

$[\text{Ir}(\text{SCN})(\text{NH}_3)_5](\text{ClO}_4)_2$ the minimum N-H...O distance is 2.96 Å suggesting that the hydrogen bonds are relatively weak. This is to be expected in view of the acidic strength of HClO_4 .

The arrangement surrounding the Ir atom is slightly distorted from a regular octahedron. Large distortions are not to be expected for low-spin d^6 complexes and it seems likely that this is caused by the difference in size of the N and S atoms. The Ir-S-C angle of 109.0° agrees well with the value found for Co-S-C in $[\text{Co}(\text{SCN})(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Snow & Boomsma, 1972) and confirms that the compound is the thiocyanato and not the isothiocyanato isomer.

We would like to thank Professor C. K. Jørgensen for suggesting this problem and for helpful discussions, and A. Regnard who carried out some preliminary measurements for us.

Acta Cryst. (1973). **B29**, 1102

The Crystal Structures of Methyl 5-Thio- α -D-ribofuranoside and Methyl 5-Thio- β -D-ribofuranoside

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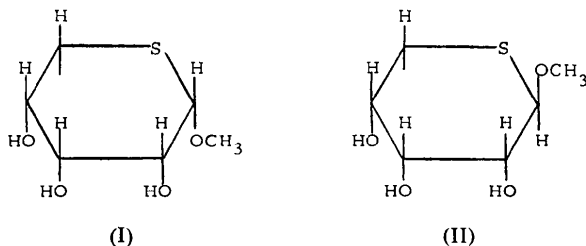
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(Received 16 October 1972; accepted 15 January 1973)

The crystal structures of methyl 5-thio- α -D-ribofuranoside and methyl 5-thio- β -D-ribofuranoside, $\text{C}_6\text{H}_{12}\text{O}_4\text{S}$, have been determined from Cu $K\alpha$ radiation data and refined to R values of 0.03 and 0.04 respectively. Both structures have space group $C2$ with four molecules in unit cells of $a=12.26$ (1), $b=4.942$ (6), $c=13.76$ (1) Å, $\beta=105.07$ (8) $^\circ$ and of $a=12.39$ (3), $b=4.786$ (9), $c=14.57$ (4) Å, $\beta=109.96$ (7) $^\circ$, respectively. The molecules have the 4C_1 ring conformation. In the α configuration, this gives rise to a *synaxial* O...O interaction at 2.99 Å with no intramolecular hydrogen bond formation. In the β compound, one hydroxyl hydrogen [H(2)] has three oxygen nearest neighbour distances of 2.5, 2.6 and 2.7 Å, the shortest of which may correspond to a weak intramolecular hydrogen bond between vicinal hydroxyl groups. The bond lengths are normal with a mean C-S distance of 1.815 Å and a ring angle at the sulfur atom of 98° . In both structures, the molecules are hydrogen-bonded into layers, two molecules wide, with van der Waals interactions between the layers.

Introduction

This paper is the second of a series describing crystal structural studies on some thioribofuranosides supplied to us by Professor N. A. Hughes, of the University of Newcastle upon Tyne, U. K. The first was that on methyl 1-thio- α -D-ribofuranoside (Girling & Jeffrey, 1971, 1973); this work has determined the structure of two compounds with the sulfur atom in the pyranose ring, methyl 5-thio- α -D-ribofuranoside (I) and methyl 5-thio- β -D-ribofuranoside (II).



Experimental

The compounds I and II were recrystallized from three different solvents: ethanol, ethanol-benzene and

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benzene. No polymorphism was observed. The crystals used for data collection were elongated in the **b** direction with dimensions 0.11 × 0.45 × 0.21 mm for I and 0.01 × 0.47 × 0.02 mm for II; larger crystals could not be obtained for II. Preliminary cell dimensions from film measurements were refined by a least-squares fit to the 2θ's of twenty computer centered reflections measured using Cu Kα radiation on a CAD-3 diffractometer at room temperature. The intensities of all symmetry independent reflections were measured using a θ-2θ scan with a variable scan width, and Ni-filtered

Cu Kα radiation. For I, the data were taken on a CAD-3 diffractometer with 6° per min scan rate and a background time equal to the scan. For II, a Picker FACS I diffractometer was used with a 1° per min scan rate and two 10-sec backgrounds. For I, 19 reflections of the 681 measured were less than two standard deviations above background. For II, owing to the very small crystals, the number of these 'unobserved' reflections was 218 out of 693 measured, and data were less accurate owing to the poor background-to-intensity ratio.

Table 1. Atomic parameters with their estimated standard deviations for methyl 5-thio-α- and methyl 5-thio-β-D-ribose

Positional parameters are expressed as fractions of the lattice translations. Thermal parameters are defined by the expression $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Non-hydrogen parameters × 10⁴; hydrogen parameters × 10².

