Gómez Beltrán, F., Valero Capilla, A. & Alcalá Aranda, R. (1978). *Cryst. Struct. Commun.* **7**, 153–157, 255–258.
Gómez Beltrán, F., Valero Capilla, A. & Alcalá Aranda, R. (1979). *Cryst. Struct. Commun.* **8**, 87–91.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Nardelli, M., Musatti, A., Domiano, P. & Andreetti, G. D. (1965). *Ric. Sci. Parte* 2 *Sez. A*. **8**, 807–810.
Valero Capilla, A., Alcalá Aranda, R. & Gómez Beltrán, F. (1980). *Cryst. Struct. Commun.* **9**, 147–150.

Acta Cryst. (1984). C**40**, 951–955

The Structures of 15,18,34,37-Tetramethoxy-1,4,7,10,13,20,23,26,29,32-decaoxa-[13.13]parabenzenophane, $C_{32}H_{48}O_{14}$, and its 1:2:2 Complex with Sodium Thiocyanate and Water, $C_{32}H_{48}O_{14}.2(NaSCN.H_2O)$*

By John D. Owen

Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Hertfordshire AL5 2JQ, England

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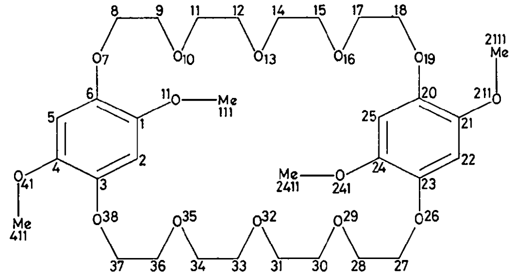
Abstract. $C_{32}H_{48}O_{14}$ (I): $M_r = 656{\cdot}7$, $C2/c$, $a = 32{\cdot}705$ (4), $b = 7{\cdot}637$ (2), $c = 13{\cdot}645$ (3) Å, $\beta = 98{\cdot}469$ (16)°, $V = 3370{\cdot}9$ (12) Å^3, $Z = 4$, $D_x = 1{\cdot}294$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}1$ cm^{-1}, $F(000) = 1408$, $T = 293$ K, $R = 0{\cdot}044$ for 1684 observations. The crystals are formed by packing of discrete molecules separated by normal van der Waals contacts. The oxygen atoms of each half of the centrosymmetrical molecule are almost coplanar with the benzene ring. $2(NaSCN.H_2O).(I)$: $M_r = 854{\cdot}9$, $P\bar{1}$, $a = 13{\cdot}178$ (3), $b = 13{\cdot}708$ (2), $c = 23{\cdot}567$ (4) Å, $\alpha = 83{\cdot}054$ (13), $\beta = 89{\cdot}816$ (14), $\gamma = 94{\cdot}162$ (20)°, $V = 4214{\cdot}5$ (12) Å^3, $Z = 4$, $D_x = 1{\cdot}347$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}2$ cm^{-1}, $F(000) = 1808$, $T = 293$ K, $R = 0{\cdot}089$ for 2727 observations. One sodium cation is six-coordinated, the other is eight-coordinated. The molecules form dimers, joined by hydrogen-bonded waters and anions and the benzene rings are stacked within the molecule, within the dimer and between dimers forming infinitely stacked chains along $[1\bar{1}1]$.

Introduction. 'Crown ether' compounds containing benzene rings were among the first to be prepared (Pedersen, 1967). These contained benzenes with two oxygen atoms in the *ortho* position, and many more have been prepared since (Gokel & Korzeniowski, 1982). These molecules form cavities which can accept small organic molecules or alkali-metal cations. Benzocrowns with oxygens in the *meta* position are much rarer (Van Keulen, Kellogg & Piepers, 1979; Elben, Fuchs, Frensch & Vögtle, 1979) and no structures of complexes have been reported. *para* substitution is also rare (Helgeson, Timko & Cram, 1974; Helgeson, Tarnowski, Timko & Cram, 1977; Kawashima, Kawashima, Otsubo & Misumi, 1978) and again no complexes have been reported. Model building indicated that the presence of methoxy groups on the benzene ring should aid complexation with alkali-metal cations, since a cavity surrounded by several oxygens can be formed at each end of a molecule such as (I). The preparation and characterization of (I) will be reported elsewhere (Parsons, 1983). The structures of (I) and its complex with $2(NaSCN.H_2O)$ are the first reported for a *para*-substituted benzo-crown molecule, and were undertaken to compare the conformations of the free and complexed molecules.



