Preparation and Physicochemical Characterization of Anionic Uranyl β-Ketoenolates

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New classes of anionic uranyl β-ketoenolates of formula $[UO_2L_2X]^-$ {L = 1,3-diphenylpropane-1,3-dionate (dppd), 4,4,4-trifluoro-1-phenylbutane-1,3-dionate (tfpbd), or 1-phenylbutane-1,3-dionate (pbd); X = Cl^-, Br^-, I^-, $[NO_3]^-$, $[O_2CMe]^-$, or $[NCS]^-$} and $[L_2O_2U(\mu\text{-}X)UO_2L_2]^-$ (X = F^-, and also Cl^- only in the case of L = dppd) have been synthesized and characterized by a number of physical measurements. The different ability of the various anionic ligands to enter into the co-ordination sphere of the uranyl ion, their potentially different bonding modes, and the possible correlations between physical parameters and the nature of either the chelate substituents or the anionic ligand are discussed.

ALTHOUGH series of five-co-ordinate neutral uranyl β-ketoenolates $[UO_2L_2L']$ (L = β-ketoenolate anion, L′ = adducted neutral ligand) have been prepared and their physicochemical properties discussed,[1-10] there has been no report of the interaction of anionic ligands with such complexes which, in principle, would lead to the formation of anionic uranyl β-ketoenolate species. We have tested the reactivity of a series of anionic ligands ranging from halide to nitrate, acetate, and thiocyanate ions, towards anhydrous uranyl β-ketoenolates and/or the related aqua- or methanol adducts, in order to examine the ability of the ligands to enter the co-ordination sphere of the metal and the potentially different bonding modes. Spectroscopic measurements on the new complexes obtained allow a discussion of the possible correlations between physical parameters and the nature of either the chelate substituents or of the anionic ligands.

EXPERIMENTAL

Reagents.—Reagent-grade uranyl acetate dihydrate, 1,3-diphenylpropane-1,3-dione (Hdppd), 1-phenylbutane-1,3-dione (Hpbd), 4,4,4-trifluoro-1-phenylbutane-1,3-dione (Htfpbd), and tetraethylammonium salts (Fluka products) were used without further purification. Methanol, acetone, ethyl acetate, and acetonitrile used as solvents were distilled before use. Acetonitrile for conductimetric measurements was carefully purified as reported in the literature.[11]

Preparation of the Complexes.—$[UO_2L_2(OH_2)]$ *and* $[UO_2L_2]$ (L = dppd, pbd, *or* tfpbd). The aqua-adducts and related anhydrous forms were prepared as previously reported.[3]

$[UO_2L_2(HOMe)]$ *and* $[UO_2L_2(dmso)]$ (L = dppd, pbd, *or* tfpbd; dmso = *dimethyl sulphoxide*). The methanol adducts were obtained by recrystallization of the corresponding aqua-species from methanol, while the dimethyl sulphoxide adducts were prepared by reaction of the methanol adducts with an excess of dmso in MeCN. Analytical and some physical data of these new neutral complexes are summarized in Table 1.

$[NEt_4][UO_2(dppd)_2X]$ (X = Cl^-, Br^-, I^-, $[NO_3]^-$, $[O_2CMe]^-$ *or* $[SCN]^-$). To $[UO_2(dppd)_2]$ or $[UO_2(dppd)_2(HOMe)]$ dissolved in the minimum volume of ethyl acetate was added an equimolar amount of the appropriate tetraethylammonium salt dissolved in a little MeCN or MeOH, at room temperature with stirring. The resulting solutions, concentrated when necessary, were left to stand and the microcrystalline products which formed overnight or in a few days were filtered off, washed with a little ethyl acetate, and dried *in vacuo*. The halogeno-species were also obtained as well shaped crystals from acetone–methanol (1 : 1) by slow concentration in air.

