

$\omega$  scans  
 Absorption correction:  
 $\psi$  scan (SDP; Enraf-  
 Nonius, 1985)  
 $T_{\min} = 0.986$ ,  $T_{\max} =$   
 1.000  
 3410 measured reflections  
 2509 independent reflections

$R_{\text{int}} = 0.0130$   
 $\theta_{\max} = 28.96^\circ$   
 $h = -1 \rightarrow 11$   
 $k = -1 \rightarrow 10$   
 $l = -20 \rightarrow 20$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 2.4%

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.0308$   
 $wR(F^2) = 0.0876$   
 $S = 1.014$   
 2509 reflections  
 143 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0487P)^2$   
 $+ 0.0159P]$   
 where  $P = \max[0, (F_o^2$   
 $+ 2F_c^2)/3]$

$(\Delta/\sigma)_{\max} = 0.081$   
 $\Delta\rho_{\max} = 0.278 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.225 \text{ e } \text{Å}^{-3}$   
 Extinction correction:  
 SHELXL93  
 Extinction coefficient:  
 0.019 (2)  
 Atomic scattering factors  
 from *International Tables*  
 for *Crystallography* (1992,  
 Vol. C, Tables 4.2.6.8 and  
 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
C11	0.02022 (5)	0.28215 (7)	-0.24307 (2)	0.0571 (2)
C12	0.33418 (5)	0.37513 (8)	-0.50554 (3)	0.0632 (2)
N1	0.16555 (14)	0.3256 (2)	-0.37948 (7)	0.0417 (3)
C2	0.0269 (2)	0.2767 (2)	-0.35773 (9)	0.0405 (3)
N3	-0.10331 (15)	0.2220 (2)	-0.41167 (8)	0.0469 (3)
C4	-0.0909 (2)	0.2142 (2)	-0.50074 (9)	0.0432 (3)
N5	0.0427 (2)	0.2626 (2)	-0.53269 (8)	0.0446 (3)
C6	0.1598 (2)	0.3141 (2)	-0.46908 (9)	0.0401 (3)
C7	-0.2214 (2)	0.1523 (3)	-0.56372 (11)	0.0558 (5)
C8	-0.3283 (2)	0.0871 (2)	-0.61796 (10)	0.0442 (4)
N9	-0.44441 (15)	0.0197 (2)	-0.67764 (9)	0.0465 (3)
C10	-0.5912 (2)	-0.0418 (3)	-0.6495 (2)	0.0601 (5)
C11	-0.4189 (3)	-0.0252 (3)	-0.76840 (12)	0.0590 (5)

Table 2. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ )

C11—C2	1.722 (2)	C4—C7	1.395 (3)
C12—C6	1.730 (2)	N5—C6	1.301 (3)
N1—C2	1.329 (2)	C8—C7	1.205 (3)
N1—C6	1.331 (2)	C8—N9	1.305 (3)
C2—N3	1.309 (3)	N9—C11	1.450 (2)
N3—C4	1.353 (2)	N9—C10	1.462 (3)
C4—N5	1.357 (2)		
C2—N1—C6	110.8 (2)	N5—C6—N1	129.4 (2)
N3—C2—N1	128.55 (13)	N5—C6—C12	115.67 (12)
N3—C2—C11	116.1 (2)	N1—C6—C12	114.9 (2)
N1—C2—C11	115.3 (2)	C8—C7—C4	175.1 (2)
C2—N3—C4	114.1 (2)	C7—C8—N9	178.8 (2)
N3—C4—N5	123.6 (2)	C8—N9—C11	120.4 (2)
N3—C4—C7	118.7 (2)	C8—N9—C10	120.3 (2)
N5—C4—C7	117.69 (14)	C11—N9—C10	118.3 (2)
C6—N5—C4	113.54 (13)		

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KA1174). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

### References

- Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.  
 Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.  
 Galli, R., Neuenschwander, M. & Engel, P. (1989). *Helv. Chim. Acta*, **72**, 1324–1336.  
 Gillespie, R. J. & Hargittai, I. (1991). In *The VSEPR Model of Molecular Geometry*. Massachusetts: Allyn and Bacon.  
 Himbert, G. (1979). *Angew. Chem.* **91**, 432–433.  
 Himbert, G. & Brunn, W. (1985). *Liebigs Ann. Chem.* pp. 2206–2216.  
 Himbert, G., Feustel, M. & Jungs, M. (1981). *Liebigs Ann. Chem.* pp. 1907–1927.  
 Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.  
 Sheldrick, G. M. (1990). *SHELXTL. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 685–706. Dordrecht: Kluwer Academic Publishers.  
 Wegner, G. (1974). *Chimia*, **28**, 475–484.

