Crystal Structure of Tetracaesium Octaisothiocyanatouranate(IV)

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The structure of $Cs_4[U(NCS)_8]$ has been determined by single-crystal *X*-ray diffraction methods from diffractometer data on 845 reflections and refined to *R* 0.06. Crystals are tetragonal, space group *P*4/*n* with a_0 = 11.958(6), c_0 = 11.170(6) Å, *Z* = 2. The two sets of four nitrogen atoms co-ordinated to the uranium atom [at distances of 2.38(3) and 2.46(3) Å, respectively] are arranged at the vertices of an almost perfect square antiprism. The results are discussed in relation to the structure of $[NEt_4]_4[U(NCS)_8]$ and spectral data for both compounds.

THE structure of $[NEt_4]_4[U(NCS)_8]$ was investigated by Countryman and McDonald[1] who found that the uranium atom was surround by eight nitrogen atoms arranged at the vertices of a cube. Later studies[2] have shown analogous compounds of the types $[NEt_4]_4[M(NCS)_8]$ (M = Th, Pa, Np, and Pu) and $[NEt_4]_4[M(NCSe)_8]$ (M = Pa and U) to be isostructural with this uranium compound, and that they all exhibit a single strong ν(CN) in their i.r. spectra, as expected from group theoretical considerations for eight-co-ordinate compounds with O_h (cubic) symmetry. Compounds of the type $Cs_4[M(NCS)_8]$ (M = U and Pu) were found,[2] on the basis of *X*-ray powder results, not to be isostructural with the first-named compounds and, furthermore, i.r. studies[2]

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[1] R. Countryman and W. S. McDonald, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2213.

[2] Z. M. S. Al-Kazzaz, K. W. Bagnall, D. Brown, and B. Whittaker, *J.C.S. Dalton*, 1972, 2273.

showed the strong ν(CN) vibration to be split, suggesting a lower symmetry for these compounds. In addition, it was noted [2] that the solid-state visible–near-i.r. spectra of $[NEt_4]_4[U(NCS)_8]$ and $Cs_4[U(NCS)_8]$ were quite different, but that spectra of the compounds dissolved in non-aqueous solvents (methyl cyanide and nitromethane) were virtually identical with each other and with the solid-state spectrum of $Cs_4[U(NCS)_8]$ suggesting that in solution the cubic stereochemistry of the $[U(NCS)_8]^{4-}$ anion in $[NEt_4]_4[U(NCS)_8]$ transformed to the unknown stereochemistry of the anion in $Cs_4[U(NCS)_8]$. However, it was also noted that only a single C–N vibration was observed for solution-i.r. spectra of both complexes.

In view of these spectral results the structure of $Cs_4[U(NCS)_8]$ has been investigated by single-crystal *X*-ray techniques; the results are discussed in relation to those reported previously for $[NEt_4]_4[U(NCS)_8]$.

EXPERIMENTAL

Crystal Data.—$Cs_4[U(NCS)_8]$, $M = 1234$, Tetragonal, $a_0 = 11.958(6)$, $c_0 = 11.170(6)$ Å, $U = 1597.2$ Å^3, $Z = 2$, $D_c = 2.6$ g cm^{-3}, $F(000) = 1\,088$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 121.1 cm^{-1}. Space group $P4/n$, from systematic absences ($hk0$, $h + k = 2n$) and Laue symmetry, $4/m$.

TABLE 1

Fractional co-ordinates and anisotropic temperature * factors ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	2 500	2 500	1 883(2)	357(9)	357(9)	619(16)	0	0	0
Cs	4 170(2)	6 122(2)	2 514(2)	1 336(25)	592(16)	982(20)	−133(15)	34(17)	−145(13)
S(1)	−630(10)	3 739(8)	−981(11)	1 242(93)	669(67)	1 366(102)	13(62)	−777(84)	76(65)
S(2)	1 311(8)	6 051(8)	4 223(8)	941(72)	690(60)	741(63)	152(54)	−166(55)	−129(52)
N(1)	918(22)	3 030(20)	714(24)	635(178)	523(164)	744(192)	−109(138)	−166(155)	203(146)
N(2)	1 797(19)	4 068(22)	3 101(25)	408(141)	630(178)	970(206)	39(134)	55(152)	−108(176)
C(1)	273(29)	3 307(21)	6(30)	918(261)	115(152)	725(257)	−48(166)	−2(216)	−58(151)
C(2)	1 578(23)	4 885(25)	3 561(26)	525(189)	396(179)	574(154)	78(154)	185(154)	−40(160)

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*kh + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

Crystals for data collection were prepared as described previously [2] and sealed in thin-walled Lindemann glass capillaries.

