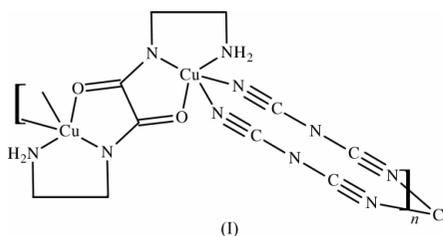


**catena-Poly[[[ $\mu$ -*N,N'*-bis(2-aminoethyl)-oxamido]dicopper(II)]-di- $\mu$ -dicyanoamido]****Sheng Chu, Xiao-Qing Wang,\*  
Ru-Ji Wang and Guang-Qiu Shen**Department of Chemistry, Tsinghua University,  
Beijing 100084, People's Republic of ChinaCorrespondence e-mail:  
xqwang@tsinghua.edu.cn**Key indicators**Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.040  
 $wR$  factor = 0.073  
Data-to-parameter ratio = 19.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

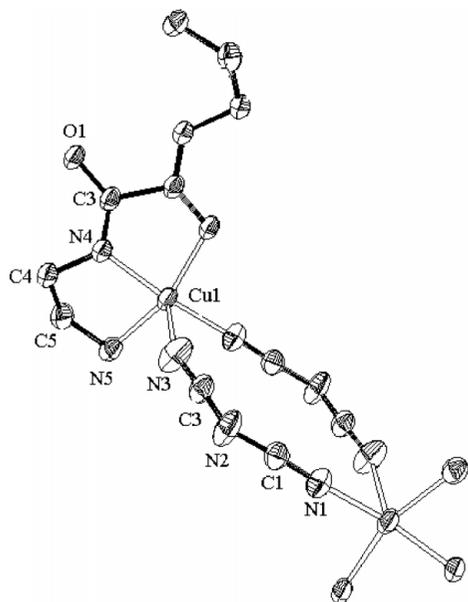
A new polymeric copper complex,  $[\text{Cu}_2(\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2)(\text{C}_2\text{N}_3)_2]_n$  or  $[\text{Cu}_2(\text{oxen})[\text{N}(\text{CN})_2]_2]_n$  [oxenH<sub>2</sub> is *N,N'*-bis(2-aminoethyl)-oxamide], has been synthesized and its structure determined by X-ray diffraction methods. In the polymer chain, oxen and dicyanamide (dca) groups both act as bridges to link Cu<sup>II</sup> cations, illustrating the potential of oxen and dca in coordination chemistry and supramolecular polymer chemistry.

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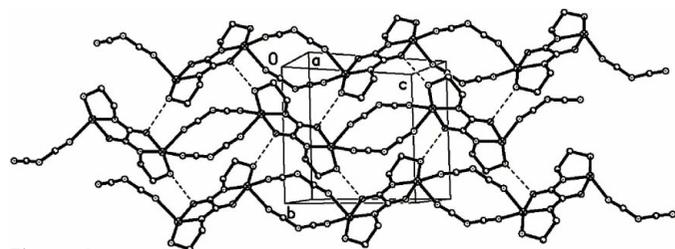
Supramolecular polymer chemistry, an important branch of modern chemical science, is developing as the combination of supramolecular chemistry and polymer chemistry (Lehn, 1995, 1999; Kholbystov *et al.*, 2001). Inorganic crystal engineering is an important branch of supramolecular polymer chemistry research, because it offers the prospect of deliberately designing new materials with useful properties (Zhang *et al.*, 2001; Braga, 1999).



