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Interaction of Metal Ions with Humic-like Models. Part 6*. Molecular Structure, Spectral and Thermal Properties of Diaquabis(2,6-dimethoxybenzoato)dioxouranium(VI) Monohydrate

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Abstract

The crystal and molecular structure of $[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$ (DMB = 2,6-dimethoxybenzoate), complex **I**, has been determined by X-ray diffraction and refined to a final R value of 0.0411. The compound belongs to the space group $P2_1/a$ with cell constants a = 12.649(4), b = 14.418(5), c = 13.460(4) Å and Z = 4. As in the analogous complex $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$ (DHB = 2,6-dihydroxybenzoate), compound **II**, the uranyl ion is bound to two bidentate carboxylate groups and two water molecules, but the point-symmetry is lower because the carboxylates, and the water molecules, are in vicinal positions. The lack of hydrogen-bonds between carboxylate groups and *ortho*-methoxy substituents and, possibly, steric factors account for the rotation of the phenyl rings with respect to the equatorial plane of the metal, the dihedral angle between the 'best planes' being about 77°. Detectable changes in the bond distances and angles within the carboxylate groups are produced by the non-planarity of the ligand. Spectroscopic and thermal properties of complexes **I** and **II** are also compared.

Introduction

Structural investigations have shown that in the metal complexes of 2,6-dihydroxybenzoic acid the phenolic groups take part in an extensive network of hydrogen-bonding with the carboxylate groups and water molecules [1, 2]. These contacts play an important role in determining the ion environment, the structure and the packing of the complex units.

In particular, in the dioxouranium(VI) complex, where the carboxylate groups act as bidentate, a high degree of planarity was observed for the entire molecule because of the strong contacts between adjacent carboxylate and phenolic groups [2].

In order to show the structural differences arising in metal complexes from the methyl substitution of phenolic groups in the *ortho* position to carboxylate, we have extended the investigation to the metal derivatives of 2,6-dimethoxybenzoic acid [3, 4].

The present paper reports the structure of $[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$ and compares the structural, spectroscopic and thermal properties of this complex with those of $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$, described previously [2].

Experimental

Materials

2,6-Dimethoxybenzoic acid (Merck) was twice recrystallized from water. Uranyl acetate dihydrate was reagent grade.

Preparation of the Complex

Uranyl acetate dihydrate (1.5 mmol) and 2,6-dimethoxybenzoic acid (3.0 mmol) were dissolved

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*Part 5 is ref. [2].

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TABLE I. Atomic Coordinates.[a]

