Reactivity of Uranyl Ion with Quinquedentate Chelating Hydrazine Derivatives. Part 1. 2,6-Diacetylpyridine bis(2′-pyridylhydrazone)

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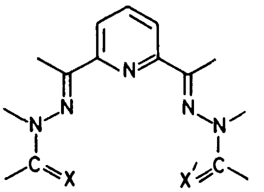
Uranyl nitrate reacts with 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2dapp) to give $[UO_2(H_2dapp)(NO_3)]_2$-$[UO_2(NO_3)_4]$ (1) or a mixture (2) of ionic mononuclear species, in each of which H_2dapp acts as a quinquedentate chelating ligand, depending on the experimental conditions. The complexes have been characterized by a number of physicochemical measurements including the *X*-ray analysis of (1). Crystals of (1) are triclinic with a = 14.071(9), b = 10.801(7), c = 10.122(6) Å, α = 63.86(7), β = 75.65(9), γ = 78.86(9)°, space group $P\bar{1}$, and Z = 1. The structure has been solved by conventional techniques, and refined to a final R of 0.07. The unit cell contains two very highly distorted eight-co-ordinated cations $[UO_2(H_2dapp)(NO_3)]^+$, related by a centre of symmetry and with the N_5O donor set in a symmetrically twisted ' equatorial plane ' [U–N (mean) 2.62 Å, N–U–N (mean) 59.5°, and U–O 2.48 Å for the unidentate nitrate group], and an uranyl tetranitrate counter anion $[UO_2(NO_3)_4]^{2-}$ [two bidentate nitrates (U–O 2.53 Å) and two unidentate (U–O 2.45 Å)], at the centre of symmetry, in a hexagonal bipyramidal arrangement. The nature of the solvent(s), the high stabilizing effect of the 5,5,5,5 chelation mode, and reactivity tests, which allow the isolation of $[UO_2(H_2dapp)(NO_3)][BPh_4]$ (3) and $[UO_2(H_2dapp)][ClO_4]_2$ (4), are discussed. Owing to the deprotonation of the diazapropenic sequences =C=N–NH–, the neutral complex $[UO_2(dapp)]$ (6), containing U–N covalent bonds, can be obtained by the action of non-hydroxylated bases on (1)—(4). Like uranyl amides, compound (6) reacts with alcohols to give alkoxy-derivatives. Polymeric $[\{(UO_2)_2(H_2dapp)(OCH_3)_4 \cdot x CH_3OH\}_n]$ (7) has been isolated.

ALTHOUGH considerable attention has been paid in the last few years to polychelation around the uranyl ion, only a few examples of complexes with quinquedentate chelating ligands have been reported.[1,2] *X*-Ray determinations on [*NN*′-bis(salicylidene)-1,5-diamino-3-oxapentane]dioxouranium(VI) [1] and [*NN*′-bis(salicylidene)-1,5-diamino-3-azapentane]dioxouranium(VI) [2] have shown that the ligands co-ordinate through the oxygen and nitrogen atoms, giving rise to equatorial puckered pentagons, with formations of four 6,5,5,6-membered rings around the uranyl moiety. No examples of polychelation with formation of four five-membered rings are known.

We have approached this problem by considering a series of potentially quinquedentate chelating hydrazine derivatives containing the sequences of donor atoms



X=X′=N, O, or S
X≠X′=N, O, or S

shown above, in order to examine the effects of the ring contraction and the nature of the different donor atoms on the co-ordination. We first tested the reactivity of the 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2-dapp), which has been shown [3] to behave as a penta-azachelating, almost planar, ligand towards 3*d* transition-metal ions, giving cationic and neutral complexes, owing to the possibility of deprotonation of the diazapropenic groups =C=N–NH–.[4-7] In this paper we report the preparation, the physicochemical characterization, and the reactivity of the cationic and neutral complexes obtained, and the unusual structure, determined by *X*-ray diffraction, of $[UO_2(H_2dapp)(NO_3)]_2[UO_2(NO_3)_4]$. Some structural results have already been published.[8]

EXPERIMENTAL

Reagents.—Reagent-grade uranyl nitrate hexahydrate, uranyl dichloride trihydrate, 2,6-diacetylpyridine, silver perchlorate dihydrate, sodium tetraphenylborate, triethylamine, sodium hydride, methyl-lithium (Fluka pure products), and 2-hydrazinopyridine (EGA product) were used without further purification. Ethyl acetate, acetonitrile, acetone, ethanol, methanol, isopropyl alcohol, and pyridine were dried or purified before use as reported.[9] 1,8-Bis(dimethylamino)naphthalene (proton sponge, Aldrich product) was recrystallized from benzene and maintained under an inert atmosphere in a dry-box.

Preparation of the Ligand 2,6-*Diacetylpyridine Bis*(2′-*pyridylhydrazone*) (H_2dapp)—The ligand was prepared as reported in the literature [5] and recrystallized from acetone, m.p. 195—196 °C; ^{1}H n.m.r. ($CDCl_3$), δ 2.43 (s, 6 H, methyl protons), 6.16—7.83 (three complex multiplets, 11 H, pyridine protons), and 7.93 (s, 2 H, hydrazone protons).

Preparation of the Complexes.—$[UO_2(H_2dapp)(NO_3)]_2$-$[UO_2(NO_3)_4]$ (1). A solution of H_2dapp (1 mmol) in ethyl acetate (30 cm^3) was slowly added to a solution of uranyl nitrate hexahydrate (1 mmol) in the same solvent (40 cm^3) at room temperature, with stirring. The orange-red product immediately formed was stirred for 1 h, filtered off, washed with several portions of ethyl acetate, and dried under vacuum. The same product was obtained using different mol ratios of reagents $\{H_2dapp : [UO_2(NO_3)_2] \cdot 6H_2O =$ 2 : 3 and 1 : 5$\}$ both at room temperature and at reflux, m.p. >300 °C (decomp.) (Found: C, 24.3; H, 2.05; N, 14.75; U, 37.95. $C_{38}H_{38}N_{20}O_{24}U_3$ requires C, 24.35; H, 2.05; N, 14.95; U, 38.1%); i.r. spectrum (KBr pellet), 3 283m, 3 183w, 3 089w, 3 030w, 1 641(sh), m, 1 617s, 1 598ms, 1 579ms, 1 550ms, 1 522ms, 1 484s, 1 464s, 1 442s, 1 414ms, 1 385vs, 1 347(sh), m, 1 285vs, 1 251ms, 1 207m, 1 185ms, 1 154ms, 1 120w, 1 108w, 1 094m, 1 032ms, 1 004ms, 955s, 940vs, 910(sh), m, 878w, 866w, 851w, 836w, 812ms, 810ms, 786ms, 777s, 754m, 745m, 738m, 724m, 633m, 553m, 525m, and 485m cm^{-1}. Red crystals were obtained from ethyl acetate–acetonitrile (8 : 2 v/v) in the presence of uranyl nitrate.

