Structures of α,α'-Di(2-methoxyethoxy)stilbene and its Complex with Sodium Thiocyanate

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Abstract. (1) *cis*-α,α'-Di(2-methoxyethoxy)stilbene, $C_{20}H_{24}O_4$, $M_r = 328 \cdot 41$, monoclinic, $P2_1/a$, $a = 20 \cdot 640$ (4), $b = 9 \cdot 542$ (1), $c = 9 \cdot 400$ (2) Å, $\beta = 96 \cdot 17$ (2)°, $V = 1840 \cdot 6$ (6) Å^3, $Z = 4$, $D_x = 1 \cdot 19$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1 \cdot 5418$ Å, $\mu = 6 \cdot 70$ cm^{-1}, $F(000) = 704$, $T = 291$ K, $R = 0 \cdot 060$ for 2545 observed reflections. (2) *cis*-α,α'-Di(2-methoxyethoxy)-stilbene–sodium thiocyanate monohydrate, $C_{20}H_{24}O_4$.NaSCN.H_2O, $M_r = 427 \cdot 50$, monoclinic, $P2_1/n$, $a = 24 \cdot 698$ (8), $b = 8 \cdot 731$ (2), $c = 10 \cdot 544$ (3) Å, $\beta = 94 \cdot 75$ (2)°, $V = 2266$ (1) Å^3, $Z = 4$, $D_x = 1 \cdot 25$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 1 \cdot 95$ cm^{-1}, $F(000) = 904$, $T = 291$ K, $R = 0 \cdot 048$ for 2654 observed reflections. The conformation of the molecule as a free ligand is completely different from that in its NaSCN complex. In the free ligand (1) a circular arrangement is observed but one of the terminal methoxy oxygens is oriented outwards from the cavity. Twisting about the double bond is highly significant (17°) and both phenyl groups are deconjugated with respect to the C=C bond. In the complex (2) the Na cation is hexacoordinated to the four ether oxygens, to the SCN anion (through N) and to a water molecule, forming a distorted octahedron. The polyether chain is tightly folded in a conformation where the two terminal units are genuine 'corners' ($ag^{\pm}g^{\pm}$) with *gauche* bonds of the same sign.

Introduction. Recently we have reported the structures of a series of oligoethylene glycol dimethyl ethers (glymes) complexed with alkaline-earth metal thiocyanates (Wei, Tinant, Declercq, Van Meerssche & Dale, 1987*b*). Generally, for the same cation, the ligand wraps around the cation in a conformation which depends on the polyether length: short ligands – up to five oxygens – adopt circular arrangements while longer

chains fold in partial helical conformations. However, because of the high flexibility of the glymes the situation is far more complicated and it was difficult to rationalize all the parameters governing the conformations observed.

With the aim of studying its complexing properties, α,α'-di(2-methoxyethoxy)stilbene has been synthesized (De Man, 1988). To our knowledge, structures of such linear ligands, analogous to triglyme but with a double bond in the central unit, have not been described so far in free or complexed form (Allen *et al.*, 1979). Obviously this more preorganized ligand may give interesting complexes with new structural features as well as with new stability and selectivity properties (Cram, 1986; Vogtle & Weber, 1979). In view of the analogy with our previous work, we have decided to determine the structure of this ligand and some of its complexes. In this paper we compare the free molecule with its sodium thiocyanate complex.

Experimental. Crystals of (1) were obtained by crystallization from a petroleum/ethyl acetate mixture; (2) by slow evaporation from acetone, D_m not measured. Crystal sizes: (1) $0 \cdot 42 \times 0 \cdot 28 \times 0 \cdot 11$ mm; (2) $0 \cdot 50 \times 0 \cdot 24 \times 0 \cdot 11$ mm. Lattice parameters refined using (1) 30, (2) 15 reflections in the range $5° \leq 2\theta \leq 25°$. For (1), Huber four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation. 3324 $hk\pm l$ independent reflections with $(\sin\theta)/\lambda \leq 0 \cdot 60$ Å^{-1}; $0 \leq h \leq 24$, $0 \leq k \leq 11$, $-11 \leq l \leq 11$, 2545 with $I \geq 2 \cdot 5\sigma(I)$. For (2), Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation. 4425 $hk\pm l$ independent reflections with $(\sin\theta)/\lambda \leq 0 \cdot 62$ Å^{-1}; $0 \leq h \leq 29$, $0 \leq k \leq 10$, $-12 \leq l \leq 12$, 2654 with $I \geq 2 \cdot 5\sigma(I)$. Standard reflections (1): $\overline{2}10$ (2): $63\overline{2}$ checked

