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## Basic Salts with »Very Short« Hydrogen Bonds; the Crystal Structure of $\alpha$ -Picoline-*N*-oxide Hemihydrochloride Sesquihydrate (Dunlop's Salt)

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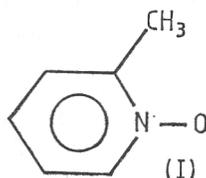
Type A acid salts of many simple carboxylic acids (HX) crystallise with anions,  $\text{XHX}^-$ , which are symmetrical and which contain »very short« OHO-bonds with  $\text{O}\dots\text{O}$  less than 250 pm. Such compounds also reveal anomalous IR spectra. The Glasgow work on such crystal structures has benefited from a long collaboration with Hadži's spectroscopic group at Ljubljana. The importance of such joint studies in helping the understanding of strong hydrogen bonding is discussed.

Some organic bases form analogous basic salts, which have similarly anomalous spectra. An example, discovered by Hadži in 1962, is the hemihydrobromide of  $\alpha$ -picoline-*N*-oxide,  $\text{B} \cdot \frac{1}{2}\text{HBr}$ , where  $\text{B} = \text{C}_6\text{H}_7\text{NO}$ , for which he predicted the formula  $\text{BHB}^+ \text{Br}^-$ . Preliminary X-ray work confirmed this and the presence of a »very short« OHO-bond. Hitherto unpublished crystallographic work is summarised.

Dunlop's salt is the sesquihydrated hemihydrochloride of the same base. A careful X-ray study has been made (1040 reflexions;  $R = 3.7\%$ ):  $\text{B} \cdot \frac{1}{2}\text{HCl} \cdot \frac{3}{2}\text{H}_2\text{O}$  has a structure corresponding to  $\text{BHB}^+ \text{Cl}^- \cdot 3\text{H}_2\text{O}$ ; the cation lies across a centre of symmetry, with  $\text{O}\dots\text{O} = 241.4(3)$  pm. At one stage the salt was supposed to include a symmetrical  $\text{ClHCl}^-$  anion; but our more precise work shows the anion to be  $\text{Cl}^- \dots \text{H}-\text{OH}$  (or  $\text{HO}-\text{H} \dots \text{Cl}^-$ ) symmetrised by disorder across a twofold axis of the crystal, with  $\text{Cl}^- \dots \text{O} = 297(1)$  pm. The spectrum of DSALT is almost identical with that of the hemihydrobromide.

### INTRODUCTION

Twenty-five years ago, Hadži prepared a basic salt of  $\alpha$ -picoline-*N*-oxide (2-methyl-pyridine-*N*-oxide;  $\text{B} = \text{C}_6\text{H}_7\text{NO}$ , formula (I)). It was the hemihydrobromide,  $\text{B} \cdot \frac{1}{2}\text{HBr}$ . From its IR spectrum, he predicted<sup>1</sup> that the crystal



\* Festschrift of Professor Dušan Hadži.

structure would be ionic,  $\text{BHB}^+ \text{Br}^-$ , and that the two B units in the positive ion would be linked by a very strong OHO-bond.

In Glasgow, since 1947, we had been interested in acid salts of the general composition  $\text{MX} \cdot \text{HX}$ , where M is a metal atom (or  $\text{NH}_4$ ) and HX a simple carboxylic acid. Crystal-structure analysis showed some of these anomalous salts to be normal salts with extra »acid of crystallisation«. Discrete  $\text{X}^-$  and HX units could be recognised; so that a more explicit formulation would be  $\text{M}^+ \text{X}^- \cdot \text{HX}$ . These were called Type B acid salts. More interesting were those of Type A, whose crystal structures required them to be formulated as  $\text{M}^+ \text{XHX}^-$ ; the anion lay across a symmetry element of the crystal — usually a centre of inversion, but sometimes a twofold axis or a mirror-plane — so that the two X units were equivalent. Unlike the great majority of hydrogen bonds, those in  $\text{XHX}^-$  were symmetrical, or apparently so. Further, the OHO-bonds in Type A crystals are »very short«<sup>2</sup>; the O...O distance is almost always in the range 255–242 pm (= 2.55–2.42 Å), to be contrasted with 276 pm in ice or 265 pm in a typical carboxylic-acid dimer.

#### SPECTROSCOPIC WORK ON HYDROGEN BONDING AT LJUBLJANA

At Ljubljana in the 1950's, Hadži established a school devoted to the spectroscopic study of hydrogen-bonded materials; some of his early students became prominent in the field, notably Bratos and Novak. The esteem in which their work was held was shown, in the Summer of 1957, when the IUPAC conference on hydrogen bonding attracted to Ljubljana an impressive group of distinguished scientists. The proceedings were summarised,<sup>3</sup> and Hadži edited a fuller account of the papers read.<sup>4</sup>

In February 1954, Hadži wrote to me (J.C.S.) about his special interest in short OHO-bonds. His letter stimulated a long collaboration between spectroscopist and crystallographer which has been particularly valuable to us in Glasgow. (See papers by Hadži, Novak and Blinc<sup>5,6,7</sup>). Above all, we have been encouraged to seek and study Type A compounds; for their »very short« OHO-bonds are crucial in the general problem of understanding the hydrogen bond.

In water vapour, the asymmetric O—H stretching frequency ( $\nu_3$ ) produces a prominent band near  $3750 \text{ cm}^{-1}$  ( $1 \text{ cm}^{-1} = 2.998 \times 10^{10} \text{ hz}$ ). Crystals containing free OH-groups always absorb near this frequency. However, when the group is engaged in hydrogen bonding, the spectrum changes: the band moves to lower frequency; the peak-height diminishes; but the peak broadens, so that its integrated intensity increases. It had been known for a long time that these changes were accompanied by a shortening of the overall O...O distance; and, when neutron diffraction came to be applied, it became evident that there was also a lengthening of O—H, which was not surprising. These correlations were quantified by Nakamoto, Margoshes and Rundle<sup>8</sup>, and subsequently by many others (e.g. Novak<sup>9</sup>). For instance, a plot of the change in frequency ( $-\Delta\nu_3$ ), against the O...O distance, shows an accelerating fall as the distance changes from 300 pm, in the weakest OHO-bonds, to  $\sim 255$  pm in rather strong bonds, in which  $\nu_3$  has dropped to  $\sim 2000 \text{ cm}^{-1}$ .

