Table 2. *Significant bond lengths (Å) and angles (°)*

PO_3F^{2-}

P—F	1.601 (1)	F—P—O(1)	103.10 (7)
P—O(1)	1.508 (1)	F—P—O(2)	104.22 (7)
P—O(2)	1.510 (1)	F—P—O(3)	103.90 (8)
P—O(3)	1.511 (1)	O(1)—P—O(2)	115.73 (7)
		O(1)—P—O(3)	113.40 (7)
		O(2)—P—O(3)	114.50 (7)

$Ni(H_2O)_6^{2+}$

Ni—O(4)	2.034 (1) × 2	O(4)—Ni—O(5)	91.18 (5)
Ni—O(5)	2.079 (1) × 2	O(4)—Ni—O(6)	89.52 (5)
Ni—O(6)	2.070 (1) × 2	O(5)—Ni—O(6)	90.79 (5)
O—H(mean)	0.80 (4)	O(4)—Ni—O(6^i)	90.48 (5)
		O(5)—Ni—O(6^i)	89.21 (5)
		O(4)—Ni—O(5^i)	88.82 (5)
		H—O—H(mean)	107 (4)

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Hydrogen-bond geometry (Å, °)*

$D \cdots A$	$D \cdots A$	$H \cdots A$	H atom	Angle at H
O(1)···O(4^i)	2.774 (2)	1.98 (4)	H(41)	170 (3)
O(1)···O(6^{ii})	2.778 (2)	1.99 (4)	H(61)	173 (4)
O(1)···N^{ii}	2.830 (2)	2.01 (4)	H(1)	173 (4)
O(2)···O(6^{iii})	2.789 (2)	1.97 (4)	H(62)	174 (4)
O(2)···N^{iv}	2.935 (2)	2.07 (4)	H(3)	148 (4)
O(3)···O(4^v)	2.703 (2)	1.90 (4)	H(42)	171 (4)
O(3)···N	2.846 (2)	1.99 (4)	H(2)	171 (3)
O(5)···F	2.841 (2)	2.05 (4)	H(51)	176 (5)
O(5)—O(2^v)	2.683 (2)	1.87 (4)	H(52)	179 (4)

Symmetry code: (i) $x, y, 1+z$; (ii) $1-x, -y, 1-z$; (iii) $-x, -y, 1-z$; (iv) $x-1, y, z$; (v) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

The title compound was prepared from a mixture (molar ratio 1:1) of aqueous solutions of $(NH_4)_2PO_3F.H_2O$ and $Ni(NO_3)_2.6H_2O$. Green single crystals were grown by slow evaporation at room temperature. The IR spectrum revealed the presence of both NH_4^+ and PO_3F^{2-} ions. Crystals decomposed in air; to collect data, they were mounted in sealed glass capillaries. In spite of this, crystal decay was observed during data collection. The final intensities of standard reflections dropped by up to 73 % of their initial values. Intensities were collected with a scan amplitude of 1.5° and speed of 0.6° s^{-1}. Calculations were performed with *DIRDIF* (Beurskens et al., 1984), *XRAY*80 (Stewart, Kundell & Baldwin, 1980), *PESOS* (Martínez-Ripoll & Cano, 1975) and *PLUTO* (Motherwell & Clegg, 1978). The weighting scheme applied by *PESOS* was $w = K/F(f)F(s)$, where $K = 0.5785$, $F(s) = 6.4971 - 21.0696(\sin\theta/\lambda) + 18.9012(\sin\theta/\lambda)^2$ and $F(f) = a + bF_{obs} + cF_{obs}$. The values of a, b and c were as follows:

a	b	c	
1.1255	−0.2964	0.0269	$F_{obs} < 7.5$
0.2515	0.0118	0.0	$7.5 < F_{obs} < 20.0$
−0.0032	0.0235	0.0	$20.0 < F_{obs} < 29.0$
−0.3053	0.0329	0.0	$29.0 < F_{obs}$

