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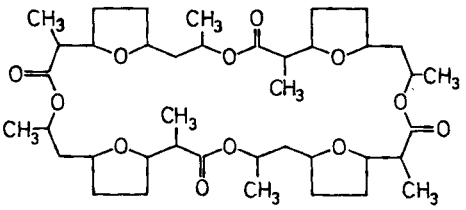
74. The Crystal Structure of the NaNCS Complex of Nonactin

dination with the K^+ ion (K^+...O, 2.73–2.88 Å) replacing its solvent shell. Assuming standard *van der Waals* and ionic radii (O, 1.40 Å; K^+, 1.33 Å; Na^+, 0.95 Å) the central cavity within a cube of oxygen atoms has a minimum radius of 1.02 Å, and is therefore slightly too big for Na^+. Such factors are relevant to the selectivity of these compounds and we have now carried out a crystal structure analysis of the Na^+ complex to establish the nature of the coordination. We find that the cubic coordination is deformed such that the four carbonyl oxygen atoms are closer to the cation (Na^+...O, 2.395–2.438 Å) than are the ether oxygen atoms (Na^+...O, 2.744–2.791 Å). This change is accomplished with only very small changes in the ligand conformation.



1

Crystallographic Data. – Sodium thiocyanate complex of nonactin, $C_{40}O_{12}H_{64}$. NaNCS, M.W. 818. Monoclinic, $a = 15.550$, $b = 19.592$, $c = 15.311$ Å, $\beta = 90°$, $U = 4665$ Å^3, $Z = 4$. Space group C2/c (C_{2h}^6), $D_m = 1.18$, $D_x = 1.16$. Cell constants were obtained from 30° precession photographs (CuKα radiation) and diffractometer measurements (MoKα radiation). They are accurate to about 0.15%. The crystals used for this analysis were a mixture of 72% nonactin and 28% monactin.

Data collection. – The intensities of the 4300 reflections within the range $\theta < 28°$ were measured with a computer-controlled four-circle diffractometer (*Hilger & Watts* Y290), using graphite-monochromatized MoKα radiation, from a crystal with dimensions 0.4 × 0.3 × 0.15 mm. The reflections were processed in the usual way, giving 3396 unique reflections with intensities significantly greater than zero. Absorption corrections ($\mu_{Mo} = 1.4$ cm^{-1}) were not applied.

Structure analysis. – The unit cell contains four formula units. Because there are eight general positions in the space group C2/c, it follows that the nonactin molecule has a symmetry

Table 1. *Fractional coordinates* (estimated standard deviations × 10^4 in parentheses)

	X	Y	Z		X	Y	Z
Na	.5000 (0)	.2687 (4)	.2500 (0)	C(14)	.6212 (10)	.2303 (13)	−.0211 (10)
C(1)	.3986 (8)	.3683 (8)	.3891 (10)	C(15)	.5876 (9)	.3017 (11)	−.0244 (10)
C(2)	.3411 (9)	.4145 (9)	.3406 (12)	O(16)	.6369 (6)	.3456 (7)	.0342 (6)
C(3)	.3597 (10)	.4104 (8)	.2439 (11)	O(17)	.4677 (5)	.3509 (5)	.3651 (7)
O(4)	.3487 (6)	.3410 (5)	.2177 (6)	C(18)	.3554 (15)	.4901 (11)	.3683 (18)
C(5)	.3178 (10)	.3392 (9)	.1282 (9)	C(19)	.3000 (12)	.4521 (9)	.1835 (14)
C(6)	.2317 (9)	.3025 (9)	.1234 (8)	C(20)	.3139 (12)	.4126 (12)	.1008 (13)
C(7)	.2269 (8)	.2307 (8)	.1603 (8)	C(21)	.1369 (9)	.1976 (9)	.1520 (11)
O(8)	.2875 (5)	.1881 (5)	.1110 (6)	O(22)	.3860 (5)	.1906 (5)	.2175 (5)
C(9)	.3625 (8)	.1714 (7)	.1474 (8)	C(23)	.3794 (12)	.0473 (9)	.1108 (16)
C(10)	.4127 (9)	.1214 (8)	.0921 (9)	C(24)	.5658 (12)	.0830 (10)	.0567 (15)
C(11)	.5069 (9)	.1267 (8)	.1130 (10)	C(25)	.6490 (11)	.1226 (13)	.0668 (14)
O(12)	.5328 (5)	.1960 (5)	.1005 (6)	C(26)	.5897 (12)	.3460 (16)	−.1144 (10)
C(13)	.6211 (8)	.1958 (9)	.0688 (10)				

Table 2. *Anisotropic vibrational parameters, expressed in the form*

$exp(-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl))$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	.071	.086	.076	.000	.015	.000
C(1)	.066	.135	.114	.009	–.002	–.058
C(2)	.064	.124	.172	.007	.007	–.040
C(3)	.103	.084	.135	.003	.008	–.002
O(4)	.115	.098	.079	–.012	–.004	.019
C(5)	.114	.134	.081	–.005	–.004	.033
C(6)	.099	.150	.063	.029	.005	.004
C(7)	.079	.119	.073	.014	.002	–.013
O(8)	.069	.133	.083	.003	–.016	–.033
C(9)	.073	.094	.080	.000	–.001	–.018
C(10)	.081	.136	.098	.001	–.012	–.044
C(11)	.096	.107	.130	.008	.012	–.049
O(12)	.072	.132	.119	.010	.014	–.015
C(13)	.061	.178	.107	–.008	.006	–.041
C(14)	.077	.321	.095	–.038	.020	–.059
C(15)	.071	.266	.103	–.048	.008	.029
O(16)	.076	.230	.096	–.047	.015	.042
O(17)	.065	.131	.126	.009	.018	–.036
C(18)	.204	.127	.285	.042	.004	–.120
C(19)	.152	.090	.206	.026	.035	.046
C(20)	.135	.212	.154	–.016	–.011	.097
C(21)	.072	.159	.126	–.024	.010	–.039
O(22)	.080	.108	.077	.013	–.010	–.022
C(23)	.135	.098	.287	–.022	.036	–.080
C(24)	.114	.149	.243	.022	.023	–.097
C(25)	.100	.263	.174	.047	.015	–.080
C(26)	.126	.471	.061	–.082	–.001	.062

Table 3. *Calculated hydrogen atom fractional coordinates*

	X	Y	Z		X	Y	Z
H(2)	.274	.400	.353	H(19)**	.322	.505	.177
H(3)	.426	.426	.232	H(20)*	.374	.428	.071
H(5)	.364	.312	.088	H(20)**	.260	.421	.056
H(6)*	.185	.333	.160	H(21)*	.090	.228	.188
H(6)**	.214	.299	.055	H(21)**	.138	.146	.179
H(7)	.246	.232	.229	H(21)***	.118	.195	.084
H(10)	.403	.133	.023	H(23)*	.415	.011	.071
H(11)	.517	.113	.181	H(23)**	.311	.044	.095
H(13)	.662	.224	.114	H(23)***	.388	.035	.180
H(14)*	.688	.232	–.044	H(24)*	.572	.031	.083
H(14)**	.581	.199	–.064	H(24)**	.544	.082	–.011
H(15)	.521	.301	–.001	H(25)*	.681	.109	.128
H(18)*	.343	.496	.438	H(25)**	.691	.113	.011
H(18)**	.312	.523	.332	H(26)*	.562	.396	–.103
H(18)***	.422	.505	.355	H(26)**	.552	.320	–.165
H(19)*	.233	.450	.205	H(26)***	.656	.352	–.137

element of the space group, a twofold rotation axis or a centre of symmetry. The NCS anion must either lie along a twofold rotation axis or be statistically disordered.