Methyl-5-thio-α-D-ribose

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} or <i>B</i>	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(5)	798 (1)	0*	1513 (1)	43 (1)	398 (1)	39 (1)	3 (2)	15 (1)	-35 (2)
C(1)	-354 (4)	1024 (1)	2043 (4)	34 (3)	252 (3)	39 (3)	-13 (8)	7 (3)	-18 (7)
C(2)	-91 (5)	419 (1)	3162 (5)	34 (3)	143 (2)	51 (3)	8 (8)	22 (2)	14 (7)
C(3)	1012 (4)	1466 (1)	3835 (4)	45 (4)	135 (2)	30 (2)	2 (8)	12 (3)	16 (6)
C(4)	2015 (4)	623 (1)	3456 (4)	31 (3)	139 (2)	41 (3)	-11 (7)	7 (2)	6 (7)
C(5)	1947 (4)	1676 (1)	2410 (4)	39 (4)	306 (3)	37 (3)	-18 (9)	14 (3)	-7 (8)
C(6)	-1234 (5)	4261 (2)	810 (4)	78 (5)	488 (4)	30 (3)	62 (13)	-5 (3)	-14 (10)
O(1)	-663 (3)	3752 (1)	1858 (2)	49 (3)	258 (2)	27 (2)	11 (6)	-2 (2)	0 (5)
O(2)	-1021 (4)	1133 (1)	3546 (4)	38 (2)	208 (2)	56 (2)	1 (6)	27 (2)	0 (5)
O(3)	940 (3)	4323 (1)	3895 (2)	53 (3)	155 (2)	33 (2)	12 (6)	3 (2)	-3 (6)
O(4)	3064 (3)	1447 (1)	4152 (3)	35 (3)	248 (2)	47 (2)	-24 (6)	1 (2)	39 (5)
H(2)	-10 (1)	22 (2)	36 (1)	0 (1)					
H(3)	12 (1)	46 (2)	44 (1)	5 (2)					
H(4)	32 (1)	26 (2)	40 (1)	1 (1)					
H(5)	-10 (1)	-1 (2)	17 (1)	2 (1)					
H(6)	-1 (1)	-10 (2)	32 (1)	1 (1)					
H(7)	11 (1)	8 (2)	46 (1)	3 (1)					
H(8)	20 (1)	-13 (2)	35 (1)	1 (1)					
H(9)	27 (1)	12 (2)	23 (1)	1 (1)					
H(10)	19 (1)	37 (2)	24 (1)	2 (1)					
H(11)	-7 (1)	38 (2)	3 (1)	4 (3)					
H(12)	-17 (1)	27 (2)	5 (1)	9 (1)					
H(13)	-19 (1)	57 (2)	7 (1)	8 (2)					

Methyl 5-thio-β-D-ribose

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} or <i>B</i>	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(5)	1836 (2)	0*	1557 (2)	58 (2)	424 (2)	37 (2)	-11 (1)	15 (1)	50 (1)
C(1)	3324 (19)	-1057 (4)	2189 (16)	56 (11)	414 (7)	41 (9)	-31 (3)	16 (8)	-22 (3)
C(2)	3790 (22)	-70 (4)	3203 (20)	41 (10)	225 (7)	43 (8)	-14 (5)	21 (7)	3 (4)
C(3)	3113 (10)	-915 (3)	3842 (8)	61 (10)	114 (5)	25 (6)	-16 (2)	9 (7)	-29 (2)
C(4)	1859 (9)	-185 (4)	3436 (8)	40 (9)	83 (6)	40 (6)	-16 (3)	16 (6)	-12 (3)
C(5)	1258 (16)	-1262 (3)	2457 (12)	55 (11)	348 (10)	37 (7)	2 (3)	9 (7)	9 (2)
C(6)	3857 (15)	-1404 (4)	768 (14)	98 (16)	871 (8)	61 (12)	-30 (4)	39 (11)	-50 (4)
O(1)	3996 (7)	-181 (3)	1639 (6)	82 (8)	441 (11)	47 (5)	-56 (3)	39 (5)	-27 (2)
O(2)	4961 (6)	-659 (2)	3646 (9)	32 (9)	56 (8)	59 (6)	12 (2)	10 (6)	22 (2)
O(3)	3230 (7)	-3797 (2)	3961 (6)	72 (8)	161 (10)	36 (5)	31 (2)	20 (5)	16 (1)
O(4)	1253 (9)	-793 (2)	4090 (6)	68 (10)	184 (17)	42 (6)	-28 (2)	34 (6)	0 (1)
H(2)	52 (1)	-13 (3)	39 (1)	3					
H(3)	34 (1)	-37 (3)	45 (1)	3					
H(4)	15 (1)	-10 (3)	44 (1)	3					
H(5)	33 (2)	-20 (3)	21 (2)	3					
H(6)	37 (2)	5 (3)	30 (2)	3					
H(7)	36 (1)	3 (3)	46 (1)	3					
H(8)	17 (1)	13 (3)	32 (1)	3					
H(9)	4 (1)	-12 (3)	21 (1)	3					
H(10)	13 (1)	-21 (3)	24 (1)	3					
H(11)	30 (1)	-13 (3)	2 (1)	3					
H(12)	37 (1)	-31 (3)	7 (1)	3					
H(13)	44 (1)	-17 (3)	5 (1)	3					

* Not varied owing to cell-origin definition.

Table 2. Observed and calculated structure factors for (a), and (b) II

Columns are: *l* (for I) or *h* (for II) index, $10|F_{obs}|$, $10|F_{calc}|$. Asterisks indicate unobserved reflections.

(a)

Table (a) showing observed and calculated structure factors for reflections (a). Columns include indices (l, h), observed intensity (10|F_obs|), and calculated intensity (10|F_calc|). Asterisks indicate unobserved reflections.

(b)

Table (b) showing observed and calculated structure factors for reflections (b). Columns include indices (l, h), observed intensity (10|F_obs|), and calculated intensity (10|F_calc|). Asterisks indicate unobserved reflections.

