A trinucleating ligand based on 1,8-naphthalenediol: synthesis, structural and magnetic properties of a linear $Cu^{II}Cu^{II}Cu^{II}$ complex

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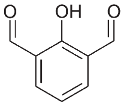
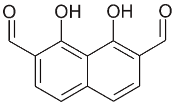
The extension of Robson-type ligands from dinucleating based on 2,6-diformylphenol to trinucleating based on 2,7-diformyl-1,8-naphthalenediol is demonstrated by the synthesis, structural and magnetic characterization of the first trinuclear Cu^{II} complex using a 1,8-naphthalenediol derived ligand.

In 1970, Robson introduced the symmetrical dialdehyde 2,6-diformylphenol **I** and its substituted analogues as precursors for the synthesis of dinucleating ligands (compartmental ligands, Robson type ligands).[1] Since then, an innumerous number of studies employed these ligand systems either in a non-cyclic or a macrocyclic version,[2] and with variations of the bridging unit, *e.g.* 1,8-naphthyridine,[3] pyrazolate,[4] and thiophenol.[5] The synthesis of homo- as well as hetero-dinuclear transition metal complexes allowed the detailed investigations of their magnetochemical and electrochemical properties. These studies provided important insight into the molecular and electronic structure of dinuclear metallo-proteins and the co-operativity of such sites in catalysis.



I



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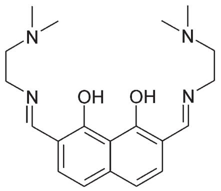

H_2L

In order to extend these ligand systems to trinucleating ligand systems we have previously established a streamlined synthesis for the dialdehyde 2,7-diformyl-1,8-naphthalenediol **II** which we regard as the '*one ring- and one donor-increased*' derivative of 2,6-diformylphenol **I**.[6] Analogously, we have synthesized 2-formyl-1,8-naphthalenediol as the '*one ring- and one donor-increased*' derivative of salicylaldehyde and applied it to the formation of extended salen-like ligands based on the 1,8-naphthalenediol backbone.[7–9] Herein we report the synthesis of the first trinucleating ligand H_2L based on 1,8-naphthalenediol and its trinuclear $Cu^{II}Cu^{II}Cu^{II}$ complex.

The reaction of **II** with *N*,*N*-dimethylethylenediamine results in the formation of a brown solid which was directly used for the complex synthesis. In order to evaluate whether the potentially trinucleating ligand H_2L selectively coordinates distinct compartments, we have initially reacted H_2L under basic conditions with only two equivalents of $CuCl_2 \cdot 2H_2O$ and obtained a brown crystalline solid (**1**).† The FTIR spectrum shows no band at 1686 cm^{-1} (C=O stretch of **II**)[6] but a new band at 1638 cm^{-1} characteristic of C=N stretches. Thus, the FTIR indicates the complete transformation of the aldehyde to imine groups. The MALDI-TOF mass spectrum of **1** exhibits prominent ions at mass-to-charge ratios (*m*/*z*) of 650, 632, and 615, with mass and isotopic distribution patterns corresponding to $[LCu_3Cl_3]^+$, $[LCu_3Cl_2OH]^+$, and $[LCu_3Cl_2]^+$, respectively. Thus, not a dinuclear but a trinuclear Cu complex is formed, which is corroborated by elemental analysis. Single-crystal X-ray diffraction establishes that **1** is a mixture of $[LCu_3Cl_3(OCH_3)(HOCH_3)]$ (75%, Fig. 1a) and $[LCu_3Cl_4(HOCH_3)]$ (25%).‡ According to the stoichiometry of the reaction and in order to provide more chloride ions to avoid a methoxo-bridged species, we reacted the ligand H_2L with three equivalents of $CuCl_2 \cdot 2H_2O$ and obtained a brown crystalline solid (**2**).§ The C=N stretch is slightly shifted to 1644 cm^{-1} and the MALDI-TOF mass spectrum exhibits the prominent ions at mass-to-charge ratios (*m*/*z*) 650 and 615 for $[LCu_3Cl_3]^+$ and $[LCu_3Cl_2]^+$, respectively. However, the peak at 632 observed in **1** is not observed in the mass spectrum of **2**. Single-crystal X-ray diffraction clearly establishes that **2** has to be formulated as $[LCu_3Cl_4(HOCH_3)]$ (Fig. 1b).¶

