

Table 1. Atomic coordinates for non-H atoms with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta).$$

| | x | y | z | B_{eq} (Å ²) |
|--------|------------|-------------|------------|----------------------------|
| O(2') | 0.4733 (2) | 0.4823 (1) | 0.3456 (1) | 4.77 (7) |
| O(10A) | 0.8293 (3) | -0.0014 (2) | 1.1491 (1) | 6.9 (1) |
| O(10B) | 0.9365 (3) | 0.1647 (3) | 1.0928 (2) | 10.9 (2) |
| N(1') | 0.6120 (2) | 0.3172 (2) | 0.2987 (2) | 5.0 (1) |
| N(3') | 0.5941 (2) | 0.3583 (2) | 0.4734 (2) | 4.6 (1) |
| C(2) | 0.6820 (3) | 0.1701 (2) | 0.5674 (2) | 4.7 (1) |
| C(2') | 0.5526 (2) | 0.3934 (2) | 0.3708 (2) | 3.9 (1) |
| C(3) | 0.7004 (3) | 0.2596 (2) | 0.4738 (2) | 4.3 (1) |
| C(4) | 0.6764 (3) | 0.2106 (2) | 0.3539 (2) | 4.5 (1) |
| C(5) | 0.5791 (4) | 0.0993 (3) | 0.3387 (2) | 5.9 (1) |
| C(6) | 0.7353 (4) | 0.2188 (3) | 0.6808 (2) | 5.6 (1) |
| C(7) | 0.7048 (4) | 0.1319 (3) | 0.7741 (2) | 5.5 (1) |
| C(8) | 0.7865 (4) | 0.1629 (3) | 0.8830 (2) | 6.3 (2) |
| C(9) | 0.7573 (5) | 0.0700 (3) | 0.9715 (2) | 7.3 (2) |
| C(10) | 0.8507 (4) | 0.0844 (3) | 1.0758 (2) | 6.1 (1) |

Table 2. Bond lengths (Å) and angles (°) between non-H atoms, and hydrogen bonds (Å)

| | | | |
|-------------------|-----------|---------------------|-----------|
| O(2')—C(2) | 1.241 (3) | C(2)—C(6) | 1.523 (3) |
| O(10A)—C(10) | 1.311 (3) | C(3)—C(4) | 1.548 (3) |
| O(10B)—C(10) | 1.188 (3) | C(4)—C(5) | 1.513 (4) |
| N(1')—C(2') | 1.341 (3) | C(6)—C(7) | 1.511 (4) |
| N(1')—C(4) | 1.452 (3) | C(7)—C(8) | 1.514 (4) |
| N(3')—C(2') | 1.332 (3) | C(8)—C(9) | 1.508 (4) |
| N(3')—C(3) | 1.453 (3) | C(9)—C(10) | 1.490 (4) |
| C(2)—C(3) | 1.510 (3) | | |
| C(2')—N(1')—C(4) | 111.7 (2) | N(1')—C(4)—C(5) | 111.6 (2) |
| C(2')—N(3')—C(3) | 111.9 (2) | C(3)—C(4)—C(5) | 116.3 (2) |
| C(3)—C(2)—C(6) | 113.7 (2) | C(2)—C(6)—C(7) | 112.7 (2) |
| O(2')—C(2')—N(1') | 125.4 (2) | C(6)—C(7)—C(8) | 113.8 (3) |
| O(2')—C(2')—N(3') | 125.9 (2) | C(7)—C(8)—C(9) | 111.5 (3) |
| N(1')—C(2')—N(3') | 108.6 (2) | C(8)—C(9)—C(10) | 114.3 (3) |
| N(3')—C(3)—C(2) | 112.4 (2) | O(10A)—C(10)—O(10B) | 122.3 (2) |
| N(3')—C(3)—C(4) | 101.2 (2) | O(10A)—C(10)—C(9) | 113.2 (3) |
| C(2)—C(3)—C(4) | 117.3 (2) | O(10B)—C(10)—C(9) | 124.5 (3) |
| N(1')—C(4)—C(3) | 100.6 (2) | | |

