Rational Design of a Ferromagnetic Trinuclear Copper(II) Complex with a Novel in-situ Synthesised Metalloligand

Ming-Liang Tong,*[a,b] Yin-Miao Wu,[a] Ye-Xiang Tong,[a] Xiao-Ming Chen,*[a]
Ho-Chol Chang,[c] and Susumu Kitagawa*[c]

Keywords: Magnetic properties / Copper / N ligands / Nucleophilic addition

An interesting ferromagnetic linear trinuclear copper(II) compound containing an in-situ synthesised functional ligand has been rationally obtained and crystallographically characterised, confirming a new route to magnetic polynuclear clusters.

Introduction

Multi-metal-centred complexes or metal-complex assemblies with highly ordered solid-state structures have attracted much attention in the past few decades.[1,2] In homometallic systems, either ferromagnetic or antiferromagnetic behaviours can occur depending on the bridging ligand shape, bridging angles, and other factors.[3] Although high spin multiplicities of the ground state, along with ferromagnetic behaviour, have been achieved by applying the concept of strict orthogonality[4] between two magnetic orbitals in designing molecules, the rational design and synthesis of novel metal clusters with large ground spin-states is still a challenging and central topic in the field of molecular magnetism. The development of new metalloligands,[2,5] which have been found to play an important role not only in mediating magnetic interactions but also in introducing a catalytic site in metal assembled complexes, is undoubtedly one of best methods for meeting this challenge. Recently, in our attempt to synthesise coordination polymers with metal(II) salts and sodium dicyanamide [Na(dca)],[6] an unexpected product, namely [Cu(dcaOMe)$_2$] (**1**) [dcaOMe = di(methoxycarbimido)aminato], was formed by an interesting in situ nucleophilic addition reaction of the ligand (Scheme 1). We speculated that a series of functional polydentate ligands may be designed and generated by using other nucleophiles with potential ligation sites instead of MeOH, and that these ligands may be used in the synthesis of homo- and heterometallic clusters. We report here the successful use of pyrazole to furnish an interesting ferromagnetically coupled linear trinuclear copper(II) compound [Cu$_3$(dcadpz)$_2$(pz)$_2$(ClO$_4$)$_2$](ClO$_4$)$_2$·H$_2$O [**2**; dcadpz = di(pyrazolecarbimido)aminato; pz = pyrazole], which contains an interesting metalloligand as a ferromagnetic coupler.

Results and Discussion

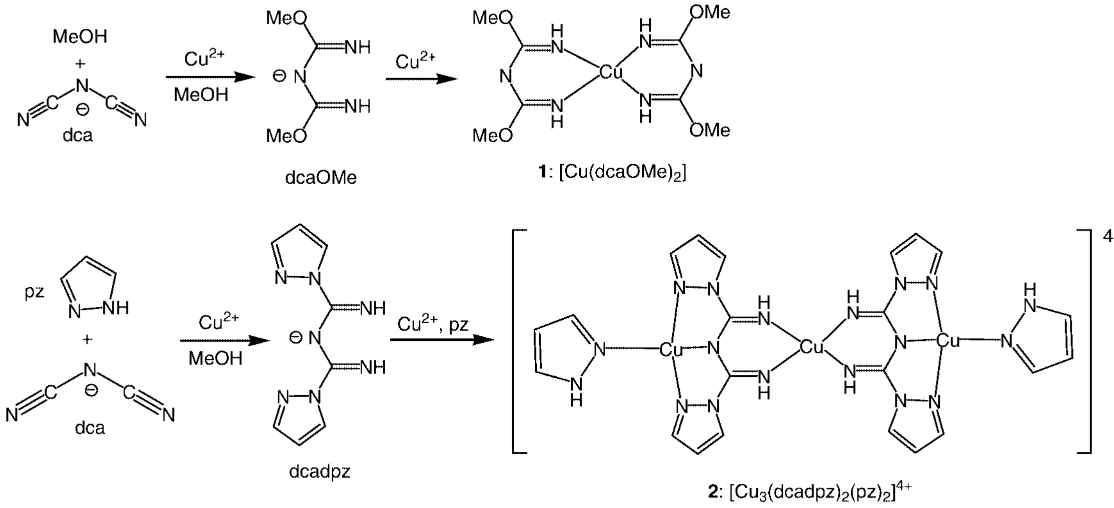
Single-crystal X-ray analysis revealed that **1** is a neutral planar Cu^{II} complex (Figure 1, top). The Cu^{II} atom is coordinated in a planar-square geometry to four nitrogen atoms from two dcaOMe ligands. The Cu1−N bond lengths are 1.939(2) and 1.946(2) Å. The dcaOMe ligand is apparently formed by the addition reaction of dca and MeOH. Although this product was synthesised by the addition of methanol and dicyanimide in the presence of zinc chloride, followed by the replacement of zinc by copper(II) using an ammoniacal solution of copper(II) sulfate,[7,8] no X-ray structural analysis had been done prior to our work.

