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Structural and magnetic investigations on new molecular quantum rings

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Received 21 March 2006; accepted after revision 9 June 2006

Available online 18 December 2006

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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Keywords: Copper; Cluster compounds; Sandwich complexes; Magnetic properties

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 $\{\text{Cu}_N[(\text{RSiO}_2)_N]_2\} \cdot N(\text{ligand})$ ($N = 6, 8, 10$; $R = \text{Et, Ph, Me, \dots}$; ligand = EtOH, DMF, ...) 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

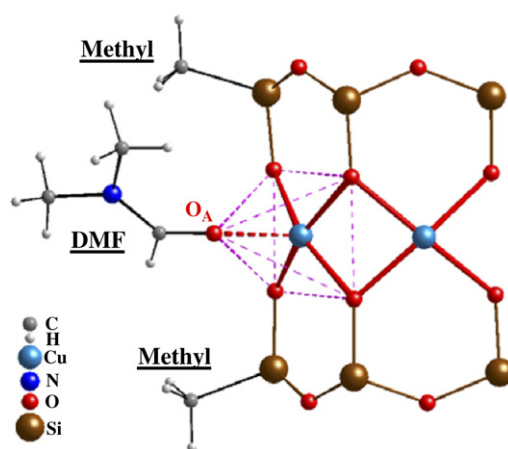


Fig. 2. A fragment representing the main building blocks of the molecular ring structure, typical for all three complexes. Only two methyl groups and one DMF molecule are shown for clarity. The square-pyramidal configuration of Cu(II) atoms arises from the apical bonding (O_A) with solvent.

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

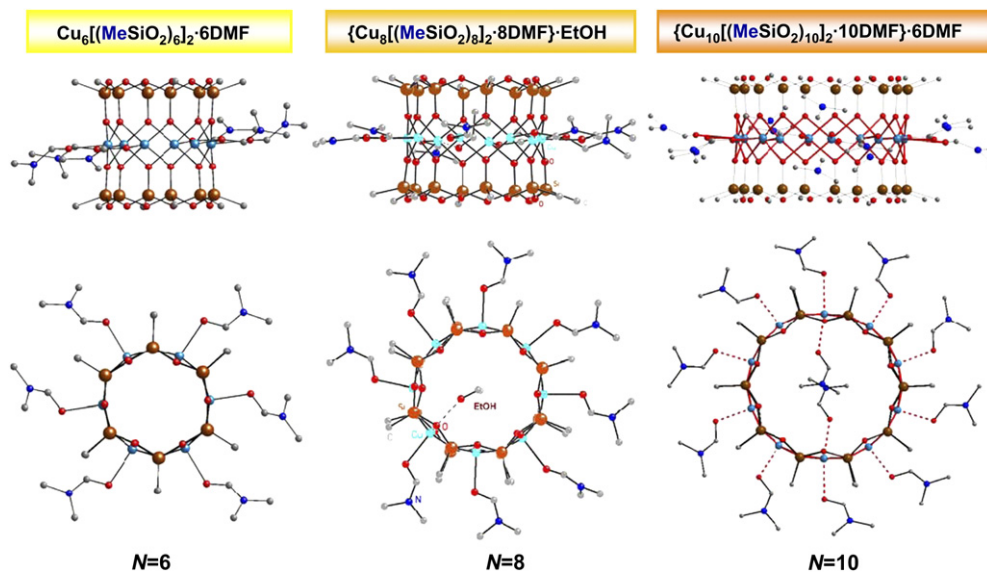


Fig. 1. Side view (upper row) and top view (lower row) of the molecular structure of three ring-shaped polynuclear Cu(II) cyclomethylsiloxanolate complexes. Hydrogen atoms are omitted for clarity.

96.50° for **3**. The coordination environment of the copper atoms is a slightly distorted oxygen square-pyramidal configuration. The apical positions of all copper polyhedra in **1**, **2** and **3** are occupied by DMF oxygen atoms and the Cu–O_A bonds are always significantly longer than the equatorial Cu–O distances. The Cu–O_A bonds vary in the range of 2.231–2.372 Å (av. 2.273 Å for **1**; av. 2.303 Å for **2**; av. 2.362 Å for **3**). Thus, the methyl family offers the possibility to study the evolution of the static and dynamic magnetic properties of molecular quantum rings upon increasing the number of magnetic sites from $N = 6$ to 8 and to 10. It should be noted that there is only one structural difference observed for the present methyl family: one additional molecule of the EtOH solvent is present inside the molecular skeleton for complex **2**; and two additional DMF solvent molecules are located inside the molecule for complex **3**, cf. Fig. 1.

