H···O contacts (involving H atoms in the *ortho* positions and generally occurring in pseudo-related pairs) which may contribute to the stability of this arrangement. These distances have not been listed as they are of borderline significance and, furthermore, involve calculated H positions. Deviations from a true centrosymmetric relationship between the tppo ligands are reflected in the angles between the normals to the planes of pseudo-related phenyl groups [rings (1) and (4), $2 \cdot 8°$; (2) and (5), $12 \cdot 7°$; (3) and (6), $10 \cdot 0°$]. Angles around the P atoms range from 109 to 114° for O—P—C (mean 111°) and from 106 to 110° for C—P—C (mean 108°). Bond distances in the ligands are in the expected ranges. The degree of coplanarity of the C atoms in each of the six phenyl rings is high, all deviations from the respective least-squares planes being $<0 \cdot 01$ Å. The molecular packing is illustrated in Fig. 2. The combination of two factors, namely the positions of the centres of gravity of the molecules (V is near the point $\frac{1}{4},\frac{1}{2},\frac{1}{4}$) and the intramolecular pseudo-symmetry described above, results in a structure which is approximately *B*-centred (excluding V and its

immediate neighbours). Thus, pairs of molecules related by crystallographic inversion centres are also related by translations of approximately $\frac{1}{2},0,\frac{1}{2}$. This can be seen in Fig. 2. The molecules at the top left and lower right, for example, occupy the equipoints x,y,z and $1 - x$, $1 - y$, $1 - z$. For these (and for the *c*-glide related pair) the pseudo-centring of the tppo ligands is evident in this projection.

We thank Dr G. Gafner, South African Council for Scientific and Industrial Research, for the services of the national X-ray Data Collection Facility in providing the diffractometer data. MRC wishes to acknowledge useful discussions with Dr P. J. Wheatley during his visit to this laboratory.

References

CAVE, J., DIXON, P. R. & SEDDON, K. R. (1978). *Inorg. Chim. Acta*, **30**, L349–L352.
COETZER, J. (1970). *Acta Cryst.* **B26**, 872–874.
DRAKE, J. E., VEKRIS, J. & WOOD, J. S. (1968). *J. Chem. Soc. A*, pp. 1000–1005.
GELLATLY, B. J. & CAIRA, M. R. (1979). Unpublished results.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
KEPERT, D. L. (1972). *The Early Transition Metals.* New York: Academic Press.
PREEZ, J. G. H. DU & GIBSON, M. L. (1970). *J. S. Afr. Chem. Inst.* **23**, 184–190.
SHELDRICK, G. M. (1977). *SHELX.* Program for crystal structure determination. Univ. of Cambridge, England.
WET, J. F. DE (1980). The *CRISTEP* desk-plotter system. *J. Appl. Cryst.* To be published.
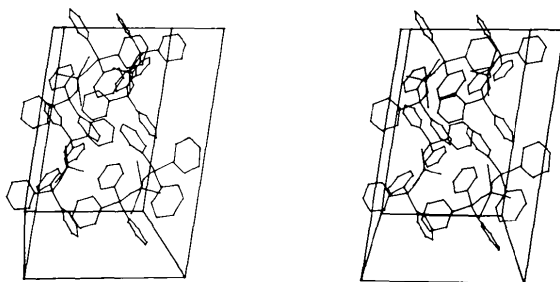WET, J. F. DE, CAIRA, M. R. & GELLATLY, B. J. (1978). *Acta Cryst.* **B34**, 762–766.

Fig. 2. Stereoscopic view down [010]. The origin is at the top left with *c* across and *a* down.

Structure of the Potassium Thiocyanate Complex of 3,6,9,12,15-Pentaoxa-21-azabicyclo[15.3.1]henicosa-1(21),17,19-triene-2,16-dione

BY S. B. LARSON AND N. K. DALLEY

Department of Chemistry and the Thermochemical Institute,* Brigham Young University, Provo, Utah 84602, USA

Abstract. $C_{15}H_{19}NO_7 \cdot KSCN$, monoclinic, $P2_1/m$, $a = 7 \cdot 8833$ (12), $b = 14 \cdot 2868$ (20), $c = 8 \cdot 6449$ (13) Å, $\beta = 91 \cdot 383$ (10)°, $V = 972 \cdot 44$ Å^3, $Z = 2$, $D_c = 1 \cdot 44$, $D_m = 1 \cdot 44$ Mg m^{-3}; colorless to pale-orange prismatic crystals, m.p. 470–471·5 K; model refined to $R = 0 \cdot 066$ and $R_w = 0 \cdot 036$. The potassium is positioned in the cavity of the polyether ring and is coordinated to every hetero-atom in the ring.

