Crystal structure of 13,27-dichloro-29,30-dihydroxy-3,9,17,23-tetramethyl-6,20-dioxa-3,9,17,23-tetraazatri-cyclo[23.3.1.1^{11,15}]triaconta-1(29),11,13,15(30),25,27-hexaene-(aqua)magnesium hydrate, $\text{Mg}[\text{C}_{28}\text{H}_{40}\text{Cl}_2\text{N}_4\text{O}_4(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$

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Abstract

$\text{C}_{28}\text{H}_{44}\text{Cl}_2\text{MgN}_4\text{O}_6$, triclinic, $P\bar{1}$ (No. 2), $a = 10.397(3)$ Å, $b = 11.152(3)$ Å, $c = 14.728(5)$ Å, $\alpha = 74.25(2)^\circ$, $\beta = 80.51(2)^\circ$, $\gamma = 77.00(2)^\circ$, $V = 1591.6$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.056$, $wR_{\text{ref}}(F^2) = 0.174$, $T = 293$ K.

Source of material

The compound was the product of a side reaction in the synthesis of the ligand itself [1]. The presence of Mg was confirmed by ICP analysis. Found: Mg, 3.5%. Calc.: Mg, 3.8%.

Experimental details

While all of several selected crystals showed unambiguous cell parameters and allowed a solution by direct methods, none of them resulted in an R -factor smaller than 12%. After studying the data file with PLATON [2,3], the non-merohedral twinning was

suggested. The overlapped reflections (those with severely distorted background or visible deformation) were removed from the data file; the remaining reflection file was re-processed using PLATON.

Discussion

A great number of macroheterocycles containing phenolic ring as part of their molecular framework have been synthesized [4]. The coordination of relatively large alkali and alkaline earth cations inside the macrocyclic hosts have been reported, while comparatively little attention has been given to magnesium cation complexes. This lack of interest is likely caused by the relatively small radius and the low coordination number of Mg^{2+} ion, which reduce the interactions between macrocyclic donor atoms, and the cation. Here we report a crystal structure of magnesium complex with phenolic oxaza macrocycle 13,27-dichloro-29,30-dihydroxy-3,9,17,23-tetramethyl-6,20-dioxa-3,9,17,23-tetraazatri-cyclo[23.3.1.1^{11,15}]triaconta-1(29),11,13,15(30),25,27-hexaene.

The Mg ion has a slightly distorted octahedral coordination. The deviations of the four coordinated O atoms and Mg from the least squares plane containing these atoms are all less than 0.02 Å. The two nitrogen atoms are at apical positions at significantly longer interatomic distances from the central ion. The C–O–C angles of the ligand chain are larger than tetrahedral, while C–N–C are very close to tetrahedral. With the exceptions of those contained in the phenolic groups, all torsion angles of C–C bonds are ($\pm$) *gauche* (40° – 80°), and all torsion angles about C–O are *trans* (170° – 180°). Each nitrogen is involved in one *trans* and one *gauche* C–C–N–C torsion angle. The coordinated water molecule forms two hydrogen bonds with nitrogen atoms of the macrocyclic ring, which gives additional stability to the complex. The other water molecule is connected to a phenolic oxygen atom by a hydrogen bond. Despite the short O6...O3 distance (2.83 Å), there is only a weak interaction between them ($\angle \text{O3–H3O–O6} = 115^\circ$). Unlike anhydrous Mg^{2+} , the hydrated $\text{Mg}(\text{H}_2\text{O})^{2+}$ cation fits well in the macrocyclic cavity interacting with seven crown ether donor atoms either by direct coordination or by means of hydrogen bonding. We have reported similar coordination via a water molecule in the Li–18-crown-6 complex cation [5]. The remaining hydrogen atom of the hydrate water molecule is oriented towards the phenyl group of the complex forming a weak O–H...phenyl hydrogen bond [6].

