

Table 2. Conformational effects of oxygen-bridge substitution

These values represent the averages of those structures reported by Cody (1980, 1981).

C-X-C	3,5-	C(4)-X (Å)	X-C(1') (Å)	C(4)-X-C(1') (°)	Conformation
O	I	1.376	1.394	119.6	Skewed, twist-skewed
	Other	1.380	1.377	120.0	Skewed, twist-skewed
C	I	1.484	1.523	116.3	Skewed, twist-skewed
	Other	1.514	1.512	115.5	Twist-skewed, perpendicular

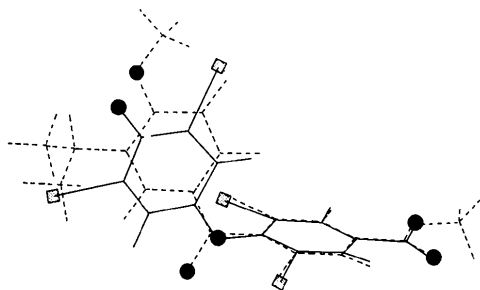


Fig. 4. Superposition of title compound (dashed) with that of 4-(4-hydroxy-3,5-diiodophenoxy)-3,5-diiodobenzoic acid (Cody & Strong, 1980). The squares are iodine and filled circles oxygen.

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α,α' -Dithiobisformamidinium Dinitrate, [(NH₂)₂CSSC(NH₂)₂]⁺[NO₃]₂⁻ at 110 K

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Abstract. C₂H₈N₄S₂²⁺·2NO₃⁻, monoclinic, *C2/c*, *a* = 10.871 (5), *b* = 8.113 (4), *c* = 11.580 (5) Å, β = 100.32 (2)°, *V* = 1004.8 Å³, *Z* = 4. The structure was refined on *F* (including positional parameters for hydrogen atoms) to *R* = 0.038 and *R_w* = 0.039 for 1055 reflections having *F*_o² > 3σ(*F*_o²). The dication has crystallographically imposed twofold symmetry with the following stereochemistry: C–N 1.311 (3) and 1.301 (3) Å; C–S 1.786 (2) Å; S–S 2.022 (1) Å;

The observation that these ketone-bridged thyroid hormone analogues have significant nuclear receptor binding affinity (Cheung, unpublished results) suggests that they could be used as photo-affinity probes of the active site on thyroid hormone-binding proteins.

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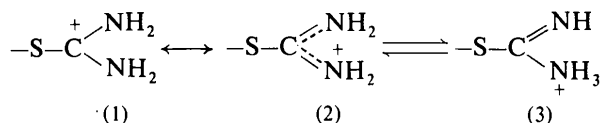
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planar configuration around the carbon atom; C–S–S–C torsional angle 97.9 (1)°; S–S–C–N torsional angles 6.6 (2) and 6.8 (2)°. An extensive hydrogen-bonding network links nitrate oxygen atoms with hydrogen atoms [O...N 2.837 (3), 2.862 (3), 2.888 (3) and 2.970 (3) Å].

Introduction. In the course of studies on the interaction of metal(III) species with thiourea under acidic conditions colourless crystals of the title compound appeared as the result of redox reactions. Several possible structures exist for the cation.

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Although the structures of several rhenate derivatives (Lis, 1979, 1980) and of the dichloride (Villa, Manfredotti, Nardelli & Tani, 1972), and dibromide and diiodide compounds (Foss, Johnsen & Tvedten, 1958) are known, it was only for the chloride derivative that hydrogen atoms could be located and refined, thereby establishing unequivocally mode (2) as the preferred resonance structure. We became interested in the influence of strong hydrogen bonding between nitrate and dithiobisformamidinium ions.

Colourless crystals were obtained from a solution of 1.5 g thiourea nitrate in 100 ml of 0.5 mol dm⁻³ nitric acid by oxidation with 50 ml of 1.023 vol.% hydrogen peroxide using a modification of earlier methods (de Barry Barnett, 1910; Storch, 1890). The microcrystalline product formed within a few minutes and was dried on filter paper. In large amounts it decomposes spontaneously at room temperature, whereas isolated single crystals are stable particularly if they are cooled.

