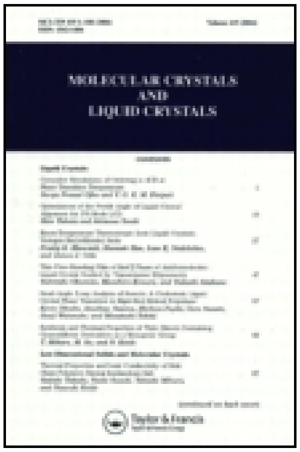


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferromagnetic Interaction in a Pyrimidine-Bridged Copper(II) Nitrate Complex

Kensuke Nakayama [a], Mitsutoshi Nakagawa [a], Takayuki Ishida [a], Yoshimitsu Ishikawa [a], Masanori Yasui [a], Fujiko Iwasaki [a] & Takashi Nogami [a]

[a] Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo, 182, Japan

Version of record first published: 04 Oct 2006

To cite this article: Kensuke Nakayama, Mitsutoshi Nakagawa, Takayuki Ishida, Yoshimitsu Ishikawa, Masanori Yasui, Fujiko Iwasaki & Takashi Nogami (1997): Ferromagnetic Interaction in a Pyrimidine-Bridged Copper(II) Nitrate Complex, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 379-384

To link to this article: http://dx.doi.org/10.1080/10587259708044590

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 379–384
Reprints available directly from the publisher
Photocopying permitted by license only

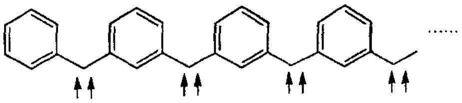
FERROMAGNETIC INTERACTION IN A PYRIMIDINE-BRIDGED COPPER(II) NITRATE COMPLEX

KENSUKE NAKAYAMA, MITSUTOSHI NAKAGAWA, TAKAYUKI ISHIDA, YOSHIMITSU ISHIKAWA, MASANORI YASUI, FUJIKO IWASAKI, AND TAKASHI NOGAMI
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

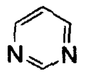
Abstract Linear polymeric complexes $[PM_2 \cdot Cu(NO_3)_2]_n$ (PM =pyrimidine) and $[L \cdot Cu(hfac)_2]_n$ (L = PM, 4- and 5-methylpyrimidine, and quinazoline) have been synthesized and characterized. The copper(II) spins were ferromagnetically coupled for all cases.

INTRODUCTION

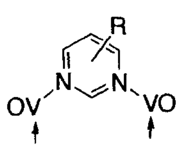
The intramolecular magnetic interactions of several dinuclear transition-metal complexes containing pyrimidines or related compounds have been investigated.[1-4] The superexchange interaction was discussed on the basis of spin polarization mechanisms on the π systems of the heteroaromatic ligands,[2-4] just like those on the *m*-phenylenes in the organic high-spin poly(*m*-phenylenecarbenes) (**A**)[5,6] and poly[*m*-phenylene(phenylmethyls)].[5,7] We previously reported that the pyrimidine-bridged bis(oxovanadium) complexes are high-spin (triplet) molecules in their ground states (**B**).[3] Among them, PM·$[VO(hfac)_2]_2$ (PM = pyrimidine, hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) showed a ferromagnetic transition at 0.14 K, and this result was interpreted as ferromagnetic assembly of high-spin molecules.[3]



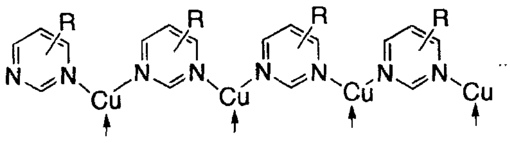
A



PM : pyrimidine



B

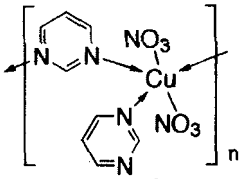


C

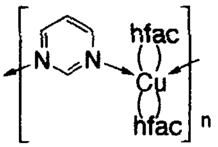
We extended the investigation from dinuclear complexes to polynuclear complexes and found that polynuclear copper(II) complexes afforded ferromagnetic linear chains (C).[8] We report here the magnetic property and crystal structure of a novel complex [$PM_2 \cdot Cu(NO_3)_2$] (**1**) and also those of a series of [$L \cdot Cu(hfac)_2]_n$ [L = PM (**2**), 4-methylpyrimidine (**3**), 5-methylpyrimidine (**4**), and quinazoline (**5**)][8] for comparison. The pyrimidine bridges in all of the polymeric complexes were proved to play a role of ferromagnetic exchange couplers.

