1.* Selected bond distances and angles are listed in Table 2. As shown in the *ORTEP* plot, the two P atoms coordinate to the metal center with an average W—P distance of 2·510 (2) Å, which is similar to those reported in [$(OC)_4WPPh_2CH(CH_2CH_2PPh_2)$-$CH_2PPh_2$] (1), 2·523 (2) and 2·522 (2) Å (Churchill, Rheingold & Keiter, 1981), and [$(CO)_4W$-{Ph_2PNHN=$C(Ph)CH_2PPh_2$}] (2), 2·531 (2) and 2·497 (1) Å (Al-Jibori, Hall, Hutton & Shaw, 1984). The P—W—P bond angle, 80·06 (6)°, is smaller than those in (1) [87·58 (6)°] and (2) [87·8 (1)°]. This observation is apparently due to the coplanar, rigid ligand, which forces the decrease in the P—W—P bond angle. The four atoms P1, C31, C36 and P2 are coplanar; distances from the least-squares plane [P1, C31, C36, P2] are P1 −0·001 (3), C31 0·015 (9), C36 −0·014 (9), and P2 0·001 (3) Å. As expected, the W atom is located in the same plane; its deviation from the plane is 0·018 (7) Å.

The metal—C bond distances of carbonyls *trans* to phosphorus sites are in the range 1·953 (8)–1·999 (8) Å, whereas the other two metal bonds (*cis* to phosphorus) are 1·956 (8)–1·993 (8) Å, and they are all normal bond lengths. Generally, those metal–C bonds *trans* to phosphorus sites in metal carbonyl systems have shorter distances; however, in the present species there is no significant difference. All W—C—O bond angles range from 172·9 (8)–179·7 (6)°, deviating slightly from linearity.

The diastereotropic property of methyl groups on the isopropyl unit can be observed by ^1H NMR spectroscopy, which shows absorptions at 1·34 (*dd*, J = 6·8 Hz, $J_{P—H}$ = 16·6 Hz, 12 H) and 0·68 p.p.m. (*dd*, J = 7·0 Hz, $J_{P—H}$ = 15 Hz, 12 H). In this crystalline structure, all the methyl groups point toward the $W(CO)_4$ moiety, as shown in Fig 1, in order to minimize steric interaction.

Table 2. *Selected bond distances* (Å) *and bond angles* (°)

W1—P1	2·510 (2)	W2—P3	2·497 (2)
W1—P2	2·509 (2)	W2—P4	2·499 (2)
W1—C1	1·960 (8)	W2—C5	1·993 (8)
W1—C2	1·963 (7)	W2—C6	1·953 (8)
W1—C3	1·956 (8)	W2—C7	1·999 (8)
W1—C4	1·994 (7)	W2—C8	1·960 (8)
P1—C11	1·864 (7)	P3—C41	1·885 (7)
P1—C14	1·865 (8)	P3—C44	1·861 (7)
P1—C31	1·806 (6)	P3—C61	1·828 (7)
P2—C21	1·852 (7)	P4—C51	1·851 (9)
P2—C24	1·871 (7)	P4—C54	1·851 (8)
P2—C36	1·859 (6)	P4—C66	1·847 (7)
C1—O1	1·17 (1)	C5—O5	1·160 (9)
C2—O2	1·164 (9)	C6—O6	1·18 (1)
C3—O3	1·178 (9)	C7—O7	1·140 (9)
C4—O4	1·147 (9)	C8—O8	1·18 (1)
P1—W1—P2	80·06 (6)	P3—W2—P4	79·82 (7)
P1—W1—C4	173·2 (2)	P3—W2—C7	174·5 (3)
P2—W1—C2	174·1 (2)	P4—W2—C6	174·6 (2)
C1—W1—C3	169·8 (3)	C5—W2—C8	169·3 (3)
C11—P1—C14	101·8 (3)	C41—P3—C44	102·6 (3)
C21—P2—C24	101·8 (3)	C51—P4—C54	99·8 (4)
W1—C1—O1	174·7 (6)	W2—C5—O5	174·9 (6)
W1—C2—O2	179·7 (6)	W2—C6—O6	179·3 (7)
W1—C3—O3	173·1)6)	W2—C7—O7	178·8 (8)
W1—C4—O4	177·0 (8)	W2—C8—O8	172·9 (8)

