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Dialkylcarbamato Complexes of Transition Elements. 2. Crystal and Molecular Structure of Di-μ_3-oxo-dodeca(diethylcarbamato)tetrauranium(IV)

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The crystal and molecular structure of the title compound, which is a by-product of the synthesis of tetrakis(diethylcarbamato)uranium(IV), has been determined from three-dimensional x-ray diffraction data. The substance crystallizes in the space group $P\bar{1}$, with cell dimensions a = 17.164 (4) Å, b = 14.014 (6) Å, c = 12.478 (4) Å, α = 112.76 (4)°, β = 93.12 (3)°, and γ = 122.58 (2)°; d_c = 1.799 g/cm^3 for Z = 1; R = 0.039 for 4095 independent observations. The title compound is a tetranuclear species, containing both diethylcarbamato and μ_3-oxo ligands. The molecule has a central core constituted by a nearly planar U_4O_2 system with tricoordinate oxygen atoms bridging three uranium atoms, the U–O bond distances ranging from 2.147 (7) to 2.294 (7) Å. Three different geometries for the diethylcarbamato ligands, none of which is monodentate, have been observed; the related U–O bond distances range from 2.313 (14) to 2.682 (7) Å. The two nonequivalent uranium atoms are eight-coordinate. No U–O stretching vibration associated with the central U_4O_2 system was observed in the infrared down to 250 cm^{-1} and the compound has a normal magnetic susceptibility for a uranium(IV) compound at room temperature. A possible mechanism for the formation of the complex is proposed.

The chemistry of dialkylcarbamato complexes of transition elements is still largely unexplored[2] and this may be mainly due to the difficulties encountered in their preparation and to the unstable character of the O_2CNR_2 group toward hydrolysis, which makes the use of solvents free from protonic activity necessary. On the other hand, the dialkylcarbamato should be similar to the carboxylato group, O_2CR, both electronically and stereochemically. It is therefore expected that the dialkylcarbamato groups should give a large variety of structural arrangements, namely, monodentate, bidentate, terminal, and bridging ones, as it has already been found[3] for the carboxylato ligands. It is, however, to be noted that the presence of two R groups per ligand is expected to alter the solubility of dialkylcarbamato vs. the corresponding carboxylato complexes considerably, favoring the solubilization of the former compounds in hydrophobic solvents. This, together with the strong nucleophilic character of the carbamato nitrogen, could offer new possibilities of chemical reactivity in nonaqueous solvents.

In the course of our studies on tetrakis(dialkylcarbamato)uranium(IV) derivatives,[2] we have found a reaction by-product of formula $U_4O_2(O_2CNEt_2)_{12}$ which has been investigated by x-ray diffraction analysis. We want now to report the crystal and molecular structure of this product, which has been shown to exhibit several still unreported features, of considerable interest for coordination chemists.

Experimental Section

Anhydrous UCl_4 was prepared either from uranium oxides as described elsewhere[2] or from uranium metal and chlorine[4] at 250 °C.

Preparation of $U_4O_2(O_2CNEt_2)_{12}$. The tetrameric compound could be separated from the main product, $U(O_2CNEt_2)_4$, only by operating in a saturated hydrocarbon as solvent. The yields were variable, mainly depending on the degree of water content in the solvent and in the gas. The one reported here represents a typical preparation, carried out by distilling the solvent over sodium and $LiAlH_4$ and by drying the CO_2 through concentrated sulfuric acid.

Anhydrous UCl_4 (8.18 g, 21.53 mmol) was introduced under a CO_2 atmosphere in a 250-mL flask containing Et_2NH (17.7 mL, 172.3 mmol) dissolved in 100 mL of heptane, previously treated with carbon dioxide for 3 h at room temperature. The exothermic reaction began immediately with formation of a light green precipitate and a green solution. After 20 h of stirring the reaction mixture was filtered under nitrogen. The filtered solution was concentrated under reduced pressure and the resulting green solid was collected by filtration and dried in vacuo (0.25 g, 2.0% yield). The green substance is soluble in aromatic hydrocarbons and moderately soluble in heptane (the solubility of $U(O_2CNEt_2)_4$ in heptane is negligible[2]) and is moderately stable to air and moisture. Anal. Calcd for $C_{60}H_{120}N_{12}O_{26}U_4$: C, 30.31; H, 5.09; N, 7.07. Found: C, 29.77, 31.01; H, 4.91, 5.43; N, 7.13. Magnetic susceptibility measurement: χ_U^{cor} = 3240 × 10^{-6} cgsu (diamagnetic correction = −222 × 10^{-6} cgsu), corresponding to μ_{eff} = 2.76 μ_B.

