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Controlled Copper-Mediated Chlorination of Phenol Rings under Mild Conditions

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The very unusual case of copper-mediated chlorination of phenol rings under mild conditions at room temperature is reported. Reaction of the ligand 1,7-bis(2-hydroxyphenyl)-2,6-diaza-4-hydroxylheptane (H_3L1) with $CuCl_2$ in acetonitrile leads to either the formation of a tetranuclear copper(II) complex $[Cu_4(HL3)_2(\mu\text{-}Cl)_2Cl_2](CH_3CN)$ (**1**) or a linear trinuclear complex $[Cu_3(HL1)_2Cl_2(CH_3CN)_2](CH_3CN)_2$ (**2**), depending on the reaction conditions. Both compounds have been fully characterized, including the determination of their 3D structures by X-ray diffraction. The unprecedented tetranuclear compound **1** is constituted of a dichlorido-bridged dimer of di-μ-phenoxido-dinuclear species, whereas the trinuclear complex **2** presents a linear array of copper(II) ions, held together through di-μ-phenoxido bridges of the central and external ions. The magnetic susceptibility of the two compounds was investigated, revealing either very strong ($J < -500$ cm^{-1}) or strong (J value around $-370(1)$ cm^{-1}) antiferromagnetic dominant interactions among the Cu^{II} ions for **1** and **2**, respectively. The tetranuclear complex **1** is obtained, under dry conditions, through the in situ formation of ligand HL3 (H_3L3 = 1,7-bis(2-hydroxy-5-chlorophenyl)-2,6-diaza-4-hydroxylheptane) by oxidative chlorination of $(HL1)^{2-}$. In the presence of traces of water, **1** is partially hydroxylated at the ortho position of one of the phenyl rings. The use of trimethylorthoformate as the dehydrating agent prevents the formation of hydroxylated ligands. Several partly chlorinated/hydroxylated products (identified as H_3L2) have also been obtained through slight variations of the synthetic procedures (presence or absence of water and/or triethylamine in the reaction mixtures). These partially chlorinated and/or hydroxylated coordination species are mutually isomorphous to either **1** or **2**. Several "modified" ligands have been isolated and characterized by ^{1}H NMR and MS, after reaction with sodium sulfide of the complexes formed.

Introduction

Polynuclear transition complexes containing nitrogen and phenolic oxygen donor atoms are of considerable interest in inorganic and biomimetic chemistry due to their potential application in catalysis, their biological relevance, and potentially interesting magnetic properties.[1−10] For example, the extensively investigated "metallosalen-type" coordination compounds have long been employed as catalysts for the selective epoxidation of olefins and the oxidation of hydro-

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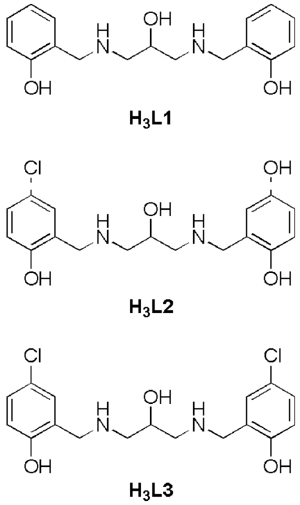

Figure 1. Schematic representations of the ligands **H_3L1**, **H_3L2**, and **H_3L3**.

carbons[11,12] and in recent years for DNA cleavage.[13,14] Nowadays, selective and mild processes to produce functionalized derivatives through the activation of C−H bonds have become of great interest and significance for chemists.[15−19] Halogenation reactions are valuable tools for such purpose with saturated hydrocarbons, but mild conditions for such functionalization reactions have not yet been reported.

In the course of our studies on biomimetic oxidations using salen-type ligands, a variety of copper(II) complexes of the potentially N_2O_3 donor 1,7-bis(2-hydroxyphenyl)-2,6-diaza-4-hydroxylheptane (Figure 1, **H_3L1**) have recently been investigated.[20] Generally, a linear trinuclear copper(II) compound is obtained with two doubly deprotonated ligands **HL1** present in the crystal structures.[20]

In the present study, reactions of **H_3L1** with $CuCl_2$ in MeCN under various synthetic conditions lead to a series of mutually isomorphous tetranuclear and trinuclear compounds. In addition to the original ligand **H_3L1**, two different kinds of “new” ligands, namely, **H_3L2** and **H_3L3** (Figure 1), are observed, which are generated in situ by (partial) hydroxylation and (partial/total) chlorination at the ortho and para positions of the phenol rings of the initial **H_3L1** unit. Such chlorination and hydroxylation of the phenol rings is most surprising and rare, considering that almost all halogenation reactions developed so far are performed under photochemical conditions or involve the combination of stoichiometric amounts of oxidative halogenation reagents like H_2O_2, hypervalent iodine, and trimethylsilyl, under various thermal conditions.[15,21−24] To the best of our knowledge, only one example of a relatively mild homogeneous chlorination of a pyrazole-based ligand coordinated to copper(II) has been reported so far.[25] The catalytic chlorination of phenols in heterogenized systems has been reported in a few cases.[26−28]

In the present report, the unusual and controlled homogeneous chlorination of the ligand **H_3L1** mediated by copper(II) chloride is described.

