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The Crystal Structure of Thiourea Parabanic Acid

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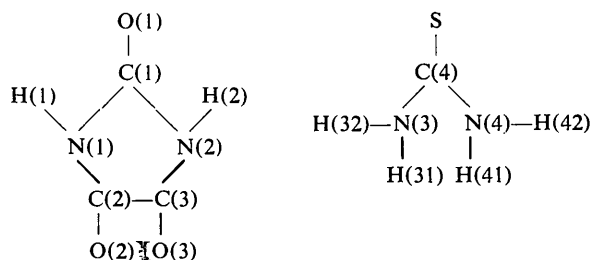
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The crystal structure of thiourea parabanic acid has been determined from its three-dimensional Patterson function. The structure has been refined by least-squares methods with anisotropic thermal parameters (for all but the hydrogen atoms) to $R=9.7\%$ for observed reflexions. The planar (010) complex crystallizes in the $P2_1$ system (b unique) and exhibits a new intermolecular contact between sulphur and carbon atoms on adjacent layers in the structure. In the absence of other intermolecular bonds in the b direction, this contact determines the position of the complex relative to the screw axis.

Introduction

In the course of determining the structure of urea parabanic acid (Colman & Medlin, 1970) the substitution of one of the light atoms for a heavier atom was considered. Crystals of the 1:1 complex of thiourea parabanic acid (TUPBA)



were grown and, although they are not isomorphous with urea parabanic acid, the structure was determined in order to investigate hydrogen bonding facilities on the three parabanic acid carbonyl groups.

Experimental

Faintly yellow coloured crystals of TUPBA were grown by adding excess thiourea to a concentrated

water solution of parabanic acid. The tabular prismatic crystals have a well defined zone axis [010] along which they are elongated. There is a well pronounced cleavage plane perpendicular to this unique axis and the possibility of hydrogen bonding in this direction seemed remote. Whilst no other cleavages, as such, were found it is possible to cut the crystal along two other planes, *viz.* ($\bar{1}01$) and (601), the former being the plane of the plate. The ($\bar{2}01$) face is also well developed. The crystals melt at 213°C.

The unit-cell dimensions were determined by calibrating a Weissenberg film with NaCl lines and from goniometric measurements of the angle between the faces. These latter measurements were made independently on two separate crystals. The dimensions are: $a=10.984 \pm 0.019$, $b=6.298 \pm 0.003$, $c=6.238 \pm 0.012$ Å; $\beta=115^\circ 34' \pm 02'$. The only systematic extinction condition is along $(0, 2n+1, 0)$ and the space group $P2_1$ is therefore defined unequivocally. The measured density of 1.59 g.cm^{-3} compares satisfactorily with the value calculated (1.63 g.cm^{-3}) for two asymmetric units of molecular weight 190 in a cell of the above dimensions.

Four layers of unintegrated data were collected about both the b and the [102] axes. In all, 639 of the 900 reflexions accessible to Cu $K\alpha$ radiation were recorded. Absorption corrections for both sets of data were considered negligible since the optimum thickness $2/\mu$ is 0.6 mm for TUPBA and is approximately 3

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times the crystal diameter in each case. Scaling was done by the Wilson (1942) method.

Structure determination

The sharpened three-dimensional Patterson function showed a high density of peaks on $v=0, \frac{1}{2}$ and peaks elsewhere in the cell were generated by the sharpening procedure (which was to use $|F_o/f|^2$ for the coefficients where f is the oxygen form factor). The orientation of the thiourea molecule was determined from an image found in the origin (see Fig. 1) and the parabanic acid molecule was located by searching for peaks approximately 3 Å from the two nitrogen atoms in thiourea. In fact the $v=0$ section of the Patterson function shows a complete image of the complex. The existence of two large peaks on $v=\frac{1}{2}$ led to an ambiguity in the sulphur atom position but this was resolved using the geometry of the complex in the cell. Since the complex is perpendicular to the screw axis an undistorted image of the complex should be evident in the true S-S peak. The sulphur position was subsequently identified (see Fig. 2), and it remained only to resolve an uncertainty of π in the orientation of the complex. The genuine Harker peaks are, with one exception, light atom-light atom vectors and they were swamped by other features of the structure on $v=\frac{1}{2}$. The incorrect orientation had an R index of 0.57, *i.e.* the most probable value for a random set of non-centrosymmetric points (Wilson, 1950), whilst the alternative position gave $R=0.31$.