References

Berndt, A. L. (1974). *Acta Cryst.* B30, 529–530.
Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A. J., Noordik, J. H., Beurskens, G., Parthasarathi, V., Bruins Slot, H. J., Haltiwanger, R. C. & Surits, J. M. M. (1984). *DIRDIF* system. Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands.
Durand, J., Cot, L., Berraho, M. & Rafiq, M. (1987). *Acta Cryst.* C43, 611–613.
Durand, J., Cot, L. & Galigné, J. L. (1974). *Acta Cryst.* B30, 1565–1569.
Durand, J., Cot, L. & Galigné, J. L. (1978). *Acta Cryst.* B34, 388–391.
Durand, J., Granier, W., Cot, L. & Galigné, J. L. (1975). *Acta Cryst.* B31, 1533–1535.
Durand, J., Larbot, A., Cot, L., Duprat, M. & Dabosi, F. (1983). *Z. Anorg. Allg. Chem.* 504, 163–172.
Galigné, J. L., Durand, J. & Cot, L. (1974). *Acta Cryst.* B30, 697–701.
Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS.* Instituto Rocasolano, CSIC, Serrano 119, Madrid-6, Spain.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Payen, J. L., Durand, J., Cot, L. & Galigné, J. L. (1979). *Can. J. Chem.* 57, 886–889.
Serafini, A., Labarre, J. F., Granier, W. & Cot, L. (1976). *J. Chim. Phys.* 73, 13–15.
Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1980). The *XRAY*80 system. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

(±)-*cis*-6-Acetylamino-5-hydroxy-1,3-dioxepane

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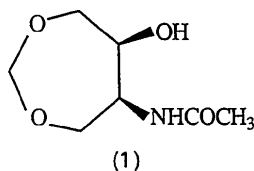
Abstract

The 1,3-dioxepane ring adopts a twist-boat conformation with the acetylamino and hydroxy groups occupying *cis* positions with respect to the ring. Two intramolecular hydrogen bonds [N—H···OH of 2.774(4) and O—H···OCH$_2$ of 2.808(3) Å] fix the conformation, and to-

gether with two intermolecular hydrogen bonds cause the broadening of —OH and —NH stretching bands in the IR (KBr) spectrum at 3290–3180 cm^{-1}.

Comment

As part of our research on polyfunctional synthon syntheses (Dumić, Proštenik & Butula, 1978; Proštenik, Dumić & Butula, 1984; Dumić, Proštenik, Fabijanić & Butula, 1984; Dumić, Filić, Vinković & Kamenar, 1992) the structure determination of the title compound (1) was undertaken in order to establish the configuration of 3,4,8,8a-tetrahydro-6H-[1,3]dioxepino-[5,6-d]oxazole. Details of the synthetic work will be published elsewhere (Dumić, Vinković, Butula & Kamenar, 1992).

(1)

The acetylamino and hydroxy groups are *cis* with respect to the 1,3-dioxepane ring (Fig. 1) which adopts a twist-boat conformation. All bond distances (Table 2) are in agreement with the distances given by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) for the corresponding types of bonds, with the exception of C(1)—O(2) and C(2)—C(3) of 1.401(4) and 1.508(5) Å respectively, which are slightly shorter than expected. There are two intramolecular hydrogen bonds; one between the acetylamino and the hydroxo group, N(1)—H···O(3), and one between the hydroxo group and a ring O atom, O(3)—H···O(2). While the former restricts free rotation around the single bond N(1)—C(4), the latter fixes the conformation of the dioxepane ring. They both, together with the intermolecular hydrogen bonds (Fig. 2, Table 3), cause the observed broadening of the —OH and —NH stretching bands in the IR (KBr) spectrum.
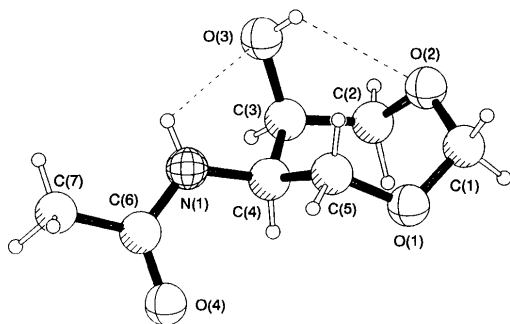

Fig. 2. *PLUTON* drawing of the unit cell of $C_7H_{13}NO_4$. Hydrogen bonds are represented by dashed lines.

