

Han-Ping Zhang,<sup>a</sup> Yi-Zhi Li,<sup>b</sup>  
Hong Zhou,<sup>a,c</sup> Zhi-Quan Pan<sup>a\*</sup>  
and Cheng-Gang Wang<sup>a</sup><sup>a</sup>Hubei Key Laboratory of Novel Chemical Reactions & Green Chemical Technology, Wuhan Institute of Chemical Technology, Wuhan 430073, People's Republic of China, <sup>b</sup>Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and <sup>c</sup>College of Chemistry and Molecular Science of Wuhan University, Wuhan 430072, People's Republic of China

Correspondence e-mail: llyyz@nju.edu.cn

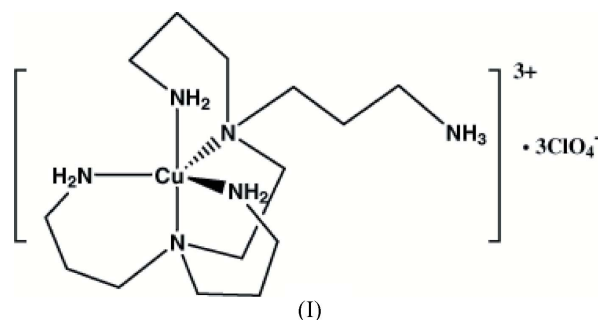
## Key indicators

Single-crystal X-ray study  
 $T = 298\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$   
Disorder in solvent or counterion  
 $R$  factor = 0.060  
 $wR$  factor = 0.146  
Data-to-parameter ratio = 11.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**[*N,N,N'*-Tris(3-aminopropyl)-*N'*-(3-ammonio-propyl)ethane-1,2-diamine]copper(II) tris(perchlorate)**

In the title complex,  $[\text{Cu}(\text{C}_{14}\text{H}_{37}\text{N}_6)](\text{ClO}_4)_3$ , the  $\text{Cu}^{\text{II}}$  atom adopts a slightly distorted trigonal bipyramidal coordination and one amino group in the complex is protonated. The  $\text{Cu}-\text{N}$  bond distances in the equatorial plane are in the range 2.074 (4)–2.173 (4) Å. Two N atoms occupy the axial positions with  $\text{Cu}-\text{N}$  contacts of 2.048 (3) and 2.056 (3) Å. All of the perchlorate anions are disordered. In the crystal structure, there are many  $\text{N}-\text{H}\cdots\text{O}$  intermolecular hydrogen bonds between cations and anions, forming a three-dimensional network.

## Comment

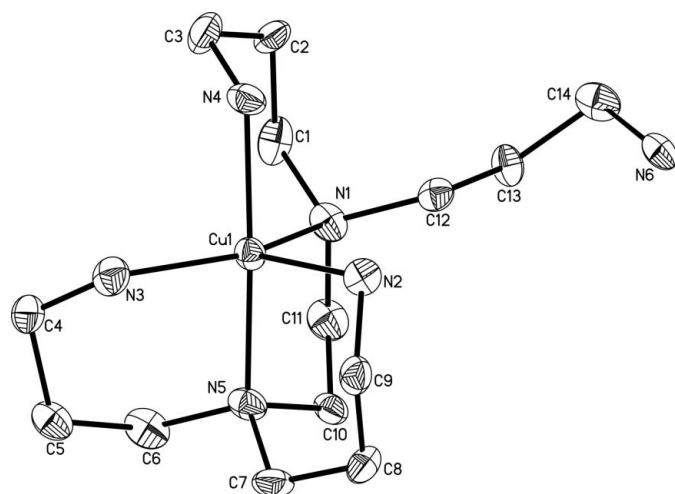
Polyamines have become a rapidly growing area of research due to their potential in performing programmed tasks such as molecular recognition and transfer (Wagnon *et al.*, 1989), supramolecular self-assembly (Rodriguez *et al.*, 2003) and mimics of metalloenzyme active sites (Jitsukawa *et al.*, 2001), while their strong coordination ability with most metals and high thermal stability lead to the convenient formation of a variety of molecular complexes (Jiang *et al.*, 2003), giving polyamines many practical applications in softening water, industrial cleaning, detoxifying drugs, separation and extraction (Joo *et al.*, 2003). Up to the present, many linear primary amines have been synthesized, but few polyamines with branched chains of primary amines have been reported.



In order to understand better the interaction of metal-polyamines, a hexaamine complex, (I), was obtained by reaction between *N,N,N',N'*-tetrakis(3-aminopropyl)ethane-1,2-diamine and copper(II) perchlorate. The crystal structure of the complex has been determined by X-ray diffraction. A perspective view of the cation is given in Fig. 1. The coordination around copper(II) is best described as slightly distorted trigonal bipyramidal; one aminopropyl N atom does not coordinate with copper(II) because of protonation. The  $\text{Cu}-\text{N}$  bond distances in the equatorial plane are in the range

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**Figure 1**

A view of the cation of the title complex, showing the labelling of the non-H atoms and 30% probability displacement ellipsoids. All H atoms have been omitted for clarity.