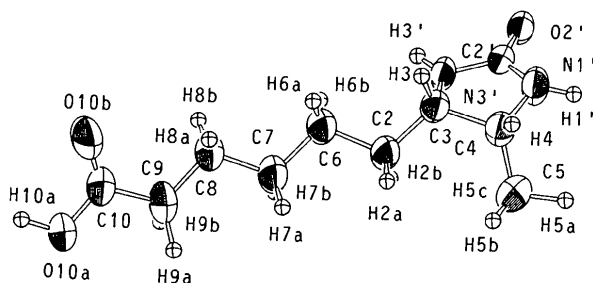


Fig. 1. Perspective view of desthiobiotin with the atomic numbering used.

crystal structure of (\pm)-desthiobiotin has previously been determined (Chen, Parthasarathy & DeTitta, 1976). Their crystal has a different packing system from that of the present one, but the molecular conformations in both crystals are similar. The crystal structure of biotin has also been reported (Traub, 1956; Bonnemere, Hamilton, Steinrauf & Knappe, 1965).

| D (at x,y,z) | A | D...A |
|-----------------|----------------------|-----------|
| O(10A) | O(2') ⁱ | 2.657 (2) |
| N(1') | O(10B) ⁱⁱ | 2.889 (3) |
| N(3') | O(2') ⁱⁱⁱ | 2.887 (2) |

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

References

- BEURSKENS, P. T. (1984). Tech. Rep. 1984. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- BONNEMERE, C., HAMILTON, J. A., STEINRAUF, L. K. & KNAPPE, J. (1965). *Biochemistry*, **4**, 240–245.
- CHEN, C.-S., PARTHASARATHY, R. & DETITTA, G. T. (1976). *J. Am. Chem. Soc.* **98**, 4983–4990.
- GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- IZUMI, Y., KANO, Y., INAGAKI, K., KAWASE, N., TANI, Y. & YAMADA, H. (1981). *Agric. Biol. Chem.* **45**, 1983–1989.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- TANAKA, M., IZUMI, Y. & YAMADA, H. (1988). *Vitamin*, **62**, 306–315.
- TRAUB, W. (1956). *Nature (London)*, **178**, 649–650.

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Monoprotonated Perchlorate Salt of Tris(2-pyridyl)methanol

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Abstract. 2-[Bis(2-pyridyl)hydroxymethyl]pyridinium perchlorate, C₁₆H₁₄N₃O⁺.ClO₄⁻, $M_r = 363.8$, monoclinic, $P2_1/c$, $a = 12.301$ (3), $b = 13.300$ (4), $c = 10.817$ (3) Å, $\beta = 110.94$ (2)°, $V = 1652.8$ (8) Å³, $Z =$

4, $D_x = 1.462$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.26$ mm⁻¹, $F(000) = 752$, $T = 293$ (1) K, $R = 0.053$ for 2504 observed reflections. The C—O bond length is 1.407 (4) Å; the C—C(OH)

bond lengths are 1.523 (4), 1.532 (3) and 1.548 (5) Å with the middle value that of the protonated pyridyl ring. Maximum deviation from regular tetrahedral geometry about C₁ is 115.1 (2)°. The hydroxyl H is hydrogen bonded to a pyridyl ring N atom (N2c) in the same cation at *ca* 1.92 Å. The N—H of the protonated ring has a bond length of 0.87 (4) Å. The perchlorate Cl—O bond lengths range from 1.392 (4) to 1.413 (3) Å and the maximum deviation from regular tetrahedral geometry is 106.3 (2)°.

