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Acetylacetonebis(acetylacetonato)dioxouranium(VI)

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Abstract. $[U(C_5H_7O_2)_2(C_5H_8O_2)O_2]$, orthorhombic, $P2_1cn$, $a = 13·571$ (4), $b = 7·925$ (2), $c = 18·185$ (5) Å, $M_r = 568·4$, $Z = 4$, $D_x = 1·933$ Mg m^{-3}, $R = 0·041$, 2037 observed reflections. The coordination polyhedron around U is a pentagonal bipyramid, with the O atoms of the UO_2 group in the apical positions. The UO_2 group is nearly linear and perpendicular to the equatorial pentagonal plane. The acetylacetone molecule coordinates to U through only one O, exhibiting a monodentate dangling complexation.

Introduction. As part of a study of actinide chelate complexes with β-diketones, the synthesis and structure determination of the title compound, $[U(acac)_2(Hacac)O_2]$ (Hacac = acetylacetone) has been undertaken.

Earlier studies of uranyl complexes with chelating agents like $HCOO^-$, $acac^-$, ac^- and $C_2O_4^{2-}$ have shown the coordination of U to be bipyramidal with a linear UO_2 group and five (Frasson, Bombieri & Panattoni, 1966; Howatson & Grev, 1975; Mentzen, Puaux & Sautereau, 1978) or occasionally six (Alcock, 1973; Jayadevan, Singh Mudher & Chackraburtty, 1975) O atoms arranged equatorially. The present investigation was undertaken to find out how the title complex conforms to this pattern.

The complex was precipitated by mixing aqueous solutions of $U(NO_3)_2O_2$ and Hacac. The precipitate was recrystallized from Hacac, the final product being small compact light-orange crystals.

The diffraction data were collected on a Syntex $P2_1$ computer-controlled four-circle diffractometer. The parameters of the cell were determined by least squares from the coordinates of 15 reflections. The intensities of 3261 independent reflections were measured up to $2\theta = 60°$ with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). A standard reflection, measured after every 50 reflections, gave no indication of crystal decay. The intensities were corrected for Lorentz and polarization effects and for absorption (Coppens, Leiserowitz & Rabinovich, 1965), the absorption coefficient for Mo $K\alpha$ being 10·18 mm^{-1} (Roof, 1959). 2037 reflections had $I > 3\sigma(I)$. The position of U was determined from a Patterson synthesis, and the remaining 23 non-hydrogen atoms were located from a subsequent Fourier synthesis. The structure was refined by block-diagonal least squares (Lindgren, 1977) with anisotropic thermal parameters for the atoms of the UO_2 group and an overall scale factor. Scattering factors used were those of Doyle & Turner (1968) for C and O, and for U those of Cromer & Waber (1965). Atomic positions are given in Table 1.* The structure factors were weighted according to $w = (a + |F_o| + c|F_o|^2)^{-1}$ (Cruickshank, 1965) with $a = 20·0$ and $c = 0·008$.

Table 1. *Fractional atomic coordinates* ($\times 10^5$)

	x	*y*	*z*
U	0	−4414 (5)	83927 (2)
O(1)	6702 (115)	5889 (151)	91146 (71)
O(2)	−5801 (90)	−14629 (135)	76570 (59)
O(3)	−5715 (81)	21416 (136)	78873 (58)
O(4)	12039 (101)	6025 (149)	75146 (72)
O(5)	13664 (107)	−24447 (192)	83265 (69)
O(6)	−3740 (98)	−28127 (160)	91257 (69)
O(7)	−14737 (94)	3004 (138)	89657 (65)
O(8)	−28259 (121)	22726 (210)	82960 (77)
C(1)	−10791 (156)	45675 (230)	72342 (111)
C(2)	−3464 (112)	31217 (199)	73820 (87)
C(3)	4851 (124)	29393 (207)	69768 (94)
C(4)	12265 (133)	17728 (217)	70365 (96)
C(5)	21010 (164)	17680 (267)	65579 (102)
C(6)	25024 (229)	−46782 (302)	84001 (131)
C(7)	15215 (147)	−39515 (255)	85838 (103)
C(8)	8541 (166)	−48393 (249)	89768 (109)
C(9)	−1253 (102)	−42653 (139)	92176 (63)
C(10)	−7559 (169)	−54681 (257)	96321 (122)
C(11)	−16695 (251)	−5421 (336)	101906 (174)
C(12)	−20346 (139)	4279 (217)	95240 (105)
C(13)	−29047 (132)	12623 (222)	95272 (91)
C(14)	−33340 (128)	21097 (211)	89334 (91)
C(15)	−43580 (150)	28474 (230)	89712 (99)

Discussion. A stereoscopic view (*ORTEP*, Johnson, 1965) of the molecule is shown in Fig. 1. Bond

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34558 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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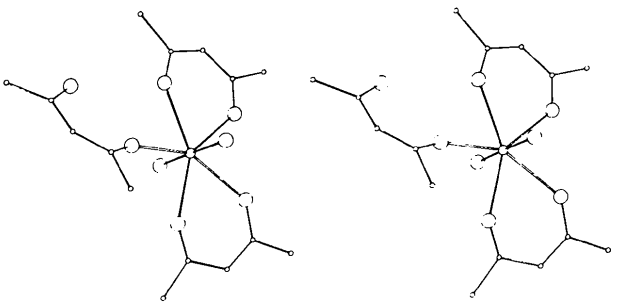

Fig. 1. A stereoscopic view of the molecule.

