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Copper(II) dimers with ferromagnetic intra- and intermolecular exchange interactions

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Dimers based on Cu^{II} azomethine complexes exhibited both intra- and intermolecular ferromagnetic exchange interactions, as found from magneto-structural correlations.

Multinuclear coordination compounds with Shiff base ligands belong to multispin systems manifesting intramolecular ferromagnetic exchange interactions between paramagnetic centers.[1–9] We synthesised binuclear copper chelates based on tridentate azomethines containing N_4, N_2S_2 and N_2OS ligand environments with aromatic **1** or heterocyclic **2**, **3** coordination fragments.

The above chelates† were synthesised by refluxing methanol (**1**, **2**) or butanol (**3**) solutions of *N*-[2-(2,3-dihydrobenzothiazol-2-yl)phenyl]-4-methylbenzenesulfonamide **4**, *N*-{2-[(2-aminobenzimidazol-1-ylimino)methyl]phenyl}-4-methylbenzenesulfonamide **5** or 1-[(2-hydroxybenzylidene)amino]-1,3-dihydrobenzimidazole-2-thione **6** with $[Cu(OAc)_2{\cdot}H_2O]_2$.

The preferred tautomeric forms of ligands **4**–**6** have been proved by IR and ^{1}H NMR‡ spectroscopy and the data are consistent with published data on the tautomerism of azomethine[11] and azole[12] compounds.

EXAFS spectroscopy data (Table 1)§ revealed the formation of coordination units CuN_2S_2 (**1**), CuN_4 (**2**) and $CuNOS_2$ (**3**).

The copper–donor and copper–copper distances determined by EXAFS are in good agreement with those obtained from X-ray structural data (Table 1, Figure 1)¶ and close to the values observed in binuclear copper complexes with bridging sulfur atoms.[12] Both copper atoms are pentacoordinated (the coordination polyhedron is a distorted tetrahedral pyramid). Both six-membered metallocycles [Cu(1)N(1)C(9)C(8)C(7)N(2) and Cu(2)N(1′)C(7′)C(8′)C(13′)N(2′)] possess the envelope conformation (copper atoms deviate from the plane of other atoms by 0.68 and 0.70 Å). These cycles are bent along N(1)···N(2) and

† **1**: ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.3 (s, 6H, 2Me), 6.7–7.7 (m, 24H, H_{arom}), 8.0 (s, 2H, HC=N). Found (%): C, 54.23; H, 3.77; N, 6.38. Calc. for $C_{40}H_{32}Cu_2N_4O_4S_4$ (%): C, 54.10; H, 3.63; N, 6.31.

2: Found (%): C, 54.11; H, 3.57; N, 15.08. Calc. for $C_{42}H_{34}Cu_2N_{10}O_4S_2$ (%): C, 54.01; H, 3.67; N, 15.00.

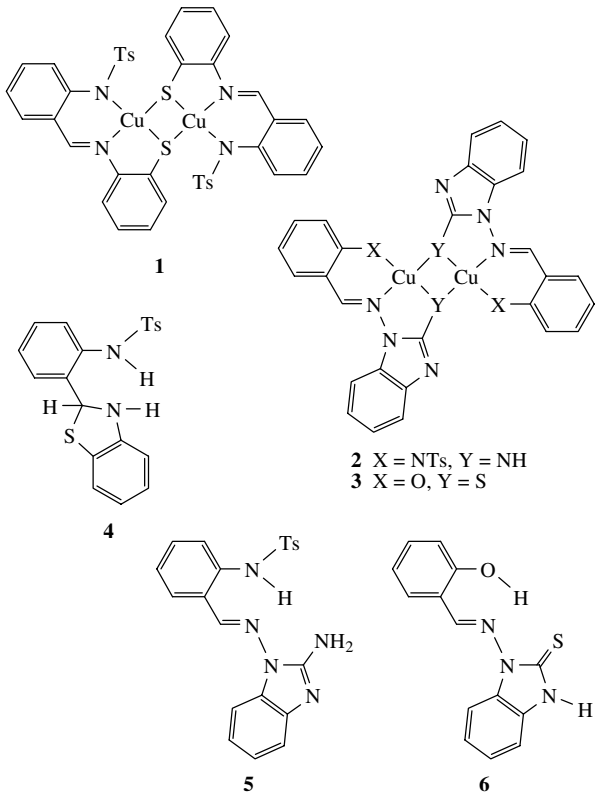
3: Found (%): C, 50.91; H, 2.78; N, 12.81. For $C_{28}H_{18}Cu_2N_6O_2S_2$ (%): C, 50.82; H, 2.74; N, 12.70.