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Structure of Tetrakis(1-ethoxy-4,4,4-trifluoro-1,3-butanedionato)uranium(IV)

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Abstract. [$U(C_6H_6F_3O_3)_4$], M_r = 970·46, monoclinic, $P2_1$, a = 10·034 (1), b = 15·181 (2), c = 11·842 (1) Å, β = 111·25 (2)°, V = 1681·2 (7) Å^3, Z = 2, D_x = 1·917 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 4·694 mm^{-1}, $F(000)$ = 928, T = 295 K, R = 0·027 for 2371 unique reflections with $I > 3\sigma(I)$. The U atom is eight coordinated by the O atoms of four independent β-diketone ligands, forming a dodecahedral

0108-2701/89/121881-04$03.00

Table 1. *Final positional coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B (Å^2)
U	0·85852 (2)	0·000	0·72379 (2)	3·54 (5)*
O(11)	0·7986 (6)	0·0242 (4)	0·5207 (5)	4·9 (1)
C(11)	0·718 (1)	0·0484 (9)	0·314 (1)	6·0 (2)
C(12)	0·6967 (7)	0·005 (1)	0·4210 (7)	4·5 (1)
C(13)	0·590 (1)	−0·0549 (8)	0·403 (1)	5·5 (2)
C(14)	0·5736 (9)	−0·0974 (7)	0·5046 (9)	4·5 (3)
C(15)	0·458 (1)	−0·2160 (9)	0·572 (1)	6·0 (3)
C(16)	0·562 (1)	−0·288 (1)	0·603 (1)	8·5 (4)
O(12)	0·6470 (7)	−0·0834 (5)	0·6156 (6)	4·9 (1)
O(13)	0·4736 (8)	−0·1595 (6)	0·4754 (7)	6·1 (2)
F(11)	0·6092 (8)	0·0340 (7)	0·2114 (6)	10·4 (3)*
F(12)	0·8339 (6)	0·0197 (7)	0·3003 (5)	9·4 (2)*
F(13)	0·7273 (9)	0·1353 (5)	0·3296 (7)	9·0 (2)*
O(21)	1·0313 (6)	0·0222 (4)	0·9061 (5)	4·7 (1)
C(21)	1·2137 (9)	0·012 (1)	1·0971 (8)	5·7 (2)
C(22)	1·0581 (8)	−0·003 (1)	1·0164 (7)	4·8 (2)
C(23)	0·968 (1)	−0·0416 (8)	1·065 (1)	5·0 (2)
C(24)	0·8236 (9)	−0·0625 (7)	0·9885 (9)	4·4 (2)
C(25)	0·601 (1)	−0·1239 (9)	0·982 (1)	6·6 (3)
C(26)	0·605 (2)	−0·217 (1)	0·942 (1)	9·4 (4)
O(22)	0·7721 (7)	−0·0509 (5)	0·8788 (6)	4·8 (1)
O(23)	0·7475 (8)	−0·0985 (6)	1·0487 (7)	5·9 (2)
F(21)	1·2420 (8)	−0·009 (1)	1·2113 (6)	11·2 (3)*
F(22)	1·2506 (8)	0·0938 (5)	1·0944 (8)	9·0 (2)*
F(23)	1·2964 (8)	−0·0346 (6)	1·0566 (9)	10·3 (3)*
O(31)	0·9271 (7)	−0·1443 (5)	0·7572 (6)	5·3 (1)
C(31)	1·037 (1)	−0·2759 (9)	0·834 (1)	6·2 (3)
C(32)	1·043 (1)	−0·1869 (7)	0·7850 (9)	4·8 (2)
C(33)	1·165 (1)	−0·1608 (9)	0·7709 (9)	5·4 (2)
C(34)	1·172 (1)	−0·0788 (8)	0·7149 (9)	4·7 (2)
C(35)	1·304 (1)	0·013 (1)	0·625 (1)	7·5 (3)
C(36)	1·227 (1)	0·012 (2)	0·503 (1)	9·6 (4)
O(32)	1·0794 (6)	−0·0207 (4)	0·6871 (6)	5·1 (2)
O(33)	1·2913 (8)	−0·0659 (6)	0·6901 (7)	5·9 (2)
F(31)	0·9881 (9)	−0·2689 (6)	0·9261 (7)	9·6 (2)*
F(32)	0·947 (1)	−0·3291 (5)	0·7611 (8)	9·2 (3)*
F(33)	1·1630 (8)	−0·3171 (6)	0·8816 (8)	9·3 (3)*
O(41)	0·6965 (6)	0·1019 (5)	0·7330 (6)	4·6 (1)
C(41)	0·576 (1)	0·2105 (9)	0·799 (1)	5·9 (2)
C(42)	0·7024 (9)	0·1839 (7)	0·7643 (8)	4·3 (2)
C(43)	0·799 (1)	0·2439 (8)	0·7626 (9)	4·8 (2)
C(44)	0·9179 (9)	0·2205 (7)	0·7313 (8)	4·1 (2)
C(45)	1·120 (1)	0·2729 (9)	0·687 (1)	5·7 (2)
C(46)	1·076 (2)	0·274 (1)	0·554 (1)	8·9 (4)
O(42)	0·9473 (6)	0·1461 (5)	0·7111 (5)	4·2 (1)
O(43)	0·9950 (7)	0·2910 (6)	0·7220 (6)	5·7 (2)
F(41)	0·4515 (7)	0·2038 (6)	0·7053 (7)	8·4 (2)*
F(42)	0·5848 (7)	0·2908 (6)	0·8422 (8)	11·2 (2)*
F(43)	0·5660 (7)	0·1553 (6)	0·8848 (7)	9·0 (2)*