Dca (dicyanamide,  $[\text{N}(\text{CN})_2]^-$ ) and *trans*-oxen [*N,N'*-bis(2-aminoethyl)oxamido<sup>2-</sup>] have been shown to be useful species for the construction of one- and two-dimensional coordination architectures (Groeneman *et al.*, 1998; Choi & Suh, 1999; Batten *et al.*, 2000; Manson *et al.*, 1998). Dca itself can act as a monodentate, bidentate (two types of binding) or tridentate ligand. In the last few years, coordination polymers containing dca as ligand have attracted much attention and led to many homometallic or heterometallic networks of varied topologies and magnetic properties (van Albada *et al.*, 2000; Hvastijova *et al.*, 1999). When other ligands are introduced, different kinds of structures can be obtained, such as one-dimensional chains (Sun *et al.*, 2001; Escuer *et al.*, 2000), ladders (Wang *et al.*, 2000), two-dimensional sheets (Marshall *et al.*, 2002; Jensen *et al.*, 2001), and three-dimensional interpenetrating diamondoid nets (Wang *et al.*, 2000). Therefore, we chose dca and oxen groups as ligands to construct a new coordination polymer. Here we report the synthesis and structure of the title polymeric complex, (I).


**Figure 1**

The structure of a section of the polymeric title compound, with 50% probability ellipsoids, showing the atomic numbering scheme for the asymmetric unit.


**Figure 2**

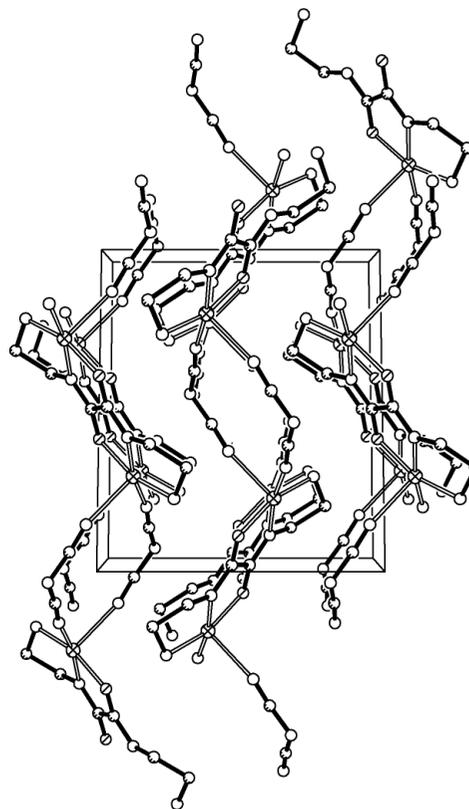
Three polymer chains of the title complex, showing hydrogen bonds as dashed lines.

The structure of (I), with the atomic numbering, is shown in Fig. 1. The repeat unit of the polymer is a dinuclear one, containing two centrosymmetrically related  $\text{Cu}^{2+}$  cations, with oxen and dca groups connecting the cations together. The  $\text{Cu}^{2+}$  cations exhibit square-based pyramidal coordination geometry; the basal plane is formed by two N atoms and one O atom from an oxen group and one N atom from a dca group. The apical site is occupied by one N atom from another dca group, with a bond length of 2.343 (3) Å. The chain polymeric structure is depicted in Fig. 2. In the chain, oxen and dca groups both act as bridging ligands, alternately connecting copper cations. Fig. 3 shows the packing, viewed along the *a* axis. An intermolecular hydrogen-bond network is present (Table 1), through which the polymer chains are connected into a two-dimensional structure and copper ions are arranged in a net.

The IR spectrum shows the characteristic CN stretching vibration at 2250 and 2350  $\text{cm}^{-1}$ , C=O at 1105  $\text{cm}^{-1}$ , and N—H at 3145 and 3380  $\text{cm}^{-1}$ .

## Experimental

To a stirred solution of  $\text{Cu}(\text{oxen})\cdot 2\text{H}_2\text{O}$  (0.136 g, 0.5 mmol) in  $\text{H}_2\text{O}$  (20 ml) was added an equimolar amount of  $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$  (0.185 g,


**Figure 3**

A packing view along the *a* direction.

0.5 mmol); the solution changed from purple to blue immediately. A solution of  $\text{Na}(\text{dca})$  (0.045 g, 0.5 mmol) in ethanol was then added. The solution was stirred for 30 min at room temperature. The filtered solution was allowed to evaporate at room temperature. After 7 d, green crystals of the title complex were obtained.

