Reactivity of Uranyl Ion with Quinquedentate Chelating Hydrazine Derivatives. Part 2.† 2,6-Diacetylpyridine Bis(4-methoxybenzoylhydrazone)

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The new quinquedentate chelating ligand 2,6-diacetylpyridine bis(4-methoxybenzoylhydrazone) (H_2dapmb) reacts with uranyl nitrate and perchlorate to give the monocationic species [UO_2(Hdapmb)][NO_3] (1) and [UO_2(Hdapmb)][ClO_4] (2) respectively, and in the presence of nitric and perchloric acid solutions to give the adducts [UO_2(H_2dapmb)][NO_3]$_2$ (5) and [UO_2(H_2dapmb)][ClO_4]$_2$ (6) respectively. The six-co-ordinate isomeric form [UO_2(H_2dapmb)(ONO_2)][NO_3] (4) has been isolated under different experimental conditions. All the complexes have been fully deprotonated to neutral species [UO_2(dapmb)] (3), under a range of experimental conditions. Complex (3) can be isolated in two different crystalline forms, α and β, depending on the experimental conditions. All the species have been characterized by a number of analytical and physico-chemical measurements, including the determination of the crystal structure of the two isomers of (3). The red (α) form is monoclinic, space group $P2_1/c$, with a = 8.229(5), b = 10.564(6), c = 29.662(9) Å, and β = 101.05(8)°, while the orange (β) form is orthorhombic, space group $P2_12_12_1$, with a = 15.266(8), b = 14.953(6), and c = 10.790(6) Å. An accurate structure determination was carried out for the monoclinic modification (automatic diffractometer, Mo-K_α radiation; 2 342 observed reflections; R = 0.040), while the investigation of the orthorhombic form was undertaken merely to ascertain whether or not its configuration was the same as that of the monoclinic form. The geometry of [UO_2(dapmb)] in the two forms is very similar, the only significant difference being the conformation of a carbon atom in a methoxy-group. Seven-fold co-ordination of U^{VI} was found, with the five donor atoms in the equatorial plane and the linear UO_2 group normal to the plane. Interconversion reactions on the various compounds have been studied.

RECENTLY [1,2] we studied the interaction of uranyl ion with 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2dapp), a ligand containing a sequence of five nitrogen-donor atoms [*see* Figure 1 (I)].

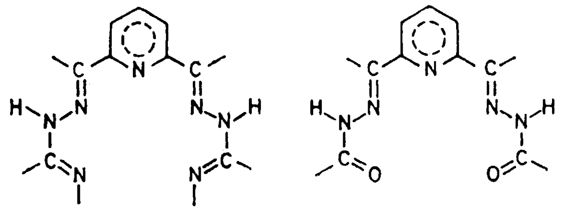
(I) (II)

FIGURE 1 Schematic drawing of the sequences of donor atoms in quinquedentate chelating ligands derived from hydrazine

In all cases H_2dapp behaves as a quinquedentate chelating ligand with the formation of four five-membered rings around the metal. From *X*-ray structural analysis it has been shown that such chelation is also maintained in the case of [UO_2(H_2dapp)(ONO_2)]$_2$[$UO_2(NO_3)_4$] causing considerable distortion of the equatorial plane of the complex cation. The non-planarity of the co-ordinated ligand is mainly due to steric hindrance between the hydrogen atoms on the two pyridine rings of the hydrazone residues.[3]

In order to achieve planar equatorial multi-chelation of the uranyl moiety we have synthesized the new quinquedentate ligand 2,6-diacetylpyridine bis(4-methoxybenzoylhydrazone) (H_2dapmb) containing the sequence of donor atoms (II) in Figure 1 and studied its reactions with uranyl nitrate, acetate, and perchlorate.

The synthesis of a series of ionic and neutral complexes, whose physico-chemical characterization is due to the ability of aroylhydrazones to co-ordinate either in the keto or enol form,[4-8] is reported here.

X-Ray analyses of two different crystalline forms of the neutral species, the red monoclinic and the orange orthorhombic, have been obtained in order to ascertain possible structural differences.

EXPERIMENTAL

Reagents.—Reagent-grade uranyl nitrate hexahydrate, uranyl acetate dihydrate (Fluka products), and 2,6-diacetylpyridine (Ega Chemie product) were used without further purification. Solvents were distilled before use. The compound 4-methoxybenzoylhydrazine was prepared as described previously.[9]

2,6-*Diacetylpyridine Bis*(4-*methoxybenzoylhydrazone*) (H_2dapmb).—To a hot solution of 2,6-diacetylpyridine (0.01 mol) was added a hot ethanolic solution of 4-methoxybenzoylhydrazine (0.02 mol) with stirring, and the mixture heated under reflux for 3 h. During the reaction the formation of a white product was observed. After cooling, the white product was collected by filtration and washed several times with hot ethanol. Recrystallization from absolute ethanol affords 3.155 g (90% yield) of H_2dapmb, m.p. 214—216 °C (Found: C, 65.5; H, 5.7; N, 15.4. $C_{25}H_{25}N_5O_4$ requires C, 65.35; H, 5.55; N, 15.25%).

Infrared (KBr pellets) bands at: 3 290m [ν(NH)], 1 665vs, br [ν(C=O) and ν(C=N)?], 1 610s [ν(C=C), pyridine ring], 1 583m (pyridine ring), 1 535ms [amide (II)], 1 505 [ν(C=C), pyridine ring], 1 465ms (pyridine ring), 1 250vs [ν_{asym} (O–CH_3)], and 1 025ms [ν_{sym} (O–CH_3)] cm^{-1}.

Hydrogen-1 n.m.r. data ([$^2H_6$]dmso) (dmso = dimethyl sulphoxide): δ 10.77 (s, 2 H, NH), δ 7.97, 7.10 (two multi-

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† Part 1 is ref. 2.

plets, 11 H, aromatic and pyridine protons), δ 3.90 (s, 6 H, $-O-CH_3$), δ 2.57 (s, 6 H, $CH_3-C=N-$).

$[UO_2(Hdapmb)][NO_3]$ (1).—To a solution of uranyl nitrate (1 mmol) in thf–EtOH (thf = tetrahydrofuran) (50 cm^3, 1 : 1 v/v) was added a suspension of H_2dapmb (1 mmol) in thf (40 cm^3) over 30 min at room temperature with stirring. During the addition an orange product precipitated. The mixture was left stirring overnight to complete the reaction. The orange product was filtered off, washed with absolute ethanol (2 × 10 cm^3) and thf (2 × 10 cm^3), and dried *in vacuo*. The yield of (1) was 0.712 g (90%) (Found: C, 37.9; H, 3.2; N, 10.55; U, 30.5. $C_{25}H_{24}N_6O_9U$ requires C, 37.95; H, 3.05; N, 10.65; U, 30.15%).

Infrared (KBr pellets) bands at: 3 180w,br, 1 605vs,br, 1 586ms, 1 543ms, 1 500s, 1 438ms (sh), 1 429s, 1 382vs, 1 265, 1 260s, 1 183, 1 170s, 1 038s, 1 023ms, 917vs, and 907ms (sh) cm^{-1}.

The same product was obtained using uranyl nitrate in excess (1 : 10). By crystallization of the crude product from a hot ethanol–acetonitrile (7 : 3 v/v) mixture the orange orthorhombic β form of $[UO_2(dapmb)]$ (3) was obtained.

