The trend in bond lengths is consistent with this suggested formula. A C=N bond, 1·282 Å long, is localized between C(8) and N(3). The other C—N distances in the molecule show a hybrid character, resonating between single and double bonds. C(9)—O(1) is significantly longer than the expected exocyclic C—O distance in pentatomic rings. N(1)—N(2) is somewhat shorter than a N—N single bond.

The C—C bond length in the phenyl ring averages 1·380 Å (1·394 Å after thermal motion correction). A hydrogen bond is localized between the O atoms of the ethanol molecule and the betaine molecule: the O···O distance is 2·763 Å with the H atom well aligned between the two O atoms, the O—H···O angle being 158°.

All the intermolecular distances are normal. Least-squares planes through several atomic groups in the molecule were computed. The equations of the best planes with deviations from planarity are reported in Table 4. The three fused rings are slightly twisted, the extent of the torsional buckling being shown by the deviations from plane *E* in Table 4. The phenyl ring is planar (plane *D*), within the limits of experimental error, and makes an angle of 70·4° with the mean plane through the fused rings.

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The Crystal and Molecular Structure of an NH_4^+–Tetranactin Complex

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$C_{44}H_{72}O_{12}.NH_4SCN$, $M_r = 869·17$, crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 15·889$ (8), $b = 20·695$ (10), $c = 15·371$ (8) Å, $\beta = 90·48$ (5)°, $Z = 4$, $D_x = 1·142$ g cm^{-3}. The final R value was 0·080 for 5527 observed reflexions. The NH_4^+ cation is trapped in the tetranactin molecule and forms strong hydrogen bonds with the other O atoms.

Introduction

The nactins exhibit a very high selectivity for the NH_4^+ ion in ion transport through lipid bilayer membranes (Scholer & Simon, 1970; Eisenman, Krasne & Ciani, 1975). In the alkali-metal–nactin complexes, a distorted cubic coordination is completed with the four tetrahedrally oriented carbonyl O atoms and the four tetrahedrally oriented ether O atoms (Dobler, Dunitz & Kilbourn, 1969; Iitaka, Sakamaki & Nawata, 1972) and a strong interaction was observed between the cation and the carbonyl groups (Kyogoku, Ueno, Akutsu & Nawata, 1975). This coordination geometry may well fit the NH_4^+ ion, which possesses a tetrahedral symmetry, but no strong interaction was observed between

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Table 1. *The positional* ($\times 10^4$) *and thermal* ($\times 10^4$) *parameters for non-hydrogen atoms and the* NH$_4^+$ *atoms*

