molecules which are related by a crystallographic twofold axis. A related NS_2Cl donor set has been reported for a series of binuclear macrocyclic complexes of Pd^{II} (Lehn, Parker & Rimmer, 1985).

We thank the SERC for support and Johnson Matthey plc for generous loans of platinum metals.

References

ATKINSON, N., BLAKE, A. J., DREW, M. G. B., FORSYTH, G., LAVERY, A. J., REID, G. & SCHRÖDER, M. (1989). *J. Chem. Soc. Chem. Commun.* pp. 984–986.

BLAKE, A. J., HYDE, T. I., REID, G. & SCHRÖDER, M. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1397–1399.

BLAKE, A. J., REID, G. & SCHRÖDER, M. (1990). *J. Chem. Soc. Dalton Trans.* In the press.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

GOULD, R. O. & TAYLOR, P. (1985). *CALC.* Program for molecular geometry calculations. Fortran77 version. Univ. of Edinburgh, Scotland.

LEHN, J.-M., PARKER, D. & RIMMER, J. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1517–1521.

MALLINSON, P. D. & MUIR, K. W. (1985). *J. Appl. Cryst.* 18, 51–53.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

16-Crown-5 Derivative of 1,6-Anhydro-β-D-glucopyranose: Structure of [1,6-Anhydro-2,4-di-O-(3,6,9-trioxaundecane-1,11-diyl)-β-D-glucopyranose]sodium Tetraphenylborate

By PETER LUGER AND LOUIS DENNER

Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-1000 Berlin 33, Germany

AND MILOSLAV ČERNÝ, JINDŘICH JINDŘICH AND TOMÁŠ TRNKA

Department of Organic Chemistry, Charles University, 128 40 Prague 2, Albertov 2030, Czechoslovakia

Abstract. $[Na(C_{14}H_{24}O_8)][B(C_6H_5)_4]$, $M_r = 662.56$, orthorhombic, $P2_12_12_1$, $a = 29.865 (5)$, $b = 12.163 (3)$, $c = 9.499 (2)$ Å, $V = 3450.5$ Å^3, $Z = 4$, $D_x = 1.275$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1.5418$ Å, $\mu = 8.29$ cm^{-1}, $F(000) = 1408$, $T = 295$ K, final $R = 0.049$ and $wR = 0.068$ for 3195 reflections having $I > 2\sigma(I)$. In the 1:1 complex of the Na$^+$ 16-crown-5 cation and the tetraphenylborate anion the sodium ion is 0.77 Å above the crown center and is coordinated to the five oxygen atoms of the crown and to O(1) of the sugar moiety belonging to a symmetry-related molecule *via* the screw axis in the z direction. The integration of the 1,6-anhydro sugar fragment into the 16-crown-5 ether does not affect the rather rigid conformation of this fused ring system but causes certain changes in the crown ether geometry when compared to a previously determined 16-crown-5 complex.

Introduction. A great number of chiral crown ethers so far described in the literature (Stoddart, 1987) contain a sugar molecule as a chiral component, usually a modified sugar alcohol or a hexose, the polyether part being 15-crown-5 or 18-crown-6. The complexing ability of these compounds is sensitive to

the configuration of the sugar moiety and to geometrical changes of the polyether ring. It has been shown that the presence of an additional hydroxyl group in the polyether ring may modify the formation of complexes and makes the introduction of a pendant arm possible (Pugia, Knudsen, Cason & Bartsch, 1987). These aspects were taken into account in our effort to prepare a new type of crown ether containing 1,6-anhydro-β-D-glucopyranose as a chiral component.

The starting compound used in our synthesis was 1,6:3,4-dianhydro-2-*O*-toluene-*p*-sulfonyl-β-D-galactopyranose (Černý, Gut & Pacák, 1961) which was converted into the title compound by reaction with tetraethylene glycol followed by intramolecular cyclization and complex formation with sodium tetraphenylborate (Jindřich, 1987). This paper describes the results of the crystallographic analysis of the complex and gives evidence for its previously suggested structure.