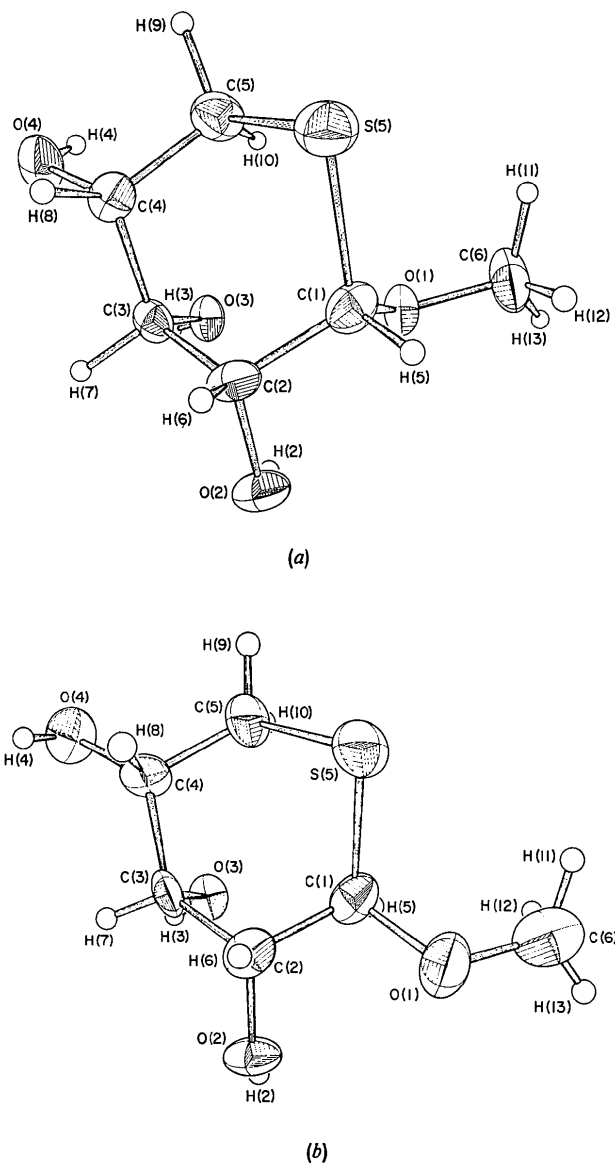


Fig. 1. The thermal ellipsoids at the 50% probability level, and the atomic nomenclature of (a) methyl 5-thio- α -D-ribofuranoside, (b) methyl 5-thio- β -D-ribofuranoside.

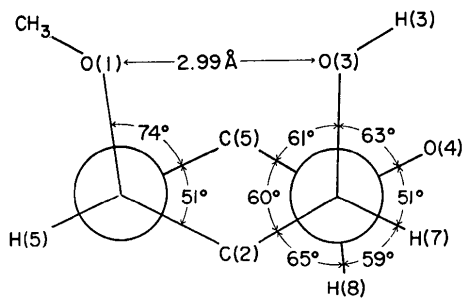


Fig. 2. Synaxial non-bonding 1,3 interaction in methyl 5-thio- α -D-ribofuranoside. Molecule viewed in the direction of the C(3)–C(4), C(1)–S(5) bonds.

Crystal data

Methyl 5-thio- α -D-ribofuranoside

Methyl 5-thio- β -D-ribofuranoside

$C_6H_{12}O_4S$, M.W. 180.2

m.p. 74–6°C

m.p. 127–9°C

Monoclinic, space group $C2$, from systematic extinction; $h+k$ odd missing for hkl and structure solution

$Z=4$

$\mu(\text{Cu } K\alpha) = 34.3 \text{ cm}^{-1}$

$a = 12.26 (1)$

$a = 12.39 (3)$

$b = 4.942 (6)$

$b = 4.786 (9)$

$c = 13.76 (1) \text{ \AA}$

$c = 14.57 (4) \text{ \AA}$

$\beta = 105.07 (8)^\circ$

$\beta = 109.96 (7)^\circ$

$D_m = 1.479 \text{ g cm}^{-3}$

$D_m = 1.471 \text{ g cm}^{-3}$

(flotation)

(flotation)

$D_x = 1.484 \text{ g cm}^{-3}$

$D_x = 1.474 \text{ g cm}^{-3}$

Structure solution and refinement

The squared structure amplitudes were used to calculate Patterson syntheses for both structures from which atomic positions of the non-hydrogen atoms were easily located for I. The Patterson synthesis of II failed to reveal the sulfur–sulfur vectors unambiguously, because of the more limited and less accurate data. The molecular orientation and origin of II was subsequently deduced from packing considerations by means of models. Anisotropic full-matrix least-squares heavy-atom refinement of I and II gave agreement indices R of 0.049 and 0.067 respectively. The hydrogen atoms were located in both structures from difference maps, despite the poor data for II. Anomalous dispersion corrections (Cromer & Liberman, 1970) for sulfur and oxygen atoms were then added

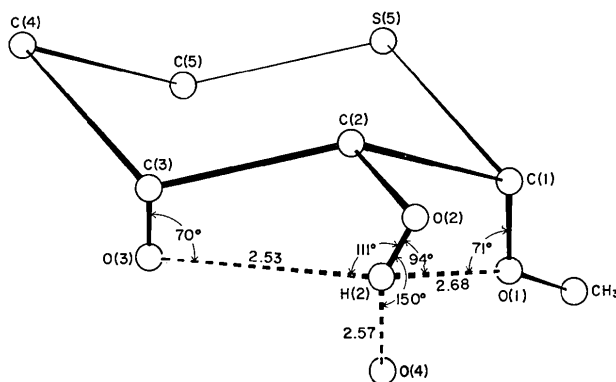


Fig. 3. The environment of H(2) in the crystal structure of methyl 5-thio- α -D-ribofuranoside. The dashed lines show the three nearest neighbour oxygen atoms at distances close to the van der Waals separation of 2.6 Å.

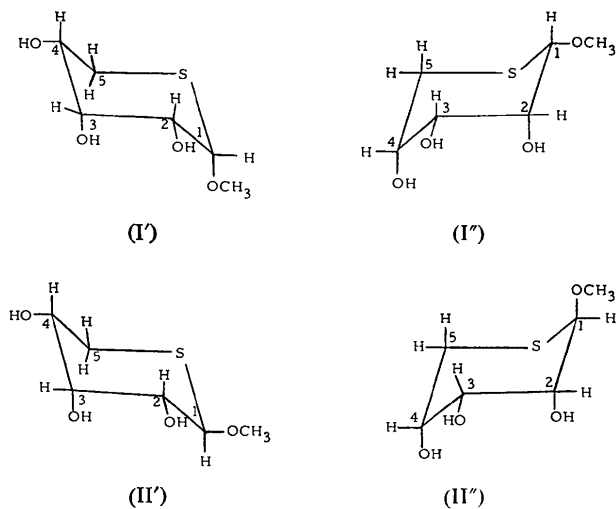
and a full-matrix least-squares refinement of all heavy atoms anisotropically and hydrogen atoms isotropically yielded a final unweighted R of 0.033 for I and 0.044 for II. The function minimized was $w(|F_o| - K|F_c|)^2$ where K is a single scale factor. The hydrogen temperature factors were held constant in II because of the small number of data. It was noted during the refinement of II that when $\omega = 1.0$ the F_{obs} of reflections with high standard deviations gave relatively poor agreement with F_{calc} . A final full-matrix least-squares refinement for II with weights $[\omega = 1/\sigma(F)^2]$ derived from counting statistics (Shiono, 1970) resulted in a wR of 0.019 with valence distances and angles which were close to the expected values. A similar refinement for I yielded no significant improvement and the positional and thermal parameters reported are from the statistically weighted refinement of II and the unweighted ($\omega = 1.0$) refinement of I.