Still stronger hydrogen bonds have been discovered, most obviously in Type A crystals. In the region of 255 pm, there is evidence that the character

of the OHO-bond changes rather suddenly. The dissociation energies of long bonds may be up to  $10 \text{ kJ mol}^{-1}$ ; this increases to  $\sim 50 \text{ kJ}$  when  $\text{O} \dots \text{O}$  is  $\sim 260 \text{ pm}$ ; below  $\sim 255 \text{ pm}$ , it perhaps rises to values not far short of those associated with covalent bonds. Though, to be sure, it may be difficult to measure the dissociation energy of the bond in a Type A compound, or indeed to define the quantity.

These changes in properties are reflected in theoretical interpretations of hydrogen bonding. In elementary terms, we attribute most bonds to a weak electrostatic attraction between a dipolar OH-group and the partial negative charge on the acceptor atom to which the group is directed:  $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}} \dots \overset{\delta-}{\text{O}}$ . As the bond shortens overall, and strengthens, additional attraction comes from some sort of electron delocalisation. It may become dominant in a bond which is »very short«, and possibly symmetrical. It is this latter possibility that makes strong hydrogen bonding specially interesting.

The spectra of compounds involving these exceptionally strong bonds no longer show the band obviously connected with the O—H stretch ( $\nu_3$ ). Instead, extending over many hundreds of wave-numbers, there is a broad region of absorption: a »background« culminating somewhere in the range  $1500\text{--}700 \text{ cm}^{-1}$ . Examples may be seen in Figure 2. Hadži<sup>10</sup> designated such spectra as Type (ii); and the broad absorption as the »D band«, though, as he points out, it may not be what is normally meant by a band. Within the D band, there are often »negative peaks«, or »windows«, such as are to be seen in Figure 2 near  $900 \text{ cm}^{-1}$ . This phenomenon has been discussed by Hadži and Bratos<sup>11</sup>.

The strongest hydrogen bond known is in the bifluoride anion,  $\text{HF}_2^-$ . As early as 1958, Blinc published a perceptive discussion of this bond and its symmetry<sup>12</sup>, with special reference to the IR spectrum of  $\text{KHF}_2$ . The first simple bifluoride to have its crystal structure accurately determined was  $\text{NaHF}_2$  by McGaw and Ibers<sup>13</sup> using neutrons. The space group, if it is has been correctly chosen, imposes symmetry on the anion. Therefore this structure is of Type A. The site of the anion has the symmetry  $3m (= D_{3d})$ , which, formally, requires the proton to be at a centre of inversion lying on a mirror-plane; and the two F-atoms to be symmetry related. The distance  $\text{F} \dots \text{F}$  was found to be  $226.4(3) \text{ pm}$ , and each  $\text{F—H} = 113 \text{ pm}$ . The neutron measurements can be covered equally well by either of two models: the proton vibrates, with a certain amplitude along the  $\text{F} \dots \text{F}$  line, in a single-minimum potential-energy well; or, in a double-minimum, it is disordered between two close sites, not more than  $10 \text{ pm}$  on either side of the mid-point, and with rather smaller amplitude. By introducing spectroscopic considerations, McGaw and Ibers favoured the model with the single minimum. The hydrogen bond in  $\text{NaHF}_2$  is now regarded, by most workers, as genuinely symmetrical.

However, a remarkable result was reported by Williams and Schneemeyer, in 1973<sup>14</sup>, who were studying the bifluoride of *p*-toluidine with neutrons. Here there are no constraints on the symmetry of the anion. The  $\text{F} \dots \text{F}$  distance is  $226.0(4) \text{ pm}$ , and the same as in  $\text{NaHF}_2$ . Yet the proton is off-centre; its distances from the F-atoms are  $102.5(6) \text{ pm}$  and  $123.5$ . The difference may be plausibly explained by consideration of the differing environments of the F-atoms: the second engages in two relatively strong  $\text{N—H} \dots \text{F}$  contacts, with  $\text{H} \dots \text{F}$   $160.8(6)$  and  $167.5 \text{ pm}$ , whereas the first engages only in one, much

weaker, contact of 177.7 pm. Such a difference causes the proton to shift 10.5 pm from the mid-point. This fits the idea of a shallow potential-energy well, perhaps non-parabolic in shape.

We return to the problems of O—H...O-bonds when they become »very short«. How short must they be before the proton is vibrating about the mid-point, in a single-minimum potential? A type A crystal structure ensures a suitably symmetrical environment, though it does not rule out a close double minimum. Most workers in this field would regard 242 pm as short enough, provided it is supported by work of due precision. About bonds as long as 250 pm there would be argument<sup>15</sup>. Of course, mere shortness may not be the only important factor. There may well be others.

#### $\alpha$ -PICOLINE-N-OXIDE HEMIHYDROBROMIDE, AND SOME OTHER TYPE A BASIC SALTS

A sample of this hemihydrobromide was sent to Glasgow in 1962. A preliminary X-ray study was made by Mills<sup>16</sup>. Using photographic-visual estimates of intensity, he examined two projections of the structure, which confirmed Hadži's prediction<sup>1</sup>: the structure was of Type A; the BHB<sup>+</sup> unit was across a centre of symmetry; and the O...H...O distance was roughly estimated to be 230 pm. We did not have a diffractometer in Glasgow at that time. So, when Mills went to Buffalo, he took with him some of Hadži's material, and collected a fuller set of data. Unfortunately, there was a secular fall-off in intensity, which was attributed to damage to the crystal caused by exposure to X-rays. For this, and other, reasons, a definitive structure analysis was never completed. However, Mill's thesis contained partial three-dimensional data. As an exercise in the new Glasgow system of crystallographic programs<sup>17</sup>, Dr. Mallinson has recently used these data to re-examine this structure. The results showed a hydrogen bond of length 238(4) pm, which is not significantly shorter than the average lengths found in most Type A structures. Some details of this recent work are given in the Experimental section.

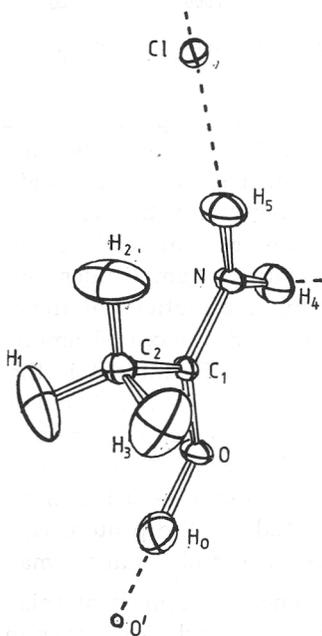
Meantime another Type A basic salt — though this classification was not then in use — had been recognised in North America at a somewhat earlier date. It was acetamide hemihydrochloride, a compound first described by Strecker in 1857<sup>18</sup>:  $B \cdot \frac{1}{2}HCl$ , where B now stands for  $CH_3 \cdot CO \cdot NH_2$ . In 1958 Albert and Badger<sup>19</sup> reported a striking similarity between its IR spectrum and that of potassium hydrogen bis-phenylacetate, an acid salt of Type A.<sup>20</sup> (Both spectra are in fact of Hadži's Type (ii).) On this basis, they suggested a correspondingly symmetrical structure. In confirmation, they cited X-ray work by Hughes and Takei.<sup>21</sup> Further support came in 1960 when Peterson and Worsham<sup>22</sup> reported neutron-diffraction work, and found O...H...O = 241 pm. However, neither of these analyses was of any precision, nor were they ever reported in any detail.

