

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

### THE CRYSTAL STRUCTURES OF AMMONIUM AND SODIUM 2-AMINO-3,5-DICHLOROBENZOATES

Z. Rzączyńska<sup>a</sup>; R. Mrozek<sup>a</sup>; M. Sikorska-Iwan<sup>a</sup>; T. Głowiak<sup>b</sup>

<sup>a</sup> Department of General Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland <sup>b</sup> Faculty of Chemistry, University of Wrocław, Wrocław, Poland

**To cite this Article** Rzączyńska, Z. , Mrozek, R. , Sikorska-Iwan, M. and Głowiak, T.(2008) 'THE CRYSTAL STRUCTURES OF AMMONIUM AND SODIUM 2-AMINO-3,5-DICHLOROBENZOATES', *Journal of Coordination Chemistry*, 49: 3, 189 – 199

**To link to this Article:** DOI: 10.1080/00958970008022571

**URL:** <http://dx.doi.org/10.1080/00958970008022571>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## THE CRYSTAL STRUCTURES OF AMMONIUM AND SODIUM 2-AMINO-3,5- DICHLOROBENZOATES

Z. RZĄCZYŃSKA<sup>a,\*</sup>, R. MROZEK<sup>a</sup>,  
M. SIKORSKA-IWAN<sup>a</sup> and T. GŁOWIAK<sup>b</sup>

<sup>a</sup>*Department of General Chemistry, Faculty of Chemistry,  
Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 2,  
20-031 Lublin, Poland;* <sup>b</sup>*Faculty of Chemistry, University of Wrocław,  
F. Joliot-Curie 14, 50-383 Wrocław, Poland*

(Received 8 February 1999)

The crystal structures of ammonium and sodium 2-amino-3,5-dichlorobenzoates were determined by the X-ray diffraction method. The ammonium salt crystallizes in the monoclinic system (space group  $P2_1/c$ ) with  $a = 13.941(3)$ ,  $b = 9.128(3)$ ,  $c = 7.349(2)$  Å,  $\beta = 90.80(3)^\circ$  and  $Z = 4$ . The structure consists of an ammonium cation hydrogen bonded to a carboxylate oxygen of the 2-amino-3,5-dichlorobenzoate anion. The sodium salt of 2-amino-3,5-dichlorobenzoic acid crystallizes in the triclinic system (space group  $P\bar{1}$ ) with  $a = 8.033(2)$ ,  $b = 8.944(2)$ ,  $c = 17.350(3)$  Å,  $\alpha = 76.72(3)^\circ$ ,  $\beta = 79.69(3)^\circ$ ,  $\gamma = 72.54(3)^\circ$  and  $Z = 4$ . The compound is a polymer in which the sodium ions are coordinated by carboxylate oxygen atoms of the organic ligand and water molecules in an octahedral arrangement. IR spectra of the salts are discussed.

**Keywords:** Crystal structure; IR spectra; 2-amino-3,5-dichlorobenzoates; sodium; ammonium

### INTRODUCTION

The structural investigation of ammonium and sodium salts of 2-amino-3,5-dichlorobenzoic acid was undertaken as part of an investigation of a series of 2-amino-3,5-dichlorobenzoates. In a previous paper, lanthanide(III) complexes with 2-amino-3,5-dichlorobenzoic acid were described and the mode

\* Corresponding author.

of metal–ligand coordination was discussed on the basis of infrared (IR) spectra in the range of carboxylate group absorption.<sup>1</sup> The coordination mode may be also postulated from the shift of symmetric and asymmetric vibrations of the carboxylate group compared to those of the sodium salt of this ligand.<sup>2</sup> In the present paper we show the carboxylate group coordination with sodium and ammonium ions and compare the complex structures using suitable IR spectra.

## EXPERIMENTAL

To a solution of sodium hydroxide (10 cm<sup>3</sup>, 1 M) was added a suspension of 2-amino-3,5-dichlorobenzoic acid (2.06 g, 10 cm<sup>3</sup>) and the mixture was heated until dissolution of the acid. The solution obtained was purified by heating with active carbon and filtering. From the solution, dark brown crystalline needles of the sodium salt were obtained after a few days. Crystals of the ammonium salt were obtained by an analogous procedure.

### Spectroscopic Measurements

The IR spectra of the acid and its salts in the solid state were recorded with a Specord M80 spectrophotometer over the range 4000–400 cm<sup>-1</sup> in KBr discs.