A detailed analysis of the magnetic properties, in particular at high temperatures, reveals a strong ferromagnetic Cu–Cu exchange interaction ($2J/k_B = -50.4$ K) for the $N = 6$ compound with an $S = 3$ high-spin ground state, a moderately strong ferromagnetic interaction ($2J/k_B = -27.6$ K) for $N = 8$, and an antiferromagnetic interaction ($2J/k_B = +17.2$ K) with a non-magnetic $S = 0$ ground state for $N = 10$. These results, together with structural data enabled us to correlate structural parameters, such as the average Cu–Cu distance, the average Cu–O–Cu bridging angle and the average diameter of the molecular rings, with the sign and strength of the magnetic exchange coupling J , cf. Table 1.

2. Experiment

The X-ray diffraction measurements were performed employing a Smart CCD diffractometer (Mo $K\alpha$ -radiation, graphite-monochromator, ω -scan technique). The structure was solved by direct methods and refined by full-matrix least-squares against F^2 in the anisotropic (H-atoms isotropic) approximation, using the SHELXTL-97 package [3]. Variable-temperature magnetic susceptibility measurements in the temperature range 2–350 K and magnetic fields up to 5 T were carried out using a Quantum Design SQUID magnetometer

MPMS-XL. These measurements were complemented by isothermal magnetization runs at temperatures between 2 and 250 K for fields up to 5 T. All magnetic measurements were performed on polycrystalline samples of **1**, **2** and **3**.

3. Energy spectrum

Heisenberg rings with $S = 1/2$ have been investigated extensively in the past [4–8]. For an isotropic nearest neighbour exchange interaction, the model is exactly soluble, and the energy spectrum as well as the thermodynamics can, in principle, be calculated using Bethe ansatz techniques [4]. For small rings up to $N = 7$, the complete set of eigenstates can also be obtained from more elementary symmetry considerations [7]. Yet, a more realistic model of the materials under investigation would include perturbations away from this soluble limit. In particular, anisotropies in the exchange couplings and the local g -tensors could be important. Furthermore, inhomogeneous local environments of the magnetic centers might lead to a deformation of the exchange bridges and thus to site-dependent exchange couplings. Possibly, there also exist exchange paths for next nearest neighbour interactions. For an understanding of the influence of these perturbations on the energy spectrum, a complete numerical diagonalization and a comparison with detailed thermodynamic and spectroscopic measurements would be desirable.

In the search for a minimal model, one can try for the present to ignore these complications. Assuming only nearest neighbour interactions, the simplest exchange Hamiltonian of a ring of N spin $S = 1/2$ objects with a cyclic boundary condition $S_{N+1} = S_1$, takes the form

$$H = 2J \sum_{i=1}^N \left(S_i \cdot S_{i+1} + \frac{1}{4} \right). \quad (1)$$

This way of writing the exchange interaction is convenient for spin $S = 1/2$, since $P_{ij} = 2(S_i \cdot S_j + 1/4)$ then acts as a permutation operator of the spin states on sites i and j . The states with full ferromagnetic alignment and a total spin of $S_{\text{tot}} = S_{\text{max}} = N/2$ have the energy $E_{\text{FM}} = JN$ and delimit the spectrum on one side, whereas

Table 1
Comparison of the structural and magnetic parameters of polynuclear Cu(II) complexes

	(Cu–Cu) distances, Å	(Cu–O–Cu) angle	(Diameter), Å	$\langle 2J/k_B \rangle$, K
{Cu ₆ [(PhSiO ₂) ₆] ₂ ·6EtOH}	2.807	92.25°	5.614	–60 (FM)
{Cu ₆ [(MeSiO ₂) ₆] ₂ ·6DMF}	2.839	93.02°	5.677	–50.4 (FM)
{Cu ₈ [(MeSiO ₂) ₈] ₂ ·8DMF}·EtOH	2.882	95.26°	7.575	–27.6 (FM)
{Cu ₁₀ [(MeSiO ₂) ₁₀] ₂ ·10DMF}·6DMF	2.911	96.50°	9.410	+17.2 (AFM)