Recently we have repeated these analyses with better accuracy. With X-rays at room temperature we (Muir and Speakman<sup>23</sup>) find O...H...O = 245.2(14) pm; and (Speakman, Lehmann, Allibon and Semmingsen<sup>24</sup>) with neutrons, at 120 K, 242.6(3) pm. Figure 1 shows an ORTEP<sup>25</sup> drawing based on the latter. The following formulae set out the chemical analogy between this basic salt and the acid salt, sodium hydrogen diacetate<sup>26</sup>:



The spectra of these two compounds, shown in Figure 2, are very similar, apart from the bands due to N—H-stretching in the former. (For the spectroscopy of acetamide hemihydrochloride see papers by Bertulozza et al.<sup>27</sup> and Spinner<sup>28</sup>.) However, the crystal structures are quite different, though both are of Type A. The first is monoclinic, with the cation centred on a point of inversion; whilst the second has an elegant, high-symmetry structure in the cubic system, with the hydrogen-diacetate unit centred across a twofold axis.

Good neutron-diffraction work yields information about the vibrational motions, of the atomic nuclei, within the molecule, which is more accurate than would be obtainable from X-ray analysis. For instance, it may be applied to support the idea that the OHO-bond undergoes a marked change of character when its overall length falls below  $\sim 255$  pm. Consider a molecule containing a C—O—H (or N—O—H) group. Any vibrational motion of the proton, relative to the rest of the group, may be analysed into three components: *S*, stretching of the O—H bond; *B*, bending at the C—O—H angle; and *T*, twisting about the C—O bond (e. g. Novak<sup>9</sup>). As is well known, the ease of these motions is



AHHCL 120K, ND2

Figure 1. ORTEP drawing showing part of the structure of acetamide hemihydrochloride, based on neutron diffraction. (The ellipsoids are drawn to correspond to 50% probability limits; H(0) lies on a centre of symmetry.)

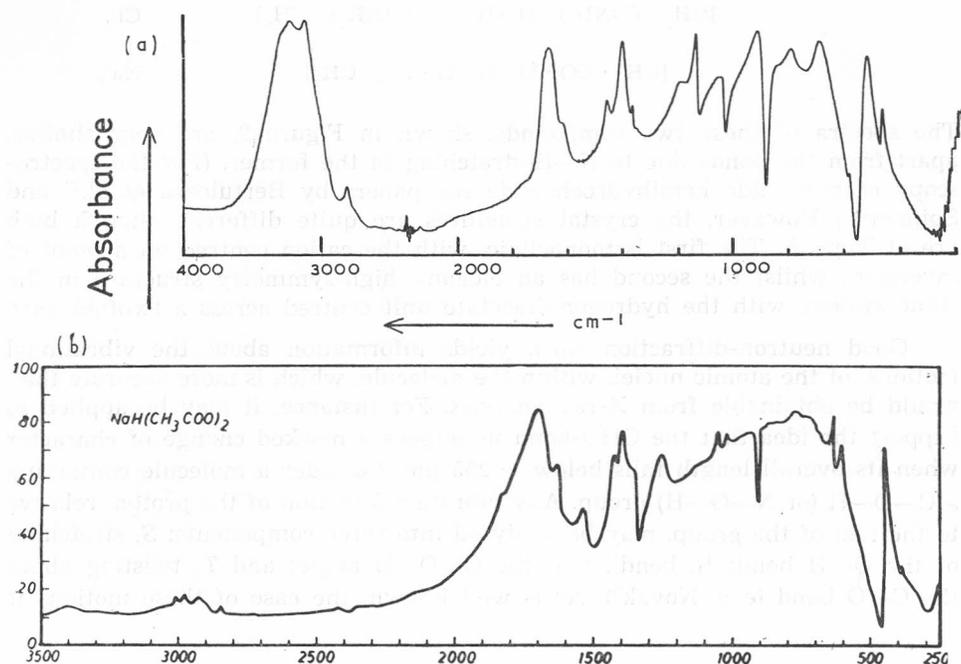


Figure 2. The IR spectra of (a) acetamide hemihydrochloride, and (b) sodium hydrogen diacetate. (KBr discs;  $1 \text{ cm}^{-1} = 2.998 \times 10^{10} \text{ Hz}$ .)

in the order  $T > B > S$ ; and the corresponding frequencies are in the reverse order,  $S > B > T$ . When the O—H group becomes involved in hydrogen bonding, the  $S$ -frequency diminishes, as we have stated already; but, for nearly all hydrogen bonds, the trend remains the same, until we pass the frontier to »very short« bonds. Then the order of relative amplitudes may be reversed. When we represent the anisotropic amplitudes by ellipsoids, like those in Figure 1., an ellipsoid, showing the motions of the proton, with respect to its neighbouring O-atoms, is »inverted«: maximal amplitude comes to be parallel, and minimal transverse, to the O—H line. (It is the minimal that is parallel to the bond in a free O—H-group, or one that is not strongly hydrogen bonded.) This is true for all the Type A structures known to us, for which good neutron measurements are available.<sup>29</sup> For example, from our study of acetamide hemihydrochloride at 120 K, we estimate — using the usual and reasonable assumptions — the r.m.s. amplitude of the proton,  $\text{H}(0)$  relative to the O-atoms, to be 15(1) pm parallel to  $\text{O} \dots \text{O}$ , and 8 pm normal to it.

There is theoretical evidence in support of this idea, notably in work by Janoschek<sup>30</sup> which indicates corresponding changes in the shape of the potential-energy field when the OHO-bond becomes »very short«.

Rough X-ray work and accurate neutron work have been done on a basic salt of dimethylacetamide ( $\text{B} = \text{CH}_3\text{CO} \cdot \text{N}(\text{CH}_3)_2$ ):  $\text{BHB}^+ \text{AuCl}_4^-$ .<sup>31</sup> The structure is of Type A; and, with neutrons,  $\text{O} \dots \text{O} = 243.0(16) \text{ pm}$ .