Preliminary precession and Weissenberg photographs established symmetry and systematic absences consistent with the monoclinic space groups *C2/c* or *Cc*. Data collection: Picker FACS-I diffractometer with modified Nonius low-temperature device; crystal habit: elongated octahedron 0.20 × 0.10 × 0.10 mm, lattice constants at 110 K determined by least-squares refinement of 12 hand-centred reflections with 0.3305 < (sin θ)/λ < 0.4077 Å⁻¹, 1636 reflections (excluding reflections for which *h* + *k* = 2*n* + 1) with 0.0431 < (sin θ)/λ < 0.7049 Å⁻¹, θ-2θ scan, graphite-monochromated Mo *K*α radiation (λ = 0.7107 Å), scan speed 2.0° in 2θ min⁻¹, 10 s background at each end of

Table 1. *Positional and isotropic thermal parameters for [(NH₂)₂CSSC(NH₂)₂][NO₃]₂*

The isotropic thermal parameters *B* (Å²) for non-hydrogen atoms are taken from the final isotropic refinement. Hydrogen atoms were not included at this stage.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
S	0.53466 (6)	0.14457 (8)	0.67462 (5)	1.42 (5)
C(1)	0.4348 (2)	0.2852 (3)	0.5831 (2)	1.2 (2)
N(1)	0.3498 (2)	0.3728 (3)	0.6208 (2)	1.7 (1)
N(2)	0.4543 (2)	0.2920 (3)	0.4748 (2)	1.5 (1)
N(3)	0.7055 (2)	0.1153 (2)	0.3768 (2)	1.6 (1)
O(1)	0.6447 (2)	0.2185 (2)	0.3119 (2)	1.9 (1)
O(2)	0.7912 (2)	0.0335 (2)	0.3430 (2)	1.8 (1)
O(3)	0.6818 (2)	0.0882 (2)	0.4779 (1)	2.1 (1)
H(11)	0.158 (3)	0.131 (5)	0.306 (3)	1.4
H(12)	0.198 (3)	0.058 (5)	0.425 (3)	1.4
H(21)	0.402 (3)	0.354 (5)	0.419 (3)	1.4
H(22)	0.489 (4)	0.233 (5)	0.040 (3)	1.4

the reflection, scan range 1.1° below *K*α₁ to 1.0° above *K*α₂, rescan option (Lenhart, 1975) for weaker reflections, six standard reflections showed no significant variation, Lorentz and polarization corrections, all calculations with a local modification of the Northwestern University Crystallographic Computing Library (Waters & Ibers, 1977). The structure was solved using *MULTAN78*. Anisotropic refinement, assuming space group *C2/c*, converged at values for *R* and *R_w* of 0.047 and 0.055, respectively. The four independent hydrogen atoms were then unambiguously located. They were given a fixed temperature factor, *B* = 1.4 Å² and, in subsequent cycles of refinement, their positional parameters were varied. Final refinement using the 1055 unique data with *F_o*² > 3σ(*F_o*²) converged at values for *R* and *R_w* (on *F*) of 0.038 and 0.039 for a model described by 85 variable parameters.* The weighting scheme {*w* = 1/[σ² counting + (0.03 *I*)²]} showed no dependency of the minimized function upon the magnitude of *F_o* or (sin θ)/λ. The final difference synthesis was essentially featureless, although the top three peaks (maximum density <0.35 e Å⁻³; hydrogen atoms 0.89 to 0.63 e Å⁻³) lay near the oxygen atoms of the nitrate group.

In view of this and the very low and nearly isotropic temperature factors, especially for the crystallographically unique half of the dimeric cation, which in space group *C2/c* possesses twofold symmetry, no investigation of the alternative noncentrosymmetric space group *Cc* seemed warranted. Final atomic parameters are given in Table 1.

Discussion. The structure of the dication (Fig. 1) is generally quite similar to that observed in other dithiobisformamidinium species. The asymmetry in the S—C—N angles, also observed previously, but not commented upon, may be attributed to 1–4 S'...N and 1–5 S'...H interactions which are relieved by an opening up of the bond angle. The complete thiourea group is essentially planar, the C—S—S'—C' torsion angle of 97.9 (2)° lies within the observed extremes of 104.8° (for the iodo salt, Foss *et al.*, 1958) and 88.8° (for a rhenate salt, Lis, 1979); similarly, the S'—S—C—N torsion angles of 6.8 (2) and 6.6 (2)° fall within the limits of 1.6° (for the dibromo salt, Foss *et al.*, 1958) and 15.6° (for the dichloro salt, Villa *et al.*, 1972). Thus the dication conformation conforms to those previously observed (for a short review, see Villa *et al.*, 1972).