### X-ray Structure Determinations

Preliminary Weissenberg photographs revealed crystal systems, space groups and approximate unit cell dimensions. Crystallographic data and the refinement procedures are given in Table I. Intensities were corrected for extinction for Lorentz and polarization effects, but not for absorption. The structures were solved by heavy-atom methods using SHELXS 86<sup>3</sup> and refined by full-matrix least-squares methods using the SHELXL 93 program.<sup>4</sup> Hydrogen atoms were located from a difference Fourier map and refined. Several cycles of refinement of the coordinates with anisotropic thermal parameters for non-hydrogen atoms and isotropic parameters for H atoms reduced the *R* values to 0.060 and 0.034 for ammonium and sodium salts, respectively. Scattering factors were those incorporated in SHELXL 93. Final atomic parameters for the non-hydrogen atoms are listed in Tables II and III.

TABLE I Crystal data and summary of intensity data collection and structure refinement

	1	2
Formula	C <sub>7</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>10</sub> Cl <sub>2</sub> NNaO <sub>5</sub>
<i>M<sub>r</sub></i>	223.05	282.05
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
Temp. <i>T</i> °C	22	23
Cell constants	25 reflections, 20.0 < $\theta$ < 45.0	25 reflections, 20.0 < $\theta$ < 35.0
<i>a</i> , Å	13.941(3)	8.033(2)
<i>b</i> , Å	9.128(3)	8.944(2)
<i>c</i> , Å	7.349(2)	17.350(3)
$\alpha$ , °		76.72(3)
$\beta$ , °	90.80(3)	79.69(3)
$\gamma$ , °		72.54(3)
Cell volume, Å <sup>3</sup>	935.1(3)	1149.2(4)
<i>Z</i>	4	4
<i>F</i> (000)	456	576
Radiation $\lambda$ , Å	CuK $\alpha$ , 1.54180	MoK $\alpha$ , 0.71069
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	1.584	1.630
<i>D<sub>m</sub></i> , (flotation CCl <sub>4</sub> /C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> g cm <sup>-3</sup> )	1.59	1.63
$\mu$ , cm <sup>-1</sup>	60.18	6.06
Crystal size, mm	0.10 × 0.15 × 0.35	0.20 × 0.25 × 0.45
Scan width		1.2 + 0.35 tan $\theta$
No. of standard reflections		3 (100 ref.)
Decay of standards		< 3%
Reflection measured	1905	3973
2 $\theta$ range, deg.	6.3–162.6	4.5–55.0
Range of <i>h</i> , <i>k</i> , <i>l</i>	–17 → 17, 0 → 11, 0 → 8	0 → 9, –10 → 11, –21 → 22
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
No. of observed reflections	1501	2877
Weights <sup>a</sup> ( <i>a</i> , <i>b</i> , <i>f</i> )	0.1071, 1.8833, 1/3	0.0593, 0.3490, 1/3
GOF	1.079	1.044
$R_1 = \sum( F_o  -  F_c ) / \sum( F_o )$	0.0600	0.0343
$wR_2 = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]} \right\}^{1/2}$	0.1813	0.0997
Function minimized		$\sum w(\Delta F^2)^2$
Largest diff. peak and hole (e/Å <sup>-3</sup> )	0.408, –0.403	0.297, –0.372

<sup>a</sup> $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$  where  $P = [f \cdot (\max \text{ of } 0 \text{ or } F_o^2) + (1 - f) \cdot F_c^2]$ .

## RESULTS AND DISCUSSION

IR spectra of 2-amino-3,5-dichlorobenzoic acid and its ammonium and sodium salts were recorded. In the IR spectrum of the free acid several bands can be clearly distinguished. The bands at 3488 and 3392 cm<sup>-1</sup> may be assigned to  $\nu$ (as) and  $\nu$ (sym) stretching vibrations of the NH<sub>2</sub> group and the  $\nu$ (NH<sub>2</sub>) deformation vibration occurs at 1616 cm<sup>-1</sup>.<sup>5</sup> The band at 1676 cm<sup>-1</sup> is assigned to vibrations of C=O group. Bands at 1572, 1456,

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses in the structure of  $\text{C}_6\text{H}_2\text{Cl}_2\text{NH}_2\text{COONH}_4$ 

	$x/a$	$y/b$	$z/c$	$U_{eq}^*$
Cl(1)	0.5019(1)	0.3032(1)	0.1189(2)	0.0586(5)
Cl(2)	0.2332(1)	-0.1040(1)	0.2279(2)	0.0577(5)
O(1)	0.0592(2)	0.4040(4)	0.2645(5)	0.0479(8)
O(2)	0.1648(2)	0.5802(3)	0.2389(5)	0.0501(9)
N(1)	0.3478(4)	0.5154(5)	0.1844(8)	0.0579(13)
N(2)	0.0523(3)	0.7460(5)	0.4832(7)	0.0445(9)
C(1)	0.2212(3)	0.3351(4)	0.2220(6)	0.0343(9)
C(2)	0.3180(3)	0.3753(4)	0.1896(6)	0.0374(9)
C(3)	0.3825(3)	0.2596(5)	0.1619(6)	0.0399(10)
C(4)	0.3590(3)	0.1151(5)	0.1698(7)	0.0427(10)
C(5)	0.2637(3)	0.0791(5)	0.2077(7)	0.0402(10)
C(6)	0.1970(3)	0.1875(5)	0.2314(6)	0.0377(9)
C(7)	0.1435(3)	0.4462(5)	0.2430(6)	0.0372(9)

