Crystal Structures and Magnetic Properties of Two Phases from Imidazolate-bridged Copper(II) 4,6-Nonanedionate Complexes

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A helical chain $[\mathrm{Cu(dnbm)}(\mu\text{-im})]_n$ and a tetrancuclear macrocycle $[\mathrm{Cu(dnbm)}(\mu\text{-im})]_4$ (Hdnbm = 4,6-nonanedione, Him = imidazole) were selectively prepared and structurally characterized. Their magnetic properties obeyed one-dimensional chain and square models, respectively.

Oligonuclear and polymeric copper(II) coordination compounds attract much attention in materials chemistry.[1,2] Some peculiar enzyme functions are based on oligonuclear copper clusters, where imidazolates play a role of bridging ligands.[3] Copper(II) imidazolate systems afford a variety of structures of self-assembled supramolecular coordination complexes, e.g., oligonuclear cycles[4–9] and discrete linear systems.[10–15] Although $[\mathrm{Cu(dnbm)}(\mu\text{-im})]_x$ is known (Hdnbm and Him stand for 4,6-nonanedione and imidazole, respectively),[16] the crystal structure has not yet been reported. Generally, there are difficulties in preparing single crystals of polymeric coordination compounds, and also in specifying compounds as polymers or macrocycles solely from spectroscopic and elemental analyses. We will report here full characterization of two phases of $[\mathrm{Cu(dnbm)}(\mu\text{-im})]_x$.

The reaction of $[\mathrm{Cu(dnbm)_2}]$ with two molar equiv of imidazole in refluxing ethanol for 2 h followed by gradual concentration at 50 °C afforded polymeric $[\mathrm{Cu(dnbm)}(\mu\text{-im})]_n$ (**1**) as fine needles (mp. 153–156 °C). On the other hand, a reaction was conducted at room temperature, to give $[\mathrm{Cu(dnbm)}(\mu\text{-im})]_4$ (**2**) with good crystal habit as blocks (mp 113–114 °C). The polymeric form was favored under thermal equilibrium conditions, probably because of the low solubility of **1** even at high temperatures.

Figure 1 shows the molecular structure of **1**.[17] A dinuclear unit $[\{\mathrm{Cu(dnbm)}(\mu\text{-im})\}_2]$ is crystallographically independent, which constructs a helix in a tetragonal $P4_2/n$ space group. The intramolecular nearest-neighboring Cu1···Cu2 and Cu2···Cu1* distances are 5.9016(10) and 5.8973(11) Å, respectively. The Cu ions have a $\mathrm{CuN_2O_2}$ coordination environment with two N atoms from two imidazolates and two O atoms from a dnbm ligand. The O1–Cu1–N1, O2–Cu1–N4#, O3–Cu2–N3, and O4–Cu2–N2 bond angles are somewhat smaller than 180°, and the coordination structure is distorted from square-planar toward tetrahedral (d-SP).

There are eight copper ions in a pitch, contrary to the expectation from the cis N–Cu–N configuration, which seems suitable for a 4-fold axis involving four copper ions. The Cu1···Cu2···Cu1* angle [134.66(2)°] is considerably larger than, while the Cu2···Cu1*···Cu2* angle [89.64(2)°] is close to, the ideal right angle. The alternating irregular angles are responsible for the formation of a $\mathrm{Cu_8}$-based chain and not a $\mathrm{Cu_4}$-based helix or a tetrameric macrocycle.

As Figure 2 shows the molecular structure of **2**,[17] four Cu ions construct a rectangle arrangement affording a [2 × 2]-molecular grid. A half of the molecule of **2** is crystallographically independent owing to centrosymmetry in a space group $P\bar{1}$. The intramolecular Cu1···Cu2 and Cu1···Cu2† distances are 5.8928(10) and 5.8694(7) Å, respectively. The Cu2†···Cu1···Cu2 and Cu1···Cu2···Cu1† angles are 90.45(12) and 89.55(12)°, respectively.