The standard deviations in the final positional parameters of II are at least twice as large as those in I reflecting the poorer counting statistics and fewer data of the former. No observed reflections were removed or weighted zero for any reason during the refinement. The absolute configuration of both sugars was confirmed at the 99.9% confidence level by the methods of Ibers & Hamilton (1964). The final atomic positional and thermal parameters are given in Table 1 and the structure factors in Table 2. The atomic numbering and thermal ellipsoids are shown in Fig. 1. The atomic scattering factors for carbon and oxygen were those from *International Tables for X-ray Crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used.

Results and discussion

Both molecules have the normal 4C_1 conformation, as shown in I' and II'. For II, this was anticipated because the alternative 1C_4 conformation, II'', has three axial substituents, which causes conformational instability when an alternative with less axial groups is possible. The 1C_4 conformation, I'', is also observed to predominate for some α -methyl ribopyranoside derivatives in non-polar solvents, by reason of this bonding $O(2)H \cdots O(4)H$ interaction (*cf.* Lemieux, 1971).^{*} However, this is not observed in this crystal structure; neither is there any evidence for an intramolecular hydrogen bond between the syn-axial groups $O(3)H$ to $O(1)-CH_3$ in I', which could provide additional stability for the 1C_4 conformer. The $O(3) \cdots O(1)$ separation is 2.99 Å and H(3) points away from O(1) and towards O(4) and an adjacent molecule, forming an intermolecular hydrogen bond with a H(3) to O(4) distance of 2.2 Å, see Fig. 2. Of the two equatorial

hydroxyls, O(4)H forms a normal intermolecular hydrogen bond to O(2) on an adjacent molecule [$O(4) \cdots O(2)$, 2.79 Å; $H(4) \cdots O(2)$, 2.12 Å]; but H(2) has either close van der Waals contacts or possibly weak hydrogen bonds to three nearest neighbour oxygens, including two vicinal oxygens O(1) and O(3) in the same molecule, as shown in Fig. 3. Crystallographic evidence for intramolecular hydrogen bonding between vicinal hydroxyls is rare in the crystal structures of carbohydrates, although there is strong spectroscopic evidence for such intramolecular bonding in 1,2 diols (Kuhn, 1954). In carbohydrates, the geometry for vicinal bonds is generally unfavorable relative to *synaxial* or intermolecular hydrogen-bonding. Stronger evidence for vicinal hydrogen bonding has been observed in the crystal structure of methyl α -D-altropyranoside (Gatehouse & Poppleton, 1971) where there is also no intramolecular hydrogen bonding between the *synaxial* $O(3)-H$ and $O(1)-CH_3$ groups.



In this structure, therefore, hydrogen bonding provides no obvious reason why the 4C_1 ring conformation is preferred over the 1C_4 , as found in the methyl 1-thio- α derivative. It is possible that a difference in the conformational energy terms arising from the anomeric effect (Lemieux, 1964), according to whether the sulfur is in the 1 or 5 position, is the significant factor in this distinction between these two thio-ribofuranosides.

The conformation about the glycosidic bond $C(1)-O(1)$ is *synclinal (gauche)* with respect to the ring S in both derivatives, with $S(5)-C(1)-O(1)-C(6)$ torsion angles of 71 and -69° for I and II, respectively. In I, this orientation for the methyl group is that of least van der Waals repulsions, since the *-sc*, (-60°), and *ap* (180°) orientations result in van der Waals overlap between the methyl group and O(2) and O(3) respectively. In II, the *ap* orientation is eliminated by the repulsive interaction between the CH_3 and O(2).

* In the α configuration, both I' and I'' have two axial substituents and the formation of an intramolecular hydrogen bond between $O(2)H$ and $O(4)H$ should stabilize the latter, 1C_4 , conformation, as in the crystal structure of methyl 1-thio- α -D-ribofuranoside (Girling & Jeffrey, 1973).

The $+sc$ orientation would involve a weaker van der Waals repulsion between the CH_3 and $\text{H}(6)$, leading to a slightly higher conformational energy than the observed $-sc$ orientation, which has no such van der Waals interactions (see Fig. 1). In both structures, the conformation observed is consistent with the orientation favored by the 'exo-anomeric effect' (cf. Lemieux, 1971; Jeffrey, Pople & Radom, 1973).

The bond distances and bond angles for I and II are given in Table 3. Those of II are subject to large standard deviations and with the exception of the C-S bonds, there is a systematic trend for most of the bond distances to appear short. This is associated with larger values and a greater spread of the thermal parameters shown in Table 1. In I, the C-S bond lengths are not significantly different, and the mean value of 1.817 Å can be compared with the C(1)-S(1) value of 1.802 Å in methyl 1-thio- α -D-ribofuranoside (Girling & Jeffrey, 1973). The mean C-C distance is 1.514 Å and the mean C-O distance excluding C(1)-

O(1) is 1.434 Å. There is, therefore, an indication of the usual anomeric bond shortening in the C(1)-O(1) distance of 1.405 Å (Berman, Chu & Jeffrey, 1967; Jeffrey, Pople & Radom, 1973). The S valence angle is more acute than for a cyclic oxygen, and this agrees with the 99.1° observed for C(1)-S(1)-C(6) in methyl 1-thio- α -D-ribofuranoside. The O-H bond distances are consistently 'observed' short, i.e. 0.5 to 0.7 Å, and this is especially so in II, where the data were less accurate. This is commonly observed in carbohydrate structures, in contrast to the C-H distances which are observed closer to the internuclear separations, and is probably due to the greater electronegativity of the oxygen atoms. The torsion angles are given in Table 4. In the comparison of the two rings, the distortion due to the *synaxial* repulsion in I might be expected to result in a wider distribution of the ring torsion angles and this is observed. The substituent torsion angles correspond closely except, of course, for the differences due to the α and β configuration.

