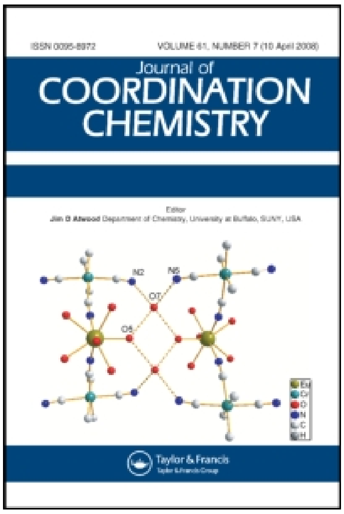

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Crystal Structure, Thermal Analysis and Spectroscopic Study of Sodium 3,4-Diaminobenzoate

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CRYSTAL STRUCTURE, THERMAL ANALYSIS AND SPECTROSCOPIC STUDY OF SODIUM 3,4-DIAMINOBENZOATE

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The structure and infrared spectrum of sodium 3,4-diaminobenzoate have been studied. The sodium salt crystallizes in the orthorhombic system, space group *Pcab* with $a = 6.1940(10)$, $b = 14.285(3)$, $c = 21.348(4)$ Å, and $Z = 8$. The compound is polymeric in which Na ions are coordinated to six oxygen atoms, with Na–O distances ranging from 2.3380(14)–2.5856(18) Å. The compound dehydrates at 340 K and is decomposed at 485 K. IR spectra of the salt are discussed.

Keywords: Sodium 3,4-diaminobenzoate; IR spectra; Thermal analysis; X-ray structure

INTRODUCTION

Metal compounds with 3,4-diaminobenzoic acid (DABA) were reported as the haloplatinate(II) and halopalladate(II). These compounds have shown cytotoxicity against P388 lymphocytic leukemia cells. DABA is bonded with the metal through both nitrogen atoms of the amino groups [1]. In the sodium salt as well as in lanthanide complexes, which were described earlier, the metal ions coordinate with 3,4-diaminobenzoic ligands with oxygen atoms of the carboxylate group [2].

Free DABA exists in the solid state in the zwitterion form and thus the acid molecules are connected by a quite different system of hydrogen bonds than is typical of carboxylic acids [3,4]. During a systematic investigation of lanthanide complexes with aminobenzoic acids the authors frequently used a spectroscopic criterion in evaluating the mode of carboxylate group–metal ion coordination. Sodium 3,4-diaminobenzoate salt was used as a reference [5]. The crystal structure of Na(DAB) and its IR spectrum are presented below.

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EXPERIMENTAL

X-ray Structure Determination

A suitable crystal was obtained by slow evaporation of an aqueous solution. The crystal system, space group and approximate unit cell dimensions were determined from Weissenberg photographs. Intensities of reflections were measured on a Kuma KM-4 diffractometer using MoK_{α} radiation. Crystallographic data and the refinement details are given in Table I. Intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct method using SHELXS-97 and refined by full-matrix least-squares methods using the SHELXL97 program [6,7]. The positions of all hydrogen atoms were determined from difference Fourier maps. Several cycles of refinement of coordinates and thermal parameters (anisotropic for non-hydrogen and isotropic for hydrogen atoms) reduced the R value to 0.0359. Scattering factors were those incorporated in SHELXL97. Final atomic and selected bonding parameter are listed in Tables II and III.

IR Spectra

IR spectra of complexes were recorded over the range 4000–400 cm^{-1} using a Perkin Elmer 1725X FTIR spectrometer. Samples were prepared as KBr discs.

Thermal Analysis

The thermal stability of the salt in air was determined using a Setsys 16/18 TG, DTA instrument. Samples (10.3 mg) were heated in Al_2O_3 crucibles at 293–1273 K in flowing air with a heating rate of 10 K min^{-1}. Products of decomposition were calculated from