Data for Cu₆[(PhSiO₂)₆]₂·6EtOH have been taken from literature [1].

the other boundary of the spectrum is given by the energy E_{AFM} of the antiferromagnetic state with $S_{\text{tot}} = 0$. The total width of the spectrum is equal to $|(E_{\text{FM}} - E_{\text{AFM}})/J| = 8.60555$ for $N = 6$, and $|(E_{\text{FM}} - E_{\text{AFM}})/J| = 11.3022$ for $N = 8$ [5]. For a ferromagnetic exchange interaction $J < 0$, the first low-lying states are single-magnon excitations with a finite energy gap of $\Delta = 2|J| \cdot [1 - \cos(2\pi/N)]$ above the high-spin ground state with $S_{\text{tot}} = S_{\text{max}}$. For $N = 6$ and $N = 8$, this yields $\Delta/|J| = 1$ and $\Delta/|J| = (2 - \sqrt{2}) = 0.5858$, respectively. For temperatures below Δ , higher energy levels are frozen out and the magnetic system behaves as a large single spin with $S = S_{\text{tot}}$. Consequently, the temperature dependence of χT should exhibit a characteristic plateau of width $\Delta/2$ at $\chi T|_{T \rightarrow 0} = (N_A \mu_B^2 g^2)/k_B \cdot S_{\text{max}}(S_{\text{max}} + 1)/3$. For high temperatures T the effective moment decreases, and for T much larger than the total width of the spectrum, the individual spins are independent leading to an asymptotic value of $\chi T|_{T \rightarrow \infty} = (N_A \mu_B^2 g^2)/k_B \cdot N/4$. For an antiferromagnetic exchange interaction, the high-temperature asymptotic value of χT is identical to the ferromagnetic case, whereas χT decreases at lower temperature and shows a plateau at $\chi T|_{T \rightarrow 0} = 0$, the width of which is also determined by a finite-size gap.

Fig. 3 shows the experimental susceptibility data for the three different complexes. Complexes **1** and **2** exhibit a pronounced ferromagnetic behaviour at high temperatures with an increase of the effective magnetic moment upon cooling. This contrasts with the magnetic behaviour of complex **3**, where the effective magnetic moment decreases all the way below room temperature indicating an antiferromagnetic exchange interaction. For compounds **1** and **3**, we thus conclude that the molecular ground state is a high-spin state with $S_{\text{tot}} = 3$ for $N = 6$

and a non-magnetic state with $S_{\text{tot}} = 0$ for $N = 10$. On the contrary, the magnetic behaviour of compound **2** appears to be more complex showing an unusual behaviour below 20 K: while the high-temperature analysis of the data clearly reveals a ferromagnetic character of the magnetic interactions, the decrease of χT below 20 K seems to indicate the presence of significant antiferromagnetic correlations. Apparently, the energy spectrum for compound **2** is markedly different from that of a simple idealized homogeneous quantum ring. Thus, our data do not provide experimental evidence of a high-spin $S = 4$ ground state for compound **2** with $N = 8$.

Furthermore, a closer look at the susceptibility data in Fig. 3 reveals that χT does not show a low-temperature plateau for the six-membered ring either, although the low-temperature magnetization $M(H)$ is satisfactorily described by a Brillouin function with $S = 3$. Because of the large distances between the molecules in the crystal, we believe that the absence of a plateau in χT cannot be explained by intermolecular interactions. More likely causes of this unusual behaviour are either an effective crystal zero-field splitting of the ground-state spin S_{max} multiplet or significant site-dependent variations of the exchange interactions due to deformations of the ring geometry. Such inhomogeneities can lead to a reduction of the magnon gap, but do not affect the value of the effective moment χT for $T \rightarrow 0$, since the ground state is still given by the fully ferromagnetically polarized states with $S_{\text{tot}} = S_{\text{max}}$. On the contrary, an effective zero-field splitting reduces the degeneracy of the ground state and can also lead to an increase of $\chi T|_{T \rightarrow 0}$.