$[UO_2(Hdapmb)][ClO_4]$ (2).—To an ethanolic solution (50 cm^3) of uranyl perchlorate (1 mmol) was added a suspension of the ligand (1 mmol) in absolute ethanol (100 cm^3) over 45 min, at room temperature with stirring. An orange product started to precipitate when almost half of the ligand suspension was added. The mixture was left stirring overnight to complete the reaction, the product was then separated by filtration, washed several times with absolute ethanol, and dried *in vacuo*. The yield of (2) was 0.724 g (87.5%) (Found: C, 35.9; H, 3.20; Cl, 4.35; N, 8.25; U, 29.1. $C_{25}H_{24}ClN_5O_{10}U$ requires C, 36.25; H, 2.9; Cl, 4.30; N, 8.45; U, 28.75%).

Infrared (KBr pellets) main bands at: 3 280w,br, 1 600vs,br, 1 552ms, 1 544ms, 1 504vs, 1 454ms, 1 441ms, 1 407ms, 1 370vs,br, 1 268vs, 1 252s, 1 179, 1 173vs, 1 100vs,br, 1 036s, 989m, 925vs, and 908ms (sh) cm^{-1}.

The same product was obtained using a 1 : 10 mol ratio of ligand to uranyl perchlorate.

$[UO_2(dapmb)]$ (3).—Uranyl acetate dihydrate (1 mmol) and H_2dapmb (1 mmol) in EtOH (100 cm^3) were heated under reflux for 1 h. We obtained 0.680 g (93.5% yield) of a yellow-orange product which was filtered off, washed with hot ethanol (partial dissolution), and dried *in vacuo*. By crystallization of the crude product from EtOH–acetonitrile (7 : 3 v/v) the red monoclinic α form was isolated (Found: C, 40.85; H, 3.05; N, 9.55; U, 32.45. $C_{25}H_{23}N_5O_6U$ requires C, 41.25; H, 3.15; N, 9.65; U, 32.75%).

Infrared (KBr pellets) main bands at: 1 604s, 1 585s, 1 553ms, 1 500vs, 1 451ms, 1 440m, 1 422m, 1 399s, 1 360vs,br, 1 249vs, 1 168vs, 1 035s, 1 022s (sh), 989m, 911s, and 902vs cm^{-1}.

$[UO_2(H_2dapmb)(ONO_2)][NO_3]$ (4).—To the neutral complex (3) (0.5 g, 6.88 × 10^{-4} mol), suspended in absolute ethanol (100 cm^3), was slowly added 0.56 mol dm^{-3} HNO_3 (12 cm^3, 6.7 × 10^{-3} mol) at room temperature and with stirring. The mixture was left to react overnight, the yellow product formed was filtered off, washed with two portions of an EtOH–HNO_3 mixture (10 cm^3 absolute EtOH + 1 cm^3 0.56 mol dm^{-3} HNO_3), and dried *in vacuo*. The yield of complex (4) was 0.604 g (71%) (Found: C, 34.85; H, 2.95; N, 11.15; U, 27.55. $C_{25}H_{25}N_7O_{12}U$ requires C, 35.15; H, 2.95; N, 11.5; U, 27.9%).

Infrared (KBr pellets) main bands at: 3 180m,br, 1 607vs, 1 560s, 1 543s, 1 508s, 1 429s,br, 1 382s, 1 337vs, 1 310vs, 1 267vs, 1 178s, 1 157s, 928s, and 903m cm^{-1}.

The same product was obtained either from (3) by using 2 mol dm^{-3} HNO_3 in excess or from (1) with both 0.56 mol dm^{-3} and 2 mol dm^{-3} HNO_3 in excess.

$[UO_2(H_2dapmb)][NO_3]_2$ (5).—To an ethanolic (25 cm^3) suspension of H_2dapmb (1 mmol) was added an ethanolic solution (10 cm^3) of uranyl nitrate (1 mmol) slowly, at room temperature and with stirring. An orange product (1) was formed. The slow addition of 0.56 mol dm^{-3} HNO_3 (10 cm^3, 5.6 × 10^{-3} mol) to the mixture gave rise to the progressive solvation of the orange product forming an orange solution. After two thirds of the nitric acid had been added a yellow product started to precipitate.

When the nitric acid had all been added, the reaction mixture was left to react for 3 h at room temperature.

The yellow product was filtered off, washed with an EtOH–HNO_3 mixture (10 cm^3 absolute EtOH + 1 cm^3 0.56 mol dm^{-3} HNO_3), and dried *in vacuo*. We obtained 0.742 g of (5) (87% yield) (Found: C, 35.3; H, 3.10; N, 11.2; U, 27.6. $C_{25}H_{25}N_7O_{12}U$ requires C, 35.15; H, 2.95; N, 11.5; U, 27.9%).

Infrared (KBr pellets) main bands at: 3 180m,br, 1 604s,br, 1 551s,br, 1 504s, 1 456ms,br, 1 443ms,br, 1 381vs, 1 334s, 1 309s, 1 269s, 1 178s, 1 022ms, 942s, and 903wm cm^{-1}.

The same product was isolated from the reaction of H_2dapmb and uranyl nitrate in the presence of both 0.56 mol dm^{-3} and 2 mol dm^{-3} HNO_3 in excess.

$[UO_2(H_2dapmb)][ClO_4]_2$ (6).—To the neutral complex (3) (0.5 g, 6.88 × 10^{-4} mol) suspended in absolute ethanol (100 cm^3), was added 2 mol dm^{-3} $HClO_4$ (10 cm^3, 2 × 10^{-2} mol) slowly at room temperature and with stirring. After addition of the perchloric acid was complete, the mixture was left to react overnight. The yellow product was filtered off, washed with an EtOH–$HClO_4$ mixture and dried *in vacuo*. The yield of (6) was 0.787 (85%) (Found: C, 32.05; H, 2.55; Cl, 7.50; N, 7.30; U, 25.75. $C_{25}H_{25}Cl_2N_5O_{14}U$ requires C, 32.35; H, 2.70; Cl, 7.65; N, 7.55; U, 25.65%).

Infrared (KBr pellets) main bands at: 3 280m,br, 1 604vs, 1 545s, 1 502ms, 1 458m, 1 441m, 1 330s, 1 262s, 1 176vs, 1 093vs,br, 942s, and 908m (sh) cm^{-1}.

Physical Measurements.—Infrared spectra (400—4 000 cm^{-1}), either of KBr discs or Nujol or hexachlorobutadiene mulls, were recorded on a Perkin-Elmer 621 spectrophotometer. Hydrogen-1 and ^{13}C n.m.r. spectra for solutions in deuteriated dimethyl sulphoxide were recorded on a Varian HL 100 equipped with Fourier-transform facility.