*Acta Cryst.* (1996). **C52**, 2006–2008

## 1-(4-Amino-6-methyl[1,3]oxazolo[5,4-d]pyrimidin-2-yl)-1-deoxy-D-ribose 5-Benzoate Dihydrate

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(Received 31 March 1995; accepted 29 January 1996)

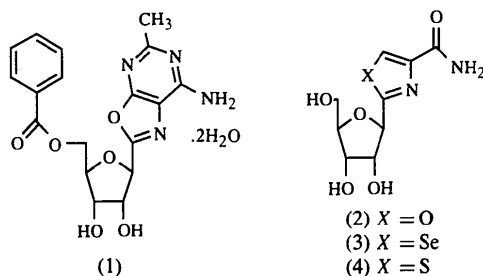
### Abstract

In the crystal structure of the title compound, C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>·2H<sub>2</sub>O, the [1,3]oxazolo[5,4-d]pyrimidine ring is planar and seems to possess a  $\pi$ -stacking interaction with the phenyl ring of the ester group.

### Comment

Although the crystal structures of 2,4-dimethyl-5-(4-nitrophenyl)oxazole (Pompa, Albano, Bellon & Scatturin, 1965), 2-methyl-4-(bromomethyl)-5-(4-nitrophenyl)oxazole (Scatturin & Zannetti, 1959), 2-methyl-

4-(chloromethyl)-5-(4-nitrophenyl)oxazole (Scatturin & Zannetti, 1956; Albano, Bellon, Pompa & Scatturin, 1963), 2-(chloromethyl)-4-methyl-5-(4-nitrophenyl)oxazole (Scatturin & Zannetti, 1959), 2-(4-pyridyl)-1,3-oxazole (Brufani, Giacomello & Stein, 1961) and the organic scintillator 1,4-bis-2-(5-phenyloxazolyl)benzene ('POPOP'; Ambats & Marsh, 1965) have been determined, there are no reports of the crystal structures of the [1,3]oxazolo[5,4-*d*]pyrimidine ring system. Owing to the strong interest in C-nucleosides and in the synthesis and potential bioactivity of oxazofurin, (2), and its derivatives (Franchetti, Cristalli, Grifantini, Cappellacci, Vittori & Nocentini, 1990; Franchetti, Messini, Cappellacci, Grifantini, Guarracino, Marongiu, Piras & La Colla, 1993; Freeman & Scheuerman, 1989; Goldstein, Li, Hallows, Langs, Franchetti, Cappellacci & Grifantini, 1994), we have synthesized the title compound, (1), and determined its crystal structure.



The antitumor and antiviral C-nucleosides selenazofurin, (3), tiazofurin, (4), and some of their derivatives exhibit unusually short Se or S to furanose O atom distances (Burling, Gabrielsen & Goldstein, 1991; Cappellacci, Franchetti, Grifantini, Messini, Abu Sheikha, Nocentini, Moraca & Goldstein, 1995; Goldstein, Takusagawa, Berman, Srivastava & Robins, 1983; Goldstein, Mao & Marquez, 1988; Goldstein, Kennedy & Hennen, 1990; Burling & Goldstein, 1992) which may have a profound effect on their bioactivity. It has been suggested that this conformational preference is a result of an electrostatic interaction between the partial positive charge on the Se or S atom and a partial negative charge on the furanose O atom (Goldstein, Bell & Marquez, 1990; Burling & Goldstein, 1992). The O(3) atom in (1), which is more electronegative than the Se atom in selenazofurin or the S atom in tiazofurin, does not possess a partial positive charge. Indeed, it is likely that there is a repulsive interaction between negatively charged furanose and oxazole O atoms in (1) (Goldstein, Li, Hallows, Langs, Franchetti, Cappellacci & Grifantini, 1994). Thus, (1) adopts the conformation shown in Fig. 1 and does not display the close heteroatom contact. The [1,3]oxazolo[5,4-*d*]pyrimidine ring portion of the heterocyclic system in (1) is planar and possesses a  $\pi$ -stacking interaction with the phenyl ring of the ester group. There are two water molecules in the crystal structure.

