Reactivity of Uranyl Ion with Quinquedentate Chelating Hydrazine Derivatives. Part 3.† 2,6-Diacetylpyridine (2′-Pyridylhydrazone) (4″-Toluoylhydrazone)

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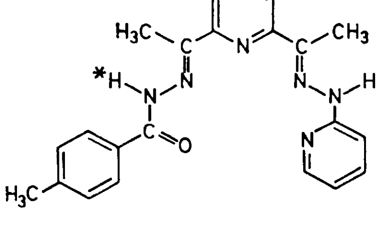
The new title ligand HH*dappt reacts with $[UO_2][NO_3]_2.6H_2O$ in ethanol to give $[UO_2(Hdappt)][NO_3]$ (1) in which the ligand is co-ordinated in its semienolized monodeprotonated form, with formation of four fused five-membered rings around the uranyl moiety. The related complex $[UO_2(Hdappt)][BPh_4]$ (2) has been synthesized by the action of an excess of $Na[BPh_4]$ on (1). Compounds (1) and (2) when treated with a number of non-hydroxylated bases are transformed to deep violet $[UO_2(dappt)]$ (3) which, owing to the presence of only one reactive U–N covalent bond, reacts with hydroxylated species such as benzoic and acetic acid to give monomeric products in which the equatorial co-ordination number is increased from five to six; $[UO_2(Hdappt)(O_2CC_6H_5)]$ (4) and $[UO_2(Hdappt)(O_2CCH_3)]$ (5), in both of which the carboxylate group is unidentate, have been isolated. Both the ligand and complexes have been characterized by physicochemical measurements.

In previous papers [1-4] we have reported the synthesis and physicochemical characterization of a number of charged and neutral complexes of the uranyl ion, obtained by the reaction of uranyl salts with 2,6-diacetylpyridine bis(2′-pyridylhydrazone), (H_2dapp), and 2,6-diacetylpyridine bis(4′-methoxybenzoylhydrazone), (H_2dapmb), in all of which the symmetrical ligands behave as quinquedentate donors with formation of four fused five-membered rings around the uranyl moiety. It has been shown that H_2dapp reacts with uranyl nitrate and perchlorate in ethanol at room temperature to give 1 : 1 charged adducts, whereas reactions of H_2dapmb, under the same experimental conditions, result in the formation of complexes in which the ligand is present as its semienolized monodeprotonated form.

Reaction with non-hydroxylated bases in aprotic solvents causes further deprotonation of the charged species with formation of the neutral $[UO_2(dapp)]$ [3] and $[UO_2(dapmb)]$.[4] The former complex is sensitive to the attack of hydroxylated reagents, which results in release of the ligand in the reaction with water and the formation of polymeric alkoxy-species in the reaction with methanol and ethanol. This is consistent with the known relative weakness of U–N covalent bonds, compared to U–O bonds. Because of this sensitivity $[UO_2(dapp)]$ is not a suitable complex for study of the reactivity of U–N covalent bonds towards hydroxylated reagents.

In order to overcome this difficulty we have now synthesized the mixed 2,6-diacetylpyridine (2′-pyridylhydrazone) (4″-toluoylhydrazone), HH*dappt. This ligand reacts with uranyl nitrate under the above experimental conditions to give the charged species $[UO_2(Hdappt)][NO_3]$ (1), which can be deprotonated to the neutral $[UO_2(dappt)]$ (3) which contains only one reactive covalent U–N bond. The latter complex reacts with species such as benzoic and acetic acid to give products in which the equatorial co-ordination number is increased from five to six, and yet the U–N bond is retained. The rates of these changes can be slow enough to be followed by standard repetitive scanning spectrophotometry.



HH*dappt

In this paper we report the preparation and the physicochemical characterization of the new ligand and the derived complexes.