Precise unit-cell parameters (24 °C) were obtained by least-squares refinement from the θ values of 25 reflections measured on a Philips PW 1100 diffractometer with Mo-K_α radiation.

All intensities were collected by the ω scan method on a Philips diffractometer by use of a graphite monochromator and Mo-K_α radiation with a prismatic crystal of dimensions *ca.* 0.09 × 0.12 × 0.30 mm. 845 Independent reflections with $h > 0$, $k \geqslant 0$, $l \geqslant 0$ were measured between θ 3 and 20°.

Scan width of 1.2°, scan speed of 2.40° per min, and two 15 s background counts were chosen. Intensities were then corrected for Lorentz and polarisation effects and placed on an approximately absolute scale by Wilson's method.[3] No absorption correction was applied. The 714 reflections having a net intensity $> 3\sigma(I)$ were used in the structure refinement [$\sigma(I)$ based on counting statistics].

Structure Determination.—Since these are only two formula units per unit cell, the uranium atoms must occupy special positions having four-fold site-symmetry. The structure was resolved by the standard heavy-atom method and refined by full-matrix least-squares procedures by use of unit weights, the function minimised being $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic thermal vibration parameters were used for all atoms.

Convergence was reached with R 0.06 (calculated on the observed reflections) and no parameter shift was $> 0.1\sigma$. A final difference-Fourier map showed no relevant residues. All calculations for the structure determination were performed on a CDC 6600 computer with the '*X*-Ray '70' system of crystallographic programmes.[4]

Atomic scattering factors for all atoms were from ref. 5, and the anomalous dispersion corrections [6] have been applied to the uranium and caesium atoms ($\Delta f'$ and $\Delta f''$).

Final atomic co-ordinates and thermal parameters are listed in Table 1 with their estimated standard deviations. Observed and calculated structure factors are given in Supplementary Publication No. SUP 21327 (2pp., 1 microfiche).*

RESULTS AND DISCUSSION

As suggested from the solid-state spectral results [2] the configuration of the $[U(NCS)_8]^{4-}$ ion in $Cs_4[U(NCS)_8]$ is quite different from that in $[NEt_4]_4[U(NCS)_8]$.[1] Thus, whereas the co-ordination polyhedron about the uranium atom in the latter compound is a cube, that in $Cs_4[U(NCS)_8]$ is very close to a square antiprism. A view of the structure of the $[U(NCS)_8]^{4-}$ anion down the *a* axis (Figure 1) reveals the axial symmetry of the UN_8 group: the uranium atom is lying in the crystallographic four-fold axis.

Bond lengths and angles are listed in Table 2, which also contains intra- and inter-molecular contacts.

The two independent U–N bond distances were 2.38 and 2.46 Å, the mean (2.42 Å) being close to the U–N distance (2.38 Å) reported for $[NEt_4]_4[U(NCS)_8]$. The N ··· N distances for the two sets of four coplanar nitrogen atoms are 2.82 and 2.91 Å, respectively, compared with the two independent N ··· N distances along the cube edges in $[NEt_4]_4[U(NCS)_8]$ of 2.74 and 2.77 Å. The alternative shape parameters calculated for the antiprismatic configuration in $Cs_4[U(NCS)_8]$ (l/s 1.08 and $\theta = 56.7°$), are close to the values (1.057 and 57.3°, respectively) given by Hoard and Silverton [7] for the most

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[3] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

[4] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-Ray '70,' System of Crystallographic Programmes, Version of July 1970, University of Maryland.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[7] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

favourable case. In addition, the angle of twist (47.3°) is close to the ideal value (45°).

