Crystal structure of hexaaquamagnesium(II) bis(hydrogen-*cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate) dihydrate, $[Mg(H_2O)_6][C_{18}H_{13}O_4]_2 \cdot 2H_2O$

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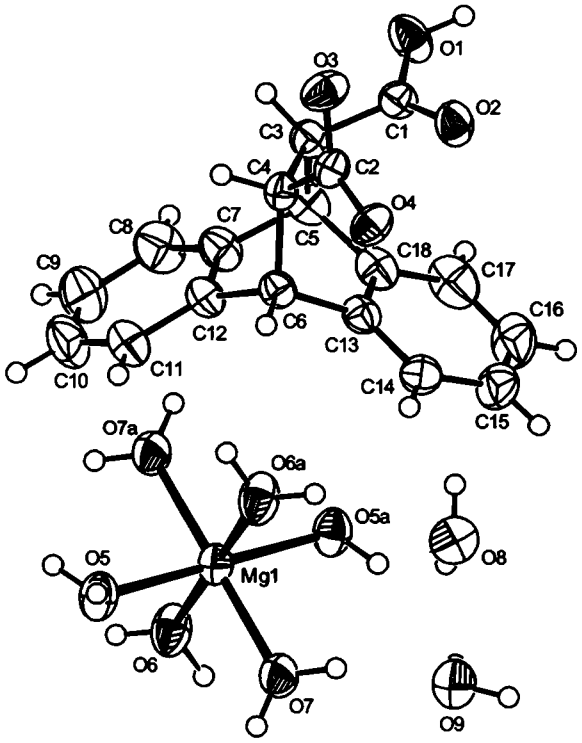

Abstract

$C_{36}H_{46}MgO_{18}$, monoclinic, $P12_1/c1$ (no. 14),
$a = 18.3358(7)$ Å, $b = 12.1644(5)$ Å, $c = 8.5208(2)$ Å,
$\beta = 96.087(2)°$, $V = 1889.8$ Å^3, $Z = 2$,
$R_{gt}(F) = 0.040$, $wR_{ref}(F^2) = 0.102$, $T = 298$ K.

Source of material

The title compound was crystallized by slow evaporization from the aqueous solution prepared by the reaction of equimolar amounts of $Mg(NO_3)_2$ solution and dicarboxylic acid, which was synthesized by a cycloaddition reaction of maleic anhydride with anthracene and hydrolyzation with NaOH solution.

Discussion

The role of magnesium in biological systems has been explored in very much detail [1]. There are many examples of the binding of magnesium to oxygen-containing ligands such as carboxylates, hydroxyls, and water. In nature, magnesium binds nucleic acids via water molecules while it can bind to proteins directly [2]. The role of water molecules in the inner coordination to magnesium cations in enzymes was investigated by ab initio molecular orbital calculation [3]. The interactions between magnesium-bound water molecules and carboxylate groups can facilitate the catalytic activity of enzymes by changing the pK_a of the water molecule and controlling the orientation of required functional groups. A detailed knowledge of the coordination of magnesium could provide a guideline for drug designs of certain metalloproteins. To our knowledge, no crystal structures of metal ion complexes of the carboxylate of the anthracene adduct have been reported.

The bond lengths of C1—O1 and C1—O2 are 1.309(2) Å and 1.215(2) Å, respectively, while the bond lengths of C2—O3 and C2—O4 are 1.265(2) Å and 1.251(2) Å, respectively, indicating that the ligand is in the form of the monocarboxylate group while the other group is protonated. Thus, Mg(II) cation is attached to two carboxylate groups from different molecules. In addition to the electrostatic interactions, the crystal structure is stabilized by a network of hydrogen bonds and van der Waals interactions. Intermolecular hydrogen bonds are formed between the carboxylic and the adjacent carboxylate groups. The intermolecular distance between the stacked aromatic rings is approximately 4.1 Å indicating π-π interaction.

