$a = 14.685\ (2)$ Å
$b = 8.679\ (3)$ Å
$c = 17.769\ (3)$ Å
$\beta = 111.75\ (1)°$
$V = 2103.4\ (7)$ Å^3
$Z = 4$
$D_x = 1.408$ Mg m^{-3}
$D_m = 1.406$ Mg m^{-3}
D_m measured by flotation
in KI

$\theta = 11.2$–$12.3°$
$\mu = 0.112$ mm^{-1}
$T = 289.2$ K
Prism
$0.25 \times 0.20 \times 0.20$ mm
Colourless

Data collection

Rigaku AFC-5R diffractom-
eter
$\omega/2\theta$ scans
Absorption correction: none
4149 measured reflections
3986 independent reflections
2187 reflections with
$I > 2\sigma(I)$

$R_{int} = 0.035$
$\theta_{max} = 25°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 10$
$l = -21 \rightarrow 19$
3 standard reflections
every 150 reflections
intensity decay: -0.55%

Refinement

Refinement on F
$R = 0.085$
$wR = 0.052$
$S = 1.341$
2187 reflections
258 parameters
H atoms not refined
Weighting scheme based
on measured s.u.'s
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction:
Zachariasen type 2
Gaussian isotropic
Extinction coefficient:
3.138×10^{-6}
Scattering factors from *Inter-
national Tables for X-ray
Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (3)*

O(1)—C(7)	1.412 (6)	C(1)—C(7)	1.503 (6)
O(1)—B(1)	1.426 (7)	C(7)—C(8)	1.550 (7)
O(2)—C(18)	1.411 (6)	C(7)—C(19)	1.579 (7)
O(2)—B(2)	1.422 (9)	C(8)—C(9)	1.482 (6)
N(1)—C(9)	1.274 (7)	C(8)—C(18)	1.581 (7)
N(1)—B(1)	1.591 (7)	C(12)—C(18)	1.518 (7)
N(2)—C(20)	1.291 (7)	C(18)—C(19)	1.548 (7)
N(2)—B(2)	1.602 (8)	C(19)—C(20)	1.489 (7)
O(1)—C(7)—C(8)	110.9 (4)	O(2)—C(18)—C(8)	108.7 (5)
O(1)—C(7)—C(19)	108.1 (5)	O(2)—C(18)—C(19)	111.6 (5)
C(8)—C(7)—C(19)	86.9 (4)	C(8)—C(18)—C(19)	86.9 (4)
C(7)—C(8)—C(9)	119.1 (5)	C(7)—C(19)—C(18)	91.1 (4)
C(7)—C(8)—C(18)	91.0 (4)	C(7)—C(19)—C(20)	113.4 (4)
C(9)—C(8)—C(18)	117.2 (5)	C(18)—C(19)—C(20)	119.3 (5)

Date collection and cell refinement for all complexes: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Programs used to solve structure: *SIR*88 (Burla *et al.*, 1989) for (1) and (2), *SAPI*91 (Fan, 1991) for (3). Programs used to refine structure: *DIRDIF*92 (Beurskens *et al.*, 1992) for (1) and (3), *DIRDIF*94 (Beurskens *et al.*, 1994) for (2) and *TEXSAN* (Molecular Structure Corporation, 1992) for all complexes. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1049). Services for accessing these data are described at the back of the journal.

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7-Methyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene

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Abstract

The title compound, C$_{14}$H$_{24}$N$_4$, is known to act as a macrocyclic ligand and its conformation has been determined to facilitate future comparisons with its coordinated forms. The aliphatic macrocyclic strand is disordered with respect to a mirror plane perpendicular to the pyridine ring and contains an ordered tertiary

N atom; the four donor N atoms are approximately coplanar.