Direct methods were used to elucidate the structure. The observed relative F_o-values were put on an absolute scale by *Wilson*'s method and converted to E-values. The computer program *Multan* [6] was used to evaluate the signs for the 294 reflections with $E > 1.8$, and the resultant E-map revealed peaks for 21 of the 30 symmetry-independent non-hydrogen atoms. (No clear indications were found for the methyl groups C(18) and C(26), for the methylene groups C(19), C(20), C(24), C(25) of the tetrahydrofurane rings, and for the atoms of the NCS group). A subsequent F_o-*Fourier* map with signs based on these 21 atoms showed peaks for all non-hydrogen atoms of the nonactin molecule, but only a single peak was found for the NCS anion, at $x \sim 0$, $y \sim 0.38$, $z \sim 0.21$, indicating that the anion, as in the KNCS complex [4], is disordered and not

Table 4. *Molecular topography.* Bond lengths and angles

C(2)–C(1)–O(16)	1.473	1.371	112.8	C(9)–C(10)–C(11)		1.503	109.9
O(16)–C(1)–O(17)		1.187	122.4	C(9)–C(10)–C(23)		1.568	109.1
C(2)–C(1)–O(17)			124.8	C(11)–C(10)–C(23)			110.3
C(1)–C(2)–C(3)		1.510	110.2	C(10)–C(11)–O(12)		1.429	108.1
C(1)–C(2)–C(18)		1.557	111.1	C(10)–C(11)–C(24)		1.521	115.4
C(3)–C(2)–C(18)			106.9	O(12)–C(11)–C(24)			106.8
C(2)–C(3)–O(4)		1.427	107.6	Na–O(12)–C(11)	2.744		109.3
C(2)–C(3)–C(19)		1.543	116.4	Na–O(12)–C(13)		1.458	117.1
O(4)–C(3)–C(19)			105.3	C(11)–O(12)–C(13)			108.0
Na–O(4)–C(3)	2.791		109.5	O(12)–C(13)–C(14)		1.533	107.4
Na–O(4)–C(5)		1.454	115.7	O(12)–C(13)–C(25)		1.499	106.3
C(3)–O(4)–C(5)			109.2	C(14)–C(13)–C(25)			113.8
O(4)–C(5)–C(6)		1.522	110.4	C(13)–C(14)–C(15)		1.493	116.3
C(6)–C(5)–C(20)		1.500	113.8	C(14)–C(15)–O(16)		1.460	110.4
O(4)–C(5)–C(20)			104.6	C(14)–C(15)–C(26)		1.629	121.4
C(5)–C(6)–C(7)		1.517	117.6	O(16)–C(15)–C(26)			101.3
C(6)–C(7)–C(8)		1.466	107.8	C(1)–O(16)–C(15)			120.5
C(6)–C(7)–C(21)		1.547	113.7	Na–O(17)–C(1)	2.438		126.9
O(8)–C(7)–C(21)			107.5	C(3)–C(19)–C(20)		1.499	98.5
C(7)–O(8)–C(9)		1.334	119.1	C(5)–C(20)–C(19)			105.4
O(8)–C(9)–C(10)		1.512	112.1	Na–O(22)–C(9)	2.395		127.9
O(8)–C(9)–O(22)		1.193	124.5	C(11)–C(24)–C(25)		1.517	99.7
C(10)–C(9)–O(22)			123.3	C(13)–C(25)–C(24)			104.2

Table 5. *Torsion angles for the asymmetric unit of the 32-membered ring and for the 2 tetrahydrofurane rings*

C(15)–O(16)–C(1)–C(2)	–177.4	C(13)–C(14)–C(15)–O(16)	58.0
O(16)–C(1)–C(2)–C(3)	–152.2	C(14)–C(15)–O(16)–C(1)	–107.2
C(1)–C(2)–C(3)–O(4)	57.9		
C(2)–C(3)–O(4)–C(5)	148.0	C(19)–C(3)–O(4)–C(5)	23.2
C(3)–O(4)–C(5)–C(6)	–120.9	C(3)–O(4)–C(5)–C(20)	2.0
O(4)–C(5)–C(6)–C(7)	–55.4	O(4)–C(5)–C(20)–C(19)	–27.3
C(5)–C(6)–C(7)–O(8)	–60.7	C(5)–C(20)–C(19)–C(3)	39.3
C(6)–C(7)–O(8)–C(9)	103.4	C(20)–C(19)–C(3)–O(4)	–38.2
C(7)–O(8)–C(9)–C(10)	173.8		
O(8)–C(9)–C(10)–C(11)	156.1	C(24)–C(11)–O(12)–C(13)	–21.5
C(9)–C(10)–C(11)–O(12)	–55.9	C(11)–O(12)–C(13)–C(25)	–2.8
C(10)–C(11)–O(12)–C(13)	–146.3	O(12)–C(13)–C(25)–C(24)	25.8
C(11)–O(12)–C(13)–C(14)	119.5	C(13)–C(25)–C(24)–C(11)	–36.9
O(12)–C(13)–C(14)–C(15)	58.1	C(25)–C(24)–C(11)–O(12)	36.2