$[NEt_4][UO_2(tfpbd)_2X]$ (X = Cl^- *or* Br^-). Equimolar amounts of $[UO_2(tfpbd)_2L']$ (L′ = OH_2 or HOMe) and the appropriate tetraethylammonium salt in MeCN were allowed to react for 2 h at room temperature and the resulting solutions slowly evaporated. The oily products formed were worked up with diethyl ether until yellow powders were obtained which were washed with a little cold ethyl acetate and finally dried *in vacuo*. The salt $[NEt_4][UO_2(pbd)_2Cl]$ was prepared following the same procedure as for the tfpbd analogue.

$[NEt_4][L_2O_2U(\mu\text{-}F)UO_2L_2]$ (L = dppd, pbd, *or* tfpbd). For L = dppd, a methanolic solution of tetraethylammonium fluoride was slowly added to the $[UO_2(dppd)_2L']$ (L′ = OH_2 or HOMe) dissolved in the same solvent in a mol ratio of 1 : 2 at 60 °C. The resulting solution was left to react for 1 h at 60 °C with stirring and then brought to room temperature. The microcrystalline product which formed was filtered off, washed with small portions of MeOH, and dried *in vacuo*. The same procedure was followed for the analogous fluoride-bridged complexes of pbd and tfpbd, but using as solvent mixtures of ethyl acetate and MeCN.

$[NEt_4][(dppd)_2O_2U(\mu\text{-}Cl)UO_2(dppd)_2]$. Equimolar amounts of $[UO_2(dppd)_2]$ and $[NEt_4][UO_2(dppd)_2Cl]$ dissolved in anhydrous benzene were allowed to react in a dry-box for 48 h with stirring. The initial deep red solution

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gradually became yellow and a flocculent yellow precipitate was formed which was filtered off, washed with benzene, and dried *in vacuo*. Any attempt to isolate the analogous chloride-bridged species of pbd and tfpbd failed.

Analytical and some physical data for the anionic complexes are reported in Table 2. Uranium was determined gravimetrically as the tetraphenylarsonium salt of uranyl pyridine-2,6-dicarboxylate.[12]

TABLE 1

Analytical and some physical data for the new neutral complexes

Complex	Analysis (%) * C	H	F	M.p. (θ_c/°C)	Characteristic i.r. absorptions (cm^{-1})
$[UO_2(dppd)_2(HOMe)]$	49.75 (49.75)	3.40 (3.45)		150—277	1 530vbr [ν(C=O) and ν(C=C)], 914 [$\nu_3(UO_2)$]
$[UO_2(pbd)_2(HOMe)$	40.4 (40.4)	3.45 (3.50)		130—255	1 550 [ν(C=O)], 1 517 [ν(C=C)], 916 [$\nu_3(UO_2)$]
$[UO_2(tfpbd)_2(HOMe)]$	34.45 (34.4)	2.20 (2.20)	15.5 (15.55)	150—275	1 610, 1 575 [ν(C=O)], 1 535 [ν(C=C)], 918 [$\nu_3(UO_2)$]
$[UO_2(dppd)_2(dmso)]$	48.5 (48.35)	3.50 (3.50)		225—226	1 527vbr [ν(C=O) and ν(C=C)], 895 [$\nu_3(UO_2)$], 995 [ν(S=O)]
$[UO_2(pbd)_2(dmso)]$	39.25 (39.4)	3.60 (3.60)		187—189	1 560 [ν(C=O)], 1 515 [ν(C=C)], 905 [$\nu_3(UO_2)$], 997 [ν(S=O)]
$[UO_2(tfpbd)_2(dmso)]$	34.0 (33.95)	2.25 (2.30)	14.5 (14.65)	180—182	1 610, 1 575 [ν(C=O)], 1 535 [ν(C=C)], 910 [$\nu_3(UO_2)$], 992 [ν(S=O)]

* Calculated values are given in parentheses.