EXPERIMENTAL

Reagents.—Reagent-grade uranyl nitrate hexahydrate (Fluka), 2,6-diacetylpyridine, 2-pyridylhydrazine (Ega), sodium tetraphenylborate and pure benzoic acid (C. Erba) were used without further purification. 4-Toluoylhydrazine was prepared as reported.[5] Glacial acetic acid, benzene, and acetonitrile were carefully purified and dried.[6,7]

Physical Measurements.—Infrared spectra (400—4000 cm^{-1}) were recorded for KBr pellets or Nujol and hexachlorobutadiene mulls between KBr plates on a Perkin-Elmer 621 spectrophotometer. Proton and ^{13}C n.m.r. spectra at 60 and 25.16 MHz respectively, for solutions in 99% $[^2H_6]$dimethyl sulphoxide, were obtained on Varian T-60 and Varian HL-100 (Fourier transform) instruments. Electronic spectra for solutions in acetonitrile (200—600 nm) were recorded on a Cary-17D double-beam spectrophotometer at 25 °C. Molar conductivities at 25 °C were measured on 5×10^{-4} mol dm^{-3} solutions in acetonitrile with an LKB 3216B conductivity bridge.

Preparation of the Ligand.—2,6-*Diacetylpyridine* (2′-*Pyridylhydrazone*) (4″-*Toluoylhydrazone*), HH*dappt.—To a solution of 2,6-diacetylpyridine (6.52 g) in absolute ethanol (100 cm^3) was added dropwise with stirring a solution of 2-hydrazinopyridine (4.36 g) dissolved in the same solvent, and the mixture left to react under nitrogen for 24 h. The resulting pale yellow solution was concentrated until a white product began to precipitate. This product (0.85 g), separated and crystallized from acetone, was identified [3] as

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† Part 2 is ref. 4.

pure 2,6-diacetylpyridine bis(2′-pyridylhydrazone), m.p. 195—196 °C. The filtered solution was evaporated to dryness and the crude solid residue dissolved in the minimum volume of dichloromethane. The solution was then adsorbed on a silica column (100 × 3 cm) pretreated with ethyl acetate–n-hexane (70 : 30) and eluted with the same mixture of solvents. The yellow isomer (0.4 g) of 2,6-diacetylpyridine mono(2′-pyridylhydrazone) was thus separated from the white one (3.2 g), *Z*- and *E*-Hdapmp respectively, both of which were recovered and recrystallized from dichloromethane–n-hexane.

To the solution of *E*-Hdapmp (3 g) in a mixture of absolute ethanol (100 cm³) and dichloromethane (15 cm³) was slowly added with stirring an equimolar amount of 4-toluoylhydrazine dissolved in the same mixture, and the resulting solution left to react under reflux for several hours, the progress of the reaction being checked by t.l.c. The solution was then evaporated to dryness under reduced pressure and the crude product dissolved in dichloromethane. The addition of n-hexane resulted in the precipitation of the pure HH*dappt (1.6 g) as white needles. Analytical and physicochemical data for both the intermediate isomers and the final ligand are reported in Tables 1 and 2.

Preparation of the Complexes.—$[UO_2(Hdappt)][NO_3]$ (1). (*a*) Solid HH*dappt (1 g) was added to a stirred refluxing solution of uranyl nitrate hexahydrate (1.32 g) in absolute ethanol (100 cm³). At first the ligand dissolved readily, but near the end of the addition the orange complex began to precipitate. It was stirred for 2 h and the complex filtered off, washed with ethanol, and dried under vacuum.

(*b*) A suspension of *E*-Hdapmp (0.64 g) in ethanol (30 cm³) was added to a stirred solution of $[UO_2][NO_3]_2 \cdot 6H_2O$ (1.29 g) in ethanol (50 cm³) at room temperature. After a few minutes, during which the initial suspension dissolved, a yellow product precipitated and was stirred for 2 h. A suspension of 4-toluoylhydrazine (0.375 g) in ethanol (50 cm³) was then slowly added with stirring and the mixture refluxed for 3 h, the progress of the reaction being followed by the disappearance of the 4-toluoylhydrazine by t.l.c. The orange complex formed was recovered as in (*a*).