* Starred atoms were refined anisotropically.

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and fold angles* (°)

	Ligand (1)	Ligand (2)	Ligand (3)	Ligand (4)
U—O(1)	2·288 (6)	2·251 (6)	2·287 (8)	2·275 (7)
U—O(2)	2·404 (7)	2·423 (7)	2·429 (7)	2·416 (7)
O(1)—C(2)	1·28 (1)	1·29 (1)	1·27 (1)	1·29 (1)
C(1)—C(2)	1·52 (2)	1·53 (1)	1·48 (2)	1·52 (2)
C(1)—F(1)	1·322 (15)	1·315 (14)	1·350 (15)	1·343 (15)
C(1)—F(2)	1·320 (15)	1·300 (21)	1·282 (16)	1·314 (16)
C(1)—F(3)	1·332 (17)	1·309 (16)	1·340 (15)	1·352 (16)
C(2)—C(3)	1·36 (2)	1·37 (2)	1·35 (1)	1·34 (1)
C(3)—C(4)	1·43 (2)	1·437 (15)	1·424 (16)	1·417 (14)
C(4)—O(3)	1·33 (1)	1·34 (1)	1·34 (1)	1·35 (1)
O(3)—C(5)	1·483 (15)	1·445 (15)	1·457 (21)	1·483 (14)
C(5)—C(6)	1·47 (2)	1·50 (2)	1·37 (2)	1·47 (2)
C(4)—O(2)	1·27 (1)	1·22 (1)	1·24 (1)	1·21 (1)
O(1)—U—O(2)	71·3 (2)	71·6 (2)	70·7 (3)	70·4 (2)
C(2)—C(1)—F(1)	112 (1)	113 (1)	109 (1)	112 (1)
C(2)—C(1)—F(2)	111 (1)	111 (1)	115 (1)	114 (1)
C(2)—C(1)—F(3)	109 (1)	109 (1)	115 (1)	110 (1)
F(1)—C(1)—F(2)	108 (1)	107 (1)	103 (1)	107 (1)
F(1)—C(1)—F(3)	107 (1)	109 (1)	105 (1)	106 (1)
F(2)—C(1)—F(3)	109 (1)	107 (1)	108 (1)	107 (1)
O(1)—C(2)—C(1)	111 (1)	112 (1)	113 (1)	112 (1)
O(1)—C(2)—C(3)	128 (1)	129 (1)	127 (1)	128 (1)
C(2)—C(3)—C(4)	120 (1)	119 (1)	119 (1)	120 (1)
C(3)—C(4)—O(3)	114 (1)	113 (1)	115 (1)	113 (1)
C(3)—C(4)—O(2)	127 (1)	125 (1)	126 (1)	125 (1)
C(4)—O(3)—C(5)	120 (1)	119 (1)	119 (1)	116 (1)
O(3)—C(5)—C(6)	111 (1)	107 (1)	115 (2)	110 (1)
Folding along				
O(1)—O(2)	1·6 (4)	7·9 (12)	15·8 (5)	14·0 (3)

