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A New Polynuclear Coordination Type for (Salicylaldoxime)copper(II) Complexes: Structure and Magnetic Properties of an (Oxime)Cu_6 Cluster

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A previously unseen coordination mode is reported for (salicylaldoxime)copper complexes utilising a linked zwitterionic NO_2^{2-} donor set.

Introduction

The strength and selectivity of binding of Cu^{II} cations by salicylaldoxime derivatives arises from the stability[1] of the 14-membered pseudomacrocyclic structure of the resulting complexes,[2] and ca. 25% of the world's copper is recovered by solvent extraction using kerosene-soluble reagents of this type, e.g. $\mathbf{L^1}$ (Figure 1a).[3] We have recently developed extractants based on salicylaldoxime, which are capable of transporting metal *salts*. These (e.g. $\mathbf{L^2}$ in Figure 1b) have hydrophobic 3-aminomethyl groups, for example, which become protonated on uptake of the metal salt, providing binding sites for the attendant anions in a tritopic assembly of the type $[Cu\mathbf{L}_2X_2]$, shown in Figure 1b. By linking two salicylaldoximes through 3-aminomethyl groups it is possible to generate helical dinuclear copper(II) complexes, $[Cu_2(\mathbf{L^3}\text{-}2H)_2]$ (Figure 1c), which are capable of encapsulating anions.[4] The cavity size decreases and the helicity of the assembly increases markedly on protonation of the amino groups, and uptake of an anion occurs when the "copper-only" complex is treated with an acid.[4]

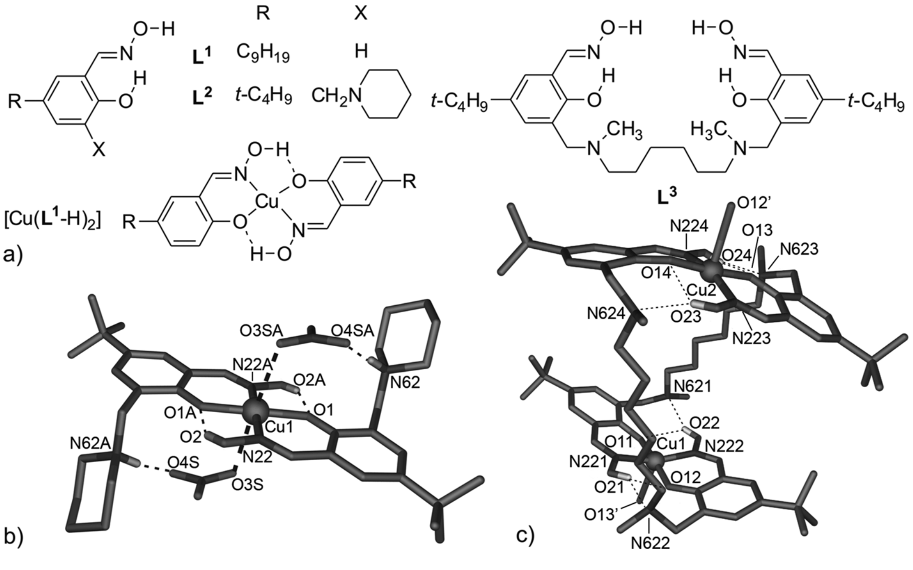

Figure 1. (a) Salicylaldoxime ligands and the 14-membered pseudomacrocyclic Cu^{II} complex formed by the commercial extractant $\mathbf{L^1}$; (b) the tritopic $Cu(NO_3)_2$ complex, $[Cu(\mathbf{L^2})_2(NO_3)_2]$ formed[9] by the 3-piperidinomethyl derivative $\mathbf{L^2}$, and (c) a recently reported[4] dicopper helicate $[Cu_2(\mathbf{L^3}\text{-}2H)_2]$ formed by the strapped bis(salicylaldoxime) $\mathbf{L^3}$.

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Phenolic oximes are versatile ligands that are also capable of forming polynuclear complexes with metals such as Mn,[5] Co,[5a,6] Ni[5a,6a] and Fe,[5a,7] including a single-molecule magnet with the highest energy barrier to magnetisation reversal currently known.[8] No such salicylaldoximato-bridged Cu^{II} complexes have been reported.

