splitting for $UCl_5 \cdot TCAC$ in the other solvents studied is 896, 879, and 917 cm^{-1}, for CS_2, benzene, and CCl_4, respectively. The reason for this variation is not at all clear at present. However, because the Γ_8' levels tend to split increasingly with decreasing symmetry, it may be that these energy level differences reflect the symmetry lowering or magnitude of distortion from octahedral symmetry.

Esr Spectra

Finally, we report the first esr measurements made on pure U(V) compounds, namely, powdered samples of $UCl_5 \cdot TCAC$, $UCl_5 \cdot SOCl_2$, $UCl_5 \cdot PCl_5$, $RbUCl_6$, and $(n\text{-}C_3H_7)_4NUCl_6$. All of these compounds produced an extremely broad signal similar to that for the compound $UCl_5 \cdot SOCl_2$, shown in Figure 6. The average g values were all approximately 1.1, with the sign undetermined. This may be compared with the value of $\backsim 1.25$ determined for U(V) ions in a matrix of ThO_2.[24] The value of g is expected to be negative, since $g = -1.14$ for Pa(IV)[12] and $g = -0.60$ for Np(IV)[13] and since Karraker[5] has *calculated* a g value for $UCl_5 \cdot SOCl_2$ of -1.18. Agreement of this latter value with our experimental values is quite reasonable.

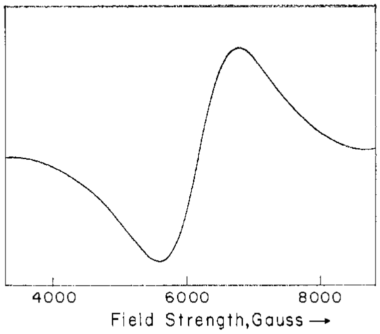

Figure 6.—Esr spectrum of powdered $UCl_5 \cdot SOCl_2$; $\nu = 9.442$ Mc.

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Diethyldithiocarbamates of Quadrivalent Actinides[1]

By J. P. Bibler[2] and D. G. Karraker

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Diethyldithiocarbamates of Th(IV), U(IV), Np(IV), and Pu(IV) were synthesized by the reaction between MCl_4 or $[(C_2H_5)_4N]_2MCl_6$ (M = Th, U, Np, or Pu) and LiL $[L = S_2CN(C_2H_5)_2^-]$ in anhydrous ethanol. Elemental analyses show that the products have the formula ML_4, and comparison of the infrared spectra of ML_4 compounds and the sulfur-bonded ZnL_2 indicates that all are similarly bonded. X-Ray diffraction data indicate that all four compounds are isomorphous. Proton magnetic resonance spectra established the spectroscopic equivalence of all C_2H_5 radicals in $CDCl_3$ and C_6D_6 solutions of ThL_4 and UL_4. The proposed structure for the ML_4 compounds is an eight-coordinate metal ion, bonded by four four-atom chelate rings to the ligands.

Introduction

The objective of this investigation was the synthesis and study of sulfur-bonded coordination compounds of the actinides. Qualitative information on actinide(IV) coordination can be obtained from the existence of such compounds. A comparison of the stability of compounds in which actinides are bonded to sulfur with the stability of analogous oxygen-bonded compounds might provide valuable information on the nature of the bonding.

Previous investigators have attempted to synthesize uranium(IV) dialkyldithiocarbamates but obtained uranyl derivatives instead.[3] Uranyl dialkyldithiocarbamates have been investigated thoroughly,[4-6] and an early investigation[7] mentioned a thorium precipitate that was not characterized. The preparation and preliminary results on the crystal structure of uranium(IV) diethyldithiocarbamate were reported[8] during the preparation and review of this paper.

Experimental Section

Reagents. $[(C_2H_5)_4N]_2MCl_6$.—These compounds were prepared by a modification of the method of Bradley, *et al.*[9] The M(IV) hydroxides were precipitated from aqueous solution by addition of base, washed free of excess base, and dehydrated by washing with absolute ethanol. A suspension of the M(IV) hydroxide in absolute ethanol was dissolved by bubbling gaseous HCl into the chilled suspension; $[(C_2H_5)_4N]_2MCl_6$ was precipitated by addition of an ethanol solution of $(C_2H_5)_4NBr$. The solid product was collected by filtration, washed with absolute ethanol, and vacuum dried.