(I)

Experimental. Data for both structures collected on a CAD-4 diffractometer, intensities of 2 standard reflections changed insignificantly during data collections; no absorption corrections; scattering factors calculated from published analytical coefficents (*International Tables for X-ray Crystallography*, 1974); structure solution and refinement with *SHELX* (Sheldrick, 1976); data reduction and final geometry with local programs on a Prime 550 computer.

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* Crystal Structures of Complexes between Alkali-Metal Salts and Cyclic Polyethers. 14. Part 13: Owen (1983).

0108-2701/84/060951-05$01.50

Table 1. *Fractional coordinates* ($\times 10^4$) *and* U_{iso}/U_{eq} *values* (Å^2 $\times 10^4$) *for the non-hydrogen atoms of* (I)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm iso}/U_{\rm eq}$*
C(1)	4123·0 (7)	−702 (3)	1693 (2)	375 (8)*
C(2)	3746·2 (7)	−1084 (3)	2005 (2)	394 (8)*
C(3)	3379·8 (7)	−468 (3)	1486 (2)	365 (8)*
C(4)	3382·1 (7)	593 (3)	659 (2)	388 (8)*
C(5)	3757·7 (7)	939 (3)	334 (2)	412 (9)*
C(6)	4122·5 (7)	272 (3)	838 (2)	381 (8)*
O(7)	4479·8 (5)	498 (2)	416 (1)	452 (6)*
C(8)	4781·8 (8)	1689 (4)	904 (2)	519 (10)*
C(9)	4614·4 (8)	3478 (4)	1010 (2)	553 (10)*
O(10)	4458·0 (5)	4177 (2)	65 (1)	518 (7)*
C(11)	4260·5 (10)	5803 (4)	134 (2)	688 (12)*
C(12)	4092·0 (10)	6452 (4)	−860 (3)	777 (14)*
O(13)	3751·3 (6)	5424 (3)	−1272 (1)	798 (9)*
C(14)[a]	3565·9 (19)	6726 (9)	−2036 (4)	534 (20)
C(15)[a]	3176·5 (18)	5820 (9)	−2508 (4)	533 (20)
C(14)[b]	3517·4 (18)	5597 (10)	−2257 (4)	607 (20)
C(15)[b]	3194·0 (17)	6963 (9)	−2234 (4)	562 (20)
O(16)	2871·3 (6)	6014 (3)	−1804 (2)	816 (9)*
C(17)	2615·5 (9)	7462 (4)	−1707 (2)	692 (12)*
C(18)	2266·5 (8)	6918 (4)	−1187 (2)	542 (10)*
O(19)	1981·2 (5)	5877 (2)	−1850 (1)	442 (6)*
O(11)	4498·8 (5)	−1277 (2)	2155 (1)	512 (6)*
C(111)	4506·9 (8)	−2201 (4)	3063 (2)	629 (11)*
O(41)	3008·9 (5)	1253 (2)	228 (1)	522 (6)*
C(411)	3009·6 (9)	2490 (4)	−549 (2)	687 (12)*

[a] Occupancy 0·487 (8).

[b] Occupancy 0·513 (8).

(I): yellowish prisms, crystal 0·25 × 0·25 × 0·28 mm; cell dimensions from 23 reflections, $9 < \theta < 18°$, data collected for all planes with k and $l \geq 0$, where $1·5 < \theta < 23°$; 2666 planes measured, 2338 unique ($R_{\rm int} = 0·046$), 1684 [$I \geq 2\sigma(I)$] classed as observed, index range h −35/34, k 0/8, l 0/14. The asymmetric unit is half a molecule, the other half being related by a crystallographic centre of symmetry. Multisolution direct methods used to solve structure; H atoms placed in calculated positions, methyl H atoms located on Fourier difference maps; all non-hydrogen atoms except C(14) and C(15) refined by least squares with anisotropic temperature factors, H atoms given common $U_{\rm iso}$ [refined value 0·071 (2) Å^2] and methyl H's also a common $U_{\rm iso}$ [refined value 0·082 (4) Å^2]. Two alternative sites found on difference maps for each of C(14) and C(15), so atoms were located in these positions with occupancy p and $1-p$; p refined to 0·487 (8). H atoms with same occupancy placed in positions calculated from the geometry of each pair. $R = 0·044$, $wR = 0·044$, $w \propto 1/[\sigma^2(F_o) + 0·0005F_o{}^2]$; max. Δ/σ on final cycle 0·10, $\Delta\rho$ within −0·25 and 0·16 e Å^{-3}.