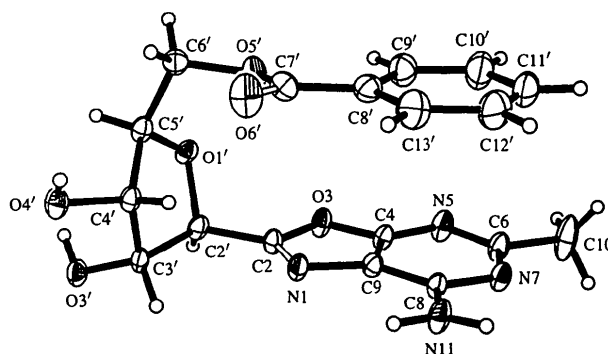


Fig. 1. Displacement ellipsoid plot (XP in SHELXTL-Plus; Sheldrick, 1988) of the molecular structure and atom numbering of (1). Ellipsoids are drawn at the 50% probability level for non-H atoms. The two water molecules have been omitted.

## Experimental

Compound (1) was prepared by the partial hydrolysis of (1*R*)-1-(4-amino-6-methyl[1,3]oxazolo[5,4-*d*]pyrimidin-2-yl)-1-deoxy-D-ribose 2,3,5-tribenzoate. Colorless crystals of (1) were obtained by crystallization from aqueous methanol.

### Crystal data

$C_{18}H_{18}N_4O_6 \cdot 2H_2O$   
 $M_r = 422.4$   
 Monoclinic  
 $P2_1$   
 $a = 7.1551$  (7) Å  
 $b = 13.5277$  (11) Å  
 $c = 9.9826$  (9) Å  
 $\beta = 90.748$  (8)°  
 $V = 966.15$  (15) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.452$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 38 reflections  
 $\theta = 13$ – $16^\circ$   
 $\mu = 0.108$  mm<sup>-1</sup>  
 $T = 183$  K  
 Cube  
 $0.43 \times 0.43 \times 0.40$  mm  
 Colorless

### Data collection

Siemens R3m/V diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: none  
 2508 measured reflections  
 2273 independent reflections  
 2218 observed reflections  
 $[F > 2.0\sigma(F)]$

$R_{int} = 0.036$   
 $\theta_{max} = 27.5^\circ$   
 $h = 0 \rightarrow 9$   
 $k = 0 \rightarrow 17$   
 $l = -12 \rightarrow 12$   
 3 standard reflections monitored every 97 reflections  
 intensity decay: none

### Refinement

Refinement on  $F$   
 $R = 0.048$   
 $wR = 0.062$   
 $S = 1.95$   
 2218 reflections  
 271 parameters  
 $w = 1/[\sigma^2(F) + 0.0005F^2]$   
 $(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.26$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U <sub>eq</sub>
N(1)	0.0505 (4)	3/4	0.1836 (3)	0.0198 (7)
C(2)	0.0697 (4)	0.6757 (3)	0.2620 (3)	0.0179 (8)
O(3)	0.0720 (3)	0.5834 (3)	0.2008 (2)	0.0223 (7)
C(4)	0.0508 (5)	0.6065 (3)	0.0681 (3)	0.0194 (9)
N(5)	0.0436 (4)	0.5372 (3)	-0.0269 (3)	0.0239 (8)
C(6)	0.0272 (5)	0.5792 (3)	-0.1486 (3)	0.0238 (10)
N(7)	0.0165 (4)	0.6764 (3)	-0.1766 (3)	0.0202 (7)
C(8)	0.0156 (4)	0.7434 (3)	-0.0759 (3)	0.0165 (8)
C(9)	0.0383 (4)	0.7066 (3)	0.0557 (3)	0.0177 (8)
C(10)	0.0213 (8)	0.5094 (4)	-0.2645 (4)	0.0431 (14)
N(11)	-0.0034 (4)	0.8387 (3)	-0.1079 (3)	0.0238 (8)
O(1')	-0.0913 (3)	0.6345 (3)	0.4641 (2)	0.0205 (6)
C(2')	0.0836 (4)	0.6719 (3)	0.4121 (3)	0.0183 (8)
C(3')	0.1130 (4)	0.7724 (3)	0.4774 (3)	0.0176 (8)
C(4')	-0.0892 (4)	0.8097 (3)	0.4872 (3)	0.0180 (8)
C(5')	-0.1983 (4)	0.7152 (3)	0.5194 (3)	0.0186 (8)
C(6')	-0.3974 (5)	0.7123 (3)	0.4658 (3)	0.0226 (9)
C(7')	-0.4431 (5)	0.7695 (3)	0.2393 (3)	0.0258 (10)
C(8')	-0.4569 (5)	0.7341 (4)	0.0985 (4)	0.0262 (10)
C(9')	-0.4461 (6)	0.6340 (4)	0.0663 (4)	0.0320 (11)
C(10')	-0.4667 (6)	0.6051 (4)	-0.0665 (4)	0.0412 (14)
C(11')	-0.4956 (6)	0.6746 (5)	-0.1667 (4)	0.0404 (13)
C(12')	-0.5033 (6)	0.7724 (4)	-0.1355 (4)	0.0410 (13)
C(13')	-0.4843 (6)	0.8031 (4)	-0.0041 (4)	0.0366 (12)
O(3')	0.2020 (3)	0.7646 (3)	0.6039 (2)	0.0210 (6)
O(4')	-0.1040 (3)	0.8824 (3)	0.5894 (2)	0.0243 (7)
O(5')	-0.4008 (3)	0.6957 (3)	0.3229 (2)	0.0263 (7)
O(6')	-0.4677 (4)	0.8543 (3)	0.2736 (3)	0.0378 (9)
O(7)	-0.5938 (4)	0.4846 (3)	0.5058 (3)	0.0352 (8)
O(8)	0.2975 (4)	0.9682 (3)	0.6575 (3)	0.0341 (8)