Experimental. Crystallization from acetone/water; colorless plate-shaped single crystals; crystal size 0.2 × 0.4 × 0.5 mm. Stoe four-circle diffractometer controlled by a DEC Micro PDP-11 computer. Lattice

parameters from least-squares refinement of 56 reflections with $60 < 2\theta < 70°$. At room temperature one octant of independent reflections measured in ω–2θ scan mode up to $(\sin\theta/\lambda)_{max} = 0.583$ Å^{-1} with Ni-filtered Cu $K\alpha$ radiation. Number of reflections 3321, 126 unobserved with $I < 2\sigma(I)$, h, k, l 0 to 34, 0 to 14, 0 to 11. Two standard reflections measured every 40 min showed insignificant statistical intensity variations. Reflection intensities corrected by Lorentz and polarization factor, no absorption correction. Structure solution easily obtained with MULTAN77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Conventional full-matrix least-squares refinement of atomic positional and thermal parameters, scale factor and an isotropic extinction parameter with the XTAL system (Hall & Stewart, 1987). Quantity minimized $\sum w(|F_o| - |F_c|)^2$. Unobserved reflections included if $|F_c| > |F_o|$.

During the refinement carbon atom C(11) of the crown showed unusually large thermal parameters and its position tended to diverge. A redetermination from a difference synthesis gave an extended diffuse maximum, so that high flexibility at this ring site or disorder was assumed. It was treated as follows: the bond length C(10)—C(11) was fixed at 1·50 Å and the corresponding H atoms were placed in calculated positions with a common isotropic temperature factor. The positional parameters of these six atoms were held constant during the later refinement cycles. The remaining non-H atoms were refined with anisotropic thermal parameters and all other H atoms were located from a difference Fourier map and refined with isotropic temperature factors.

Final $R = 0.049$ and $wR = 0.068$, based on 3195 reflections and 588 variables, goodness of fit $S = 2.42$, $w = 1/\sigma^2(F)$, $\sigma^2(F)$ values from counting statistics, max. $(\Delta/\sigma) = 0.03$, largest peak in final difference map $= 0.51$, largest hole $= 0.32$ e Å^{-3}.* Atomic scattering factors for C and N atoms from Cromer & Mann (1968), H-atom scattering factors from Stewart, Davidson & Simpson (1965). Final atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) are given in Table 1.

Discussion. The results of this X-ray analysis confirm the structure as a 1:1 complex of the tetraphenylborate with an Na$^+$ 16-crown-5 macrocycle where the 1,6-anhydro sugar is integrated in the crown ether. The atomic numbering scheme, the molecular structure of the crown and the coordination of the