$[UO_2(H_2dapp)(NO_3)][NO_3]$ *and* $[UO_2(H_2dapp)][NO_3]_2$ *mixture* (2). Several preparations of the mixture (2) were performed using different solvents [ethyl acetate–acetonitrile (3 : 1), ethyl acetate–methanol (3 : 1), acetonitrile, or absolute ethanol]. In each case equimolar amounts of H_2dapp and uranyl nitrate hexahydrate were allowed to react at room temperature with stirring, and the orange product formed was then filtered off, washed with the reaction solvent(s), and dried under vacuum. The same product was obtained from ethanol or acetonitrile at reflux. Attempts to recrystallize the crude product from a number of solvents failed to separate the mixture of isomers, m.p. >300 °C (decomp.) (Found: C, 31.05; H, 2.55; N, 17.15; U, 31.95. $C_{19}H_{19}N_9O_8U$ requires C, 30.85; H, 2.55, N, 17.05; U, 32.2%); i.r. spectrum (KBr pellet), 3 423br, 3 365br, 3 263br, m, 3 148br, m, 1 644(sh), m, 1 615vs, 1 594s, 1 574ms, 1 539(sh), ms, 1526s, 1 491ms, 1 460vs, 1 423s, 1 381vs, 1 295vs, 1 280(sh), ms, 1 265ms, 1 251ms, 1 194s, 1 171m, 1 155s, 1 110w, 1 105w, 1 093ms, 1 025ms, 1 008ms, 925s, 915s, 866w, 838w, 814m, 807m, 780ms, 762m, 754m, 736m, 719m, 635m, 508w, and 479w cm^{-1}.

$[UO_2(H_2dapp)(NO_3)][BPh_4]$ (3). To a methanolic solution of $Na[BPh_4]$ was added the solid mixture (2) in a mol ratio of 2 : 1 at room temperature, with stirring. After a few minutes, during which partial solubilization of the initial suspension was noted, a yellowish product precipitated, which was stirred for 2 h and then filtered off, washed with methanol, and dried under vacuum, m.p. >300 °C (decomp.) (Found: C, 51.35; H, 4.15; N, 11.2; U, 23.3. $C_{43}H_{39}BN_8O_5U$ requires C, 51.8; H, 3.90; N, 11.25; U, 23.9%]. Infrared spectrum (KBr pellet); 3 310br, 3 060w, 3 000w, 2 980w, 1 645(sh), m, 1 620vs, 1 600s, 1 582s, 1 552ms, 1 530s, 1 492vs, 1 475vs, 1 440br, s, 1 425s, 1 381vs, 1 350m, 1 330m, 1 295(sh), s, 1 275vs, 1 250s, 1 185ms, 1 150s, 1 120mw, 1 115mw, 1 090ms, 1 060w, 1 022m, 1 005m, 923vs, 870w, 840w, 802m, 782m, 771 ms, 750ms, 735s, 708s, 632m, 620m, 610ms, 555w, 490w, and 470w cm^{-1}. The same compound was obtained from a suspension of (1) in acetonitrile with $Na[BPh_4]$ in a mol ratio of 1 : 4.

$[UO_2(H_2dapp)][ClO_4]_2$ (4). To an ethanolic solution of uranyl perchlorate, obtained after filtration from the AgCl formed in the reaction between stoicheiometric amounts of uranyl chloride and silver perchlorate, was added an equimolar amount of H_2dapp, dissolved in dichloromethane, at room temperature and with stirring. The brown product, formed in few minutes, was allowed to react for 2 h, then filtered off, washed with several small portions of ethanol, and dried under vacuum. Brilliant brown crystals were obtained by recrystallization from acetonitrile, m.p. >300 °C (decomp.) (Found: C, 28.15; H, 2.50; Cl, 8.45; N, 11.9; U, 28.9. $C_{19}H_{19}Cl_2N_7O_{10}U$ requires C, 28.0; H, 2.35; Cl, 8.70; N, 12.05; U, 29.3%). Infrared spectrum (KBr pellet); 3 165w, br, 3 080w, br, 3 015w, br, 1 614s, 1 599s, 1 577m, 1 549m, 1 526m, 1 491m, 1 454m, br, 1 423m, 1 377w, 1 351w, 1 332w, 1 283m, 1 267m, 1 253m, 1 157s, br, 1 138s, br, 1 100vs, 1 004m, 938(sh), m, 919s, 866w, 833w, br, 808m, 776ms, 756m, 712m, 675w, br, 635m, 624ms, 565w, br, 518w, 483w, 414w, and 383w cm^{-1}.

$[H_4dapp][NO_3]_2$ (5). To a suspension of H_2dapp in methanol was added an excess of dilute HNO_3 at room temperature. After 2 h of vigorous stirring the white-yellow product formed was filtered off, washed with aqueous methanol until neutral, then with methanol and diethyl ether, and finally dried under vacuum. It was recrystallized from hot methanol, m.p. >300 °C (Found: C, 48.5; H, 4.35; N, 26.5. $C_{19}H_{21}N_9O_6$ requires C, 48.4; H, 4.45; N, 26.75%). Infrared spectrum (KBr pellet): 3 260br, 1 598vs, 1 575s, 1 565s, 1 514s, 1 448(sh), s, 1 433vs, 1 405(sh), m, 1 361ms, 1 330ms, 1 302(sh), m, 1 286vs, 1 273vs, 1 163vs, 1 137vs, 1 098m, 1 083m, 989ms, 880m, 860m, 848s, 808s, 766vs, 729s, 651m, 628m, and 536w cm^{-1}.