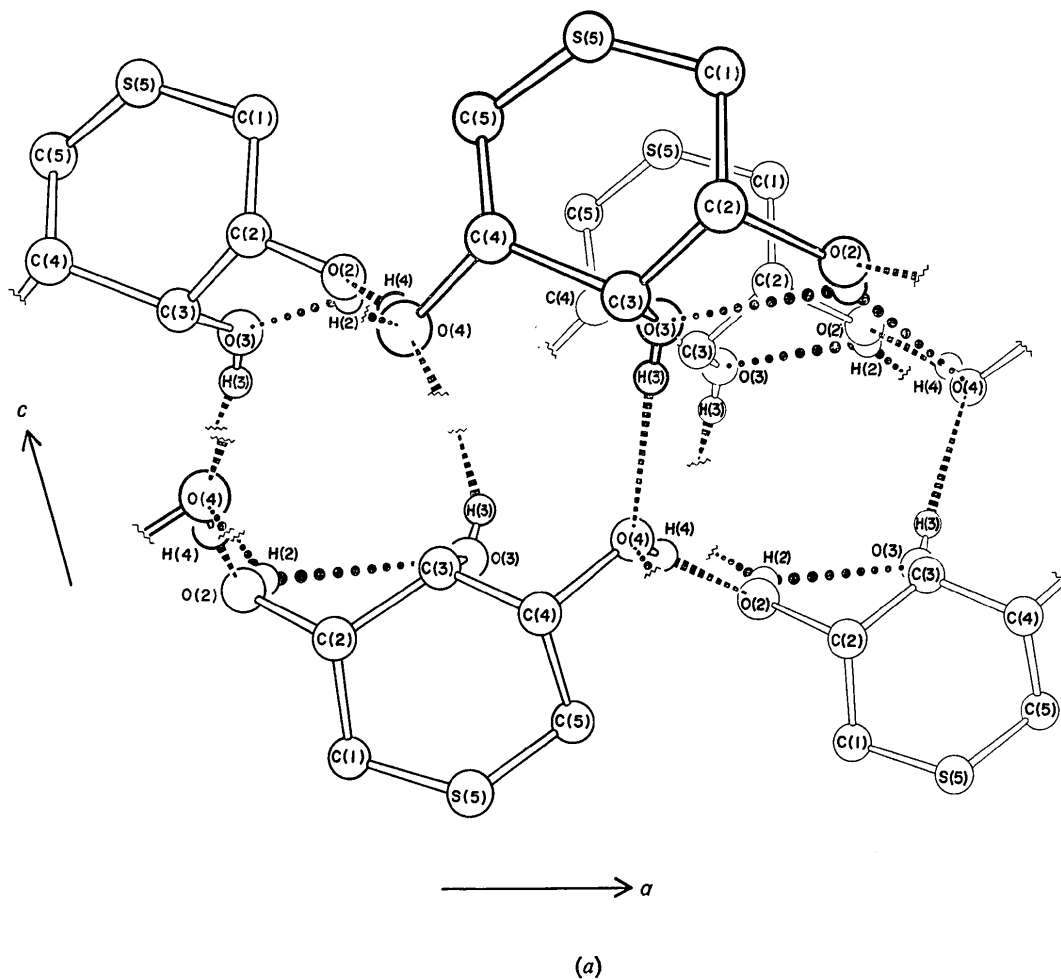


Fig. 4. (a) Perspective view down the b axis of the hydrogen bonding in methyl 5-thio- α -D-ribofuranoside. (The methoxyl group and the methylene hydrogen atoms have been omitted for clarity.) The weak vicinal interaction between $\text{H}(2)$ and $\text{O}(3)$ is included.