every 50 reflections: no significant deviation. Both structures solved by *SHELXS*86 (Sheldrick, 1985). For (1) 21, for (2) all, H atoms from difference Fourier synthesis; those of methyl group C(14) of (1) calculated (C–H = 1·08 Å, H–C–H = 109·5°). Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using F; H isotropic with common refined temperature factor. Weighting scheme: $w = 1/(\sigma^2 + gF^2)$, $g = 0·03652$ for (1) and $0·00032$ for (2). (1): $R = 0·060$, $wR = 0·073$, $S = 0·54$ for 2545 observed reflections. (2): $R = 0·048$, $wR = 0·049$, $S = 1·79$ for 2654 observed reflections. Final maximum shift to e.s.d. = (1) 0·18, (2) 0·17. Maximum and minimum heights in final difference Fourier synthesis = (1) 0·20 and −0·40, (2) 0·45 and −0·32 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1.* Bond lengths, coordination distances, valence angles and selected torsion angles are compared in Table 2.

A stereoscopic view of the free ligand 1, showing the atom numbering, is presented in Fig. 1 (*PLUTO*, Motherwell & Clegg, 1978). It shows clearly that the molecule is preorganized to coordinate equatorially to a spherical cation: a single change of sign of the *gauche* bond C12–C13 ($g^+ \rightarrow g^-$)† would orient all the four oxygens to point towards a common center in a planar arrangement. As open-chain neutral ligands, podands usually do not have a preformed intramolecular cavity inside which a cation can nest (Weber & Vogtle, 1981). The conformations in which a lone pair on each of the ether oxygens points towards a common center are obviously unstable because of dipole repulsions (Dale, 1980). The double bond in the central unit of the polyether chain enforces convergence of the oxygen atoms. The oxygens O1 and O3 in the central unit can only avoid repulsion of their lone pairs by torsions around the C–O and C=C bonds. *Anti* conformations of the C–O bonds are impossible because of steric overcrowding between the methylene and phenyl hydrogen atoms. The torsion angles observed for C11–C1–O1–C2 and C1–C11–O3–C12 are *ca* 105° (Table 2c), *i.e.* difficult to classify between g and a. In this situation torsion around the ethylenic bond is necessary to avoid, to some degree, the repulsion of the lone pairs. This torsion is important, the torsion angle O1–C1–C11–O3 taking a value of 16·6 (6)° (Table 2c). In the terminal units, the repulsion between the lone pairs is probably also the reason why one unit (O2) is

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and interatomic distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51715 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† $a = anti$ (±120, $\pm180°$), $g = gauche$, g^+ (0, 120°), g^- (0, −120°) (Dale, 1980).

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å²)