Uranium was determined gravimetrically as the tetraphenylarsonium salt of dioxobis(pyridine-2,6-dicarboxylato)uranate(VI).[10]

Crystal Data.—*Red form* (α) *monoclinic modification*. $C_{25}H_{23}N_5O_6U$, $M = 727.5$, Monoclinic, $a = 8.229(5)$, $b = 10.564(6)$, $c = 29.662(9)$ Å, $\beta = 101.05(8)°$, $U = 2\,530.7$ Å^3, $D_m = 1.92$ (by flotation), $Z = 4$, $D_c = 1.909$ g cm^{-3}, $F(000) = 1\,392$, space group $P2_1/c$ (C_{2h}^5, no. 14).[11]

Alternate non-standard setting: $a = 8.229$, $b = 10.564$, $c = 29.223$ Å, $\beta = 94.99°$, space group $P2_1/n$ (transformation matrix $\bar{1}00$, $0\bar{1}0$, 101). Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 61.6 cm^{-1}.

Crystal size: 0.10 × 0.12 × 0.20 mm. Cell data were obtained from the least-squares refinement of the setting angles for 25 high-order reflections. Intensities wese collected up to $(\sin\theta)/\lambda$ 0.595 Å^{-1} on a Philips PW 1100 fully-automatic diffractometer in the θ—2θ scan mode.

The range of each scan consisted of the base width of 1.1° at $2\theta = 0°$ and an increment, $\Delta(2\theta) = 0.15 \tan \Theta°$, to allow for spectral dispersion; scan speed was 0.03° s^{-1}, while background counts were taken at the extremes of the scan for a time equal to 10 s.

Reflections measured were $\pm h$, $+k$, and $+l$ up to the indices 9, 12, and 35. A total of 4 796 reflections were collected of which 83 were equivalent and 266 systematic absences. 2 342 Independent reflections with $I > 3\sigma(I)$, $\sigma(I)$ being based on counting statistics, were corrected for Lorentz and polarization effects and used in the determination and refinement of the structure. Three standard reflections remained constant to within $\pm 3\%$ throughout data collection.

As a check on possible variations in the transmission factor, eight strong reflections were measured at $\chi = 90$ and 10° intervals from $\Phi = 0$ to 370°. The maximum variation from the mean was *ca.* 6%, suggesting that absorption was not a serious problem; however the impossibility of deriving the correct geometrical shape for the badly developed crystal makes us unable to perform any reliable absorption correction.

TABLE 1

Atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for the red monoclinic form

Atom	*x/a*	*y/b*	*z/c*
U	−905(1)	33(1)	1 214(0)
O(1)	−2 018(13)	1 209(11)	857(4)
O(2)	245(12)	−1 129(10)	1 568(3)
O(3)	−2 913(11)	26(17)	1 667(3)
O(4)	−1 692(13)	−1 457(11)	647(4)
O(5)	−7 752(15)	309(12)	3 093(4)
O(6)	−2 948(17)	−5 796(13)	−868(4)
N(1)	−517(14)	1 548(12)	1 860(4)
N(2)	1 654(15)	1 398(12)	1 322(4)
N(3)	1 026(15)	−332(11)	674(4)
N(4)	−1 683(13)	1 595(11)	2 153(4)
N(5)	637(17)	−1 258(14)	335(5)
C(1)	−2 835(22)	717(18)	2 017(6)
C(2)	−4 166(17)	640(14)	2 295(5)
C(3)	−4 009(21)	1 382(18)	2 693(6)
C(4)	−5 228(19)	1 312(15)	2 973(5)
C(5)	−6 548(21)	469(16)	2 830(6)
C(6)	−6 695(20)	−255(19)	2 443(5)
C(7)	−5 506(17)	−158(19)	2 172(5)
C(8)	742(20)	2 320(16)	1 971(5)
C(9)	1 983(17)	2 229(13)	1 663(4)
C(10)	3 330(19)	3 051(15)	1 729(5)
C(11)	4 530(22)	2 885(18)	1 458(6)
C(12)	4 235(16)	1 956(13)	1 116(4)
C(13)	2 789(20)	1 220(16)	1 061(5)
C(14)	2 443(18)	247(15)	695(5)
C(15)	−788(20)	−1 763(17)	351(6)
C(16)	−1 366(23)	−2 824(18)	34(6)
C(17)	−363(18)	−3 210(15)	−278(5)
C(18)	−858(23)	−4 189(18)	−583(6)
C(19)	−2 324(22)	−4 840(25)	−576(6)
C(20)	−3 383(22)	−4 392(18)	−287(6)
C(21)	−2 866(22)	−3 416(18)	28(6)
C(22)	−7 657(30)	1 074(26)	3 512(8)
C(23)	940(24)	3 237(21)	2 365(7)
C(24)	3 666(21)	−135(25)	401(6)
C(25)	−1 902(32)	−6 373(26)	−1 129(9)

Structure determination. The uranium atom was located from a three-dimensional Patterson synthesis (R factor of 0.18). A Fourier map phased on the co-ordinates of this atom provided the locations of all other non-hydrogen atoms. Refinements (unit weight to each 'observed' reflection, anisotropic thermal parameters only for uranium) minimizing $\Sigma w(|F_o| - |F_c|)^2$ converged to R 0.040 and the weighted residual R' was 0.052 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$.

The shifts were then all < 0.01 Å. From a final difference Fourier, essentially featureless, the positions of all the hydrogen atoms could not be deduced.

Scattering factors used were those for neutral atoms[12] and the scattering curve for U was corrected for anomalous dispersion.[13] The positional parameters for the non-hydrogen atoms are reported in Table 1. The final values of observed and calculated structure amplitudes, thermal parameters, and least-squares planes data are listed in Supplementary Publication No. SUP 22744 (24 pp.).*

The calculations were performed on a CDC/CRYBER '76 computer (Centro Calcolo Elettronico Interuniversitario Italia Nord-Orientale, Casalecchio, Bologna), using the *X*-Ray System.[14]

Orange form (β), *orthorhombic modification.* $C_{25}H_{23}N_5O_6U$, Orthorhombic, $a = 15.266(8)$, $b = 14.953(6)$, $c = 10.790(6)$ Å, $U = 2\,463.1$ Å^3, $Z = 4$, space group $P2_12_12_1$ (D_2^4, no. 19),[11] Mo-K_α radiation, $\lambda = 0.710\,7$ Å.

The data set [1 069 independent reflections with $I > 3\sigma(I)$] was obtained, with a procedure similar to that described for the α form, from an apparently atypical crystal, a cuboid of side 0.25 mm. It was impossible to apply any absorption correction, although in this case absorption was a very serious problem, and so diffraction data were accordingly limited in accuracy. However, the investigation of the orthorhombic form was undertaken merely to ascertain whether or not the configuration of the molecule was the same as in the monoclinic form. During the refinement (final R value 0.059) some bond distances were found to have different values to those expected on the basis of the α form structure determination.

The estimated standard deviations for the atomic co-ordinates were very high, since the number of observed reflections (1 069) was rather low with respect to the large number of variables (154).

RESULTS AND DISCUSSION

The reactions of H_2dapmb with uranyl salts and the transformations which the various compounds undergo under suitable conditions are summarized in the Scheme.

It can be observed that the ligand reacts with uranyl nitrate and perchlorate, independent of mol ratios, at room temperature in thf–absolute ethanol to give $[UO_2(Hdapmb)][NO_3]$ (1) and $[UO_2(Hdapmb)][ClO_4]$ (2) respectively. The ligand is present in both of these complexes as its semi-enolized monodeprotonated form.