Complex **2** is a symmetrical linear trinuclear copper(II) complex. The crystallographically asymmetric unit consists of 1.5 Cu^{II} centres, one dcadpz ligand, one pz ligand, two ClO$_4^-$ ions and 0.5 disordered lattice water molecules (Figure 1, bottom). The central Cu1 atom is located at an inver-

---

[a] State Key Laboratory of Optoelectronic Materials & Technologies and School of Chemistry and Chemical Engineering, Sun Yat-Sen University,
Guangzhou 510275, China
Fax: (internat.) +86-20/8411-2245
E-mail: cestml@zsu.edu.cn
cescxm@zsu.edu.cn
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,
Fuzhou 350002, China
[c] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501, Japan
E-mail: kitagawa@sbchem.kyoto-u.ac.jp

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 1

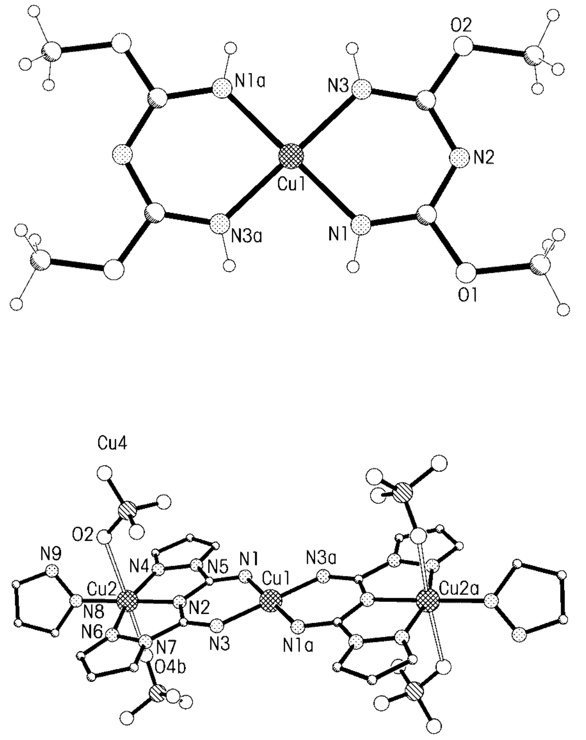


Figure 1. The coordination environment of the copper atoms in **1** (top) and **2** (bottom); selected bond lengths (Å): Cu(1)−N(1) 1.939(2), Cu(1)−N(3) 1.946(2) for **1**; Cu(1)−N(3) 1.949(4), Cu(1)−N(1) 1.955(4), Cu(2)−N(8) 1.957(4), Cu(2)−N(2) 1.958(4), Cu(2)−N(4) 1.976(4), Cu(2)−N(6) 1.980(4), Cu(2)−O(2) 2.518(5), Cu(2)−O(4b) 2.561(6) for **2**

