## CRYSTAL STRUCTURE AND THERMAL STABILITY OF AMMONIUM ADIPATE $(NH_{4})_{2}C_{6}H_{8}O_{4}$

I. A. Teslya, A. I. Tursina, L. D. Iskhakova, L. M. Avdonina, and V. V. Marugin

An x-ray structural investigation of ammonium adipate  $(NH_4)_2AD$  has been carried out  $(CAD-4, \lambda Mo, R = 0.041, R_W = 0.038, 938$  reflections). The parameters of the monoclinic cell are: a = 6.150(1), b = 8.897(1), c = 8.690(1) Å,  $\beta = 98.21(1)^{\circ}$ , Z = 2, space group  $P2_1/c$ . The dependence of the geometry of the adipate ion on the character of the hydrogen bonds and on the size and coordination environment of the cation has been examined. The influence of H bonds on the packing of the molecules in the structure has been analyzed. A thermographic investigation of the compound has been carried out, and the parameters of the model of the kinetic equation of the decomposition step to  $NH_4HAD$  have been found.

The use of ammonium adipates in the electronics industry has caused the need for investigations of the physicochemical properties and structure of these compounds. The interpretation of their structures is important not only from the crystal-chemical point of view, but also because it is the means for establishing the composition of compounds due to the lack of reliable chemical methods of analysis for the adipate ion.

The literature data on ammonium adipates are restricted to the results of goniometric measurements of crystals of the neutral salt (monoclinic, a:b:c = 0.6880:1:0.9787,  $\sigma$  = 82°14') and a salt of unknown composition (triclinic, a:b:c = 0.8474:1:0.5496,  $\alpha$  = 90°20',  $\beta$  = 95°10',  $\gamma$  = 100°56' [1]) and data on the solubility of the neutral salt at 14°C [2] and its dissociation pressure at t > 100°C [3].

The purpose of the present work was to determine the structure and thermal stability of ammonium adipate  $(NH_4)_2C_6H_8O_4$  (the composition was established during the x-ray structural investigation).

## EXPERIMENTAL

The crystals of ammonium adipate  $(NH_4)_2AD$  were obtained by means of the isothermal evaporation of solutions containing ammonia and adipic acid  $(H_2AD)$  in a 2:1 mole ratio at room temperature. The experimental set of intensities was obtained on a CAD-4 autodiffractometer (MoK $\alpha$ ,  $\omega/\theta$  scan technique, single crystal measuring 0.28 × 0.21 × 0.087 mm). The unit-cell parameters are: a = 6.150(1), b = 8.897(1), c = 8.690(1) Å,  $\beta$  = 98.21(1)°, Z = 2, space group P2<sub>1</sub>/c,  $\rho_{cal}$  = 1.272 g/cm<sup>3</sup>. A total of 1633 independent nonzero reflections were recorded in the range 0 <  $\theta$  < 32°. The treatment of the data and all the calculations were carried out with the use of the ENX-SDP system of programs on a PDP 11/t55 computer. The structure was solved by the direct method (MULTAN 11/82). The coordinates of the hydrogen atoms were located on the basis of difference Fourier syntheses. The final refinement of the positional and thermal parameters (in the anisotropic approximation for the nonhydrogen atoms and the isotropic approximation for the hydrogen atoms) was performed by introducing a single weighting scheme and taking into account the secondary extinction on the basis of 936 reflections with I > 3\sigma(I) and gave R = 0.041, R\_W = 0.038, and S = 0.349. The extinction coefficient  $\varepsilon$  = 8.7(1)·10<sup>-6</sup>.

The coordinates of the atoms are presented in Table 1, and the molecular structure is depicted in Fig. 1, which also presents the principal bond lengths and bond angles. The packing of the molecules is shown in Fig. 2.

Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Substances. Translated from Zhurnal Strukturnoi Khimii, Vol. 31, No. 6, pp. 123-127, November-December, 1990. Original article submitted October 13, 1988.