The ability of the solvent to deprotonate the ligand is due to the highly increased acidity of the aroyl hydrazone proton caused by its co-ordination with the uranyl ion. It is known, in fact, that co-ordination to transition metals may increase the acid dissociation constant of some hydrazone systems by a factor of 10^5—10^8.[15]

Further deprotonation of (1) and (2) to give the neutral

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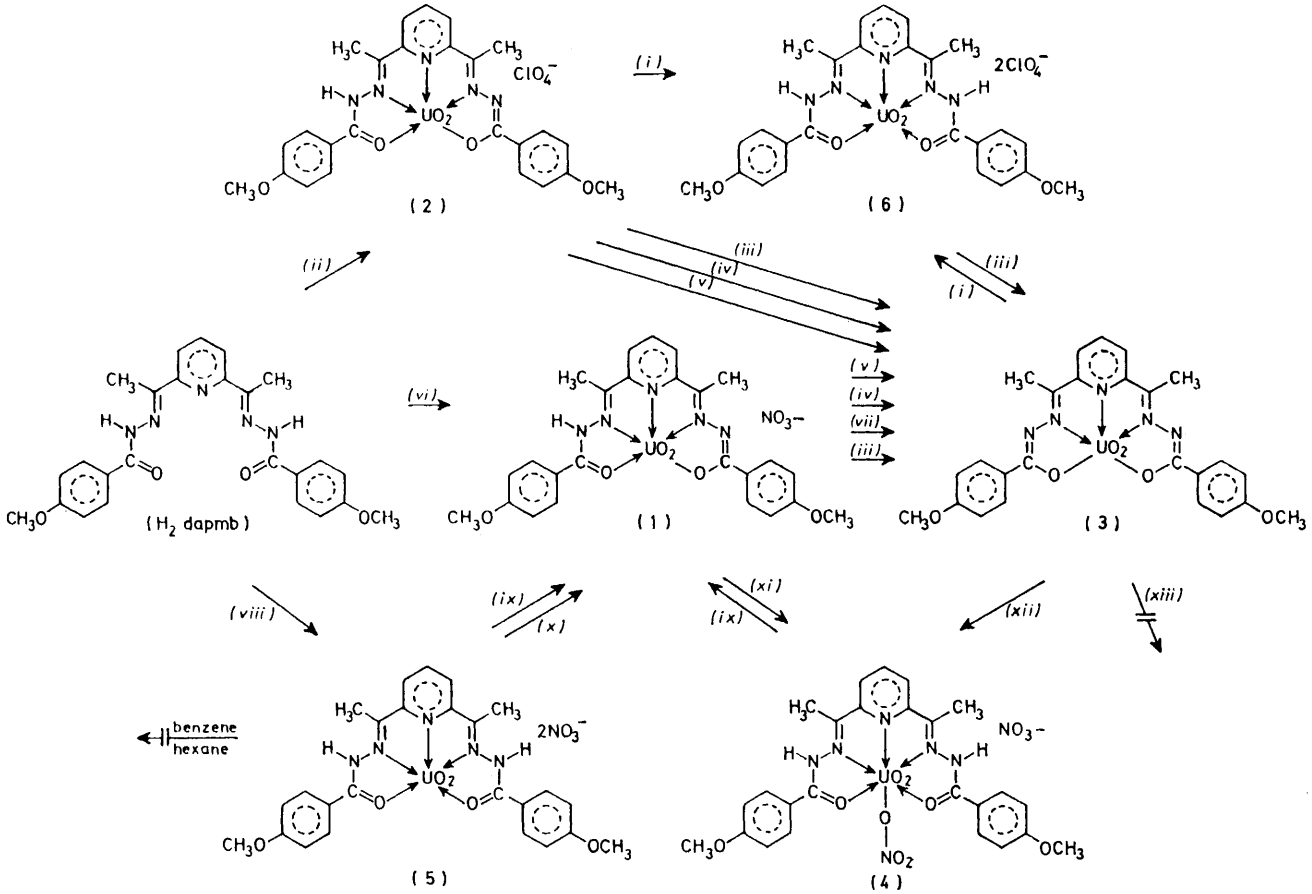
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

complex [UO_2(dapmb)] (3) can be achieved by using solvents with high dielectric constants (50% aqueous ethanol, water, dmso, acetonitrile, *etc.*) either slowly at room temperature or rapidly by heating. Complex (3) is normally obtained by refluxing H_2dapmb with uranyl acetate in absolute ethanol which causes deprotonation of both secondary imino-hydrogens by the acetate ions.



SCHEME (*i*) 1 mol dm^{-3} $HClO_4$ in excess, ethanol, room temperature (r.t.); (*ii*) [UO_2][ClO_4]$_2$, absolute ethanol, r.t.; (*iii*) water, r.t.; (*iv*) CH_3CN, reflux; (*v*) dmso, r.t. and 80 °C; (*vi*) [UO_2][NO_3]$_2$·$6H_2O$, absolute ethanol, r.t.; (*vii*) 50% aqueous ethanol, r.t.; (*viii*) [UO_2][NO_3]$_2$·$6H_2O$, 0.56 mol dm^{-3} HNO_3, ethanol, r.t.; (*ix*) absolute ethanol, r.t.; (*x*) ethyl acetate, r.t.; (*xi*) 0.56 or 1 mol dm^{-3} HNO_3 in excess, ethanol, r.t.; (*xii*) 0.56 or 1 mol dm^{-3} HNO_3 in excess; (*xiii*) dmso, r.t.

Both (1) and (2) are transformed into the neutral complex (3) in various solvents with elimination of the strong acids HNO_3 and $HClO_4$ respectively. This behaviour is indicative of the stability of the neutral complex towards these acids at least at low concentrations (2.5×10^{-2} mol dm^{-3}). By treating (3) with HNO_3 (0.14 mol dm^{-3}) in mol ratios of 1 : 1 and 1 : 5 at room temperature, the neutral complex remains unchanged even after 16 h. In fact complete protonation, accompanied by formation of the adduct [UO_2(H_2dapmb)(ONO_2)][NO_3] (4), may only be achieved by using more concentrated nitric acids solutions (>0.56 mol dm^{-3}) in excess.

The adduct (4) is stable only in acidic media (pH <1) or in aprotic solvents (benzene, n-hexane) in which it is also insoluble. By suspending (4) in absolute ethanol at room temperature, monodeprotonation with quantitative formation of (1) occurs.

In order to confirm that the formation of the adduct only occurs in acidic media, the reaction of H_2dapmb and uranyl nitrate (1 : 1) was carried out in the presence of 0.56 mol dm^{-3} HNO_3 (mol ratio 1 : 10) in ethanol at room temperature. The adduct [UO_2(H_2dapmb)][NO_3]$_2$ (5) was isolated. This reacts with absolute ethanol, as does the complex (4), giving (1) in quantitative yield. Both (4) and (5) are fully deprotonated by the action of aqueous ethanol (50%) or water either at room temperature or when heated, thus giving the neutral complex (3).

The adduct [UO_2(H_2dapmb)][ClO_4]$_2$ (6) is obtained either by treating 2 mol dm^{-3} $HClO_4$ with the neutral complex (3) or by the reaction of H_2dapmb and uranyl perchlorate (1 : 1) in the presence of an excess of 2 mol dm^{-3} $HClO_4$.

