Inorg. Chem. **2008**, *47*, 9128−9130

Inorganic Chemistry
Communication

A Conducting Coordination Polymer Based on Assembled Cu_9 Cages

**Salomé Delgado,*,[†] Pablo J. Sanz Miguel,[†] José L. Priego,[‡] Reyes Jiménez-Aparicio,[‡]
Carlos J. Gómez-García,[§] and Félix Zamora*,[†]**

*Departamento de Química Inorgánica, Universidad Autónoma de Madrid, 28049 Madrid, Spain,
Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense
de Madrid, 28040 Madrid, Spain, and ICMol Parque Científico de la Universidad de Valencia,
46980 Paterna, Valencia, Spain*

Received July 31, 2008

We report on a novel highly semiconducting 1D coordination polymer architecture obtained by the reaction of a Cu^{II} salt with 2,2′-dipyridyldisulfide under microwave solvothermal conditions. This reaction proceeds with an unusual C−S and S−S bond cleavage of the 2,2′-dipyridyldisulfide ligand. The unprecedented architecture of this coordination polymer consists of a 1D chain formed by the assembling of Cu_9 cluster cages. The electrical conductivity behavior of this novel material suggests new perspectives for the use of coordination polymers as electrical conducting materials.

The singular properties of 1D structures based on inorganic compounds are of special relevance in the search for new materials.[1,2] Coordination polymers have gained great attention during the last years in the field of materials science because of their interesting properties including magnetism,[3] catalysis,[4] nonlinear optics,[5] and molecular sensing.[6] However, despite electrical conductivity being an area of high interest, in the case of coordination polymers, it is still poorly developed.[1,7] Recenty, theoretical calculations have pointed out their potential as electrical conductors.[8] The search for nanotechnological applications for these polymers, and in particular as molecular wires, has became of current interest because of the variety of organizations that they may offer on several surfaces.[9] A wide range of 1D, 2D, and 3D architectures of coordination polymers have already been reported, but the development of new structures could still produce a variety of novel materials. Hydro(solvo)thermal methods have proven to be a fruitful strategy in the preparation of highly stable coordination polymers. This is, in part, due to many interesting synthetic reactions that can take place during the preparation process,[10] including redox, ligand oxidative coupling, and substitution reactions, which result in products that are inaccessible, or not easily attainable, by other conventional methods.[11] It is expected that novel architectures can be achieved with the use of innovative synthetic procedures such as ultrasound and microwave.[1] However, examples of coordination polymers synthesized by the latter procedure are very scarce.[12]

Finally, the use of organosulfur ligands is especially attractive for the development of new structural types because of their versatility in coordination binding modes. In addition, they show a rich redox chemistry[13] based on both oxidative formation and reductive cleavage of the disulfide bonds, which has been explored as an attractive route toward functional ligands and novel materials. Moreover, the

---

* To whom correspondence should be addressed. E-mail: salome.delgado@uam.es (S.D.), felix.zamora@uam.es (F.Z.). Fax: +34 91 4974833.

[†] Universidad Autónoma de Madrid.

[‡] Universidad Complutense de Madrid.

[§] ICMol Parque Científico de la Universidad de Valencia.

(1) Kitagawa, S.; Noro, S. *Comprehensive Coordination Chemistry*; Elsevier: Oxford, U.K., 2004; Vol. *7*, p 231.

(2) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15*, 353.

(3) Brammer, L. *Chem. Soc. Rev.* **2004**, *8*, 476.

(4) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

(5) Hou, H.; Meng, X.; Song, Y.; Fan, Y.; Zhu, Y.; Lu, H.; Du, C.; Shao, W. *Inorg. Chem.* **2002**, *41*, 4068.

(6) (a) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970. (b) Beauvais, L. G.; Sores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763.

(7) Janiak, C. *Dalton Trans.* **2003**, 2781.

