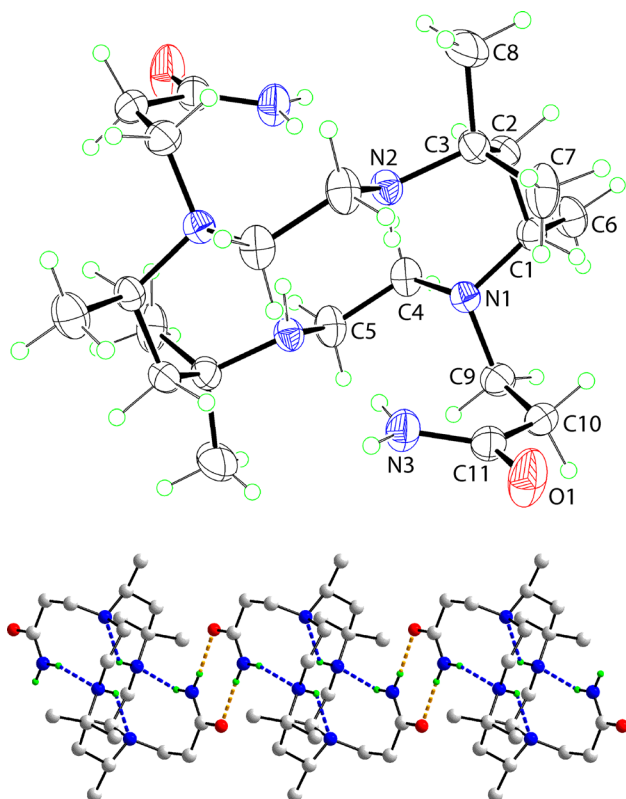


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# Crystal structure of *rac*-1,8-bis(2-carbamoylethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $C_{22}H_{46}N_6O_2$



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## Abstract

$C_{22}H_{46}N_6O_2$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 8.5777(3)$  Å,  $b = 9.0205(4)$  Å,  $c = 9.9270(3)$  Å,  $\alpha = 67.899(3)^\circ$ ,  $\beta = 71.106(3)^\circ$ ,  $\gamma = 63.774(4)^\circ$ ,  $V = 626.83(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $R_{gt}(F) = 0.0400$ ,  $wR_{ref}(F^2) = 0.1162$ ,  $T = 298(2)$  K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## 1 Source of material

The title macrocycle was prepared as detailed in the literature, with colourless crystals being obtained by the slow evaporation of its hot methanolic solution during the synthesis [5]. **M.pt** (uncorrected): 458 K. **Elemental analysis** (Leco CHNS-932 elemental analyzer): Calculated (%): C, 61.93; H, 10.87; N, 19.70. Found (%): C, 61.97; H, 10.90; N, 19.68. **IR** (Shimadzu IR 20 spectrophotometer, KBr,  $cm^{-1}$ ): 3265 (m)  $\nu(NH_2)$ , 3120 (w)  $\nu(N-H)$ , 2967 (m)  $\nu(C-H)$ , 1682 (s)  $\nu(C-O)$ , 1385 (s)  $\nu(CH_3)$ , 1180 (w)  $\nu(C-C)$ .  **$^1H$  NMR** (Bruker AVANCE 400 NMR spectrometer, DMSO- $d_6$ , ppm):  $\delta$ :  $CH_3$  0.85 (d, e), 1.04 (s, e), 1.16 (s, a);  $NH_2$  9.57 (s), 7.29 (s);  $CH_2$ , CH and NH; 5.36 (s), 3.32 (s), 1.66 (t), 2.36 (m), 2.67 (m), 2.75 (m) and 2.84 (m).

**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.10 × 0.08 × 0.03 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
$\mu$ :	0.58 mm <sup>-1</sup>
Diffraction, scan mode:	XtaLAB synergy, $\omega$
$\theta_{max}$ , completeness:	67.1°, >99%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	15,023, 2230, 0.035
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2\sigma(I_{obs})$ , 1922
$N(param)_{refined}$ :	148
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>
O1	0.97133 (18)	0.4285 (2)	0.70510 (14)	0.0890 (5)
N1	0.50316 (13)	0.32964 (13)	0.75915 (12)	0.0365 (3)
N2	0.39251 (15)	0.68935 (14)	0.54783 (12)	0.0394 (3)
H1N	0.4755 (16)	0.5899 (14)	0.5671 (17)	0.047*
N3	0.85728 (17)	0.3777 (2)	0.56063 (14)	0.0568 (4)
H2N	0.782 (2)	0.344 (2)	0.551 (2)	0.068*
H3N	0.913 (2)	0.433 (2)	0.4831 (15)	0.068*
C1	0.37289 (16)	0.42064 (17)	0.87007 (14)	0.0387 (3)
H1	0.440666	0.446194	0.915466	0.046*
C2	0.23948 (17)	0.59343 (18)	0.80078 (15)	0.0438 (3)
H2A	0.155085	0.639294	0.881117	0.053*
H2B	0.174679	0.570573	0.751718	0.053*
C3	0.30465 (19)	0.73626 (17)	0.68944 (15)	0.0445 (3)
C4	0.4224 (2)	0.25550 (19)	0.70363 (15)	0.0464 (3)
H4A	0.310689	0.342395	0.678089	0.056*
H4B	0.396483	0.161473	0.783121	0.056*
C5	0.5342 (2)	0.18897 (19)	0.56970 (16)	0.0509 (4)
H5A	0.630633	0.082750	0.601034	0.061*
H5B	0.461984	0.163173	0.530500	0.061*
C6	0.2721 (2)	0.3150 (2)	0.99730 (17)	0.0579 (4)
H6A	0.189897	0.301727	0.960338	0.087*
H6B	0.208822	0.373588	1.073147	0.087*
H6C	0.354613	0.203919	1.037814	0.087*
C7	0.4285 (3)	0.7647 (2)	0.75189 (17)	0.0619 (5)
H7A	0.538411	0.668205	0.754716	0.093*
H7B	0.373827	0.776489	0.850242	0.093*
H7C	0.450390	0.867332	0.689708	0.093*
C8	0.1409 (3)	0.9006 (2)	0.6629 (2)	0.0830 (6)
H8A	0.176794	0.993177	0.593749	0.124*
H8B	0.079227	0.928983	0.754833	0.124*
H8C	0.064088	0.882824	0.623443	0.124*
C9	0.66221 (19)	0.19921 (17)	0.81635 (16)	0.0466 (3)
H9A	0.728155	0.124876	0.751277	0.056*
H9B	0.626415	0.129018	0.913104	0.056*
C10	0.78344 (18)	0.2726 (2)	0.82988 (16)	0.0492 (4)
H10A	0.713893	0.350637	0.891446	0.059*
H10B	0.873156	0.178505	0.883140	0.059*
C11	0.87685 (18)	0.3667 (2)	0.69145 (16)	0.0521 (4)

