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Pseudosymmetry in ammonium [(carboxymethyl)sulfanyl]acetate

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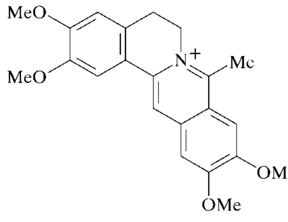
The structure of the title compound, $NH_4^+\cdot C_4H_5O_4S^-$, is composed of monocarboxylate anions of [(carboxymethyl)-sulfanyl]acetic acid linked into infinite chains *via* strong $O-H\cdots O^-$ hydrogen bonds. The three-dimensional structure is completed by the ammonium cations, which interlink neighbouring chains *via* $N-H\cdots O$ hydrogen bonds. Solution and refinement in the true space group *Pn* led to an unambiguous position for the single carboxyl H atom. In the higher symmetry space group *P*2/*n*, the carboxylate anion would be located on a twofold axis.

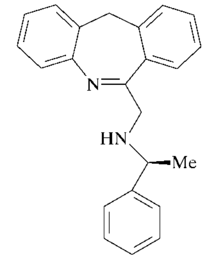
Comment

Sodium borohydride ($NaBH_4$) is a valuable reducing agent in modern organic synthesis and is the reagent of choice in many reductions of C—O, C—N and even C—C multiple bonds. The reactivity of $NaBH_4$ can be readily modified and enhanced through its reaction with various additives and modifying agents (Perisamy & Thirumalaikumar, 2000).

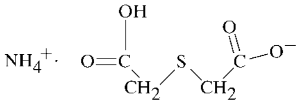
Over the past decade we have been interested in the (stereo)selective synthesis of various natural or medicinally significant products (Ziółkowski *et al.*, 1999; Biała *et al.*, 2002). In some cases, borohydride reduction was the key step. Recently, we have studied selective reductions of prochiral fragments of intermediates in the stereoselective synthesis of natural protoberberines and mianserin. Thus, the intermediate compounds (I) and (II) were prepared (Sotomayor *et al.*, 1996; Pawłowska *et al.*, 2003) and subjected to reduction with a variety of acyloxyborohydrides. The best results (65–70% diastereomeric excess) were obtained with tris(trimethyl-acetoxyborohydride) (Pawłowska *et al.*, 2004). In the search for even better diastereo-control, we focused our attention on [(carboxymethyl)sulfanyl]acetic acid, (III) [alternative names: 2,2′-thiobis(acetic acid), mercaptodiacetic acid, thiodiglycolic acid], which has not previously been used as a substituent for borohydride modifications. We surmise that the molecule of (III) combines steric demands with a remarkable ability to form complexes with transition metals (Efimenko *et al.*, 1991), thus making it a good reagent for borohydride derivatization. Having experienced some problems with the solubility of the protoberberine precursor, (I), in the same solvent as the reducing agent, we decided to make the reagent water-soluble and stable by transforming the acid into its monoammonium salt. Thus, the title [(carboxymethyl)sulfanyl]acetic acid ammonium salt, (IV), was prepared from 1,4-oxathiane-2,6-dione, (V), by the action of aqueous ammonia.



Protoberberine precursor (I)



Mianserin precursor (II)



$NH_4^+\cdot HO-C(=O)-CH_2-S-CH_2-C(=O)-O^-$

(IV)

Initially, the diffraction data for (IV) were collected at room temperature on a conventional four-circle diffractometer. Although the structure could be solved and refined in both centrosymmetric and non-centrosymmetric space groups (*P*2/*n* and *Pn*, respectively), better results (see below) were obtained in the latter, for which there was also a slight preference in terms of the intensity statistics (mean $|E^2-1| = 0.801$). However, although the structure was qualitatively reasonable, some features were unsatisfactory, for instance, discrepancies in N—H distances, or relatively high and unequal isotropic displacement parameters for these H atoms. For this reason, a complete sphere of low-temperature data was collected on an area detector. We present here and discuss only the low-temperature data, which provide a strong indication that the lower-symmetry space group *Pn* is correct.

