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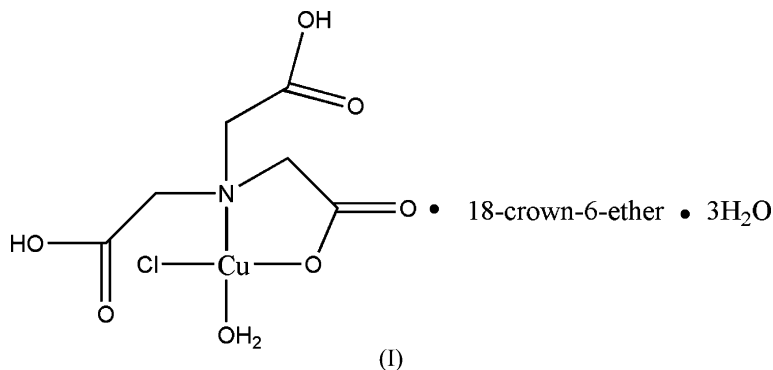
## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å  
H-atom completeness 96%  
Disorder in solvent or counterion  
 $R$  factor = 0.037  
 $wR$  factor = 0.076  
Data-to-parameter ratio = 10.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.A sandwich strand supramolecular complex:  
aquachloro(nitrilotriacetato- $\kappa^2N,O$ )copper(II)  
18-crown-6-ether trihydrateReceived 31 December 2005  
Accepted 7 March 2006

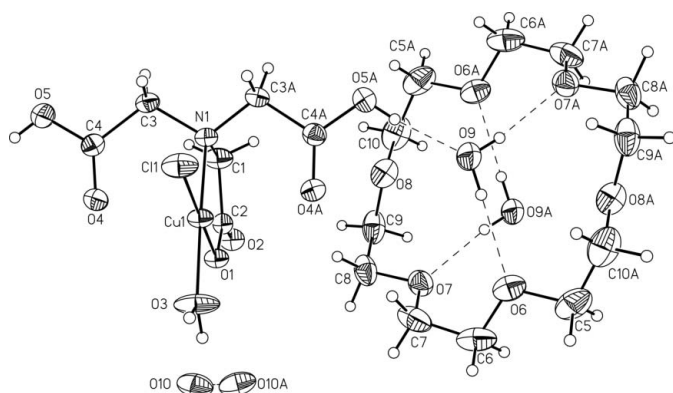
The unexpected title compound,  $[\text{Cu}(\text{C}_6\text{H}_8\text{NO}_6)\text{Cl}(\text{H}_2\text{O})] \cdot \text{C}_{12}\text{H}_{24}\text{O}_6 \cdot 3\text{H}_2\text{O}$ , was synthesized by crystallization of a mixture containing  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , nitrilotriacetic acid ( $\text{H}_3\text{NTA}$ ),  $\text{KOH}$ , 18-crown-6 and  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ . The complex consists of a hydrogen-bonded polymeric structure, in which discrete  $\text{Cu}(\text{H}_2\text{NTA})(\text{H}_2\text{O})\text{Cl}$  units interact *via* the carboxyl groups and the coordinating water molecules with the crown ether molecules. No direct metal–crown ether bond exists in the infinite sandwich-type hydrogen-bonded structure. The copper complex lies on a mirror plane, which passes through Cu and all the coordinating atoms. The crown ether molecule lies on an inversion centre. One water molecule is disordered across the mirror plane.

## Comment

Matching hydrogen-bond donors and acceptors to form hydrogen-bonded aggregates is a popular strategy in the design of supramolecular complexes. Crown ethers are effective hydrogen-bond acceptors by virtue of their electro-negative O atoms from the viewpoint of crystal engineering. Research on crown ethers and transition metals has received more attention recently. Metal salts with 15-crown-5 and 12-crown-4 have been prepared and their structures determined (Steed *et al.*, 2001; Junk *et al.*, 2001). Complexes obtained by the cocrystallization of hydrated metal salts (Co, Ni, Cu, Zn, Sn and Ga) with aqueous 18-crown-6 ethers have been reported (Steed *et al.*, 1998; Junk *et al.*, 2004). Various anions, such as  $\text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ , affect the structure of metal–crown ether complexes.