Comment

The title compound, (I), is known to act as a tetraaza macrocyclic ligand (L) towards several transition metal ions. For example, with nickel(II), it forms [Ni(L)]-(ClO$_4$)$_2$, with the coordination about the metal centre being approximately square planar (Alcock *et al.*, 1986). Compounds such as (I) are sufficiently flexible to vary their mode of coordination, and we have therefore determined its crystal structure in order to compare its conformation with those found in metal complexes. The structure of the related ligand β-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene has also been reported (Drew *et al.*, 1986), but this has methyl groups on two C atoms of the macrocyclic ring and not on a donor N atom as in (I).

(I)
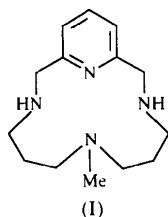
The molecular structure of (I) is represented in Fig. 1. Bond lengths and angles are unexceptional but confirm the bond orders given in the scheme above.
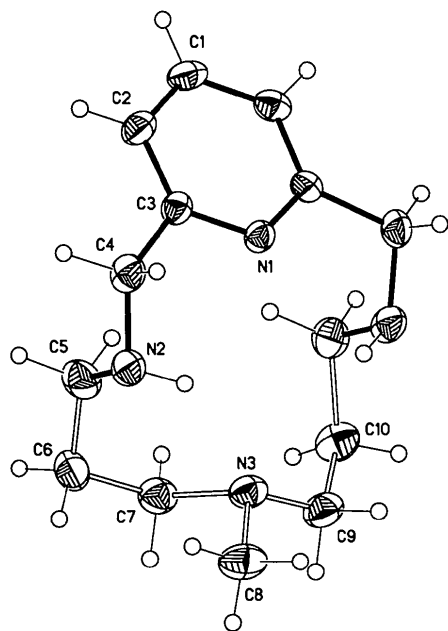
The pyridine ring is planar (r.m.s. deviation 0.004 Å) and the four N atoms are approximately coplanar (r.m.s. deviation 0.04 Å). The angle between these two planes is 47.4 (1)°, which can be compared with a value of 49.2° in the related macrocycle (Drew *et al.*, 1986) with methyl groups at C4 and C4', but not at N3 (as labelled in Fig. 1). Atoms C1, N1 and N3 are located on the mirror plane (*i.e.* $y = \frac{1}{4}$), and the complete molecule is generated from the asymmetric unit by reflection across this plane. The ring segment from C6 to C10 *via* N3 (and including C8) is disordered and the alternative positions (not shown in Fig. 1) are generated by reflection across the mirror plane.

The macrocycle is folded in such a way that all atoms with the exception of C4 and C8 (and their symmetry equivalents) are on the same side of the N$_4$ plane. The NH protons were fitted from an electron-density map and point inwards, thus implying that the NH lone pairs point away from the macrocyclic cavity. The separations between adjacent N atoms in the N$_4$ plane are N1···N2 2.849 (2) and N2···N3 3.238 (2) Å; the *trans* separations are much greater at N1···N3 3.928 (3) and N2···N2^i 4.624 (3) Å [symmetry code: (i) x, $\frac{1}{2} - y$, z]. There is no evidence of either inter- or intramolecular hydrogen bonding; the shortest potential hydrogen-bond interaction involves atoms N2 and N3 at a separation of 3.238 (2) Å (*cf.* the sum of the van der Waals radii of 3.10 Å).

Experimental

To a stirred solution of freshly prepared 2,6-pyridinecarb-aldehyde (9.81 g, 72.7 mmol) in ethanol (150 ml) was added a solution of Cu(NO$_3$)$_2$.4H$_2$O (17.56 g, 72.7 mmol) in water (150 ml). To the resulting pale-green solution was added dropwise, with stirring, a solution of 1,7-diamino-4-methyl-4-azaheptane (9.54 g, 72.7 mmol) in ethanol (30 ml). The resulting deep-blue solution was stirred while heating under reflux for 2 h, during which time an intense violet colour developed. The solution was then placed under a dry nitrogen atmosphere and cooled to 278 K. Sodium tetrahydroborate (7 g, 184.2 mmol) was added in small portions over a period of 30 min. The solution was stirred at room temperature for 30 min, and then heated to reflux for a further 30 min, before being left to stir overnight at room temperature. The copper was removed by treating the mixture with Na$_2$S.9H$_2$O (40 g, 167 mmol) followed by heating to reflux for 30 min. The solution was then cooled and the black copper sulfide was removed by filtration through a bed of Celite. The filtrate was extracted with dichloromethane (7 × 200 ml), the combined extracts dried with anhydrous MgSO$_4$, and the di-chloromethane removed by evaporation to leave an orange–white gel. The pure ligand was obtained by sublimation of the gel.

