distances [2·208 (6), 2·231 (6) Å] are substantially longer than the corresponding Ni—O bond lengths [2·103 (9), 2·116 (9) Å]. Distortion of the Ni and Co coordination polyhedra is caused in part by the limited bites of the bidentate carboxylate groups; the O—Co—O and O—Ni—O angles are 59·6 (2) and 62·4 (3)°, respectively.

In both the Co^{II} and Ni^{II} structures, the tet-b ligand is folded about the N(2)—M—N(4) axis. For reasons unknown to us, the tet-b ligand is folded about the N(1)—Cu—N(3) axis in the [Cu(tet-b)(o-SC$_6$H$_4$-CO$_2$)].H$_2$O complex which contains an approximately trigonal-bipyramidal CuN$_4$S unit (Hughey et $al.$, 1979). Significant differences between the bound and free carboxylate groups of the title complex were not detected. As indicated by the dihedral angles of 29·5 (4) and 25·4 (4)°, neither carboxylate group is coplanar with its attached benzene ring. A somewhat larger carboxylate/phenyl dihedral angle (79·0°) was observed for the o-SC$_6$H$_4$CO$_2$ anion bound to Cu(tet-b) and attributed in part to intramolecular S···H—N bonding. Only intermolecular hydrogen bonding was observed in the title complex [between O(3) and H(N1), H(N3) of adjacent molecules, Table 2]. The remaining structural features for both the tet-b and dithiodibenzoate units are typical. The observed C—N, C—C, and C⩰C bond distances span the ranges 1·48 (1)–1·51 (1), 1·50 (1)–1·54 (1), and 1·36 (1)–1·41 (1) Å, respectively. The CSSC dihedral angle [83·2 (4)°] lies between

those reported for perfluorodiphenyl disulfide (76·5°, Woodward, Brown, Lee & Massey, 1976) and diphenyl disulfide (96·2°, Lee & Bryant, 1969), while the S—S bond length [2·063 (3) Å] is comparable to those in $(C_6F_5)_2S_2$ [2·059 (4) Å] and $(C_6H_5)_2S_2$ [2·03 (0·5) Å].

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Structure of 1,4,7,10,13-Pentaoxa-16-thiacyclooctadecane at 101 K

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Abstract. $C_{12}H_{24}O_5S$, $M_r = 280·38$, orthorhombic, $Pbca$, $a = 8·295$ (3), $b = 20·372$ (7), $c = 8·476$ (3) Å, $V = 1432·3$ Å^3, $Z = 4$, $D_x = 1·30$ Mg m^{-3}, $F(000) = 608$, μ(Mo $K\alpha$) = 0·226 mm^{-1}, colorless crystals, m.p. 303 K. The structure was determined from three-dimensional X-ray diffraction data collected at 101 K, solved by direct methods, and refined to $R = 0·092$ ($R_w = 0·071$) for a total of 834 unique intensities [$I > \sigma(I)$]. The title compound is isomorphous with the hexaether 1,4,7,10,13,16-hexaoxacyclooctadecane [Dunitz & Seiler (1974). $Acta$ $Cryst.$ B**30**, 2739–2741]. The structure is disordered in that the S-atom position has an occupancy of 0·5 S and 0·5 O.

Introduction. The title compound was synthesized according to the procedure by Hui (Hui, 1972; Bradshaw, Hui, Chan, Haymore, Izatt & Christensen, 1974) and recrystallized from hexane. Systematic

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absences determined from precession photographs ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; and $hk0$, $h = 2n + 1$) indicated the unambiguous space group *Pbca*. A crystal (0·25 × 0·35 × 0·35 mm) was mounted on a Picker four-circle goniostat (Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å) equipped with a Furnass graphite monochromator. All experimental data were collected at 101 K using a gas-flow cooling system (Huffman, 1974) due to the low melting point of the solid. Accurate unit-cell dimensions were determined by a least-squares refinement of 12 reflections centered at $\pm2\theta$ using an automated top-bottom/left-right aperture system. Three-dimensional diffraction data to a maximum 2θ of 50° (sin $\theta/\lambda = 0·595$ Å^{-1}) were recorded for 1843 reflections (including redundancies) using the $\theta/2\theta$ scan mode. The scan speed was 3° min^{-1} with a 2θ range from 1° below $K\alpha_1$ to 1° above $K\alpha_2$. Single background time at extremes of scan was 10 s. The equivalent reflections were averaged to yield 937 unique intensities of which 834 had $I \geq \sigma(I)$, $\sigma(I)$ calculated considering only counting statistics. The structure was solved by direct methods and refined by least-squares analysis. Only the observed data were used in the refinement process. Hydrogen positions