TABLE I Crystal data and structure refinement details

Formula	$C_6H_3(NH_2)_2COONa \cdot 2H_2O$
M_r	210.17
Crystal system	Orthorhombic
Space group	*Pcab*
T (K)	293
Wavelength (Å)	0.71069
a (Å)	6.194(2)
b (Å)	14.285(3)
c (Å)	21.348(4)
Volume (Å^3)	888.9(6)
Z	8
F(000)	880
Absorption coefficient (cm^{-1})	0.158
Density (calculated) mg/m^3	1.478
Crystal size mm	0.25 × 0.25 × 0.40
Reflections measured	1860
2θ rang for data collection, deg.	4.0–54.2
Index ranges	$0 \leq h \leq 7$, $0 \leq k \leq 18$, $0 \leq l \leq 27$
Data [$I > 2\sigma(I)$]/parameters	1615/172
Goodness-of-fit on F^2	1.035
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0359$, $wR2 = 0.0987$
R indices (all data)	$R1 = 0.0427$, $wR2 = 0.1014$
Extinction coefficient	0.039(2)
Largest diff. peak and hole (e Å^{-3})	0.657 and − 0.175

TABLE II Final atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non-hydrogen atoms with esd values in parentheses for sodium 3,4-diaminobenzoate

Atom	*X/a*	*y/b*	*z/c*	U_{eq}^*
Na	– 0.08976(12)	0.26318(5)	0.50619(3)	0.0298(2)
O(1)	0.1792(2)	0.32642(9)	0.44204(5)	0.0313(3)
O(2)	0.3631(2)	0.44911(10)	0.40638(6)	0.0384(4)
O(3)	0.1556(2)	0.29327(10)	0.58797(6)	0.0337(3)
O(4)	– 0.3563(3)	0.38668(11)	0.50189(7)	0.0413(4)
N(1)	0.1918(3)	0.44251(10)	0.17112(6)	0.0273(3)
N(2)	– 0.2267(3)	0.36500(11)	0.16648(7)	0.0316(4)
C(1)	0.1055(3)	0.37743(10)	0.33885(7)	0.0223(4)
C(2)	0.1980(3)	0.41276(10)	0.28398(7)	0.0220(4)
C(3)	0.0915(3)	0.40879(9)	0.22655(7)	0.0217(3)
C(4)	– 0.1157(3)	0.36945(10)	0.22410(7)	0.0241(4)
C(5)	– 0.2052(3)	0.33254(11)	0.27855(8)	0.0263(4)
C(6)	– 0.0967(3)	0.33581(11)	0.33541(7)	0.0256(4)
C(7)	0.2240(3)	0.38442(11)	0.40036(7)	0.0243(4)

*$U_{eq} = (1/3)\sum_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$.

TABLE III Selected bond lengths (Å) and angles (°) for the complex

Na–Na^a	3.1198(5)	O(1)–Na–O(3)	84.48(5)
Na–Na^b	3.1198(5)	O(1)–Na–O(1)^a	107.57(6)
Na–O(1)	2.3380(14)	O(3)–Na–O(1)^a	157.14(6)
Na–O(3)	2.3543(15)	O(1)–Na–O(4)	100.50(6)
Na–O(1)^a	2.3585(14)	O(3)–Na–O(4)	109.62(6)
Na–O(4)	2.4180(17)	O(1)^a–Na–(4)	87.68(6)
Na–O(3)^a	2.4869(16)	O(1)–Na–O(3)^a	171.21(5)
Na–O(4)^b	2.5850(18)	O(3)–Na–O(3)^a	87.02(5)
O(1)–C(7)	1.247(2)	O(1)^a–Na–O(3)^a	81.19(5)
O(2)–C(7)	1.270(2)	O(4)–Na–O(3)^a	80.23(6)
N(1)–C(3)	1.421(2)	O(1)–Na–O(4)^b	84.30(5)
N(2)–C(4)	1.411(2)	O(3)–Na–O(4)^b	79.42(5)
C(1)–C(2)	1.398(2)	O(1)^a–Na–O(4)^b	82.50(5)
C(2)–C(3)	1.394(2)	O(4)–Na–O(4)^b	170.01(7)
C(3)–C(4)	1.402(3)	O(3)^a–Na–O(4)^b	96.38(5)
C(4)–C(5)	1.392(2)	C(7)–O(1)–Na	146.43(12)
C(5)–C(6)	1.388(2)	O(1)–C(7)–O(2)	124.21(15)
C(6)–C(1)	1.388(2)	H(2)–N(1)–H(3)	105(2)
C(7)–C(1)	1.508(2)	H(4)–N(2)–H(5)	107(2)

Symmetry code: $^a x-1/2, -y+1/2, z$; $^b x+1/2, -y+1/2, z$.

