Electronic Supplementary Information

Temperature-dependent zero-field splitting in copper(II) dimer studied by EPR

Matvey V. Fedin,[a] Ekaterina F. Zhilina,[b] Dmitrii L. Chizhov,[b] Inna A. Apolonskaya,[c] Grigory G. Alexandrov,[c] Mikhail Kiskin,[c] Alexey A. Sidorov,[c] Artem S. Bogomyakov,[a] Galina V. Romanenko,[a] Igor L. Eremenko,[c] Vladimir M. Novotortsev,[c] Valery N. Charushin [b]

[a]*International Tomography Center SB RAS, 630090, Novosibirsk, Russia*
[b]*I.Ya. Postovsky Institute of organic synthesis UB RAS, 620990, Yekaterinburg, Russia*
[c]*N.S. Kurnakov Institute of general and inorganic chemistry RAS, 117907, Moscow, Russia*

1. X-ray structure of compound I at room temperature

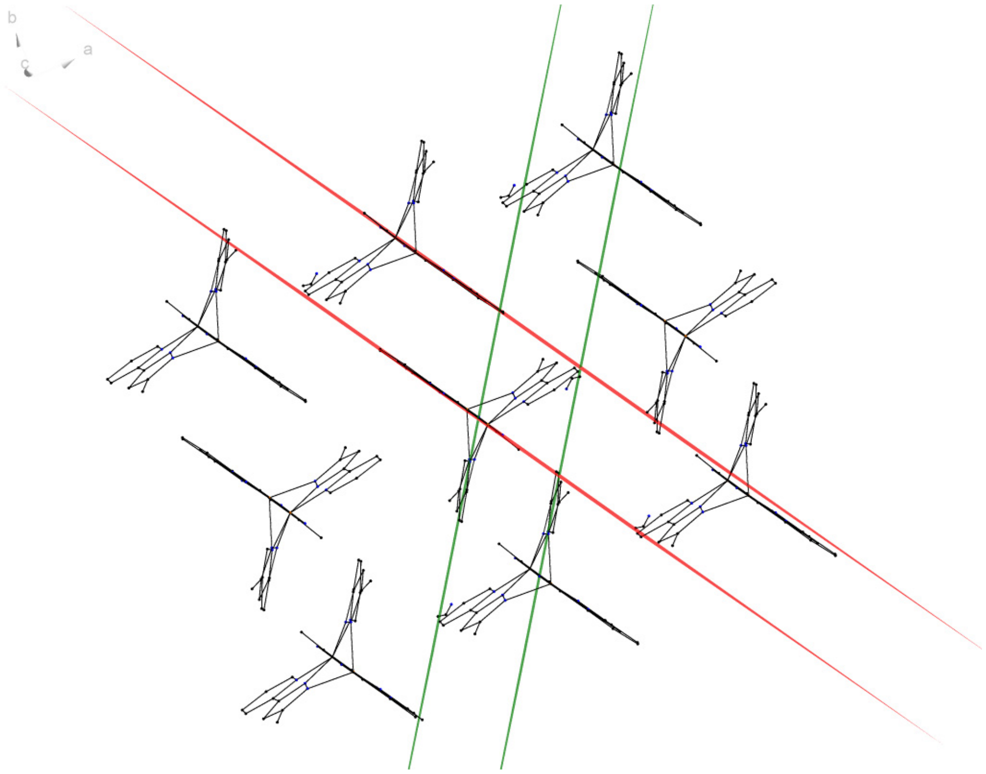

Figure S1. Crystal structure fragment of **I**. Red lines refer to the planes of **L** molecules and green lines – to the planes of **L**^{1} molecules.