Experimental

Crystal data

$C_7H_{13}NO_4$	$V = 425.0$ (2) Å^3
$M_r = 175.18$	$Z = 2$
Monoclinic	$D_x = 1.37$ Mg m^{-3}
Pn	$D_m = 1.38$ Mg m^{-3}
$a = 8.767$ (1) Å	Mo $K\alpha$
$b = 7.117$ (2) Å	$\lambda = 0.7101$ Å
$c = 7.260$ (2) Å	$\mu = 0.105$ mm^{-1}
$\beta = 110.23$ (2)°	$T = 293$ K
Cell parameters from 18	Irregular pyramid
reflections	0.36 × 0.30 × 0.26 mm
$\theta = 9{-}12°$	Colourless

Data collection

Philips PW1100 diffractome-	$\theta_{max} = 29.97°$
ter	$h = -12 \rightarrow 11$
ω scans	$k = 0 \rightarrow 9$
Absorption correction:	$l = 0 \rightarrow 10$
none	3 standard reflections
1015 measured reflections	frequency: 120 min
1014 independent reflections	intensity variation: 3.4%
904 observed reflections	
$[F > 3.0\sigma(F)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.003$
Final $R = 0.032$	$\Delta\rho_{max} = 0.158$ e Å^{-3}
$wR = 0.041$	$\Delta\rho_{min} = -0.120$ e Å^{-3}
$S = 0.7693$	Atomic scattering factors
904 reflections	from *International Tables*
159 parameters	*for X-ray Crystallogra-*
All H-atom parameters re-	*phy* (1974, Vol. IV, Table
fined	2.2B)
$w = 0.7348/[\sigma^2(F) +$	
$0.000867F^2]$	

Fig. 1. *PLUTON* drawing of $C_7H_{13}NO_4$ showing the labelling scheme of the non-H atoms. Intramolecular hydrogen bonds are represented by dashed lines.

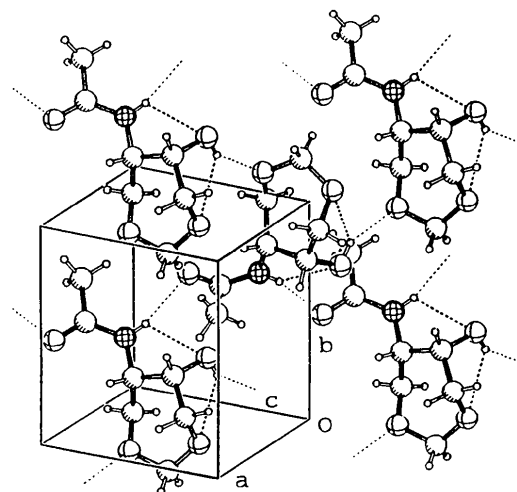Data collection: Philips PW1100/10 software 1974. Cell refinement: Philips PW1100/10 software 1974. Data reduction:

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0.5055 (5)	−0.1874 (4)	0.5434 (5)	0.0430 (9)
C(2)	0.5637 (5)	0.1010 (5)	0.4162 (6)	0.049 (1)
C(3)	0.5120 (4)	0.2659 (4)	0.5111 (5)	0.0369 (9)
C(4)	0.5334 (4)	0.2296 (4)	0.7263 (5)	0.0354 (8)
C(5)	0.4639 (5)	0.0429 (4)	0.7628 (5)	0.041 (1)
C(6)	0.5400 (4)	0.4475 (4)	0.9887 (5)	0.0328 (8)
C(7)	0.4580 (5)	0.6074 (5)	1.0513 (5)	0.046 (1)
O(1)	0.5605 (3)	−0.1081 (3)	0.7333 (4)	0.0441 (7)
O(2)	0.4524 (4)	−0.0522 (3)	0.3946 (4)	0.0442 (7)
O(3)	0.3491 (3)	0.3201 (3)	0.4036 (4)	0.0448 (7)
O(4)	0.6662	0.3782 (3)	1.1011	0.0442 (6)
N(1)	0.4670 (4)	0.3834 (3)	0.8054 (4)	0.0366 (7)

Table 2. *Geometric parameters* ($\mathring{A}$, °)