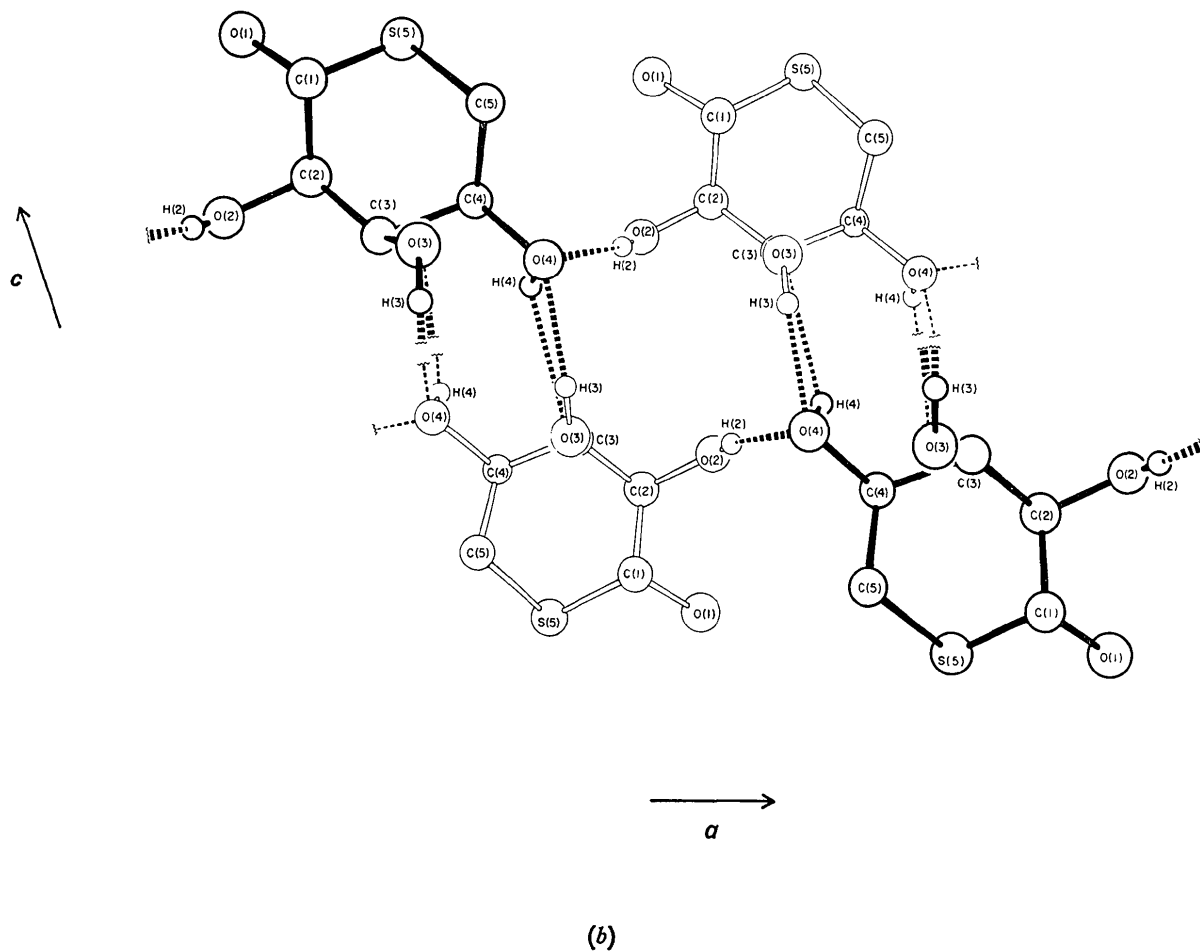


Fig. 4. (*cont.*). (b) Hydrogen bonding (dotted lines) in methyl 5-thio- β -D-ribose.

The hydrogen bonding is shown in Fig. 4. In I, it forms a series of infinite helical chains extending in the **b** direction, if we include a very weak vicinal interaction of 2.5 Å between H(2) and O(3), *i.e.* \cdots O(2)–H \cdots O(3)–H \cdots O(4)–H \cdots O(2) \cdots . There is an additional weak interaction between H(2) and O(4) on an adjacent molecule at 2.6 Å, which is not regarded as a hydrogen bond, although the corresponding O(2) \cdots O(4) distance is 2.79 Å. With the exception of O(2)–H \cdots O(3), which has been discussed above, the hydrogen distances and angles are normal: O(3) \cdots O(4) 2.85 Å, O(4) \cdots O(2) 2.79 Å, H(3) \cdots O(2) 2.2 Å, H(4) \cdots O(2) 2.1 Å, O(3)–H(3)–O(4) 168°, O(4)–H(4)–O(2) 174°. All other intermolecular O \cdots O and O \cdots C distances are greater than 3.25 Å. The intermolecular O \cdots H or C \cdots H distances are greater than 2.5 Å, and the H \cdots H distances are 2.5 Å or greater, except for H(9) \cdots H(13) and H(12) \cdots H(13) at 2.4 and 2.3 Å, respectively.

In II, the hydrogen–oxygen interactions form a chain of molecules in the **a** direction linked in pairs by a double-stranded arrangement, the geometry of which

is shown in detail in Fig. 5. Of these interactions, only that between O(4) and H(3) qualifies as a reasonably strong hydrogen bond. A similar type of double-stranded interaction between two parallel hydroxyl bonds has previously been observed in potassium gluconate monohydrate (Jeffrey & Fasiska, 1972), with shorter O \cdots H distances, 1.9 and 2.2 Å. The molecules displaced in the **a** direction are linked by a single hydrogen bond, O(2) \cdots O(4) 2.88 Å, H(2) \cdots O(2) 2.50 Å. (There is some uncertainty concerning the position of H(2) in this low precision analysis, since the separation of O(2) to the atom O(4) is shorter, *i.e.* 2.78 Å, in the molecule below that shown in Fig. 5, although the H(2) position observed gives a H(2) \cdots O(4) distance which is 2.94 Å.

Despite the differences in hydrogen bonding, the molecular packing, shown in Fig. 6, reflects the similarity in the crystal data of the two compounds. In both structures, alternate (002) planes correspond to hydrolytic and non-hydrolytic interfaces, the former by hydrogen bonding between the hydroxyls and the latter by van der Waals contacts between the methyl

Table 3. Bond lengths and angles (other than 109.5°) for methyl 5-thio- α -D-ribose (I) and methyl 5-thio- β -D-ribose (II)

Bond lengths	I	II
S(5)-C(1)	1.821 (5) Å	1.83 (2) Å
S(5)-C(5)	1.813 (5)	1.80 (2)
C(1)-C(2)	1.517 (8)	1.47 (2)
C(2)-C(3)	1.516 (7)	1.51 (2)
C(3)-C(4)	1.513 (8)	1.50 (2)
C(4)-C(5)	1.512 (8)	1.46 (2)
C(1)-O(1)	1.405 (6)	1.40 (2)
C(2)-O(2)	1.420 (9)	1.40 (2)
C(3)-O(3)	1.418 (7)	1.39 (2)
C(4)-O(4)	1.448 (6)	1.43 (2)
C(6)-O(1)	1.452 (6)	1.35 (2)

Bond angles	I	II
C(1)-S(5)-C(5)	98.5 (3)°	97 (1)°
S(5)-C(1)-C(2)	111.5 (4)	113 (1)
C(1)-C(2)-C(3)	118.2 (4)	115 (2)
C(2)-C(3)-C(4)	111.7 (4)	114 (1)
C(3)-C(4)-C(5)	112.6 (4)	115 (1)
S(5)-C(1)-O(1)	113.2 (3)	109 (1)
C(1)-O(1)-C(6)	112.5 (4)	120 (1)
C(3)-C(2)-O(2)	111.2 (4)	111 (2)
C(2)-C(3)-O(3)	108.4 (4)	107 (1)
C(4)-C(3)-O(3)	111.3 (4)	109 (1)
C(4)-C(5)-S(5)	109.4 (4)	113 (1)
C(2)-C(1)-O(1)	110.6 (4)	112 (2)
C(3)-C(4)-O(4)	110.0 (4)	113 (1)
C(5)-C(4)-O(4)	110.6 (4)	112 (1)
C(1)-C(2)-O(2)	110.2 (4)	113 (1)

Table 4. Torsion angles for methyl 5-thio- α -D-ribose (I) and methyl 5-thio- β -D-ribose (II)

