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(μ_2-Bicarbonato-κ^2O,O')[μ_2-1,4,8,11,14,18,23,27-octaaza-6,16,25(1,3)-tribenzenabicyclo[9.9.9]nonacosaphane]dicopper(II) triperchlorate acetonitrile solvate

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In the title complex, $[Cu_2(CHO_3)(C_{36}H_{54}N_8)](ClO_4)_3\cdot C_2H_3N$, at 180 K, the triamino caps of the dicopper(II) cryptate are approximately eclipsed and the benzene rings are arranged so as to form three arms of a twisted triskelion motif. The coordination geometry of one Cu atom is trigonal–bipyramidal, while the second resembles more closely a square pyramid. The latter arrangement accommodates a perchlorate anion coordinated loosely to Cu to give a very distorted octahedral geometry. The cryptate complexes adopt an approximately hexagonal close-packed (hcp) arrangement.

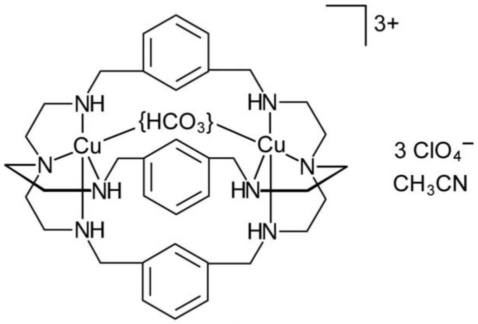
Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.006 Å
R factor = 0.052
wR factor = 0.137
Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title complex, $[C_{37}H_{55}Cu_2N_8O_3]^{3+}(ClO_4^-)_3\cdot C_2H_3N$, (I), contains a dicopper(II) complex of the *meta*-xylyl-linked cryptand $C_{36}H_{54}N_8$ (denoted hereinafter as L), in which the metal centres are bridged by a bicarbonate anion, HCO_3^- (Fig. 1). The intracomplex Cu1···Cu2 separation is 6.0853 (11) Å. In projection along the Cu···Cu axis (Fig. 2), the triamino caps at each end of the cryptate appear close to eclipsed, and the benzene rings adopt an arrangement that resembles three arms of a twisted triskelion motif. The C—OH bond of the bridging bicarbonate anion projects into a gap between two of the arms.



(I)

The environments of atoms Cu1 and Cu2 differ significantly (Table 1). For Cu1, the coordination geometry is trigonal–bipyramidal, with Cu1 lying 0.231 (2) Å (towards the centre of the complex) from the equatorial plane defined by atoms N2, N3 and N4. Atoms N1 and O2 lie in the axial coordination sites. For Cu2, the coordination geometry resembles more closely a square pyramid, with Cu2 lying 0.283 (2) Å from the basal plane defined by atoms N5, N6, N7 and O3. Atom N8 lies in the apical coordination site. The distortion towards square-pyramidal geometry for Cu2 reflects a ‘flattening’ of this end of the cryptand away from the open side to which the bicarbonate C—OH bond projects. This accommodates a perchlo-

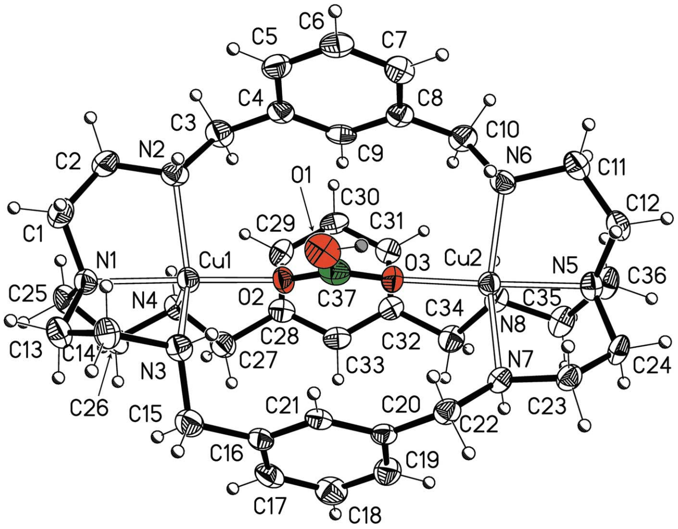


Figure 1
The cryptate unit in (I), showing displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary radii. The bicarbonate anion is highlighted in colour.