environment. The bidentate ligands span the *m* edges of the polyhedron leading to the *mmmm* stereoisomer in the Hoard & Silverton [*Inorg. Chem.* (1963), **2**, 235–243] classification.

Introduction. The uranium(IV) β-diketonates are examples illustrating eight coordination of the metal. The theoretical stereochemistry leads to seven possible geometries (Kepert, 1982), but the two most stable structures, the square antiprism and the dodecahedron, are those which have been observed experimentally for a large number of compounds. The case of tetrakis bidentate chelates offers different possible stereoisomers depending on the edges spanned by the ligands. Moreover, with asymmetric β-diketones it is interesting to investigate the influence of the substituent effect on the observed stereochemistry, particularly in the presence of electronegative fluorinated groups. The incorporation of fluorinated substituents in β-diketonato chelates of actinides enhances the extremely interesting property of volatility, and these chelates have been investigated for different applications in the nuclear field (Katz & Seaborg, 1957; Swain & Karraker, 1970). They have also been studied by ^{19}F NMR spectroscopy in solution to observe intramolecular motions of the ligand (Martin-Rovet, Folcher & Kiener, 1981). We previously reported the structures of two of these chelates: tetrakis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato) (Navaza, de Rango & Charpin, 1980) and tetrakis(1,1,1-trifluoro-2,4-pentanedionato) (Charpin, Lance & Navaza, 1985), known as U(tfba)$_4$ and U(tfaa)$_4$, respectively.

Experimental. A green crystal, approximate size 0·4 × 0·3 × 0·2 mm, suitable for X-ray analysis was mounted on a CAD-4 Enraf–Nonius diffractometer equipped with a graphite monochromator. Cell constants were obtained from the setting angles of 25 reflections in the range $8 < \theta < 12°$. A total of 3244 reflections were measured by $\omega/2\theta$ scans, ω scan width: $(0{\cdot}8 + 0{\cdot}35\,\tan\theta)°$, background measured on each side of the scan one-sixth of the time, $1 \le 2\theta \le 25°$, $-11 < h < 11$, $0 < k < 18$, $0 < l < 14$. Three standard reflections (108, $2\bar{8}6$, 3,13,5) measured every hour showed intensity variations within counting statistics (decay of 0·1% in 44 h). A double empirical absorption correction was applied, first from ψ scans, max., min. transmission 0·998, 0·864

(North, Phillips & Mathews, 1968), then using *DIFABS*, max., min. transmission 0·394, 0·732 (Walker & Stuart, 1983); Lorentz–polarization effects were corrected. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a MicroVAX II computer with Enraf–Nonius *SDP* (Frenz, 1985). From 3062 unique reflections, 2371 with $I > 3\sigma(I)$ were used in full-matrix least-squares refinements based on *F*. Heavy-atom method; U and F atoms only were given anisotropic thermal parameters, H atoms localized in theoretical positions, then constrained to ride on their C atoms. Final *R* values: $R_F = 0{\cdot}027$, $wR_{F^2} = 0{\cdot}034$, $w = 1/(\sigma F)^2$ with $\sigma F = [\sigma I^2 + (pF^2)^2]^{1/2}$, $p = 0{\cdot}05$, max. peak height in final Fourier map: 0·86 e Å^{-3}, $S = 1{\cdot}17$, max. $\Delta/\sigma = 0{\cdot}26$ [*x* of C(36)]. The structure belongs clearly to the non-centrosymmetric group and the absolute configuration has been obtained unambiguously.