Thus, changing the cation from $[NEt_4]^+$ to Cs^+ in compounds of the type $M^I_4[U(NCS)_8]$ (M^I = cation) results in a change in the $[U(NCS)_8]^{4-}$ anion configuration from cubic to square antiprismatic, an observation which gives a measure of support to the suggestion [1] that the shape of the $[NEt_4]^+$ cation is responsible for the cubic arrangement adopted by the anion in $[NEt_4]_4[U(NCS)_8]$. It is noticeable that the cruciform-shaped $[NEt_4]^+$ ions fit comfortably against square cube faces of the anion co-ordination polyhedron in the latter compound whilst in $Cs_4[U(NCS)_8]$ the Cs^+ ions spurn the square faces of the antiprism, preferring instead the environment of the triangular faces. Figure 2 illustrates the packing of $[U(NCS)_8]^{4-}$ and Cs^+ ions.

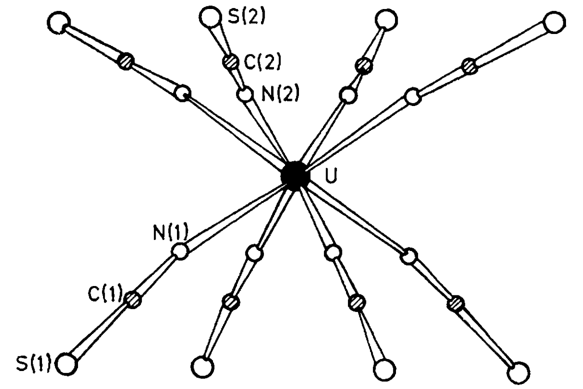

FIGURE 1 The $[U(NCS)_8]^{4-}$ structure viewed along the *a* axis with the labelling of the atoms

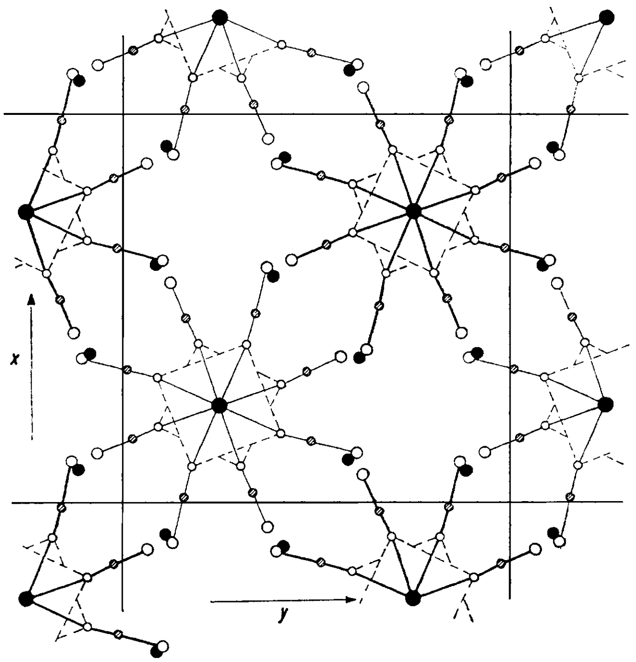

FIGURE 2 Projection of the structure down the four-fold axis showing packing of $[U(NCS)_8]^{4-}$ and Cs^+ ions. Large closed circles, U; large open circles, S; small closed circles, Cs; small open circles, N; hatched circles, C; thick lines, atoms at *z ca.* 0.2; thin lines, atoms at *z ca.* 0.8

The packing in the caesium compound is noticeably more crowded than that in the tetraethylammonium analogue and it is therefore scarcely surprising that the U–N–C groups in the former compound do not retain the linearity exhibited in $[NEt_4]_4[U(NCS)_8]$. Pertinent bond angles and bond lengths for $Cs_4[U(NCS)_8]$ are listed in Table 2; mean bond lengths (N–C 1.145, and C–S 1.62 Å) are close to those found for the anion in $[NEt_4]_4$-$[U(NCS)_8]$. The caesium atoms make short contacts (Table 2) with all three types of atoms in the pseudohalogen groups. In particular, each caesium atom forms contacts with three different anionic units.

