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## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$   
 $R$  factor = 0.043  
 $wR$  factor = 0.103  
Data-to-parameter ratio = 17.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>. $\mu$ -1,5-Dicyanamido-bis[chloro(1,4,7-triazacyclononane)copper(II)] perchlorate

In the title compound,  $[\text{Cu}_2(\text{C}_2\text{N}_3)\text{Cl}_2(\text{C}_6\text{H}_{15}\text{N}_3)_2]\text{ClO}_4$ , two  $[\text{CuCl}_2(\text{tacn})]$  units ( $\text{tacn} = 1,4,7$ -triazacyclononane) are linked by a single bridging dicyanamide ligand. The geometry about each  $\text{Cu}^{\text{II}}$  atom is deformed square-pyramidal or deformed trigonal-bipyramidal, formed by three N atoms of  $\text{tacn}$ , one of the terminal N atoms of the dicyanamide ligand and a  $\text{Cl}^-$  anion.

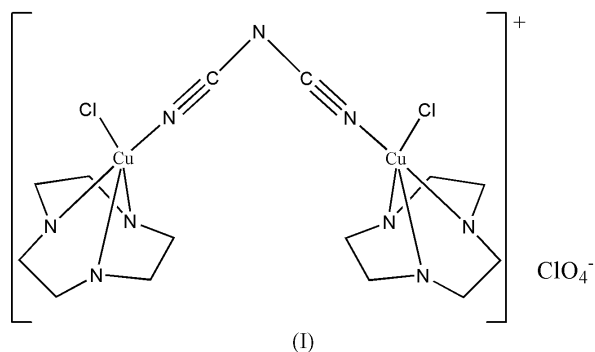
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## Comment

Binuclear copper(II) complexes form an extremely active area of research in modern coordination chemistry (Sessler & Sibert, 1993; Edterurtas *et al.*, 1991) because of their crucial role in bioinorganic chemistry as model compounds for binuclear active sites in proteins (Collin *et al.*, 1988; Casellato *et al.*, 1979). Many model complexes containing various bridging ligands, such as oxalate (Zhang *et al.*, 2000), azide (Chaudhuri *et al.*, 1986), thiocyanate (Haasnoot *et al.*, 1984), terephthalate and tetracarboxylatobenzene (Chaudhuri *et al.*, 1988), and benzoate (Burger *et al.*, 1996), have been prepared and their structures characterized. During the course of our studies on binuclear copper(II) complexes, we obtained the title compound, (I). The synthesis and crystal structure of (I) are reported here.



The title compound consists of  $[\text{Cu}_2\{\text{N}(\text{CN})_2\}\text{Cl}_2(\text{tacn})_2]^+$  cations and  $\text{ClO}_4^-$  anions (Fig. 1). Atom Cu1 is situated in a distorted square-pyramidal geometry, with atom N2 of  $\text{tacn}$  at the apical position. The  $\text{Cu1}-\text{N2}$  bond distance of  $2.272(3)\text{ \AA}$  is longer than the other  $\text{Cu1}-\text{N}$  bonds of  $\text{tacn}$  [ $2.011(3)$ – $2.068(3)\text{ \AA}$ ; Table 1]. Atom Cu2 shows a distorted trigonal bipyramidal coordination geometry, with atoms N6 and N9 at the axial positions.

The  $\text{N}(\text{CN})_2^-$  anion links two  $[\text{Cu}(\text{tacn})\text{Cl}_2]$  units in a 1,5-bridging mode. The  $\text{C7}-\text{N5}-\text{C8}$  bond angle is  $120.2(4)^\circ$ , which is typical for the dicyanamide ligand in a 1,5-bridging mode (Vangdal *et al.*, 2002; Carranza *et al.*, 2002).

Experimental

A solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.5 mmol) in methanol (5 ml) was added to a solution of tacn (0.5 mmol) in methanol (15 ml), affording a clear deep-blue solution. The reaction mixture was stirred for 30 min at room temperature, then a solution of NaN(CN)<sub>2</sub> (0.045 g, 0.5 mmol) in water (5 ml) was slowly added dropwise. The deep-blue mixture was stirred for another 2 h, then filtered to remove any insoluble particles. Finally, NaClO<sub>4</sub> (ca 0.1 g) was added to the filtrate. After a month, crystals of (I) suitable for X-ray study were obtained by slow evaporation of the filtrate at room temperature (yield 65%).

