

Uranium(IV) Complexes with O-and N-Donor Ligands

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New complexes of U(IV) with O and N-donor ligands are reported. The ligands (TH), variedly substituted monobasic bidentate triazene-1-oxides, have been used. UCl_4 and TH were refluxed in ethanolic medium in varied ratios. The complexes obtained were invariably in 1:4 molar ratio. The complexes were characterised by elemental analysis, conductance measurements in nitromethane, magnetic moment values were obtained at room temperature, IR in the range 200-400 cm^{-1} in KBr discs and electronic spectral studies. U(IV) was found to possess the coordination number eight.

INTRODUCTION

A large number of U(IV) complexes, using $RCO-CH_2-COR'$ ligands, UL_4 , have been reported^{1,2}. More complicated variations of this kind of ligands are known, several Th(IV)³ and uranyl(VI)⁴ complexes of which have been reported, but only a few of these ligands have been applied to actinide elements in more than one oxidation states. UCl_4 is the usual starting material for synthesis of other U(IV) compounds. Various adducts of UCl_4 are formed with O and N-donors having two to seven ligand molecules and having a variety of structures.⁵ UCl_4 (CH_3CN)₄ is a nearly dodecahedron⁶ and with bulky neutral ligands octahedral complexes are obtained: *Cis*- $UCl_4(OPPh_3)_2$ and *trans*- $UCl_4(HMPA)_2$. The complex $U(NCS)_4$ adds three $Me_3CCONMe_2$ ligands to give a pentagonal bipyramidal seven coordinate complex with all NCS (two axial) coordinated through nitrogen.⁷ The studies of actinide complexes including uranium are of considerable interest because they have been used in solvent extraction procedures.⁸ The instability of some of the complexes may make them useful in fractional sublimations⁹ and their high thermal and radiation stabilities suggest their use as organic moderators.¹⁰ Recent observations of intermolecular energy

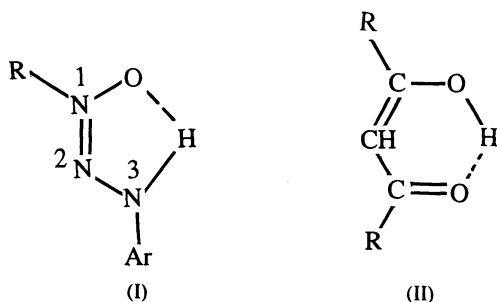
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transfer in several actinide β -diketone complexes indicate their potential applications as liquid lasers.¹¹ The result of investigations of the present study reports the coordination potentialities of U(IV) with variedly substituted triazene-1-oxides which are as fascinating as β -diketones with the only difference that in this case the protonating hydrogen is linked to the N-atom (I) instead of O-atom in case of β -diketones (II).



EXPERIMENTAL

Ligands were synthesized by following the method of Elkins and Hunter¹², that is, by coupling substituted hydroxylamines with benzene diazonium chloride or substituted benzene diazonium chloride at 0–5°C in presence of sodium acetate to control pH. The crude precipitate of substituted triazene-1-oxides was filtered under suction, washed thoroughly with water and recrystallised from alcohol or aqueous alcohol.

The general preparative method of the complexes reported in the present work consists in treating an aqueous solution of tetravalent uranium with the ligand and then adjusting the pH of the solution by adding alkali (ammonia, sodium hydroxide, etc.) until the complex separates from the aqueous phase. The crude products are finally recrystallised from ethanol. The colour of uranium(IV) complexes obtained were green to dark brown.

RESULTS AND DISCUSSION

Complexes obtained are of type UT_4 (Table 1). The colours of the complexes varied from green to brown which were similar to those obtained with β diketones¹². The complexes were mono-molecular in freezing benzene and non-electrolyte ($0.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in nitromethane. The magnetic moments were 2.2 BM less than the theoretical M_J values (3.58 BM). The electronic spectral bands were found to be broad ones compared to trivalent lanthanides. Infrared spectra (Table 2) indicated the bonding of uranium (IV) both through $\overset{3}{N}$ — and $\overset{1}{N} \rightarrow O$ donor groups.

The electronic configuration of uranium is $5f^3 6d^1 7s^2$. Uranium(IV) has the configuration $5f^2$ after the noble gas core (Rn), since triazene-1-oxides are bidentate ligands and it is expected that uranium(IV) is 8-coordinate in the present

TABLE 1
CHARACTERISATION DATA OF UT₄ (TETRATRIAZENE-1-OXIDATO) URANIUM(IV)

Complexes	Substituents		Analysis %; Found: (Calcd.)			
	R	Ar	M	N	C	H
UT ₄	CH ₃	C ₆ H ₅	28.21 (28.40)	19.89 (20.04)	39.72 (40.09)	3.66 (3.82)
UT ₄	C ₆ H ₅	C ₆ H ₅	21.73 (21.91)	15.18 (15.46)	52.87 (53.03)	3.29 (3.68)
UT ₄	CH ₃	C ₆ H ₄ CH ₃ (<i>p</i>)	26.41 (26.62)	18.48 (18.79)	42.61 (42.95)	4.19 (4.47)
UT ₄	C ₆ H ₅	C ₆ H ₄ CH ₃ (<i>p</i>)	21.79 (21.95)	15.09 (15.35)	58.68 (59.03)	4.13 (4.38)
UT ₄	CH ₃	C ₆ H ₄ NO ₂ (<i>p</i>)	23.01 (23.37)	12.76 (22.00)	32.79 (33.00)	2.51 (2.75)
UT ₄	C ₆ H ₅	C ₆ H ₄ NO ₂ (<i>p</i>)	18.36 (18.79)	17.38 (17.69)	45.13 (45.49)	2.61 (2.84)

TH = Monobasic bidentate Triazene-1-oxide; T = Triazene-1-oxide, an ion.