Results and Discussion

1. Synthesis and Chlorination/Hydroxylation Experiments. The reaction of 1 equiv of ligand **H_3L1** with 2 equiv of copper(II) chloride in commercial, undried acetonitrile leads to a dark red solution. A green precipitate rapidly develops, which is eliminated by filtration, and the solution is left unperturbed for the slow evaporation of the solvent. A mixture of two types of dark crystals is obtained, corresponding to a tetranuclear copper(II) complex containing partially hydroxylated and chlorinated ligands and to a trinuclear copper(II) complex exhibiting altered ligands, solely resulting from partial hydroxylation (see the Supporting Information). Synthetic efforts directed toward the selective preparation of each compound have successfully led to the pure tetranuclear tetrachlorinated product formulated as $[Cu_4(\mathbf{HL3})_2(\mu\text{-}Cl)_2Cl_2](CH_3CN)$ (**1**) and to the pure trinuclear complex $[Cu_3(\mathbf{HL1})_2Cl_2(CH_3CN)_2](CH_3CN)_2$ (**2**). Thus, the reaction of 2 equiv of copper(II) chloride with 1 equiv of **H_3L1** in acetonitrile in the presence of trimethylorthoformate, to remove traces of water, exclusively produces complex **1**, where the initial coordinated **HL1** has been dichlorinated to **HL3** (Figure 2). If the reaction is performed under anhydrous conditions and with the addition of triethylamine (1 equiv), the pure trinuclear complex **2** is obtained (Figure 3), whose coordinated **HL1** ligands have not been chemically modified. Any other experimental procedures yield mixtures of coordination compounds showing partial hydroxylated/chlorinated ligands (see the Supporting Information PDF and CIF files for details).

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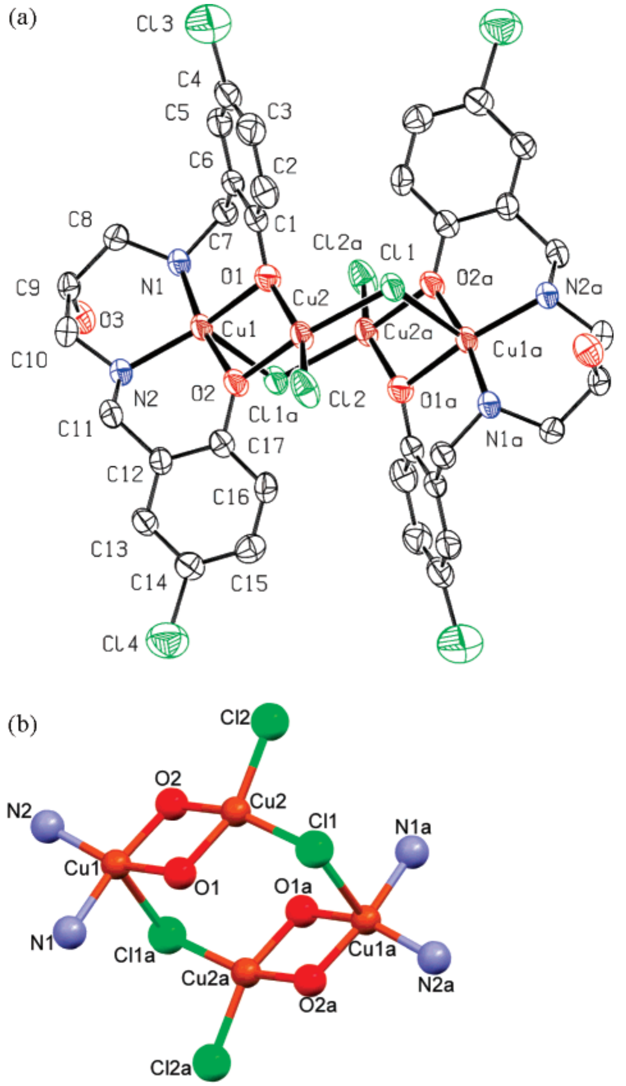

Figure 2. (a) Displacement ellipsoid plot (50% probability level) of the tetranuclear compound **1** showing the crystallographic numbering scheme; hydrogen atoms and solvent molecule have been omitted for clarity. (b) Arrangement of the Cu atoms in the phenoxido- and chlorido-bridged tetranuclear core.

