Octathiocyanato- and Octaselenocyanato-complexes of the Tetravalent Actinide Elements

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Octathiocyanato-actinide(IV) complexes of the types $(NEt_4)_4M(NCS)_8$ (M = Th, Pa, U, Np, and Pu) and $Cs_4M(NCS)_8$ (M = U and Pu) and the octaselenocyanato-complexes $(NEt_4)_4Pa(NCSe)_8$ and $(NEt_4)_4U(NCSe)_8$ have been prepared by reactions in non-aqueous media. Crystallographic and spectral results are reported for the complexes together with some chemical properties.

NUMEROUS hydrated thorium(IV) and uranium(IV) thiocyanato-complexes are known, but relatively few anhydrous complexes have been characterised;[1] protactinium(IV), neptunium(IV), and plutonium(IV) analogues have not hitherto been recorded. It has been shown[2] that the thiocyanate groups are bonded to the metal *via* the nitrogen atom in the recently prepared[3] compound $(NEt_4)_4U(NCS)_8$ and that the eight nitrogen atoms are arranged at the vertices of an almost perfect cube. This compound is only the second known example of discrete, eight-co-ordinate cubic stereochemistry, and it appeared worthwhile to study the preparation and properties of analogous complexes formed by the larger (Th and Pa) and smaller (Np and Pu) tetravalent actinide ions. We report now the preparation of the series of complexes $(NEt_4)_4M(NCS)_8$ (M = Th, Pa, Np, and Pu) and $Cs_4M(NCS)_8$ (M = U and Pu), and of the first examples of actinide(IV) selenocyanato-complexes, $(NEt_4)_4M(NCSe)_8$ (M = Pa and U), together with details of their crystallographic and spectral properties.

Preparation of the Complexes.—Treatment of either the appropriate actinide tetrachloride or tetraethylammonium hexachloro-complex[3] in anhydrous methyl cyanide with stoicheiometric amounts of potassium thiocyanate and tetraethylammonium chloride (1 : 8 : 4 in the former instance and 1 : 8 : 2 in the latter instance)

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[1] K. W. Bagnall, *M.T.P. Int. Rev. Sci.*, 1972, **7**, 139.

[2] R. Countryman and W. S. McDonald, *J. Inorg. Nuclear Chem.*, 1971, **31**, 2213.

[3] P. Gans and J. W. Marriage, *J.C.S. Dalton*, 1972, 1738.

yields the octathiocyanato-complexes $(NEt_4)_4M(NCS)_8$, (M = Th to Pu inclusive) which are purified by recrystallisation from methyl cyanide. The solubilities in this solvent increase markedly from thorium through to plutonium; the octathiocyanato-complexes are also appreciably soluble in nitromethane but virtually insoluble in methylene dichloride, ethyl acetate, and isopentane.

The analogous octaselenocyanato-complexes of protactinium(IV) and uranium(IV) are obtained in an identical manner from reactions involving the appropriate tetrachloride, potassium selenocyanate, and tetraethylammonium chloride. They are somewhat more soluble in methyl cyanide than are the thiocyanato-complexes but crystallise readily on the addition of methylene dichloride and isopentane, in which solvents they are insoluble.

$Cs_4U(NCS)_8$ and $Cs_4Pu(NCS)_8$ form, in acetone solution, on the addition of caesium thiocyanate to the appropriate dicaesium hexachloro-complex (8 : 1 mole ratio). Removal of the solvent by vacuum evaporation followed by recrystallisation from a mixture of nitromethane and methylene dichloride yields the pure complexes which are soluble in acetone, nitromethane, methyl cyanide, and water but are insoluble in methylene dichloride, benzene, and isopentane.

All the complexes decompose when treated with aqueous ammonia, the insoluble actinide(IV) hydroxides being formed. The protactinium(IV) complexes decompose as a result of oxidation on exposure to the atmosphere, and on the addition of solvents which have not been thoroughly flushed with an inert gas such as nitrogen or argon.