Ring angles	I	II
C(1)-C(2)-C(3)-C(4)	-53.0°	-53.1°
C(2)-C(3)-C(4)-C(5)	60.2	54.9
C(3)-C(4)-C(5)-S(5)	-68.1	-60.1
C(4)-C(5)-S(5)-C(1)	59.2	54.1
C(5)-S(5)-C(1)-C(2)	-51.2	-52.2
S(5)-C(1)-C(2)-C(3)	52.8	56.0

Substituent angles	I	II
O(4)-C(4)-C(5)-S(5)	167.2	169.0
O(4)-C(4)-C(3)-O(3)	63.4	60.4
O(4)-C(4)-C(3)-C(2)	-175.2	-175.1
O(3)-C(3)-C(4)-C(5)	-61.1	-64.6
O(3)-C(3)-C(2)-O(2)	-59.3	-62.6
O(3)-C(3)-C(2)-C(1)	70.0	67.8
O(2)-C(2)-C(3)-C(4)	178.2	176.5
O(2)-C(2)-C(1)-S(5)	-177.7	-174.1
O(2)-C(2)-C(1)-O(1)	55.6	-50.4
O(1)-C(1)-C(2)-C(3)	-74.1	179.7
O(1)-C(1)-S(5)-C(5)	74.1	-177.6
C(6)-O(1)-C(1)-S(5)	71.0	-68.9
C(6)-O(1)-C(1)-C(2)	-162.1	164.8

and methylene groups and sulfur atoms. The molecules are therefore hydrogen bonded into layers separated by van der Waals interactions.

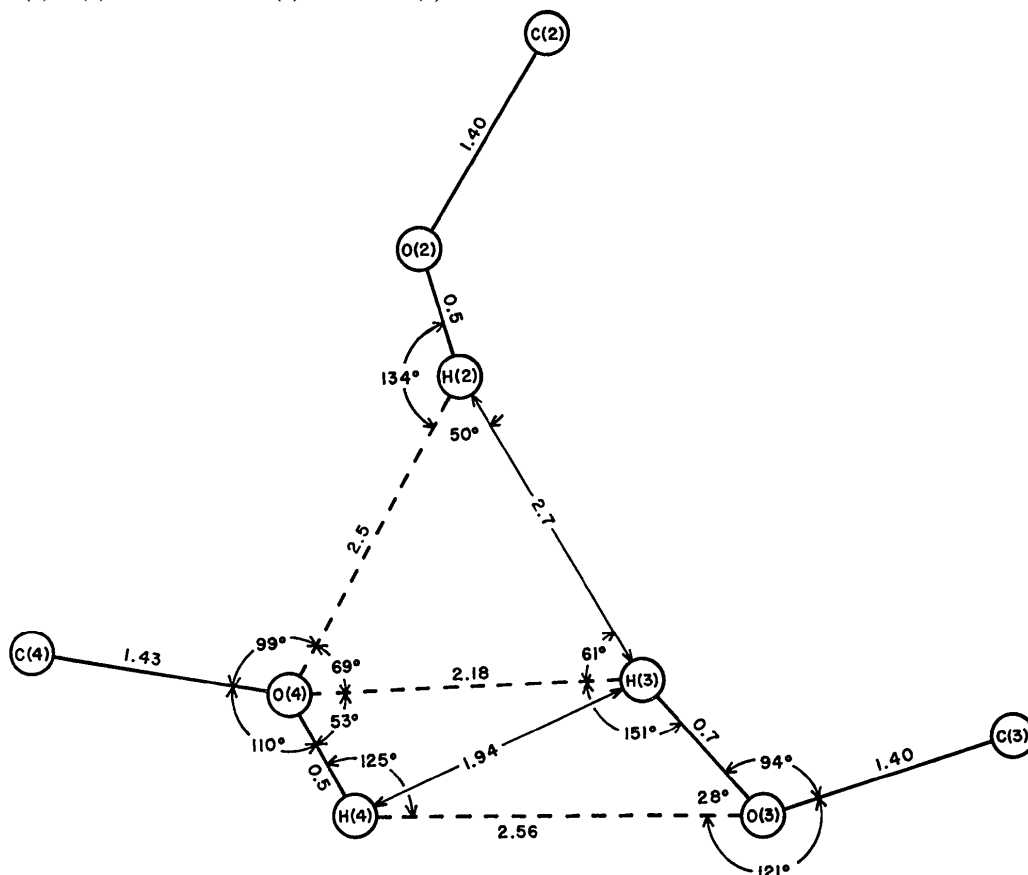


Fig. 5. Detail of the O(3)H...O(4)H hydrogen bonding in methyl 5-thio- β -D-ribose. The distance O(3)...O(4) is 2.85 Å.