Atom[b]	x/a	y/b	z/c
U	0.11270(0)	0.24080(0)	0.16960(0)
O(1)	0.03730(60)	0.34370(40)	0.12570(60)
O(1)'	0.18640(60)	0.13690(40)	0.21350(60)
O(2)	0.17620(60)	0.29270(60)	0.35820(50)
O(2)'	0.28470(50)	0.33160(40)	0.27260(50)
O(3)	0.45350(70)	0.21970(50)	0.45850(60)
O(3)'	0.25330(70)	0.49270(50)	0.44990(70)
O(4)	−0.00670(60)	0.20280(60)	0.27650(60)
O(4)'	−0.05390(50)	0.14740(40)	0.07730(60)
O(5)	0.24100(60)	0.28610(50)	0.07280(50)
O(5)'	0.09500(60)	0.20290(50)	−0.01820(50)
O(6)	0.28120(70)	0.10480(50)	−0.08200(60)
O(6)'	0.14840(70)	0.40650(40)	−0.12810(60)
C(1)	0.26740(70)	0.32610(60)	0.35830(70)
C(2)	0.35780(80)	0.35770(70)	0.46060(70)
C(3)	0.45050(80)	0.30260(70)	0.51040(70)
C(4)	0.53210(80)	0.32780(90)	0.60400(90)
C(5)	0.52270(110)	0.41270(100)	0.64760(90)
C(6)	0.42870(100)	0.47220(80)	0.59870(90)
C(7)	0.34630(90)	0.44410(70)	0.50310(80)
C(8)	0.23750(130)	0.58150(90)	0.48870(130)
C(9)	0.54280(100)	0.15470(90)	0.51630(110)
C(10)	0.18110(80)	0.24850(50)	−0.01320(80)
C(11)	0.22020(80)	0.25860(60)	−0.10670(70)
C(12)	0.27700(80)	0.18450(60)	−0.13470(70)
C(13)	0.33010(100)	0.19940(80)	−0.20810(80)
C(14)	0.31760(100)	0.28750(80)	−0.25720(90)
C(15)	0.25940(90)	0.35800(70)	−0.23160(90)
C(16)	0.20990(80)	0.34380(60)	−0.15660(80)
C(17)	0.13450(160)	0.49540(90)	−0.17550(140)
C(18)	0.33940(130)	0.02950(80)	−0.10310(120)
O(7)	0.02260(90)	0.03120(70)	−0.10880(90)
HC(4)	0.60440(350)	0.28350(350)	0.64680(350)
HC(5)	0.59110(350)	0.43820(350)	0.71800(350)
HC(6)	0.41970(350)	0.53820(350)	0.63660(350)
HC(81)	0.15660(350)	0.61150(350)	0.43440(350)
HC(82)	0.30400(350)	0.62770(350)	0.49130(350)
HC(83)	0.23020(350)	0.57490(350)	0.56580(350)
HC(91)	0.53420(350)	0.09040(350)	0.46680(350)
HC(92)	0.53010(350)	0.13030(350)	0.58920(350)
HC(93)	0.62460(350)	0.18080(350)	0.53480(350)
HC(13)	0.38010(350)	0.14610(350)	−0.22720(350)
HC(14)	0.35410(350)	0.29670(350)	−0.31730(350)
HC(15)	0.25550(350)	0.42600(350)	−0.27170(350)
HC(171)	0.07800(350)	0.53960(350)	−0.14770(350)
HC(172)	0.08550(350)	0.48770(350)	−0.26370(350)
HC(173)	0.20910(350)	0.53070(350)	−0.16600(350)
HC(181)	0.34070(350)	−0.03110(350)	−0.05700(350)
HC(182)	0.43200(350)	−0.04980(350)	−0.08340(350)
HC(183)	0.31010(350)	0.01150(350)	−0.18690(350)

[a] The standard deviations of the least significant figure(s) are given in parentheses. Standard deviations for hydrogen atoms have been arbitrarily enhanced by about three-fold with respect to the other atoms. [b] The numbering scheme is that of Fig. 2.

in hot water until a clear yellow solution was obtained. On standing overnight at 40 °C pale yellow crystals precipitated which were filtered off, washed with water and air-dried. Analytical data: Found: C, 31.50; H, 3.49; H_2O, 8.0%. Calcd. for $UO_2(C_{18}H_{18}O_8)\cdot 3H_2O$: C, 31.47; H, 3.52; H_2O, 7.87%.

Analytical and Spectroscopic Measurements

Elemental analyses, thermal and spectral measurements were carried out as described previously [1, 2].

Crystal Data and Structure Determination

$C_{18}H_{24}O_{13}U$, M = 686.4, monoclinic, a = 12.649(4), b = 14.418(5), c = 13.460(4) Å, β = 110.60(3)°, V = 2297.8 Å^3, Z = 4, MoK$_\alpha$ radiation, $\lambda = 0.7107$ Å.

Intensity data were collected on a Philips four-circle diffractometer. A total of 5759 reflections was collected and corrected for Lorentz, polarization and absorption effects. The diffracted intensities were averaged to 5543 structure amplitudes but only 3982 reflections with $[F_0 > 6\sigma(F_0)]$ were considered observed. The structure was solved using the SHELX-76 package of programs [5]. The final R values are: $R = 0.0411$ and $R_w = 0.0433$.

The observed and calculated structure factors are available as Supplementary Material. Final fractional coordinates are given in Table I.

