

References

- BEACH, J. E., BLAIR, A. M. J. N., CLARKE, A. J., COX, J. S. G., KING, J., LEE, T. B., LOVEDAY, D. E. E., MOSS, G. F., ORR, T. S. C., RITCHIE, J. T. & SHEARD, P. (1970). *Adv. Drug Res.* **5**, 115–121.
- CAIRNS, H., COX, D., GOULD, K. J., INGALL, A. H. & SUSCHITZKY, J. L. (1985). *J. Med. Chem.* **28**, 1832–1842.
- GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
- SHEARD, P. & SUSCHITZKY, J. L. (1984). *Progress in Medicinal Chemistry*, Vol. 21, edited by G. P. ELLIS & G. B. WEST. Amsterdam: Elsevier.

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Synthesis and Structure of Bis(ototato)dioxouranium(VI) Pentahydrate

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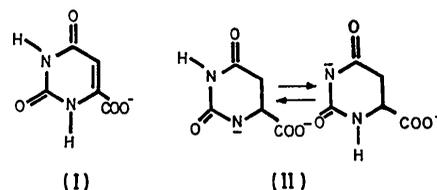
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Abstract. Dioxobis(1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidincarboxylato)uranium(VI) pentahydrate, $[\text{UO}_2(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$, $M_r = 670.29$, monoclinic, $C2/c$, $a = 16.167$ (4), $b = 10.384$ (2), $c = 10.866$ (3) Å, $\beta = 97.62$ (2)°, $V = 1808.0$ (7) Å³, $Z = 4$, $D_m = 2.51$, $D_x = 2.462$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 86.5$ cm⁻¹, $F(000) = 1264$, $T = 295$ (2) K, final $R = 0.022$, $wR = 0.029$ for 1533 observed reflections with $F_o \geq 5.0\sigma(F_o)$. The U atom is seven-coordinate and has a pentagonal-bipyramidal coordination. The ototate ion acts as a monodentate ligand through the carboxylate group.

Introduction. Orotic acid is a key compound involved in the *de novo* biosynthesis of pyrimidine bases of nucleic acids in living organisms (Leberman, Kornberg & Simms, 1955; Genchev, 1970; Lehninger, 1970). The overall process of enzymatic phosphoribosylation of orotic acids from phosphoribosyl pyrophosphate ultimately requires an unsubstituted N(1) nitrogen atom (Victor, Greenberg & Sloan, 1979). Metal ions make orotic acid available in the form of its reactive N(3)H dianion where N(1) is unsubstituted, thus contributing to the phosphoribosylation at the N(1) site (Sander, Wright & McCormick, 1965). It is also known to display bacteriostatic and cytostatic properties (*Small Medical Encyclopedia*, 1967).

Orotic acid, besides being biologically important, is also an interesting potentially multidentate ligand, since coordination may occur through the two N atoms of the pyrimidine ring, the two carbonyl oxygens and the carboxylic group. However, complexity of the pyrimidine system results also from pH changes.

Between pH 3 and 9 orotic acid is present in aqueous solutions mainly as the ototate anion (I). N(3)H with N(1) unsubstituted is obtained by abstraction of a second proton ($\text{p}K = 9.45$) and, according to previous observations on related uracil anion systems, should be present together with the N(1)H tautomer (II) (Psoda, Kazimierzczak & Shugar, 1974; Bensaude, Aubard, Dreyfus, Dodin & Dubois, 1978).



Although the crystal structures of orotic acid monohydrate (Takusagawa & Shimada, 1973) and ammonium orotate monohydrate (Solbakk, 1971) are known, very few structural studies of metal complexes with this ligand have been published. Crystal data of the complexes diammine(ototate)copper(II) (Mutikainen & Lumme, 1980) and tetraaqua(ototate)nickel(II) hydrate (Sabat, Zglinska & Jerowska-Trzebiatowska, 1980) indicate that complexation stabilizes the N(3)H tautomer and coordination to the metal occurs *via* carboxylate oxygen and the N(1) atom as chelation sites. The crystal structures of two complexes of 5-nitroorotic acid with Cu^{II} have also been reported recently (Arrizabalaga, Castan & Daham, 1983).