Table 2. *Fractional coordinates* ($\times 10^4$) *and* U_{iso}/U_{eq} *values* (Å^2 $\times 10^3$) *for the non-hydrogen atoms of* $2(NaSCN.H_2O).(I)$ (U_{eq} *defined as in Table* 1)

	x	y	z	$U_{\rm iso}/U_{\rm eq}$*
Na(1)	539 (3)	512 (2)	2272 (2)	60 (1)*
Na(2)	−2340 (3)	2712 (3)	4862 (2)	71 (2)*
C(1)	−479 (6)	2290 (6)	2913 (4)	44 (2)
C(2)	−546 (7)	3011 (6)	3274 (4)	51 (3)
C(3)	−1422 (7)	3062 (6)	3573 (4)	51 (3)
C(4)	−2252 (7)	2398 (6)	3517 (4)	49 (3)
C(5)	−2200 (7)	1694 (6)	3148 (4)	46 (2)
C(6)	−1321 (6)	1652 (6)	2851 (3)	41 (2)
O(7)	−1174 (4)	974 (4)	2479 (2)	50 (2)
C(8)	−2021 (7)	275 (7)	2385 (4)	54 (3)
C(9)	−1715 (8)	−279 (7)	1916 (4)	69 (3)
O(10)	−833 (5)	−746 (5)	2088 (3)	73 (2)
C(11)	−508 (9)	−1397 (9)	1723 (5)	94 (4)
C(12)	462 (8)	−1771 (8)	1921 (5)	82 (3)
O(13)	1196 (5)	−963 (5)	1902 (3)	74 (2)
C(14)	2152 (8)	−1204 (8)	2129 (5)	79 (3)
C(15)	2725 (8)	−306 (8)	2238 (5)	81 (3)
O(16)	2198 (5)	179 (4)	2648 (3)	61 (2)
C(17)	2369 (8)	−179 (8)	3225 (4)	74 (3)
C(18)	1675 (7)	268 (7)	3601 (4)	63 (3)
O(19)	656 (4)	−162 (4)	3522 (2)	58 (2)
C(20)	−73 (7)	88 (6)	3880 (4)	45 (2)
C(21)	−998 (7)	−486 (6)	3929 (4)	48 (2)
C(22)	−1773 (7)	−273 (6)	4262 (4)	50 (3)
C(23)	−1656 (6)	521 (6)	4571 (4)	44 (2)
C(24)	−745 (6)	1079 (6)	4530 (4)	46 (2)
C(25)	44 (7)	874 (6)	4195 (4)	49 (2)
O(26)	−2376 (4)	824 (4)	4922 (2)	58 (2)
C(27)	−3373 (7)	335 (7)	4948 (4)	62 (3)
C(28)	−3985 (8)	870 (7)	5318 (4)	69 (3)
O(29)	−4029 (5)	1849 (5)	5068 (3)	68 (2)
C(30)	−4699 (9)	2401 (8)	5364 (5)	91 (4)
C(31)	−4497 (9)	3428 (9)	5152 (5)	99 (4)
O(32)	−3509 (6)	3755 (6)	5273 (3)	98 (3)
C(33)	−3211 (10)	4777 (10)	5194 (6)	114 (5)
C(34)	−2164 (10)	4953 (10)	5323 (6)	118 (5)
O(35)	−1495 (5)	4505 (5)	4961 (3)	85 (2)
C(36)	−1214 (9)	5079 (8)	4451 (5)	82 (3)
C(37)	−780 (7)	4454 (7)	4047 (4)	63 (3)
O(38)	−1581 (5)	3713 (5)	3965 (3)	72 (2)
O(11)	370 (4)	2146 (4)	2613 (3)	56 (2)
C(111)	1152 (8)	2945 (8)	2534 (5)	75 (3)
O(41)	−3090 (5)	2473 (5)	3869 (3)	67 (2)
C(411)	−4058 (7)	2133 (8)	3682 (4)	65 (3)
O(211)	−1026 (5)	−1276 (5)	3599 (3)	65 (2)
C(2111)	−1945 (8)	−1903 (8)	3641 (5)	79 (3)
O(241)	−718 (5)	1902 (5)	4831 (3)	65 (2)
C(2411)	228 (8)	2309 (8)	4976 (5)	75 (3)
S(1)*t*	2194 (3)	2643 (2)	548 (2)	110 (2)*
C(1)*t*	1614 (9)	1912 (9)	1055 (6)	71 (5)*
N(1)*t*	1176 (10)	1401 (8)	1399 (5)	114 (6)*
S(2)*t*	487 (2)	4516 (3)	8256 (2)	95 (2)*
C(2)*t*	532 (8)	4188 (8)	7645 (6)	72 (5)*
N(2)*t*	572 (9)	3913 (8)	7195 (5)	112 (6)*
O(1)*w*	−2075 (7)	2414 (8)	5863 (4)	134 (5)*
O(2)*w*	−489 (7)	2652 (7)	6514 (4)	134 (5)*