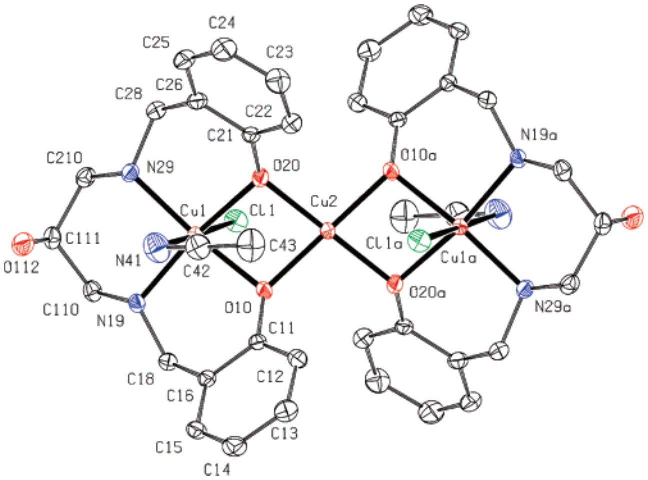

Figure 3. Displacement ellipsoid plot (50% probability level) of the trinuclear compound **2** showing the crystallographic numbering scheme; hydrogen atoms and the uncoordinated acetonitrile molecules have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**[a]

Cu1−O1	1.992(4)	Cu1−O2	1.943(4)
Cu1−N1	2.001(5)	Cu1−N2	2.020(4)
Cu1−Cl1a	2.715(2)	Cu2−Cl1	2.262(1)
Cu2−Cl2	2.209(2)	Cu2−O1	1.972(4)
Cu2−O2	1.961(4)	Cu1−Cu2	3.086(1)
O1−Cu1−N1	94.3(2)	O2−Cu1−O1	76.6(2)
N1−Cu1−N2	94.9(2)	O2−Cu1−N2	94.7(2)
O1−Cu1−N2	157.5(2)	O2−Cu1−N1	170.5(2)
Cl1a−Cu1−O1	94.9(1)	Cl1a−Cu1−O2	87.9(1)
Cl1a−Cu1−N2	105.7(1)	Cl1a−Cu1−N1	90.0(1)
Cl1−Cu2−O1	96.4(1)	Cl1−Cu2−Cl2	96.71(6)
Cl2−Cu2−O2	96.6(1)	O2−Cu2−O1	76.7(2)
Cl2−Cu2−O1	156.5(1)	Cl1−Cu2−O2	159.9(1)
Cu1−O2−Cu2	104.4(2)	Cu1−O1−Cu2	102.3(2)
Cu1a−Cl1−Cu2	104.09(6)		

[a] a = 1 − x, $-y$, $-z$.

2. Description of the Structures. 2a. Description of [Cu_4($HL3$)$_2$(μ-Cl)$_2$$Cl_2$]($CH_3CN$) (1). A thermal ellipsoid plot showing the crystallographic numbering scheme is depicted in Figure 2, and relevant bond lengths and angles are given in Table 1. The asymmetric unit of compound **1** consists of a [Cu_2(**HL3**)Cl_2] molecule, whereas—after the application of a center of inversion—the entire complex is made up of a [Cu_4(**HL3**)$_2$]$^{4+}$ cation, two bridging Cl^- anions, two monodentate Cl^- anions, and one MeCN solvent molecule. The basal plane of the five-coordinated Cu1 ion consists of two amine nitrogens (Cu−N distances 2.001(5) and 2.020(4) Å) and two phenolic oxygens (Cu−O distances 1.992(4) and 1.943(4) Å). The axial position is occupied by a bridging chloride atom (Cu−Cl = 2.715(2) Å). The angles around Cu1 in the basal plane vary from 76.6(2)° to 94.9(2)°, and only the Cl1a−Cu1−N2 angle (105.7(1)°) deviates significantly from the expected value of 90°. The geometry around Cu1 can thus be best described as a distorted square-pyramidal configuration with a τ parameter value of 0.22 (τ = 0 and 1 for a perfect square-pyramidal and trigonal-bipyramidal geometries, respectively).[29]