Experimental. Nearly colorless crystals were obtained from the reaction of tris(2-pyridyl) methanol [tris(2-pyridyl)carbinol], py₃COH, with tetrakis(methyl sulfoxide)ruthenium(II) chloride in perchloric acid (0.10*M*). Four-circle Nicolet P1 autodiffractometer, graphite-monochromated Mo *K*α radiation, ω scan technique. Cell parameters for a rectangular parallelepiped crystal of 0.25 × 0.45 × 0.80 mm from least-squares procedures on 15 reflections ($2\theta > 25^\circ$). Maximum value of $(\sin\theta)/\lambda = 0.650 \text{ \AA}^{-1}$. No significant changes observed in six check reflections measured every 300 reflections. 3783 independent reflections collected and 2504 satisfied $I \geq 3\sigma(I)$, $R_{\text{int}} = 0.019$; range $h = -15$ to 15, $k = 0$ to 17, $l = 0$ to 14; no absorption correction applied. Structure solved by direct methods using the *SHELXTL* direct methods program (Sheldrick, 1978). H atoms located by difference Fourier after second refinement cycle. At convergence, R (based on F) = 0.053, wR (based on F) = 0.060, $S = 2.89$, and $w = 1/(\sigma_F^2)$ where $\sigma_F^2 = \{[\sigma(F_o)]^2 + (0.01|F_o|)^2\}$, $(\Delta/\sigma)_{\text{max}} = 0.03\sigma_p$ for 235 parameters (25 anisotropic non-H atoms and two refined isotropic H atoms). Largest residual feature in the final difference Fourier map was 0.42 e Å⁻³. Extinction parameter of the form $[1 + 0.002(x)F_c^2 \sin^{-1}(2\theta)]^{-1/4}$ where $x = 0.00043$ (Larson, 1967). Scattering factors for all atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations on a Data General Eclipse S-200 computer using versions of the Nicolet (Syntex) *E-XTL* or *SHELXTL* interactive crystallographic software as modified at Crystalytics Company. Fig. 1

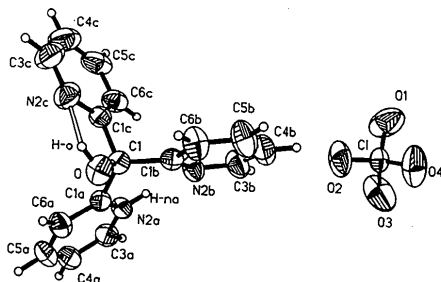


Fig. 1. The molecular structure and numbering scheme for $[py_2(py.H)COH](ClO_4)$. Ellipsoids are at the 50% probability level.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10$) with e.s.d.'s in parentheses

B_{eq} is defined as one third of the trace of the orthogonalized B_{ij} tensor.

| Cation | x | y | z | B_{eq} |
|--------|----------|----------|----------|-----------------|
| C1 | 2415 (2) | 7056 (2) | 1961 (3) | 32 (1) |
| O | 2441 (2) | 7810 (2) | 1059 (2) | 44 (1) |
| C1a | 3434 (2) | 7258 (2) | 3255 (3) | 32 (1) |
| N2a | 3815 (2) | 6513 (2) | 4140 (2) | 34 (1) |
| C3a | 4628 (3) | 6640 (3) | 5342 (3) | 42 (1) |
| C4a | 5107 (3) | 7567 (3) | 5709 (4) | 50 (1) |
| C5a | 4759 (3) | 8334 (3) | 4823 (4) | 55 (1) |
| C6a | 3921 (3) | 8190 (2) | 3592 (4) | 46 (1) |
| C1b | 2431 (2) | 6032 (2) | 1340 (3) | 32 (1) |
| N2b | 2822 (2) | 5257 (2) | 2145 (3) | 41 (1) |
| C3b | 2788 (3) | 4346 (3) | 1606 (4) | 54 (1) |
| C4b | 2372 (3) | 4184 (3) | 269 (4) | 57 (1) |
| C5b | 1964 (4) | 4979 (3) | -542 (4) | 62 (1) |
| C6b | 1991 (3) | 5924 (3) | -16 (3) | 50 (1) |
| C1c | 1275 (2) | 7149 (2) | 2253 (3) | 35 (1) |
| N2c | 658 (2) | 7956 (2) | 1717 (3) | 50 (1) |
| C3c | -350 (4) | 8097 (4) | 1917 (4) | 68 (2) |
| C4c | -732 (3) | 7452 (4) | 2664 (4) | 72 (2) |
| C5c | -68 (3) | 6623 (4) | 3226 (4) | 59 (1) |
| C6c | 953 (3) | 6465 (3) | 3013 (3) | 42 (1) |
| Anion | | | | |
| Cl | 3107 (1) | 736 (1) | 1113 (1) | 40 (1) |
| O1 | 2139 (3) | 193 (3) | 1141 (4) | 98 (2) |
| O2 | 2953 (3) | 1783 (2) | 1199 (3) | 76 (1) |
| O3 | 4130 (3) | 409 (2) | 2121 (3) | 99 (1) |
| O4 | 3214 (3) | 519 (2) | -97 (3) | 89 (1) |

