CHEMISTRY LETTERS, pp. 151-154, 1975. Published by the Chemical Society of Japan

HYDROGEN BOND IN THE NH_4^+-TETRANACTIN COMPLEX[1)]

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The molecular structure of the NH_4^+-tetranactin complex was determined by the X-ray diffraction method. The ammonium H atoms form strong hydrogen bonds to the ether O atoms in tetrahedral directions. They also interact electrostatically with the carbonyl O atoms. No signs of rotational disorder were detected for the NH_4^+ ion at 21° C.

Nonactins (Fig.1), one of the electrically neutral ionophore, exhibit a high NH_4^+ selectivity in cation transport through lipid bilayer membrane[2),3)]. The existence of a strong ion-dipole interaction between the cation and the carbonyl O atoms has been shown for alkali metal complexes of nonactins[4-7)] on the basis of IR, Raman and NMR spectroscopies. On the other hand, it has been suggested that the strong interaction between NH_4^+ and ether O atoms dominates in ammonium complexes of nonactins[8),9)] in connection with cation selectivity. The present letter

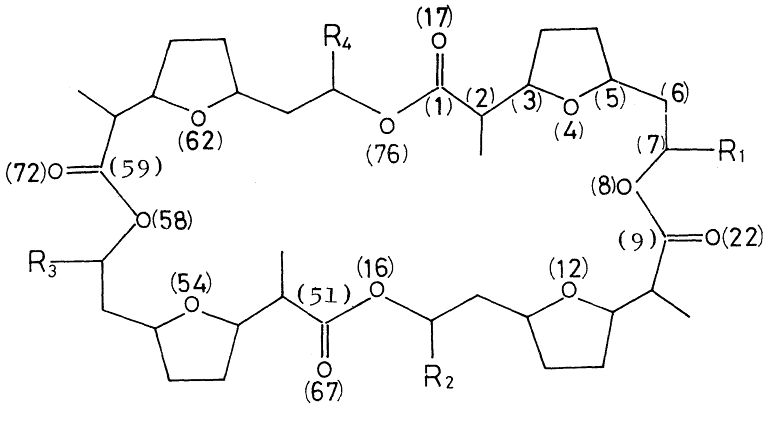

Fig. 1. Structures of tetranactin and nonactin
R1=R2=R3=R4=ethyl: tetranactin, R1=R2=R3=R4=methyl: nonactin.

describes the coordination geometry of oxygen atoms around the NH_4^+ ion in the ammonium tetranactin complex determined by the X-ray diffraction method.

For the X-ray diffraction experiment, a single crystal of the NH_4^+-tetranactin complex of Form I$^{10,11)}$ was used (Table 1). Reflexion data were collected on a Philips PW 1100 computer-controlled 4-circle X-ray diffractometer with Cu Kα radiation (graphite monochromated) by a θ-2θ scan method. The crystal structure of the NH_4^+ complex was assumed to be isomorphous with that of the Rb^+ complex$^{11)}$. The atomic parameters of the nitrogen atom which was put into the structure in place of the rubidium ion were refined along with those of 12 oxygen and 44 carbon atoms by the block-diagonal least-squares method using the intensity data of the NH_4^+-tetranactin crystal. The positions of 76 hydrogen atoms (including those of the NH_4^+ ion) and the SCN^- anion (disordered) were found on a difference Fourier map. At present, the R index was 8 % for 5527 reflexions ($Fo > 3\sigma Fo$) assuming

Table 1. Crystal Data

NH_4^+-tetranactin ($C_{44}H_{72}O_{12}\cdot NH_4SCN$), Form I crystal, F.W.=869.11, Space group=$P2_1/n$, a=15.889, b=20.695, c=15.371 Å, β=90.48°, Z=4, μ(Cu Kα)=12.7 cm^{-1}, Number of observed independent reflexions: 5703, measured at 21° C , Crystal dimension: 0.375×0.350×0.325 mm.

Table 2. Interatomic distances (Å) and angles (°) of NH_4^+

N—H1	0.88 (5)	∠H1—N—H2	105 (5)	∠H2—N—H3	108 (5)
N—H2	0.79 (5)	∠H1—N—H3	116 (4)	∠H2—N—H4	114 (5)
N—H3	0.92 (5)	∠H1—N—H4	108 (4)	∠H3—N—H4	107 (4)
N—H4	0.80 (4)				

Estimated standard deviations in the least significant digit are given in parentheses.

Table 3. Thermal vibrations*' of N and H atoms of NH_4^+

	D1	D2	D3		D1	D2	D3
N :	0.22,	0.23,	0.25	H3 :	0.20,	0.28,	0.37
H1 :	0.13,	0.26,	0.40	H4 :	0.21,	0.25,	0.33
H2 :	0.21,	0.29,	0.32				

(*' Root mean square displacement Di (Å) along the i-th principal axis of vibration ellipsoids) anisotropic temperature factors for C, O, N, S and H of NH_4^+ and isotropic ones for N of SCN^- and H. The estimated standard deviations were about 0.008 Å for C-C bond, 0.05 Å for N-H bond and 0.4° for C-C-C angle. The geometry of NH_4^+ (Table 2) as well as the thermal vibrations of the individual atoms of NH_4^+ (Table 3) were normal and no signs of rotational disorder of NH_4^+ were observable.

