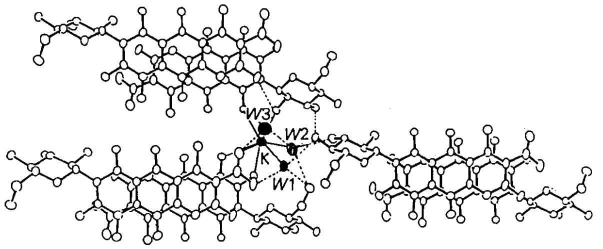

Fig. 2. Molecular packing environment of carminic acids around a potassium ion, viewed along the *b* axis. Ionic interactions with the potassium ion (full circle) are shown by thin lines, and hydrogen bonds by the dotted lines. Shaded circles represent waters of crystallization.

form. This is the first insight. Although its physiological role is at present unclear, the potassium ion appears to stabilize the molecular structure of anionic carminic acid by the neutralization. As is obvious from Fig. 2 and Table 4, extensive ionic interactions are observed between K^+ and the polarizable atoms of the carminic acid and water molecules. In addition to the oxygen atom of the carboxyl anion, those of the 5-, 6- and 8-hydroxyl groups also participate in the interactions.

A structural feature of the crystal is the extensive stacking of anthraquinone rings. The dihedral angle between the aromatic rings is 4·9 (2)° and their average interplanar spacing is 3·5 Å: the carboxyl group and glucose ring jut out from the stacking layers. The formation of these infinite stacking layers would result in the profound red colouration characteristic of carminic acid.

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Structure of Bis(18-crown-6)potassium* Dioxotetrathiocyanatouranate–Water

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Abstract. $[K(C_{12}H_{24}O_6)]_2[UO_2(NCS)_4(H_2O)]$, $M_r = 1127\cdot22$, monoclinic, $C2/c$, $a = 26\cdot780\ (4)$, $b = 8\cdot661\ (2)$, $c = 24\cdot814\ (2)$ Å, $\beta = 129\cdot08\ (1)°$, $V = 4467\cdot6$ Å^3, $D_x = 1\cdot676$ g cm^{-3}, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 38\cdot709$ cm^{-1}, $F(000) = 2240$, $T = 293$ K, $R = 0\cdot035$ for 4097 observed reflections with

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* 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

0108-2701/87/081544-03$01.50

$F^2 > 3\sigma(F^2)$. The uranyl ion is surrounded by four thiocyanate ions and one water molecule in its equatorial plane. The potassium ion is coordinated by six oxygen atoms of the crown ether and also by one S atom of NCS^- ion forming a hexagonal pyramid. A stable coordination compound has therefore been formed in this system. It may be more effective to extract uranium with this system than with an ammonium system.

Introduction. Recently several systems for the extraction of uranium with crown ethers have been studied. It was reported that the extractability of uranium with crown ethers is different in various thiocyanate solutions (Jin & Xu, 1982). Therefore the correlated study of structure and extraction efficiency in these compounds is of great interest. We synthesized some complexes and determined their structures. The structure of $[(18\text{-crown-}6)NH_4]_2[UO_2(NCS)_4(H_2O)]$ has previously been reported (Wang, Zheng, Zhang, Chen, Shen & Yang, 1987). In the present work we report the structure of the title compound.