UCl_4, $NpCl_4$.—Anhydrous UCl_4 and $NpCl_4$ were prepared by passing a stream of dry nitrogen, saturated with CCl_4, over UO_2

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[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

[2] ORAU Summer Research Participant at the Savannah River Laboratory.

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or NpO_2 at ~600°.[10] The oxides were contained in a ceramic combustion boat in a horizontal, externally heated glass tube. The anhydrous chlorides sublimed to a cool zone on the wall of the tube.

Solvent.—All solvents were reagent grade and were further purified by passage through 4-Å molecular sieves. Dissolved oxygen was removed by alternately evacuating the solvent to about 0.5 atm and purging with dry nitrogen.

Infrared Spectra.—Infrared spectra were measured in paraffin oil mulls with a Perkin-Elmer Model 521 infrared spectrophotometer. All samples were prepared in a nitrogen atmosphere; CsBr, KBr, and NaCl plates were used to support the samples. The precision of infrared wavelengths is estimated to be ± 3 cm^{-1}; the accuracy is ± 5 cm^{-1}.

X-Ray Diffraction Data.—X-Ray powder diffraction photographs were taken with a 57.3-mm-diameter Debye–Scherrer camera, Ilford G film, and nickel-filtered copper radiation. Samples were loaded into glass capillaries and sealed with wax in an inert atmosphere to prevent decomposition during the 10-hr exposure. The intensity of the diffraction lines was measured from the film with a Jarrell-Ash Model JA-203 microdensitometer. The d values obtained have an estimated accuracy of ± 0.01 Å; line intensities have an estimated precision of $\pm 10\%$.

Pmr Spectra.—Proton magnetic resonance (pmr) spectra for ThL_4 and UL_4 were obtained with a Varian A-60 nmr spectrometer. Deuteriobenzene was the solvent used for 20–60°; $CDCl_3$ was the solvent used between -60 and 20°.

Analyses.—The chelates were dissolved in strong nitric acid, and organic material was destroyed by wet-ashing with nitric and sulfuric acids. After wet-ashing, thorium was determined by EDTA titration; uranium was determined by reduction to uranium(IV) in a lead reductor and titration with standard ceric solution; and neptunium and plutonium were determined by coulometric titration.

Sulfur analyses were performed gravimetrically after oxidation of weighed samples in a Parr bomb and precipitation of $BaSO_4$.

Carbon, hydrogen, and nitrogen were determined with an F & M Model 185 CHN analyzer. Because of the personal hazard involved in handling the α-emitting ^{237}Np and ^{239}Pu in dry compounds, neptunium and plutonium compounds were not analyzed for carbon, hydrogen, or nitrogen.

Syntheses.—The general method of preparation was by the reaction of an anhydrous ethanol solution of lithium diethyldithiocarbamate and the metal chloride (MCl_4 or $[(C_2H_5)_4N]_2MCl_6$) in a nitrogen atmosphere at room temperature. Lithium diethyldithiocarbamate was selected because of the solubility of lithium chloride in the ethanol solvent. Lithium diethyldithiocarbamate was freshly prepared for each reaction by dissolving a weighed piece of oxide-free lithium in ethanol (0.05 mole of lithium/80 ml of ethanol). The ethanol solution of lithium ethoxide was cooled in liquid nitrogen, and equimolar quantities of carbon disulfide and diethylamine were added successively, with stirring and cooling.

Solid $[(C_2H_5)_4N]_2MCl_6$ or an ethanol solution of UCl_4 or $NpCl_4$ was added to the solution of lithium diethyldithiocarbamate, and the slurry was agitated until the reaction was judged complete; the time varied among different actinides. Products were collected on a filter, washed, and agitated with benzene to dissolve the actinide diethyldithiocarbamates. The benzene solution was filtered to separate undissolved solids, and the actinide diethyldithiocarbamates were precipitated by dilution of the benzene solution with about five volumes of petroleum ether (bp 20–40°).

UL_4, NpL_4, and PuL_4 products obtained by this procedure are slightly impure, as evidenced by pmr spectra and CHN analyses for the UL_4 product and by infrared spectra for all three products. Recrystallization of UL_4 from benzene in the presence of diethylamine apparently reduced decomposition in solution, and a pure product was obtained, as evidenced by elemental analysis, pmr spectra, and the correspondence of infrared spectra to that of ThL_4. This procedure was followed in preparing NpL_4 and PuL_4. Recrystallization of ThL_4 from benzene with no diethylamine present yielded a pure product. Infrared spectra identified pure products. Synthetic data are summarized in Table I.

