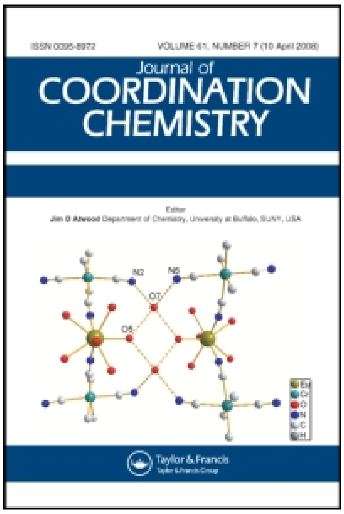

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Synthesis, Characterization and Crystal Structure of a Novel Complex of Maleic Acid with Gadolinium(III)

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NOVEL COMPLEX OF MALEIC ACID WITH GADOLINIUM(III)

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A novel ionic complex of gadolinium(III) with maleic acid, $[Gd(C_4H_3O_4)_2(H_2O)_7](C_4H_3O_4).H_2O$, was synthesized and characterized by elemental analysis, molar conductance, TG, DTA and IR. The structure of the complex was determined by single-crystal X-ray diffraction methods and refined to $R=0.024$, $R_w=0.029$ for 4906 reflections with $I \geqslant 3\sigma(I)$. Crystals are triclinic with $a=10.317(2)$, $b=16.627(3)$, $c=7.192(3)$ Å, $\alpha=91.99(2)$, $\beta=109.18(2)$, $\gamma=72.00(2)°$, $\mu(MoK_\alpha)=31.047\,cm^{-1}$, and $Z=2$. The space group is Pr. The gadolinium ion is coordinated by two bimaleates and seven waters forming a positive complex, and another bimaleate anion compensates for charge. The metal coordination number is nine and the coordination polyhedron is a distorted, monocapped square antiprism.

Keywords: Gadolinium(III), maleic acid, synthesis, crystal structure

INTRODUCTION

Complexes of lanthanides with dicarboxylic acids often have special structures and interesting fluorescent properties. Studies of complexes of lanthanides with maleic acid, $Ln_2L_3.nH_2O$ and $Ln(HL)_3.nH_2O$, are known from previous investigations[1,2] and the crystal structure of $Nd_2(C_4H_2O_4)_3.12H_2O$ has been reported.[3] In this paper, we report a novel ionic complex of Gd(III) with maleic acid, $[Gd(C_4H_3O_4)_2(H_2O)_7]\notin(C_4H_3O_4).H_2O$. It has been characterized by elemental analysis, molar conductance, TG, DTA and IR methods; its crystal structure has been determined by single-crystal X-ray diffraction methods.

EXPERIMENTAL

Preparation of $[Gd(HL)_2(H_2O)_7](HL).H_2O$

Freshly prepared $Gd(OH)_3$ (1.0 mmol) was added to an aqueous solution of H_2L (8.0 mmol, H_2L = maleic acid), with continuous stirring. The solution was evaporated at 60°C until some crystals were formed at the surface. It was cooled to room temperature, filtered, the crystals washed with anhydrous ethanol and dried *in vacuo* at room temperature over P_2O_5.

The product was dissolved in an H_2L solution in EtOH–H_2O (1:4, v/v), which was allowed to evaporate at room temperature over P_2O_5 in a desiccator. A single crystal obtained from the solution was used for the X-ray analysis.

Microanalysis for C and H was performed with a model 1106 elemental analyser, and gadolinium was determined by EDTA titration. Anal. Calcd. for

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$[Gd(C_4H_3O_4)_2(H_2O)_7](C_4H_3O_4).H_2O$: Gd, 24.32; C, 22.29; H, 3.90%. Found: Gd, 24.54; C, 22.26; H, 3.55%. Molar conductance was measured in DMF at 25°C using a DDS-11A conductivity apparatus at a concentration of 2.301×10^{-3} mol dm^{-3}. The molar conductance of the complex is 80.9 S cm^2 mol^{-1}, which indicates the complex to be a 1:1 electrolyte.[4] IR spectra were recorded using a Nicolet-5DX FIR spectrometer in KBr discs.