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2 × 10^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Na	0·16597 (4)	0·0291 (1)	0·5609 (1)	5·00 (4)
C(1)	0·2509 (1)	0·0150 (3)	0·8210 (4)	5·3 (1)
O(1)	0·28488 (8)	0·0668 (2)	0·9028 (3)	6·38 (9)
C(2)	0·2056 (1)	0·0263 (3)	0·8935 (4)	4·7 (1)
O(2)	0·17537 (7)	−0·0297 (2)	0·8028 (3)	4·72 (7)
C(3)	0·1928 (1)	0·1475 (3)	0·9122 (4)	5·7 (1)
O(3)	0·2117 (1)	0·1845 (3)	1·0428 (4)	8·4 (1)
C(4)	0·2083 (1)	0·2198 (3)	0·7906 (5)	5·6 (1)
O(4)	0·17553 (9)	0·2077 (2)	0·6816 (3)	5·99 (8)
C(5)	0·2541 (1)	0·1840 (3)	0·7341 (5)	5·5 (1)
O(5)	0·25008 (8)	0·0709 (2)	0·6910 (3)	5·48 (8)
C(6)	0·2902 (1)	0·1769 (4)	0·8461 (6)	7·1 (2)
C(7)	0·1715 (2)	0·2999 (3)	0·5911 (7)	8·4 (2)
C(8)	0·1381 (2)	0·2758 (4)	0·4806 (7)	8·8 (2)
O(9)	0·1525 (1)	0·1816 (3)	0·4052 (4)	7·8 (1)
C(10)	0·1237 (–)	0·1672 (–)	0·2932 (–)	13·0 (1)
C(11)	0·1113 (–)	0·0499 (–)	0·2642 (–)	20·0 (1)
O(12)	0·1117 (1)	−0·0220 (3)	0·3722 (4)	8·2 (1)
C(13)	0·0684 (1)	−0·0474 (3)	0·4228 (6)	8·1 (2)
C(14)	0·0743 (2)	−0·1233 (6)	0·5419 (5)	8·3 (2)
O(15)	0·09956 (9)	−0·0662 (3)	0·6481 (3)	6·38 (9)
C(16)	0·1108 (2)	−0·1354 (5)	0·7631 (5)	7·3 (2)
C(17)	0·1354 (1)	−0·0674 (4)	0·8693 (4)	6·4 (1)
B	0·3992 (1)	0·4610 (3)	0·6238 (4)	4·13 (9)
C(101)	0·41707 (9)	0·5848 (3)	0·5783 (3)	4·23 (8)
C(102)	0·4040 (1)	0·6318 (3)	0·4489 (4)	5·4 (1)
C(103)	0·4216 (1)	0·7309 (4)	0·4007 (5)	6·6 (1)
C(104)	0·4533 (1)	0·7873 (3)	0·4790 (5)	6·5 (1)
C(105)	0·4669 (1)	0·7429 (3)	0·6055 (5)	6·0 (1)
C(106)	0·4489 (1)	0·6448 (3)	0·6528 (4)	4·9 (1)
C(201)	0·4348 (1)	0·3697 (3)	0·5605 (3)	4·29 (8)
C(202)	0·4365 (1)	0·2618 (3)	0·6091 (4)	5·4 (1)
C(203)	0·4663 (1)	0·1843 (3)	0·5586 (5)	6·5 (1)
C(204)	0·4959 (1)	0·2120 (4)	0·4522 (5)	6·8 (1)
C(205)	0·4948 (1)	0·3160 (4)	0·3995 (5)	7·2 (1)
C(206)	0·4649 (1)	0·3930 (3)	0·4513 (5)	5·9 (1)
C(301)	0·3493 (1)	0·4451 (3)	0·5526 (3)	4·35 (9)
C(302)	0·3148 (1)	0·5208 (3)	0·5818 (5)	6·0 (1)
C(303)	0·2735 (1)	0·5151 (5)	0·5161 (6)	7·7 (2)
C(304)	0·2650 (1)	0·4353 (6)	0·4177 (6)	8·8 (2)
C(305)	0·2977 (1)	0·3596 (6)	0·3866 (5)	8·4 (2)
C(306)	0·3392 (1)	0·3637 (4)	0·4552 (4)	6·1 (1)
C(401)	0·3967 (1)	0·4450 (2)	0·7964 (3)	4·08 (8)
C(402)	0·4358 (1)	0·4463 (3)	0·8800 (4)	4·9 (1)
C(403)	0·4350 (1)	0·4390 (3)	1·0250 (4)	5·6 (1)
C(404)	0·3950 (1)	0·4260 (3)	1·0963 (4)	5·8 (1)
C(405)	0·3562 (1)	0·4187 (3)	1·0186 (4)	5·5 (1)
C(406)	0·3571 (1)	0·4285 (3)	0·8725 (4)	4·64 (9)

sodium are shown in Fig. 1. A list of bond lengths and angles appears in Tables 2 and 3 and some selected torsion angles are listed in Table 4. In the tetraphenylborate anion the B—C distances vary between 1·648 (4) and 1·655 (5) Å (average 1·652 Å), being in agreement with previous results found for this anion, for example by Nolte & Gafner (1974).

