MicroVAX II computer with use of the *SHELXTL-Plus* program package (Sheldrick, 1988) with atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates are given in Table 2, bond distances and angles in Table 3.* The molecular structure and atomic-numbering scheme are shown in Fig. 1. The geometry about the Li^+ ion can be classified as trigonal bipyramidal. The O(3), N(2) and N(4) atoms occupy equatorial positions in the trigonal plane, while the remaining N(1) and N(3) atoms occupy axial positions. Equatorial placement of the $CF_3SO_3^-$ ion is dictated by the preference of the phenanthroline ligand for chelation, with N—Li—N angles near 80°. The Li^+ ion is coplanar with respect to the least-squares plane defined by the three equatorial atoms, and deviation from the plane is 0·026 Å. Although the in-plane angles differ from the ideal (120°) of a regular trigonal bipyramid, the sum of the three angles is 360°. The Li—N-distance ranges are 2·115 (9)–2·166 (9) Å and the short Li—O bond distance of 2·072 (9) Å reflects a strong electrostatic attraction between the lithium and trifluoromethanesulfonate ions (Humphrey, Lamanna, Brookhart & Husk, 1983). The dihedral angles between the equatorial plane and the two phenanthroline molecular planes are 100·4 and 79·5°.

Chemically equivalent bond distances and angles in the two phenanthroline ligands are normal and in good agreement with each other. The two ligands are essentially planar, with maximum deviations of atoms from their least-squares planes of 0·027 and 0·051 Å, respectively. The dihedral angle between these ligands is 59·5°. Bond distances and angles within the $CF_2SO_3^-$ ion are normal (Lawrance, 1986).

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* Fractional atomic coordinates for H atoms, anisotropic temperature factors for non-H atoms, least-squares-planes information and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51792 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of the 15-Crown-5–$NaClO_4$ (1/1) Complex

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Abstract. 1,4,7,10,13-Pentaoxacyclopentadecane–sodium perchlorate (15-C-5/$NaClO_4$), $C_{10}H_{20}O_5.NaClO_4$, $M_r = 342·71$, monoclinic, $P2_1/c$, $a = 9·928$ (1), $b = 10·162$ (1), $c = 15·944$ (2) Å, $\beta = 97·35$ (1)°, $V = 1595·4$ (2) Å^3, $Z = 4$, $D_x = 1·43$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 2·54$ cm^{-1}, $F(000) = 716·0$, room temperature, $R = 0·053$ and $S = 2·18$ for 2006 independent reflections. The Na cation forms a 1/1 complex with 15-C-5. In this complex, Na^+ is seven-coordinated to the five macrocyclic O atoms (av. Na—O 2·42 Å) and two of the O atoms of the bidentate perchlorate anions (av. Na—O 2·51 Å). The Na^+ ion lies 0·77 Å above the least-squares plane of the ether O atoms. All structural parameters of the crown ether are

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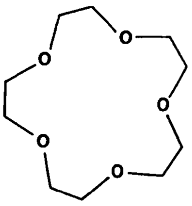
in agreement with related crown-ether complexes, including relatively short aliphatic C—C bonds (av. 1·49 Å).

Introduction. In order better to understand the factors involved in the complexation of alkali-metal cations by crown ethers, we have investigated the geometry of the complexes of a series of crown ethers having a central macrocyclic frame of 13–15 atoms, with Li^+, Na^+ and K^+. We were especially interested in the parameters that determine the specificity and selectivity of a certain crown ether to a particular cation. Previously it has been shown that the size and shape of the central cavity of the macrocycle plays a most important role in complexation (Pedersen, 1967; Dally, 1978; Poonia & Bajav, 1979). During our experiments it was apparent that the flexibility of the crown molecule, the type and nature of the counter-ion and the solvent environment also have a significant influence on the interaction between the crown ether and the cation.

One of the most interesting studies turned out to be the series of complexes of 15-crown-5 [15-C-5, (1)] and benzo-15-crown-5 [B-15-C-5, (2)] with various sodium and potassium salts. Although the structures of alkali-metal complexes of B-15-C-5 have been extensively studied (Dally, 1978; Poonia & Bajav, 1979; Weber & Vögtle, 1981; Hilgenfeld & Saenger, 1982), only very few structural studies have been done on the related complexes of 15-C-5, its more flexible analog (Groth, 1981; Cambillau, Bram, Corset & Riche, 1982). Here we present the crystal and molecular structure of the complex of 15-C-5 with $NaClO_4$ (1*a*), a complex which is a good structural representative of the 15-C-5/Na complexes.



