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Key indicators

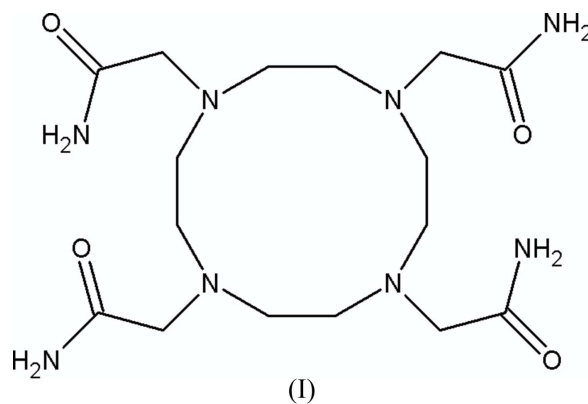
Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.042
 wR factor = 0.111
Data-to-parameter ratio = 17.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.1,4,7,10-Tetrakis(carbamoylmethyl)-1,4,7,10-
tetraazacyclododecane

The centrosymmetric title compound, $\text{C}_{16}\text{H}_{32}\text{N}_8\text{O}_4$, crystallizes one half-molecule in the asymmetric unit. Single crystals were grown from water and, even though the compound contains hydrogen-bonding groups, no water molecules of crystallization were found. Two of the four pendant arms form intramolecularly hydrogen bonds to preorganize the compound into a shape similar to that required for ligation.

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Comment

It is well known that macrocyclic ligands produce enhanced thermodynamic stability with metal ions compared with their open-chain analogues. Our interest with the title macrocycle, (I), concerns its complexing ability with the heavy post-transition elements, lead and bismuth. The chemistry of lead is of interest in relation to its toxicity and effects on intelligence in human subjects (Bryce-Smith, 1986). Bismuth has become of increasing interest in complexes such as the subsalicylate in treating gastric and duodenal ulcers (Baxter, 1992). The architecture of this ligand (see scheme), capable for forming five-membered rings through its four N-donor and four O-donor atoms, should bode well for good complexing ability to lead(II) and bismuth(III). The present ligand has also been used by Amin *et al.* (1996) in its lanthanide(III) complex form as a catalyst for the hydrolytic cleavage of RNA. One of the authors (RCL) was involved in the synthesis of the first example of a bismuth(III) complex with a nitrogen donor macrocycle (Luckay *et al.*, 1995), and on the basis of these studies, the present macrocycle should also show good binding tendencies with bismuth(III). Furthermore, the role of the lone pair in bismuth(III) in determining coordination geometry would be examined. Also of interest is the preorganization of the ligand before ligation of a metal.



There are only three types of hydrogen bonds formed by this centrosymmetric compound in its crystalline state

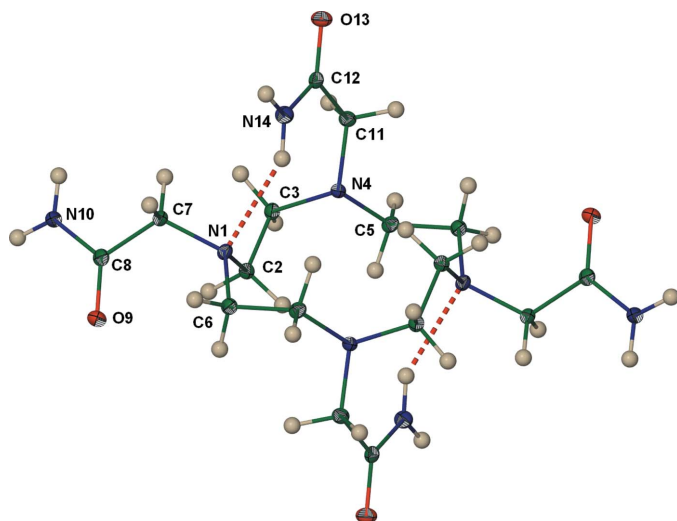


Figure 1
The molecular structure of the title compound, showing atom labels and 50% probability displacement ellipsoids for non-H atoms. Unlabeled atoms are related by the symmetry operator $(1-x, 1-y, 1-z)$. The red dashed lines represent the intramolecular hydrogen bonds.