TABLE 2

Analytical data and physical properties of the anionic complexes [a]

Complex	Analysis (%) [b]					M.p. (θ_c/°C)	Λ
	C	H	N	X	U		S cm^2 mol^{-1}
(1) $[NEt_4][UO_2(dppd)_2Cl]$	51.9 (51.7)	4.75 (4.75)	1.55 (1.60)	4.00 (4.05)	27.15 (27.0)	278—280	133
(2) $[NEt_4][UO_2(dppd)_2Br]$	49.05 (49.25)	4.15 (4.55)	1.45 (1.50)	8.30 (8.65)	25.55 (25.7)	292—294	137
(3) $[NEt_4][UO_2(dppd)_2I]$	46.95 (46.85)	4.45 (4.30)	1.25 (1.45)	12.95 (13.05)	24.3 (24.45)	268—288	155
(4) $[NEt_4][UO_2(dppd)_2(NO_3)]$	49.95 (50.2)	4.40 (4.60)	3.05 (3.10)		25.75 (26.2)	278—280	143
(5) $[NEt_4][UO_2(dppd)_2(O_2CMe)]$	53.1 (53.05)	5.00 (4.95)	1.40 (1.55)		25.95 (26.3)	235—237	135
(6) $[NEt_4][UO_2(dppd)_2(NCS)]$	52.35 (51.75)	4.90 (4.65)	3.10 (3.10)		26.45 (26.3)	261—262	136
(7) $[NEt_4][UO_2(tfpbd)_2Cl]$	38.1 (38.8)	4.00 (3.70)	1.60 (1.60)	4.30 (4.10)	27.3 (27.5)	160—165	137
(8) $[NEt_4][UO_2(tfpbd)_2Br]$	36.7 (36.9)	3.25 (3.50)	1.55 (1.55)	8.40 (8.80)	26.35 (26.15)		148
(10) $[NEt_4][UO_2(pbd)_2Cl]$	43.9 (44.35)	4.85 (5.00)	1.90 (1.85)	4.55 (4.70)	30.85 (31.4)		150
(12) $[NEt_4][(dppd)_2O_2U(\mu\text{-}F)UO_2(dppd)_2]$	51.7 (51.6)	4.10 (4.05)	0.80 (0.90)	1.10 (1.20)	30.2 (30.1)	338—340	
(13) $[NEt_4][(tfpbd)_2O_2U(\mu\text{-}F)UO_2(tfpbd)_2]$	37.65 (37.2)	3.00 (2.85)	0.95 (0.90)	15.9 (15.95)	31.05 (30.75)		
(14) $[NEt_4][(pbd)_2O_2U(\mu\text{-}F)UO_2(pbd)_2]$	42.2 (43.2)	4.15 (4.20)	1.10 (1.05)	1.20 (1.40)	35.7 (35.7)	210—220	
(15) $[NEt_4][(dppd)_2O_2U(\mu\text{-}Cl)UO_2(dppd)_2]$	50.8 (51.1)	3.95 (4.00)	0.80 (0.85)	2.30 (2.20)	30.1 (29.8)	230—240	

[a] The complexes $[NEt_4][UO_2(tfpbd)_2I]$ and $[NEt_4][UO_2(pbd)_2Br]$, (9) and (11) respectively, were obtained only in solution. [b] Calculated values are given in parentheses.

Physical Measurements.—Molar conductivities at 25 °C were measured on 10^{-3}—10^{-4} mol dm^{-3} solutions in MeCN using an LKB 3216B conductivity bridge. Infrared spectra (400—4 000 cm^{-1}) were recorded on a Perkin-Elmer 621 i.r. spectrophotometer in KBr discs, far i.r. spectra (100—400 cm^{-1}) as Nujol mulls between polyethylene plates on a Beckman i.r. 11 instrument. Hydrogen-1 n.m.r. spectra for MeCN solutions of comparable concentration for each series were obtained on a Varian T60 spectrometer at 34 °C using $SiMe_4$ as internal standard.