(1)

Experimental. 15-C-5 (1) was purchased from Sigma and used without further purification. The complex (1*a*) was obtained by mixing solutions of equimolar amounts of (1) and $NaClO_4$. Crystallized by slow evaporation from methanol/water (1/1) solution; colorless single crystals, well formed prisms, 0·3 × 0·3 × 0·4 mm; Enraf–Nonius CAD-4 automatic four-circle diffractometer; Mo radiation, graphite monochromator. Lattice parameters were determined by least-squares fit of 24 reflections in the range $20 < 2\theta < 27°$, monoclinic, space group $P2_1/c$. Intensity data were collected in the $\omega/2\theta$ scan mode, $4 \leq 2\theta \leq 54°$, $-h00 \rightarrow hkl$, in 1 shell; 3 orientation check reflections ($\bar{5}11$; 060; 0,2,10) measured every 100 reflections, 3 intensity check reflections (600; $\bar{1}51$; $\bar{2}19$) measured every 60 min. Intensity of check reflections varied on average by 2% and decayed during data collection by about 6%. Intensity data were reduced, corrected for Lorentz and polarization effects and for radiation damage. Owing to the shape of the crystal and the small absorption coefficient no absorption correction was applied. 3910 reflections were measured, of which 2914 are unique. For the Patterson function, direct methods and the refinement, only those reflections for which $F_o \geq 4{\cdot}0\sigma(F_o)$ were included (2006 reflections, 69% of the total).

The structure was solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The best phase set, with a CFOM of 2·73, yielded a preliminary model with all non-H atoms of the structure, including the perchlorate, clearly recognizable, in the electron density map. The H atoms were located by successive cycles of least-squares refinements and difference electron density maps. Conventional full-matrix least-squares techniques were used for refinement of atomic parameters (Cruickshank, 1970; Sheldrick, 1976). All non-H atoms were refined anisotropically (9 parameters per atom), while all H atoms were refined isotropically (4 parameters per atom). A weighting scheme based on $w = a/[\sigma^2(F) + bF^2]$ ($a = 1{\cdot}00$, $b = 0{\cdot}0005$) was introduced and optimized in the final stages of refinement. The overall scale factor was also refined. Altogether, 270 parameters (P) were refined simultaneously using 2006 observations (O), $O/P = 7{\cdot}43$. Final $R = 0{\cdot}053$, $wR = 0{\cdot}061$. Final $S = 2{\cdot}18$. In the final cycle of refinement, the maximum shift/e.s.d. ratio was 0·005, and the average was 0·001. In the final difference map, max. and min. electron densities around the perchlorate anion were 0·54 and −0·27 e Å^{-3}, respectively, and elsewhere in the molecule were 0·19 and −0·17 e Å^{-3}, respectively.

Discussion. The final structural results are presented in Tables 1 and 2* and in Figs. 1 and 2. Fig. 1 is a top view of the structure of the complex (1*a*), including also the numbering scheme used. Fig. 2 is a side view of the structure of (1*a*). As expected, the complex obtained is a 1/1 crown/Na adduct, in which the Na cation appears paired with the perchlorate counter-ion. Each unit of $[(1).Na^+.ClO_4^-]$ is electronically neutral and interacts only weakly with the neighboring molecules in the crystal (Fig. 3). The Na cation in the inclusion

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* Lists of observed and calculated structure factors, anisotropic thermal parameters and a full list of structural parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51693 (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 and temperature factors*