Both structures demonstrate that the ligand L^{2-} is capable of coordinating three metal ions that are arranged in a linear fashion. The two terminal Cu^{II} ions are coordinated by an N_2O compartment of L^{2-} while the central Cu^{II} ion is coordinated by the O_2 compartment of L^{2-}. In **2**, the central Cu^{II} ion is additionally bridged to the two terminal Cu^{II} ions by two external Cl^- ions, while in the main component of **1**, one Cl^- ion is substituted by a CH_3O^- bridge. The fivefold coordination of the central Cu^{II} ion is completed by a coordinated MeOH, and the fivefold coordination of each of the two terminal Cu^{II} ions is completed by Cl^- ligands. While the molecular structures of both compounds are very similar, we will focus our discussion on **2**.

The trinuclear molecule exhibits no symmetry, which is exemplified by the differences in the coordination geometries of the three Cu^{II} ions (Fig. 2). While the coordination environment of Cu3 is close to square-pyramidal (τ = 0.08),[10] the coordination environments of Cu2 (τ = 0.19) and Cu1 (τ = 0.24) exhibit severe distortions towards trigonal-bipyramidal. In Cu3 the basal plane consists of the N_2O compartment of the ligand and the bridging Cl4. The terminal Cl3 occupies the apical position. The basal plane at Cu2 is comprised of the two aryl oxide donors and the two bridging chlorides Cl2 and Cl4, while the methanol molecule

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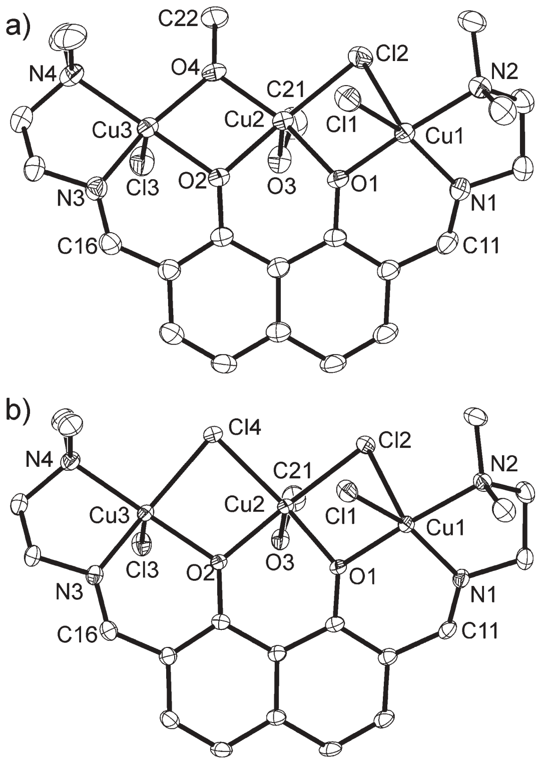