Table I. Summary of Crystal Data for $U_4O_2(O_2CNEt_2)_{12}$

Mol formula	$U_4O_2(O_2CNEt_2)_{12}$
Mol wt	2377.8
Crystal shape	Prismatic
Crystal size, mm	0.11 × 0.17 × 0.19
Space group	$P\bar{1}$
Unit cell data, Å or deg	a = 17.164 (4)
	b = 14.014 (6)
	c = 12.478 (4)
	α = 112.76 (4)
	β = 93.12 (3)
	γ = 122.58 (2)
Volume, Å^3	2194.6
Density (calcd, Z = 1), g cm^{-3}	1.799
Radiation used in data collection	Mo Kα (λ 0.71069 Å)
Linear absorption coefficient, μ, cm^{-1}	111.1
No. of independent reflections used in the least-squares refinement	4095

X-Ray Analysis. Crystals of the title compound were sealed in thin-walled glass capillaries under an inert atmosphere. A series of Weissenberg photographs showed triclinic symmetry. The space group $P\bar{1}$ was assumed and the successful refinement confirmed this assignment. The unit-cell parameters were refined by a least-squares fit to the setting angles measured for 26 reflections on the diffractometer. The crystal data are given in Table I.

Data Collection. The crystal selected for data collection was prismatic and bounded by the following eight planes: 100, $1\bar{1}0$, $\bar{1}00$, $\bar{1}10$, $\bar{7}24$, $\bar{1}\bar{1}5$, $70\bar{9}$, $11\bar{5}$. The maximum crystal dimensions were approximately 0.11 × 0.17 × 0.19 mm.

The crystal was mounted with the c axis parallel to the spindle axis of a computer-operated Siemens AED diffractometer; Zr-filtered Mo Kα radiation was used. A total of 6858 reflections were collected within a hemisphere up to θ = 24°, using the θ–2θ scan method and "five-points" technique.[5] A total of 4095 reflections with intensities greater than $3\sigma(I)$, where $\sigma^2(I)$ = total counts + $(0.005I)^2$, were used for the structure determination. The variation of the intensity of a selected standard reflection, checked every 15 reflections, reached a maximum of 3% during the data collection run; the scale factor was adjusted on the assumption that all other intensities varied at the same rate. The integrated intensities were reduced to F^2 by applying Lorentz and polarization factors. An absorption correction was applied according to the method proposed by Busing and Levy;[6] the transmission factors ranged from 0.21 to 0.35.

Solution and Refinement of the Structure

The structure was solved by the application of the heavy-atom technique. Block-matrix, least-squares refinements on F were