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

TABLE III Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses in the structure of  $\text{C}_6\text{H}_2\text{Cl}_2\text{NH}_2\text{COONa} \cdot 3\text{H}_2\text{O}$ 

	$x/a$	$y/b$	$z/c$	$U_{eq}$
Na(1)	0.1860(1)	0.6766(1)	0.0316(1)	0.0347(2)
Na(2)	0.3796(1)	0.9305(1)	0.0915(1)	0.0396(3)
Cl(11)	-0.2980(2)	0.4493(1)	0.4124(1)	0.0818(3)
Cl(12)	-0.3870(1)	-0.1104(1)	0.3920(1)	0.0706(3)
Cl(21)	0.2111(2)	0.4231(1)	0.4342(1)	0.0868(4)
Cl(22)	0.1179(2)	-0.1216(1)	0.3949(1)	0.0759(3)
O(11)	-0.1926(3)	0.1615(2)	0.1022(1)	0.0396(4)
O(12)	-0.2532(3)	0.4200(2)	0.1000(1)	0.0412(5)
O(21)	0.2597(3)	0.1956(2)	0.1107(1)	0.0586(6)
O(22)	0.2621(4)	0.4350(3)	0.1183(1)	0.0657(7)
O(1)	0.6633(3)	0.9646(3)	0.0503(1)	0.0433(5)
O(2)	0.4776(3)	0.6864(2)	0.0353(1)	0.0377(4)
O(3)	0.0914(3)	0.8815(3)	0.1159(2)	0.0490(5)
O(4)	-0.1000(3)	0.6714(3)	0.0273(1)	0.0381(4)
O(5)	-0.0458(4)	0.7297(4)	0.2602(2)	0.0937(9)
O(6)	-0.5476(4)	0.7816(3)	0.2215(2)	0.0694(7)
N(11)	-0.2400(4)	0.5064(3)	0.2375(2)	0.0505(7)
N(21)	0.2688(4)	0.4992(3)	0.2605(2)	0.0602(8)
C(11)	-0.2722(3)	0.2476(3)	0.2265(1)	0.0325(5)
C(12)	-0.2685(4)	0.3581(3)	0.2718(2)	0.0371(6)
C(13)	-0.3025(4)	0.3163(4)	0.3544(2)	0.0491(7)
C(14)	-0.3387(5)	0.1752(4)	0.3918(2)	0.0554(8)
C(15)	-0.3419(4)	0.0705(3)	0.3458(2)	0.0464(7)
C(16)	-0.3085(4)	0.1044(3)	0.2640(2)	0.0387(6)
C(17)	-0.2364(3)	0.2791(3)	0.1369(1)	0.0304(5)
C(21)	0.2200(3)	0.2551(3)	0.2392(1)	0.0329(6)
C(22)	0.2343(4)	0.3530(3)	0.2891(2)	0.0397(6)
C(23)	0.2025(5)	0.3010(4)	0.3713(2)	0.0520(8)
C(24)	0.1658(5)	0.1581(4)	0.4042(2)	0.0564(9)
C(25)	0.1561(4)	0.0642(3)	0.3540(2)	0.0471(7)
C(26)	0.1799(4)	0.1113(3)	0.2730(2)	0.0375(6)
C(27)	0.2493(4)	0.2990(3)	0.1495(2)	0.0368(6)

1416  $\text{cm}^{-1}$  and at 880, 828  $\text{cm}^{-1}$  might be classified as skeletal vibrations and  $\nu\text{C}(\text{Ar})\text{-H}$  vibrations. The band at 720  $\text{cm}^{-1}$  is due to the  $\text{C-Cl}$  group.<sup>6</sup>

In the spectra of the salts the  $\text{C=O}$  bands at 1676  $\text{cm}^{-1}$  disappear and two peaks corresponding to the  $\text{COO}$  groups are observed. In the ammonium salt the asymmetric carboxylate group band  $\nu(\text{as})$  is split into two bands at 1584 and 1540  $\text{cm}^{-1}$  and the symmetric band,  $\nu(\text{sym})$ , is at 1404  $\text{cm}^{-1}$ . The magnitude of separation  $\Delta\nu = \nu(\text{as}) - \nu(\text{sym})$  is 180 and 136  $\text{cm}^{-1}$ .