$2(NaSCN.H_2O).(I)$: colourless needles, crystal 0·18 × 0·18 × 0·20 mm; cell dimensions from 24 reflections, $10 < \theta < 14°$; data collected for all planes with $l \geq 0$ and $1·5 < \theta < 20°$; 4051 planes measured, 3922 unique ($R_{\rm int} = 0·023$), 2728 [$I \geq 2\sigma(I)$] classed as observed, index range h ±12, k −12/13, l 0/22. Multisolution direct methods used to solve structure; H atoms placed in calculated positions; methyl H atoms located by Fourier difference maps, water H atoms not found; NaSCN and water O atoms given anisotropic temperature factors, rest isotropic; methyl H atoms given a common $U_{\rm iso}$ [refined value 0·068 (8) Å^2], rest of H atoms treated similarly [refined $U_{\rm iso} = 0·102$ (6) Å^2]. The 220 reflection suffered from double reflection and was omitted, giving $R = 0·089$, $wR = 0·094$, for 2727 observations, $w \propto 1/[\sigma^2(F_o)]$; max. Δ/σ in final cycle 0·11, $\Delta\rho$ −0·45 to 0·57 e Å^{-3}.

Table 3. *Bond lengths* (Å) *and torsion angles* (°) *in* (I), *e.s.d.'s* 0·2–0·5°

Primed atoms are related to those in Table 1 by $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

C(1)–C(2)	1·392 (3)	C(11)–C(12)	1·472 (4)
C(1)–C(6)	1·384 (3)	C(12)–O(13)	1·410 (4)
C(1)–O(11)	1·369 (3)	O(13)–C(14)^a	1·502 (6)
C(2)–C(3)	1·382 (3)	O(13)–C(14)^b	1·451 (6)
C(3)–C(4)	1·391 (3)	C(14)^a–C(15)^a	1·508 (11)
C(3)–O(19′)	1·382 (3)	C(15)^a–O(16)	1·491 (6)
C(4)–C(5)	1·391 (3)	C(14)^b–C(15)^b	1·490 (11)
C(4)–O(41)	1·370 (3)	C(15)^b–O(16)	1·472 (6)
C(5)–C(6)	1·384 (3)	O(16)–C(17)	1·405 (4)
C(6)–O(7)	1·387 (3)	C(17)–C(18)	1·489 (4)
O(7)–C(8)	1·433 (3)	C(18)–O(19)	1·439 (3)
C(8)–C(9)	1·487 (4)	O(11)–C(111)	1·423 (3)
C(9)–O(10)	1·419 (3)	O(41)–C(411)	1·421 (3)
O(10)–C(11)	1·409 (3)		

C(2)–C(1)–O(11)–C(111)	−6
C(5)–C(4)–O(41)–C(411)	−6
C(5)–C(6)–O(7)–C(8)	110
C(6)–O(7)–C(8)–C(9)	−57
O(7)–C(8)–C(9)–O(10)	−59
C(8)–C(9)–O(10)–C(11)	174
C(9)–O(10)–C(11)–C(12)	−178
O(10)–C(11)–C(12)–O(13)	70
C(11)–C(12)–O(13)–C(14)^a	160
C(11)–C(12)–O(13)–C(14)^b	−177
C(12)–O(13)–C(14)^a–C(15)^a	−177
C(12)–O(13)–C(14)^b–C(15)^b	−85
O(13)–C(14)^a–C(15)^a–O(16)	77
C(14)^a–C(15)^a–O(16)–C(17)	83
O(13)–C(14)^b–C(15)^b–O(16)	−79
C(14)^b–C(15)^b–O(16)–C(17)	173
C(15)^a–O(16)–C(17)–C(18)	161
C(15)^b–O(16)–C(17)–C(18)	−175
O(16)–C(17)–C(18)–O(19)	−73
C(3)–O(19′)–C(18′)–C(17′)	173
C(4)–C(3)–O(19′)–C(18′)	65