TABLE 2
MAJOR INFRARED BANDS (cm⁻¹) OF TH AND UT₄ COMPOUNDS

Compounds	Substituents		³ v(N—H)	¹ v(N → O)	v(U—N)	v(N—O)
	R	Ar				
TH	CH ₃	C ₆ H ₃	3200 s	1300 m	—	—
TH	C ₆ H ₃	C ₆ H ₅	3190 s	1290 m	—	—
UT ₄	CH ₃	C ₆ H ₅	—	1240 s	480 m	430 m
UT ₄	C ₆ H ₅	C ₆ H ₅	—	1235 s	475 m	430 m
UT ₄	CH ₃	C ₆ H ₄ CH ₃ (<i>p</i>)	—	1245 s	480 m	430 m
UT ₄	C ₆ H ₅	C ₆ H ₄ CH ₃ (<i>p</i>)	—	1240 s	475 m	430 m
UT ₄	CH ₃	C ₆ H ₄ NO ₂ (<i>p</i>)	—	1245 s	480 m	430 m
UT ₄	C ₆ H ₃	C ₆ H ₄ NO ₂ (<i>p</i>)	—	1240 s	475 m	430 m

studies. The Russel-Saunders term for uranium(IV) is ³H₄. The monomeric neutral UT₄ indicates that all the four TH ligands protonate and leads to the formation of a neutral uranium(IV) complex. The actinides resemble the lanthanides in that they too have incompletely filled orbitals. While the 4f-orbitals of the latter are effectively shielded by the 5s²5p⁶ outer shells, the 5f-orbitals of actinides are poorly shielded and sometimes left bare depending on the oxidation

state. It is because of the poor shielding of the 5f-orbitals of the actinides that they are under a much greater crystal field effect than the 4f-orbitals of the lanthanides. It has been found from experiments that the crystal field effect in an actinide compound is about one-tenth that in a first transition series metal ions and at least ten times more than that in a lanthanide¹³. An important reason for the lower value of μ_{exp} than μ_J is believed due to the magnetic exchange phenomenon through the super exchange. Another line of argument is an exposure of the 5fⁿ electrons of an actinide to a crystal field which may lead to a considerable quenching of the orbital magnetic moment.

The absorption spectrum of lighter actinide complex such as U(IV) results from the Laporte forbidden f-f transitions. The absorption bands are broad similar to the broad bands observed in the transition metal complexes. This is because of the fact that the energies of 5f and 6d-orbitals are comparable and unlike 4f-orbitals 5f-orbitals are not deep seated. As such 5f-orbitals, such as uranium(IV), face greater exposure to the surrounding ligands and also due to the effect of the vibrations of the ligands the absorptions are broadened. Charge transfer transitions also lead to broadening of the bands. Because of the complexity of spectral and low symmetry of complexes, spectra are not easily used as means of deducing stereochemistry except when used as "finger prints" for comparison with spectra of previously characterised compound.¹⁴

Triazene-1-oxides exhibit two major characteristic bands $\nu(\overset{3}{\text{N}}-\text{H})$ at about 3200 cm^{-1} and $\nu(\overset{1}{\text{N}} \rightarrow \text{O})$ at about 1300 cm^{-1} .¹⁵⁻²⁰ On complexation $\nu(\overset{3}{\text{N}}-\text{H})$ band disappears and $\nu(\overset{1}{\text{N}} \rightarrow \text{O})$ band is considerably lowered by about 60 cm^{-1} due to electron drainage. This indicates bonding of uranium(IV) both through $\overset{3}{\text{N}}-\text{H}$ and $\overset{1}{\text{N}} \rightarrow \text{O}$ donor groups. Appearance of new bands at about 480 cm^{-1} and 430 cm^{-1} have been assigned to $\nu(\text{U}-\overset{1}{\text{N}})$ and $\nu(\text{U}-\text{O})$ bands.²¹ Uranium(IV) gives many eight-coordinate complexes, both neutral²², for example $\text{U}(\text{acac})_4$ or $\text{U}(\text{oxine})_4$, and ionic²³, for example $\text{U}(\text{NCS})_8$ and $\text{U}(\text{NCSe})_4^-$. Our results are in conformity with these observations. On the basis of the similar IR bands of $\text{UCl}_4(\text{CH}_3\text{CN})_6$ and UT_4 it is believed that UT_4 complexes also have dodecahedral stereochemistry.

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