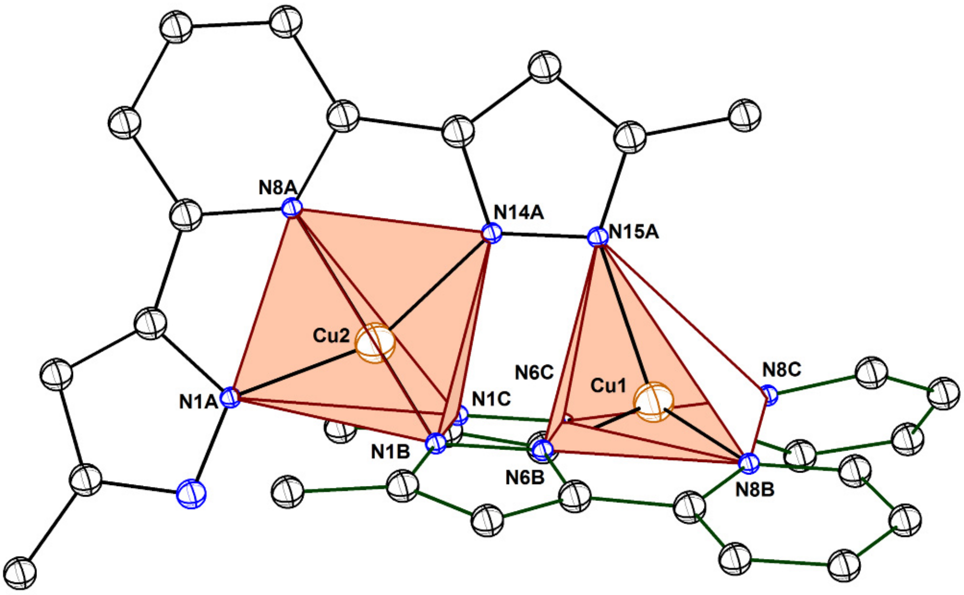

Figure S2. Coordination polyhedra of Cu1 and Cu2 atoms in compound **I** (T = 296(2)K). H- and F-atoms are omitted for clarity.

2. Qualitative consideration of exchange interaction pathways in the dimer I

Mutual orientation of two copper centers in studied dimer **I** implies that qualitatively three super-exchange pathways are possible along each N-N link (marked 1, 2 and 3 in Figure S3). The coordination polyhedra are very distorted, therefore for a qualitative understanding of these pathways let us first consider the limiting cases of relevant undistorted geometries. Assume that Cu1 coordination is precisely square-pyramidal with Cu1–N15A being the elongated axis (this is a very reasonable approximation according to XRD data). Consider then two model cases where (i) Cu2 coordination is precisely trigonal-bipyramidal with N1A–Cu2–N14A being a trigonal axis, and (ii) Cu2 coordination is precisely square-pyramidal with Cu2–N1C being the elongated axis. These two limiting situations are sketched in Figure S3. The d_{z2} orbital of Cu1 is directed along elongated bond in Cu1 unit, and electron is localized on the d_{x2-y2} orbital in orthogonal plane. In case (i) the d_{z2} orbital in Cu2 unit is directed along the trigonal axis, and spin density is found on this d_{z2} orbital (Figure S3a). In case (ii), however, d_{z2} orbital of Cu2 is directed along elongated tetragonal axis (Figure S3b), and electron is localized on the d_{x2-y2} orbital in orthogonal plane. In case (i) one would find that all three exchange pathways are relatively inefficient, because none of them connects two ground d-orbitals with the high electron density. In case (ii), however, one would in principle expect also some antiferromagnetic exchange via pathway 2, since it connects d-orbitals with high electron density in both Cu1 and Cu2, whereas a weak ferromagnetic exchange remains via pathways 1 and

3, since each of these pathways includes one orbital with a high and one orbital with a low electron density. Thus, exchange interaction between two copper ions should be noticeably different for two model cases (i) and (ii) shown in Figures S3a and S3b.

The consideration above refers to the ground electron orbitals of two ions and exchange interactions between them. However, anisotropic part of exchange, which contributes to the apparent *D* values, originates from the interaction between ground electron orbital of one ion and the excited orbital of another ion. It is more difficult to draw qualitative conclusions on these types of interactions, but it is clear that anisotropic parts of exchange should experience noticeable change on passing from situation shown in Figure S3a to S3b as well.