2.074 (4)–2.173 (4) Å. Atoms N4 and N5 occupy the axial positions with Cu–N4 and Cu–N5 distances of 2.048 (3) and 2.056 (3) Å, respectively. There are many N–H···O intermolecular hydrogen bonds between cations and anions in the crystal structure, forming a three-dimensional network (Table 1).

## Experimental

*N,N,N',N'*-Tetrakis(3-aminopropyl)ethane-1,2-diamine (*L*) was first synthesized by the reaction between diaminoethane and acrylonitrile, followed by hydrogenation. The title copper(II) complex was obtained by reaction of *L* and copper(II) perchlorate. To an ethanol solution (20 ml) containing *L* (0.4617 g, 1.6 mmol) was added dropwise an ethanol solution (15 ml) containing CuCl<sub>2</sub> (0.5438 g, 3.2 mmol) with stirring at room temperature. After an ethanol solution (10 ml) of NaClO<sub>4</sub> (1.0 g, 82 mmol) had been added, a blue solid was formed which was filtered off and dried in air. Blue needle-shaped crystals were obtained by slow evaporation of a 78% ethanol solution at room temperature.

### Crystal data

[Cu(C <sub>14</sub> H <sub>37</sub> N <sub>6</sub> )](ClO <sub>4</sub> ) <sub>3</sub>	<i>Z</i> = 4
<i>M<sub>r</sub></i> = 651.39	<i>D<sub>x</sub></i> = 1.634 Mg m <sup>−3</sup>
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.3315 (11) Å	<i>μ</i> = 1.19 mm <sup>−1</sup>
<i>b</i> = 18.131 (2) Å	<i>T</i> = 298 (2) K
<i>c</i> = 15.8484 (18) Å	Needle, blue
<i>β</i> = 99.092 (2)°	0.30 × 0.10 × 0.08 mm
<i>V</i> = 2647.7 (5) Å <sup>3</sup>	

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	14355 measured reflections
<i>φ</i> and <i>ω</i> scans	5180 independent reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2000)	4129 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>T<sub>min</sub></i> = 0.716, <i>T<sub>max</sub></i> = 0.911	<i>R<sub>int</sub></i> = 0.039
	<i>θ<sub>max</sub></i> = 26.0°

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.060$   
 $wR(F^2) = 0.146$   
*S* = 1.05  
 5180 reflections  
 464 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 1.99P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.48 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.65 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N2–H2C···O5 <sup>i</sup>	0.90	2.30	3.132 (5)	153
N2–H2C···O5 <sup>ii</sup>	0.90	2.56	3.407 (18)	158
N6–H6C···O5 <sup>i</sup>	0.89	2.51	3.064 (6)	121
N6–H6E···O5 <sup>ii</sup>	0.89	2.47	2.906 (18)	110
N3–H3C···O4 <sup>iii</sup>	0.90	2.38	3.246 (5)	161
N3–H3C···O2 <sup>iii</sup>	0.90	2.38	3.058 (12)	132
N2–H2D···O10 <sup>iii</sup>	0.90	2.16	2.961 (10)	147
N2–H2D···O12 <sup>iii</sup>	0.90	2.44	3.317 (5)	164
N3–H3D···O7 <sup>iii</sup>	0.90	2.11	2.979 (5)	162
N3–H3D···O7 <sup>iii</sup>	0.90	2.16	2.899 (13)	139
N4–H4C···O7 <sup>iii</sup>	0.90	2.45	3.160 (5)	136
N4–H4C···O12 <sup>iii</sup>	0.90	2.52	3.310 (10)	146
N4–H4C···O12 <sup>iii</sup>	0.90	2.57	3.152 (5)	123
N4–H4D···O3 <sup>iii</sup>	0.90	2.05	2.903 (13)	158
N4–H4D···O2 <sup>iii</sup>	0.90	2.47	3.250 (5)	146
N6–H6C···O1 <sup>iii</sup>	0.89	1.96	2.775 (18)	151
N6–H6C···O1 <sup>iii</sup>	0.89	2.25	3.103 (5)	161
N6–H6D···O11 <sup>iv</sup>	0.89	1.94	2.823 (10)	169
N6–H6D···O10 <sup>iv</sup>	0.89	2.24	2.957 (5)	138
N6–H6D···O9 <sup>iv</sup>	0.89	2.42	3.135 (5)	138
N6–H6E···O6 <sup>i</sup>	0.89	2.08	2.842 (15)	143
N6–H6E···O6	0.89	2.14	2.919 (6)	145

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

All H atoms were placed in calculated positions, with C–H = 0.89–0.97 Å, and included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C,N})$ . All of the perchlorate anions are disordered. The site-occupancy factors of the perchlorate Cl and O atoms were obtained by setting free variables; the site-occupancy factors of the Cl and O atoms are as follows: 0.852 (6) for Cl1, O1, O2, O3 and O4; 0.148 (6) for Cl1', O1', O2', O3' and O4'; 0.780 (13) for Cl2, O5, O6, O7 and O8; 0.220 (13) for Cl2', O5', O6', O7' and O8'; 0.741 (5) for Cl3, O9, O10, O11 and O12; 0.259 (5) for Cl3', O9', O10', O11' and O12'.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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