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[(1,4,8,11-Tetraazacyclotetradeca-1,4,8,11-tetrayl)tetraacetamide-$\kappa^6N^1,N^4,N^8,N^{11},O^1,O^8$]copper(II) sulfate 4.5-hydrate

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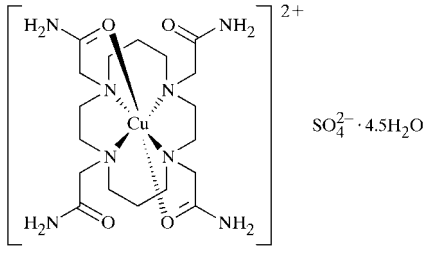
The crystal structure of the title copper(II) complex, $[Cu(C_{18}H_{36}N_8O_4)]SO_4\cdot4.5H_2O$, formed with the tetraamide cyclam derivative 2-(4,8,11-triscarbamoylmethyl-1,4,8,11-tetraazacyclotetradec-1-yl)acetamide (TETAM), is described. The macrocycle lies on an inversion centre occupied by the hexacoordinated Cu atom. The four macrocyclic tertiary amines form the equatorial plane of an axially Jahn–Teller elongated octahedron. Two O atoms belonging to two diagonally opposite amide groups occupy the apical positions, giving rise to a *trans*-III stereochemistry, while both the remaining pendant side arms extend outwards from the macrocyclic cavity and are engaged in hydrogen bonds with sulfate anions and co-crystallized water molecules.

Comment

Owing to their novel physico-chemical and structural properties, substituted tetraaza macrocycles have attracted widespread interest and have provided practical solutions to challenging everyday problems, where selective metal-complex formation plays a key role. For example, lanthanide complexes of *N*-carbamoyl-substituted cyclen derivatives have been found to exhibit interesting chiroptical properties (Parker & Williams, 1996) or to promote RNA cleavage efficiently (Amin *et al.*, 1994). In contrast, the 14-membered cyclam analogues bearing dangling amide groups have been studied much less extensively, while crystallographic data are scarce (Meyer *et al.*, 1998). A monoacetamide cyclam-based copper(II) complex has been structurally characterized by means of IR and visible absorption spectroscopy (Kaden, 1984); the pH-dependent solution behaviour observed suggested the formation of a square-planar tetracoordinated species below pH 10, while apical ligation of the deprotonated amide N atom at higher pH values afforded a pentacoordinated square-pyramidal species. The crystal structure of the title copper(II) complex of 2-(4,8,11-triscarbamoylmethyl-1,4,8,11-tetraazacyclotetradec-1-yl)-acetamide, (I), is reported herein in order to investigate further the structural features related to the presence of pendant acetamide arms attached to the cyclam scaffold.



(I)

Compound (I) crystallizes in the centrosymmetric space group *C*2/*c*, with half a molecular unit belonging to the asymmetric unit. The second half unit is generated by an inversion centre at $(\frac{3}{4},\frac{1}{4},\frac{1}{2})$, which is occupied by the Cu atom, leading to a planar N_4 basal coordination. According to the extended Dale nomenclature developed for heteroatom-containing macrocycles (Meyer *et al.*, 1998), the cyclam fragment exhibits an anangular [3′,4′,3′,4′]-*C* ring conformation, with four pseudocorners located at C1, C4, and the symmetry-related atoms C1′ and C4′, delimiting a parallelogram of 4.98 (C1···C4) by 3.84 Å (C1···C4′), with a C4···C1···C4′ angle of 99.4°. Starting at τ_1, defined as the N1—C1—C2—N2 torsion angle, the following sequence along the cycle is observed: 59.2 (2), −169.6 (1), 175.6 (2), −66.2 (2), 67.3 (2), −174.2 (1) and 157.9 (1)°. It can be easily observed that this macrocyclic conformation forces the amine N atoms to adopt a type III configuration according to Bosnich's formalism (Bosnich *et al.*, 1965; Frémond *et al.*, 2000), which results in a *trans* layout of the four acetamide substituents. The five- and six-membered chelate rings have been characterized by