In the sodium salt the asymmetric carboxylate stretch is at 1584  $\text{cm}^{-1}$  but the symmetric band is split into bands at 1432, 1408 and 1380  $\text{cm}^{-1}$ . Separation values are 152, 176 and 204  $\text{cm}^{-1}$ , and suggest different kinds of carboxylate groups in both investigated compounds.<sup>7</sup>

### The Ammonium Salt Structure

The crystal structure of the ammonium salt of 2-amino-3,5-dichlorobenzoic acid of formula  $\text{C}_6\text{H}_2\text{Cl}_2\text{NH}_2\text{COONH}_4$  is shown in Figure 1. The crystal

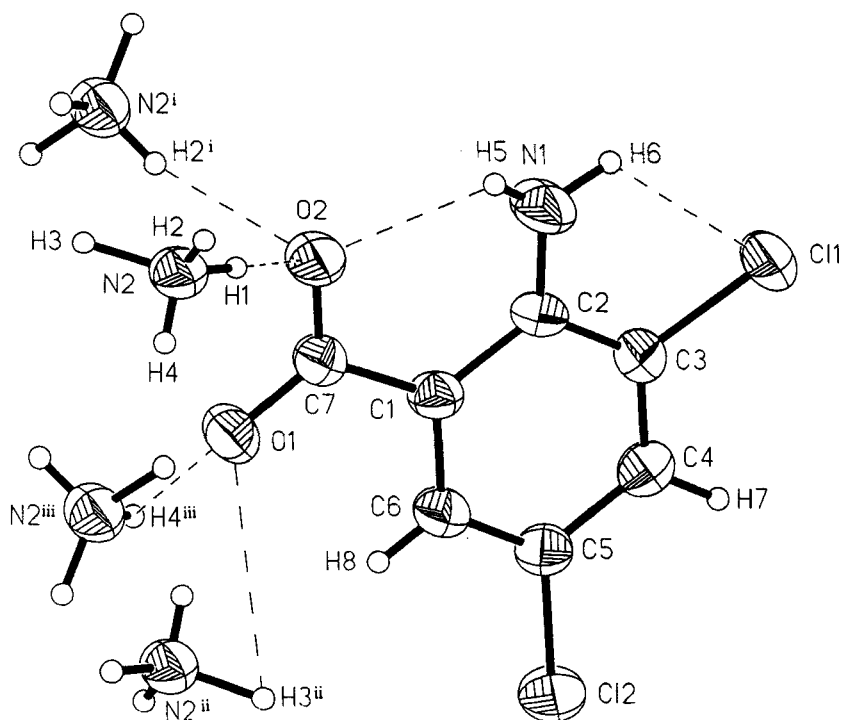


FIGURE 1 The structure of  $\text{C}_6\text{H}_2\text{Cl}_2\text{NH}_2\text{COONH}_4$ ; symmetry code: (i)  $x, 1.5 - y, -0.5 + z$ ; (ii)  $-x, -0.5 + y, 0.5 - z$ ; (iii)  $-x, 1 - y, 1 - z$ .

structure consists of the  $\text{NH}_4^+$  cations hydrogen bonded to oxygen atoms of the carboxylate group of the  $\text{C}_6\text{H}_2\text{Cl}_2\text{NH}_2\text{COO}^-$  anions. The same mode of coordination is observed in ammonium acetate.<sup>8</sup> The ammonium group participates in four  $\text{N-H}\cdots\text{O}$  hydrogen bonds to oxygen atoms of four different 2-amino-3,5-dichlorobenzoate ions. The nitrogen atom arrangement is approximately tetrahedral. Selected bond lengths are given in Table IV. Distances  $\text{C-O}(1)$  1.248(5) and  $\text{C-O}(2)$  1.259(5) Å are typical of a deprotonated carboxyl group. In the structure the mean  $\text{C-C}$  bond length in the ring is 1.392 Å, but two  $\text{C-C}$  distances are considerably shorter;  $\text{C3-C4}$  is 1.361(6) and  $\text{C5-C6}$  is 1.370(6) Å. The shortening of the  $\text{C-C}$  bonds is observed in the case when an electron withdrawing substituent is adjacent to the carbon ring,<sup>9</sup> such as chloro substituents in 3 and 5 positions. The largest  $\text{C-C}$  distance, 1.422(5) Å, is observed between  $\text{C}(1)$  and  $\text{C}(2)$ .  $\text{COO}$  and  $\text{NH}_2$  substituents in *ortho* positions influence both the  $\text{C}(1)\text{-C}(2)$  distance and the angle at substituted carbon atoms.  $\text{C}(6)\text{-C}(1)\text{-C}(2)$  and  $\text{C}(1)\text{-C}(2)\text{-C}(3)$  angles are  $119.3(4)^\circ$  and  $116.2(4)^\circ$ . Similar angles are  $119.7(1)^\circ$  and  $117.4(2)^\circ$  in *ortho*-aminobenzoic acid.<sup>10</sup> The decrease in the angles results from intramolecular interactions and from repulsion between the amino and carboxylic groups.