were obtained from a difference Fourier map. Positional parameters of all the atoms, anisotropic temperature factors of the non-H atoms and the isotropic temperature factors of the H atoms were refined. Tables 1 and 2 list the coordinates and isotropic temperature factors for the atoms in one asymmetric unit.* The final discrepancy index was $R = 0·092$ ($R_w = 0·071$). The weights were based on counting statistics with allowance for experimental error (Stout & Jensen, 1968). The 'goodness of fit' $[\sum w(\Delta F)^2/(n - m)]^{1/2}$ for the last cycle was 1·44. A final difference Fourier map showed no significant features. Atomic-scattering factor tables were taken from *International Tables for X-ray Crystallography* (1968).

Discussion. Fig. 1 shows the ring conformation and atom-numbering scheme of the compound. The symmetry of the space group *Pbca* with $Z = 4$ requires that the molecule have a center of inversion and therefore that the S/O position be disordered with 0·5 occupancy factors for each atom. This disorder was confirmed in the latter stages of refinement. The structure was refined using *GENLS* (Larson, 1977) which allows the fractional occupancy factors of the disordered atoms to be varied but requires the sum of the factors to be 1·0. In the final refinement deviations from the 50/50 arrangement were insignificant. Bond lengths, bond angles, and torsion angles are shown in Table 3. The C—S bond lengths of 1·687 (7) and 1·641 (7) Å are intermediate between the normal C—S (1·81 Å) and C—O (1·43 Å) bond distances. As in previously reported uncomplexed S-containing macrocycles, the S atom is directed out of the cavity and gives the

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Table 1. *Fractional coordinates* (×10⁴) *and isotropic U values* (×10³) *for the non-*H *atoms with e.s.d.'s in parentheses*

$\bar{U}$ is the average of the three eigenvalues of each anisotropic vibration tensor.

	x	y	z	$\bar{U}$ (Å²)
S(1)	184 (3)	−1375 (1)	−2825 (2)	34 (2)
C(2)	−6 (10)	−2007 (3)	−1639 (8)	36 (4)
C(3)	1259 (8)	−2066 (3)	−386 (7)	36 (4)
O(4)	915 (5)	−1617 (2)	862 (4)	27 (2)
C(5)	2334 (8)	−1440 (3)	1712 (7)	34 (4)
C(6)	1911 (8)	−887 (3)	2786 (6)	34 (4)
O(7)	1507 (5)	−329 (2)	1899 (4)	30 (2)
C(8)	914 (8)	198 (3)	2849 (6)	31 (3)
C(9)	630 (10)	760 (3)	1758 (7)	38 (4)

Table 2. *Fractional coordinates* (×10³) *and isotropic U values* (×10³) *for the* H *atoms with e.s.d.'s in parentheses*

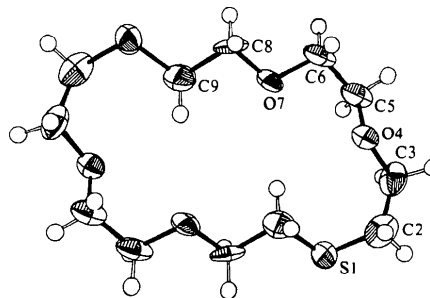|	x	y	z	U (Å²)
H(2a)	26 (7)	−235 (3)	−233 (8)	38 (16)
H(2b)	−82 (7)	−203 (2)	−134 (6)	0 (14)
H(3a)	244 (8)	−197 (3)	−79 (7)	36 (15)
H(3b)	123 (8)	−251 (4)	19 (9)	71 (20)
H(5a)	314 (5)	−130 (2)	98 (5)	0 (10)
H(5b)	263 (8)	−179 (3)	238 (9)	51 (18)
H(6a)	113 (7)	−101 (3)	333 (6)	22 (16)
H(6b)	281 (6)	−80 (2)	349 (5)	0 (10)
H(8a)	−21 (7)	10 (3)	320 (6)	26 (14)
H(8b)	174 (5)	30 (2)	360 (5)	4 (11)
H(9a)	153 (7)	92 (3)	144 (7)	26 (16)
H(9b)	−4 (7)	65 (3)	90 (7)	35 (16)

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule with 75% probability thermal ellipsoids, showing atom numbering. The H atoms are drawn as spheres of radius 0·1 Å for artistic purposes.