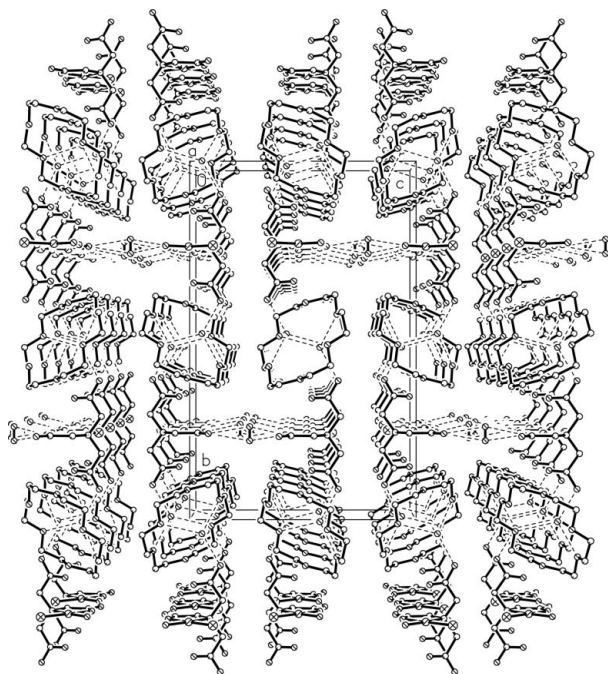


Nitrilotriacetic acid ( $\text{H}_3\text{NTA}$ ) is one of the important derivatives of glycine. A number of complexes containing NTA have been studied over many years, including not only rare-earth complexes (Martin & Jacobson, 1972*a,b*; Chen *et*



**Figure 1**

A view of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (A)  $x, \frac{3}{2} - y, z$  for the Cu complex,  $1 - x, 2 - y, 2 - z$  for the crown ether molecule.] Dashed lines indicate hydrogen bonds.



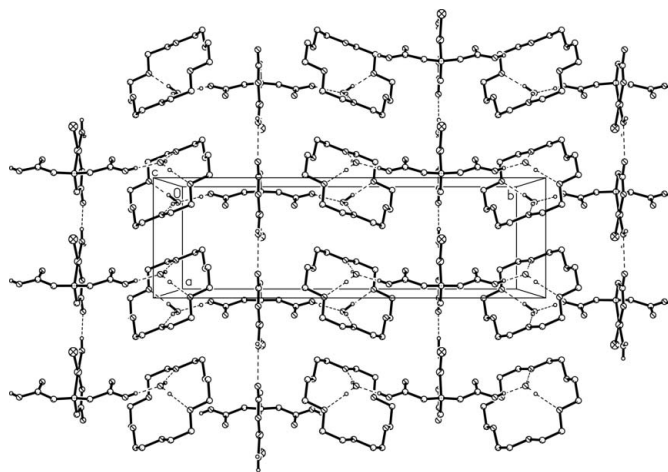
**Figure 2**

Hydrogen-bonded (dashed lines) layers viewed along the  $a$  axis. H atoms not involved in hydrogen bonding have been omitted.

*al.*, 2000), but also  $4f-3d$  heteronuclear clusters (Liu *et al.*, 2000; Jiang *et al.* 2005).

Here, instead of being a simple anion, the NTA ligand is involved in the cocrystallization process to synthesize the title complex, (I). A displacement ellipsoid drawing of (I) is shown in Fig. 1, and Figs. 2 and 3 show the hydrogen-bonded network. Selected bond lengths and angles are listed in Table 1. The copper complex lies on a mirror plane, which passes through all the coordinating atoms; one water molecule is disordered across this mirror plane. The crown ether molecule lies on an inversion centre.

The X-ray crystal structure shows extensive intermolecular hydrogen bonding involving  $\text{Cu}(\text{H}_2\text{NTA})(\text{H}_2\text{O})\text{Cl}$  units, the uncoordinated water molecules and the crown ether molecule.



**Figure 3**

Packing diagram, viewed along the  $c$  axis, showing the hydrogen-bonded (dashed lines) three-dimensional network. H atoms not involved in hydrogen bonding have been omitted.

Since  $\text{H}_3\text{NTA}$  is not completely deprotonated, the tetra-coordinated  $\text{Cu}^{\text{I}}$  ion is chelated by an  $\text{H}_2\text{NTA}^-$  ligand only through N1 and O1, while O3 of the coordinated water molecules and the Cl1 ion occupy the remaining positions. The  $\text{Cu}^{\text{II}}$  unit resembles a butterfly with two pendant protonated carboxyl groups as the wings. The wings link to the water molecule O9 *via* hydrogen bonds (Table 2), and the water molecules also hydrogen bond to the crown ether O atoms, stabilizing the extensive sandwich array of  $\text{Cu}(\text{H}_2\text{NTA})(\text{H}_2\text{O})\text{Cl}$  units between successive macrocyclic 18-crown-6 ether units. Every 18-crown-6 ether ligand associated with two water molecules on opposite sides adopts the conventional conformation with pseudo- $D_{3d}$  symmetry (Schurhammer *et al.*, 2003). This gives rise to a hydrogen-bonded one-dimensional chain with a succession of  $\text{Cu}(\text{H}_2\text{NTA})(\text{H}_2\text{O})\text{Cl}$ ,  $\text{H}_2\text{O}$  and 18-crown-6 molecules. The chains are connected *via* hydrogen bonds between the coordinated water molecules of one chain and the coordinated carboxylate O atoms of another chain, yielding a two-dimensional layer (Fig. 2). The layers are further linked by the rest of the disordered water molecules which connect the coordinated water molecules, as shown in Fig. 3.

