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Interaction of Metal Ions with Humic-like Models. Part 5.* The Crystal and Molecular Structure of Diaquabis(2,6-dihydroxybenzoato)-dioxouranium(VI) Octahydrate

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Abstract

The crystal and molecular structure of the complex $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$ (DHB = 2,6-dihydroxybenzoato) has been determined from single-crystal X-ray analysis and refined to a final R value of 0.033 for 3620 observed reflections. The complex crystallizes in the monoclinic system, space group $C2/m$, with $a = 6.704(3)$, $b = 20.171(6)$, $c = 9.454(4)$ Å and $Z = 2$. The coordination about the uranyl group, which is linear, involves two bidentate carboxylate groups and two water molecules in *trans* positions giving rise to an irregular hexagonal bipyramid. Intramolecular hydrogen bonds between phenolic and carboxylate groups forming six-membered rings allow the molecule to be nearly planar. Spectroscopic (IR, NMR and electronic absorption) data and thermal properties of the compound are also reported.

Introduction

The study of metal complexes formed by polyhydroxybenzoic acids can provide reliable information about the binding of metals to humic substances which are of primary importance to the environmental behavior of trace elements [1]. In this connection, we have already reported spectroscopic, analytical and structural results concerning the interaction of 2,6-dihydroxybenzoic acid with some divalent ions [2–4]. As part of this research, we have now studied the interaction of dioxouranium(VI) with the above ligand.

This paper reports the crystal and molecular structure, together with thermal and spectroscopic data, of the title compound which was obtained by reaction of uranyl acetate with 2,6-dihydroxybenzoic acid in aqueous solution.

Experimental

Materials

2,6-Dihydroxybenzoic acid (Merck, 97%) was recrystallized twice from water and dried *in vacuo*. Uranyl acetate dihydrate was of commercial grade.

Preparation of the Complex

The complex was prepared by mixing stoichiometric amounts of the acid and uranyl acetate dihydrate in hot water. On standing at 50 °C yellow crystals precipitated, which were filtered off, washed with water and air-dried. Analytical data were consistent with the formula $UO_2(C_{14}H_{10}O_8)\cdot 10H_2O$: Calc.: C, 22.23; H, 3.99; H_2O, 23.82. Found: C, 22.43; H, 3.85; H_2O, 23.5.

Analytical and Spectroscopic Measurements

C, H and N were determined using a Perkin-Elmer 240 B elemental analyser. Thermal studies were performed on a Perkin-Elmer thermogravimetric apparatus in nitrogen atmosphere at a scanning rate of 5 °C min^{-1}. IR spectra were recorded on a Perkin-

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*Part 4 is L. Strinna Erre, G. Micera, P. Piu, F. Cariati and G. Ciani, *Inorg. Chem.*, in press.

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Elmer 683 spectrophotometer in KBr pellets or as samples spread over NaCl plates in the range 4000–300 cm^{-1}. Electronic spectra were taken on Beckman Acta M IV spectrophotometer.

Crystal Data and Structure Analysis

$C_{14}H_{30}O_{20}U$, M = 756.4, monoclinic, a = 6.704(3), b = 20.171(6), c = 9.454(4) Å, β = 99.57(3)°, V = 1260.6 Å^3, D_c = 1.99 g cm^{-3}, D_m = 2.03 g cm^{-3}, Z = 2, (Mo-K$_\alpha$) = 0.7107 Å^3, space group $C2/m$.

Data were collected on a four-circle Philips PW 1100 automated diffractometer with graphite monochromatized Mo-K$_\alpha$ radiation. A total of 3620 reflections was collected of which 848 were systematically absent for space group conditions. The 2772 remaining reflections were corrected for Lorentz, polarization and absorption effects using the RIFLUP program [5]. The diffracted intensities were averaged to 1627 structure amplitudes using the SORT program*. The structure was solved and refined using the SHELX-76 program. The final conventional R value was 0.033. The uranium atom lies in position 2a(000) of space group $C2/m$ and thus the molecular point group symmetry is at least $2/m$ (C_{2h}).

The positional and thermal parameters with their estimated standard deviations are listed in Tables I and II, respectively.

Results and Discussion

Thermal Analysis

Thermogravimetric analysis of the complex showed ten water molecules which were removed in two separate steps. Seven molecules were lost in the range 40–90 °C, whereas the three remaining molecules were released at temperatures up to 125 °C. The red anhydrous complex decomposed at 200 °C. U_3O_8 was the residue.