Standard deviations, given in parentheses, refer to the least significant digits. Thermal factors are those in the expression: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(NH$_4$)	4492 (3)	2528 (2)	1461 (3)	41 (2)	25 (1)	52 (2)	1 (1)	−2 (2)	0 (1)
H$_1$(NH$_4$)	4045 (30)	2295 (22)	1332 (30)	102 (30)	25 (16)	50 (32)	25 (18)	13 (25)	22 (19)
H$_2$(NH$_4$)	4351 (29)	2748 (21)	1851 (31)	68 (30)	24 (15)	76 (32)	−10 (17)	9 (25)	−1 (18)
H$_3$(NH$_4$)	4959 (29)	2303 (20)	1639 (34)	67 (28)	18 (14)	108 (41)	2 (16)	16 (28)	3 (19)
H$_4$(NH$_4$)	4618 (29)	2728 (21)	1036 (29)	51 (30)	28 (16)	76 (29)	4 (18)	−4 (24)	−17 (17)
C(1)	5824 (3)	3592 (3)	2596 (4)	43 (2)	28 (2)	66 (3)	−7 (2)	−4 (2)	3 (2)
C(2)	5337 (3)	3946 (3)	3271 (4)	51 (3)	25 (2)	70 (3)	−1 (2)	−6 (2)	−7 (2)
C(3)	4407 (3)	3932 (3)	3042 (4)	49 (3)	23 (2)	88 (4)	2 (2)	−4 (3)	−3 (2)
O(4)	4145 (2)	3248 (2)	3059 (2)	46 (2)	26 (1)	74 (2)	2 (1)	4 (2)	−6 (1)
C(5)	3289 (3)	3191 (3)	3397 (4)	46 (3)	33 (2)	86 (4)	5 (2)	3 (3)	−10 (2)
C(6)	3295 (4)	2811 (3)	4221 (4)	56 (3)	39 (2)	64 (3)	−0 (2)	11 (3)	−13 (2)
C(7)	3630 (3)	2131 (3)	4139 (4)	45 (3)	41 (2)	53 (3)	−4 (2)	2 (2)	−5 (2)
O(8)	3067 (2)	1792 (2)	3524 (2)	41 (2)	33 (1)	53 (2)	0 (1)	5 (1)	−4 (1)
C(9)	3398 (3)	1474 (2)	2859 (3)	43 (2)	27 (1)	47 (3)	3 (2)	4 (2)	5 (2)
C(10)	2741 (3)	1131 (2)	2328 (3)	49 (3)	25 (1)	50 (3)	−2 (2)	4 (2)	0 (2)
C(11)	2961 (3)	1154 (2)	1371 (3)	49 (3)	21 (1)	52 (3)	−0 (1)	1 (2)	2 (2)
O(12)	2968 (2)	1826 (2)	1109 (2)	50 (2)	23 (1)	48 (2)	−2 (1)	−9 (1)	2 (1)
C(13)	2638 (3)	1886 (3)	225 (3)	53 (3)	27 (2)	43 (2)	−1 (2)	−6 (2)	0 (2)
C(14)	1830 (3)	2287 (3)	244 (3)	44 (2)	33 (2)	50 (3)	−5 (2)	−8 (2)	3 (2)
C(15)	1944 (3)	2972 (3)	561 (3)	45 (2)	30 (2)	46 (3)	−1 (2)	−4 (2)	1 (2)
O(16)	2521 (2)	3281 (2)	−45 (2)	44 (2)	27 (1)	45 (2)	−3 (1)	−7 (1)	1 (1)
O(17)	5694 (2)	3608 (2)	1819 (2)	58 (2)	46 (1)	58 (2)	1 (1)	−15 (2)	5 (1)
C(18)	5653 (5)	4653 (4)	3312 (6)	71 (4)	42 (2)	132 (6)	−8 (3)	−3 (4)	−15 (3)
C(19)	3839 (4)	4247 (3)	3699 (5)	65 (4)	25 (2)	132 (6)	12 (2)	7 (4)	−13 (3)
C(20)	2993 (4)	3904 (3)	3509 (5)	60 (4)	41 (2)	127 (6)	9 (2)	12 (4)	−9 (3)
C(21)	3622 (4)	1739 (4)	4985 (4)	71 (4)	58 (3)	59 (4)	−10 (3)	0 (3)	0 (3)
O(22)	4144 (2)	1466 (2)	2708 (2)	43 (2)	46 (1)	57 (2)	6 (1)	6 (2)	−5 (1)
C(23)	2698 (5)	424 (3)	2650 (4)	104 (5)	31 (2)	64 (4)	−10 (2)	5 (3)	10 (2)
C(24)	2342 (3)	831 (3)	759 (4)	56 (3)	24 (1)	60 (3)	−4 (2)	3 (2)	−3 (2)
C(25)	2503 (4)	1199 (3)	−82 (4)	64 (3)	34 (2)	55 (3)	−2 (2)	−2 (2)	−4 (2)
C(26)	1134 (3)	3357 (3)	556 (4)	49 (3)	41 (2)	63 (3)	4 (2)	3 (2)	−2 (2)