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Table II. Fractional Coordinates and Thermal Parameters of Nonhydrogen Atoms[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U(1)	−0.07933 (3)	−0.04168 (3)	0.09421 (3)	3.89 (2)	4.52 (2)	5.09 (2)	6.01 (3)	4.31 (3)	6.27 (3)
U(2)	0.13151 (3)	−0.05668 (4)	0.14888 (4)	3.29 (2)	4.36 (2)	5.62 (2)	4.67 (3)	2.02 (3)	6.07 (3)
O	−0.0499 (4)	0.0312 (6)	−0.0410 (6)	3.4 (3)	4.9 (3)	4.9 (3)	5.5 (5)	3.0 (5)	6.7 (5)
Ligand (1)									
O(1)	−0.1326 (5)	−0.2596 (6)	0.0074 (6)	4.1 (3)	4.7 (3)	6.0 (4)	5.3 (6)	3.0 (5)	6.1 (6)
O(2)	−0.0110 (5)	−0.2717 (7)	0.0561 (7)	3.3 (3)	4.6 (3)	7.3 (4)	4.3 (5)	3.2 (6)	6.6 (6)
C(1)	−0.1000 (7)	−0.3228 (9)	0.0055 (9)	4.8 (5)	4.1 (4)	5.1 (5)	5.6 (8)	3.3 (8)	6.1 (8)
N	−0.1639 (6)	−0.4532 (8)	−0.0537 (9)	3.9 (4)	3.5 (4)	7.4 (5)	4.1 (7)	1.0 (7)	3.6 (7)
C(2)	−0.2658 (10)	−0.5201 (13)	−0.1185 (12)	6.1 (7)	5.5 (7)	9.1 (7)	6.1 (13)	5.7 (12)	7.6 (12)
C(3)	−0.3292 (14)	−0.5599 (18)	−0.0464 (17)	5.7 (12)	12.8 (11)	12.6 (11)	9.9 (20)	7.0 (19)	13.1 (19)
C(4)	−0.1315 (9)	−0.5344 (12)	−0.0632 (11)	5.2 (6)	3.9 (6)	9.0 (7)	5.5 (11)	2.1 (10)	4.9 (11)
C(5)	−0.0994 (12)	−0.5619 (16)	−0.1690 (15)	8.8 (10)	9.1 (10)	11.6 (10)	14.3 (17)	7.8 (16)	8.0 (16)
Ligand (2)									
O(1)	0.0593 (6)	0.1632 (7)	0.2453 (7)	7.6 (4)	5.0 (4)	5.9 (4)	8.6 (7)	3.6 (7)	4.4 (6)
O(2)	0.1851 (5)	0.1569 (7)	0.2860 (7)	5.4 (4)	4.2 (3)	7.5 (4)	4.9 (6)	0.6 (7)	5.6 (6)
C(1)	0.1494 (8)	0.2173 (10)	0.2972 (10)	6.4 (6)	4.0 (5)	5.6 (6)	4.6 (9)	1.5 (9)	5.2 (9)
N	0.2095 (9)	0.3476 (11)	0.3663 (13)	6.9 (6)	5.5 (6)	11.6 (9)	5.7 (10)	−1.4 (12)	5.6 (11)
C(2)	0.1815 (15)	0.4267 (19)	0.3577 (18)	14.1 (13)	8.0 (13)	9.9 (12)	10.4 (22)	11.6 (21)	7.5 (21)
C(3)	0.1459 (24)	0.4388 (30)	0.4500 (29)	25.2 (25)	18.1 (24)	14.6 (24)	22.6 (43)	21.8 (40)	16.3 (40)
C(4)	0.3118 (15)	0.4175 (19)	0.4370 (19)	10.4 (13)	8.2 (13)	11.9 (13)	7.7 (23)	3.3 (21)	8.3 (22)
C(5)	0.3730 (18)	0.4589 (23)	0.3669 (23)	12.6 (17)	11.6 (17)	12.4 (17)	9.7 (30)	1.9 (28)	8.6 (28)
Ligand (3)									
O(1)	−0.2395 (5)	−0.1776 (7)	−0.0400 (8)	3.4 (3)	6.6 (4)	10.0 (5)	6.4 (6)	5.2 (7)	10.4 (8)
O(2)	−0.2777 (5)	−0.0922 (7)	−0.1299 (8)	3.3 (3)	6.6 (4)	9.2 (5)	5.2 (6)	3.9 (7)	10.6 (8)
C(1)	−0.2993 (8)	−0.1654 (11)	−0.0855 (12)	3.7 (5)	6.0 (6)	8.6 (7)	6.0 (9)	4.2 (9)	7.6 (11)
N	−0.3907 (7)	−0.2322 (12)	−0.0787 (14)	2.4 (4)	10.4 (8)	17.9 (11)	5.3 (9)	5.6 (11)	21.3 (16)
C(2)	−0.4211 (13)	−0.3206 (18)	−0.0262 (17)	3.3 (12)	12.1 (11)	15.2 (11)	6.0 (20)	7.6 (19)	16.1 (19)
C(3)	−0.3966 (17)	−0.2552 (22)	0.0978 (22)	7.3 (17)	15.0 (16)	19.4 (16)	10.6 (29)	15.2 (27)	23.3 (27)