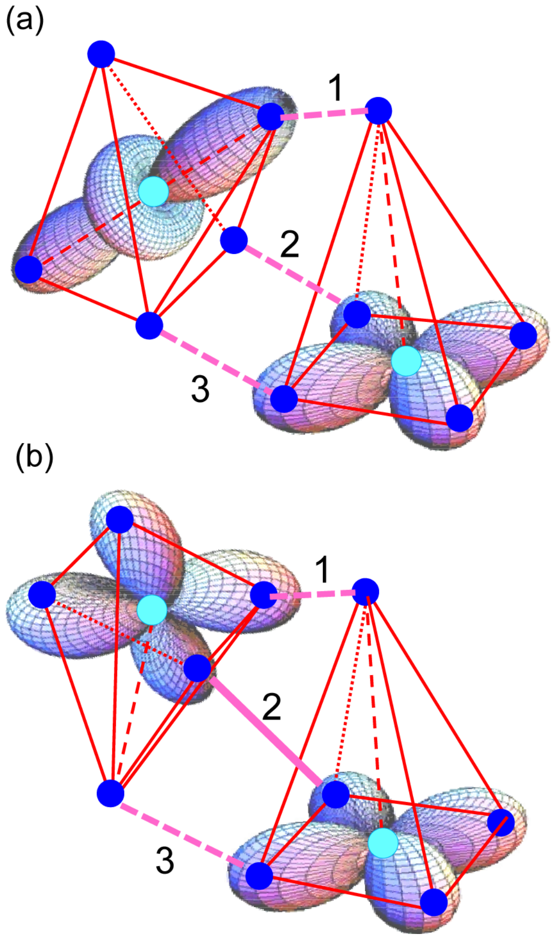

Figure S3. Model dimeric cluster with the exact trigonal-bipyramidal (a) and square-pyramidal (b) geometry of Cu2 coordination unit (on the left), and exact square-pyramidal geometry of Cu1 coordination unit (on the right); ●-Cu, ●-N. The structure of d-orbitals occupied by unpaired electron is sketched, and exchange interaction pathways indicated.

In real compound **I** the geometries of both copper(II) units are strongly distorted over the whole temperature range, so the ground orbitals are the mixtures of those shown in Figures S3a,b. In Cu1 unit Cu1–N15A bond is noticeably larger than two other bonds Cu1–N6C and Cu1–N6B (2.16 vs. 1.99 and 1.97 A at 295 K), and the direction of d-orbitals should be very close to the model case shown in Figure S3a. In Cu2 unit the geometry corresponds to the intermediate case between trigonal-bipyramidal and square-pyramidal. At low temperature the square-pyramidal character is more pronounced ($\tau_5 = 0.384$ at 103 K), whereas at high temperature geometry gets closer to trigonal-bipyramidal ($\tau_5 = 0.447$ at 295 K). In addition, the Cu2–N1B bond experiences noticeable shortening by ≈0.03 A when the temperature is lowered from 295 to 103 K, whereas the other Cu2-N1C bond is simultaneously lengthened by 0.017 A. Although these changes are quite small, the absolute difference in bond lengths $\delta = d_{\mathrm{Cu2\text{-}N1C}} - d_{\mathrm{Cu2\text{-}N1B}}$ is also small, and it changes from $\delta = 0.075$ A at 103 K to $\delta = 0.030$ A at 295 K (i.e. by a factor of ~2). Again, in agreement with the changes in τ_5 (which characterizes geometry via angles between Cu–N bonds), the changes of the bond lengths also indicate gradual rearrangement toward square-pyramidal geometry when the temperature decreases. Note, that the observation of weak ferromagnetism (J~5 cm^{-1}) by magnetic susceptibility measurements is fully consistent with the above conclusions on exchange interaction pathways.

Resuming, this qualitative consideration shows that slight structural changes found by X-ray in the studied dimer should be conjugated with the redistribution of exchange interaction pathways, including their anisotropic parts, which can explain the dependence of the apparent D value on temperature. Quantum chemistry calculations, though they could not be performed for this demanding task up to date, may potentially bring more evidence to this situation.