* Lists of structure factors and anisotropic thermal parameters and a table detailing the stereochemistry of this and other dithiobisformamidinium compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36770 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

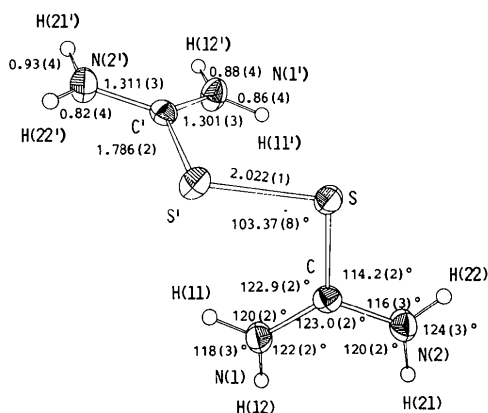


Fig. 1. Molecular diagram of the dithiobisformamidinium dication. Bond distances in Å and bond angles in degrees are shown. Thermal ellipsoids are drawn at the 70% probability level, except for hydrogen atoms which are drawn artificially small.

The hydrogen-bonding network is quantified in Table 2 and illustrated in Fig. 2. All four hydrogen atoms are involved in hydrogen bonding with two of the nitrate oxygen atoms. The close contact between O(1) and N(2) [O(1)···H(22) 2.44 (4), O(1)···N(2) 3.098 (3) Å, O(1)···H(22)—N(2) 138 (3)°] represents a hydrogen bond of dubious authenticity. The nitrate group is localized, as indicated by participation of only two of the oxygen atoms in hydrogen bonding, loss of threefold symmetry in O—N—O bond angles and a small but highly significant contraction of the N—O(1) bond [N(3)—O(1) 1.234 (2); N(3)—O(2) 1.262 (2), N(3)—O(3) 1.263 (3) Å; O(2)—N(3)—O(3) 118.7 (2), O(1)—N(3)—O(2) 120.8 (2) and O(1)—N(3)—O(3) 120.4 (2)°]. A close S···O(3) contact of 3.043 (2) Å arises as a result of a hydrogen bridge linking O(3) to H(22) (see Fig. 2). Since the sulphur atoms may be slightly polarized (δ^+) by the formally cationic carbon atom this may also represent a weak dipolar interaction. On the other hand, despite the opening up of the S—C(1)—N(1) angle noted above, the S'···N(1) and H(11)···S' distances of 3.090 (2) and 2.59 (3) Å, respectively, are both much shorter than the values of ~ 3.4 and ~ 3.1 Å which might be expected if these separations were determined solely by van der Waals interactions. In any event, dipolar and other intermolecular interactions do not result in substantive changes in molecular stereochemistry compared with

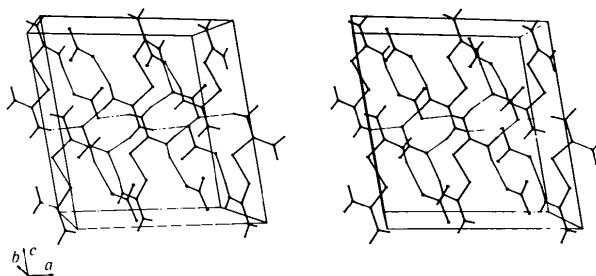


Fig. 2. Unit-cell diagram, illustrating hydrogen bonds (thin lines) for [(NH₂)₂CSSC(NH₂)₂][NO₃]₂.

Table 2. Hydrogen-bonding network for [(NH₂)₂CSSC(NH₂)₂][NO₃]₂

	Distance (Å)		Angle (°)
O(2)···H(21)	1.99 (4)	N(1)—H(11)···O(2)	153 (3)
O(2)···H(11)	2.07 (4)	N(2)—H(21)···O(2)	162 (3)
O(3)···H(12)	1.96 (4)	N(1)—H(12)···O(3)	175 (3)
O(3)···H(22)	2.18 (4)	N(2)—H(22)···O(3)	162 (4)
O(2)···N(2)	2.888 (3)	H(11)···O(2)—N(3)	112 (1)
O(2)···N(1)	2.862 (3)	H(21)···O(2)—N(3)	132 (1)
O(3)···N(1)	2.837 (3)	H(21)···O(2)···H(11)	115 (1)
O(3)···N(2)	2.970 (3)	H(12)···O(3)—N(3)	114 (1)
		H(22)···O(3)—N(3)	97 (1)
		H(22)···O(3)···H(12)	148 (1)

that observed in related structures or that expected for the isolated cation free from intermolecular forces.

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