$$B_{eq} = (8/3)\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}
(a) Compound (1)				
C1	2570 (1)	2184 (2)	4545 (2)	3·85 (3)
O1	3034 (1)	2666 (2)	5610 (2)	4·47 (3)
C2	3231 (1)	1680 (3)	6695 (3)	5·03 (4)
C3	3585 (1)	2448 (3)	7924 (3)	5·37 (5)
O2	4176 (1)	2977 (2)	7543 (2)	5·52 (3)
C4	4501 (2)	3804 (5)	8616 (4)	7·61 (8)
C5	1898 (1)	2161 (2)	4924 (2)	3·85 (3)
C6	1667 (1)	3274 (2)	5675 (2)	4·61 (4)
C7	1047 (1)	3262 (3)	6071 (3)	5·43 (5)
C8	639 (1)	2123 (3)	5720 (3)	5·42 (5)
C9	869 (1)	1014 (3)	4998 (3)	5·10 (4)
C10	1488 (1)	1017 (2)	4597 (2)	4·43 (4)
C11	2775 (1)	1818 (2)	3289 (2)	3·85 (3)
O3	3433 (1)	1599 (2)	3268 (2)	4·54 (3)
C12	3765 (1)	2631 (3)	2522 (3)	4·86 (4)
C13	4462 (1)	2216 (4)	2634 (4)	6·22 (6)
O4	4538 (1)	1051 (3)	1759 (3)	7·06 (4)
C14	5172 (2)	481 (6)	2025 (6)	11·25 (12)
C15	2370 (1)	1587 (2)	1919 (2)	3·86 (3)
C16	1833 (1)	2409 (3)	1482 (3)	4·66 (4)
C17	1495 (1)	2223 (3)	139 (3)	5·72 (5)
C18	1686 (2)	1214 (3)	−776 (3)	5·84 (5)
C19	2211 (1)	390 (3)	−356 (3)	5·35 (5)
C20	2557 (1)	575 (2)	980 (3)	4·55 (4)
(b) Compound (2)				
Na	1788 (1)	2515 (1)	1921 (1)	4·26 (2)
S	2031 (1)	3367 (2)	5928 (1)	11·96 (4)
C21	1828 (2)	4019 (5)	4535 (4)	6·38 (8)
N	1688 (1)	4445 (4)	3534 (4)	7·15 (8)
C1	1137 (1)	847 (3)	−604 (2)	3·44 (5)
O1	1586 (1)	639 (2)	261 (2)	3·91 (4)
C2	1618 (2)	−771 (3)	976 (3)	4·57 (6)
C3	1221 (2)	−814 (4)	1954 (4)	5·28 (7)
O2	1318 (1)	438 (3)	2796 (2)	5·45 (5)
C4	990 (2)	407 (7)	3836 (4)	7·13 (10)
C5	973 (1)	−477 (3)	−1422 (2)	3·58 (5)
C6	1349 (1)	−1217 (4)	−2104 (3)	4·34 (6)
C7	1195 (2)	−2475 (4)	−2863 (3)	5·19 (7)
C8	664 (2)	−2988 (4)	−2923 (3)	5·18 (7)
C9	294 (2)	−2272 (4)	−2245 (3)	4·91 (7)
C10	441 (1)	−1025 (4)	−1494 (3)	4·39 (6)
C11	906 (1)	2221 (3)	−673 (2)	3·24 (5)
O3	1060 (1)	3299 (2)	268 (2)	3·55 (3)
C12	1276 (1)	4702 (3)	−198 (3)	4·28 (6)
C13	1813 (1)	4478 (4)	−706 (3)	4·79 (7)
O4	2193 (1)	4020 (2)	313 (2)	4·57 (4)
C14	2689 (2)	3480 (7)	−112 (5)	7·46 (11)
C15	484 (1)	2724 (3)	−1670 (2)	3·22 (5)
C16	544 (1)	2456 (4)	−2948 (3)	4·11 (6)
C17	148 (1)	2950 (4)	−3872 (3)	4·76 (6)
C18	−300 (1)	3725 (4)	−3532 (3)	4·58 (6)
C19	−354 (1)	4033 (4)	−2272 (3)	4·14 (6)
C20	32 (1)	3524 (3)	−1346 (3)	3·64 (5)
O5	2616 (1)	1511 (3)	2719 (3)	5·83 (5)

oriented inwards and the other (O4) outwards. The resulting conformational sequence along the chain is: $ag^{\pm}a \mp 102 \pm 17 \mp 110\ ag^{\pm}a$. It differs from the circular arrangement which is characterized by the sequence $ag^{\pm}a$ with alternating signs. This latter conformation is the most familiar; it has been observed in many linear polyether complexes, *e.g.* triglyme.Ca(SCN)₂, tetra-glyme.Ca, Sr, and Ba bis(thiocyanates) (Wei *et al.,* 1987a) and tetraglyme.HgCl₂ (Iwamoto, 1973). Thus the main difference with respect to the circular arrangement is the relative orientation of the two terminal units, for which the *gauche* bonds are of opposite signs. In the conformation adopted by the

Table 2. Molecular geometry

Table 2. (cont.)