	x	y	z	U_{eq}/U_{iso}* (Å^2)
Na	0·2600 (1)	0·9890 (1)	0·3105 (1)	0·0503 (6)
Cl	0·2349 (1)	0·9975 (1)	0·1150 (1)	0·0581 (4)
O(6)	0·3579 (3)	1·0063 (2)	0·1735 (2)	0·0903 (21)
O(7)	0·1243 (3)	1·0028 (3)	0·1665 (2)	0·0998 (25)
O(8)	0·2241 (5)	1·1094 (5)	0·0646 (3)	0·1594 (40)
O(9)	0·2284 (5)	0·8727 (4)	0·0762 (3)	0·1469 (37)
O(1)	0·4349 (2)	0·8317 (2)	0·3610 (1)	0·0650 (15)
C(1)	0·3859 (5)	0·7273 (4)	0·4075 (3)	0·0777 (27)
C(2)	0·2567 (6)	0·6807 (3)	0·3595 (3)	0·0836 (31)
O(2)	0·1597 (2)	0·7828 (2)	0·3431 (1)	0·0729 (16)
C(3)	0·0712 (5)	0·7970 (5)	0·4057 (3)	0·0885 (33)
C(4)	−0·0152 (4)	0·9134 (6)	0·3823 (4)	0·0951 (36)
O(3)	0·0708 (2)	1·0274 (2)	0·3877 (1)	0·0705 (16)
C(5)	0·0088 (5)	1·1453 (5)	0·3546 (3)	0·0905 (35)
C(6)	0·1110 (6)	1·2533 (4)	0·3720 (3)	0·0935 (34)
O(4)	0·2245 (3)	1·2217 (2)	0·3303 (1)	0·0695 (15)
C(7)	0·3416 (6)	1·2944 (4)	0·3586 (3)	0·0857 (31)
C(8)	0·4625 (5)	1·2228 (4)	0·3349 (3)	0·0824 (29)
O(5)	0·4647 (2)	1·0978 (2)	0·3750 (1)	0·0616 (14)
C(9)	0·5751 (4)	1·0167 (5)	0·3580 (3)	0·0809 (29)
C(10)	0·5577 (4)	0·8873 (4)	0·3997 (3)	0·0793 (29)
H(11)†	0·449 (4)	0·659 (4)	0·421 (3)	0·082 (12)
H(12)	0·370 (3)	0·763 (3)	0·466 (2)	0·058 (10)
H(21)	0·206 (6)	0·624 (6)	0·387 (4)	0·131 (21)
H(22)	0·272 (4)	0·656 (4)	0·307 (3)	0·078 (13)
H(31)	0·011 (5)	0·723 (5)	0·408 (3)	0·094 (14)
H(32)	0·139 (5)	0·806 (5)	0·457 (3)	0·094 (16)
H(41)	−0·073 (5)	0·919 (5)	0·420 (3)	0·097 (15)
H(42)	−0·043 (5)	0·921 (5)	0·313 (4)	0·114 (17)
H(51)	−0·013 (4)	1·122 (4)	0·292 (3)	0·073 (11)
H(52)	−0·053 (5)	1·164 (4)	0·384 (3)	0·085 (15)
H(61)	0·147 (4)	1·256 (4)	0·438 (3)	0·087 (13)
H(62)	0·086 (6)	1·343 (6)	0·350 (4)	0·148 (23)
H(71)	0·342 (4)	1·368 (5)	0·332 (3)	0·084 (13)
H(72)	0·354 (4)	1·300 (4)	0·422 (3)	0·090 (14)
H(81)	0·548 (5)	1·268 (4)	0·349 (3)	0·096 (15)
H(82)	0·461 (5)	1·208 (4)	0·274 (3)	0·100 (16)
H(91)	0·557 (6)	1·009 (4)	0·284 (4)	0·122 (20)
H(92)	0·650 (6)	1·079 (5)	0·372 (3)	0·107 (16)
H(101)	0·639 (5)	0·842 (4)	0·382 (3)	0·099 (15)
H(102)	0·571 (4)	0·902 (4)	0·462 (3)	0·084 (13)

* For non-H atoms U_{eq} is $\frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

† Numbering system for H atoms is H(*mn*), where *m* is the C-atom number and *n* is the H-atom number on that C atom [*e.g.* H(102) is the second H atom on C(10)].

