triangle is reflected in variations of the other bonds and angles associated with the molybdenum atoms as shown in Table 2. The longer Mo—Co bond is that associated with the molybdenum whose cyclopentadienyl ring is on the upper, or capped, face of the metal triangle, *i.e.* Mo(2). Normally this lengthening would be assumed to be a mechanism to reduce the steric interactions between the cyclopentadienyl group and the other atoms on the upper face. However, the closest contact on this upper face is between the alkylidyne carbon and C(2) and Mo(1), at 2·36 Å, yet this causes no marked distortions around Mo(1). The Mo—C_{ap} [Mo(1)—C_{ap} 2·069 (3) Å, Mo(2)—C_{ap} 2·087 (3) Å] distances are slightly shorter than in (2), and are also slightly shorter than in the related compound $(\mu_3\text{-CPh})Co_2Mo(CO)_8(\eta^5\text{-}C_5H_5)$, (3) (Beurich & Vahrenkamp, 1982), but not significantly so. These other two structures have Mo—C_{ap} distances of 2·11 (1) and 2·10 (1) Å respectively. The Co—C_{ap} distances are essentially identical in all three structures [1·933 (3) Å in (1), 1·94 (1) Å in (2) and 1·93 (1) Å in (3)].

The carbonyl groups on the cobalt atom are all as expected with no unusual variations in bond lengths or angles. The carbonyl groups on the molybdenum atoms, on the other hand, show deviations from the expected norm. The main deviation of note for the carbonyl groups is that those attached to Mo(2) show marked deviations from linearity. The Co(1) and Mo(1) carbonyls all have angles close to the expected 180° [range 175·8 (3)–178·6 (3)°], whereas those on Mo(2) show angles of 168·6 (3)° [C(3)—O(3)] and 171·3 (3)° [C(4)—O(4)]. The closest contact for carbonyl C(3)—O(3) is H(Cp11) at 2·6 Å, while the closest contact for C(4)—O(4) is C(3) at 2·63 Å. These distances are similar to those found for all the other carbonyl groups except for the close interaction of the alkylidyne carbon with C(2) (2·36 Å) and so presumably the distortion is due to subtle interactions, both intra- and intermolecular.

A further point of note is the tilting of the cyclopentadienyl ligands with respect to the metal. The metal—$(\eta^5\text{-}C_5H_5)$ distances range from 2·367 to 2·299 Å for ring 2 [on Mo(2)] and from 2·378 to 2·306 Å for ring 1 [on Mo(1)]. This tilting appears to be a common feature of metal–cyclopentadienyl interactions and this range of distances is as expected.

We thank Mr D. Craig for the collection of the data for this structure.

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Acta Cryst. (1991). C**47**, 2345–2348

Structure of (*N,N'*-Bissalicylidene-1,5-diamino-3-azapentane)dioxouranium(VI) Ethanol Solvate

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(*Received* 10 *December* 1990; *accepted* 11 *June* 1991)

Abstract. [*N,N'*-(3-Aza-1,5-pentanediyl)bis(salicylideneiminato)]dioxouranium(VI) ethanol solvate, $C_{18}H_{19}N_3O_4U.C_2H_6O$, $M_r = 625{\cdot}466$, orthorhombic, $Pca2_1$, $a = 9{\cdot}912\ (10)$, $b = 11{\cdot}438\ (19)$, $c = 19{\cdot}599\ (38)$ Å, $V = 2222{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}869$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 69{\cdot}29$ cm^{-1}, $F(000) = 1191{\cdot}7$, room temperature, final $R = 0{\cdot}069$ for 1654 unique observed reflexions. The ethanol molecules are not coordinated to the uranium but occupy channels running through the lattice. They cause distortion of the molecules of the complex in which the angles between the planes of the benzene rings and the equatorial coordination plane of the uranium are decreased.