(8) (a) Alexandre, S. S.; Soler, J. M.; Sanz Miguel, P. J.; Nunes, R. W.; Yndurain, F.; Gómez-Herrero, J.; Zamora, F. *Appl. Phys. Lett.* **2007**, *90*, 193107. (b) Calzolari, A.; di Felice, R.; Alexandre, S. S.; Zamora, F. *J. Am. Chem. Soc.* **2008**, *130*, 5552.

(9) (a) Amo-Ochoa, P.; Rodriguez-Tapiador, M. I.; Castillo, O.; Olea, D.; Guijarro, A.; Alexandre, S. S.; Gomez-Herrero, J.; Zamora, F. *Inorg. Chem.* **2006**, *45*, 7642. (b) Garcia-Couceiro, U.; Olea, D.; Castillo, O.; Luque, A.; Roman, P.; de Pablo, P. J.; Gomez-Herrero, J.; Zamora, F. *Inorg. Chem.* **2005**, *44*, 8343. (c) Olea, D.; Alexandre, S. S.; Amo-Ochoa, P.; Guijarro, A.; de Jesus, F.; Soler, J. M.; de Pablo, P. J.; Zamora, F.; Gomez-Herrero, J. *Adv. Mater.* **2005**, *17*, 1761. (d) Mateo-Martí, E.; Welte, L.; Amo-Ochoa, P.; Sanz Miguel, P. J.; Gómez-Herrero, J.; Martín-Gago, J. A.; Zamora, F. *Chem. Commun.* **2008**, *945*.

(10) Zhang, J.-P.; Zheng, J.-P.; Zheng, S.-L.; Huang, X.-C.; Chen, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 206.

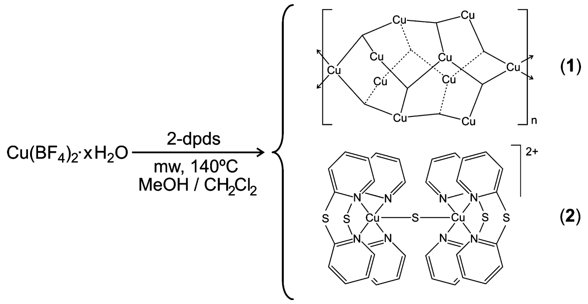
(11) Chen, X.-M.; Tong, M.-L. *Acc. Chem. Res.* **2007**, *40*, 162.

(12) Amo-Ochoa, P.; Givaja, G.; Miguel, P. J. S.; Castillo, O.; Zamora, F. *Inorg. Chem. Commun.* **2007**, *10*, 921, and references cited therein.

(13) (a) Humphrey, S. M.; Mole, R. A.; Rawson, J. M.; Wood, P. T. *Dalton Trans.* **2004**, 1670. (b) Caradoc-Davies, P. L.; Hanton, L. R. *Dalton Trans.* **2003**, 1754. (c) Horikoshi, R.; Mochida, T.; Moriyama, H. *Inorg. Chem.* **2002**, *41*, 3017.

10.1021/ic801314s CCC: $40.75

Scheme 1



incorporation of thiolate−S as a bridge between adjacent transition-metal sites in coordination polymers is highly desirable in terms of magnetic, conductive, and luminescent behavior because the orbital energies are better matched for S and there will be greater delocalization of the spin density toward the bridging atom.[14]

Recently, we have focused our research on the study of 1D coordination polymers for the development of new molecular wires.[9,15] In this Communication, we report the reaction between Cu(BF$_4$)$_2$·H$_2$O and 2-dpds (2-dpds = 2,2′-dipyridyldisulfide) under microwave conditions, which give rise to a semiconductor 1D coordination polymer showing a new architecture generated by an unusual cleavage of C−S and S−S bonds of the 2,2′-dipyridyldisulfide ligand.

The treatment of Cu(BF$_4$)$_2$·H$_2$O with 2-dpds under solvothermal microwave conditions leads to the formation of separated crystals of a Cu^{I} yellow crystalline solid characterized as $\{[Cu_9(C_5H_5NS)_8(SH)_8](BF_4)\}_n$ (**1**) and $\{[Cu^{II}(2\text{-dps})_2]_2(\mu\text{-}S)\}(BF_4)_2(CH_2Cl_2)_4$ (**2**; 2-dps = 2,2′-dipyridylsulfide) (Scheme 1). In addition, pale-yellow orthorhombic crystals of elemental sulfur S$_8$ (S.I.) were obtained as a concomitant byproduct.