Adduct (6) undergoes the same reactions as (4) and (5). Furthermore at room temperature strong neutral ligands such as dmso and pyridine-*N*-oxide do not give addition products with complex (3), thus indicating great stability of the planar multi-chelation around the uranyl moiety.

Infrared Spectra.—Infrared spectra (KBr pellets, Nujol and hexachlorobutadiene mulls) of all the species isolated have shown some band shifts which define the co-ordination mode of the complex well. In particular there are some characteristic vibrations of the co-ordinated ligand both in the keto and enol forms that may be compared to those of the similar complexes with transition metals previously reported.[4-8]

The amide (I) band[16] ν(C=O), which occurs at 1 665 cm^{-1} in the free ligand, is lowered by co-ordination with the uranyl ion by *ca.* 50 cm^{-1} both in the monodeprotonated species [(1) and (2)] and the adducts [(4), (5), and (6)]; these features parallel the analogous lowering of *ca.* 20—30 cm^{-1} observed in transition-metal aroylhydrazone complexes.[4,7,8]

In the monodeprotonated complexes (1) and (2) an increase in the intensity of the band centred at 1 600 cm^{-1}, due to the C=N–N=C residue,[4-8] can be observed together with the appearance of a strong band at 1 037 cm^{-1} due to ν(C–O–),[17-20] in addition to the ν(NH) bands at 3 180 and 3 280 cm^{-1} respectively.

On the other hand, the spectrum of the neutral species (3) has neither absorption bands due to ν(NH) stretching or the amide (I) band ν(C=O) but shows the same strong absorptions at *ca.* 1 610 and 1 037 cm^{-1}.

In order to define the nature of the nitrate groups in the ionic complexes (1), (4), and (5) a comparative analysis of their i.r. spectra (KBr pellets, Nujol and hexachlorobutadiene mulls) has been carried out, conductometric and ^{1}H and ^{13}C n.m.r. measurements being precluded by their relative insolubility in the solvents in which they are stable.

Repeated grindings of complex (4) with KBr lead to a gradual decrease in the intensity of the mono-co-ordinated nitrate group and $\nu_3(UO_2)$ absorption bands at 1 429 and 928 cm^{-1} respectively. This parallels the increase in intensity of the ionic nitrate group absorption at 1 382 cm^{-1} and the appearance of a new $\nu_3(UO_2)$ band at 942 cm^{-1}, due to solid–solid interaction between the complex and KBr, as previously noted for other related uranyl complexes.[2]

On the other hand, i.r. spectra of (4) in hexachlorobutadiene and Nujol mulls have bands at 1 426, 1 381, and 928 cm^{-1}, whereas the absorption at 942 cm^{-1} is absent.

However, repeated grindings with KBr of species (1) and (5) do not modify the spectra at all, which show only ionic nitrate groups absorbing at 1 382 cm^{-1} and $\nu_3(UO_2)$ at 917 and 942 cm^{-1}.

These features indicate that species (4) is hexa-co-ordinated on the equatorial plane of the uranyl ion with a mono-co-ordinated nitrate group, while the second nitrate group is ionic. On the contrary, species (1) and (5) are penta-co-ordinated and all the nitrate groups are ionic. As far as the $\nu_3(UO_2)$ stretching vibration as a function of the charge of the complex is concerned, it is interesting to note that in penta-co-ordinated bis-cationic complexes (5) and (6) it occurs at 942 cm^{-1}. In the penta-co-ordinated mono-cationic species (1) and (2) a lowering to 917 and 925 cm^{-1} respectively, is observed. Following this trend the neutral complex (3) has $\nu_3(UO_2)$ at 902 cm^{-1}. Furthermore, a lowering of $\nu_3(UO_2)$ from 942 cm^{-1} for penta-co-ordinated bis-cationic species (5) to 928 cm^{-1} for hexa-co-ordinated mono-cationic species (4) parallels the findings for analogous five-co-ordinate uranyl complexes.[2]

TABLE 2

25.16 MHz proton noise-decoupled ^{13}C n.m.r. spectral data ([^{2}H$_6$]dmso) for H$_2$dapmb and the neutral complex (3)

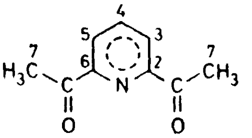
H$_2$dapmb		[UO$_2$(dapmb)]		
Carbon atoms	δ[a]	Carbon atoms	δ[a]	Δδ[b]
C(1),C(15)	164.6 (s)[c]	C(1),C(15)	175.6	−11
C(5),C(19)	161.9 (s)	C(5),C(19)	161.8	0.1
C(9),C(13)	154.2 (s)	C(9),C(13)	161.3	−7.1
C(8),C(14)	152.9 (s)	C(8),C(14)	157.8	−4.9
C(11)	137.2 (d)	C(11)	142.2	−5.0
C(3),C(7),-C(21),C(17)	130.4 (d)	C(3),C(7),-C(21),C(17)	130.9	−0.5
C(2),C(16)	125.9 (s)	C(2),C(16)	127.4	−1.5
C(10),C(12)	120.4 (d)	C(10),C(12)	124.9	−4.5
C(4),C(6),-C(20),C(18)	113.5 (d)	C(4),C(6),-C(20),C(18)	113.8	−0.3
C(22),C(25)	55.4 (q)	C(22),C(25)	55.4	
C(23),C(24)	12.3 (q)	C(23),C(24)	15.1	−2.8

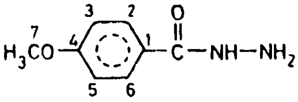
[a] Measured in p.p.m. from SiMe$_4$. [b] Δδ = δ(H$_2$dapmb) − δ[UO$_2$(dapmb)]. [c] s = Singlet, d = doublet, q = quartet.

Hydrogen-1 *and* ^{13}C *N.M.R. Spectra.*—Since complexes (1) and (2) are only slightly soluble in [^{2}H$_6$]dmso in which they are slowly deprotonated to the neutral complex (3), and species (4), (5), and (6) are almost insoluble in all the solvents in which they are stable, we have limited the n.m.r. investigation to a comparison of the spectra of the neutral complex (3) and the ligand.

TABLE 3

25.16 MHz proton noise-decoupled ^{13}C n.m.r. spectral data ([^{2}H$_6$]dmso) for 2,6-diacetylpyridine and 4-methoxybenzoylhydrazine





Carbon atoms	δ *	Carbon atoms	δ *
C=O	190.6	C=O	165.8
C(2),C(6)	152.2	C(4)	161.5
C(4)	139.0	C(2),C(6)	128.8
C(3),C(5)	124.6	C(1)	125.6
C(7),C(8)	25.2	C(3),C(5)	113.6
		C(7)	55.3

* Measured in p.p.m. from SiMe$_4$.

The ^{1}H n.m.r. spectrum ([^{2}H$_6$]dmso) of (3) suggests a symmetric structure, similar to that of the free ligand, with a diamagnetic shift of the protons near to the co-ordinated atoms.

The protons *ortho* to the –C(O)=N–N=C group and the γ protons of the pyridine co-ordinated to the uranyl ion are deshielded, the chemical shift changing from δ 7.9 in the free ligand to δ 8.56 in the neutral complex. The chemical shift of the aromatic protons *meta* to the co-ordinated group $-C(O)=N-N=C$ and the β pyridine protons is, as expected, only slightly affected by co-ordination and is moved *ca.* 0.07 p.p.m. downfield.