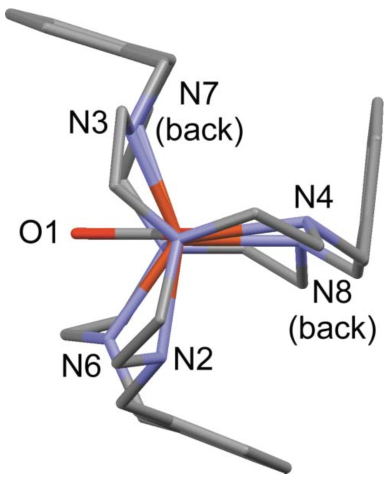


Figure 2
A projection of the cryptate in (I) along the Cu1$\cdots$Cu2 vector, showing the triamino caps in an approximately eclipsed orientation, and the benzene rings forming three arms of a triskelion-like motif. The C37—O1 bond of the bicarbonate bridge projects between two of the arms. H atoms have been omitted.

rate anion, which approaches Cu2 [Cu2—O1*A* 3.035 (3) Å], suggesting a very distorted octahedral geometry (Fig. 3). Atom O1*A* also accepts a hydrogen bond from the OH group of the bicarbonate anion [O1$\cdots$O1*A* 2.935 (5) Å, H1$\cdots$O1*A* 2.10 Å and O1—H1$\cdots$O1*A* 173.8°].

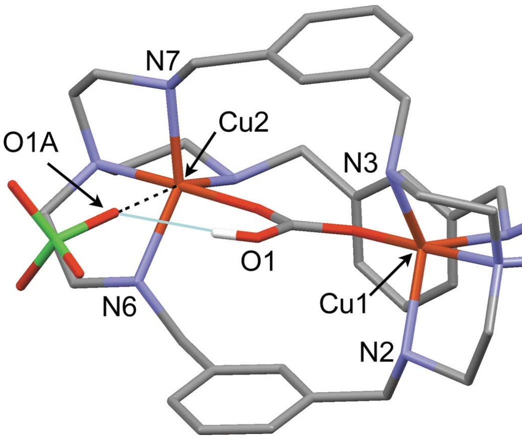


Figure 3
Detail of (I), showing a perchlorate anion approaching atom Cu2, giving rise to a distorted octahedral arrangement. The same O atom (O1*A*) also accepts a hydrogen bond from the bicarbonate anion. To accommodate the perchlorate anion, the cryptate is 'flattened' at the Cu2 end, reflected most clearly in the N6—Cu2—C7 and N2—Cu1—N3 angles (Table 1). H atoms bound to C and N atoms have been omitted.

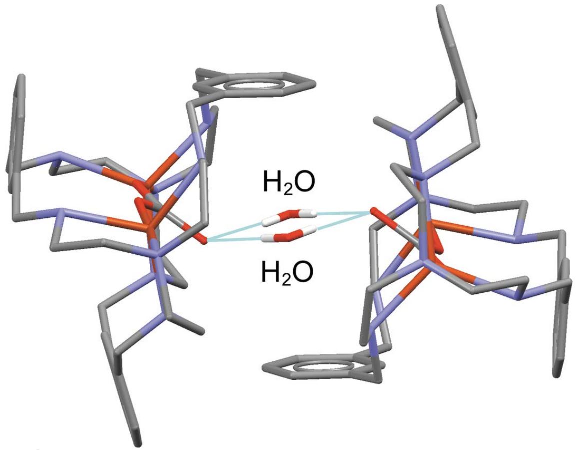


Figure 4
The hydrogen-bonded dimeric units in the carbonate-bridged cryptate $[Cu_2L(CO_3)](ClO_4^-)_2 \cdot 2H_2O$ (Dussart *et al.*, 2002), illustrating the unusual arrangement of the benzene rings that facilitates edge-to-face interactions between cryptates. H atoms bound to C and N atoms have been omitted.