The O3–Cu2–N3 and O4–Cu2–N2 bond angles are much smaller than 180°, implying a d-SP structure at Cu2, while the Cu1 coordination structure is nearly square-planar (n-SP). This finding is similar to that of bisimidazolato Cu compounds possessing a d-SP/n-SP-mixed tetranuclear framework.[18] As the side view shows (Figure 2b), the two basal planes are slightly canted with each other by 7.3(1)°.

We measured magnetic susceptibilities (χ_{mol}) of polycrystalline specimens of the present compounds on a SQUID magnetometer. The χ_{mol} value of **1** increased on cooling from 300 K,

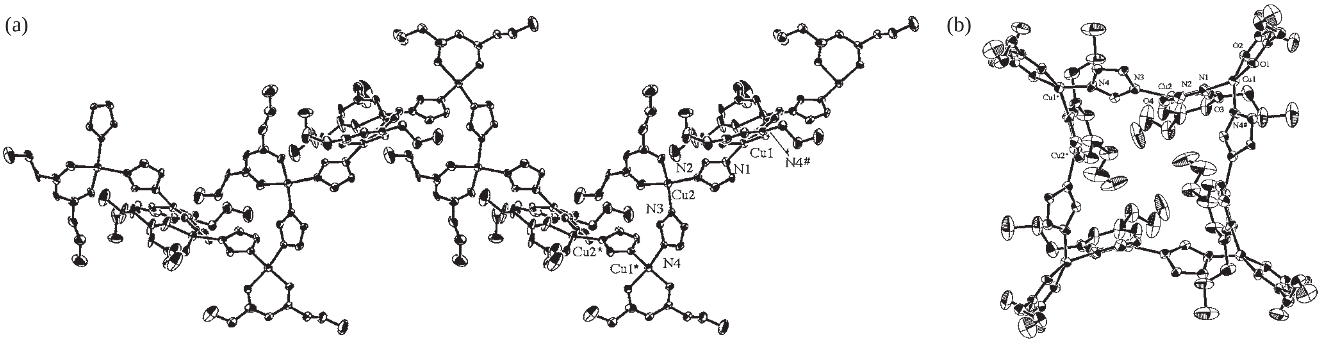

Figure 1. X-ray crystal structure of **1**. (a) Side and (b) top views of a chain. Eight repeating units are drawn. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. Symmetry operation codes of * and # are $-y$, $-1/2+x$, $-1/2+z$ and $1/2+y$, $-x$, $1/2+z$, respectively. Selected bond lengths (Å) and angles (°): Cu1–O1, 1.918(3); Cu1–O2, 1.932(4); Cu1–N1, 1.954(5); Cu1–N4#, 1.954(5); Cu2–O3, 1.923(4); Cu2–O4, 1.920(4); Cu2–N2, 1.981(5); Cu2–N3, 1.944(5); O1–Cu1–N1, 158.46(19); O2–Cu1–N4#, 156.73(18); O3–Cu2–N3, 159.08(19); O4–Cu2–N2, 161.3(2).