0108-2701/91/112345-04$03.00

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$)

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

	x	y	z	U_{eq}
U(1)	4516 (1)	4262 (1)	5000	49 (1)
O(1)	4260 (7)	3910 (13)	3571 (11)	61 (5)
O(2)	4813 (8)	4719 (14)	6412 (12)	73 (6)
O(3)	4419 (7)	2062 (12)	5513 (12)	91 (7)
O(4)	3421 (7)	4486 (14)	5527 (10)	85 (6)
N(1)	5698 (7)	3080 (15)	4833 (36)	99 (12)
N(2)	5398 (8)	5716 (17)	4026 (11)	72 (7)
N(3)	4075 (7)	6749 (15)	4687 (10)	58 (7)
C(1)	4814 (10)	1115 (15)	6052 (17)	56 (7)
C(2)	4469 (14)	118 (21)	6705 (18)	88 (10)
C(3)	4842 (13)	−859 (25)	7247 (17)	101 (12)
C(4)	5535 (14)	−932 (21)	7103 (17)	119 (12)
C(5)	5897 (13)	−20 (22)	6434 (17)	83 (10)
C(6)	5531 (11)	1057 (16)	5878 (16)	66 (8)
C(7)	5916 (9)	1985 (15)	5141 (36)	81 (8)
C(8)	6224 (11)	3872 (21)	4055 (20)	91 (11)
C(9)	6126 (11)	5391 (19)	4253 (20)	84 (10)
C(10)	5292 (12)	7228 (19)	4173 (18)	81 (10)
C(11)	4549 (11)	7591 (21)	3909 (16)	69 (8)
C(12)	3598 (9)	7323 (17)	5145 (29)	78 (8)
C(13)	3110 (10)	6781 (19)	5967 (16)	58 (8)
C(14)	2701 (10)	7642 (21)	6556 (16)	66 (8)
C(15)	2185 (9)	7219 (19)	7309 (18)	75 (9)
C(16)	2079 (10)	5914 (24)	7411 (19)	85 (9)
C(17)	2492 (11)	4939 (24)	6844 (16)	77 (9)
C(18)	3043 (10)	5334 (17)	6070 (15)	55 (8)
O(5)	3069 (12)	928 (23)	5026 (51)	238 (16)
C(19)	2653 (17)	1640 (31)	4345 (46)	260 (37)
C(20)	2305 (20)	902 (26)	3686 (34)	248 (26)

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

U(1)—O(1)	1·749 (13)	U(1)—O(2)	1·780 (14)
U(1)—O(3)	2·267 (12)	U(1)—O(4)	2·243 (13)
U(1)—N(1)	2·609 (14)	U(1)—N(2)	2·515 (16)
U(1)—N(3)	2·636 (15)	O(3)—C(1)	1·365 (22)
O(4)—C(18)	1·282 (22)	N(1)—C(7)	1·218 (26)
N(1)—C(8)	1·574 (34)	N(2)—C(9)	1·488 (26)
N(2)—C(10)	1·522 (25)	N(3)—C(11)	1·536 (25)
N(3)—C(12)	1·216 (25)	C(1)—C(2)	1·412 (29)
C(1)—C(6)	1·423 (30)	C(2)—C(3)	1·364 (34)
C(3)—C(4)	1·374 (37)	C(4)—C(5)	1·382 (31)
C(5)—C(6)	1·436 (29)	C(6)—C(7)	1·460 (33)
C(8)—C(9)	1·534 (28)	C(10)—C(11)	1·533 (32)
C(12)—C(13)	1·447 (31)	C(13)—C(14)	1·353 (27)
C(13)—C(18)	1·445 (25)	C(14)—C(15)	1·396 (27)
C(15)—C(16)	1·314 (30)	C(16)—C(17)	1·420 (31)
C(17)—C(18)	1·453 (28)	O(5)—C(19)	1·332 (56)
C(19)—C(20)	1·254 (53)		