Table 2. Selected geometric parameters (Å, °)

N(1)—C(2)	1.280 (4)	N(1)—C(9)	1.407 (4)
C(2)—O(3)	1.389 (5)	C(2)—C(2')	1.501 (4)
O(3)—C(4)	1.367 (4)	C(4)—N(5)	1.334 (5)
C(4)—C(9)	1.363 (6)	N(5)—C(6)	1.344 (5)
C(6)—N(7)	1.347 (6)	C(6)—C(10)	1.493 (6)
N(7)—C(8)	1.354 (5)	C(8)—C(9)	1.412 (4)
C(8)—N(11)	1.334 (6)	O(1')—C(2')	1.452 (4)
O(1')—C(5')	1.448 (5)	C(2')—C(3')	1.521 (6)
C(3')—C(4')	1.536 (5)	C(3')—O(3')	1.411 (4)
C(4')—C(5')	1.534 (6)	C(4')—O(4')	1.422 (5)
C(5')—C(6')	1.516 (4)	C(6')—O(5')	1.445 (4)
C(7')—C(8')	1.487 (5)	C(7')—O(5')	1.335 (5)
C(7')—O(6')	1.210 (6)	C(8')—C(9')	1.394 (7)
C(8')—C(13')	1.397 (6)	C(9')—C(10')	1.389 (6)
C(10')—C(11')	1.387 (7)	C(11')—C(12')	1.361 (9)
C(12')—C(13')	1.381 (6)		
C(2)—N(1)—C(9)	103.4 (2)	N(1)—C(2)—O(3)	116.0 (3)
N(1)—C(2)—C(2')	129.9 (4)	O(3)—C(2)—C(2')	114.0 (3)
C(2)—O(3)—C(4)	102.7 (3)	O(3)—C(4)—N(5)	122.1 (4)
O(3)—C(4)—C(9)	108.7 (3)	N(5)—C(4)—C(9)	129.1 (3)
C(4)—N(5)—C(6)	110.4 (4)	N(5)—C(6)—N(7)	127.1 (3)
N(5)—C(6)—C(10)	115.8 (4)	N(7)—C(6)—C(10)	117.1 (3)
C(6)—N(7)—C(8)	120.0 (3)	N(7)—C(8)—C(9)	116.9 (4)
N(7)—C(8)—N(11)	118.1 (3)	C(9)—C(8)—N(11)	125.0 (3)
N(1)—C(9)—C(4)	109.2 (3)	N(1)—C(9)—C(8)	134.6 (4)
C(4)—C(9)—C(8)	116.2 (3)	C(2')—O(1')—C(5')	109.6 (3)
C(2)—C(2')—O(1')	108.8 (2)	C(2)—C(2')—C(3')	113.9 (3)
O(1')—C(2')—C(3')	105.9 (3)	O(1')—C(3')—C(4')	101.3 (3)
C(2')—C(3')—O(3')	112.0 (3)	C(4')—C(3')—O(3')	112.4 (2)
C(3')—C(4')—C(5')	102.8 (3)	C(3')—C(4')—O(4')	110.6 (3)
C(5')—C(4')—O(4')	112.5 (3)	O(1')—C(5')—C(4')	106.0 (3)
O(1')—C(5')—C(6')	110.2 (3)	C(4')—C(5')—C(6')	115.3 (3)
C(5')—C(6')—O(5')	110.9 (3)	C(8')—C(7')—O(5')	111.2 (4)
C(8')—C(7')—O(6')	124.4 (4)	O(5')—C(7')—O(6')	124.4 (3)
C(7')—C(8')—C(9')	121.8 (4)	C(7')—C(8')—C(13')	119.0 (4)
C(9')—C(8')—C(13')	119.2 (4)	C(8')—C(9')—C(10')	119.3 (4)
C(9')—C(10')—C(11')	120.7 (5)	C(10')—C(11')—C(12')	120.1 (4)
C(11')—C(12')—C(13')	120.4 (5)	C(8')—C(13')—C(12')	120.5 (5)
C(6')—O(5')—C(7')	120.1 (3)		