The least-squares refinement of atomic coordinates in certain non-centrosymmetric space groups leads to difficulties resulting from the independence of $|F_o|$ of one or more of the coordinate parameters. In the space group $P2_1$ (b unique) a gross shift of all the y coordinates affects only the phase angle of the structure factors. The problem was overcome by holding half of the y coordinates constant on every cycle (*cf.* Karle & Karle, 1968). An arbitrary spread of $b/10$ was applied to the y coordinates which had starting values near $y=0.2$. It is not possible to refine using least-squares if all the atoms have initial values $y_j=0$ since $\delta F/\delta y_j=0$ for all j under these conditions. Anisotropic thermal parameters

$$\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

were introduced at $R=0.16$ and the refinement subsequently converged to $R=0.135$.

The three strongest diffraction amplitudes 020, 040 and $\bar{2}01$ all had negative $\Delta(=|F_o|-|F_c|)$ at this stage and data were collected from crystals dipped in liquid air in order to correct for secondary extinction effects which were apparently present.

The hydrogen atoms [with the exception of H(2)] were located from a difference map at $R=0.125$ and since it was not possible to refine the y coordinates of these atoms, they were adjusted to the value for the nitrogen atom to which they were covalently bound, as were the thermal parameters. The standard deviations for the y coordinates of the hydrogen atoms were

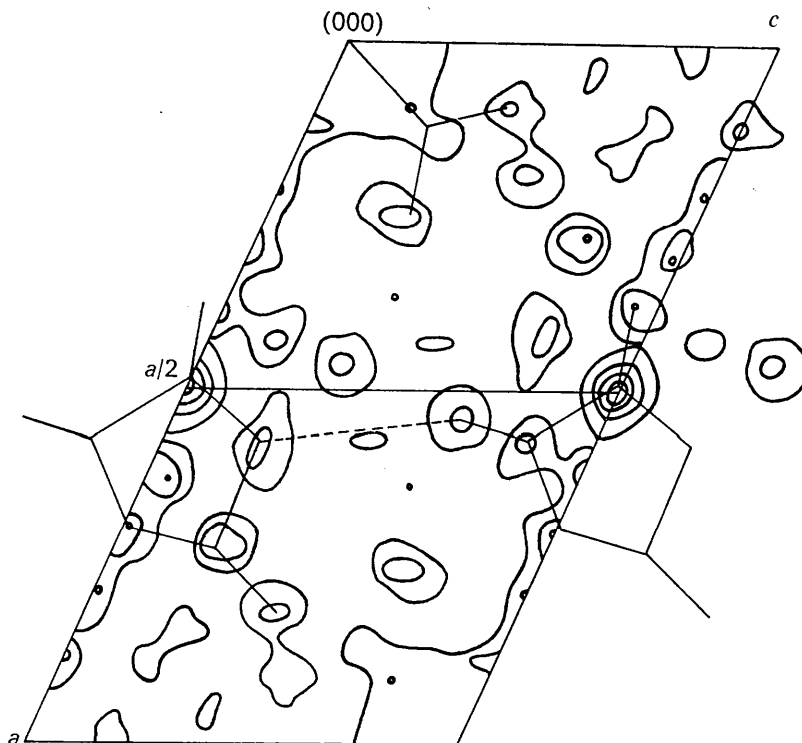


Fig. 1. The $v=0$ section of the sharpened Patterson function of TUPBA.

estimated from the relative standard deviations of x , y and z coordinates of the heavy atoms.

The final parameters are given in Table 1 and the structure factors in Table 2.

parabanic acid and thiourea structures are in C(3)-O(3) (increased from 1.212 to 1.250 Å) and in C(4)-N(4) (increased from 1.329 to 1.402 Å). The percentage double bond character of the ring bonds in TUPBA is

Discussion

The molecular dimensions are shown in Fig. 3 and the only significant changes in bond lengths from the