$[UO_2(dapp)]$ (6). Compounds (1), (2), (3), or (4), suspended in dry acetonitrile, were added to a solution of ' proton sponge ' in the same solvent at room temperature with magnetic stirring. The black product rapidly formed was stirred for 30 min, filtered off, washed with acetonitrile, and dried under vacuum, m.p. >300 °C (decomp.) (Found: C, 37.55; H, 2.95; N, 15.8; U, 38.7. $C_{19}H_{17}N_7O_2U$ requires C, 37.2; H, 2.75; N, 16.0; U, 38.8%). Hydrogen-1 n.m.r. spectrum ($CDCl_3$): δ 3.52 (s, 6 H, methyl protons) and 6.83—9 (multiplets, 11 H, pyridine protons). Infrared spectrum (KBr pellet): 1 609s, 1 583s, 1 564m, 1 527ms, 1 504s, 1 472vs, 1 451(sh), ms, 1 431s, 1 391vs, 1 374vs, 1 358s, 1 321vs, 1 295(sh), ms, 1 275s, 1 255s, 1 247s, 1 194(sh), m, 1 154vs, 1 140vs, 1 114(sh), ms, 1 111ms, 1 063vs, 993vs, 975s, 923(sh), vs, 915(sh), vs, 911vs, 899s, 880(sh), ms, 848m, 832m, 796ms, 761s, 724s, 690w, 637w, 628ms, 536w, 522w, 409w, 386w, and 362w cm^{-1}. Black brilliant microcrystals were obtained by slow recrystallization from dry acetonitrile.

$[\{(UO_2)_2(H_2dapp)(OCH_3)_4\cdot x CH_3OH\}_n]$ (7). A suspension of (6) in dry methanol was stirred for 12 h at room temperature in a dry-box filled with nitrogen. The colour of the solid gradually changed from black to yellow. The resulting product was then filtered off, washed with dry methanol, and dried under vacuum (Found: C, 27.9; H, 3.40; N, 9.65; U, 45.9. $C_{24}H_{35}N_7O_9U_2$ requires C, 27.65; H, 3.65; N, 9.40; U, 45.7%). Infrared spectrum (KBr pellet): 3 284ms, 2 811m, 1 611s, 1 579ms, 1 564m, 1 528m, 1 456ms, 1 440vs, 1 375m, 1 364m, 1 338w, 1 295w, 1 279w, 1 263m, 1 168m, 1 152m, 1 143m, 1 105w, 1 050w, 1 021s, 1 007vs, 911vs, 885m, 847w, 807m, 782w, 766ms, 735m, 643w, 637w, 548w, 490w, 422w, 422m, and 415br, m cm^{-1}.

Characteristic i.r. absorptions in the spectrum of some of the compounds taken in Nujol and hexachlorobutadiene mulls are reported and discussed in the text. Uranium was determined gravimetrically as the tetraphenylarsonium salt of uranyl pyridine-2,6-dicarboxylate.[10]

Physical Measurements.—Infrared spectra (400—4 000 cm^{-1}) were recorded on a Perkin-Elmer 621 spectrophotometer in KBr disks and as Nujol or hexachlorobutadiene mulls. Hydrogen-1 n.m.r. spectra for deuteriochloroform solutions were obtained on a Varian T60 spectrometer at 34 °C using $SiMe_4$ as internal standard.

Crystal Data.—$C_{38}H_{38}N_{20}O_{24}U_3$, (1), $M = 1\,872.9$, Triclinic, $a = 14.071(9)$, $b = 10.801(7)$, $c = 10.122(6)$ Å, $\alpha = 63.86(7)$, $\beta = 75.65(9)$, $\gamma = 78.86(9)^\circ$, $U = 1\,331.7$ Å^3, $Z = 1$, $D_c = 2.33$ g cm^{-3}, $F(000) = 874$, space group $P\bar{1}$ (C_i^1, no. 2), Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) $= 87.6$ cm^{-1}.

A red needle-shaped crystal (*ca.* 0.6 × 0.3 × 0.2 mm) with a somewhat irregular cross section was coated with cyanoacrylate adhesive, sealed in a Lindemann glass capillary tube, and used to obtain the cell data and subsequent intensity measurements. Intensity data, up to $\theta = 25^\circ$, were collected on a Philips PW 1100 diffractometer by use of graphite-monochromatized Mo-K_α radiation, with the $0\bar{1}1$ axis nearly coincident with the diffractometer Φ axis. Accurate cell parameters were obtained by least-squares refinement using 25 high-angle reflections. The ω—2θ scan technique was used with a symmetric scan of 1.2° for 30 s and the associated two background counts for 10 s. Three standard reflections monitored every hour showed no significant variations due to crystal deterioration during data collection. All reflections with an intensity less than three times the estimated standard deviation of the total counts were considered as non-observed, reducing the total number of reflections from 4 502 to 3 137. The intensities were corrected for Lorentz and polarization effects; although desirable, no absorption correction was applied because of the difficulty of approximating the shape of the crystal.

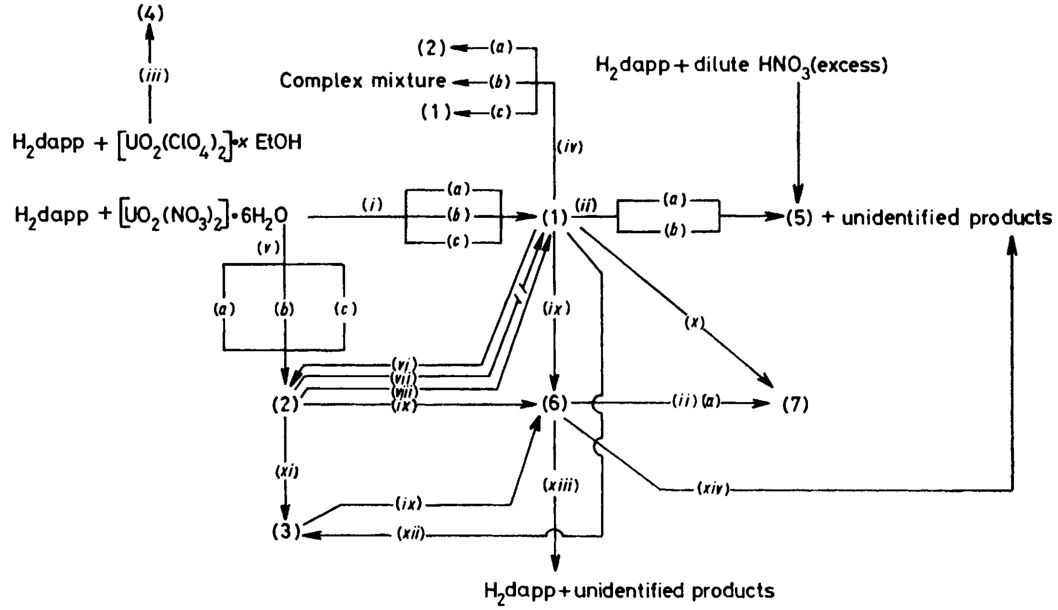
Structure Determination and Refinement.—The Patterson function, calculated from this data set, gave the positions of the uranium atoms. From these, the first electron-density distribution, calculated with phases obtained from structure-factor calculations on U atoms ($R = 0.20$) clearly revealed all the remaining non-hydrogen-atom positions ($R = 0.16$). The structure was refined by full-matrix least-squares methods, with anisotropic thermal parameters only for the heavy atoms. Unit weights were used throughout, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, and scattering factors were those for neutral atoms,[11] with corrections for anomalous dispersion included for U.[12] After seven cycles, the refinement converged when R was 0.070 and no positional parameter shift was $>0.01\sigma$. However, the geometry for the unidentate nitrate group of the $[UO_2(NO_3)_4]^{2-}$ anion was unsatisfactory. This group comprises the atoms with the largest thermal vibrations. A final difference Fourier, with all atoms of this nitrate omitted, showed quite broad peaks for the O(6) and O(7) atoms (*ca.* 2.5 e Å^{-3}) and at least three more significant peaks, possibly corresponding to alternative sites. By varying the occupancy factors, some models for the disorder were tried, but the data were not sufficient for a satisfactory analysis. Since the main chemical interest lies elsewhere, and is not affected by this disorder, we have not pursued the matter further, and in Table 1 the atomic parameters for O(6) and O(7) are those derived from the refinement. The structure refinement was limited by the number of data (3 137 for 338 variables) and by the neglect of absorption and this is the main cause for the large deviations observed for some chemically equivalent distances and angles.