TABLE I

SYNTHETIC DATA

Product	Color	Reaction material	Mixing time, hr	Chemical yield,[b] %
ThL_4[a]	White	$[(C_2H_5)_4N]_2ThCl_6$	16	65
UL_4	Dark beige	$[(C_2H_5)_4N]_2UCl_6$	0.5	75
		UCl_4	0.2	6
NpL_4	Orange	$[(C_2H_5)_4N_2]NpCl_6$	0.5	95
		$NpCl_4$	0.2	10
PuL_4	Black	$[(C_2H_5)_4N]_2PuCl_6$	16	50

[a] L = $S_2CN(C_2H_5)_2^-$. [b] After recrystallization; calculated from the quantity of actinide. Lithium diethyldithiocarbamate was usually in excess.

Results

Analyses of the products are summarized in Table II; infrared absorption data for solid samples are shown in Table III, with absorption data for ZnL_2 included for comparison.

Infrared Spectra.—Infrared absorption spectra for all four ML_4 products were essentially the same and correspond rather closely with the spectrum of ZnL_2. The 950–1200-cm^{-1} region of the spectrum reflected the purity of the product. Impure products characteristically showed a double absorption from 1010 to 1090 cm^{-1} and a single absorption near 995 cm^{-1}.[11] This pattern was absent in the spectra of pure samples.

X-Ray powder diffraction data for lines of strongest intensity (Table IV) show that all four compounds are isomorphous.

Pmr Spectra.—Proton magnetic resonance spectra at room temperature and at $-58°$ for C_6D_6 solutions of ThL_4 showed only two sets of signals. A triplet of relative magnitude 3, centered at -0.83 ppm relative to tetramethylsilane as an internal standard, was assigned to equivalent methyl protons; a quartet of relative magnitude 2, centered at -4.0 ppm, was assigned to equivalent methylene protons. Although the spectrum of the paramagnetic UL_4 derivative showed larger chemical shifts and a slight temperature dependence, the equivalence of ethyl groups again was apparent (one triplet due to $-CH_3$ groups at -1.76 ppm in C_6D_6 at 20° and one quartet due to $-CH_2-$ groups at -5.79 ppm). The equivalence of these groups does not imply directly that all diethyldithiocarbamate ligands are bonded in an equivalent manner, although such a model is not unreasonable. The absence of pmr signals due to coordinated ethanol, ethoxide, or water in conjunction with infrared and analytical data establish that these ligands could only be present to the extent of a few per cent.

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(11) The abstract of this paper (Abstract L-32) submitted at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, arrived at erroneous conclusions from an interpretation of the infrared spectra of compounds now known to be impure.

Table II

Elemental Analyses

	Anal, %									
	C		H		N		S		Metal	
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Th[S_2CN(C_2H_5)_2]_4$	29.13	29.19	4.85	4.94	6.80	6.76	31.06	30.90	28.2	27.5
$U[S_2CN(C_2H_5)_2]_4$	28.92	28.98	4.82	4.85	6.76	6.81	30.84	31.80	28.6	28.2
$Np[S_2CN(C_2H_5)_2]_4$							30.88	31.80	28.6	28.1
$Pu[S_2CN(C_2H_5)_2]_4$							30.80	28.91	28.76	28.43

Table III

Infrared Absorption Bands (cm^{-1})[a]