We and others have previously described several comparable dicopper(II) cryptates, with various diatomic and polyatomic anionic bridges. The conformation of *L* is observed to be dependent on the nature of the bridging group. In the cyanide-bridged complex $[Cu_2L(CN)](ClO_4^-)_3$, the cryptate adopts regular C_{3h} point symmetry, with a Cu$\cdots$Cu separation of 5.081 (2) Å (Bond *et al.*, 2005). With polyatomic bridging groups, such as methyl carbonate (Dussart *et al.*, 2002), imidazole (Pierre *et al.*, 1995; Harding *et al.*, 1995), cyanate and azide (Harding *et al.*, 1996), the Cu$\cdots$Cu separation is much greater (and variable, ranging from *ca* 5.66 to 6.24 Å) and the threefold symmetry about the Cu$\cdots$Cu axis is lost. In each case, the benzene rings of the cryptand adopt the triskelion arrangement observed in (I) (Fig. 2). Each of these cryptates is also flattened at one end in the manner of (I), accommodating a perchlorate anion that approaches one Cu atom. In the carbonate-bridged complex, $[Cu_2L(CO_3)](ClO_4^-)_2 \cdot 2H_2O$ (Dussart *et al.*, 2002), the cryptand adopts a less regular arrangement (Fig. 4) in which one of the benzene rings is rotated *ca* 90° with respect to the arrangement observed in the other cases. This appears to be driven by the formation of hydrogen-bonded dimeric units *via* water molecules that bridge the carboxylate anions in neighbouring cryptates; the arrangement of the benzene rings facilitates edge-to-face interactions between cryptates. Flattening of the cryptate is not observed in this case.

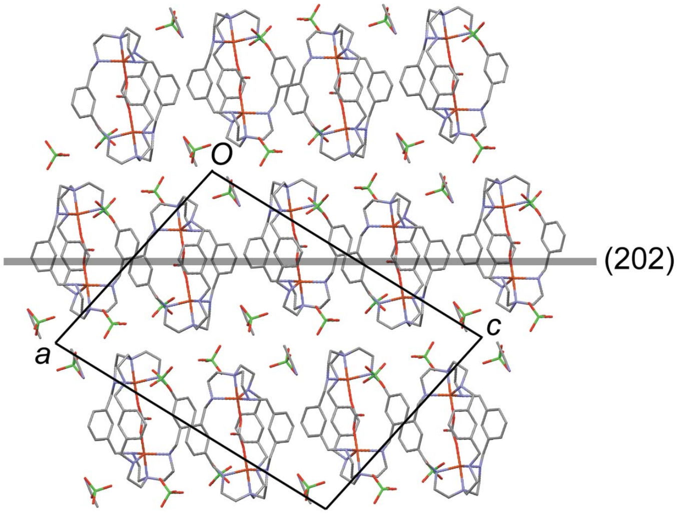


Figure 5
A projection of (I) along the *b* direction, showing layers of cryptates lying in the (202) planes, with their Cu$\cdots$Cu vectors approximately perpendicular to these planes. The perchlorate anions and acetonitrile solvent molecules lie between the layers. H atoms have been omitted.

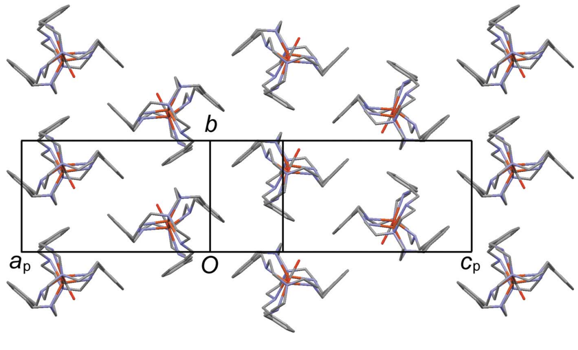


Figure 6
A projection on to a single layer in (202), showing face-to-face and edge-to-face arrangements between benzene rings in adjacent cryptands of (I). If the cryptands are considered to be cylindrically symmetric, the arrangement approximates hexagonal close-packed. H atoms have been omitted.

In the crystal structure of (I), the cryptate complexes lie in layers in the (202) planes (Fig. 5), with the Cu$\cdots$Cu vectors lying approximately perpendicular to the layer planes. Projection on to a single layer (Fig. 6) highlights a combination of offset face-to-face and edge-to-face interactions between the benzene rings. If the cryptands are considered to be cylindrically symmetric, the layers are essentially close-packed in two dimensions. These layers stack in an *ABAB* manner (Fig. 5), so that the overall packing arrangement approximates hexagonal close-packed (hcp). The perchlorate anions and acetonitrile molecules are situated between the cryptand layers.