Table 4. *Bond lengths* (Å) *and torsion angles* (°) *in* 2(NaSCN.H_2O).(I), *e.s.d.'s* 0·8–1·3°

Na(1)–O(7)	2·453 (6)	O(16)–C(17)	1·414 (11)
Na(1)–O(10)	2·482 (7)	C(17)–C(18)	1·484 (12)
Na(1)–O(13)	2·504 (8)	C(18)–O(19)	1·449 (10)
Na(1)–O(16)	2·415 (7)	O(19)–C(20)	1·365 (10)
Na(1)–O(19)	2·988 (7)	C(20)–C(21)	1·398 (11)
Na(1)–O(11)	2·495 (7)	C(20)–C(25)	1·380 (11)
Na(1)–N(1)*t*	2·378 (12)	C(21)–C(22)	1·354 (11)
Na(2)–O(26)	2·571 (7)	C(21)–O(211)	1·406 (10)
Na(2)–O(29)	2·462 (7)	C(22)–C(23)	1·382 (11)
Na(2)–O(32)	2·450 (9)	C(23)–C(24)	1·373 (11)
Na(2)–O(35)	2·661 (8)	C(23)–O(26)	1·375 (9)
Na(2)–O(38)	2·538 (8)	C(24)–C(25)	1·369 (11)
Na(2)–O(41)	2·592 (8)	C(24)–O(241)	1·402 (10)
Na(2)–O(241)	2·484 (7)	O(26)–C(27)	1·430 (10)
Na(2)–O(1)*w*	2·376 (10)	C(27)–C(28)	1·478 (12)
C(1)–C(2)	1·387 (11)	C(28)–O(29)	1·404 (10)
C(1)–C(6)	1·382 (11)	O(29)–C(30)	1·435 (12)
C(1)–O(11)	1·359 (9)	C(30)–C(31)	1·441 (14)
C(2)–C(3)	1·361 (11)	C(31)–O(32)	1·388 (12)
C(3)–C(4)	1·388 (12)	O(32)–C(33)	1·417 (13)
C(3)–O(38)	1·386 (10)	C(33)–C(34)	1·424 (16)
C(4)–C(5)	1·381 (11)	C(34)–O(35)	1·442 (13)
C(4)–O(41)	1·395 (10)	O(35)–C(36)	1·388 (11)
C(5)–C(6)	1·361 (11)	C(36)–C(37)	1·494 (13)
C(6)–O(7)	1·374 (9)	C(37)–O(38)	1·442 (11)
O(7)–C(8)	1·453 (10)	O(11)–C(111)	1·442 (11)
C(8)–C(9)	1·485 (12)	O(41)–C(411)	1·416 (10)
C(9)–O(10)	1·404 (11)	O(211)–C(2111)	1·429 (11)
O(10)–C(11)	1·401 (12)	O(241)–C(2411)	1·390 (10)
C(11)–C(12)	1·468 (14)	S(1)*t*–C(1)*t*	1·614 (14)
C(12)–O(13)	1·413 (11)	C(1)*t*–N(1)*t*	1·133 (13)
O(13)–C(14)	1·416 (11)	S(2)*t*–C(2)*t*	1·560 (14)
C(14)–C(15)	1·448 (13)	C(2)*t*–N(2)*t*	1·170 (14)
C(15)–O(16)	1·440 (11)		