Introduction. The ligand of the title compound is a cyclic polyether containing a pyridine ring and carbonyl oxygens as well as ether oxygens. It has been shown to form a very stable complex with potassium (Izatt, Lamb, Asay, Maas, Bradshaw & Christensen,

---

1977). This study was initiated to determine the role, if any, of the carbonyl oxygens and the pyridine ring in the complexation of the cation.

The ligand and complex were synthesized by R. E. Asay (Izatt et al., 1977). Preliminary determination of lattice parameters was made using a precession camera. The data indicated a monoclinic space group, either $P2_1$ or $P2_1/m$. The conditions and procedures for data collection have been described previously (Dalley & Larson, 1979a) except that the scan speed was 2° min^{-1}. Lattice parameters were obtained by a least-squares refinement of the 2θ values of 15 centered reflections [20° < 2θ < 30°, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å)]. Intensities for 2257 independent reflections were measured to a 2θ limit of 55° (sin $\theta/\lambda = 0.650$ Å^{-1}) and were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ scans (coefficient range 1.0–1.35) was also made to account for crystal shape (0.5 × 0.5 × 0.1 mm). The data included eight systematically extinct reflections ($0k0$, k odd) and 501 reflections having $I < 2\sigma(I)$.

The trial structure was obtained by direct methods. Phases for 199 of the 400 reflections with highest E's were determined by MULTAN (Germain, Main & Woolfson, 1971), space group $P2_1$ being assumed. The $20\bar{1}$, 504 and $51\bar{2}$ reflections were used to define the origin. An E map calculated from these phases showed many peaks from which a reasonable model was determined. This model showed that the K$^+$ ion, the pyridine N, the O opposite the N in the polyether ring and the thiocyanate ion were roughly in a plane near the quarter level of y. This suggested the presence of a mirror plane bisecting the polyether ligand and, thus, the space group should be $P2_1/m$. Accordingly, this model was refined using a full-matrix least-squares procedure (Busing, Martin & Levy, 1962) with the assumption that $P2_1/m$ was the correct space group. With the aid of calculated positions, the H atoms were located on a difference map. The calculated positions were input initially before these positions were refined.

A weighted refinement varying all atomic positions, non-hydrogen anisotropic thermal parameters and hydrogen isotropic thermal parameters was terminated when changes in the parameters were less than 10% of their uncertainties. The final weighted R was 0.036 and the unweighted R was 0.066. The goodness of fit was 3.03 with $m = 2257$ and $n = 172$. The final positional parameters of the nonhydrogen atoms are listed in Table 1.* The $20\bar{1}$ reflection was omitted from the refinement owing to secondary extinction. The weights

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35067 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($\times 10^3$)

	x	y	z	U_{eq}/U (Å^2)
K$^+$	7608 (1)	2500	5569 (1)	45
S(14)	1197 (2)	2500	3475 (1)	75
C(15)	2779 (5)	2500	4736 (4)	54
N(16)	3910 (5)	2500	5627 (4)	70
N(1)	6437 (3)	2500	2453 (3)	34
C(2)	6007 (3)	3300 (2)	1726 (2)	38
C(3)	6556 (3)	4203 (2)	2442 (3)	42
O(4)	6851 (2)	4160 (1)	3966 (2)	44
C(5)	7420 (4)	5035 (2)	4689 (3)	49
C(6)	7483 (4)	4880 (2)	6420 (3)	52
O(7)	8721 (2)	4184 (1)	6776 (2)	45
C(8)	9170 (4)	4157 (2)	8382 (3)	54
C(9)	10290 (4)	3322 (2)	8691 (3)	56
O(10)	9304 (3)	2500	8447 (3)	50
C(11)	5155 (3)	3326 (2)	315 (3)	49
C(12)	4716 (5)	2500	−392 (4)	54
O(13)	6677 (2)	4915 (1)	1710 (2)	62
H(51)	655 (3)	551 (2)	440 (2)	10 (6)
H(52)	851 (3)	521 (2)	426 (2)	23 (7)
H(61)	629 (3)	453 (2)	677 (3)	50 (9)
H(62)	783 (3)	551 (2)	689 (3)	27 (7)
H(81)	808 (3)	417 (2)	902 (3)	34 (8)
H(82)	977 (3)	471 (2)	852 (3)	40 (9)
H(91)	1093 (3)	342 (2)	973 (3)	22 (6)
H(92)	1119 (4)	333 (2)	810 (3)	52 (11)
H(111)	488 (4)	396 (2)	4 (3)	49 (9)
H(121)	413 (5)	250	−116 (4)	53 (15)