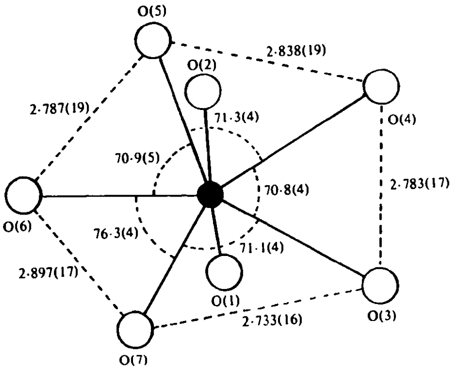

Fig. 2. The coordination in [U(acac)$_2$(Hacac)O$_2$]. Some distances (Å) and angles (°) are noted.

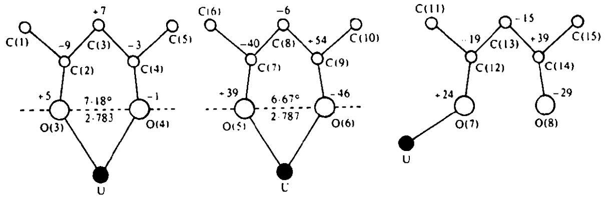

Fig. 3. The numbering of the atoms of the ligands. The deviations of the least-squares planes (Å × 10^3), the ligand bite distances (Å) and the magnitude of the fold over the O···O line are noted.

Table 2. *Bond distances* (Å) *and angles* (°)

U–O(1)	1·793 (13)	C(1)–C(2)	1·540 (25)
U–O(2)	1·750 (11)	C(2)–C(3)	1·355 (23)
U–O(3)	2·373 (11)	C(3)–C(4)	1·370 (24)
U–O(4)	2·429 (13)	C(4)–C(5)	1·471 (28)
U–O(5)	2·443 (15)	C(6)–C(7)	1·488 (36)
U–O(6)	2·358 (13)	C(7)–C(8)	1·351 (29)
U–O(7)	2·329 (12)	C(8)–C(9)	1·471 (26)
O(3)–C(2)	1·241 (19)	C(9)–C(10)	1·486 (25)
O(4)–C(4)	1·271 (21)	C(11)–C(12)	1·518 (36)
O(5)–C(7)	1·299 (25)	C(12)–C(13)	1·353 (26)
O(6)–C(9)	1·211 (17)	C(13)–C(14)	1·398 (24)
O(7)–C(12)	1·272 (23)	C(14)–C(15)	1·508 (26)
O(8)–C(14)	1·354 (22)	O(7)–O(8)	2·700 (20)
O(1)–U–O(2)	176·2 (6)	O(5)–O(6)–O(7)	107·1 (6)
O(1)–U–O(3)	93·2 (5)	O(6)–O(7)–O(3)	107·2 (5)
O(1)–U–O(4)	89·2 (5)	O(7)–O(3)–O(4)	109·2 (5)
O(1)–U–O(5)	87·0 (6)	O(3)–C(2)–C(3)	122·7 (15)
O(1)–U–O(6)	93·3 (5)	C(2)–C(3)–C(4)	129·8 (16)
O(1)–U–O(7)	89·6 (6)	C(3)–C(4)–O(4)	121·9 (16)
O(2)–U–O(3)	87·5 (4)	O(5)–C(7)–C(8)	124·1 (19)
O(2)–U–O(4)	87·6 (5)	C(7)–C(8)–C(9)	127·0 (17)
O(2)–U–O(5)	90·2 (5)	C(8)–C(9)–O(6)	120·3 (14)
O(2)–U–O(6)	88·1 (5)	O(7)–C(12)–C(13)	124·3 (17)
O(2)–U–O(7)	94·2 (5)	C(12)–C(13)–C(14)	126·5 (16)
O(3)–O(4)–O(5)	108·3 (6)	C(13)–C(14)–O(8)	119·6 (16)
O(4)–O(5)–O(6)	107·1 (6)	U–O(7)–O(8)	121·8 (6)