TABLE I. Atomic Coordinates.[a]

Atom[b]	x/a	y/a	z/c
U	0.00000(0)	0.00000(0)	0.00000(0)
O(1)	0.25190(90)	0.00000(0)	−0.03060(70)
O(2)	0.03470(60)	0.11090(20)	0.11620(40)
O(3)	0.06180(70)	0.22030(20)	0.25910(40)
O(4)	0.12290(120)	0.00000(0)	0.26030(60)
O(5)	0.50000(0)	0.20230(30)	0.50000(0)
O(6)	0.19880(90)	0.10130(30)	0.46770(60)
O(7)	0.37670(160)	0.00000(0)	0.66320(110)
C(1)	0.00000(0)	0.14410(40)	0.00000(0)
C(2)	0.00000(0)	0.21600(30)	0.00000(0)
C(3)	0.03100(80)	0.25200(30)	0.13020(50)
C(4)	0.03210(90)	0.32110(30)	0.13060(60)
C(5)	0.00000(0)	0.35460(40)	0.00000(0)
HO(3)	0.03540(350)	0.16670(150)	0.20660(250)
HC(4)	0.05330(350)	0.34540(150)	0.20750(250)
HC(5)	0.00000(0)	0.40870(250)	0.00000(0)

[a] The standard deviations of the least significant figure(s) are given in parentheses. [b] The labeling scheme is that of Fig. 2. O(5), O(6) and O(7) are oxygens of crystallization water molecules.

Infrared Spectra

IR data for the hydrate and anhydrous complexes, together with those for the corresponding sodium salt, are reported in Table III. For other metal derivatives of DHB, namely $[Cu(DHB)_2(H_2O)_2]$ and $[M(H_2O)_6](DHB)_2 \cdot 2H_2O$, almost identical stretching frequencies were observed for the

TABLE II. Thermal Parameters (×10^4)[a].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	298(2)	151(2)	267(2)	0(0)	38(1)	0(0)
O(1)	444(31)	252(29)	549(35)	0(0)	167(27)	0(0)
O(2)	541(22)	202(17)	258(16)	12(14)	37(15)	−12(17)
O(3)	686(28)	328(22)	245(17)	−3(16)	47(17)	25(20)
O(4)	1034(57)	260(31)	326(29)	0(0)	−117(32)	0(0)
O(5)	937(54)	408(39)	321(29)	0(0)	103(32)	0(0)
O(6)	924(41)	557(33)	567(30)	−98(26)	56(28)	−77(30)
O(7)	1039(76)	1189(87)	783(63)	0(0)	206(56)	0(0)
C(1)	337(34)	214(36)	326(34)	0(0)	35(27)	0(0)
C(2)	311(32)	154(33)	280(30)	0(0)	47(25)	0(0)
C(3)	378(25)	233(24)	294(22)	−25(20)	36(19)	13(21)
C(4)	430(29)	210(24)	468(30)	−99(24)	59(23)	0(23)
C(5)	342(37)	207(38)	550(47)	0(0)	48(34)	0(0)

[a] In the form: $\exp[-2\pi^2 \Sigma U_{ij} a_i^* a_j^* h_i h_j]$.

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*'SORT' (Sorting and Averaging) is a local version of programs originating from Brookhaven National Laboratory and from the State University of New York at Buffalo.

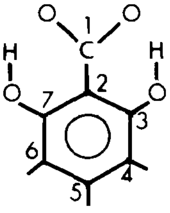
TABLE III. Stretching Frequencies (cm^{-1}) of the Carboxylate and Uranyl Groups.

Compound	$\nu_{as}(COO)$	$\nu_s(COO)$	$\Delta\nu$	$\nu_{as}(O-U-O)$
$[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$	1598s	1445s	153	920s
$[UO_2(DHB)_2]$	1597s	1446s	151	943s
$Na(DHB)\cdot 1.5H_2O$	1595s	1400s	195	–

carboxylate groups, either coordinate or uncoordinate [3]. This finding was explained as due to the intramolecular hydrogen bonding between carboxylate and phenolic groups. Compared to the above complexes and to the sodium salt, the dioxouranium(VI) derivatives display a shift of $\nu_s(COO)$ to higher frequency and, simultaneously, a decrease of $\Delta(\nu_{as}(COO) - \nu_s(COO))$ which achieves values typical of bidentate carboxylate groups. However, the hydrogen bonding is still effective in influencing the vibrational modes of the carboxylate group, as in the analogous 2,6-dimethoxybenzoate complex where hydrogen bonding is not operating, a further decrease of $\Delta\nu$ is observed [6].