The lone electron pair of the amino nitrogen atom is engaged with  $\pi$  electrons of a ring. Consequently, the  $\text{C-N}$  distance is 1.345(5) Å and the  $\text{C}(2)\text{-N}(1)\text{-H}(5)$  and  $\text{C}(2)\text{-N}(1)\text{-H}(6)$  angles are close to  $120^\circ$ . In the structure of *ortho*-aminobenzoic acid there are two molecules per asymmetric unit: one is neutral form with  $\text{C-N}$  distance 1.386(3) Å and the other in a zwitterionic form with  $\text{C-N}$  distance 1.455(4) Å.<sup>11</sup>

TABLE IV Selected bond lengths (Å) in ammonium and sodium 2-amino-3,5-dichlorobenzoates

Compound	$\text{C}_7\text{H}_8\text{Cl}_2\text{N}_2\text{O}_2$	$\text{C}_7\text{H}_{10}\text{Cl}_2\text{NNaO}_5$	
Molecule	<b>1</b>	<b>1</b>	<b>2</b>
$\text{C}(1)\text{-C}(2)$	1.422(5)	1.407(4)	1.404(4)
$\text{C}(2)\text{-C}(3)$	1.403(6)	1.393(4)	1.369(4)
$\text{C}(3)\text{-C}(4)$	1.361(6)	1.369(4)	1.370(5)
$\text{C}(4)\text{-C}(5)$	1.400(6)	1.371(4)	1.368(4)
$\text{C}(5)\text{-C}(6)$	1.370(6)	1.376(4)	1.368(4)
$\text{C}(6)\text{-C}(1)$	1.391(5)	1.386(4)	1.392(4)
$\text{C}(1)\text{-C}(7)$	1.493(6)	1.505(3)	1.509(3)
$\text{C}(7)\text{-O}(1)$	1.248(5)	1.260(3)	1.239(3)
$\text{C}(7)\text{-O}(2)$	1.259(5)	1.255(3)	1.239(3)
$\text{C}(2)\text{-N}(1)$	1.345(5)	1.392(4)	1.379(4)
$\text{C}(3)\text{-Cl}(1)$	1.745(4)	1.737(3)	1.735(3)
$\text{C}(5)\text{-Cl}(2)$	1.732(4)	1.744(3)	1.745(3)

TABLE V Hydrogen bond lengths (Å) and angles (°) with e.s.d.'s in parentheses for C<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>NH<sub>2</sub>COONH<sub>4</sub>

<i>D-H...A</i>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	$\angle D-H...A$
N(1)-H(5)···O(2)	0.72(6)	2.15(6)	2.655(6)	128(6)
N(1)-H(6)···Cl(1)	0.93(7)	2.35(6)	2.937(3)	120(5)
N(2)-H(1)···O(2)	0.98(6)	1.87(6)	2.838(6)	168(5)
N(2)-H(2)···O(2) <sup>i</sup>	0.83(9)	2.10(9)	2.903(6)	163(8)
N(2)-H(3)···O(1) <sup>ii</sup>	1.07(8)	1.80(8)	2.780(6)	151(6)
N(2)-H(4)···O(1) <sup>iii</sup>	0.81(6)	2.00(6)	2.794(6)	168(6)

Symmetry code: (i)  $x, 1.5 - y, 0.5 + z$ ; (ii)  $-x, 0.5 + y, 0.5 - z$ ; (iii)  $-x, 1 - y, 1 - z$ .

In this structure the C2-N1 distance is one of the shortest for an aromatic carbon atom and a nitrogen atom of an amino group. The NH<sub>2</sub> group is proton donor for two intramolecular hydrogen bonds, N-H···O and N-H···Cl; the nitrogen atom is not an acceptor. The hydrogen bonds are detailed in Table V. A very short hydrogen bond length (2.655(6) Å) exists in this structure.