shows the atom-numbering scheme, Table 1 contains atomic parameters for non-H atoms, Table 2 contains bond lengths and bond angles for the $[py_2(py.H)COH]^+$ cation and the ClO_4^- anion.*

Related literature. Tris(2-pyridyl)methanol (Keene, Snow & Tiekink, 1988) as well as several compounds with the ligand coordinated to transition metals have been reported. Symmetric (N,N',N'') coordination is found in methylmercury(I) (Canty, Chaichit, Gatehouse & George, 1981). Two isomers of cobalt(III) have been reported, one in which both ligands are bound in a symmetric mode (Szalda & Keene, 1986) while the second has a mixed mode of coordination with one ligand bound in a symmetric mode but the other in an asymmetric (N,N',O) mode (White & Faller, 1982). A mixed mode of coordination was also found for two ruthenium(II) complexes, $[Ru(py_3COH)_2]^{2+}$ (Keene, Szalda & Wilson, 1987) and $[Ru(NH_3)_3(py_3COH)]^{2+}$ (Moritz, Diamantis, Keene, Snow & Tiekink, 1988); the conjugate base of each complex with proton loss from the coordinated $-COH$ group was also reported. The dimer $[(CH_3)In(py_3CO)]_2^{2+}$ has the O atoms serving as the

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and deviations, and the atomic coordinates for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54878 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0377]