(a) Bond distances (Å)

Ligand	(1)	(2)
O1–C1	1·387 (2)	1·389 (3)
C5–C1	1·469 (3)	1·478 (4)
C11–C1	1·343 (3)	1·328 (4)
C2–O1	1·415 (3)	1·442 (3)
C3–C2	1·492 (4)	1·481 (5)
O2–C3	1·401 (3)	1·416 (4)
C4–O2	1·395 (4)	1·416 (5)
C6–C5	1·388 (3)	1·382 (4)
C10–C5	1·394 (3)	1·393 (4)
C7–C6	1·370 (4)	1·393 (4)
C8–C7	1·393 (4)	1·382 (5)
C9–C8	1·369 (4)	1·359 (5)
C10–C9	1·371 (3)	1·378 (4)
O3–C11	1·376 (2)	1·398 (3)
C15–C11	1·474 (3)	1·484 (3)
C12–O3	1·427 (3)	1·439 (3)
C13–C12	1·485 (4)	1·484 (5)
O4–C13	1·402 (4)	1·425 (4)
C14–O4	1·414 (4)	1·419 (5)
C16–C15	1·384 (3)	1·387 (4)
C20–C15	1·391 (3)	1·384 (4)
C17–C16	1·387 (4)	1·390 (4)
C18–C17	1·377 (4)	1·369 (4)
C19–C18	1·363 (4)	1·373 (4)
C20–C19	1·388 (4)	1·379 (4)

Anion

N–C21		1·145 (5)
S–C21		1·616 (5)

Coordination distances

Na–N		2·421 (4)
Na–O1		2·419 (4)
Na–O2		2·380 (4)
Na–O3		2·495 (4)
Na–O4		2·426 (4)
Na–O5		2·317 (4)

(b) Bond angles (°)

Ligand	(1)	(2)
C5–C1–O1	115·3 (2)	116·5 (2)
C11–C1–O1	117·5 (2)	118·0 (2)
C11–C1–C5	127·2 (2)	125·3 (2)
C2–O1–C1	114·9 (2)	117·4 (2)
C3–C2–O1	108·1 (2)	112·0 (3)
O2–C3–C2	110·3 (2)	109·2 (3)
C4–O2–C3	112·5 (2)	113·1 (3)
C6–C5–C1	119·8 (2)	120·4 (3)
C10–C5–C1	121·6 (2)	120·7 (3)
C10–C5–C6	118·5 (2)	118·8 (3)
C7–C6–C5	120·9 (2)	120·3 (3)
C8–C7–C6	120·0 (2)	119·6 (3)
C9–C8–C7	119·2 (2)	120·3 (3)
C10–C9–C8	121·2 (2)	120·5 (3)
C9–C10–C5	120·2 (2)	120·4 (3)
O3–C11–C1	117·2 (2)	118·7 (2)
C15–C11–C1	127·2 (2)	125·4 (2)
C15–C11–O3	115·6 (2)	115·9 (2)
C12–O3–C11	115·3 (2)	114·7 (2)
C13–C12–O3	107·1 (2)	112·2 (3)
O4–C13–C12	109·8 (2)	108·6 (2)
C14–O4–C13	111·2 (3)	112·8 (3)
C16–C15–C11	122·4 (2)	120·9 (2)
C20–C15–C11	119·2 (2)	120·5 (2)
C20–C15–C16	118·2 (2)	118·5 (2)
C17–C16–C15	120·5 (2)	120·2 (3)
C18–C17–C16	120·6 (2)	120·4 (3)
C19–C18–C17	119·6 (2)	119·7 (3)
C20–C19–C18	120·3 (2)	120·3 (3)
C19–C20–C15	120·8 (2)	120·8 (3)