### The Sodium Salt Structure

The sodium salt of 2-amino-3,5-dichlorobenzoic acid with formula C<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>NH<sub>2</sub>COONa · 3H<sub>2</sub>O crystallizes in the triclinic space group *P* $\bar{1}$ . It forms a centrosymmetric tetramer in which sodium ions are coordinated by oxygen atoms of carboxylate groups and water molecules. The octahedra in the tetramer are connected by two water molecules which form the edges of neighbouring octahedra (Figure 2). The coordination polyhedron of Na ions takes the form of significantly distorted octahedron just as observed in the sodium salts of phthalic<sup>12</sup> and acetic acids.<sup>13,14</sup> The Na(1) ion is surrounded by three carboxylate oxygen atoms from two different 2-amino-3,5-dichlorobenzoate anions and by three water oxygen atoms. The O(11)<sup>i</sup> and O(12)<sup>i</sup> atoms are from one acid molecule, so the carboxylate group is bidentate-chelating. The O(22) oxygen atom comes from another acid molecule in which the carboxylate group bridges two sodium ions. Among the water molecules, one is a monodentate ligand and two are bidentates, bridging the Na(1) and Na(2) ions (Figure 3).

In the coordination environment of the Na(2) ion there are five water oxygen atoms and only one O(21)<sup>ii</sup> carboxylate oxygen atom of a 2-amino-3,5-dichlorobenzoate ion. Two water molecules with O(1) and O(1)<sup>i</sup> atoms create a binary centrosymmetric bridge between Na(2) and Na(2)<sup>i</sup> ions. The Na-O<sub>water</sub> distances vary in the range 2.327(2)–2.468(3) Å while the



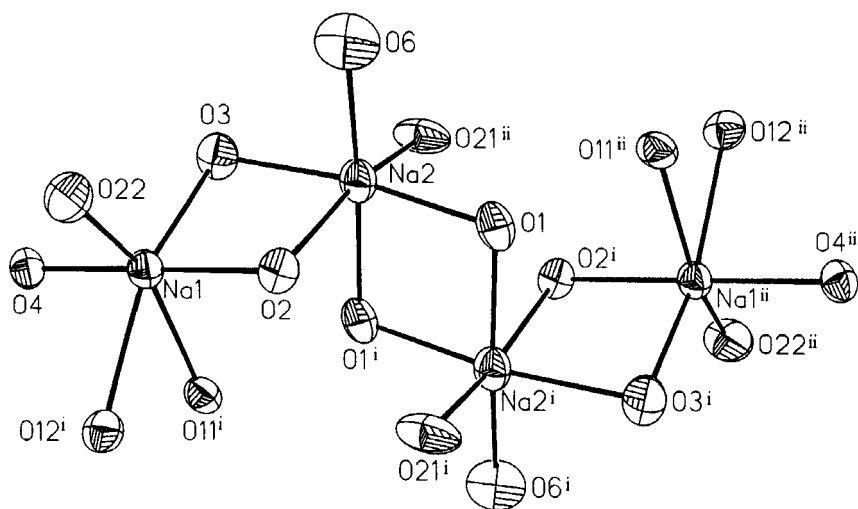


FIGURE 2 The coordination environments of sodium ions in tetrameric  $C_6H_2Cl_2NH_2COONa \cdot 3H_2O$ .

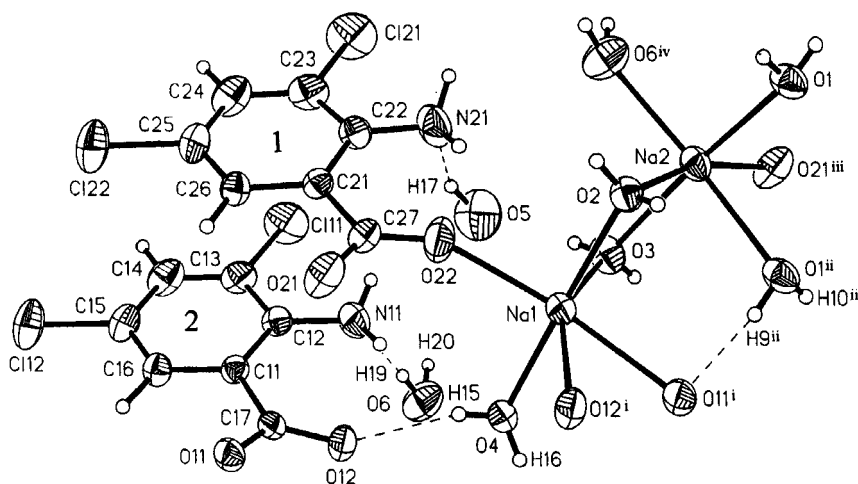


FIGURE 3 A section of the crystal structure of  $C_6H_2Cl_2NH_2COONa \cdot 3H_2O$ ; symmetry code: (i)  $-x, 1-y, -z$ ; (ii)  $1-x, 2-y, -z$ ; (iii)  $x, 1+y, z$ ; (iv)  $1+x, y, z$ .

