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ACTINIDE COMPLEXES WITH CHELATING LIGANDS CONTAINING SULFUR AND AMIDIC NITROGEN DONOR ATOMS

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CONTENTS

A. INTRODUCTION

During the last few years much interest has been directed towards the chemistry of sulfur chelating ligands and their related transition metal complexes and a number of good reviews have been published [1—7]. The abundance of literature dealing with the chemistry and properties of sulfur donor chelate complexes obviates the necessity for another exhaustive review in this general area but does reveal the need for a more precise and detailed examination of the actinide complexes, especially in view of the many good papers published of late.

Recently the chemistry of the actinide amide compounds has increased considerably and the phthalocyanine compounds have been studied in detail in relation to their ability to stabilize a particular oxidation state of the actinides. There has been considerable recent interest in coordination chemistry centered around the role of actinide ions as templates in the cyclization and condensation reactions which produce complexes of macrocyclic ligands. These metal ions have a rich and diverse chemistry because they exhibit high coordination numbers and novel coordination geometries unknown or unusual for *d* transition metals and because they have available 5*f* valence orbitals which may in some cases possess the appropriate energy and spatial extension to be of chemical significance.

Many reviews on various aspects of the chemistry of the actinides have been published with particular attention being paid to aqueous solutions [8—11], the structural and preparative aspects of actinides [12], their halides [13—19], organometallic [16,17] and carboxylic compounds [20] and to their electronic spectra [19]. In a previous review [21] we discussed the behavior of the actinides, in their various oxidation states, towards the most usual organic chelating ligands: tropolone, 8-hydroxyquinoline, β-diketones, Schiff bases and azo-derivatives. All these ligands are bidentate or polydentate with oxygen or nitrogen donor atoms, and have received the greatest attention. Particular attention has been directed towards preparative methods, the geometry of coordination of the adducts on varying the bite and the coordination power of the chelating ligands and their IR, NMR, UV and PES spectroscopy. However no attention was paid to An—SR, An—SeR, An—SR_2 and An—NR_2 bonds present in actinide complexes with chelating ligands. The purpose of this review is to cover the lack of information in this field and to draw, where possible, some general conclusions concerning the physicochemical behavior of actinide chelate compounds with particular regard to the stability and reactivity of the various An—L bonds and to the ability of the actinide ions to alter the normal course of a number of organic cyclooligomerization reactions via unusual requirements of coordination geometry and ionic radius.

B. DITHIOCARBAMATE LIGANDS

The reaction of CS_2 with primary or secondary amines, both aliphatic or aromatic, gives rise to the dithiocarbamate salts of general formula $[H_2NR_2]$-$[R_2NCSS]$. The corresponding alkali metal salts are obtained using an alkali hydroxide as the proton acceptor according to the reaction [22—24]

$$R_2NH + CS_2 + MOH \xrightarrow{H_2O} R_2NCSSM + H_2O$$

The structure of the dithio complexes can be represented by the valence bond formalism shown in Fig. 1. The extent to which resonance form c contributes to the structure and its effect on the physicochemical properties of these compounds has been the subject of considerable study [5]. A detailed IR investigation of a great number of dithiocarbamate complexes has shown [26,27] that the resonance for c does indeed contribute considerably to the structure. These conclusions have been based on an IR band in the region 1550—1480 cm^{-1}. The energy of this band lies between the stretching frequency region assigned to C—N single bonds (1250—1350 cm^{-1}) and that assigned to C=N double bonds (1690—1590 cm^{-1}) [25] and can be best explained as vibration of a polar $C=N^+$ bond [26,27]. The C=N stretching frequencies of a series of N,N-diethyldithiocarbamate complexes vary with the probable arrangement of sulfur donors around the central atom and decrease in the order: planar > tetrahedral > octahedral > distorted octahedral or pyramidal [27].

(i) *Actinide(VI) dithio- and diselenocarbamate complexes*

Uranyl(VI) dithiocarbamate complexes were mentioned but not characterized as early as 1908 [22,34]. At a later date a number of complexes of general formula $UO_2(DTC)_2$ (HDTC= diethyldithiocarbamic acid) were reported [35]. A series of uranyl(VI) dithiocarbamates has also been prepared in more recent years and reported as stable crystalline species containing ethanol of crystallization [36]. The highly colored solutions formed when UO_2^{2+} is treated with dithiocarbamate ligands have been used in the colorimetric determination of uranium [37,38], and the quantitative precipitation of UO_2^{2+} with dithiocarbamates under acid conditions has been reported [39,40]. In 1956 uranyl(VI) dithiocarbamate complexes with the stoicheiometry $K[UO_2(R_2DTC)_3]$ were reported and on the basis of spectrophotometric data it was wrongly suggested that they could be best described as the double salt $UO_2(DTC)_2 \cdot K_2UO_2(DTC)_4$ [41]. The crystal and molecular structure of $[(CH_3)_4N][UO_2DTC)_3]$ revealed the existence of a trianionic complex [42]. The configuration about the uranium atom is depicted in Fig. 2. The positions of the carbon atoms of the ethyl groups were not exactly defined and have been drawn with dashed lines. Six sulfur atoms are arranged equatorially around the linear uranyl(VI)

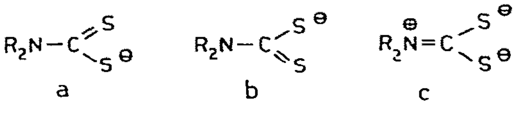


Fig. 1. Valence bond formalism for dithiocarbamates.

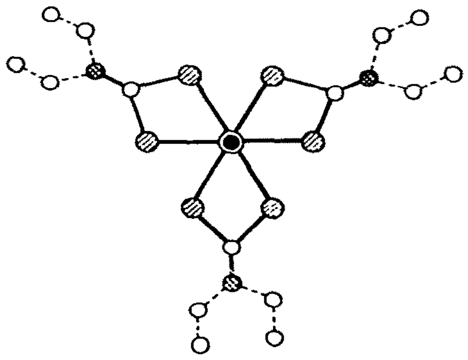


Fig. 2. The configuration about the uranium atom for $[(CH_3)_4N][UO_2(DTC)_3]$.

group. They are not coplanar but staggered with respect to the plane which contains the uranium atom and perpendicular to the uranyl(VI) axis; an average U—S bond of 2.80 Å and an S—U—S angle of 73.5° have been reported.

A series of complexes of the type $UO_2(DTC)_2(L)$ (L = neutral monodentate ligand) has been reported [43,44,49]. The red $UO_2(DTC)_2(Ph_3PO)$ and the orange-red $UO_2(DTC)_2(Ph_3AsO)$ complexes were prepared according to the reaction

$$K[UO_2(DTC)_3]H_2O + L \rightarrow UO_2(DTC)_2(L) + KDTC + H_2O$$

using acetone as solvent. $UO_2(DTC)_2(Ph_3AsO)$ can also be obtained by addition of triphenylarsine oxide to a solution of $UO_2(DTC)_2(Ph_3PO)$ in *sym*-dichloroethane and this reaction appears to be immediate from spectral measurements. This may be explained by assuming that the $U—OAsPh_3$ bond is stronger than $U—OPPh_3$ as already found [45]. The crystal structures of the two isomorphous complexes show that the two dithiocarbamate ligands are chelated, in one plane, to the uranium atom through the sulfur atoms. In the same plane the monodentate ligand Ph_3AsO or Ph_3PO is coordinated through the oxygen atom. The uranyl group is normal to the equatorial plane; the coordination polyhedron is thus a slightly irregular pentagonal bipyramid, the uranium atom having coordination number seven. The U—O bond lengths of the linear uranyl(VI) group are 1.71 ± 0.03 Å for $UO_2(DTC)_2(Ph_3AsO)$ and 1.67 ± 0.03 and 1.72 ± 0.03 Å for $UO_2(DTC)_2(Ph_3PO)$. The U—S distances, averaging 2.84 Å, are equal in the two molecules. The U—O (ligand) and As—O and P—O distances agree with the corresponding values found in the $UO_2(NO_3)_2(Ph_3PO)_2$ and $UO_2(CH_3COO)_2(Ph_3PO)_2$ complexes [46,47] confirming the strong π contribution to the As—O and P—O bonds (Fig. 3).

Yellow-orange crystals of $UO_2(DTC)_2(Me_3NO)$ have been obtained by reacting $UO_2(NO_3)_2 \cdot 6\ H_2O$ in methanol with a stoichiometric amount of potassium diethyldithiocarbamate and then adding a slight excess of trimethylamine N-oxide (Me_3NO) in methanol [48]. The basic structure of $UO_2(DTC)_2(Me_3NO)$ (Fig. 4) corresponds to that of the analogous compounds $UO_2(DTC)_2(Ph_3PO)$ and $UO_2(DTC)_2(Ph_3AsO)$. The uranium atom is in a seven coordinate pentagonal bipyramidal environment with the linear uranyl(VI) group perpendicular to the equatorial plane which contains four sulfur atoms of two carbamate groups and the oxygen atom of the ligand at the corners of an irregular pentagon. The neutral ligand approaches the central atom more closely (2.14 Å) than in $UO_2(DTC)_2(Ph_3PO)$ (2.34 Å) and $UO_2(DTC)_2(Ph_3AsO)$ (2.30 Å). The As—O and P—O bonds are practically double bond in character whereas the N—O bond in Me_3NO is a single bond. This suggests a large donor ability of the ligand Me_3NO [59]. The two U—O uranyl bond lengths (1.84 Å and 1.86 Å) are longer than those found in the arsine and phosphine oxide derivatives (mean value 1.70 Å) and the ν_3O—U—O is consequently lower ($UO_2(DTC)_2(CH_3)_3NO$, 892 cm^{-1}; $UO_2(DTC)_2(Ph_3AsO)$, 901 cm^{-1}; $UO_2(DTC)_2(Ph_3PO)$; 910, 905 cm^{-1}).

The stretching modes of the diethyldithiocarbamate groups of the com-

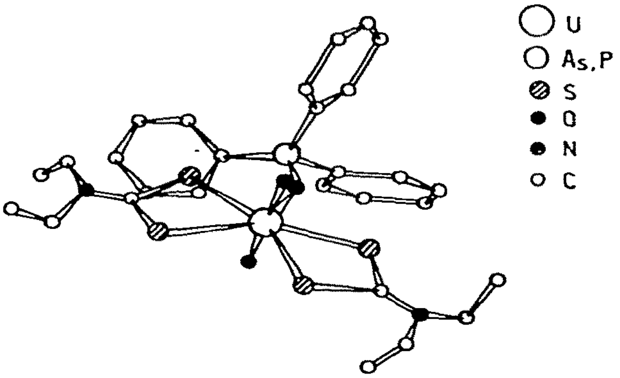


Fig. 3. A perspective view of the complex $UO_2(DTC)_2(Ph_3AsO)$ or $UO_2(DTC)_2(Ph_3PO)$.

plexes $KUO_2(DTC)_3H_2O$, $UO_2(DTC)_2(Ph_3PO)$ and $UO_2(DTC)_2(Ph_3AsO)$, in $CHCl_3$ solution have been found at 1005, 995 and 992 cm^{-1} respectively for the νC—S and at 1485, 1480 and 1479 cm^{-1} respectively for the C—N bond. The electronic spectra of these compounds are characterized by two intense bands deriving from electronic transitions localized in the uranyl system, and corresponding to the charge transfer transitions from the equatorial ligands to the uranium atoms. These cover the extremely weak band centered around 24 kK. $UO_2(DTC)_2(Ph_3PO)$ and $UO_2(DTC)_2(Ph_3AsO)$ show two band maxima or shoulders whose energy difference is about 6kK. It was suggested [43], on

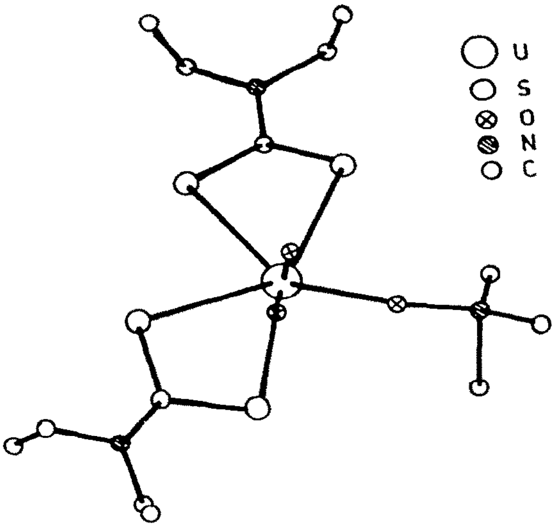


Fig. 4. The molecular structure of $UO_2(DTC)_2(CH_3)_3NO$.

the basis of comparison with Ni(DTC)$_2$ and Co(DTC)$_2$ whose charge-transfer electronic transitions differ in energy by about 6kK [3,53,54], that the two electronic transitions arise from two molecular orbitals mainly localized on the sulfur atoms to the same empty molecular orbital of uranium, thus corresponding to π(ligand) → *f*(uranium) transitions. The chemical behavior of selenium in transition metal diethyldiselenocarbamate complexes is similar to that of sulfur [50] and this has also been found recently for actinides. Crystalline precipitates of $UO_2(DSeC)_2(Ph_3PO)$ and $UO_2(DSeC)_2(Ph_3AsO)$ (HDSeC = diethyldithiocarbamic acid) were obtained by reaction of $UO_2(NO_3)_2 \cdot$ 6 H_2O in methanol with the required amounts of potassium diethyldiselenocarbamate in water-dioxan solution [51] and subsequent addition of methanolic solution of the appropriate monodentate ligand [52]. The crystal and molecular structure of $UO_2(DSeC)_2(Ph_3AsO)$ was determined by X-ray analysis (Fig. 5). Each uranium atom is in a pentagonal bipyramid environment. The linear uranyl(VI) group is perpendicular to the equatorial plane in which the four selenium atoms of the two anionic groups and the oxygen atom of the monodentate ligand occupy the corners of an irregular pentagon. The uranyl U—O distances are 1.76 and 1.72 Å (the O—U—O angle is 170°). Notable dimensional features are the four U—Se bond lengths (mean value = 2.98 Å) and the relatively short U—O (monodentate ligand) distance of 2.25 Å.

Uranyl(VI) diethyldithio- and diselenocarbamate complexes with hexamethylphosphoramide (HMPA) have been reported [56]. Molecular weight and conductivity measurements carried out in solution of *sym*-dichloroethane indicate that the complex $UO_2(DTC)_2HMPA)$ is a slightly dissociated monomeric species. The coordination geometry is expected to be similar to that of $UO_2(DTC)_2(Ph_3PO)$ [43]. The compound $UO_2(DSeC)_2(HMPA)$ was found to behave as a non-electrolyte compound, and a structure similar to that of $UO_2(DTC)(HMPA)$ has been proposed. An analogous structure has been suggested for the complexes $UO_2(DSeC)_2(Ph_3PO)$, $UO_2(DSeC)_2(Me_3NO)$ and $UO_2(DTC)(Me_3NO)$ based on elemental analysis, molecular weight and conductivity data; these complexes are monomeric and scarcely dissociated.