TG curves. A Netzsch TG apparatus coupled with a Bruker FTIR IF566 spectrophotometer identified gas-phase products of decomposition. The samples were heated to 723 K with a Netzsch DSC 204 instrument, using Al_2O_3 crucibles, in an argon atmosphere at a heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

The Sodium Salt Structure

Crystals of sodium 3,4-diaminobenzoate, $C_6H_3(NH_2)_2COONa \cdot 2H_2O$, are orthorhombic, space group *Pcab* (Fig. 1). The complex is a polymer in which sodium ions

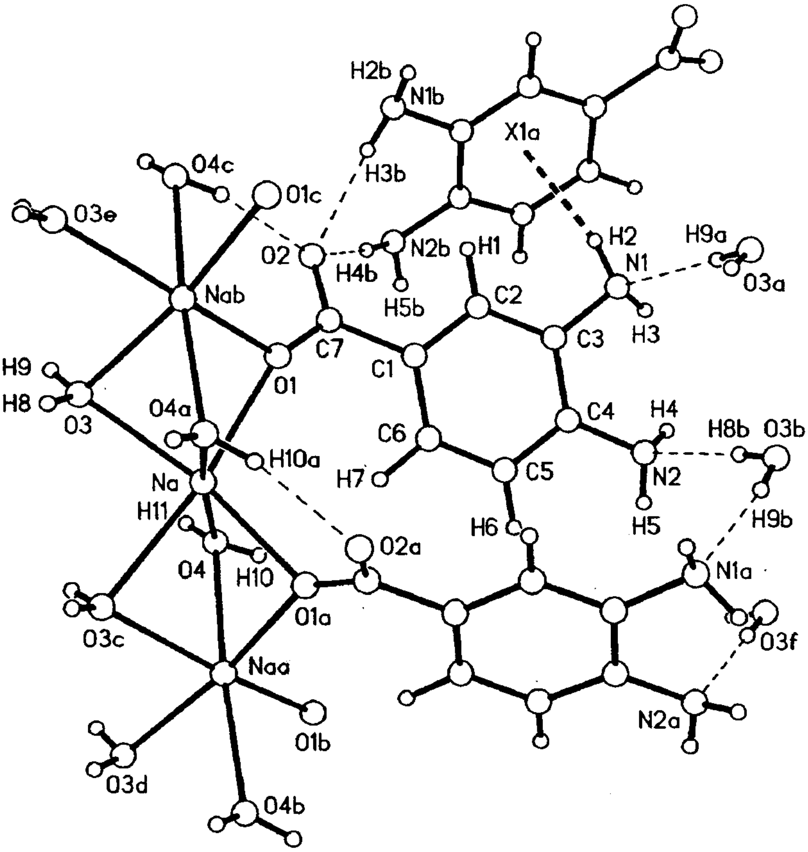

FIGURE 1 The structure of $C_6H_3(NH_2)_2COONa \cdot 2H_2O$.

are bound by water molecules and by oxygen atoms of the carboxylate groups. The carboxylate group of 3,4-diaminobenzoate in this case is bidentate, but through only one O(1) oxygen atom. Each sodium cation is surrounded by two carboxylate oxygen atoms from two different 3,4-diaminobenzoic anions and by four water oxygen atoms. The Na polyhedron ions takes the form of a significantly distorted octahedron as is observed for sodium salts of phthalic, acetic and 2-amino-3,5-dichlorobenzoate acids [8–10]. The Na–O_{water} distances vary in the range 2.3543(15)–2.5850(18) Å while the Na–$O_{carboxyl}$ bond lengths are 2.3380(14) and 2.3585(14) Å (Table III). Such large differences in bond lengths cause the significant distortion in the coordination polyhedron. Angles range from 79.42(5) to 109.62(6)° and from 157.14(6) to 171.21(5)°, respectively. The separation between adjacent Na ions in the polymeric chains is 3.1198(5) Å. Adjacent coordination polyhedra of Na atoms share the O(1)–O(3)–O(4) group.