$Na-O_{\text{carboxyl}}$  bond lengths are in the range of 2.313(2)–2.537(2) Å. Such large differences in bond lengths cause a significant distortion of the coordination polyhedra of the Na ions. The angles that would be 90° in a regular octahedral arrangement range from 52.63(6)° to 105.62(1)°. The geometry of the coordination polyhedra is given in Table VI, with the distance

TABLE VI The geometries of the coordination polyhedra around the Na ions

O(22)–Na(1)–O(4)	95.77(10)	O(1)–Na(2)–O(21) <sup>ii</sup>	92.95(10)
O(22)–Na(1)–O(2)	85.10(10)	O(1)–Na(2)–O(6) <sup>iii</sup>	93.22(10)
O(4)–Na(1)–O(2)	179.09(9)	O(21) <sup>ii</sup> –Na(2)–O(6) <sup>iii</sup>	104.20(9)
O(22)–Na(1)–O(11) <sup>i</sup>	151.24(9)	O(1)–Na(2)–O(3)	171.62(9)
O(4)–Na(1)–O(11) <sup>i</sup>	90.60(9)	O(21) <sup>ii</sup> –Na(2)–O(3)	92.04(10)
O(2)–Na(1)–O(11) <sup>i</sup>	88.76(8)	O(6) <sup>iii</sup> –Na(2)–O(3)	92.08(11)
O(22)–Na(1)–O(3)	105.61(10)	O(1)–Na(2)–O(2)	88.03(9)
O(4)–Na(1)–O(3)	93.39(9)	O(21) <sup>ii</sup> –Na(2)–O(2)	164.26(9)
O(2)–Na(1)–O(3)	86.09(8)	O(6) <sup>iii</sup> –Na(2)–O(2)	91.42(9)
O(11) <sup>i</sup> –Na(1)–O(3)	101.95(9)	O(3)–Na(2)–O(2)	85.35(8)
O(22)–Na(1)–O(12) <sup>i</sup>	99.97(8)	O(1)–Na(2)–O(1) <sup>iv</sup>	84.23(9)
O(4)–Na(1)–O(12) <sup>i</sup>	84.84(8)	O(21) <sup>iv</sup> –Na(2)–O(1) <sup>iv</sup>	86.50(8)
O(2)–Na(1)–O(12) <sup>i</sup>	95.30(8)	O(6) <sup>iii</sup> –Na(2)–O(1) <sup>iv</sup>	169.14(9)
O(11) <sup>i</sup> –Na(1)–O(12) <sup>i</sup>	52.63(6)	O(3)–Na(2)–O(1) <sup>iv</sup>	89.36(10)
O(3)–Na(1)–O(12) <sup>i</sup>	154.40(9)	O(2)–Na(2)–O(1) <sup>iv</sup>	77.97(8)

Symmetry code: (i)  $-x, -y + 1, -z$ ; (ii)  $x, y + 1, z$ ; (iii)  $x + 1, y, z$ ; (iv)  $-x + 1, y + 2, -z$ .

between Na(1)–Na(2) ions 3.526(2) Å. This value is similar to that in sodium acetate trihydrate.<sup>14</sup> Adjacent coordination polyhedra of Na(1) and Na(2) atoms share an edge through the atoms O(2)–O(3). In 2-amino-3,5-dichlorobenzoate ions there is evidence of ionized carboxyl groups. The C–O bond lengths are in the range 1.239(3)–1.260(3) Å. The O–C–O angle is 122.8(2)° in the chelating group and 123.3(2)° in the bridging one.

C–N distances are 1.392(3) and 1.379(4) Å. These are relatively long in comparison with the ammonium salt and might be explained by the participation of the nitrogen atom of the NH<sub>2</sub> groups as proton acceptors in hydrogen bonds. H–N–H angles in the H···NH<sub>2</sub> group are close to tetrahedral.

The 2-amino-3,5-dichlorobenzoate ion of (2) is bonded to the cation by the C–O group that is hydrogen bonded to a water molecule in the coordination polyhedron. The carboxylate groups are proton acceptors in O–H···O and N–H···O hydrogen bonds. The water molecules in the coordination sphere are involved two or one hydrogen bonds as proton donors while the water molecule O(5) participates in three hydrogen bonds with two 2-amino-3,5-dichlorobenzoate ions and water molecule. Hydrogen bond geometry is given in Table VII.