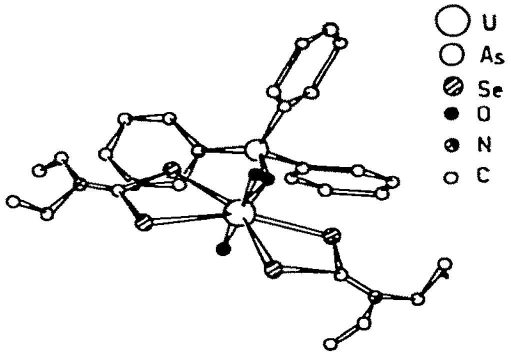


Fig. 5. The molecular structure of $UO_2(DSeC)_2(Ph_3AsO)$.

TABLE 1

Crystallographic data for uranyl(VI) dithio- and diselenocarbamate complexes

Compound	Space group	a(Å)	b(Å)	c(Å)	β(°)	Z	Coord. no.	Ref.
$[(CH_3)_4N][UO_2(DTC)_3]$	$Pna2_1$ orthorombic	19.03	17.21	9.41		4	6	42
$UO_2(DTC)_2(Ph_3PO)$	$P2_1/n$ monoclinic	18.32	9.16	20.97	111.39	4	5	43
$UO_2(DTC)_2(Ph_3AsO)$	$P2_1/n$ monoclinic	18.28	9.13	20.95	111.18	4	5	43
$UO_2(DTC)_2(Me_3NO)$	$P2_12_12_1$ orthorombic	13.82	11.36	14.40		4	5	48
$UO_2(DSeC)_2(Ph_3AsO)$	$P2_1/n$ monoclinic	18.59	9.14	21.33	111.52	4	5	52

TABLE 2

Salient bond distances (Å) and angles (°) of uranyl(VI) dithio- and diselenocarbamate complexes

Complex	U—O apical bond length	U—O equatorial length	Average U—S (U—Se) equatorial bond length	S—U—S(Se—U—Se) chelate angle	Ref.
$[(CH_3)_4N][UO_2(DTC)_3]$	1.72 1.69		2.80	73.5	42
$UO_2(DTC)_2(Ph_3AsO)$	1.71 1.71	2.30	2.85	62.3	43
$UO_2(DTC)_2(Ph_3PO)$	1.67 1.72	2.34	2.84	61.9	43
$UO_2(DTC)_2(Me_3NO)$	1.84 1.86	2.14	2.86	62	48
$UO_2(DSeC)_2(Ph_3PO)$	1.76 1.77	2.25	2.98	64.5	52

An appreciable conductivity was found for $UO_2(DSeC)_2(Me_3NO)$; however it was not comparable with the values encountered for uni-univalent electrolytes. In the IR spectra the antisymmetric stretch ν_3O—U—O for $UO_2(DSeC)_2(Ph_3AsO)$ is lower than that found for the corresponding phosphine oxide derivative (Table 3) thus confirming a systematic trend observed for uranyl complexes with Ph_3PO or Ph_3AsO [43,47,57,58].

Values of the ν_3O—U—O frequency of different complexes were related to

TABLE 3

Infrared (cm^{-1}) and conductivity data for uranyl(VI) dithio- and diselenocarbamates

Complex	Λ[a]	ν_3O—U—O	νX—O (X = P, As, N)	Ref.
$K[UO_2(DTC)_3]\cdot H_2O$	55	880, 860		43
$UO_2(DTC)_2(Ph_3PO)$	4	910, 905	1130, 1117 (P—O)	43
$UO_2(DTC)_2(Ph_3AsO)$	6	901	880sh (As—O)	43
$UO_2(DTC)_2(Me_3NO)$	3.4	892	948, 939 (N—O	48
$UO_2(DTC)_2(HMPA)$	—	900	1085 (P—O)	56, 162
$UO_2(DSeC)_2(Ph_3PO)$	4.6	905	1130, 1120 (P—O	162
$UO_2(DSeC)_2(Ph_3AsO)$	3.0	899	872 (As—O)	162
$UO_2(DSeC)_2(Me_3NO)$	25.4	897	950, 941 (N—O)[b]	162
$UO_2(DSeC)_2(HMPA)$	—	902	1095 (N—O)	56

[a] Molar conductivity (cm^2 ohm^{-1} mol^{-1}) of 10^{-3} M solutions in nitromethan at 25°C.

[b] The bands should be due to the C—N and N—O bond stretching modes respectively [63]; in the complexes such an assignment is uncertain.

the donor ability of the ligands coordinated to the uranium by an oxygen atom [59], showing that the larger the ligand donation, the lower the stretching frequency of the uranyl group. On this basis the arsine oxide is a better donor than the phosphine oxide, a finding which is supported by the stronger U—O(ligand) bond observed in the Ph_3AsO complexes [60].

The change in position of the ν_3O—U—O stretching frequency with ligands is probably due to vibrational and electronic interactions. Vibrational interactions [155,156] arise from the coupling of the antisymmetric stretch with bending vibrations of the bond to the equatorial ligands. Electronic vibrations arise from an electronic transfer to uranyl ion from the equatorial ligands; such a transfer depends on the donor ability of the ligand. It has been found [157] that for a series of complexes formulated as $UO_2(L)_2(NO_3)_2$ (L = neutral monodentate ligand) ν_3O—U—O moved to lower frequencies along a series of ligands following the spectrochemical series in order of increasing field. From other results [158] it appears that correlation between the uranyl ν_3 stretching and the position of a given ligand within the spectrochemical series is doubtful; the shift of ν_3O—U—O does not always occur. Furthermore $UO_2(DSeC)_2(Me_3NO)$ exhibits ν_3O—U—O at 897 cm^{-1}. A shift to lower frequencies can also be observed in the spectra of $UO_2(DTC)_2(Me_3NO)$ and $UO_2(NO_3)_2(Me_3NO)$ when compared with those of the corresponding Ph_3PO and Ph_3AsO analogues [43,58].

Therefore according to the literature [59], a larger donor ability of Me_3NO has been found with respect to both the phosphine and arsine oxide. It may also be noted that νP—O and νAs—O occur at considerably lower frequencies on coordination (the free ligand values are 1195 cm^{-1} [61] and 880 cm^{-1} [62] respectively) while the νN—O and νC—N (free ligand, 937 and 945 cm^{-1} [63]) are generally displaced towards higher frequencies [64].

(ii) Actinide(V) dithiocarbamate complexes

Two protoactinium(V) diethyldithiocarbamate complexes have been prepared by the reaction of protoactinium(V) chloride or bromide and sodium diethyldithiocarbamate in methylene chloride [65]. The complexes are of the type $Pa(DTC)_4X$ (X = Cl, Br) and it is significant to note that the complex $Pa(DTC)_5$ has not been prepared; the protoactinium(V) ionic radius (0.90 Å) appears to be too small to form a pentakis-complex. The complexes $Pa(DTC)_4X$ are air sensitive, but stable in anhydrous oxygen-free media. A reaction occurs when they are dissolved in ethanol with the probable formation of an alkoxide species, for example the dark-red $Pa(DTC)_4Cl$ gives a pale-yellow solid which shows bands characteristic of ethoxy groups in the 1000—1100 cm^{-1} region in its IR spectrum.

The C=N frequencies for $Pa(DTC)_4Cl$ and $Pa(DTC)_4Br$ are considerably lower than the corresponding niobium and tantalum(V) complexes (Table 4). This has been explained by assuming that the niobium(V) and tantalum(V) complexes can be formulated as $[M(DTC)_4]^+X^-$ and then the positive charge

TABLE 4

IR data (cm^{-1}) for $M(DTC)_4X$ complexes (M = Nb(V), Ta(V) and Pa(V); X = Cl^- and Br^-) [65]

Complex	νC—N	νC—S	νM—S	νM—X
$Ta(DTC)_4Cl$	1525	1004, 1015	362	
$Ta(DTC)_4Br$	1522	998, 1016	364	
$Pa(DTC)_4Cl$	1485	1000	357	317
$Pa(DTC)_4Br$	1485	1000	358	
$Nb(DTC)_4Cl$	1520	998, 1012	362	
$Nb(DTC)_4Br$	1520	998, 1012	362	

on the cation would facilitate the electron movement from the $N(C_2H_5)_2$ group towards the metal thus increasing the strength of the C=N bond. In addition a medium intensity band at 317 cm^{-1}, associated with a metal—chlorine stretching vibration, has been observed in the case of $Pa(DTC)_4Cl$.

(iii) Actinide(IV) dithio- and diselenocarbamate complexes

Quadrivalent thorium(IV), uranium(IV), neptunium(IV) and plutonium(IV) diethyldithiocarbamates are obtained by reaction of anhydrous sodium or lithium diethyldithiocarbamate with anhydrous actinide tetrachloride (Cs_2PuCl_6 or $PuCl_4 \cdot 3$ DMSO in the case of plutonium [66]) or with the hexachloride $[(C_2H_5)_4N]_2[AnCl_6]$ (An = Th(IV), U(IV), Np(IV), Pu(IV)) [67] in ethanol. Benzene is the best solvent for both extraction and recrystallisation and large well formed plates can be obtained on slow evaporation of the solvent (Table 5). The complexes can also be prepared in CH_2Cl_2 or $CHCl_3$, where no oxidation occurs, but the reaction is much slower. The preparation of Pa-$(DTC)_4$, under similar conditions, was unsuccesful [66]; However on treating $PaCl_4$ with sodium diethyldithiocarbamate in ethanol the red coloration initially observed on the surface of $PaCl_4$ rapidly disappears and there can be iso-

TABLE 5

Reaction conditions for the preparation of actinide(IV) diethyldithiocarbamates [66,67]

Complex	Starting material	Mixing time (h)	Color
$Th(DTC)_4$	$[(C_2H_5)_4N][ThCl_6]$	16	Pale yellow
$U(DTC)_4$	$[(C_2H_5)_4N][UCl_6]$; UCl_4	0.5 0.2	Yellow
$Np(DTC)_4$	$[(C_2H_5)_4N][NpCl_6]$ $NpCl_4$	0.5 0.2	Orange-red
$Pu(DTC)_4$	$[(C_2H_5)_4N][PuCl_6]$ Cs_2PuCl_6; $PuCl_4 \cdot$ DMSO	16	Black

lated from the solution a yellow solid which has a different powder pattern from the other quadrivalent actinide diethyldithiocarbamate complexes and which shows an extra band at 1040 cm^{-1} in the IR spectrum.

The An(DTC)$_4$ complexes have essentially the same IR spectra, (Table 6) with a strong band at about 1490 cm^{-1}. If the ligands are nitrogen bonded in these complexes, this peak would be expected at much lower frequency, so they have the ligands bonded to the metal exclusively through sulfur in four equivalent four-atom chelate rings.

U(DTC)$_4$ is monomeric in benzene solution [66,68] and it was suggested the uranium atom is eight coordinated through the sulfur atoms of the ligands. The crystal and molecular structure of Th(DTC)$_4$ has been investigated [69,70]. The crystals are monoclinic, space group *C*2/*c* and $z = 4$ with $a = 19.16$, $b = 11.74$, $c = 16.11$ Å, $\beta = 116.42°$. The arrangement of the eight sulfur atoms around the thorium atom was previously described as intermediate between the ideal dodecahedron and square antiprism.

A modified description of the coordination polyhedron for this compound based on the criteria [71,180] for distinguishing between dodecahedral and square antiprismatic coordination, was subsequently reported [179]. On the basis of these criteria the arrangement of the eight sulfur atoms around the thorium atom is close to that of a dodecahedron. The coordination polyhedron viewed down the crystallographic two-fold axis is shown below. The angle of intersection of the plane containing Th, S_1, S_2, S_7 and S_8 and Th, S_3, S_4, S_5 and S_6 is 89.88°, very close to that required for an idealized dodecahedron (90°) and differs considerably from that of an idealized square antiprism (77.4°) [180]. The distances of the ligand atoms from their respective planes yield average values of 0.10 and 0.06 Å for the atoms of the type A and B respectively. The chelation is along the *m* dodecahedral edges as observed for Ti(DTC)$_4$ [181], the shape of the dodecahedron being specified by the average parameters: Th—S$_A$ = 2.876 Å, Th—S$_B$ = 2.865 Å, Th—S$_A$: Th—S$_B$ = 1.00, $\vartheta_A = 34.8°$, $\vartheta_B = 82.5°$. X-ray powder patterns for quadrivalent thorium, uranium, neptunium and plutonium diethyldithiocarbamates show that they have very similar, if not identical structures and that the unit-cell volumes decrease with the increasing atomic number of the central metal atom in accordance with the actinide contraction (Table 7). The fact that no struc-

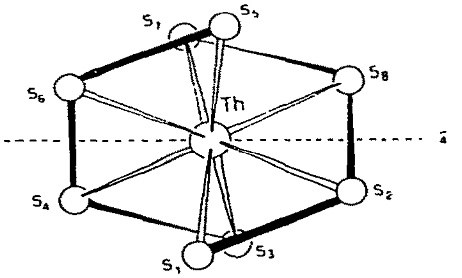


TABLE 6

IR spectra (cm^{-1}) of actinide(IV) thio, dithio and diselenocarbamate complexes

Compound[a]	Color	C—N	M—X	Ref.
Th(DMTOC)$_4$	Pale yellow	1540s	410s (S?), 480m (O?) (530m)	72
Th(DTOC)$_4$	Pale yellow	1515s	398s (S), 455s (O) (525s)	72
U(DTOC)$_4$	Yellow-brown	1515—1520s	395s (S), 455s (O) (525s)	72
Th(DMTC)$_4$	Pale yellow	1495s	365s (410s)	72
Th(DTC)$_4$	Pale yellow	1488s	360s (402s)	66, 67, 72
U(DTC)$_4$	Yellow	1490s	351s	66, 67, 72
Th(DSeC)$_4$	Yellow	1495s	355s	72
U(DSeC)$_4$	Brown	1485s	350s	72
Np(DTC)$_4$	Orange-red	1490s	—	67
Pu(DTC)$_4$	Black	1485s	—	67

[a] DMTC$^-$ = dimethyldithiocarbamate ion; DTC$^-$ = diethyldithiocarbamate ion; DMTOC$^-$ = dimethylthiocarbamate ion; DTOC$^-$ = diethylthiocarbamate ion; DSeC$^-$ = diethyldiselenocarbamate ion.

tural change is observed in the actinide complexes with possibly f^0—f^4 configurations is consistent with the decreasing role of metal—ligand electronic effect.