TABLE 1

Crystallographic properties of the actinide(IV) octathiocyanato- and octaselenocyanato-complexes [a]

Compound	Colour	Lattice parameters (Å) [b] a_0	c_0	Mol. vol. Å^3
$(NEt_4)_4Pa(NCS)_8$	Dark blue	11·65	23·05	1564
$(NEt_4)_4U(NCS)_8$	Green [c]	11·64	22·99	1556
$(NEt_4)_4Np(NCS)_8$	Pale brown	11·63	22·89	1547
$(NEt_4)_4Pu(NCS)_8$	Brown	11·60	22·88	1537
$(NEt_4)_4Pa(NCSe)_8$	Dark blue	11·82	23·49	1642
$(NEt_4)_4U(NCSe)_8$	Green	11·80	23·36	1626

[a] All possess tetragonal symmetry, space group $D^{17}_{4h} - I4/mmm$ with 2 molecules per unit cell. [b] Standard deviations (2σ) are ±0·07 and ±0·04 Å for a_0 and c_0, respectively. [c] Dimensions reported from a single crystal study, ref. 2, are a_0 = 11·64 and c_0 = 23·01 Å.

Crystallographic Properties.—The tetraethylammonium octathiocyanato-complexes are all isostructural with the uranium compound for which full structural data are available.[2] Unit-cell dimensions are listed in Table 1 together with the molecular volumes; the latter decrease, as expected, with the ionic radii of the actinide elements. Observed and calculated $\sin^2\theta$ values for $(NEt_4)_4Np(NCS)_8$ are given in Table 2. $(NEt_4)_4Pa(NCSe)_8$ and $(NEt_4)_4U(NCSe)_8$ crystallise with the same structure as their thiocyanato-analogues, the unit-cell dimensions (Table 1) being slightly larger. It appears, therefore, that the ligands are also bonded *via* the nitrogen atom in these compounds. Relatively poor quality powder photographs were obtained for the caesium octathiocyanato-metallates(IV); no attempt was made to index these powder data but it was obvious that the complexes were not isostructural with their tetraethylammonium analogues.

TABLE 2

Partial *X*-ray powder diffraction data for $(NEt_4)_4Np(NCS)_8$

$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	h,k,l	I_{est} *
0·0088	0·0088	1,1,0	S
0·0146	0·0146	1,0,3	S
0·0177	0·0176	2,0,0	W
0·0181	0·0181	0,0,4	W
0·0221	0·0221	2,0,2	M
0·0232	0·0231	2,1,1	S
0·0269	0·0269	1,1,4	M+
0·0322	0·0322	2,1,3	M+
0·0356	0·0357	2,0,4	S(d)
0·0397	0·0397	2,2,2	M−
0·0486	0·0485	3,1,2	W
0·0503	0·0503	2,1,5	M+
0·0534	0·0533	2,2,4	W+
0·0583	0·0583	3,2,1	M+
	0·0584	2,0,6	
0·0620	0·0621	3,1,4	M+
0·0676	0·0673	3,2,3	M
0·0703	0·0703	4,0,0	M
0·0725	0·0725	0,0,8	W+
0·0759	0·0758	4,1,1	M−
	0·0760	2,2,6	
0·0774	0·0775	2,1,7	M−
0·0835	0·0836	3,3,2	W+
0·0849	0·0848	3,1,6	M+
	0·0849	4,1,3	
0·0950	0·0951	3,0,7	W+
0·1030	0·1031	4,1,5	W+
0·1061	0·1060	4,2,4	M
0·1078	0·1077	2,2,8	W+
0·1110	0·1110	5,0,1	M
	0·1110	4,3,1	
	0·1111	4,0,6	
0·1136	0·1134	0,0,10	M−
	0·1138	2,1,9	
0·1164	0·1165	3,1,8	M−
0·1198	0·1199	3,3,6	M−
	0·1201	4,3,3	
0·1286	0·1286	5,2,1	M−
	0·1287	4,2,6	
0·1303	0·1303	4,1,7	M−
0·1322	0·1320	5,1,4	W+
0·1379	0·1377	5,2,3	M−
0·1409	0·1406	4,4,0	W+
0·1428	0·1429	4,0,8	M−
0·1489	0·1485	2,2,10	M
	0·1490	3,2,9	

* S, strong; M, medium; W, weak.

