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Bis(acetonitrile-κ*N*)[(1*RS*,4*RS*,8*SR*,11*SR*)-1,4,8,11-tetraazatetradecane-κ^4*N*]copper(II) bis{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} 0.31-hydrate

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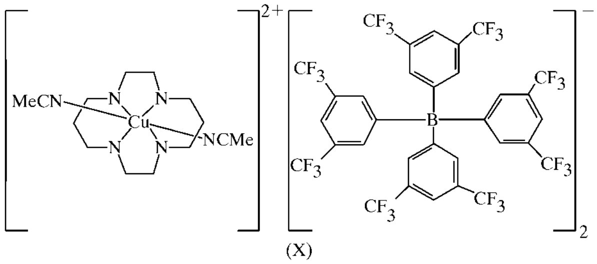
The title compound, $[Cu(C_2H_3N)_2(C_{10}H_{24}N_4)](C_{32}H_{12}BF_{24})_2\cdot 0.31H_2O$, crystallizes as an ionic species with no interactions between the ions. The $[Cu^{II}(cyclam)(MeCN)_2]^{2+}$ dication (cyclam is 1,4,8,11-tetraazatetradecane), located on a 2/*m* symmetry site, forms as a distorted octahedral species with four $Cu-N_{cyclam}$ bonds of 2.013 (2) Å and two $C-N_{MeCN}$ bonds of 2.499 (4) Å. The $[B\{C_6H_3(CF_3)\text{-}3,5\}_4]^-$ anion, located on a twofold axis, is a distorted octahedral species. A small amount of water is present, occupying sites between columns of ions.

Comment

1,4,8,11-Tetraazatetradecane (cyclam) and its derivatives have been studied extensively as ligands for transition metal complexes, including copper compounds. Among the copper(II)–cyclam complexes whose crystal structures have been reported are neutral complexes, such as $[Cu^{II}(cyclam)(SC_6F_5)_2]$, (I) [Cambridge Structural Database (Allen, 2002) refcode BUTYUK; Addison & Sinn, 1983], $[Cu^{II}(cyclam)Br_2]$, (II) (TEGPOK; Chen *et al.*, 1996; see also Matsuo *et al.*, 2001), and $[Cu^{II}(cyclam)(ClO_4)_2]$, (III) (PTZDCU; Tasker & Sklar, 1975), and ionic complexes, for example $[Cu^{II}(cyclam)(H_2O)_2][F(H_2O)_4]_2$, (IV) (JABSUA10; Emsley *et al.*, 1990; see also Matsuo *et al.*, 2001), $[Cu^{II}(cyclam)][Cu^{I}Br_3]$, (V) (QIWVAT; Willett & Vij, 2000), $[Cu^{II}Cl(cyclam)]_2[CdCl_4]$, (VI) (YUMBUD; Pickardt & Hoffmeister, 1995), [Cu^{II}(cy-



(X)

