Table 2, Fig. 1 and Fig. 2. Azide I crosses a mirror plane, so the bond distances must be equal, but the group is slightly bent. The other azide groups, in addition to being slightly bent, all have significantly different lengths for the two N–N bonds. Azide II is more asymmetric than azide III, in disagreement with the earlier findings of Choi & Boutin (1969). Azide IV, with bond lengths, as corrected by the riding model, of 1·164 and 1·196 Å, is the most asymmetric.

The distortions of the azide groups are also reflected in differences in the distances from the end N atoms to the neighboring Pb atoms, with the long N–N bonds being associated with short Pb–N bonds, and *vice versa*. This is to be expected, in the light of the electronic structures of covalently bonded azides (Pauling, 1960). This uneven Pb–N bonding for azide groups II, III, and IV accentuates the distortion of the observed N–N bond length because of the asymmetric librational motion of the azide group. Hence, it is reasonable to find that the corrected N–N bond lengths are less different than the uncorrected ones.

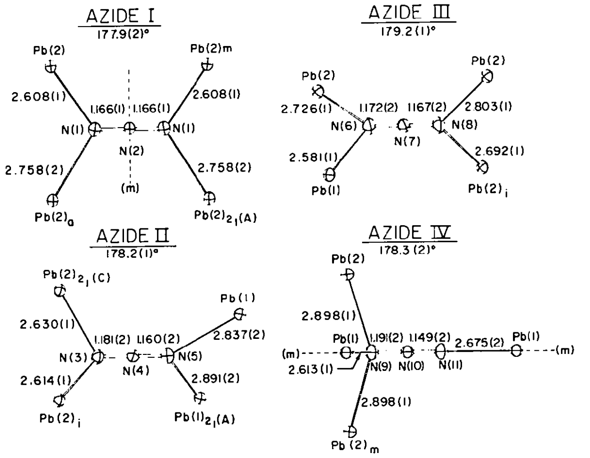
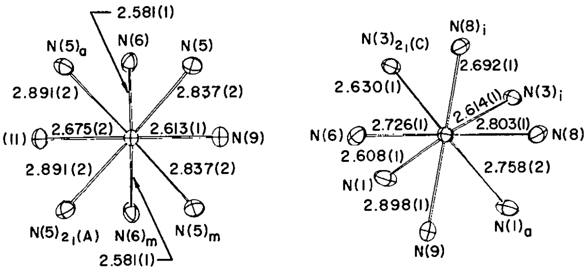


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the four azide groups and their neighboring lead atoms. The subscripts of atom designators, *e.g.* *n*, *i*, $2_1(A)$, *etc.*, indicate the symmetry operations for corresponding atoms.



(*a*) (*b*)

Fig. 2. Pb atoms and their neighboring N atoms, (*a*) for Pb(1) and (*b*) for Pb(2).

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The Potassium Thiocyanate Complex of 2,3-Naphtho-20-crown-6

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Abstract. $C_{23}H_{30}KNO_6S$, M_r = 487·66, monoclinic, $C2/c$, a = 15·698 (6), b = 20·543 (6), c = 8·274 (2) Å, β = 109·98 (2)°, 24 °C, Z = 4, D_x = 1·292 g cm^{-3}; crystallized from ethyl acetate. Full-matrix least-squares refinement [1383 data, $I \geq 2\sigma(I)$] led to R = 0·056. A twofold axis, passing through the K^+ ion, relates the two halves of the ligand; the SCN^- ion is disordered. The six O atoms lie within ±0·35 Å of their mean plane, the naphthalene C atoms within ±0·004 Å of their mean plane; both planes contain the K^+ ion and are twisted 51° about the twofold axis from each other. The K^+ ion is 6·97 Å from the center of the

naphthalene, at an average of 2·80 Å from the six O atoms and 3·26 Å from the disordered S,N of the SCN^- ion. The O and S,N coordination of the K^+ ion is approximately an hexagonal bipyramid.

Introduction. Polyether compounds containing chromophores offer the possibility of locating various metal ions and other cations at specific distances and directions from the chromophore. Studies of the effects of ions on the reactivity and spectra of a chromophore can then be made in which the geometries of the complexes are fixed and known. The title crown–metal complex is one of several under study (Sousa & Larson, 1977). Its crystal structure determination was undertaken because it seems likely (Live & Chan, 1976; Sousa & Johnson, 1977) that the conformation of the crystalline complex will resemble the most probable conformation(s) in a solution or a glass.