Crystal data

[Cu<sub>2</sub>(C<sub>2</sub>N<sub>3</sub>)Cl<sub>2</sub>(C<sub>6</sub>H<sub>15</sub>N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> *D*<sub>x</sub> = 1.718 Mg m<sup>-3</sup>  
*M*<sub>r</sub> = 621.90 Mo *K*α radiation  
 Monoclinic, *P*2<sub>1</sub>/*n* Cell parameters from 864 reflections  
*a* = 17.882 (6) Å *θ* = 2.3–26.0°  
*b* = 7.494 (3) Å *μ* = 2.14 mm<sup>-1</sup>  
*c* = 18.596 (6) Å *T* = 293 (2) K  
*β* = 105.200 (5)° Block, blue  
*V* = 2404.9 (14) Å<sup>3</sup> 0.24 × 0.18 × 0.12 mm  
*Z* = 4

Data collection

Bruker SMART CCD area-detector 4901 independent reflections  
 diffractometer 3372 reflections with *I* > 2σ(*I*)  
 φ and ω scans *R*<sub>int</sub> = 0.047  
 Absorption correction: multi-scan *θ*<sub>max</sub> = 26.4°  
 (SADABS; Sheldrick, 1996) *h* = -22 → 22  
*T*<sub>min</sub> = 0.592, *T*<sub>max</sub> = 0.773 *k* = -6 → 9  
 13116 measured reflections *l* = -23 → 23

Refinement

Refinement on *F*<sup>2</sup> *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0444*P*)<sup>2</sup> + 0.6189*P*]  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.043 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
*wR*(*F*<sup>2</sup>) = 0.103 (Δ*σ*)<sub>max</sub> = 0.001  
*S* = 1.05 Δ*ρ*<sub>max</sub> = 0.59 e Å<sup>-3</sup>  
 4901 reflections Δ*ρ*<sub>min</sub> = -0.42 e Å<sup>-3</sup>  
 289 parameters  
 H-atom parameters constrained

Table 1

Selected geometric parameters (Å, °).

Cu1—N4	1.969 (4)	Cu2—N6	1.979 (4)
Cu1—N1	2.011 (3)	Cu2—N9	2.011 (3)
Cu1—N3	2.068 (3)	Cu2—N8	2.114 (3)
Cu1—N2	2.272 (3)	Cu2—N7	2.196 (4)
Cu1—Cl1	2.2909 (12)	Cu2—Cl2	2.2833 (12)
N4—Cu1—N1	168.44 (15)	N6—Cu2—N9	174.88 (14)
N4—Cu1—N3	90.63 (14)	N6—Cu2—N8	92.69 (14)
N1—Cu1—N3	82.20 (14)	N9—Cu2—N8	83.21 (12)
N4—Cu1—N2	106.10 (14)	N6—Cu2—N7	94.31 (16)
N1—Cu1—N2	81.89 (13)	N9—Cu2—N7	82.09 (13)
N3—Cu1—N2	81.48 (13)	N8—Cu2—N7	81.71 (13)
N4—Cu1—Cl1	93.88 (11)	N6—Cu2—Cl2	93.84 (11)
N1—Cu1—Cl1	91.37 (10)	N9—Cu2—Cl2	91.26 (9)
N3—Cu1—Cl1	167.41 (11)	N8—Cu2—Cl2	147.77 (10)
N2—Cu1—Cl1	108.43 (9)	N7—Cu2—Cl2	129.09 (10)

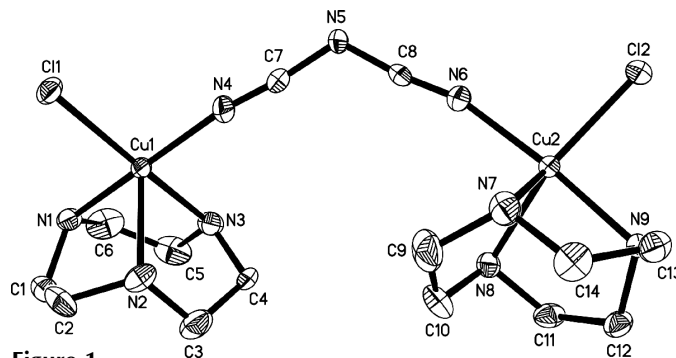


Figure 1

A perspective view of the complex cation in (I), shown with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

The C-bound H atoms were included in the riding-model approximation, with C—H distances of 0.97 Å and with *U*<sub>iso</sub>(methylene H) = 1.5*U*<sub>eq</sub>(C).

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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