C(1)-N(1)	33%
C(1)-N(2)	16%
C(2)-N(1)	25%
C(3)-N(2)	25%

Table 1. TUPBA structure parameters

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B_{11} ($\times 10^4$)	B_{22} ($\times 10^4$)	B_{33} ($\times 10^4$)	B_{12} ($\times 10^4$)	B_{13} ($\times 10^4$)	B_{23} ($\times 10^4$)
O(1)	4533 (7)	2308 (30)	148 (11)	39 (11)	202 (112)	88 (31)	23 (49)	-26 (14)	-30 (88)
O(2)	8978 (6)	1947 (34)	5213 (11)	24 (10)	191 (65)	161 (33)	-26 (58)	19 (14)	22 (104)
O(3)	7364 (6)	1884 (28)	8052 (10)	38 (10)	158 (60)	64 (27)	-13 (52)	14 (14)	-83 (81)
N(1)	6820 (7)	2045 (33)	2090 (11)	42 (14)	231 (78)	108 (34)	46 (75)	39 (19)	41 (148)
N(2)	5616 (7)	2025 (40)	4243 (11)	34 (13)	222 (74)	85 (36)	-13 (88)	13 (16)	-54 (123)
C(1)	5576 (8)	1948 (44)	1983 (14)	23 (15)	244 (99)	117 (42)	48 (91)	8 (20)	0 (158)
C(2)	7790 (8)	2201 (46)	4378 (15)	28 (14)	186 (103)	103 (41)	53 (72)	11 (20)	-38 (143)
C(3)	6927 (9)	1916 (68)	5840 (15)	44 (16)	171 (98)	85 (43)	51 (86)	-7 (21)	68 (136)
S	2705 (2)	2090 (16)	4640 (3)	38 (4)	176 (25)	111 (10)	-26 (24)	7 (5)	-20 (41)
N(3)	194 (8)	2104 (47)	1510 (14)	31 (13)	530 (132)	149 (47)	-12 (106)	-2 (21)	-92 (182)
N(4)	1765 (8)	1829 (42)	-131 (14)	54 (15)	207 (130)	117 (39)	-49 (60)	25 (19)	67 (96)
C(4)	1461 (9)	1906 (45)	1832 (17)	30 (14)	198 (121)	161 (48)	55 (83)	31 (21)	44 (148)
H(1)	6626 (133)	2045 (500)	491 (288)	as for N(1)					
H(2)	4834 (123)	2025 (500)	5831 (209)	as for N(2)					
H(31)	9345 (141)	2104 (500)	96 (248)	as for N(3)					
H(32)	102 (138)	2104 (500)	3000 (259)	as for N(3)					
H(41)	771 (148)	1829 (500)	-1925 (243)	as for N(4)					
H(42)	2716 (140)	1829 (500)	-78 (232)	as for N(4)					

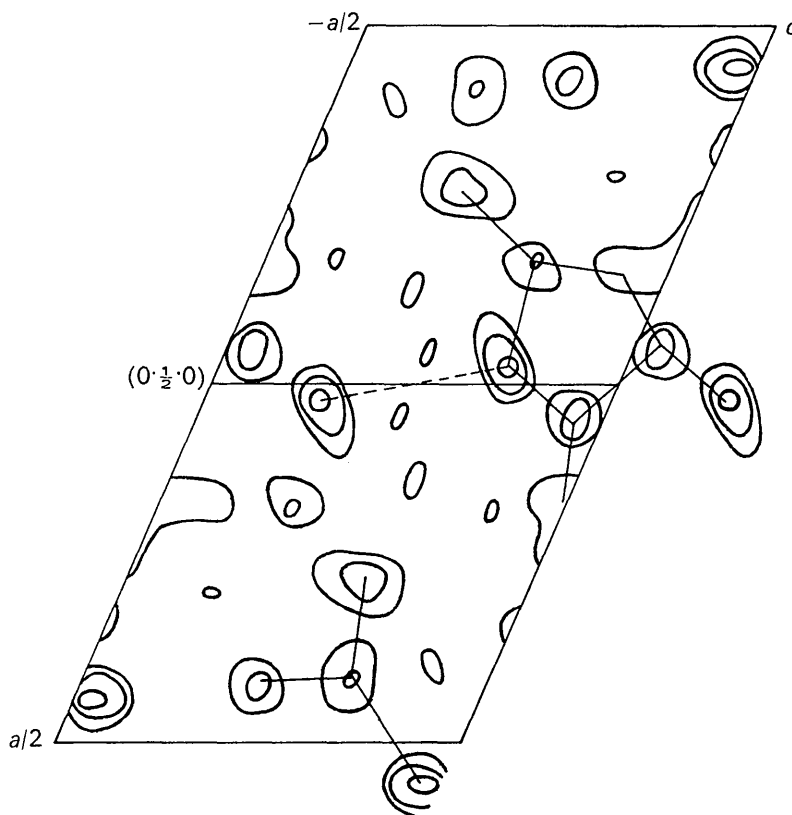


Fig. 2. The Harker section $v = \frac{1}{2}$ of the sharpened Patterson function of TUPBA.