A single crystal of approximate dimensions 0·12 × 0·37 × 0·43 mm [μ for Mo $K\alpha = 2{\cdot}86$ cm^{-1}] was used. The diffraction conditions hkl: $h + k = 2n$, $h0l$: $l = 2n$, the absence of other non-related conditions, and the monoclinic symmetry indicate the space groups $C2/c$ or Cc. Diffraction data were measured at 24 °C with a Picker FACS-I automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation. Cell parameters were determined by a least-squares fit to the angular settings of 16 reflections ($35° \le 2\theta \le 40°$, $\alpha_1\alpha_2$ doublet clearly resolved, λ for Mo $K\alpha_1 = 0{\cdot}70926$ Å). The 2891 unique reflections (including 1508 'unobserved') in the $+h + k \pm l$ region were collected for $2\theta \le 55°$ using the θ–2θ scan method [scan speed of 1° (2θ) min^{-1}; 20 s background; scan ranges of 1·5° (2θ) plus the $\alpha_1\alpha_2$ divergence; three standard reflections measured after every 50 data]. The data were reduced and standard deviations calculated as reported previously (Wei & Ward, 1976); least-squares refinement weights were $w = 1/[(\sigma_F)^2 + (0{\cdot}02F)^2]$; extinction corrections were not applied; absorption corrections (Templeton & Templeton, 1973) ranged from 1·027 to 1·099.

The crystal structure was solved in $C2/c$ with the

Table 1. *Fractional coordinates* ($\times 10^4$; *for* H $\times 10^3$) *and hydrogen isotropic thermal parameters* (Å^2)

	x	y	z	$B_{\rm iso}$
K	5000	6730 (0·6)	7500	
NS	5604 (2)	13161 (1)	6666 (3)	
C(1)	5401 (3)	11294 (2)	8202 (5)	
C(2)	5784 (3)	10720 (2)	8886 (6)	
C(3)	5409 (2)	10121 (2)	8216 (4)	
C(4)	5780 (3)	9510 (2)	8878 (5)	
C(5)	5414 (2)	8931 (2)	8226 (4)	
C(6)	5841 (3)	8309 (2)	9084 (5)	
O(7)	6007 (1)	7844 (1)	7950 (3)	
C(8)	6863 (3)	7888 (2)	7754 (6)	
C(9)	6966 (3)	7321 (2)	6736 (6)	
O(10)	6845 (1)	6739 (1)	7543 (3)	
C(11)	6996 (3)	6170 (2)	6714 (7)	
C(12)	6751 (3)	5584 (3)	7533 (7)	
O(13)	5798 (2)	5557 (1)	7069 (3)	
C(14)	5497 (4)	5012 (3)	7782 (8)	
C(15)	5119 (12)	13193 (4)	7282 (28)	
H(1)	565 (3)	1171 (2)	854 (5)	7·0 (10)
H(2)	631 (3)	1069 (2)	979 (5)	5·6 (10)
H(3)	629 (2)	951 (2)	985 (4)	4·1 (7)
H(4)	643 (3)	843 (2)	1006 (5)	6·0 (9)
H(5)	545 (3)	809 (2)	957 (5)	4·9 (8)
H(6)	734 (2)	788 (2)	886 (5)	3·9 (7)
H(7)	689 (3)	833 (2)	721 (5)	6·8 (10)
H(8)	650 (3)	732 (2)	561 (6)	5·4 (9)
H(9)	756 (3)	731 (2)	665 (4)	5·7 (9)
H(10)	766 (3)	618 (2)	673 (5)	6·7 (9)
H(11)	666 (3)	620 (2)	555 (5)	4·8 (8)
H(12)	691 (3)	515 (2)	716 (5)	5·8 (8)
H(13)	708 (3)	562 (2)	891 (6)	5·7 (8)
H(14)	574 (2)	502 (2)	894 (6)	4·6 (9)
H(15)	572 (4)	465 (3)	769 (6)	7·6 (13)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Symmetry code: (i) $1 - x$, y, $\frac{3}{2} - z$; (ii) $1 - x$, $2 - y$, $1 - z$; (iii) x, $2 - y$, $\frac{1}{2} + z$.