EXPERIMENTAL

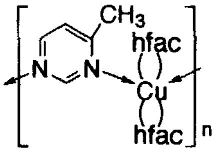
Complex **1** was synthesized from copper(II) nitrate trihydrate and 2-equiv. of pyrimidine in methanol at room temperature. Resulting dark blue crystals were collected in 75% yield. They were analytically pure and used for magnetic and X-ray diffraction studies. Anal. Calcd for $C_8H_8CuN_6O_6$: C, 27.63; H, 2.32; N, 24.17%. Found: C, 27.32; H, 2.44; N, 24.11%. The preparation of **2** - **5** were previously reported.[8,9]



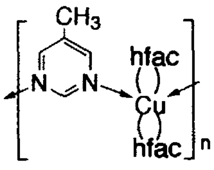
1



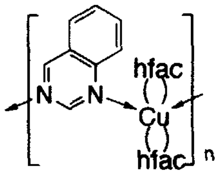
2



3

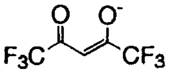


4



5

hfac =



The X-ray diffraction data were recorded on a RIGAKU AFC7R four-circle diffractometer using Mo K_α radiation. The paramagnetic susceptibility was measured on an MPMS-7 SQUID magnetometer (Quantum Design) down to 1.8 K at 0.5 T. The diamagnetic contribution was estimated from the Pascal atomic constants.

RESULTS AND DISCUSSION

Crystal Structures

Figure 1 shows the X-ray crystal structure of **1**. There are two types of pyrimidine molecules in **1**. One is a bidentate bridge in the polymer backbone and another a monodentate pendant. All of the copper ions are symmetrically equivalent; the neighboring Cu···Cu distances are 6.01 Å and the repeating units are correlated by a glide reflection within a chain. The Cu-N(equatorial) and Cu-N(axial) bond lengths are

2.05 and 2.32 Å, respectively, in the chain. Although the coordination structure is considered to be a square-pyramid, two oxygen atoms of nitrate ions are located nearly *trans* to the axial pyrimidine nitrogen with the Cu···O distances of 2.72 and 2.79 Å.

The shortest inter-chain Cu···Cu distance is 7.63 Å which is longer than the intra-chain one. We can not find any appreciable overlap of π-orbitals among the heteroaromatic rings or ligands and any atomic distance within the sum of van der Waals radii in inter-chain directions. Thus, this structure can be regarded as a quasi-one-dimensional system.

The crystal structures of **2**, **3**, and **5** were described elsewhere.[8] They similarly possess linear chain structures. The linear chain structure of **3** has a 4_1 screw symmetry with the intra-chain Cu···Cu distance of 6.17 Å. The structure of **2** is basically similar to that of **3**, in spite of a different space group. In the crystal of **5**, there are two types of

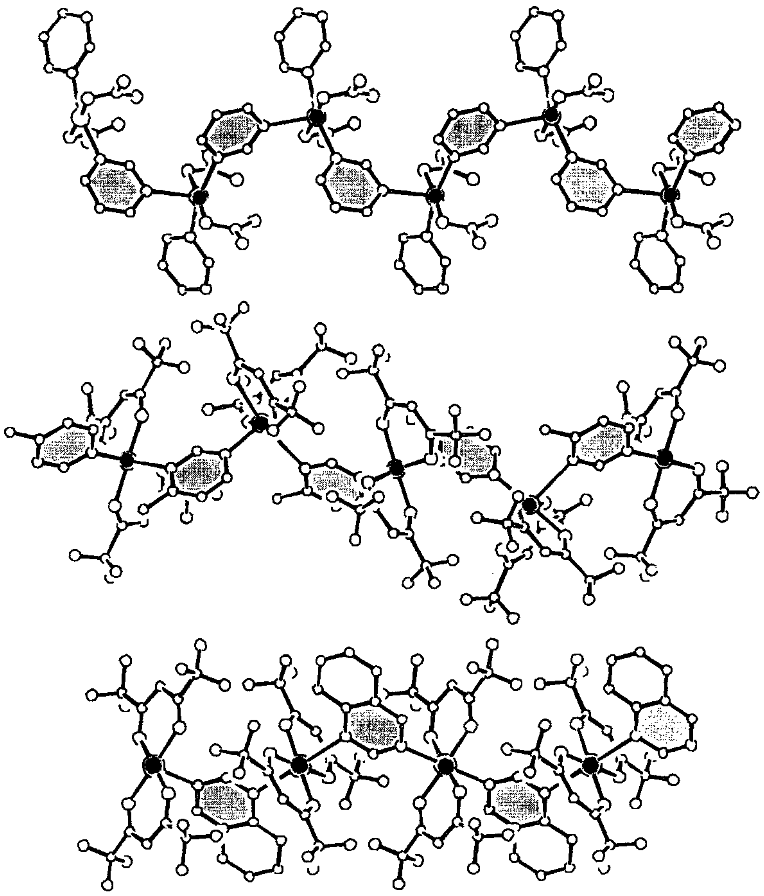


FIGURE 1 Crystal structures of **1**, **3**, and **5**. Bridging pyrimidine rings and copper ions are shaded. Hydrogen atoms are omitted for the sake of clarity.

copper ions which are located on the centers of symmetry. The quinazoline molecules are arranged in a head-to-head fashion. Both of two nitrogen atoms of quinazoline are coordinated at axial positions of the copper ions with the Cu-N bond lengths of 2.45 and 2.19 Å.

