Synthesis and Characterisation of Uranium(IV) Nitrate Complexes with Piperazines

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Uranium(IV) complexes of empirical formula $U(NO_3)_4L_2$ (L = piperazine, 1-methyl-, 2-methyl-, 1-phenyl-, 1,4-dimethyl-, 2,6-dimethyl-, or 2,5-dimethyl-piperazine) have been prepared by a new method involving the *in situ* reaction of uranium(IV) nitrate with the ligands. Infrared spectral studies indicate the nitrate groups to be co-ordinated in a chelating bidentate fashion and the piperazines in a chair conformation. The electronic spectra and magnetic properties are also discussed.

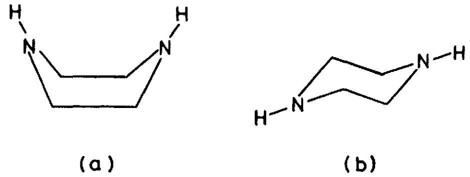
Piperazines which exist in the chair conformation in their free state can form complexes in which they are either in boat form (a) or in chair form (b), giving chelated and non-chelated polymeric complexes respectively. Bearing this property in mind, we have already synthesised a wide variety of complexes of some actinides [1-4] with these highly basic ligands.

In this paper we report complexes of $U(NO_3)_4$ with piperazine (pipz), 1-methylpiperazine (1Me-pipz), 2-methylpiperazine (2Me-pipz), 1-phenylpiperazine (1Ph-pipz), 1,4-dimethylpiperazine (1,4Me_2-pipz), 2,6-dimethylpiperazine (2,6Me_2-pipz), and 2,5-dimethylpiperazine (2,5Me_2-pipz).

Results and Discussion

Synthesis.—Uranium(IV) nitrate complexes were prepared by a new method of direct interaction of the salt with piperazines. Green complexes of formula $U(NO_3)_4L_2$ were obtained by mixing ethanolic solutions of the bases with an ethanolic solution of uranium(IV) nitrate prepared *in situ* according to reaction (1). To the best of our knowledge this is the first report of the isolation of uranium(IV) nitrate complexes by this route. Moreover, this is also the first report of uranium(IV) nitrate complexes with N-donors. In their effort to obtain uranium(IV) nitrate complexes by a similar process of direct interaction of the salt with bases, Bagnall *et al.*[5] attempted the isolation of uranium(IV) nitrate from green uranium(IV) solution in acetone by evaporation *in vacuo* at room temperature. However, as the green solid separated in the last stages of evaporation it was oxidised spontaneously to uranium(VI). Recently du Preez and van Vuuren[6] employed the green filtrate in acetone for conductometric titrations after removing the precipitated silver chloride; however, they did not use this solution for the isolation of uranium(IV) nitrate complexes. These workers appear to use only (two) indirect methods for the synthesis of uranium(IV) nitrate complexes. In one of these, $Cs_2U(NO_3)_6$ is suspended in a suitable solvent and excess of ligand is added.[6-11] The complexes obtained, usually in the form of oils, are treated with 2-methylbutane or dried under vacuum for a long time to give green products. In the other method the corresponding uranium(IV) chloride complex is dissolved in an appropriate solvent and a solution of $AgNO_3$ in acetonitrile is added to precipitate the green uranium(IV) nitrate complex.[5,11,12] It was admitted[8] that the major problem with the first method is the elimination of liberated caesium nitrate. This is, however, overcome by selecting a solvent in which the complex dissolves but the caesium nitrate does not. Thus a single solvent cannot be used throughout. Moreover, this method cannot be employed for the cases where insoluble uranium(IV) nitrate complexes are obtained because it may not be possible to separate them from caesium nitrate. The second method can be applied only in cases where the corresponding uranium(IV) chloride complexes are soluble. The present method is applicable to all types of products, *i.e.* soluble, insoluble, and oils, and there is no fear of contamination with any impurity. The general applicability of this method was tested by synthesising and identifying (by elemental analyses and i.r. spectroscopy) the following known uranium(IV) nitrate complexes: $U(NO_3)_4\cdot2.5dma$,[5] $U(NO_3)_4\cdot4tppo$,[7] $U(NO_3)_4\cdot2hmpa$,[8] and $U(NO_3)_4\cdot3dmso$.[12,*]

$$UCl_4 + 4AgNO_3 \longrightarrow U(NO_3)_4 + 4AgCl\downarrow \quad (1)$$


(a) (b)