C(4)	−0.4616 (13)	−0.2057 (18)	−0.1090 (17)	5.6 (12)	11.4 (11)	13.2 (11)	7.3 (20)	6.5 (19)	15.1 (19)
C(5)	−0.5121 (21)	−0.2889 (26)	−0.2260 (26)	17.2 (21)	17.1 (21)	17.1 (21)	21.3 (38)	8.8 (36)	15.9 (36)
Ligand (4)									
O(1)	−0.1384 (7)	0.0778 (9)	0.1586 (8)	10.5 (6)	9.8 (6)	8.6 (5)	17.7 (10)	10.0 (9)	11.7 (9)
O(2)	−0.1328 (6)	0.1730 (8)	0.0469 (7)	6.4 (4)	7.5 (4)	7.0 (4)	10.6 (8)	7.2 (7)	9.5 (8)
C(1)	−0.1459 (9)	0.1563 (11)	0.1354 (12)	6.5 (6)	5.9 (6)	8.3 (7)	9.7 (10)	8.1 (11)	8.2 (11)
N	−0.1663 (12)	0.2259 (14)	0.2231 (12)	19.9 (13)	15.2 (10)	11.9 (9)	32.0 (22)	20.7 (18)	20.0 (17)
C(2)	−0.2260 (20)	0.1688 (26)	0.3167 (24)	15.6 (20)	16.0 (19)	20.5 (19)	23.6 (33)	5.4 (31)	15.8 (32)
C(3)	−0.1399 (21)	0.2477 (26)	0.3868 (25)	20.9 (20)	12.4 (20)	14.6 (20)	23.4 (35)	7.7 (34)	1.9 (34)
C(4)	−0.1710 (14)	0.3231 (17)	0.2072 (17)	15.7 (11)	9.0 (11)	13.1 (11)	19.9 (20)	13.6 (19)	13.1 (19)
C(5)	−0.2632 (19)	0.2604 (24)	0.1312 (24)	16.3 (18)	17.7 (17)	21.2 (17)	26.5 (31)	20.0 (29)	25.7 (29)
Ligand (5)									
O(1)	0.2267 (7)	−0.1276 (8)	0.1897 (8)	8.0 (5)	6.6 (5)	9.2 (5)	10.6 (9)	−1.3 (8)	5.7 (8)
O(2)	0.2116 (7)	−0.0099 (10)	0.3473 (8)	6.4 (5)	10.9 (6)	7.9 (5)	11.3 (9)	4.0 (8)	11.7 (9)
C(1)	0.2528 (9)	−0.0610 (12)	0.2999 (12)	5.0 (6)	6.9 (7)	9.4 (7)	7.0 (11)	3.1 (11)	11.8 (12)
N	0.3278 (9)	−0.0357 (11)	0.3851 (11)	8.9 (7)	9.5 (7)	9.3 (7)	14.0 (13)	0.9 (11)	8.0 (12)
C(2)	0.3802 (13)	−0.0870 (17)	0.3305 (16)	7.9 (10)	9.0 (10)	10.7 (10)	10.6 (18)	−4.9 (17)	7.6 (17)
C(3)	0.4473 (20)	−0.0171 (26)	0.2933 (24)	13.5 (19)	21.3 (18)	17.0 (19)	26.8 (33)	10.9 (31)	20.8 (32)
C(4)	0.3591 (14)	0.0530 (17)	0.5185 (17)	10.4 (11)	11.6 (11)	11.0 (11)	12.8 (20)	4.9 (18)	14.1 (19)
C(5)	0.4325 (19)	0.1797 (24)	0.5510 (23)	15.0 (18)	12.6 (18)	14.7 (18)	15.6 (32)	3.2 (30)	10.2 (30)
Ligand (6)									
O(1)	0.0089 (5)	−0.0693 (6)	0.2516 (6)	5.5 (3)	5.0 (3)	4.9 (3)	6.0 (6)	4.2 (6)	6.4 (6)
O(2)	−0.1269 (5)	−0.0884 (8)	0.2520 (7)	6.3 (4)	8.2 (4)	7.6 (4)	11.1 (7)	8.4 (7)	11.9 (8)
C(1)	−0.0664 (8)	−0.1019 (10)	0.2893 (10)	6.5 (6)	4.9 (5)	5.2 (5)	6.0 (9)	6.2 (9)	6.9 (9)
N	−0.0775 (7)	−0.1496 (9)	0.3652 (8)	5.5 (4)	6.5 (5)	5.9 (4)	7.9 (8)	7.2 (8)	8.4 (8)
C(2)	−0.0085 (10)	−0.1708 (12)	0.4038 (12)	8.7 (7)	6.7 (7)	6.1 (7)	9.5 (12)	5.5 (11)	7.3 (12)
C(3)	−0.0413 (12)	−0.3069 (16)	0.3283 (15)	14.1 (10)	11.0 (9)	7.2 (10)	19.0 (17)	10.2 (16)	11.4 (16)
C(4)	−0.1619 (10)	−0.1850 (12)	0.4073 (12)	8.1 (7)	7.9 (7)	6.6 (7)	9.9 (12)	8.8 (12)	10.5 (12)
C(5)	−0.2551 (14)	−0.3138 (18)	0.3184 (17)	8.6 (11)	9.0 (11)	11.9 (11)	8.0 (20)	7.9 (19)	11.3 (19)