O(1)—U(1)—O(2)	175·8 (6)	O(1)—U(1)—O(3)	91·6 (5)
O(2)—U(1)—O(3)	92·1 (6)	O(1)—U(1)—O(4)	89·8 (5)
O(2)—U(1)—O(4)	92·5 (6)	O(3)—U(1)—O(4)	86·8 (5)
O(1)—U(1)—N(1)	95·6 (10)	O(2)—U(1)—N(1)	83·6 (10)
O(3)—U(1)—N(1)	70·2 (5)	O(4)—U(1)—N(1)	156·5 (6)
O(1)—U(1)—N(2)	84·1 (5)	O(2)—U(1)—N(2)	91·8 (6)
O(3)—U(1)—N(2)	136·4 (5)	O(4)—U(1)—N(2)	136·3 (5)
N(1)—U(1)—N(2)	67·1 (6)	O(1)—U(1)—N(3)	88·0 (5)
O(2)—U(1)—N(3)	89·7 (5)	O(3)—U(1)—N(3)	155·1 (5)
O(4)—U(1)—N(3)	68·3 (5)	N(1)—U(1)—N(3)	134·6 (5)
N(2)—U(1)—N(3)	68·3 (5)	U(1)—O(3)—C(1)	137·0 (11)
U(1)—O(4)—C(18)	138·6 (12)	U(1)—N(1)—C(7)	133·7 (18)
U(1)—N(1)—C(8)	113·7 (13)	C(7)—N(1)—C(8)	112·3 (19)
U(1)—N(2)—C(9)	117·4 (11)	U(1)—N(2)—C(10)	114·8 (11)
C(9)—N(2)—C(10)	109·0 (15)	U(1)—N(3)—C(11)	112·8 (11)
U(1)—N(3)—C(12)	129·2 (14)	C(11)—N(3)—C(12)	117·6 (17)
O(3)—C(1)—C(2)	116·6 (18)	O(3)—C(1)—C(6)	121·7 (15)
C(2)—C(1)—C(6)	121·4 (17)	C(1)—C(2)—C(3)	118·7 (24)
C(2)—C(3)—C(4)	121·0 (22)	C(3)—C(4)—C(5)	122·8 (21)
C(4)—C(5)—C(6)	118·4 (22)	C(1)—C(6)—C(5)	117·5 (17)
C(1)—C(6)—C(7)	124·7 (16)	C(5)—C(6)—C(7)	117·8 (19)
N(1)—C(7)—C(6)	123·1 (21)	N(1)—C(8)—C(9)	108·9 (17)
N(2)—C(9)—C(8)	107·9 (16)	N(2)—C(10)—C(11)	109·9 (16)
N(3)—C(11)—C(10)	109·6 (15)	N(3)—C(12)—C(13)	128·1 (18)
C(12)—C(13)—C(14)	118·9 (17)	C(12)—C(13)—C(18)	118·8 (16)
C(14)—C(13)—C(18)	122·1 (17)	C(13)—C(14)—C(15)	123·4 (19)
C(14)—C(15)—C(16)	117·7 (18)	C(15)—C(16)—C(17)	122·6 (19)
C(16)—C(17)—C(18)	121·4 (20)	O(4)—C(18)—C(13)	123·9 (17)
O(4)—C(18)—C(17)	123·4 (17)	C(13)—C(18)—C(17)	112·6 (17)
O(5)—C(19)—C(20)	112·2 (30)		

Introduction. The molecules of the unsolvated form of the title compound (UO_2saldien) have a 'butterfly' shape with the planes of the two benzene rings inclined at about 30° to the equatorial coordination plane of the uranium (Akhtar & Smith, 1973; Benetollo, Bombieri & Smith, 1979). UO_2saldien has been observed (Akhtar, McKenzie, Paine & Smith, 1969) to form a series of solvates with small organic molecules, including ethanol, acetonitrile, benzene, and chloroform. The resulting solvates range in colour from pale yellow to red. We thought to determine the structures of a number of these solvates in order to determine the extent to which the UO_2saldien molecule was distorted by the solvent molecules and to see if there was any correlation between such distortion and the colour of the crystals. So far we have been able to obtain suitable crystals of only the ethanol solvate and we now report its structure.

Experimental. UO_2saldien.EtOH was obtained as orange-red crystals by following the procedure described by Augustin, Kerrinnes & Langenbeck (1964). The composition was confirmed by microanalysis. (Found: C 38·35, H 3·89, N 6·78, calculated for $C_{20}H_{25}N_3O_5U$: C 38·41, H 4·03, N 6·72.)

X-ray reflexion data from a small (0·30 × 0·25 × 0·15 mm) block-shaped crystal were collected on a Nicolet *R3m* four-circle automatic diffractometer operating in the ω-scan mode and using Mo $K\alpha$ radiation. Unit-cell parameters were determined by least squares from the setting angles of 21 well-centred and well-distributed reflexions in the range $4 < 2\theta < 21°$. An empirical absorption correction was applied from azimuthal scans on nine reflexions (294 measurements) and gave max. and min. transmission factors of 0·052 and 0·025 respectively. Reflexion data in the range $3·5 < 2\theta < 55°$ and having $0 \le h < 13$, $0 \le k < 15$, and $0 \le l < 26$ were collected. Two check reflexions were monitored every 100 reflexions and showed no evidence of decay. 2754 measurements were made of 2686 unique reflexions, of which 1654 were accepted as observed [$|F| > 3\sigma(F)$]. R_{int} was 0·0101. Structure solved by Patterson and difference Fourier methods and refined by cascade blocked-diagonal least squares [function minimized $\sum w(F_o - F_c)^2$] with weights $w = 1/[\sigma^2(F) + 0·00003F^2]$ to a final R of 0·0691 ($wR = 0·0415$). 261 refined parameters including a weighting parameter. About one third of the hydrogen atoms were found from a low-θ difference Fourier map. H atoms, except for the hydroxyl of the ethanol, which was not located, were inserted with calculated bond lengths and angles and constrained to ride each on its neighbouring heavy atom. The (isotropic) hydrogen thermal parameters were each fixed at 1·2 times U_{eq} for the adjacent heavy atom.