The An(DTC)$_4$ complexes react with oxygen and water. Th(DTC)$_4$ can be stored in an inert atmosphere without decomposition, but U(DTC)$_4$, Np(DTC)$_4$ and Pu(DTC)$_4$ decompose slowly to form products which are insoluble in benzene or chloroform. Th(DTC)$_4$ solutions in CHCl$_3$ are stable for days in the absence of oxygen but decomposition products precipitate from U(DTC)$_4$ solutions within 1 day.

Many of the basic features of the Mossbauer effect in ^{237}Np are now well understood [10,177]. The different valence states of neptunium are easily distinguished by their isomer shifts, and magnetic phenomena can be studied from the hyperfine splitting. Mossbauer studies for Np(DTC)$_4$ have been carried out but the absence of data for other neptunium chelates does not allow any correlation to be drawn.

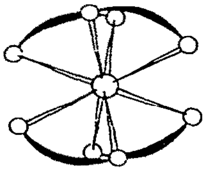


Fig. 6. The coordination polyhedron of Th(DTC)$_4$; view down the crystallographic two-fold axis.

TABLE 7

Unit-cell dimensions for the quadrivalent actinide(IV) diethyldithiocarbamates [66]

Complex	Unit-cell	Lattice parameters (Å)				Cell volume (Å^3)
		a	b	c	β(°)	
Th(DTC)$_4$	Monoclinic	19.16	11.74	16.11	116.42	3245.4
U(DTC)$_4$	Monoclinic	19.04	11.67	16.03	116.40	3190.4
Np(DTC)$_4$	Monoclinic	19.01	11.64	16.00	116.49	3168.5
Pu(DTC)$_4$	Monoclinic	18.96	11.61	15.92	116.50	3136.3

U(salen)(DTC)$_2$ (H_2salen = N,N′-ethylene-bis-salicylidenealdimine) was obtained by adding Tl(DTC) to a solution of U(salen)(Cl)$_2$ · 2 THF in 2 : 1 molar ratio using tetrahydrofuran as solvent [75]. By reacting Th(salen)(Cl)$_2$ · 2 THF with Tl(DTC) a white product which was analysed for Th(salen)(DTC)$_2$ was obtained [75].

The insertion of CX_2 (X = O, S, Se) and of COS into the metal—nitrogen bond of thorium(IV) and uranium(IV) dialkylamides An(NR_2)$_4$ has been studied [72]. A violent exothermic reaction occurs when CX_2 or COS is introduced into a solution of An(NR_2)$_4$ (R = CH_3, C_2H_5, iso-butyl) in n-hexane. Thorium diethylcarbamate and diethyloxothiocarbamate are the most stable with respect to decomposition on standing at room temperature and in the case of the uranium(IV) compounds, oxidation of the products resulting from the insertion of CO_2 or COS occurs. The IR spectra of the diethyldithiocarbamates produced by the insertion reaction are identical with those compounds produced by other methods [66,67]. ^{1}H NMR spectra of An(DTC)$_4$ show that the two ethyl groups of the ligand are equivalent [67,72], a singlet being observed for the dimethyl derivatives and a triplet and a quartet for the diethyl ones. However in the spectrum of thorium(IV) diethyloxothiocarbamate in $CDCl_3$, using a 60 MHz instrument, an equal intensity splitting of the triplet and quartet occurred. In the latter case this gives rise to a quintet made up of two overlapping quartets. From these observations it appears that the chemical shift at 60 MHz in $CDCl_3$ solution is equal to the coupling constant. At 100 MHz in $CDCl_3$ the quartet was split into two quartets of equal intensity centered at τ = 6.48, but the two triplets overlapped to form a quartet centered at 8.85 τ. In C_6D_6 solution at 60 MHz the quartet is also split in the same way. This behavior indicates that rotation about the R_2N—C bond is slow compared with the NMR time scale as had been observed with COS insertion products of silylamines [73]. The resolution of the spectrum becomes worse as the $CDCl_3$ solution is cooled to —50°C and at 50°C there is little change in the spectrum.

Recently it has been shown that it is possible to prepare dialkyldithiocarbamate complexes of uranium(IV) starting from uranium(IV) tetrachloride, dialkylamide and CS_2 [159] without the preliminary synthesis of tetrakys-(dialkylamido)uranium(IV) [72]. In hydrocarbon solvents the formation of $U(DTC)_4$ probably occurs via the substitution reaction of the chlorine ligands of UCl_4 by the DTC^- anion formed in the preliminary fast reaction of Et_2NH and CS_2.

$2\ Et_2NH + CS_2 \rightarrow [NH_2Et_2][NEt_2CS_2]$

$4[NH_2Et_2][NEt_2CS_2] + UCl_4 \rightarrow 4[NH_2Et_2]Cl + U(S_2CNEt_2)_4$

The first strongly exothermic reaction was followed spectroscopically in toluene and the C—S stretching vibration of CS_2 at 2160 cm^{-1} was found to disappear a few minutes after the mixing of the reagent and was replaced by the typical bands of the dithiocarbamate group. No evidence has been found of the $U—NR_2$ group being formed and inserting CS_2. Cryoscopic molecular weight measurements confirm the monomeric nature of $U(DTC)_4$ in solution at the freezing temperature of benzene. Dry oxygen in toluene oxidizes $U(DTC)_4$ at room temperature and, after recrystallization from tetrahydrofuran, the reaction product was characterized as the tetrahydrofuran adduct $UO_2(DTC)_2 \cdot 1.5$ THF. The absorption of dioxygen was found to be almost exactly 1 mol per uranium. The presence of coordinated tetrahydrofuran was indicated by the two bands at 1010 and 860 cm^{-1} in the IR spectrum attributable to the asymmetric and symmetric C—O stretching vibrations, respectively [160].

Carbon disulfide inserts into the uranium(IV)—nitrogen amidic bond of the complex $Cp_2U[N(C_2H_5)_2]_2$ ($Cp = \eta^5C_5H_5$) to give the corresponding dithiocarbamate $Cp_2U(DTC)_2$. This was verified by its mass spectrum which shows the highest peak at *m/e* 664 and by ^1H NMR spectrum [161].

(iv) Actinide(III) dithiocarbamate complexes

Neutral trivalent $Pu(DTC)_3$ was obtained by reaction between anhydrous plutonium tribromide and the stoicheiometric amount of sodium diethyldithiocarbamate in anhydrous ethanol; the presence of water causes the precipitation of basic salts and oxygen must be excluded to prevent oxidation to $Pu(DTC)_4$ [69,74]. $Pu(DTC)_3$ is soluble in CH_3CN and can be recrystallized from anhydrous CH_2Cl_2. It is insoluble in benzene which may therefore be used for the separation of $Pu(DTC)_3$ from small amounts of the very soluble $Pu(DTC)_4$ formed during the precipitation.

Attempts to prepare $U(DTC)_3$ and $Np(DTC)_3$ have been unsuccessful; reactions involving neptunium trichloride or tribromide yield initially dark brown solutions of presumably trivalent complexes which are rapidly oxidized even in the absence of oxygen and deposit red crystals of $Np(DTC)_4$. Uranium(III) is even less stable than neptunium(III) and attemps to prepare $U(DTC)_3$ have resulted only in the formation of $U(DTC)_4$ even with methylene dichloride as the solvent [74]. By treating the tris-diethyldithiocarbamate complexes with sodium diethyldithiocarbamate and tetraethylammonium bromide in 1 : 1 : 1

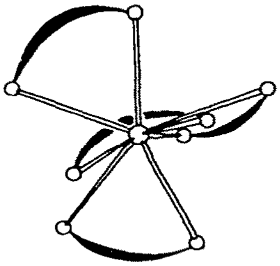
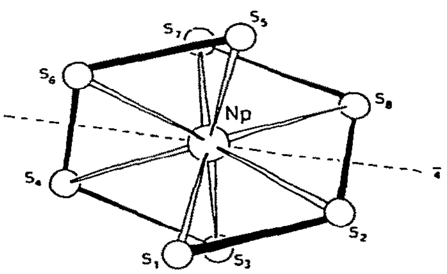


Fig. 7. The coordination polyhedron in the [Np(DTC)$_4$]$^-$ ion.

ratio in anhydrous alcohol, complexes of the type (NEt$_4$)[An(DTC)$_4$] (An = Np(III) and Pu(III)) have been obtained [74]. The pure product has been obtained by recrystallisation from methyl cyanide—ether or from methylene dichloride. These tetrakis complexes are soluble in anhydrous methyl cyanide and methylene dichloride, less soluble in alcohol and insoluble in ether, carbond tetrachloride and isopentane.

The IR spectra of Pu(DTC)$_3$ and [An(DTC)$_4$]$^-$ (An = Np(III), Pu(III)) are very similar to those reported previously for other diethyldithiocarbamate complexes. The C—N stretching vibration occurs at 1480 cm^{-1} in the [An(DTC)$_4$]$^-$ complexes.

Despite the close similarity between the ionic radii of Pu^{3+} (1.00 Å) and Nd^{3+} (0.995 Å) X-ray powder diffraction results indicate Pu(DTC)$_3$ and Nd(DTC)$_3$ possess a different crystal form. The tetrakis-diethyldithiocarbamate complexes are isostructural and possess monoclinic symmetry, space group $P2_1/c$ (C^5_{2h}) with $Z = 4$ in a unit cell of dimensions $a = 11.68$, $b = 20.49$, $c = 19.14$ Å; $\beta = 106.5°$. The neptunium atom is coordinated to eight sulfur atoms (see Fig. 7) and the angle of intersection of the planes containing Np, S$_1$, S$_2$, S$_7$ and S$_8$ and Np, S$_3$, S$_4$, S$_5$ and S$_6$ is 90.03°; the distances of the ligand atoms from their respective planes yield an average distance of 0.09 A; thus on the basis of the dihedral angle and the average distances of the atoms from their respective planes the earlier description of the polyhedron (Fig. 7) as a grossly distorted dodecahedron is misleading. The dodecahedron can be described by two perpendicular trapezoids and one of them is sufficiently



Chelation in NEt$_4$ NP(DTC)$_4$

rotated about an axis perpendicular to it to bring one sulfur atom close to the plane of the second trapezoid. The chelation in $NEt_4Np(DTC)_4$ [179] is along the *m* dodecahedral *m* edge, the shape of the distorted dodecahedron being specified by the average parameters Np—S = 2.885 Å, $Np—S_B$ = 2.844 Å, $Np—S_A : Np—S_B = 1.01$, $\vartheta_A = 36.1°$, $\vartheta_B = 79.6°$ [179]. The mean Np—S distance [2.87 Å) compares favorably with the values of 2.87 and 2.80 Å found for $Th(DTC)_4$ [69,70] and $[(CH_3)_4N][UO_2(DTC)_3]$ [42].

C. DITHIOCARBOXYLATE LIGANDS

The reaction of CS_2 with a variety of nucleophiles X^- gives rise to compounds known as dithioacids. The deprotonated forms of these compounds interact strongly with metal ions to form compounds where both the sulfur atoms are bound to the metal ion. The most versatile reaction for the preparation of both dithioaliphatic and dithioaromatic acids is the addition of CS_2 to a Grignard reagent [5,76].

(i) Actinide(VI) dithiocarboxylate complexes

Two monomeric complexes of formula $UO_2(DTA)_2(L)$ and $UO_2(DBA)_2(L)$ (HDTA = dithioacetic acid, HDBA = dithiobenzoic acid; L = Ph_3PO and Ph_3AsO) have been synthesised and characterised [57]. They have been prepared using the following reactions

$$UO_2(NO_3)_2 \cdot 6\,H_2O + 2\,KDTA \xrightarrow{CH_3OH} UO_2(DTA)_2 + 2\,KNO_3 + 6\,H_2O$$

$$UO_2(DTA)_2 + L \rightarrow UO_2(DTA)_2(L)$$

$$UO_2(CH_3COO)_2 \cdot 2\,H_2O + 2\,HDBA + L \rightarrow UO_2(DBA)_2(L) + 2\,H_2O +$$

$$+ 2\,CH_3COOH$$

and for $UO_2(DBA)_2(Ph_3PO)$ a complete X-ray structural determination has been carried out (Table 8). The crystals are monoclinic, space group $P2_1/c$ with $a = 16.782$, $b = 11.001$, $c = 15.687$ Å; $\beta = 113°29'$; $z = 4$. The X-ray analysis shows that the geometry of the coordination polyhedron in the molecule is a slightly irregular pentagonal bipyramid. Two dithioacetate groups are chelated to the central atom. The four sulfur atoms lie in the equatorial plane and the fifth atom is the oxygen of the triphenylphosphine oxide. The uranyl group is linear and normal to the plane. All distances and angles in the molecule are comparable with the corresponding ones found in $UO_2(DTC)_2$-(Ph_3PO) and $UO_2(DTC)_2(Ph_3AsO)$ showing that the substitution of $N(C_2H_5)_2$ by a methyl group in the chelated ligands has no detectable influence on the bonding of the coordinated atoms. (Fig. 8). The U—S distances (mean 2.85(1) Å) are larger by ca. 0.05 Å than the U—S distance (mean 2.80 Å) in $[(CH_3)_4N]$-$UO_2(DTC)_3]$ [42]. There is no evidence for the formation of monomeric six or bridging five coordinate complexes. For uranyl(VI) acetate compounds,

TABLE 8

Comparison between the crystallographic data of $UO_2(DTA)_2(Ph_3PO)$ and uranyl(VI) acetate and nitrate analogs

Complex	Unit-cell	Space group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Z	Coord. no.	Ref.
$UO_2(DTA)_2(Ph_3PO)$	Mono-clinic	$P2_1/c$	16.73	11.00	15.68		113.29		4	5	57
$[UO_2(CH_3COO)_2 \cdot (Ph_3PO)]_2$	Triclinic	$P1$ or $P\bar{1}$	8.35	11.02	13.68	101.50	91.12	109.12	2	5	47
$UO_2(CH_3COO)_2 \cdot (Ph_3PO)_2$	Mono-clinic	$P2_1/c$	9.88	19.14	10.88		116.30		2	6	175
$UO_2(NO_3)_2(Ph_3PO)_2$	Mono-clinic	$P2_1/c$	11.01	19.02	10.93		128		2	6	46, 175
$UO_2(NO_3)_2(Ph_3AsO)_2$	Mono-clinic	$P2_1/c$	11.09	19.28	10.88		128.1		2	6	46