Table 6. *Observed structure factors*

Every *h k l_i* is followed by values $10 \cdot F_o$ for l_i, l_{i+1}, l_{i+2}, etc.

```
0  0  2* 302,   0,1714,   0, 608,   0, 811,   0,  25,   0, 151,   0,  62,   0,  37,   0,  23,
0  2  0*1997, 769, 334,1477,  66,  75, 106, 147, 459, 293,  30,   0,  55,  62,   0,  40,   0,  28,
0  2 20*  27*  0  4  0*1679,1273,  85,  99, 428, 350, 320,  59,  74, 141,  79,   0, 143,  52,   9,
0  4 15*  24,   0,  38*  0  6  0* 728, 793,  94, 187, 594,  92,  85,   0, 230,  27, 152,  60, 225,
0  6 13*  66,  57,  58,  14,  38,  15*  0  8  0* 539, 201, 104, 314, 193,   0,   0, 159,  14,  67,
0  8 10* 125, 129,  92,  66,  38,  27,   0,   0*  0 10  0* 175,  83, 134,  90, 136, 120, 122, 108,
0 10  8*  35,  81,  76,  36,   0,   0,  33,  31*  0 12  0*  57, 392, 192,  81, 113,  46,  80, 108,
0 12  8*  60,  88,  98,  63,  16,  33*  0 14  0*  51, 328,  17,  24,   0, 150,  29, 194,  49,  21,
0 14 10*   9,  26,  42,   0,   0,   0,  27*  0 16  0*   0,  23,  55,  80,  99, 124,   9,  28,   9,
0 16  9*  51,  30,  22,   0,   0,   0,  15*  0 18  0*   0,  57,  23,   0,   0,   0,  48,   9,  14,
0 18  9*  14,   0,  18*  0 20  0*   0,   0,  27,  13,  17,   0,   0,   0,   0,   0,   0,  19,
1  1-18*   0,  17,   0,  26,   0,  38,   0, 145,  73, 274, 393, 639,  33, 225, 213,1026,  32,1459,
1  1  0* 221,1336, 384,2545,  74, 437, 474, 630,  42, 229, 100,  90,  40,  78,  21,  38,  10,  38,
1  1 19*  39*  1  3-18*  42,   0,  10,  25,  20,  21,  16, 120, 147, 187, 417,  36, 450, 107, 312,
1  3 -3*1674, 105, 299, 152, 487, 204, 569, 275, 268, 180, 378,  58,  49, 103,   0,  78,  27,  81,
1  3 15*  29,  32,  17*  1  5-19*   0,  33,   0,  22,  92,   0,  41,  20,  55,  54, 217,  37,  76,
1  5 -6* 259, 160,  88, 534, 445,  49, 222, 475, 299, 640, 268, 253, 143, 133,  56,  70,  75, 201,
1  5 12*  44,  96, 101,  32,  19*  1  7-18*  32,   0,   0,  84,   0,  87,  63,   8,  97,  43,  30,
1  7 -7* 100,  91,  58,  61, 593, 455, 710, 484, 191, 185, 699, 720, 120,  81,  48,  80, 229, 111,
1  7 11* 228, 155,  23,  60,  29*  1  9-15*   0,   0,  82,  69,  17, 119,  20,  26,   0,  74,  77,
1  9 -4* 268, 200,  47, 270, 127, 273, 343, 125, 336, 396,  46,  29,  73, 252, 140,  42,  76,  34,
1  9 14*  33,  10,   0,  39*  1 11-15*  25,   0,  16,  37,  77,  89,  99,  22,  78,  50,   0, 212,
1 11 -3* 226, 104, 131, 126,  25, 131,  52, 144,   0,  48,  42,  70,  84,  19,   0,  37,  28,  22,
1 11 18*   0*  1 13-13*  24,  23,   9,  53, 112, 240,   8, 108,   0,   0, 142, 205,  77, 456,  34,
1 13  2* 165, 114,  37,  13, 120,  28,  32,  28,  94,  44,   0,  22*  1 15-13*  18,   0,  23,   0,
1 15 -9*  41, 104,  23, 216,  65,  92,   0,  69,  48, 166,  79,  70,  87,  77,  20,  69,  38,  63,
1 15  9*   0,  35,  36,   0*  1 17-10*   0,  34,  16,   0,   0,  25,  69, 108,  31,  45,  34,  25,
1 17  2*  54,   0,  53,  23,   0,  29,  41,  29,  20,   0,   0,   8,   0,  32*  1 19 -9*   0,   0,
1 19 -7*   0,  13,  19,   0,   0,  44,   0,  13,   0,  49,  29,  40,   0,  21,  55,   0,  30,   0,
1 19 11*  33,   0*  1 21 -6*  10,   0,   0,  24,  10,   0,   0,  14,  17,   0,   0,   0,
1 23 -8*   0,   0,   0,   0,  11,   0,   0,  25,   0,  33,   0,   0,   0,  11*  1 25 -3*   0,   0,
1 25 -1*  25*  2  0-18*  33,   0,   0,   0, 101,   0,  37,   8, 323,   0, 650,   0, 730,   0,1088,
2  0 -2* 134,   0, 364,   0,  93,   0,  59,   0, 234,   0, 371,   0, 397,   0,  84,   0,  29,   0,
2  0 16*  36,   0,   0,   0,  32*  2  2-17*  20,  14,  45,  70,  66,  66,  24, 234,   0, 101, 365,
2  2 -6* 453, 166, 627, 543, 233, 759, 103, 297,  72,1042, 257, 356,   0, 436,  46, 152, 217, 125,
2  2 12*  93,  77,   9,  44,  35*  2  4-18*  23,   0,  41,  45,   0,  78,   0,  33, 153,  80, 292,
2  4 -7*  46, 444, 322, 220, 279, 232, 238, 776, 450,  73, 183, 825,  38,  35,  24, 294, 153,  34,
2  4 11* 194, 123,  26,  20,  48,  45*  2  6-16*  35,   0,  35,  54, 159,   0,   0,  91,  28,   0,
2  6 -6* 137, 225, 311, 113,  61,  91,  91, 346, 301, 116, 776, 315, 149, 213, 194, 152, 122, 170,
2  6 12*  73,  51,   0,  13,  30*  2  8-15*  36,  77,  43,  72,  31, 164,  51, 127, 121, 130, 156,
2  8 -4* 417, 172, 162, 606, 523, 367, 560, 586,  90, 374,  43, 101, 266,  75, 149,  81,   0,   0,
2  8 14*   0,   0,  44*  2 10-18*   0,   0,   0,   0,  14,  68,  77, 104,  40,   0,  51, 120,  27,
2 10 -5* 295,  38, 191, 213, 210,  35, 234, 250, 170, 214, 103, 190,  99, 172, 124,  47,  36,   9,
2 10 13*  16,  25,   0,  21*  2 12-13*  19,  44,  92,  74, 169,  14,  38,  30, 118,  87, 183,  51,
2 12 -1* 183, 178, 197,  58,  97,  82,  65,   0,  83,  85,  36,  36,  13,   9,  10,   0,   0,  37,
2 14-16*  27,   0,   0,   0,  10,  42,  35, 127,   0, 167,  85,   0,  66,  27, 140, 140,  91,  81,
2 14  2* 132,  46,   0,  50,   0,  67,  17,  67,  18,   0,  19,  28*  2 16-11*  10,   0,  28,   0,
2 16 -7*  83,   0,  74,  36,   0,  22,  43,  44,  55,   0,  23,  39,   0,  25,  18,   0,  25,   0,
2 16 11*  24,   0,   0,   0*  2 18-12*   0,   0,   0,   0,  36,  35,  13,  20,   0,  28,  60,  32,
2 18  0*   0,  83,  50,  67,   0,  53,  50,  41,  40,  47,   0,   0,   0,   0,   0*  2 20-12*   0,
2 20 -6*   0,  22,  22,  34,  28,   0,  27,  25,  25,  23,  30,   0,  36,  30,   0,   0,  35,
2 22 -8*   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,   0,
2 24  2*  36,  24*  3  1-19*  22,   0,   0,  27,  24,  40, 245,  24, 120,  28,  36,  41, 472, 121,
3  1 -5* 198, 236,  60,1124,2337,1467,1078,  59, 194, 195, 932, 117, 297,  15, 252,  93,  96,  44,
3  1 13*   0,  34,  87,   0,  57*  3  3-16*  49,  13,  36,  94,  33, 138,   0, 132, 128, 231, 186,
3  3 -5* 308, 385,  14,  66,1042, 127,1613, 106,  73,  10, 131,  45, 109,  11, 186, 139,  57, 157,
3  3 13*  81,   0,  42,   0*  3  5-17*  18,  63,  28,   8, 101, 104,  38,   0, 319, 209, 229,  46,
3  5 -5* 229, 164, 394, 504, 472, 648,  69, 213, 271, 629, 911, 322, 125,  91,  40, 113,   0, 111,
3  5 13*  87,  13,   0,   0,   0,   0*  3  7-19*   0,   0,  25,   0,  43,  52,  84,  77, 122,  87,
3  7 -9* 235,  21,  58, 209, 263,  71,  95, 486, 521, 239, 205, 345, 168, 614, 379, 301,  92, 158,
3  7  9*   0,   0,  14,  44,  65,   0,  21*  3  9-15*  10,  56,   0,  55,   0,  35,  43, 140, 106,
3  9 -6* 188, 272, 482,  75, 153, 404,  62,  50,  30, 258, 269, 217,  58, 103, 101,  28,  26,  68,
3  9 12*  41,  64,  34,  14*  3 11-18*  30,   0,   0,   0,  52,  16,  89,  22,  53,  40,  37,  48,
3 11 -6*  65,  23, 224,  95,  74, 147, 176, 203, 194,  71,  73, 149,   0,   0, 105,  43,  65,  47,
3 11 12*   0,   0,  10*  3 13-14*  34,  10,  63,  21,  46,  43,  82,  71,  75,  87,  92, 114,   0,
3 13 -1* 162, 109, 178,  43,  36, 109,   0,  55,  65,   0,  45,  25,   0,   0,   0,  23,
3 15-12*  33,   0,  33,  27,  52,  23,  24,   0,   0,  48,  57,  53,  18,  25,  24,  45,  95,  30,
3 15  6*   0,   0,  53,   0,  34,   0*  3 17-14*   0,   0,   0,   0,  10,  35,  16,   0,  65,  38,
3 17 -4*  77,  19,  58,  19,  94,  56,  39,   0,  48,  64,  81,  26,  33,  17,   0,   0,
3 19 -9*   0,   0,   0,  39,  25,  52,  53,  73,  38,  27,  26,  31,  64,  50,  65,  50,  40,   0,
3 19 13*   0*  3 21 -9*   0,   0,   0,   0,   0,   0,   0,  10,   0,  22,   0,  10*  3 23  0*   0,
3 23  1*  33,   0,   0,  15*  3 25 -1*   0,   0,   0*  4  0-16*  67,   0, 146,   0,  71,   0,  95,
4  0 -8*  64,   0, 391,   0, 443,   0, 120,   0,1651,   0,1094,   0, 395,   0, 289,   0, 518,   0,
4  0 10* 112,   0,  64,   0,  56,   0,  95*  4  2-17*  14,  39,  34, 112,  85, 117,  84,  39, 177,
4  2 -8*  68,   0, 616, 165, 431, 457, 343, 110,  88, 849, 412, 303, 626, 222,  25,  17, 427, 137,
4  2 10*  99, 123,  57,   0,  80,  52,  66*  4  4-16*  38,   0,   0, 143, 134,  43, 223, 239,  87,
4  4 -7* 133, 158, 435, 491, 422, 432, 515, 392, 484,  67, 216,  82, 291, 418,  38,  74, 122,   0,
4  4 11* 196,  19,  36,  54,  31,   0,  27*  4  6-19*   0,   0,   0,   0,  36,  13,  63,  59,  64,
4  6-10* 169, 296,   0, 171, 367, 464, 497, 223, 579, 926, 509,  33,   0,  41,  62, 638, 199,  35,
4  6  8* 109,  26,  25,  42,  32,  64,   9,  27,   0,   0,   0,   0*  4  8-15*   0,  52,   0,   0,
4  8-11*  28,  63,  29, 150,  38, 196, 320,  56, 184, 779, 151, 290, 186, 118, 161, 381, 286,  92,
4  8  7*   0,  88,  68, 112,  97,  69,  18,  53,  55,  37*  4 10-14*  38,   0,   0,  33,   0,  79,
4 10 -8*  66,  55,  16, 252, 158, 166,  84,  98, 100, 229, 365, 235, 338, 127,  43,  26,  25,   4,
4 10 10* 135,   0,  68,  46,  40,  27,   0,   0,   0*  4 12-16*  11,  45,  24,  32,  27,  10,  58,
4 12 -9*  41,  81, 194,  34,  72,   0, 110, 229, 138, 151, 135,  14, 126,  55,  28,   0,  24,  20,
```

Table 6 (cont.)