Like Bagnall *et al.*,[5] we also tried to isolate uranium(IV) nitrate by the vaporation of its solution in ethanol, but here too it was oxidised to uranium(VI) after a longer time (48 h).

All the complexes are non-hygroscopic and can be kept in air for 3—4 h without visible moistening. However, they are oxidised to yellow uranium(VI) if exposed to air for 1—2 d. They do not melt but decompose to black solids at *ca.* 300 °C. Due to their insolubility, molecular-weight and molar conductance determinations could not be performed. Analytical data are given in Table 1.

Infrared Spectral Studies (4 000—250 cm^{-1}).—The NH stretch which appears at *ca.* 3 400 cm^{-1} for the free piperazines is observed as a broad band in the region 3 400—3 150 cm^{-1} for the complexes studied. This downward shift,[13,14] which is indicative of co-ordination of the NH nitrogen atom, receives support from an additional observation; the shift in the δ(NH) frequency which appears at *ca.* 1 650 cm^{-1} for the free piperazines and in the range 1 625—1 620 cm^{-1} for the complexes.[13] The broadness of the band due to ν(NH) may be caused by hydrogen bonding.[15] The CH stretch of NCH_3 which appears at 2 750 and 2 810 cm^{-1} in the i.r. spectra of 1-methyl- and 1,4-dimethyl-piperazine is not observed in the i.r. spectra of the complexes. It presumably shifts to higher frequencies, and is

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* dma = Dimethylacetamide, tppo = triphenylphosphine oxide, hmpa = hexamethylphosphoramide, and dmso = dimethyl sulphoxide.

Table 1. Analytical and magnetic data for the complexes

Complex	Analysis[a]/% M	C	H	N	S^b/c.g.s. units	θ^c/K	$\mu_{eff.}$ 88	299 K
(1) $U(NO_3)_4(pipz)_2$	35.8	14.75	3.40	12.50	0.941	33.12	2.39	2.83
	(36.1)	(14.6)	(3.30)	(12.75)				
(2) $U(NO_3)_4(1Me\text{-}pipz)_2$	34.50	17.55	3.40	8.20	0.862	44.08	2.36	2.82
	(34.7)	(17.5)	(3.50)	(8.15)				
(3) $U(NO_3)_4(2Me\text{-}pipz)_2$	34.5	17.5	3.50	8.10	0.933	44.15	2.37	2.82
	(34.7)	(17.5)	(3.50)	(8.15)				
(4) $U(NO_3)_4(1Ph\text{-}pipz)_2$	29.1	29.8	3.40	7.20	0.880	44.00	2.41	2.81
	(29.4)	(29.6)	(3.45)	(6.90)				
(5) $U(NO_3)_4(1,4Me_2\text{-}pipz)_2$	33.1	20.7	4.40	12.00	0.921	68.00	2.36	2.79
	(33.35)	(20.15)	(3.90)	(11.75)				
(6) $U(NO_3)_4(2,6Me_2\text{-}pipz)_2$	33.2	20.1	4.00	11.8	0.925	69.00	2.39	2.81
	(33.35)	(20.15)	(3.90)	(11.75)				
(7) $U(NO_3)_4(2,5Me_2\text{-}pipz)_2$	33.4	20.15	4.00	11.8	0.948	77.01	2.33	2.80
	(33.35)	(20.15)	(3.90)	(11.75)				

[a] Required values are given in parentheses. [b] Slopes of plots $1/\chi_M$ *vs.* T. [c] Obtained by extrapolating the plots mentioned in *b* to $1/\chi_M = 0$.