Experimental. Yellow crystal (0·15 × 0·25 × 0·25 mm). D_m not determined. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters from 25 reflections (θ range 14·5–15°), 4863 independent reflections measured with $2\theta_{\max} = 54°$, $h = -34$ to 34, $k = 0$ to 11, $l = 0$ to 31, 4097 reflections with $F^2 > 3\sigma(F^2)$ considered observed and were used in the refinement. Three standard reflections $\bar{18},\bar{2},8$, $18,\bar{2},\bar{10}$ and $15,3,\bar{4}$ every 3600 s (2·1% variation). Lp correction but no empirical absorption correction. Systematic absences, hkl: $h+k = 2n+1$, $h0l$: $l = 2n+1$. Structure solved by Patterson method, difference Fourier syntheses. No attempts were made to locate the H atoms. Full-matrix least-squares refinement on F with anisotropic temperature factors. 254 variables, $(\Delta/\sigma)_{\max}$ 0·00, $R = 0{\cdot}035$, $wR = 0{\cdot}041$ where $w = 1$ for $F^2 > 3\sigma(F^2)$, $w = 0$ for $F^2 < 3\sigma(F^2)$. Correction for isotropic extinction, extinction coefficient = $3{\cdot}26 \times 10^{-8}$. Max. value in final difference density map was 1·601 e Å^{-3} located near the U atom. Calculation performed on a PDP 11/44 computer with *SDP* program supplied by Enraf–Nonius (1983). Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic coordinates and thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
U	0·000	0·22127 (4)	0·250	2·827 (5)
K	0·15563 (5)	0·2425 (2)	0·61240 (5)	3·76 (3)
S(1)	−0·11959 (7)	−0·2844 (2)	0·13059 (8)	4·98 (4)
S(2)	0·0674 (1)	0·4416 (3)	0·47412 (8)	6·72 (6)
O(1)	0·0666 (1)	0·2236 (5)	0·2511 (2)	4·16 (9)
O(2)	0·000	0·5074 (7)	0·250	4·7 (2)
O(3)	0·2632 (2)	0·4145 (6)	0·6505 (2)	5·2 (1)
O(4)	0·1882 (2)	0·5204 (6)	0·6868 (2)	4·5 (1)
O(5)	0·1162 (1)	0·3031 (6)	0·6937 (2)	4·4 (1)
O(6)	0·0763 (2)	0·0371 (5)	0·6124 (2)	4·9 (1)
O(7)	0·1480 (2)	−0·0712 (6)	0·5731 (2)	5·4 (1)
O(8)	0·2231 (2)	0·1473 (7)	0·5672 (2)	5·7 (1)
N(1)	−0·0512 (2)	−0·0084 (6)	0·1775 (2)	4·3 (1)
N(2)	0·0639 (2)	0·3156 (7)	0·3691 (2)	5·1 (2)
C(1)	−0·0795 (2)	−0·1233 (7)	0·1581 (2)	3·3 (1)
C(2)	0·0659 (3)	0·3669 (8)	0·4133 (3)	4·3 (2)
C(3)	0·2542 (3)	0·575 (1)	0·6554 (3)	5·9 (2)
C(4)	0·2479 (3)	0·5920 (9)	0·7118 (3)	5·7 (2)
C(5)	0·1786 (3)	0·5329 (9)	0·7374 (3)	4·9 (2)
C(6)	0·1144 (3)	0·4637 (9)	0·7058 (3)	5·1 (2)
C(7)	0·0569 (2)	0·229 (1)	0·6656 (3)	5·4 (2)
C(8)	0·0644 (3)	0·061 (1)	0·6606 (3)	5·6 (2)
C(9)	0·0808 (3)	−0·1209 (9)	0·6043 (4)	6·8 (2)
C(10)	0·0869 (3)	−0·138 (1)	0·5479 (4)	7·4 (3)
C(11)	0·1565 (4)	−0·078 (1)	0·5216 (3)	6·8 (2)
C(12)	0·2222 (3)	−0·015 (1)	0·5538 (3)	6·6 (2)
C(13)	0·2827 (2)	0·219 (1)	0·5971 (3)	6·6 (2)
C(14)	0·2743 (3)	0·388 (1)	0·6012 (3)	6·6 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

U–O(1)	1·767 (2)	O(5)–C(6)	1·430 (4)
U–O(2)	2·478 (3)	O(5)–C(7)	1·425 (4)
U–N(1)	2·442 (3)	O(6)–C(8)	1·435 (4)
U–N(2)	2·440 (3)	O(6)–C(9)	1·400 (4)
K–S(2)	3·179 (1)	O(7)–C(10)	1·452 (5)
K–O(3)	2·824 (2)	O(7)–C(11)	1·433 (4)
K–O(4)	2·816 (2)	O(8)–C(12)	1·444 (5)
K–O(5)	2·854 (2)	O(8)–C(13)	1·411 (5)
K–O(6)	2·771 (2)	N(1)–C(1)	1·156 (4)
K–O(7)	2·850 (2)	N(2)–C(2)	1·153 (4)
K–O(8)	2·785 (2)	C(3)–C(4)	1·519 (5)
S(1)–C(1)	1·625 (3)	C(5)–C(6)	1·494 (5)
S(2)–C(2)	1·618 (3)	C(7)–C(8)	1·486 (6)
O(3)–C(3)	1·433 (5)	C(9)–C(10)	1·513 (6)
O(3)–C(14)	1·448 (4)	C(11)–C(12)	1·502 (6)
O(4)–C(4)	1·439 (4)	C(13)–C(14)	1·496 (7)
O(4)–C(5)	1·437 (4)		