sion centre and is coordinated in a perfectly square-planar geometry to four nitrogen atoms from two dcadpz ligands, with Cu1−N bond lengths of 1.949(4) and 1.955(4) Å, similar to those in **1**. Each of the terminal Cu2 atoms is coordinated in an elongated [4+2] distorted octahedral geometry with four nitrogen atoms in the equatorial positions [Cu2−N$_{basal}$ bond lengths of 1.957(4)−1.980(4) Å], with three nitrogen atoms coming from a dcadpz ligand and the fourth from a monodendate pz ligand. The two oxygen atoms from two different perchlorate ions in the apical positions complete the octahedral geometry, with two long Cu2−O bond lengths of 2.518(5) and 2.561(6) Å. Each trinuclear Cu$_3$ unit is further connected to four adjacent Cu$_3$ units through quadruple μ-ClO$_4^-$ bridges, resulting in a two-dimensional coordination layer (Figure 2). The uncoordinated ClO$_4^-$ and the lattice water molecules are located between the layers and form hydrogen bonds with the imido groups, resulting in a three-dimensional network (Figure S1). It is interesting to note that the magnetic orbital of Cu1 is regarded as $d_{x^2-y^2}$ and is directed towards the four basal N atoms from the two dcadpz ligands, a situation similar to that found in the pioneering building block [Cu(opba)]$^{2-}$ [opba = *o*-phenylenebis(oxamato)].[2] The magnetic orbital of Cu2, mainly $d_{x^2-y^2}$, lies in the N$_4$(basal) plane and points towards the four basal donors.

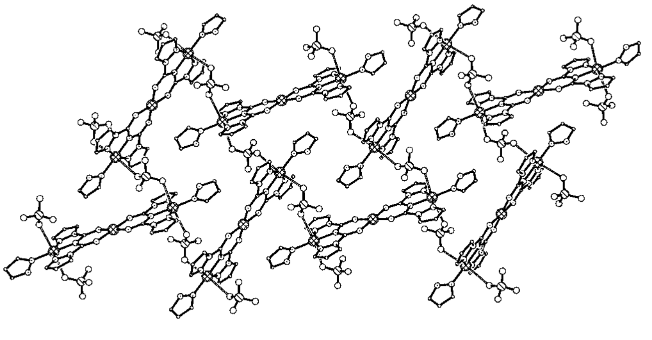


Figure 2. Perspective view of the 2D coordination layer along the *b* axis in **2**

The orientations of the magnetic orbits in **2** are verified by its magnetic behaviour. The value of the magnetic moment at room temperature is 3.25 μ_B per Cu$_3$ formula unit, consistent with three unpaired electrons per Cu$_3$ unit with $g = 2.17$. Upon lowering the temperature, the magnetic moment (μ_{eff}) gradually increases from 3.25 μ_B at 300 K to reach a maximum of 3.88 μ_B at 4.6 K (Figure 3), which is similar to the value (3.87 μ_B) of three ferromagnetically coupled Cu^{II} atoms. The plot of χ_M^{-1} versus T (50−300 K) obeys the Curie−Weiss Law [$\chi_M = C/(T - \theta)$] at 10 kOe with a Weiss constant, θ, of 1.74 K, and a Curie constant, *C*, of 1.30 cm^3 mol^{-1} K, indicating a significant ferromagnetic coupling between the three $S = 1/2$ spins within the Cu_3 unit through the dcadpz bridges. From the structural analysis, **2** is considered to consist of well-separated tri-copper(II) units connected by perchlorate ligands, with the closest Cu2···Cu2′ distance being 6.364 Å. The temperature dependence of μ_{eff} was analysed by an isolated three-spin model[1,9−11] ($H = -2J(S_{Cu2}\cdot S_{Cu1} + S_{Cu1}\cdot S_{Cu2'})$) with MAGMUN4.0.[12] The best-fit parameters were $J = 7.18$ cm^{-1} with an averaged *g* value of 2.15. The three copper(II) ions are ferromagnetically coupled and each Cu_3 unit has a ground spin-multiplicity of 3/2, which is supported by the field dependence of the magnetization [Figure 3 (inset)], The *M*(*H*) data show a linear behaviour from 0 to 20 kOe. The slope then starts to reduce and reaches a value of 2.92 Nβ at 50 kOe, which is very close to the saturated value of 3 Nβ per Cu_3 formula unit with $S = 3/2$. The existence of a ferromagnetic interaction in **2** apparently results from the spin orbital orthogonality: the central Cu atom is antisymmetric whereas the terminal Cu atom is symmetric, and hence the two $d_{x^2-y^2}$ orbitals are orthogonal to each other. This orthogonality is advantageous for ferromagnetic coupling. Magnetic susceptibility $\chi_M(T)$ and magnetization *M*(*H*) measurements on single-phase polycrystalline samples of **1** were also performed to confirm the valence of the copper ion in **1**. The magnetic behaviour of **1** obeys the Curie−Weiss Law in the range 2−300 K with an effective magnetic moment of 1.81 μ_B at 300 K (Figure S2), consistent with the single unpaired electron of Cu^{II} in **1**.