Unlike the perchlorate anion, which forms a discrete 3:2 crown-metal complex  $[\text{Cu}(\text{H}_2\text{O})_3(18\text{-crown-6})]_2[\text{ClO}_4]_4 \cdot 18\text{-crown-6}$  (Steed *et al.*, 1998) due to its poor coordinating ability, two carboxylic acid groups of NTA show a strong ability to bond water molecules, which interact with the ether units *via* hydrogen bonds. A similar sandwich structure has been reported for  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  (Steed *et al.*, 1998; Junk *et al.*, 2004) *via* metal-bound water molecules to two individual crown ligands or metal-bound water molecules to other water molecules then to crown ligands. It is worth noting that enough KOH has been added to neutralize the ligand, but the complex still contains two carboxylic acid groups. This shows that the  $-\text{COOH}$  groups play an important role in stabilizing the hydrogen-bonded structure, as does the 18-crown-6 (Kou *et al.*, 2002).

Experimental

A solution (5 ml) of nitrilotriacetic acid (19.1 mg, 0.1 mmol) in water was neutralized by an aqueous solution (5 ml) of KOH (16.8 mg, 0.3 mmol) and 18-crown-6 (79.3 mg, 0.3 mmol) with stirring. An aqueous solution (5 ml) of CuCl<sub>2</sub>·2H<sub>2</sub>O (17.0 mg, 0.1 mmol) was added to the above mixture. An aqueous solution (5 ml) of GdCl<sub>3</sub>·6H<sub>2</sub>O (28.4 mg, 0.1 mmol) was finally added to the mixture. Light-blue crystals suitable for X-ray diffraction analysis separated after several days (yield: 15%).

Crystal data

[Cu(C <sub>6</sub> H <sub>8</sub> NO <sub>6</sub> )Cl(H <sub>2</sub> O)]·C <sub>12</sub> H <sub>24</sub> O <sub>6</sub> ·3H <sub>2</sub> O	<i>D</i> <sub>x</sub> = 1.447 Mg m <sup>-3</sup>
<i>M</i> <sub>r</sub> = 625.50	Mo <i>K</i> α radiation
Orthorhombic, <i>Pnma</i>	Cell parameters from 1435 reflections
<i>a</i> = 7.542 (2) Å	<i>θ</i> = 2.4–25.0°
<i>b</i> = 24.569 (5) Å	<i>μ</i> = 0.92 mm <sup>-1</sup>
<i>c</i> = 15.493 (3) Å	<i>T</i> = 293 (2) K
<i>V</i> = 2870.8 (10) Å <sup>3</sup>	Plate, light blue
<i>Z</i> = 4	0.30 × 0.11 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2559 independent reflections
<i>ω</i> scans	2189 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2000)	<i>R</i> <sub>int</sub> = 0.035
<i>T</i> <sub>min</sub> = 0.763, <i>T</i> <sub>max</sub> = 0.955	<i>θ</i> <sub>max</sub> = 25.0°
13134 measured reflections	<i>h</i> = -8 → 8
	<i>k</i> = -29 → 25
	<i>l</i> = -18 → 17

Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.037	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.01 <i>P</i> ) <sup>2</sup> + 3 <i>P</i> ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.076	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>S</i> = 1.07	(Δ/σ) <sub>max</sub> = 0.001
2559 reflections	Δρ <sub>max</sub> = 0.40 e Å <sup>-3</sup>
236 parameters	Δρ <sub>min</sub> = -0.40 e Å <sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Cu1—O3	1.943 (3)	Cu1—N1	2.074 (3)
Cu1—O1	1.958 (2)	Cu1—Cl1	2.238 (1)
O3—Cu1—O1	86.5 (1)	O3—Cu1—Cl1	94.19 (9)
O3—Cu1—N1	172.3 (1)	O1—Cu1—Cl1	179.30 (8)
O1—Cu1—N1	85.8 (1)	N1—Cu1—Cl1	93.53 (8)

Table 2

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>
O5—H5C···O9 <sup>i</sup>	0.78 (3)	1.77 (3)	2.549 (3)	173.8 (3)
O9—H9C···O7 <sup>ii</sup>	0.86	1.97	2.820 (3)	169
O9—H9D···O6	0.86	2.07	2.909 (3)	167
O3—H3D···O10 <sup>i</sup>	0.86	1.86	2.666 (3)	156
O3—H3D···O10	0.86	1.86	2.666 (3)	156
O3—H3C···O2 <sup>iii</sup>	0.86	1.89	2.716 (3)	161

Symmetry codes: (i) *x*, -*y* + ½, *z*; (ii) -*x* + 1, -*y* + 2, -*z* + 2; (iii) *x* - 1, *y*, *z*.

H atoms were located in difference Fourier maps. All H atoms were allowed for as riding atoms. Those bonded to C atoms were refined with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C), giving C—H bond distances in the range 0.90 (4)–1.10 (8) Å. The carboxylic acid H atom was refined freely. H atoms of water molecules were positioned geometrically with O—H = 0.86 Å and *U*<sub>iso</sub>(H) = 0.05 Å<sup>2</sup> and then fixed in position. One water molecule is disordered across a mirror plane, and its H atoms were not located.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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