Anion

N–C21–S		178·2 (4)

Around the cation

N–Na–O1		162·2 (3)
N–Na–O2		100·1 (3)
O1–Na–O2		71·7 (3)
N–Na–O3		100·9 (3)
O1–Na–O3		65·6 (3)
O2–Na–O3		97·6 (3)

	(2)
N–Na–O4	100·7 (3)
O1–Na–O4	86·2 (3)
O2–Na–O4	157·9 (3)
O3–Na–O4	71·2 (3)
N–Na–O5	98·4 (3)
O1–Na–O5	97·5 (3)
O2–Na–O5	90·9 (3)
O3–Na–O5	157·1 (3)
O4–Na–O5	93·3 (3)

(c) Torsion angles in the ligand ($\sigma = 0.6°$)

|	(1)	(2)
C5–C1–O1–C2	78·8	−44·4
C11–C1–O1–C2	−102·5	138·7
O1–C1–C5–C6	41·8	−51·5
O1–C1–C5–C10	−135·6	126·8
C11–C1–C5–C6	−136·8	125·2
C11–C1–C5–C10	45·8	−56·5
O1–C1–C11–O3	16·6	−11·3
O1–C1–C11–C15	−165·1	169·5
C5–C1–C11–O3	−164·8	172·0
C5–C1–C11–C15	13·4	−7·1
C1–O1–C2–C3	−165·3	−72·2
O1–C2–C3–O2	−67·5	−58·6
C2–C3–O2–C4	175·0	−174·3
C1–C11–O3–C12	−109·7	121·6
C15–C11–O3–C12	71·8	−59·1
C1–C11–C15–C16	38·3	−47·0
C1–C11–C15–C20	−146·3	135·3
O3–C11–C15–C16	−143·4	133·8
O3–C11–C15–C20	32·0	−43·8
C11–O3–C12–C13	180·0	−68·8
O3–C12–C13–O4	72·6	−64·6
C12–C13–O4–C14	−169·9	168·0
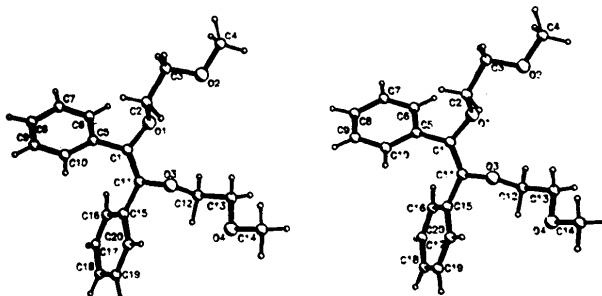
Fig. 1. Stereoscopic view of the free ligand (1).

ligand, the four ether oxygens are, however, approximately coplanar (max. deviation from their mean plane 0·1 Å) (Table 3).

The orientation of the phenyl rings in (1) is also of interest. Both rings are twisted out of the ethylenic bond plane so that C11–C1–C5–C10 = 45·8 (6)° and C1–C11–C15–C16 = 38·3 (6)°. As a result they are almost perpendicular to each other, the dihedral angle between their mean planes being 118°. In this conformation, the conjugation of each aromatic group with the double bond is almost completely lost. The C=C bond length of 1·343 (3) Å is typical of a non-conjugated double bond. In the polyether moiety the distances C–C and C–O are as expected. The valence angles between the phenyl rings and the double bond are significantly larger than 120°: C5–C1–C11 = C1–C11–C15 = 127·2 (2)°. They indicate the

Table 3. *Mean planes and distances of some atoms from these planes (Roberts and Sheldrick, 1975)*

	(1)		(2)	
Mean plane through	O1, O2, O3, O4		O1, O3, N, O5	
Equation	$0.0481x + 0.9453y$		$0.5664x + 0.5843y$	
	$-0.3227z = 1.1379$		$-0.5812z = 2.851$	
Distances (Å)				
	O1	0.082	O1	−0.286
	O2	−0.029	O2	−2.347
	O3	−0.103	O3	0.271
	O4	0.050	O4	2.326
	C1	−0.109	Na	−0.040
	C5	−0.359	N	−0.196
	C11	−0.022	O5	0.211
	C15	0.115		

steric repulsion between the two aromatic rings in a *cis* configuration. Similar values have been observed in other *cis*-stilbenes (Tinant, Touillaux, Declercq, Van Meerssche, Leroy & Weiler, 1983).