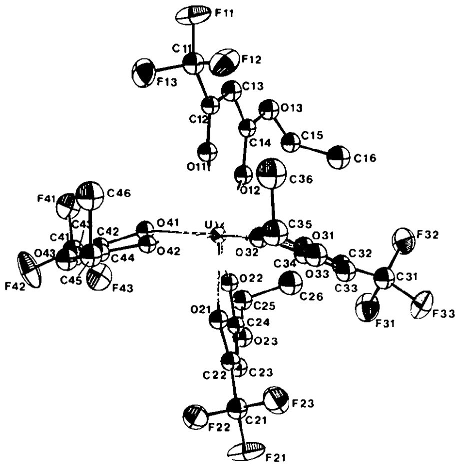

Fig. 1. *ORTEP* (Johnson, 1976) drawing of the molecule with the numbering scheme used.

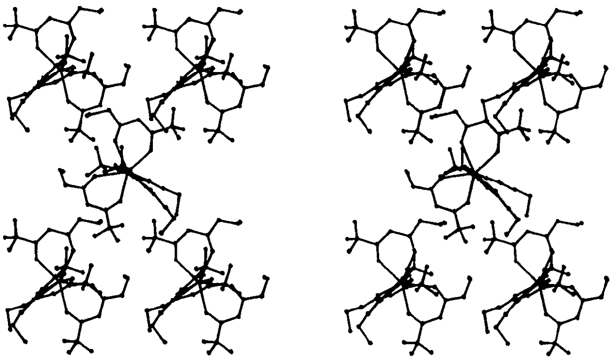

Fig. 2. Stereoscopic view of the crystal structure.

Discussion. Final atomic coordinates and thermal parameters are given in Table 1. The main geometrical features of the four crystallographically independent β-diketone ligands are reported in Table 2.* Figs. 1 and 2 show *ORTEP* (Johnson, 1976) views of the molecule and the crystal packing, respectively.

The coordination polyhedron around the U atom in this chelate is a dodecahedron formed by eight O atoms of the four ligands. It can be divided into two nearly planar trapezes [O(11), O(12), O(21), O(22) (−0·14, +0·21, +0·14, −0·21 Å) and O(31), O(32), O(41), O(42) (−0·10, +0·15, +0·10, −0·16 Å), each containing the U atom at the level −0·02 and +0·10 Å respectively] with dihedral angle 88·2 (2)°. The stereoisomer type is *mmmm* in the Hoard & Silverton (1963) notation.

The four ligands, which are almost identical, largely differ by the folding along the O—O line, from quasi-planarity for ligand (1), to 14 and 15° angles for ligands (3) and (4), and an intermediate value (8°) for ligand (2) probably due to the packing effect. The most interesting feature in this asymmetric β-diketone is the significant difference in the bond lengths U—O, on the CF_3 and OC_2H_5 sides: 2·28 and 2·42 Å respectively, which was not evident for U(tfba)$_4$ ($R = CF_3$, $R' = C_6H_5$: Navaza *et al.*, 1980), or Th(tta)$_4$ ($R = CF_3$, $R' = C_4H_3S$: Lenner & Lindquist, 1979) (the uranium compound being isomorphous to the thorium one) and suggested, though within the e.s.d., for U(tfaa) ($R = CF_3$, $R' = CH_3$: Charpin *et al.* 1985).

It is also interesting to consider the stereochemistries encountered in the formation of asymmetric β-diketonates. The *llll* antiprism in U(tfaa)$_4$, and the *gggg* dodecahedron in U(tfba)$_4$ were original solutions. The *mmmm* dodecahedron observed for the compound described here seems to be analogous to the configuration described for the tta compound: however, in these two propeller-like molecules, it can be observed that in the former the CF_3 groups are not situated on the same side of the bisecting trapezes as they are in the latter.

