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Structural and magnetic investigations on new molecular quantum rings

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Abstract

We report on a comparative investigation of the structural and magnetic properties of three oxygen-bridged polynuclear ($N = 6, 8, 10$) Cu(II) cyclomethylsiloxanolate complexes, $\text{Cu}_6[(\text{MeSiO}_2)_6]_2 \cdot 6\text{DMF}$ (**1**), $\{\text{Cu}_8[(\text{MeSiO}_2)_8]_2 \cdot 8\text{DMF}\} \cdot \text{EtOH}$ (**2**) and $\{\text{Cu}_{10}[(\text{MeSiO}_2)_{10}]_2 \cdot 10\text{DMF}\} \cdot 6\text{DMF}$ (**3**). All three molecular complexes have a planar ring-shaped configuration of the copper $S = 1/2$ spins. The analysis of the magnetic data, with particular emphasis placed on the high-temperature behaviour, together with the structural information enables us to correlate the evolution of the exchange coupling J between the magnetic $S = 1/2$ centers of the quantum ring as a function of the number N of magnetic sites to the structural changes of the molecular crystals. **To cite this article:** Volodymyr Pashchenko et al., *C. R. Chimie* 10 (2007).

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1. Introduction and structural aspects

The synthesis of new magnetic clusters with unprecedented spin topologies is a central topic in the field of molecular magnetism. Among the various strategies that have been developed, the design of molecules containing quantum rings with different values of the spin S and numbers N of magnetic sites represents an interesting approach [1].

In the previously reported ring-shaped molecular complex $\text{Cu}_6[(\text{PhSiO}_2)_6]_2 \cdot 6\text{EtOH}$ [1], it was demonstrated that the six copper ions within the ring are ferromagnetically coupled [$2J/k_B = -60$ K, cf. Eq. (1)] with a total spin $S_{\text{tot}} = 3$ ground state. In order to study in more detail the mechanisms leading to the formation of a high-spin ground state and the influence of the various radicals R or ligand groups of the molecule on the magnetic behaviour of the quantum ring, we have attempted to expand the existing class of molecular magnets by synthesizing new isostructural molecular complexes.

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Recently, a large series of copper-containing siloxanolate complexes $\{\text{Cu}_N(\text{RSiO}_2)_N\}_2 \cdot N(\text{ligand})$ ($N = 6, 8, 10$; $R = \text{Et, Ph, Me, \dots}$; $\text{ligand} = \text{EtOH, DMF, \dots}$) having a sandwich-like molecular structure has been obtained [1,2]. Here we report on the structural and magnetic properties of three representatives of the methyl family: oxygen-bridged polynuclear ($N = 6, 8, 10$) Cu(II) cyclomethylsiloxanolate complexes, $\text{Cu}_6[(\text{MeSiO}_2)_6]_2 \cdot 6\text{DMF}$ (**1**), $\{\text{Cu}_8[(\text{MeSiO}_2)_8]_2 \cdot 8\text{DMF}\} \cdot \text{EtOH}$ (**2**) and $\{\text{Cu}_{10}[(\text{MeSiO}_2)_{10}]_2 \cdot 10\text{DMF}\} \cdot 6\text{DMF}$ (**3**). Compound **1** crystallizes in the monoclinic system, space group $P1\ 2_1/n1$ (No. 14), empirical formula $[\text{C}_{30}\text{H}_{78}\text{Cu}_6\text{N}_6\text{O}_{30}\text{Si}_{12}]$, with $a = 13.3683(14)\ \text{\AA}$, $b = 15.388(2)\ \text{\AA}$, $c = 17.4383(14)\ \text{\AA}$, $\beta = 98.88(7)^\circ$, and $Z = 2$; compound **2** – monoclinic system, space group $P2_1/c$ (No. 14), empirical formula $[\text{C}_{42}\text{H}_{110}\text{Cu}_8\text{N}_8\text{O}_{41}\text{Si}_{16}]$, with $a = 18.710(5)\ \text{\AA}$, $b = 19.936(5)\ \text{\AA}$, $c = 28.837(7)\ \text{\AA}$, $\beta = 90.2(6)^\circ$, and $Z = 4$; compound **3** – monoclinic system, space group $P1\ 2_1/n1$ (No. 14), empirical formula $[\text{C}_{68}\text{H}_{172}\text{Cu}_{10}\text{N}_{16}\text{O}_{56}\text{Si}_{20}]$, with $a = 18.028(2)\ \text{\AA}$, $b = 18.856(3)\ \text{\AA}$, $c = 21.249(3)\ \text{\AA}$, $\beta = 103.54(5)^\circ$, and $Z = 2$. All details of the synthesis and the single-crystal X-ray analysis will be published elsewhere [2]. These cluster compounds are distinct in that all three of them exhibit a very similar molecular structure consisting of rings of $N = 6, 8$ or 10 Cu(II) atoms sandwiched by two N -membered cyclomethylsiloxanolate ligands (see Figs. 1 and 2). The methyl group, attached to each of the $2N$ Si atoms, points away from the molecule. Within the rings, adjacent Cu^{2+} ions are linked by pairs of siloxanolate oxygen atoms which