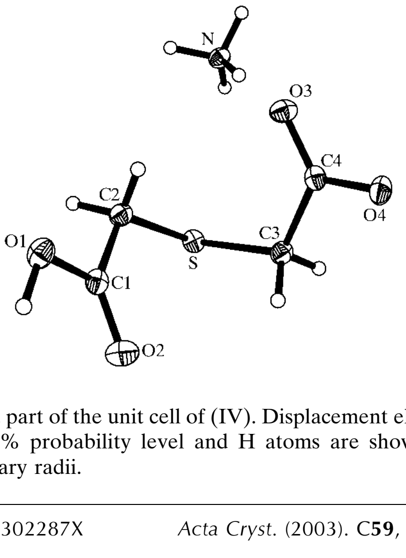


Figure 1
The independent part of the unit cell of (IV). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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The asymmetric unit of (IV) (Fig. 1) consists of the monoanion of acid (III) and an ammonium cation. Bond distances and angles are summarized in Table 1. There are three types of hydrogen bonds stabilizing the present structure. One type is between carboxyl and carboxylate groups, leading to a zigzag chain of anions with an overall direction parallel to $[\bar{1}01]$. The second type describes the three N—H···O linkages involving carboxyl and carboxylate O atoms, and the third type describes N—H···S hydrogen bonds (Fig. 2 and Table 2). The ammonium ions thus link the chains into a three-dimensional array.

There are some similarities between the structure of (IV) and that of ammonium hydrogen glutarate (with the S atom replaced by a methylene group; Macdonald & Speakman, 1971). One dissimilarity lies in the overall molecular conformation; the glutarate anion forms a planar zigzag chain that is almost linear, whereas the hydrogen thiobiacetate anion is twisted in all structures, so that the S and C atoms are not in the same plane. Even more important is the difference in overall packing in these structures. Ammonium hydrogen glutarate consists of alternate planes of glutarate dianions and ammonium cations perpendicular to the *a* direction in the orthorhombic lattice. The anions pass approximately parallel to the *a* direction (perpendicular to the layers).

An additional distinction in the structure of (IV) is the presence of very strong O—H···O$^-$ hydrogen bonds between carboxyl and carboxylate groups. The significant difference between the two C—O distances [1.244 (2) and 1.279 (2) Å for C4—O3 and C4—O4, respectively] may indicate a partial localization of negative charge at O4, consistent with the very short O—H···O4 contact. On the other hand, the C—O distances involving atom C1 [1.320 (2) and 1.212 (2) Å for C1—O1 and C1—O2, respectively] correspond to those expected for carboxylic acids [1.308 (19) and 1.214 (19) Å, respectively (Allen *et al.*, 1987; Maurin, 1998)]. Comparison with thiobiacetic acid (Kepert *et al.*, 1999) is also instructive. In that compound, the usual centrosymmetric carboxylic acid dimers are observed, with O···O and H···O distances of 2.675 and 1.894 Å, respectively, leading to infinite chains of molecules. The C—O bond distances of 1.299 and 1.221 Å, respectively, are normal for carboxylic acids. The molecule of thiobiacetic acid is approximately planar.

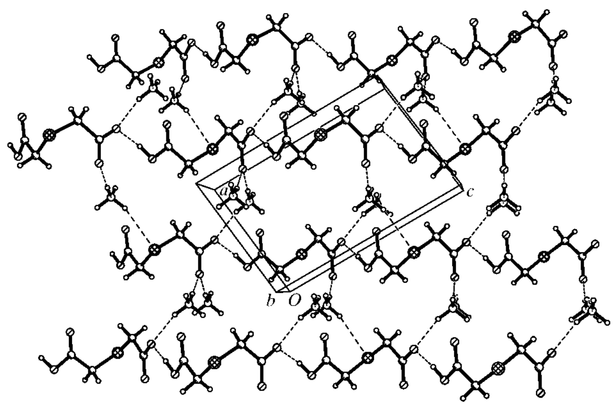

Figure 2
The crystal packing diagram for (IV), viewed along the *b* direction. Hydrogen bonds are shown as dashed lines.

We now present our reasons for rejecting the centrosymmetric space group *P*2/*n*. The corresponding refinement presented serious problems, the most important of which involved the carboxyl H atom. The special position of the S atom on the twofold axis would, in an ordered structure, imply either the presence of the dicarboxylic acid itself or of its dianion, both inconsistent with the single ammonium cation. The localization of an H atom in the vicinity of one carboxyl O atom resulted, however, in a close H···H contact between molecules related by the inversion centre, and its position could not be refined. The only possible solutions were a localization of this H atom on the inversion centre, or a description of the structure as partially disordered. Nevertheless, such a procedure led to much worse overall results for the initial room-temperature data than refinement in the space group *Pn* (*wR*2 = 0.1349 and 0.0775, respectively). These findings were then confirmed by the low-temperature structure solution and refinement (*wR*2 = 0.0738 in *Pn*).

The previously solved structures of potassium and rubidium hydrogen thiobiacetates (Herbertsson, 1976) were presented as an isomorphous pair in space group *P*2/*c*, but were not entirely satisfactory (carboxyl H atom not located, high *R* values). The cells can be transformed with the matrix $(100, 0\bar{1}0, \bar{1}0\bar{1})$ to a cell analogous to that of (IV). We assume, therefore, that these structures are isomorphous with (IV) and should have been refined in the same non-centrosymmetric space group. There is, however, one obvious qualitative distinction between the potassium/rubidium and ammonium salts, namely that the ammonium cation can act as a hydrogen-bond donor.