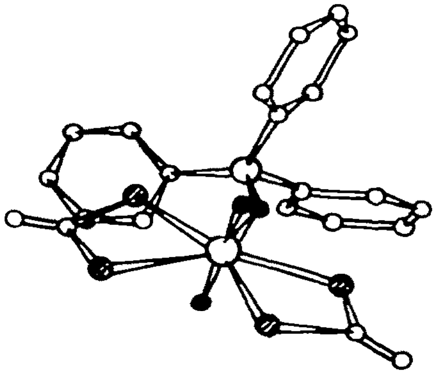


Fig. 8. A perspective view of the $UO_2(DTA)_2(Ph_3PO)$ molecule.

instead, monomeric and dimeric complexes can be obtained by varying the solvent and the reaction conditions [47,56,162]. The monomeric complexes of the type $UO_2(CH_3COO)_2(L)_2$ (L = neutral monodentate ligand) are hexacoordinated species in the equatorial plane of the uranyl(VI) group as $UO_2(NO_3)_2(Ph_3PO)_2$ and $UO_2(NO_3)_2(Ph_3AsO)_2$ [71]. The dimer $[UO_2(CH_3COO)(Ph_3PO)]_2$ has two $UO_2(CH_3COO)_2(Ph_3PO)$ molecules related by a center of

TABLE 9

Physico-chemical data for dithioacetate and dithiobenzoate uranyl(VI) complexes and their comparison with uranyl(VI) acetate analogs

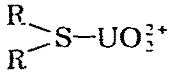
Complex	Λ_M [a]	ν_3O—U—O	νX—O (X = P, As)	Color	Ref.
$UO_2(DTA)(Ph_3PO)$	7 [b]	918	1132, 1120	Orange-red	57
$UO_2(DBA)(Ph_3PO)$	9 [b]	920	1137, 1123	Red	57
$UO_2(CH_3COO)_2(Ph_3PO)_2$	11.9 [b]; 2.4 [c] 3.2	912, 905	1150, 1132	Green-yellow	47
$[UO_2(CH_3COO)_2(Ph_3PO)]_2$	6.4 [b,e]; 2.1 [c] 2.5 [d]	926, 920	1138, 1120	Light yellow	47
$UO_2(DTA)(Ph_3AsO)$	11 [b]	910	882	Orange-yellow	57
$UO_2(DBA)(Ph_3AsO)$	12 [b]	912	862, 858	Red	57
$UO_2(CH_3COO)_2(Ph_3AsO)_2$	22.7 [b], 11.9 [c] 18.8 [d]	895	871, 867	Green-yellow	47
$[UO_2(CH_3COO)_2(Ph_3AsO)]_2$	12.4 [b], 8.1 [c] 11.3 [d]	921, 910	880	Yellow	47

[a] Molar conductance values at 25°C in ohm^{-1} cm^2 mol^{-1}. [b] In nitromethane. [c] In *sym*-dichloroethane. [d] In *sym*-dichloromethane. [e] The compound undergoes slow decomposition in this solvent.

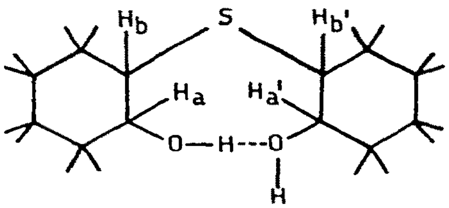
symmetry and bridged by acetate groups so that the resulting coordination number of the uranium is seven [47].

Conductivity measurements show that the dithiocarboxylate complexes are slightly dissociated in nitromethane and practically undissociated in *sym*-dichloroethane. The complexes are essentially monomeric in this solvent; however values lower than the theoretical were observed at 37°C, indicating that neutral ligands had been partially lost. This occurred to a greater extent for the Ph_3PO complexes than for the Ph_3AsO analogs. The two charge transfer bands expected for (sulfur)—*f*(uranium) transitions are found at 25 and 30.5 kK and 26.3 and 31.3 kK respectively in the electronic spectra of $UO_2(DTA)_2(Ph_3PO)$ and $UO_2(DTA)_2(Ph_3AsO)$. The very intense band centered around 33.2 kK is ascribed to the dithioacetate groups. The first charge-transfer band for $UO_2(DBA)_2(Ph_3PO)$ is found at 28 kK and that for the arsine oxide analog at 27.8 kK; however the second band of these complexes is apparently masked by the absorption due to the dithiobenzoate groups (32.2 kK), in the order of increasing frequencies: $DTC^- < DTA^- < DBA^-$ (Table 9).

D. ACTINIDE(VI) THIOETHER COMPLEXES

The formation of coordinate bonds of the type  $R_2S{-}UO_2^{2+}$ with the typically-soft sulfur atom is not to be expected because the uranyl(VI) ion is a hard Lewis acid [77]. Although many attempts to isolate thioether—uranyl(VI) complexes have been unsuccessful, one example is reported [78] in which a thioetheric sulfur atom is directly coordinated to uranium(VI).

The complex *cis*-dichloro *meso*-bis-(*trans*-2-hydroxycyclohexyl)sulphide dioxouranium(VI) ($UO_2(OSO)(Cl)_2$) [78], is obtained by reaction of $UO_2Cl_2 \cdot 3\,H_2O$ in ethyl acetate with an excess of the ligand bis-(2-hydroxycyclohexyl)sulphide (OSO) in the same solvent at room temperature. The ligand (OSO) (Fig. 9) synthesized by reaction (70°C, 1 h) of an excess of disodium sulphide with cyclohexene oxide in alcoholic media, is, on the basis of IR and ^1H NMR spectra, a mixture of *meso* and racemic stereoisomers in the *trans*-equatorial conformation and does not contain the *cis* form with equatorial hydroxy-groups for which significant differences should be expected for the H_a and H_a' proton signals. The crystal structure of the complex $UO_2(OSO)(Cl)_2$ containing the ligand in the *meso* form has been determined [78] (Fig. 10). The crystals are triclinic, space group $P\bar{1}$ with $a = 11.274$, $b = 10.173$, $c = 9.367$ Å, $\alpha = 111.41°$, $\beta = 97.46°$ and $\gamma = 111.29°$ with $z = 2$. The uranium atom is seven coordinate with the uranyl(VI) group perpendicular to the equatorial plane. The organic ligand is terdentate, being coordinated to uranium through the two oxygen and the sulfur atoms. The uranyl(VI) U—O distances are normal. The two independent U—Cl distances (2.67 Å) are consistent with the sum of the crystal radii (2.68 Å) [79] and with the values found in other uranyl(VI) compounds [80—82], but they are significantly greater



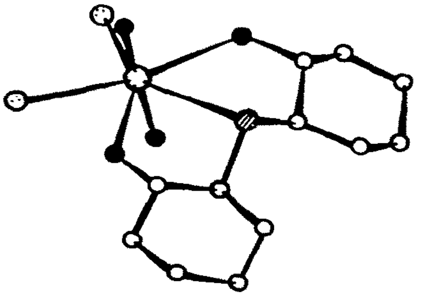


Fig. 9. The ligand bis-(2-hydroxycyclohexyl)sulfide.

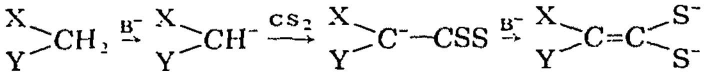
Fig. 10. The molecular structure of $UO_2(OSO)Cl_2$.

than those found in compounds of uranium(IV) [83,84]. The U—O (ligand) distances are chemically equivalent and are comparable with the values usually found for U—O(alcohol) bonds [85,86]. The U—S distance (2.94 Å), is ca. 0.1 Å longer than U—S bonds in dithioacetate or -carbamate uranyl(VI) complexes [43,57].

The difference of 0.4 Å between U—S(thioether) and U—O(ether) bond distance (2.55 Å) [142] compares well with the difference in covalent radii of oxygen and sulfur. Because of the almost symmetrical disposition assumed by the ligand the entire molecule can be considered to approximate to C_s symmetry. The shift of 0.4 ppm in the ^1H NMR spectrum observed on coordination for both peaks relative to the protons of the carbon atoms in positions α to the oxygen and sulfur atoms respectively, indicate a comparable bonding interaction between uranium and the oxygen and sulfur atoms. The strong bands at 264, 251 and 223 cm^{-1} in the IR spectrum of the complex have not been assigned but they are certainly associated with the O—U—O bending and the U—Cl asymmetric and symmetric stretching vibrations in a *cis* configuration.

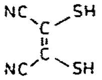
E. 1,1 AND 1,2 DITHIOLATE LIGANDS

Organic compounds of the type H_2CXY react with CS_2 in the presence of a base to give either a dithioacid or a 1,1-ethylene dithiolate according to the mechanism [32,164]



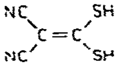
$$\begin{matrix}X\\Y\end{matrix}\!\!>\!CH_2 \xrightarrow{B^-} \begin{matrix}X\\Y\end{matrix}\!\!>\!CH^- \xrightarrow{CS_2} \begin{matrix}X\\Y\end{matrix}\!\!>\!C^-\!\!-\!CSS \xrightarrow{B^-} \begin{matrix}X\\Y\end{matrix}\!\!>\!C\!=\!C\!<\!\begin{matrix}S^-\\S^-\end{matrix}$$

The formation of 1,1-ethylene dithiolates depends on the base used and the electron withdrawing character of the X and Y groups [5]. The maleondinitrilethiol ligand



H_2mnt

has the same formula as the ligand



H_2imnt

The first ligand forms a five membered chelate ring while the second forms a four membered chelate ring. The strength of the metal—sulfur bond is of particular importance in complexes of the dithiolate ligands and is intimately related to the existence of any metal—ligand π-bonding which occurs upon chelate ring formation. The molecular orbitals of the 1,1 and 1,2-dithiolate ligand systems, which are perpendicular to the principal plane of the ligands, are delocalized over the atoms which comprise the chelating part of the ligands and can overlap with the metal orbitals of corresponding symmetry. In general the more substantial metal—ligand π-bonding is found to occur in complexes of the 1,2-dithiolates as evidenced by the consistently shorter metal—sulfur bond length observed in their structures. The many facile and reversible electron transfer reactions which these complexes undergo and other chemical and physical studies support the notion of electron delocalization in the π-system of these complexes. The π-bonding in complexes containing the 1,1-dithiolato ligand systems appears to be considerably less important. The four membered chelate rings are highly strained, and the complexes are, in general, unable to undergo the easy and reversible oxidation and reduction reactions characteristic of the 1,2-dithiolate complexes [7].

(i) Actinide(VI) and actinide(IV) dithiolate complexes

Many attempts have been made to prepare uranium(IV) complexes with thiols [66,87]. Uranium(IV) tetrachloride reacts with sodium *cis*-1,2-dicyanoethylene-1,2-dithiolate in a number of solvents but the ultimate result is the decomposition of the ligand. Reaction also occurs between toluene-3,4-dithiol and uranium(IV) tetrachloride in the presence of ammonia and for lithium metal, but no pure compound has been isolated [66].

Reaction of UCl_4 and sodium dithiolates in anhydrous oxygen-free methanol and under a nitrogen atmosphere also gives no pure compound but on addition of $(C_6H_5)_4AsCl$ to this solution, a crystalline solid can be obtained which can be recrystallized from $CH_2Cl_2/(CH_3)_2CO$. It is sparingly soluble in CH_2Cl_2, but very soluble in polar solvents such as DMSO, DMF or pyridine. Analytical and conductivity data agree with the formation of a 4 : 1 electrolyte of the type: $[(C_6H_5)_4As]_4[U(S_2C_2(CN)_2)_4]$ (ref. 87). The magnetic moment (2.62 BM) agrees with the values found for other uranium(IV) complexes. The complex can be recrystallized, without precautions to exclude air, without any change, but if it is recrystallized from pyridine and methanol, the colour of the solution changes from brown to olive-green and dark crystals of $[(C_6H_5)_4As]_2[UO_2(S_2C_2(CN)_2)_2(py)]$ are obtained. The same uranyl(VI) complex can be prepared by the reaction in methanol of $UO_2(CH_3COO)_2 \cdot 2\ H_2O$ and $Na_2S_2C_2(CN)_2$. The uranyl(VI) complex shows in its IR spectrum a band at 895 cm^{-1} due to the ν_3O—U—O.

Anionic uranyl(VI) complexes with the ligands H_2mnt and H_2imnt have been prepared by reaction of $UO_2(NO_3)_2 \cdot 6\ H_2O$ with the sodium salts of the two ligands and addition to the resulting solution of tetraalkylammonium salts [88]. The complexes $[N(C_2H_5)_4]_2[UO_2(mnt)_2]$, $[N(n\text{-}C_3H_7)_4]_2[UO_2(mnt)_2]$ and $[N(C_2H_5)_4]_2[UO_2(imnt)_2]$ always contain one or two molecules of solvent; attempts to prepare the corresponding Cs^+ or $(CH_3)_4N^+$ analogs failed. These complexes are soluble in $(CH_3)_2CO$, CH_3CN, C_5H_5N, CH_3NO_2, sparingly soluble in EtOH and insoluble in H_2O and lose the solvent molecule when treated with neutral monodentate ligands (L) according to the reaction [89]

$$[UO_2(mnt)_2(S)_n]^{2-} + L \rightarrow [UO_2(mnt)_2(L)]^{2-} + n\ S$$

$$[UO_2(imnt)_2(S)_n]^{2-} + L \rightarrow [UO_2(imnt)_2(L)]^{2-} + n\ S$$

where $n = 1$ or 2 and L = Ph_3PO, Ph_3AsO and PyN—O. These complexes can be recrystallized from acetone/water and probably have a pentagonal bipyramidal structure like $UO_2(DTC)_2(Ph_3PO)$. $[UO_2(imnt)_2(S)_n]^{2-}$ gives with acetylacetone a mixture of $[UO_2(imnt)_3]^{4-}$ and $UO_2(acac)_2$ and with sodium diethyldithiocarbamate a mixture of $[UO_2(DTC)_3]^-$ and $[UO_2(imnt)_3]^{4-}$.