In order to obtain information on the splitting of the low-lying states, we have recorded ESR spectra for the

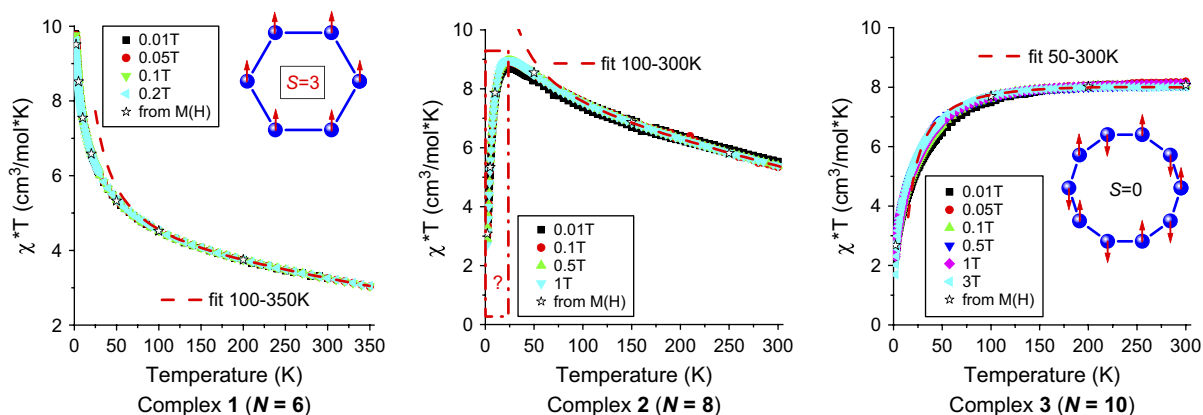


Fig. 3. Effective magnetic moment χT as a function of temperature T for three polynuclear Cu(II) cyclomethylsiloxanolate complexes. Symbols correspond to the raw magnetic data collected at various applied magnetic fields in the range 0.01–3T. Star symbols denote the susceptibility data extracted from isothermal magnetization measurements. The dashed lines are fits to the high-temperature approximation in Eq. (3) with the parameter J given in the text.

methyl family compounds at a temperature of $T = 1.5$ K. In the frequency range 26–134 GHz, the frequency-field dependences of the resonance absorptions exhibit a gap at zero field suggesting that two levels are separated by 25–30 GHz for all three compounds. This would correspond to a zero-field splitting parameter D of the order of 1 K. This value is not surprising insofar as similar axial magnetic anisotropies for effective high-spin ground states have also been reported for other compounds [1,5]. On the level of the microscopic Hamiltonian in Eq. (1), anisotropies would need to be included as anisotropic exchange terms and g -tensors, since a single-ion anisotropy term is not possible for spins with $S = 1/2$. The coordination of the copper ions in the rings suggests that the main axes of the local g -tensors point outwards in the radial direction. How such local anisotropies can lead to an effective zero-field splitting D is an interesting open question. In principle, one might hope to extract information on the local g -tensors from ESR measurements at higher temperatures. Yet, the ESR spectra at room temperature are still strongly exchange- and angular-averaged and the g -tensor is related more to the lattice as a whole than to the individual magnetic centers. At high temperatures $T \gg |J/k_B|$, ESR measurements for all members of the present methyl family reveal the same average g -factor for copper Cu^{2+} of $g = 2.09$. It should be noted that the knowledge of the molecular g -tensor could provide, in principle, interesting information on the nature of the N -coupled ring state, especially if it is possible to correlate this molecular tensor obtained at low temperatures with the N individual local g -tensors.

The structural data of the present methyl family also provide some indications in favor of inhomogeneities of the exchange couplings. The copper atoms in the rings have a strictly planar configuration with an average square-root deviation from the plane of the order of $\delta = 0.0002$ Å (for $N = 6$); $\delta = 0.0006$ Å (for $N = 8$) and $\delta = 0.0013$ Å (for $N = 10$). This makes it easy to find out small structural deformations of the symmetry of the ring as a whole by comparing the distances between the nearest neighbour copper positions within the plane. For the ring-shaped complexes **1** and **3** with $N = 6$ and $N = 10$, respectively, we have found three and five pairs with identical distances between the copper atoms in the range 2.8113–2.8613 Å (an average value of about 2.839 Å) and 2.8696–2.9301 Å (av. 2.911 Å), respectively. In the case of compound **2** ($N = 8$) all Cu–Cu distances are non-equivalent and lie in the range 2.8371–2.9116 Å, yielding an average value of about 2.882 Å. The marked variations for compound **2** could be important in explaining the unexpected feature of χT below 20 K. For relatively weak