Bond distances and angles

NS–C(15)	1·054 (8)	C(9)–H(9)	0·96 (4)
NS–C(15$^{\rm i}$)	1·652 (9)	C(11)–H(10)	1·04 (5)
O(7)–C(6)	1·424 (5)	C(11)–H(11)	0·93 (4)
O(7)–C(8)	1·411 (4)	C(12)–H(12)	1·01 (5)
O(10)–C(9)	1·413 (5)	C(12)–H(13)	1·09 (4)
O(10)–C(11)	1·415 (5)	C(14)–H(14)	0·90 (4)
O(13)–C(12)	1·412 (5)	C(14)–H(15)	0·85 (6)
O(13)–C(14)	1·420 (5)		
C(1)–C(1$^{\rm i}$)	1·392 (9)	NS–C(15)–NS$^{\rm i}$	173·6 (7)
C(1)–C(2)	1·356 (6)	C(6)–O(7)–C(8)	115·4 (4)
C(2)–C(3)	1·396 (6)	C(9)–O(10)–C(11)	113·5 (4)
C(3)–C(3$^{\rm i}$)	1·419 (7)	C(12)–O(13)–C(14)	113·0 (4)
C(3)–C(4)	1·412 (5)	C(1$^{\rm i}$)–C(1)–C(2)	119·6 (3)
C(4)–C(5)	1·351 (5)	C(1)–C(2)–C(3)	122·3 (4)
C(5)–C(5$^{\rm i}$)	1·437 (7)	C(2)–C(3)–C(3$^{\rm i}$)	118·1 (5)
C(5)–C(6)	1·504 (6)	C(2)–C(3)–C(4)	124·6 (4)
C(8)–C(9)	1·479 (6)	C(3$^{\rm i}$)–C(3)–C(4)	117·3 (2)
C(11)–C(12)	1·493 (7)	C(3)–C(4)–C(5)	124·4 (3)
C(14)–C(14$^{\rm i}$)	1·467 (10)	C(4)–C(5)–C(5$^{\rm i}$)	118·3 (4)
C(1)–H(1)	0·95 (5)	C(4)–C(5)–C(6)	120·0 (4)
C(2)–H(2)	0·91 (4)	C(5$^{\rm i}$)–C(5)–C(6)	121·6 (2)
C(4)–H(3)	0·92 (3)	C(5)–C(6)–O(7)	114·3 (3)
C(6)–H(4)	1·03 (4)	O(7)–C(8)–C(9)	107·9 (3)
C(6)–H(5)	0·95 (4)	C(8)–C(9)–O(10)	109·9 (3)
C(8)–H(6)	0·97 (4)	O(10)–C(11)–C(12)	109·5 (3)
C(8)–H(7)	1·03 (5)	C(11)–C(12)–O(13)	108·8 (4)
C(9)–H(8)	0·97 (4)	O(13)–C(14)–C(14$^{\rm i}$)	109·7 (4)

Coordination of K^+ ion

K–O(7)	2·733 (3)	O(7)–K–NS$^{\rm iii}$	81·52 (7)
K–O(10)	2·884 (2)	O(10)–K–O(10$^{\rm i}$)	179·33 (6)
K–O(13)	2·796 (3)	O(10)–K–O(13)	60·97 (8)
K–NS$^{\rm ii}$	3·255 (3)	O(10)–K–O(13$^{\rm i}$)	119·70 (10)
O(7)–K–O(7$^{\rm i}$)	66·31 (5)	O(10)–K–NS$^{\rm ii}$	86·61 (7)
O(7)–K–O(10)	57·45 (7)	O(10)–K–NS$^{\rm iii}$	93·34 (7)
O(7)–K–O(10$^{\rm i}$)	121·89 (10)	O(13)–K–O(13$^{\rm i}$)	60·83 (5)
O(7)–K–O(13)	118·41 (9)	O(13)–K–NS$^{\rm ii}$	84·56 (6)
O(7)–K–O(13$^{\rm i}$)	165·50 (11)	O(13)–K–NS$^{\rm iii}$	102·31 (7)
O(7)–K–NS$^{\rm ii}$	91·87 (7)	NS$^{\rm ii}$–K–NS$^{\rm iii}$	172·14 (8)

program *MULTAN* (Germain, Main & Woolfson, 1971). Other programs used include the Zalkin (1974) system, *ORTEP* (Johnson, 1965), and *ABSOR* (Templeton & Templeton, 1973).