Spectral Properties.—A single, strong C–N stretching vibration is observed in the i.r. spectra of solid complexes of the types $(NEt_4)_4M(NCS)_8$ and $(NEt_4)_4M(NCSe)_8$, as would be expected from group-theoretical considerations for eight-co-ordinate ions with O_h (cubic) symmetry.[4] The bands are observed between 2045 and 2055 cm^{-1} (Table 3), positions which are little different from those for thiocyanate and selenocyanate ions in their respective potassium salts. The C–S vibration, expected

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[4] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

TABLE 3

Infrared spectral results (cm^{-1}) for the actinide(IV) complexes

Compound	ν(C–N) * Solid	Solution
$(NEt_4)_4Th(NCS)_8$	2045	
$(NEt_4)_4Pa(NCS)_8$	2042	
$(NEt_4)_4U(NCS)_8$	2045	2060 [a]
$(NEt_4)_4Np(NCS)_8$	2045	
$(NEt_4)_4Pu(NCS)_8$	2055	
$Cs_4U(NCS)_8$	2050	2045 [a]
$Cs_4Pb(NCS)_8$	2050, 2100sh	2040 [b]
$(NEt_4)_4Pa(NCSe)_8$	2043	
$(NEt_4)_4U(NCSe)_8$	2040	

[a] In nitromethane. [b] In acetone.

* All CN vibrations are very strong.

as a very weak band at *ca.* 800 cm^{-1} for nitrogen bonded thiocyanate groups,[4] could not be identified in the various spectra, possibly because of the appearance of a medium intensity band associated with the tetraethylammonium ion at 780 cm^{-1}. The C–S band has not been observed in the spectra of the caesium complexes either, although the intensity of the C–N stretching vibration (very strong) indicates [4-6] that the thiocyanate ion is also *N*-bonded in these compounds. This is confirmed by the results of Bailey *et al.*[4] who quote the following i.r. bands (cm^{-1}) for a sample of $K_4U(NCS)_8$: ν(CN), 2057s and 2015sh; ν(CS) 926w and 790w; δ(NCS) 478m. Preparative conditions were, however, not provided for this compound. Although we have been unable to resolve the strong C–N vibration in the spectra of our samples of $Cs_4U(NCS)_8$ [the band is resolved for $Cs_4Pu(NCS)_8$, Table 3] the peak is slightly asymmetric on the low wavelength side.

The splitting observed by Bailey *et al.*[4] for $Cs_4U(NCS)_8$, and by ourselves for the plutonium analogue, suggests that, unlike that in the tetraethylammonium complex, the anion in the caesium salts does not possess cubic (O_h) symmetry. This is supported by the observed solid state spectra for the two uranium complexes. Thus, as shown in Figure 1 and Table 4, the spectrum of $Cs_4U(NCS)_8$ is somewhat different from that of $(NEt_4)_4U(NCS)_8$. In contrast to this observation $(NEt_4)_4U(NCSe)_8$ exhibits a spectrum which is virtually identical with that of the latter complex.

TABLE 4

Spectral results for the octathiocyanato-complexes

$(NEt_4)_4Pa(NCS)_8$ [a]		$(NEt_4)_4U(NCS)_8$ [a]		$(NEt_4)_4U(NCS)_8$ [b]		$Cs_4U(NCS)_8$ [a]		$(NEt_4)_4Np(NCS)_8$ [a]	
Position (nm) [c]	*I* [d]	Position (nm) [c]	*I* [d]	Position (nm)	*I* [d]	Position (nm) [c]	*I* [d]	Position (nm) [c]	*I* [d]
592	VS [e]	460	S	458	W	466	S	441	S
1200	S,br	490	S	478	sh	474	W	469	M
1578	W	511	sh			490	W	473	sh
1690	VW	518	S	507	S	513	S	490	M
1840	sh	575	W	580	M	581	S	510	M
1890	S	621	S			620	sh	528	S
1950	sh	690	S	650	sh	650	S	539	S
		780	M	685	sh	680	S	548	sh
		826	sh	701	S	701	S	565	W
		917	S			750	VW	619	W
		1008	M			836	sh	640	M
		1098	S	880	sh	870	sh	664	VW
		1121	sh			900	S	690	sh
		1160	S	930	M	928	sh	708	S
		1190	sh			956	sh	729	S
		1270	VW	1070	sh	1078	sh	749	S
		1416	M,b	1115	sh	1113	S	780	W
		1488	vw,b	1188	S,b	1188	S	791	S
		1568	sh			1253	sh	849	M
		1590	M,b			1271	sh	879	sh
		1649	sh			1380	VW	911	M
		1690	VW	1455	sh	1480	sh	925	M
				1585	S,b	1550	S,b	968	VW,sh
						1617	S,b	991	M
						1715	sh	1018	S
						1930	W	1190	W
								1200	W
								1390	W,sh
								1470	W,b
								1510	W,sh
								1709	S
								1810	M

[a] Solid state spectrum at 77 K. [b] Solution spectrum in anhydrous methyl cyanide. [c] Band positions correspond to the spectra illustrated in Figures 1 and 2. [d] Relative intensity: S, strong; M, medium; W, weak; b, broad; sh, shoulder. [e] Only observed for very thin samples.

