Inorg. Chem. **2010**, *49*, 5350–5352
DOI: 10.1021/ic100594n

Inorganic Chemistry
Communication

Multidentate Ligands for the Synthesis of Multimetallic Complexes. 2. Formation of a Planar Cu_4OH Motif

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Received March 30, 2010

The reaction of the multidentate Schiff base species TrenSal, TrenBrSal, and TEtSal with copper acetate is reported. The heptadentate ligands generate a tetrametallic L_2Cu_4OH motif that contains an internalized hydroxide anion. In contrast, the hexadentate TEtSal ligand is found to form an open trimetallic motif. The importance of L_2Cu_4OH to the family of copper complexes with an endohedral hydroxide anion is discussed. [(TrenBrSal)$_2$Cu$_4$OH][OAc] is analyzed by temperature-dependent magnetic measurements.

We are studying the manner in which ligands support the formation of multimetallic complexes.[1] Our strategy uses flexible, multidentate, salicylidene, Schiff base ligands. These have been chosen for their ability to encapsulate metal cations in such a manner that the three terminal phenoxide donors assemble into a secondary binding motif. When divalent metals (e.g., Ni,[1g] Zn,[1g] Pb[1b]) are used, a charge imbalance between the encapsulated cation and the ligand is created, which leaves a residual charge on the complex. This facilitates the binding of an additional metal center between pairs of complexes. Significantly, there are no structurally characterized copper(II) complexes of this type of ligand. Because copper(II) has a marked preference for tetragonal and square-base-pyramidal geometries, we formed the opinion that when challenged with multidentate ligands such as [tris(2-hydroxybenzylidene)amino]ethylamine (TrenSal), it would display an alternative structural motif to that of nickel and zinc.

From the outset, the products of the reaction of TrenSal and [tris(2-hydroxy-5-bromobenzylidene)amino]ethylamine (TrenBrSal) with copper displayed mass spectrometric evidence that their complexes were not the same as those of nickel and zinc.[1g,2,3] An X-ray study of the Cu(TrenBrSal) complex confirmed the presence of a fourth metal and a bridging hydroxide ion (Figure 1), thus generating a novel triple-decker sandwich $[L_2M_4OH]^+$ motif. Salicylidene units operate in pairs to create planar motifs for two of the metal centers (Cu1 and Cu1*), which are incorporated into layers one and three. The remaining salicylidene along with the apical nitrogen (N2) of Tren forms the middle layer, again creating a planar environment for the metal. However, as a heptadentate ligand, the TrenSal units cannot satisfy the coordination demands of the coppers in the central layer and a water molecule is deprotonated to form an hydroxide bridge between Cu2 and Cu2*. The four coppers create a planar motif, with the bridging hydroxide sitting above the plane by 0.163 Å [∠Cu−OH−Cu* 171.1(9)°; ∠Cu···OH···Cu* 174.1 (6)°]. The coppers do not form a square but a parallelogram [∠Cu···Cu···Cu 112.69(2)° and 67.32(2)°] defined by two long [3.558(1) Å] and two short [3.544(1) Å] Cu···Cu distances. The nature of the core supports the formation of two formal bonds to the hydroxide [Cu2−O4

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(2) μ_2-Hydroxodi[[[tris(2-hydroxybenzylidene)amino]ethylamine copper] copper] acetate. Anal. Calcd for $C_{56}H_{58}N_8Cu_4O_9 \cdot 2H_2O$: C, 52.66; H, 4.89; N, 8.77. Found: C, 52.18; H, 4.81; N, 9.23. FTIR [ν/cm^{-1} (KBr)]: 1625 (C=N), 1535, 1450 (C=C), 1320 (C−O), 760 (aromatic). MS (EI; m/z): $[M]^+/[M - CuOH]^+/[M - CuOHSal]^+$ 1181 (100%), 998 (55%). λ_{max}(DMF, ε/dm^3 mol^{-1} cm^{-1}) 371 nm (14 100). μ_{eff}: 3.0 μ_B (300 K).