C(1)—O(1)	1.411 (4)	C(2)—C(3)	1.508 (5)
C(1)—O(2)	1.401 (4)	C(3)—O(3)	1.424 (4)
C(4)—C(5)	1.523 (5)	C(2)—O(2)	1.435 (5)
C(5)—O(1)	1.430 (5)	C(6)—C(7)	1.498 (5)
C(3)—C(4)	1.530 (5)	C(6)—O(4)	1.228 (3)
C(4)—N(1)	1.448 (5)	C(6)—N(1)	1.342 (4)
O(1)—C(1)—O(2)	112.9 (3)	C(3)—C(2)—O(2)	109.9 (3)
C(4)—C(5)—O(1)	109.7 (3)	O(4)—C(6)—N(1)	122.3 (3)
C(5)—C(4)—N(1)	110.5 (3)	C(7)—C(6)—N(1)	116.4 (3)
C(5)—C(4)—C(3)	114.2 (3)	C(7)—C(6)—O(4)	121.3 (3)
C(3)—C(4)—N(1)	110.7 (3)	C(1)—O(1)—C(5)	115.3 (3)
C(4)—C(3)—O(3)	110.6 (3)	C(1)—O(2)—C(2)	113.9 (3)
C(4)—C(3)—C(2)	112.7 (3)	C(4)—N(1)—C(6)	122.1 (3)
C(2)—C(3)—O(3)	111.3 (3)		

Table 3. *Hydrogen-bond geometry* ($\mathring{A}$, °)

D—H···A	D···A	D—H	D—H···A	Symmetry code for A
O3—H(O3)···O2	2.808 (3)	0.82 (4)	109 (4)	x,y,z
H1—H(N1)···O3	2.774 (4)	0.83 (3)	103 (2)	x,y,z
O3—H(O3)···O1	2.836 (3)	0.82 (4)	150 (4)	$-0.5 + x, -y, -0.5 + z$
N1—H(N1)···O4	3.054 (3)	0.83 (3)	166 (3)	$-0.5 + x, 1 - y, -0.5 + z$

STRUFA (*ZOAK7*; Vicković, 1975). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Software used to prepare material for publication: *PLUTON* (Spek, 1982).

The ω-scan width was 1.20° with an ω-scan rate of 2.4° min^{-1}. To define the origin of the space group the x and z coordinates of O(4) were fixed. Refinement was performed by the full-matrix least-squares method.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Dumić, M., Filić, D., Vinković, M. & Kamenar, B. (1992). In preparation.
Dumić, M., Proštenik, M. V. & Butula, I. (1978). *Croat. Chem. Acta,* 51, 259–264.

Dumić, M., Proštenik, M. V., Fabijanić, J. & Butula, I. (1984). *Croat. Chem. Acta,* 57, 405–409.
Dumić, M., Vinković, M., Butula, I. & Kamenar, B. (1992). In preparation.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Proštenik, M. V., Dumić, M. & Butula, I. (1984). *Croat. Chem. Acta,* 57, 281–288.
Sheldrick, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
Spek, A. L. (1982). *The EUCLID Package.* In *Computational Crystallography,* edited by D. Sayre. Oxford: Clarendon Press.
Vicković, J. (1975). *Proc. Yugosl. Cent. Crystallogr.* 10, 77.

Structure of Bis(dipicolinato)ferrate(III) Dihydrate

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Abstract

The Fe atom is octahedrally surrounded by two tridentate dipicolinate anions. These two ligands are orthogonal to each other. The two water molecules are linked through the proton required for electricial neutrality and form an H_5O_2 cation. The protons of these two water molecules are bonded to the O atoms of the carboxylate groups which are not coordinated to the Fe atom. Metal–nitrogen and metal–oxygen distances are comparable to those of other transition-metal dipicolinate complexes.

Comment

The complexation of metal ions by 2,6-pyridine-dicarboxylic acid (H_2dpa) has been extensively studied. Part of the interest results from the unique ability of the ligand to form stable chelates, as indicated by the slow exchange rates (Erikson, Grenthe & Puigdomenech, 1987; Ducommun, Helm, Laurenczy & Merbach, 1989) and thermodynamic