Fig. 1 (a) Molecular structure of the main component [$LCu_3Cl_3(OCH_3)(HOCH_3)$] in crystals of **1**·MeOH; (b) molecular structure of [$LCu_3Cl_4(HOCH_3)$] in crystals of **2**·MeOH. Selected interatomic distances in Å: **1** (**2**), Cu1–Cu2 = 3.095(1) (3.121(1)), Cu2–Cu3 = 3.014(1) (3.117(1)), Cu1–N1 = 1.946(2) (1.948(2)), Cu1–N2 = 2.023(2) (2.032(2)), Cu1–O1 = 1.964(2) (1.978(2)), Cu1–Cl1 = 2.232(1) (2.232(1)), Cu1–Cl2 = 2.668(1) (2.666(1)), Cu2–O1 = 1.916(2) (1.919(2)), Cu2–O2 = 1.953(2) (1.974(2)), Cu2–O3 = 2.421(2) (2.317(2)), Cu2–Cl2 = 2.252(1) (2.256(1)), Cu2–O4 = 1.885(5) (Cu2–Cl4 = 2.280(1)), Cu3–N3 = 1.931(2) (1.934(2)), Cu3–N4 = 2.052(2) (2.032(2)), Cu3–O2 = 1.992(2) (1.995(2)), Cu3–Cl3 = 2.610(1) (2.565(1)), Cu3–O4 = 1.925(5) (Cu3–Cl4 = 2.309(1)).

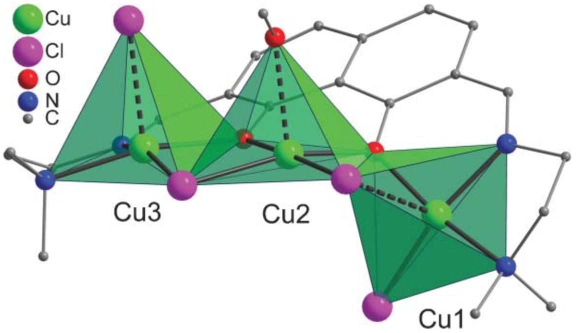

Fig. 2 Molecular structure of **2** demonstrating the unsymmetrical arrangement of the coordination polyhedra.

occupies the apical position. Contrarily, the basal plane at Cu1 consists of the N_2O compartment of the ligand and the terminal chloride Cl1 whereas the apical position is occupied by the bridging Cl2. This results in the unsymmetrical arrangement of coordination polyhedra shown in Fig. 2, where the basal planes of Cu3 and Cu2 share a common edge with an angle of the basal planes of 5.2°. On the other hand the edge-sharing motif between Cu1 and Cu2 involves the apical ligand of Cu1, which results in an angle between the basal planes of 63.7°.

In order to obtain a first insight into the coupling between the Cu^{II} ions of this new trinucleating ligand, we have measured the magnetic susceptibility of **2** (Fig. 3). In the temperature range 20 to 120 K, the effective magnetic moment per trimer, μ_{eff}, is 1.82–1.83 μ_B, indicating a S_t = ½ ground state. Below 20 K, μ_{eff} decreases slightly with decreasing temperature due to saturation effects and/or intermolecular antiferromagnetic interactions. Above 130 K there is a slight increase in μ_{eff} with increasing temperature reaching a value of 2.02 μ_B at 290 K indicating the thermal population of a higher total spin state.

The coupling of the three local S_i = ½ spin states yields three total spin states S_t (one S_t = 3/2 and two S_t = ½). Due to the differences in the bridging motif, the interaction between Cu1 and Cu2 (J_{12}) should be different to that of Cu2 and Cu3 (J_{23}). The naphthalenediol backbone could provide a long distance pathway between Cu1 and Cu3 (J_{13}). The adequate spin-Hamiltonian which has to be used is shown in eqn (1).

$$H = -2J_{12}S_1S_2 - 2J_{23}S_2S_3 - 2J_{13}S_1S_3 + \sum_{i=1}^{3}\mu_B g_i S_i B \quad (1)$$

There is no analytical solution for this case of three different J values and we have analyzed the magnetic properties by full-matrix-diagonalization.[11] The S_t = ½ spin ground state indicates dominant antiferromagnetic interactions. The increase of μ_{eff} above 130 K is due to thermal population of the excited S_t = 3/2 state. Simulations indicate that this state has to be at an energy of ~500 cm^{-1} above the spin ground state. The energy of the second S_t = ½ spin state depends on the ratios and magnitudes of the three J_i values and has a small influence on the energy of the S_t = 3/2 state. However, there is a manifold of solutions of the spin-Hamiltonian to fit the experimental data but the marginal temperature dependence does not allow the evaluation of the three coupling constants.