Experimental. The title complex was obtained by mixing aqueous solutions of sodium orotate and uranyl nitrate in a 2:1 molar ratio. Upon evaporation of the

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Table 1. Positional ($\times 10^4$) and equivalent isotropic thermal ($\times 10^3$) parameters of the non-hydrogen atoms with e.s.d.'s in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
U	5000	4351.9 (2)	7500	21.7 (2)
O(U)	5418 (3)	4351 (3)	9088 (3)	39 (2)
W(1)	6330 (2)	5143 (3)	7006 (3)	34 (2)
W(2)	5000	6676 (5)	7500	49 (4)
W(3)	4770 (4)	1652 (8)	597 (5)	67 (4)
N(1)	6982 (2)	1219 (3)	6135 (3)	25 (2)
C(2)	7447 (3)	554 (4)	5397 (4)	25 (2)
O(2)	7852 (2)	1085 (3)	4657 (3)	39 (2)
N(3)	7433 (3)	-760 (3)	5533 (4)	22 (2)
C(4)	7001 (3)	-1417 (4)	6328 (4)	24 (2)
O(4)	7019 (2)	-2615 (3)	6329 (3)	39 (2)
C(5)	6558 (3)	-650 (4)	7122 (4)	27 (2)
C(6)	6545 (3)	633 (4)	6974 (4)	25 (2)
C(7)	6026 (3)	1502 (4)	7703 (4)	28 (2)
O(1)	5891 (2)	2610 (3)	7210 (3)	33 (2)
O(3)	5769 (2)	1066 (4)	8624 (3)	28 (2)

solution at room temperature crystals precipitated slowly over a period of several days. D_m measured by flotation.

Syntex $P2_1$ diffractometer, Mo $K\alpha$ Zr-filtered radiation, θ - 2θ scan, $2\theta \leq 55.0^\circ$, scan speed variable 1.00 - $12.00^\circ \text{ min}^{-1}$, scan range 0.9° below $K\alpha_1$, 0.9 above $K\alpha_2$, background counting 0.5 s of scan time. Crystal $0.26 \times 0.20 \times 0.41$ mm. Cell parameters from 15 independent reflections ($20 \leq 2\theta \leq 22^\circ$), data form $-h, \pm k, \pm l$. No significant intensity variation for three reflections monitored every 67 reflections. Lp and empirical ϕ -scan absorption correction applied (Syntex, 1976). Data collected/unique/ R_{int} 3492/1609/0.006.

The U atom was deduced from a Patterson synthesis. Subsequent difference Fourier synthesis revealed the positions of all the other non-hydrogen atoms. The structure was refined with *SHELX76* (Sheldrick, 1976) in space group $C2/c$ (attempts to refine it in Cc led to negative U s) by full-matrix least squares in which $\sum w\Delta^2$ was minimized. H atoms located from ΔF maps, except those of uracil calculated at a distance of 1.0 Å. Non-H atoms anisotropic, H atoms isotropic. Weighting scheme for the last steps of refinement $w = 1.574/[\sigma^2(F_o) + 0.00035F_o^2]$. Two reflections showing poor agreement were given zero weight during final refinement cycles, $R = 0.024$ and $wR = 0.030$ for all data; $\Delta\rho_{max} = 0.71$, $\Delta\rho_{min} = 0.77 \text{ e \AA}^{-3}$ in the vicinity of the U atom. $(\Delta/\sigma)_{max} = 0.589$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters of the non-H atoms are given in Table 1,* bond lengths and angles in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44110 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The U atom lies on a twofold axis perpendicular to the U-O(U) bond and passes through W(2), Fig. 1. It has a pentagonal-bipyramidal coordination which is the preferred geometry for seven-coordinated uranyl compounds (Lintredt, Heeg, Ahmad & Glick, 1982). The equatorial pentagon formed by the carboxylic O(1) of the two monodentate orotate ligands and the oxygen atoms of three water molecules is planar with a maximum deviation from the least-squares plane of $0.029(1)$ Å for O(1). The coordination sphere is completed by the linear uranyl group nearly perpendicular to the equatorial plane with a maximum deviation from 90° of less than 2° .

The uranyl bonds fall in the normal range (Lintredt *et al.*, 1982; Mackinnon & Taylor, 1983; Burns, 1983; Toivonen & Laitinen, 1984). The pyrimidine ring is planar, the maximum deviation from the best plane being $0.024(7)$ Å for C(5). The mutual angle of the best planes of the two pyrimidine rings is only $6.6(3)^\circ$, each forming a $33.0(1)^\circ$ angle with the coordination pentagon.