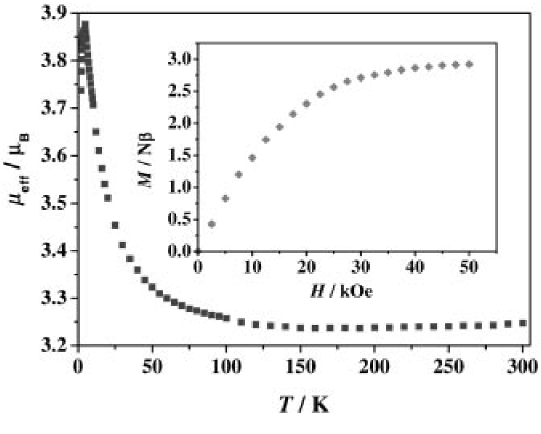


Figure 3. Temperature-dependent magnetic susceptibility plotted as μ_{eff} versus *T* and field-dependent magnetization plotted as *M* versus *H* (inset) at 2 K for a powdered sample of **2**

It is interesting to note that the neutral $Cu(dcadpz)_2$ metalloligand[13] features a planar structure and an intriguing functionality, possessing as it does three lone pairs on either side of the peripheral nitrogen atoms. Therefore, it may behave as a bis-bidentate ligand to connect two metal ions and may further act as a trinuclear building unit to generate low-dimensional coordination magnetic materials. In addition, it is characterised by its spin distribution. There is one unpaired electron arising from the central Cu^{2+} ion, and this electron occupies a $d_{x^2-y^2}$ orbital that is delocalised not only towards the nearest nitrogen atoms, but also towards the six peripheral donor atoms. Such a magnetic orbital interaction means that the $Cu(dcadpz)_2$ segment could be a very useful ferromagnetic coupler. Moreover, what interests us is that the metalloligand presented here can also be easily modified by adopting other starting materials instead of pyrazole. A new route for the synthesis of novel ferromagnetic couplers can therefore be anticipated that is quite different from another recently reported ferromagnetic coupler [$Cu(bptap)_2$], in which bptap was formed by the hydrolysis of tris(2-pyridyl)triazine in the presence of anhydrous $Cu(OAc)_2$ in absolute methanol.[11]

In summary, we provide here a rational strategy for the synthesis of an interesting polydentate ligand and its metal cluster by a simultaneous in-situ addition reaction of dicyanamide and pyrazole, followed by metal coordination. Investigation of this synthetic strategy towards other substituted pyrazole derivatives and the assembly of heteronuclear metal complexes constructed with this metalloligand is under way.

Experimental Section

Synthesis of 1 and 2: Purple crystals of **1** were synthesised by the reaction of $Cu(BF_4)_2\cdot 6H_2O$ (0.237 g, 1.0 mmol) and Na(dca) (0.089 g, 1.0 mmol) in MeOH at 50 °C in ca. 84% yield (0.136 g). The reaction of $Cu(ClO_4)_2\cdot 6H_2O$ (0.555 g, 1.5 mmol), Na(dca) (0.089 g, 1.0 mmol) and pyrazole (0.136 g, 2.0 mmol) in MeOH at 50 °C led to the formation of deep blue crystals of **2** in 78% yield (0.298 g).
1: $C_8H_{16}CuN_6O_4$ (323.8): calcd. C 29.72, H 4.99, N 26.01; found C 29.46, H 4.92, N 25.78
2: $C_{22}H_{26}Cl_4Cu_3N_{18}O_{17}$ (1147.0): calcd. C 23.10, H 2.29, N 22.06; found C 22.81, H 2.18, N 21.83. The IR spectra of **1** and **2** clearly indicate the absence of characteristic peaks for cyano groups, suggesting the transformation of cyano groups into carbimido groups during the reaction.