The complex of (1) with sodium thiocyanate is presented in the stereoview of Fig. 2. A water molecule (O5) completes the coordination sphere of the cation.

(a) Coordination of Na

The coordination around the Na cation is sixfold and has a distorted octahedral geometry. The four ether oxygen atoms are coordinated at distances ranging from 2·380 (4) to 2·495 (4) Å (Table 2a). The coordination sphere is completed by the SCN anion (through the N atom) and by the water molecule O5. From the sum of the van der Waals radii (1·4 Å for O, 1·5 Å for N) (Pauling, 1960) and the effective ionic radii (1·02 Å for Na^+ with coordination VI) (Shannon, 1976), one may expect distances $Na^+\cdots O$ of 2·42 Å and $Na^+\cdots N$ of 2·52 Å. The mean value for the four ether oxygens–Na distances is 2·43 (2) Å, in agreement with predicted values. The $Na^+\cdots N$ and $Na^+\cdots O5(w)$ are shorter than the sum of radii because of the higher electronegativity of the donor atoms, especially N which carries a negative charge. The $O\cdots O$ and $O\cdots N$ distances range from 2·662 (4) to 3·670 (4) Å; the distance $O1\cdots O3$ of 2·662 (4) Å is shorter than the sum of the van der Waals radii but these atoms are adjacent to the double bond, while $O1\cdots O2 = 2·811$ (4) Å and $O3\cdots O4 = 2·866$ (4) Å correspond to the sum of radii. Consequently, the angles $O1\cdots Na\cdots O2$, $O1\cdots Na\cdots O3$ and $O3\cdots Na\cdots O4$ deviate more significantly from the value of 90° expected for a regular octahedron.

(b) Conformation of the ligand

Distances and valence angles are very similar in the complex and in the free ligand (Table 2a,b). The orientation of the phenyl groups is also similar: torsion angles C11—C1—C5—C10 and C1—C11—C15—C16 in (2) are, respectively, −56·5 (6) and −47·0 (6)°, *i.e.* they are twisted out of the ethylenic plane by 10° more than in the free ligand. This greater degree of deconjugation is reflected perhaps in the slightly shorter

C=C and longer C—C_{ar} in bonds in (2) (Table 2a). The torsion around the ethylenic bond [O1—C1—C11—O3 = −11·3 (6)°] is less than in (1).

As shown in Fig. 2 and by a comparison of the torsion angles along the chain (Table 2c), the ligand has approximate twofold symmetry with the diad perpendicular to the central C=C bond. The conformation of the two arms of the ligand is completely different from that observed for (1). Two C—O bonds, O1—C2 and O3—C12, located symmetrically with respect to the C=C bond, which were *anti* in (1) are *gauche* in (2) and have the same sign. Moreover, the *gauche* bond C12—C13 now has the same sign as its symmetrical counterpart C2—C3. This leads to a conformational sequence which contains two genuine corners $(g^{\pm}g^{\pm})$ (Dale, 1980): $ag^{\pm}g^{\pm} \mp 139 \pm 11 \mp 122\, g^{\pm}g^{\pm}a$. The result is a tight folding which brings O2 and O4 to opposite sides of a plane containing O1, O3, N, O5w and the Na^+ cation (Fig. 2, Table 3). This is clearly quite different from the circular arrangement expected from the free ligand structure from known structures of short linear polyethers, particularly (because of similar ionic radii) that of triglyme.Ca(SCN) (Wei *et al.*, 1987a). The reason might be that Na does not satisfy the 'cavity' size which would be obtained in a horseshoe arrangement containing a central double bond. We plan to study the structures of other alkali-metal and alkaline-earth thiocyanate complexes of (1) in order to verify this hypothesis.