Spectra recorded for $(NEt_4)_4U(NCS)_8$ and $(NEt_4)_4Np(NCS)_8$ in anhydrous methyl cyanide or nitromethane are quite different from the solid state transmission spectra of these compounds. In fact, apart from intensity and resolution differences, the solution spectrum of $(NEt_4)_4U(NCS)_8$ is extremely similar to the solid state

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[5] S. Fronaeus and R. Larson, *Acta Chem. Scand.*, 1962, **16**, 1447.

[6] C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.

transmission spectrum of $Cs_4U(NCS)_8$. This is apparent from the results shown in Table 4 where the band positions are compared. This suggests that on dissolution in methyl cyanide or nitromethane the cubic stereochemistry of the $U(NCS)_8^{4-}$ anion in the tetraethylammonium complex is destroyed, the arrangement of the NCS groups transforming to that of the anion in $Cs_4U(NCS)_8$, probably either dodecahedral or square antiprismatic. However, attempts to confirm these deductions by examination of the solution i.r. spectra of $(NEt_4)_4U(NCS)_8$ and $Cs_4U(NCS)_8$ have been inconclusive. Thus, in each instance only a single, strong C–N vibration is observed (Table 3) for nitromethane solutions of the complexes, whereas, as pointed out by Grey and Smith [7] more bands should be observed for square antiprismatic (2) or dodecahedral stereochemistry (4). Whilst the possibility remains that the vibrations are very close in energy the problem will only be solved satisfactorily by the elucidation of the structure of $Cs_4U(NCS)_8$ using X-ray techniques. The spectrum of $Cs_4U(NCS)_8$ in nitromethane is virtually identical with that of the solid compound.

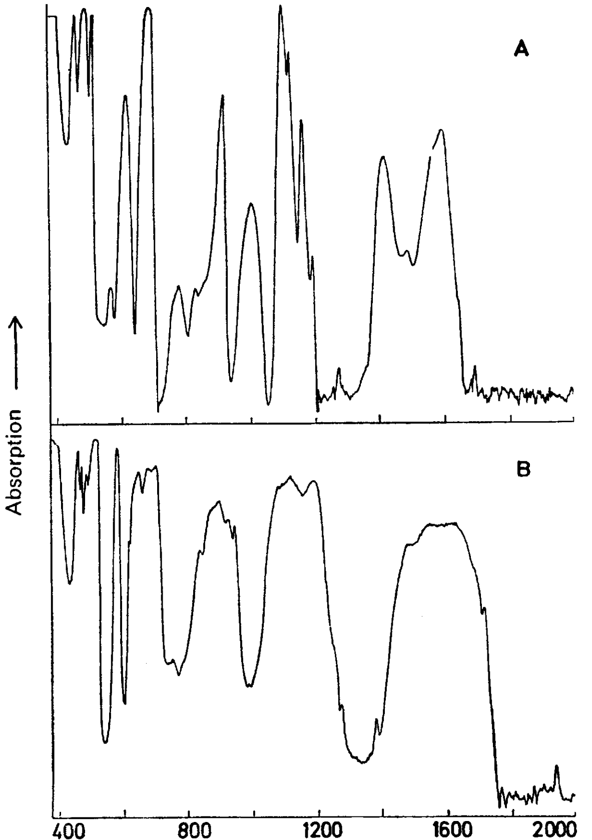

FIGURE 1 A, solid state spectrum of $(NEt_4)_4U(NCS)_8$; B, solid state spectrum of $Cs_4U(NCS)_8$

Low-temperature, solid state transmission spectra for $(NEt_4)_4Pa(NCS)_8$ and $(NEt_4)_4Np(NCS)_8$ are illustrated in Figure 2; associated band positions are given in Table 4. These are the first recorded solid state spectra for Pa^{IV} and Np^{IV} compounds in which the actinide(IV) ion is known to exhibit cubic stereochemistry. As might be anticipated the spectrum of $(NEt_4)_4Pa(NCS)_8$ is quite different from those of solid $PaCl_4$ (dodecahedral) and UF_4 (square antiprismatic) and of the six-co-ordinate complexes Cs_2PaCl_6 and $PaCl_4(tppo)_2$.[8] * The spectrum of $(NEt_4)_4Pa(NCSe)_8$ is virtually identical with that of the isostructural octathiocyanato-complex.

