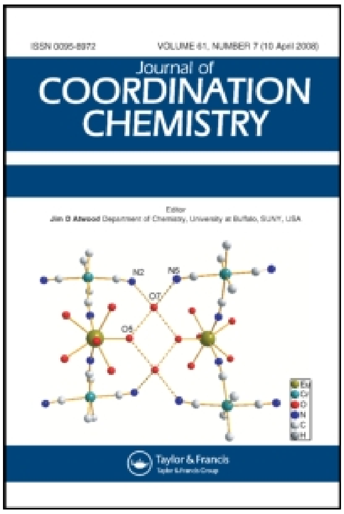

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A novel mixed-valence copper coordination polymer: synthesis, characterization and crystal structure

Guang Fan[a]; Gang Xie[a]; Sanping Chen[a]; Shengli Gao[a]; Qizhen Shi[a]
[a] Department of Chemistry, Shaanxi Key Laboratory of Physical Inorganic Chemistry, Northwest University, Xi'an, Shaanxi, P.R. China

To cite this Article Fan, Guang , Xie, Gang , Chen, Sanping , Gao, Shengli and Shi, Qizhen(2006) 'A novel mixed-valence copper coordination polymer: synthesis, characterization and crystal structure', Journal of Coordination Chemistry, 59: 7, 791 — 795

To link to this Article: DOI: 10.1080/00958970500376229

URL: http://dx.doi.org/10.1080/00958970500376229

Journal of Coordination Chemistry
Vol. 59, No. 7, 10 May 2006, 791–795

Taylor & Francis
Taylor & Francis Group

A novel mixed-valence copper coordination polymer: synthesis, characterization and crystal structure

GUANG FAN, GANG XIE, SANPING CHEN,
SHENGLI GAO* and QIZHEN SHI

Department of Chemistry, Shaanxi Key Laboratory of Physical Inorganic Chemistry,
Northwest University, Xi'an, Shaanxi 710069, P.R. China

(*Received in final form 28 July 2005*)

Hydrothermal reaction of copper(II) nitrate trihydrate with 2-pyrazinecarboxylic acid in the presence of phosphorous acid gave a novel mixed-valence coordination polymer, $[Cu(I)Cu(II)(C_5H_3N_2O_2)_2(NO_3)(H_2O)]_n$ (**1**), which has been structurally characterized. Crystal data: triclinic, $P\bar{1}$, $a = 6.2266(6)$, $b = 8.0148(7)$, $c = 14.443(1)$ Å, $\alpha = 74.698(1)$, $\beta = 84.865(1)$, $\gamma = 84.532(1)^\circ$, $V = 690.51(11)$ Å^3, $Z = 2$, $R_1 = 0.0262$. The complex features linear –Cu(1)(2-pyrazinecarboxylate)–Cu(2)–$(NO_3)(H_2O)$(2-pyrazinecarboxylate)–Cu(3)(2-pyrazinecarboxylate)–Cu(2)$(NO_3)(H_2O)$(2-pyrazinecarboxylate)– strands cross-linked by water molecules to form a two-dimensional sheet, further connected by intralayer $Cu(2)\cdots NO_3^-$ interactions to form a novel cavity. Other characteristic data are given.

Keywords: Hydrothermal reaction; Copper; 2-Pyrazinecarboxylic acid; Mixed-valency; Coordination polymer; Crystal structure

1. Introduction

Studies of mixed-valence complexes are of great interest both in biochemistry and inorganic chemistry [1–3]. Such complexes may not only serve as possible models for copper proteins or provide valuable information on electron-transfer mechanisms, but also have potential applications in fields such as nonlinear optics, electric and magnetic materials [4, 5]. Pyrazine is an excellent bridging ligand and has been extensively studied. In addition, carboxylate ligands are equally capable of bridging when paramagnetic metals are involved, and represent an important class of ligand in inorganic and bioinorganic chemistry [6]. 2-Pyrazinecarboxylic acid (2-pac) is a versatile bridging ligand. It allows the design of novel mixed-valency Cu(I)/Cu(II) and mixed-metal compounds, some of which have been structurally characterized [7–14].

---

*Corresponding author. Email: gaoshli@nwu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500376229

Here we describe the hydrothermal synthesis and characterizations of novel mixed-valence Cu(I)/Cu(II) coordination polymer containing 2-pac **1**.

2. Experimental

2.1. *Materials and measurements*

2-Pyrazinecarboxylic acid was purchased from Acros. All other chemicals were of analytical grade and used without further purification. Elemental analyses were performed on a Vario EL III instrumentanalyzer. IR spectra were recorded on a BEQ VZNDX 550 FTIR instrument (KBr pellets) in the range 4000–400 cm^{-1}.