The complex $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$ exhibits a strong absorption at 920 cm^{-1} which is attributable to the ν_3 vibration of the UO_2 moiety. The band shifts to 943 cm^{-1} in the spectrum of the anhydrous compound. This indicates strengthened U–O bonds [7], probably as a consequence of the absence of the hydrogen bonding to water molecules.

TABLE IV. ^1H NMR Chemical Shifts (δ/ppm).



Compound	C–H-5	C–H-4, C–H-6
DHB	7.32	6.45
$[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$	7.34	6.46

NMR and Electronic Spectra

The ^1H and ^{13}C NMR chemical shifts for the ligand and the complex, measured in CD_3OD downfield from TMS used as an internal standard, are listed in Tables IV and V. It is apparent from the data that the signals corresponding to the C–H-4, C–H-5 and C–H-6 hydrogens and the C-4, C-5 and C-6 carbon atoms, which are far away from the carboxylate group, are practically unaffected upon uranyl coordination. The major chemical shift variations with respect to the free ligand are observed for the C-1 (6.97 ppm) and C-2 (1.88 ppm) atoms. These findings strongly support the hypothesis that the uranyl ion is bound to the carboxylate group of DHB also in solution.

In either CH_3OH or H_2O solution the electronic absorption spectrum shown in Fig. 1 was observed, suggesting that the same species is formed.

Molecular Structure

A view of the structure projected down the O–U–O axis is shown in Fig. 2. The uranium atom is eight-coordinate and lies in a crystallographic inversion center. In particular the equatorial plane of uranium is occupied by six oxygen atoms, two from water molecules and four from bidentate carboxylates giving rise to an irregular hexagonal bipyramid. The coordinate groups are mutually in the *trans* position allowing the molecular structure to assume a C_{2h} point group symmetry.

The most relevant bond distances and angles are reported in Table VI. The uranyl group is linear and has U–O distances (1.760(6) Å) which are comparable to those usually found in related compounds [8, 9]. Also the U–O distances in the equatorial plane (average value: 2.47 Å) are within the ranges reported for other hexacoordinate uranyl complexes [8].

TABLE V. ^{13}C NMR Chemical Shifts (δ/ppm).

Compound	C-4, C-5, C-6	C-3, C-7	C-2	C-1
DHB	108.64	136.86	162.42	173.23
$[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$	108.65	136.24	164.30	180.20
Δppm		−0.62	+1.88	+6.97

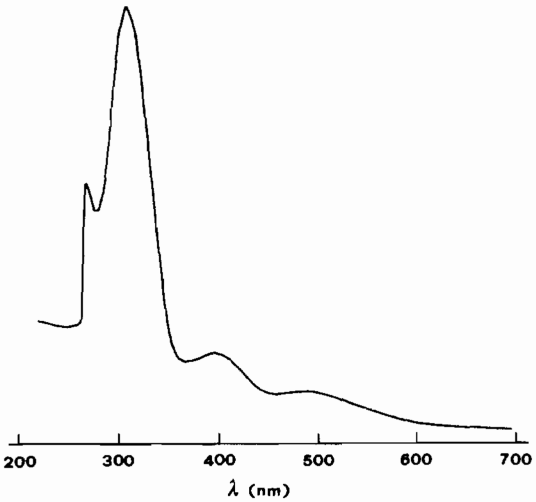


Fig. 1. Absorption spectrum of $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$ in water or methanol.

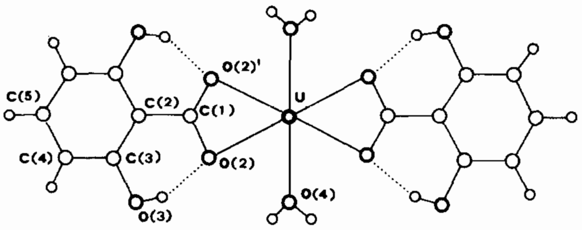


Fig. 2. Perspective view of $[UO_2(DHB)_2(H_2O)_2]$ along the O–U–O axis. The oxygen atoms of the uranyl group, O(1) and O(1)′, are not shown.

