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Potassium 3-Dithiocarboxy-3-aza-5-aminopentanoate Dihydrate

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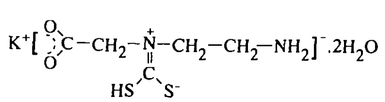
Abstract

The synthesis and crystal structure of the title compound, $K^+.C_5H_9N_2O_2S_2^-.2H_2O$, are described. The structure consists of potassium cations, 3-dithiocarboxy-3-aza-5-aminopentanoate anions and molecules of water. The anion exists in two tautomeric forms, each described by two resonance structures.

Comment

Dithiocarbamates are organosulfur compounds with wide applications. They are used as accelerators in vulcanization, as high-pressure lubricants, as well as fungicides and pesticides (Kaushik, Bhushan & Sharma, 1984). Also, dithiocarbamates are often used for the synthesis of transition metal complexes (Coucouvanis, 1970). As dithiocarbamates themselves, dithiocarbamate–metal complexes have been used in agriculture for controlling insects and fungi, in the treatment of alcoholism, *etc.* (Kitson, 1985).

In this paper, we report the synthesis and crystal structure of potassium 3-dithiocarboxy-3-aza-5-aminopentanoate dihydrate, (I). The structure consists of 3-dithiocarboxy-3-aza-5-aminopentanoate anions, K^+ cations and molecules of water (Fig. 1) held together by Coulomb forces and hydrogen bonds. Intramolecular hydrogen bonds are of the N—H···O and O*w*—H···O types. It is interesting that O1 appears as a fourfold acceptor. Hydrogen bonds are weak [2.813 (1)–3.00 (1) Å] and bent, with the exception of O*w*2—H*w*22···O1 which is of normal length, 2.738 (3) Å, and almost linear.



$$K^+[\,{}^{O}_{O^-}\!\!>C-CH_2-\overset{+}{N}(=C(SH)S^-)-CH_2-CH_2-NH_2]^-.2H_2O$$

(I)

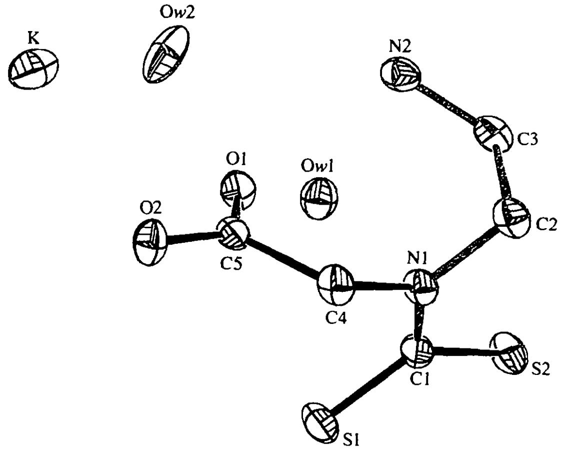
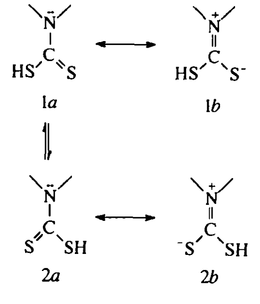


Fig. 1. The numbering of atoms and geometry of the title compound. Displacement ellipsoids are drawn at the 40% probability level.

The coordination number of the K^+ cation is six and includes pairs of O2 and O*w*2 atoms from two different asymmetric units, and a pair of O*w*1 atoms from a third asymmetric unit. The polyhedron around K^+ is a very irregular body.

The bond lengths and angles in the 'outer' parts of the anion are normal, but in the C4—N1—C2 and N1—C1—S2 regions, bond lengths and angles are different from the expected ones. The angles around the N1 and C1 atoms are near to 120° and the N1—C1 bond has multiple-bond character [1.351 (4) Å]. Furthermore, the fact that the C1—S1 and C1—S2 bond lengths are almost the same and that the position of the H atom H(S) could not be determined suggests a rapid intramolecular hydrogen migration (1 ⟷ 2). This part of the molecule can be presented schematically as a resonance hybrid, with *b* being the predominant form.