$[UO_2(Hdappt)][BPh_4]$ (2). To a suspension of (1) in ethanol was added with stirring a large excess of $Na[BPh_4]$, dissolved in the same solvent, and the resulting mixture left to reflux for 3 h. The brownish orange product formed was filtered off, washed with ethanol, and dried under vacuum.

$[UO_2(dappt)]$ (3). To compound (1) (0.6 g) suspended in anhydrous acetonitrile (10 cm³) was slowly added with stirring an excess of 1,8-bis(dimethylamino)naphthalene (proton sponge), dissolved in the same solvent (10 cm³). The deep violet product which formed rapidly was stirred under nitrogen for 15 h and then filtered off, washed with acetonitrile and n-pentane, and dried under vacuum (0.52 g, 95%, as brilliant microcrystals).

$[UO_2(Hdappt)(O_2CC_6H_5)]$ (4). To a suspension of (3) (0.2 g) in anhydrous benzene (20 cm³) was added with stirring an excess of benzoic acid dissolved in the same solvent (20 cm³), under nitrogen at room temperature. During the addition a deep yellow product began to precipitate. The mixture was left to react for several hours and then the product was filtered off, washed with benzene, and dried under vacuum.

$[UO_2(Hdappt)(O_2CCH_3)]$ (5). This complex was obtained as a yellow powder in the same manner as (4) but using purified acetic acid.

Analytical and physical data for all the complexes are reported in Table 3. Uranium was determined gravimetrically as the tetraphenylarsonium salt of dioxobis(pyridine-2,6-dicarboxylato)uranate(VI).[8]

RESULTS AND DISCUSSION

The condensation of 2,6-diacetylpyridine with 2-pyridylhydrazine leads to the formation of 2,6-diacetylpyridine mono(2′-pyridylhydrazone) which exists in two geometrical forms, *E*- and *Z*-Hdapmp, respectively. In the *Z* configuration intramolecular hydrogen bonding is possible between the imino-group and the heterocyclic nitrogen of the substituted pyridine residue, as occurs in the closely related *Z* isomer of pyridine-2-carbaldehyde 2′-pyridylhydrazone.[9] The *E* isomer can only participate in intermolecular hydrogen bonding. Proton n.m.r.

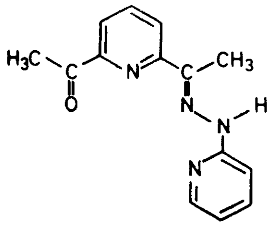
TABLE 1

Analytical and physical data for *Z*- and *E*-Hdapmp isomers and HH*dappt

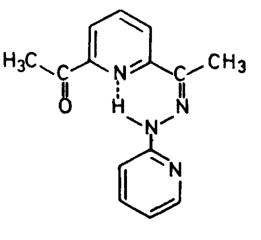
Compound	M.p. (θ_c/°C)	Analysis (%) [a] C	H	N	¹H N.m.r.[b]	Characteristic absorptions (cm⁻¹)
Z-Hdapmp	133—134	66.15 (66.15)	5.30 (5.50)	22.0 (22.05)	2.43 (s, 3 H, CH_3CO), 2.82 (s, 3 H, CH_3CN), 6.60—8.67 (m, 7 H, pyridine H), 13.75 (s, 1 H, =NH)	3 175 ν(N–H) 1 712 ν(C=O) 1 600 [c] 1 570 ν(C=N)? 1 500 ν(N–H)
E-Hdapmp	160—161	65.95 (66.15)	5.80 (5.50)	22.05 (22.05)	2.45 (s, 3 H, CH_3CO), 2.65 (s, 3 H, CH_3CN), 6.68—8.47 (m, 7 H, pyridine H), 9.95 (s, 1 H, =NH)	3 285 ν(N–H) 1 695 ν(C=O) 1 600 [c] 1 565 ν(C=N)? 1 520 ν(N–H)
HH*dappt	229—230	68.15 (68.4)	5.95 (5.70)	21.55 (21.75)	2.42 (s, 3 H, $C_6H_4CH_3$-*p*), 2.50 (s, 3 H, CH_3C=N–NH), 2.57 (s, 3 H, CH_3C=N–NH *), 6.70—8.27 (m, 11 H, aromatic and pyridine H) 9.93 (s, 1 H, =NH) 10.73 (s, 1 H, =NH *)	3 260 ν(N–H*) 3 175 ν(N–H) 1 660 ν(C=O) 1 645 ν(C=N) [d] 1 598 [e] 1 566 ν(C=N) [f]