Crystal data

Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level.

$C_{14}H_{24}N_4$

$M_r = 248.37$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Orthorhombic
Pnma
$a = 15.3046\,(10)$ Å
$b = 14.5739\,(10)$ Å
$c = 6.4175\,(6)$ Å
$V = 1431.41\,(19)$ Å^3
$Z = 4$
$D_x = 1.153$ Mg m^{-3}
D_m not measured

Cell parameters from 2239
reflections
$\theta = 2.66–25.49°$
$\mu = 0.071$ mm^{-1}
$T = 180\,(2)$ K
Needle
$0.23 \times 0.09 \times 0.06$ mm
Colourless

Data collection

Siemens SMART CCD area-
detector diffractometer
ω scans
Absorption correction: none
3319 measured reflections
1327 independent reflections

1043 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 25.49°$
$h = -16 \rightarrow 17$
$k = -6 \rightarrow 17$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.122$
$S = 1.162$
1327 reflections
114 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.3663P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.141$ e Å^{-3}
$\Delta\rho_{min} = -0.181$ e Å^{-3}
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 5.01 cm. Coverage of the unique set was over 97% complete to at least 28° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model, with U(H) equal to 1.2 (or 1.5 for methyl H atoms) times U_{eq} of the parent atom. Attempted refinement in space group $Pn2_1a$ (non-standard setting of $Pna2_1$) did not remove the need for a disorder model and gave poorer results, *i.e.* $R = 0.075$.

Data collection: *SMART* (Siemens, 1994*b*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.29389 (12)	1/4	0.0318 (3)	0.0377 (5)
N2	0.20591 (11)	0.40863 (10)	0.1844 (2)	0.0533 (5)
N3	0.07865 (13)	1/4	0.3651 (3)	0.0481 (6)
C1	0.32440 (17)	1/4	-0.3924 (4)	0.0501 (7)
C2	0.31645 (11)	0.33153 (12)	-0.2853 (3)	0.0454 (5)
C3	0.30072 (10)	0.32915 (10)	-0.0728 (2)	0.0383 (4)
C4	0.28524 (12)	0.41379 (11)	0.0589 (3)	0.0497 (5)
C5	0.12707 (13)	0.40163 (13)	0.0595 (3)	0.0613 (6)
C6†	0.0365 (8)	0.3963 (9)	0.1530 (16)	0.058 (2)
C7†	0.0142 (2)	0.2992 (3)	0.2239 (6)	0.0537 (9)
C8†	0.0834 (3)	0.3061 (3)	0.5638 (6)	0.0643 (11)
C9†	0.0558 (2)	0.1602 (3)	0.4108 (6)	0.0551 (10)
C10†	0.0526 (8)	0.0970 (9)	0.2241 (14)	0.059 (2)

† Site occupancy = 0.50.

Table 2. *Selected torsion angles (°)*

C1—C2—C3—C4	-176.08 (18)	C9—N3—C7—C6	-176.1 (6)
C5—N2—C4—C3	-62.53 (19)	C8—N3—C7—C6	62.5 (6)
N1—C3—C4—N2	-49.1 (2)	C5—C6—C7—N3	51.6 (7)
C2—C3—C4—N2	127.94 (18)	C8—N3—C9—C10	-177.7 (6)
C4—N2—C5—C6	-179.4 (6)	C7—N3—C9—C10	63.1 (6)
C4'—N2'—C5'—C10	176.8 (5)	N3—C9—C10—C5'	45.3 (9)
N2—C5—C6—C7	-81.4 (6)	C9—C10—C5'—N2'	49.9 (8)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

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