## Crystal data

$[\text{Cu}_2(\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2)(\text{C}_2\text{N}_3)_2]$   
 $M_r = 431.39$   
 Monoclinic,  $P2_1/n$   
 $a = 7.0622$  (6) Å  
 $b = 9.6969$  (8) Å  
 $c = 11.3531$  (9) Å  
 $\beta = 105.308$  (2)°  
 $V = 749.89$  (11) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.910$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2360 reflections  
 $\theta = 2.8\text{--}30.5^\circ$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $T = 293$  (2) K  
 Prism, green  
 0.20 × 0.10 × 0.07 mm

## Data collection

Bruker SMART APEX CCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 1997)  
 $T_{\text{min}} = 0.650$ ,  $T_{\text{max}} = 0.818$   
 5902 measured reflections

2166 independent reflections  
 1667 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -13 \rightarrow 9$   
 $l = -14 \rightarrow 15$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.073$   
 $S = 1.06$   
 2166 reflections  
 109 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.48$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.39$  e Å<sup>-3</sup>

**Table 1**  
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N5-H5A \cdots O1^i$	0.90	2.05	2.941 (3)	168
$N5-H5B \cdots N2^{ii}$	0.90	2.33	3.180 (4)	157

Symmetry codes: (i)  $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (ii)  $-x, 2 - y, 2 - z$ .

H atoms were positioned geometrically and refined with riding model constraints.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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## References

- Albada, G. A. van, Quiroz-Castro, M. E., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2000). *Inorg. Chim. Acta*, **298**, 221–225.
- Batten, S. R., Jensen, P., Moubaraki, B. & Murray, K. S. (2000). *Chem. Commun.* pp. 2331–2332.
- Braga, D. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3705–3713.
- Bruker (1997). *SADABS*, *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Choi, H. J. & Suh, M. P. (1999). *Inorg. Chem.* **26**, 6309–6320.
- Escuer, A., Mautner, F. A., Sanz, N. & Vicente, R. (2000). *Inorg. Chem.* **8**, 1668–1673.
- Groeneman, R. H., MacGillivray, L. R. & Atwood, J. L. (1998). *Chem. Commun.* pp. 2735–2736.
- Hvastijova, M., Kohout, J., Mrozinski, J. & Jager, L. (1999). *Pol. J. Chem.* **2**, 271–278.
- Jensen, P., Batten, S. R., Moubaraki, B. & Murray, K. S. (2001). *J. Solid State Chem.* **2**, 352–361.
- Kholbystov, A. N., Blake, A. J., Champness, N. R., Lemenovskii, D. A., Majouga, A. G. & Zyk, N. V. (2001). *Coord. Chem. Rev.* **222**, 155–192.
- Lehn, J.-M. (1995). *Supramolecular Chemistry – Concepts and Perspectives*. Weinheim: VCH.
- Lehn, J.-M. (1999). *Chem. Eur. J.* **5**, 2445–2463.
- Manson, J. L., Lee, D. W., Rheingold, A. L. & Miller, J. S. (1998). *Inorg. Chem.* **23**, 5966–5971.
- Marshall, S. R., Rheingold, A. L., Dawe, L. N., Shum, W. W., Kitamura, C. & Miller, J. S. (2002). *Inorg. Chem.* **14**, 3599–3601.
- Sun, B. W., Gao, S., Ma, B. Q. & Wang, Z. M. (2001). *Inorg. Chem. Commun.* **4**, 72–75.
- Wang, Z. M., Luo, J., Sun, B. W., Yan, C. H., Gao, S. & Liao, C. S. (2000). *Acta Cryst.* **C56**, 786–789.
- Zhang, H. X., Kang, B. S., Zhou, Z. Y., Chan, A. S. C., Yu, K. B., Chen, Z. N. & Ren, C. (2001). *Inorg. Chem. Commun.* **12**, 695–698.