The two insets in Fig. 3 show the relative error surface for varying J_{12} and J_{23} with a fixed value of $J_{13} = -50$ cm^{-1} (left inset) and J_{13} = +10 cm^{-1} (right inset). The solid line in Fig. 3 is a

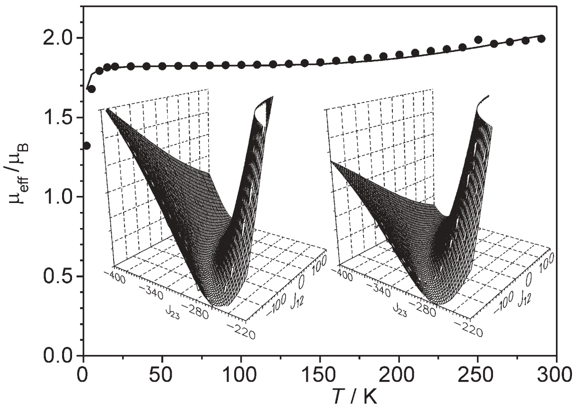

Fig. 3 Temperature dependence of the effective magnetic moment, μ_{eff}, of **2**·MeOH at 1 T. The solid line is a simulation using the spin-Hamiltonian parameters given in the text, which represent only one solution out of a manifold of solutions. The insets show the relative error over the (J_{23}, J_{12}) parameter space, calculated for $J_{13} = -50$ cm^{-1} (left), and J_{13} = +10 cm^{-1} (right).

characteristic fit result with $J_{12} = -291$ cm^{-1}, $J_{23} = -162$ cm^{-1}, and $J_{13} = 0$ with g_1, g_2, and g_3 fixed at 2.11, a typical value for Cu^{II} in a tetragonal coordination environment. This results in the S_t = 3⁄2 state at ~510 cm^{-1} and the excited S_t = ½ at ~560 cm^{-1}.

There are several examples of dinuclear Cu^{II}Cu^{II} complexes synthesized with dinucleating ligands based on **I**.[12,13] The edge-bridged complexes with a phenoxide/chloride bridging unit exhibit antiferromagnetic couplings with the J values in the range from −80 to −190 cm^{-1}. The study of the magnetochemical properties by varying the exogenous bridging ligand from chloride to other mononuclear monoatomic bridges demonstrated that besides the Cu–OPh–Cu angle, the nature of the exogeneous bridge has a strong modulating effect.[12]

In summary, we have demonstrated for the first time the use of 2,7-diformyl-1,8-naphthalenediol **II** as a building block for the synthesis of trinucleating ligands, exemplified by the trinuclear Cu complex of L^{2-}. We are currently investigating the general applicability of **II** for the development of various kinds of trinucleating ligands to synthesize trinuclear complexes relevant for magnetostructural correlations and biomimetic catalyses. A special focus in the study of the trinuclear complexes will be the influence of the third remote metal ion on biomimetic transformations/catalyses. This third metal ion might play a role as a general Lewis acid, might provide a nucleophile and/or might preorganize the substrate to the catalytic active site by pre-coordination.