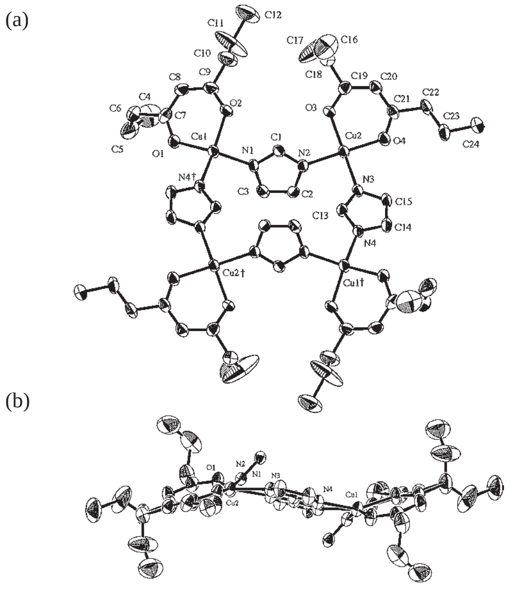

Figure 2. X-ray crystal structure of **2**. (a) Top and (b) side views. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted. Symmetry operation code of † is $1 - x$, $2 - y$, $-z$. Selected bond lengths (Å) and angles (°): Cu1–O1, 1.913(3); Cu1–O2, 1.929(4); Cu1–N1, 1.935(4); Cu1–N4†, 1.932(5); Cu2–O3, 1.919(4); Cu2–O4, 1.918(3); Cu2–N2, 1.957(3); Cu2–N3, 1.967(4); O1–Cu1–N1, 154.9(2); O2–Cu1–N4†, 152.2(2); O3–Cu2–N3, 162.6(2); O4–Cu2–N2, 171.5(2).

reached a broad maximum around 60 K, and gradually decreased (Figure 3a). This behavior clearly indicates the presence of dominant antiferromagnetic coupling. An extrapolation of the χ_{mol} curvature to 0 K seems to give a non-zero χ_{mol} intercept. Usually such behavior is related to an infinite Heisenberg $S = 1/2$ antiferromagnetic chain, as originally predicted by Bonner and Fisher.[19] On further cooling, the χ_{mol} value of **1** decreased with a turning point around 10 K. The origin of this anomaly is not clear at present. To estimate the exchange coupling within a chain, we used the data above 15 K. Assuming an equally spaced $S = 1/2$ magnetic chain and the Heisenberg spin Hamiltonian as $H = -\Sigma 2JS_i \cdot S_{i+1}$, we applied a numerical fitting,[19] giving $2J/k_{\mathrm{B}} = -89.8(7)$ K with $g = 2.04(2)$.[20]

The χ_{mol} vs. T plot of **2** (Figure 3b) exhibited a distinctly different feature from that of **1**. Namely, zero χ_{mol} value is suggested at $T \rightarrow 0$ K. A Curie impurity is assumed, as indicated by a sharp upturn at the lowest temperature region. A square model involving four $S = 1/2$ spins leads to the spin Hamiltonian as $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1)$. The experimental data of **2** were fitted to the corresponding van Vleck equation[5,6,9] to give $2J/k_{\mathrm{B}} = -81.0(2)$ K, $g = 2.061(2)$,[20] and $C_{\mathrm{imp}} = 0.0203(2)\,\mathrm{cm^3\,K\,mol^{-1}}$.

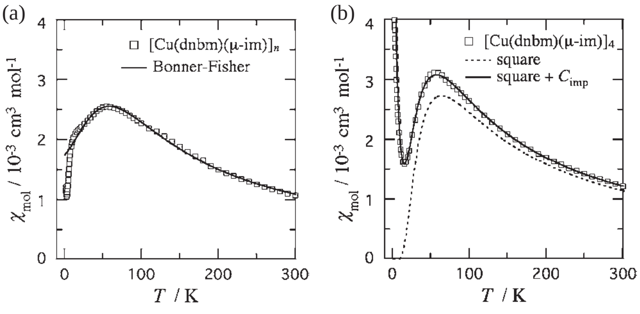

Figure 3. Temperature dependence of molar magnetic susceptibility (χ_{mol}) for (a) **1** and (b) **2**. The solid and dotted lines represent the best fit curves. See the text for the equations and parameters.

We have to think of possible fittings to alternating-chain and square models, which involve J and αJ as coupling parameters ($0 < \alpha < 1$). The χ_{mol} value would approach null at 0 K in the case of alternating chains. The present behavior guarantees the approximation with $\alpha = 1$ to be valid. We tried to fit the data of **2** to a rectangle model,[6] but eventually found that the analysis based on equal spacing satisfactorily reproduced the experimental results. The structurally common bridges Cu–N(eq)–N(eq)–Cu afford comparable magnitudes of couplings. Hence, though an alternating parameter α should be introduced, α was found to be close to unity.