The interesting structure of **1** results in a quasi-1D Cu^{I} polymer. It represents a novel 1D coordination polymer architecture type based on the assembling of Cu$_9$ cages (Figure 1). Three different copper atoms are included in the structure: Cu1, Cu2, and Cu3 in a 4:1:4 ratio. Coordination geometries are trigonal-planar for Cu1 and tetrahedral for Cu2 and Cu3. Figure 1 shows a schematic view of a monomer of **1** (a Cu$_9$ cluster) and the polymer skeleton, extended along the *c* axis (see Figure SI-4 in the Supporting Information for packing details). Copper cations are bridged by tetrahedral sulfur atoms (S2a and S2b) from 2-pyridylthione ligands, forming cavities interconnected by Cu2. These cavities are delimited by eight Cu$_3$S$_3$ hexagons, with a volume of ca. 100 Å^3.

A view of the binuclear complex **2** is depicted in Figure SI-5 in the Supporting Information. The solid-state structure of **2** consists of two centrosymmetric [Cu^{II}(2-dpds)$_2$] units connected by a linear sulfur bridge; the structure is completed by two BF$_4$ counteranions and four dichloromethane solvent molecules. Few examples containing a linear sulfur bridge between two transition metals have been reported so far (see reference in Table SI-6 in the Supporting Information), with this complex being the first example with copper.

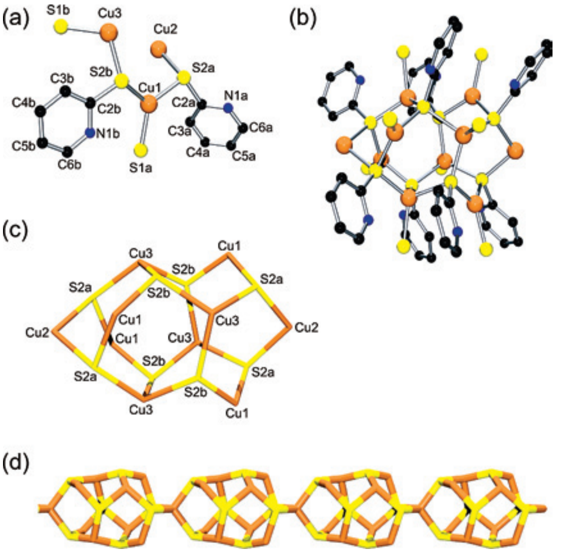


Figure 1. (a) View of cation 1 with an atomic numbering scheme. (b and c) Schematic views of a $[Cu_9(C_5H_5NS)_8(SH)_8]^+$ cluster (**1**). Cu1 and Cu3 bind additional high-spin terminal ligands; sulfur atoms in the skeleton bind a C$_5$H$_5$N ring (pyridine-2-thione ligands). (d) Representation of the $[Cu_9(C_5H_5NS)_8(SH)_8]_n^{n+}$ polymer.

The metal coordination geometry of the copper atoms is described as square-pyramidal, with the sulfur bridging atom in the apical position; the basal plane positions are occupied by two 2-dps acting as N,N′-bidentate ligands. Both 2-dps ligands are cis-positioned and are in a head−head arrangement, with S2a and S2b pointing out of the dimer; intraligand dihedral angles are 64.01° (A ring) and 70.67° (B ring). The metal is placed 0.258 Å out of the basal plane toward the apical position [Cu1−S1, 2.6666(7) Å]. Cu−N distances are usual, ranging from 2.018(5) Å (Cu1−N1a) to 2.033(5) Å (Cu1−N1b). The 2-dps sulfur atoms (S2a and S2b) are involved in a double S2a···S2b intramolecular interaction [3.341(2) Å], forming strands; besides, the cationic dimer is surrounded by BF$_4^-$ and CH$_2$Cl$_2$.