[a] Calculated values are given in parentheses. [b] δ in p.p.m. relative to $SiMe_4$; s = singlet, m = multiplet. [c] Pyridine ring I breathing band. [d] Pyridylhydrazone residue. [e] Pyridine ring I breathing band and substituted benzene ring skeletal vibrations. [f] Benzoylhydrazone residue.

spectra of solutions of similar concentration in [$^2H_6$]dimethyl sulphoxide show a minor deshielding of the imino-proton for the *E* isomer, which resonates at δ 9.95 as compared with δ 13.75 for the *Z* isomer.



E-Hdapmp



Z-Hdapmp

In the second step of the reaction, *E*-Hdapmp reacts with 4-toluoylhydrazine to give the quinquedentate HH*dappt, the i.r. spectrum of which shows characteristic bands at 3 260 and 3 175 cm^{-1}, due to the N–H stretching of the benzoyl and pyridylhydrazone residues, respectively. The resonances of the related imino-protons in the ^{1}H n.m.r. spectrum fall at δ 10.73 and 9.93 respectively.

The ligand HH*dappt reacts with uranyl nitrate in ethanol to give the charged species [UO_2(Hdappt)][NO_3] (1), independently of the molar ratio and temperature used. Co-ordination occurs through the semienolized mono-deprotonated form of the ligand, with formation of four fused five-membered rings around the uranyl moiety, in the same way as for the symmetrical H_2dapp and H_2-dapmb;[3,4] however, H_2dapp only gives adducts.[3]

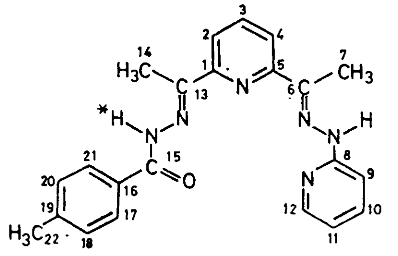
The i.r. spectrum of (1) shows some band shifts which define the co-ordination mode of the ligand. The ν(N–H) of the pyridylhydrazone residue falls at 3 210 cm^{-1}, and the amide I band [ν(C=O)], which occurs in the free ligand at 1 660 cm^{-1}, disappears and is replaced by a new band at 1 036 cm^{-1}, due to the ν(C–O) stretching vibration. The ν(C=N) stretching vibration, tentatively assigned at 1 556 cm^{-1} to the pyridylhydrazone part of the free ligand, is lowered by co-ordination to 1 526 cm^{-1} as observed for analogous complexes,[10] and the intensity of the band centred at *ca.* 1 620 cm^{-1}, due to the =C=N–N=C= absorption,[11] is increased. The asymmetric stretching $\nu_3(UO_2)$ falls at 919 cm^{-1} in good agreement with frequency values found for other charged five-co-ordinated chelated uranyl complexes.[3,4] The ionic nitrate group absorbs strongly at 1 384 cm^{-1}, as usually found, and this band is not present in the spectrum of (2), in which the nitrate group is replaced by tetraphenylborate.