Table 2. Infrared spectral absorptions of the nitrate group[a] in the complexes

Complex	$\nu_{1(4)}{}^b$	ν_2	$\nu_3{}^d$	$\nu_{4(1)}{}^b$	$\nu_5{}^d$	ν_6	$(\nu_2 + \nu_3) - (\nu_2 + \nu_5) = \Delta_1$	$(\nu_2 + \nu_{1(4)}) - (\nu_2 + \nu_{4(1)}) = \Delta_2$
(1)	1 475s	1 020s	750w	1 310s	715w	815s	1 770 − 1 720 = 50	2 530 − 2 310 = 220
(2)	1 475s	1 025s	760w	1 310s	715w	815s	1 760 − 1 710 = 50	2 530 − 2 320 = 210
(3)	1 470s	1 020s	760w	1 310s	715w	810s	1 760 − 1 710 = 50	2 540 − 2 320 = 220
(4)	1 470s	1 025s	760w	1 310s	715w	815s	1 760 − 1 700 = 60	2 540 − 2 310 = 230
(5)	1 470s	1 020s	760w	1 310s	710w	815s	1 770 − 1 720 = 50	2 530 − 2 300 = 230
(6)	1 470s	1 020s	760w	1 315s	710w	815s	1 770 − 1 720 = 50	2 530 − 2 320 = 210
(7)	1 475s	1 025s	760w	1 310s	715w	810s	1 770 − 1 710 = 60	2 530 − 2 320 = 210

[a] For these fundamentals, the main subscripts and those in parentheses pertain to the bidentate and unidentate nitrates respectively. For other fundamentals, the subscripts pertain to both kinds of nitrates. [b] $\nu_{1(4)} = \nu(N{=}O)\ [\nu_{asym}(NO_2)]^c \equiv \nu_{3(h.c)}$; $\nu_{4(1)} = \nu_{asym}(NO_2)[\nu_{sym}(NO_2)]^c \equiv \nu_{3(l.c.)}$; $\nu_{3(h.c.)}$ and $\nu_{3(l.c.)}$ are the high- and low-energy components of the splittings, on co-ordination, of ν_3 for ionic nitrate. [c] Sat Pal, A. K. Trikha, and B. S. Manhas, *Synth. React Inorg. Metal-Org. Chem.*, 1984, **14**, 1111. [d] Splittings of ν_4 for ionic nitrate.

mixed with the other CH bands occurring around 2 900 cm^{-1}, on co-ordination of the NCH_3 nitrogen atom.[16]

The i.r. spectrum[17] of $PdCl_2(1,4Me_2\text{-}pipz)$, in which the piperazine has been shown to exist in boat form by *X*-ray diffraction studies,[18] exhibits a large number of new bands of low and medium intensity in addition to changes in the bands characteristic of the free ligand. Except for the additional bands due to the metal–ligand and nitrate groups, the i.r. spectra of the present complexes are quite simple and no new bands of low and medium intensity assignable to the boat conformation[17] appear, thus showing that the piperazines retain their chair conformations in the complexes. The complexes are thus non-chelated polymers.

The appearance of a strong band around 1 310 cm^{-1} (Table 2) and the absence of bands characteristic of ionic nitrate (1 390, 830 cm^{-1}) indicate the presence of co-ordinated nitrates only.[19] The significant and fairly uniform ranges of the differences in separations between the nitrate-group combination bands, $(\nu_2 + \nu_{1(4)}) - (\nu_2 + \nu_{4(1)})$ and $(\nu_2 + \nu_3) - (\nu_2 + \nu_5)$, for the two modes of nitrate binding (200—300 and 20—25 cm^{-1} for bidentate and 90—200 and 5—25 cm^{-1} for unidentate nitrate) have been considered a fairly reliable i.r. spectral criterion for distinguishing these modes of nitrate binding.[19–27] On the basis of the magnitudes of these separations (Table 2), chelating bidentate nitrates are present in our complexes.