ν_3O—U—O moves from higher to lower frequencies on changing the nature of the neutral monodentate ligand, in the order: Ph_3PO < pyN—O < Ph_3AsO. The compound $Cp_2U[N(C_2H_5)_2]_2$, obtained from the reaction sequence [161]

$$UCl_4 + 4\ LiN(C_2H_5)_2 \xrightarrow{THF} [U[N(C_2H_5)_2]_4 + 4\ LiCl$$

$$U[N(C_2H_5)_2]_4 + 2\ C_5H_6 \xrightarrow{Pentane} Cp_2U[N(C_2H_5)_2]_2 + 2\ NH(C_2H_5)_2$$

reacts with toluene-3,4-dithiol (H_2TDT), *o*-mercaptophenol (H_2OMP) and 1,2-ethanedithiol (H_2EDT) to give the substituted Cp_2UX. A variable temperature ^{1}H NMR investigation of Cp_2U(TDT) shows the apparent existence of dimeric composition as the room temperature singlet for the Cp protons splits into two peaks having an intensity ratio of approximately 2/1 at −60°C. A possible explanation is a rapid monomer—dimer equilibrium which is slowed down at low temperature. This dimeric tendency is also seen in the mass spectra which show *m/e* 984 and 920 for $[Cp_2U(OMP)]_2$ and $[Cp_2U(EDT)]_2$, respectively. The mass spectrum of $[Cp_2U(TDT)]_2$ does not show the expected dimer; however it is much less volatile than the other complexes as reflected by the fact that a higher temperature is needed to obtain a spectrum and that its peaks are of low intensity [161].

TABLE 10

Physico-chemical data for uranyl(VI) dithiolate complexes [89]

Complex	Color	Λc [a]	M.p. (°C)	ν_3O—U—O (cm^{-1})	Other bands (cm^{-1})
$(NEt_4)_2[UO_2(mnt)_2PyO]$	Green	148	138—141	905	1220 νN—O
$(NPr_4)_2[UO_2(mnt)_2PyO]$	Green	140	173—178	905	1220 νN—O
$(NEt_4)_2[UO_2(i\text{-}mnt)_2PyO]$	Red	158	165—167	905	1216 νN—O
$(NPr_4)_2[UO_2(i\text{-}mnt)_2PyO]$	Red	139	204—210	905	1216 νN—O
$(NEt_4)_2[UO_2(mnt)_2Ph_3PO]$	Green	155	175—180	909	1146 νP—O
$(NPr_4)_2[UO_2(mnt)_2Ph_3PO]$	Green	146	180—185	909	1119 νP—O
$(NEt_4)_2[UO_2\text{-}(i\text{-}mnt)_2Ph_3PO]$	Orange	146	202—205	909	1147 νP—O
$(NPr_4)_2[UO_2\text{-}(i\text{-}mnt)_2Ph_3PO]$	Orange	135	206—208	909	1126 νP—O
$(NEt_4)_2[UO_2\text{-}(mnt)_2Ph_3AsO]$	Green	151	180—183	900	878 νAs—O
$(NPr_4)_2[UO_2\text{-}(mnt)_2Ph_3AsO]$	Green	141	170—175		
$(NEt_4)_2[UO_2\text{-}(i\text{-}mnt)_2Ph_3AsO]$	Orange	141	208—212	900	
$(NPr_4)_2[UO_2\text{-}(i\text{-}mnt)_2Ph_3AsO]$	Orange	150	210—212	900	

[a] Λc (cm^2 ohm^{-1} mol^{-1}) in nitromethane (c = 10^{-3} mol l^{-1}) at 25°C.

F. ACTINIDE ALKYLXANTHATE COMPLEXES

In general xanthates are formed by the reaction between a metal alkoxide and carbon disulfide. Their structure can be represented by the valence bond formalism of Fig. 11.

IR studies agree that resonance forms *a* and *b* best describe the structure of the xanthate complexes [27—29,33]. The minor importance of resonance form *c* is reflected in the structure of a number of xanthate complexes [5] in which the xanthate ligands contain two significantly different C—S bonds. It must be noted however that a different situation has been found in the crystal structures of potassium ethylxanthate [30] and tris-ethylxanthate arsenic(III) [31]. The attempted preparation of actinide(IV) ethylxanthate complexes by reaction of the actinide(IV) tetrachloride with potassium ethylxanthate in ethanol, methyl cyanide, acetone or chloroform does not yield any identificable products [66], but the red-orange uranyl(VI) complexes UO_2-

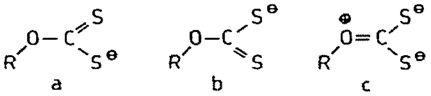
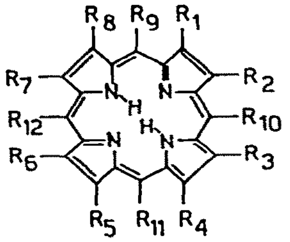


Fig. 11. Valence bond formalism of alkylxanthates.

$(ROCS_2)_2$ (R = methyl, ethyl, n- and iso-propyl, n- and iso-butyl, iso-amyl and cyclohexyl) have been isolated in poor yield from concentrated aqueous solutions of uranyl(VI) nitrate and the potassium alkylxanthate. They are very readily hydrolyzed and are much less stable with respect to decomposition than are the corresponding N,N-dialkyldithiocarbamates [35]. The ability of the sulfur atoms to accept electrons released under the mesomeric effect of the $—NR_2$ group has been proposed [5,66] as an important factor explaining the stability of dithiocarbamate complexes. When the $—NR_2$ group is replaced in xanthate derivatives by —OR, which has a much smaller mesomeric effect, little evidence for the double-bond character in the C—O bond is found and xanthalates are almost invariably less stable than dithiocarbamates.

G. ACTINIDE PORPHYRIN COMPLEXES

The porphyrins are compounds formed by adding substituents to the nucleus of porphine [165]. The naturally occurring porphyrins are generally formed by adding substituents to positions 1—8 and are named according to the number and type of substituent (Fig. 12). Upon removal of the pyrrole protons, porphyrins readily complex with a variety of metals. While free porphyrins are biologically unimportant, metalloporphyrins are widely found in nature. Porphyrins, in common with other macrocyclic ligands, have a central hole of essentially fixed size. In certain complexes the metal is unable to fit into this hole and lies out of the porphyrin plane. The ligand *meso*-tetraphenylporphin (H_2TPP) has four phenyl groups in the 9, 10, 11, 12 positions and reacts with thorium(IV) tetrakis-acetylacetonate to give $Th(TPP)(acac)_2$, the first example of a porphyrin complex of an actinide element [166]. This complex has been synthesized by refluxing for 3—4 h a 1,2,4-trichlorobenzene solution of H_2TPP and tetrakis-(2,4-pentanedionato)thorium(IV), purifying the residue by chromatography on alumina and recrystallizing the eluate from chloroform/methanol. $Th(TPP)(acac)_2$ is stable to air and water and reacts rapidly with HCl to form H_4TPP^{2+}. The mass spectrum shows a parent peak at *m/e* 943 attributable to the loss of an acac fragment. The ^1H NMR spectrum



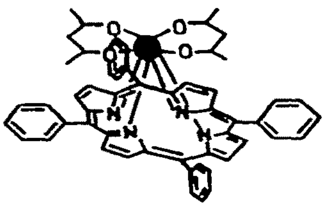


Fig. 12. The metal-free porphyrins.

Fig. 13. The proposed structure of $Th(TPP)(acac)_2$.

has peak at 8.87 δ (singlet, pyrrole) 8.27 δ (multiplet, *ortho*), 7.77 δ (multiplet, *meta* and *para*), 4.13 δ (singlet, methyne of the acac), 1.10 δ (singlet, methyl of the acac). A structure involving eight-coordination can be tentatively proposed. (Fig. 13).

H. PHTHALOCYANINE LIGAND

The phthalocyanine molecule (H_2Pc) (Fig. 14) contains a ring system of four isoindole units linked by aza nitrogen atoms [90—100]; it is therefore closely related to the naturally occurring prophyrins but has aza rather than methyne corner links. The two central hydrogen atoms of the structure are replaceable by a wide range of metals and the compounds obtained are usually insoluble in common solvents, but have some slight solubility in higher boiling aromatic solvents such as quinoline, chlorobenzene and chloronaphthalene.

Metal-free phthalocyanine exists in three polymeric forms (α, β and γ) [90,101] while most other phthalocyanines exist in two (α and β) [101—106,109]. The polymorphic forms differ in their IR spectra, X-ray diffraction patterns [102,104,110], reflectance spectra [101] conductivity, and resistivity.

Complete structural studies were carried out with the metal-free derivative [100], and the nickel [107], platinum [108] manganese(II) and iron(II) [108a] complexes. Metal-free phthalocyanine and beryllium, cobalt(II), nickel-(II), copper(II), manganese(II) and iron(II) phthalocyanines are isomorphous [108]. The phthalocyanines form long flat ribbon-like monoclinic crystals (space group $P2_1/a$), the surface of the ribbon being the (001) plane and the (010) axis. In the metal-free phthalocyanine, identical molecules occur along the *b* axis at intervals of 4.72 Å. The perpendicular distance between planes is 3.38 Å, close to that observed in graphite (3.4 Å). The nearest intermolecular approach is 3.35 Å.

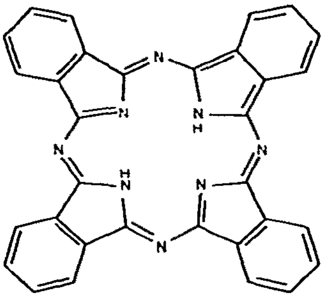


Fig. 14. The metal-free phthalocyanine.

TABLE 11

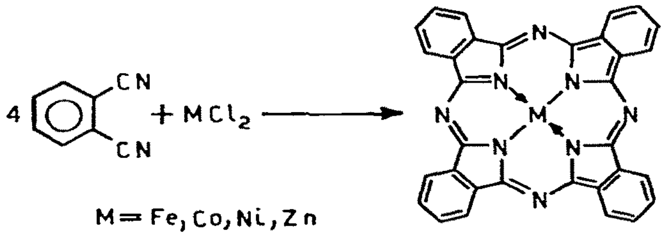
Cell constants of metal free phthalocyanine and some metal phthalocyanine complexes [176][a]

	a(Å)	b(Å)	c(Å)	β(°)
H_2Pc	19.85	4.72	14.8	122.2
Be(II)	21.2	4.84	14.7	121.0
Mn(II)	20.2	4.75	15.1	121.7
Fe(II)	20.2	4.77	15.0	121.6
Co(II)	20.2	4.77	15.0	121.3
Ni(II)	19.9	4.71	14.0	121.9
Cu(II)	19.6	4.79	14.6	120.6
Pt(II)	23.9	3.81	16.9	129.6

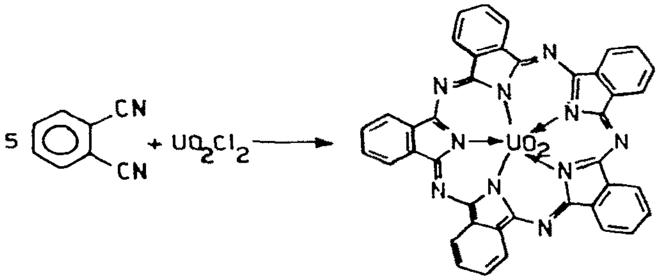
[a] Space group $P2_1/a$.

(i) *Actinide(VI) phthalocyaninate complexes*

Phthalocyanine metal complexes may be prepared by various methods, the most interesting being at a temperature greater than ca. 200°C in a solvent such as quinoline or trichlorobenzene, in which the metal ion serves as a template in the cyclization and condensation reaction which produces complexes of macrocyclic ligands [110—115]. In the absence of basic solvents or additives such as urea, ring halogenation may occur. The basic additives or their decomposition products are believed to function as halogen acceptors, thus minimizing ring attack.



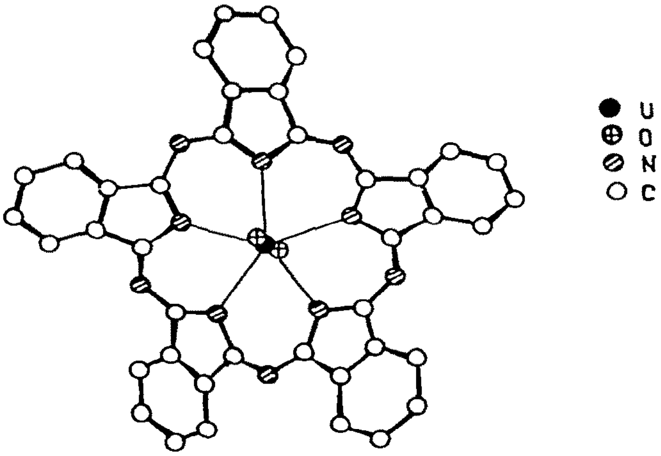
The same reaction has been also studied with uranyl(VI) [116]. First it was assumed that the reaction between dicyanobenzene and UO_2^{2+} yielded a normal tetradentate phthalocyanine complex even though satisfactory analytical data were not obtained [117—119]. Mass spectral data subsequently suggested that five dicyanobenzene subunits might be coordinated to uranyl(VI) ion [120] and the so called uranyl(VI) phthalocyanine is in reality a complex of the superphthalocyanine ligand, an expanded five-subunit analog of phthalocyanine [121,122]. Thus the reaction of anhydrous uranyl(VI) chloride with *o*-dicyanobenzene in dry dimethylformamide is



The presence of large quantities of water in the reagents reduces the yield and promotes the formation of the metal-free phthalocyanine. The yield of the condensation also falls when uranyl(VI) nitrate or acetate are substituted for the chloride and more traces of the UO_2(Spc) complex are produced in the reaction with UO_2Br_2, UO_2F_2 or UO_2SO_4. The condensation procedure employing UO_2Cl_2, phthalic anhydride and urea, with or without molybdate catalyst [90], fails to produce UO_2(Spc). The analytical and mass spectral data provide no evidence for ring chlorination during the synthesis. The UO_2(Spc) condensation is invariably accompanied by the formation of the metal-free phthalocyanine, H_2Pc. The strong preference of the uranyl(VI) ion to achieve a pentagonal-bipyramidal or hexagonal-bipyramidal coordination geometry doubtless alters the normal course of the cyclization. The IR spectrum of the blue-black UO_2(SPc) gives no evidence for C≡N which is commonly observed in (phthalocyaninato)M-(*o*-dicyanobenzene) [123,124]. In this case the extra nitrile is apparently coordinated as an independent, displaceable ligand [123,124]. A strong band at 925 cm^{-1}, due to the antisymmetric stretching ν_3O—U—O, is observed in the IR spectrum of UO_2(SPc). An X-ray diffraction study [122] indicates that the reaction above reported does occur and that five *o*-dicyanobenzene units have cyclized in the presence of uranyl(VI) ion, to yield the UO_2(SPc) superphthalocyanine complex. The blue-black crystals of UO_2(SPc) are monoclinic, space group $P2_1/c$, with a = 8.210, b = 21.667, c = 18.467 Å, β = 103.16° and Z = 4. The molecular structure (Fig. 15) shows that the coordination geometry of the uranium atom approximates an idealized compressed pentagonal bipyramid. The two axial ligands are oxygen atoms with an average U—O bond length of 1.74 Å. The equatorial coordination is by five nitrogen atoms. The cyclopentakis(2-iminoisoindoline) ligand is severely and irregularly distorted from the planarity, presumably as a consequence of appreciable steric strain within the macrocycle. The resulting polyhedron is reported in Fig. 16.