Results and Discussion

Thermal Behaviour

Thermogravimetric measurements (Fig. 1) showed the three water molecules to be lost in a single step over the range 75–100 °C. Compared to those of the analogous complex $UO_2(DHB)_2\cdot 3H_2O$ formed upon partial dehydration of **II**, the water molecules of

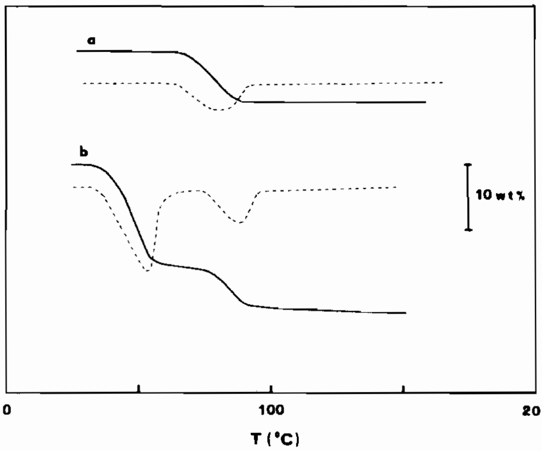

Fig. 1. TG (——) and DTG (– – –) curves of $[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$ (a) and $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$ (b).

TABLE II. IR Absorption Data (cm^{-1}).

Compound	ν_{as}(COO)	ν_s(COO)	$\Delta(\nu_{as} - \nu_s)$	ν_3(U–O)
$[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$	1550s	1440s	110	940s, 950s
$[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$	1597s	1446s	151	920s
$Na(DMB)\cdot 0.25H_2O$	1619s	1417s	202	

TABLE III. Selected Bond Distances (Å) and Angles (°) in $[UO_2(2,6\text{-}DMB)_2(H_2O)_2]\cdot H_2O$.[a]

Uranyl group:			
U–O(1)	1.750(6)	U–O(1)′	1.753(6)
U–O(2)	2.493(7)	U–O(5)	2.499(8)
U–O(2)′	2.499(6)	U–O(5)′	2.518(7)
U–O(4)	2.486(9)	U–O(4)′	2.440(6)
O(2)–U–O(2)′	51.1(2)	O(5)–U–O(5)′	51.5(2)
Carboxylate groups:			
C(1)–O(2)	1.25(1)	C(10)–O(5)	1.26(1)
C(1)–O(2)′	1.25(1)	C(10)–O(5)′	1.25(1)
C(1)–C(2)	1.52(1)	C(10)–C(11)	1.52(2)
O(2)–C(1)–O(2)′	119.0(9)	O(5)–C(10)–O(5)′	120.3(9)
Aromatic rings:			
C(2)–C(3)	1.38(1)	C(11)–C(12)	1.41(1)
C(2)–C(7)	1.40(1)	C(11)–C(16)	1.38(1)
C(3)–C(4)	1.37(1)	C(12)–C(13)	1.39(2)
C(4)–C(5)	1.38(2)	C(13)–C(14)	1.41(2)
C(5)–C(6)	1.42(2)	C(14)–C(15)	1.37(2)
C(6)–C(7)	1.40(1)	C(15)–C(16)	1.38(2)
C(3)–O(3)	1.39(1)	C(12)–O(6)	1.34(1)
O(3)–C(9)	1.46(1)	O(6)–C(18)	1.40(2)
C(7)–O(3)′	1.34(1)	C(16)–O(6)′	1.33(1)
O(3)′–C(8)	1.42(2)	O(6)′–C(17)	1.41(2)

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

$[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$ are lost at a slightly lower temperature.

Infrared Spectra

The relevant IR absorptions for the dioxouranium(VI) complexes of DMB and DHB as well as for the sodium DMB salt are listed in Table II. It is significant that different $\Delta(\nu_{as} - \nu_s)$ values are observed for the carboxylate groups of **I** and **II**, although bidentate coordination has been detected in both cases (see structural results). Such behaviour may be explained by the lack of contacts between the CO_2 groups and the *ortho*-methoxy substituents in complex **I**. Consequently, stretching frequencies more consistent with a bidentate coordination are observed for this complex.