were based on counting statistics with allowance for some experimental error, $\sigma(F) = F\sigma(I)/2I$ (Stout & Jensen, 1968). Atomic scattering factor tables for O, C and S were obtained from Cromer & Waber (1965) and those for the other atom types were taken from *International Tables for X-ray Crystallography* (1968). Anomalous-dispersion corrections for K or S were not made. The negative charge on the thiocyanate ion was divided equally between the sulfur and the nitrogen by averaging the S and S$^-$ and N and N$^-$ tables respectively. Refinement of this final model in space group $P2_1$ resulted in unreasonable bond lengths.

Discussion. The conformation of the complex is illustrated in Fig. 1. Bond lengths and bond and torsion angles are listed in Table 2. The ligand is composed of three portions, each exhibiting characteristic features. The pyridine moiety shows geometrical features consistent with previously reported pyridine-containing compounds (Pretorius & Boeyens, 1978; Pelizzi & Pelizzi, 1979). Likewise, the ester portion composed of C(3), O(4), C(5) and O(13) has bond lengths and angles typical of both non-cyclic esters (Kroon & Kanters, 1973) and cyclic esters (Dalley & Larson, 1979a,b). The C—O and C—C bonds involving C(5), C(6), O(7), C(8), C(9) and O(10), averaging 1.423 (2) and 1.508 (6) Å respectively, are consistent with those of other cyclic polyethers (Dalley, 1978). The angles in this portion [averaging 112.2 (6)° for O centered and

108·7 (3)° for C centered] are characteristic of other cyclic polyethers.

The torsion angles for the polyether portion [magnitudes averaging 65 (3)° about C—C bonds and 172 (7)° about C—O bonds] are consistent with those of other cyclic polyethers and show that the ligand has little strain (Dalley, 1978). The torsion angles in the other portions of the ligand are as expected.

The interatomic distances from the donor atoms of the ring to the potassium ion as well as to the other donor atoms are listed in Table 3. The average K—O distance is 2·78 (2) Å and the K—N(1) distance is

2·826 (2) Å. These distances are very close to the sums of the respective van der Waals radii of 2·73 and 2·83 Å (Pauling, 1960), and demonstrate interaction of the potassium ion with all hetero-atoms of the ring. The potassium ion also interacts with two anions. The distances are 2·917 (4) Å from one thiocyanate N and 3·395 (2) Å from the S of another anion. These distances as well as the C—N and C—S distances of 1·164 (5) and 1·637 (4) Å, respectively, are similar to those observed in the structure of KSCN (Akers, Peterson & Willet, 1968). The K—N—C angle is 138°. Hazell (1963) analyzed several thiocyanates and suggested that these geometrical features imply a partial C—N triple bond and a partial C—S double bond.

There is considerable thermal motion in the anion, especially for S and N. The anion is linear [179·7 (4)°] as expected. Angles involving the K⁺ ion are listed in Table 4.

The almost regular hexagon formed by the donor atoms of the ligand can be seen in Fig. 1. The diagonals of the hexagon range from 5·54 to 5·60 Å. The ligand is fairly planar, as indicated in Fig. 2. The coordination of the cation to the anions is also easily seen. The deviations of the donor atoms from their least-squares plane are N(1) +0·15 Å, O(4) −0·14 Å, O(7) +0·12 Å, O(10) −0·11 Å, with a standard deviation of 0·14 Å. The donor atoms are in a slight chair conformation. The K⁺ ion deviates from this plane by −0·21 Å and can be seen in Fig. 2 to have an oscillating motion in the cavity. The pyridine ring is also planar as are the four-atom groupings centered at C(2) and C(3). The dihedral angle between the plane of the donor atoms and the pyridine ring is 2·8°.