TABLE VI. Selected Bond Distances (Å) and Angles (°) in $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$.[a]

Distances		Angles	
U–O(1)	1.760(6)	O(2)–U–O(2)′	51.7(1)
U–O(2)	2.486	O(2)–C(1)–O(2)′	116.6(3)
U–O(4)	2.462(6)	U–O(2)–C(1)	95.8(2)
C(1)–O(2)	1.275(6)	C(2)–C(1)–O(2)	121.7(2)
C(1)–C(2)	1.450(10)	C(1)–C(2)–C(3)	120.9(2)
C(2)–C(3)	1.415(6)	C(2)–C(3)–O(3)	121.1(5)
C(3)–O(3)	1.361(6)		
C(3)–C(4)	1.394(9)		
C(4)–C(5)	1.392(7)		
C(4)–HC(4)	0.87(3)		
C(5)–HC(5)	1.09(5)		

[a] The standard deviations of the least significant figure(s) are given in parentheses.

Intramolecular hydrogen bonds occur between the carboxylate oxygen atoms and the *ortho*-phenolic groups to form six-membered rings. As a consequence, the entire molecule is nearly planar, the dihedral angle formed by the aromatic ring with the coordination plane being 5.20(0.15)° and that with the carboxylate group 2.35(0.25)° only (Table VII). In this way the molecular symmetry is very near to that of D_{2h}. The position of three hydrogen atoms has been determined. In particular the structural parameters of the intramolecular bonds between the carboxylate and phenolic groups are: O(3)–HO(3)···O(2) = 163.9(2.1)°, O(3)–HO(3) = 1.19(5) Å, HO(3)···O(2) = 1.41(5) Å and O(2)···O(3) = 2.578(6) Å.

The comparison of the structural data for the complex with those expected for a free carboxylate group [10] shows that upon coordination both the C–O distances are lengthened by about 0.05 Å and, at the same time, the O–C–O angle is restricted from 122° to 116.6(3)°. A similar trend was observed for dioxouranium(VI) complexes containing bidentate carboxylate or nitrate groups [8, 9]. In the latter case [9] this finding was explained by considering that the HOMO orbital energy variation mainly accounts for the change of the overall energy

TABLE VII. Least-Squares Planes Data.

Plane	
1	$0.9954(1)X - 0.0957(14)Z = 0.0000$ (equatorial plane)
2	$0.9999(1)X - 0.0051(24)Z = 0.0000$ (aromatic ring)
3	$0.9989(1)X - 0.0461(28)Z = 0.0000$ (carboxylate group)

Dihedral angles (°) between planes

1–2,	5.20(0.15)
1–3,	2.35(0.21)
2–3,	2.85(0.17)

Deviations (A × 10^3) from the planes[a]

Plane 1: U* O(1), O(2)* –54(4), O(2′)* 54(4), O(4)* 180(8), C(1) O(1), C(2) O(1), O(3) –224(5), HO(3) –271(20)

Plane 2: C(2)* O(1), C(3)* –3(5), C(4)* 4(6), C(5)* O(1), C(1) O(1), O(3) –5(5), HO(3) –10(21)

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[a] Deviations for atoms defining the planes are marked with asterisks.

of the ligand due to geometrical distortion upon complex formation. Thus, the electrons of the HOMO orbital of the nitrate are stabilized and shifted towards the symmetry-adapted 5f orbitals in the equatorial plane of uranium. Such an explanation should be applicable to the carboxylate group also.

Molecular Packing and Hydrogen Bonding

Although ten water molecules per uranium atom are present in the cell, only two of them are directly bound to the metal, the remaining eight being crystallization waters. All the water molecules are part of a three-dimensional network of hydrogen bonds. Short contacts inherent in such an interaction are listed in Table VIII and whether or not the position of the hydrogen atoms of water was determined.

TABLE VIII. Hydrogen-bond Distances (Å).[a]

$O(4)\cdots O(6)$	2.82	$O(5)\cdots O(6)^{ii}$	2.85
$O(5)\cdots O(6)$	2.85	$O(6)\cdots O(6)^{iii}$	2.83
$O(7)\cdots O(6)$	2.88	$O(7)\cdots O(6)^{iv}$	2.88
$O(3)\cdots O(5)^{i}$	2.85		

[a] Superscripts refer to the following equivalent positions relative to x, y, z: i: $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; ii: $1 - x, y, 1 - z$; iii: $-x, y, 1 - z$; iv: $x, -y, z$.

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