C(2)–C(1)–O(11)–C(111)	−18
C(37)–O(38)–C(3)–C(4)	−178
C(5)–C(4)–O(41)–C(411)	−28
C(5)–C(6)–O(7)–C(8)	2
C(6)–O(7)–C(8)–C(9)	173
O(7)–C(8)–C(9)–O(10)	59
C(8)–C(9)–O(10)–C(11)	173
C(9)–O(10)–C(11)–C(12)	175
O(10)–C(11)–C(12)–O(13)	−62
C(11)–C(12)–O(13)–C(14)	175
C(12)–O(13)–C(14)–C(15)	−164
O(13)–C(14)–C(15)–O(16)	61
C(14)–C(15)–O(16)–C(17)	84
C(15)–O(16)–C(17)–C(18)	−172
O(16)–C(17)–C(18)–O(19)	71
C(17)–C(18)–O(19)–C(20)	173
C(18)–O(19)–C(20)–C(21)	−164
C(22)–C(21)–O(211)–C(2111)	−2
C(22)–C(23)–O(26)–C(27)	−5
C(25)–C(24)–O(241)–C(2411)	−25
C(23)–O(26)–C(27)–C(28)	−176
O(26)–C(27)–C(28)–O(29)	62
C(27)–C(28)–O(29)–C(30)	174
C(28)–O(29)–C(30)–C(31)	167
O(29)–C(30)–C(31)–O(32)	−63
C(30)–C(31)–O(32)–C(33)	−169
C(31)–O(32)–C(33)–C(34)	−178
O(32)–C(33)–C(34)–O(35)	61
C(33)–C(34)–O(35)–C(36)	87
C(34)–O(35)–C(36)–C(37)	−164
O(35)–C(36)–C(37)–O(38)	60
C(36)–C(37)–O(38)–C(3)	175

Discussion. The final parameters are in Tables 1 and 2[*] and stereopairs (Johnson, 1971) of the two molecules in Figs. 1 and 2. Bond lengths and torsion angles are given in Tables 3 and 4 and details of the H-bonding scheme in Fig. 3.

(I): The crystals are formed from discrete molecules separated by normal van der Waals distances. Each molecule contains a crystallographic centre of symmetry (at $\frac{1}{4}, \frac{1}{4}, 0$ for the molecule in Table 1), so the two benzene rings are parallel, but are not stacked either within or between molecules. The molecule is made up of two approximate planes, *ca* 1·8 Å apart, containing the benzene atoms and seven O atoms. Bond lengths and angles are as expected for crown ethers, except around C(14) and C(15). Here, the bond angles at O(13) and O(16) form pairs 97 and 127° for each conformer due to inadequate description of the disorder. The conformers differ in their torsion angles; the major difference is the torsions about the C(14)–C(15) bonds which are +*gauche* in the *a* conformer and −*gauche* in the *b*. The conformations around C(1)–O(11) and C(4)–O(41) should allow conjugation of the

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles, deviations from the mean planes and H-bonding geometry parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39287 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

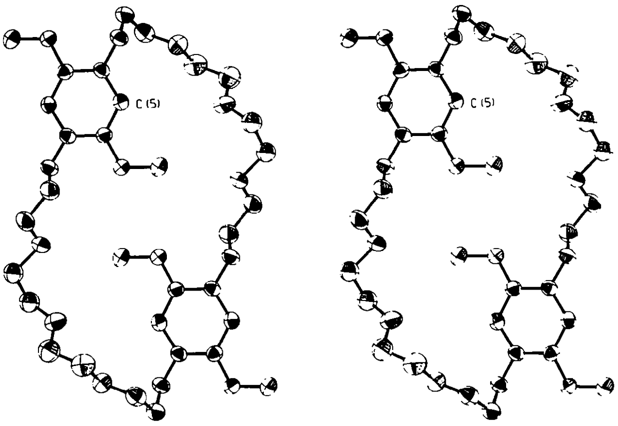

Fig. 1. The molecule of (I), showing 50% thermal ellipsoids.

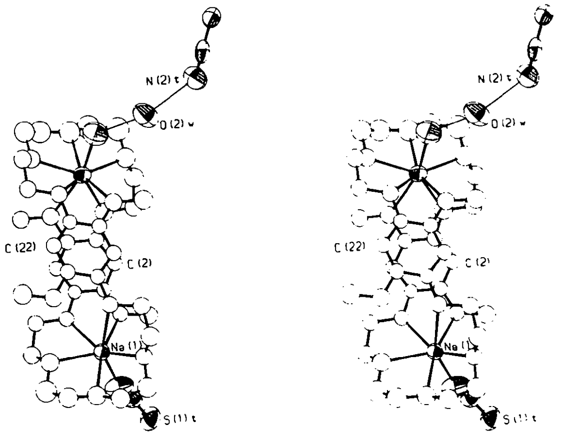

Fig. 2. The molecule of $2(NaSCN.H_2O).(I)$ showing 50% thermal ellipsoids.