Results and Discussion

When an attempt was made to incorporate a PF_6^- anion into the dinuclear $[Cu_2(\mathbf{L^3}\text{-}2H)_2]$ complex by the addition of $NaPF_6$ in water, a major rearrangement was observed, which resulted in the isolation of the first polynuclear (salicylaldoxime)copper(II) complex, $[Cu_6(\mathbf{L^3}\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)](PF_6)_3$ (Figure 2). The $Cu^{II}{}_3(\mu_3\text{-}O)^{4+}$ units are held together by doubly deprotonated salicylaldoxime ligands in an arrangement, which is similar to that found in Mn^{III} complexes[5] containing $[Mn_3(salox\text{-}2H)_3(\mu_3\text{-}O)]^-$. The new hexanuclear copper complex has a helical structure in which two $Cu^{II}{}_3(\mu_3\text{-}O)^{4+}$ units are linked by the three straps between the salicylaldoximate units. The twist of 23.55(6)° from a trigonal prismatic arrangement of the two Cu_3 triangles arises in part from the intramolecular hydrogen bonds between each alkylammonium NH group and its neighbouring phenolate oxygen atom [N6···O1 2.775(10) Å] and, together with the incorporation of a proton between μ_3-oxygen atoms (see below), contributes to the close approach of the two $Cu_3(\mu_3\text{-}O)$ cores; the separation of the least-squares planes through the $Cu_3(\mu_3\text{-}O)$ units is 3.29(4) Å.

The coordination environment of the Cu^{II} atom is unlike those of any previously reported salicylaldoximato complexes.[2,4,9,10] Each Cu^{II} atom is coordinated to an oxime N and phenolate O donor from one ligand and an oximate O donor of a neighbouring ligand. The distorted square-planar coordination site is completed by a bond to a central μ_3-O atom with bond lengths and *cis* bond angles falling in the ranges 1.898(5)–1.909(8) Å and 83.3(3)–92.64(18)°, respectively (Table S1, Supporting Information).

The in-plane Cu^{II}–Cu^{II} distance is 3.2397(19) Å, falling in the range 3.045–3.393 Å reported for other approximately planar $Cu_3(\mu_3\text{-}O)$ cores.[11] The central μ_3-O atoms are displaced by 0.364(11) Å from the Cu_3 planes towards the centre of the assembly. This *endo* arrangement of the μ_3-O atoms, accompanied by charge neutrality arguments, suggests that a proton is sandwiched between them in an O–H···O hydrogen-bonded arrangement [O···O 2.561(16) Å]. Similar $[Cu_6(O)(OH)]$ arrangements have been observed in H-bonded dimerised complexes of monoanionic α- and β-aminooximes.[11c,12] The commitment of the N–H bonds of the alkylammonium groups to H-bond to their neighbouring phenolates results in the PF_6^- counterions making their closest contacts with the adjacent α-methylene groups. The shortest involves C62, with a C62···F1 distance of 3.17(3) Å.