All calculations were performed on a CDC 7600 computer with the '*X*-Ray 72 system '.[13] Structure-factor tables and thermal parameters are given in Supplementary Publication No. SUP 22662 (25 pp.).*

RESULTS AND DISCUSSION

The Scheme summarizes the transformations which the various compounds undergo under suitable conditions.

Treatment of H_2dapp with uranyl nitrate in ethyl acetate in different mol ratios and at different temperatures affords the same red product (1), very slightly soluble in all the common organic solvents, in which it does not change. It analyzes for a compound with a mol ratio U : H_2dapp of 3 : 2. Infrared spectra of KBr pellets, although rather complex, show significant bands at 3 283 cm^{-1} [ν(N–H)], at 1 484, 1 464, and 1 285 cm^{-1} (stretching vibrations of co-ordinated uni- and bidentate nitrate groups),[14-18] and at 955 and 940 cm^{-1}, which can be assigned to the asymmetric stretchings of uranyl groups in different environments. Characteristic bands of co-ordinated pyridine residues, with minor



SCHEME All steps at room temperature unless stated otherwise. (*i*) Ethyl acetate, (*a*) 1 : 1, (*b*) 2 : 3, (*c*) 1 : 1, reflux; (*ii*) (*a*) dry MeOH, (*b*) excess of dilute HNO_3; (*iii*) EtOH, 1 : 1; (*iv*) (*a*) absolute EtOH, (*b*) 95% EtOH, (*c*) dry Pr^{i}OH; (*v*) (*a*) MeCN, 1 : 1, (*b*) $MeCO_2Et$–MeCN, 1 : 1, (*c*) EtOH, 1 : 1, r.t. or reflux; (*vi*) MeCN, reflux; (*vii*) $MeCO_2Et$, reflux; (*viii*) $[UO_2(NO_3)_2]\cdot 6H_2O$, 2 : 1, $MeCO_2Et$; (*ix*) MeCN, non-hydroxylated bases; (*x*) H_2dapp, 1 : 1, non-hydroxylated bases, dry MeOH; (*xi*) Na[BPh$_4$], 1 : 2, MeOH; (*xii*) Na[BPh$_4$], 1 : 4, MeCN; (*xiii*) H_2O; (*xiv*) dilute HNO_3

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

shifts or splittings with respect to the free ligand, are present at 1 617, 1 579, 1 550, and 1 442 cm^{-1}, in accordance with assignments for related complexes.[19,20] The ν(C=N) stretching frequency, tentatively assigned at 1 565 cm^{-1} in the free ligand,[19] is lowered to 1 522 cm^{-1} by co-ordination. The presence of a strong absorption at 1 385 cm^{-1}, accompanied by a weak one at 812 cm^{-1}, bands typical for ionic nitrates,[14,15,21-23] has been reasonably demonstrated to arise from solid–solid interactions between the complex and KBr during the grinding. For i.r. spectra of (1) in KBr pellets at different concentrations, it was noted that, although in all cases the presence of absorptions due to co-ordinated nitrate groups was accompanied by strong free-nitrate bands, the relative intensity of these absorptions varied with each spectrum while the spectrum of (1) in hexachlorobutadiene showed only bands characteristic of co-ordinated nitrate groups, without absorptions in the 1 350—1 400 cm^{-1} range.