Crystal Structure Characterisation: X-ray diffraction data collection were carried out on a Bruker CCD diffractometer, using graphite-monochromated Mo-K_α radiation. All non-H atoms were refined anisotropically.
1: Purple crystals. $C_8H_{16}CuN_6O_4$, $M_r = 323.81$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.018(3)$, $b = 5.6635(14)$, $c = 11.632(3)$ Å, $\beta = 99.703(6)°$, $V = 650.6(3)$ Å^3, $Z = 2$, $D_c = 1.653$ g cm^{-3}, $\mu = 17.00$ cm^{-1}. Data collection ($4.01 \leq 2\theta \leq 26°$) was performed at 293 K on a Bruker CCD diffractometer (Mo-K_α, $\lambda = 0.71073$ Å). The structure was solved by direct methods and refined with full-matrix least-squares (SHELX-97),[14] giving a final R_1 value of 0.0400 for 98 parameters and 1032 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.1142 for all 1192 reflections.
2: Deep blue crystals, 293 K. $C_{22}H_{26}Cl_4Cu_3N_{18}O_{17}$, $M_r = 1147.03$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.362(6)$, $b = 12.469(7)$, $c = 17.570(8)$ Å, $b = 92.208(9)°$, $V = 2049.5(19)$ Å^3, $Z = 2$, $D_c = 1.859$ g cm^{-3}, $\mu = 18.96$ cm^{-1}. Final R_1 value of 0.0639 for 295 parameters and 3126 unique reflections with $I > 2\sigma(I)$ and wR_2 of 0.1895 for all 3991 reflections.
CCDC-204851 (**1**) and -204852 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the

Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the NSFC (20001008 & 20131020), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (200122) and the Talent Training Program Foundation of the Higher Education Department of Guangdong Province (Q02017). M.-L. T. is grateful to JSPS for a postdoctoral fellowship.

---

[1] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.

[2] O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647−657.

[3] Y. Rodríguez-Martín, M. Hernández-Molina, F. S. Delgado, J. Pasán, C. Ruiz-Pérez, J. Sanchiz, F. Lloret, M. Julve, *CrystEngCommun* **2002**, *4*, 522−535.

[4] O. Kahn, J. Galy, Y. Journaux, J. Jaid, I. Morgenstern-Badarau, *J. Am. Chem. Soc.* **1982**, *104*, 2165−2176.

[5] S.-I. Noro, S. Kitagawa, M. Yamashita, T. Wada, *Chem. Commun.* **2002**, 222−223.

[6] M.-L. Tong, J. Ru, Y.-M. Wu, X.-M. Chen, H.-C. Chang, K. Mochizuki, S. Kitagawa, *New J. Chem.* **2003**, *27*, 779−782.

[7] G. Rembarz, E. Fischer, K.-Ch. Röber, R. Ohff, H. Crahmer, *J. Prakt. Chem.* **1969**, *311*, 889−893.

[8] G. Götz, H. U. Kibbel, *Z. Chem.* **1975**, *15*, 278−281.

[9] X. Chen, S. Zhan, C. Hu, Q. Meng, Y. Liu, *J. Chem. Soc., Dalton Trans.* **1997**, 245−250.

[10] J. Tercero, C. Diaz, J. Ribas, J. Mahía, M. A. Maestro, *Inorg. Chem.* **2002**, *41*, 5373−5381.

[11] T. Kajiwara, A. Kamiyama, T. Ito, *Chem. Commun.* **2002**, 1256−1257.

[12] *MAGMUN4.0* was developed by Dr Zhiqiang Xu (zxu@hpower.com)and Kathy Minzhen He (heminzhen@yahoo.com) in collaboration with Prof. L. K. Thompson (lthomp@mun.ca) and Dr O. Waldmann (waldmann@physik.uni-erlangen.de).

[13] The neutral $Cu(dcadpz)_2$ metalloligand has been isolated and crystallographically characterised. Crystal data for $Cu(dcadpz)_2$: $C_{16}H_{16}CuN_{14}$, tetragonal, space group $P4_2/n$ (No. 86), $M_r = 467.97$, $a = b = 22.285(8)$, $c = 3.8905(15)$ Å, $V = 1932.2(12)$ Å^3, $Z = 4$. $R_1 = 0.0618$, $wR_2 = 0.0956$.

[14] G. M. Sheldrick, SHELXS-97, *Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997.

Received April 8, 2003