TABLE 1. Coordinates of Atoms ( $\times 10^4$ ,  $\times 10^3$ for H) and Their Isotropic Equivalent Temperature Parameters  $B_{iso}^{eq}(A^2)$ 

Atom	x/a	<b>y</b> /b	z/c	B <sup>eq</sup> iso	
N	2715(2)	3766(2)	699(2)	2,52(2)	
O(1)	1699(2)	6867(1)	470(2)	3,17(2)	
O(2)	5047(2)	7477(2)	1565(2)	3,20(2)	
C(1)	19(3)	9824(2)	854(2)	2,68(3)	
C(2)	2246(3)	9297(2)	1661(2)	3,18(3)	
C(3)	3035(3)	7775(2)	1180(2)	2,23(3)	
HN(1)	128(3)	336(2)	53(2)	3,3(4)	
HN(2)	345(3)	345(2)	6(2)	4,2(5)	
HN(3)	333(3)	337(2)	168(2)	4,9(5)	
HN(4)	261(3)	481(2)	76(2)	4,6(5)	
HC(11)	42(3)	576(2)	360(2)	3,5(4)	
HC(12)	109(3)	406(2)	400(2)	3,4(4)	
HC(21)	219(4)	577(3)	781(3)	6,3(6)	
HC(22)	338(3)	493(2)	648(2)	4,7(5)	



Fig. 1

Fig. 1. Structure of a molecule of ammonium adipate with the principal bond lengths and bond angles.

Fig. 2. Packing of molecules in the structure of ammonium adipate.

The thermographic investigation of the samples was carried out on the Q-1500D derivatograph of a Paulik-Paulik-Erdey system and a THY-2000C derivatograph from Setaram (France). The temperature was scanned in the 20-500°C range at the rate of 5 deg/min. Weighed portions with masses from 30 to 40 mg were placed in platinum crucibles, and calcined aluminum oxide served as the standard. The x-ray diffraction investigation of the decomposition products of the adipate was carried out on a FR-522 monochromator-camera system (CuKa radiation, germanium as an internal standard).

## RESULTS AND DISCUSSION

A comparison of the unit-cell parameters of  $(NH_4)_2AD$  with the goniometric data in [1] reveals that (NH4)2AD was also studied in the work cited.

The structure of  $(NH_4)_2AD$  has the form of a three-dimensional array, in which the  $C_6H_8O^{2-1}$ adipate ions (AD) are bound to the ammonium ions both by forces of electrostatic interaction and by a three-dimensional system of hydrogen bonds.

The adipate ion in the structure of  $(NH_4)_2AD$  is centrosymmetric in analogy to the adipate ion in the structures of the acid  $H_2AD$  [4], bis(N-methylethylenediamine)copper(II) adipate dihydrate [5], and hexamethylene diammonium adipate [6]. The symmetry center is lost in the acid salts, for example, in lithium acid adipate LiHAD [7].

The structure of AD under consideration contains a planar fragment of our carbon atoms of the type -C(2)-C(1)-C(1')-C(2')-. The terminal atoms of the hydrocarbon chain [C(3) and C(3')] deviate 1.256(2) Å from the mean-square plane drawn through them, and each carboxylate group is turned at an angle  $\varphi = 77.5^{\circ}$  to it.

It is seen from a comparison of the structures of  $H_2AD$  [4], LiHAD [7], and  $(NH_4)_2AD$  that the geometry of the adipate ion (the planarity of the  $C-(C)_4-C$  fragment and the

values of the angle  $\varphi$ ) depends on the character of the hydrogen bonds and on the size and coordination environment of the cation. The planarity of this fragment can be characterized by the values of the largest deviations ( $\Delta$ ) from the mean-square plane drawn through all six carbon atoms of AD.

In  $H_2AD$  and LiHAD strong hydrogen bonds of the OH...O type with the participation of the carboxyl groups (the O...O contacts measure 2.64 [4] and 2.486(2) Å [7], respectively) form parallel to the axis of the hydrocarbon fragments and join the latter in infinite chains extended in the same direction. These bonds tend to be located in the plane of the hydrocarbon fragments; for example, in  $H_2AD$  the deviation of the atoms from the plane of

 $-C < \bigcirc C - H - O \\ O - H - O$ 

are almost planar, and the values of the angle  $\varphi$  for the carboxyl groups are small; the values of  $\Delta$  and  $\varphi$  are equal to 0.044 Å and 6.2° and to 0.040 Å and 2.9°, respectively. In LiHAD the tiny lithium atoms are accommodated between the layers of HAD ions, and the te-trahedral environment typical of lithium is achieved by rotating each carboxylate group through an angle  $\varphi = 67.7^{\circ}$ .