The thiocyanate anion is almost linear with N—C—S = 178·2 (4)°. In all the alkaline-earth.glyme
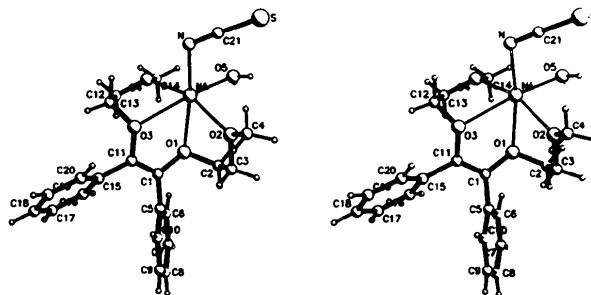

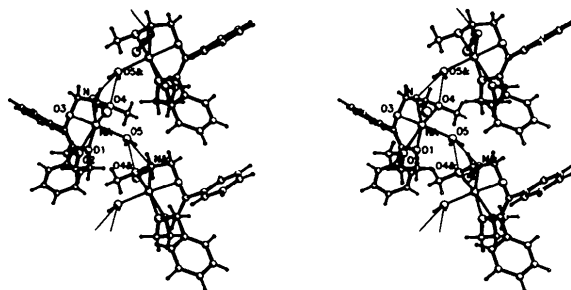Fig. 2. Stereoscopic view of the complex (2).

Fig. 3. Stereoscopic view of hydrogen bonding in the complex.

thiocyanates the anion was bound through N in an approximately linear manner (M^{2+}···NCS$^-$ 180°) (Wei et al., 1987a,b). In the present structure the angle Na$^+$···NCS$^-$ = 112·4 (3)° and, in addition to being coordinated to Na, the N atom is hydrogen bonded to a symmetry-related water molecule. Such non-linear arrangements are relatively uncommon but have already been reported for some alkali-metal thiocyanate complexes (Weber & Saenger, 1980; Suh, Weber, Kaftory, Saenger, Sieger & Vogtle, 1980). The other hydrogen atom of the water molecule is H-bonded to the ether oxygen O4. The distances are: O5—H51···N (O5 0·5−x, 0·5+y, 0·5−z): O···N 2·887, H···N 1·98 Å; O5—H52···O4 (O5 0·5−x, 0·5+y, 0·5−z): O···O 3·016, H···O 2·33 Å. A stereoscopic view of the hydrogen bonds between the complex units is presented in Fig. 3.

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Structure of Catalpol Hexaacetate*

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Abstract. [1S-(1α,4aα,7β,7aα)]-5-Acetoxy-7-acetoxymethyl-6α,7α-epoxy-1-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)-1,4a,5,6,7,7a-hexahydrocyclopenta[c]pyran,‡ C$_{27}$H$_{34}$O$_{16}$, M_r = 614·6, monoclinic, $P2_1$, a = 5·877 (2), b = 12·735 (5), c = 20·759 (9) Å, β = 95·62 (3)°, V = 1546 (1) Å^3, Z = 2, D_x = 1·32 Mg m^{-3}, Mo $K\alpha$, λ = 0·7107 Å, μ = 0·103 mm^{-1}, F(000) = 648, T = 293 K, R = 0·053 for 2099 observed reflections. The X-ray analysis confirms the structure previously assigned on the basis of chemical and spectroscopic studies. The five-membered ring is intermediate between a half-chair and an α-envelope, whilst the dihydropyran ring adopts a sofa conformation. The β-glucose moiety is a distorted $^4C_1$ chair. The packing in the crystal is entirely due to intermolecular C—H···O contacts and van der Waals forces.

Introduction. Catalpol (1) is a naturally occurring iridoid glucoside which was isolated from the aerial parts of the plant *Penstemon apateticus* (Schrophulariaceae). The sample used was collected in Cofre de Perote (Estado de Veracruz, Mexico). This plant

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