TABLE 2

(*a*) Bond distances (Å) and bond angles (°), with estimated standard deviations

U–N(1)	2.38(3)	U–N(2)	2.46(3)
N(1)–C(1)	1.15(4)	N(2)–C(2)	1.14(4)
C(1)–S(1)	1.63(4)	C(2)–S(2)	1.61(3)
U–N(1)–C(1)	169(3)	U–N(2)–C(2)	170(2)
N(1)–C(1)–S(1)	178(3)	N(2)–C(2)–S(2)	178(3)
N(1)–U–N(1^{I})	113.6(9)	N(2)–U–N(2^{I})	113.0(9)
N(1)–U–N(1^{II})	72.6(9)	N(2)–U–N(2^{II})	72.3(8)

(*b*) Contacts (Å)

N(1) · · · N(2)	3.12(4)	Mean (*l*) 3.085
N(1) · · · N(2^{II})	3.05(4)	
N(1) · · · N(1^{II})	2.82(4)	Mean (*s*) 2.865
N(2) · · · N(2^{II})	2.91(3)	

U · · · Cs	4.821(2)	Cs · · · N(2^{III})	3.55(2)
Cs · · · S(2)	3.92(1)	Cs · · · C(2^{III})	3.54(3)
Cs · · · N(2)	3.81(2)	Cs · · · S(2^{IV})	3.92(1)
Cs · · · C(2)	3.63(3)	Cs · · · S(1^{V})	3.58(1)
Cs · · · N(1^{III})	3.44(3)	Cs · · · S(2^{VI})	3.66(1)
Cs · · · C(1^{III})	3.42(3)	Cs · · · S(1^{VII})	3.68(1)
Cs · · · S(1^{III})	3.98(1)		

Roman numeral superscripts denote the following equivalent positions relative to *x*, *y*, *z*:

I	$\frac{1}{2} - x, \frac{1}{2} - y, z$	V	$\frac{1}{2} + x, \frac{1}{2} + y, z$
II	$x, \frac{1}{2} - y, z$	VI	$\frac{1}{2} + x, 1 - y, 1 - z$
III	$\frac{1}{2} - x, y, z$	VII	$\frac{1}{2} + x, 1 - y, z$
IV	$\frac{1}{2} - x, \frac{1}{2} - y, z$		

The foregoing structural results for $Cs_4[U(NCS)_8]$ substantiate the earlier deduction,[2] based on solid-state visible–near-i.r. spectral data, that the co-ordination polyhedron around the uranium atom is different from that in $[NEt_4]_4[U(NCS)_8]$. In addition, it can now be concluded from these spectral data and those for non-aqueous solutions of the two compounds that the cubic arrangement around the uranium atom in $[NEt_4]_4[U(NCS)_8]$ transforms to square antiprismatic when the compound is dissolved in either methyl cyanide or nitromethane. The presence of a single C–N vibration in the solution i.r. spectra [2] is probably due to an accidental coincidence of the energies of the two vibrations expected on the basis of group theoretical considerations.

$[NEt_4]_4[U(NCSe)_8]$ Is isostructural with $[NEt_4]_4[U(NCS)_8]$ and the solid-state visible–near-i.r. spectra of these compounds are virtually identical.[2] In view of these facts, and the different spectrum exhibited by solid $Cs_4[U(NCS)_8]$, it is possible that the presence of cubic or square antiprismatic configurations around the uranium atom in cations of the type $[U(NCS)_8]^{4-}$ can in future be established directly from spectral studies. However, as indicated in a recent publication,[8] it is essential to restrict the use of solid-state spectral data for the deduction of stereochemistries in actinoid compounds to those instances where the compounds involved are of similar chemical composition.

[4/2390 *Received, 15th November, 1974*]

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[8] D. Brown, B. Whittaker, and N. Edelstein, Report AERE-R 7481, 1973.