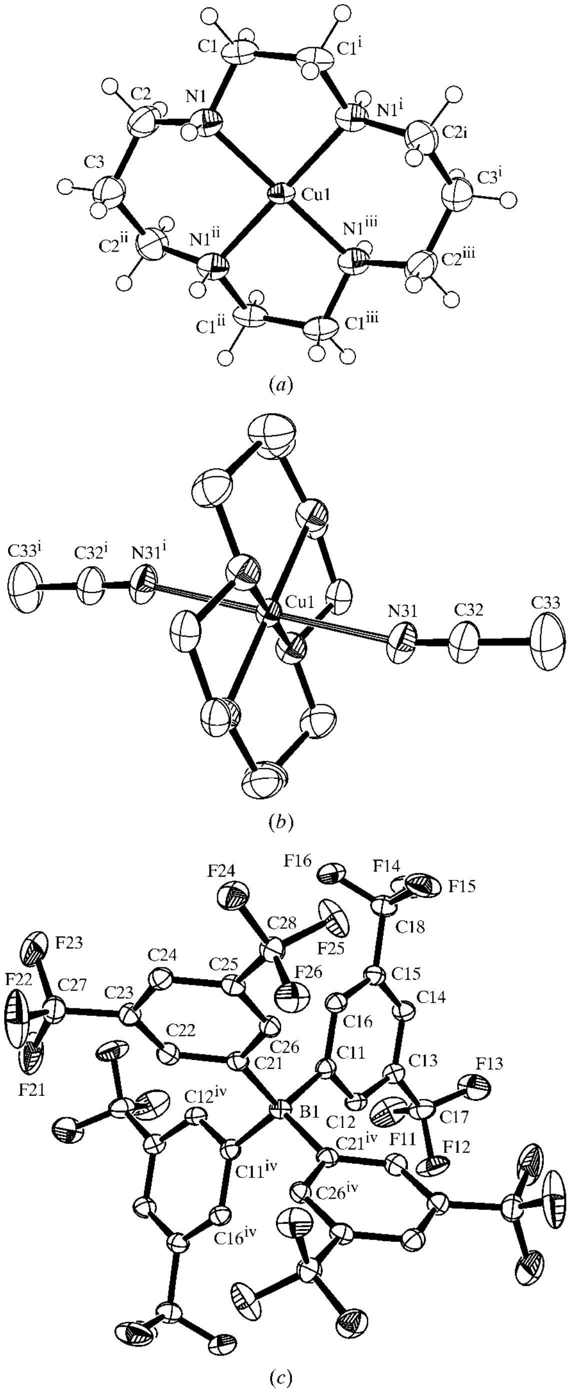


Figure 1
The asymmetric unit of (X), with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. (*a*) The planar Cu^{II}(cyclam) section of the $[Cu^{II}(cyclam)(NCMe)_2]^{2+}$ dication; (*b*) the $[Cu^{II}(cyclam)(NCMe)_2]^{2+}$ dication; (*c*) the $[B\{C_6H_3(CF_3)\text{-}3,5\}_4]^-$ anion. H atoms have been drawn as circles of arbitrary radii in (*a*) and have been omitted from (*b*) and (*c*) for clarity. [Symmetry codes: (i) $x, -y, -z$; (ii) $1 - x, y, z$; (iii) $1 - x, -y, -z$; (iv) $-x + \frac{1}{2}, y, -z + \frac{1}{2}$.]

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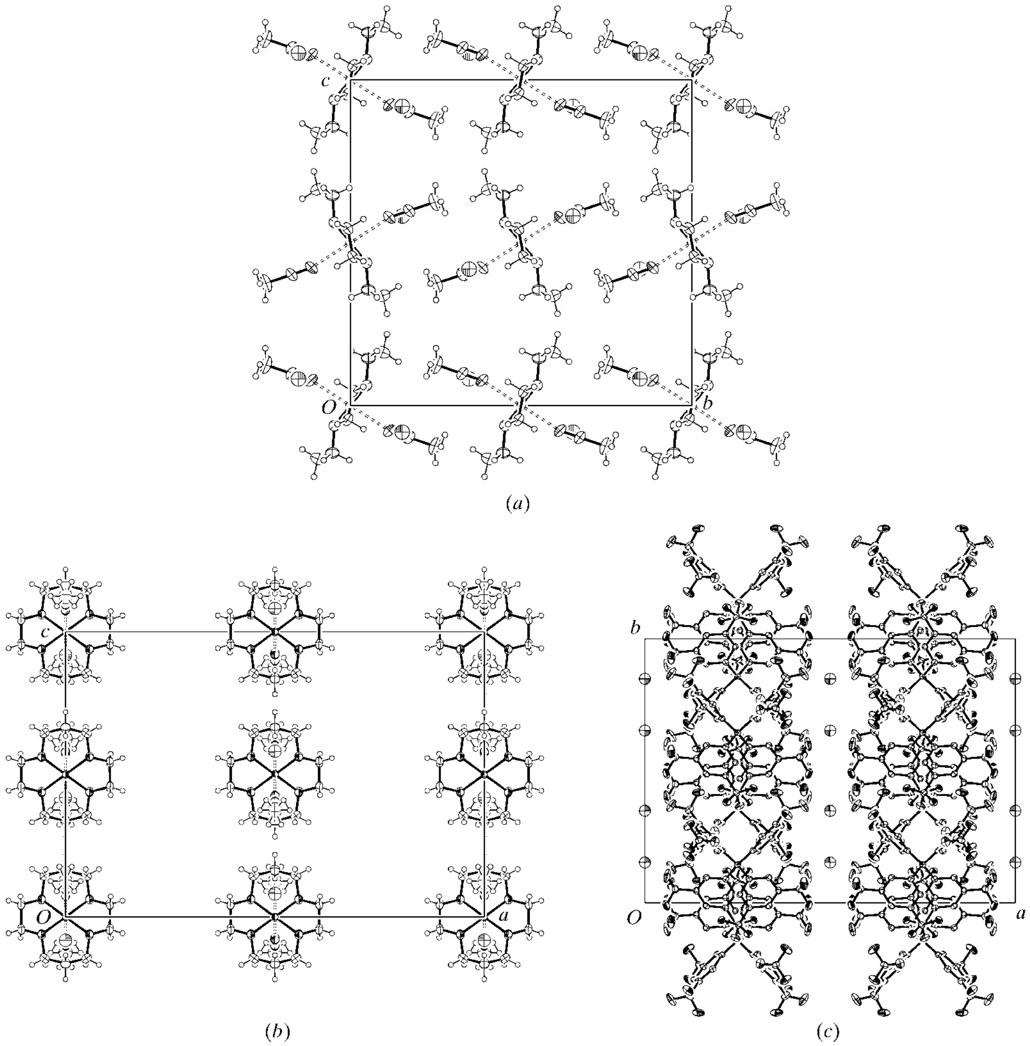