Table 2. Bond lengths (Å) and bond angles (°) with *e.s.d.*'s in parentheses

| | | | |
|-------------|-----------|-------------|------------|
| Cation | | | |
| C1—O | 1.407 (4) | O—H—O | 0.82 (4) |
| C1—C1a | 1.532 (3) | C1a—N2a | 1.342 (4) |
| C1—C1b | 1.523 (4) | C3a—N2a | 1.338 (3) |
| C1—C1c | 1.548 (5) | C1b—N2b | 1.324 (4) |
| C1a—C6a | 1.368 (4) | C3b—N2b | 1.338 (4) |
| C3a—C4a | 1.363 (5) | C3c—N2c | 1.323 (4) |
| C4a—C5a | 1.360 (5) | C3c—N2c | 1.346 (6) |
| C5a—C6a | 1.376 (5) | N2a—Hna | 0.874 (35) |
| C1b—C6b | 1.377 (4) | C1c—C6c | 1.376 (5) |
| C3b—C4b | 1.367 (5) | C3c—C4c | 1.371 (7) |
| C4b—C5b | 1.351 (5) | C4c—C5c | 1.377 (6) |
| C5b—C6b | 1.375 (5) | C5c—C6c | 1.372 (6) |
| | | | |
| O—C1—C1a | 107.1 (2) | C1a—N2a—C3a | 123.3 (3) |
| O—C1—C1b | 108.9 (3) | C1b—N2b—C3b | 118.1 (3) |
| O—C1—C1c | 109.4 (2) | C1c—N2c—C3c | 117.5 (3) |
| C1a—C1—C1b | 115.1 (2) | C1a—N2a—Hna | 115.5 (20) |
| C1a—C1—C1c | 107.8 (2) | C3a—N2a—Hna | 121.2 (20) |
| C1b—C1—C1c | 108.5 (2) | C1—O—Ho | 102 (3) |
| C1—C1a—N2a | 119.0 (2) | C1—C1b—N2b | 117.7 (3) |
| C1—C1a—C6a | 122.7 (2) | C1—C1b—C6b | 120.1 (3) |
| N2a—C1a—C6a | 118.1 (2) | N2b—C1b—C6b | 122.1 (3) |
| N2a—C3a—C4a | 119.5 (3) | N2b—C3b—C4b | 123.0 (3) |
| C3a—C4a—C5a | 118.6 (3) | C3b—C4b—C5b | 118.4 (4) |
| C4a—C5a—C6a | 121.1 (3) | C4b—C5b—C6b | 119.9 (3) |
| C1a—C6a—C5a | 119.3 (3) | C1b—C6b—C5b | 118.6 (3) |
| C1—C1c—N2c | 113.3 (3) | C3c—C4c—C5c | 119.2 (4) |
| C1—C1c—C6c | 123.0 (3) | C4c—C5c—C6c | 118.9 (4) |
| N2c—C1c—C6c | 123.7 (3) | C1c—C6c—C5c | 118.3 (3) |
| N2c—C3c—C4c | 122.4 (4) | | |
| | | | |
| Anion | | | |
| Cl—O1 | 1.401 (4) | Cl—O3 | 1.408 (3) |
| Cl—O2 | 1.413 (3) | Cl—O4 | 1.392 (4) |
| | | | |
| O1—Cl—O2 | 111.8 (2) | O2—Cl—O3 | 110.9 (2) |
| O1—Cl—O3 | 110.9 (2) | O2—Cl—O4 | 109.0 (2) |
| O1—Cl—O4 | 106.3 (2) | O3—Cl—O4 | 107.8 (2) |

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Structure of Ethyl 1-*p*-Anisyl-7,8-dimethoxy-4,5-dimethyl-3-phenyl-3a,4,5,9b-tetrahydropyrazolo[3,4-*c*]isoquinoline-3a-carboxylate

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Abstract. Ethyl 7,8-dimethoxy-1-(4-methoxyphenyl)-4,5-dimethyl-3-phenyl-3a,4,5,9b-tetrahydropyrazolo-

bridging atoms and one pyridyl group of each ligand coordinated to each In^{III} and the third non-coordinated (Canty, Titcombe, Skelton & White, 1988). py₃COH can also coordinate as a bidentate (*N,N*) ligand with dimethylgld (Canty, Minchin, Healy & White, 1982).

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References

- CANTY, A. J., CHAICHT, N., GATEHOUSE, B. M. & GEORGE, E. E. (1981). *Inorg. Chem.* **20**, 4293–4300.
- CANTY, A. J., MINCHIN, N. J., HEALY, P. C. & WHITE, A. H. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1795–1802.
- CANTY, A. J., TITCOMBE, L., SKELTON, B. W. & WHITE, A. H. (1988). *J. Chem. Soc. Dalton Trans.* pp. 35–45.
- KEENE, F. R., SNOW, M. R. & TIEKINK, E. R. T. (1988). *Acta Cryst.* **C44**, 937–938.
- KEENE, F. R., SZALDA, D. J. & WILSON, T. A. (1987). *Inorg. Chem.* **26**, 2211–2216.
- LARSON, A. E. (1967). *Acta Cryst.* **23**, 664–665.
- MORITZ, P. S., DIAMANTIS, A. A., KEENE, F. R., SNOW, M. R. & TIEKINK, E. R. T. (1988). *Aust. J. Chem.* **41**, 1353–1362.
- SHELDRIK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Germany.
- SZALDA, D. J. & KEENE, F. R. (1986). *Inorg. Chem.* **25**, 2795–2799.
- WHITE, D. L. & FALLER, J. W. (1982). *Inorg. Chem.* **21**, 3119–3122.

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