(3) μ_2-Hydroxodi[[[tris(2-hydroxy-5-bromobenzylidene)amino]ethylamine copper] copper] acetate. Anal. Calcd for $C_{56}H_{52}Br_6N_8Cu_4O_9$: C, 39.22; H, 3.06; N, 6.53. Found: C, 38.95; H, 3.34; N, 6.88. FTIR [ν/cm^{-1} (KBr)]: 1625 (C=N), 1455 (C=C), 815 (aromatic). MS (EI. m/z): $[M]^+$ 1654. λ_{max}-(DMF, ε/dm^3 mol^{-1} cm^{-1}): 377 nm (16 900). μ_{eff}: 2.8 μ_B (300 K). Crystal data: $[Cu_4L_2(OH)][MeCOO] \cdot 2DMF \cdot H_2O$: $C_{62}H_{68}Br_6Cu_4N_{10}O_{12}$, M = 1878.88, monoclinic, $P2_1/c$, a = 20.2739(4) Å, b = 12.8700(2) Å, c = 26.2491(6) Å, β = 98.759(1)°, V = 6769.2(2) Å^3, Z = 4, T = 123 K. Data measured with a Nonius Kappa CCD diffractometer (λ = 0.710 73 Å); 75 527 reflections, R_{int} = 0.1232. Final refinement to convergence was on F^2. R = 0.0543 (F, 7499 obsd data only) and R_w = 0.0982, all 13 282 data), GOF = 1.003, 851 refined parameters, residual electron density max and min 1.007 and −1.271 e Å^{-3}.

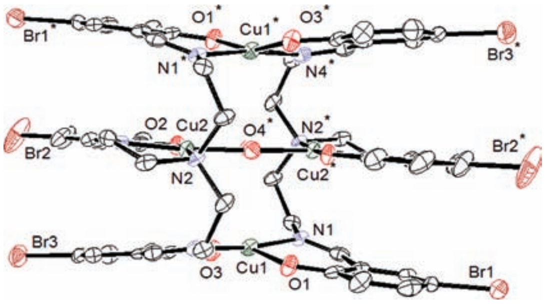

Figure 1. X-ray crystal structure of [(TrenBrSal)$_2$Cu$_4$OH][OAc].[3] The hydrogen atoms, acetate, and included solvent (DMF or H_2O) have been omitted for clarity. The central OH anion is disordered about a center of symmetry. This precludes finding the hydroxyl hydrogen atom. However, the presence of the OH group has been confirmed using bond valence sum analysis.[4] Other possible sites for this hydrogen atom have been considered and rejected on the basis of bond geometries (e.g., oxygen atoms of the ligand) and the lack of suitable hydrogen-bond acceptors. There are two independent half-molecules in the unit cell with slightly different metrical parameters. Values for only one of the molecules are given in the text. The thermal ellipsoids are shown at 50%.

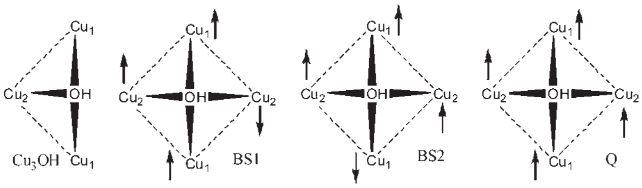

Figure 2. Schematic representation of the Cu$_3$OH and Cu$_4$OH motifs where the hydroxide adopts an unusually obtuse (> 145°) Cu−OH−Cu angle.[5] Three forms of the Cu$_4$OH motif are shown, identified by their respective spin states: two triplet forms (BS1 and BS2) and the quintet form (Q).

1.95(2) Å] with two longer interactions with the apical coppers [Cu1···O4 2.92(2) and 2.93(2) Å] in the layers above and below.