In all the structures that we are aware of and which contain the orotate ligand, whether it is complexed to a metal or not, the respective bond lengths in the pyrimidine ring are quite similar, which shows that

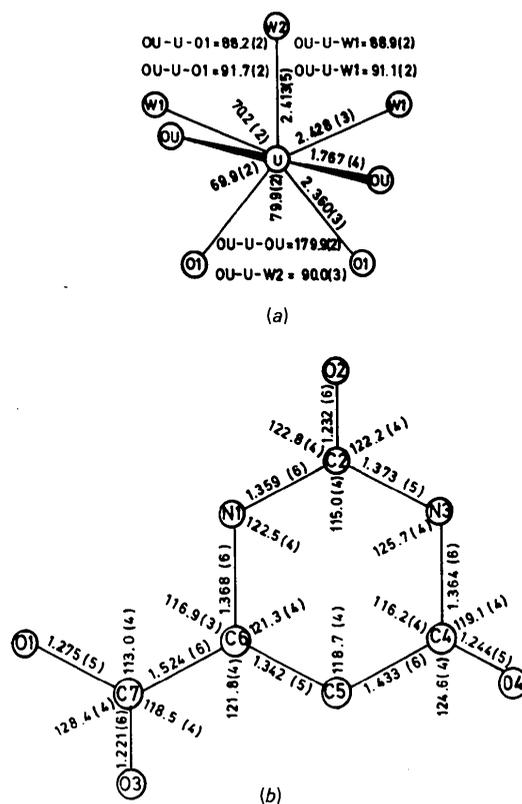


Table 2. Some interatomic distances (Å) and angles (°) in orotate ligands

	Present work	A	B	C	D	E	F
C(7)—O(3)	1.221	1.197	1.247	1.227	1.241	1.225	1.209
C(7)—O(1)	1.275	1.306	1.250	1.285	1.256	1.267	1.284
C(6)—N(1)—C(2)	122.9	122.7	122.6	117.9	118.3	118.7	118.1
C(2)—N(3)—C(4)	125.7	126.4	126.5	126.5	125.8	127.3	120.7
N(1)—C(2)—O(2)	122.8	124.1	123.1	124.4	122.8	123.3	121.1
N(3)—C(2)—O(2)	122.2	121.2	121.9	118.2	119.3	119.5	118.1
N(3)—C(4)—O(4)	119.1	119.5	120.2	120.6	119.8	121.5	120.2
C(5)—C(4)—O(4)	124.6	125.0	125.0	125.2	126.0	126.4	124.0

References: *A* Takusagawa & Shimada (1973). *B* Solbakk (1971). *C* Mutikainen & Lumme (1980). *D* Sabat, Zglinska & Jerowska-Trzebiatowska (1980). *E*, *F* Arrizabalaga, Castan & Daham (1983).

metal complexation has no effect on the pyrimidine bond lengths. On the other hand, complexation and/or protonation do cause changes in the bond angles of the pyrimidine ring and the bond lengths of the carboxyl group. These changes are in agreement with two empirical rules which have been established on the bases of previous structural work (Terzis & Mentzafos, 1983, and references therein): (1) The magnitude of the valence angle of N atoms in six-membered heterocyclic rings depends on the exocyclic attachment to the N atoms. The angle is considerably larger when the N is protonated than when it is not. (2) The proton, being a better electron sink than a coordinated metal, is more effective than the metal in inducing structural changes. In Table 2 we see that the angle C(2)—N(3)—C(4) is 'large', 125.7–127.3°, in all structures where N(3) is protonated, but 'small', 122.6° in structure *F* where the proton has been substituted with Cu^{II}. Similarly, the angle C(6)—N(1)—C(2) is 'large', 122.6–122.9°, in structures *A* and *B* and the present work where N(1) is protonated, but 'small', 117.9–118.7°, in the structures *C*, *D*, *E* and *F* where the proton is substituted by Ni^{II} or Cu^{II}. Looking at the carboxylic group we have two extreme situations in structures *A* and *B*. In *A* the carboxyl group is protonated at O(1) and we have a long (single) C(7)—O(1) bond of 1.306 Å and a short (double) C(7)—O(3) of 1.197 Å. In *B* there is no proton and because of resonance the two bonds are practically equal at 1.250 and 1.247 Å respectively. In all other structures the proton is substituted by a metal and the bond length is intermediate between those in *A* and *B*.