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
U	0.0	0.0	0.0
U′	0.345 1(1)	0.231 1(1)	−0.269 8(1)
O(1)	0.102 6(24)	0.053 2(34)	0.002 0(36)
O(2)	0.085 5(18)	−0.080 9(26)	−0.204 2(28)
O(3)	0.028 1(16)	0.128 5(22)	−0.280 8(24)
O(4)	0.102 1(22)	0.043 7(31)	−0.442 3(34)
O(5)	0.102 9(25)	−0.220 1(37)	0.087 5(38)
O(6)	0.051 1(27)	−0.390 4(38)	0.047 9(40)
O(7)	0.189 4(29)	−0.351 1(39)	0.035 4(41)
O(8)	0.414 9(12)	0.335 4(17)	−0.245 4(18)
O(9)	0.272 4(12)	0.129 7(16)	−0.292 2(18)
O(10)	0.358 2(13)	0.407 6(19)	−0.532 3(20)
O(11)	0.365 2(15)	0.251 8(21)	−0.615 7(23)
O(12)	0.381 4(17)	0.462 4(24)	−0.768 1(26)
N(1)	0.066 8(20)	0.026 4(29)	−0.309 6(31)
N(2)	0.099 9(26)	−0.328 5(37)	0.062 7(38)
N(3)	0.367 4(16)	0.373 8(23)	−0.641 7(25)
N(4)	0.520 1(15)	0.211 7(21)	−0.439 3(23)
N(5)	0.526 3(14)	−0.023 8(20)	−0.315 0(22)
N(6)	0.458 0(14)	−0.005 4(19)	−0.201 0(21)
N(7)	0.327 2(14)	0.048 9(20)	0.008 3(21)
N(8)	0.228 8(14)	0.295 8(20)	−0.063 3(21)
N(9)	0.194 4(15)	0.414 3(21)	−0.331 3(23)
N(10)	0.190 8(15)	0.429 1(21)	−0.110 0(23)
C(1)	0.561 9(18)	0.328 8(25)	−0.553 9(28)
C(2)	0.639 9(20)	0.321 2(28)	−0.660 1(31)
C(3)	0.682 4(20)	0.192 1(29)	−0.655 2(31)
C(4)	0.645 2(18)	0.073 7(25)	−0.538 6(27)
C(5)	0.563 7(17)	0.091 5(24)	−0.434 7(25)
C(6)	0.433 7(24)	−0.112 5(33)	−0.081 7(36)
C(7)	0.475 5(21)	−0.260 6(30)	−0.059 1(32)
C(8)	0.362 2(17)	−0.084 1(24)	0.038 8(26)
C(9)	0.337 5(18)	−0.195 2(26)	0.180 7(28)
C(10)	0.273 1(20)	−0.160 1(28)	0.288 8(31)
C(11)	0.239 6(19)	−0.024 4(27)	0.261 8(29)
C(12)	0.267 1(18)	0.076 4(25)	0.119 9(27)
C(13)	0.226 6(19)	0.222 1(26)	0.077 0(28)
C(14)	0.177 4(24)	0.278 2(34)	0.197 7(36)
C(15)	0.157 2(21)	0.458 4(30)	−0.458 4(32)
C(16)	0.098 3(24)	0.578 7(34)	−0.509 7(36)
C(17)	0.069 7(22)	0.658 3(32)	−0.423 2(34)
C(18)	0.101 4(22)	0.611 5(31)	−0.291 7(33)
C(19)	0.160 6(19)	0.486 0(27)	−0.248 7(29)

Since conductivity measurements and ^{1}H n.m.r. spectra were prevented by insolubility, the correct assignment of the bonding mode of the ligand and the geometry around the uranyl units was determined by carrying out an *X*-ray diffractometric analysis of (1). Final positional parameters are listed in Table 1, bond lengths and angles in Table 2, and details of planes in Table 3. The analysis shows a quite unusual molecular structure in which two highly distorted eight-co-ordinated complex cations are electronically balanced by the unexpected uranyl tetranitrate counter anion. It is known that uranyl tetranitrate salts are obtained from

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses, taking into account the accuracy of cell dimensions

(*a*) Distances

(*i*) In $[UO_2(H_2dapp)(NO_3)]^+$

U′–O(8)	1.76(2)	N(5)–N(6)	1.37(3)
U′–O(9)	1.75(2)	N(6)–C(6)	1.28(3)
U′–O(10)	2.48(2)	C(6)–C(7)	1.53(5)
U′–N(4)	2.66(2)	C(6)–C(8)	1.48(4)
U′–N(6)	2.64(2)	C(8)–N(7)	1.35(3)
U′–N(7)	2.61(2)	N(7)–C(12)	1.34(3)
U′–N(8)	2.59(2)	C(12)–C(13)	1.47(4)
U′–N(9)	2.60(2)	C(13)–C(14)	1.55(5)
O(10)–N(3)	1.28(4)	C(13)–N(8)	1.28(3)
N(3)–O(11)	1.23(3)	N(8)–N(10)	1.35(3)
N(3)–O(12)	1.21(3)	N(10)–C(19)	1.40(4)
N(4)–C(5)	1.31(3)	C(19)–N(9)	1.33(4)
N(4)–C(1)	1.40(3)	N(9)–C(15)	1.36(4)
C(5)–N(5)	1.38(3)	C_{py}–C_{py}	mean 1.39(3)

(*ii*) In $[UO_2(NO_3)_4]^{2-}$

U–O(1)	1.66(4)	O(3)–N(1)	1.25(4)
U–O(2)	2.54(3)	N(1)–O(4)	1.25(4)
U–O(3)	2.52(2)	O(5)–N(2)	1.31(6)
U–O(5)	2.45(3)	N(2)–O(6)	1.12(6)
O(2)–N(1)	1.22(3)	N(2)–O(7)	1.22(5)

(*b*) Angles

(*i*) In $[UO_2(H_2dapp)(NO_3)]^+$

O(8)–U′–O(9)	178.3(0.8)	N(4)–C(5)–N(5)	116.1(2.0)
N(4)–U′–N(6)	59.2(0.5)	C(5)–N(5)–N(6)	118.5(2.1)
N(6)–U′–N(7)	60.4(0.6)	N(5)–N(6)–C(6)	118.2(2.3)
N(7)–U′–N(8)	60.8(0.6)	N(6)–C(6)–C(7)	123.9(2.8)
N(8)–U′–N(9)	59.4(0.7)	N(6)–C(6)–C(8)	115.1(2.8)
N(9)–U′–O(10)	63.7(0.6)	C(7)–C(6)–C(8)	121.0(2.2)
O(10)–U′–N(4)	66.6(0.6)	C(6)–C(8)–N(7)	117.1(1.9)
U′–O(10)–N(3)	121.6(1.5)	C(6)–C(8)–C(9)	119.4(2.3)
U′–N(4)–C(1)	121.6(1.5)	N(7)–C(8)–C(9)	123.4(2.3)
U′–N(4)–C(5)	121.2(1.4)	C(8)–N(7)–C(12)	117.4(1.8)
U′–N(6)–N(5)	117.1(1.1)	N(7)–C(12)–C(11)	123.3(2.3)
U′–N(6)–C(6)	121.7(1.8)	N(7)–C(12)–C(13)	114.8(1.9)
U′–N(7)–C(8)	119.5(1.6)	C(11)–C(12)–C(13)	121.8(2.4)
U′–N(7)–C(12)	121.7(1.3)	C(12)–C(13)–N(8)	116.3(2.7)
U′–N(8)–C(13)	123.4(1.6)	C(12)–C(13)–C(14)	120.9(2.1)
U′–N(8)–N(10)	114.8(1.3)	C(14)–C(13)–N(8)	122.7(2.3)
U′–N(9)–C(15)	123.8(1.9)	C(13)–N(8)–N(10)	119.4(2.4)
U′–N(9)–C(19)	119.0(1.8)	N(8)–N(10)–C(19)	115.5(2.6)
O(10)–N(3)–O(11)	119.3(2.0)	N(10)–C(19)–C(18)	119.7(3.0)
O(10)–N(3)–O(12)	118.8(2.6)	N(10)–C(19)–N(9)	115.2(2.1)
O(11)–N(3)–O(12)	121.8(3.0)	N(9)–C(19)–C(18)	125.1(2.8)
N(4)–C(1)–C(2)	122.7(2.5)	C(19)–N(9)–C(15)	116.3(2.2)
N(4)–C(5)–C(4)	124.8(1.9)	C_{py}–C_{py}–C_{py}	mean 118.6(2.0)