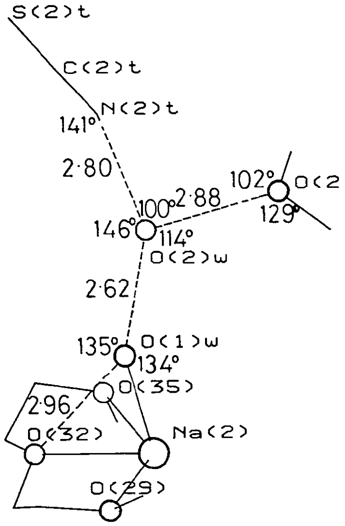

Fig. 3. The hydrogen-bonding geometry in $2(NaSCN.H_2O).(I)$. O(211') is related to that in Table 1 by $-x$, $-y$, $1-z$. E.s.d.'s are 0·01–0·015 Å for lengths and 0·4–1·0° for angles.

oxygen p orbitals to the ring π system, and this is confirmed by the C(1)—O(11) and C(4)—O(41) distances being significantly shorter than C(6)—O(7) and C(3)—O(19') [O(38) in formula (I)], where the conformation cannot allow significant conjugation.

$2(NaSCN.H_2O).(I)$: There are two Na^+ cations complexed to each molecule of the ligand, separated by 8·169 (5) Å. The benzene rings within the molecule are stacked in the usual manner, *ca* 3·5 Å apart, and are almost parallel [2·9 (3)° between planes]. The complex molecules form dimers linked by hydrogen bonds involving two water molecules, an anionic N, and a methoxy O atom (Fig. 3). The dimers also have benzene rings [C(20)···C(25)] stacked, but they are *ca* 3·9 Å apart and overlap only about 50%. The other benzene ring of the molecule [C(1)···C(6)] is stacked with that of another dimer at *ca* 3·6 Å, but the overlap only involves the C(5)—C(6) bond. Thus the crystals are formed by packing of hydrogen-bonded dimers stacked along [$1\bar{1}1$].

Na(1) has five O and one N at normal distances, and a seventh atom, O(19) at 2·988 (7) Å, much further away. It is notable that O(19), the furthest from Na(1) and the anionic nitrogen, N(1)*t*, the closest, form the apices of the distorted pentagonal bipyramid of atoms around Na(1). Na(2) is eight-coordinated, in no regular shape. However, O(241), O(26), O(29), O(32) and O(35) form a reasonable plane with Na(2). O(38) and O(41) lie on one side of this plane, and a water oxygen O(1)*w*, the closest atom, lies on the other. O(1)*w* is hydrogen-bonded to O(2)*w* which then forms H-bonds to the nitrogen of the second anion, N(2)*t*, and also to a methoxy oxygen atom, O(211), on the other molecule of the dimer (Fig. 3). O(211) is not coordinated to either cation in the neighbouring molecule [nearest distance, Na(1)···O(211) = 4·174 (7) Å]. Bond lengths and angles are again as expected. The methoxy torsion angles should allow different degrees of conjugation, but the accuracy of the structure determination precludes discussion of the effects on the bond lengths. The conformation of the ligand is very different in several respects from that found in the structure of the uncomplexed ligand. Most obviously, the benzene rings are stacked, but less obvious is the fact that the benzene ring C(1)···C(6) has undergone a 180° rotation about the axis through O(7), C(6), C(3), O(38). This implies that the molecule is very flexible indeed, and confirms the impressions gained by investigations using space-filling models.

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References

Elben, U., Fuchs, H. B., Frensch, K. & Vögtle, F. (1979). *Justus Liebigs Ann. Chem.* **8**, 1102–1111.

Gokel, G. W. & Korzeniowski, S. H. (1982). *Macrocyclic Polyether Synthesis*. Berlin: Springer-Verlag.

Helgeson, R. C., Tarnowski, T. L., Timko, J. M. & Cram, D. J. (1977). *J. Am. Chem. Soc.* **99**, 6411–6418.

Helgeson, R. C., Timko, J. M. & Cram, D. J. (1974). *J. Am. Chem. Soc.* **96**, 7380–7382.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2*B*. Birmingham: Kynoch Press.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Kawashima, N., Kawashima, T., Otsubo, T. & Misumi, S. (1978). *Tetrahedron Lett.* pp. 5025–5028.

Owen, J. D. (1983). *Acta Cryst.* C**39**, 861–863.

Parsons, D. G. (1983). Private communication.

Pedersen, C. J. (1967). *J. Am. Chem. Soc.* **89**, 7017–7036.

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

Van Keulen, B. J., Kellogg, R. M. & Piepers, O. (1979). *J. Chem. Soc. Chem. Commun.* pp. 285–286.