As for U–O, two absorptions attributable to ν_3 are displayed by the spectrum of complex **I**, probably due to a solid-state effect. The higher-frequency shift of this mode, as compared to that for **II**, is in accord with the slightly shorter U–O distance observed in $[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$. A similar trend has been observed on passing from $[UO_2(DHB)_2(H_2O)_2]\cdot 8H_2O$ to the anhydrous complex, as observed previously [2].

Description of the Structure

A perspective view of the complex $[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$ is shown in Fig. 2, bond distances and angles being listed in Table III. The uranyl group shows six-coordination in the equatorial plane with bonds to two bidentate carboxylate groups and two water molecules. The third water molecule does not interact with the metal ion. There are no unusual bond lengths within the coordination polyhedron

TABLE IV. Least-Squares Planes Data.

Plane	
1	$-0.4408(15)X + 0.8442(8)Y - 0.3049(17)Z = 2.0016(59)$ (equatorial plane)
2	$0.7356(32)X + 0.4384(40)Y - 0.5164(44)Z = 0.9973(462)$ (phenyl ring **I**)
3	$-0.6283(37)X - 0.2974(45)Y - 0.7189(33)Z = 2.1941(267)$ (phenyl ring **II**)
4	$-0.3740(47)X + 0.9167(21)Y - 0.1409(49)Z = 3.0358(318)$ (carboxylate group **I**)
5	$-0.4848(42)X + 0.8315(28)Y - 0.2712(51)Z = 1.8733(191)$ (carboxylate group **II**)

Dihedral angles (°) between planes:

1–4,	11.0(3)
1–5,	3.3(3)
1–2,	78.3(2)
1–3,	75.8(3)
2–4,	78.5(3)
3–5,	75.4(3)

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

Plane 1:	U* 4(1), O(2)* −49(8), O(2′)* −31(6), O(4)* 19(8), O(4′)* −42(6), O(5)* 10(7), O(5′)* −30(7), C(1) −151(9), C(2) −450(10), C(5) −1028(14), C(10) 37(8), C(11) 106(9), C(14) 178(12)
Planc 2:	C(2)* −8(10), C(3)* 9(10), C(4)* −8(11), C(5)* 6(14), C(6)* −4(13), C(7)* 6(11), C(1) −27(9), O(3) 31(9), C(9) −126(14), O(3′) −20(9), C(8) 6(16).
Plane 3:	C(11)* −16(10), C(12)* 21(10), C(13)* −19(12), C(14)* 1(12), C(15)* 6(12), C(16)* 4(10), C(10) −231(10), O(6) 8(8), C(18) −3(16), O(6′) 51(8), C(17) 68(19)
Plane 4:	C(1)* 7(9), O(2)* −3(9), O(2′)* −1(6), C(2)* −3(10), U −387(1), C(2) −3(10), C(3) −1170(10), C(4) −1223(13), C(5) −57(14), C(6) 1174(12), C(7) 1193(10)
Plnae 5:	C(10)* 10(9), O(5)* −3(7), O(5′)* −3(7), C(11)* −4(9), U 132(1), C(11) −4(9), C(12) −1209(9), C(13) −1274(12), C(14) −86(12), C(15) 1088(11), C(16) 1137(9)

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

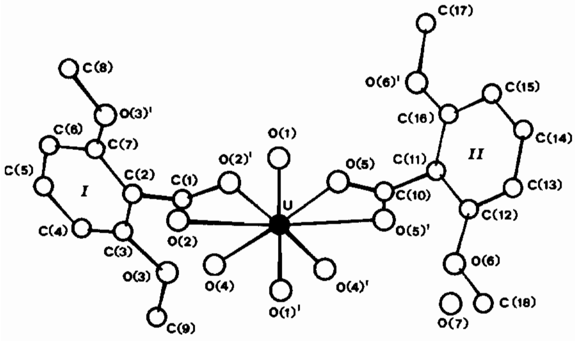

Fig. 2. Perspective view of $[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$ showing the numbering scheme used.

as the U–O distances are in the range commonly reported for related complexes [6].