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Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.25 × 0.26 × 0.36 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.69 cm ⁻¹
Diffractometer, scan mode:	Siemens P4, $\omega/2\theta$
$2\theta_{\max}$:	46.12°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4514, 4259
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3174
$N(\text{param})_{\text{refined}}$:	403
Programs:	SHELXS-86 [7] SHELXL-97 [8], ORTEP-3 [9], PLATON [2,3]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(12A)	2i	0.6287(5)	0.234(4)	0.309(3)	0.055
H(4A)	2i	0.676(1)	0.840(2)	0.525(2)	0.058
H(4B)	2i	0.815(4)	0.7682(6)	0.4734(5)	0.058
H(10A)	2i	0.8531(5)	0.229(3)	0.333(1)	0.056
H(10B)	2i	0.932(3)	0.3212(5)	0.262(2)	0.056
H(33A)	2i	0.449(2)	0.8095(8)	0.101(1)	0.067
H(33B)	2i	0.5344(6)	0.867(2)	0.1476(6)	0.067
H(33C)	2i	0.5175(6)	0.728(2)	0.188(2)	0.067
H(8A)	2i	0.7426(7)	0.275(4)	0.477(1)	0.065
H(8B)	2i	0.651(3)	0.391(1)	0.416(1)	0.065
H(14A)	2i	0.446(4)	0.493(2)	0.109(2)	0.050
H(2A)	2i	0.6813(9)	1.004(2)	0.387(2)	0.050
H(2B)	2i	0.650(2)	0.987(2)	0.288(2)	0.050

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(16A)	2i	0.702(3)	0.6225(7)	-0.013(2)	0.051
H(16B)	2i	0.538(3)	0.6620(8)	0.010(1)	0.051
H(21A)	2i	1.058(2)	0.812(3)	-0.076(1)	0.071
H(21B)	2i	1.0261(6)	0.696(2)	-0.098(2)	0.071
H(19A)	2i	0.7857(6)	0.766(2)	-0.113(2)	0.072
H(19B)	2i	0.817(1)	0.908(3)	-0.118(2)	0.072
H(18A)	2i	0.6582(6)	0.931(3)	0.0062(9)	0.065
H(18B)	2i	0.590(3)	0.8731(9)	-0.052(2)	0.065
H(5A)	2i	0.732(2)	0.614(1)	0.595(2)	0.063
H(5B)	2i	0.586(4)	0.6570(6)	0.561(1)	0.063
H(22A)	2i	1.0862(7)	0.567(4)	0.0383(5)	0.070
H(22B)	2i	1.192(4)	0.6539(6)	0.0121(8)	0.070
H(24A)	2i	1.055(1)	0.872(2)	0.061(2)	0.054
H(24B)	2i	1.176(3)	0.8105(5)	0.1018(6)	0.054
H(7A)	2i	0.631(3)	0.4268(7)	0.565(2)	0.074
H(7B)	2i	0.791(3)	0.401(2)	0.564(2)	0.074
H(34A)	2i	1.219(3)	0.5919(6)	0.1844(5)	0.071
H(34B)	2i	1.1006(8)	0.510(3)	0.1995(4)	0.071
H(34C)	2i	1.086(1)	0.6190(8)	0.259(2)	0.071
H(26A)	2i	1.209(5)	0.875(1)	0.235(1)	0.048
H(28A)	2i	0.905(2)	0.988(2)	0.412(3)	0.048
H(32A)	2i	0.9650(6)	0.393(2)	0.464(2)	0.084
H(32B)	2i	1.040(2)	0.3695(9)	0.370(2)	0.084
H(32C)	2i	0.9855(8)	0.261(3)	0.444(1)	0.084
H(31A)	2i	0.489(1)	0.762(2)	0.436(1)	0.074
H(31B)	2i	0.486(1)	0.872(1)	0.338(2)	0.074
H(31C)	2i	0.478(1)	0.907(2)	0.439(1)	0.074
H(30)	2i	0.743(5)	0.702(5)	0.322(3)	0.067
H(31)	2i	0.802(6)	0.563(3)	0.315(4)	0.067
H(40)	2i	0.722(6)	1.038(4)	0.118(4)	0.095
H(41)	2i	0.665(7)	1.163(6)	0.130(4)	0.095