All further bonding data of this moiety are as expected [average phenyl C—C 1·388 (3) Å, angle C—B—C 109·5 (20)°] and need no further discussion. In the 16-crown-5 ring the average C—C bond length in the crown is 1·50 (2) Å with the usual shortening to values below 1·50 Å if both C atoms have oxygen neighbours. The average C—O bond is 1·424 (8) Å [values in the disordered fragment O(9)—C(10)—C(11)—O(12) not considered]. The conformation of the 16-membered macrocycle is rather different from the typical 'crown' arrangement being otherwise found. Very common are O—C—C—O torsion angles close to a $+sc$ or $-sc$ (*gauche*) con-

formation and the *ap* conformation (*trans*) along C—O bonds. This pattern is, for example, roughly realized in the only 16-crown-5 derivative previously investigated, *viz* 15,15-bis(dodecyclmethyl)-16-crown-5 with NaSCN (Czugler, Weber, Kálmán, Stensland & Párkányi, 1982). In the present structure major deviations from this pattern are observed at the O(9)—C(10)—C(11)—O(12) fragment, which was shown in the refinement to be affected by some disorder, and in the crown ether segment O(2)—C(2)—C(3)—C(4)—O(4) being part of the anhydro sugar.

The sodium cation is not exactly in the crown center but 0·77 Å above a least-squares plane calculated through the five ether O atoms of the crown. The Na⁺ cation is coordinated to these five O atoms and to an O(1)′ oxygen atom of the sugar anhydro ring related to the crown molecule *via* the screw axis in the *z* direction [symmetry operation for O(1)′: ½ − *x*, −*y*, −½ + *z*]. Hence in this structure the Na⁺ ion is sixfold coordinated with Na⁺···O distances in the crown between 2·407 (4) and 2·495 (4) Å and an Na···O(1)′ distance of 2·403 (4) Å. The average Na···O distance of 2·44 Å is consistent with the usual Na···O ether contacts for five- to eight-coordinated sodium in crown ether complexes (Shoham & Cohen, 1989). In the 16-crown-5 complex with NaSCN (Czugler *et al.*, 1982) the sodium ion also had sixfold coordination (five oxygens of the crown plus nitrogen of SCN⁻) with Na⁺···O = 2·43 Å and Na⁺ 0·57 Å above the plane of the crown. In a recently described structure of a 15-crown-5 complex with NaClO₄ (Shoham & Cohen, 1989) the displacement of Na⁺ from the center of the crown is also 0·77 Å (with respect to the least-squares plane of the five ether oxygens), although the coordination number is seven and two contacts with perchlorate oxygens outside the crown exist. A relation was stated
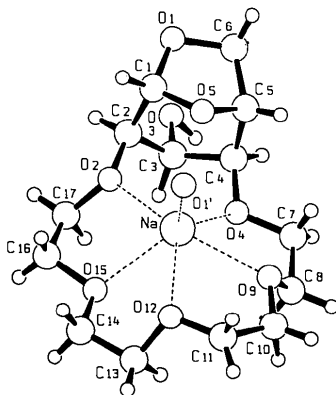
Table 2. *Bond lengths (Å) for the* 16-*crown*-5 *moiety and* Na···O *coordination contacts (Å), with e.s.d.'s in parentheses*