The Cu2 atom has a distorted square-planar geometry consisting of two phenolic oxygens (Cu−O distances 1.972(4) and 1.961(4) Å), one chloride atom, and one bridging chloride atom (Cu−Cl distances 2.209(2) and 2.262(1) Å, respectively). The angles around Cu2 span from 76.7(2)° to 96.71(6)°. One important structural feature is the spatial arrangement of the four Cu^{II} ions (see Figure 2b). The Cu1 and Cu2 ions are bridged by two phenolic oxygens with angles of 102.3(2)° and 104.4(2)°, whereas Cu2a and Cu1 are connected via a single chloride bridge (Cu1−Cl1a−Cu2a angle of 104.09(6)°). The distances between Cu1−Cu2, Cu1−Cu2a, and Cu2−Cu2a are 3.086(1), 3.935(1), and 3.997(1) Å, respectively. Such cluster arrangement is extremely rare as, to the best of our knowledge, only one tetranuclear copper(II) structure with this type of framework is hitherto known.[30] The lattice is stabilized by hydrogen-bonding interactions along the *c* axis between the H1N atom of the amine nitrogen N1 and the alcoholic oxygen atom

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**[a]

Cu1−Cl1	2.606(1)	Cu1−O10	2.002(2)
Cu1−O20	2.019(2)	Cu1−N19	2.029(2)
Cu1−N29	2.016(3)	Cu1−N41	2.930(3)
Cu2−O10	1.945(2)	Cu2−O20	1.942(2)
Cu1−Cu2	2.9722(6)		
Cl1−Cu1−O10	87.07(7)	Cl1−Cu1−O20	85.97(6)
Cl1−Cu1−N19	100.15(7)	Cl1−Cu1−N29	101.87(7)
Cl1−Cu1−N41	176.20(7)	O10−Cu1−O20	78.05(9)
O10−Cu1−N19	93.1(1)	O10−Cu1−N29	167.78(9)
O10−Cu1−N41	91.0(1)	O20−Cu1−N19	169.0(1)
O20−Cu1−N29	94.1(1)	O20−Cu1−N41	90.43(9)
N19−Cu1−N29	93.5(1)	N19−Cu1−N41	83.2(1)
N29−Cu1−N41	79.6(1)	O10−Cu2−O20	81.28(9)
O10−Cu2−O20a	98.72(9)	Cu1−O10−Cu2	97.7(1)
Cu1−O10−C11	121.5(2)	Cu1−O20−Cu2	97.21(9)

[a] a = −*x*, 1 − *y*, −*z*.

O3 of a neighboring ligand, with a N1···O3 distance of 3.035(7) Å and a N1−H1N···O3 angle of 151.8(2)°.

2b. Description of [$Cu_3(HL1)_2Cl_2(CH_3CN)_2$]($CH_3CN$)$_2$ (2). A thermal ellipsoid plot showing the crystallographic numbering scheme is depicted in Figure 3, and relevant bond lengths and angles are presented in Table 2. The linear trinuclear compound **2**, in which the Cu2 atom lies on an inversion center, contains one [Cu_3(**HL1**)$_2$]$^{2+}$ cation, two semicoordinating Cl^- anions, and two very weakly coordinated MeCN solvent molecules. The terminal copper atoms are hexacoordinated with an elongated octahedral geometry.

The basal plane of the Cu1 ion consist of two amine nitrogen atoms (Cu−N distances 2.016(3) and 2.029(2) Å) and two phenolate oxygen atoms (Cu−O distances 2.002(2) and 2.019(2) Å). The axial positions are occupied by a chloride atom (Cu−Cl distance 2.606(1) Å) and—at best a semicoordinating distance—a nitrogen atom of the MeCN molecule (Cu−N distance 2.930(3) Å). The two terminal Cu1 and Cu1a ions are both coordinated to $HL2^{2-}$ in a cis fashion with respect to the phenolate moieties. The central Cu2 ion has a square-planar geometry due to the site symmetry, with Cu−O distances of 1.942(2) and 1.945(2) Å.

Each phenolate unit bridges to the central Cu2 atom of the trinuclear moiety, resulting in a CuO4 chromophore. The dihedral angle between the two planes of Cu1−O10−Cu2 and Cu1−O20−Cu2 amounts to 18.3°. The Cu1−Cu2 distance is 2.9722(6) Å, whereas the Cu1−O−Cu2 angles are 97.21(9)° and 97.7(1)°. The lattice is stabilized by hydrogen bonds between the H atoms of the amine nitrogen and the alcoholic oxygen atom of the ligand, with N···O distances of 2.911(3) and 2.884(3) Å, and also by hydrogen bonds between the H atom of the amine nitrogen and the H atom of the alcoholic oxygen atom to the chloride atom of a neighboring ligand, with N/O···Cl distances of 3.146(3) and 3.277(2) Å.