(*ii*) In $[UO_2(NO_3)_4]^{2-}$

O(1)–U–O(2)	92.5(1.5)	O(2)–N(1)–O(3)	116.8(3.1)
O(1)–U–O(3)	89.7(1.3)	O(2)–N(1)–O(4)	121.8(3.1)
O(1)–U–O(5)	79.1(1.5)	O(3)–N(1)–O(4)	119.9(2.5)
O(2)–U–O(3)	49.2(0.7)	U–O(5)–N(2)	126.3(2.9)
O(3)–U–O(5)	113.5(1.0)	O(5)–N(2)–O(6)	145.2(3.9)
O(5)–U–O(2) *	114.1(1.1)	O(5)–N(2)–O(7)	94.0(4.0)
U–O(2)–N(1)	96.7(2.2)	O(6)–N(2)–O(7)	120.4(4.7)
U–O(3)–N(1)	96.7(1.5)		

* Atom at $\bar{x}$, $\bar{y}$, $\bar{z}$.

very concentrated (14—20 mol dm^{-3}) nitric acid solutions.[24]

TABLE 3

Least-squares planes [with the deviations (Å) of relevant atoms in square brackets] given by $Px + Qy + Rz = S$, where x, y, and z are fractional unit-cell co-ordinates

	P	Q	R	S
(*i*) In $[UO_2(H_2dapp)(NO_3)]^+$				
Plane (1): N(4), N(6), N(7), N(8), N(9), O(10)	10.311	8.446	6.200	3.908
[N(4) 0.52, N(6) −0.48, N(7) −0.07, N(8) 0.56, N(9) −0.46, O(10) −0.07, U′ −0.07, N(3) −0.94, C(5) −0.02, N(5) −0.63, C(6) −0.89, C(8) −0.64, C(12) 0.23, C(13) 0.78, N(10) 1.00, C(19) 0.31]				
Plane 2: N(4), C(5), N(5), C(6)	12.131	4.162	7.129	4.079
[N(4) −0.02, C(5) 0.04, N(5) −0.04, C(6), 0.02, U′ −0.85, C(1) 0.16, C(4) 0.21, C(6) 0.13]				
Plane (3): N(6), C(6), C(8), N(7)	12.563	4.659	6.569	4.401
[N(6) 0.01, C(6) −0.01, C(8) 0.01, N(7) −0.01, U′ −0.76, N(5) 0.23, C(7) −0.03, C(9) 0.12, C(12) 0.10]				
Plane (4): N(7), C(12), C(13), N(8)	12.946	6.037	4.337	4.522
[N(7) −0.05, C(12) −0.08, C(13) 0.08, N(8) −0.05, U′ 0.17, C(8) −0.17, C(11) −0.43, C(14) 0.31, N(10) 0.06]				
Plane (5): N(8), N(10), C(19), N(9)	12.698	4.434	0.049	4.252
[N(8) −0.04, N(10) 0.07, C(19) −0.07, N(9) 0.04, U′ 1.14, C(13) −0.39, C(18) −0.27, C(15) −0.25]				
Plane (6): O(10), N(3), O(11), O(12)	13.774	−0.090	1.333	4.183
[O(10), N(3), O(11), O(12) 0.00, U′ 0.19]				
(*ii*) In $[UO_2(NO_3)_4]^{2-}$				
Plane (7): O(2), O(3), O(5), O(2),[a] O(3),[a] O(5)[a]	12.583	6.579	3.592	0.000
[O(2) −0.19, O(3) 0.19, O(5) 0.16, U 0.00, O(4) −0.02, N(1) −0.10, N(2) −0.68, O(1) 1.61]				
Plane (8): O(2), O(3), N(1), O(4)	13.498	4.995	3.555	0.000
[O(2), 0.02, O(3) 0.02, N(1) −0.07, O(4) 0.02, U 0.00, O(5) 0.60, N(2) −0.07, O(6) −1.09, O(7) 0.93]				
Plane (9): O(5), N(2), O(6), O(7)	1.409	−2.255	7.949	1.347
[O(5) −0.01, N(2) 0.03, O(6) −0.01, O(7) −0.01, U −1.35]				

Angles (°) between the mean planes:

(1)–(2)	30.1	(3)–(5)	42.4
(1)–(3)	26.3	(3)–(6)	36.1
(1)–(4)	20.3	(4)–(5)	25.1
(1)–(5)	41.4	(4)–(6)	34.8
(1)–(6)	54.6	(5)–(6)	32.1
(1)–(7)	20.6	(7)–(8)	10.5
(2)–(3)	5.9	(7)–(9)	86.4
(2)–(4)	25.4	(8)–(9)	88.2
(2)–(5)	48.0	(7)–(L)[b]	10.1
(2)–(6)	38.4	(1)–(L′)[b]	4.4
(3)–(4)	19.5	(L)–(L′)[b]	26.6

[a] Atom at $\bar{x}$, $\bar{y}$, $\bar{z}$. [b] L indicates the least-squares line defined by O(1)–U–O(1)[a] and L′ that defined by O(8)–U′–O(9); for a plane and line the angle is to the normal of the plane.