Table 3. *Bond distances (Å) and bond and torsion angles (°)*

1	2	3	4	1–2	1–2–3	1–2–3–4
C(9')	S(1)	C(2)	C(3)	1·687 (7)	102·5 (3)	−81·3 (6)
S(1)	C(2)	C(3)	O(4)	1·641 (7)	115·5 (5)	78·3 (6)
C(2)	C(3)	O(4)	C(5)	1·498 (10)	109·5 (5)	−154·8 (5)
C(3)	O(4)	C(5)	C(6)	1·427 (7)	111·8 (5)	170·0 (5)
O(4)	C(5)	C(6)	O(7)	1·427 (8)	107·8 (5)	−65·8 (6)
C(5)	C(6)	O(7)	C(8)	1·491 (8)	110·0 (4)	173·4 (5)
C(6)	O(7)	C(8)	C(9)	1·402 (7)	112·9 (4)	176·9 (5)
O(7)	C(8)	C(9)	S(1')	1·430 (7)	106·4 (4)	176·4 (4)
C(8)	C(9)	S(1')	C(2')	1·490 (8)	107·5 (4)	165·7 (5)

molecule an elliptical shape (Dalley, Smith, Larson, Matheson, Christensen & Izatt, 1975).

The title compound is isomorphous with the hexaether 1,4,7,10,13,16-hexaoxacyclooctadecane (Dunitz & Seiler, 1974). The unit-cell origin and atomic labels for this structure were chosen to correspond to the hexaether structure solved by Dunitz & Seiler. It is interesting that replacement of an O by an S atom essentially leaves the packing arrangement and conformation unchanged. The longer C–S bond lengths, smaller C–S–C bond angles, and the larger size of the S atom evidently offset each other to yield virtually the same conformation as the hexaether.

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Sodium Thiocyanate Complex of 1,4,7,10,13-Pentaoxa-16-thiacyclooctadecane

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Abstract. $C_{12}H_{24}O_5S.NaSCN$, $M_r = 361·458$, monoclinic, $P2_1/c$, $a = 17·289$ (8), $b = 13·7203$ (14), $c = 7·7412$ (9) Å, $\beta = 104·967$ (15)°, $V = 1773·9$ Å^3, $Z = 4$, $D_x = 1·35$, $D_m = 1·35$ Mg m^{-3} (flotation in CCl$_4$ and heptane), $F(000) = 768$, colorless crystals, m.p. 383 K. The structure was solved by direct methods and refined to $R = 0·048$ ($R_w = 0·023$) for a total of 2961 unique reflections. The Na$^+$ ion sits in a cavity formed by the five atoms to which it is coordinated. There is no interaction between the S atom of the polyether and the Na$^+$ ion. The N of the thiocyanate ion completes the sixfold coordination to the Na$^+$ ion.

Introduction. The complex was prepared by allowing the solvent to evaporate from an equimolar salt–ligand

mixture dissolved in methanol. A crystal was shaped to a suitable size (0·33 × 0·40 × 0·43 mm) for X-ray intensity measurements. Preliminary data obtained on a General Electric XRD-5 diffractometer were used to determine the space group. Systematic absences (0*k*0, $k = 2n + 1$, and *h*0*l*, $l = 2n + 1$) indicated the unambiguous space group $P2_1/c$. Intensity data were collected using a Syntex P1 automated diffractometer employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). Accurate lattice parameters were determined by a least-squares refinement of 15 2θ measurements, 25° < 2θ < 34°. Integrated intensities were measured by a $\theta/2\theta$ scan. The scan rate was 2° min^{-1} over the peak width with a 2θ range from 1° below $K\alpha_1$ to 1° above $K\alpha_2$. Background counts at extremes of scan were taken with the total background time equalling the scan time. A total of 3109 unique