Several partly chlorinated and/or hydroxylated products were also characterized by single-crystal studies as either trinuclear or tetranuclear complexes (see the Supporting Information). All tetranuclear complexes are mutually isomorphous (same space groups, very similar cell axes and M−L distances) to **1**. Similarly, all trinuclear products show the same space group, very similar cell parameters, and M−L distances as those in **2**. Details are given in the Supporting Information figures and tables.

3. Spectroscopy and Magnetism. The diffuse-reflectance spectrum recorded for a powder sample of the dark red-brown compound **1** shows a very broad tail-shaped band with a maximum at about 18.8 × 10^3 cm^{-1} and a weak broad shoulder at about 9−12 × 10^3 cm^{-1}, most likely originating from a mixture of d−d and charge-transfer (CT) bands. No attempts were undertaken to resolve these d−d bands for two species. The dark green compound **2** shows a broad signal with a maximum at 16.1 × 10^3 cm^{-1}. This d−d band is most likely originating from the two chromophores with slightly different geometries at the Cu^{II} centers. Also at 24.1 × 10^3 cm^{-1} the CT bands are observed.

For a better characterization, and to understand the magnetic exchange coupling between the copper(II) ions in the present compounds, electron paramagnetic resistance (EPR) and magnetic susceptibility measurements were performed at variable temperatures.

X-band EPR spectra of polycrystalline powders of the complexes were recorded at room temperature (RT) and at 77 K. Compound **1** exhibits an almost EPR-silent behavior from 0 to 800 mT, with only (both at RT and at 77 K) a weak axial $S = {}^1/_2$ signal with $g_\perp = 2.07$, $g_\| = 2.29$ and a weak $A_\|$ value of 12.0 mT. This signal likely arises from very small quantities of monomeric impurities, known to be often present in bulk polynuclear compounds. The EPR spectrum of compound **2** reveals a very broad (approximately 240 mT) isotropic signal at RT, with $g = 2.15$, with no hyperfine splittings resolved, probably due to exchange broadening. At 77 K, this signal is sharpened up with a $g_\perp = 2.07$ and a very weak unresolved $g_\|$ value of 2.20. This behavior was also observed in earlier reported, related trinuclear compounds.[31,32]

The magnetic susceptibility of powdered samples of **1** and **2** was measured in the ranges of 5−400 and 5−300 K, respectively. The tetranuclear compound **1** remains essentially diamagnetic up to ca. 300 K, as can be seen from the plot of $\chi_m T$ vs T shown in Figure 4. Such a behavior implies a very strong dominant antiferromagnetic interaction with an interaction constant <−500 cm^{-1} that can be ascribed to interactions within the copper pairs through the di-μ-phenoxido bridges. The EPR silent spectra are in good agreement with these observations. A rough estimation of the dominant interaction constant in **1** was obtained by fitting the experimental data showing a slight increase in $\chi_m T$ between 300 and 380 K to a simple dimer model[33]

$$\chi_M = (1-\rho)\frac{2N_A\beta^2 g^2}{k_B T}[3+\exp(-J/k_B T)]^{-1} + 2\rho\left(\frac{N_A\beta^2}{k_B T}\right) + \text{TIP}$$

Attempts at fitting to a tetranuclear model only resulted in ill-defined interaction constants, as a result of too little

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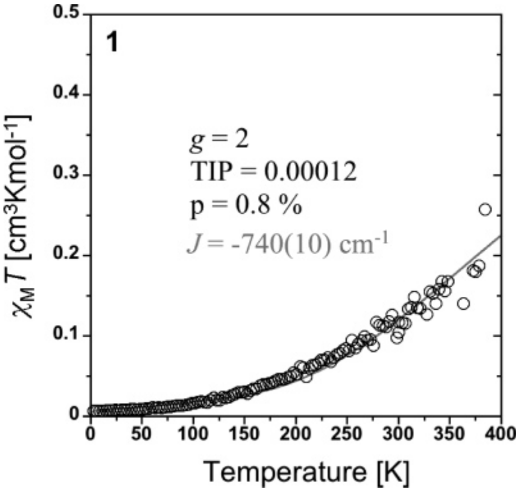

Figure 4. Plot of the temperature dependence of χ_mT vs T for compound **1**. The solid line represents the calculated curve for a dimer model with an interaction constant of $J = -740(10)$ cm^{-1} with $g = 2.0$ (see text).