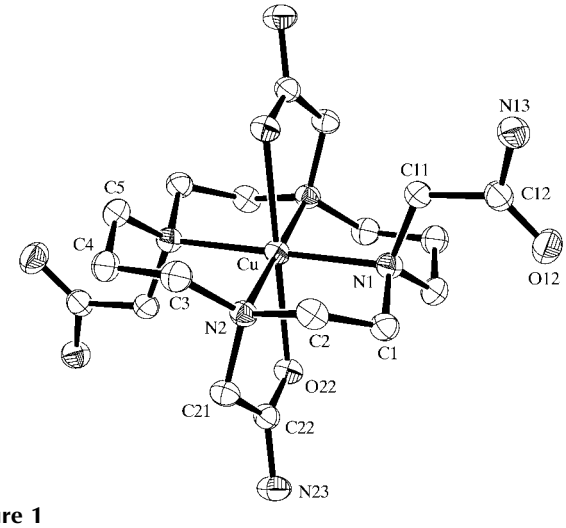


Figure 1
A view of the cation of (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids. For the sake of clarity, H atoms have been omitted.

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puckering analysis (Cremer & Pople, 1975). For both independent five-membered chelate rings (N1—C1—C2—N2—Cu and N2—C21—C22—O22—Cu), the closest pucker descriptor is a half-chair twisted along C1—C2 (Q = 0.465 Å and φ = 91.8°) and N2—C21 (Q = 0.238 Å and φ = 311.0°), respectively. The six-membered chelate ring (N2—C3—C4—C5—N1′—Cu) exhibits a chair conformation, in agreement with the observed puckering parameters (Q = 0.657 Å, θ = 174.6° and φ = 166.0°). The average bond distances [Csp^3—Csp^3 = 1.520 (5) Å and Csp^3—N = 1.493 (5) Å] are typical of tetraaza macrocycles (Meyer *et al.*, 1998).

The coordination sphere around the metal centre exhibits a distorted octahedral geometry. The distances and angles within the basal plane reveal a regular rectangular arrangement of the four N atoms [Cu—N1 = 2.152 (1) Å, Cu—N2 = 2.049 (2) Å and N1—Cu—N2 = 86.24 (5)°]. Two acetamide O atoms complete the octahedron at the apical positions [Cu—O22 = 2.356 (1) Å, N1—Cu—O22 = 85.72 (4)° and N2—Cu—O22 = 78.49 (5)°]. The axial elongation results from the well known Jahn–Teller effect. The acetamide C═O groups show a double-bond character whether the carbonyl is coordinated [1.241 (2) Å] or not [1.231 (2) Å]. The calculated N2/C21/C22/(N23,O22) mean plane exhibits a higher r.m.s. deviation (0.1346 Å) than that corresponding to N1/C11/C12/(N13,O12) (0.0972 Å), due to the Cu—O22 interaction. The angle between these mean planes [88.71 (6)°] is very close to the N1—Cu—N2 coordination angle [86.24 (5)°].

The hydrogen-bonding pattern found in the structure of (I) seems responsible for the above arrangement. In particular, the specific orientation of the uncoordinated acetamide moiety is due to the N13—H131···O*W*1—H*W*11···O12 hydrogen bonds, which involve a water molecule as both acceptor and donor in the same asymmetric unit (Table 1). The sulfate anions bridge the complexes and water molecules by means of their O atoms, giving rise to a hydrogen-bond network. Indeed, they act as acceptors in medium-strength interactions (H···O 1.783–2.052 Å).

In order to obtain a more accurate description of the amide and water H atoms, their bond distances were restrained to the mean values derived from neutron experiments: N—H = 1.009 Å (Wilson & Prince, 1999) and O*W*—H*W* = 0.970 Å (Blessing, 1988). Table 1 shows the dissociation energies (D_E) corresponding to the N—H···O and O*W*—H*W*···O contacts, which were calculated according to the simple expression obtained for X—H···O (X is C, N or O) closed-shell hydrogen-bond interactions: D_E (kJ mol^{-1}) = 25000 × exp[−3.6 × d(H···O) (Å)] (Espinosa *et al.*, 1998). At this stage, it should be noted that weaker C—H···O interactions have not been taken into account. Inspection of the D_E values reported in Table 1 leads to an estimated interaction energy between the O*W*1 water molecule and the C11/C12/(O12,N13) acetamide group of roughly 33 kJ mol^{-1}. The interaction energy corresponding to a sulfate anion bridging TETAM and water molecules is approximately 134 kJ mol^{-1}. Thus, it might be concluded that the crystal cohesion in (I) is mainly ensured by the hydrogen-bond network involving the sulfate counterions.