We utilized a simple imidazolate anion for linking copper(II) diketonates without preorganization of the ligands. It should be noted that the combination of simple copper(II) diketonates and imidazolate ion is versatile for supramolecular chemistry.

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References and Notes

1 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspective*, VCH, Weinheim, **1995**.

2 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

3 A. Messerschmidt, R. Huber, *Eur. J. Biochem.* **1990**, *187*, 341.

4 P. Chaudhuri, I. Karpenstein, M. Winter, C. Butzlaff, E. Bill, A. X. Trautwein, U. Florke, H.-J. Haupt, *J. Chem. Soc., Chem. Commun.* **1992**, 321.

5 P. Chaudhuri, I. Karpenstein, M. Winter, M. Lengen, C. Butzlaff, E. Bill, A. X. Trautwein, U. Flörke, H.-J. Haupt, *Inorg. Chem.* **1993**, *32*, 888.

6 G. Kolks, S. J. Lippard, J. V. Waszezak, H. R. Lilienthal, *J. Am. Chem. Soc.* **1982**, *104*, 717.

7 S. Mukherjee, T. Weyhermüller, E. Bill, P. Chaudhuri, *Eur. J. Inorg. Chem.* **2004**, 4209.

8 W. A. Alves, G. Cerchiaro, A. Paduan-Filho, D. M. Tomazela, M. N. Eberlin, A. M. D. C. Ferreira, *Inorg. Chim. Acta* **2005**, *358*, 3581.

9 T. Higa, M. Moriya, Y. Shimazaki, T. Yajima, F. Tani, S. Karasawa, M. Nakano, Y. Naruta, O. Yamauchi, *Inorg. Chim. Acta* **2007**, *360*, 3304.

10 C. A. Koch, C. A. Reed, G. A. Brewer, N. P. Rath, W. R. Scheidt, G. Gupta, G. Lang, *J. Am. Chem. Soc.* **1989**, *111*, 7645.

11 E. Colacio, M. Ghazi, R. Klevekas, M. Klinga, F. Lloret, J. M. Moreno, *Inorg. Chem.* **2000**, *39*, 2770; E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Liveskas, M. Klinga, J. M. Moreno, *Inorg. Chem.* **1998**, *37*, 3040.

12 N. Matsumoto, K. Inoue, M. Ohba, H. Okawa, S. Kida, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2283.

13 J. M. Dominguez-Vera, N. Galvez, E. Colacio, R. Cuesta, J.-P. Costes, J.-P. Laurent, *J. Chem. Soc., Dalton Trans.* **1996**, 861.

14 R. Boca, M. Hvastijova, J. Kozisek, M. Valko, H. Ehrenberg, H. Fuess, W. Haase, I. Svoboda, R. Werner, *Inorg. Chem. Commun.* **2005**, *8*, 548.

15 Y. F. Song, C. Massera, M. Quesada, I. A. Koval, P. Gamez, A. M. M. Lanfredi, J. Reediik, *Eur. J. Inorg. Chem.* **2004**, 4566.

16 T. Kogane, R. Hirota, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 91.

17 CCDC reference numbers 702612 and 702613.

18 J. Peisach, P. Aisen, W. E. Blumberg, *The Biochemistry of Copper*, Academic Press, **1966**, 90; J. A. J. Jarvis, A. F. Wells, *Acta Crystallogr.* **1960**, *13*, 1027.

19 J. C. Bonner, M. E. Fisher, *Phys. Rev.* **1964**, *135*, A640.

20 These g factors were determined from the fitting of the magnetic data. The powder ESR spectra indicated comparable magnitudes of g_{iso} (2.12 and 2.10 for **1** and **2**, respectively).

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