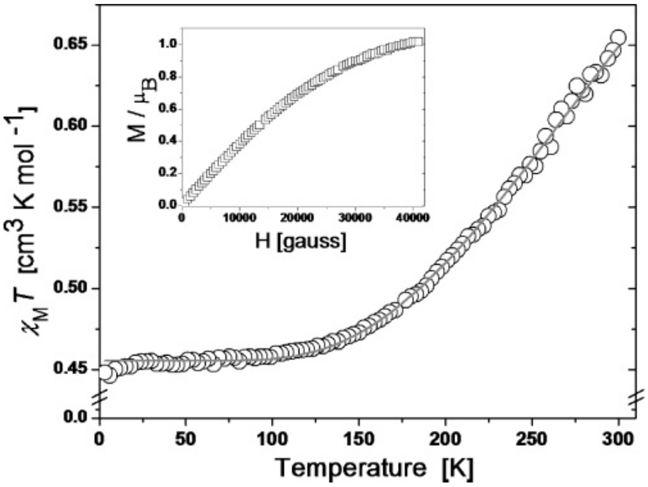

Figure 5. A plot of the temperature dependence of χ_mT vs T for compound **2**. The solid line represents the calculated curve for the parameters $J = -370(1)$ cm^{-1} and $g = 2.20$ (see text). Inset: Field dependence of magnetization measured at 2 K for **2**.

data defining these parameters, e.g., at high temperatures. The dominant interaction is simply too strong. For the same reason, g was fixed to 2 (no EPR signal) and the parameters TIP and the fraction of paramagnetic impurity ρ were fixed to values determined from the region of 5−100 K. The dominant interaction is thus evaluated at ca. −740(10) cm^{-1} (see Figure 4), which is reasonable for a di-μ-phenoxido-bridged system with Cu−O−Cu angles of around 102−105°.

The temperature dependence of the product χ_mT of the trinuclear compound **2** is shown in Figure 5. The value of χ_mT at RT is lower than that of the three uncoupled copper(II) ions (0.655 cm^3 K mol^{-1} instead of 1.125 cm^3 K mol^{-1} for $g = 2.0$), suggesting the presence of a strong antiferromagnetic interaction among the metal centers. Then χ_mT decreases to reach a plateau at a χ_mT value of 0.455 cm^3 K mol^{-1} below 125 K, which is a little above that expected for a $S = {}^1/_2$ ground state (0.375 cm^3 K mol^{-1} for $g = 2$). This behavior was modeled using the spin Hamiltonian[31−33]

$$H = g\beta S_zH - J_1(S_1\cdot S_2 + S_{1a}\cdot S_2) - J_2(S_1\cdot S_{1a})$$

The first term of this Hamiltonian corresponds to the Zeeman term, for which a single isotropic g tensor has been considered for the two different Cu^{II} ions in the compound. The second and third terms are isotropic nearest-neighbor (J_1) and next-nearest-neighbor interactions (J_2), respectively. In this compound, where the trinuclear array is perfectly linear and the dominant nearest-neighbor interaction is antiferromagnetic, J_2 can be neglected and has thus been set to zero. Considering the presence of TIP (temperature-independent paramagnetism), the resulting expression is given in the following equation

$$\chi T = \frac{Ng^2\beta^2}{4k_B} F(T) + \mathrm{TIP}$$

$$F(T) = \frac{1 + \exp(J_1/k_BT) + 10\exp(3J_1/2k_BT)}{1 + \exp(J_1/k_BT) + 2\exp(3J_1/2k_BT)} + \mathrm{TIP}$$

The set of parameters that best fits this equation (the solid line in Figure 5) is $g = 2.20(1)$ and $J_1 = -370(1)$ cm^{-1}. The TIP value was fixed to 60 × 10^{-6} cm^3 mol^{-1} per copper center.

In this case, similar to those of previous examples,[20,31,32] the magnetic orbital of the Cu^{II} ions is the $d_{x^2-y^2}$, which points in the direction of the oxygen atoms of the ligand, and the magnetic behavior must then depend on the geometry of the Cu(μ−OR)Cu unit. The Cu−Cu separation is large, indicating that no direct exchange mechanism is likely to contribute to the magnetic coupling. Therefore, the strong antiferromagnetic coupling in the complex is ascribed to superexchange mechanisms within the central-terminal copper(II) pairs. The value here obtained is in very good agreement with some other linear related Cu^{II} compounds[20,32] and also in good agreement with the isostructural iodide compound,[31] for which a J value of −474(3) cm^{-1} has been obtained. It indeed follows the previously proposed magnetostructural correlations in this type of linear trinuclear copper(II) compound.[34]

4. Ligand Extraction and Preliminary Mechanistic Studies. Ligand extraction experiments, after formation of the chlorinated and/or hydroxylated products, have been performed to characterize the newly formed ligands present in the final crystal structures (details of these experiments are given in the Supporting Information). Mass spectrometry analyses have confirmed the formation of the chlorinated and/or hydroxylated organic molecules. Several cases of chlorination of pyrazolate ligands have been reported in the literature with strong oxidizing/halogenating reagents.[22,35,36] Only one literature example showed the alteration of the ligand, i.e., 3-phenyl-5-(6-methyl-2-pyridyl)pyrazole, through chlorination of the C-4 position mediated by CuCl$_2$ in DMF, under mild conditions.[25] The present experiments thus

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represent the first case of chlorination of phenol rings under mild conditions.