C(27)	1235 (4)	4050 (3)	821 (5)	79 (4)	42 (2)	91 (5)	14 (3)	3 (3)	−6 (3)
C(28)	3931 (5)	1069 (4)	4907 (5)	89 (5)	54 (3)	87 (5)	2 (3)	−10 (4)	17 (3)
C(51)	3193 (3)	3596 (2)	271 (3)	43 (2)	24 (1)	56 (3)	5 (2)	−9 (2)	−3 (2)
C(52)	3712 (3)	3894 (3)	−444 (4)	51 (3)	26 (2)	61 (3)	−1 (2)	−9 (2)	4 (2)
C(53)	4635 (3)	3875 (2)	−190 (4)	47 (3)	24 (1)	64 (3)	0 (2)	−3 (2)	3 (2)
O(54)	4875 (2)	3191 (2)	−152 (2)	45 (2)	27 (1)	61 (2)	−0 (1)	7 (1)	5 (1)
C(55)	5740 (3)	3115 (3)	−455 (4)	40 (2)	31 (2)	68 (3)	−0 (2)	6 (2)	1 (2)
C(56)	5745 (4)	2718 (3)	−1265 (4)	56 (3)	36 (2)	59 (3)	2 (2)	9 (2)	7 (2)
C(57)	5384 (3)	2042 (3)	−1177 (3)	49 (3)	37 (2)	49 (3)	3 (2)	3 (2)	3 (2)
O(58)	5919 (2)	1700 (2)	−542 (2)	43 (2)	31 (1)	53 (2)	1 (1)	7 (1)	3 (1)
C(59)	5546 (3)	1402 (3)	117 (3)	52 (3)	27 (2)	46 (3)	−2 (2)	5 (2)	−7 (2)
C(60)	6182 (3)	1044 (2)	688 (3)	47 (3)	23 (1)	58 (3)	6 (2)	2 (2)	−2 (2)
C(61)	5925 (3)	1090 (2)	1621 (3)	50 (3)	25 (1)	51 (3)	4 (2)	1 (2)	0 (2)
O(62)	5949 (2)	1771 (2)	1862 (2)	54 (2)	26 (1)	48 (2)	7 (1)	−12 (1)	−1 (1)
C(63)	6257 (3)	1841 (3)	2758 (3)	50 (3)	34 (2)	44 (3)	7 (2)	−8 (2)	−2 (2)
C(64)	7075 (3)	2203 (3)	2745 (3)	46 (3)	38 (2)	51 (3)	9 (2)	−8 (2)	−7 (2)
C(65)	7027 (3)	2881 (3)	2386 (3)	46 (3)	39 (2)	45 (3)	3 (2)	−1 (2)	−5 (2)
O(66)	6454 (2)	3236 (2)	2955 (2)	48 (2)	33 (1)	50 (2)	6 (1)	−7 (1)	−4 (1)
O(67)	3355 (2)	3638 (2)	1034 (2)	54 (2)	43 (1)	52 (2)	−4 (1)	−14 (2)	−6 (1)
C(68)	3404 (4)	4602 (3)	−578 (5)	63 (4)	31 (2)	129 (6)	2 (2)	−17 (4)	19 (3)
C(69)	5240 (4)	4170 (3)	−833 (4)	63 (3)	29 (2)	86 (4)	−9 (2)	−1 (3)	11 (2)
C(70)	6046 (4)	3806 (3)	−615 (5)	51 (3)	34 (2)	102 (5)	−7 (2)	11 (3)	2 (2)
C(71)	5404 (4)	1654 (3)	−2012 (4)	78 (4)	49 (3)	54 (3)	3 (3)	1 (3)	−5 (2)
O(72)	4797 (2)	1397 (2)	234 (2)	41 (2)	50 (1)	58 (2)	−1 (1)	6 (1)	8 (1)
C(73)	6234 (5)	337 (3)	399 (4)	100 (5)	35 (2)	78 (4)	18 (3)	5 (3)	−9 (2)
C(74)	6494 (4)	752 (3)	2281 (4)	67 (3)	29 (2)	71 (4)	12 (2)	−5 (3)	6 (2)
C(75)	6325 (4)	1148 (3)	3099 (4)	74 (4)	37 (2)	59 (3)	10 (2)	−12 (3)	9 (2)
C(76)	7865 (4)	3238 (3)	2391 (4)	52 (3)	51 (2)	74 (4)	−6 (2)	5 (3)	−12 (3)
C(77)	7809 (5)	3920 (4)	2084 (5)	82 (4)	50 (3)	96 (5)	−18 (3)	18 (4)	−9 (3)
C(78)	5069 (5)	973 (4)	−1927 (5)	91 (5)	47 (3)	88 (5)	−8 (3)	−6 (4)	−17 (3)
S$_1$(SCN)	9054 (4)	1540 (4)	1678 (6)	120 (4)	103 (3)	233 (7)	38 (3)	11 (4)	17 (4)
S$_2$(SCN)	9847 (4)	1654 (3)	1406 (5)	111 (4)	88 (3)	202 (6)	−40 (3)	−39 (4)	34 (3)
C$_1$(SCN)	8526 (12)	1183 (8)	1264 (12)	147 (14)	45 (6)	118 (13)	18 (7)	−4 (11)	3 (7)
C$_2$(SCN)	10166 (12)	1328 (7)	1605 (13)	138 (13)	28 (4)	147 (15)	−9 (6)	19 (11)	14 (7)