From Table 3 we see some systematic differences in the exocyclic angles of the two carbonyls. For the carbonyl C(4)—O(4) the angle C(5)—C(4)—O(4) is in all structures larger than N(3)—C(4)—O(4) by about 5°. This is consistent with the predictions of VSEPR theory (Gillespie, 1970) since N(3) is more electronegative than C(5). For the carbonyl C(2)—O(2) no such systematic difference is observed since the carbonyl is bonded to two N atoms. And in the present structure where both nitrogens are protonated

Table 3. Bond lengths (Å) and angles (°) involving hydrogen bonds

Symmetry position of atom <i>Y</i> : (a) <i>x</i> , <i>y</i> , <i>z</i> ; (b) $-x$, $-y$, $-z$; (c) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$.				
<i>X</i> —H... <i>Y</i>	<i>X</i> —H	H... <i>Y</i>	<i>X</i> ... <i>Y</i>	<i>X</i> —H... <i>Y</i>
N(1)—HN(1)...O(2) (c)	1.000	2.004	2.951	157.1
N(3)—HN(3)...O(4) (c)	0.999	1.913	2.864	157.9
<i>W</i> (1)—H(1 <i>A</i>)...O(2) (c)	0.716	1.983	2.697	174.3
<i>W</i> (1)—H(1 <i>B</i>)...O(4) (a)	0.970	1.788	2.724	161.0
<i>W</i> (2)—H(2 <i>B</i>)... <i>W</i> (3) (b)	1.015	1.714	2.688	159.3
<i>W</i> (3)—H(3 <i>B</i>)...O(3) (a)	0.834	2.226	2.914	140.1
E.s.d.'s	0.1	0.1	0.006	2.0

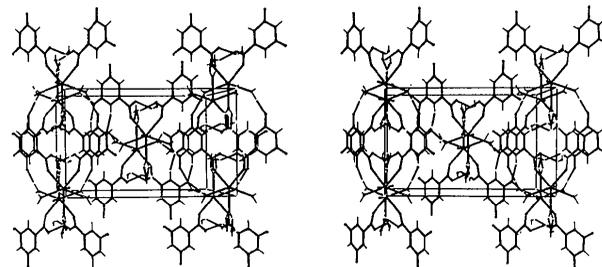


Fig. 2. ORTEP view (Johnson, 1976) of the molecular packing with the hydrogen bonds indicated by bold lines.

(therefore equivalent) the two angles N(1)—C(2)—O(2) and N(3)—C(2)—O(2) are equal. In structures *A* and *B* where again both nitrogens are protonated the angle difference is 'small', 2.9 and 2.2° respectively. In the other structure where N(1) is coordinated to a metal the situation approaches that of the C(4)—O(4) carbonyl since, as we mentioned before, a complexed metal is not as good an electron sink as the proton.

In all structures known to date where the orotate is complexed to a metal it acts either as a bidentate ligand through O(1) and N(1) (Mutikainen & Lumme, 1980; Sabat, Zglinska & Jerowska-Trzebiatowska, 1980; Arrizabalaga, Castan & Daham, 1983) or as a tridentate ligand through O(1), N(1), N(3) (Arrizabalaga, Castan & Daham, 1983). The present is the only structure where it is monodentate, through O(1), and it is perhaps a testimony to the 'hardness' of the uranyl ion (Pearson, 1963).

The hydrogen bonding is extensive. There are many potential donor and acceptor sites, nearly all of them being used. The hydrogen bonds are listed in Table 3 and shown in the ORTEP (Johnson, 1976) stereoview of the molecular packing in Fig. 2.

References

- ARRIZABALAGA, P., CASTAN, P. & DAHAM, F. (1983). *Inorg. Chem.* **22**, 2245–2252.
 BENSUADE, O., AUBARD, J., DREYFUS, M., DODIN, C. & DUBOIS, J. E. (1978). *J. Am. Chem. Soc.* **100**, 2823–2827.
 BURNS, J. H. (1983). *Inorg. Chem.* **22**, 1174–1178.
 GENCHEV, D. D. (1970). *Dokl. Bolg. Akad. Nauk.* **23**, 435–439.
 GILLESPIE, R. J. (1970). *J. Chem. Educ.* **47**, 18–23.