## THE DISCOVERY OF DUNLOP'S SALT

In his work on the adducts of  $\alpha$ -picoline-*N*-oxide, Hadži<sup>1</sup> reported a straight hydrochloride,  $B \cdot HCl$ , but no hemihydrochloride,  $B \cdot \frac{1}{2}HCl$ , corresponding to the hemihydrobromide. As we had experienced difficulties in our X-ray work on this latter, Dunlop<sup>32</sup> attempted to prepare  $B \cdot \frac{1}{2}HCl$ , expecting it to be isomorphous with  $B \cdot \frac{1}{2}HBr$ , and hoping it might be more stable in the X-ray beam. His method was to mix the free base with concentrated aqueous HCl, in various molar ratios between 1:1 and 2:1. At first the product was always the neutral salt,  $B \cdot HCl$ , recognisable by its spectrum, which is shown in Figure 3(b) and which agrees with that given by Hadži.<sup>1</sup> Then one day — »by chance«, as it seemed — Dunlop found crystals with a different appearance. Some of them were a new compound, which we may now call Dunlop's salt (DSALT).

The difficulties of preparing DSALT, and of purifying it, we shall discuss in the Experimental section. But, at this point, we should emphasise that some impurity may not necessarily invalidate the results of crystal-structure analysis, always provided that good single crystals can be picked out from the sample.

The spectrum of DSALT, shown in Figure 3(a), is totally different from that of  $B \cdot HCl$  (b). It is of Hadži's Type (ii), and indeed closely similar to that of the hemihydrobromide.

Crystals from the 1972 preparation were found to have a density of 1.35  $g\ cm^{-3}$ . This density, together with the unit-cell dimensions, gave 1294 a. m. u. for the total contents of the cell. This could be approximately explained by 8 units of composition  $B \cdot HCl \cdot H_2O$ , though such a formula did not account for the spectrum.

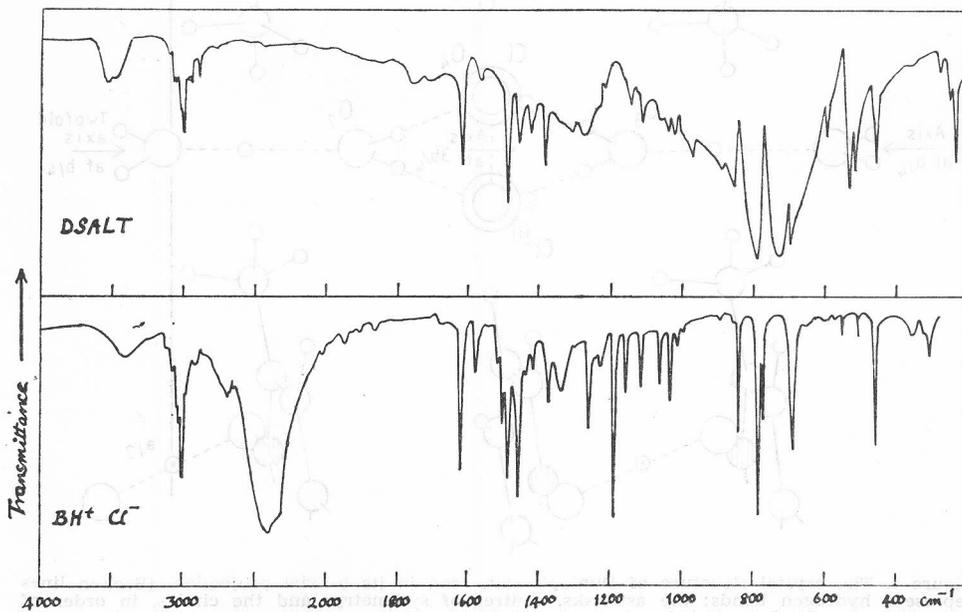


Figure 3. The IR spectrum of (a) Dunlop's salt, and (b)  $\alpha$ -picoline-*N*-oxide hydrochloride.

To elucidate this problem, Dunlop collected X-ray intensity data, and, starting with an open mind, executed a preliminary structure analysis, using the Cl-atom in an application of the heavy-atom method of solving the phase problem.<sup>32</sup> A general view of his findings appears in Figure 4. As we now know, this view was correct in the sense that all the atoms shown are in, or near, their proper positions. The atoms represented by the double circles were taken to be Cl. Some neutron-diffraction data were also collected at about this time; and they supported the same general structure.<sup>32</sup>

If we accept Figure 4, it represents a remarkable disproportionation: a compound of composition  $2(B \cdot HCl \cdot H_2O)$ , the monohydrate of a neutral salt, has actually crystallised as  $BHB^+ ClHCl^- \cdot 2H_2O$ , the dihydrate of a salt