NH_4^+ and carbonyl O atoms in the IR spectra (Pioda, Wachter, Dohner & Simon, 1967) or in the Raman spectra (Asher, Phillies & Stanley, 1974). Nevertheless, even in solution, NH_4^+ is held rigidly in the central cavity of nonactin (Davis, 1975). The crystal structure analysis of an NH_4^+–tetranactin complex was undertaken in order to clarify the relation between the ion selectivity of nactins and the molecular structure of the complex, especially the arrangement of NH_4^+ in the complex. The main points of the present study have already been published and show that the ammonium H atoms form strong hydrogen bonds to the ether O atoms in tetrahedral directions (Nawata, Sakamaki & Iitaka, 1975). Recently the crystal structure of an NH_4^+–nonactin complex has been reported (Neupert-Laves & Dobler, 1976). A comparison of the structures of the ammonium ion complexes with tetranactin and nonactin is therefore made in the present paper.

Experimental

The crystals grown from ethyl acetate–acetone solution (1 : 1, v/v), are prisms, well developed along [101]. The crystal used was cut to the dimensions 0·38 × 0·35 × 0·33 mm.

Crystal data

$C_{44}H_{72}O_{12}.NH_4SCN$, $M_r = 869·17$, monoclinic, $a = 15·889\,(8)$, $b = 20·695\,(10)$, $c = 15·371\,(8)$ Å, $\beta = 90·48\,(5)°$, $Z = 4$, $D_x = 1·142$ g cm^{-3}, $F(000) = 1888$. Space group $P2_1/n$, Cu $K\alpha$ radiation, $\lambda = 1·5418$ Å, $\mu(\text{Cu}\,K\alpha) = 10·2$ cm^{-1}.

Table 2. *Bond lengths* (Å)

The values in parentheses are for chemically equivalent atoms, for which the atomic numbering is expressed by adding 50 to that of the original atoms. $H_i(NH_4)$ and $N(NH_4)$ are abbreviated as H_i and N respectively.

C=O		–C–C–	
C(1)–O(17)	1·211 (1·203)	C(1)–C(2)	1·492 (1·511)
C(9)–O(22)	1·210 (1·205)	C(2)–C(3)	1·517 (1·515)
Mean	1·207	C(2)–C(18)	1·549 (1·559)
		C(3)–C(19)	1·507 (1·513)
–C–O–		C(5)–C(6)	1·490 (1·493)
C(3)–O(4)	1·475 (1·467)	C(5)–C(20)	1·558 (1·531)
C(5)–O(4)	1·465 (1·463)	C(6)–C(7)	1·511 (1·519)
C(7)–O(8)	1·475 (1·470)	C(7)–C(21)	1·533 (1·514)
C(11)–O(12)	1·449 (1·458)	C(9)–C(10)	1·499 (1·526)
C(13)–O(12)	1·457 (1·465)	C(10)–C(11)	1·516 (1·497)
C(15)–O(16)	1·460 (1·466)	C(10)–C(23)	1·545 (1·531)
Mean	1·464	C(11)–C(24)	1·511 (1·523)
		C(13)–C(14)	1·530 (1·501)
–C–O–		C(13)–C(25)	1·513 (1·531)
C(9)–O(8)	1·328 (1·330)	C(14)–C(15)	1·511 (1·509)
C(51)–O(16)	1·338 (1·356)	C(15)–C(26)	1·513 (1·522)
Mean	1·338	C(19)–C(20)	1·546 (1·520)
		C(24)–C(25)	1·524 (1·526)
N–H_i		C(21)–C(28)	1·477 (1·512)
N–H_1	0·88	C(26)–C(27)	1·499 (1·492)
N–H_2	0·79	Mean	
N–H_3	0·92	C(sp^2)–C(sp^3)	1·507
N–H_4	0·80	C(sp^3)–C(sp^3)	1·518
Mean	0·85		

Table 3. *Bond angles* (°)