[a] Anisotropic thermal factor defined by $\exp[-{}^1/_4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)]$. Standard deviations in parentheses, in this and following tables, refer to the last digit quoted.

performed for each atom and the function minimized was $\sum w(F_o - F_c)^2$ with Cruickshank's weighting scheme.[7] Neutral scattering factors for nonhydrogen atoms were taken from Cromer and Mann,[8] while those for hydrogen were from Stewart, Davidson, and Simpson.[9] The calculations included both $\Delta f'$ and $\Delta f''$ corrections for the anomalous dispersion effects of the uranium atom.[10] With the exception of ORTEP,[11] all the computer programs were written by Immirzi.[12]

The positions of the two independent uranium atoms were determined from a three-dimensional Patterson map. From subsequent Fourier syntheses, the positions of the other 49 independent nonhydrogen atoms were deduced.

Attempts to locate hydrogen atoms from Δf maps were unsuccessful; therefore the usual tetrahedral geometry and a C–H bond length of 1.0 Å were assumed and the positions calculated. In the final anisotropic refinement, the hydrogen atom contributions were calculated from these fixed positions and the temperature factors were set to 10.0 and 12.0 Å^2 for hydrogens of methylene groups and methyl groups, respectively. The refinement converged to give a final agreement factor $R = 0.039$. At convergence, the shifts of the positional parameters pertaining to the $U_4O_2C_{12}O_{24}$ fragment (with the exclusion of ligand 5) were less than 0.5σ. Maximum shifts up to values of about σ were observed only for the peripheral atoms, which showed very large thermal parameters. A final difference Fourier synthesis showed no peaks greater than 0.6 e/Å^3 which were not within 1 Å of the uranium atoms. Positional and anisotropic thermal parameters from the final least-squares cycle are reported in Table II.

Table III. Calculated Fractional Coordinates ($\times 10^4$) of the Hydrogen Atoms

	x	*y*	*z*		*x*	*y*	*z*
Ligand (1)				Ligand (4)			
H1(C2)	−2728	−4637	−1431	H1(C2)	−2875	1803	3020
H2(C2)	−2899	−6024	−1995	H2(C2)	−2759	639	2530
H1(C3)	−3995	−6058	−902	H1(C3)	−1496	2429	4863
H2(C3)	−3063	−4785	343	H2(C3)	−995	3515	4415
H3(C3)	−3234	−6172	−221	H3(C3)	−878	2351	3925
H1(C4)	−730	−4865	134	H1(C4)	−1534	3993	2928
H2(C4)	−1855	−6189	−675	H2(C4)	−1162	3724	1742
H1(C5)	−791	−6191	−1802	H1(C5)	−2829	3070	1058
H2(C5)	−466	−4817	−1691	H2(C5)	−3219	2065	1601
H3(C5)	−1590	−6141	−2500	H3(C5)	−2847	1795	416
Ligand (2)				Ligand (5)			
H1(C2)	2383	5175	3750	H1(C2)	4085	−1046	3852
H2(C2)	1306	3853	2758	H2(C2)	3307	−1769	2488
H1(C3)	1174	4891	4591	H1(C3)	4936	−413	2538
H2(C3)	1933	4788	5296	H2(C3)	5113	845	3682
H3(C3)	856	3466	4305	H3(C3)	4335	123	2318
H1(C4)	3326	4910	5232	H1(C4)	3004	465	5395
H2(C4)	3199	3554	4538	H2(C4)	3797	213	5680
H1(C5)	4523	5190	4204	H1(C5)	5102	2139	5829
H2(C5)	3766	5347	3583	H2(C5)	4436	2592	6342
H3(C5)	3639	3991	2890	H3(C5)	4397	2151	4910
Ligand (3)				Ligand (6)			
H1(C2)	−4976	−3926	−610	H1(C2)	574	−1086	3989
H2(C2)	−3944	−3735	−517	H2(C2)	10	−1485	4928
H1(C3)	−4149	−3186	1386	H1(C3)	67	−3188	3573
H2(C3)	−4233	−2104	1313	H2(C3)	−509	−3317	2380
H3(C3)	−3201	−1912	1406	H3(C3)	−1072	−3715	3319
H1(C4)	−5071	−2121	−560	H1(C4)	−1467	−1847	4878
H2(C4)	−4260	−1091	−935	H2(C4)	−1712	−1144	4287
H1(C5)	−5684	−2916	−2729	H1(C5)	−3137	−3380	3461
H2(C5)	−5535	−3891	−2508	H2(C5)	−2496	−3876	2942
H3(C5)	−4724	−2861	−2885	H3(C5)	−2741	−3173	2351