The singlet due to the protons of the $-OCH_3$ group is not shifted in the complex (δ 3.90) while the singlet due to the methyl protons of the $CH_3-C=N-$ group experiences a deshielding of 0.55 p.p.m. due to the co-ordination of the imino-nitrogen atoms with the uranyl ion.

Further information on the structure of (3) in solution has been obtained from comparison of (3) and H_2dapmb using 25.16 MHz proton noise-decoupled ^{13}C n.m.r. spectra.

The chemical shift, δ, (p.p.m. from $SiMe_4$) and the chemical-shift changes, Δδ (p.p.m.), accompanying the co-ordination of the ligand in complex (3) are reported in Table 2. The spectra indicate that the two compounds have the same symmetry; *i.e.* a plane of symmetry, which bisects the pyridine ring. Hence, they give the same number of signals (Figure 2).

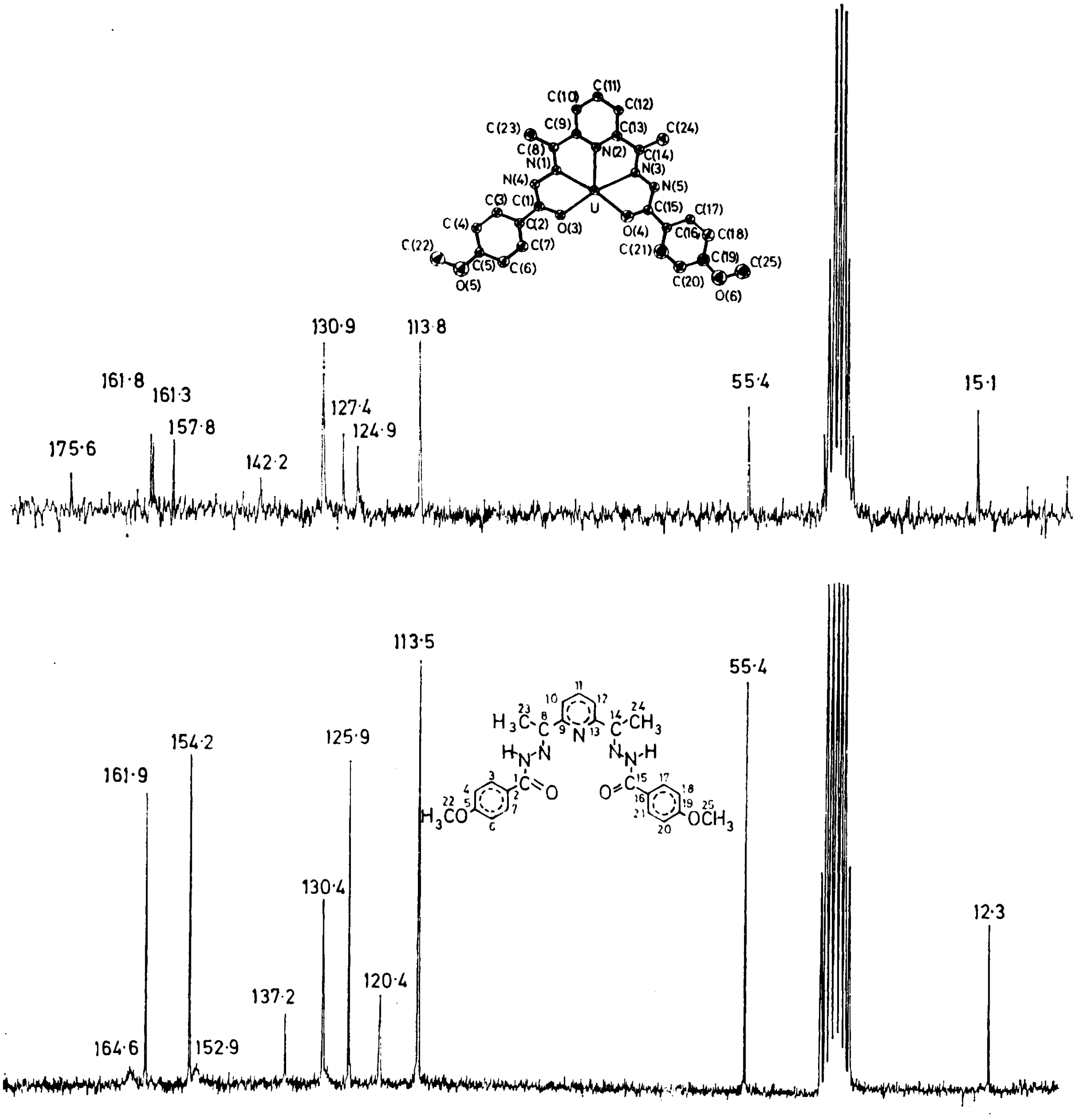
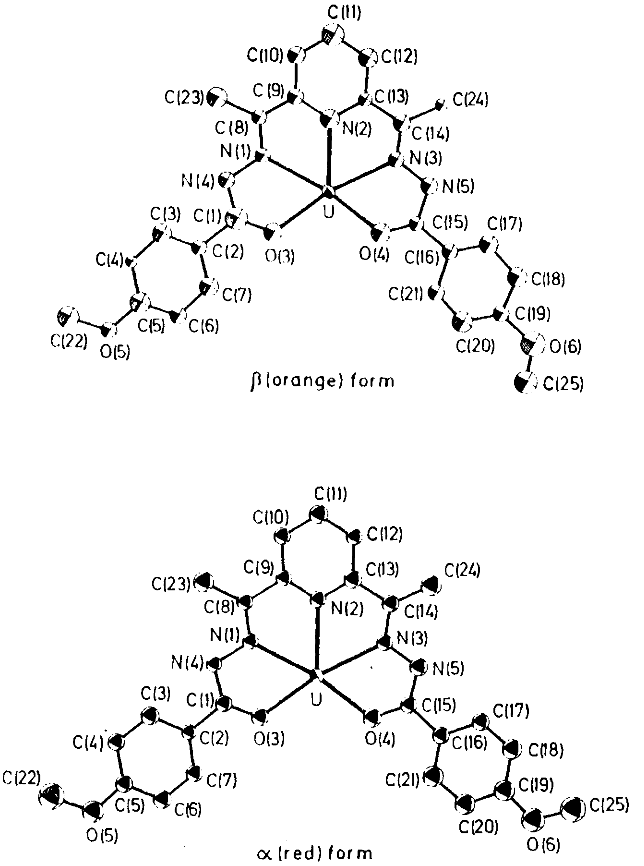


FIGURE 2 25.16 MHz proton noise-decoupled ^{13}C n.m.r. spectra of H_2dapmb and $[UO_2(dapmb)]$ in $[^2H_6]$dmso

The assignments for the ligand have been deduced taking into account the shifts of the carbon atoms of the fragments which form the H_2dapmb molecule (2,6-diacetylpyridine and *p*-methoxybenzoylhydrazine) reported in Table 3.

The numbering scheme of the carbon atoms in both the ligand and complex (3) is the same, see Figure 2.