A small but significant number of [Cu$_n$OH] (n = 2−4) species that incorporate hydroxide ions with obtuse angles (∠Cu−OH−Cu > 145°) have been reported (Figure 2).[5] Sugiura et al. and Burkhardt et al. have prepared species that are essentially pyramidal in nature (∠Cu−OH−Cu 144−152°).[5a,b] McKee and Tandon[5c] have produced a series of closely related species using a macrocyclic ligand that enforces a planar motif on the Cu$_4$OH unit. The cavity in which the hydroxide sits is not completely symmetric, and although the ∠Cu−OH−Cu angles are all at 90° or 180°, there are two distinct Cu−OH distances (2.127 and 2.082 Å), indicating that there are primary and secondary Cu−OH interactions (cf. [(TrenBrSal)$_2$Cu$_4$OH]$^+$). A trimetallic species has been reported by Kuhn et al.[5d] In this system, a multidentate ligand is employed that initially assembles a Cu$_2$OH core to which a third copper associates. The hydroxide is roughly equidistant from the three coppers (Cu1−OH 2.171 Å; Cu2−OH 1.984 Å) and is raised above the plane of the three metals by 0.153 Å. In this case, the bridged hydroxide (∠Cu−OH−Cu 170.23°) is bisected by the third copper. A final complex in this series is the dimetallic Cu$_2$OH species reported by Harding et al. that displays the shortest Cu−OH distance (1.957 Å).[5e] Viewing the T-shaped and dimetallic species as multicopper complexes with missing vertices places them much closer in nature to that of McKee and Tandon and [(TrenBrSal)$_2$Cu$_4$OH]$^+$.

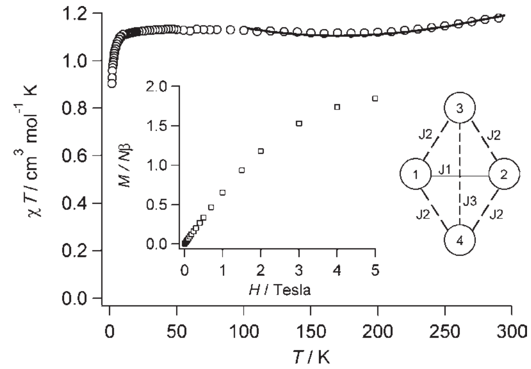

Figure 3. Temperature-dependent magnetic susceptibility of [(TrenBrSal)$_2$Cu$_4$OH][OAc]. The solid line represents a fit of the data in the range 290−100 K.[6] The inset shows magnetization versus the applied field at 2 K.

Only the complex reported by Burkhardt et al. has been subjected to extensive magnetochemical analysis. They report a χT value of 0.77 cm^3 K mol^{-1}, indicative of strong antiferromagnetic coupling within the Cu$_4$OH core. This is consistent with the earlier study by McKee and Tandon, who report that $\mu_{\rm eff}$ values of their Cu$_4$OH complexes (~1.3 μ_B at ambient temperature) are lower than expected for four isolated copper centers.[5c] The temperature-dependent magnetic behavior of [(TrenBrSal)$_2$Cu$_4$OH][OAc][6] is shown in Figure 3. The value of χT at 290 K is 1.19 cm^3 K mol^{-1}, which is lower than that expected for four noninteracting copper(II) centers (1.82 cm^3 mol^{-1} K for g = 2.2), indicating strong antiferromagnetic coupling. As the temperature is lowered, the value of χT decreases, reaching a shallow local minimum at around 160 K, consistent with the presence of competing exchange interactions. χT drops sharply below 10 K. The coupling scheme used to model the data was as follows: J_1 represents the Cu2−O4−Cu2* coupling, J_2 represents the Cu1−Cu2 interactions, and J_3 represents the Cu1−Cu1* interaction. For the data above 100 K, it was possible to model the data using only two J parameters (J_2 = 0): g = 2.22; J_1 = −346 cm^{-1}; J_2 = 0 cm^{-1}; J_3 = +39 cm^{-1}.[6] The value of J_1 is consistent with that (−440 cm^{-1}) reported by Harding et al. for the related linear Cu$_2$OH complex.[5e] Given the Cu1−Cu1* separation, the magnitude of J_3 is perhaps surprising, although this competing interaction is required to reproduce the local minimum in χT. Entering these J values into MAGPACK reveals an S=1 ground state for the complex.

Density functional theory (DFT) calculations were conducted on both [(TrenBrSal)$_2$Cu$_4$OH]$^+$ and a simplified model, which represent the complex in its singlet, triplet, and quintet forms using a range of functional and basis sets (Table 1). The relative energies of these single-point calculations on [(TrenBrSal)$_2$Cu$_4$OH]$^+$ indicate that the quintet and triplet forms are of equal energy but that the singlet form is less favorable. Furthermore, there is significant spin contamination (S^2) of the triplet state, which is attributed to intrusion of the quintet state.