RESULTS AND DISCUSSION

Analytical, spectroscopic, and conductimetric data indicate for all the complexes, except the fluoro-species, mononuclear anionic species of type $[UO_2L_2X]^-$, in which the uranyl moiety is equatorially surrounded by four oxygen atoms derived from the two diketonate ligands and by the anionic ligand. The *X*-ray structure of $[UO_2(dppd)_2(NO_3)]^-$ shows[13] that the approximately linear uranyl group is perpendicular to the equatorial plane in which four oxygen atoms from two bidentate dppd ligands and the oxygen atom of the unidentate

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nitrate group [U–O(nitrate) 2.43(2) Å] occupy the corners of a quasi-regular pentagon. The stretching vibrations of the co-ordinated nitrate group have been assigned at 1 449 and 1 290 cm^{-1}. In these complexes acetate acts as a unidentate ligand as indicated by the positions of both the asymmetric and symmetric ν(O–C–O) stretching vibrations at 1 635 and 1 370 cm^{-1} respectively, being shifted to higher and lower frequencies, respectively, compared with the free ion.[14] Free acetate ion absorbs at 1 582 and 1 425 cm^{-1}.

Information on the bonding mode of the thiocyanate group in $[NEt_4][UO_2(dppd)_2(NCS)]$ (6) can be obtained by comparing its vibrational spectrum with those of uranyl complexes in which thiocyanate is either *N*-bonded unidentate [14,15] or bridging.[16,17] In the former case ν(C–N) falls at *ca.* 2 080 cm^{-1}, at *ca.* 2 160 cm^{-1} in the latter. The values of ν(C–N) at 2 063 cm^{-1} and ν(C–S) at 775 cm^{-1} in the present case indicate that the thiocyanate group is unidentate and co-ordinated to uranium through the nitrogen atom. Moreover, the conductivity values of all the mononuclear species, including the halogeno-complexes (Λ 120—160 S cm^2 mol^{-1}) are consistent with 1 : 1 species.[18] Far-i.r. spectra of the complexes $[UO_2(dppd)_2X]^-$ (X = halide), even if not well resolved, show characteristic U–X stretching vibrations at *ca.* 220 cm^{-1} (X = Cl^-) and at 145 cm^{-1} (X = Br^-). The U–I stretching frequency, not detectable in the spectrum of $[NEt_4][UO_2(dppd)_2I]$ (3), probably lies at <100 cm^{-1}. All the fluoride-bridged complexes show a U–F stretch at *ca.* 400 cm^{-1} as is normally found,[14] while for the chloride-bridged species $[NEt_4][(dppd)_2O_2U(\mu\text{-}Cl)UO_2(dppd)_2]$ (15) no band can be reasonably assigned to a U–Cl vibration due to the broadness of the spectrum in the 200—300 cm^{-1} region.

Co-ordination of the diketone results in a shift of the carbonyl asymmetric-stretching vibration, the position and possible splitting of which depend on the nature of the carbonyl substituents but are rather insensitive to the nature of the anionic ligand. Three or four, sometimes broad, bands are present in the carbonyl-stretching region (1 500—1 610 cm^{-1}) of nearly all the complexes. While the lowest vibration at *ca.* 1 520 cm^{-1} can be ascribed to ν(C=C) (enol ring), in accordance with assignments for a variety of metal β-ketoenolates,[19-24] the ν(C=O) stretching assignments are not unambiguous because of the presence of C=C phenyl ring(s) stretches. Considering the chloro-complexes (1), (7), and (10), if the band at 1 590—1 600 cm^{-1} is selected as due to C=C phenyl stretching,[25] it is likely that the band at 1 610 cm^{-1} for the tfpbd species (7) and the bands at 1 564 and 1 545 cm^{-1} for the pbd (10) and dppd species (1) respectively are mainly due to C=O stretching, in accordance with the conclusions of Haigh and Thornton [3] for a series of neutral uranyl β-diketonate adducts and with the general finding that strong electronegative groups, like trifluoromethyl, cause an increase in the frequency of the perturbed carbonyl absorption band. Moreover, the presence of a phenyl group acting as an electron sink through resonance with the other carbonyl group can explain the presence of a second perturbed carbonyl absorption at 1 573 cm^{-1} in the spectrum of species (7). The bands at 1 608 and 1 561 cm^{-1} of bis[4,4,4-trifluoro-1-(2-furyl)butane-1,3-dionato]copper(II) and at 1 615 and 1 580 cm^{-1} of bis[4,4,5,5,6,6,6-heptafluoro-1-(2-furyl)hexane-1,3-dionato]copper(II) have been explained in this manner.[26] In conclusion, the C=O stretching decreases in the order tfpbd > pbd > dppd.