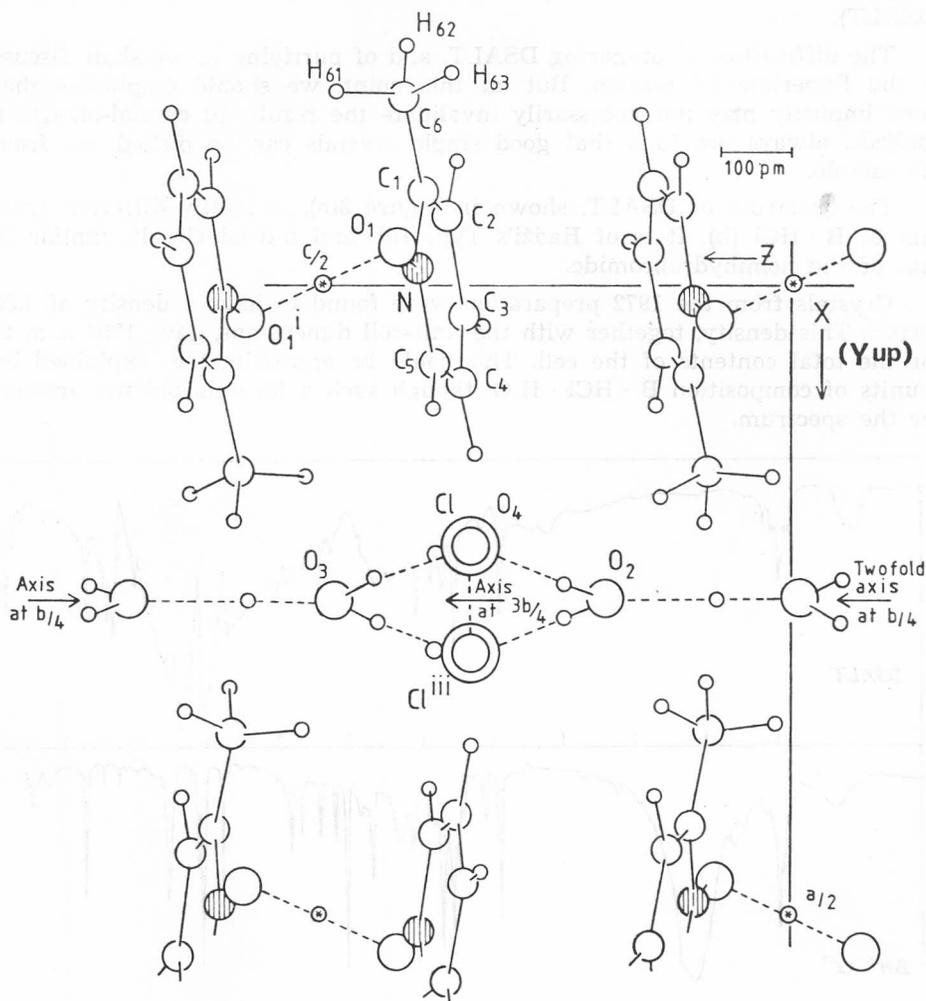


Figure 4. The crystal structure of Dunlop's salt, seen in its *b*-axial projection. (Broken lines represent hydrogen bonds; the asterisks, centres of symmetry; and the circles, in order of increasing size, H, C (or N if hatched), O and Cl. The H-atoms are numbered according to the C- or O-atom to which they are attached.)

that is both acidic and basic. The being four such units in the cell, the implications of the the space group were that the cation and anion are each in special positions; as is shown in the diagram,  $\text{BHB}^+$  lies across a centre of symmetry, and  $\text{ClHCl}^-$  across a twofold axis. DSALT appeared to be a Type A structure in both units.

The anion was of very special interest. For many years there had been speculative research directed towards finding a hydrogen-bichloride unit which might resemble the bifluoride anion, and perhaps involve a strong hydrogen bond with a central proton. For instance, we may cite Waddington's work<sup>33</sup> from the spectroscopic side. And there is at least one crystal in which careful X-ray work, by Schroeder and Ibers<sup>34</sup>, seems to have demonstrated a symmetrical  $\text{ClHCl}$ -unit, though the proton was not directly located. The compound has the formula  $\text{Cs}^+ \text{Cl}^- \cdot 1/3 (\text{H}_3\text{O}^+ \text{HCl}_2^-)$ . Along a threefold axis of the crystal, Cl-atoms are strung out at intervals that are, alternately, 362 and 314(2) pm. The longer distance is double the van der Waals radius of chlorine. (Pauling's estimate was 180 pm.) The shorter distance, being 46 pm less than  $2 \times 180$  pm, must correspond to a hydrogen bond. The H-atom was not actually located. But, at the relevant site, the crystal symmetry is exactly that found in  $\text{NaHF}_2$ ; and it was concluded that this too is a Type A structure, with the proton centrally placed on the mirror-plane.

Returning to DSALT, we face the question, whether we have a similar hydrogen-bichloride anion here, as we have sketched it in Figure 5(a). Before such a claim can be put forward with conviction, we must examine our results more carefully, and the evidence upon which they depend. The  $\text{Cl} \dots \text{Cl}$  distance was surprisingly short,  $\sim 280$  pm, which would mean a contraction of 70 pm below the van der Waals contact distance. The preliminary X-ray

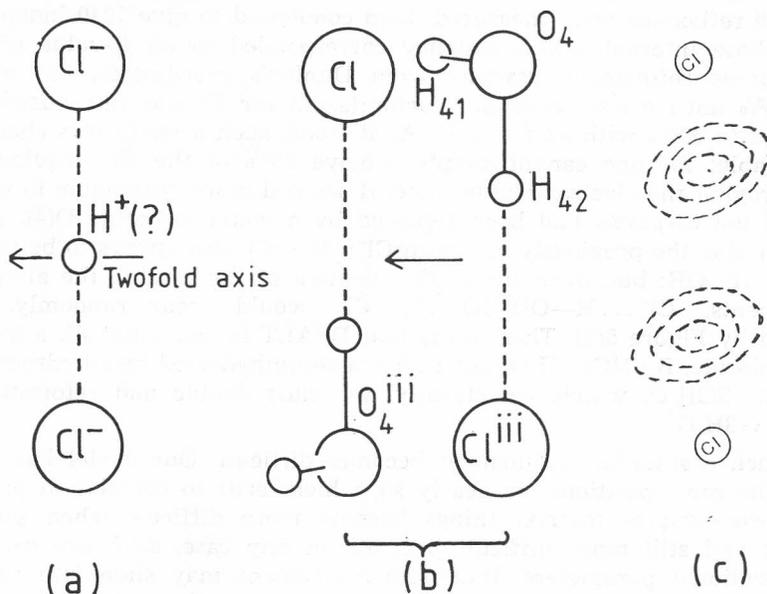


Figure 5. (a) Model of the hypothetical, symmetrical  $\text{Cl}^- - \text{H}^+ - \text{Cl}^-$  unit, (b) model for the actual disordered  $\text{Cl}^- \dots \text{H} - \text{OH}$  unit in Dunlop's salt, (c) an excerpt from the »difference« neutron-scattering density in the region of this hydrogen bond. (Contours, representing negative density, are drawn at intervals of  $-0.3 \text{ pm}^{-6}$  ( $= -0.3 \times 10^{-15} \text{ m pm}^{-6}$ )).

work was unlikely to locate an H-atom between a pair of heavy Cl-atoms. Neutron diffraction might do better; the proton has a neutron-scattering amplitude of  $-3.8$  fm, compared with  $+6.5$  for the C nucleus, or  $+9.6$  fm for Cl ( $1 \text{ fm} = 10^{-15} \text{ m}$ ), and it might appear, in a »difference-density« map, as a negative peak. An excerpt from this map, in Figure 5(c), certainly shows no evidence for a central proton. What does appear is a pair of symmetry-related negative peaks  $70$  pm from each Cl-atom. This was much too close to be acceptable; in the HCl molecule, the Cl—H distance is  $128$  pm, which would be considerably increased by strong hydrogen bonding. (The Fourier series is basic to the understanding of crystal-structure analysis. In practice, the series can never be infinite and, when it is severely restricted — as it was in our neutron work on DSALT — the »termination of series« errors may produce false peaks and especially at positions close to a heavy scatterer. At that stage of our work, we were inclined to discount the two small negative peaks for this reason.)

Furthermore, the early diffraction work on DSALT gave unusually high vibrational parameters for Cl. Isotropised m. s. amplitudes were  $1100 \text{ pm}^2$  from the X-ray analysis, and  $900 \text{ pm}^2$  with neutrons, which may be contrasted with  $600 \text{ pm}^2$  from our X-ray study of acetamide hemihydrochloride.<sup>23</sup> Finally, neither of the preliminary diffraction analyses was precise.