The structure was refined by full-matrix least squares to $R_1 = (\Sigma|F_o - F_c|)/\Sigma F_o = 0{\cdot}056$, $R_2 = \{[\Sigma w(F_o - F_c)^2]/\Sigma w(F_o)^2\}^{1/2} = 0{\cdot}051$, $R_1 = 0{\cdot}131$ including the 1598 zero-weighted data for which $I \leq 2\sigma(I)$, the standard deviation of an observation of unit weight = 1·30. Composite 'NS' atoms [consisting of $f(\mathrm{N}) + f(\mathrm{S})$ in scattering amplitude] were refined at half-occupancy, as was C(15), for the disordered SCN^- ion. Average and maximum shift-to-error ratios for the last least-squares cycle were 0·01 and 0·13. The final difference map showed densities ranging from +0·31 to −0·24 e $Å^{-3}$ with no indication of incorrectly placed or missing atoms. Scattering factors used were those of Doyle & Turner (1968) for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for H and the anomalous scattering factors of Cromer & Liberman (1970) for the non-hydrogen atoms (assumed zero for H). Atomic parameters are listed in Table 1,* interatomic distances and angles in Table 2.

Discussion. An important feature of the crystal structure of the title compound is the twofold rotation axis: the K^+ ion lies on this axis; the disordered SCN^- ion lies across this axis; and the naphtho-crown ligand is related, one-half to the other, by this axis. Fig. 1 shows the molecular structure and the numbering of the atoms.

The six crown O atoms, which coordinate the K^+ ion, lie within ±0·35 Å of a plane containing the K^+ ion. The C—O and C—C distances in the crown portion of the ligand average 1·416 and 1·482 Å; the C—O—C and O—C—C angles average 114·0 and 109·2°. The naphthalene portion of the ligand is planar with all ten C atoms within ±0·004 Å of a plane which also contains the K^+ ion; the crown methylene carbon atom C(6), bonded to the naphthalene, lies 0·07 Å from this plane; and the C—C distances in the aromatic rings average 1·389 Å. The plane of the naphthalene portion is rotated 51° about the twofold axis from the plane of the six O atoms.*

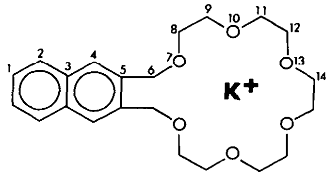

Fig. 1. The molecular structure indicating the numbering of the atoms.

No strong intermolecular interactions are observed in the packing of the complex into the crystal lattice (Fig. 2). The SCN^- ion (at x, $2-y$, $-\frac{1}{2}+z$) lies midway between two K^+ ions (at x,y,z; x, y, $-1+z$), but the ends of the SCN^- ion do not point directly towards the K^+ ions. The S,N—K distance is 3·255 Å, the S,N—K—O angles range from 81·5 to 102·3°, the K—O distances average 2·804 Å and the O—K—O angles are close to 60, 120 or 180°; the coordination about the K^+ ion is a distorted hexagonal bipyramid. A similar coordination of K^+ was reported for the K^+SCN^- complex of 18-crown-6 (Seiler, Dobler & Dunitz, 1974).

The features of the structure which are most significant for the spectral studies are: the naphthalene portion of the ligand is planar and is not significantly distorted by attachment of the crown portion to it; the

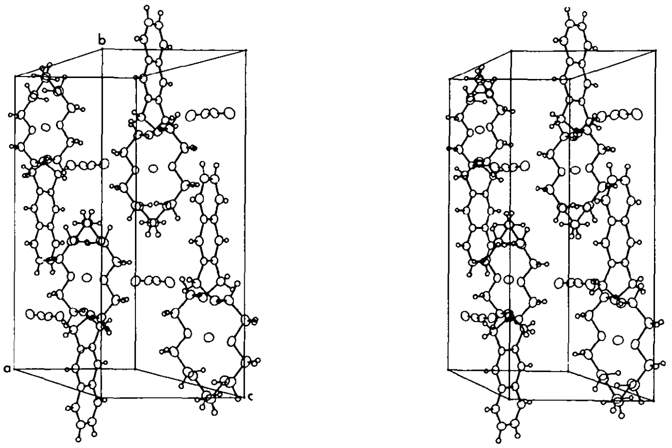

Fig. 2. The title compound viewed along (Ī00) (*ORTEP*, Johnson, 1965).