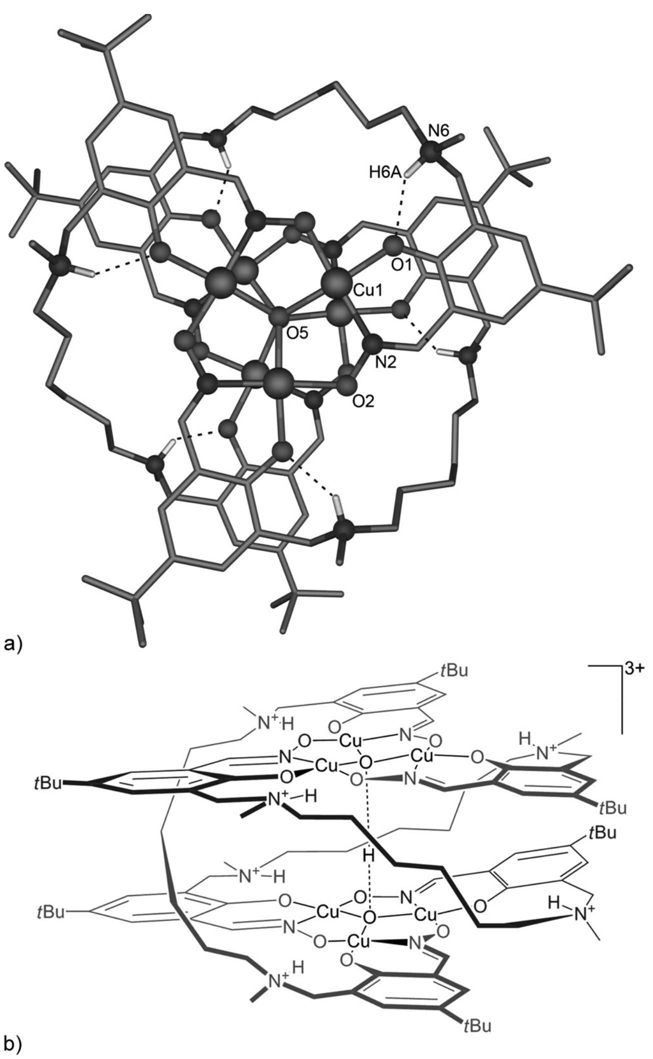

Figure 2. (a) Solid-state structure of the cation $[Cu_6(\mathbf{L^3}\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)]^{3+}$ viewed along the threefold axis through the μ_3-O atoms and the interaction of their alkylammonium protons with the phenolate O atoms [N6···O1 2.775(9) Å and N6–H6···O1 133.1°]. (b) Schematic representation showing the three straps and the interplane $(\mu_3\text{-}O)\cdots H\cdots(\mu_3\text{-}O)$ hydrogen bond.

The HR-MS spectra contain two isotopic groups of strong signals in the ranges *m*/*z* = 689.2284–692.8940 and 1033.3346–1038.8344 which represent the complex species $[Cu_6(\mathbf{L^3}\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)]^{3+}$ $(C_{96}H_{145}N_{12}O_{14}Cu_6)^{3+}$ and $[Cu_6(\mathbf{L^3}\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)\text{-}H]^{2+}$ $(C_{96}H_{144}N_{12}O_{14}Cu_6)^{3+}$. The calculated theoretical *m*/*z* values for the lowest-mass tri- and dications are 689.2260 $(C_{96}H_{145}N_{12}O_{14}Cu_6)^{3+}$ and 1033.3350 $(C_{96}H_{144}N_{12}O_{14}Cu_6)^{2+}$ (Figure 3), proving the cluster is quite stable in the gas phase.

Significant quantities of $[Cu_6(\mathbf{L^3}\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)](PF_6)_3$ were prepared by combining $\mathbf{L^3}$, $Cu(OAc)_2$ and $NaPF_6$ in a methanol/water mixture, allowing its magnetic properties to be studied. Solid-state dc magnetisation measurements were performed in the range 300–2 K in a field of 0.1 T. The $\chi_M T$ value (Figure 4) of ca. 1.9 $cm^3\,K\,mol^{-1}$ at 300 K is below the spin-only (g = 2.00) value expected for six non-interacting Cu^{II} ions of ca. 2.25 $cm^3\,K\,mol^{-1}$. The value decreases with decreasing temperature to a value of ca. 1 $cm^3\,K\,mol^{-1}$ at ca. 90 K, where it plateaus briefly until ca. 60 K, finally decreasing sharply to a value of ca.