2.2. $[Cu(I)Cu(II)(C_5H_3N_2O_2)_2(NO_3)(H_2O)]_n$ *(1)*

Dark red plates of **1** were obtained from a mixture of 2-pyrazinecarboxylic acid (0.124 g, 1 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1 mmol) and H_3PO_3 (0.2 cm^3, 50%), which was placed in a sealed plastic bottle and kept at 85° for 24 h under autogenous pressure. Yield: 76%. Anal. Calcd For $Cu_2C_{10}H_8N_5O_8$ (%): C, 26.78; H, 1.39; N, 15.49. Found: C, 26.50; H, 1.78; N, 15.45.

2.3. *Crystallography*

A suitable single crystal of dimensions $0.35 \times 0.12 \times 0.28$ mm^3 was mounted on Bruker Smart Apex CCD diffractometer equipped with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected using ω and φ scan modes in the range $2.64 < \theta < 29.15$ at 273 K. Among 4434 measured reflections, 2949 were considered observed reflections with $I > 2\sigma(I)$ and used in the refinement. Corrections for Lorentz polarization factor and absorption were applied. The structure was solved by direct methods and refined with full-matrix least-squares techniques based on F^2 using the SHELXTL package [15–17]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms were generated geometrically and allowed to ride on their parent atoms. Crystal data, data collection parameters and refinement statistics for **1** are listed in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Description of the structure*

Complex **1** exhibits a two-dimensional wave-like structure built up from one-dimensional mixed-valence chains of $Cu(I)Cu(II)(C_5H_3N_2O_2)_2(NO_3)(H_2O)$ (figure 1), cross-linked by water molecules (figure 2). Within the chain, three copper atoms are crystallographically distinguishable. Both Cu(1) and Cu(3) are divalent and Cu(2) is univalent. The one-dimensional mixed-valence chain consists of alternating $Cu(I)(NO_3)(H_2O)$ and $Cu(II)(C_5H_3N_2O_2)_2$ fragments. All water molecules coordinated to Cu(2) in the same chain are arranged in a *trans* orientation with the neighboring chain, as for NO_3^-. Coordination planes of Cu(1) and Cu(3) are not coplanar,

Table 1. Summary of crystallographic data for the complex.

Formula	$C_{10}H_8Cu_2N_5O_8$
Formula weight	453.29
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	6.2266(6)
b (Å)	8.0148(7)
c (Å)	8.0148(7)
α (°)	74.698(1)
β (°)	84.865(1)
γ (°)	84.532(1)
Volume (Å^3)	690.51(1)
Z	2
F(000)	450
Temperature (K)	273(2)
Total reflections	4108
Observed reflections ($I > 2\sigma(I)$)	2949
Goodness of fit	1.057
R_{int}	0.0136
R_1, wR_2 ($I > 2\sigma(I)$)	0.0262, 0.0697
R_1, wR_2 (all data)	0.0282, 0.0707

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Cu(1)–O(1)	1.936(2)	Cu(1)–N(1)	1.986(2)
Cu(2)–N(2)	1.970(2)	Cu(2)–N(4)	1.983(2)
Cu(2)–O(5)	2.363(3)	Cu(2)–O(8)	1.983(4)
Cu(3)–O(3)	1.963(1)	Cu(3)–N(3)	1.996(2)
Cu(3)–O(5)	2.436(2)		
O(1)–Cu(1)–O(1)	180.0	O(1)–Cu(1)–N(1)	83.96(8)
N(1)–Cu(1)–N(1)	180.0	N(2)–Cu(20)–N(4)	140.16(9)
O(3)–Cu(3)–O(3)	180.0	O(3)–Cu(3)–N(3)	83.13(7)
N(3)–Cu(3)–N(3)	180.0	O(3)–Cu(3)–O(5)	90.29(6)
N(3)–Cu(3)–O(5)	89.41(7)	O(5)–Cu(3)–O(5)	180.0
Cu(2)–O(5)–Cu(3)	123.14(7)	O(2)–C(1)–O(1)	125.8(2)