Experimental

A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (178 mg, 0.48 mmol) dissolved in MeOH (5 ml) was added dropwise to the cryptand ligand, $C_{36}H_{54}N_8$ (121 mg, 0.2 mmol), dissolved in methanol (5 ml). The dark blue–green solution became turbid immediately, and a blue-green powder was filtered off after 2 h. Slow recrystallization from acetonitrile over several days yielded green laths of the acetonitrile solvate of (I). The acetonitrile solvent in the crystal structure is not retained over the period required for CHN analysis, which agrees with an unsolvated complex. Spectroscopic analysis: IR (Nujol, ν, cm^{-1}): 3436 (*s*), 2877 (*w*), 1635 (*ms*), 1450 (*m*), 1400 (*sh*), 1121 (*vs*), 801, 757, 702 (*w*), 627 (*ms*). CHN analysis {%, values in parentheses calculated for $[C_{37}H_{55}Cu_2N_8O_3](ClO_4)_3$}: C 40.74 (40.96), H 5.00 (5.11), N 9.97 (10.32). It is notable that, when the recrystallization system incorporates methanol, the product of recrystallation is the methyl carbonate-bridged dicopper(II) cryptate, rather than the bicarbonate-bridged complex (Dussart *et al.*, 2002).

Crystal data

$[Cu_2(CHO_3)(C_{36}H_{54}N_8)](ClO_4)_3\cdot C_2H_3N$
$M_r = 1126.37$
Monoclinic, $P2_1/n$
$a = 19.690$ (4) Å
$b = 8.862$ (2) Å
$c = 26.828$ (5) Å
$\beta = 100.721$ (2)°
$V = 4599.6$ (16) Å^3
$Z = 4$
$D_x = 1.627$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 2245 reflections
$\theta = 4.8$–24.0°
$\mu = 1.18$ mm^{-1}
$T = 180$ (2) K
Lath, green
0.24 × 0.10 × 0.02 mm

Data collection

Bruker–Nonius X8APEX-II CCD area-detector diffractometer
Thin–slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.319$, $T_{max} = 0.977$
16940 measured reflections
8362 independent reflections
5186 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 25.5°$
$h = -23 \rightarrow 23$
$k = -10 \rightarrow 6$
$l = -32 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.137$
$S = 0.99$
8362 reflections
613 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.938 (3)	Cu2—N6	2.070 (3)
Cu1—N1	2.054 (3)	Cu2—N7	2.084 (3)
Cu1—N3	2.097 (4)	Cu2—N8	2.256 (4)
Cu1—N2	2.153 (3)	C37—O3	1.241 (5)
Cu1—N4	2.167 (4)	C37—O2	1.257 (5)
Cu2—O3	1.957 (3)	C37—O1	1.370 (6)
Cu2—N5	2.054 (3)		
O2—Cu1—N1	177.34 (14)	O3—Cu2—N5	178.32 (14)
O2—Cu1—N3	96.54 (13)	O3—Cu2—N6	94.51 (13)
N1—Cu1—N3	84.59 (14)	N5—Cu2—N6	84.18 (14)
O2—Cu1—N2	97.41 (12)	O3—Cu2—N7	97.17 (12)
N1—Cu1—N2	83.86 (13)	N5—Cu2—N7	84.50 (13)
N3—Cu1—N2	125.14 (14)	N6—Cu2—N7	145.49 (14)
O2—Cu1—N4	94.56 (12)	O3—Cu2—N8	96.71 (13)
N1—Cu1—N4	82.82 (13)	N5—Cu2—N8	82.65 (13)
N3—Cu1—N4	124.02 (14)	N6—Cu2—N8	105.63 (14)
N2—Cu1—N4	107.32 (14)	N7—Cu2—N8	105.08 (13)

H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C—H = 0.95 Å for the benzene rings and C—H = 0.99 Å for the methylene groups. In all cases, $U_{iso}(H) = 1.2U_{eq}(C)$. All H atoms bound to N atoms could be distinguished in a difference Fourier map, but were included in

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calculated positions and allowed to ride, with N—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. The calculated positions were in good agreement with those indicated by the difference Fourier map. The H atom of the bicarbonate bridge could not be distinguished, but the C37—O1 bond length, together with the requirement for charge balance, confirms the presence of the OH group. The H atom was placed in a calculated position in the plane of the HCO_3^- group, so as to form the best hydrogen bond (AFIX 83 in *SHELXL97*). It was subsequently allowed to ride, with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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