EXPERIMENTAL

Compounds were prepared and handled in inert (nitrogen or argon) atmosphere boxes (water content <20 p.p.m.; oxygen content <20 p.p.m.) to afford protection from moisture and oxygen and because of the radioactive hazards associated with the α-emitting isotopes ^{231}Pa, ^{237}Np, and ^{239}Pu which were used in this work.

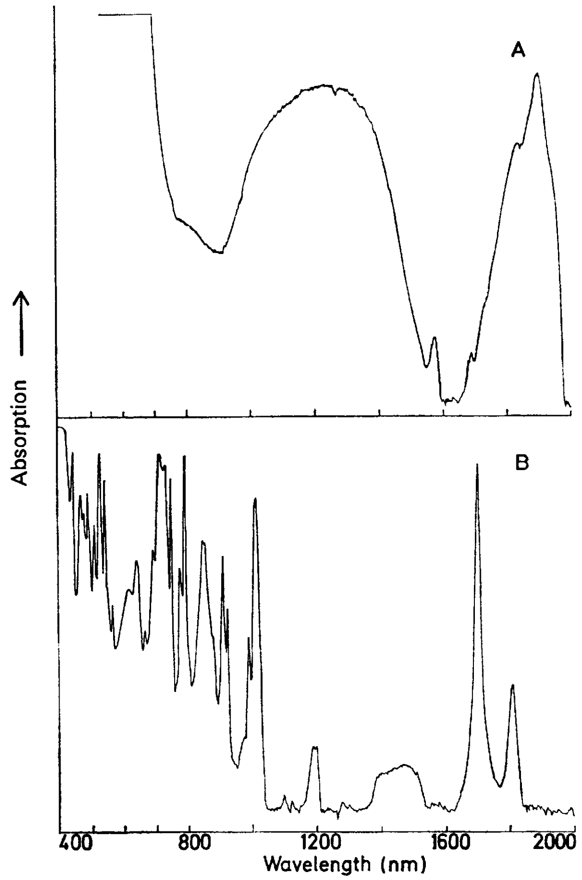

FIGURE 2 A, solid state spectrum of $(NEt_4)_4Pa(NCS)_8$; B, solid state spectrum of $(NEt_4)_4Np(NCS)_8$

Materials.—Thorium,[9] protactinium,[10] uranium,[11] and

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* tppo = triphenylphosphine oxide.

[7] I. E. Grey and P. W. Smith, *Austral. J. Chem.*, 1969, **22**, 311.

[8] D. Brown and B. Whittaker, to be published.

[9] B. C. Smith and M. A. Wassef, *J. Chem. Soc.* (*A*), 1968, 1817.

[10] D. Brown and P. J. Jones, *J. Chem. Soc.* (*A*), 1967, 719.

[11] J. A. Hermann and J. F. Suttle, *Inorg. Synth.*, 1957, **5**, 143.

neptunium[12] tetrachlorides, Cs_2UCl_6,[13] $(NEt_4)_2PuCl_6$,[14] and Cs_2PuCl_6[13] were prepared according to the methods in the references cited. Methyl cyanide was purified as described previously;[15] all other solvents were distilled, flushed with argon to remove oxygen, and stored in contact with degassed molecular sieves. Potassium thiocyanate and selenocyanate were obtained from B.D.H. Ltd. and used as supplied.

NN-*Tetraethylammonium Octathiocyanatometallates*(IV).—The appropriate tetrachloride (0·05—0·3 g), or $(NEt_4)_2PuCl_6$ (0·20 g), was mixed with the stoicheiometric quantities of potassium thiocyanate (1 : 8 mole ratio) and tetraethylammonium chloride (1 : 4 mole ratio) in methyl cyanide (1—5 ml). The reaction mixture was heated for several minutes following which the precipitated potassium chloride was removed by centrifugation and, if necessary, the precipitated product was extracted from it into hot methyl cyanide. The thorium, protactinium, and uranium *products* crystallised in high yield (90—95%) from the methyl cyanide supernatant; the more soluble neptunium and plutonium octathiocyanato-complexes were isolated by vacuum evaporation of the supernatant following which they were purified by recrystallisation from the minimum volume of hot methyl cyanide.