O(1)–U–O(1′)	178·7 (2)	C(6)–O(5)–C(7)	111·4 (3)
O(1)–U–O(2)	89·34 (7)	C(8)–O(6)–C(9)	110·1 (2)
O(1)–U–N(1)	96·52 (9)	C(10)–O(7)–C(11)	111·7 (3)
O(1)–U–N(1′)	84·56 (9)	C(12)–O(8)–C(13)	113·6 (3)
O(1)–U–N(2)	92·7 (1)	U–N(1)–C(1)	157·5 (2)
O(1)–U–N(2′)	86·9 (1)	U–N(2)–C(2)	149·1 (3)
O(2)–U–N(1)	144·65 (6)	S(1)–C(1)–N(1)	179·7 (5)
O(2)–U–N(2)	70·43 (7)	S(2)–C(2)–N(2)	178·7 (3)
N(1)–U–N(1′)	70·9 (1)	O(3)–C(3)–C(4)	107·1 (3)
N(1)–U–N(2′)	143·56 (9)	O(4)–C(4)–C(3)	107·4 (3)
N(1)–U–N(2)	74·99 (9)	O(4)–C(5)–C(6)	107·0 (3)
N(2)–U–N(2′)	140·9 (1)	O(5)–C(6)–C(5)	108·6 (3)
S(2)–K–O(3)	88·98 (6)	O(5)–C(7)–C(8)	108·3 (3)
S(2)–K–O(4)	87·51 (5)	O(6)–C(8)–C(7)	108·8 (3)
S(2)–K–O(5)	108·02 (5)	O(6)–C(9)–C(10)	107·2 (4)
S(2)–K–O(6)	107·46 (6)	O(7)–C(10)–C(9)	108·3 (3)
S(2)–K–O(7)	107·65 (6)	O(7)–C(11)–C(12)	107·6 (3)
S(2)–K–O(8)	87·43 (6)	O(8)–C(12)–C(11)	108·7 (3)
K–S(2)–C(2)	110·8 (1)	O(8)–C(13)–C(14)	107·4 (3)
C(3)–O(3)–C(14)	111·1 (3)	O(3)–C(14)–C(13)	109·3 (3)
C(4)–O(4)–C(5)	110·6 (3)		

Discussion. Final atomic parameters are listed in Table 1.* Selected bond distances and angles are in Table 2. The structure with atomic numbering is shown in Fig. 1. Fig. 2 is a perspective view of the unit cell.

In the structure, the U atom is located on the twofold axis. The linear O=U=O bond distance, U—O(1), is 1·767 Å as usual. The uranyl ion is equatorially coordinated by four N atoms from the linear NCS^- ions and one O atom from the water molecule forming a pentagonal bipyramid which is close to our previously reported structure of $[(18\text{-crown-6})NH_4]_2[UO_2(NCS)_4(H_2O)]$. In the equatorial plane, the bond angle N(2)—U—N(1) is 75°, which is larger than other angles formed by neighboring atoms. This is attributed to the repulsive effect of NCS^- groups on some ether atoms.

The potassium ion is coordinated by six ether O atoms in the range 2·77–2·86 Å and also by one S atom from NCS^- ion at a distance of 3·18 Å. It is thus surrounded by seven atoms forming a distorted hexagonal pyramid and is about 0·39 Å from the average plane of the six ether O atoms. This may be the reason why K is not situated at the center of the crown ether as usual (Seiler, Dobler & Dunitz, 1974). Obviously, a stable molecule of this complex is formed through the potassium ion coordination and is different from the structure of $[(18\text{-crown-6})NH_4]_2[UO_2(NCS)_4(H_2O)]$. It is possible that the extraction efficiency of uranium with crown ether in the potassium thiocyanate system is much better than in the ammonium thiocyanate system. If potassium ions coexist in various thiocyanate solutions, the extraction efficiency of uranium with crown ether may be further increased.

In the crown-ether ring, the six O atoms are alternately about 0·20 Å above and below their mean plane. The average bond distance C—C is 1·502, C—O 1·432, K—O 2·817 Å. The average angle O—C—C is 108·0, C—O—C 111·4, K—O—C 114·5°. The torsion angles about C—C bonds are close to 66°, those about C—O bonds are close to 177°. All these data are similar to those reported by Wang *et al.* (1987) and Dunitz, Dobler, Seiler & Phizackerley (1974).

In the molecule, the angle K—U—K′ is 177°; the uranium pentagonal bipyramid is neatly sandwiched between the two crown ethers. The crystal is stabilized by van der Waals forces.

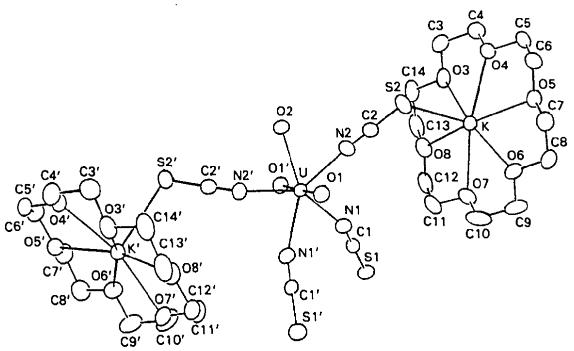

Fig. 1. Molecular structure and numbering scheme.

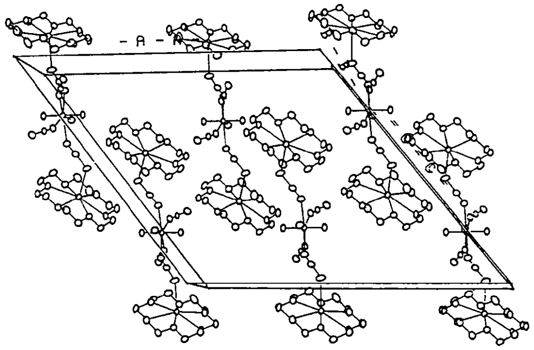

Fig. 2. A perspective view of the unit cell.

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* Lists of observed and calculated structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43863 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.