In the structure of  $(NH_4)_2AD$  the coordination environment of the  $NH_4$  cation is formed by the oxygen atoms of carboxylate groups which are simultaneously acceptors in hydrogen bonds of the NH...O type. When an ammonium ion forms fairly strong H bonds, its coordination polyhedron is usually a distorted tetrahedron. In the structure under consideration, it is formed as a result of rotation of the carboxylate groups through an angle  $\varphi = 77.5^{\circ}$ . The placement of the large ammonium cations between the adipate ions (see Fig. 2) violates the planarity of the adipate fragment as a result of the aforementioned deviation of the terminal carbon atoms ( $\Delta = 0.333$  Å).

The lengths of the  $C(sp^3)-C(sp^3)$  and  $C(sp^3)-C(sp^2)$  bonds in the structure of  $(NH_4)_2AD$  are equal within the range of the tripled error in their determination. Such equalization of the bonds occurs in all adipate ions with  $-COO^-$  groups.

The lengths of the  $C(sp^3)$ -H bonds are equal to 0.99(2)-1.02(2) Å (the mean value is 1.01 Å).

The idealized model of a carboxylate group obtained in [8] on the basis of a statistical treatment of the structural data for 70 compounds containing -COO<sup>-</sup> and -COOH groups is distinguished by the equality of the two C-O bonds [1.25(2) Å] and of the values of the CCO angles  $[117(2)^{\circ}]$ . In a more recent report [9] the geometry of a -COO<sup>-</sup> group was characterized by bond lengths equal to 1.252(2) Å and an OCO angle equal to  $125.6(2)^{\circ}$ . As a whole, the structure of the carboxylate groups in  $(NH_4)_2AD$  conforms to the idealized model within the range of error. In addition, the slight difference between the lengths of the C-O bonds correlates with the difference between the strengths of the hydrogen bonds in which the O(1) and O(2) atoms participate as acceptors (see Fig. 2, Table 2).

The NH<sub>4</sub><sup>+</sup> ion is a slightly distorted tetrahedron with  $R_{N-H} = 0.90$  to 0.95(2) Å and HNH angles equal to 104-114(2)°. It is coordinated by four oxygen atoms from the carboxylate groups of four adipate ions. The mean N...O distance, which is equal to 2.812 Å, is close to the mean value of  $R_{N...O}$  for an ammonium ion coordination number of 4 (2.86 Å) [10].

The ammonium ion forms ordinary hydrogen bonds (Table 2).

H bonds	Distance, Å	N <del>-H</del> O angle, deg	Symmetry elements for $0_i$ atoms
I NII(4) O(1) II NH(1) O(1)' III NH(2) O(2)'' IV NH(3) O(2)'''	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	464(2) 457(2) 473(2) 470(2)	$ \begin{vmatrix} x, y, z \\ \overline{x}, \frac{1}{2} - y, \overline{z} \\ 1 - x, 1 - y, \overline{z} \\ 1 - x, y - \frac{1}{2}, \frac{1}{2} - z \end{vmatrix} $

TABLE 2. Geometric Characteristics of the Hydrogen Bonds in the Structure of  $(\rm NH_4)_2AD$ 

The packing of the adipate ions in the crystal structure is caused by the hydrogen bonds and is organized in the following manner. Layers parallel to the XY plane, in which each NH<sub>4</sub> ion binds three adipate ions by means of hydrogen bonds of types I-III (Fig. 2), can be identified in the structure. These layers are joined to form a three-dimensional framework by hydrogen bonds of type IV. The parallel hydrocarbon fragments of the adipate ions are oriented in a layer in such a manner that the angle between the normals to the planar fragment and to the layer is equal to  $103.4^{\circ}$ . The hydrocarbon fragments in two neighboring layers, which are related by the c plane, are at a  $37.5^{\circ}$  angle relative to one another. The shortest contact between the hydrogen atoms of neighboring hydrocarbon fragments exceed 3 Å.

The compound  $(NH_4)_2AD$ , which was investigated here, is the most stable compound among the ammonium adipates [11].

The thermographic investigation in air (including the visual thermal analysis) showed that the decomposition of  $(NH_4)_2AD$  is preceded by cracking of the sample and the conversion of the single crystal into a finely crystalline state at 72°C [a slight endothermic effect is observed on the dT( $\tau$ ) curve at that temperature].