$Cs_4U(NCS)_8$ *and* $Cs_4Pu(NCS)_8$.—1 : 8 Mole ratios of the appropriate dicaesium hexachlorometallate(IV), Cs_2MCl_6 (0·2—0·3 g), and caesium thiocyanate were mixed in acetone (5 ml). The reaction mixture was heated for 10 min following which the precipitated caesium chloride was removed by centrifugation. The *product* was isolated by vacuum evaporation of the acetone and purified by dissolution in nitromethane from which solvent it precipitated on the addition of dichloromethane. This dissolution–precipitation cycle was repeated three times, the nitromethane solution being centrifuged to remove caesium chloride before the addition of the dichloromethane.

$(NEt_4)_4Pa(NCSe)_8$ *and* $(NEt_4)_4U(NCSe)_8$.—These complexes were prepared in a similar manner to their thiocyanato-analogues. The *products* were appreciably more soluble in methyl cyanide from which solvent they crystallised on the addition of dichloromethane–isopentane mixture.

Analysis.—The metals and thiocyanate were determined as described previously.[16] The results are given in Table 5. $(NEt_4)_4Pu(NCS)_8$ and $Cs_4Pu(NCS)_8$ were identified by *X*-ray powder diffraction analysis.

Physical Measurements.—Solid state i.r. and visible spectra were recorded as described previously.[16] Solution i.r. spectra were recorded for dilute solutions of the complex in nitromethane contained in a fixed path-length (0·05 mm) cell. Compensation for the weak bands of nitromethane in the region of interest (1800—2200 cm^{-1}) was achieved by use of a variable path-length cell containing the solvent. *X*-Ray powder photographs were obtained for samples in thin-walled silica capillaries using a Debye–Scherrer 19 cm camera with filtered copper radiation (35 kV; 15 mA). Capillaries containing the radioactive isotopes were coated with Bostikote as a safety precaution.[17] Since the structure type was known[2] it was possible to calculate the powder pattern expected for $(NEt_4)_4U(NCS)_8$ using the Programme Genstruck[18] and then index the observed reflections by comparison with the calculated pattern. The indexed reflections were refined by a least-squares method using the programme Cohen[18] with the appropriate wavelength (λ_mCu-K_α = 1·54178 Å). The agreement limit was set to 0·0004 for values of $\sin^2\theta$.

TABLE 5

Analytical results

	Found		Required	
Compound	Metal (%)	SCN (%) or SeCN (%)	Metal (%)	SCN (%) or SeCN (%)
$(NEt_4)_4Th(NCS)_8$[a]	18·95	38·1	19·05	38·15
$(NEt_4)_4Pa(NCS)_8$	18·95	38·05	19·0	38·2
$(NEt_4)_4U(NCS)_8$	19·4	38·05	19·45	37·95
$(NEt_4)_4Np(NCS)_8$	19·2	38·15	19·4	38·0
$(NEt_4)_4U(NCSe)_8$	14·85	52·4[b]	14·9	52·55
$(NEt_4)_4Pa(NCSe)_8$	14·3	52·6[b]	14·5	52·75
$Cs_4U(NCS)_8$	19·2	37·2	19·3	37·6

[a] Found: C, 39·9; H, 6·6; N, 14·0; S, 21·3. Calc. for $C_{16}H_{20}N_{12}S_8Th$: C, 39·5; H, 6·6; N, 13·8; S, 21·1%. [b] Based on the gravimetric determination of Se.

We thank the S.R.C. for a grant towards the cost of using U.K.A.E.A., A.E.R.E. facilities for the work with protactinium, neptunium, and plutonium and one of us (Z. M. S. Al.-K.) thanks the Iraq Ministry of Oil for the award of a scholarship.

[2/1113 *Received*, 17*th May*, 1972]

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[12] K. W. Bagnall and J. B. Laidler, *J. Chem. Soc.* (*A*), 1966, 516.

[13] K. W. Bagnall, A. M. Deane, T. L. Markin, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, 1961, 1611.

[14] J. L. Ryan, *J. Phys. Chem.*, 1961, **65**, 1856.

[15] D. Brown and P. J. Jones, *J. Chem. Soc.* (*A*), 1967, 247.

[16] Z. M. Al-Kazzaz, K. W. Bagnall, and D. Brown, *J. Inorg. Nuclear Chem.*, in the press.

[17] K. W. Bagnall and J. H. Freeman, *J. Chem. Soc.*, 1956, 4579.

[18] J. A. C. Marples and J. L. Shaw, Brit. Report AERE-R 5210 (1966).