(*a*)

(*b*)

(*c*)

Figure 2
The orientation of molecules in the unit cell; (*a*) the $[Cu^{II}(cyclam)(NCMe)_2]^{2+}$ dication viewed normal to (100) and (*b*) the $[Cu^{II}(cyclam)(NCMe)_2]^{2+}$ dication viewed normal to (010). The acetonitrile molecule is approximately perpendicular to the plane of the figure, showing the disorder of the terminal methyl group. (*c*) The $[B(C_6H_3(CF_3)\text{-}3,5)_4]^-$ anion viewed normal to (001), with water molecules disordered between the columns. H atoms have been omitted for clarity.

clam)][$CdCl_3(H_2O)_2$]Cl, (VII) (YUMCAK; Pickardt & Hoffmeister, 1995), $[Cu^{II}(NCS)(cyclam)][SCN]$, (VIII) (ZUZJUZ; Lu *et al.*, 1996), and $[Cu^{II}(cyclam)][BH_4]_2$, (IX) (HAFSUC; Antsyshkina *et al.*, 1992). In complexes (I)–(VII), copper is six-coordinated, with the four N atoms of the cyclam ligand in the equatorial sites of a distorted octahedral structure. The axial ligands in (I)–(IV) are the other bound ligands [*viz.* SC_6F_5 in (I), Br in (II), $OClO_3$ in (III) and OH_2 in (IV)], while in (V)–(VII), the axial sites are occupied by halides, including bridging ligands from the halometallate anions. In contrast to the situation in (I)–(VII), the Cu centre in (VIII) has essentially a distorted square-pyramidal geometry, with the bound isothiocyanate ligand in the axial site; however, there is also a weak Cu$\cdots$S interaction with a neighbouring cation, at a distance of only ~0.185 Å less than the sum of the van der Waals radii.

In order to study the effect of a large non-interacting anion on the structure of a copper(II)–cyclam complex, a complex with the $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$ anion was sought. The title compound, (X), was obtained on recrystallizing the reaction product obtained from cyclam, $Cu(ClO_4)_2{\cdot}6H_2O$ and $Na[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ from MeCN/Et_2O solution.

Complex (X), in space group *Cmca*, exists as an ionic species, with no interactions between the distorted octahedral $[Cu^{II}(cyclam)(NCMe)_2]^{2+}$ dications (Figs. 1*a* and 1*b*) and the distorted tetrahedral $[B\{C_6H_3(CF_3)\text{-}3,5\}_4]^-$ anions (Fig. 1*c*). The arrangement of these molecules in the unit cell is shown in Fig. 2. As in complexes (I)–(VII), the equatorial sites in the dication of (X) are occupied by the four cyclam N atoms; the uniform $Cu-N_{cyclam}$ bond length is 2.013 (2) Å and is within the range found in the other Cu(cyclam) complexes. The axial $Cu-N_{MeCN}$ bond lengths are much longer [2.499 (3) Å]. The distortion from an ideal octahedral geometry is small, as shown by the N—Cu—N bond angles (Table 1). The equatorial N—Cu—N angles [$N1-Cu1-N1^{i}$ and $N1^{iii}-Cu1-N1^{ii}$; symmetry codes: (i) $x, -y, -z$; (ii) $1-x, y, z$; (iii) $1-x, -y, -z$] within the five-membered rings are, as expected, smaller than those within the six-membered rings (N1—Cu1—