4	12	9*	76,	39,	58,	23,	17,	0,	0*	4	14-16*	8,	0,	33,	32,	10,	29,	23,	32,	17,				
4	14	-7*	62,	33,	16,	0,	84,	0,	119,	33,	77,	35,	21,	34,	85,	33,	57,	45,	96,	21,				
4	14	11*	27,	29,	0,	0,	39*	4	16-13*	42,	0,	0,	0,	25,	42,	47,	39,	38,	0,	28,				
4	16	-2*	0,	0,	33,	79,	31,	32,	0,	30,	49,	84,	0,	38,	0,	0,	23*	4	18	-8*	0,			
4	18	-7*	0,	34,	89,	26,	105,	32,	35,	22,	32,	49,	44,	81,	69,	0,	17,	35,	0,	27,				
4	18	12*	43*	4	20	-4*	10,	43,	36,	35,	36,	38,	0,	26,	48,	26*	4	22	8*	0,	31,			
4	24	-4*	19,	0,	0,	0,	15,	0,	0,	0,	0,	0,	0,	0*	5	1-17*	47,	0,	78,	48,	54,			
5	1-12*	25,	156,	53,	22,	297,	283,	45,	134,	32,	953,	528,	239,	265,	247,	294,	226,	49,	152,					
5	1	6*	46,	344,	62,	387,	58,	24,	98,	149,	54,	58,	10,	27,	26*	5	3-16*	28,	0,	79,				
5	3-13*	183,	29,	0,	218,	158,	339,	139,	32,	447,	267,	152,	217,	194,	478,	98,	395,	38,	501,					
5	3	5*	432,	68,	283,	188,	78,	81,	49,	92,	85,	129,	42*	5	5-15*	0,	33,	134,	9,	105,				
5	5-18*	193,	185,	0,	257,	138,	559,	368,	1018,	772,	173,	78,	48,	233,	328,	512,	156,	94,	52,					
5	5	8*	49,	79,	14,	18,	24,	28,	91,	17*	5	7-15*	39,	21,	45,	61,	135,	59,	53,	44,				
5	7	-7*	46,	52,	237,	213,	685,	497,	280,	304,	219,	223,	113,	69,	113,	98,	0,	102,	0,	68,				
5	7	11*	36,	0,	62,	31,	48,	0,	0,	0*	5	9-17*	11,	0,	27,	27,	41,	78,	41,	98,				
5	9	-9*	0,	71,	87,	27,	103,	288,	107,	38,	246,	80,	39,	28,	448,	127,	110,	108,	112,	73,				
5	9	9*	69,	67,	36,	72,	63,	96,	0,	0*	5	11-16*	37,	57,	0,	50,	9,	53,	56,	48,				
5	11	-8*	164,	0,	0,	43,	90,	72,	90,	0,	124,	177,	247,	127,	105,	61,	29,	67,	31,	72,				
5	11	10*	46,	38,	90,	27,	24*	5	13-16*	11,	0,	0,	0,	19,	42,	38,	9,	54,	19,	52,				
5	13	-5*	55,	186,	45,	78,	37,	104,	0,	99,	67,	11,	75,	25,	64,	138,	0,	106,	0,	0,				
5	13	14*	15*	5	15-14*	39,	21,	0,	10,	27,	23,	18,	0,	48,	27,	91,	0,	54,	0,	136,				
5	15	1*	0,	93,	0,	36,	0,	46,	98,	115,	31,	23,	14*	5	17-12*	53,	0,	35,	31,	8,				
5	17	-7*	27,	59,	45,	61,	32,	36,	0,	30,	61,	28,	64,	0,	40,	32,	19,	0,	24,					
5	19-12*	0,	0,	0,	15,	0,	0,	31,	29,	55,	21,	34,	19,	0,	31,	0,	39,	38,	14,					
5	19	6*	35*	5	21	-5*	32,	0,	0,	0,	0,	0,	20,	22,	10,	0,	0,	21,	0,	0,				
5	23	-3*	21,	0,	26,	0,	0,	0,	0,	0*	6	0-16*	26,	0,	40,	0,	54,	0,	38,	0,				
6	0-18*	19,	0,	46,	0,	99,	0,	325,	0,	321,	0,	583,	0,	773,	0,	427,	0,	87,	0,					
6	0	8*	163,	0,	253,	0,	89,	0,	32*	6	2-16*	45,	38,	21,	22,	46,	0,	22,	58,	67,				
6	2	-7*	18,	200,	292,	96,	51,	127,	737,	58,	312,	330,	182,	448,	213,	263,	87,	77,	55,	154,				
6	2	11*	51,	55,	27,	46,	56,	0,	0*	6	4-16*	22,	49,	53,	20,	143,	44,	62,	106,	124,				
6	4	-7*	62,	126,	451,	362,	181,	118,	250,	359,	431,	111,	386,	161,	54,	294,	104,	24,	59,	8,				
6	4	11*	101,	38,	38,	60,	39*	6	6-15*	39,	33,	78,	144,	0,	16,	68,	209,	47,	42,	224,				
6	6	-4*	303,	354,	85,	41,	167,	193,	69,	183,	152,	81,	187,	75,	40,	16,	32,	42,	0,	9,				
6	6	14*	49,	0*	6	8-16*	18,	0,	31,	87,	0,	95,	90,	29,	180,	0,	127,	82,	59,	159,				
6	8	-2*	113,	59,	101,	158,	21,	57,	152,	48,	39,	64,	55,	0,	29,	81,	61,	67,	14,	0,				
6	10-13*	17,	98,	54,	38,	62,	74,	0,	151,	31,	127,	174,	35,	21,	158,	29,	125,	61,	62,					
6	10	5*	77,	84,	25,	23,	30,	39,	105,	48,	62,	0,	0*	6	12-16*	24,	0,	0,	0,	65,				
6	12-11*	23,	0,	0,	61,	0,	67,	43,	19,	80,	88,	160,	166,	65,	76,	59,	26,	54,	58,					
6	12	7*	0,	0,	109,	27,	90,	48,	0*	6	14-11*	0,	39,	26,	0,	23,	23,	0,	57,	39,				
6	14	-2*	18,	169,	31,	158,	28,	59,	19,	54,	37,	117,	36,	109,	27,	22*	6	16-13*	51,	0,				
6	16	-9*	22,	72,	21,	56,	41,	0,	28,	31,	52,	83,	21,	74,	29,	50,	28,	33,	87,	40,				
6	16	9*	24,	0,	23,	0,	0,	11*	6	18-11*	35,	0,	0,	0,	17,	0,	42,	30,	25,	26,				