Although the conformation of the NH_4^+-tetranactin complex was substantially identical with those of alkali metal complexes of tetranactin[11], a remarkable difference was observed for the distances between the central ion and the surrounding oxygen atoms. N-to-ether O distances (2.859～2.929 Å) were significantly shorter than those of N-to-carbonyl O (2.971～3.048 Å), indicating the existence of stronger interactions between NH_4^+ and the ether O atoms than those between NH_4^+ and the carbonyl O atoms, contrary to that observed in the alkali metal complexes[11,12].

As shown in Fig.2.(a) and (b), the ether O atoms are located in proximity to H atoms of NH_4^+ (1.95～2.15 Å), and the ether O-to-H directions make the small angles (10°～13°) with those of the lone-pair orbitals of the ether O atoms. Accordingly, strong hydrogen bonding can be expected for the interactions between NH_4^+ and the ether O (Fig.2). Each carbonyl O atom, on the other hand, is in the

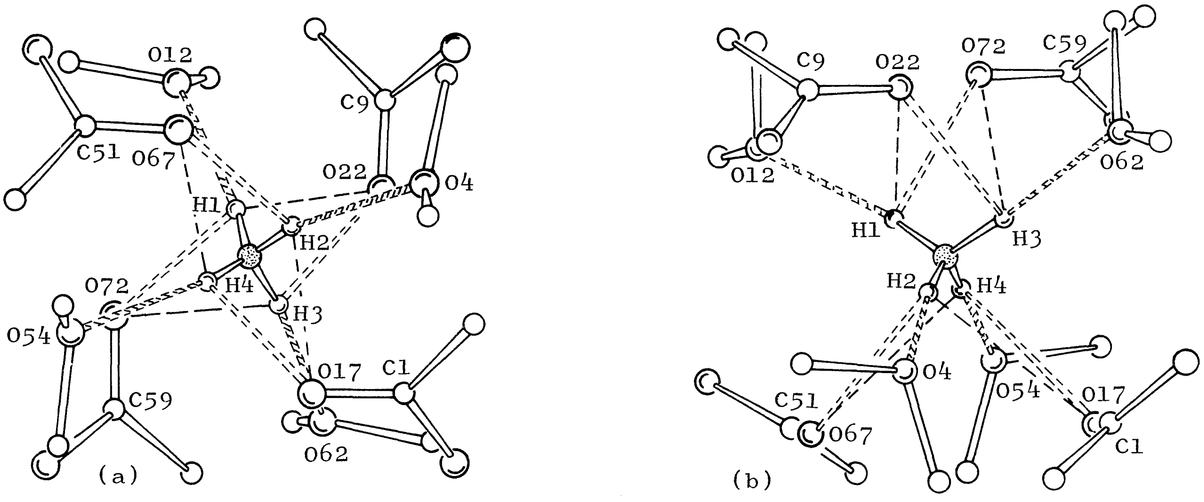

Fig. 2. The coordination geometry of the carbonyl O (O67, O22, O17, O72) and the ether O (O12, O4, O62, O54) atoms around the ammonium ion in the NH_4^+-tetranactin complex; (a) viewed down along [010] and (b) along [001]. Hydrogen bonds are shown by broken double lines with shading. Weak and strong interactions are indicated by the interatomic bonds of broken single lines and broken double lines, respectively. ◯ = O, ◌ = N, ○ =C, and ⊖ = H.

position to interact electrically with N^+, and lies in proximity to the two H atoms of NH_4^+ (2.72～2.87 Å) and the carbonyl O-to-H directions make the angles of 71°～78° with those of the lone-pair orbitals of the carbonyl O atoms, which are quite larger than those found in the case of the ether O atoms. It is noteworthy that the one of the two H atoms lying in proximity to the carbonyl O (e.g. H1 for O22 in Fig. 2) approaches to the carbonyl carbon atom (3.08～3.14 Å), and is under the influence of repulsive forces caused by the positive partial charge of the carbon atom. The net electrostatic interactions between these H and O atoms may therefore be greatly reduced. In the NH_4^+-tetranactin complex, the ammonium H atoms participate in strong hydrogen bonding to the ether O atoms in tetrahedral directions (∠O····H–N: 168°～176°) and at the same time they interact electrostatically with the carbonyl O atoms (∠O····H–N: 96°～102°).

The samples of tetranactin were isolated by Dr. K. Ando of Chugai Pharmaceutical Co., Ltd., to whom the authors' thanks are due. Thanks are also due to Dr. Y. Harada of Faculty of Pharmaceutical Sciences, University of Tokyo, for preparing the computer programs for the HITAC 8800/8700 at the Computer Centre of the University of Tokyo.

A Footnote and References

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(Received November 29, 1974)