C(1)—O(1)	1·424 (5)		
C(1)—C(2)	1·523 (5)	C(1)—O(5)	1·410 (5)
O(1)—C(6)	1·452 (6)	C(2)—O(2)	1·422 (4)
C(2)—C(3)	1·533 (5)	O(2)—C(17)	1·426 (5)
C(3)—O(3)	1·435 (6)	C(3)—C(4)	1·524 (6)
C(4)—O(4)	1·432 (5)	C(4)—C(5)	1·533 (6)
O(4)—C(7)	1·418 (6)	C(5)—O(5)	1·441 (5)
C(5)—C(6)	1·516 (7)	C(7)—C(8)	1·477 (9)
C(8)—O(9)	1·417 (7)	O(9)—C(10)	1·378 (4)
C(10)—C(11)	1·500 (−)	C(11)—O(12)	1·348 (4)
O(12)—C(13)	1·414 (6)	C(13)—C(14)	1·470 (8)
C(14)—O(15)	1·439 (6)	O(15)—C(16)	1·420 (6)
C(16)—C(17)	1·498 (7)		
Na···O(4)	2·472 (3)	Na···O(2)	2·423 (3)
Na···O(12)	2·495 (4)	Na···O(9)	2·407 (4)
Na···O(1)′	2·403 (4)	Na···O(15)	2·442 (3)

Note: O(1)′ is symmetry related to O(1) by ½ − *x*, −*y*, −½ + *z*.

Table 3. *Bond angles (°) for the* 16-*crown*-5-*moiety, with e.s.d.'s in parentheses*

O(1)—C(1)—C(2)	110·3 (3)	C(4)—C(5)—C(6)	113·9 (4)
O(1)—C(1)—O(5)	106·1 (3)	O(5)—C(5)—C(6)	101·8 (3)
C(2)—C(1)—O(5)	109·7 (3)	C(1)—O(5)—C(5)	102·1 (3)
C(1)—O(1)—C(6)	106·5 (3)	O(1)—O(6)—C(5)	103·6 (3)
C(1)—C(2)—O(2)	104·3 (3)	O(4)—C(7)—C(8)	109·3 (4)
C(1)—C(2)—C(3)	111·1 (3)	C(7)—C(8)—O(9)	108·4 (4)
O(2)—C(2)—C(3)	111·9 (3)	C(8)—O(9)—C(10)	107·8 (5)
C(2)—O(2)—C(17)	114·7 (3)	O(9)—C(10)—C(11)	114·7 (6)
C(2)—C(3)—O(3)	107·7 (3)	C(10)—C(11)—O(12)	118·3 (6)
C(2)—C(3)—C(4)	113·0 (3)	C(11)—O(12)—C(13)	113·1 (5)
O(3)—C(3)—C(4)	110·8 (3)	O(12)—C(13)—C(14)	106·8 (4)
C(3)—C(4)—O(4)	106·4 (3)	C(13)—C(14)—O(15)	107·4 (5)
C(3)—C(4)—C(5)	111·9 (3)	C(14)—O(15)—C(16)	112·1 (4)
O(4)—C(4)—C(5)	109·2 (3)	O(15)—C(16)—C(17)	107·8 (4)
C(4)—O(4)—C(7)	114·5 (3)	O(2)—C(17)—C(16)	106·9 (3)
C(4)—C(5)—O(5)	107·2 (3)		

between the 'size' of the crown cavity and the displacement of the sodium cation. It is interesting to note that the cavity size of the present 16-crown-5 macrocycle is almost the same as reported by Shoham & Cohen for the 15-crown-5, when measured *via* O···O distances across the macrocyclic ring. These distances range from 4·04 to 4·62 Å in the present structure (4·37 to 4·74 Å in the 16-crown-5