In the centrosymmetric $[UO_2(NO_3)_4]^{2-}$ anion the uranyl group is surrounded by an irregular hexagon of four oxygen atoms from two bidentate nitrate groups and two oxygen atoms from two unidentate nitrate groups. The resulting bipyramidal arrangement is shown in Figure 1 and it is noteworthy that this complex, together with the three isomorphous tetranitrates $M_2[UO_2(NO_3)_4]$ ($M = NH_4$, Rb, or Cs),[25] represents the only uranyl compound containing both bi- and unidentate nitrates. The U–O (unidentate) bond length (2.45 Å) seems to be somewhat shorter than the U–O (bidentate) (2.52 and 2.54 Å) and a review [26-35] of these distances in uranyl nitrates and nitrato-complexes confirms this. The unidentate nitrate plane is virtually normal to the equatorial plane (Table 3), even if the highest temperature factors of the peripheral oxygen atoms, expected on the basis of previous *X*-ray determinations, may indicate some disorder or some degree of free oscillation in a relatively large hole in the packing. The unrealistic uranyl distance, surprisingly short (1.66 Å), represents the ' dustbin ' for all sorts of errors: no correction for absorption, the use of inadequate uranium factors, and the neglect of anisotropic refinement [the shortest U–O uranyl distances have been found (1.50 and 1.54 Å) in the chloroform solvate of dioxobis(quinolin-8-olato)(quinolin-8-ol)uranium(VI)].[36]

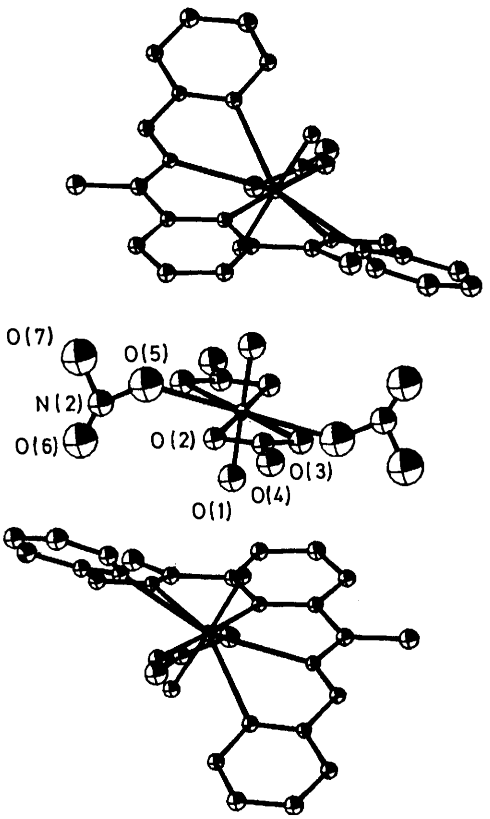

FIGURE 1 Molecular structure of $[UO_2(H_2dapp)(NO_3)]_2[UO_2(NO_3)_4]$, viewed along the c axis

The two monocations $[UO_2(H_2dapp)(NO_3)]^+$, well separated from the counter anion, comprise a system of four five-membered rings with an unidentate nitrate group in the co-ordination sphere of UO_2^{2+} (Figure 2). Although the U–N bond lengths (between 2.59 and 2.66 Å) (Table 2) compare well with analogous distances in related compounds,[1,2,17,37] the six-co-ordination around the uranyl ion makes the system so distorted that an 'equatorial plane' cannot be defined, and the envelope of the six donor atoms assumes a fully extended twist form, towards the symmetry point group $D_2(222)$ (Figure 3). This unique structure of the cations can be accounted for only by a high stabilizing effect of the 5,5,5,5-chelation mode of bonding. The four five-membered rings can be regarded as approximately planar, and a lack of electronic delocalization in the co-ordinated ligand is observed. The C(6)–N(6) and C(13)–N(8) distances (both 1.28 Å) and N(5)–N(6) and N(8)–N(10) (1.37 and 1.35 Å) are consistent with double and single bonds respectively, whereas C(5)–N(5) and C(19)–N(10) (1.38 and 1.40 Å respectively) agree with an N–C_{ph} length.

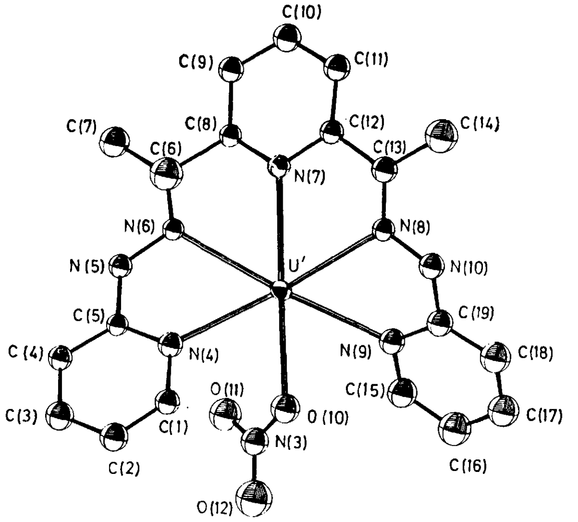

FIGURE 2 Projection of the structure of $[UO_2(H_2dapp)(NO_3)]^+$ onto the mean plane of the N_5O donor set. The O(8) and O(9) atoms overlap the uranium atom and are omitted for clarity. The atom-numbering system is also shown, together with the 50% probability ellipsoids

On the basis of the structural results and bearing in mind that i.r. studies on various solid uranyl tetranitrate salts [38,39] are stated to indicate the presence of ionic nitrate, we can assume that the solid–solid interactions in KBr pellets derive from both the uranyl tetranitrate anion and the complex monocations, as confirmed also by analogous observations on compounds (2) and (3), reported below.

The insolubility of (1) in the reaction medium and the nature of the solvent (stereoelectronic effects and polarity) could determine the extent of complex formation since the use of more polar, protic and aprotic, solvent mixtures leads to the formation of ionic mononuclear species. Reactions between uranyl nitrate and H_2dapp in a mol ratio of 1 : 1 in ethyl acetate–acetonitrile (3 : 1) or ethyl acetate–methanol (3 : 1), as well as in MeCN or absolute ethanol, at room temperature result, for instance, in the formation of a mixture (2) of ionic mononuclear species, which analyzes for a U : H_2dapp : NO_3 ratio of 1 : 1 : 2. Infrared spectra of (2), both as KBr pellets and as hexachlorobutadiene or Nujol mulls, display characteristic N–H stretching bands in the 3 360—3 420 cm^{-1} region, co-ordinated nitrate absorptions at 1 460 and 1 280 cm^{-1}, a strong ionic nitrate absorption at 1 381 cm^{-1}, two strong bands, of nearly equal intensity, at 915 and 925 cm^{-1} assignable to two asymmetric stretchings $\nu_3(UO_2)$, and a series of weak doublets in the 600—800 region. Solid–solid interactions were observed also in this case, the intensity of the band at 1 381 cm^{-1} being dependent on the concentration of the KBr pellet.