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† Synthesis of **1**: [LCu$_3$Cl$_{3.25}$(OCH$_3$)$_{0.75}$(HOCH$_3$)]. A mixture of 2,7-diformyl-1,8-naphthalenediol (200 mg, 0.925 mmol), *N*,*N*-dimethylethylenediamine (204 mg, 2.31 mmol, 2.5 eq.), and Na$_2$SO$_4$ (500 mg) in CH$_2$Cl$_2$ (40 ml) was heated at 40 °C for 2 h under Ar. After cooling to room temperature, the brown solution was filtered and the solvent was removed under reduced pressure. The brown solid was suspended in heptane and the suspension was heated at reflux for 2 h. Filtration afforded the crude ligand, which was dissolved in MeOH (80 mL) and treated with a solution of CuCl$_2$·2H$_2$O (315 mg, 1.85 mmol, 2.0 eq.) in MeOH (30 mL) and with a solution of Et$_3$N (187 mg, 1.85 mmol, 2.0 eq.) in MeOH (33 mL). The mixture was heated at reflux for 2 h. After cooling to room temperature and filtration, vapour diffusion of Et$_2$O resulted in the deposition of dark brown crystals. Yield: 111 mg (25% based on Cu). MS-MALDI-TOF (CH$_2$Cl$_2$/DCTB): *m*/*z* 650 (22%) [LCu$_3$Cl$_3$]$^+$, 632 (100) [LCu$_3$Cl$_2$OH]$^+$, 615 (44) [LCu$_3$Cl$_2$]$^+$; FT-IR (KBr): $\tilde{\nu}$/cm^{-1} = 2923, 2815, 1638 (C=N), 1568, 1385, 1135, 1068. Anal. Calcd for C$_{21.75}$H$_{34.25}$N$_4$O$_{4.75}$Cl$_{3.25}$Cu$_3$ (**1**·H$_2$O): C 35.61 H 4.71 N 7.63. Found: C 35.38 H 4.43 N 7.31.

‡ Crystal data for **1**·MeOH: C$_{22.75}$H$_{36.25}$Cl$_{3.25}$N$_4$O$_{4.75}$Cu$_3$, M = 747.64, triclinic, a = 10.283(1) Å, b = 10.941(1) Å, c = 13.382(1) Å, α = 79.52(1)°, β = 87.86(1)°, γ = 82.82(1)°, V = 1468.7(2) Å^3, T = 198(2) K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo-Kα) = 2.49 mm^{-1}, 16597 reflections measured, 6990 unique (R_{int} = 0.048) and 5934 observed reflections [$I \geqslant 2\sigma(I)$], 365 refined parameters. R = 0.031, wR^2 = 0.075, CCDC 619201. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612555g

§ Synthesis of **2**: [LCu$_3$Cl$_4$(HOCH$_3$)]. The synthesis of **2** is analogous to that of **1** except for the use of 3 equivalents of CuCl$_2$·2H$_2$O (473 mg, 2.77 mmol, 3.0 eq.). Yield: 111 mg (18% based on Cu). MS-MALDI-TOF (CH$_2$Cl$_2$/DCTB): *m*/*z* 650 (100%) [LCu$_3$Cl$_3$]$^+$, 615 (26) [LCu$_3$Cl$_2$]$^+$; FT-IR (KBr): $\tilde{\nu}$/cm^{-1} = 2921, 1644 (C=N), 1571, 1376, 1154, 1068. Anal. Calcd for C$_{21}$H$_{34}$N$_4$O$_5$Cl$_4$Cu$_3$ (**2**·2H$_2$O): C 33.11 H 4.541 N 7.79. Found: C 33.06 H 4.37 N 7.41.

¶ Crystal data for **2**·MeOH: C$_{22}$H$_{34}$Cl$_4$N$_4$O$_4$Cu$_3$, M = 750.95, triclinic, a = 10.1794(5) Å, b = 10.7731(5) Å, c = 13.4671(7) Å, α = 78.786(5)°, β = 87.043(5)°, γ = 83.440(5)°, V = 1438.52(12) Å^3, T = 100(2) K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo-Kα) = 2.605 mm^{-1}, 21300 reflections measured, 6942 unique (R_{int} = 0.0392) and 6031 observed reflections [$I \geqslant 2\sigma(I)$], 344 refined parameters. R = 0.0281, wR^2 = 0.0658, CCDC 619202. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612555g

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