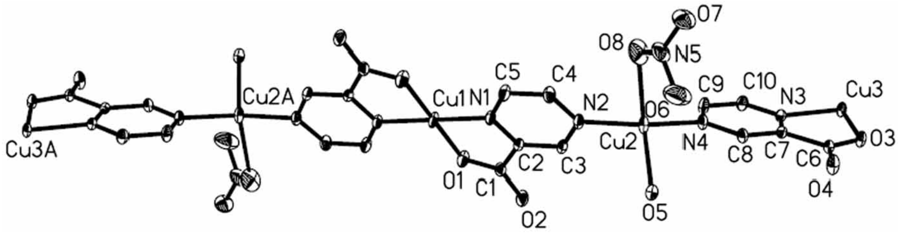

Figure 1. A fragment of the one-dimensional chain in **1** with atom labelling (atoms drawn at 30% probability level); hydrogen atoms are omitted for clarity.

with an interplanar angle of 62.6°. Cu(1) is situated in a distorted square planar environment, bonded to two oxygen and two nitrogen atoms of two chelating 2-pyrazinecarboxylate ligands. Additionally, Cu(1) interacts weakly with two NO_3^- ions (Cu(1)–O(7) = 2.594 Å), positioned perpendicularly to the [CuN_2O_2] plane, giving a pseudo-octahedral geometry.

The coordination sphere of Cu(2) is a distorted tetrahedron. Cu(2) is coordinated to two crystallographically inequivalent nitrogen donors (N(2) and N(4); Cu(2)–N(2) = 1.970(2), Cu(2)–N(4) = 1.983(2) Å) from two 2-pyrazinecarboxylate

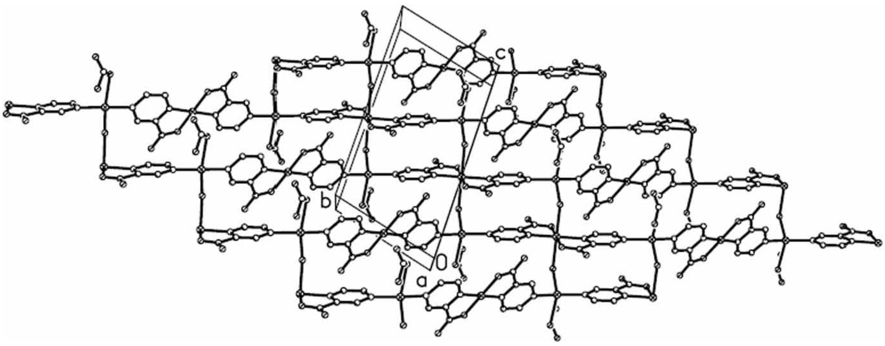

Figure 2. Illustration of the 2-dimensional network layer in the structure; hydrogen atoms are omitted for clarity.

molecules, one water molecule (Cu(2)–O(5) = 2.221(2) Å) and a nitrate oxygen atom (Cu(2)–O(8) = 2.367(7) Å). Bond angles around Cu(2) are 140.16(9) for N(2)–Cu(2)–N(4), 103.46(8) for N(2)–Cu(2)–O(5), 88.51(2) for N(2)–Cu(2)–O(8), 103.9(2) for N(4)–Cu(2)–O(8), 100.64(7) for N(4)–Cu(2)–O(5) and 123.54(2) for O(8)–Cu(2)–O(5).

Cu(3) is bonded to two nitrogen (N(3)) and two oxygen (O(3)) atoms from two 2-pyrazinecarboxylate molecules, with Cu(3)–N(3) = 1.996(2), Cu(3)–O(3) = 1.963(2) Å, N(3)–Cu(3)–N(3) = 180.0 and N(3)–Cu(3)–O(3) = 83.13(7)°; the axial positions are occupied by two water molecules with Cu(3)–O(5) = 2.436(2) Å. By comparison, bond distances and angles around Cu(1) and Cu(3) involving 2-pyrazinecarboxylate molecules are quiet similar to the corresponding values found in $Cu(C_5H_3N_2O_2)_2$ and $Cu(C_5H_3N_2O_2)_2(H_2O)_2$ [6], respectively.

Crystal packing of the complex (figure 2) involves two different channels. The larger one is enclosed by four Cu(I) and four Cu(II) ions, six 2-pyrazinecarboxylates and two water molecules, with a cross-sectional size of 4.097 × 18.954 Å. The other consists of two Cu(I) and two Cu(3) ions, two 2-pyrazinecarboxylates and two water molecules, with a cross-sectional size of 4.097 × 6.722 Å. Furthermore, chains from each pair of adjacent layers are criss-crossed through the interaction $Cu(2)\cdots NO_3^-$(O(7)), yielding a three-dimensional polymer with rectangular channels (figure 3). This structure is quiet different from those of α- or β-$[Cu_2X(C_5H_3N_2O_2)_2(H_2O)]_n$ (X = Cl, Br) [7] and $[Cu(I)Cu(II)(C_5H_3N_2O_2)_2(H_2O)(ClO_4)]_n$ [14].