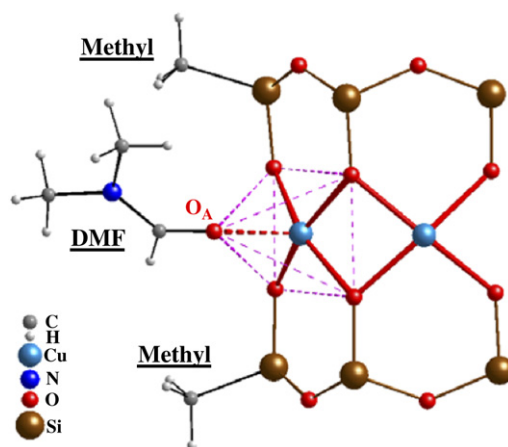


Fig. 2. A fragment representing the main building blocks of the molecular ring structure, typical for all three complexes. Only two methyl groups and one DMF molecule are shown for clarity. The square-pyramidal configuration of Cu(II) atoms arises from the apical bonding (O_A) with solvent.

provide the magnetic exchange path for the Cu(II) $S = 1/2$ spins. These equatorial Cu–O bonds in **1**, **2** and **3** vary in the range of $1.928\text{--}1.985\ \text{\AA}$ (av. $1.957\ \text{\AA}$ for **1**; av. $1.951\ \text{\AA}$ for **2**; av. $1.960\ \text{\AA}$ for **3**), which is close to the expected values for copper atoms with a square-pyramidal coordination environment. The Cu–O–Cu angles, which mainly determine the magnetochemical behaviour of the polynuclear clusters, in **1**, **2** and **3** vary in the range $91.2\text{--}97.7^\circ$, which is typical for other copper-containing organosiloxanes. The average value of the Cu–O–Cu angle is about 93.02° for **1**, 95.26° for **2** and

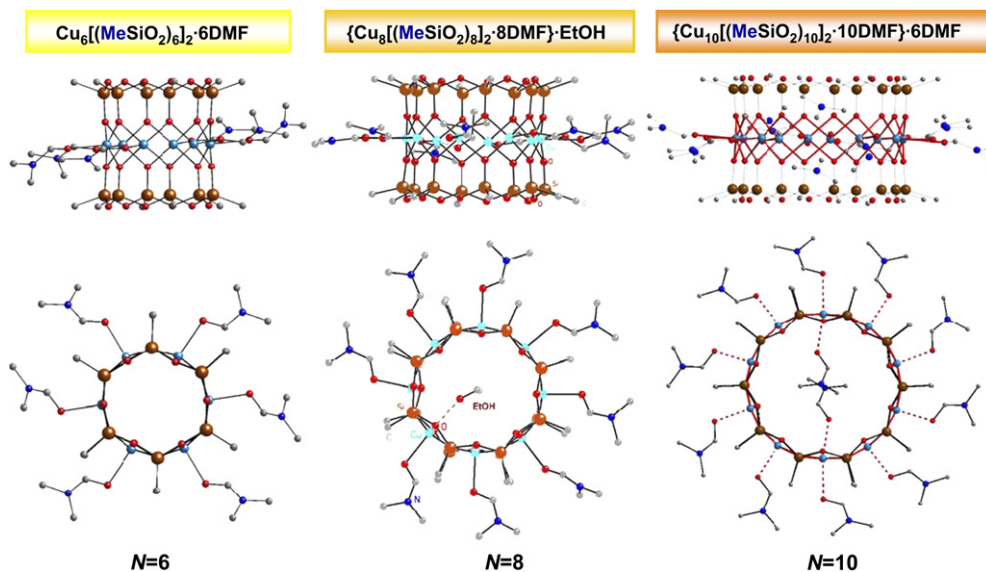


Fig. 1. Side view (upper row) and top view (lower row) of the molecular structure of three ring-shaped polynuclear Cu(II) cyclomethylsiloxanolate complexes. Hydrogen atoms are omitted for clarity.

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