The shifts on the final cycle of refinement were all less than 0.034 of the corresponding e.s.d.'s: the final difference Fourier map showed max. and min. densities of 1·1 and $-1{\cdot}2$ e Å^{-3} and showed no peak which could be interpreted as an atom. Analysis of variance against sinθ and against $|F|$ showed no unusual features; neither did the normal probability plot. Atomic scattering factors, linear absorption coefficients, and f' and f'' values were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) except for the uranium values which were taken from Roof (1959) (μ) and Roof (1961) (f' and f''). The *SHELXTL* suite of crystallographic programs (Sheldrick, 1983) was used throughout on a Nova3 computer.

The atomic parameters are listed in Table 1* and principal bond lengths and angles are in Table 2. The structure is illustrated in Figs. 1, 2 and 3.

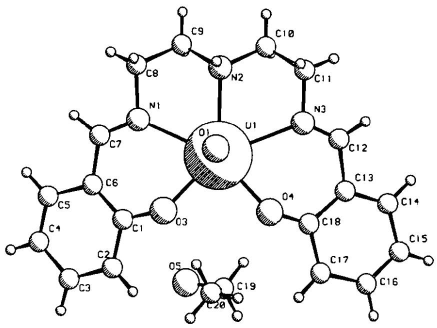

Fig. 1. One molecule of the complex, showing the atom-numbering scheme.

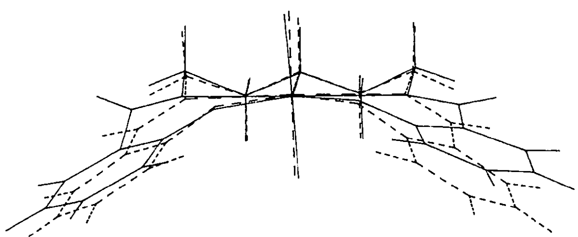

Fig. 2. The complex molecule from the solvated (solid lines, present work) and unsolvated (broken lines; Benetollo, Bombieri & Smith, 1979) crystals, superimposed to show the changes in dihedral angle. A least-squares fit on the uranium and its five equatorial ligand atoms has been used to effect the superposition of the two different conformations.

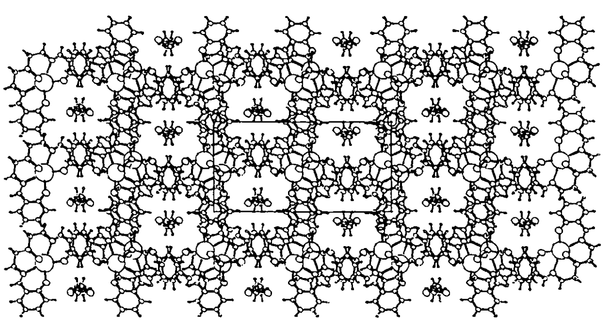

Fig. 3. The crystal structure viewed along [001] showing the channels occupied by ethanol molecules.

Discussion. The ethanol, although not bonded to it, causes a marked flattening of the complex molecule. The dihedral angles between the planes of the benzene rings and the equatorial coordination plane of the uranium differ both from one benzene to the other and from those found in the (unsolvated) parent compound. This is illustrated in Fig. 2. The dihedral angles concerned are 21·5 [C(1)—C(6)] and 27·5° [C(13)—C(18)] compared with 30·3° for both benzene planes of the (symmetrical) unsolvated molecule. The conjugation of the π-electron systems is therefore likely to be greater in the solvate and this may be correlated with its more intense and redder colour. Although the shape of the complex molecule is thus significantly modified, there are no exceptionally short intermolecular contacts and no obvious candidate for the hydrogen bond which the ethanol is expected to contribute was found.