The electronic nature of the ketoenolate substituents affects in the same order the uranyl asymmetric stretching, $\nu_3(UO_2)$, so that electron-donor substituents tend to decrease ν_3 due to a build up of negative charge around the uranium atom, while the opposite effect operates in the case of tfpbd species. $\nu_3(UO_2)$ is rather insensitive to the nature of the anionic ligand; in the dppd series no trend is observed on passing from chloro- to iodo-species and, within the limit of experimental error, very similar values of $\nu_3(UO_2)$ are found for the nitrato-, acetato-, and isothiocyanato-complexes. In contrast, a regular decrease in $\nu_3(UO_2)$ in the order $Br^- > [NO_3]^- > Cl^- > [NCS]^-$ has been observed for a series of neutral quinoline *N*-oxide complexes of the type $[UO_2X_2(qno)_2]$ (X = Cl^-, Br^-, $[NO_3]^-$, or $[NCS]^-$) and has been correlated with an electronic interaction of the anionic ligand with the uranyl ion.[27] However, molecular-symmetry or solid-state effects can play an important role in levelling any discriminating behaviour.

The unequivocal assignment of the U–O(β-ketoenolate) vibration modes is difficult due to their interaction with those of the ligand. However, based on a comparison of the spectra of related complexes,[3,7,8] the bands at *ca.* 465, 425, and 415 cm^{-1} for the tfpbd, pbd, and dppd complexes respectively can be tentatively assigned to the ν(U–O) vibration. This trend and the relative intensities of the peaks are similar to those reported for neutral uranyl,[8] copper, and nickel [7] complexes with various β-diketones. All the characteristic i.r. absorption bands discussed above are collected in Table 3.

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If the i.r. spectra do not provide any suitable characteristic vibration of the proton ring which is sufficiently sensitive for the detection of relatively minor perturbations due to the co-ordinated anionic ligand, such effects, although rather small, can be seen from the ^{1}H n.m.r. spectra of the three series of mononuclear halogeno-complexes including the species (9) and (11), only obtained in solution in the presence of an excess of iodide and bromide respectively. This implies that the bonding effects in other parts of the complexes can be transferred to the diketonate chelate ring through the uranium atom. An increasing shielding of the ring CH proton on passing from the iodo- to the chloro-species, which parallels the pK_a of the halides, is observed (Table 3). The chemical shift of the ring CH proton for the mononuclear fluoro-complexes in solution, as reported below, confirms this trend even though it deviates to some extent from the previously almost linear relation, and is reasonable due to the very high electron density of fluoride. When the halide is kept constant, the sharp single resonance of the ring proton is a function of the nature of the carbonyl substituents, increasing in the order pbd < tfpbd < dppd with the influence of the substituents in deshielding being in the order Ph > CF_3 > Me.