However, a comparative examination of complexes **I** and **II** reveals remarkable differences as far as the molecular geometry is concerned. In fact, the symmetry of complex **I**, due to the *cis* position of the carboxylates, and consequently of the water molecules, is lower than that of **II**. Remarkable differences in the internal geometry of the ligand molecules are also observed. Indeed, while DHB is nearly planar in complex **II**, a rotation of the phenyl ring with respect to the CO_2 plane is observed for DMB in complex **I**, the dihedral angle being *ca.* 77° (Table IV). This value may be compared to the tilt of 56.2° in the free acid [7] and to the angles of 58.5 and 87.0° observed in the complexes $[Cu(DMB)_2(H_2O)]_2$ and $[Cu(DMB)(CH_3COO)(H_2O)]_2$, respectively [3].

A further comparative examination reveals that, with respect to complex **II**, $[UO_2(DMB)_2(H_2O)_2]\cdot H_2O$ exhibits: i) C–O (carboxylate) bond lengths 0.025(8) Å shorter; ii) U–O(carboxylate) distances 0.016(7) Å longer; iii) C(carboxylate)–C(phenyl) bonds 0.07(10) Å longer; iv) O–C–O angles 3.05(9)° larger. These differences can be interpreted as due to the lack of intramolecular contacts between the carboxylate groups and the *ortho*-methoxy substituents and, possibly, to steric factors, which allow the rotation of the phenyl ring with respect to the CO_2 plane. In this way the p_z orbital of the C (carboxylate) atom interacts to a lesser extent with the π orbitals of the aromatic ring and is more able to combine with the π orbitals within the CO_2 group, in agreement with the bond length variations observed on passing from complex **II** to complex **I**. The net result is that in complex **I** the π flux from the

TABLE V. Molecular Packing and Hydrogen-bond Distances (Å).[a]

O(5)′·····O(7)	2.77(1)	O(2)′·····O(4)	2.67(1)
O(4)′·····O(7)[a]	2.62(1)	O(3) ·····O(4)[c]	2.89(1)
O(4)′·····O(5)[b]	2.75(1)		

[a]Superscripts refer to the following equivalent positions relative to x, y, z: $^a -x, -y, -z$; $^b -\frac{1}{2}+x, \frac{1}{2}-y, z$; $^c \frac{1}{2}+x, \frac{1}{2}-y, z$.

phenyl ring is reduced, thus hindering the formation of stronger U–O (carboxylate) bonds.

Table IV also shows that the dihedral angle between the equatorial plane of the metal and that of the C(2)–carboxylate group, 11.0(3)°, is higher than the corresponding one involving the C(10)–carboxylate group, 3.3(3)°. Such a feature, already observed in [$Cu(DMB)_2(H_2O)]_2$ [3], may be described as a folding of the whole carboxylate about the O···O axis and is most likely accounted for by crystal-packing forces, which are mainly due to hydrogen-bonding contacts involving water molecules (Table V).

Acknowledgement

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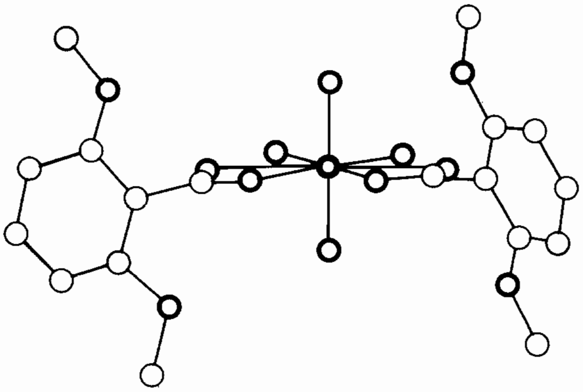

Fig. 3. Perspective view of [$UO_2(DMB)_2(H_2O)_2$]$\cdot H_2O$ showing the folding of the ligand about the O···O axis of the carboxylate group.

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