6	18	-1*	0,	24,	26,	19,	0,	27,	13,	0,	0,	0,	0*	6	20	-9*	30,	0,	0,	25,	0,			
6	20	-2*	26,	44,	17,	10,	0*	6	22	-6*	15,	0,	0,	0,	0,	0,	0,	18,	0,	0,				
6	24	-4*	0,	16,	16,	0,	0,	0,	0,	0*	7	1-16*	0,	19,	0,	13,	48,	45,	91,					
7	1	-9*	152,	165,	0,	110,	373,	64,	347,	368,	476,	285,	707,	312,	544,	173,	199,	65,	28,	96,				
7	1	9*	198,	20,	93,	0,	22,	28,	22*	7	3-15*	17,	73,	20,	78,	69,	35,	55,	217,	97,				
7	3	-6*	182,	123,	109,	171,	268,	124,	197,	63,	92,	320,	42,	95,	45,	38,	120,	78,	62,	82,				
7	3	12*	52,	0,	28,	26,	18*	7	5-17*	21,	10,	0,	78,	49,	0,	132,	61,	16,	144,	119,				
7	5	-6*	163,	87,	0,	124,	19,	39,	92,	48,	39,	207,	536,	109,	20,	176,	71,	18,	78,	61,				
7	5	12*	49,	51,	40*	7	7-18*	0,	0,	42,	46,	49,	41,	38,	119,	17,	93,	137,	168,	89,				
7	7	-5*	102,	28,	137,	176,	182,	82,	45,	112,	67,	202,	50,	141,	81,	101,	43,	22,	45,	33,				
7	7	13*	38,	32,	44,	15*	7	9-16*	28,	47,	0,	0,	35,	20,	29,	98,	103,	108,	15,	31,				
7	9	-4*	30,	69,	162,	88,	11,	0,	60,	174,	0,	78,	92,	11,	58,	60,	74,	40,	63,	44,				
7	11-12*	25,	34,	0,	85,	27,	0,	52,	0,	78,	137,	63,	117,	137,	61,	23,	0,	133,	8,					
7	11	6*	78,	41,	28,	60,	58,	30,	41*	7	13-15*	50,	8,	0,	0,	36,	16,	13,	31,	42,				
7	13	-6*	83,	21,	90,	91,	46,	92,	126,	63,	157,	69,	149,	36,	53,	36,	45,	0,	45,	41,				
7	13	12*	18,	21,	33*	7	15-14*	0,	34,	0,	14,	0,	49,	27,	42,	82,	18,	134,	30,	27,				
7	15	-1*	63,	17,	46,	47,	42,	73,	32,	70,	35,	48,	0,	0,	0,	0*	7	17	-7*	36,	17,			
7	17	-5*	33,	42,	52,	47,	29,	49,	26,	43,	16,	43,	33,	45,	39,	0,	30*	7	19-18*	48,				
7	19	-7*	34,	0,	0,	17,	28,	0,	36,	17,	29,	14,	10,	0,	22,	0,	0,	0,	0,	0,				
7	19	11*	0*	7	21	-5*	26,	29,	29*	7	23	-1*	0,	0,	0*	8	0-14*	0,	0,	116,	8,	0,		
8	0	-8*	108,	0,	196,	0,	539,	0,	513,	0,	761,	0,	850,	0,	84,	0,	38,	0,	132,	0,				
8	8	10*	156,	0,	99,	0,	29*	8	2-15*	48,	17,	0,	110,	111,	32,	310,	50,	148,	39,	39,				
8	2	-4*	460,	80,	45,	178,	635,	529,	222,	88,	75,	497,	16,	203,	104,	218,	151,	30,	43,	87,				
8	2	14*	23,	0,	0*	8	4-17*	11,	0,	51,	27,	26,	77,	113,	22,	225,	35,	127,	56,	91,				
8	4	-4*	45,	224,	263,	259,	163,	437,	147,	271,	112,	112,	87,	52,	145,	156,	94,	53,	35,	108,				
8	4	14*	22*	8	6-14*	28,	31,	0,	41,	96,	110,	64,	28,	66,	36,	62,	84,	267,	34,	134,				
8	6	1*	221,	81,	45,	214,	52,	113,	177,	117,	43,	12,	41,	69,	84,	52,	0,	28,	15,					
8	8-17*	31,	44,	0,	63,	41,	61,	54,	69,	98,	59,	34,	19,	103,	29,	21,	64,	210,	51,					
8	8	1*	0,	148,	114,	59,	90,	26,	134,	33,	49,	33,	33,	41,	36,	56*	8	10-16*	0,	8,				
8	10-14*	78,	0,	0,	35,	0,	0,	84,	61,	14,	34,	70,	24,	0,	155,	23,	39,	162,	76,					
8	10	4*	23,	72,	28,	61,	71,	56,	13,	40,	42*	8	12-15*	0,	0,	15,	51,	26,	33,	13,				
8	12	-8*	65,	80,	43,	128,	88,	53,	111,	31,	58,	164,	31,	160,	60,	56,	62,	17,	64,	0,				
8	12	10*	23,	17,	0*	8	14-10*	22,	19,	40,	67,	0,	183,	26,	35,	43,	43,	24,	185,	0,				
8	14	3*	133,	23,	0,	32,	38,	47,	38,	20*	8	16-12*	32,	0,	0,	0,	45,	10,	53,	48,				
8	16	-4*	48,	60,	49,	47,	30,	38,	20,	49,	9,	45,	39,	29,	41*	8	18	-4*	45,	0,	32,			
8	18	-1*	37,	36,	32,	47,	10,	32,	35,	0,	20,	15,	0,	15,	0*	8	20	-7*	0,	0,	0,			
8	20	-3*	0,	0,	0,	38,	0,	0,	0,	0,	0,	0,	0*	8	22	-7*	0,	0,	0,	0,	0,			
8	22	0*	41,	0,	0,	0,	0,	16*	9	1-18*	0,	0,	0,	0,	28,	53,	0,	51,	47,	54,				
9	1	-8*	134,	174,	40,	425,	59,	259,	267,	175,	232,	371,	33,	51,	178,	76,	15,	210,	201,	8,				
9	1	10*	50,	61,	54,	40,	36,	0,	0,	0,	0*	9	3-18*	0,	0,	0,	0,	48,	0,	34,				
9	3-11*	128,	72,	74,	266,	20,	28,	183,	0,	331,	81,	153,	306,	48,	83,	64,	141,	171,	41,					
9	3	7*	115,	304,	44,	113,	36,	103,	50,	45,	0,	0,	0*	9	5-13*	64,	66,	86,	15,	8,				
9	5	-8*	135,	11,	88,	58,	127,	121,	73,	159,	197,	159,	101,	262,	121,	225,	17,	61,	187,	59,				