TABLE 3

Characteristic i.r. absorptions (cm^{-1}) and ring CH proton chemical shifts (δ) for the anionic complexes

Complex	ν(C=O)	ν(C=C)	$\nu_3(UO_2)$	ν(U–O)	Other absorptions	δ(CH)/p.p.m.
(1)	1 545	1 520	892	425	220 [ν(U–Cl)]	7.35
(2)	1 540	1 525	892	428	145 [ν(U–Br)]	7.38
(3)	1 540	1 523	892	428		7.45
(4)	1 537	1 519	900	423	1 449 [$\nu_{asym}(NO_2)$], 1 290 [$\nu_{sym}(NO_2)$]	7.42
(5)	1 545	1 520	895	425	1 635 [ν_{asym}(O–C–O)], 1 370 [ν_{sym}(O–C–O)]	7.33
(6)	1 540	1 520	893	430	2 063 [ν(C–N)], 775 [ν(C–S)]	7.40
(7)	1 610—1 573	1 535	915	465		7.03
(8)	1 612—1 570	1 532	915	463		7.07
(9)						7.13
(10)	1 564	1 522	908	412		6.61
(11)						6.65
(12)	1 540	1 515	897	423	402 [ν(U–F)]	7.47
(13)	1 610—1 575	1 532	918	465	405 [ν(U–F)]	7.08
(14)	1 565	1 520	903	415	407 [ν(U–F)]	6.68
(15)	1 545	1 515	905	428		7.40

The high electron density of fluoride is also responsible for the fact that only bridged, very stable, binuclear fluoro-complexes of the type $[L_2O_2U(\mu\text{-}F)UO_2L_2]^-$ are obtained in the solid state. It is known that series of very stable binuclear fluoro-complexes can be formed even under conditions where the formation of a stable mononuclear complex would have been expected.[28] Furthermore, in the displacement series for the uranyl ligands $[CO_3]^{2-} \geqslant [O_2]^{2-} \geqslant [OH]^- > F^- > [C_2O_4]^{2-}$, *etc.*, fluoride occupies one of the first places. In other words, the strength of the chemical affinity of fluoride for uranyl is large and the UO_2–F bond strength is comparable with that of the hydroxide O–H bond. Hydrogen-1 n.m.r. measurements on the present series of fluoro-complexes indicate that the bridge between the two uranium atoms can be broken in solution by an excess of a strong neutral ligand such as dimethyl sulphoxide (dmso), according to the reaction (1). Addition of dmso to a solution of each bridged complex in MeCN results in the splitting of the single sharp resonance of the ring CH proton into two equivalent peaks (by integration), of which that at lower field is coincident with the resonance of pure $[UO_2L_2(dmso)]$ and that at higher field is reasonably assigned to $[UO_2L_2F]^-$ (Table 4).

$$[L_2O_2U(\mu\text{-}F)UO_2L_2]^- + \text{dmso} \longrightarrow [UO_2L_2F]^- + [UO_2L_2(\text{dmso})] \quad (1)$$

TABLE 4

Ring CH proton chemical shift (δ/p.p.m.) of the species involved in the reaction $[L_2O_2U(\mu\text{-}F)UO_2L_2]^-$ (A) + dmso $\longrightarrow$ $[UO_2L_2F]^-$ (B) + $[UO_2L_2(dmso)]$ (C) in MeCN solutions {Values for $[UO_2L_2(dmso)]$ prepared independently are in parentheses.}

	Complex		
L	(A)	(B)	(C)
dppd	7.47	7.23	7.40 (7.40)
tfpbd	7.08	6.96	7.13 (7.13)
pdb	6.68	6.55	6.67 (6.67)

As reported in the Experimental section, a chloride-bridged complex, structurally analogous to the fluoro-complex, was obtained only in the case of L = dppd. This rather unstable species readily reacts with weak neutral ligands giving the corresponding neutral adduct. Such behaviour, together with the fact that the stability of the halogeno-complexes diminishes down Group 7, so that only fluoro- and chloro-species have been obtained for all the series, leads to the conclusion that the ability of halide to act as a bridge decreases in the order of diminishing stability of the halogeno-complexes, reflecting the hard acid nature of the uranyl ion.

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