Least-squares analysis (Schomaker, Waser, Marsh & Bergman, 1959) on four sets of atoms gave the following planes:

Imidazole ring

$$-0.529x + 6.290y + 0.122z = 0.986$$

Parabanic acid

$$-0.015x + 6.292y + 0.252z = 1.370$$

Thiourea

$$0.721x + 6.272y - 0.535z = 1.248$$

TUPBA

$$1.626x + 5.540y - 0.294z = 1.829$$

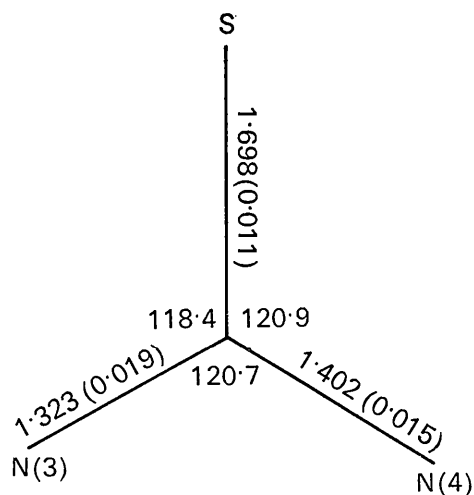
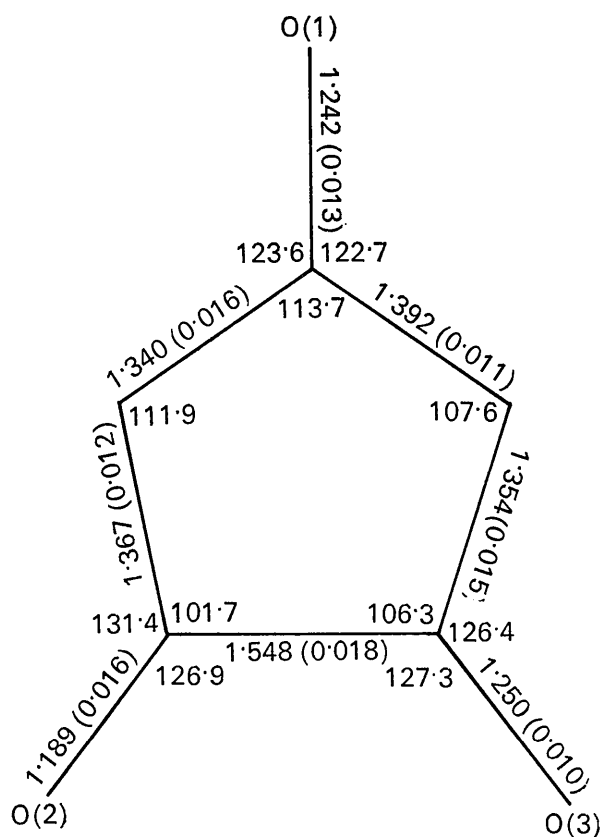


Fig. 3. Dimensions of thiourea and parabanic acid molecules in TUPBA.

The complex is in fact not planar at atomic dimensions and the best-fit plane to TUPBA passes between the two molecules. The most significant displacements ($>2.5\sigma$) from the first two planes are

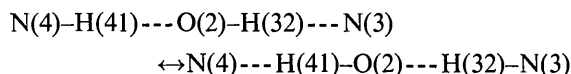
	Displacement in multiples of standard deviations	
	Imidazole ring	Parabanic acid
O(1)	12.7	4.2
O(2)	-7.8	
O(3)	-4.5	
C(1)		-3.7
C(2)		3.9

There are no significant displacements from the thiourea plane.

The complex unit is stabilized by a system of hydrogen bonds into sheets in the (020) plane. The planar packing of the molecules is shown in Fig. 4 and the dimensions of the hydrogen bonds shown in this Figure are given in Table 3.

The six hydrogen atoms are all engaged in hydrogen bonds, two with each of O(2) and O(3) and one with each of O(1) and S.

During the final least-squares cycles the z coordinates of H(32) and H(41) oscillated with amplitude approximately 0.6 and 0.2 Å respectively and it is interesting that both of these protons participate in weak hydrogen bonding to O(2). The possibility of transitions of the type



was considered, but neither the magnitude nor the direction of the oscillation are adequately in accord with such a situation. Further, C(2)-O(2) has no single-bond character.