Two cases of the coordination structures around copper ions have been found in the complexes: 1) N(axial)—Cu—N(equatorial) for **1** - **3**, and 2) N(axial)—Cu—N(axial) for **5**. Ferromagnetic couplings were observed for both cases (see below).[10]

Magnetic Properties

The SQUID measurements of **1** - **5** revealed the presence of ferromagnetic interactions between the Cu(II) spins, as indicated by the positive Weiss constants and the increases of the effective magnetic moments with a decrease of temperature (Figure 2).

The Weiss constant of **1** was obtained to be +0.71 K from the Curie-Weiss plot. In order to confirm the presence of ferromagnetic interaction, the magnetization curve of **1** was measured at 1.8 K. The obtained curve was found to exceed the theoretical Brillouin function of S = 1/2, and fall between the theoretical S = 1 and 3/2 curves. The exchange parameter J/k_B between the neighboring Cu(II) spins can be estimated to be +0.89 K with the Landé g factor of 2.23 based on a Heisenberg linear-chain model.[11]

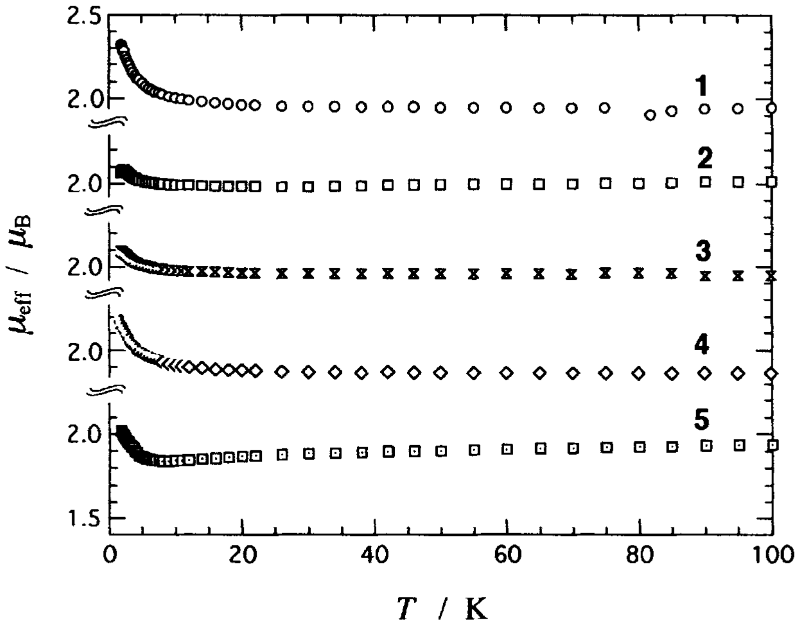


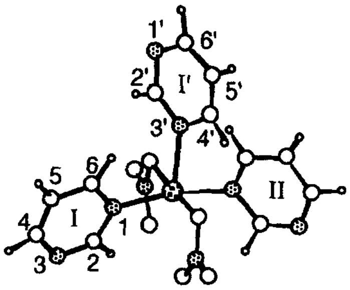
FIGURE 2 The temperature dependences of the effective magnetic moments for **1** - **5**.

Similar magnetic measurements on **2** - **5** revealed that the copper(II) spins were ferromagnetically correlated in all of the complexes. We obtained J/k_B = +0.2 - +0.7 K and g = 2.0 - 2.2. Thus, pyrimidine rings can be regarded as ferromagnetic exchange couplers in these polymeric systems of **1** - **5**.

The ac susceptibility measurements of **5** revealed that the ferromagnetic transition occurred at about 0.12 K (T_C).[8] A ferromagnetic S-shaped M-H curve was obtained below T_C, while a linear paramagnetic feature was observed above T_C.[8] This fact implies that the high-spin polymers are ferromagnetically correlated. The polynuclear copper(II) complexes (**C**) were designed on the analogy of organic high-spin materials such as **A**, and the ferromagnetic interactions were realized in the present systems. Ferromagnet **5** is an example of ferromagnetic assembly of high-spin polymers.