#### A PRECISE X-RAY STUDY OF DUNLOP'S SALT

In the Summer of 1979 one of us (J.C.S.) at last succeeded in repeating Dunlop's preparation of DSALT. The identity of the materials was proved by the spectrum and cell dimensions. In August, 1980, we collected a full set of X-ray intensity data. (Details are given in the Experimental section.) Over 5000 reflexions were measured, then condensed to give 1040 independent terms, whose internal self-consistency corresponded to an  $R$ -value of  $2.7\%$ . Least-squares refinement, starting from Dunlop's coordinates, did not fall below  $10\%$  until a site-occupancy factor (s.o.f.) for Cl was introduced. Then  $R$  dropped to  $6.2\%$  with s.o.f. =  $0.71$ . As it stood, such a result was chemically unreasonable; for one cannot simply remove  $29\%$  of the  $\text{Cl}^-$ , leaving holes and destroying the electrostatic balance. It seemed more reasonable to suppose that half the Cl-atoms had been replaced by a water molecule O(4). At any particular site, the previously supposed  $\text{Cl}^- \cdots \text{H}^+ \cdots \text{Cl}^-$  has always to be replaced by  $\text{Cl}^- \cdots \text{H}-\text{OH}$ ; but, over any sizable domain of the crystal, the alternative arrangements,  $\text{Cl}^- \cdots \text{H}-\text{OH}/\text{HO}-\text{H} \cdots \text{Cl}^-$  would occur randomly, as is suggested by Figure 5(b). This means that DSALT is not, after all, a monohydrated chloride,  $\text{B} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , but rather a sesquihydrated hemihydrochloride,  $\text{B} \cdot \frac{1}{2}\text{HCl} \cdot \frac{3}{2}\text{H}_2\text{O}$ , which, structurally, we must double and reformulate as  $\text{BHB}^+ \text{Cl}^- \cdot 3\text{H}_2\text{O}$ .

In such a situation, refinement becomes difficult. Our model has Cl and O(4) in the same positions, or nearly so, which leads to correlation problems in the least-squares matrix; things become more difficult when s.o.f. are involved; and still more difficult because, in any case, s.o.f. are correlated with vibrational parameters. Indiscreet refinement may slide into catastrophe... The only way out is to restrict the number of correlated parameters to be refined at any stage, to be guided by what is chemically reasonable, and to treat any results with caution.

There is no a priori requirement that the half-atoms Cl and O(4) must be in exactly the same positions, or at exactly the same distance from the twofold axis which formally relates them. Refinement proceeded more quickly when O(4) was supposed to be further from the axis. This led to the s.o.f.,  $\text{Cl}:\text{O}(4) = 0.46(1):0.54$ . This difference is not significant; for the standard deviations will have been underestimated because the factors are related, being constrained to add up to unity.

At appropriate stages in the analysis, all the H-atoms which appear in Figure 4 were located in »difference-density« maps, and were refined with isotropic vibrational parameters. The resulting hydrogen-bonding scheme is reasonable, many of the H-atoms involved have s.o.f. of 0.5, as is found in most forms of ice. All other atoms were allowed anisotropic parameters. At convergence,  $R = 3.7\%$ . Coordinates are collected in Table I.

Because of the correlation problems, some uncertainty might attach to some of the details of this structure. Fortunately, in the Summer of 1981, we obtained a much purer sample of DSALT. From this a satisfactory elemental analysis could be made as follows:

<i>Anal.</i> $\text{C}_6\text{H}_7\text{NO} \cdot \frac{1}{2}\text{HCl} \cdot \frac{3}{2}\text{H}_2\text{O}$ (154.4)	calc'd.: C 46.7; H 6.9; N 9.1; Cl 11.5%
	found: C 46.7; H 5.8; N 9.2; Cl 11.4%
$\text{C}_6\text{H}_7\text{NO} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ (163.6) for comparison	calc'd.: C 44.1; H 6.2; N 8.6; Cl 21.7%

TABLE I

Fractional Atomic Coordinates for Dunlop's Salt ( $\times 10^3$  for H-Atoms;  $\times 10^4$  for Others; Atoms with Site-Occupancy Factors Less than Unity are Asterisked. Standard Deviations in Parenthesis

	<i>x</i>	<i>y</i>	<i>z</i>
Cl*	2073(2)	5740(4)	3385(2)
C(1)	—698(1)	1446(3)	3921(1)
C(2)	—507(1)	—476(3)	3676(1)
C(3)	222(1)	—1000(3)	3485(1)
C(4)	787(1)	382(3)	3528(2)
C(5)	604(1)	2268(3)	3771(2)
C(6)	—1481(1)	2123(4)	4131(2)
N	—118(1)	2742(2)	3965(1)
O(1)	—287(1)	4638(2)	4198(1)
O(2)*	2500	2500	1970(2)
O(3)*	2500	2500	4922(2)
O(4)*	2061(7)	5506(14)	3387(8)
H(0)*	0	500	500
H(2)	—94(1)	—141(3)	364(1)
H(3)	33(1)	—235(3)	336(2)
H(4)	127(1)	8(2)	344(1)
H(5)	96(1)	324(3)	383(1)
H(61)	—148(1)	277(2)	476(2)
H(62)	—184(1)	80(3)	407(2)
H(63)	—153(1)	340(3)	373(2)
H(21)*	250	250	155(2)
H(22)	245(4)	329(4)	223(3)
H(31)*	250	250	48(4)
H(32)	237(2)	324(3)	452(2)
H(41)*	207(1)	485(2)	374(2)
H(42)*	233	671	337

This composition, along with the structural results from the X-ray analysis, leaves us in no doubt that DSALT is correctly seen as the sesquihydrated hemihydrochloride of  $\alpha$ -picoline-*N*-oxide.

The density of the pure material was 1.296 g cm<sup>-3</sup>, which comes into agreement with the formulation above. We attribute the higher densities found in 1972, and later, to contamination of the earlier samples with B · HCl, as is explained in more detail in the Experimental section.

Crystal Data. C<sub>12</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>2</sub> · 3H<sub>2</sub>O, *M* = 308.8, m. p. 44–47 °C, Orthorhombic, space group Pccn, *a* = 1756.0(3), *b* = 679.4(4), *c* = 1332.5(4) pm, *V*<sub>c</sub> = 1589.7 × 10<sup>6</sup> pm<sup>3</sup>, *D*<sub>obs</sub> = 1.296, *Z* = 4, *D*<sub>calc</sub> = 1.294 g cm<sup>-3</sup>,  $\mu$  (Mo *K* $\alpha$ ) = 2.2 cm<sup>-1</sup>.