Table 2. *Molecular structural parameters: bond lengths* (Å), *selected bond angles* (°), *selected torsion angles* (°)

O(7)—Na	2·513 (4)	O(1)—Na	2·421 (3)
O(2)—Na	2·406 (3)	O(3)—Na	2·406 (3)
O(4)—Na	2·417 (3)	O(5)—Na	2·423 (3)
C(10)—C(9)	1·494 (7)	O(6)—Na	2·507 (4)
O(6)—Cl	1·442 (4)	O(7)—Cl	1·454 (4)
O(8)—Cl	1·389 (4)	O(9)—Cl	1·408 (4)
C(1)—O(1)	1·416 (5)	C(10)—O(1)	1·412 (5)
C(2)—C(1)	1·485 (7)	O(2)—C(2)	1·416 (6)
C(3)—O(2)	1·419 (5)	C(4)—C(3)	1·481 (8)
O(3)—C(4)	1·435 (6)	C(5)—O(3)	1·418 (5)
C(6)—C(5)	1·496 (8)	O(4)—C(6)	1·417 (6)
C(7)—O(4)	1·403 (6)	C(8)—C(7)	1·493 (7)
O(5)—C(8)	1·421 (5)	C(9)—O(5)	1·424 (5)
O(7)—Na—O(6)	54·7 (1)	O(2)—Na—O(6)	117·8 (1)
O(1)—Na—O(6)	89·7 (1)	O(1)—Na—O(7)	128·2 (1)
O(2)—Na—O(7)	93·3 (1)	O(2)—Na—O(1)	69·6 (1)
O(3)—Na—O(7)	95·5 (1)	O(3)—Na—O(1)	120·7 (1)
O(4)—Na—O(6)	97·1 (1)	O(4)—Na—O(7)	89·7 (1)
O(4)—Na—O(1)	135·5 (1)	O(4)—Na—O(2)	138·8 (1)
O(5)—Na—O(6)	86·6 (1)	O(5)—Na—O(7)	133·2 (1)
O(5)—Na—O(1)	68·5 (1)	O(5)—Na—O(2)	130·8 (1)
O(5)—Na—O(3)	112·1 (1)	O(5)—Na—O(4)	68·1 (1)
C(10)—O(1)—C(1)	113·9 (3)	C(2)—C(1)—O(1)	107·5 (4)
O(2)—C(2)—C(1)	112·6 (3)	C(3)—O(2)—C(2)	114·4 (4)
C(4)—C(3)—O(2)	107·1 (4)	O(3)—C(4)—C(3)	108·0 (4)
C(5)—O(3)—C(4)	115·7 (4)	C(6)—C(5)—O(3)	107·4 (4)
O(4)—C(6)—C(5)	107·9 (4)	C(7)—O(4)—C(6)	113·9 (4)
C(8)—C(7)—O(4)	108·8 (3)	O(5)—C(8)—C(7)	106·7 (4)
C(9)—O(5)—C(8)	113·5 (3)	C(10)—C(9)—O(5)	106·8 (3)
O(1)—C(1)—C(2)—O(2)	−56·58	C(1)—C(2)—O(2)—C(3)	−90·27
C(2)—O(2)—C(3)—C(4)	174·29	O(2)—C(3)—C(4)—O(4)	−66·54
C(3)—C(4)—O(3)—C(5)	170·52	C(4)—O(3)—C(5)—C(6)	175·81
O(3)—C(5)—C(6)—O(4)	61·93	C(5)—C(6)—O(4)—C(7)	−164·05
C(6)—O(4)—C(7)—C(8)	159·65	O(4)—C(7)—C(8)—O(5)	−60·48
C(7)—C(8)—O(5)—C(9)	179·94	C(8)—O(5)—C(9)—C(10)	−176·11
O(5)—C(9)—C(10)—O(1)	62·63	C(9)—C(10)—O(1)—C(1)	−163·95
C(10)—O(1)—C(1)—C(2)	−179·54		

complex is present in a non-classical seven-coordinated geometry, where the Na ion is directly coordinated by the five ether O atoms of the crown ether, which are arranged in a pentagon, and two of the four O atoms of the bidentate perchlorate anion. The observed mean Na—O distance of 2·42 Å (Table 2) to the macrocyclic O atoms is consistent with the usual Na—O ether bond length which ranges around 2·35–2·50 Å for five- to eight-coordinated complexes with macrocyclic ligands (Dally, 1978; Poonia & Bajav, 1979; Owen, 1980). The Na—O distance to the two perchlorate O atoms is significantly longer (mean 2·51 Å) and could be accounted for by the bidentate symmetrical interaction of the perchlorate with the Na ion combined with spatial interference with the crown ether. The five macrocyclic O atoms are roughly coplanar, forming a least-squares plane (l.s.p.) with an average deviation of 0·28 Å. The Na cation lies 0·77 Å above the center of this plane and the perchlorate ion is exactly on the opposite side to the Na cation such that the O(6)—Na—O(7) plane is practically perpendicular to the l.s.p. of the macrocyclic O atoms. The perchlorate anion is well ordered and its two O atoms closest to the Na atom form a rather strong bond with it. The Cl—O bond length is significantly longer for the two interacting O atoms compared to the other two O atoms (1·44, 1·45 *vs* 1·39, 1·40 Å) and with usual distances in perchlorate ions. These observations suggest a rather specific electronic interaction between the counter-ion and the central cation.