The use of sulphur in hydrogen bonding has been reviewed by Wallwork (1962) and Donohue (1969). The observed N(2)-S distance of 3.312 (0.011) Å is within the range of data reviewed. There is some doubt about the least-squares solution for H(2). It was originally assigned a coordinate 1 Å from N(2) and on the line joining N(2)-S although a difference Fourier synthesis gave the position near the final least-squares coordinate. In the final Fourier synthesis the peak height at the least-squares coordinate for H(2) is 0.12 e.Å⁻³ but there is a peak of height 2.5 e.Å⁻³ midway between N(2) and S on the line joining these two atoms. The least-squares

hydrogen bond dimensions are shown in Table 3, but if H(2) is located by the method of Donohue (1969), then the dimensions are

$$\begin{aligned} \text{H}(2)-\text{S} &= 2.5 \text{ \AA} \\ \angle \text{N}(2)-\text{H}(2)-\text{S} &= 160^\circ. \end{aligned}$$

In either case the H(2)-S approach implies that a hydrogen bond has formed.

The separation of the screw related sheets is 3.15 Å and therefore carbon-oxygen contacts similar to those found in urea parabanic acid (Colman & Medlin, 1970) do not occur. However the sulphur atom is involved in a number of contacts which are shorter than the predicted van der Waals approaches of 3.25 Å for S---O and 3.55 Å for S---C. The first of these contacts (3.15 Å) may not be significant since it is within the plane of the complex and may therefore be a result of the hydrogen bonding configuration in this plane. On the other hand the S---C contacts are between screw related layers and therefore are not influenced by other intermolecular bonds. The contact lengths and angles are

S---C(2) ^s	3.23 Å (0.03)
C(4)-S---C(2) ^s	90.2°
S---C(3) ^s	3.31 Å (0.03)
C(4)-S---C(3) ^s	85.1°

Although the two approaches are nearly equal, the difference in the lengths of C(2)-O(2) and C(3)-O(3) implies that there may be some genuine asymmetry in the contact. The large standard deviations of the contact lengths derive from the large standard deviations of all *y* coordinates in the structure. The geometry of the contact is illustrated in Fig. 4 where the sulphur atom is seen to lie almost directly above the centre of C(2)-C(3) on the screw-related layer. There are, of course, four such contacts with parabanic acid molecules above and below the thiourea plane.

A further item of experimental evidence on the contacts concerns the existence of peaks in the final ρ_o and $\rho_o-\rho_c$ electron density maps. Only two significant peaks which are not in the plane of the complex are found in either of these maps and they are approximately 0.8 Å above and below the C(2)-C(3) bond on the line

Table 3. *Hydrogen bonds in TUPBA*

A-H---B							
A	H	B	A-B	$\sigma(A-B)$	H-B	$\sigma(H-B)$	$\angle AHB$
N(4)	H(42)	O(1)	2.985	0.016	1.962	0.218	171°
N(2)	H(2)	S	3.312	0.011	2.127	0.185	127
N(1)	H(1)	O(3)	2.830	0.011	2.012	0.175	146
N(3)	H(32)	O(2)	3.129	0.014	2.216	0.200	155
N(4)	H(41)	O(2)	3.184	0.012	1.995	0.176	172
N(3)	H(31)	O(3)	2.924	0.013	1.996	0.199	160