Thanks are expressed to Dr G. Folcher, and N. Keller for preparing crystals of the compound.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and fuller lists of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52139 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Crystal Chemistry of *cyclo*-Hexaphosphates. IV. Structures of Tris(ethylenediammonium) *cyclo*-Hexaphosphate Dihydrate and Copper Bis(ethylenediammonium) *cyclo*-Hexaphosphate Hexahydrate

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Abstract. Tris(ethylenediammonium) *cyclo*-hexaphosphate dihydrate, $[C_2H_{10}N_2]_3P_6O_{18}.2H_2O$, $M_r = 696{\cdot}204$, monoclinic, $P2_1/n$, $a = 11{\cdot}064\,(5)$, $b = 12{\cdot}317\,(5)$, $c = 9{\cdot}342\,(5)$ Å, $\beta = 90{\cdot}53\,(5)°$, $V = 1273\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}816$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}528$ mm^{-1}, $F(000) = 724$, $T = 295$ K, final $R = 0{\cdot}030$ for 2530 unique reflections. Copper bis(ethylenediammonium) *cyclo*-hexaphosphate hexahydrate, $Cu[C_2H_{10}N_2]_2P_6O_{18}.6H_2O$, $M_r = 769{\cdot}694$, monoclinic, $P2_1/a$, $a = 13{\cdot}378\,(8)$, $b = 11{\cdot}574\,(6)$, $c = 8{\cdot}687\,(3)$ Å, $\beta = 103{\cdot}15\,(3)°$, $V = 1310\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}951$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}344$ mm^{-1}, $F(000) = 790$, $T = 295$ K, final $R = 0{\cdot}032$ for 3646 unique reflections. In the first compound two kinds of ethylenediammonium groups coexist, one with no internal symmetry, the second one centrosymmetric. Layers containing P_6O_{18}, water molecules and the centrosymmetric organic groups alternate along the *b* axis. Layers of the first kind of ethylenediammonium groups alternate with those of the second type. The second compound can also be described as a layer organization: layers containing the P_6O_{18} ring anions and $[Cu(H_2O)_6]$ octahedra alternate with layers containing the organic groups, along the *a* axis. For both compounds, H-atom positions have been refined and the networks of hydrogen bonds are described.

Introduction. A series of ethylenediammonium–divalent cation–*cyclo*-tetraphosphate compounds has been previously reported by the authors. These compounds have very different stoichiometries: $Ca[eda]P_4O_{12}.15/2H_2O$ (Averbuch-Pouchot, Durif & Guitel, 1988);* $M[eda]P_4O_{12}.5H_2O$ for M = Pb or Sr (Bagieu-Beucher, Durif & Guitel, 1988); $M[eda]_3[P_4O_{12}]_2.14H_2O$ for M = Cu, Ni, Co, Mn, Mg, Zn and Cd (Averbuch-Pouchot & Durif, 1989).

The present work reports the first results we obtained in a similar systematic study, but this time with a larger-ring phosphoric anion: P_6O_{18}.

Experimental.

(I) *Tris*(*ethylenediammonium*) *cyclo-hexaphosphate dihydrate*, $3[NH_3(CH_2)_2NH_3]^{2+}.(P_6O_{18})^{6-}.2H_2O$

Single crystals were prepared by using a process deriving from the Boullé metathesis reaction (Boullé, 1938) but involving in the present case the use of $Ag_6P_6O_{18}.H_2O$, recently described (Averbuch-Pouchot, 1989).

The reaction is:

$$3(eda)Cl_2 + Ag_6P_6O_{18}.H_2O \rightarrow 6AgCl + (eda)_3P_6O_{18}.$$

After filtration of the insoluble silver chloride the resulting solution is kept at room temperature until the formation of large stout colourless monoclinic prisms of $(eda)_3P_6O_{18}.2H_2O$.

Crystal size: 0·30 × 0·30 × 0·35 mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. Systematic absences: $h0l$ $(h + l =$

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* eda = $C_2H_{10}N_2$.

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