Table 6 (cont.)

9	5	10°	86,	42,	93,	27,	0,	0,	34°	9	7-17°	39,	0,	0,	0,	55,	34,	30,	75,	61,
9	7	-8°	39,	98,	88,	8,	8,	32,	163,	0,	36,	29,	40,	63,	0,	43,	72,	63,	38,	21,
9	7	18°	31,	0,	51,	53°	9	9-16°	31,	0,	0,	41,	27,	73,	55,	82,	49,	96,	36,	84,
9	9	-4°	38,	65,	260,	70,	195,	62,	46,	55,	49,	20,	87,	22,	58,	20,	18,	51,	0,	0,
9	9	16°	0°	9	11-13°	72,	0,	31,	13,	0,	30,	107,	58,	48,	45,	22,	79,	82,	182,	93,
9	11	2°	112,	34,	43,	37,	41,	70,	41,	29,	21,	57,	25,	0°	9	13-13°	28,	29,	0,	0,
9	13	-9°	50,	30,	21,	122,	44,	57,	72,	78,	29,	109,	75,	135,	40,	36,	54,	25,	34,	19,
9	13	9°	42,	20,	0,	0,	15°	9	15-12°	11,	0,	0,	0,	10,	45,	49,	44,	90,	29,	0,
9	15	-1°	85,	17,	64,	59,	39,	0,	29,	19,	32,	38°	9	17	-7°	27,	26,	26,	0,	24,	53,
9	17	-1°	25,	47,	34,	32,	0,	0,	18,	0,	0,	32°	9	19	-6°	15,	0,	0,	0,	0,	0,
9	19	6°	26,	0,	0,	0,	0°	9	21	2°	28°	9	23	-1°	16,	0,	0,	0°	10	0-14°	65,	0,
10	0-12°		25,	0,	113,	0,	131,	0,	289,	0,	151,	0,	403,	0,	35,	0,	319,	0,	145,	0,
10	0	6°	46,	0,	53,	0,	99,	0,	9°	10	2-15°	0,	42,	41,	28,	44,	38,	72,	115,	44,
10	2	-6°	194,	71,	249,	139,	178,	269,	103,	68,	252,	74,	53,	0,	73,	78,	36,	42,	56,	165,
10	2	12°	28,	0,	20,	0,	0,	0°	10	4-13°	56,	47,	0,	189,	53,	0,	122,	18,	112,	183,
10	4	-3°	63,	217,	58,	155,	53,	42,	222,	344,	86,	28,	33,	73,	117,	35,	181,	39,	0,	17,
10	6-12°		43,	62,	108,	47,	9,	22,	31,	43,	72,	23,	126,	198,	91,	33,	46,	133,	173,	60,
10	6	6°	48,	67,	36,	116,	42,	62,	38,	0,	20,	0,	19°	10	0-12°	0,	53,	16,	0,	42,
10	8	-7°	47,	37,	68,	125,	92,	83,	194,	102,	89,	114,	101,	0,	67,	17,	124,	74,	31,	26,
10	8	11°	34,	49°	10	10-14°	24,	29,	30,	24,	33,	54,	60,	38,	35,	47,	100,	131,	28,	180,
10	10	0°	19,	14,	12,	41,	22,	92,	23,	52,	16,	0,	45,	22°	10	12	-9°	19,	41,	74,	27,
10	12	-5°	81,	26,	49,	29,	44,	157,	87,	95,	43,	37,	0,	22,	35,	34,	0,	0,	0,	0,
10	12	14°	38°	10	14-13°	16,	32,	0,	43,	0,	20,	17,	57,	67,	9,	36,	60,	20,	28,	46,
10	14	2°	47,	24,	8,	35,	30,	53,	31°	10	16-11°	19,	0,	0,	0,	0,	0,	0,	37,	25,
10	16	-2°	0,	40,	62,	53,	19,	17,	0,	10,	0,	0,	0,	26,	0,	27°	18	18	-3°	36,	38,
10	18	2°	32,	27,	0,	18°	10	20	-5°	8,	0,	0,	33,	0,	33,	0,	30,	0,	0,	0,	38,
10	20	8°	25°	10	22	-3°	0,	0,	0,	0°	11	1-16°	0,	0,	0,	20,	0,	73,	91,	20,	12,
11	1	-7°	114,	21,	8,	22,	112,	85,	72,	37,	134,	58,	94,	106,	139,	36,	38,	64,	26,	27,
11	1	11°	54,	17,	28,	23°	11	3-12°	32,	97,	124,	145,	69,	33,	72,	44,	174,	201,	129,	47,
11	3	0°	95,	209,	89,	122,	11,	48,	78,	22,	152,	0,	80,	57,	17,	30,	0°	11	5-12°	24,
11	5-11°		23,	61,	126,	86,	72,	108,	48,	153,	210,	11,	224,	204,	71,	33,	89,	117,	60,	99,
11	5	7°	50,	144,	72,	46,	31,	38°	11	7-16°	0,	0,	0,	53,	0,	53,	8,	38,	31,	71,
11	7	-6°	47,	57,	18,	97,	27,	162,	189,	174,	153,	91,	12,	8,	107,	41,	51,	69,	42,	31,
11	7	12°	26,	0,	0,	36°	11	9-10°	41,	31,	45,	81,	47,	30,	152,	84,	39,	48,	19,	129,
11	9	2°	41,	54,	120,	71,	58,	74,	13,	38,	35°	11	11	-9°	67,	48,	26,	88,	36,	125,	44,
11	11	-2°	38,	59,	52,	73,	92,	64,	91,	73,	22,	35,	16,	24°	11	13-10°		10,	0,	0,	49,
11	13	-6°	44,	32,	47,	0,	35,	9,	45,	77,	27,	0,	28,	34,	34,	42,	0,	30,			
11	15-10°		38,	0,	21,	17,	0,	28,	43,	32,	32,	27,	18,	10,	0,	33,	19,	22,	14,		
11	17	-6°	21,	0,	34,	0,	17,	0,	0,	0,	20°	11	19	0°	6,	28,	8,	24°	11	21	-1°	33,
12	0-10°		13,	0,	106,	0,	133,	0,	54,	0,	143,	0,	148,	0,	21,	8,	104,	0,	53,	0,	
12	0	8°	81,	0,	44°	12	2-15°	0,	15,	0,	0,	37,	75,	68,	42,	0,	58,	86,	148,	0,	
12	2	-2°	77,	52,	116,	66,	95,	77,	69,	38,	12,	116,	63,	0,	19,	32°	12	4-16°	19,	0,	
12	4-12°		10,	32,	107,	60,	44,	92,	82,	83,	208,	92,	224,	212,	36,	86,	16,	81,	29,	111,	
12	4	6°	62,	123,	24,	41,	28,	0°	12	6-13°	0,	0,	17,	0,	45,	68,	119,	0,	43,	55,	
12	6	-3°	100,	176,	244,	145,	134,	57,	123,	60,	112,	55,	106,	43,	55,	33,	0,	0,	37,		
12	8	-14°	27,	0,	39,	27,	63,	51,	35,	65,	131,	9,	116,	24,	53,	32,	172,	101,	63,	30,	
12	8	4°	42,	64,	84,	16,	65,	39,	31,	41,	37°	12	10-13°		0,	0,	0,	52,	34,	35,	77,
12	10	-6°	91,	78,	35,	53,	26,	117,	43,	28,	59,	124,	37,	22,	59,	67,	22,	0,	0,	25,	
12	12-13°		0,	0,	0,	8,	0,	41,	0,	46,	75,	16,	49,	34,	69,	17,	26,	9,	85,	60,	
12	12	5°	9,	17,	22°	12	14	-7°	0,	0,	0,	0,	14,	30,	37,	0,	21,	30,	35,	0,	
12	16	-3°	20,	0,	0,	0,	0,	0,	0,	38,	0,	0,	32,	0,	34°	12	18	1°	0,	0,	0,
12	18	6°	38,	31°	12	20	-2°	29°	13	1-10°	22,	21,	40,	51,	0,	194,	90,	25,	83,	119,	33,
13	1	1°	52,	46,	257,	82,	43,	12,	68,	33,	54,	33°	13	3-13°	26,	0,	0,	22,	65,	108,	
13	3	-7°	38,	23,	58,	124,	93,	172,	126,	77,	22,	61,	57,	154,	30,	58,	38,	31,	33,	52,	
13	3	15°	50°	13	5-10°	38,	100,	58,	41,	18,	47,	33,	93,	129,	49,	191,	28,	175,	67,	57,	
13	5	5°	54,	114,	56,	0,	21,	63,	0,	44°	13	7-11°	25,	37,	45,	52,	72,	38,	29,	40,	
13	7	-3°	29,	59,	164,	176,	54,	33,	65,	41,	66,	64,	63,	29,	36°	13	9-12°	0,	0,	0,	
13	9	-9°	24,	39,	44,	46,	98,	13,	29,	37,	64,	24,	0,	94,	42,	30,	68,	57,	52,	39,	
13	9	10°	50°	13	11-12°	19,	0,	0,	0,	0,	44,	65,	49,	43,	38,	25,	57,	43,	31,	62,	
13	11	3°	59,	28,	59,	61,	0,	43°	13	13	-6°	0,	0,	20,	29,	26,	56,	33,	40,	31,	39,
13	13	4°	24°	13	15	-5°	15,	0,	0,	0,	0,	35,	0,	0,	0,	0,	0,	15,	0,	22,	
13	17	-5°	29,	0,	0,	0,	15,	0,	0°	13	19	-1°	36,	0,	0,	19°	14	0-10°	54,	0,	45,
14	0	-6°	67,	0,	27,	0,	82,	0,	102,	0,	131,	0,	145,	0,	65,	0,	13,	0,	67,	0,	
14	0	12°	30°	14	2-14°	0,	0,	0,	0,	37,	32,	43,	21,	32,	165,	28,	121,	33,	104,	43,	
14	2	1°	36,	52,	140,	47,	82,	52,	69,	41,	24°	14	4	-9°	48,	68,	28,	41,	161,	55,	91,
14	4	-2°	67,	30,	36,	36,	69,	41,	35,	74,	36,	53,	44,	60,	0,	0,	0,	15,			
14	6-13°		15,	0,	0,	18,	26,	80,	57,	58,	35,	27,	34,	27,	41,	44,	113,	84,	71,	24,	
14	6	5°	55,	71,	41,	29°	14	8-10°	27,	0,	0,	74,	51,	46,	63,	32,	31,	9,	0,	99,	
14	8	2°	38,	21,	39,	33,	52,	45,	33,	34,	25,	26,	0°	14	16	-6°	22,	31,	76,	45,	21,
14	10	-1°	16,	24,	16,	30,	36,	44,	0,	0,	0,	32°	14	12	-7°	40,	0,	30,	42,	36,	39,
14	12	-1°	37,	40,	31,	35,	0,	0,	0,	0,	0,	26°	14	14	-3°	38,	0,	0,	35,	0,	0,
14	14	6°	38,	0,	0,	0°	14	16	-6°	29,	29,	48,	44,	0,	0,	42,	0,	0,	0,	0,	31,
14	18	-4°	22,	0,	0,	0,	27°	15	1	-8°	24,	24,	56,	55,	67,	75,	24,	61,	41,	24,	36,
15	1	3°	43,	57,	84,	39,	40,	38,	49°	15	3-12°	11,	0,	0,	0,	0,	0,	96,	65,	99,	
15	3	-3°	45,	50,	104,	37,	40,	42,	40,	42,	43,	47,	47,	0,	35,	0,	0,	0,	0,		
15	5	-7°	50,	49,	32,	35,	56,	40,	74,	46,	52,	55,	35,	63,	0,	32,	57,	0,	0,	0,	
15	5	13°	25°	15	7	-9°	34,	56,	0,	55,	68,	56,	13,	38,	23,	50,	31,	84,	54,	46,	17,
15	7	8°	53,	0,	0,	22°	15	9	-6°	39,	28,	0,	47,	53,	22,	43,	32,	27,	44,	0,	47,
15	9	6°	49,	37,	43°	15	11	-3°	25,	51,	0,	30,	0,	0,	0,	44,	37,	51,	0,	0,	0,
15	11	10°	38°	15	13	-8°	0,	0,	24,	0,	44,	0,	0,	0,	0,	0,	0,	29,	51,	24,	35,
15	15	-4°	36,	0,	0,	19°	15	17	3°	22°	16	0	-4°	125,	0,	60,	0,	59,	0,	49,	0,	81,
16	0	6°	60°	16	2	-7°	35,	0,	90,	61,	32,	69,	55,	37,	54,	30,	66,	78,	32,	49,	0,
16	2	9°	38,	0,	0,	35°	16	4	-8°	27,	0,	0,	10,	29,	43,	42,	0,	61,	67,	0,	58,
16	4	4°	40,	48,	0,	0,	40°	16	6-11°	0,	0,	43,	0,	32,	59,	33,	31,	22,	0,	42,	
16	6	0°	56,	62,	50,	40,	0,	40,	0,	10,	0,	0,	0°	16	8	-5°	37,	0,	37,	28,	66,