The absolute structure could not be determined by refinement of the Rogers  $\eta$  parameter (Rogers, 1981) or by inversion of the structure. Therefore, only the relative stereochemistry is shown in Fig. 1. H atoms were included using a riding model with C—H = 0.96 Å. Water H atoms were not located.

Data collection: Churchill, Lashewycz & Rotella (1977). Data reduction: UCLA (Strouse, 1981). Program(s) used to solve structure: MITHRIL (Gilmore, 1984). Program(s) used to refine structure: SHELXTL-Plus (Sheldrick, 1988). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

Funds for the purchase of the Siemens R3m/V diffractometer system were made available from the National Science Foundation under grant CHE-85-14495.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Albano, V., Bellon, P. L., Pompa, F. & Scatturin, V. (1963). *Ric. Sci. Parte 2, Sez. A3*, 1143; *Chem. Abstr.* (1964), **61**, 1342.
- Ambats, I. & Marsh, R. E. (1965). *Acta Cryst.* **19**, 942–948.
- Brufani, M., Giacomello, G. & Stein, M. L. (1961). *Gazz. Chim. Ital.* **91**, 767.
- Burling, F. T., Gabrielsen, B. & Goldstein, B. M. (1991). *Acta Cryst. C47*, 1272–1275.
- Burling, F. T. & Goldstein, B. M. (1992). *J. Am. Chem. Soc.* **114**, 2313–2320.
- Cappellacci, L., Franchetti, P., Grifantini, M., Messini, L., Abu Sheikha, G., Nocentini, G., Moraca, R. & Goldstein, B. M. (1995). *Nucleosides Nucleotides*, **14**, 607–610.
- Churchill, M. R., Lashewycz, R. A. & Rotella, F. J. (1977). *Inorg. Chem.* **16**, 265–271.
- Franchetti, P., Cristalli, G., Grifantini, M., Cappellacci, L., Vittori, S. & Nocentini, G. (1990). *J. Med. Chem.* **33**, 2852–2856.
- Franchetti, P., Messini, L., Cappellacci, L., Grifantini, M., Guarracino, P., Marongiu, M. E., Piras, G. & La Colla, P. (1993). *Nucleosides Nucleotides*, **12**, 359–368.
- Freeman, F. & Scheuerman, R. A. (1989). Unpublished data.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Goldstein, B. M., Bell, J. E. & Marquez, V. E. (1990). *J. Med. Chem.* **33**, 1123–1127.
- Goldstein, B. M., Kennedy, S. D. & Hennen, W. J. (1990). *J. Am. Chem. Soc.* **112**, 8265–8268.
- Goldstein, B. M., Li, H., Hallows, W. H., Langs, D. A., Franchetti, P., Cappellacci, L. & Grifantini, M. (1994). *J. Med. Chem.* **37**, 1684–1688.
- Goldstein, B. M., Mao, D. T. & Marquez, V. E. (1988). *J. Med. Chem.* **31**, 1026–1031.
- Goldstein, B. M., Takusagawa, F., Berman, H. M., Srivastava, P. C. & Robins, R. K. (1983). *J. Am. Chem. Soc.* **105**, 7416–7422.
- Pompa, F., Albano, V., Bellon, P. & Scatturin, V. (1965). *Ric. Sci. Parte 2, Sez. A8*, 1150; *Chem. Abstr.* (1966), **64**, 18555.
- Rogers, D. (1981). *Acta Cryst.* **A37**, 734–741.
- Scatturin, V. & Zannetti, R. (1956). *Ric. Sci.* **26**, 523; *Chem. Abstr.* (1956), **50**, 16256.
- Scatturin, V. & Zannetti, R. (1959). *Ann. Chim. (Rome)*, **49**, 68; *Chem. Abstr.* (1959), **53**, 13724.
- Sheldrick, G. M. (1988). *SHELXTL-Plus Structure Determination Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
- Strouse, C. (1981). *UCLA Crystallographic Computing Package*. University of California, Los Angeles, USA.