The Mg(II) cation is bound to six water molecules at the inner coordination and four water molecules at outer coordination. The bond lengths between the magnesium cation and oxygen atoms of inner water molecules are in the range of 2.030(1) Å – 2.117(1) Å. The outer water molecules are 4.174 Å and 4.543 Å apart from the Mg ion. The distances between Mg and each oxygen atom of the carboxylic and the carboxylate group (O1, O2, O3, and O4) are 6.248 Å, 4.135 Å, 5.239 Å, and 3.909 Å, respectively. The Mg ion is closer to the carboxylate group with C2 (4.751 Å) than to the carboxylic group with C1 (5.334 Å). The carboxylate group is twisted with the dihedral angle O3–C2–C4–C3 of 61.1° while the carboxylic group is twisted with the dihedral angle O2–C1–C3–C4 of 19.6°. The aromatic rings are bent inclining to each other with the angle of 108.2°. The unit cell of the title compound consists of alternative layers between hydrophobic (aromatic moiety of anthracene adducts) and hydrophilic groups (Mg(II) cation).

Table 1. Data collection and handling.

Crystal:	colorless cube, size 0.20 × 0.20 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.3 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	52.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16930, 3856
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3116
$N(param)_{refined}$:	307
Programs:	SIR97 [4], SHELXL-97 [5], ORTEP-II [6], maXus [7]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.259(2)	0.193(2)	0.565(3)	0.093(9)
H(3)	4e	0.3498	0.3502	0.8379	0.033(4)
H(4)	4e	0.3118	0.4877	0.9656	0.037(4)
H(5)	4e	0.3953	0.4009	0.5913	0.049(5)
H(6)	4e	0.2743	0.6624	0.8406	0.033(4)
H(8)	4e	0.5203	0.4776	0.7095	0.065(7)
H(9)	4e	0.5842	0.6123	0.8607	0.088(8)
H(10)	4e	0.5225	0.7459	0.9840	0.089(8)
H(11)	4e	0.3954	0.7488	0.9587	0.064(6)
H(14)	4e	0.2009	0.7187	0.5811	0.054(6)
H(15)	4e	0.1713	0.6878	0.3137	0.068(7)
H(16)	4e	0.2328	0.5570	0.1857	0.084(8)
H(17)	4e	0.3238	0.4516	0.3229	0.067(6)
H(5O)	4e	−0.006(1)	0.099(2)	0.277(3)	0.065(7)
H(5P)	4e	0.068(2)	0.056(3)	0.270(4)	0.11(1)
H(6O)	4e	0.088(2)	0.105(2)	−0.184(3)	0.086(8)
H(6P)	4e	0.132(2)	0.082(2)	−0.027(3)	0.10(1)
H(7O)	4e	−0.062(1)	0.201(3)	−0.079(3)	0.090(9)
H(7P)	4e	−0.102(2)	0.106(2)	−0.170(3)	0.093(9)
H(8O)	4e	0.087(2)	0.609(2)	−0.011(3)	0.075(8)
H(8P)	4e	0.015(1)	0.651(2)	−0.031(3)	0.065(7)
H(9O)	4e	0.116(2)	0.343(3)	0.078(4)	0.10(1)
H(9P)	4e	0.084(2)	0.255(3)	0.154(3)	0.10(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4e	0.29200(7)	0.2340(1)	0.6223(2)	0.0366(7)	0.0404(7)	0.0768(9)	0.0043(5)	−0.0021(6)	−0.0216(6)
O(2)	4e	0.20067(6)	0.3526(1)	0.6284(2)	0.0336(6)	0.0442(7)	0.0594(7)	0.0057(5)	−0.0081(5)	−0.0096(5)