distances and angles are given in Table 2. The UO$_2$ group is nearly linear, with a mean U–O distance of 1·77 Å, and perpendicular [90·6 (5)°] to the equatorial plane. The two chelated acac ligands have an average bite distance of 2·785 Å. Of the secondary U–O distances, those to O(3) and O(6), adjacent to O(7) of the monodentate Hacac, are slightly shorter (mean 2·365 Å) than those to O(4) and O(5) (mean 2·436 Å). The coordination polyhedron is depicted in Fig. 2. The geometry of the three ligands and the numbering of the atoms are shown in Fig. 3. The ligand rings are planar, having a five-atom resonance structure, with C–CH and C–O lengths intermediate between single and double bonds, as in other related structures (Allard, 1972; Lenner, 1978; Soling, 1975, 1976). The ligand planes are folded from the central atom over the O···O line, with a mean fold angle of 6·9 (7)°. The monodentate Hacac molecule has a similar geometry to the acac ligands, with the exception of a long (1·35 Å) O(8)–C(14) bond, due to O(8) also bonding to a H atom. The dangling O(8) is 0·93 (3) Å out of the plane of the five O atoms coordinating equatorially to U, and has a distance to U of 4·40 (2) Å. The least-squares plane of the Hacac ligand is at 32·5 (6)° to the equatorial coordination plane.

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Structure of *cis*-Bis(1-methylimidazole)bis(*o*-nitrophenolato)cobalt(II)

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Abstract. $C_{20}H_{20}CoN_6O_6$, $[Co(C_4H_6N_2)_2(C_6H_4NO_3)_2]$, monoclinic, $P2_1/c$, $a = 13{\cdot}745\,(5)$, $b = 8{\cdot}010\,(2)$, $c = 21{\cdot}841\,(7)$ Å, $\beta = 114{\cdot}18\,(1)°$, $Z = 4$, $D_m = 1{\cdot}51\,(1)$, $D_c = 1{\cdot}51$ Mg m^{-3}. Least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) led to a final, unweighted R value (on F) of 0·040. The Co^{II} ions are octahedrally coordinated to two 1-methylimidazole molecules and two chelated *o*-nitrophenolate ions. The Co—O(phenolic oxygen) bond lengths are 1·972 (2) and 1·978 (2) Å and the Co—O(nitro group) bond lengths are 2·248 (3) and 2·219 (4) Å. The O—Co—O bond angles are 78·4 (1) and 81·3 (1)°. The structure demonstrates the feasibility of metal-ion complexation by nitrated tyrosine residues.

Introduction. In recent years there has been increasing interest in the modification of specific residues in enzymes and proteins so that they will bind lanthanide-ion nuclear-magnetic-resonance shift reagents. These shift reagents can serve as probes of the structures of the proteins in solution. Of particular promise as a modification technique has been the nitration of tyrosine residues. The *o*-nitrophenol portion of a nitrated tyrosine residue is isoelectronic with acetylacetone and it has been suggested that the chelation of metal ions by this group should be facile. Riordan & Sokolovsky (1971) and Riordan & Vallee (1972) have shown that tyrosine residues of a large variety of proteins can be specifically nitrated at the 3-position and thus it appears that chelated lanthanide-ion shift reagents could be widely used in the study of protein structure. Indeed, Marinetti, Snyder & Sykes (1976, 1977) have recently applied this approach to the study of the structure of bovine pancreatic trypsin inhibitor.

Although the use of nitrated tyrosine residues seems plausible there are a number of factors which are troubling. Firstly, it is known that the nitro group is an exceedingly weak Lewis base. Secondly, examination of space-filling models of *o*-nitrophenol suggests that coordination to metal ions should be difficult because the ligand has a relatively small bite. Thirdly, the stability constants of complexes of *o*-nitrophenol or *N*-acetyl-L-3-nitrotyrosine ethyl ester with lanthanide elements have been found to be small and of the order of 10^2 *M* (Postmus, Magnusson & Craig, 1966; Marinetti, Snyder & Sykes, 1975). Because these factors suggest that the *o*-nitrophenolate group is a poor chelating ligand we decided to determine the structure of a metal complex containing this group in order to establish the nature of the bonding. The structure of *cis*-bis(1-methylimidazole)bis(*o*-nitrophenolato)cobalt(II) reported here unambiguously demonstrates the chelation of metal ions by the nitrophenolate group but also suggests that this group should be a poor ligand toward large metal ions such as the lanthanides.

The complex was prepared by stirring 1·5 g of diaquabis(*o*-nitrophenolato)cobalt(II) with 0·8 ml of 1-methylimidazole in 0·1 litre of CH_2Cl_2 for several hours and then filtering the solution to remove undissolved material. Dark red prisms of the complex were obtained by slow evaporation of the CH_2Cl_2 solution in a refrigerator. Intensity data were collected on a crystal of dimensions 0·60 × 0·36 × 0·30 mm mounted in a thin-walled glass capillary with the crystal's longest dimension (the crystallographic **a** direction) parallel to the capillary walls. The 0·30 mm dimension was perpendicular to the well developed (010) faces; other bounding planes belonged to the {100} and {001}

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