$N1^{ii}$ and $N1^{i}—Cu1—N1^{iii}$), *viz.* 86.05 (13) *versus* 93.95 (13)°, respectively. The $N_{axial}—Cu—N_{equatorial}$ angles are 93.55 (9) and 86.45 (9)°, with an $N_{axial}—Cu—N_{axial}$ angle of 180°. The Cu—N≡C(Me) fragment is nearly linear [Cu1—N31—C32 = 166.3 (3)°], and the terminal methyl group is disordered. The configurations of the four chiral N centres in (X) are 1*RS*, 4*RS*, 8*SR* and 11*SR*. On the basis of the puckering parameters of Cremer & Pople (1975), the six-membered chelate rings have near chair-shaped conformations [Q = 0.591 (4) Å, θ = 12.6 (3)° and φ = 180.0 (14)°], while the five-membered rings have twist conformations [Q = 0.454 (3) Å and φ = 270.0 (3)°].

The C—B—C bond angles in the anion of (X) are clustered around the ideal tetrahedral angle of 109.5°, being between 105.7 (2) and 113.04 (11)°.

Water molecules are disordered between columns of anions, which form parallel to (011) (Fig. 2*c*), with approximately one-third of a water atom present in the formula unit. Hydrogen bonding is both intra- and intermolecular; see Table 2 for details.

Experimental

To a solution of cyclam (0.5 mmol) in ethanol (10 ml) was added $Cu(ClO_4)_2·6H_2O$ (0.5 mmol) in H_2O (5 ml), followed by $Na[B\{C_6H_3(CF_3)_3\text{-}3,5\}_4]$ (1 mmol) in Me_2CO (5 ml). The reaction mixture was left overnight, and then the solvent was evaporated and the residue recrystallized from $MeCN/Et_2O$. Purple crystals of (X) (m.p. 481–483 K) formed slowly.

Crystal data

$[Cu(C_2H_3N)_2(C_{10}H_{24}N_4)]$-$(C_{32}H_{12}BF_{24})_2·0.31H_2O$
M_r = 2077.56
Orthorhombic, *Cmca*
a = 25.7320 (6) Å
b = 18.3516 (4) Å
c = 17.5412 (4) Å
V = 8283.4 (3) Å^3
Z = 4
D_x = 1.666 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 477 reflections
θ = 2.9–27.5°
μ = 0.42 mm^{-1}
T = 120 (2) K
Block, purple
0.22 × 0.12 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ–ω scans
Absorption correction: empirical (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.920, T_{max} = 0.983
32 892 measured reflections
4855 independent reflections
3525 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 27.5°
$h = -33 \rightarrow 25$
$k = -22 \rightarrow 23$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.139
S = 1.02
4855 reflections
315 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 12.7378P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

H atoms were refined using a riding model employing the appropriate AFIX commands of *SHELXL*97 (Sheldrick, 1997). The H atom on water molecule O31 could not be located because the amount of water in the structure is small. However, the assignment of water at this location is justified because of the solvent-accessible areas (50 Å^3 per void) identified by *PLATON* (Spek, 2003).

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.013 (2)	Cu1—N31	2.499 (3)
$N1^{i}—Cu1—N1^{iii}$	93.95 (13)	$N1—Cu1—N31^{i}$	86.44 (9)
$N1—Cu1—N1^{i}$	86.05 (13)	N1—Cu1—N31	93.56 (9)

Symmetry codes: (i) $x, -y, -z$; (iii) $1 - x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
$N1—H1\cdots F15^{v}$	0.93	2.25	3.055 (3)	145
C22—H22···F21	0.95	2.39	2.733 (3)	101

Symmetry code: (v) $x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* in *OSCAIL for Windows* (McArdle, 1994, 2000) and *ORTEP*-3 *for Windows* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1648). Services for accessing these data are described at the back of the journal.

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