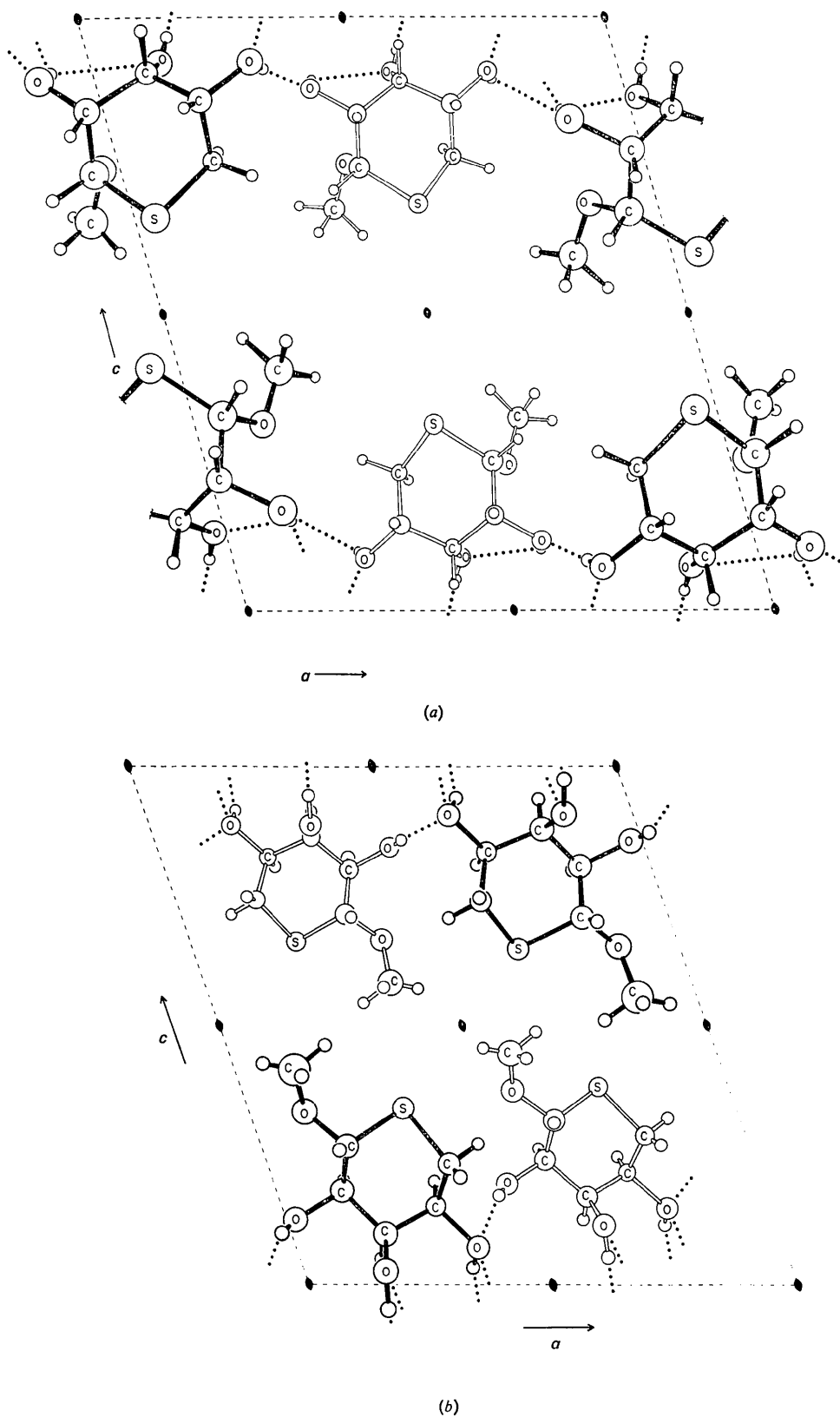


Fig. 6. Molecular packing viewed down the b axis. The dotted lines indicate hydrogen bonds. (a) Methyl 5-thio- α -D-ribofuranoside, (b) methyl 5-thio- β -D-ribofuranoside.

This research is supported by Grant No. GM-11293 of the U.S. Public Health Service, National Institutes of Health.

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Acta Cryst. (1973). **B29**, 1111

Structure Cristalline du Polychélate Co-2,3-PYD.2H₂O

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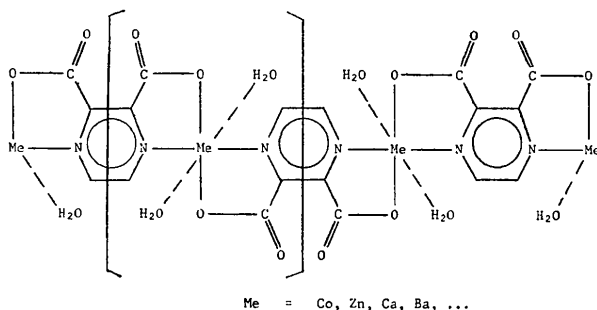
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(Reçu le 13 juin 1972, accepté le 1 décembre 1972)

The crystal structure of the polychelate Co-2,3-PYD.2H₂O (C₆H₂N₂O₄Co.2H₂O) was determined by the symbolic addition method with data collected on a single-crystal diffractometer, using Mo K α radiation. The crystals are orthorhombic, space group *Pcca*, with eight molecules in a unit cell of dimensions $a = 8.037$, $b = 13.977$ and $c = 15.478$ Å. The hydrogen atoms were found from a difference Fourier synthesis. The refinement was carried out by least-squares calculations with anisotropic temperature factors included for all atoms except hydrogen. No corrections were made neither for absorption or extinction. The final *R* value on *F* is 0.034 for 1542 reflexions. The structure consists of chains of molecules parallel to the [010] direction; the molecules are linked by hydrogen bonds.

Introduction

Le polychélate Co-2,3-PYD.2H₂O a été synthétisé par le Dr Antinelli (Antinelli, 1970) à partir d'un poids égal d'acide pyrazine-2,3-dicarboxylique et d'acétate de cobalt. L'analyse chimique et l'analyse thermogravimétrique ont permis d'établir la formule brute C₆H₂N₂O₄Co.2H₂O. L'auteur (Antinelli) a proposé, par analogie avec d'autres polychélates, une formule développée du type:



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Aucune étude n'a pu confirmer cette formule. L'objet du présent travail est donc de vérifier cette hypothèse. Ce polychélate est particulièrement intéressant car il peut contribuer à la synthèse de composés fortement magnétiques.

Partie expérimentale

La méthode de préparation du Co-2,3-PYD.2H₂O a été décrite précédemment (Antinelli, 1970). Soulignons que le thermogramme indique une perte en poids de 12,8% dû au départ des deux molécules d'eau entre 135 et 320°C, et que l'analyse thermique différentielle détermine le point de décomposition de ce polychélate à 360°C (Antinelli, 1970). De plus, une bande d'absorption a été observée à la spectrométrie infrarouge vers 3205 cm⁻¹ (Antinelli, 1970), laissant prévoir les liaisons hydrogène autour de 2,8 Å.

Le cristal choisi pour l'étude cristallographique est une sphère d'environ 0,1 mm de rayon, obtenue par polissage d'un gros monocristal. La forme de l'échantillon a été dictée pour minimiser l'effet de l'absorption. Les règles de non-extinction (*hkl*: aucune extinction, *0kl*: $l = 2n$, *h0l*: $l = 2n$ et *hk0*: $h = 2n$) établies par photographies Weissenberg et par photographies de précession indiquent que le polychélate Co-2,3-PYD,