Thermogravimetric measurements were performed using a PCT-2 thermobalance in air at a heating rate of 10°C min^{-1}. α-Al_2O_3 was used as reference material. The complex loses all waters between 58–234°C. Calcd. H_2O: 22.2%. Found: 22.3%. The anhydrous complex decomposes at 262°C, finally to Gd_2O_3 at 774°C.

Crystal structure determination

Intensity data for a crystal of dimensions $0.59 \times 0.52 \times 0.44$ mm were collected on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan mode [scan width: $0.65 + 0.35 \tan\theta$]. A total of 5096 reflections in the range $1° \leqslant \theta \leqslant 27°$ were measured. An empirical absorption correction was applied (max. and min. transmission factors 0.998 and 0.948, respectively). Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 20° and 40°.

Crystal data

$GdC_{12}H_{27}O_{20}$, $M = 648.58$, triclinic, space group $P\bar{1}$, $a = 10.317(2)$, $b = 16.627(3)$, $c = 7.192(3)$ Å, $\alpha = 91.99(2)$, $\beta = 109.18(2)$, $\gamma = 72.00(2)°$, $V = 1105.1$ Å^3, $D_c = 1.952$ g cm^{-3}, $Z = 2$, $\mu(MoK_\alpha) = 31.047$ cm^{-1} and $F(000) = 648$.
The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure in which the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where $w = 1$ for all observed reflections. Non-hydrogen atoms were refined with anisotropic thermal parameters. Most hydrogen atoms were located from a ΔF map and included in the refinement using fixed thermal parameters; others were positioned on geometrical grounds. Refinement converged at $R = 0.024$, $R_w = 0.029$ and $(\Delta/\sigma)_{max} = 0.29$ for 4906 data with $I \geqslant 3\sigma(I)$. The greatest residual electron density peak in the final difference map was 0.76 eÅ^{-3}.

All calculations were carried out on a PDP11/44 computer using the SDP-PLUS program. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

RESULTS AND DISCUSSION

IR spectra

Selected infrared data for NaHL and $[Gd(HL)_2(H_2O)_7](HL).H_2O$ are listed in Table I. At 3582 cm^{-1} and 1686 cm^{-1} are, respectively, the γ_{OH} and $\gamma_{C=O}$ modes of the carboxylic group.[5] In comparison with the IR spectrum of NaHL, $\gamma_{C=O}$ of the complex is displaced from 1704 to 1687 cm^{-1}; this can be attributed to hydrogen bonds between carboxylic groups and waters. The $\gamma_{as(COO^-)}$ and $\gamma_{s(COO^-)}$ modes of the complex are similar to those of NaHL, which demonstrates that there is a free bimaleate anion in the complex.[6,7]

TABLE I
Infrared data for NaHL and the complex (cm⁻1).

	ν_{OH}	$\gamma_{C=O}$	$\gamma_{as(COO^-)}$	$\gamma_{s(COO^-)}$
NaHL	3589.6(m)	1704.5(m)	1583.3(s) 1504.9(s)	1397.9(m) 1369.4(m)
Complex	3581.7(m)	1686.6(m)	1568.3(s) 1508.3(s)	1400.3(m) 1365.1(m)