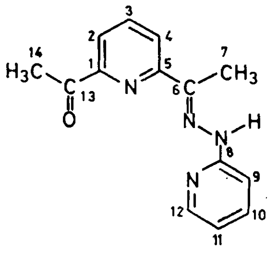
The ionic nature of complexes (1) and (2) is confirmed by the values of the molar conductivity, 108 and 86 S cm^2 mol^{-1} respectively, for 5×10^{-4} mol dm^{-3} solutions, typical of 1 : 1 electrolytes in acetonitrile.[12]

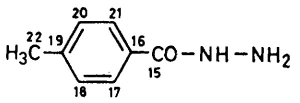
Owing to the ability of the diazapropene sequence =C=N–NH– to be deprotonated,[3,13-21] compounds (1) and (2), when treated with a number of non-hydroxylated bases, *e.g.* pyridine, sodium hydride, methyl-lithium, and 1,8-bis(dimethylamino)naphthalene (proton sponge) in anhydrous acetonitrile, are transformed, very easily and quantitatively using the proton sponge, to the same neutral deep violet compound [UO_2(dappt)] (3). Complex (3) is non-conducting in acetonitrile solution, and

TABLE 2

25.16-MHz Proton-noise-decoupled ^{13}C n.m.r. spectral data ([$^2H_6$]dimethyl sulphoxide) for HH*dappt and the fragments which form this molecule [a]







HH*dappt				*E*-Hdapmp		*p*-Toluoylhydrazine	
Carbon	δ_C	Carbon	δ_C	Carbon	δ_C	Carbon	δ_C
C^{15}=O	n.v.[b]	C^{16}	131.1	C^{13}=O	199.4	C^{15}=O	161.1
C^8	157.3	C^{17}—C^{21}	128.8	C^8	157.2	C^{19}	141.0
C^{13}	157.2	C^{18}—C^{20}	128.4	C^1	155.4	C^{16}	130.6
C^5	154.9	C^4, C^2	119.6, 119.2	C^5	151.9	C^{17}—C^{21}	128.9
C^1	154.0	C^{11}	115.8	C^{12}	147.6	C^{18}—C^{20}	127.0
C^{12}	147.4	C^9	107.3	C^6	143.3	C^{22}	21.0
C^6	143.9	C^{22}	21.1	C^3, C^{10}	138.1, 137.5		
C^{19}	141.6	C^{14}	12.4	C^2	123.2		
C^3	138.0	C^7	11.2	C^4	120.0		
C^{10}	136.8			C^{11}	116.0		
				C^9	107.3		
				C^{14}	25.5		
				C^7	11.1		

[a] In p.p.m. from $SiMe_4$. [b] n.v. = Not visible.

TABLE 3

Analytical and physical data for the complexes

Complex	Analysis (%) [a]				Characteristic i.r. absorptions (cm^{-1})	$\lambda_{max.}$/nm
	C	H	N	U		
(1) $[UO_2(Hdappt)][NO_3]$ [b]	36.65 (36.8)	2.95 (2.95)	13.4 (13.65)	33.05 (33.2)	3 210 ν(N–H) 1 618 ν(=C=N–N=C=) 1 384 $\nu(NO_3)$ 1 036 ν(C–O) 919 $\nu_3(UO_2)$	528, 443, 380, 359
(2) $[UO_2(Hdappt)][BPh_4]$ [c]	56.0 (56.7)	3.95 (4.20)	8.60 (8.65)	24.2 (24.45)	3 320 ν(N–H) 1 618 ν(=C=N–N=C=) 1 030 ν(C–O) 918 $\nu_3(UO_2)$	529, 441, 377, 350
(3) $[UO_2(dappt)]$	40.45 (40.35)	3.20 (3.05)	12.9 (12.85)	36.25 (36.4)	1 610 ν(=C=N–N=C=) 1 028 ν(C–O) 908 $\nu_3(UO_2)$	525, 440, 378, 357, 346 (sh)
(4) $[UO_2(Hdappt)(O_2CC_6H_5)]$	44.85 (44.85)	3.05 (3.35)	10.65 (10.8)	30.55 (30.65)	1 595 ν_{asym}(O–C–O) 1 380 ν_{sym}(O–C–O) 1 033 ν(C–O) 910 $\nu_3(UO_2)$	
(5) $[UO_2(Hdappt)(O_2CCH_3)]$	39.6 (39.3)	3.30 (3.40)	11.45 (11.95)		1 598 ν_{asym}(O–C–O) 1 380 ν_{sym}(O–C–O) 1 032 ν(C–O) 910 $\nu_3(UO_2)$	