The large equatorial radius of uranium in uranyl(VI) complexes and the 2.55 Å U—N distance observed in other seven-coordinate uranyl(VI) complexes [55,85,86,125,126] seem to preclude the formation of a UO_2(Pc) complex and favour the formation of a larger macrocycle.

The use of substituted phthalonitrile in the superphthalocyanine condensation has also been reported [163]. It is possible to prepare the more soluble



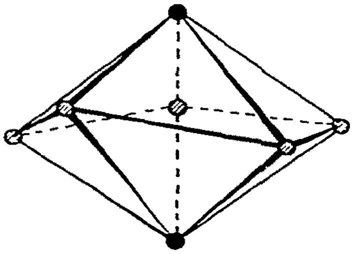


Fig. 15. A perspective view, essentially perpendicular to the mean plane of the macrocycle, of the UO_2(SPc) molecule.

Fig. 16. Perspective view of the axially compressed pentagonal bipyramidal coordination polyhedron of the UO_2(SPc) molecule.

pentamethyl derivative $UO_2(Me_5Spc)$ using 4-methylphthalonitrile and anhydrous UO_2Cl_2 in dimethylformamide. 270 MHz ^1H NMR studies indicate that the product obtained is a mixture of isomers. ^1H NMR studies also suggest that in solution UO_2(SPc) is distorted from planarity and reveals that the five subunit macrocycle is stereochemically dynamic. The analysis of ring current induced ^1H NMR shifts indicates considerably reduced π electron delocalization in UO_2(SPc) compared to M(Pc) derivatives. It appears that the inherent strain evidenced by such a molecular structure and the accompanying impairment of electronic delocalization, lead to significant destabilization of UO_2(SPc) and $UO_2(Me_3SPc)$ with respect to phthalocyanine and metallophthalocyanine products. The electronic spectra of the five-subunit macrocycles are considerably different from those of the M(Pc) derivatives. UO_2(SPc) exhibits a strong, broad absorption at rather long wavelength (914 nm) with a pronounced shoulder at about 810 nm and a strong short wavelength transition at 424 nm. For $UO_2(Me_5SPc)$ the methyl substitution causes small displacements of 10 and —5 nm respectively, in the above maxima.

The chemical stability of this UO_2(SPc) complex [127] has been studied. The reaction of UO_2(SPc) with various metal salts in dimethylformamide-1-chloronaphthalene at 60—130°C results both in displacement of the uranyl ion and contraction of the ring system according to the scheme on p. 259. Products have been confirmed by IR, mass and visible spectra and the yields are practically quantitative. An example of this reaction, monitored spectrophotometrically, is reported in Fig. 17. Anhydrous metal salts such as $CuCl_2$, $CoCl_2$ and $ZnCl_2$, when dissolved in dimethylformamide, react with UO_2-

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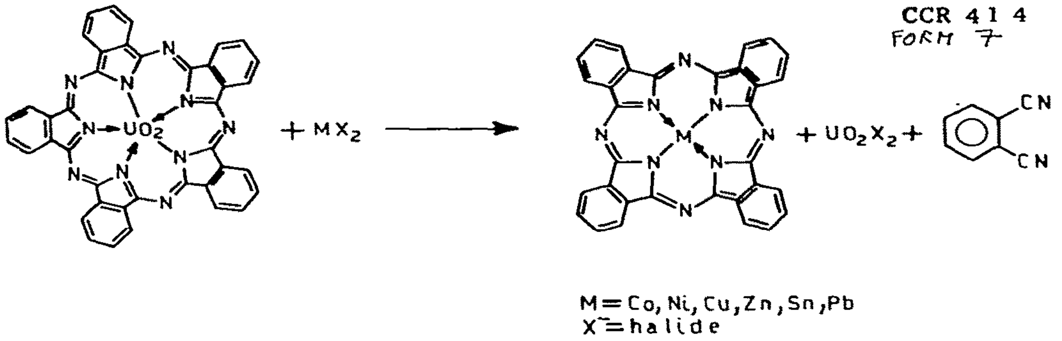
FORM 7



(SPc) to produce the corresponding M(Pc) complex in high yield. Under the same conditions the larger Sn^{2+} and Pb^{2+} ions also induce the contraction along with the formation of Sn(Pc) and Pb(Pc) respectively. Anhydrous ThCl$_4$ in DMF causes decomposition of UO$_2$(SPc) with no phthalocyanine production. The methylated derivative UO$_2$(Me$_4$SPc) reacts with CuCl$_2$ in dimethylformamide to yield Cu(Me$_4$Pc). That the Cu(Pc) does not arise via metallation of initially formed H$_2$Pc was demonstrated kinetically by showing that CuCl$_2$ converted added H$_2$Pc to Cu(Pc) at a far slower rate than the rate of UO$_2$(SPc) contraction.

Under identical conditions, metallation of the free H$_2$Pc is far slower. Also reaction with trivalent metal salts such as lanthanide trihalides yields the cor-

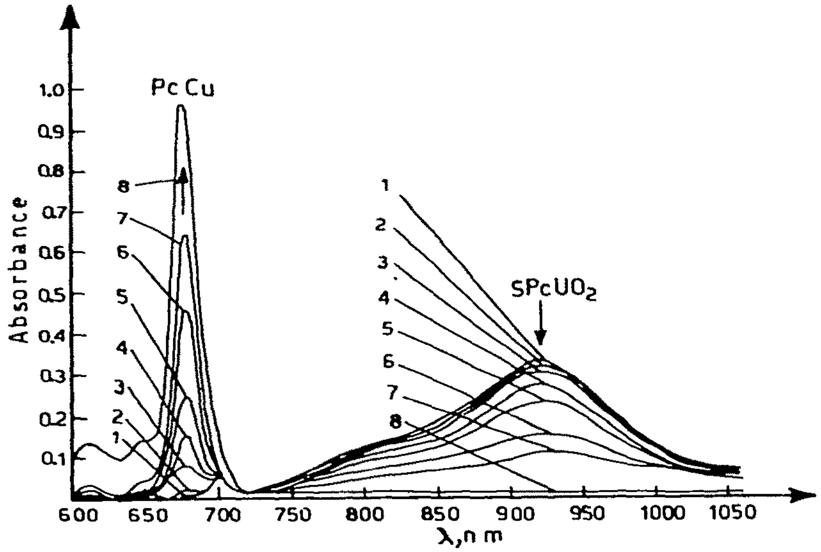


Fig. 17. Spectrophotometric record of the reaction of UO$_2$(SPc) with CuCl$_2$ in 200/1 1-chloronaphthalene/DMF at 75°C (Cu(Pc) = cupric phthalocyanine).

TABLE 12

Contraction and transmetallation reaction of UO_2(SPc) and UO_2(Me_5SPc) [127,163]

Starting complex	Metal salt [a]	Solvent	Temp. (°C)	Reaction time (h)	Products	Yield %
UO_2(SPc)	$CuCl_2$	DMF	120	3	Cu(Pc)	95
UO_2(SPc)	$CuCl_2$	1-pentanol	120	15	Cu(Pc)	87
UO_2(SPc)	Cu(tfacac)$_2$	DMF	123	13	Cu(Pc)	25
					UO_2(SPc)	75
UO_2(SPc)	Cu(tfacac)$_2$	Toluene	195 [b]	10	Cu(Pc)	33
					UO_2(SPc)	67
UO_2(Me_5SPc)	$CuCl_2$	DMF	75	47	Cu(Me_4Pc)	95
UO_2(SPc)	$CoCl_2$	Quinoline	120	1.5	Co(Pc)	59
UO_2(SPc)	$ZnCl_2$	DMF	135	30	Zn(Pc)	45
UO_2(SPc)	$ZnCl_2 \cdot 4\,H_2O$	DMF	135	30	H_2Pc	49
					Zn(Pc)	26
UO_2(SPc)	$NiSO_4 \cdot 6\,H_2O$	DMF	140	50	Ni(Pc)	82
UO_2(SPc)	$SnCl_2$	DMF	120	2.5	Sn(Pc)	82
UO_2(SPc)	$ErCl_3$	DMF	116	4	Er(Pc)Cl	37

[a] tfacac = trifluoroacetylacetonato. [b] Sealed tube reaction.

responding M(Pc)X compounds. Reaction with sodium or potassium in refluxing mesitylene produces the corresponding metal phthalocyanine. Treatment of UO_2(SPc) with aqueous and non aqueous acids under a variety of conditions results in demetallation accompanied by ring contraction.

(ii) Actinide(IV) phthalocyaninate complexes

$ThCl_4$ and phthalodinitrile (molar ratio 1 : 1 or 1 : 2) at 230—250°C interact with evolution of HCl [127—129]. After extraction of the blue-black solidified melt with acetone, a solution of the residue in quinoline gives an electronic spectrum characteristic of phthalocyanine—metal complexes [90]. This contains only one absorption band. The thorium: chloride ratio and the evolution of HCl indicates that some of the benzene rings of the phthalocyanine are chlorinated. The chlorinated product does not sublime: it decomposes with formation of metal-free phthalocyanine derivatives.

Using ThI_4 and phthalodinitrile at 240°C, it is possible to prevent halogenation of the benzene ring. After extraction of excess of nitrile and sublimation at 550°C and 10^{-5} torr, which involves evolution of iodine, dark violet crystals of diphthalocyanine—thorium(IV), Th(Pc)$_2$, can be obtained. Dark-violet diphthalocyanine uranium(IV), U(Pc)$_2$, is formed analogously from UI_4 and phthalodinitrile [130]. These products are thermally very stable and are air resistant. Th(Pc)$_2$ can be sublimed at 600°C in a N_2 stream at 1 atm. and both Th(Pc)$_2$ and U(Pc)$_2$ are sparingly soluble in C_6H_6 or THF but more soluble in py, quinoline, 1,2,4-trichlorobenzene, 1-Cl-naphthalene or hexamethyl bromide of phosphoric acid [130]. IR spectra of both complexes are almost identical and very similar to that of the analogous tin complex [128]. $Th(Pc)_2$ is diamagnetic while $U(Pc)_2$ is paramagnetic (3.1 BM between 100 and 239 K), the mass spectrometric molecular weights are 1256 for $Th(Pc)_2$ and 1262 for $U(Pc)_2$. The molecules are barely fragmented at an electron energy of 50 eV, which confirms the very great stability of the compounds in agreement with the behavior on sublimation. For these compounds antiprismatic or bipyramidal structures have been suggested, as for the tin compound [131], because the mutual steric hindrance between the two ligands would be less in the archimedian antiprismatic arrangement [131].

The thermal stability of $Th(Pc)_2$ and $U(Pc)_2$ has been studied by differential thermal analysis and thermovolumetric analysis [167] and compared with a series of lanthanide bisphthalocyaninate complexes of the type Ln(Pc)(HPc). As Fig. 18 shows, two intense endothermic peaks have been recorded on the heating curves of the Ln(Pc)(HPc) complexes whereas on the heating curves for $Th(Pc)_2$ and $U(Pc)_2$ there is a single endothermic peak at 676 and 693°C respectively. The endothermic peak at higher temperature is attributed both for Ln(Pc)(HPc) and $Th(Pc)_2$ or $U(Pc)_2$ to the decomposition of the complexes to a black substance. The endothermic peak at lower temperature in the lanthanide complexes has been ascribed to the reaction [167]

$$2\ Ln(Pc)(HPc) \rightarrow [Ln_2(Pc)_3] + H_2 + 4\ C_8H_4N_2$$

where $C_8H_4N_2$ = phthalonitrile. The crystal and molecular structure of $U(Pc)_2$, more recently determined by X-ray diffraction analysis (132), confirms the

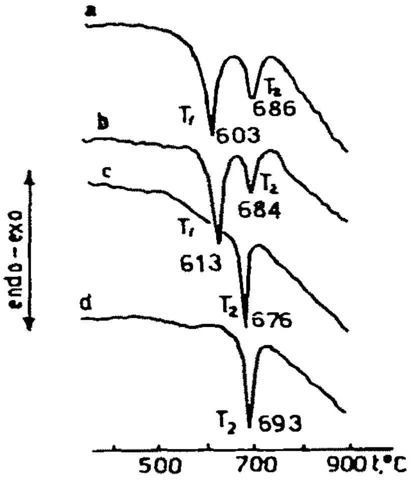


Fig. 18. Differential thermal analysis of the bisphthalocyaninate complexes (heating rate 10 K min^{-1}) in an argon atmosphere: (a) Gd(Pc)(HPc); (b) Yb(Pc)(HPc); (c) $Th(Pc)_2$; (d) $U(Pc)_2$.

eight coordination around the central metal ion. The crystals are of monoclinic symmetry and have a space group $C2/c$ with $a = 18.74$, $b = 18.73$, $c = 15.61$ Å, $\beta = 113.6°$, $Z = 4$. The asymmetric unit contains half a formula unit of U(Pc)$_2$. The structure of the molecule is reported in Fig. 19. The nitrogen atoms of the pyrrole rings of two phthalocyanine ligands are in an 8-fold coordination around the uranium atom. The four pyrrole nitrogen atoms of each ligand form a square with a side of 2.80 Å. The uranium atom is equidistant from all the pyrrole nitrogen atoms (2.43 Å) and the distance of the uranium atom from the planes defined by the pyrrole nitrogen atoms of the two ligands is 1.40 Å. The two phthalocyanine groups are rotated by about 37° from a prismatic configuration about the uranium atom so that the geometry with respect to the nitrogen atoms deviates by about 8° from that of a square antiprism. They are not planar but saucer-shaped with the four nitrogen atoms at the base of the saucer. The sp^2 orbitals at the nitrogen atoms forming σ-bonds to the uranium atom are thus bent so as to be directed towards the uranium atom. The mean bond lengths and angles do not differ appreciably from those of other metal—phthalocyaninato complexes such as Cu(Pc) [133], Pt(Pc) [134], Sn(Pc) [137], Mn$_2$(Pc)$_2$(py)$_2$O [135] or from the metal free H$_2$Pc [136]. A comparison of U(Pc)$_2$ with the complexes reported above, indicates that the uranium(IV) does not show any special properties and that the bonding between the ligand and the actinide atom is comparable to that for other metals.