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

1	2	3	4	1–2	1–2–3	1–2–3–4
C(2')	N(1)	C(2)	C(3)	1·344 (3)	116·5 (2)	−176·2 (2)
N(1)	C(2)	C(3)	O(4)	(a)	118·3 (2)	−23·9 (3)
C(2)	C(3)	O(4)	C(5)	1·491 (3)	114·3 (2)	179·0 (2)
C(3)	O(4)	C(5)	C(6)	1·333 (3)	115·2 (2)	173·4 (2)
O(4)	C(5)	C(6)	O(7)	1·464 (3)	107·4 (2)	63·7 (3)
C(5)	C(6)	O(7)	C(8)	1·513 (4)	108·8 (2)	165·3 (2)
C(6)	O(7)	C(8)	C(9)	1·422 (3)	112·5 (2)	172·1 (2)
O(7)	C(8)	C(9)	O(10)	1·425 (3)	109·0 (2)	−67·3 (3)
C(8)	C(9)	O(10)	C(9')	1·504 (4)	108·3 (2)	178·9 (2)
C(9)	O(10)	C(9')		1·421 (3)	111·5 (2)	

Distances and angles involving atoms out of the polyether ring

O(13)	C(3)	C(2)	N(1)	1·203 (3)	122·6 (2)	158·0 (2)
O(13)	C(3)	O(4)	C(5)	(a)	123·0 (2)	−2·9 (3)
O(13)	C(3)	C(2)	C(11)	(a)	(a)	−19·0 (3)
C(11)	C(2)	C(3)	O(4)	1·378 (3)	118·3 (2)	159·1 (2)
C(11)	C(2)	N(1)	C(2')	(a)	123·3 (2)	0·7 (4)
C(12)	C(11)	C(2)	N(1)	1·369 (3)	119·0 (3)	0·1 (4)
C(12)	C(11)	C(2)	C(3)	(a)	(a)	176·9 (3)
C(11')	C(12)	C(11)	C(2)	(a)	119·0 (3)	−0·8 (5)

Average C—H bond distances

Pyridine ring	0·88 (11)
Polyether ring	1·00 (7)

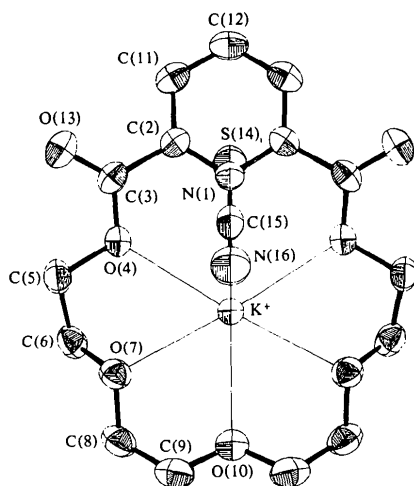(a) Listed earlier in the table.

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound with 50% probability thermal ellipsoids for the atoms. The H atoms are omitted.

Table 3. *Interatomic distances* (Å)

Distances between ring donor atoms		Distances between K⁺ and the ring, and in the thiocyanate ion	
N(1)–O(4)	2·723 (2)	K⁺–N(1)	2·826 (2)
N(1)–O(7)	4·762 (3)	K⁺–O(4)	2·803 (2)
N(1)–O(10)	5·603 (3)	K⁺–O(7)	2·757 (2)
O(4)–O(7)	2·812 (2)	K⁺–O(10)	2·796 (2)
O(4)–O(10)	4·900 (2)	K⁺–N(16)	2·917 (4)
O(4)–O(4')	4·742 (2)	K⁺–S(14')	3·395 (2)
O(4)–O(7')	5·543 (2)	S(14)–C(15)	1·637 (4)
O(7)–O(10)	2·838 (2)	C(15)–N(16)	1·164 (5)
O(7)–O(4')	2·543 (2)		
O(7)–O(7')	4·812 (2)		

Table 4. K—O—C, K—N—C *and* K—S—C *angles* (°)