The formation of **1** and **2** implies cleavage of two bonds from the 2-dpds ligand: S−S and S−C(sp^2). Although S−S bond cleavage in dithiodipyridine is easy under solvothermal conditions, C−S bond cleavage is much less frequent and has only been recently reported.[11] The activation of this bond, as well as the removal of organosulfur compounds present in a petroleum-based feedstock, is a fundamental task toward the discovery of new organic syntheses.[16] A feasible mechanism that can explain the formation of compounds **1** and **2** can be postulated, considering 2-dps and S$_8$ as byproducts. This process assumes the homolitic rupture of the S−S and S−C(sp^2) bonds, with subsequent formation of two free-radical intermediates, [2-pyS$^\bullet$] and [2-py$^\bullet$]. Recombination of both radicals entails the 2-dps (as a minor product) ligand. Furthermore, self-recombination of the radicals should also

---

(14) Alexandre, S. S.; Soler, J. M.; Sanz Miguel, P. J.; Nunes, R. W.; Yndurain, F.; Gómez-Herrero, J.; Zamora, F. *Appl. Phys. Lett.* **2007**, *90*, 193107.

(15) (a) Delgado, S.; Barrilero, A.; Molina-Ontoria, A.; Medina, M. E.; Pastor, C. J.; Jiménez-Aparicio, R.; Priego, J. L. *Eur. J. Inorg. Chem.* **2006**, *14*, 2746. (b) Delgado, S.; Molina-Ontoria, A.; Medina, M. E.; Pastor, C. J.; Jiménez-Aparicio, R.; Priego, J. L. *Inorg. Chem. Commun.* **2006**, *9*, 1289.

(16) Choudhary, T. V.; Malandra, J.; Green, J.; Parrot, S.; Johson, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3299.

take place. Under this presumption, all dissolutions were examined by means of electrospray ionization mass spectrometry: two peaks at *m*/*z* 221.02 and 158.01, attributed to deprotonated cations of the 2-dpds and 2,2′-bipy ligands, respectively, are detected together with a peak at *m*/*z* 189.05, assignable to the monoprotonated 2-dps cation. The reduction of Cu^{II} to Cu^{I} observed in this reaction probably is emphasized under microwave conditions. Although methanol can also serve as a reducing agent, by use of CH_2Cl_2 instead of methanol, **1** is also obtained. It has been established that Cu^{II} ions could be reduced to Cu^{I} in the presence of N-containing ligands under hydro(solvo)thermal conditions.[17] In addition, it is well-known that the presence of thiolate groups in the reaction media may also cause a reduction of the copper.[18] To our knowledge, it is the first time that use of a microwave technique has allowed the preparation of new architecture of coordination networks.

In order to confirm the oxidation state of the copper centers in compounds **1** and **2**, several techniques were used. The X-ray photoelectron spectrum of **1** shows shoulder peaks of $^2P_{3/2}$ and $^2P_{1/2}$ at 932.6 and 952.4 eV, respectively, indicating the presence of Cu^{I} in the complex[19] (Figure SI-1 in the Supporting Information). This observation is in agreement with the diamagnetism observed in the magnetic measurements carried out in the temperature range 2−300 K (S.I.). Complex **2** presents a room temperature magnetic moment of 2.77 μ_B per Cu^{II} dimer, which remains constant when the temperature is decreased. Only at very low temperatures does the magnetic moment decrease to reach a value of ca. 2.69 μ_B at 2 K (Figure SI-2 in the Supporting Information). This behavior indicates that compound **2** is essentially paramagnetic with a very weak antiferromagnetic coupling. Accordingly, we have fit the magnetic behavior to the Bleaney−Bowers[20] formula for an $S = {}^1/_2$ dimer. The very low zJ value (-0.12 cm^{-1}) confirms the presence of a very weak antiferromagnetic coupling between the Cu^{II} centers of the dinuclear molecule, as expected for a linear Cu−S−Cu bridge in apical positions, because the overlap of the magnetic orbitals of both Cu^{II} ions ($d_{x^2-y^2}$) is expected to be negligible.