4 was synthesised according to ref. 10. ^{1}H NMR ($CDCl_3$) δ: 2.4 (s, 3H, Me), 4.3 (s, 1H, $NH_{benzothiazoline}$), 6.4 (s, 1H, $CH_{benzothiazoline}$), 6.6–8.2 (m, 12H, H_{arom}), 12.2 (s, 1H, NH_{Ts}).

5: ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.2 (s, 3H, Me), 6.5 (s, 2H, NH_2), 6.9–7.6 (m, 11H, H_{arom}), 8.1 (dd, 1H, H_{arom}), 8.8 (s, 1H, HC=N), 10.0 (s, 1H, NH_{Ts}). Found (%): C, 62.33; H, 4.77; N, 17.34. Calc. for $C_{21}H_{19}N_5O_2S$ (%): C, 62.21; H, 4.72; N, 17.27.

6: ^{1}H NMR ([$^2H_6$]DMSO) δ: 6.8–7.5 (m, 7H, H_{arom}), 7.8 (dd, 1H, H_{arom}), 10.05 (s, 1H, HC=N), 10.5 (s, 1H, NH), 12.95 (s, 1H, OH). Found (%): C, 62.40; H, 4.28; N, 16.66. Calc. for $C_{14}H_{11}N_3OS$ (%): C, 62.24; H, 4.12; N, 15.60.

‡ Measured on UNITY-300 (Varian).



N(1′)···N(2′) lines by 31.0° and 30.2°, respectively. Taking into account short intramolecular contacts between the π systems of two ligands [*e.g.*, C(6′)···C(9) 3.245(3), C(2)···C(7′) 3.396(3) and C(2′)···C(7) 3.455(3) Å] we can propose the presence of intramolecular stacking interactions.

An intrinsic feature of **1** is the sufficiently strong antiferromagnetic exchange interaction, which is similar to the other complexes containing a Cu_2S_2 fragment[14] and results in the diamagnetism of the sample. Compound **1** is diamagnetic both in the solid state (Faraday method) and in solution of $CDCl_3$ (^{1}H NMR, Evans method). In view of these data, both intra- and intermolecular ferromagnetic exchange interaction observed†† for possessing the same sulfur bridging fragment chelate **3** (Figure 2) are highly unexpected.

Complex **2** with the Cu_2N_2 bridging fragment shows the same magnetic behaviour (Figure 3). Experimental $\mu_{eff}(T)$ curve fitting by the Bleany–Bowers model (taking into account the intermolecular exchange zJ') gave the following optimal parameters:

For **2**: $g = 2.07$, $J = 6.7\pm0.8$ cm^{-1}, $zJ' = 0.33\pm0.05$ cm^{-1}
For **3**: $g = 2.01$, $J = 8.3\pm1.3$ cm^{-1}, $zJ' = 0.58\pm0.08$ cm^{-1}

Therefore, we concluded that a fragment annelated to the polymetallic core could essentially change both steric and electronic structures of an exchange cluster in Cu^{II} azomethine dimers. The reconstruction of an exchange cluster provoked by a fragment annelated to the spin coupled system is able to change the sign of J.

Table 1 Structural features of the nearest atom environment of copper atoms in complexes **1**–**3** as observed from the EXAFS spectroscopy data (d is the interatomic distance, c.n. is the coordination number and σ^2 is the Debye–Waller factor).

Compound	c.n.	d/Å	σ^2/Å^2	Donor atom	R-factor (%)
1	2	1.978 [1.965(3)][a]	0.0038	N	7.2
	1	2.186 [2.214(1)]	0.0043	S	
	1	2.316 [2.342(1)]	0.0037	S	
	1	2.661 [2.654(1)]	0.0042	O	
	1	2.854 [2.8136(7)]	0.0040	Cu	
	4	2.96 [2.915(3)]	0.0031	C	
2	2	1.97	0.0031	N	7.4
	2	2.00	0.0031	N	
	4	2.79	0.0044	C/N	
	1	3.01	0.0059	Cu	
3	2	1.94	0.0024	N/O	8.4
	1	2.24	0.0073	S	
	1	2.30	0.0079	S	
	1	2.92	0.0063	Cu	

[a]The corresponding averaged values according to X-ray diffraction analysis of complex **1** are given in parentheses.