average exchange interactions within the molecule, slight changes in the copper–copper distances might have a significant effect on the strength of the exchange couplings and one might also speculate about variations of the distances as a function of temperature by a dynamical coupling of the spin system to lattice distortions [9]. On the basis of the comparison of the experimental data for the three complexes at low temperatures, we note that, probably, the ferromagnetically coupled ring with $N = 8$ with a rather weak amplitude of the exchange interaction is most sensitive to inhomogeneities in the exchange interaction.

4. High-temperature approximation

From the discussion of the magnetic properties in Section 3, we expect that a composite analysis is useful for treating “low-” and “high-temperature” regions separately. For low temperatures, the details of the energy spectrum are important and for the optimization of the magnetic model it would be very useful to obtain direct experimental information about the splitting of the low-lying energy levels. This can be obtained, for example, from spectroscopic investigations on single crystals. We are currently trying to solve this problem by restoring the level structure experimentally. At high temperatures, the level splitting is not visible any longer and the effects of a crystal field (a magnetic anisotropy of the molecule as a whole) or of inhomogeneities of the exchange couplings within the ring can be neglected. The magnetic properties are then only sensitive to average values of the microscopic parameters. This fact can be explored to estimate the order of magnitude of the average exchange coupling J .

To obtain an estimate of J , we can use an expansion of the magnetic quantities in powers of J/T , where from now on, J denotes the average exchange interaction within the ring. To this end, we start from the partition function

$$Z = \text{tr} \left[e^{-H/k_B T} \right], \quad (2)$$

and expand the exponential in the trace in a power series. Taking appropriate derivatives with respect to the temperature and the magnetic field, series expansions for all thermodynamic quantities can be obtained. For the susceptibility, the first terms for $S = 1/2$ are given by (see also Ref. [10])

$$T\chi|_{h=0} = \frac{N_A \mu_B^2 g^2 N}{k_B} \left\{ 1 - \frac{J}{T} + O\left(\frac{J^3}{T^3}\right) \right\}. \quad (3)$$

We have compared this high-temperature approximation with results of a complete numerical diagonalization for spin $S = 1/2$ rings with $N = 6, 8, 10$ and conclude that Eq. (3) is in satisfactory agreement with the exact solution for temperatures above $3J$.

Fig. 3 shows fits of the high-temperature approximation in Eq. (3) to the experimental susceptibility data in the high-temperature region. The range of the temperature interval for the fit is chosen as wide as possible, but compatible with the requirement $T \geq 3J$ mentioned above. Since the magnetic data presented in Fig. 3 are not yet corrected for a temperature-independent contribution χ_{TIP} resulting from a diamagnetic core contribution from the sample and a signal from the sample holder, these contributions have been accounted for by including an additional fitting parameter together with the parameter J . As the nearest oxygen environment of the copper atoms has a similar square-pyramidal configuration for all three complexes, we have assumed that the average spectroscopic g -factor for the local Cu^{2+} centers is fixed and equal to $g = 2.09$. It should be noted that the presence of a χ_{TIP} comparable with the magnitude of the susceptibility of the spin system may significantly affect the total temperature dependence of χT in the high-temperature region. The estimates for the exchange coupling J obtained from the fits are shown in Table 1 together with important structural parameters of the rings.

There is a well-known relationship between the singlet–triplet splitting (or the magnitude and sign of the exchange integral $2J$) and the Cu–O–Cu bridging angle for the simple case of dihydroxo-bridged copper(II) dimers. According to the empirical works by Hatfield and Hodgson, there is a linear relation between the Cu–O–Cu bridging angle (as the Cu–Cu distance) within the Cu–O₂–Cu group and the value of exchange parameter $2J$ for this class of materials [11]. Two critical structural parameters, such as a critical Cu–O–Cu bridging angle of 97.5° and a critical Cu–Cu distance of 2.888 \AA , can be defined, which characterize the change of sign in the magnetic interaction. Given a fixed Cu–O bond length, these critical parameters are strictly connected to each other by geometry.