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(6) Direct current magnetic measurements were carried out using a Quantum Design MPMS-XL SQUID magnetometer in a field of 10 kOe. $\hat{H} = -2J_1(\hat{S}_1\hat{S}_2) - 2J_2(\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4 + \hat{S}_1\hat{S}_4) - 2J_3(\hat{S}_3\hat{S}_4)$.

Table 1. DFT Calculations on $[(\text{TrenBrSal})_2\text{Cu}_4\text{OH}]^+$ and a Simplified Model (M06-L/ecp1)[a]

	singlet[b]	triplet[b]	quintet[b]
BP86/6-31G*		−25 045.050 989, $S^2 = 2.003$	−25 045.051 163, $S^2 = 6.006$
BLYP/6-31G*		−25 041.772 036, $S^2 = 2.755$	−25 041.766 763, $S^2 = 6.006$
B3LYP/6-31G*	−25 042.648 290	−25 042.767 260, $S^2 = 3.009$	−25 042.767 256, $S^2 = 6.009$
B3LYP/ecp2[c]	−3 920.798 867	−3920.917 828, $S^2 = 3.012$	−3920.917 822, $S^2 = 6.011$
M06-L/ecp1[d]		−2922.951 254, $S^2 = 3.011$	−2922.951 279, $S^2 = 6.012$

[a] For the model the aryl rings have been replaced by an aliphatic chain. The model compound has been geometry optimized. [b] Energies in hartrees. [c] ecp2, basis set 6-31G* for all atoms except bromine and copper. [d] ecp1, basis set 6-31G* for all atoms except copper.

By extending the analysis by applying broken-symmetry calculations to the simplified model compound at the HF/ecp1 level of theory, we were able to demonstrate that one of the triplet states (BS1; Figure 2) was of lower energy than the quintet state (Q) and the triplet state, where the spins on Cu2 and Cu2* are parallel (BS2; Figure 2). Within this solution, it is possible to confirm the presence of superexchange between Cu2 and Cu2* via the OH group, which is an integral component of the magnetochemical analysis (Table 2).

Table 2. Broken-Symmetry Calculations on a Simplified Model of $[(\text{TrenBrSal})_2\text{Cu}_4\text{OH}]^+$ at the HF/ecp1 Level of Theory[a]

	total energy	spin density Cu1	spin density Cu2
singlet	−2904.890 523 105 716		
triplet BS1	−2905.570 999 712	0.880 38	0.872 37
		0.880 55	−0.879 12
triplet BS2	−2905.407 360 387	0.834 55	0.872 88
		−0.883 00	0.008 48
quintet	−2905.575 036 701	0.979 08	0.985 44
		0.879 00	0.875 86

[a] The spin density on Cu1 for the BS2 model is inconsistent with magnetic analysis.

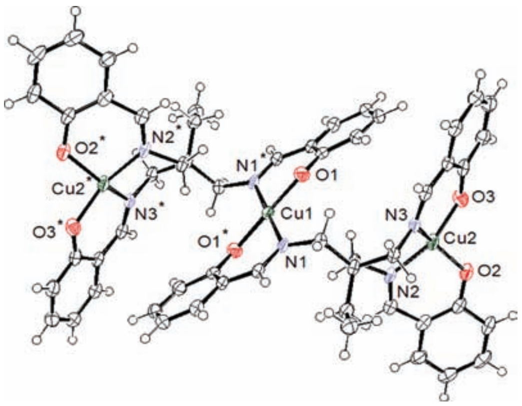

Figure 4. X-ray crystal structure of $[(\text{TEtSal})_2\text{Cu}_3]$. There are two independent half-molecules in the unit cell. Thermal ellipsoids are shown at 50%.