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LEBERMAN, J., KORNBURG, A. & SIMMS, E. S. (1955). *J. Biol. Chem.* **215**, 403–415.
- LEHNINGER, A. (1970). *Biochemistry*, p. 661. New York: Worth Publishers Inc.
- LINTREDT, R. L., HEEG, M. J., AHMAD, N. & GLICK, M. D. (1982). *Inorg. Chem.* **21**, 2350–2356.
- MACKINNON, P. J. & TAYLOR, J. C. (1983). *Polyhedron*, **2**, 217–224.
- MUTIKAINEN, I. & LUMME, P. (1980). *Acta Cryst.* **B36**, 2233–2237.
- PEARSON, R. C. (1963). *J. Am. Chem. Soc.* **85**, 3533–3539.
- PSODA, A., KAZIMIERCZAK, Z. & SHUGAR, D. (1974). *J. Am. Chem. Soc.* **96**, 6832–6839.
- SABAT, M., ZGLINSKA, D. & JEROWSKA-TRZEBIATOWSKA, B. (1980). *Acta Cryst.* **B36**, 1187–1188.
- SANDER, E. G., WRIGHT, L. D. & MCCORMICK, D. B. (1965). *J. Biol. Chem.* **240**, 3628–3630.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- Small Medical Encyclopedia* (1967). Vol. 6, p. 970. Moscow: IZD.
- SOLBAKK, J. (1971). *Acta Chem. Scand.* **25**, 3006–3018.
- Syntax (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California, USA
- TAKUSAGAWA, F. & SHIMADA, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2011–2019.
- TERZIS, A. & MENTZAFOS, D. (1983). *Inorg. Chem.* **22**, 1140–1143.
- TOIVONEN, J. & LAITINEN, R. (1984). *Acta Cryst.* **C40**, 7–9.
- VICTOR, J., GREENBERG, L. B. & SLOAN, D. L. (1979). *J. Biol. Chem.* **254**, 2647–2655.

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Structure of Di- μ -carbonyl-bis[η^5 -methylcyclopentadienylcobalt(II)](Co–Co)

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Abstract. $[\text{Co}_2(\text{C}_6\text{H}_7)_2(\text{CO})_2]$, $M_r = 332.13$, $C2/m$, $a = 7.989$ (4), $b = 8.573$ (4), $c = 9.934$ (4) Å, $\beta = 114.76$ (1)°, $U = 617.8$ (2) Å³, $Z = 2$, $D_x = 1.79$ Mg m⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.67$ mm⁻¹, $F(000) = 336$, $T \sim 220$ K, final $R = 0.037$ and $wR = 0.045$ for 1307 unique reflections with $F \geq 3\sigma(F)$. The structure is isomorphous with the analogous Ni complex, the $2/m$ symmetry reducing the number of unique atoms to 11. The carbonyl ligands asymmetrically bridge the two Co atoms, extending away from the neighbouring methyl substituent on the cyclopentadienyl rings which lie across the crystallographic mirror plane.

Introduction. The deformation electron density of a series of dinuclear organometallic structures is currently being studied (Gregson & Howard, 1984; Howard, Louca & McIntyre, 1987) in order to investigate the nature of metal–metal bonds and the role played by bridging carbonyl ligands. The Ni analogue of this Co complex has revealed no accumulation of electron density between the two metal atoms, the linkage between which has a formal bond order of one, based on simple electron counting rules. As a useful comparison we have chosen to investigate the title complex, first reported by Hersh, Hollander & Bergman (1983), which formally has a bond order of two. This preliminary experiment is intended to confirm that the

complex satisfies certain criteria which would enable us to carry out an accurate deformation electron density study.

Experimental. $[\text{Co}_2(\text{CO})_2(\text{MeCp})_2]$ prepared by a method similar to that proposed by Hersh *et al.* (1983); brown crystals obtained by recrystallization from toluene. Rectangular plane crystal, $0.1 \times 0.25 \times 0.32$ mm, mounted under N_2 in a Lindemann-glass capillary. Intensity data collected using a Nicolet $P3m$ diffractometer with graphite monochromator and N_2 gas-flow cooling device. Cell parameters determined by least-squares refinement using 15 accurately centred reflections in the range $29 \leq \theta \leq 31^\circ$. 1415 unique reflections were recorded using ω - 2θ scan techniques, $2\theta_{\text{max}} = 70^\circ$, 1307 [$F \geq 3\sigma(F)$] used in analysis. h 0– ± 12 , k 0–13, l 0–16. Check reflections showed no systematic variation, Lorentz and polarization factors applied, no absorption correction. Structure solved by heavy-atom method, all atoms located by successive electron-density difference syntheses. Blocked-cascade least-squares refinement using *SHELXTL* (Sheldrick, 1981) on 64 parameters. Isotropic thermal parameters for H, minimized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F) + 0.0004F^2]^{-1}$, $\sigma(F)$ from counting statistics, $R = 0.037$, $wR = 0.043$, $S = 1.7$. Max. height in final difference Fourier synthesis 1.5 e \AA^{-3} . Max. shift/e.s.d. = 0.003. Atomic scattering factors including corrections for