One extension of the group of compounds with phthalocyanine ligands to other actinides was first detected radiochemically for protactinium(IV) and

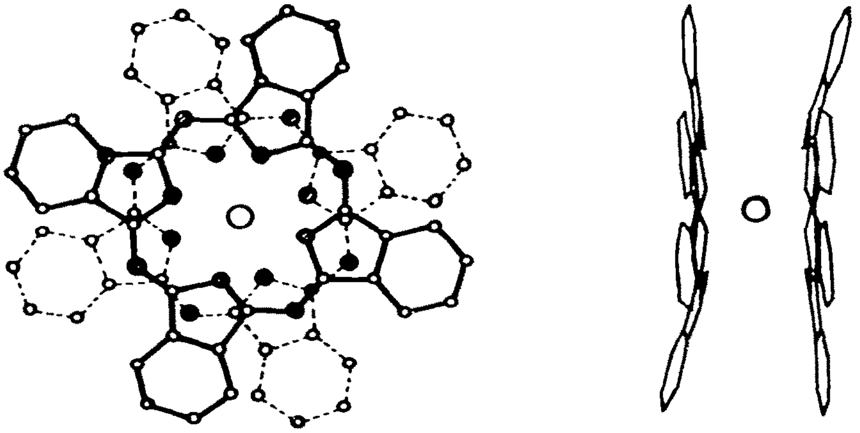


Fig. 19. Molecular structure of U(Pc)$_2$: (a) projection of the molecule onto the plane of the pyrrole nitrogen atoms; (b) projection of the molecule along the crystallographic two fold axis.

neptunium(IV) [138,139] through the reactions

$$^{232}\text{Th(Pc)}_2\ (\text{n}, \gamma)\ ^{233}\text{Th(Pc)}_2 \xrightarrow[t_{1/2}\ =\ 22.1\ \text{min}]{\beta^-} {}^{233}\text{Pa(Pc)}_2\ (\beta^-)\ t_{1/2} = 27.4\ \text{days}$$

$$^{238}\text{U(Pc)}_2\ (\text{n}, \gamma)\ ^{239}\text{U(Pc)}_2 \xrightarrow[t_{1/2}\ =\ 23.5\ \text{min}]{\beta^-} {}^{239}\text{Np(Pc)}_2\ (\beta^-)\ t_{1/2} = 2.35\ \text{days}$$

The existence of Pa(Pc)_2 and Np(Pc)_2 is shown by the observation that the specific activities of ^{232}Pa and ^{239}Np remain constant in the sublimates obtained on repeated sublimation of the irradiated Th(Pc)_2 and U(Pc)_2. $^{239}\text{Np(Pc)}_2$ was also chemically synthesized on the tracer scale from irradiated uranium metal, (^{238}U + ^{239}Np) using the normal synthetic method for the preparation of U(Pc)_2 from UI_4 and phthalodinitrile, yielding U(Pc)_2 + $^{239}\text{Np(Pc)}_2$. This preparation also indicates the possible existence of the hitherto unrecorded NpI_4 [138,139]. Weighable quantities of Pa(Pc)_2 were prepared in the same way as the thorium(IV) and uranium(IV) compounds from PaI_4 and phthalodinitrile [138,139].

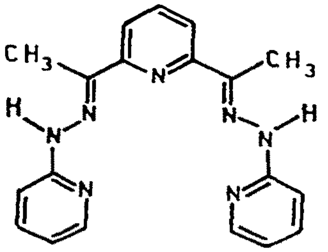
PaI_5 may also be used as starting material. This is surprising since Pa^{V} can otherwise be converted into Pa^{IV} only with very strong reducing agents. PaPc_2, like ThPc_2 and UPc_2 can be sublimed without decomposition and is stable in air, whereas Pa^{IV} compounds are generally extremely sensitive to O_2 and moisture. In the preparation of An(Pc)_2 (An = Pa(IV), Th(IV), U(IV)) the electron donor—acceptor complexes (EDA complexes), $\text{An(Pc)}_2\text{I}_2$, are proposed as intermediates. The sandwich configuration of the MPc_2 complexes is thus formed immediately. By analogy with SnPcI_2 [106] a monophthalocyaninato actinide diiodide should have been expected as the first stage. The EDA complexes are also formed from AnPc_2 and I_2 in naphthalene. The black completely insoluble compounds lose I_2 at 250°C. For EDA complexes of aromatic hydrocarbons with I_2, the excitation energy for the EDA bond is a linear function of the ionization energy of the hydrocarbons. The EDA band of MPc_2I_2 complexes (λ = 530 nm) fits well into this system.

The IR spectrum from 4000 to 400 cm^{-1} for PaPc_2 is practically identical with the corresponding spectra of ThPc_2 and UPc_2 and is characteristic of metal phthalocyanines. It may be assumed from spectra of MPc_2 complexes between 4000 and 10 000 cm^{-1} (absence of *f—f* transitions) and from their ESR spectra that the compounds have a center of symmetry.

ThI_4 reacts with perfluorophthalodinitrile at 240°C to give a perfluorophthalocyaninato compound having the composition $\text{Th(Pc}^f\text{)I}$. This is in contrast to the reaction with phthalonitrile. In $\text{Th(Pc}^f\text{)I}$ thorium has the formal oxidation number 3. It has been found by mass spectrometry that $\text{Th(Pc}^f)_2$ is formed from $\text{Th(Pc}^f\text{)I}$ by thermal decomposition (mol. wt. from mass spectrometry 1830). These complexes are the first known example of the existence of the perfluorophthalocyanine ring [138,139].

I. ACTINIDE(VI) COMPLEXES WITH 2,6-DIACETYLPYRIDINE-BIS(2'-PYRIDYLHYDRAZONE)

The ligand 2,6-diacetylpyridine-bis(2'-pyridylhydrazone)



can be obtained by reaction of 2,6-diacetylpyridine and 2-pyridylhydrazine in alcoholic media [142]. It is a pentadentate ligand capable of undergoing depro-

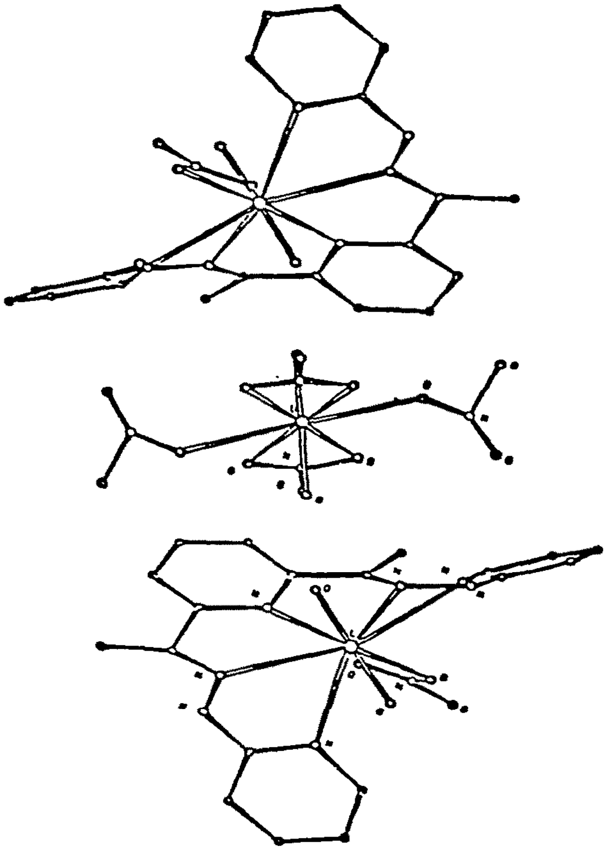


Fig. 20. The molecular structure of $[UO_2(H_2L)(NO_3)]_2[UO_2(NO_3)_4]$.

tonation reactions when it is coordinated to transition metal ions allowing ionic complexes to be transformed into neutral complexes, as found for other polyaza ligands derived from pyridine-2-aldehyde [140,141,143—150].

2,6-diacetylpyridine-bis(2′-pyridylhydrazone) has been utilized for preparing the first pentaaza complex, with diazinic sequences, of uranyl(VI) ion, containing uranyl(VI)—nitrogen amidic bonds [151]. Treatment of UO_2-$(NO_3)_2 \cdot 6\ H_2O$ in ethylacetate with the ligand in different ratios and at different temperatures affords the same red product with a uranium : ligand ratio of 3 : 2 [151]. The IR spectrum of this compound shows a band at 3283 cm^{-1} due to N—H, a more intense one at 940 cm^{-1} due to ν_3 O—U—O and bands characteristic of coordinated pyridine [153] in the region 1620—1440 cm^{-1}. An X-ray investigation [152] has been carried out on this compound as spectroscopic evidence does not provide unambiguous information on the bonding mode of the ligand and geometry around the uranium. The crystals are triclinic, space group $P\bar{1}$, $a = 14.07$, $b = 10.80$, $c = 10.12$ Å; $\alpha = 63.8$, $\beta = 75.6$, $\gamma = 78.8°$; $z = 1$. The molecular structure of the complex is unusual: two highly distorted octacoordinated complex cations are electrically balanced by the unexpected uranyl(VI) tetranitrate counteranion. The resulting molecular structure, viewed along the *c* axis, is shown in Fig. 20. The unit cell contains two cations $[UO_2(H_2L)NO_3]^+$ related by a center of symmetry and a $[UO_2(NO_3)_4]^{2-}$ anion at the center of symmetry. The cation comprises a

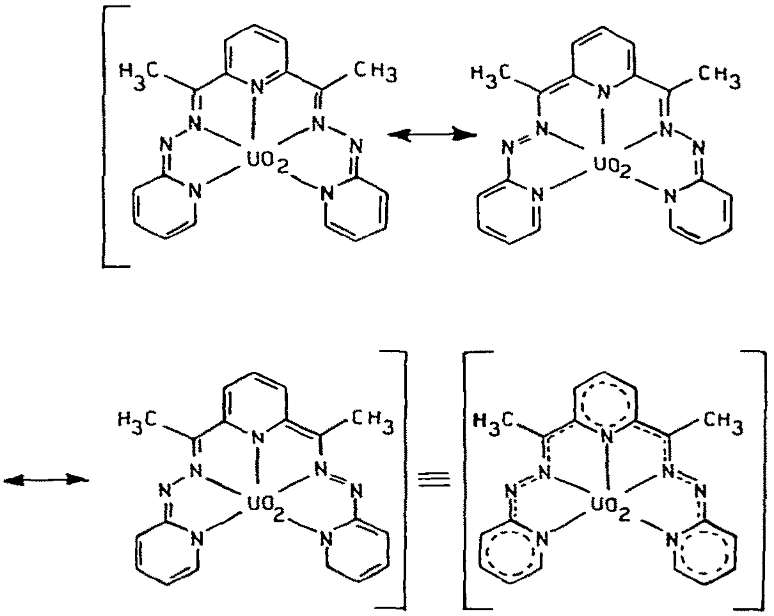


Fig. 21. Equivalent resonance forms (1, 2, 3) in terms of the valence bond structure and delocalized electronic structure (4) of the complex $UO_2(L)$.

system of four strained five-membered rings with a monodentate nitrate group in the coordination sphere of the UO_2^{2+}. In the anion two nitrate groups coordinate as bidentate and two as monodentate nitrate groups, leading to the 6-fold coordination of oxygen atoms in the equatorial plane normal to uranyl group [154].

By suspending $[UO_2(H_2L)(NO_3)]_2[UO_2(NO_3)_4]$ in anhydrous acetonitrile in the presence of an excess of 1,8-bis(dimethylamino)naphthalene deprotonation of the ligand occurs and a black product, stable in the solid state, has been quantitatively obtained. This black compound is non-conducting in nitrobenzene solution and although the IR spectrum is rather complex, there is no evidence for N—H and NO_3^- stretching vibrations, and the ν_3O—U—O is lowered to 911 cm^{-1}. 2,6-diacetylpyridine-bis(2′-pyridylhydrazone) is easily recovered from this black compound when it is treated with dilute mineral acids and water. The structure reported in Fig. 21 has been proposed for this black compound; it is highly stabilized by the presence of the 5-5-5-5 chelation mode, which allows the highest resonance of the system.

J. ACTINIDE(IV) AMIDE COMPLEXES

The complexes of the last section contain the amidic An—NR_2 bond which is stabilized by the extensive mesomeric nature of the organic ligands. It is also possible to prepare complexes in which such a mesomeric stabilizing effect is not present. The starting material for the preparation of uranium(IV) amide complexes is tetrakis-(diethylamido)-uranium(IV), $U[N(C_2H_5)_2]_4$ synthesized by the reaction of lithium diethylamide with uranium(IV) tetrachloride in diethylether [168—170]. After filtration of LiCl and removal of the solvent, the uranium amide was purified by distillation under vacuum. An emerald-green liquid which crystallizes at 35.5—36.5°C was obtained. In the crystalline state the complex exists as a dimer, with two nitrogen atom bridges between two uranium atoms [170]. Its molecular structure (Fig. 22) shows five nitrogen atoms which are at the corners of a distorted trigonal bipyramid. Two of these bipyramids share an edge to make a dimeric complex located on a center of symmetry. The uranium atoms are 4.00 Å apart. The three nonbridging U—N distances average 2.22 Å whereas the bridging U—N distances are 2.47 and 2.57 Å. This compound undergoes an aminolysis reaction when treated with a secondary amine [173] and the trinuclear $U_3(CH_3NCH_2CH_2NCH_3)_6$, ($U_3(DMED)_6$), and the tetranuclear $U_4(CH_3NCH_2CH_2NCH_3)_8$, ($U_4(DMED)_8$) [174], have been synthesized this way according to the reactions

$$3\ U[N(C_2H_5)_2]_4 + 6\ CH_3NHCH_2CH_2NHCH_3 \rightarrow U_3(CH_3NCH_2CH_2NCH_3)_6$$

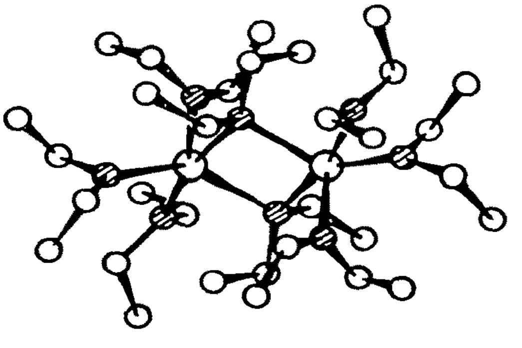
$$+\ 12\ HN(C_2H_5)_2$$

and

$$4\ U[N(C_2H_5)_2]_4 + 8\ CH_3NHCH_2CH_2NHCH_3 \rightarrow U_4(CH_3NCH_2CH_2NCH_3)_8 + 16\ HN(C_2H_5)_2$$

at 77 K using pentane as solvent. The structural analysis [173] of the trinuclear compound shows that this complex is a cluster containing three uranium atoms in a line bridged by nitrogen atoms. The central uranium atom is on a center of symmetry and is 3.543 Å from the terminal atoms; the uranium atoms are joined by triple nitrogen bridge bonds, each of which is from a different dimethylethylenediamine ligand. The central uranium atom is on a center of symmetry with six chemically equivalent nitrogen atoms about it at the corners of an elongated trigonal antiprism with an average U—N distance of 2.37 Å. The two equivalent terminal uranium atoms are at the center of a distorted trigonal prism of six nitrogen atoms, including both nitrogen atoms of each of the three dimethylene ligands. The six nitrogen neighbors of the terminal uranium atoms define a figure which is closer to a trigonal prism than to a regular octahedron (Fig. 23).