Table 6 (cont.)

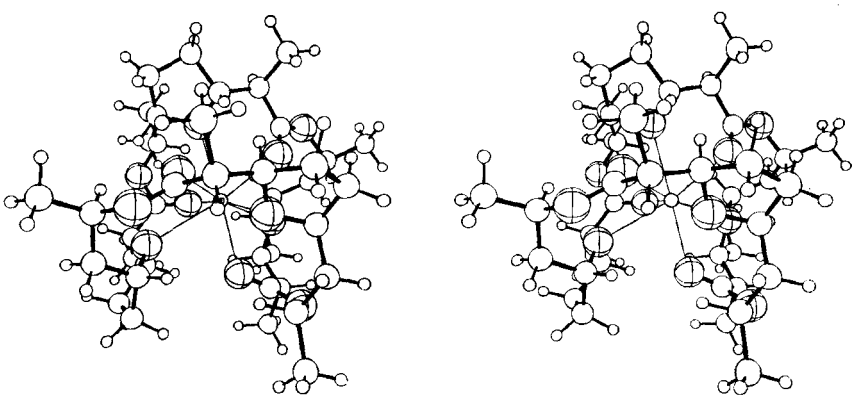
16	8	0*	44,	0,	0,	0,	0,	0,	0,	0,	0,	0,	0,	22*	16	10	-7*	48,	0,	0,	0,
16	10	-1*	41,	29,	0,	0,	0,	0,	0,	0,	41,	0,	35*	15	12	-3*	38,	0,	0,	0,	18,
16	12	2*	33*	16	14	-1*	34*	16	16	-1*	22,	0,	0,	19*	17	1	-10*	33,	0,	0,	0,	0,	0,
17	1	-4*	10,	67,	0,	38,	37,	31,	33,	41,	42,	66*	17	3	-9*	0,	0,	0,	0,	20,	0,
17	3	-2*	24,	33,	44,	44,	37,	61,	0,	44,	41,	31*	17	5	-8*	49,	0,	0,	41,	43,	30,
17	5	0*	12,	0,	56,	38,	43,	0,	0,	37,	0,	27*	17	7	-9*	22,	0,	0,	0,	0,	15,
17	7	-3*	38,	0,	0,	0,	0,	35,	34,	0,	0,	0,	0,	33,	25*	17	9	0*	43,		
17	11	-4*	55,	0,	40,	0,	35,	0,	0,	0,	43*	17	13	-3*	37,	0,	0*	18	0	-6*	15,	0,
18	0	2*	54*	18	2	-8*	0,	15,	21,	0,	0,	0,	0,	42,	27,	56,	61,	33,	0,	21,	0,
18	2	7*	40*	18	4	-9*	25,	0,	0,	0,	0,	0,	0,	0,	46,	10,	25,	28,			
18	6	-1*	38,	42,	0,	0,	32*	18	8	-5*	40,	38,	0,	0,	0,	37,	32,	26,	19,	0,	0,
18	8	5*	15*	18	10	2*	11,	0,	22*	18	12	-1*	27*	19	1	-3*	26,	0,	0,	35*	19	3	0*	21,
19	3	2*	32*	19	5	-6*	22,	0,	0,	33,	0,	0,	0,	39,	40*	19	7	-4*	27,	22,	29,	29,
19	7	0*	39,	0,	27,	36,	0,	30*	19	9	-1*	0,	0*	20	0	-2*	16*	20	2	-2*	44,	0,	0,
20	2	1*	29*	20	4	0*	0,																

along the dyad. Three cycles of full-matrix least-squares analysis (anisotropic temperature factors for Na and O atoms in the third cycle) were followed by a difference *Fourier* map. The refinement was completed by eight cycles of block-diagonal least-squares analysis with anisotropic temperature factors for all atoms (except the anion) and hydrogen atoms held fixed at calculated positions (stereochemical assumptions: H—C—H, local C_{2v} symmetry, bond angle 111°, H—C distance 1.09 Å; —C—H, equal angles with the three attached bonds; methyl groups, staggered conformation, H—C—H bond angle 109°). The final R factor, based on 2205 reflections with $F_o > 2\sigma(F_o)$ and $F_o > 1.3$ was 17.2%. The high R factor is probably due to the disorder of the thiocyanate anion. Various attempts to describe the disorder in terms of a reasonable model were unsuccessful and had to be abandoned. The 28% monactin content of the crystals may also affect the quality of the structure analysis.

Results. – The results are summarized in the Tables and Fig. 4. Fractional coordinates, vibrational parameters and calculated hydrogen atom positions are given in Tables 1, 2 and 3. Standard deviations were estimated by inversion of the least-squares normal equations. Bond lengths and angles and torsion angles relevant to the conformation of the ligand are given in Tables 4 and 5 and in Fig. 4. The corresponding standard deviations for bond lengths of C–C and C–O bonds are between 0.015–0.032 Å, for the bond angles between 1.1–2.1°. The standard deviations for the Na^+...O distances are 0.01 Å. A list of observed structure factors is given in Table 6.

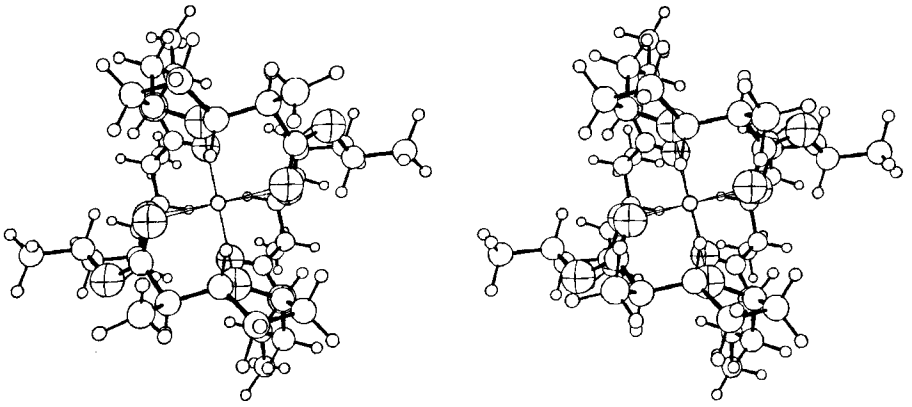
Discussion. – The structure of the Na^+ complex of nonactin is depicted in Fig. 1. Fig. 2 shows how very similar the Na^+ and K^+ complex are.