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32804 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* See previous footnote.

K^+ ion lies on the twofold axis and at a distance of 6·97 Å from the center [the midpoint of the C(3)–C(3^i) bond] and 4·52 Å from the end [the midpoint of the C(5)–C(5^i) bond] of the naphthalene.

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2,2′-Biquinolyl*

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Abstract. $C_{18}H_{12}N_2$, monoclinic, $P2_1/c$, $Z = 2$, $M_r = 256{\cdot}3$; $a = 14{\cdot}013\,(11)$, $b = 3{\cdot}919\,(4)$, $c = 11{\cdot}656\,(8)$ Å, $\beta = 97{\cdot}03\,(5)°$ at 28 °C; $a = 13{\cdot}971\,(11)$, $b = 3{\cdot}853\,(4)$, $c = 11{\cdot}589\,(7)$ Å, $\beta = 97{\cdot}50\,(4)°$ at -160 ± 5 °C, μ(Mo $K\alpha$) = 0·764 cm^{-1}. The structure was refined to $R = 0{\cdot}065$ for 1407 observed intensities. The configuration is *trans*; the two halves of the molecule are related by a center of symmetry imposed by the space group. The sp^2–sp^2 single-bond length between the two quinoline systems is 1·492 (3) Å.

Introduction. Clear, prismatic crystals were obtained by recrystallization of commercial 2,2′-biquinolyl from ethanol. A small crystal of dimensions 0·37 × 0·27 × 0·23 mm was selected. Intensity data were collected at -160 ± 5 °C with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) on a Picker FACS-1 diffractometer equipped with a standard gas-flow cooling system (Huffman, 1974). Systematic absences of $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$ identified the space group as $P2_1/c$. Unit-cell parameters at 28 °C and at -160 ± 5 °C were refined by least squares with the orientation and Bragg angles of 14 reflections carefully centered at $\pm 2\theta$. 4327 reflections (including extinctions) were scanned in the range $1 \le 2\theta \le 55°$ with the θ–2θ scan technique, a scan rate of 2° min^{-1} and 20 s background counts at both ends of the scan range of $(2{\cdot}5 + 0{\cdot}692 \tan\theta)°$. Three standard reflections were measured every 30 reflections. No significant trends were observed. Intensities, I, were assigned variances $\sigma^2(I)$ according to counting statistics plus a term $(0{\cdot}03I)^2$ to allow for unaccountable errors. Lorentz and polarization corrections were made in the usual manner. Of 1407 unique reflections 1215 had $(F_o)^2 \geq \sigma(F_o)^2$.

The structure was solved from the Patterson function and refined with the full-matrix least-squares program *XFLS*3 of Busing, Martin & Levy (1974). The function minimized was $\Sigma\, w(|F_o|^2 - |F_c|^2)^2$ with $w = 1/\sigma^2(F_o)^2$.

Table 1. *Final positional parameters with standard deviations in parentheses*

	x	y	z
N(1)	0·12176 (8)	0·0928 (3)	−0·02146 (9)
C(2)	0·04968 (10)	−0·0217 (4)	0·03161 (11)
C(3)	0·06306 (10)	−0·1799 (4)	0·14380 (11)
C(4)	0·15414 (11)	−0·2145 (4)	0·20109 (12)
C(5)	0·33151 (11)	−0·1151 (4)	0·19993 (12)
C(6)	0·40452 (11)	0·0081 (4)	0·14347 (13)
C(7)	0·38392 (11)	0·1607 (4)	0·03224 (13)
C(8)	0·29086 (11)	0·1853 (4)	−0·02086 (12)
C(9)	0·21366 (10)	0·0597 (4)	0·03556 (11)
C(10)	0·23368 (10)	−0·0927 (4)	0·14803 (12)
H(3)	0·0073 (10)	−0·263 (4)	0·1742 (13)
H(4)	0·1639 (10)	−0·327 (4)	0·2776 (14)
H(5)	0·3454 (10)	−0·223 (4)	0·2754 (14)
H(6)	0·4714 (12)	−0·013 (5)	0·1784 (14)
H(7)	0·4354 (12)	0·256 (4)	−0·0048 (14)
H(8)	0·2739 (10)	0·291 (4)	−0·0975 (13)

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