The formation of the chlorinated and the hydroxylated ligands **H_3L2** and **H_3L3** (Figure 1 and Supporting Information) appears to be a quite complicated and interesting process in which a bridging phenolato ligand appears to play a key role. When such groups bind to metal centers, the para-phenolic position (as well as the ortho positions, but to a lesser extent) is known to be activated.[37] However, how the deprotonated phenol then reduces both copper(II) ions to copper(I) can only be hypothesized, and a full explanation is left for a subsequent study.

Concluding Remarks

A series of unique chairlike tetranuclear and linear trinuclear complexes have been isolated and characterized from the reaction of the phenolic ligand **H_3L1** (1,7-bis(2-hydroxyphenyl)-2,6-diaza-4-hydroxylheptane) with $CuCl_2$. The tetranuclear compounds are essentially diamagnetic over the temperature range of 5−350 K, which is indicative of very strong antiferromagnetic interactions (<-500 cm^{-1}) among the phenoxido-bridged pairs of copper(II) centers. The magnetic behavior of the trinuclear compound shows a strong antiferromagnetic exchange ($J = -370$ cm^{-1}), with a low-temperature leveled-off magnetism for one unpaired electron. Whereas several linear trinuclear copper(II) complexes have been obtained from **H_3L1** without ligand modification,[20] the present coordination compounds show that, depending on the synthetic conditions, chlorinated and hydroxylated modified phenolic ligands can be generated. The original ligand **H_3L1** has thus been chlorinated upon coordination to $CuCl_2$ in MeCN, most surprisingly without adding any oxidizing agent. The modified ligands could be isolated and characterized. The present report describes an unusual example of homogeneous copper-mediated chlorination of phenol rings with specific dichlorination, which is highly regioselective for para or ortho substitution.

Experimental Section

General. C,H,N analyses were performed on a Perkin-Elmer 2400 Series II analyzer. Ligand-field spectra were obtained on a Perkin-Elmer Lambda900 spectrophotometer using the diffuse-reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a Jeol RE2x electron-spin-resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were obtained on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000−300 cm^{-1}, res. 4 cm^{-1}). Magnetic susceptibility measurements (5−300 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 G). Data were corrected for the magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.[33]

Preparation of the Ligand H_3L1. The ligand 1,7-bis(2-hydroxyphenyl)-2,6-diaza-4-hydroxylheptane (**H_3L1**) was synthesized from salicylaldehyde and 1,3-diamino-2-propanol by reductive amination using $NaBH_4$ in dried methanol.[20] $C_{17}H_{22}N_2O_3$ (ESI-MS: $m/z = 303$). Anal. Calcd: C, 67.5; H, 7.3; N, 9.3. Found: C, 67.3; H, 7.1; N, 9.5. ^{1}H NMR (300 MHz, chloroform-*d*): δ 7.17 (t, 2H), 6.97 (d, 2H), 6.79 (q, 4H), 3.94 (m, 5H), 2.66 (d, 4H).

Table 3. Crystallographic Data for Coordination Compounds **1** and **2**

	1	**2**
formula	$C_{36}H_{39}Cl_8Cu_4N_5O_6$	$C_{42}H_{52}Cl_2Cu_3N_7O_6$
molecular weight	1175.48	1026.44
cryst syst	monoclinic	monoclinic
T (K)	293(2)	173(2)
space group	$C2/c$	$P2_1/c$
a (Å)	20.824(1)	11.992(2)
b (Å)	12.187(1)	17.992(3)
c (Å)	18.739(1)	11.908(2)
β (deg)	118.415(1)	114.19(3)
V (Å^3)	4182.7(5)	2343.7(9)
Z	4	2
D_{calc} (g cm^{-3})	1.867	1.454
F(000)	2360	1058
μ (mm^{-1})	2.570	1.516
cryst size (mm^3)	0.18 × 0.16 × 0.12	0.30 × 0.30 × 0.30
shape, color	prism, dark red-brown	prism, dark green
θ_{min}, θ_{max} (deg)	2.0−29.3	2.9−27.5
total reflns	25 354	36 196
total unique reflns	5275 ($R_{int} = 0.042$)	5284 ($R_{int} = 0.065$)
no. of ref params	272	285
R1[a], wR2[b], S[c]	0.059, 0.163, 1.00	0.038, 0.091, 1.04
min and max resd dens (e/Å^3)	−1.19, 1.31	−0.33, 1.16

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Goodness-of-fit $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters.