The fact that the Na cation is found 'above' and not 'inside' the central cavity has been observed in other related systems (Dally, 1978; Poonia & Bajav, 1979; Hilgenfeld & Saenger, 1982) and can be explained by both the actual 'size' of the cavity and the preferred specific interactions of the cation with the lone pairs of the ether O atoms (Shoham, Lipscomb & Olsher, 1983; Shoham, Christianson, Bartch, Heo, Olsher & Lipscomb, 1984). The diagonal distance between the opposite O atoms across the macrocyclic ring is 4·01–4·51 Å, which means that the adjusted van der Waals diameter of the cavity in (1*a*) is 1·21–1·71 Å (Dally, 1978; Shoham *et al.*, 1983). The effective cavity size is therefore too small to accommodate the Na^+ cation within the plane of the five macrocyclic ether O atoms, since the empirical effective diameter for a seven-coordinated Na^+ ion has been calculated to be

2·44–2·72 Å (Shannon, 1976). The central cavity size is similar in the two analogous complexes of 15-C-5/sodium enolate [(*1b*); Cambillau *et al.*, 1982] and B-15-C-5/$NaClO_4$ [(*2a*); Owen, 1980]. In (*1b*) the central Na ion is seven-coordinated, the mean Na—O distance is 2·49 Å, and the Na ion lies 1·05 Å above the plane of the ether O atoms . In (*2a*) the central Na ion is also seven-coordinated, although the interaction with the perchlorate is not symmetrical (Na—O distances of 2·43 and 2·63 Å), the mean Na—O distance is 2·44 Å, and the Na ion lies 0·77 Å above the plane of the ether O atoms.

The crown ether (1) in (*1a*) adopts the expected 'crown' conformation in which the macrocycle is rather flat (av. deviation of 0·31 Å from the l.s.p. of the entire crown ether), with three O atoms pointing to one side of the mean plane of the molecule (toward the Na ion) and the other two [O(3) and O(5)] to the other side. Because of the odd number of O atoms, two neighboring O atoms [O(1) and O(2)] are forced to lie on the same side of the molecular plane. All bond lengths and bond angles in (*1a*) are within the expected ranges (Dally, 1978), with the exception of the relatively short aliphatic C—C bonds (mean value of 1·49 Å). Such short C—C distances were observed in similar macrocyclic systems (Dally, 1978; Maverick, Seiler, Schweizer & Dunitz, 1980; Shoham *et al.*, 1984) and may be explained by the interaction with the adjacent C—O ether linkages (Hilgenfeld & Saenger, 1982). With the exception of the torsion angle C(1)—C(2)—O(2)—C(3) (−90·27°), all C—C—O—C torsion angles are close to the antiperiplanar (*trans*) conformation (180°), while all O—C—C—O torsion angles are close to the synclinal (*gauche*) conformation (60°). These values are similar to those of larger complexed and uncomplexed crown ethers (Dally, 1978; Poonia & Bajav, 1979; Hilgenfeld & Saenger, 1982). These usual structural parameters observed in (*1a*) indicate that no significant ring strain is encountered by the macrocycle upon complexation. The overall conformation of 15-C-5 in (*1a*) is also rather similar to the conformation of 15-C-5 in a number of transition-metal complexes reported recently (Arte, Feneau-Dupont, Declercq, Germain & Van Meerssche, 1979; Holt, Alcock, Hendrixson, Malpass, Ghirardelli & Palmer, 1981; Dejehet, Debuyst, Mullie, Arietta, Germain & Van Meerssche, 1983; Dejehet, Debuyst, Spirlet, Declercq & Van Meerssche, 1983; Brügge, Fölsing, Knöchel & Dreissig, 1985; Harrison, Giorgetti & Bünzli, 1985; Lee, Hsieh, Lee, Chiu & Chang, 1985; Rath & Holt, 1985) where the metal/(1) ratio varies between 1/1 and 1/3. Since the structure of the free macrocycle (1) is not known as yet, it is difficult to point out the detailed conformational change (if any) that takes place during complexation. No unusually short intermolecular contacts have been found in the crystal packing.