#### THE STRUCTURE OF DUNLOP'S SALT

The atom-numbering system, corresponding to Table I, is explained in Figure 4. The diagram also shows our final structure, based on the X-ray analysis, with the understanding that the double circles now represent half-atoms of Cl or O(4) which are nearly congruent. The nature of this disorder is illustrated in Figure 5(b). The principal bond-lengths and angles, within the cation, are listed in Table II. The mean plane of the six atoms of the

TABLE II

*Interatomic Distances (pm), and Angles (°), in the Cation of Dunlop's Salt.*  
(Standard Deviations in Parentheses.)

N—O(1)	135.8(2)			C(1)—N—O(1)	117.7(1)
		C(2)—H(2)	99(2)	C(5)—N—O(1)	118.7(1)
N—C(1)	134.8(2)	C(3)—H(3)	95(2)	N—C(1)—C(2)	116.2(2)
C(1)—C(2)	138.7(3)	C(4)—H(4)	89(2)	C(1)—C(2)—C(3)	121.4(2)
C(2)—C(3)	135.3(3)	C(6)—H(61)	94(2)	C(2)—C(3)—C(4)	119.9(2)
C(3)—C(4)	136.6(3)	C(6)—H(62)	110(2)	C(3)—C(4)—C(5)	119.1(2)
C(4)—C(5)	136.0(3)	C(6)—H(63)	102(2)	C(4)—C(5)—N	119.9(2)
C(5)—N	133.4(2)			C(5)—N—C(1)	123.5(2)
C(1)—C(6)	147.6(3)	O(1) · H(0)	120.7(2)	C(2)—C(1)—C(6)	124.3(2)
				N—C(1)—C(6)	119.4(2)
				N—O(1) · H(0)	107.7(1)

pyridine ring is expressed by the equation,  $0.1372 X' - 0.2103 Y + 0.9686 Z' = 468.79$  pm, in which *X'*, *Y* and *Z'* are absolute orthogonal coordinates with respect to axes chosen to be parallel to *a*, *b* and *c*\*. Deviations from this plane are small. Symmetry requires the mean planes of the two halves of the cation to be parallel. They need not be co-planar; and, indeed, the cation is buckled by a rotation about the N—O bonds, the result of which is that the perpendicular distance between the mean planes amounts to 200 pm. (The same cation occurs in the hemihydrobromide of  $\alpha$ -picoline-*N*-oxide, and it has exactly the same configuration.)

The hydrogen bond connecting the two base units is »very short«: O...O = 241.4(3) pm. Other details of this bond are in Table III, which also contains information about the other hydrogen bonds. The most interesting of these is that between Cl and O(4), across the twofold axis at 3*b*/4;

TABLE III

Geometrical Details of the Hydrogen Bonding in Dunlop's Salt. (Distances, pm, with Standard Deviations in Parentheses. When Needed an Equivalent-Position Superscript is Defined.)

A—H $\cdots$ B	A $\cdots$ B	A—H	H $\cdots$ B	A—H $\cdots$ B
O(1) $\cdots$ H(0) $\cdots$ O(1 <sup>i</sup> ) $i = x, 1 - y, 1 - z$	241.4(3)	120.7(2)	(120.7)	(180°)
O(4)—H(42) $\cdots$ Cl <sup>ii</sup> $ii = 1/2 - x, 3/2 - y, z$	297.0(10)	95	200.3	178°
O(3)—H(3) $\cdots$ O(2 <sup>iii</sup> ) $iii = x, 1/2 - y, 1/2 + z$	272.9(4)	75(3)	198	(180°)
O(2)—H(22) $\cdots$ O(4)	288.7(10)	65(3)	226(3)	164(4)°
O(3)—H(32) $\cdots$ O(4)	299.1(10)	77(3)	223(3)	176(5)°
O(2)—H(22) $\cdots$ Cl	299.4(3)	65(3)	236(3)	167(4)°
O(3)—H(32) $\cdots$ Cl	309.9(3)	77(3)	234(3)	173(3)°

Cl...O(4<sup>ii</sup>) = 297.0(10) pm, which is short for a bond of this sort. Olovsson and Jönsson<sup>35</sup> in 1976, listed details of all the hydrogen bonds that had been accurately studied with neutrons; in their table are 15 examples, with Cl...O ranging from 304 to 332 pm, and averaging 319 pm. Schroeder and Ibers<sup>34</sup> give one more example with 292(2) pm, virtually the same as in DSALT. These two relatively short Cl...O bonds are only slightly less than the Pauling value for a non-bonded contact, 320 pm; and the average value above shows no contraction at all. The electronegativity of Cl is much lower than those of F or O, lower even than that of N. Perhaps chlorine is incapable of forming a strong hydrogen bond.

One of the atoms H(41) of the water molecule, O(4), appeared prominently on a »difference« map, and its position was refined successfully. However, the other atom, H(42), was not located in the X-ray work. It was, therefore, arbitrarily put into a reasonable position on the O(4)...Cl line. No standard deviations can be assigned to any geometrical details involving this H-atom. (We may be fairly sure that H(42) is not at the mid-point between O(42<sup>ii</sup>) and Cl.) Figure 5(c) was based on the preliminary neutron work,<sup>32</sup> and it conveys some sense of half-protons roughly appropriate to our model in (b). However, as we have already pointed out, they are too close to O(4) by at least 25 pm. This deviance, though smaller, would need to be explained by the possible diffraction error described earlier.

## EXPERIMENTAL

*Preparation of Dunlop's Salt*

Hadži<sup>1</sup> first prepared the hemihydrobromide of  $\alpha$ -picoline-*N*-oxide by passing HBr gas into an ethanolic solution of the base (B). Our preparations were all done in aqueous solution, a method that had been generally successful in making acid salt. (Dunlop's unforeseen discovery of DSALT could not have been made without some source of extraneous water.) Hoping to prepare B·1/2HCl, he mixed the free base with concentrated HCl in molar ratios ranging from 2:1 to 1:1. As we have explained, such mixtures normally produced the neutral salt, B·HCl. It was only after several further attempts that DSALT was observed amongst the product. When I (J.C.S.) tried to repeat Dunlop's work some years later, I had several

failures, until »by chance« DSALT appeared. It is for this reason that preparation is so difficult. The following recipe may be successful: 2.4 g of the base, which was slightly damp, were mixed with 1.2 ml of HCl (11 M); no extra water is needed, complete dissolution occurring after gentle warming. Allowed to stand, the solution may deposit colourless, prismatic crystals, elongated parallel to the *b*-axis, and showing straight extinction between crossed polaroids. DSALT is very soluble in water. It crystallises from a concentrated solution which may contain excess acid or base, and it may be contaminated with B·HCl in particular. Further, after keeping for some time, there may be decomposition to yield B·HCl and perhaps other compounds. For these reasons, purification is also difficult, and to them we attribute our originally erroneous density.