ThL_4[b]	UL_4[b]	NpL_4[c]	PuL_4[c]	ZnL_2[b]
2230 w, b	2230 w, b	2230 w, b	2230 w, b	. . .
1488 s	1490 s	1490 s	1485 s	1500 s
1435 sh	1435 sh	1432 sh	1431 sh	1435 s
1428 s	1428 s	1428 s	. . .	1425 sh
1421 s	1422 s	1422 sh	1420 s	. . .
1374 s	1376 s	1376 s	1372 s	1375 s
1365 sh	1368 sh	1370 sh	1365 sh	. . .
1355 s	1355 s	1355 s	1351 s	1352 s
1350 sh	1350 sh	1348 sh	. . .	1340 sh
1299 w	1299 w	1300 w	1296 w	1295 s
1290 w	1291 w	1290 w	1290 sh	. . .
1264 s	1264 s	1262 s	1262 s	1268 s
1200 s	1200 s	1200 s	1204 sh	1202 s
			1197 s	1198 s
1140 s	1140 s	1140 s	1140 s	1140 s
1085 m	1085 m	. . .	. . .	1092 s
1080 sh	1080 sh	1080 sh	1085 m	1076 sh
1072 s	1072 s	1072 s	1068 s	1068 s
1060 m	1060 m	1060 sh	1060 sh	1058 sh
992 s	995 s	995 s	992 s	990 s
980 m, sh	983 m, sh	982 m, sh	982 m, sh	980 sh
912 m	913 m	910 m	908 s	910 s
840 m	840 m	840 m	837 s	845 m
				838 m
792 w	792 w	790 w	792 w	788 sh
778 sh	778 sh	775 sh	772 m	780 sh
768 m	770 m	770 m	772 m	772 m
672 m	680 m	. . .	670 s	670 w
612 w	612 w	. . .	. . .	610 w
570 sh	572 sh	. . .	. . .	562 s
560 m	560 m	. . .	. . .	555 m

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad. [b] CsBr window. [c] NaCl window.

Table IV

X-Ray Data for ML_4 Compounds

ThL_4		UL_4		NpL_4		PuL_4	
d, Å	Rel intens	d, Å	Rel intens	d, Å	Rel intens	d, Å	Rel intens
9.34	100	9.17	100	9.17	100	9.16	100
8.66	51	8.51	52	8.55	54	8.54	53
7.36	55	7.23	49	7.22	58	7.22	48
5.67	23	5.59	25	5.61	25	5.61	22
5.21	14	5.17	11	5.16	13	5.14	11
4.85	26	4.81	32	4.81	28	4.83	26
4.58	38	4.54	38	4.54	33	4.55	38
4.31	8	4.29	5	4.28	10	4.29	10
3.94	4	3.87	6	3.91	3	3.92	4
3.72	7	3.69	11	3.69	8	3.68	6
3.33	11	3.32	11	3.31	11	3.30	9
3.07	9	3.05	9	3.05	7	3.06	5
2.86	9	2.85	8	2.84	8	2.84	9
2.78	5	2.75	6	2.74	5	2.73	5
2.66	7	2.66	8	2.66	9	2.65	7
2.59	6	2.59	9	2.56	9	2.57	8
2.50	13	2.48	13	2.48	13	2.48	13
2.43	12	2.41	10	2.41	7	2.40	7
2.37	5	2.35	6	2.36	7	2.36	4
2.31	5	2.29	1	2.28	2	2.29	3
2.10	1	. . .	. . .	2.09	6	2.08	3
2.01	4	2.00	17	2.00	4	2.00	5

Discussion

The infrared spectra of all of the ML_4 compounds are identical. Absence of two strong absorptions in the 818–856 and 930–940-cm^{-1} regions[12] for uranium, neptunium, and plutonium derivatives precludes the possible formation of products of MO_2^{2+} ions. Similarly, both infrared and pmr spectra show no signals that would indicate that H_2O, $OC_2H_5^-$, or C_2H_5OH is associated in any way with the ML_4 complexes. Three prominent bands that appear in the 1130–1290-cm^{-1} region of the spectrum have been found to be characteristic of dithiocarbamates.[13] These bands were found at 1264, 1200, and 1140 cm^{-1} for ML_4 derivatives, and at 1268, 1202–1198 (doublet), and 1140 cm^{-1} for ZnL_2, a complex which is known to be sulfur bonded.[14] Further similarities between the infrared spectra of actinide and zinc diethyldithiocarbamate complexes suggest that ML_4 derivatives are also sulfur bonded. All N,N-dialkyldithiocarbamate complexes have a strong band in the 1450–1530-cm^{-1} region, which is assigned[15,16] to a polar C═N bond. This band appears at 1490 cm^{-1} for the actinide complexes and at 1500 cm^{-1} for ZnL_2.