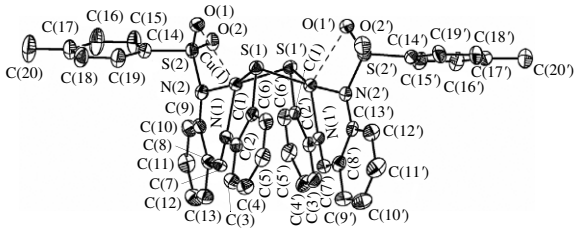


Figure 1 The general view of **1** in representation of atoms by thermal ellipsoids (p = 50%). Selected bond lengths (Å): Cu(1)···Cu(2) 2.8136(7), Cu(1)–N(2) 1.946(3), Cu(1)–N(1) 1.984(3), Cu(1)–S(1) 2.219(1), Cu(1)–S(1′) 2.339(1), Cu(1)···O(1) 2.683(1), Cu(2)···O(1′) 2.626(1), Cu(2)–N(2′) 1.941(3), Cu(2)–N(1′) 1.990(3), Cu(2)–S(1′) 2.209(1), Cu(2)–S(1) 2.346(1); selected bond angles (°): N(2)–Cu(1)–N(1) 90.41(11), N(2)–Cu(1)–S(1) 160.10(9), N(1)–Cu(1)–S(1) 90.10(8), N(2)–Cu(1)–S(1′) 100.79(9), N(1)–Cu(1)–S(1′) 122.58(9), S(1)–Cu(1)–S(1′) 95.66(4), N(2)–Cu(1)–Cu(2) 145.77(9), Cu(1)–S(1)–Cu(2) 76.05(3).

§ The EXAFS spectra of the CuK edge for all the samples were obtained at the EXAFS Station of the Siberian Synchrotron Radiation Center (SSRC). The storage ring VEPP-3 with the electron beam energy of 2 GeV and the average stored current of 70–90 mA has been used as the source of radiation. A cut-off monocrystal Si (111) was used as a monochromator. All the spectra were recorded in a transmission mode using two ionization chambers as detectors. The radial pair distribution functions around Cu atoms were obtained by the Fourier transformation of k^3-weighted spectra over the range of wave numbers 2.8–12.0 Å^{-1}. The structural parameters (the interatomic distances, the coordination numbers and Debye–Waller factors) were found by non-linear fit of theoretical spectra to experimental ones. Theoretical spectra were simulated by *ab initio* calculations of backscattering amplitudes and phases by means of FEFF7. The quality of fit was estimated from discrepancy factors between the experimental and simulated functions (R-factor).

¶ *X-ray diffraction analysis*: at 120 K crystals of **1** ($C_{43}H_{38}Cu_2N_4O_5S_4$) are monoclinic, space group $P2_1/c$, a = 14.562(2), b = 20.239(3) and c = 15.320(2) Å, β = 104.175(4) °, V = 4377.5(12) Å^3, Z = 4, (Z' = 1), M = 946.09, d_{calc} = 1.436 g cm^{-3}, μ(MoKα) = 1.210 cm^{-1}, F(000) = 1944. Intensities of 31283 reflections were measured with a Smart 1000 CCD diffractometer at 120 K [λ(MoKα) = 0.71072 Å, $2\theta < 57°$], and 10604 independent reflections (R_{int} = 0.0474) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The hydrogen atoms were located from the Fourier density synthesis. The refinement converged to wR_2 = 0.1215 and GOF = 1.081 for all independent reflections [R_1 = 0.0480 was calculated against F for 6261 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 274700. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

†† All measurements were carried out on an MPMS-5S Quantum Design SQUID magnetometer (2-300 K, magnetic field of 5 kOe). The effective magnetic moment depending on temperature calculated from the formula:

$$\mu_{eff}(T) = \sqrt{8\chi T},$$

where χ is the molar paramagnetic susceptibility corrected with taking into account the diamagnetic contribution. Theoretical curves during simulation of experimental dependences with taking into account the interdimeric exchange interactions (zJ') were determined from the equation

$$\chi = \chi_{(Cu–Cu)}/[1 - (2zJ'/Ng^2\beta^2)\chi_{(Cu–Cu)}],$$

where $\chi_{(Cu–Cu)}$ is the expression by Bleany–Bowers for magnetic susceptibility of dimer, g is the g-factor of Cu^{II} and β is Bohr magneton.