O(3)	4e	0.19285(6)	0.3822(1)	0.9676(1)	0.0343(6)	0.0494(7)	0.0555(7)	0.0026(5)	0.0081(5)	0.0193(6)
O(4)	4e	0.15491(6)	0.5363(1)	0.8482(1)	0.0312(6)	0.0466(7)	0.0399(6)	0.0097(5)	0.0047(4)	0.0065(5)
C(1)	4e	0.26395(8)	0.3263(1)	0.6670(2)	0.0314(8)	0.0326(8)	0.0392(8)	0.0018(6)	0.0040(6)	−0.0006(6)
C(2)	4e	0.20419(8)	0.4680(1)	0.8899(2)	0.0292(8)	0.0378(8)	0.0294(7)	0.0037(6)	0.0026(5)	0.0004(6)
C(3)	4e	0.31881(8)	0.3972(1)	0.7650(2)	0.0269(7)	0.0336(8)	0.0408(8)	0.0022(6)	0.0011(6)	−0.0025(6)
C(4)	4e	0.28395(8)	0.4887(1)	0.8609(2)	0.0278(7)	0.0345(8)	0.0299(7)	0.0019(6)	0.0009(5)	−0.0021(6)
C(5)	4e	0.36817(9)	0.4547(2)	0.6478(2)	0.0340(8)	0.0409(9)	0.053(1)	−0.0005(7)	0.0157(7)	−0.0114(7)
C(6)	4e	0.29940(8)	0.6032(1)	0.7898(2)	0.0328(8)	0.0318(8)	0.0339(8)	0.0006(6)	0.0051(6)	−0.0043(6)
C(7)	4e	0.41918(9)	0.5340(2)	0.7422(2)	0.0312(8)	0.046(1)	0.054(1)	−0.0060(7)	0.0084(7)	−0.0037(8)
C(8)	4e	0.4952(1)	0.5319(2)	0.7585(3)	0.034(1)	0.064(1)	0.079(1)	−0.0030(9)	0.0139(9)	−0.003(1)
C(9)	4e	0.5332(1)	0.6126(2)	0.8495(3)	0.034(1)	0.079(2)	0.084(2)	−0.016(1)	0.0000(9)	0.001(1)
C(10)	4e	0.4962(1)	0.6927(2)	0.9234(3)	0.051(1)	0.067(1)	0.071(1)	−0.025(1)	−0.005(1)	−0.005(1)
C(11)	4e	0.4203(1)	0.6950(2)	0.9081(2)	0.049(1)	0.048(1)	0.056(1)	−0.0118(9)	0.0014(8)	−0.0070(8)
C(12)	4e	0.38198(9)	0.6155(1)	0.8159(2)	0.0344(8)	0.0385(9)	0.0434(9)	−0.0073(7)	0.0038(6)	−0.0024(7)
C(13)	4e	0.27764(9)	0.5998(1)	0.6137(2)	0.0344(8)	0.0362(9)	0.0340(8)	−0.0072(7)	0.0079(6)	−0.0002(6)
C(14)	4e	0.22482(9)	0.6640(2)	0.5301(2)	0.0418(9)	0.043(1)	0.0398(9)	−0.0086(7)	0.0050(7)	0.0068(7)
C(15)	4e	0.2078(1)	0.6462(2)	0.3699(2)	0.058(1)	0.063(1)	0.039(1)	−0.013(1)	−0.0006(8)	0.0129(8)
C(16)	4e	0.2444(1)	0.5678(2)	0.2935(2)	0.076(2)	0.081(2)	0.0316(9)	−0.018(1)	0.0045(9)	0.0005(9)
C(17)	4e	0.2989(1)	0.5044(2)	0.3755(2)	0.069(1)	0.064(1)	0.043(1)	−0.015(1)	0.0240(9)	−0.0144(9)
C(18)	4e	0.31569(9)	0.5203(1)	0.5366(2)	0.0418(9)	0.044(1)	0.0381(8)	−0.0095(7)	0.0139(7)	−0.0046(7)
Mg(1)	2a	0	0	0	0.0306(4)	0.0403(4)	0.0324(4)	0.0008(3)	0.0008(3)	−0.0032(3)
O(5)	4e	0.02828(8)	0.0871(1)	0.2130(1)	0.0427(7)	0.0556(8)	0.0364(6)	0.0056(6)	0.0011(5)	−0.0079(5)
O(6)	4e	0.08986(7)	0.0653(1)	−0.0848(2)	0.0354(7)	0.077(1)	0.0443(7)	−0.0089(6)	0.0017(5)	0.0063(6)
O(7)	4e	−0.06054(7)	0.1275(1)	−0.1077(2)	0.0402(7)	0.0439(8)	0.0522(7)	0.0042(6)	−0.0064(5)	−0.0040(6)
O(8)	4e	0.07957(8)	0.3248(1)	0.1330(2)	0.0454(8)	0.0553(9)	0.0526(8)	0.0047(6)	0.0131(6)	−0.0006(6)
O(9)	4e	0.05495(8)	0.6463(1)	0.0363(2)	0.0454(8)	0.0560(8)	0.0461(7)	0.0040(6)	0.0060(6)	−0.0066(6)

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