(Table 1). That of most interest is the intramolecular hydrogen bond between donor and acceptor atoms N14 and N1, respectively. This preorganizes two of the four pendant arms of the ligand into positions pointing inwards to the center of the ligand (Fig. 1). Although the functional groups pointing inwards (the amines) are different from that of the ligated metal structures where the C=O functional group is pointing inwards, this is useful information as it shows that the flexibility of the pendant arms has small energy barriers, as the hydrogen bond is relatively weak compared with a coordination bond. The other two hydrogen bonds, which have the hydrogen-bond donor atom N10 in common, connect the individual molecules together to form a three-dimensional hydrogen-bonded network (Fig. 2). When comparing the conformation of the free ligand in the solid state with that of the coordinated state, it does not have the same conformation as in a number of the known metal–ligand complexes (Maumela *et al.*, 1995). Hence, this ligand is not highly preorganized for ligation of metals.

Experimental

The ligand was synthesized according to the method of Maumela *et al.* (1995). Characterization of the ligand was consistent with the reported NMR data. Single crystals were grown from a saturated solution of the ligand in water. After four days of slow evaporation, colorless rods were deposited.

Crystal data

$C_{16}H_{32}N_8O_4$	$D_x = 1.377 \text{ Mg m}^{-3}$
$M_r = 400.50$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2706 reflections
$a = 5.9691(7) \text{ \AA}$	$\theta = 6.4\text{--}28.1^\circ$
$b = 17.795(2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 9.4230(12) \text{ \AA}$	$T = 100(2) \text{ K}$
$\beta = 105.190(2)^\circ$	Rod, colorless
$V = 966.0(2) \text{ \AA}^3$	$0.25 \times 0.21 \times 0.12 \text{ mm}$
$Z = 2$	

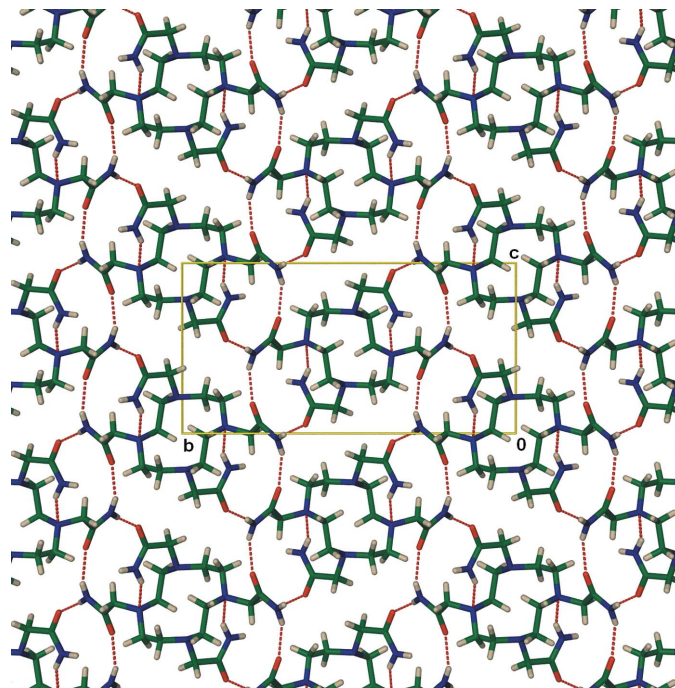


Figure 2
The molecular packing of the title compound *via* hydrogen bonds, shown as red dashed lines. Molecules are shown in closed-capped representation.

Data collection

Bruker APEX CCD area-detector diffractometer	1903 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.030$
Absorption correction: none	$\theta_{\text{max}} = 28.2^\circ$
5989 measured reflections	$h = -6 \rightarrow 7$
2230 independent reflections	$k = -23 \rightarrow 22$
	$l = -12 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.116P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
2230 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
127 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N14—H14B \cdots N1 ⁱ	0.88	2.22	3.018 (1)	152
N10—H10A \cdots O13 ⁱⁱ	0.88	2.03	2.897 (1)	168
N10—H10B \cdots O9 ⁱⁱⁱ	0.88	2.17	3.006 (1)	158

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

All H atoms were positioned geometrically (C—H = 0.99 \AA and N—H = 0.88 \AA) and constrained to ride on their parent atoms; $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

X-SEED (Barbour, 2001; Atwood & Barbour, 2003); software used to prepare material for publication: *X-SEED*.

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