Table 4. *Selected torsion angles (°), with e.s.d.'s in parentheses*

O(9)—C(10)—C(11)—O(12)	27·6 (8)	C(10)—C(11)—O(12)—C(13)	103·3 (6)
C(1)—C(2)—C(3)—C(4)	35·3 (4)	C(4)—C(3)—C(2)—O(2)	−80·8 (4)
C(1)—C(2)—O(2)—C(17)	157·1 (3)	C(4)—C(5)—C(6)—O(1)	86·1 (4)
C(1)—O(1)—C(6)—C(5)	4·0 (4)	C(4)—O(4)—C(7)—C(8)	177·8 (4)
C(1)—O(5)—C(5)—C(6)	43·2 (4)	C(5)—C(4)—O(4)—C(7)	−86·8 (4)
C(1)—O(5)—C(5)—C(4)	−76·6 (4)	C(5)—O(5)—C(1)—O(1)	−42·3 (3)
C(1)—C(2)—C(3)—O(3)	−87·4 (4)	C(6)—C(5)—C(4)—O(4)	−171·3 (3)
C(2)—C(1)—O(1)—C(6)	−95·3 (4)	C(7)—C(8)—O(9)—C(10)	−173·5 (4)
C(2)—C(1)—O(5)—C(5)	76·8 (3)	C(11)—O(12)—C(13)—C(14)	−178·3 (4)
C(8)—O(9)—C(10)—C(11)	−139·6 (6)	C(13)—C(14)—O(15)—C(16)	−174·6 (4)
C(2)—C(3)—C(4)—C(5)	−37·1 (4)	C(14)—O(15)—C(16)—C(17)	−178·0 (4)
C(2)—C(3)—C(4)—O(4)	82·0 (4)	O(1)—C(1)—C(2)—O(2)	−179·1 (3)
C(2)—O(2)—C(17)—C(16)	−173·2 (3)	O(1)—C(1)—O(5)—C(5)	−28·9 (4)
C(3)—C(2)—C(1)—O(1)	60·1 (4)	O(2)—C(2)—C(1)—O(5)	64·4 (3)
C(3)—C(2)—C(1)—O(5)	−56·3 (4)	O(2)—C(17)—C(16)—O(15)	−62·3 (5)
C(3)—C(2)—O(2)—C(17)	−82·7 (4)	O(2)—C(2)—C(3)—O(3)	156·4 (3)
C(3)—C(4)—O(4)—C(7)	152·3 (4)	O(3)—C(3)—C(4)—O(4)	−157·0 (3)
C(3)—C(4)—C(5)—O(5)	57·9 (4)	O(4)—C(7)—C(8)—O(9)	−58·9 (6)
C(3)—C(4)—C(5)—C(6)	−53·9 (4)	O(12)—C(13)—C(14)—O(15)	61·6 (5)

Fig. 1. Structure and atomic notation of the Na⁺ 16-crown-5 cation with Na···O coordination contacts in dashed lines (*SCHAKAL* representation; Keller, 1980).

complex with NaSCN) and are between 4·01 and 4·51 Å in the 15-crown-5 ring.

If a least-squares plane is calculated through all 16 atoms of the entire macrocycle an average deviation of 0·38 Å is calculated for the contributing atoms. Three of the O atoms, O(2), O(9) and O(12), are above the plane on the same side as Na and O(1)′ and the other two are below it [O(4) and O(15)]. Due to the odd number of O atoms in the crown macrocycle two neighboring O atoms have to lie on the same side of the plane. These atoms are O(9) and O(12), obviously being in a sterically unfavourable position. They are in an almost eclipsed position with respect to the C(10)—C(11) bond (torsion angle along this bond ~30°) and the C atoms between them were affected by the disorder problem mentioned above. So obviously there is some flexibility in this region of the macrocycle and an interconversion of this O—C—C—O fragment into another conformation may easily occur.

The conformation of the 1,6-anhydro system can be analyzed using the Cremer–Pople puckering parameters (Cremer & Pople, 1975) for the pyranosyl and the five-membered anhydro ring. The latter has an envelope form with the O atom O(5) as the out-of-plane atom indicated by the value of the puckering angle $\varphi = 258\cdot4\ (6)°$ and the almost zero torsion angle C(5)—C(6)—O(1)—C(1) = 4·0°. However, an exact envelope form would require $\varphi_2 = 252°$ so that this ring is distorted towards a twist form (theoretical $\varphi_2 = 270°$). The puckering parameters for the pyranosyl ring [$Q = 0\cdot625\ (4)$ Å, $\varphi = 175\cdot7\ (9)°$, $\theta = 154\cdot7\ (4)°$] indicate a distortion from a

$^1C_4$ chair (theoretical $\theta = 180°$) in the direction of a sofa conformation (theoretical $\theta = 125\cdot3°$), which is very common for all 1,6-anhydrohexopyranoses investigated so far (Strumpel, Schmidt, Luger & Paulsen, 1984).