O(66)–C(1)–C(2)	111·6 (111·9)	O(8)–C(9)–C(10)	112·0 (111·5)
O(66)–C(1)–O(17)	122·4 (123·6)	O(8)–C(9)–C(22)	123·4 (124·3)
O(17)–C(1)–C(2)	126·0 (124·5)	C(9)–C(10)–C(11)	110·4 (109·6)
C(1)–C(2)–C(3)	109·9 (109·6)	C(9)–C(10)–C(23)	107·9 (109·5)
C(1)–C(2)–C(18)	108·7 (107·9)	O(22)–C(9)–C(10)	124·7 (124·1)
C(18)–C(2)–C(3)	110·1 (111·1)	C(10)–C(11)–O(12)	107·6 (107·4)
C(2)–C(3)–O(4)	106·7 (106·6)	C(10)–C(11)–C(24)	115·9 (116·3)
C(2)–C(3)–C(19)	115·1 (116·2)	C(23)–C(10)–C(11)	110·5 (110·8)
C(3)–O(4)–C(5)	110·2 (109·6)	C(11)–O(12)–C(13)	109·7 (110·0)
C(3)–C(19)–C(20)	101·5 (101·3)	C(11)–C(24)–C(25)	101·2 (101·3)
O(4)–C(5)–C(6)	110·1 (109·7)	C(24)–C(11)–O(12)	105·0 (105·0)
O(4)–C(5)–C(20)	104·2 (104·6)	C(24)–C(25)–C(13)	103·3 (103·4)
C(19)–C(20)–C(5)	101·1 (103·3)	O(12)–C(13)–C(14)	108·9 (108·6)
C(19)–C(3)–O(4)	103·5 (104·4)	O(12)–C(13)–C(25)	105·1 (104·6)
C(20)–C(5)–C(6)	113·9 (112·2)	C(13)–C(14)–C(15)	114·6 (115·4)
C(5)–C(6)–C(7)	114·9 (115·4)	C(25)–C(13)–C(14)	113·5 (114·5)
C(6)–C(7)–O(8)	106·6 (106·6)	C(14)–C(15)–O(16)	106·3 (106·2)
C(6)–C(7)–C(21)	114·6 (113·6)	C(14)–C(15)–C(26)	113·1 (114·1)
C(7)–O(8)–C(9)	119·2 (118·0)	C(15)–O(16)–C(51)	119·0 (119·4)
C(7)–C(21)–C(28)	115·0 (114·2)	C(15)–C(26)–C(27)	114·4 (114·0)
C(21)–C(7)–O(8)	106·4 (107·0)	C(26)–C(15)–O(16)	107·8 (107·6)
H_1–N–H_2	105	Mean	
H_1–N–H_3	116	–C(sp^3)–	109·1
H_1–N–H_4	108	–C(sp^2)–	120·0
H_2–N–H_3	108	–N(sp^3)–	109·7
H_2–N–H_4	114		
H_3–N–H_4	107		

5703 independent reflexions with $I > 2\sigma(I)$ were collected on a Philips PW 1100 four-circle diffractometer at 21 °C with Cu $K\alpha$ radiation monochromated by a graphite crystal. The intensities were measured by the θ–2θ scan method with a scan speed 4° (2θ) min^{-1}. The scans were repeated twice when the total number of counts measured during a single scan was less than 10^4. The background was measured at each end of the scan for half the total scan time. Lorentz–polarization factors were applied, but no absorption correction was made. The crystal structure was determined by starting with the structure of the isomorphous Rb^+–tetranactin complex (Sakamaki, Iitaka & Nawata, 1976). The atomic parameters of 57 non-hydrogen atoms (excluding SCN^-) with anisotropic temperature factors were refined to an R value of 0·19 by the least-squares method with block-diagonal approximations. At this stage the positions of the H atoms (including those of NH_4^+) and the SCN^- (disordered) were recognized on the difference Fourier map. Subsequent refinement with anisotropic temperature factors for non-hydrogen atoms as well as for the H atoms of NH_4^+ and with isotropic temperature factors for all other H atoms and the N of SCN^- led to the final R value of 0·080 for 5527 reflexions with $|F_o| \geq 3\sigma(F_o)$. In the final least-squares calculations the following weighting system was adopted: $\sqrt{w} = 110{\cdot}0/|F_o|$ for $|F_o| > 110{\cdot}0$, $\sqrt{w} = 1{\cdot}0$ for $110{\cdot}0 \geq |F_o| > 5{\cdot}0$, and $\sqrt{w} = 0{\cdot}5$ for $|F_o| \leq 5{\cdot}0$. Atomic scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1962) and for H atoms from Stewart, Davidson & Simpson (1965). The e.s.d.'s for C–O, C–C, C–H, N–H bonds and C–C–C angles were about 0·006, 0·008, 0·05, 0·05 Å and 0·4° respectively. The final positional and thermal parameters are given in Table 1.* The atomic numbering is shown in Fig. 1. Bond lengths, bond angles, and internal rotation angles are given in Tables 2, 3 and 4* respectively.

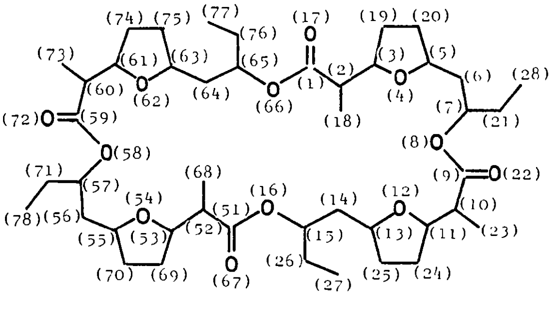

Fig. 1. Structure of tetranactin.