Experimental

The free TETAM ligand was prepared according to the method of Guilard *et al.* (2001). A methanol solution (20 ml) containing $CuSO_4{\cdot}5H_2O$ (180 mg, 0.72 mmol) and TETAM (300 mg, 0.70 mmol) was stirred for 30 min at room temperature. Evaporation of the solvent afforded a blue solid, (I), which was recrystallized from a water–methanol mixture (1:1 *v*/*v*). X-ray quality crystals of (I) were obtained by slow evaporation at room temperature.

Crystal data

$[Cu(C_{18}H_{36}N_8O_4)]SO_4{\cdot}4.5H_2O$	D_x = 1.568 Mg m^{-3}
M_r = 669.22	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 12 370 reflections
a = 18.8609 (3) Å	θ = 1.4–27.6°
b = 15.4691 (4) Å	μ = 0.92 mm^{-1}
c = 11.6010 (2) Å	T = 173 (2) K
β = 123.145 (9)°	Prism, dark blue
V = 2833.99 (10) Å^3	0.2 × 0.2 × 0.2 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	R_{int} = 0.027
φ scans	θ_{max} = 27.6°
12 370 measured reflections	h = 0 → 24
3235 independent reflections	k = 0 → 19
2814 reflections with $I > 2\sigma(I)$	l = −15 → 12

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0856P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.113	$\Delta\rho_{max}$ = 0.72 e Å^{-3}
S = 1.09	$\Delta\rho_{min}$ = −0.62 e Å^{-3}
3235 reflections	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
260 parameters	Extinction coefficient: 0.0073 (9)
H atoms treated by a mixture of independent and constrained refinement	

All H atoms (except those of the disordered water molecule) were found in the difference Fourier map and refined with a global isotropic displacement parameter of 0.038 (1) Å^2. The positions of the H(N) and H*W* atoms were restrained using the *DFIX* (*DFIX* 0.970 0.001 H*W*11 H*W*12 H*W*21 H*W*22; *DFIX* 1.009 0.001 H131 H132 H231 H232) and *DANG* (*DANG* 1.579 0.001 H*W*11 H*W*12 H*W*21 H*W*22) instructions of the *SHELXL*97 program (Sheldrick, 1997). A disordered water molecule was found in the structure, exhibiting a site-occupancy factor of 0.25. The corresponding atom O*W*3 was located 2.757, 2.868 and 2.969 Å from two equivalent O12 atoms and a symmetry-related O*W*3 atom, respectively. Since atoms H*W*31 and

Table 1
Hydrogen-bonding geometry (Å, °) and estimated dissociation energies D_E (kJ mol^{-1}).

D—H···A	D—H	H···A	D···A	D—H···A	D_E
N13—H131···O*W*1	1.009 (7)	2.24 (1)	3.052 (2)	137 (1)	7.9
N13—H131···O*W*1^{i}	1.009 (7)	2.45 (2)	3.062 (2)	119 (1)	3.7
N13—H132···O2	1.009 (18)	1.912 (18)	2.918 (2)	175 (2)	25.6
N23—H231···O22^{ii}	1.009 (10)	2.25 (1)	3.118 (2)	143 (2)	7.6
N23—H232···O1^{iii}	1.01 (2)	1.93 (2)	2.918 (2)	167 (2)	24.0
O*W*1—H*W*11···O12	0.970 (10)	1.963 (9)	2.830 (2)	148 (1)	21.3
O*W*1—H*W*12···O1^{i}	0.969 (17)	1.886 (16)	2.827 (2)	163 (2)	28.1
O*W*2—H*W*21···O2^{iv}	0.969 (18)	1.784 (18)	2.736 (2)	167 (1)	40.6
O*W*2—H*W*22···O1^{iii}	0.970 (12)	2.051 (14)	3.013 (2)	171 (2)	15.5

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

H*W*32 were not found, the corresponding data have not been included in Table 1.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1005). Services for accessing these data are described at the back of the journal.

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