Wishing to see how the spectrum of B·HCl might be affected by the presence of free base, we ground together roughly equimolar proportions of B and B·HCl. The mixture quickly liquefied, then re-solidified. The product had the IR spectrum of DSALT. Once again, DSALT materialised unexpectedly...

### The X-Ray Analysis of Dunlop's Salt

The crystal was a prism with dimensions (in mm)  $0.68 \times 0.25 \times 0.16$ , mounted in a Lindemann capillary. Intensity measurements were made on a CAD4 diffractometer, using Mo-*K* $\alpha$ -radiation, with a  $\theta/\omega$  scan and bisecting geometry. Monitoring of a standard reflexion showed no signs of crystal damage. The 5452 measured reflexions were merged to yield 1040 independent terms with  $I > 2\sigma(I)$ . Two of these showed signs of extinction errors, (200) and (002), and they were deleted in the final stages. Refinement was by full-matrix least-squares, using the program SHELX<sup>36</sup>; weighting was based on counting statistics; scattering functions were taken from International Tables, Vol. IV, 2.2B, chlorine being in its ionic form. The final values both *R* and *R*<sub>w</sub> were 3.71%. An analysis of the weighting scheme was reasonably satisfactory, though the terms with highest  $|F_o|$  and lowest  $\sin \theta$  were slightly over-weighted. Tables of structure factors and vibrational parameters may be obtained by application to the Authors.

### X-Ray Work on $\alpha$ -Picoline-N-oxide Hemihydrobromide<sup>16</sup>

Crystal Data:  $(C_6H_7NO)_2H^+ Br^-$ , *M* = 299.2, monoclinic, space group *C2/c*, *a* = 1312, *b* = 689, *c* = 1474 pm,  $\beta$  = 103.05°, *V*<sub>c</sub> =  $1298 \times 10^6$  pm<sup>3</sup>, *D*<sub>obs</sub> = 1.52, *Z* = 4, *D*<sub>calc</sub> = 1.53 g cm<sup>-3</sup>.

Mills recorded partial three-dimensional data: some 510 reflexions in the reciprocal-lattice nets *h0l*, *h3l* and *hh1* (470 independent), measured by the photographic-visual method, and not corrected for absorption. These data were used by Dr. Mallinson, with the new Glasgow system of programs<sup>17</sup>, to refine Mills' coordinates, by isotropic full-matrix analysis, for the heavier atoms. (The H-atoms, except for those of the methyl group, were placed in calculated positions, but not refined.) Convergence was at *R* = 14%, and coordinates are in Table IV.

TABLE IV

Fractional Coordinates ( $\times 10^3$ ) for  $\alpha$ -Picoline-N-oxide Hemihydrobromide, with Standard Deviations in Parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Br <sup>-</sup>	0	125(1)	250
C(1)	157(2)	406(5)	84(2)
C(2)	128(2)	227(5)	60(2)
C(3)	88(2)	167(5)	-37(2)
C(4)	85(2)	311(5)	-99(2)
C(5)	109(2)	501(5)	-76(2)
C(6)	195(3)	472(5)	177(2)
N	147(2)	538(4)	13(1)
O	180(2)	728(4)	39(1)
H(0)	250	750	0

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### IZVLEČEK

#### Bazične soli z zelo kratkimi vodikovimi vezmi; kristalna struktura adukta $\alpha$ -pikolin-N-oksida-hemivodikovklorid trihidrat (Dunlopova sol)

*J. Clare Speakman in Kenneth W. Muir*

Mnoge preproste karbonske kisline (HX) kristalizirajo z anioni (XHX)<sup>-</sup>, ki so simetrični in ki vsebujejo »zelo kratke« OHO vezi, z razdaljami O...O manjšimi od 250 pm. Takšne spojine tudi kažejo neobičajne infrardeče spektre, ki jih po Hadžiju klasificiramo kot spektre tipa »ii«. Odlikuje jih zelo široka (od 2000—400 cm<sup>-1</sup>) absorpcija asimetričnega valenčnega nihanja  $\nu$ OH z vrhom  $\nu$  območju od 600 do 1500 cm<sup>-1</sup>.

Kristalografsko jih uvrščamo v tip A. Anioni XHX<sup>-</sup> so simetrični, vodik leži na simetrijskem elementu prostorske grupe (večkrat na centru inverzije ali dvoštevni osi), obe skupini X pa sta identični in razdalje O...O vezi so vedno v območju od 242 do 255 pm (npr. v ledu je O...O razdalja 276 in 265 pm v tipičnem cikličnem dimeru karbonske kisline).

Nekatere organske baze tvorijo analogne bazične soli, ki imajo podobne neobičajne spektre tipa »ii«. Prvi tak primer je našel Hadži leta 1962, in sicer je ta spojina hemivodikovbromid  $\alpha$ -pikolin-N-oksida,  $B \cdot \frac{1}{2} \text{HBr}$ , kjer je  $B = \text{C}_6\text{H}_7\text{NO}$ , za

katerega je napovedal formulo  $\text{BHB}^+ \cdot \text{Br}^-$ . Tudi v strukturi te spojine, kot je potrdila rentgenska uklonska analiza na monokristalu, je prisotna »zelo kratka« OHO vez. Članek podaja strnjen pregled predhodnega kristalografskega dela na tej spojini.

Dunlopova sol je trihidrat hemivodikovega klorida iste baze. V članku je opisana rentgenska strukturalna analiza (1040 uklonov,  $R = 3.7\%$ ). Pokazalo se je, da ima spojina  $B \cdot \frac{1}{2} \text{HCl} \cdot \frac{3}{2} \cdot \text{H}_2\text{O}$  strukturo, ki ustreza formuli  $\text{BHB}^+ \cdot \text{Cl}^- \cdot 3\text{H}_2\text{O}$ . Kationi

ležijo na centru inverzije z razdaljo O...O enako 241,4(3) pm. Med reševanjem strukture se je dozdevalo, da kristal vsebuje  $\text{ClHCl}^-$  aniona, toda bolj podrobna analiza je pokazala, da anioni  $\text{Cl}^- \cdots \text{H} - \text{OH}$  (ali  $\text{HO} - \text{H} \cdots \text{Cl}^-$ ) kažejo simetrijo zaradi nereda okrog dvoštevne osi v kristalu, tako da je razdalja  $\text{Cl}^- \cdots \text{O} = 297(1)$  pm. Infrardeči spekter Dunlopove soli je skoraj identičen s spektrom hemivodikovegabromida.