In analogy to the above-mentioned dimer system, we attempt to correlate the structural and magnetic properties (cf. Table 1) of the present methyl family, containing similar Cu–O₂–Cu block as the main exchange path between the magnetic centers. For this purpose we have chosen the following three structural parameters: the average Cu–Cu distance, the average Cu–O–Cu bridging angle and the average diameter of the molecule (defined as the diameter of a circle going

through all N copper sites). It should be noted that the average diameter of the molecule is determined by the average Cu–Cu distance and the number N of Cu sites forming the ring. In a first approach, using the average values of distances and angles, we have neglected the existing distortions of the Cu–O₂–Cu groups producing the anisotropy of the exchange couplings within the ring and the distortions from planar geometry at the metal center, which also influence the magnitude of J . We have also assumed that the possible influence from the methyl groups and the DMF solvents on the magnetic coupling strength is identical (or negligible) for all three complexes **1**, **2** and **3**. Finally, it is necessary to notice that the parameter of exchange interaction, obtained from the high-temperature approximation, does not contain any information about the local site-dependent configuration of the magnetic interactions and simply reflects only an average value of these magnetic interactions within the ring.

The structural and magnetic parameters of the polynuclear Cu(II) cyclasiloxanolate complexes listed in Table 1 clearly demonstrate a systematic change of the exchange coupling J with the structural changes of the molecule. For a crude estimate of the critical structural parameters for the methyl rings a linear approximation is used yielding: a critical Cu–Cu distance about of 2.903 \AA , a critical Cu–O–Cu bridging angle of 96.04° and a critical diameter of the molecule of 8.686 \AA . We can consider the fair agreement of these critical parameters with those reported by Hatfield and Hodgson as an indication of the similarity of the methylsiloxanolate bridge for the N -membered rings to the dihydroxo bridge for the simplest dimers.

5. Conclusion

We have studied the structural and magnetic properties of three oxygen-bridged polynuclear Cu(II) ($N = 6, 8, 10$) 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 complexes have a ring-shaped configuration of the copper $S = 1/2$ spins. For compounds **1** and **3**, the molecular ground state has been identified as a high-spin $S = 3$ state and a non-magnetic $S = 0$ state, respectively. The analysis of the magnetic data, together with the structural information, has enabled 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 (see Table 1). Our analysis reveals indications that structure-related

inhomogeneities of the exchange couplings may have a significant influence on the low-temperature magnetic behaviour of the $N = 8$ compound **2** with a rather weak amplitude (compared with the effect of distortions) of ferromagnetic exchange interaction.

References

- [1] E. Rentschler, D. Gatteschi, A. Cornia, A.C. Fabretti, A.-L. Barra, O.I. Shchegolikhina, A.A. Zhdanov, *Inorg. Chem.* 35 (1996) 4427.
- [2] L. Zherlitsyna, N. Auner, M. Bolte, Yu. Pozdnyakova, O. Shchegolikhina, K. Lyssenko, V. Pashchenko, B. Wolf, M. Lang, F. Schütz, M. Kollar, F. Sauli, P. Kopietz (in preparation).
- [3] G.M. Sheldrick, SHELXS-97 and SHELXL-97. Programs for the determination and refinement of crystal structures, University of Göttingen, Germany, 1997.
- [4] H. Bethe, “*Zeitschrift für Physik A Hadrons and Nuclei*” 71 (1931) 205.
- [5] R. Orbach, *Phys. Rev.* 115 (1959) 1181.
- [6] L.F. Mattheiss, *Phys. Rev.* 123 (1961) 1209.
- [7] D. Kouzoudis, *J. Magn. Magn. Mater.* 189 (1998) 366; D. Kouzoudis, *J. Magn. Magn. Mater.* 173 (1997) 259.
- [8] Z. Yu, N. Lin, *J. Phys. A: Math. Gen.* 26 (1993) L881; Z. Yu, N. Lin, *Phys. Rev. B* 50 (1994) 3408.
- [9] L. Spanu, A. Parola, *Phys. Rev. Lett.* 92 (2004) 197292.
- [10] D.C. Johnston, et al., *Phys. Rev. B* 61 (2000) 9558.
- [11] W.E. Hatfield, *ACS Symp. Ser.* 5 (1975) 108; D.J. Hodgson, *Prog. Inorg. Chem.* 19 (1975) 173; Van H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfield, *Inorg. Chem.* 15 (1976) 2107.