Experimental

Ethylenediamine-*N*-monoacetic acid dihydrochloride was synthesized as described earlier (Fujii, Kyuno & Tsuchiya, 1970). Acetone and carbon disulfide were distilled before usage. All other chemicals were used as purchased without any further purification. A solution of ethylenediamine-*N*-monoacetic acid dihydrochloride (H_2edda.2HCl; 3.80 g, 0.02 mol) in 10 ml of water was neutralized by a solution of KOH (3.36 g, 0.06 mol) in 10 ml of water and then 80 ml acetone was added. CS_2 (2.4 ml, 0.04 mol) was added dropwise to the mixture which was stirred at room temperature for 3 h. The resulting white precipitate of potassium 3-dithiocarboxy-3-aza-5-aminopentanoate dihydrate was filtered, washed with acetone and air dried [yield: 3.50 g (65.3%)]. The precipitate was recrystallized twice from hot water and single crystals suitable for X-ray analysis were obtained after cooling in a refrigerator overnight.

Crystal data

$K^+.C_5H_9N_2O_2S_2^-.2H_2O$
$M_r = 268.39$
Monoclinic
$P2_1/c$
$a = 13.8156\,(12)$ Å
$b = 6.947\,(2)$ Å
$c = 12.4225\,(14)$ Å
$\beta = 111.66\,(1)^\circ$
$V = 1108.0\,(4)$ Å^3
$Z = 4$
$D_x = 1.609$ Mg m^{-3}
$D_m = 1.606$ Mg m^{-3}
D_m measured by flotation in a $CHBr_3/n\text{-}C_4H_{10}$ mixture

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.76\text{–}15.96^\circ$
$\mu = 0.848$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
$0.4 \times 0.3 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scan
Absorption correction: none
2729 measured reflections
2493 independent reflections
2031 reflections with $I > 3\sigma(I)$

$R_{\rm int} = 0.0228$
$\theta_{\rm max} = 27^\circ$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 8$
$l = -17 \rightarrow 17$
3 standard reflections frequency: 120 min intensity decay: 0.6%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.041$
$S = 0.957$
2031 reflections
144 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{\rm max} = 0.03$

$\Delta\rho_{\rm max} = 0.608$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.390$ e Å^{-3}
Extinction correction: *SDP* (Frenz, 1982)
Extinction coefficient: $1.32\,(2) \times 10^{-6}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C1	1.717 (3)	N1—C1	1.351 (4)
S2—C1	1.708 (3)	N1—C2	1.477 (4)
O1—C5	1.257 (3)	C4—C5	1.516 (3)
C2—C3	1.523 (4)	N1—C4	1.459 (4)
O2—C5	1.259 (4)	N2—C3	1.478 (4)
C1—N1—C2	121.5 (2)	S2—C1—N1	119.6 (2)
C1—N1—C4	121.1 (2)	N1—C2—C3	113.6 (2)
C2—N1—C4	117.3 (2)	N2—C3—C2	111.5 (2)
S1—C1—S2	120.9 (2)	O1—C5—O2	124.2 (2)
N1—C4—C5	115.5 (2)	O1—C5—C4	119.4 (3)
S1—C1—N1	119.6 (2)	O2—C5—C4	116.4 (3)

The title structure was solved by direct and difference Fourier methods, and refined by full-matrix least-squares techniques. Almost all H atoms were found in a difference Fourier map; the exception being H(S). However, H atoms attached to C and N atoms were placed at calculated positions (C—H and N—H = 0.95 Å) and were allowed to ride on the adjacent atom, with U(H) = 1.2U(carrier atom). Water H atoms were refined isotropically. All calculations were performed on a PDP 11/73 computer using the *SDP* (Frenz, 1982) program.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SDP*. Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *SDP*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KA1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(Ferrocenylmethyl)-6-methoxy-3-methylbenzonitrile and 10-(Ferrocenylmethyl)phenanthrene-9-carbonitrile

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Abstract

The structures of the title compounds, 2-(ferrocenylmethyl)-6-methoxy-3-methylbenzonitrile, $[Fe(C_5H_5)(C_{15}H_{14}NO)]$, (1), and 10-(ferrocenylmethyl)phenanthrene-9-carbonitrile, $[Fe(C_5H_5)(C_{21}H_{14}N)]$, (2), revealed that the cyano groups of the arylacetonitrile migrated to the aromatic systems during aryne reactions. The ori-