

SAINT (Siemens, 1995); program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1357). Services for accessing these data are described at the back of the journal.

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An *o*-xylyl cross-bridged 5,12-dioxocyclam

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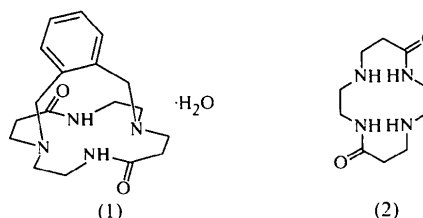
Abstract

The preparation and crystal structure of 1,10,13,18-tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene-11,17-

dione monohydrate, C₁₈H₂₆N₄O₂·H₂O, are described. The molecule has a U-shaped conformation, with the N atoms well oriented for metal complexation.

Comment

The compound 1,10,13,19-tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene-14,20-dione was synthesized during our study of the transition metal complexes of cross-bridged tetraazamacrocycles (Hubin *et al.*, 1998). Initially, our research centred on ethylene cross-bridged tetraazamacrocycles (Weisman *et al.*, 1996), but it has recently expanded to include macrocycles bridged by other groups and macrocycles containing amide groups. Recent work by others (Denat *et al.*, 1997) describes bis-amide macrocycles and corresponding reduced tetraamine species that have been cross-bridged by five-atom groups derived from *m*-xylene and 2,6-dimethylpyridine bis-electrophiles. Although no crystal structures of these molecules were reported, we considered that a four-atom bridged analogue would be more effective as a rigid ligand. 1,10,13,19-Tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene-14,20-dione was synthesized as the monohydrate, (1), by the high-dilution reaction of α, α' -dibromo-*o*-xylene and *trans*-diprotected 5,12-dioxocyclam (Tomalia & Wilson, 1985) and its crystal structure determined.



No other cross-bridged 5,12-dioxocyclams have been structurally characterized to date, although we have recently determined the crystal structure of unbridged unsubstituted 1,4,8,11-tetraazacyclotetradecane-5,12-dione, (2), and its Ni^{II} complex (Hubin *et al.*, 1999). The structures of several bis-linked substituted 5,12-dioxocyclam ligands and their Ni^{II} complexes have been determined (Dumas *et al.*, 1995); these could also be regarded as bridged dioxocyclams.

In (1), the dioxocyclam has a U-shaped conformation, with the C=O groups pointing outwards and with the *o*-xylyl bridge spanning the base of the U (Fig. 1). Compared with the unbridged species, this molecule has a clearly defined cavity in which the nitrogen donors appear to be well oriented for complexation. The bridges in the linked dioxocyclams characterized by Dumas *et al.* (1995) are much longer than that in (1) and the macrocycles have extended rather than U-shaped conformations, similar to those in the unsubstituted complex.

The asymmetric unit of (1) contains one water molecule, which is hydrogen bonded to one of the C=O groups [O11...O001 2.852(2) Å] and to a symmetry-

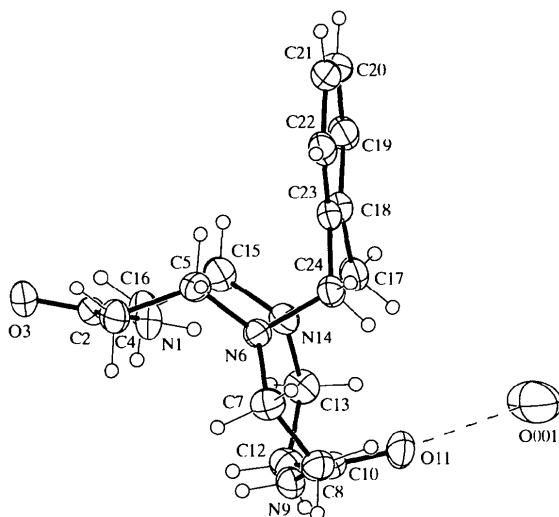


Fig. 1. View of the molecule of (1) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.

related water molecule [O001...O001]ⁱ 2.991(3) Å; symmetry code: (i) 2 - x, -y, 1 - z]. Since the second hydrogen bond is across an inversion centre, there must be disorder in the water-molecule orientations.

Experimental

Compound (1) was obtained by the substitution of α,α' -di-bromo-*o*-xylene for its *m*-xylene analogue in the literature cross-bridging reaction of (2) (Denat *et al.*, 1997). All other steps were followed according to the literature procedure; yields were 70–80%. X-ray quality crystals of (1) were obtained from the slow evaporation of a propan-2-ol solution.

Crystal data

C₁₈H₂₆N₄O₂·H₂O
M_r = 348.44
 Monoclinic
 P2₁/n
a = 9.9190 (10) Å
b = 12.898 (2) Å
c = 14.045 (2) Å
 β = 101.983 (5)°
V = 1757.7 (4) Å³
Z = 4
D_x = 1.317 Mg m⁻³
D_m not measured

Data collection

Siemens SMART diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.77, *T_{max}* = 0.96
 10 113 measured reflections
 4114 independent reflections

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 5802 reflections
 θ = 3–20°
 μ = 0.091 mm⁻¹
T = 220 (2) K
 Block
 0.5 × 0.5 × 0.4 mm
 Colourless

2954 reflections with *I* > 2 σ (*I*)
R_{int} = 0.021
 θ_{\max} = 28.48°
h = -13 → 12
k = -16 → 10
l = -17 → 18
 Intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.047
wR(*F*²) = 0.137
S = 1.061
 4114 reflections
 234 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 0.3237P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.014
 $\Delta\rho_{\max} = 0.655 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.338 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1) contains one lattice water molecule but its H atoms could not be located. The remaining H atoms were added at calculated positions and refined using a riding model, with isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: SMART (Siemens, 1994). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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