The signals relating to the carbons near the co-ordinated sites in complex (3) are remarkably deshielded in comparison to the free ligand. The effect of uranyl ion on the carbon resonance of the pyridine ring thus shifts downfield the signals for C(11), C(10), and C(12) by at least 4—5 p.p.m. It is therefore reasonable to expect that the C(9) and C(13) resonance is shifted downfield even more since they are closer to the co-ordinated nitrogen. As a consequence, the signal for C(9) and C(13) which in the free ligand was at 154.24 p.p.m. could in complex (3) be at either 157.8 or 161.3 p.p.m. The latter assignment is much more likely since it gives a deshielding of 7.06 p.p.m. whereas the 157.8 p.p.m. assignment only gives a small deshielding (3.06 p.p.m.). On this basis the signal at 157.8 p.p.m. can only be assigned to the carbon atoms C(8) and C(14) which in the free ligand were at 152.9 p.p.m.



β (orange) form

α (red) form

FIGURE 3 Projection of the molecule on to the mean plane of the co-ordination pentagon for the two crystalline forms showing the atom-numbering system. The O(1) and O(2) atoms overlap the uranium atom and have been omitted for clarity. The 50% probability thermal vibration ellipsoids are produced by the ORTEP program

X-Ray Analysis.—Depending on the method of preparation the neutral complex (3) crystallizes in two different forms. The red is obtained by crystallization of the crude product obtained from the reaction between uranyl acetate and the ligand from ethanol–acetonitrile; the orange one by crystallization of (1) from the same solvent mixture. The main difference in their i.r. spectra is the stretching frequency $\nu_3(UO_2)$ which occurs at 902 cm^{-1} for the former and at 897 cm^{-1} for the latter.

TABLE 4

(*a*) Bond lengths (Å), with standard deviations in parentheses,* for the red form

U–O(1)	1.77(1)	C(1)–C(2)	1.49(2)
U–O(2)	1.77(1)	C(2)–C(3)	1.40(2)
U–O(3)	2.32(1)	C(2)–C(7)	1.38(2)
U–O(4)	2.30(1)	C(3)–C(4)	1.42(2)
U–N(1)	2.47(1)	C(4)–C(5)	1.40(2)
U–N(2)	2.52(1)	C(5)–C(6)	1.37(2)
U–N(3)	2.49(1)	C(6)–C(7)	1.38(2)
O(3)–C(1)	1.26(2)	C(8)–C(9)	1.50(2)
O(4)–C(15)	1.30(2)	C(8)–C(23)	1.50(3)
O(5)–C(5)	1.38(2)	C(9)–C(10)	1.39(2)
O(5)–C(22)	1.47(3)	C(10)–C(11)	1.40(3)
O(6)–C(19)	1.37(3)	C(11)–C(12)	1.40(2)
O(6)–C(25)	1.40(3)	C(12)–C(13)	1.40(2)
N(1)–N(4)	1.41(2)	C(13)–C(14)	·1.48(3)
N(1)–C(8)	1.31(2)	C(14)–C(24)	1.51(3)
N(2)–C(9)	1.33(2)	C(15)–C(16)	1.48(3)
N(2)–C(13)	1.33(2)	C(16)–C(17)	1.41(3)
N(3)–C(14)	1.31(2)	C(16)–C(21)	1.38(3)
N(3)–N(5)	1.40(2)	C(17)–C(18)	1.38(2)
N(4)–C(1)	1.33(2)	C(18)–C(19)	1.39(3)
N(5)–C(15)	1.30(2)	C(19)–C(20)	1.41(3)
		C(20)–C(21)	1.40(2)

(*b*) ' Bite ' and contact distances (Å) within the ' inner core ' for the red form

N(1) · · · N(2)	2.62	O(1) · · · N(2)	3.08
N(2) · · · N(3)	2.63	O(1) · · · N(3)	3.12
N(3) · · · O(4)	2.52	O(2) · · · O(3)	2.94
O(4) · · · O(3)	3.71	O(2) · · · O(4)	2.91
O(3) · · · N(1)	2.52	O(2) · · · N(1)	3.06
O(1) · · · O(3)	2.93	O(2) · · · N(2)	3.06
O(1) · · · O(4)	2.91	O(2) · · · N(3)	2.97
O(1) · · · N(1)	3.02		

* Taking into account the accuracy of cell parameters.

In order to determine possible structural differences, an *X*-ray investigation on both the forms has been performed.

Projection of the molecule along the mean plane of the co-ordinating pentagon for the two crystalline forms is shown in Figure 3. Interatomic distances and inter-

TABLE 5

Bond angles (°), with standard deviations in parentheses,* for the red form

O(1)–U–O(2)	178.8(5)	U–N(3)–C(14)	124.7(10)
O(1)–U–O(3)	90.3(5)	N(5)–N(3)–C(14)	116.2(13)
O(1)–U–O(4)	90.1(4)	N(1)–N(4)–C(1)	108.6(12)
O(1)–U–N(1)	89.2(4)	N(3)–N(5)–C(15)	110.2(14)
O(1)–U–N(2)	89.9(4)	O(3)–C(1)–N(4)	124.9(17)
O(1)–U–N(3)	92.5(5)	O(3)–C(1)–C(2)	119.7(15)
O(2)–U–O(3)	90.8(5)	N(4)–C(1)–C(2)	115.2(15)
O(2)–U–O(4)	90.2(4)	N(1)–C(8)–C(9)	114.0(14)
O(2)–U–N(1)	90.8(4)	N(1)–C(8)–C(23)	124.0(16)
O(2)–U–N(2)	89.0(4)	C(23)–C(8)–C(9)	122.0(15)
O(2)–U–N(3)	86.5(4)	C(8)–C(9)–N(2)	116.3(13)
O(3)–U–N(1)	63.5(5)	C(8)–C(9)–C(10)	119.5(13)
O(3)–U–O(4)	106.8(5)	N(2)–C(9)–C(10)	124.1(14)
O(4)–U–N(3)	63.3(4)	C(9)–C(10)–C(11)	118.2(15)
N(1)–U–N(2)	63.3(4)	C(10)–C(11)–C(12)	117.4(15)
N(2)–U–N(3)	63.3(4)	C(11)–C(12)–C(13)	119.9(15)
U–O(3)–C(1)	123.0(12)	C(12)–C(13)–N(2)	121.7(14)
U–O(4)–C(15)	123.2(10)	N(2)–C(13)–C(14)	117.7(14)
C(5)–O(5)–C(22)	118.8(15)	C(12)–C(13)–C(14)	120.6(15)
C(19)–O(6)–C(25)	118.4(16)	C(13)–C(14)–N(3)	113.8(14)
U–N(1)–N(4)	119.8(8)	C(13)–C(14)–C(24)	123.6(15)
U–N(1)–C(8)	125.2(11)	C(24)–C(14)–N(3)	122.3(15)
N(4)–N(1)–C(8)	115.0(12)	N(5)–C(15)–O(4)	124.2(15)
U–N(2)–C(9)	121.2(10)	N(5)–C(15)–C(16)	118.0(16)
U–N(2)–C(13)	120.4(10)	O(4)–C(15)–C(16)	117.6(15)
C(9)–N(2)–C(13)	118.2(13)	C_{Ph}–C_{Ph}–C_{Ph} mean	120.0
U–N(3)–N(5)	119.0(9)		

* Taking into account the accuracy of cell parameters.

bond angles for the red form are given in Tables 4 and 5, while some least-squares planes and angles between these planes are presented in Table 6. The geometry of the complex in the two structures is very similar; the only significant difference concerns the conformation of the C(25) atom.