The problem of pseudosymmetry as presented above is quite common for structures with short carboxyl to carboxylate interactions. From a total of 7022 organic and metal–organic structures containing carboxy groups (Cambridge Structural Database, Version 5.24; Allen, 2002), 49 involve carboxylic acid H atoms with intermolecular distances closer than the sum of the van der Waals radii, and in 24 structures, this distance is even shorter than 1 Å. In 26 cases, the molecules in question are symmetry related by a centre of symmetry, a twofold axis or a mirror plane. It is interesting that, in all cases, the O···O distance is relatively short [mean value = 2.35 Å (2.57 Å for the whole group of 49)], much less then the mean value for O—H···O *D*···*A* distances in carboxylic acids (2.64 Å; Maurin, 1998). 18 of 49 structures were described as disordered in the carboxylic acid region. Such an explanation is acceptable for hydrogen bonds between carboxyl and carboxylate groups, but an alternative might be description in a lower-symmetry space group, as in the structure of (IV). The only supporting argument for disorder would be a small difference in the C—O distances of the carboxylic acid group even in the lower-symmetry space group. We believe that careful and precise measurements might resolve many dubious pseudosymmetry cases, which are fairly common not only for carboxyl–carboxylate interactions, but also for many other structures with very strong hydrogen bonds to anionic acceptor sites.

Experimental

Compound (IV) was prepared by slow addition of a 25% ammonia solution (5 ml) to 1,4-oxathiane-2,6-dione (1 g) dissolved in dioxane (20 ml). After the addition, the solvents were removed by evaporation under vacuum and the residue was heated at 503 K for 2 h. The product was recrystallized from ethanol to afford compound (IV) in 93% yield (m.p. 432–433 K). NMR spectra were in accordance with the structure.

Crystal data

$NH_4^+\cdot C_4H_5O_4S^-$
$M_r = 167.18$
Monoclinic, *Pn*
$a = 7.0429\ (8)$ Å
$b = 4.8135\ (6)$ Å
$c = 10.9047\ (12)$ Å
$\beta = 96.885\ (3)^\circ$
$V = 367.01\ (7)$ Å^3
$Z = 2$

$D_x = 1.513$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3980 reflections
$\theta = 3.3$–30.0°
$\mu = 0.40$ mm^{-1}
$T = 133\ (2)$ K
Tablet, colourless
0.35 × 0.24 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scan
3980 measured reflections
2066 independent reflections
2032 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.023$
$\theta_{\rm max} = 30.0^\circ$
$h = -9 \rightarrow 9$
$k = -6 \rightarrow 6$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.074$
$S = 1.07$
2066 reflections
124 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.0053P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.46 (5)

Crystals of (IV) were enantiomeric twins and the structure was refined accordingly. A total of 994 Friedel pairs was used to establish the Flack (1983) parameter. H atoms attached to C atoms were included at calculated positions and refined using a riding model; other H atoms were refined freely.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998).

We are grateful to colleagues from the Institute of Nuclear Chemistry and Technology in Warsaw for making their X-ray equipment available to us. The low-temperature data were collected at the Institute of Inorganic and Analytical Chemistry of the Technical University, Braunschweig. A referee contributed helpful comments regarding the structural similarity with the potassium and rubidium salts.

Table 1
Selected geometric parameters (Å, °).

C1—O2	1.2119 (17)	C4—O3	1.2443 (17)
C1—O1	1.3196 (19)	C4—O4	1.2792 (19)
O2—C1—O1	124.65 (14)	O3—C4—O4	124.32 (14)
O2—C1—C2	124.43 (15)	O3—C4—C3	121.47 (14)
O1—C1—C2	110.92 (12)	O4—C4—C3	114.21 (12)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1N···S$^{\rm i}$	0.92 (2)	2.71 (2)	3.6075 (15)	163.5 (19)
N—H4N···O3$^{\rm ii}$	0.94 (2)	1.971 (19)	2.9040 (16)	172.4 (16)
N—H3N···O4$^{\rm iii}$	0.923 (18)	1.966 (18)	2.8683 (16)	165.1 (17)
N—H2N···O3	0.87 (2)	1.99 (2)	2.8607 (16)	175 (2)
O1—H1O···O4$^{\rm iv}$	0.938 (19)	1.622 (19)	2.5418 (11)	166 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $x, 1+y, z$; (iii) $x-\frac{1}{2}, 1-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}+x, -y, z-\frac{1}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1581). Services for accessing these data are described at the back of the journal.

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