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Tri-*tert*-butyl 3-oxo-4-oxa-1,8,11-triazaspiro[5.6]dodecane-1,8,11-triacetate

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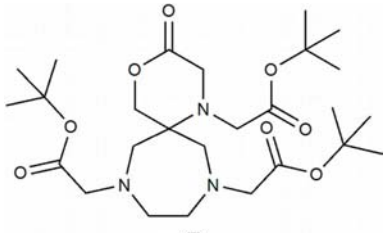
The title compound, $C_{26}H_{45}N_3O_8$, is a bicyclic molecule; the seven-membered diazepane ring has a twisted-chair conformation and the six-membered morpholine ring has a boat conformation.

Comment

The chemistry of 1,4-diazepane-based ligands is attracting increasing attention since these ligands have strong binding capabilities with different metal ions, including main group metals, transition metals and lanthanides (Comba *et al.*, 2009; Ge *et al.*, 2007, 2009; Peralta *et al.*, 2005; Rey *et al.*, 2007). In particular, it has been proposed that gadolinium(III) complexes of 6-amino-6-methylperhydro-1,4-diazepinetetraacetic acid (AAZTA) ligands are good candidates as MRI (magnetic resonance imaging) contrast agents due to their good thermodynamic stability, kinetic inertness and high relaxivity at neutral pH (Aime *et al.*, 2004).



(I)

Recently, we reported the syntheses and characterization of new bifunctional AAZTA ligands with hydroxy side chains, and the crystal structures of their gadolinium and europium complexes (Sengar *et al.*, 2008, 2009). The title compound, (I), was used as a precursor for one of the bifunctional ligands with a hydroxy arm and the complete synthesis and spectroscopic characterization of (I) was provided (Sengar *et al.*, 2009). We report herein the molecular structure of compound (I) determined by X-ray crystallography (Fig. 1).

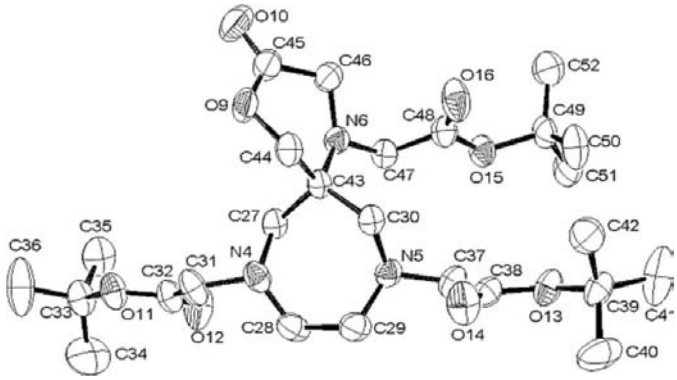


Figure 1
The molecular structure of (I), showing one of the molecules in the unit cell, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

Compound (I) crystallizes with two independent molecules in the asymmetric unit and these exhibit similar conformations. The r.m.s. deviation of the two molecules based on a fit of all non-H atoms is 0.353 Å, calculated by *PLATON* (Spek, 2009). The maximum deviations were observed for the *tert*-butyl ester groups. As expected, compound (I) contains two rings, *viz.* a seven-membered 1,4-diazepane ring with a twisted-chair conformation and a six-membered morpholine ring which adopts a boat conformation (Fig. 1). For the seven-membered ring, the approximate plane can be defined by N4/C29/N5/C27, with atoms C30, C43 and C28 deviating above and below this plane. For the six-membered ring, atoms C44 and C46 occupy the prow and stern positions, respectively. The two rings are connected to each other *via* spiro atom C43 in a near orthogonal fashion; the dihedral angles for the N5/C30/C43/N6 and N4/C27/C43/C44 planes are –87.0 (2) and −71.9 (2)°, respectively [−85.6 (2) and –72.8 (2)°, respectively, for the other molecule in the unit cell].

The diazepane and morpholine rings in the two molecules have slightly different puckering parameters (Cremer & Pople, 1975), as given in Table 1. The puckering parameters for the seven-membered ring in (I) are different from the values for the AAZTA chelate (Table 1) or the protonated diazepane (daza-3HCl-3H_2O) chelate (Romba *et al.*, 2006). This shows that a large degree of flexibility is associated with the diazepane ring, which gives rise to the different puckering parameters for noncoordinated ligands. However, upon metal coordination, the diazepane ring adopts a pseudo-chair conformation and all three N atoms coordinate to the metal ion in a facial mode (Aime *et al.*, 2008).

Experimental

Compound (I) was synthesized according to the literature procedure of Sengar *et al.* (2009). Colorless crystals suitable for X-ray analysis were obtained by slow evaporation from a dichloromethane solution of (I) in air.

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Crystal data

$C_{26}H_{45}N_3O_8$
M_r = 527.65
Triclinic, $P\overline{1}$
a = 11.1304 (17) Å
b = 15.250 (2) Å
c = 18.098 (3) Å
α = 99.305 (4)°
β = 90.010 (3)°
γ = 100.168 (3)°
V = 2982.5 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 203 K
0.24 × 0.18 × 0.13 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.962, T_{max} = 0.980
21467 measured reflections
11582 independent reflections
7769 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.170
S = 1.04
11582 reflections
667 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Puckering parameters for (I) and the AAZTA chelate.

All calculations made using *PLATON* (Spek, 2009).

	Diazepane ring		Morpholine ring		Diazepane in AAZTA†
	Molecule 1	Molecule 2	Molecule 1	Molecule 2	
q_2 (Å)	0.510 (2)	0.537 (2)	0.638 (2)	0.653 (2)	0.641 (7)
q_3 (Å)	0.676 (2)	0.675 (2)	0.031 (2)	0.026 (2)	0.633 (7)
φ_2 (°)	69.0 (3)	67.2 (2)	55.1 (2)	59.3 (2)	65.7 (6)
φ_3 (°)	323.7 (2)	323.5 (2)			16.2 (6)

† Aime *et al.* (2008).

H atoms were placed in calculated positions and refined using a riding model [C—H = 0.97 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms, and C—H = 0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene H atoms].

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3037). Services for accessing these data are described at the back of the journal.

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