In coordination of Na ions only O(1) is bonded; O(2) does not bind sodium ions. C–O bond lengths in carboxylic groups are 1.247(2) and 1.270(2) Å and the O–C–O angle is 124.21(15)°. The carboxylic group in this structure is rotated from the benzene ring plane by 25°. In the ligand the C_{phenyl}–$C_{carboxyl}$ bond has a similar length to other carboxylates, 1.508(2) Å [4,11,12].

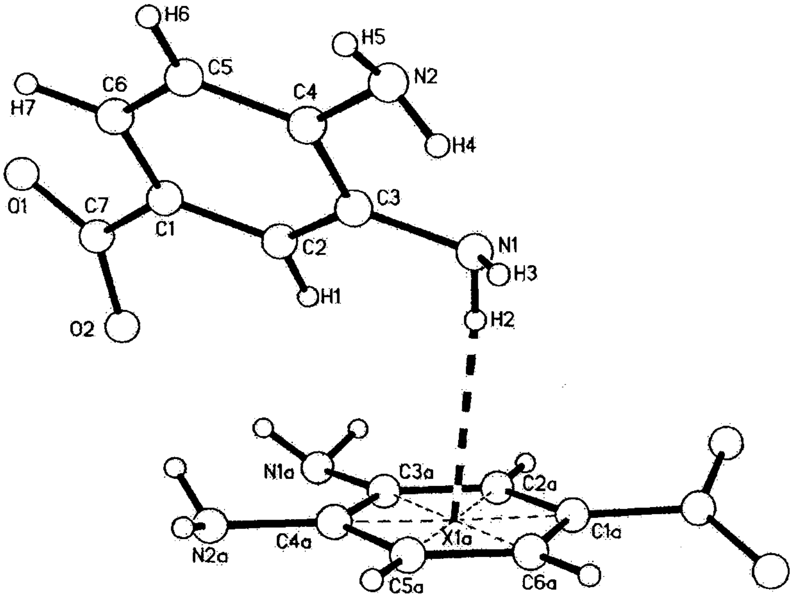

FIGURE 2 Interaction of the amino group with the π-electrons system of the phenyl ring.

C–C bond distances and C–C–C angles in the phenyl rings are similar to those for other aminobenzoic acids molecules [3].

In the aminobenzoate the C–N bond length may change depending on interactions with π-electrons of the phenyl ring. In the structure the C–N distances are 1.466(7) and 1.383(2) Å. The differences between C–N bond lengths might be explained by protonation of N(1) [3]. In Na(DAB) both N(1) and N(2) atoms are proton acceptors and C–N distances are similar, being 1.421(2) Å for N(1) and 1.411(2) Å for N(2); C–N–H and H–N–H angles are close to tetrahedral. Two hydrogen bonds O(3)–H(9)···N(1) and O(3)–H(8)···N(2) are formed with the same water molecule. The amino groups also as proton donors to the uncoordinated oxygen atom of the carboxylic group, N(1)–H(3)···O(2) and N(2)–H(4)···O(2). Each O(2) atom is also a proton acceptors from the water molecule O(4) in hydrogen bonds O(4)–H(10)···O(2) and O(4)–H(11)···O(2).

The distance between the N(1) atom and the phenyl ring centre of a neighbouring organic ligand is 3.386(2) Å (Fig. 2) This points to a weak hydrogen bond, N(1)–H(2)···X(1A). Hydrogen bond geometries use given in Table IV.

IR Spectra

In the spectrum of Na(DAB) very intense, characteristic bands ν_{as} and ν_{s} of the NH_2 group are observed at 3383, 3350 and 3324 cm^{-1}, respectively. They are shifted to higher frequencies than those of the free acid and are associated with the presence of weak hydrogen bonds. The hydrogen bond lengths in the sodium salt are 3.046(2) and 3.127(2) Å while in DABA they are 2.708(2)–2.999(2) Å [3]. Bands due to N–H vibrations occur in the free acid at 3330 and 3210 cm^{-1}.