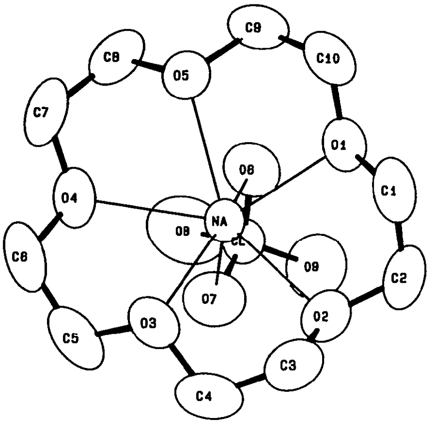

Fig. 1. Top view of (*1a*) (*ORTEP*; Johnson, 1976) with 50% probability.

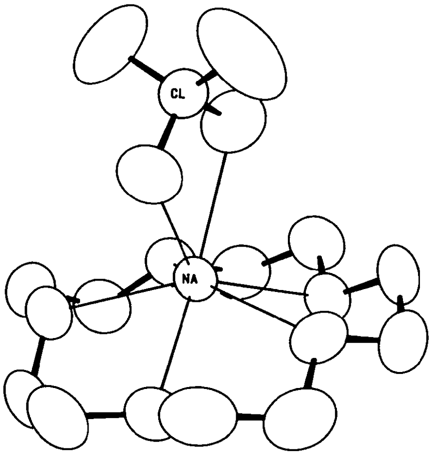

Fig. 2. Side view of (*1a*) (*ORTEP*).

A series of other B-15-C-5 and 15-C-5 complexes with sodium and potassium salts are under study in our

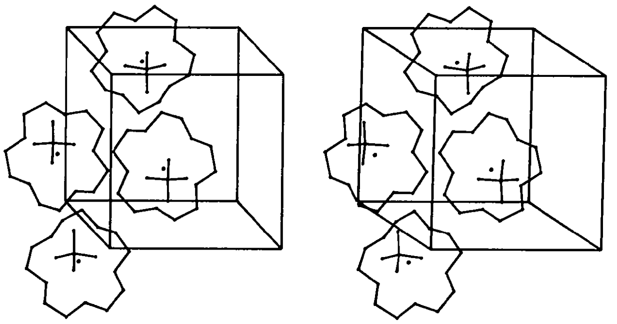

Fig. 3. Stereoview of the unit-cell packing of (*1a*) (*ORTEP*).

laboratory in order to clarify the stability and selectivity factors related to such complexes.

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The Structure of Tricarbonyl(styrene)chromium, a Crystal Active in Second-Harmonic Generation*

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Abstract. $[Cr(CO)_3(C_6H_5CH{=}CH_2)]$, $M_r = 240{\cdot}178$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}5456\,(6)$, $b = 12{\cdot}3227\,(9)$, $c = 7{\cdot}3741\,(5)$ Å, $V = 1049{\cdot}14\,(12)$ Å^3, at 291 K. $\lambda(\text{Mo}\ K\alpha_1) = 0{\cdot}70930$ Å; $Z = 4$, $D_x = 1{\cdot}520$ g cm^{-3}, $\mu = 10{\cdot}44$ cm^{-1}, $F(000) = 488$. The absolute structure was determined. $R(F) = 0{\cdot}029$ for 1306 data having $|F|_o^2 > \sigma(|F|_o^2)$; $\sigma_1 = 1{\cdot}31$. The styrene ligand is disordered, with two orientations relative to the $Cr(CO)_3$ group about equally populated. The Cr—CO linkages are nearly eclipsed with respect to $Cr—C_{ring}$ bonds, in contrast to the staggered arrangement in tricarbonyl(benzene)chromium. The molecular orientation is far from optimal for second-harmonic generation, suggesting the possibility of successful crystal 'engineering' to produce an acentric crystal of a slightly modified compound with a much enhanced generating property.

Introduction. Because of the important technical applications of second-harmonic generations (s.h.g.), there has been recent interest in the s.h.g. properties of

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