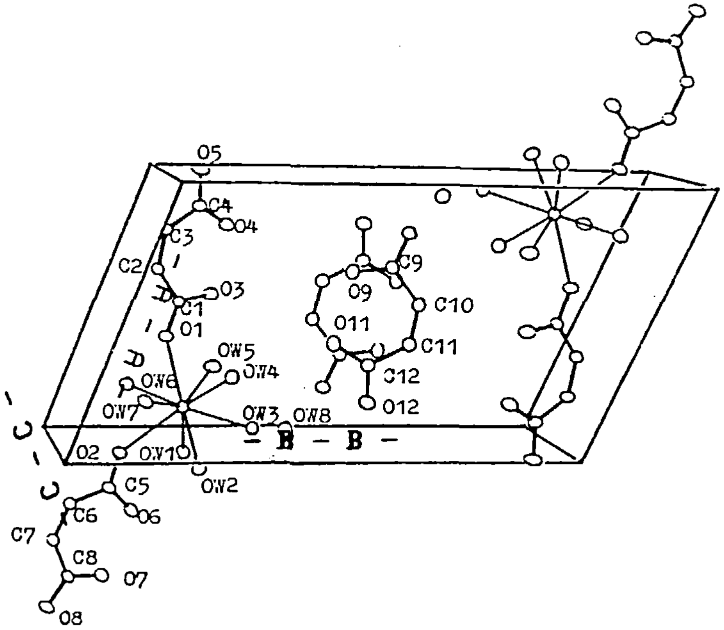

FIGURE 1 The unit cell contents of the complex.

Crystal structure

The unit cell containing the complex is shown in Figure 1. There are two molecules per unit cell. Atomic coordinates of non-hydrogen atoms are given in Table II. Selected bondlengths and angles are listed in Tables III and IV.

The gadolinium ion is coordinated by two bimaleates and seven waters to form a cation. The coordination polyhedron is a nine-coordinate, distorted, monocapped square antiprism, as shown in Figure 2 (OW3 is the capping atom).

Gd-O bondlengths in the complex are in the range 2.399(2)-2.461(2) Å. It is worth mentioning that the bonds to carboxylate oxygens are longer than those to water oxygens; only Gd-OW3 is slightly longer than Gd-O2, which seems to be inconsistent with the coordination abilities of carboxylate and water. We attribute the irregular bondlengths to the hindrance of bimaleates.

TABLE II
Atomic coordinates (× 10^4) for the complex.

	x/*a*	*y*/*b*	*z*/*c*
Gd	1201.5(1)	2386.1(1)	6533.0(2)
O1	−402(2)	1424(2)	5628(2)
O2	3781(2)	1546(2)	7675(4)
OW1	2507(2)	2955(2)	4967(4)
OW2	2380(3)	2920(2)	9589(4)
OW3	382(2)	3949(1)	6357(4)
OW4	−757(3)	2967(2)	3471(4)
OW5	−724(2)	2910(2)	7881(4)
OW6	1788(3)	1278(2)	9071(4)
OW7	1729(2)	1392(2)	4176(4)
OW8	973(3)	4099(2)	1725(4)
O3	−2615(3)	2137(2)	5534(5)
O4	−4979(2)	1983(2)	4244(4)
O5	−5948(3)	1017(2)	2804(4)
O6	5200(3)	2228(2)	9547(4)
O7	7742(3)	2053(2)	760(4)
O8	9768(2)	1094(2)	788(4)
O9	4080(3)	4376(2)	2376(6)
O10	2044(3)	5424(2)	1436(5)
O11	6637(3)	4210(2)	3363(6)
O12	8012(3)	4994(2)	3483(6)
C1	−1681(3)	1481(2)	5197(5)
C1	−2149(3)	757(2)	4266(5)
C3	−3458(3)	668(2)	3574(5)
C4	−4886(3)	1257(2)	3517(5)
C5	4998(3)	1592(2)	8549(5)
C6	6249(3)	878(2)	8433(5)
C7	7652(3)	779(2)	9119(5)
C8	8447(3)	1346(2)	288(5)
C9	3366(4)	5165(2)	1899(6)
C10	4135(4)	5788(2)	1878(7)
C11	5530(4)	5694(2)	2394(7)
C12	6805(4)	4920(2)	3135(6)

TABLE III
Selected bondlengths (Å) for the complex.

Gd-O1	2.565(2)	C1-O1	1.226(4)
Gd-O2	2.461(2)	C1-O3	1.290(4)
Gd-OW1	2.416(2)	C1-C2	1.490(4)
Gd-OW2	2.424(2)	C2-C3	1.331(4)
Gd-OW3	2.465(2)	C3-C4	1.485(4)
Gd-OW4	2.426(2)	C4-O4	1.287(4)
Gd-OW5	2.404(2)	C4-O5	1.229(4)
Gd-OW6	2.431(2)		
Gd-OW7	2.399(2)		

TABLE IV
Selected bond angles (°) for the complex.