In an attempt to interrogate the behavior of multidentate ligands with copper, we synthesized [tris(2-hydroxybenzylidene)amino]methylpropane (TEtSal).[7] This ligand system lacks an apical nitrogen donor and was expected to enforce either an adamantyl or cyclohexyl motif around the metal and the internal N_3 tripodal cap. The copper complex of TEtSal[8] is found to adopt an open trimetallic motif where pairs of ligands are used to generate three tetradentate motifs instead of encapsulating the metal in a hexadentate manner (Figure 4). This structure is again driven by copper's preference for a planar four-coordinate environment similar to that found in the simple tetradentate Schiff base complexes.[9] Indeed, the metrical parameters of the binding sites of Cu2 are consistent with those reported for Cu(Salpr), which also employs a propylene chain to separate the two imine donors.[9] The central copper (Cu1) being chelated by two didentate ligands is, however, unique. The absence of a bridging polymethylene chain allows the oxygen and nitrogen donors to adopt positions trans to one another (cf. Cu2) in a motif that is also more planar (∠O−Cu−O and ∠N−Cu−N 180°) than is found for the N_2O_2 binding motif at Cu2 [∠O−Cu−N 147.2(1)° and 155.8(1)°]. The observed room temperature magnetic moment of this material was found to be 1.39 μ_B, which is lower than what might be predicted by the spin-only formula species. However, it is consistent with data retrieved from other dimetallic CuN_2O_2 Schiff base species and is indicative of some coupling between adjacent coppers in the motif.[10]

We adopted TrenSal and TEtSal as ligands in the hope that it might generate an encapsulating motif for copper similar to that found for $[\text{Ni}_3\text{TrenSal}_2]$.[1] However, it would seem that the structure adopted by these species is driven by both the articulation at the apical linking atom and the geometric preference of the metal. Thus, for TrenSal, rather than obtain a simple trimetallic system, a more complex tetrametallic system has been isolated. This intriguing motif is another member of a rare series of Cu_4OH moieties that have importance in the magnetic and computational analysis of multimetallic copper species.

Acknowledgment. A.M. expresses his gratitude to the Nigerian government for financial assistance. J.R. acknowledges the EPSRC national services at Southampton (X-ray crystallography). J.R. and M.M. also thank the Synergy fund.

Supporting Information Available: X-ray crystallograhic data in CIF format, details of the synthesis, crystallography, magnetic measurements, and output of the theoretical calculations of $[(\text{TrenSal})_2\text{Cu}_4\text{OH}]^+$ and its simplified model. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Di[[[(2-hydroxybenzylidene)amino]methyl]propane copper]-*trans-N*,*N*,*O*,*O*-copper. Anal. Calcd for $C_{54}H_{52}N_6Cu_3O_6 \cdot 3H_2O$. C, 57.62; H, 5.19; N, 7.46. Found: C, 57.71; H, 3.37; N, 7.31. FTIR [ν/cm^{-1} (KBr)]: 1620 (C=N), 1445 (C=C), 1150 (C−O), 755 (aromatic). λ_{max}(solid): 600 nm. λ_{max}(MeCN): 370 nm ($\varepsilon = 2.37 \times 10^{-4}$ M^{-1} cm^{-1}). μ_{eff}: 1.39 μ_B (300 K). EPR: X band, 120 K, 9.4 GHz, 3250, 1550 G, $g \sim 4.2$. Crystal data: $[\text{Cu}_3\text{L}_2]\cdot 2.82\text{H}_2\text{O}$: $C_{54}H_{57.65}Cu_3N_6O_{8.82}$, $M = 1122.53$, triclinic, $P\bar{1}$, $a = 12.0221(7)$ Å, $b = 13.1610(7)$ Å, $c = 16.4888(9)$ Å, $\alpha = 77.887(3)°$, $\beta = 86.083(3)°$, $\gamma = 85.517(3)°$, $V = 2539.4(2)$ Å^3, $Z = 2$, $T = 120$ K. Data collected at Station 9.8 of the Daresbury SRS ($\lambda = 0.6911$ Å); 19 122 reflections, $R_{int} = 0.0510$. Final refinement (Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany) to convergence was on F^2. $R = 0.0487$ (F, 6863 obsd data only) and $R_w = 0.0703$, all 9185 data), GOF = 1.029, 671 refined parameters, residual electron density max and min 0.911 and −0.525 e Å^{-3}.

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