It follows that the integration of the 1,6-anhydro sugar fragment into the 16-crown-5 ether does not affect the rather rigid conformation of this fused ring system but has some influence on the crown-ether geometry when compared to the 16-crown-5 complex with NaSCN.

The packing of the complex in the crystal lattice is illustrated in Fig. 2, showing a projection of the unit cell down the z axis. An interaction between the crown and the tetraphenylborate is not directly observable, since no intermolecular contacts below van der Waals distances exist. This holds even for the hydroxyl group O(3)—H, which does not generate a hydrogen bridge as is otherwise very common at this site of the anhydro sugar.

The only short intermolecular contact is the already mentioned coordination Na$^+$···O(1)′ where O(1)′ is generated via the screw axis in the z direction at $(x,y) = (\frac{1}{4},0)$. By contacts of this type the crowns pile up in infinite screws in the z direction. Two piles exist per unit cell, at $(x,y) = (\frac{1}{4},0)$ and $(\frac{3}{4},\frac{1}{2})$, each pile surrounded by six anions per turn.
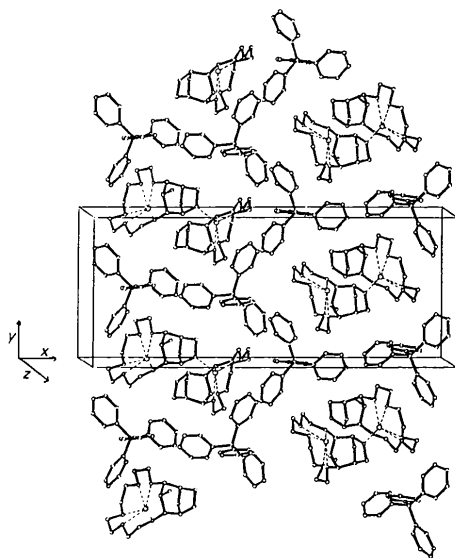
Fig. 2. Packing diagram of the title complex viewed down the c axis.

References

ČERNÝ, M., GUT, V. & PACÁK, J. (1961). *Collect. Czech. Chem. Commun.* **26**, 2542–2550.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1358–1367.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

CZUGLER, M., WEBER, E., KÁLMÁN, A., STENSLAND, B. & PÁRKÁNYI, L. (1982). *Angew. Chem.* **94**, 641–642; *Angew. Chem. Suppl.* (1982), pp. 1373–1384.

HALL, S. R. & STEWART, J. M. (1987). Editors. *XTAL2.2 Users Manual.* Univs. of Western Australia, Australia, and Maryland, USA.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

JINDŘICH, J. (1987). Thesis. Department of Organic Chemistry, Charles Univ., Prague, Czechoslovakia.

KELLER, E. (1980). *Chem. Unserer Z.* **14**, 56–60.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

NOLTE, M. J. & GAFNER, G. (1974). *Acta Cryst.* B30, 738–741.

PUGIA, M. J., KNUDSEN, B. E., CASON, C. V. & BARTSCH, R. A. (1987). *J. Org. Chem.* **52**, 541–547.

SHOHAM, G. & COHEN, N. (1989). *Acta Cryst.* C45, 1154–1158.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

STODDART, J. F. (1987). *Top. Stereochem.* 17, 207–288.

STRUMPEL, M., SCHMIDT, H. J., LUGER, P. & PAULSEN, H. (1984). *Carbohydr. Res.* 125, 185–201.