Discussion

The molecular structure of the NH_4^+–tetranactin complex (Fig. 2) seems to be similar to those of the structures of the alkali-metal complexes (Iitaka, Sakamaki & Nawata, 1972). The geometry and the thermal vibrations of the NH_4^+ group in the complex are quite normal (distances N–H = 0·79 ~ 0·92 Å, angles H–N–H = 105 ~ 116°), and there is no indication of rotational disorder of the cation (r.m.s. displacements along the three principal axes of the vibration ellipsoids are 0·17 ~0·40 Å for H_i,† 0·22 ~ 0·25 Å for N,† and 0·21 ~0·33 Å for the atoms in the 32-membered ring). It is noteworthy that the distances of N to the ether O atoms (mean value 2·890 Å) are shorter than those of N to the carbonyl O atoms (2·999 Å), whereas in the

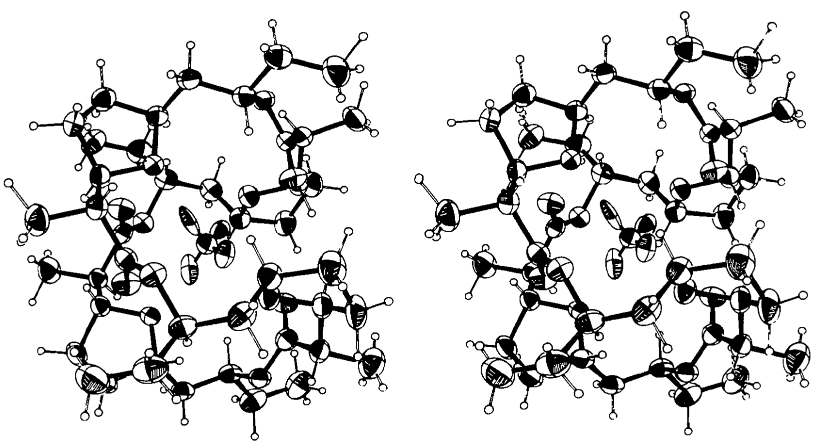

Fig. 2. Stereoscopic drawing of the NH_4^+–tetranactin complex along [101] (*ORTEP*; Johnson, 1965).

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* A list of structure factors, the positional parameters of the H atoms and the N of SCN^-, and Table 4 (internal rotation angles) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32185 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† H_i denotes the *i*th H atom bonded to the ammonium N atom and N denotes the N atom of NH_4^+.

Rb^+–tetranactin complex Rb^+-to-carbonyl O atom distances (mean value 2·909 Å) are appreciably shorter than Rb^+-to-ether O atom distances (2·940 Å), even though the ionic radius of the Rb^+ cation is nearly equal to that of the NH_4^+ (approximately 1·48 Å). As mentioned in the previous paper (Nawata, Sakamaki & Iitaka, 1975), all the H_i atoms participate in strong hydrogen bonds with the ether O atoms, while they interact electrostatically with the carbonyl O atoms (Fig. 3). The reason for the ether O atoms being involved in the hydrogen bonds may be explained by the fact that a lone-pair orbital (l.p.o.) of the ether O atom (a tetrahedral configuration being assumed) nearly points to N while none of the l.p.o.'s of the carbonyl O atom (a trigonal configuration being assumed) points to N (Table 5).

Table 5. *Coordination geometry around* NH_4^+

H_i	O(*j*)	H···O (Å)	θ_1 ; θ_2 (°) (°)	θ'_1 ; θ'_2 (°) (°)	∠N–H···O (°)	N···O (Å)
	Ether oxygen					
H_1	O(12)	1·99	12 ; 97	18 ; 51	174	2·872
H_2	O(4)	2·15	10 ; 99	21 ; 88	169	2·928
H_3	O(62)	1·95	13 ; 96	16 ; 87	172	2·858
H_4	O(54)	2·11	11 ; 98	17 ; 88	175	2·903
	Average	2·05	12 ; 98	18 ; 79	173	2·890
	Carbonyl oxygen					
H_1	O(22)*	2·73	74 ; 80	80 ; 24	97	2·972
H_1	O(72)	2·79	71 ; 79	66 ; 68	99	3·047
H_2	O(17)*	2·78	78 ; 83	75 ; 19	98	2·987
H_2	O(67)	2·73	74 ; 76	74 ; 64	102	2·991
H_3	O(22)	2·72	72 ; 75	72 ; 64	97	
H_3	O(72)*	2·87	76 ; 77	80 ; 23	92	
H_4	O(17)	2·77	75 ; 75	6 ; 68	98	
H_4	O(67)*	2·75	76 ; 82	77 ; 22	100	
	Average	2·77	75 ; 78	66 ; 44	98	2·999

θ_1; θ_2: the angles which determine the direction of the H···O bond with respect to those of the two l.p.o.'s of the ligand O atom.