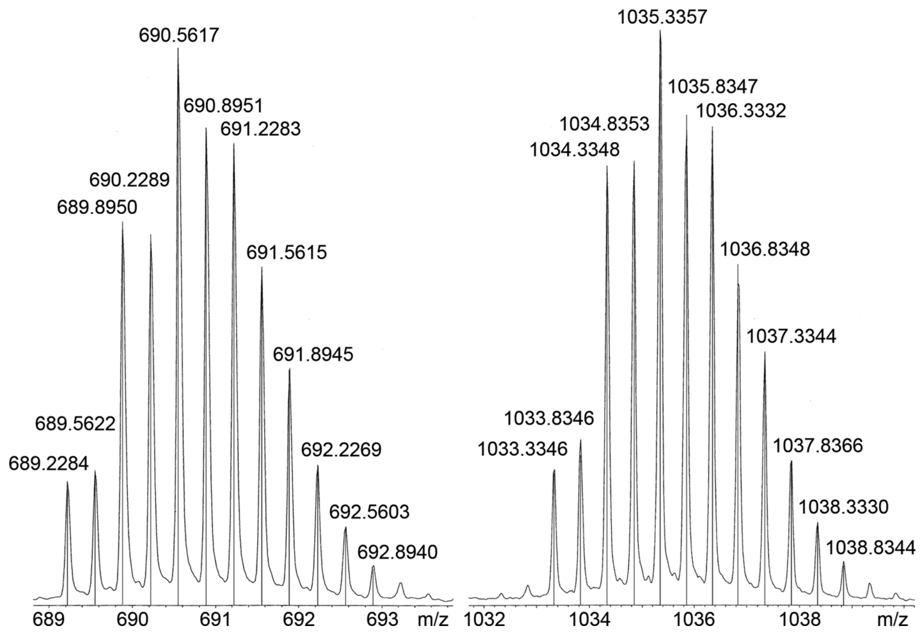

Figure 3. Selected peaks from the HR-MS (ESI) of $[Cu_6(\mathbf{L}^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)](PF_6)_3$ with accompanying theoretical model (vertical lines) for $[Cu_6(\mathbf{L}^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)]^{3+}$ $(C_{96}H_{145}N_{12}O_{14}Cu_6)^{3+}$ (left) and $[Cu_6(\mathbf{L}^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)\text{-}H]^{2+}$ $(C_{96}H_{144}N_{12}O_{14}Cu_6)^{2+}$ (right).

0.5 $cm^3\,K\,mol^{-1}$ at 2 K. The experimental data were modeled within the spin Hamiltonian formalism by use of home-written software that calculates magnetic moments from the eigenfunctions of the spin-Hamiltonian using the Hellman–Feynman theorem. Powder averaging was performed by summation along the three principal axes. Initially, the interpretation of the experimental data was attempted by use of a spin-Hamiltonian including only intratriangle isotropic exchange interactions and isotropic Zeeman terms. Such a model proved to be insufficient for the interpretation of the experimental data. The quality of fit between calculated and experimental data is improved considerably with the introduction of an antisymmetric exchange term. Hamiltonians incorporating Dzialoshinsky–Moriya exchange have been required in all previous studies of exchange-coupled triangular $[Cu^{II}_3]$ molecules.[13] If an axial model for the Zeeman terms is adopted and the g_z component of the g matrix is allowed to vary freely, a perfect fit is obtained but with an unrealistic value of g_z (ca. 2.8), whereas the perpendicular components have more realistic values of ca. 2.2. If the g_z component is restricted within the range 2.0–2.2, all best-fit g values are of the order of 2.2. Thus, during the fit of the experimental data we have used an isotropic model for the Zeeman terms and fixed the g values of the Cu centres to 2.2. We have also followed previous studies on exchange-coupled triangular $[Cu^{II}_3]$ molecules in setting $G_x = G_y = 0\ cm^{-1}$. Under these conditions the best-fit parameters obtained by spin-Hamiltonian (1) are: $J = -68.89\ cm^{-1}$; $G_z = 12.77\ cm^{-1}$. The experimental and calculated points are shown in Figure 4. Finally, addition of intertriangle or intermolecular interaction terms did not significantly improve the quality of fit.

$$\boldsymbol{H} = -2J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_1 + \hat{S}_4\cdot\hat{S}_5 + \hat{S}_5\cdot\hat{S}_6 + \hat{S}_6\cdot\hat{S}_4) + G(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_1 + \hat{S}_4\cdot\hat{S}_5 + \hat{S}_5\cdot\hat{S}_6 + \hat{S}_6\cdot\hat{S}_4) + \mu_B gB(\hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \hat{S}_4 + \hat{S}_5 + \hat{S}_6) \quad (1)$$

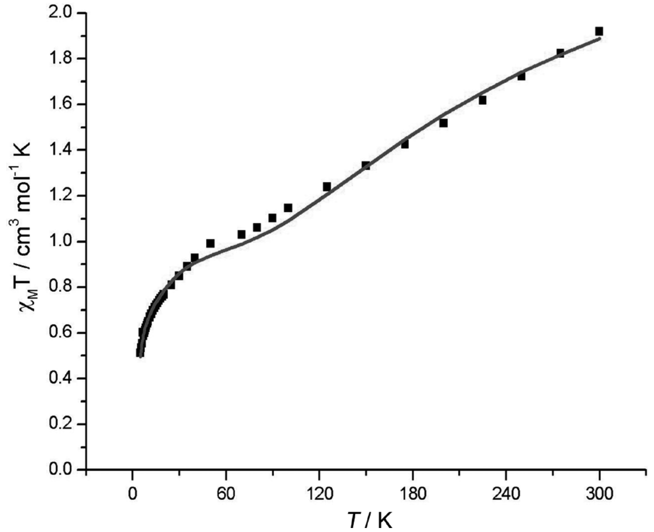

Figure 4. Plot of $\chi_M T$ vs. T for $[Cu_6(\mathbf{L}^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)](PF_6)_3$ in the 300–2 K temperature range. The solid line is the fit of the experimental data to Equation (1) with $J = -68.89\ cm^{-1}$, $G_z = 12.77\ cm^{-1}$ and g(fixed) = 2.2.