Structure of {1-[(2-Hydroxyphenyl)iminomethyl]naphthalen-2-olato-O,O',N}-piperidinenickel(II)

By YALCIN ELERMAN

Department of Engineering Physics, Faculty of Sciences, University of Ankara, Besevler, Ankara, Turkey

ERICH F. PAULUS

Hoechst AG, 623 Frankfurt/Main 80, Germany

AND HARTMUT FUESS

Strukturforschung, FB Materialwissenschaft Technische Hochschule, 6100 Darmstadt, Germany

Abstract. [Ni(C$_5$H$_{11}$N)(C$_{17}$H$_{11}$NO$_2$)], $M_r = 405.12$, monoclinic, $P2_1/n$, $a = 10.471$ (1), $b = 15.524$ (2), $c = 12.554$ (1) Å, $\beta = 113.07$ (1)°, $V = 1877.5$ Å^3, $Z = 4$, $F(000) = 848$, $D_m = 1.43$ Mg m^{-3} (pycnometrically), $D_x = 1.433$ Mg m^{-3}, Mo $K\alpha = 0.7107$ Å, $\mu = 1.043$ mm^{-1}, $T = 293$K, $R = 0.138$, $wR = 0.042$ for 3241 unique diffractometer data [$I > 1\sigma(I)$]. Nickel is in a slightly distorted square-planar environment of two oxygens [1.804(4) and 1.830(4)Å] and two nitrogens [1.848(4) and 1.947(4)Å] with O—Ni—N angles between 87.6(2) and 95.1(2)°. Ni is 0.033Å out of the plane of its ligands.

Introduction. Copper(II) and nickel(II) ions react with tridentate anionic Schiff bases, giving dimerized complexes with square planar configurations (Maggio, Pizzino & Romano, 1974). The same authors report that N-(2-hydroxyphenyl)salicylaldimine reacts with the nickel(II) ion giving a pseudo-octahedral complex by polymerization. The purpose of our study is to understand what happens when the nickel(II) ion reacts with both the monodentate ligand piperidine and the tridentate ligand N-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine. As an example we took the complex formed by the ligands N-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine and piperidine with the nickel(II) ion.

Experimental. Suitable crystals were obtained directly from the synthesis of the compound. A solution of 0.01 mol N-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine in 200 ml pure methanol was prepared and 0.6 ml piperidine was slowly added

to the solution, 0.01 mol Ni(CH$_3$COO)$_2$.4H$_2$O was dropwise dissolved in 20 ml hot methanol. The mixture of the two solutions was then refluxed for three hours. Red crystals were formed during the reflux operation.

A crystal of dimensions 0.15 × 0.15 × 0.08 mm was sealed in a Lindemann-glass capillary, 25 reflections with $2\theta > 18°$ were used for the determination of the cell parameters, one standard reflection (23$\bar{1}$), no decomposition by X-rays, 4569 measured reflections ($-14 \le h \le 1$; $0 \le \le k \le 20$; $-16 \le l \le 16$; $R_{int} = 0.016$) resulted in 3241 unique reflections (of 4823 theoretically possible ones) with intensities $I > \sigma(I)$ which were used for the structure analysis; Nicolet $R3$ computer-controlled diffractometer, $2\theta/\theta$ scan, $2\theta_{max} = 56°$; 4° min^{-1}; no correction for extinction; empirical absorption correction according to the ψ method (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968); T_{min}, $T_{max} = 0.77$, 0.87. The phase problem was solved by direct methods (Sheldrick, 1983); all the non-H atoms were located in the first electron density synthesis (E map). After a few cycles of least-squares refinement the H atoms could be included from a difference electron density synthesis. The parameter refinement was performed by the cascade least-squares method (Sheldrick, 1983), anisotropic atomic displacement parameters of the non-H atoms were refined, least-squares refinement on |F|, 245 parameters, $w = 1/\sigma^2(|F|)$ based on counting statistics, $R = 0.138$, $wR = 0.042$, $S = 1.38$; max. $\Delta/\sigma = 0.1$, the ten largest peaks in the final difference electron density synthesis were between 0.74 and 0.33 e Å^{-3}. All calculations and drawings