3.2. *Other physical data*

The thermal stability of the complex has determined by thermogravimetric analysis of polycrystalline sample in air. TGA curves show two marked weight losses of 51.0% at 238–313°C and 65.9% at 313–639°C. In the first stage, the skeleton of the complex collapses and the residue is $Cu_2(OH)_2CO_3$ (Calcd loss: 48.8%). Above 313°C, this decomposes CuO (Calcd loss 35.1%). In IR spectra, a strong broad peak at 3339 cm^{-1} and two weak to medium peaks located at 793 and 563 cm^{-1} are assigned to $\nu_{O\text{–}H}$ and in-plane wagging vibrations of water, respectively. Asymmetric and symmetric vibrations of carboxylate groups appear at 1596 and 1412 cm^{-1}, which is evidence of carboxylate binding to copper in monodentate mode. Peaks at 1469, 1320, 1061 and 793 cm^{-1} can be attributed to stretching and out-of-plane deformations

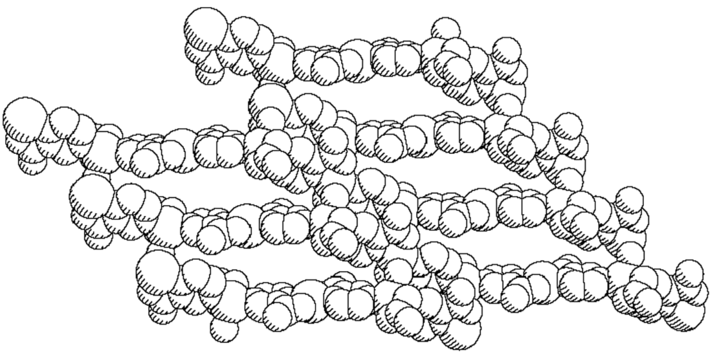

Figure 3. A perspective view of the three dimensional structure showing the rectangular channels present in it.

of nitrate, as a result of nitrate coordination in monodentate fashion. In addition, the peak at 1518 cm^{-1} is characteristic of the C=N–C group of 2-pyrazinecarboxylic acid.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 278075. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] K.D. Karlin, J. Zubieta (Eds). *Copper Coordination Chemistry: Biological and Inorganic Perspectives*, Adenine Press, New York (1985).

[2] K.D. Karlin, J. Zubieta (Eds). *Biological and Inorganic Copper Chemistry*, Adenine Press, New York (1986).

[3] P.A. Cox. *Transition Metal Oxides: An Introduction to their Electronic Structure and Properties*, Clarendron Press, Oxford (1995).

[4] C.G. Young. *Coord. Chem. Rev.*, **96**, 89 (1989).

[5] J.P. Faclker. In *Encyclopedia of Inorganic Chemistry*, K.R. Bruce (Ed.), John Wiley and Sons, New York (1992).

[6] C.L. Klein, R.J. Majeste, L.M. Trefonas, C.J. O'Connor. *Inorg. Chem.*, **21**, 1891 (1982).

[7] L.M. Zheng, X.Q. Wang, A.J. Jacobson. *J. Solid State Chem.*, **152**, 174 (2000).

[8] Y.B. Dong, M.D. Smith, H.C. zur Loye. *Solid State Sci.*, **2**, 225 (2000).

[9] Y.B. Dong, M.D. Smith, H.C. zur Loye. *Angew. Chem. Int. Edit.*, **39**, 4271 (2000).

[10] Y.B. Dong, M.D. Smith, H.C. zur Loye. *Solid State Sci.*, **2**, 861 (2000).

[11] D.M. Ciurtin, M.D. Smith, H.C. zur Loye. *Solid State Sci.*, **4**, 461 (2002).

[12] D.M. Ciurtin, M.D. Smith, H.C. zur Loye. *Abstr. Pap. Am. Chem. Soc.*, **223**, A58 (2002).

[13] D.M. Ciurtin, M.D. Smith, H.C. zur Loye. *J. Chem. Soc., Dalton Trans.*, 1245 (2003).

[14] C.M. Liu, D.Q. Zhang, J.L. Luo, N.L. Wang, H.M. Hu, D.B. Zhu. *Eur. J. Inorg. Chem.*, **19**, 3618 (2003).

[15] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Determination*, Göttingen University, Germany (1997).

[16] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, Göttingen University, Germany (1997).

[17] G.M. Sheldrick. *SHELXTL, Version V*, Siemens Industrial Automation Inc., Madison, Wisconsin, USA (1997).