K⁺–N(1)–C(2)	121·3 (1)	K⁺–O(7)–C(8)	114·5 (2)
K⁺–O(4)–C(3)	123·9 (1)	K⁺–O(10)–C(9)	112·3 (1)
K⁺–O(4)–C(5)	116·9 (1)	K⁺–N(16)–C(15)	137·6 (3)
K⁺–O(7)–C(6)	108·5 (1)	K⁺–S(14')–C(15')	106·0 (2)

$C_{15}H_{19}NO_7 . KSCN$

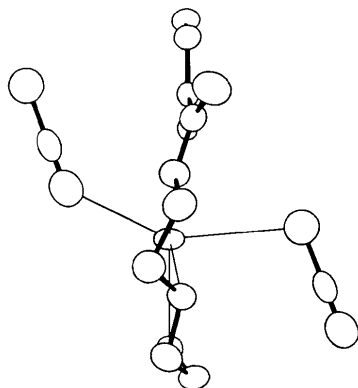Fig. 2. ORTEP (Johnson, 1965) drawing of a molecule rotated 90° clockwise [around the O(10)–N(1) vector] from the view in Fig. 1.

References

AKERS, C., PETERSON, S. W. & WILLET, R. D. (1968). Acta Cryst. B24, 1125–1126.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104–109.

DALLEY, N. K. (1978). Synthetic Multidentate Macrocyclic Compounds, edited by R. M. IZATT & J. J. CHRISTENSEN, pp. 207–243. New York: Academic Press.

DALLEY, N. K. & LARSON, S. B. (1979a). Acta Cryst. B35, 2428–2430.

DALLEY, N. K. & LARSON, S. B. (1979b). Acta Cryst. B35, 1901–1903.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.

HAZELL, A. C. (1963). J. Chem. Soc. pp. 5745–5752.

International Tables for X-ray Crystallography (1968). Vol. III, pp. 202–207. Birmingham: Kynoch Press.

IZATT, R. M., LAMB, J. D., ASAY, R. E., MAAS, G. E., BRADSHAW, J. S. & CHRISTENSEN, J. J. (1977). J. Am. Chem. Soc. 99, 6134–6136.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KROON, J. & KANTERS, J. A. (1973). Acta Cryst. B29, 1278–1283.

PAULING, L. (1960). The Nature of the Chemical Bond, 3rd ed. Ithaca: Cornell Univ. Press.

PELIZZI, C. & PELIZZI, G. (1979). Acta Cryst. B35, 126–128.

PRETORIUS, J. A. & BOEYENS, J. C. A. (1978). J. Inorg. Nucl. Chem. 40, 407–416.

STOUT, G. H. & JENSEN, L. H. (1968). X-ray Structure Determination. A Practical Guide. New York: Macmillan.

Structure of Di-μ-chloro-tetrachlorotetrakis(diethyl sulphide)diiridium(III)

BY A. F. WILLIAMS

Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, CH-1211 Genève 4, Switzerland

AND H. D. FLACK AND M. G. VINCENT*

Laboratoire de Cristallographie aux Rayons X, Université de Genève, CH-1211 Genève 4, Switzerland

Abstract. [Ir$_2$Cl$_6$\{S(C$_2$H$_5$)$_2$\}$_4$], C$_{16}$H$_{40}$Cl$_6$Ir$_2$S$_4$, monoclinic, C2/c, a = 18·884 (1), b = 12·700 (1), c = 14·436 (7) Å, β = 118·25 (1)°, Z = 4. The symmetry of the molecule is 2 with the Ir atoms on the twofold axis. Two Cl atoms bridge the Ir atoms which are octahedrally coordinated. One Ir has two mutually cis diethyl sulphide ligands in the plane of the bridging Cl atoms and the other two mutually trans diethyl sulphide groups perpendicular to the bridging Cl-atom plane. The structure was refined to R(F) = 0·029 for 975 independent reflections with I > 3σ(I).

Introduction. The title compound is one of two isomers of composition [Ir$_2$Cl$_6$\{S(C$_2$H$_5$)$_2$\}$_4$] obtained on photolysis of mer-[IrCl$_3$\{S(C$_2$H$_5$)$_2$\}$_3$] in benzene solution (Kauffman, Tsai, Gubelmann & Williams, 1980). Given the current interest in the photochemistry of coordination compounds, and the lack of any

* Present address: Department of Structure Biology, Biozentrum der Universität Basel, Klingelbergstrasse 70, CH-4056 Basel, Switzerland.