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cl(2)	2i	0.3882(2)	0.2693(2)	0.2377(1)	0.0662(9)	0.077(1)	0.0582(9)	-0.0432(8)	0.0003(7)	-0.0213(8)
Mg	2i	0.8325(1)	0.7066(1)	0.1403(1)	0.0332(8)	0.0347(9)	0.0358(9)	-0.0072(7)	-0.0044(6)	-0.0117(7)
O(1)	2i	0.8144(3)	0.8786(3)	0.1680(2)	0.037(2)	0.036(2)	0.044(2)	-0.006(1)	-0.011(2)	-0.011(2)
O(2)	2i	0.8467(3)	0.5241(3)	0.1403(2)	0.034(2)	0.037(2)	0.050(2)	-0.005(2)	-0.003(2)	-0.016(2)
O(6)	2i	0.7169(5)	0.5652(4)	0.4783(2)	0.106(3)	0.049(2)	0.039(2)	-0.025(2)	0.006(2)	-0.011(2)
N(17)	2i	0.6416(4)	0.7517(3)	0.0704(3)	0.044(2)	0.028(2)	0.044(2)	-0.005(2)	-0.008(2)	-0.008(2)
O(20)	2i	0.8877(3)	0.7688(4)	-0.0087(2)	0.048(2)	0.066(2)	0.037(2)	-0.016(2)	-0.002(2)	-0.011(2)
C(12)	2i	0.6289(5)	0.3034(5)	0.2623(4)	0.065(4)	0.029(3)	0.046(3)	-0.012(2)	-0.006(3)	-0.010(2)
C(4)	2i	0.7137(5)	0.7757(5)	0.4838(4)	0.049(3)	0.059(3)	0.045(3)	-0.019(3)	-0.001(2)	-0.021(3)
C(10)	2i	0.8515(5)	0.3156(5)	0.3024(4)	0.052(3)	0.035(3)	0.051(3)	0.001(2)	-0.014(2)	-0.007(2)
N(3)	2i	0.6627(4)	0.8248(4)	0.3925(3)	0.027(2)	0.045(2)	0.045(2)	-0.007(2)	-0.001(2)	-0.014(2)
C(33)	2i	0.5254(5)	0.7925(6)	0.1321(4)	0.050(3)	0.057(4)	0.065(4)	-0.003(3)	-0.011(3)	-0.024(3)
C(25)	2i	1.0352(5)	0.8674(4)	0.1972(3)	0.036(3)	0.035(3)	0.046(3)	-0.014(2)	-0.002(2)	-0.010(2)
C(8)	2i	0.7322(6)	0.3653(5)	0.4472(4)	0.064(4)	0.043(3)	0.054(3)	-0.021(3)	-0.005(3)	-0.002(3)
C(11)	2i	0.7377(5)	0.3625(4)	0.2424(3)	0.044(3)	0.032(3)	0.046(3)	-0.005(2)	-0.010(2)	-0.014(2)
C(14)	2i	0.5181(5)	0.4607(5)	0.1407(3)	0.040(3)	0.048(3)	0.043(3)	-0.008(2)	-0.007(2)	-0.020(3)
C(15)	2i	0.6256(5)	0.5222(4)	0.1179(3)	0.042(3)	0.035(3)	0.032(2)	-0.009(2)	-0.004(2)	-0.015(2)
N(9)	2i	0.8445(4)	0.3865(4)	0.3748(3)	0.046(2)	0.044(3)	0.045(2)	-0.010(2)	-0.014(2)	-0.004(2)
C(2)	2i	0.7028(5)	0.9465(5)	0.3428(4)	0.036(3)	0.039(3)	0.049(3)	0.000(2)	-0.005(2)	-0.017(2)
C(16)	2i	0.6257(5)	0.6402(5)	0.0391(3)	0.048(3)	0.044(3)	0.040(3)	-0.013(2)	-0.011(2)	-0.011(2)
C(21)	2i	1.0222(6)	0.7379(6)	-0.0495(4)	0.059(4)	0.074(4)	0.048(3)	-0.022(3)	0.016(3)	-0.027(3)
C(19)	2i	0.7920(6)	0.8264(6)	-0.0729(4)	0.077(4)	0.065(4)	0.038(3)	-0.030(3)	-0.016(3)	0.006(3)
C(18)	2i	0.6609(6)	0.8570(5)	-0.0139(4)	0.066(4)	0.040(3)	0.059(4)	-0.012(3)	-0.026(3)	0.000(3)
C(1)	2i	0.8481(4)	0.9335(4)	0.3071(3)	0.034(3)	0.028(2)	0.043(3)	-0.005(2)	-0.001(2)	-0.011(2)
C(5)	2i	0.6819(6)	0.6482(5)	0.5385(4)	0.060(3)	0.063(4)	0.041(3)	-0.022(3)	0.005(3)	-0.019(3)
C(13)	2i	0.5215(5)	0.3502(5)	0.2114(4)	0.047(3)	0.049(3)	0.044(3)	-0.018(2)	-0.004(2)	-0.021(3)
C(22)	2i	1.0983(6)	0.6527(6)	0.0294(4)	0.050(3)	0.062(4)	0.068(4)	-0.010(3)	0.012(3)	-0.037(3)
N(23)	2i	1.0553(4)	0.6916(4)	0.1198(3)	0.034(2)	0.046(2)	0.049(3)	-0.008(2)	0.001(2)	-0.022(2)
C(24)	2i	1.0882(5)	0.8171(5)	0.1110(4)	0.033(3)	0.055(3)	0.050(3)	-0.014(2)	0.007(2)	-0.019(3)
C(7)	2i	0.7164(7)	0.4357(5)	0.5233(4)	0.088(5)	0.054(4)	0.043(3)	-0.030(3)	-0.002(3)	-0.002(3)