The solid-state UV−vis absorption spectrum of **1** shows little absorption in the visible range. The emission spectra of the ligand 2-dpds and compound **1** show red fluorescence with emission maximum bands centered at 609 and 600 nm, respectively, upon photoexcitation at 350 nm (Figure SI-3 in the Supporting Information). In general, possible assignments for the excited states that are responsible for emission phenomena of Cu^{I} complexes are ligand-centered (LC) $\pi \rightarrow \pi^*$ transitions, ligand-to-metal (LMCT) or metal-to-ligand (MLCT) charge-transfer transitions, or metal-centered (MC) $d^{10} \rightarrow d^9s^1$ transitions.[21] Owing to the similar energy of the emission bands of the free 2-dpds ligand and **1**, the emission band in **1** is tentatively assigned to an intraligand transition. Compared with free 2-dpds, the emission in **1** is slightly red-shifted in 6 nm.

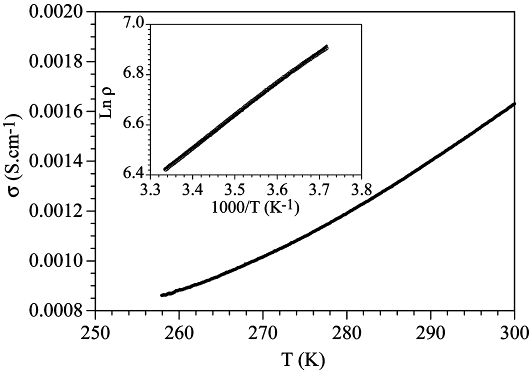


Figure 2. Thermal variation of the electrical conductivity of compound **1**. The inset shows an Arrhenius plot.

Despite the relatively long Cu−Cu distances (ca. 3.4−3.7 Å) found in the Cu_9 cages of **1**, its unusual 1D polymeric architecture and the presence of a large number of S bridges prompted us to study its electrical conductivity. These measurements show that at room temperature compound **1** presents a high room temperature conductivity of 1.6×10^{-3} S·cm^{-1} and a classical semiconducting behavior with an activation energy of 110 meV (Figure 2). Note that this is one of the very few examples of coordination polymers showing conductivity in the solid state.[1,9d]

In summary, in this work we have described the unusual simultaneous C−S and S−S bond activations in the 2-dpds ligand under microwave irradiation dielectric heating that have led to the first Cu−S−Cu linear bridge and to a 1D coordination polymer with a novel architecture type based on the assembling of metal cages with empty cavities, which constitutes one of the very few examples of conducting coordination polymer density functional theory calculations to rationalize the electrical properties of **1**, and studies on surfaces are currently in progress.

Acknowledgment. Financial support by the MEC (Projects MAT2007-66476-C02-02, MAT2007-61584 NAN2004-09183-C10-05/06, FP6-029192, CTQ2005-00397/BQU, CTQ2006-027185-E, and Consolider-Ingenio 2010 CSD 2007-00010 in Molecular Nanoscience) and Comunidad de Madrid (Project S-0505/MAT/0303). The authors are indebted to Prof. J. Gómez, Prof. J. L. García Fierro, and Dr. P. A. Postigo for their assistance.

Supporting Information Available: Details on the synthesis and characterization, electrical measurements, and X-ray crystallographic files in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.

IC801314S

---

(17) Lui, J. I. *Coord. Chem. Rev.* **2003**, *246*, 327.

(18) Higashi, L. S.; Lundeen, M.; Hilti, E.; Seff, K. *Inorg. Chem.* **1977**, *16*, 310.

(19) Cai, Y.; Wang, Y.; Li, Y.; Wang, X.; Xin, X.; Liu, C.; Zheng, H. *Inorg. Chem.* **2005**, *44*, 9128.

(20) Kahn, O. *Molecular Magnetism*; VCH Publishers, Inc.: New York, 1993; p 107.

(21) Yam, V. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999**, *28*, 323.