In the tetranuclear $U_4(DMED)_8$ [174] (Fig. 24) the four uranium atoms are at the corners of a square of side 3.6 Å, twisted so that each uranium is 0.7 Å from a mean plane. The uranium atoms are chemically and crystallographically equivalent and each is bonded to six nitrogen atoms in a highly distorted trigonal prism. Four of these nitrogen atoms act as double bridges to two neighboring uranium atoms in the ring. The other two nitrogen neighbors define an irregular polyhedron which can be described as a distorted trigonal prism. The entire tetramer has symmetry 222 and conforms approximately to the higher symmetry $\bar{4}2m$. Half of the dimethylene diamido ligands are singly coordinated to uranium at each nitrogen, while the other half of the ligands participate in bridging with both nitrogen atoms. The U—U distance in the



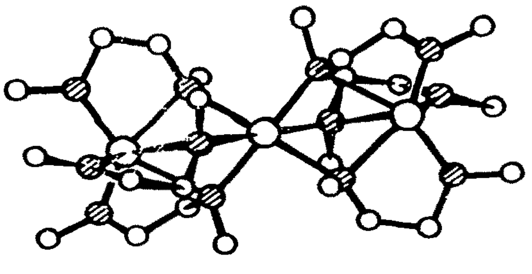


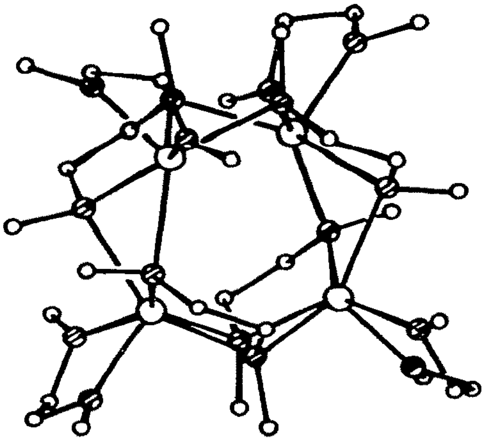
Fig. 22. The molecular structure of $U[(N(C_2H_5)_2)_4]_2$.

Fig. 23. The molecular structure of $U_3(DMED)_6$.

tetramer is slightly longer than in the trimer; so as in the trimer molecule it is unlikely that there will be any magnetic interactions above 4.2 K.

It must be noted that for the uranium amides, if the R groups of the amide are bulky, then oligomerization is prevented [171]. This occurs for the complex $U[N(C_6H_5)_2]_4$, ($U(DPA)_4$), obtained either by the aminolysis reaction or by reaction of UCl_4 with $LiN(C_6H_5)_2$. The crystal structure of this complex [171] (Fig. 25) shows that it is a monomer in the solid state and exhibits four-coordination for uranium(IV). The dark intense red color of $U(DPA)_4$ is probably due to the involvement of the aromatic rings of the amide group in the ligand in metal charge-transfer transitions. These transitions can be followed throughout the course of the aminolysis reaction, suggesting the formation of intermediates during the exchange. The original green solution of $U[N(C_2H_5)_2]_4$ slowly changes from yellow to red in a period of approximately 6 h. This color change suggests that the diethylamine groups are slowly exchanged with diphenylamide groups, shifting the visible transitions to longer wavelengths with the replacement of each diethylamide (Tables 13 and 14).

The electronic spectra of mononuclear and polynuclear uranium amides (Fig. 26) show marked similarities of these compounds suggesting that the ligand has little effect on the nature of the *f—f* transitions. The differences between spectra of $U[N(C_2H_5)_2]_4$ and $U(DPA)_4$, run in benzene and diethylether, are attributed to the complexing ability of the solvents. For the trinuclear $U_3(DMED)_6$ the close similarity of the spectra in the two solvents has been explained [173] by the assumption that the molecule is trimeric in solution with the coordination sites on the uranium atoms either filled or effectively blocked by the ligands. The large upfield shifts observed in the ^1H NMR spectra of $U[N(C_2H_5)_2]_4$, in ether solvents, agree with electronic spectra and are



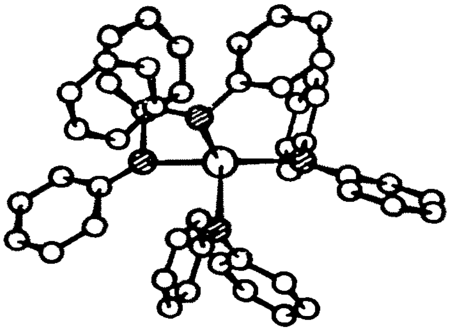


Fig. 24. The molecular structure of $U_4(DMED)_8$.

Fig. 25. The molecular structure of $U[(N(C_6H_5)_2]_4$.

TABLE 13

Cell constants for mononuclear and polynuclear uranium(IV) amide complexes

Compound	Unit-cell	Space group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Z	Color	Ref.
$U[N(C_2H_5)_2]_4$	Monoclinic	$P2_1/c$	9.326	17.283	13.867		108.43		4	Emerald-green	169
$U(DPA)_4$	Triclinic	$P\bar{1}$	10.74	20.11	9.86	92.8	111.0	99.4	2	Dark-red	171
$U_3(DMED)_6$	Monoclinic	$P2/a$	17.019	9.932	11.013		107.45		2	Yellow	173
$U_4(DMED)_8$	Orthorhombic	$Fddd$	12.02	22.73	34.32				8	Red-brown	174

TABLE 14

Salient bond distances (Å) for mononuclear and polynuclear uranium(IV) amide complexes

Compound	U—U	U—N (bridging)	U—N (terminal)	Ref.
$U[N(C_2H_5)_2]_4$	4.004	2.46, 2.57	2.22[a]	169
$U(DPA)_4$			2.21, 2.25, 2.27, 2.35	171
$U_3(DMED)_6$	3.543	2.57[a]	2.21[a]	173
$U_4(DMED)_8$	3.60[a]	2.50[a]	2.25[a]	174

[a] Average value.

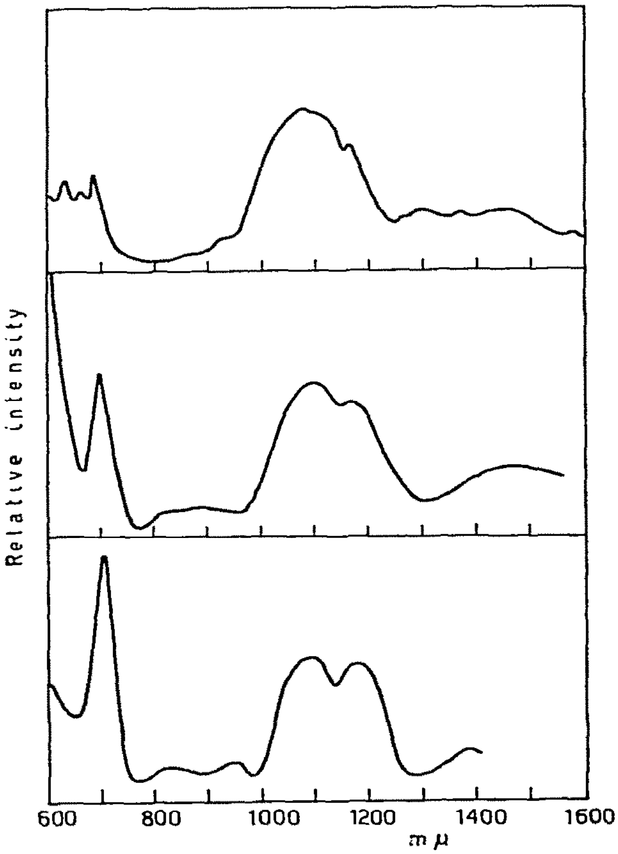


Fig. 26. The electronic spectra of mononuclear and polynuclear uranium(IV) amides: (a) mononuclear $U[N(C_6H_5)_2]_4$; (b) dinuclear $U[N(C_2H_5)_2)_4]_2$; (c) trinuclear $U_3(DMED)_6$.

TABLE 15

Magnetic data for the mononuclear $U(DPA)_4$, dinuclear $U[N(C_2H_5)_2]_4$ and trinuclear $U_3(DMED)_6$ [a]

Compound	C_M	μ_{eff}(BM)	(K)	Ref.
$U(DPA)_4$	1.00	2.84	24.8	171
$U[N(C_2H_5)_2]_4$	1.052	2.81	−2.4	169
$U_3(DMED)_6$	0.78	2.50	30.5	173

[a] The complexes follow the Curie—Weiss law $\chi_M = C_M/(T + \Theta)$ per uranium atom.

probably due to pseudocontact shifts since these solvents can coordinate to the metal ion and lower the symmetry of the molecule. The magnetic behavior of mononuclear $U(DPA)_4$, dinuclear $U[N(C_2H_5)_2]_4$ and the trinuclear $U_3(DMED)_6$ has been investigated in the temperature range 4.2—100 K. At temperatures of 20 K for $U(DPA)_4$ and 10 K for $U[N(C_2H_5)_2]_4$ the susceptibility becomes temperature independent, while above 30 K for the first complex and 20 K for the second the susceptibility follows the Curie—Weiss law; for the trinuclear complex the susceptibility follows the Curie—Weiss law throughout the measured temperature range (Table 15).

K. CONCLUSIONS

Chelate compounds of the actinide ions, in various oxidation states, containing four membered chelate rings with bidentate sulfur or selenium donors in the molecule are easy to obtain; they have been available for a long time but only recently have they been well characterized through the determination of the structures of several actinide(III), (IV) and (VI) dithio and diselenocarbamate and thiocarboxylate compounds. Some general considerations which emerge from these studies are of interest.

There are many similarities, but also some remarkable differences, between actinide complexes with dithio and diseleno groups and actinide complexes with ligands forming bidentate oxygen donor chelate rings e.g. nitrate or acetate. With the uranyl(VI) ion all of these ligands, with the exception of diselenocarbamate, give the anions $[UO_2(NO_3)_3]^-$, $[UO_2(CH_3COO)_3]^-$, $[UO_2(DTC)_3]^-$, in which the uranyl ion is hexacoordinated. These complexes, when treated with monodentate oxygen donor ligands, behave in a different manner. Uranyl(VI) nitrate gives rise only to the hexacoordinated complexes $UO_2(NO_3)_2(L)_2$; uranyl(VI) acetate gives the hexacoordinate $UO_2(CH_3COO)_2(L)_2$ and the dimeric pentacoordinated $[UO_2(CH_3COO)_2(L)]_2$. $[UO_2(DTC)_3]^-$ gives only the pentacoordinate complexes $UO_2(DTC)_2(L)$. The bite, i.e. the distance between the donor atoms of the bidentate ligand is the most important factor in determining the coordination geometry of the uranyl(VI) complexes; the bite is ca. 2.1 Å for NO_3^-, ca. 2.2 Å for CH_3COO^-, ca. 2.8 Å for

$(C_2H_5)_2NCSS^-$ and ca. 3.2 Å for $(C_2H_5)_2NCSe_2^-$ [52,178].

The anion $[UO_2(NO_3)_4]^-$ exists in the solid state and on the basis of X-ray diffraction has the structure [154] shown in Fig. 27.

$[An(CH_3COO)_5]^-$ has been reported [172] to be absorbed on an anion-exchanger and to be efficiently extracted by tertiary amines or long-chain quaternary ammonium salts dissolved in an organic diluent [172]. In these solutions the tetraacetate anions $[An(CH_3COO)_4]^-$ have been identified but it is still doubtful that they really exist. $[UO_2(DTC)_4]^-$ and $[UO_2(DSeC)_4]^-$ do not exist at all.

The acetate ion often acts as a bridging bidentate ligand giving rise to dimeric uranyl(VI) complexes; with dithioacetate and dithiobenzoate ions only mononuclear complexes have been obtained.

$U(CH_3COO)_4$ is polymeric with the uranium(IV) atom decacoordinated while $U(DTC)_4$ is a well defined monomer.

The xanthate complexes are less stable than dithiocarbamate analogs owing to the absence of an O=C bond.

When sulfur acts as a monodentate donor forming an An—SR bond it is less stable and more difficult to obtain.

It has been thought that thioethers cannot coordinate to an actinoid ion; $UO_2(OSO)(Cl)_2$ shows that when sulfur is in an appropriate position in a chelating ligand it can bind to a "hard" ion. This must be more deeply studied in the future in order to compare the strength and the reactivity of U—N (aminic), U—O (etheric) and U—S (thioetheric) bonds in chelate complexes.

Template reactions constitute an extensive class of chemical transformations in which a metal ion serves as a framework for the coordinative cyclization of an organic ligand. The possibility of creating new expanded macrocycles by performing the oligomerization reaction in the presence of large coordinatively specific actinide templates has been investigated. The present finding indicates that actinide ions may be capable of altering the normal course of a number of organic cyclo-oligomerization reactions via unusual requirements of coordination geometry and ionic radius. Much attention could be paid to this approach in the future.

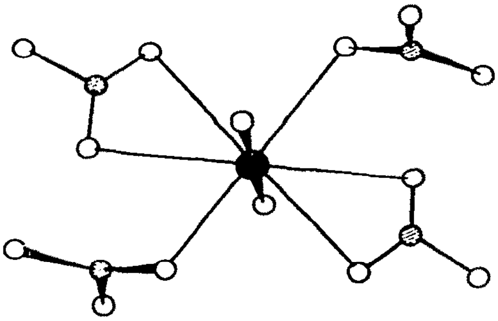


Fig. 27. The mononuclear structure of $[UO_2(NO_3)_4]^{2-}$.

The very high reactivity of the U—NR$_2$ amidic bond could be studied in more detail in the future in order to further understand its chemical properties and reactivity and to prepare new compounds by the aminolysis reaction

$$U(NR_2)_4 + x\ HNR'_2 \rightarrow U(NR_2)_{4-x}(NR'_2)_x + x\ HNR_2$$

A remarkable characteristic of these uranium—amide systems is their tendency to oligomerization. Further work on *f*-electron metal amide complexes is necessary to determine the generality of this oligomerization reaction.

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