Synthesis of $[Cu_4(HL3)_2(\mu\text{-}Cl)_2Cl_2](CH_3CN)$ (1). The addition of a solution of **H_3L1** (1 mmol, 302 mg) in 15 mL acetonitrile to a solution of $CuCl_2{\cdot}2H_2O$ (2 mmol, 340 mg) in 15 mL acetonitrile, with a molecular excess of trimethylorthoformate to remove the water, resulted in a red reaction mixture with the subsequent formation of a brown precipitate. The mixture was stirred for 30 min and then filtered. Dark red-brown crystals were obtained from the filtrate after 3 days, by slow evaporation of the solvent at RT. Yield: 280 mg (48%). Anal. Calcd for $C_{36}H_{39}Cl_8Cu_4N_5O_6$: C, 36.8; H, 3.3; N, 6.0. Found: C, 37.0; H, 3.5; N, 6.6%. IR (solid, cm^{-1}): 3362, 3211, 1595, 1474, 1456, 1406, 1320, 1256, 1195, 1163, 1123, 1084, 1038, 1005, 967, 870, 810, 781, 759, 671, 645, 549, 438, 417, 388. Experiments carried out anaerobically under the same condition (argon atmosphere) did not result in crystals of this compound, showing the reoxidation of the Cu(I) in air to be important.

Synthesis of $[Cu_3(HL1)_2Cl_2(CH_3CN)_2](CH_3CN)_2$ (2). To a suspension of $CuCl_2{\cdot}2H_2O$ (1 mmol, 170 mg) in 10 mL of acetonitrile was added a solution of **H_3L1** (0.5 mmol, 151 mg) and triethylamine (1 mmol, 101 mg) in 10 mL acetonitrile. A green precipitate formed immediately in the resulting dark brown solution. The mixture was stirred for 30 min and then filtered. Dark green crystals deposited from the filtrate after 1 day by slow evaporation of the solvent at RT. Yield: 88 mg (34%). Anal. Calcd for $C_{42}H_{52}Cl_2Cu_3N_8O_6$: C, 49.1; H, 5.1; N, 10.9. Found: C, 48.6; H, 5.5; N, 10.4%. IR (solid, cm^{-1}): 3259, 1596, 1484, 1455, 1256, 1112, 1039, 1006, 932, 873, 750, 641, 601, 580, 446, 410, 385. The use of diethylamine instead of triethylamine yielded the same compound **2**.

X-ray Crystallography. Crystallographic data and refinement details are given in Table 3. Compound **1**: Intensity data were collected using Mo Kα radiation on a Bruker AXS Smart 1000 single-crystal diffractometer, equipped with a CCD area detector at 293(2) K. The structure was solved by direct methods using the

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SIR97 program[38] and refined on F_o^2 by full-matrix least-squares procedures using the *SHELXL-97* program.[39] The data reduction was performed using the *SAINT*[40] and *SADABS*[41] programs. All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometries (C−H length of 0.95 Å) and refined "riding" on the corresponding parent atoms. Geometric calculations and molecular graphics were performed with the *PARST97*[42] program and the *PLATON* package.[43]

Compound **2**: A crystal was selected and mounted on a glass fiber, using the oil-drop method, and data were collected on a Nonius Kappa CCD diffractometer (graphite-monochromated Mo Kα radiation, ω-2θ scans) at 173 K. The structures were solved by direct methods. The programs *COLLECT*,[44] *SHELXS-97*,[45] *SHELXL-97*[39] were used for data reduction, structure solution, and structure refinement, respectively. The refinement of F^2 was done against all reflections. All non-hydrogen atoms were refined anisotropically. Crystal data are reported in Table 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper are available as CIF files in the Supporting Information (SI), and those of the other compounds mentioned in the SI have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-632368 and CCDC-632369, for compounds **1** and **2**, respectively. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., (fax, +44-(0)1223−336033; or e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Syntheses, X-ray crystal structure data, tables, figures for the partly chlorinated and/or hydroxylated compounds, and CIF files of compounds **1** and **2**; experimental details for the extraction and analysis of the various chlorinated and hydroxylated ligands obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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