If the ligands were nitrogen bonded in ML_4 series, this peak would be expected at much lower frequencies. Therefore, diethyldithiocarbamato–actinide(IV) complexes are proposed to have the ligands bonded to the metal ions through sulfur exclusively in four equivalent four-atom chelate rings. Bagnall and Holah[8] found that UL_4 is monomeric in benzene solution; probably other ML_4 compounds are also monomeric, in agreement with the expectation for chelates with an eight-coordinate metal ion.

Bagnall and Holah also proposed that the uranium atom is eight-coordinated to the sulfur atoms of the ligands. This appears to be the most reasonable hypothesis, as other probable coordination numbers require nonequivalence of the ligands. The data cannot be interpreted as establishing the equivalence of the ligands beyond reasonable doubt, but are in better

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accord with equivalent than with nonequivalent ligands. The complete crystal structure analysis for UL_4 is reported[8] to be in progress.

Pmr spectra for ThL_4 and UL_4 compounds demonstrate the spectroscopic equivalence of all of the C_2H_5 groups in solutions of these chelates. In view of the isolation of the C_2H_5 groups from the metal–sulfur bonds, it is doubtful that the pmr spectra would indicate nonequivalence of the ligands.

The ML_4 compounds react with oxygen and water. ThL_4 can be stored in an inert atmosphere without decomposition, but UL_4, NpL_4, and PuL_4 decompose slowly to form products insoluble in benzene or chloroform. ThL_4 solutions in $CHCl_3$ are stable for days in the absence of oxygen, but decomposition products precipitate from UL_4 solutions within 1 day. The greater stability of ThL_4 is also displayed by the greater ease in preparing a pure compound, compared to the other three ML_4 compounds. Measurements of the Mössbauer spectra of NpL_4 are in progress with the hope of establishing further proof of the structure.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE,
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Distribution of Some Simple and Complex Anions between Molten Lithium Nitrate–Potassium Nitrate and Tetraheptylammonium Nitrate in Polyphenyl

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The distribution of chloride, perrhenate, and $AgCl_2^-$ ions between a eutectic molten salt mixture of $LiNO_3$–KNO_3 and a solution of tetraheptylammonium nitrate in a polyphenyl solvent was studied at 150°. The distribution of the anions has been interpreted in terms of a simple anion-exchange equilibrium followed by polymerization of some species in the organic phase. The equilibrium constants for the anion exchange and the dimerization constants were calculated, and the dependence of the perrhenate distribution on the temperature was determined. The stability constants of AgCl and $AgCl_2^-$ species in the nitrate melt were derived from the distribution data. The activity coefficients of the solute and nitrate salts follow, up to a solute mole fraction of 0.1, an expression derived from a simple model of molten salt mixtures.

Introduction

In contrast to the large number of papers dealing with solvent extraction from aqueous solutions, only few attempts have been made to extend solvent extraction studies to molten salt systems. Isaac, *et al.*,[2a] have studied the extraction of some lanthanides and actinides from molten nitrate with tributyl phosphate, and Hertzog,[2b] in a similar system, extended the study to several other elements. Zangen and Marcus[3] investigated the distribution of mercury(II) halides between a nitrate melt and a polyphenyl solvent while Borkowska, *et al.*,[4] published data on the extraction of some actinides from a KCl–CuCl eutectic melt with various solvents.

The solvent extraction of the anionic species Cl^-, ReO_4^-, and $AgCl_2^-$ from a eutectic $LiNO_3$–KNO_3 melt with tetraheptylammonium nitrate, THAN, in an inert polyphenyl solvent is reported in this paper.

The only solvent extraction studies of metallic complexes involving a molten phase that have been reported are based on the distribution of a neutral species.[2a,3] The stability of metallic complexes in molten nitrates has been studied mainly through electromotive force measurements,[5,6] and owing to the nature of this experimental technique, the information obtained is most reliable for the lower complexes, since the concentration of the ligand is usually low. Thus the formation constant of $AgCl_2^-$ in molten $LiNO_3$–HNO_3[6] seems to be questionable. Solvent extraction and solubility measurements allow the coverage of a wide range of ligand concentration, and with these two independent experimental methods the stability constants of the higher complexes can be determined.

The interpretation of the distribution data in terms of equilibrium constants requires some assumptions regarding the activity coefficients of the species in both phases.

The Melt.—As in all experiments the Li : K mole ratio was maintained constant, the nitrate melt can be taken as a single component M^+A^-, with $M^+ = 0.42Li^+ +$

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