In the structure of the sodium salt each water molecule is bonded to two sodium ions and forms two hydrogen bonds with nitrogen atoms of amino groups as well as with

TABLE IV Hydrogen bond lengths (Å) and angles (°) for sodium 3,4-diaminobenzoate

$D–H\cdots A$	$D–H$	$H\cdots A$	$D\cdots A$	$\angle DH\cdots A$
N(1) – H(3) $\cdots$ O(2)^c	0.86(2)	2.19(2)	3.046(2)	176(2)
N(2) – H(4) $\cdots$ O(2)^c	0.89(2)	2.25(2)	3.127(2)	170(2)
O(3) – H(8) $\cdots$ N(2)^d	0.80(3)	2.05(3)	2.848(2)	173(3)
O(3) – H(9) $\cdots$ N(1)^e	0.80(3)	2.14(3)	2.931(2)	173(2)
O(4) – H(10) $\cdots$ O(2)^f	0.82(3)	2.02(3)	2.824(2)	168(3)
O(4) – H(11) $\cdots$ O(2)^g	0.81(3)	2.27(3)	3.056(2)	167(3)
N(1) – H(2) $\cdots$ X(1A)^h	0.92(3)	2.49(3)	3.386(2)	164(3)

Symmetry code: $^c x-1/2, -y+1, -z+1/2$; $^d -x, -y+1/2, z+1/2$; $^e -x+1/2, y, z+1/2$; $^f x-1, y, z$; $^g -x, -y+1, -z+1$; $^h x+1/2, -y+1, -z+1/2$.

uncoordinated oxygen atoms of the carboxylate group. Thus in the IR spectrum bands characteristic for water molecules connected by hydrogen bonds at 3503 cm^{-1} and deformation vibrations $\delta(H_2O)$ at 1662 cm^{-1} are observed [13,14].

The bands characteristic for asymmetric and symmetric stretching vibrations of COO occurs at 1554 and 1378, respectively. Splitting ($\Delta\nu$) of 176 cm^{-1} is connected with the fact that the carboxylate group coordinates only by one oxygen atom; a value found previously was 182 cm^{-1} [5]. The $\Delta\nu$ value of the sodium salt was the reference for predicting metal–ligand coordination in lanthanide complexes. In the neodymium(III) complex with 3,4-diaminobenzoic acid, two values of $\Delta\nu$ 124 and 207 cm^{-1} are connected with bidentate-chelating and monodentate carboxylate group coordination [2,5].

In this region there also occurs NH_2 deformation vibrations at 1602 and aromatic $\nu C_{Ar}C_{Ar}$ stretching vibrations at 1430 and 1304 cm^{-1}. Bands below 1300 cm^{-1} are connected with βCH (1379, 1339, 1160 and 1074 cm^{-1}), γCH (916, 865 and 792 cm^{-1}) and ring vibrations. Bands corresponding to Na–O stretching are probably those at 471 and 428 cm^{-1} [13–18].

Thermal Analysis

Na(DAB) compound is stable at room temperature. Upon heating, dehydration begins at about 340 K and the complex loses two water molecules; dehydration is endothermic. In the first stage, dehydration process is reflected in FTIR spectra of gaseous decomposition at 366 K; characteristic valence and deformation vibration bands of water molecules appear in ranges of 4000–3500 and 2050–1250 cm^{-1}, respectively. The anhydrous compound is stable up to 458 K and then decomposes. In the FTIR spectrum at 393 K there appear large peak for CO_2 in the range 2900–2250 and 750–600 cm^{-1}. This process is not observed on the TG curve, but slight changes are found on the DTG curve recorded in an Ar atmosphere. Release of CO_2 is probably connected with partial decarboxylation and ends abruptly at 520 K. The anhydrous compound decomposes on heating into Na_2O with intermediate stages. The first is connected with an exothermic effect and the product is sodium benzoate; this then decomposes at 673 K to Na_2O. Bands for NH_3 are observed in the range 750–1200 cm^{-1} with characteristic double-peak bands with maxima at 966 and 931 cm^{-1}. At 893 K there appear also bands characteristic of carbon oxide (2160 and 2095 cm^{-1}). At first these bands are weak but at higher temperature intensity increases [19,20].

Supplementary Material

List of atomic positions, thermal parameters, observed and calculated structures factors and complete tables of bond distances and angles are available from the authors on request.

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