θ'_1; θ'_2: the angles which determine the direction of the N–H bond with respect to those of the two l.p.o.'s of the ligand O atom.

* In these pairs, H_i's are located in proximity to carbonyl C atoms and are under the influence of repulsive forces caused by the positive partial charge of the C atoms.

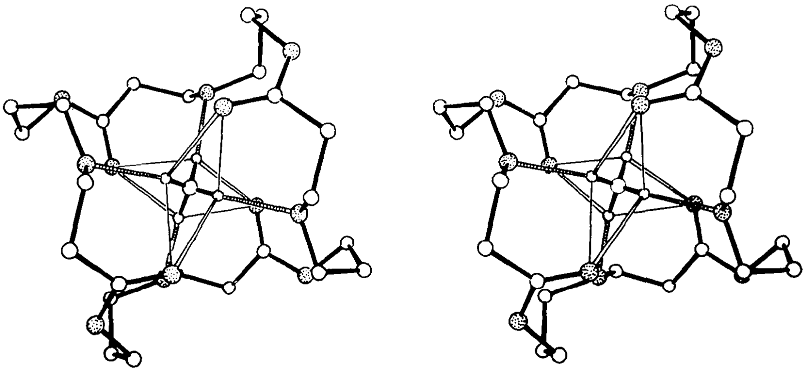
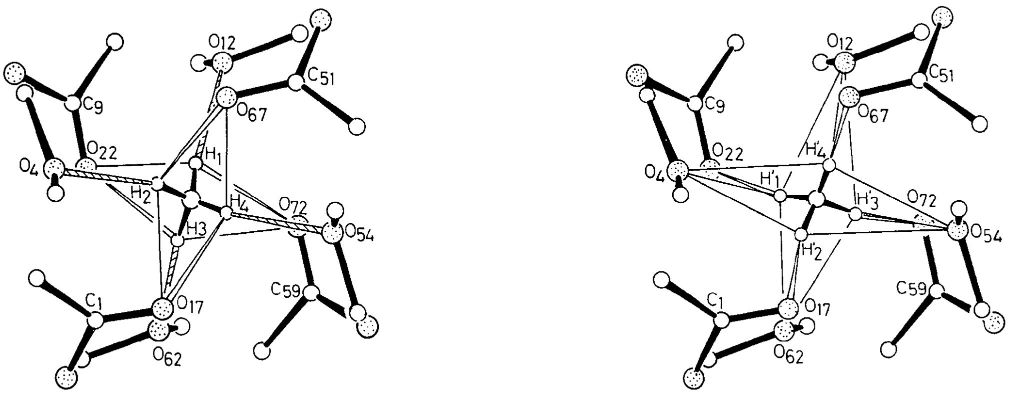


Fig. 3. Stereoscopic drawing of the 32-membered ring of the complex along [010]. Hydrogen bonds are shown as shaded bonds. Weak and strong electrostatic interactions are indicated by the interatomic single and double lines respectively. O atoms are shown as stippled circles.



(a) (b)

Fig. 4. (a) Observed and (b) hypothetical coordination geometry viewed along [010].

Table 6. *Distortion of the arrangement of ligand* O *atoms from a cube*

R.m.s. deviations are given in parentheses.

	Av. edge angle (°)	Av. edge length (Å)	Av. face diagonal length (Å)	Av. body diagonal length (Å)	N···O (Å) (ether oxygen)	N···O (Å) (carbonyl oxygen)
NH_4^+–tetranactin	88·4	3·437	4·785	5·811	2·890	2·999
	(10·3)	(0·256)	(0·489)	(0·044)	(0·026)	(0·026)
NH_4^+–nonactin*	88·8	3·454	4·828	5·881	2·857	3·078
	(9·5)	(0·269)	(0·470)	(0·066)	(0·020)	(0·062)

* Neupert-Laves & Dobler (1976).