Although the K^+ and Na^+ complexes of nonactin crystallize in different space groups (K^+ complex: orthorhombic, Pnna, $a = 20.17$, $b = 15.55$, $c = 15.33$ Å; Na^+



Nonactin-NaCNS *Nonactin-NaCNS*

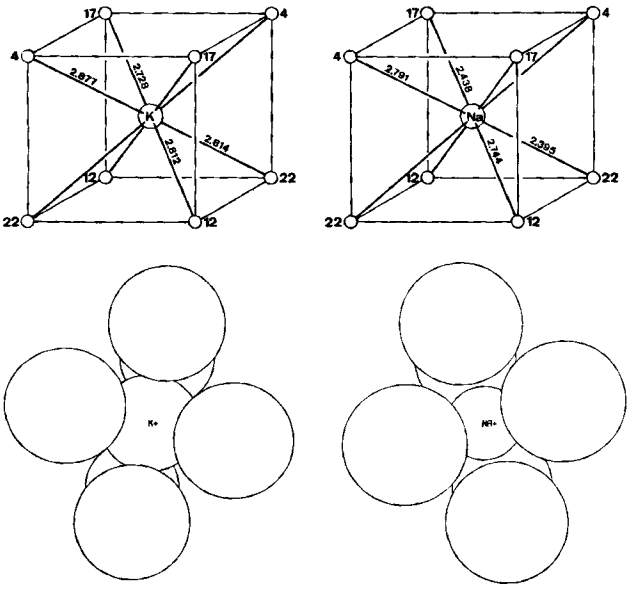
Fig. 1. *Stereoscopic view of the Na^+ complex of nonactin*



Nonactin-KCNS *Nonactin-NaCNS*

Fig. 2. *Projections of the structures of the Na^+ and K^+ complexes of nonactin along their crystallographic twofold rotation axis.* The approximate $S_4(\bar{4})$ symmetry of the ligand in both cases is evident.

complex: monoclinic, C2/c, $a = 15.55$, $b = 19.59$, $c = 15.31$ Å, $\beta = 90°$) their structures are very similar. The unit cells have approximately the same dimensions and in both structures the overall arrangement of cations and anions is that of a deformed NaCl-type structure (K^+: 0.51, 0.25, 0.25, NCS^-: 0.64, 0.21, 0.80; Na^+: 0.50, 0.27, 0.25, NCS^-: 0.02, 0.38, 0.21). The similarity between the two structures extends to the molecular parameters, in particular, to the torsion angles that describe the



K + Nonactin *Na + Nonactin*

Fig. 3. *Coordination of Na^+ and K^+ by ligand oxygen atoms.* The radii of the spheres correspond to standard *van der Waals* radii (K^+; 1.33, Na^+; 0.95, O; 1.40 Å)

conformation of the 32-membered ring. The largest changes in torsion angles occur around the bonds C(7)–O(8); 13.3°, C(10)–C(11); 9.6°, C(5)–C(6); 8.3°. For the torsion angles the differences between uncomplexed nonactin and the K^+ complex are smaller than those between nonactin and the Na^+ complex.

The Na^+ ion is coordinated (Fig. 3) by four carbonyl oxygen atoms at distances of 2.438 Å and 2.395 Å and by four ether oxygen atoms at distances of 2.791 Å for O(4), (2.877 Å in K^+ complex) and 2.744 Å for O(12), (2.812 Å in K^+ complex). The carbonyl oxygen atoms with their less crowded surroundings seem to be better able to approach the cation. This preference of Na^+ for carbonyl oxygens may also be attributed to stronger dipole interaction with carbonyl than with ether oxygen atoms. The preference of the ligand for K^+ clearly depends mainly on the change in

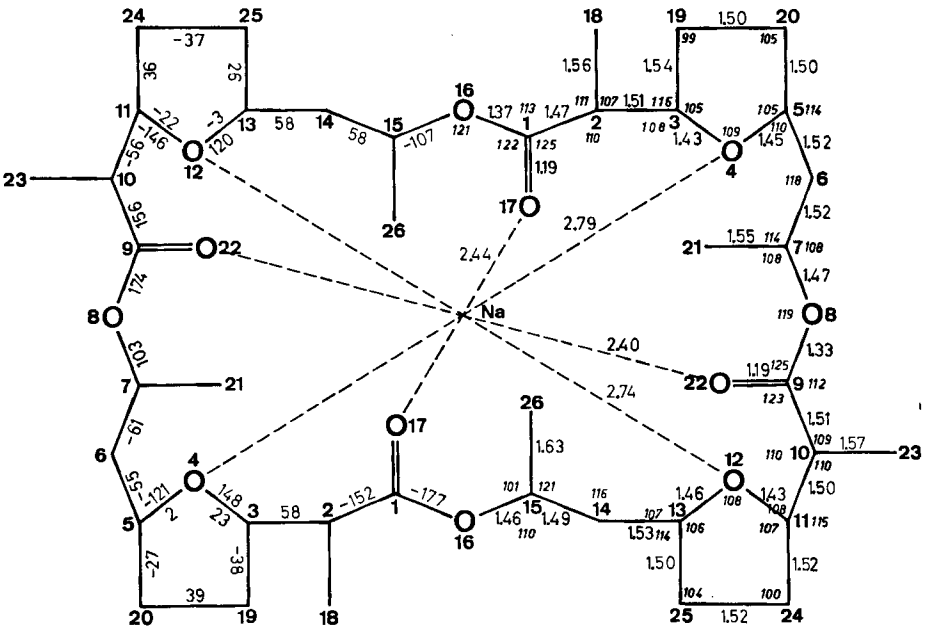


Fig. 4. *Molecular topography.* Bond lengths and bond angles are indicated in the right part of the figure, torsion angles in the left part

coordination from eight equidistant oxygens in the K^+ complex to only four first neighbours in the Na^+ complex.

It is interesting to compare these findings with recently published results of structure determinations of tetranactin complexes by *Iitaka, Sakamaki & Nawata* [7].

	Tetranactin (mean distance)	Nonactin
K^+...O (ether)	2.874 Å	2.845 Å
K^+...O (carbonyl)	2.774 Å	2.771 Å
Na^+...O (ether)	2.820 Å	2.768 Å
Na^+...O (carbonyl)	2.435 Å	2.417 Å
Rb^+...O (ether)	2.940 Å	–
Rb^+...O (carbonyl)	2.909 Å	–

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75. Eliminierungsreaktionen an Kationen in Gasphase II
Essigsäureeliminierung aus Androstanylacetaten

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Summary. Elimination of acetic acid from the molecular ions of the epimeric androstanyl-acetates is investigated applying specific ^{2}H-labelling and analysis of metastable transitions. Only 17β-androstanylacetate eliminates acetic acid in a 1,2-fashion to an extent of 16%. This contribution is shown to be a specific *cis*-elimination and after comparison with water-elimination in the corresponding alcohol a *McLafferty* type mechanism is attributed, which then appears to require a planar transition state.

Einleitung. – Molekular-Ionen von Alkylacetaten verlieren Essigsäure im wesentlichen in 1,2 und 1,3-Eliminierungsprozessen [1], während für Acetylderivate alicyclischer Alkohole 1,2-Eliminierungsprozesse nachgewiesen wurden, die als Reaktionen vom *McLafferty*-Typus gelten [2] [3]. Die strukturdiagnostische Bedeutung der *McLafferty*-Reaktion veranlasste uns zur Untersuchung der Frage, ob Koplanarität des Übergangszustandes bedingende Voraussetzung für den Ablauf dieses Reaktionstyps sein könne. An Modellen mit starrem C-Skelett und damit fixierter Konformation sollte der Nachweis mit Hilfe stereospezifischer ^{2}H-Markierung geführt werden können. In einer vorgehenden Arbeit [4] untersuchten wir die entsprechend markierten epimeren Bornylacetate und stellten fest, dass in diesem Fall *McLafferty*-Mechanismen bei der Essigsäureeliminierung bedeutungslos sind. Zwar sind 1,2-Eliminierungen wesentliche Reaktionen, aber die Übereinstimmung in allen analytischen Aspekten mit der vergleichend untersuchten Wasserelimination bei den entsprechenden Alkoholen geht so weit, dass beiden Eliminierungen die gleichen mechanistischen Abläufe zugeordnet werden müssen. Die experimentellen Daten geben Grund zur Annahme, dass hier der Eliminierung eine Ringöffnung vor-