[a] Calculated values are given in parentheses. [b] $\Lambda = 108$ S cm^2 mol^{-1}. Proton n.m.r. (from $SiMe_4$): δ 9.85 (s, 1 H, =NH), 7.08—8.63 (m, 11 H, pyridine and aromatic H), 3.35 (s, 3 H, $CH_3C{=}N{-}N{=}CO$), 3.10 (s, 3 H, $CH_3C{=}N{-}NH$), and 2.50 p.p.m. (s, 3 H, $C_6H_4CH_3$-*p*). [c] $\Lambda = 86$ S cm^2 mol^{-1}.

although its i.r. spectrum is rather complex there is no evidence for N–H and nitrate stretching vibrations, while $\nu_3(UO_2)$ is lowered to 908 cm^{-1}, following the same trend found for the bis-pyridyl- and aroyl-hydrazone species,[3,4] on passing from charged to neutral complexes. Typically, ν(C–O) stretching falls at 1 028 cm^{-1}, while new strong bands in the 1 100—1 500 cm^{-1} region may be due to vibrations of the pyridine ring in the electronic configuration induced by deprotonation, as observed in the fully nitrogenated neutral complex $[UO_2(dapp)]$ [3] and in related transition-metal complexes.[13-21]

Owing to the presence of only one reactive covalent U–N bond, compound (3) reacts with hydroxylated species such as benzoic and acetic acid to give monomeric products in which the equatorial co-ordination number of the uranyl ion is increased from five to six, and yet the U–N bond is retained. Such behaviour can be accounted for by the presence of the strong covalent U–O bond at the other side of the molecule, which has been shown [4] to be stable to the attack of hydroxylated reagents, without releasing the ligand, as is observed in the analogous reactions of $[UO_2(dapp)]$.[3] These reactions of (3) with the above organic acids in anhydrous acetonitrile result in the formation of the neutral monodeprotonated species $[UO_2(Hdappt)(O_2CC_6H_5)]$ (4) and $[UO_2(Hdappt)(O_2CCH_3)]$ (5) respectively. Both benzoate and acetate act as unidentate ligands in these complexes as indicated by the frequencies of the asymmetric and symmetric ν(O–C–O) stretching vibrations, which fall at *ca.* 1 600 and 1 380 cm^{-1} respectively (these regions of the spectra are rather complex). Thus these bands are shifted to higher and lower frequencies respectively compared to the free carboxylate ion.[22] Free benzoate and acetate absorb at about 1 590 and 1 425 cm^{-1}. Furthermore equatorial six-co-ordination lowers the $\nu_3(UO_2)$ stretching to 910 cm^{-1} compared with the same vibration in the five-co-ordinated species (1) and (2), at 919 and 918 cm^{-1} respectively, paralleling the findings for analogous uranyl complexes with quinquedentate chelating donors.[3,4]

Preliminary kinetic experiments show that the reactions of (3) with organic acids go to equilibrium, the position of which depends on the concentration of added acid. The rate of change is slow enough to be followed by repetitive scanning spectrophotometry and the spectra are characterized by a well defined isosbestic point. The mechanism of the reaction is now under investigation.

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