Acta Cryst. (1984). C**40**, 955–957

Structure and Synthesis of Bis(N^1-acetimidoylacetamidine-N^1,N^3)nickel(II) Chloride Trihydrate, $C_8H_{17.5}N_6Ni^{1.5+}.Cl^-_{1.5}.3H_2O$, at 117 K

By R. Norrestam

Structural Chemistry Group, Chemistry Department B, The Technical University of Denmark, DK-2800 Lyngby, Denmark

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Abstract. $M_r = 363{\cdot}7$, triclinic, $P\bar{1}$, $a = 7{\cdot}378\,(3)$, $b = 8{\cdot}862\,(3)$, $c = 12{\cdot}813\,(3)$ Å, $\alpha = 72{\cdot}99\,(2)$, $\beta = 79{\cdot}96\,(3)$, $\gamma = 77{\cdot}27\,(4)^\circ$, $V = 776{\cdot}0\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}557\,(1)$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 4{\cdot}4$ mm^{-1}, $F(000) = 382$, $T = 117\,(2)$ K, final $R = 0{\cdot}034$ for 1385 reflections. The crystals of the title compound, formed by evaporation of a methanolic solution of $NiCl_2$ and acetamidine, contain planar complexes of bis(N^1-acetimidoylacetamidine)nickel(II) ions. The present study thus shows that N^1-acetimidoylacetamidine can be prepared through a self-condensation reaction of acetamidine. The nickel atom is coordinated by an almost ideal square-planar arrangement of four imino nitrogen atoms. The Ni$\cdots$N distances, ranging from $1{\cdot}849$ to $1{\cdot}873\,(4)$ Å, show that the complex is of low-spin type.

Introduction. The present study is part of a research project on synthetic and structural studies of acetamidine metal complexes. So far, only one such complex has been synthetized and characterized by single-crystal diffraction techniques, *viz* the study carried out by Stephenson (1962) on a compound expected to be bis(acetonitrile)tetraammineplatinum(II) chloride monohydrate but unexpectedly shown by the outcome of the structural investigation to be bis(acetamidine)diammineplatinum(II) chloride monohydrate. Today, with pure acetamidine available (Crossland & Grevil, 1981), the conditions for more systematic studies of metal acetamidine complexes appear promising.

The specimen used in the present study was obtained by simply evaporating a methanolic solution of stoichiometric amounts (1:4) of nickel(II) chloride hexahydrate and acetamidine. Such a synthetic procedure could possibly give somewhat unpredictable results as it is known that acetamidine, which is a strong highly hygroscopic base, when exposed to atmospheric carbon dioxide yields crystalline diacetamidinium carbonate monohydrate (Norrestam, 1984). However, in the present study it is shown that acetamidine may also undergo a self-condensation reaction, possibly under the influence of nickel(II) ions, to give the simple bidentate ligand N-acetimidoylacetamidine:

$$2\,NH{=}C(CH_3){-}NH_2 \rightarrow NH{=}C(CH_3){-}NH{-}(CH_3)C{=}NH + NH_3.$$

This reaction is analogous to the self-condensation of urea by which biuret is formed. According to Oto & Ichikawa (1973), the hydrochloride of N-acetimidoylacetamidine had been prepared earlier through the reaction between $[NH_2{-}C(CH_3){-}NH_2].Cl$ (acetamidinium chloride) and $Et{-}O{-}C(CH_3){=}NH$ in an acidic (HCl) solution.

Experimental. Green prisms from methanol at 293 K, $0{\cdot}2 \times 0{\cdot}1 \times 0{\cdot}1$ mm, CAD-4 diffractometer with a cryogenic device (*cf.* van Bolhuis, 1971) operated at 117 (2) K, graphite-monochromatized Cu $K\alpha$, lattice parameters from angular settings of 12 reflections with $9 < \theta < 19^\circ$, 2117 unique reflections ($h < 5$, $|k| < 10$, $|l| < 15$) with $\theta < 74{\cdot}5^\circ$, 1385 with $\sigma(I)/I < 0{\cdot}33$ used for refinements, no significant intensity variations in 2 standard reflections, 202 and $0\bar{2}\bar{3}$, during data collection, no corrections for absorption; Ni and one Cl atom from Patterson map, remaining atoms from subsequent $\Delta\rho$ maps, least-squares minimization of $\sum w(\Delta F)^2$, anisotropic Ni and Cl atoms, isotropic C, N

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