For a hypothetical structure* obtained by a simple 90° rotation of NH_4^+, the H'_i atoms would form hydrogen bonds with the carbonyl O atom and the distances of $H'_i\cdots$O(carbonyl) and $H'_i\cdots$O(ether) would lie in the ranges 2·15 ~ 2·25 and 2·54 ~ 2·94 Å respectively. In this structure θ_1 and θ_2, defined in Table 5, would be 78 ~ 83° and 83 ~ 92° for the carbonyl O atoms, and 4 ~ 29° and 85 ~ 114° for the ether O atoms. Following Lippincott & Schroeder (1955) and Scott & Scheraga (1966), the potential energy function of the NH···OC hydrogen bonding involves a term strongly dependent on the angles θ_1 and θ_2. A rough estimate of the potential energies for the observed and hypothetical structures indicates the former to be more stable, since the hydrogen-bond distances $H'_i\cdots$O(carbonyl) in the latter are longer than distances $H_i\cdots$O(ether) in the former and all the θ_1 and θ_2 angles for the carbonyl O atoms in the latter structure are approximately 90° (the smallest angle being 78°). Furthermore, in the latter structure all the H'_i's are in proximity to the carbonyl C atoms (2·64 ~ 2·78 Å; in contrast to the corresponding distances in the former for the strong and weak electrostatic interactions, 3·51 ~ 3·56 and 3·08 ~ 3·14 Å respectively), and the repulsive forces between the partial positive charges of the carbonyl C atoms and ammonium H atoms will cause the structure to be very unstable (Fig. 4). In this intramolecular environment of tetranactin for the NH_4^+ ion, a strong interaction between the NH_4^+ ion and the ether O atoms may explain the very high selectivity of nactins for the ammonium ion.

As shown in Table 6, the N···O(ether) distances are appreciably shorter in the NH_4^+–nonactin complex than in the NH_4^+–tetranactin complex and the effect of hydrogen bonding is more clearly demonstrated in the former. This may suggest that tetranactin is less deformable than nonactin as already suggested by the crystal structure analyses of Cs^+ complexes of tetranactin and nonactin (Sakamaki, Iitaka & Nawata, 1977).

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* Hypothetical positions of H_i (hereinafter denoted as H'_i) are obtained by a 90° rotation of NH_4^+ around the approximate two-fold symmetry axis of the complex so that the N–H···O hydrogen bonds are formed with the carbonyl O atoms.

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The Crystal and Molecular Structure of Bis(cyclopentadienyl)(σ-allyl)(carbon disulphide)niobium

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Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, $a = 7{\cdot}59(1)$, $b = 13{\cdot}60(1)$, $c = 26{\cdot}47(2)$ Å, $Z = 8$. 1178 independent reflexions above background were measured on a diffractometer and the structure has been refined to R 0·070. There are two independent monomers in the asymmetric unit related by a pseudo-centre of symmetry which caused considerable difficulty in the refinement. Each Nb atom is bonded to two cyclopentadienyl rings [2·372 (22)–2·500 (21) Å], to an allyl group [2·309 (31) Å] and to carbon disulphide through a S atom [2·518 (9) Å] and a C atom [2·241 (21) Å]. This C—S bond length is 1·720 (24) Å while the other C—S retains much of its double-bond character [1·574 (23) Å]. The S—C—S angle is 136·8 (14)°. The overall geometry of the complex is similar to that usually found for $(C_5H_5)_2MX_2$ complexes.

We have carried out and report here the structure determination of bis(cyclopentadienyl)(σ-allyl)(carbon disulphide)niobium (I), a complex recently prepared by Fowles, Pu & Rice (1973). Only one structure including the carbon disulphide group bonded to a transition metal has previously been reported, namely $Pt(PPh_3)_2(CS_2)$ (Mason & Rae, 1970). In that structure the metal atom is bonded to one S and the C atom with a S—C—S angle of 136 (4)°. The dihedral angle between the CS_2 and PtP_2 planes is 6°. We were interested to see whether the bonding of the carbon disulphide group to an early transition metal would be equivalent.

The structures of a series of complexes of the form $(C_5H_5)_2MX_2$ (X=monodentate ligand) in which the metal atom is bonded to two non-parallel η^5-cyclopentadienyl rings and to two ligands X in the plane between the rings have been summarized by Prout, Cameron, Forder, Critchley, Denton & Rees (1974). Although (I) has the form $(C_5H_5)_2MX(X{-}X)$, $X{-}X$ being a bidentate ligand, its structure might be expected to be comparable.

Experimental

Crystals (red-wine plates) were prepared as described previously by Fowles, Pu & Rice (1973).

Crystal data

$C_{14}H_{15}S_2Nb$, $M_r = 340{\cdot}31$, orthorhombic, $a = 7{\cdot}59(1)$, $b = 13{\cdot}60(1)$, $c = 26{\cdot}47(2)$ Å, $Z = 8$, $U = 2732{\cdot}3$ Å^3, $D_m = 1{\cdot}68$ (2), $D_c = 1{\cdot}66$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 17{\cdot}85$ cm^{-1}; space group $P2_12_12_1$