Magnetic investigation of Cu_3–OHO–Cu_3 cores utilising oxime ligands are rare with only one other example known. Preliminary analysis of a strongly antiferromagnetic 4-amino oxime derivative by Curtis et al. with the central oxygen atom displaced by 0.233(2) Å and dihedral angles between the individual CuX_4 coordination planes of 21.4° gave a J value of ca. $-1000\ cm^{-1}$.[11c] In the present example, the dihedral angles are 9.9° between the three CuX_4 coordination planes, i.e. the molecule possesses a high degree of coplanarity, forced upon it due to the numerous H-bonding interactions and weak π–π stacking of the aromatic rings and therefore should in theory mediate strong magnetic exchange. The low J value of ca. $-70\ cm^{-1}$ is therefore somewhat surprising. One possible reason for this low value is that the central μ_3-O atom is displaced further [0.364(11) Å] than in the above example disrupting the exchange pathway. In related Cu_3OH core complexes, utilising β-amino oximes, the central hydroxide group is also substantially displaced and exhibits a comparable J value.[14]

Conclusions

The incorporation of 3-aminomethyl groups on the salicylaldoxime framework appears to make it possible for Cu^{II} to form μ_3-oxo trinuclear complexes more commonly formed by *trivalent* first transition series metals. Protonation of the 3-aminomethyl group and formation of hydrogen bonds to the neighbouring phenolate O atom reduces the charge density provided by the NO_2^{2-} donor set of the salicylaldoximate to values more comparable with those provided by NO_2^{-} donor sets in β-iminoketonate ligands, which have already been shown to give μ_3-oxo trinuclear Cu^{II} complexes. Its variable-temperature magnetic susceptibility can be modeled by incorporating only intratriangle ($J = -68.89\ cm^{-1}$) and antisymmetric ($G_z = 12.77\ cm^{-1}$) exchange.

Experimental Section

General: Variable-temperature, solid-state direct current (dc) magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet on powdered microcrystalline samples embedded in eicosane. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities by using Pascal's constants. CCDC-743326 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. *N*,*N*′-Dimethyl-*N*,*N*′-hexamethylenebis(5-*tert*-butyl-2-hydroxy-3-hydroxyiminomethyl)benzylamine (**L**^{3}) was prepared as described elsewhere.[4]

$[Cu_6(L^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)](PF_6)_3$: A suspension of **L**^{3} (50.1 mg, 0.09 mmol) in MeOH (40 mL) was heated gently to ca. 40 °C at which time $Cu(OAc)_2{\cdot}H_2O$ (36.2 mg, 0.18 mmol) and $NaPF_6$ (15.2 mg, 0.09 mmol), dissolved in 10 mL and 4 mL of H_2O, respectively, were added. After 20 min, the bright green solution was cooled to room temp., and a dark green precipitate had formed. This mixture was stirred at room temp. overnight. The precipitate was then filtered off, washed with ice-cold MeOH and dried on air to give a light green powder (57 mg, 75.9%). HR-MS (ESI): m/z = 689.2284 $[Cu_6(L^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)]^{3+}$, 1033.3346 $[Cu_6(L^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)\text{-}H]^{2+}$, 1106.3211 $[Cu_6(L^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(PF_6)]^{2+}$. $C_{96}H_{145}Cu_6F_{18}N_{12}O_{14}P_3{\cdot}6H_2O$ (2615.51): calcd. C 44.08, H 6.05, N 6.43; found C 44.07, H 6.06, N 6.41. Crystals suitable for X-ray analysis were grown within one week by slow diffusion of Et_2O into an MeCN/EtOH (1:1) solution of the complex.

Supporting Information (see footnote on the first page of this article): Crystallographic details, selected bond lengths and packing diagram for $[Cu_6(L^3\text{-}2H)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)](PF_6)_3$.

Acknowledgments

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