The same reaction carried out in acetonitrile or absolute ethanol under reflux gives the mixture (2) but of different composition, as shown by analytical results and inspection of the spectra in hexachlorobutadiene and Nujol mulls. In particular, the spectrum of the product obtained by crystallization of (2) from hot acetonitrile shows a marked increase in the intensity of the ionic nitrate and $\nu_3(UO_2)$ absorption bands at 1 381 and 925 cm^{-1} respectively, which parallels a decrease in intensity of the bands of the co-ordinated nitrate group (1 460 and 1 280 cm^{-1}) and $\nu_3(UO_2)$ (915 cm^{-1}), and a general simplification of the spectrum in the 600—800 cm^{-1} region.

The reactions of (2) with Na[BPh_4] (1 : 2 mol ratio) in methanol and of (1) with an excess (1 : 4) of Na[BPh_4] in acetonitrile give the same product $[UO_2(H_2dapp)(NO_3)][BPh_4]$ (3). Free tetraphenylborate absorbs at 1 440 cm^{-1}, medium to strong absorptions at 1 275 and 1 475 cm^{-1} indicate the presence of the unidentate nitrate group, and the single $\nu_3(UO_2)$ stretch falls at 923 cm^{-1}. Also the five-co-ordinated dicationic species $[UO_2(H_2dapp)][ClO_4]_2$ (4), easily isolated from the reaction of H_2dapp with uranyl perchlorate in absolute ethanol (strong broad absorption of the free-perchlorate group centred at 1 100 cm^{-1}), shows only a single stretch $\nu_3(UO_2)$ at 919 cm^{-1}. Finally, (1) is obtained when (2) reacts with uranyl nitrate (2 : 1) in ethyl acetate at room temperature.

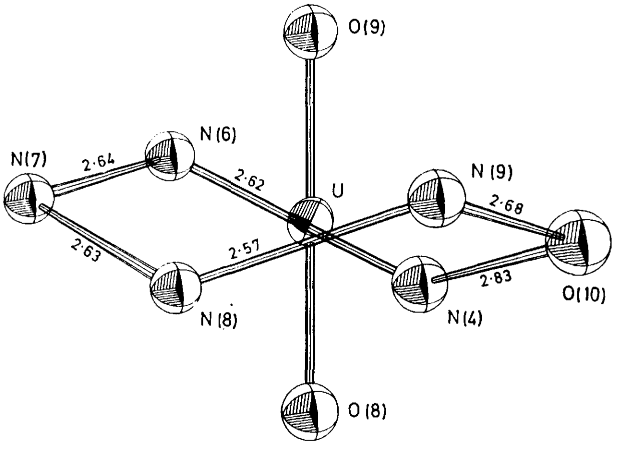

FIGURE 3 ORTEP drawing of the symmetrical or fully extended twist form of the N_5O donor set around the uranium atom. 'Bite' distances (Å) are shown

Since both the six- and five-co-ordinated species, (3) and (4), respectively, show a unique $\nu_3(UO_2)$ stretch, it is reasonable to assume that the two stretches at 915 and

925 cm^{-1} in (2) are not due to a splitting of such a vibration in a compound containing only one type of UO_2^{2+} group, as is sometimes observed,[16,40] but to the presence of a mixture of isomeric ionic species which probably differ in the co-ordination number and/or in the co-ordination mode around the uranyl moiety. The formation of (3) is, however, an indication of the presence of the species $[UO_2(H_2dapp)(NO_3)][NO_3]$ in the mixture (2).

The experimental results thus indicate that solvents with a high dielectric constant (ε) prevent complex (1) from forming, owing to either solvation of ionic nitrates, which prevent the formation of the uranyl tetranitrate anion, or to further solvolysis of that anion, if it is formed. Compound (1) suspended in acetonitrile ($\varepsilon = 36.2$) or anhydrous ethanol ($\varepsilon = 24.3$) is quantitatively transformed into (2) and $[UO_2(NO_3)_2]$, whereas it remains unchanged in Pr^iOH ($\varepsilon = 18.3$) and ethyl acetate ($\varepsilon = 6.02$). In the case of Pr^iOH stereoelectronic effects cannot be excluded. The unexpected behaviour of (1) in anhydrous methanol ($\varepsilon = 32.6$) which results in the formation (yield *ca.* 50%) of the diprotonated form of the ligand $[H_4dapp][NO_3]_2$ (5) [as indicated by a comparison of its analyses and spectra with those of an authentic sample prepared from the action of dilute nitric acid on H_2dapp or (1)], is probably due to further attack of the solvent on the solvolyzed species. Investigations on the possible mechanism are in progress.

Owing to the possibility of deprotonation of the diazapropenic sequences =C=N–NH– present in H_2dapp,[41-49] compounds (1)—(4) when treated with a non-hydroxylated base, *e.g.* pyridine, triethylamine, sodium hydride, methyl-lithium, or 1,8-bis(dimethylamino)naphthalene (' proton sponge ') in anhydrous acetonitrile, are transformed (very easily and quantitatively in the case of the proton sponge) to the same neutral black compound of formula $[UO_2(dapp)]$ (6), for which we have recently published some preliminary information.[50] Complex (6) is a non-conductor in nitrobenzene, and although the i.r. spectrum is rather complex there is no evidence for N–H and nitrate-group stretching vibrations, while $\nu_3(UO_2)$ falls at 911 cm^{-1}. The ^1H n.m.r. spectrum of freshly dissolved (6) in deuteriochloroform shows a single resonance of the methyl protons at δ 3.52, clearly indicating the symmetrical magnetic environment around the two methyl groups. This resonance is slowly split (*ca.* 48 h) into two equivalent signals at δ 3.03 and 2.55 respectively, due to an unknown reaction which is under investigation. A possible dimerization reaction, as found in the case of the zinc complex of $dapp^{2-}$, cannot be excluded.[4] The proposed structure of (6) is also supported by its reactivity which parallels that of uranyl amides,[51] due to the lability of covalent U–N bonds towards hydroxylated reagents. H_2dapp is slowly obtained by the action of water on (6). This indicates that the ligand in the neutral complex is only the bis(deprotonated) form of H_2dapp, as confirmed by the reaction of (6) with dilute nitric acid which affords (5) quantitatively. Furthermore, (6) reacts with dry methanol, at room temperature and under an inert atmosphere, giving a highly insoluble, probably polymeric, methoxyuranyl complex (7), of formula $[\{(UO_2)_2(H_2dapp)(OCH_3)_4 \cdot xCH_3OH\}_n]$ ($x = 1$ or 2), as supported by analytical and spectroscopic data, which is under investigation.

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