In the far-i.r. spectra of these complexes bands at around 530[15] and 375 cm^{-1} (refs. 3 and 4) have tentatively been assigned to the NH rocking and MN stretching modes respectively.

Electronic Reflectance Spectral (200—2 000 nm) *and Magnetic Susceptibility Measurements.*—The electronic reflectance spectra of the present uranium(IV) complexes are very weak with only a few discernible absorptions. No bands that can be assigned to the six- or eight-co-ordinate uranium(IV)[28] were observed.

The plot of $1/\chi_M$, corrected by the method of least squares, against temperature was linear and showed that the susceptibility varied according to the Curie–Weiss law $1/\chi_M = S(T - \theta)$ over the range 77—299 K. The susceptibility is, therefore, defined by the parameters S and θ (Table 1). The temperature dependence of the observed paramagnetic susceptibility and the room-temperature effective magnetic moment, *ca.* 2.8 (Table 1), are both suggestive of a cubic ligand field for uranium(IV).[29–31] However, this is unlikely since the stoicheiometric formula, assigned to these complexes on the basis of elemental analyses, together with the i.r. spectral studies suggest a co-ordination number of 12. In view of the non-availability of theoretical predictions of the magnetic properties for higher-co-ordinate uranium(IV), the present magnetic studies are not of help in confirming this proposal.

Experimental

The experimental manipulations were performed by use of Schlenk techniques.

Starting Materials.—Acetonitrile (Sarabhai) was dried by refluxing over P_2O_5. After distillation it was stored over dried molecular sieves (5 Å). Diethyl ether, absolute ethanol, and piperazines were obtained and dried as described earlier.[1-4]

Preparation of Complexes.—An absolute ethanol solution (*ca.* 10 cm^3) of the ligand (0.67—1.26 g, 7.83 mmol) was added to an ethanolic solution (20 cm^3) of uranium(IV) nitrate (1.27 g, 2.61 mmol) prepared *in situ* as described below. The green complex which precipitated immediately was separated by adding an excess of dry diethyl ether (*ca.* 50 cm^3). It was filtered in a G_4 filtration unit under anhydrous conditions, washed five or six times with ether, and finally dried *in vacuo*. A continuous flow of purified N_2 was maintained through the solution during this preparation.

The solution of uranium(IV) nitrate employed in this preparation was obtained as follows. To a solution of UCl_4 (1.00 g, 2.63 mmol) in absolute ethanol (15 cm^3) was added a solution of AnalaR $AgNO_3$ (1.78 g, 10.52 mmol) in the minimum volume (*ca.* 1 cm^3) of acetonitrile in a mole ratio of 1 : 4. The precipitated AgCl was collected in a G_4 filtration unit in the dark; it was dried at 100 °C and weighed in order to determine whether the reaction was complete; this was also tested by adding a drop of $AgNO_3$ solution to a part of the green filtrate containing uranium(IV) nitrate. The filtrate was rejected if a slight turbidity appeared.

Physical Studies.—Infrared spectra of the complexes and ligands were recorded on a Beckman IR-20 spectrophotometer and electronic reflectance spectral measurements were made on a SP 700 A u.v.–visible spectrophotometer as described earlier.[1-4] Magnetic susceptibilities were measured on a model 153 vibrating-sample magnetometer. They were corrected for diamagnetism and were independent of the field strength in all cases.

Elemental Analyses.—Uranium was estimated volumetrically by the $Ce(SO_4)_2$ oxidation method. Carbon and hydrogen analyses were performed on an automatic Coleman C,H analyser and nitrogen was determined by Kjeldahl's method, all by Mrs. H. Sohal.

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