Comparison of the IR spectrum of a sodium carboxylate with the spectrum of a salt of another metal ion with the same ligand is often used to postulate the mode of coordination.<sup>2</sup> It assumes that the sodium carboxylate is ionic. Here we describe sodium 2-amino-3,5-dichlorobenzoate. There is evident coordination between the sodium ion and carboxylate oxygen atoms in the complex. Moreover the carboxylate groups show two different

TABLE VII Hydrogen bond lengths (Å) and angles (°) with e.s.d's in parentheses for  $C_6H_2Cl_2NH_2COONa \cdot 3H_2O$ 

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$\angle D-H \cdots A$
O(1)-H(9) $\cdots$ O(11) <sup>i</sup>	0.83(4)	1.93(4)	2.753(3)	172(4)
O(1)-H(10) $\cdots$ O(4) <sup>i</sup>	0.75(5)	2.12(5)	2.803(3)	152(5)
O(2)-H(11) $\cdots$ O(12) <sup>i</sup>	0.80(4)	2.07(4)	2.857(3)	169(4)
O(3)-H(13) $\cdots$ O(5)	0.71(4)	2.06(4)	2.770(4)	174(4)
O(3)-H(14) $\cdots$ O(11) <sup>ii</sup>	0.85(5)	2.00(5)	2.833(3)	166(4)
O(4)-H(15) $\cdots$ O(12)	0.75(4)	2.12(4)	2.822(3)	156(4)
O(4)-H(16) $\cdots$ O(21) <sup>iii</sup>	0.79(3)	1.97(3)	2.769(3)	169(4)
O(5)-H(18) $\cdots$ N(21)	0.92(5)	1.88(5)	2.740(5)	155(4)
O(6)-H(19) $\cdots$ N(11)	0.81(5)	2.12(5)	2.920(4)	170(4)
N(11)-H(1) $\cdots$ O(5)	0.82(5)	2.32(5)	3.003(5)	142(4)
N(12)-H(2) $\cdots$ O(12)	0.98(4)	2.03(4)	2.700(4)	124(3)
N(21)-H(5) $\cdots$ O(22)	0.89(4)	1.97(4)	2.671(4)	135(3)
N(22)-H(6) $\cdots$ Cl(21)	0.94(5)	2.53(5)	2.916(11)	105(3)

Symmetry code: (i)  $1+x, y, z$ ; (ii)  $x, 1+x, z$ ; (iii)  $-x, 1-y, -z$ .

modes of coordination, bidentate-chelating and bidentate-bridging. This is probably the reason that the symmetric vibrations of COO groups are split into three bands. In ammonium 2-amino-3,5-dichlorobenzoate there is an ionic bond between the ammonium and  $C_6H_2Cl_2NH_2COO^-$  ions. The carboxylate group is symmetric, with C-O bond lengths 1.248(5) and 1.259(5) Å; C-C-O angles are 119.3(4)° and 119.0(4)°. Nevertheless the asymmetric band of the COO group is split. This shows that spectroscopic criteria for coordination modes should be assessed carefully.

### Supplementary Material

Lists of H atom positions, thermal parameters, observed and calculated structure factors and complete tables of bond distances and angles are available from the authors on request.

### References

- [1] R. Mrozek, Z. Rzączyńska and M. Sikorska, *Synth. React. Inorg. Met.-Org. Chem.* **27**, 707 (1997).
- [2] N.W. Alcock, V.M. Tracy and T.C. Waddington, *J. Chem. Soc., Dalton Trans.* 2243 (1976).
- [3] G.M. Sheldrick, *Acta Cryst.* **A46**, 467 (1990).
- [4] G.M. Sheldrick, *SHELXL 93. Program for Refinement of Crystal Structures* (University of Göttingen, Germany, 1994).
- [5] W. Brzyska and Z. Rzączyńska, *Polish J. Chem.* **60**, 27 (1986).
- [6] W. Brzyska and E. Świta, *Polish J. Chem.* **66**, 603 (1992).
- [7] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
- [8] I. Nahringsbauer, *Acta Cryst.* **23**, 956 (1967).
- [9] T. Więckowski and T.M. Krygowski, *Croat. Chem. Acta* **58**, 5 (1985).

- [10] H. Takazawa, S. Ohba and Y. Saito, *Acta Cryst.* **C42**, 1980 (1986).
- [11] C.K. Brown and M. Ehrenberg, *Acta Cryst.* **C41**, 441 (1985).
- [12] R.A. Smith, *Acta Cryst.* **B31**, 2345 (1975).
- [13] A. Perotti and V. Tazzoli, *J. Chem. Soc., Dalton Trans.* 1768 (1981).
- [14] T.S. Cameron, K.M. Mannan and O.R. Mohammed, *Acta Cryst.* **B32**, 87 (1976).