Several steps can be identified on the  $M(\tau)$  curve in the 100-200°C range. The first step, which is the most clearly expressed, corresponds to the endothermic effect on the  $dT(\tau)$  curve at 138°C. The calculation of the relative mass loss from the sample in this step, as well as a specially conducted x-ray diffraction investigation, indicate that 1 mole of NH<sub>3</sub> is eliminated and the acid adipate forms in this step:

$$(\mathrm{NH}_4)_2\mathrm{AD} \rightarrow \mathrm{NH}_3 \uparrow + (\mathrm{NH}_4)\mathrm{HAD}.$$

Further elimination of the residual ammonia probably occurs next. The final decomposition product in this temperature range (100-200°C) is adipic acid [the significant endothermic effect on the dT( $\tau$ ) curve at 158-160°C, which should, in all likelihood, be associated with the melting of H<sub>2</sub>AD, should be mentioned]. The formation of adipic acid is confirmed both by the agreement between the mass loss calculated from the M( $\tau$ ) curve (up to 200°C), which is equal to 18.7% of M<sub>0</sub>, and the mass loss calculated according to the stoichiometry of the reaction (NH<sub>4</sub>)<sub>2</sub>AD  $\rightarrow$  2NH<sub>3</sub>  $\uparrow$  + H<sub>2</sub>AD, which is equal to 18.8% of M<sub>0</sub>, and by the x-ray powder diffraction analysis of the residue: all the lines in its x-ray diffraction pattern are indexed in the parameters of the monoclinic cell presented in [4] for H<sub>2</sub>AD.

Vigorous decomposition of the sample then occurs in the 230-280°C temperature range. The maximum for the rate of the process at a temperature of 270°C coincides with the beginning of an exothermic effect on the  $dT(\tau)$  curve. This stage of the decomposition process probably includes decarboxylation and degradation of the hydrocarbon skeleton of the original sample accompanied by removal of the decomposition products (including the oxidation products). After completion of the experiment, a "carbonaceous" substrate remained in the crucible.

The portion of the experimental  $M(\tau)$  curve corresponding to the removal of 1 mole of  $NH_3$  with the formation of the acid adipate was approximated by the least-squares method to the model kinetic equation for topochemical reactions:

$$\frac{d\alpha}{d\tau} = z \cdot e^{\frac{-E_a}{RT}} (1-\alpha)^n,$$

where  $\alpha$  is the extent of conversion, z is the pre-exponential factor in the Arrhenius equation (sec<sup>-1</sup>),  $E_a$  is the activation energy (kcal/mole), and n is the generalized reaction order.

The parameters of the model equation were found:  $z = 9.2 \cdot 10^5 \text{ sec}^{-1}$ ,  $E_a = 17.4 \text{ kcal/mole}$ , n = 0.21.

## LITERATURE CITED

- 1. B. Bücking and M. Ladenburg, Ann. Chem., <u>217</u>, 141-143 (1983).
- 2. Z. McMater, J. Am. Chem. Soc., <u>36</u>, 742-747 (1944).
- 3. W. Biltz and G. Balz, Z. Anorg. Allg. Chem., <u>170</u>, 340-343 (1928).
- 4. J. Housty and M. Hospital, Acta Crystallogr., <u>18</u>, No. 4, 693-697 (1965).
- R. Hämäläinen, U. Turpeinen, and M. Ahlen, Acta Crystallogr., <u>B35</u>, No. 10, 2408-2410 (1979).
- 6. C. J. Brown, Acta Crystallogr., 21, No. 2, 185-190 (1966).
- 7. X. He and B. M. Graven, Acta Crystallogr., <u>C40</u>, No. 7, 1157-1159 (1984).
- 8. P. W. Borthwick, Acta Crystallogr., <u>B36</u>, No. 3, 628-632 (1980).
- 9. F. H. Allen, Acta Crystallogr., <u>B42</u>, No. 4, 515-522 (1986).
- 10. A. A. Khan and W. H. Baur, Acta Crystallogr., B28, No. 4, 683-693 (1972).
- L. M. Avdonina, L. D. Iskhakova, I. A. Teslya, et al., Zh. Neorg. Khim., <u>34</u>, No. 3, 771-775 (1990).