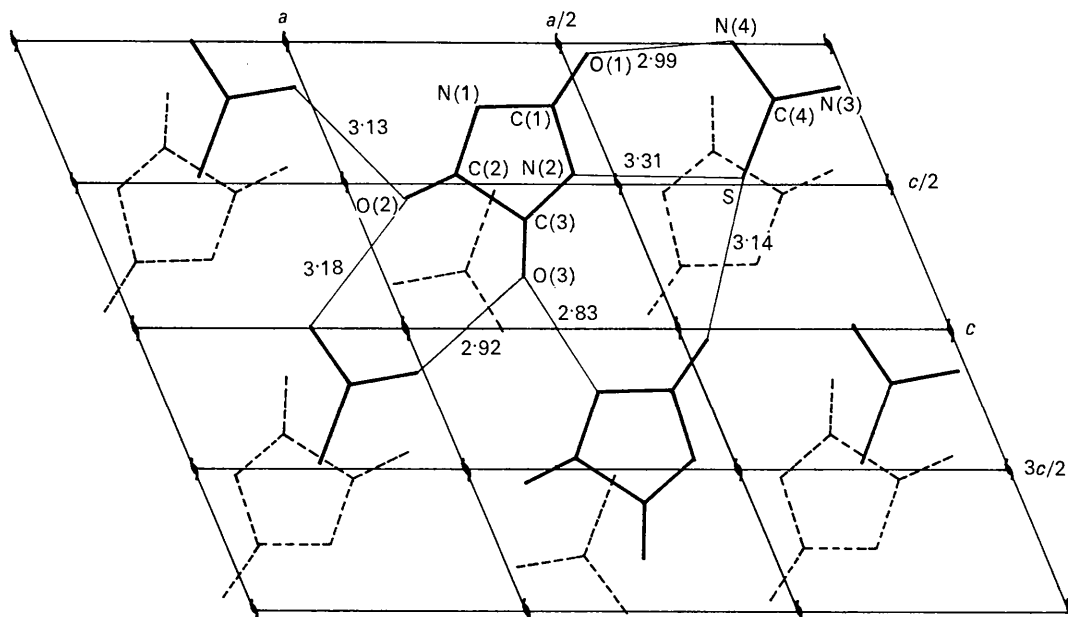


Fig. 4. The disposition of thiourea and parabanic acid molecules on symmetry related (020) planes.

through S normal to (020). Since they are over 2 Å from the sulphur atom they are not likely to result from spurious thermal motion of this atom. The peak heights are very similar, though not related by symmetry, and are 0.5 e.Å⁻³ ($\rho_o - \rho_c$) and 3.3 e.Å⁻³ (ρ_o). The standard deviation of the electron density as defined by

$$\sigma(\rho) = \frac{2}{\sqrt{V}} \sum_a ||F_o| - |F_c||^2$$

will be overestimated (Lipson & Cochran, 1966) and in this case evaluates to 0.35 e.Å⁻³. There are several peaks of density 0.5 e.Å⁻³ in the difference map but only the two in question are related either to each other or to spurious peaks in ρ_o .

Covalent bonds are associated with a bonding density located between the bound atoms and in this respect the geometry of the spurious Fourier peaks is consistent with such a concept. Salmond (1968) has discussed the valence shell expansion of sulphur in certain heterocyclic compounds. The valence shell of sulphur (3s²3p⁴) has *d* atomic orbitals available and excitation into the 3s¹3p³3d² state generates a set of six equivalent octahedral orbitals. It is not suggested that there are six equivalent orbitals in this case but the geometry of the octohedral arrangement is consistent with the geometry of the contacts and the covalent bond at the S atom. Two of the four orbitals

in the *xy* plane may participate in the S=C(4) bond and the two orbitals in the $\pm z$ directions may be active in the contact.

It is not valid to argue the influence of other crystal field forces in explaining these contacts. There are configurations of the complex relative to the screw axis which require no overlap of van der Waals radii, and therefore a genuine minimum must exist in the interaction potential function for S and C(2) in this structure.

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The Crystal Structure and Absolute Configuration of (+)₅₈₉-*cis*-Dinitrobis[(-)₅₈₉-1,2-propylenediamine]cobalt(III) chloride

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The crystal structure of (+)₅₈₉-*cis*-dinitrobis[(-)₅₈₉-1,2-propylenediamine]cobalt(III) chloride has been determined by three-dimensional X-ray methods and refined by full-matrix least-squares procedures. The structure consists of simple chloride ions and complex octahedral cations in which the two *cis* nitro groups are planar and the propylenediamine chelate rings have the λ conformation. The methyl groups of the two chelate rings occupy *trans* positions. There is some evidence for intra-ionic hydrogen bonding. The absolute configuration of the complex cation was determined from the known absolute configuration of (-)₅₈₉-1,2-propylenediamine and was confirmed by the Bijvoet method.

Introduction

The determinations of the crystal structure and of the absolute configuration of (+)₅₈₉-*cis*-dinitrobis[(-)₅₈₉-1,2-propylenediamine]cobalt(III) chloride were undertaken in order to confirm the assignment of the abso-

lute configuration of the cation that was predicted from a comparison of its circular dichroism (C.D.) spectrum with that of the (+)₅₈₉-tris(ethylenediamine)cobalt(III) ion, whose absolute configuration is known (Saito, Nakatsu, Shiro & Kuroya 1955, 1957). An account of this study and a preliminary report on the crystal structure of the compound have already been given in a previous communication (Barclay, Goldschmied, Stephenson & Sargeson, 1966).

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