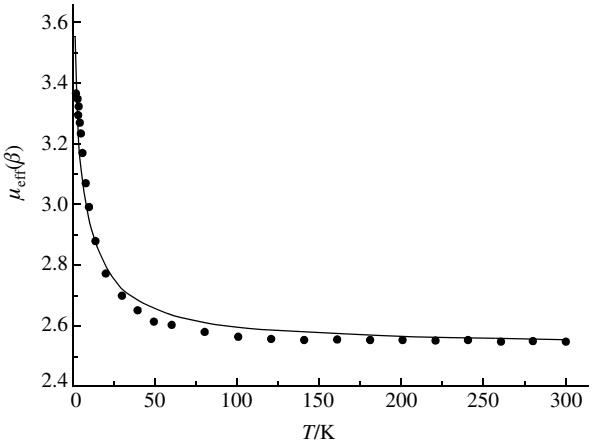


Figure 2 Temperature dependence of effective magnetic moment for **3**; solid line shows a theoretical curve.

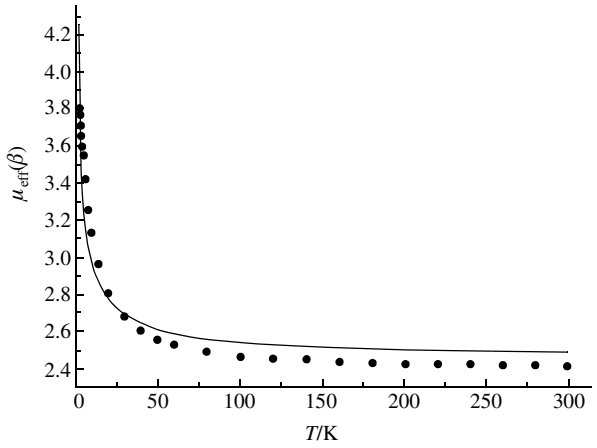


Figure 3 Temperature dependence of effective magnetic moment for **2**; solid line shows a theoretical curve.

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References

1 O. Kahn, *Molecular Magnetism*, Verlag Chemie, New York, 1993.
2 V. I. Ovcharenko and R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 (*Russ. Chem. Rev.*, 1999, **68**, 345).
3 C. Benelli and D. Gatteschi, *Chem. Rev.*, 2002, **102**, 2369.
4 V. T. Kalinnikov, Yu. V. Rakitin and V. M. Novotortsev, *Usp. Khim.*, 2003, **72**, 1123 (*Russ. Chem. Rev.*, 2003, **72**, 995).
5 R. E. P. Winpenny, *Chem. Soc. Rev.*, 1998, **27**, 447.
6 F. Tuna, L. Patron, Y. Journax, M. Andruh, W. Plass and J.-C. Trompbe, *J. Chem. Soc., Dalton Trans*., 1999, 539.
7 J.-P. Costes, F. Dahan and J. Garcia-Tojal, *Chem. Eur. J*., 2002, **8**, 5430.
8 M. Nihei, N. Hoshio, T. Ito and H. Oshio, *Polyhedron*, 2003, **22**, 2359.
9 A. K. Bondalis, J. Clemente, M. Juan and F. Dahan, *Inorg. Chem*., 2004, **43**, 1574.
10 A. S. Burlov, A. S. Antsyshkina, J. Romero, D. A. Garnovskii, A. Garcia-Vazquez, A. Sousa and A. D. Garnovskii, *Zh. Neorg. Khim.*, 1995, **40**, 1480 (*Russ. J. Inorg. Chem*., 1995, **40**, 1427).
11 A. D. Garnovskii and I. S. Vasilchenko, *Usp. Khim.*, 2005, **74**, 193 (in Russian).
12 V. I. Minkin, A. D. Garnovskii, J. Elguero, A. R. Katritzky and O. V. Denisko, *Adv. Heterocycl. Chem*., 2000, **76**, 157.
13 R. P. Houser, V. G. Young, Jr., and W. B. Tolman, *J. Am. Chem. Soc*., 1996, **118**, 2101.
14 S. Itoh, M. Nagagawa and S. Fukusumi, *J. Am. Chem. Soc*., 2001, **123**, 4087.

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