O1–Gd–OW6	65.54(8)	OW–Gd–OW1	68.89(8)
O1–Gd–OW7	66.17(8)	OW3–Gd–OW2	68.27(9)
O2–Gd–OW6	67.50(9)	OW3–Gd–OW5	69.25(9)
O2–Gd–OW7	69.47(8)	OW3–Gd–OW4	69.14(8)
OW1–Gd–OW2	88.36(9)	OW3–Gd–O1	126.78(7)
OW1–Gd–OW4	81.96(9)	OW3–Gd–OW6	134.54(9)
OW5–Gd–OW2	77.90(8)	OW3–Gd–O2	122.08(8)
OW5–Gd–OW4	81.9(1)	OW3–Gd–OW7	132.20(9)
Gd–O1–C1	139.0	Gd–O2–C5	142.8
O1–C1–O3	122.3(3)	C1–C2–C3	130.5(3)
O1–C1–C2	118.0(3)	C2–C3–C4	130.4(3)
O3–C1–C2	119.8(3)	C3–C4–O4	120.1(3)
O4–C4–O5	122.2(3)	C3–C4–O5	117.7(3)

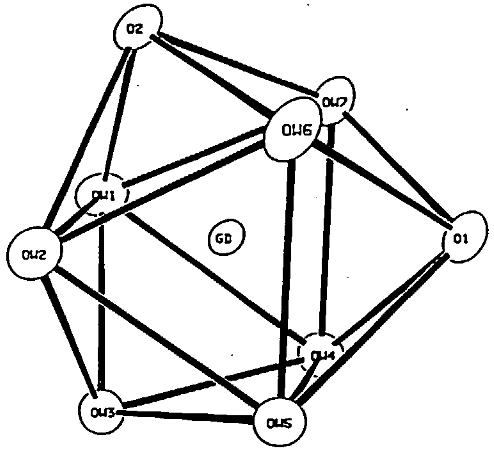

FIGURE 2 The coordination polyhedron around Gd.

Because a seven-membered chelate ring is not as stable as a five- or six-membered ring, the bimaleates coordinate to the gadolinium ion as unidentates. This coordination behaviour has been reported in the structure of $Zn(C_4H_3O_4)_2.4H_2O$.[8]

It is interesting to note that the another bimaleate is uncoordinated, but exists in the form of a simple anion. OW8 is a lattice water.

There are many hydrogen bonds between the carboxylate oxygens and waters, which increase the stability of the complex. Bondlengths and angles of hydrogen bonds are listed in Table V. The bondlengths between bimaleate and water, and between water and water, are in the range 2.760–2.979 Å; angles are in the range 135.6–177.2°. Lengths of intrabimaleate hydrogen bonds are in the range 2.400–2.468 Å' the bond angles vary between 158.1–179.2°.

TABLE V
Bondlengths (Å) and angles (°) for hydrogen bonds for the complex.*

	Length	Angle
OW1-HOW1...O4	2.825	164.4
OW1-HOW1'...OW8	2.760	172.0
OW2-HOW2...O6	2.979	135.6
OW2-HOW2'...OW8	2.818	163.4
OW3-HOW3...O12	2.797	155.2
OW3-HOW3'...O12	2.766	168.2
OW4-HOW4...O7	2.813	163.4
OW4-HOW4'...O11	2.834	167.1
OW5-HOW5...O10	2.825	159.7
OW5-HOW5'...O3	2.867	145.5
OW6-HOW6...O8	2.845	174.3
OW6-HOW6'...O5	2.872	169.5
OW7-HOW7...O5	2.774	176.9
OW7-HOW7...O8	2.779	162.8
OW8-HOW8...O10	2.796	177.2
O4-HO4...O3	2.400	179.2
O7-HO7...O6	2.422	165.1
O9-HO9...O11	2.468	158.1

*The prime indicates the OW atom is bonded to the H atom.

SUPPLEMENTARY MATERIAL

Atomic coordinates for the hydrogen atoms, thermal parameters, full lists of bondlengths and observed and calculated structure factors for the complex are available from the authors on request.

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