A remarkable feature of the solvate crystal structure is the way in which the ethanol molecules pack (head-to-tail) into parallel [001] channels in the lattice. This channel structure is probably responsible for the ease with which the various solvates can be interconverted simply by contact with the appropriate solvent. Fig. 3 shows the structure viewed along the channels. This feature, which is not found in the unsolvated parent compound, was forecast from chemical considerations by McKenzie, Paine & Selvey (1974).

We thank the Science and Engineering Research Council and the Royal Society for grants towards the purchase of the diffractometer equipment.

* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54333 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1991). C**47**, 2348–2351

Absolute Structure of $(-)_{546}$-*cis*-β-Carbonato(triethylenetetramine)cobalt(III) Perchlorate Monohydrate

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(*Received* 25 *June* 1990; *accepted* 30 *April* 1991)

Abstract. $[Co(CO_3)(C_7H_{16}N_4)]ClO_4.H_2O$, $M_r = 382{\cdot}6$, monoclinic, $P2_1$, $a = 7{\cdot}418$ (1), $b = 12{\cdot}365$ (3), $c = 8{\cdot}690$ (2) Å, $\beta = 108{\cdot}8$ (3)°, $V = 755$ (2) Å^3, $Z = 2$, D_m(flotation) = 1·69 (1), $D_x = 1{\cdot}68$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}31$ mm^{-1}, $F(000) = 396$, $T = 298$ (1) K, final $R = 0{\cdot}031$ for 3322 observed reflections. The Co^{III} ion is in a distorted octahedral environment surrounded by the four N atoms of the tetradentate trien ligand coordinated in the *cis*-β configuration. The remaining two sites are occupied by the O atoms of the chelating carbonate group. The water molecule is hydrogen bonded to the complex *via* intermolecular links with the carbonate group and the perchlorate anion.

Introduction. There has been considerable interest in the *cis*-β complexes of the triethylenetetramine ligand, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ (trien), and its derivatives. For these compounds the stereochemistry about the 'planar' secondary N atom dictates the conformations of the rings (Buckingham, Marzilli & Sargeson, 1967). Kinetic and structural studies have shown that the more stable configuration at this N atom is one in which the attached proton is directed toward the apical ring (Buckingham, Marzilli & Sargeson, 1967; Sargeson & Searle, 1967; Freeman, Marzilli & Maxwell, 1970). In this conformation the two secondary N atoms adopt the same absolute configuration (Freeman, Marzilli & Maxwell, 1970; Dellaca, Janson, Robinson, Buckingham, Marzilli, Maxwell, Turnbull & Sargeson, 1972). Exceptions are known amongst the configurational isomers of *cis*-β_1- and *cis*-β_2-$[Co(trien)(gly)]^{2+}$ (Dellaca *et al.*, 1972; Buckingham, Dwyer, Gainsford, Janson, Marzilli, Robinson, Sargeson & Turnbull, 1975). For these complexes it has been suggested that the apical ring is sufficiently flexible to adopt either the δ or the λ conformation. The present work was undertaken to establish the stereochemistry and absolute configuration of $(-)_{546}$-*cis*-β-$[Co(trien)(CO_3)]ClO_4.H_2O$, and to obtain an unambiguous description of the configuration of the 'planar' and trigonal secondary N atoms. Hitherto, the absolute configuration of the title compound has been inferred from comparative optical rotatory dispersion and circular dichroism studies, in conjunction with the results of rearrangement reactions known to occur with retention of configuration (Sargeson & Searle, 1965).

Experimental. Single crystals grown from aqueous solution. Crystal system and space group determined from oscillation and Weissenberg photographs. Structure solved by the Patterson/Fourier method with intensity data visually estimated from Weissenberg photographs, 0 to 16 layers about [0 1 0] and 0 to 4 layers about [1 0 0] with Co $K\alpha$ and Cu $K\alpha$ radiation, respectively. The absolute configuration from Friedel pairs selected from the Cu $K\alpha$ set, later confirmed by diffractometer (Siemens) measurements. Because of difficulties with refinement of thermal parameters of the perchlorate anion, data remeasured using counter methods. A crystal of *ca* (100) 0·095, (010) 0·261, (001) 0·101, (−101) 0·095 mm was mounted in a general orientation on an Enraf–Nonius CAD-4F diffractometer; Mo $K\alpha$

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0108-2701/91/112348-04$03.00