Since the crystallographic analysis of the monoclinic crystal form is more accurate (*i.e.*, lower estimated standard deviations on the bond lengths, bond angles, *etc.*) than that of the orthorhombic modification, all data in this section will pertain (unless otherwise stated) to the monoclinic crystal form. However, the corresponding data for the orthorhombic form is available on application to the authors.

TABLE 6

Angles (°) for the red form between some mean planes and the line L defined by O(1)–U–O(2) (for a plane and a line, the angle is to the normal of the plane) *

(1)–(2)	1.9	(2)–(3)	1.8
(1)–(3)	0.3	(2)–(5)	4.5
(1)–(4)	2.6	(2)–(6)	4.3
(1)–(5)	2.6	(3)–(4)	2.8
(1)–(6)	5.0	(3)–(8)	3.3
(1)–(7)	6.4	(4)–(5)	1.7
(1)–(8)	3.0	(4)–(8)	0.7
(1)–L	1.5	(5)–(7)	5.1
		(6)–(7)	11.4

Plane (1): O(3), O(4), N(1), N(2), N(3)
Plane (2): U, O(3), C(1), N(4), N(1)
Plane (3): U, N(1), C(8), C(9), N(2)
Plane (4): U, N(2), C(13), C(14), N(3)
Plane (5): U, N(3), N(5), C(15), O(4)
Plane (6): C(2)—(7)
Plane (7): C(16)—(21)
Plane (8): N(2), C(9)—(13)

* Equations of these planes and the deviations of relevant atoms from them are deposited in SUP 22744.

The crystal structure is built up of monomeric molecules. Seven-fold co-ordination of uranium(VI) is found in both α and β forms, with five atoms in the equatorial plane. The linear uranyl group, perpendicular to the plane, has been found before in many uranyl compounds (for a complete listing see Table 7 in ref. 21). The bond distances and angles reveal no surprises when compared with other equatorial five-co-ordinate uranyl complexes utilising an N_3O_2 donor set.[22] The co-ordination plane defined by the donor set, exhibits a very high degree of planarity, especially in the α form [maximum deviation being 0.05 Å for N(3)]. The uranium atom is 0.02 Å from the plane, but the most interesting feature of the complex is that it is virtually planar, except for carbon atoms C(22) and C(25) in the methoxy groups.

The four five-membered chelating rings are planar within 0.02 Å, as are the three aromatic rings, and the angles between all the planes are <5°.

In the β form the deviations of the donor atoms (from the best co-ordination plane) are as high as 0.11 Å. The four chelating rings are planar within 0.06 Å, the complex in the β form can however be considered to retain planarity. In fact, the angles between the four chelating rings and the three aromatic rings are all <10°.

The β form has a unit-cell volume 68 Å^3 smaller than that of the α form. Such a cell contraction is not uncommon. It has been recognized, for example, in the dimorphous tricarbonylphenanthrenechromium(0) (contraction 98 Å^3),[23] (antipyrine)dinitratocopper(II) (64 Å^3),[24] 3-methylcyclopropenebis(triphenylphosphine)-platinum(0) (73 Å^3),[25] and tetrakis(thiourea)mercury(II) chloride (65 Å^3).[26]

The reasons for the observed contraction are rather obscure, and we can offer no feasible explanation for its origin. In fact, there are no abnormally short intermolecular contacts either in the monoclinic or in the orthorhombic crystals, the most interesting being in the β form where there are two relatively short contacts [O(2) ··· C(12) $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ 3.13 Å and O(6) ··· C(23) $(-1 + x, y, z)$ 3.18 Å]. The shortest contact in the α form being 3.30 Å [O(3) ··· C(12) $(-1 + x, y, z)$]. Hence we conclude that the β form is more closely packed.

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REFERENCES

[1] G. Paolucci and G. Marangoni, *Inorg. Chim. Acta*, 1977, **24**, L5—L6.

[2] G. Paolucci, G. Marangoni, G. Bandoli, and D. A. Clemente, *J.C.S. Dalton*, 1980, 459.

[3] D. Wester and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 755.

[4] L. El Sayed and M. F. Iskander, *J. Inorg. Nuclear Chem.*, 1971, **33**, 435.

[5] M. F. Iskander, A. M. El Aggan, L. S. Refaat, and L. El Sayed, *Inorg. Chim. Acta*, 1975, **14**, 167.

[6] M. F. Iskander, L. El Sayed, A. F. M. Hefny, and S. E. Zayan, *J. Inorg. Nuclear Chem.*, 1976, **38**, 2209.

[7] M. F. Iskander, L. El Sayed, and M. A. Lasheen, *Inorg. Chim. Acta*, 1976, **16**, 147.

[8] M. F. Iskander and S. Saddeck, *Inorg. Chim. Acta*, 1977, **22**, 141.

[9] H. H. Fox and J. T. Gibas, *J. Org. Chem.*, 1952, **17**, 1653.

[10] G. Marangoni, S. Degetto, and U. Croatto, *Talanta*, 1973, **20**, 1217.

[11] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1969, vol. 1, p. 99.

[12] D. T. Cromer and J. A. Waber, *Acta Cryst.*, 1965, **18**, 104.

[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[14] J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, The *X*-Ray System version of June 1972. Tech. Rep. TR-192. Computer Science Center, University of Maryland, College Park, Maryland.

[15] J. F. Geldard and F. Lions, *Inorg. Chem.*, 1962, **2**, 2262; *J. Amer. Chem. Soc.*, 1962, **84**, 2262; R. W. Green, P. S. Hallman, and F. Lions, *Inorg. Chem.*, 1964, **3**, 376.

[16] M. Mashima, *Bull. Chem. Soc. Japan*, 1962, **35**, 1882; *ibid.*, 1963, **36**, 210.

[17] A. Dutta Ahmed and N. Ray Chaudhuri, *J. Inorg. Nuclear Chem.*, 1971, **33**, 189.

[18] K. E. Jabalpurwala, K. A. Venkatachalam, and M. B. Kabadi, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1027.

[19] C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy,' Academic Press, New York, 1963, pp. 187—225.

[20] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Chapman and Hall, London, 1975, pp. 122—124.

[21] D. A. Clemente, G. Bandoli, F. Benetollo, M. Vidali, P. A. Vigato, and U. Casellato, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1999.

[22] G. Bandoli, D. A. Clemente, and M. Biagini Cingi, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1709; M. N. Akhtar and A. J. Smith, *Acta Cryst.*, 1973, **B29**, 275.

[23] K. W. Muir, G. Ferguson, and G. A. Sim, *J. Chem. Soc.* (*B*), 1968, 467; J. M. Guss and R. Mason, *J.C.S. Dalton*, 1973, 1834.

[24] C. Brassy, A. Renaud, J. Delettré, and J. P. Mornon, *Acta Cryst.*, 1974, **B30**, 2246 and 2500.

[25] J. J. de Boer and D. Bright, *J.C.S. Dalton*, 1975, 662.

[26] A. Korczynski, M. Nardelli, and M. Pellinghelli, *Cryst. Struct. Comm.*, 1972, **1**, 327; P. D. Brotherton and A. H. White, *J.C.S. Dalton*, 1973, 2696.