Table 3. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(34)	2i	1.1203(5)	0.5957(6)	0.1967(4)	0.044(3)	0.061(4)	0.068(4)	0.005(3)	−0.009(3)	−0.020(3)
C(26)	2i	1.1201(5)	0.8917(4)	0.2509(3)	0.032(3)	0.038(3)	0.051(3)	−0.013(2)	−0.001(2)	−0.011(2)
C(29)	2i	0.8958(4)	0.8927(4)	0.2233(3)	0.039(3)	0.027(2)	0.038(3)	−0.009(2)	−0.007(2)	−0.003(2)
C(27)	2i	1.0709(5)	0.9412(4)	0.3284(3)	0.046(3)	0.035(3)	0.047(3)	−0.014(2)	−0.011(2)	−0.009(2)
C(28)	2i	0.9365(5)	0.9586(4)	0.3577(4)	0.052(3)	0.030(3)	0.041(3)	−0.011(2)	−0.002(2)	−0.013(2)
C(30)	2i	0.7406(5)	0.4711(4)	0.1663(3)	0.040(3)	0.033(3)	0.039(3)	−0.006(2)	−0.003(2)	−0.020(2)
C(32)	2i	0.9699(6)	0.3493(6)	0.4170(5)	0.060(4)	0.080(5)	0.074(4)	−0.012(3)	−0.028(3)	−0.014(4)
C(31)	2i	0.5167(5)	0.8429(6)	0.4021(4)	0.035(3)	0.075(4)	0.074(4)	−0.013(3)	0.002(3)	−0.018(3)
Cl(1)	2i	1.1786(1)	0.9854(2)	0.3883(1)	0.0554(9)	0.080(1)	0.075(1)	−0.0229(7)	−0.0195(7)	−0.0300(8)
O(3)	2i	0.7814(4)	0.6490(3)	0.2804(2)	0.090(3)	0.035(2)	0.037(2)	−0.010(2)	0.005(2)	−0.010(2)
O(4)	2i	0.6732(5)	1.1159(5)	0.0843(3)	0.088(3)	0.073(3)	0.071(3)	0.007(3)	−0.026(3)	−0.017(2)

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References

- Pastushok, V. N.; Bradshaw, J. S.; Bordunov, A. V.; Izatt, R. M.: Mannich Reaction as a Key Strategy for the Synthesis of Benzoazacrown Ethers and Benzocryptands. *J Org. Chem.* **61** (1996) 6888–6892.
- Spek, A. L.: PLATON, An Integrated Tool for the Analysis of the Results of a Single Crystal Structure Determination. *Acta Crystallogr. A* **46** (1990) C34.
- Spek, A. L.: PLATON - A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, The Netherlands 2002.
- Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L.: Thermodynamic and kinetic data for macrocycle interactions with cations and anions *Chem Rev.* **91** (1991) 1721–2085.
- Dalley, N. K.; Lamb, J. D.; Nazarenko, A. Y.: Crystal Structure of 1,4,7,10,13,16-Hexaoxacyclooctadecane Complex with Lithium Picrate Dihydrate. *Supramol. Chem.* **8** (1997) 345–350.
- Desiraju, G. R., Steiner, T.: *The Weak Hydrogen Bond. In: Structural Chemistry and Biology.* Oxford University Press, Oxford 2001.
- Sheldrick, G. M.: Phase annealing in SHELX-90: direct methods for larger structures. *Acta Crystallogr. A* **46** (1990) 467–473.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
- Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **30** (1997) 565.