MO Calculation

The spin distribution of the bridging pyrimidine is of great interest for clarifying the mechanism of intra-chain ferromagnetic couplings in **1** - **5**. For the sake of simplicity of calculation, we used $PM_3 \cdot Cu(NO_3)_2$ (**6**) as a monomer model of **1**. The spin distribution caused by the copper spin was calculated by means of a semiempirical UHF/ZINDO MO method.[12]



6

The magnetic orbital of the copper(II) ion in **6** was located on the equatorial plane as indicated by the spin density +0.31 on the $d_{x^2-y^2}$ orbital. In the bridging equatorial pyrimidine ring (I), the spin densities were calculated to be +0.29, -0.22, +0.23, -0.23, +0.25, and -0.24 for N(1) - C(6) atoms, respectively. The finding of the positive spin density induced on the binding nitrogen atom N(1) is compatible with the experimental results on a pyrazine-$Cu(NO_3)_2$ complex.[13] The alternating spin densities were reasonably understood from spin polarization mechanism; once a positive spin density is induced at the coordinated nitrogen atom, alternating spin densities are induced on the π-electron network of a six-membered pyrimidine ring. On the other hand, the spin densities were calculated to be negligibly small (< ± 0.06) in the axial pyrimidine ring (I'). This fact is reasonably interpreted in terms of the orthogonality between the copper $d_{x^2-y^2}$ orbital and nitrogen $n\sigma$ and $p\pi$ orbitals.

A possible mechanism of ferromagnetic coupling in **1** is as follows. The copper(II) spin can not induce any appreciable spin density on the axial pyrimidine in **6**. In actual polymeric complex **1**, however, the axial pyrimidine (I') has spin densities caused by a neighboring copper ion coordinated by N(1'). The resulting positive spin density on N(3') can induce a positive spin density on the copper ion because of the orthogonality between $d_{x^2-y^2}$(Cu) and nσ and pπ(N). The axial coordination seems to be important for the ferromagnetic coupling.

ACKNOWLEDGEMENT

Professors Kiyoshi Tanaka and Yasuhiro Nakadaira are acknowledged in performing MO calculations. This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. D. R. Corbin, L. C. Francesconi, D. N. Hendrickson, and G. D. Stucky, Inorg. Chem., 18, 3069, 3074 (1979).
2. H. Oshio and H. Ichida, J. Phys. Chem., 99, 3294 (1995); H. Oshio, J. Chem. Soc., Chem. Commun., 240 (1991).
3. S.-i. Mitsubori, T. Ishida, T. Nogami, and H. Iwamura, Chem. Lett., 285 (1994); S.-i. Mitsubori, T. Ishida, T. Nogami, H. Iwamura, N. Takeda, and M. Ishikawa, Chem. Lett., 685 (1994).
4. T. Ishida, S.-i. Mitsubori, T. Nogami, and H. Iwamura, Mol. Cryst. Liq. Cryst., 233, 345 (1993).
5. N. Mataga, Theor. Chim. Acta, 10, 372 (1967).
6. H. Iwamura, Adv. Phys. Org. Chem., 26, 179 (1990); K. Itoh, Pure Appl. Chem., 50, 1251 (1978); K. Matsuda, N. Nakamura, K. Inoue, N. Koga, and H. Iwamura, Bull. Chem. Soc. Jpn., 69, 1483 (1996).
7. A. Rajca, Chem. Rev., 94, 871 (1994); N. Ventosa, D. Ruiz, C. Rovira, and J. Veciana, Mol. Cryst. Liq. Cryst., 232, 333 (1993).
8. T. Ishida, S.-i. Mitsubori, T. Nogami, Y. Ishikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Synth. Met., 71, 1791 (1995); T. Ishida, T. Nogami, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Mol. Cryst. Liq. Cryst., 279, 87 (1996); M. Nakagawa, Y. Ishikawa, T. Kogane, T. Ishida, M. Yasui, F. Iwasaki, and T. Nogami, Mol. Cryst. Liq. Cryst., in press.
9. T. Kogane, K. Kobayashi, M. Ishii, R. Hirota, and M. Nakahara, J. Chem. Soc., Dalton Trans., 13 (1994); T. Kogane, K. Kobayashi, M. Ishii, R. Hirota, and M. Nakahara, Chem. Lett., 419 (1991).
10. Antiferromagnetic interaction was observed in a linear complex $[PM\cdot Cu(NO_3)_2\cdot 2H_2O]_n$ in which two nitrogen atoms of pyrimidine were coordinated at equatorial positions. K. Nakayama, T. Ishida, T. Nogami, unpublished results.
11. G. A. Baker, Jr., G. S. Rushbrooke, and H. E. Gilbert, Phys. Rev., 135A, 1272 (1964).
12. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Chem. Phys., 47, 2026 (1967); M. C. Zerner, G. H. Loew, R. F. Kirchner, U. T. Mueller-Westerhoff, J. Am. Chem. Soc., 102, 589 (1980); and references cited therein.
13. H. Kuramoto, M. Inoue, S. Emori, and Sugiyama, Inorg. Chim. Acta, 32, 209 (1979).