## 2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.96–0.98 Å) and refined as riding with  $U_{iso}(H) = 1.2–1.5U_{eq}(C)$ . The N-bound H atoms were located in a difference map and refined with N–H = 0.86 ± 0.01 Å.

## 3 Comment

The title macrocycle, (I; systematic name: 3-[8-(2-carbamoyl ethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecan-1-yl]propanamide) has been reported to complex, in its neutral

form, copper(II) with different binding modes as noted in the three crystallographically determined structures [5, 6]. Despite this, the crystal structure of (I) has not yet been reported. Herein, in order to redress this deficiency in the literature, the crystal and molecular structures of (I) are described along with an analysis of the calculated Hirshfeld surface.

The molecule of (I) is located about an inversion centre and is illustrated in the upper view of the figure (35 % probability ellipsoids with the unlabelled atoms related by the symmetry operation (i): 1 – *x*, 1 – *y*, 1 – *z*). The macrocycle comprises a 14-membered ring with the tertiary amine-N1 atom bearing a 2-carbamoyl ethyl substituent and the amine-N2 amine being a secondary amine. The 2-carbamoyl ethyl substituent is folded over the macrocycle to facilitate the formation of an N–H···N hydrogen bond, as detailed below. The methyl group on atom C1 occupies an equatorial position. Globally, the macrocyclic ring adopts an extended chair conformation.

While no anionic forms of (I) have been investigated crystallographically, there are three structures of copper(II) complexes where the central atom is complexed by the neutral macrocycle. In the acetate salt, isolated as a tetra-hydrate, (I) coordinates through the four nitrogen atoms. A role for the amide group interacting with the copper(II) centre is precluded as each acetate anion forms a close Cu···O interaction along with its participating in an amine–N–H···O(acetate) hydrogen bond [5]. When the counter-anion is perchlorate, rather different coordination geometries are apparent [6]. When (I) is C-racemic, as in the aforementioned acetate salt hydrate, one of the amide-O atoms also coordinates the copper(II) centre, occupying the apical position in a square-pyramidal geometry. When the isomeric meso form of (I) complexes copper(II), a similar mode of coordination is apparent but leads to a trigonal-bipyramidal geometry with the amide-O atom in an equatorial position.

As anticipated from the presence of hydrogen bonding acceptors and donors in (I), considerable interactions of this type are apparent in the crystal, both intra- and inter-molecular. An intramolecular secondary-amine–N–H···N(tertiary amine) hydrogen bond is formed between atoms within the asymmetric-unit [N2–H1n···N1: H1n···N1 = 2.374(14) Å, N2···N1 = 3.0456(16) Å with angle at H1n = 135.1(13)°]. Owing to its being positioned over the macrocycle, one amide-H atom also forms an intramolecular hydrogen bond, with the secondary amine–N atom being the acceptor [N3–H2n···N2<sup>i</sup>: H2n···N2<sup>i</sup> = 2.21(2) Å, N3···N2<sup>i</sup> = 3.041(2) Å with the angle at H2n = 161.2(16)°]. The macrocycles are connected into a linear chain along the *a*-axis via amide–N–H···O(amide) hydrogen bonds [N3–H3n···O1<sup>ii</sup>: H3n···O1<sup>ii</sup> = 2.043(15) Å, N3···O1<sup>ii</sup> = 2.910(2) Å with the angle at H3n = 176.1(17)° for (ii)

$2 - x, 1 - y, 1 - z$ ] and eight-membered  $\{\cdots\text{OCNH}\}_2$  synthons. A view of the supramolecular chain is shown in the lower image of the figure. In this image, the amide-N–H $\cdots$ O(amide) and N–H $\cdots$ N hydrogen bonds are shown as orange and blue dashed lines, respectively; for clarity, non-participating H atoms have been removed.

An analysis of the molecular packing with PLATON [7] suggests an absence of directional interactions between the chains along the  $a$ -axis and featuring conventional hydrogen bonding interactions. Therefore, in order to gain more insight into the nature of the interactions operating between chains in the crystal, an analysis of the calculated Hirshfeld surfaces was conducted in accord with literature protocols [8] and by the use of CrystalExplorer [9].

The analysis of surface contacts in (I) shows, remarkably, all surface contacts involve H atoms. The contribution from H $\cdots$ H contacts amounts to 80.1 %, which is consistent with the chains being completely adorned on the exterior by H atoms. The N–H $\cdots$ O interactions give rise to 17.0 % of the surface contacts with very minor contributions from N $\cdots$ H/H $\cdots$ N [1.6 %] and C $\cdots$ H/H $\cdots$ C [1.3 %] contacts.

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

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