. Chem.* **2009**, 48, 4661–4673; b) K. Rühlig, R. Mothes, A. Aliabadi, V. Kataev, B. Büchner, R. Buschbeck, T. Rüffer, H. Lang, *Dalton Trans.* **2016**, 45, 7960–



7979; c) M. G. F. Vaz, L. M. M. Pinheiro, H. O. Stumpf, A. F. C. Alcântara, S. Golhen, L. Ouahab, O. Cador, C. Mathonière, O. Kahn, *Chem. Eur. J.* **1999**, *5*, 1486–1495; d) C. L. M. Pereira, A. C. Doriguetto, C. Konzen, L. C. Meira-Belo, U. A. Leitão, N. G. Fernandes, Y. P. Mascarenhas, J. Ellena, A. L. Brandl, M. Knobel, H. O. Stumpf, *Eur. J. Inorg. Chem.* **2005**, 5018–5025; e) see ref.^[11b]; f) C. L. M. Pereira, E. F. Pedroso, H. O. Stumpf, M. A. Novak, L. Ricard, R. Ruiz-García, E. Rivière, Y. Journaux, *Angew. Chem. Int. Ed.* **2004**, *43*, 956–958; *Angew. Chem.* **2004**, *116*, 974; g) W. P. Barros, B. C. da Silva, N. V. Reis, C. L. M. Pereira, A. C. Doriguetto, J. Cano, K. R. Pirota, E. F. Pedroso, M. Julve, H. O. Stumpf, *Dalton Trans.* **2014**, *43*, 14586–14595.

- [22] T. Ruffer, B. Brauer, A. K. Powell, I. Hewitt, G. Salvan, Inorg. Chim. Acta 2007, 360, 3475–3483.
- [23] A. W. Addison, T. N. Rao, J. Reedjik, J. van Rijn, G. C. Verschoor, J. Chem. Soc., Dalton Trans. 1984, 1349–1356.
- [24] a) E.-Q. Gao, Q. H. Zhao, J.-K. Tang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, J. Chem. Soc., Dalton Trans. 2001, 1537–1540; b) E.-Q. Gao, J.-K. Tang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, G.-L. Wang, Inorg. Chem. 2001, 40, 3134–3140; c) J. Tercero, C. Diaz, M. Salah El Fallah, J. Ribas, Inorg. Chem. 2001, 40, 3077–3083; d) M. V. Marinho, T. R. G. Simoes, M. A. Ribeiro, C. L. M. Pereira, F. C. Machado, C. B. Pinheiro, H. O. Stumpf, J. Cano, F. Lloret, M. Julve, Inorg. Chem. 2013, 52, 8812–8819.
- [25] a) S. S. Turner, C. Michaut, O. Kahn, L. Ouahab, A. Lecas, E. Amouyal, New J. Chem. **1995**, *19*, 773–775; b) B. Cervera, J. L. Sanz, M. J. Ibáñez, G. Vila, F. Lloret, M. Julve, R. Ruiz, X. Ottenwaelder, A. Aukauloo, S. Poussereau, Y. Journaux, M. C. Muñoz, J. Chem. Soc., Dalton Trans. **1998**, 781–790.
- [26] Y. Journaux, J. Sletten, O. Kahn, Inorg. Chem. 1986, 25, 439-447.
- [27] see p. 11 in ref.^[2].
- [28] W. X. C. Oliveira, C. B. Pinheiro, M. M. da Costa, A. P. S. Fontes, W. C. Nunes, F. Lloret, M. Julve, C. L. M. Pereira, *Cryst. Growth Des.* **2016**, *16*, 4094–4107.
- [29] a) T. R. G. Simoes, R. V. Mambrini, D. O. Reiss, M. V. Marinho, M. A. Ribeiro, C. B. Pinheiro, J. Ferrando-Soria, M. Déniz, C. Ruiz-Pérez, D. Cangussu, H. O. Stumpf, F. Lloret, M. Julve, *Dalton Trans.* **2013**, *42*, 5778–5795; b) I. Unamuno, J. M. Gutiérrez-Zorrilla, A. Luque, P. Román, L. Lezama, R. Calvo, T. Rojo, *Inorg. Chem.* **1998**, *37*, 6452–6460.
- [30] a) A. Bencini, D. Benelli, D. Gatteschi, C. Zanchini, A. C. Fabretti, G. C. Franchini, *Inorg. Chim. Acta* **1984**, *86*, 169–172; b) M. Verdaguer, O. Kahn, M. Julve, A. Gleizes, *Nouv. J. Chim.* **1985**, *9*, 325–334; c) J. Ribas, A. García, R. Costa, M. Monfort, S. Alvarez, C. Zanchini, X. Solans, M. V. Domenech, *Inorg. Chem.* **1991**, *30*, 841–845.
- [31] J. Cano, E. Ruiz, P. Alemany, F. Lloret, S. Alvarez, J. Chem. Soc., Dalton Trans. 1999, 1669–1676.
- [32] R. G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.
- [33] J. Gräfenstein, E. Kraka, M. Filatov, D. Cremer, Int. J. Mol. Sci. 2002, 3, 360– 394.
- [34] F. Neese, J. Phys. Chem. Solids 2004, 65, 781-785.
- [35] L. J. Noodleman, Chem. Phys. 1981, 74, 5737–5743.
- [36] L. Noodleman, E. J. Baerends, J. Am. Chem. Soc. 1984, 106, 2316–2327.
- [37] T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka, K. Yamaguchi, Chem. Phys. Lett. 2000, 319, 223–230.
- [38] D. A. C. Ferreira, W. B. De Almeida, A. Neves, W. R. Rocha, Comput. Theor. Chem. 2012, 979, 89–95.
- [39] a) J. H. Xia, K. Matyjaszewski, *Macromolecules* 1999, *32*, 2434–2437; b)
 G. J. P. Britovsek, J. England, A. J. P. White, *Inorg. Chem.* 2005, *44*, 8125–8134.
- [40] H. O. Stumpf, Y. Pei, O. Kahn, J. Sletten, J. P. Renard, J. Am. Chem. Soc. 1993, 115, 6738–6745.
- [41] A. Earnshaw, Introduction to Magnetochemistry, Academic Press, London, 1968.
- [42] CrysAlisPro Rigaku Oxford Diffraction, CrysAlisPro Software, Rigaku Corporation, Oxford, UK, 2015.
- [43] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112-122.
- [44] L. Palatinusz, G. J. Chapuis, Appl. Crystallogr. 2007, 40, 786-790.
- [45] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [46] C. K. Johnson in *Crystallographic Computing* (Ed.: F. R. Ahmed), Munksgaard, Copenhagen, **1970**, pp. 207–219.





- [47] V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, J. Chem. Phys. 2003, 119, 12129–12137.
- [48] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
- [49] E. van Lenthe, E. J. Baerends, J. G. Snijders, J. Chem. Phys. 1993, 99, 4597– 4610.
- [50] E. van Lenthe, E. J. Baerends, J. G. Snijders, J. Chem. Phys. 1994, 101, 9783–9792.
- [51] E. van Lenthe, E. J. Baerends, J. G. Snijders, Int. J. Quantum Chem. 1996, 57, 281–293.
- [52] The ORCA Program System. F. Neese, Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 73–78.

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