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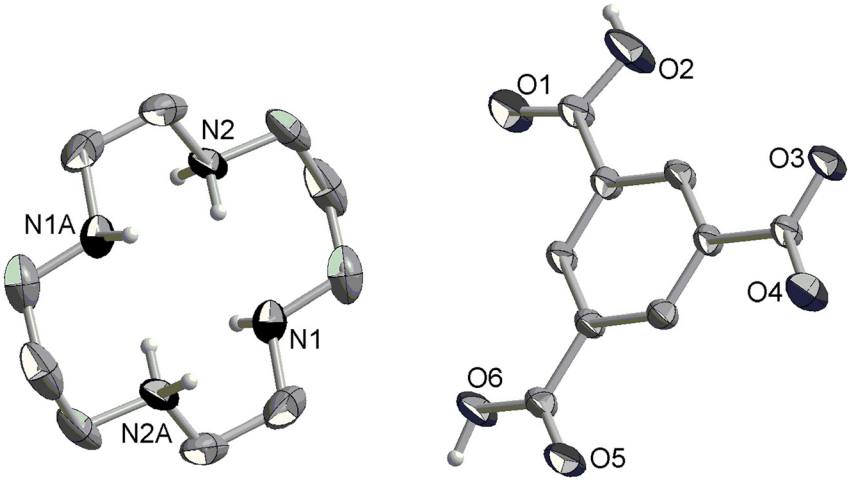
Crystal structure of 1,4,8,11-tetraazacyclotetradecane-1,8-diium bis (3,5-dicarboxybenzoate), $C_{28}H_{36}N_4O_{12}$



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Abstract

$C_{28}H_{36}N_4O_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 7.4922(11) Å, b = 8.3435(12) Å, c = 12.1563(18) Å, α = 75.207(2)°, β = 81.618(2)°, γ = 78.579(2)°, V = 716.53(18) Å^3, Z = 1, $R_{gt}(F)$ = 0.0461, $wR_{ref}(F^2)$ = 0.1335, T = 296(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.46 × 0.32 × 0.25 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8047, 3174, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 2648
$N(param)_{refined}$:	212
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

Source of material

An acetonitrile solution (20 mL) of the macrocylic L (0.100 g, 0.5 mmol) (L = 1,4,8,11-tetraazacyclotetradecane) was added to a methanol solution of trimesic acid (0.210 g, 1 mmol). Crystals of the title compound were obtained by slow evaporation.

Experimental details

The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. All the hydrogen atoms of the ligand were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5 U_{eq}(C) and the U_{iso} values of all other hydrogen atoms were set to 1.2 U_{eq}(C, N).

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5432 (2)	0.69753 (17)	0.65615 (12)	0.0417 (3)
C2	0.79566 (18)	0.82057 (16)	0.24088 (10)	0.0330 (3)
C3	0.8915 (2)	0.23285 (16)	0.48268 (11)	0.0372 (3)
C4	0.64456 (19)	0.63776 (16)	0.55489 (11)	0.0339 (3)
C5	0.66824 (18)	0.75165 (15)	0.44945 (11)	0.0328 (3)
H5	0.618750	0.864753	0.442448	0.039*
C6	0.76453 (17)	0.69831 (15)	0.35514 (10)	0.0296 (3)
C7	0.83679 (18)	0.52861 (16)	0.36689 (11)	0.0317 (3)
H7	0.902197	0.491384	0.304424	0.038*
C8	0.81226 (18)	0.41365 (15)	0.47127 (11)	0.0321 (3)
C9	0.71634 (19)	0.46858 (16)	0.56532 (11)	0.0347 (3)
H9	0.700284	0.392139	0.635079	0.042*
C10	0.8501 (3)	−0.1163 (2)	0.84942 (14)	0.0556 (4)
H10A	0.910001	−0.053996	0.780052	0.067*
H10B	0.749919	−0.156883	0.828687	0.067*
C11	0.6581 (3)	0.1465 (3)	0.87629 (16)	0.0626 (5)
H11A	0.555816	0.116421	0.850033	0.075*
H11B	0.724259	0.210483	0.810530	0.075*
C12	0.5872 (2)	0.2534 (2)	0.96058 (18)	0.0659 (6)
H12A	0.531113	0.185048	1.028727	0.079*
H12B	0.492275	0.342809	0.927909	0.079*
C13	0.7291 (3)	0.33153 (19)	0.99535 (16)	0.0581 (5)
H13A	0.782603	0.404295	0.928362	0.070*
H13B	0.670720	0.399968	1.048432	0.070*
C14	1.0158 (3)	0.2629 (2)	1.09482 (14)	0.0543 (4)
H14A	0.957227	0.327545	1.150106	0.065*
H14B	1.079381	0.335704	1.032785	0.065*
N1	0.77895 (19)	−0.00606 (17)	0.92665 (10)	0.0447 (3)
H1	0.723 (2)	−0.062 (2)	0.9872 (11)	0.054*
N2	0.87638 (18)	0.20076 (14)	1.05010 (10)	0.0409 (3)
H2A	0.930 (2)	0.144 (2)	1.0001 (13)	0.049*
H2B	0.821 (2)	0.1286 (19)	1.1024 (12)	0.049*
O1	0.5314 (2)	0.61182 (15)	0.75124 (9)	0.0749 (5)
O2	0.4681 (3)	0.85440 (15)	0.62885 (10)	0.0864 (6)
H2	0.416010	0.883790	0.686423	0.130*
O3	0.72815 (15)	0.97527 (11)	0.23239 (8)	0.0432 (3)
O4	0.88515 (18)	0.76383 (13)	0.16150 (9)	0.0550 (3)
O5	0.98699 (18)	0.18757 (13)	0.39818 (9)	0.0540 (3)
O6	0.8612 (2)	0.13295 (13)	0.57798 (9)	0.0589 (4)
H6	0.905 (3)	0.0313 (15)	0.5749 (18)	0.071*

Comment

Trimesic acid with the alpha-polymorph structure with three carboxylate groups was first reported in 1969 [5] and is still an important building block for the construction of hydrogen-bonded organic frameworks due to its predictable honeycomb crystal lattice structure formation [6–9]. In the absence of a co-crystal template, trimesic acid constructs infinite two-dimensional hydrogen-bonded networks through eight-member hydrogen bond synthons with hexagonal apertures.

The title compound was synthesized by the reaction of trimesic acid with macrocylic L. X-ray crystal structural analysis reveals that the asymmetric unit of the title structure contains half L^{2+} and one $[C_9H_5O_6]^-$.

Two macrocylic L^{2+} and two 3,5-dicarboxybenzoate anions are interconnected to form a tetragonal holes through O–H···O hydrogen bonding interactions. The tetragonal holes further interacted with each other to form two-dimensional hydrogen-bonded networks.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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