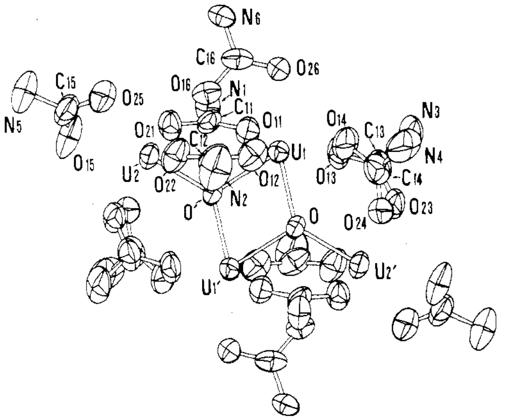
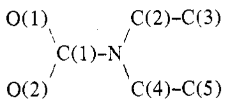


Figure 1. View of the molecular structure of $U_4O_2(O_2CNEt_2)_{12}$. The ethyl carbon atoms have been omitted for clarity.

The calculated hydrogen positions are listed in Table III. Ligand numbering is as shown, the atom number being followed when



necessary by the ligand number (1)–(6).

Discussion

Very few x-ray investigations of compounds containing dialkylcarbamato ligands have appeared in the literature. The mixed dimethylcarbamato–dimethylamido complex $W(NMe_2)_3(O_2CNMe_2)_3$ was shown to contain three terminal monodentate carbamato groups around the hexacoordinate tungsten atom. The tungsten derivative $W_2(O_2CNMe_2)_6$ contains both terminal (either mono- or bidentate) and bridging dimethylcarbamato groups.[14]

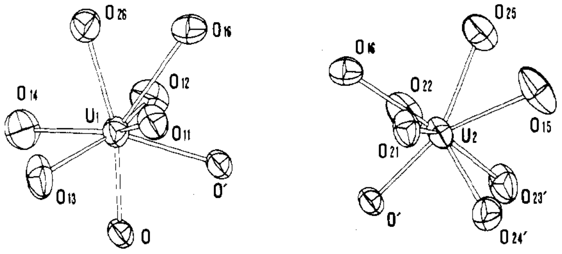


Figure 2. View of the eight-coordinate uranium atoms.

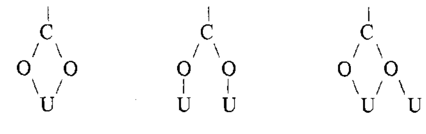


Figure 3. Different types of carbamato groups present in $U_4O_2(O_2CNEt_2)_{12}$: (a) terminal bidentate, ligand (5); (b) bridging, ligands (1)–(4); (c) terminal and bridging, ligand (6).

The crystal structure of our compound consists of discrete tetranuclear molecules, lying on a crystallographic center of symmetry; no unusually short intermolecular nonbonding distances were observed. The molecular structure is shown in Figure 1.

The two nonequivalent uranium atoms are eight-coordinate, as indicated in Figure 2. The ligands around U(1) define what might be described as a distorted bicapped trigonal prism, whereas the oxygen atoms around U(2) do not approximate any type of regular polyhedron.

In each carbamato group the O_2CN set of atoms is substantially planar. This is shown in Table V in which the deviations from least-squares planes are reported for each of the six ligands.

As indicated in Figure 3, the carbamato groups present in our molecule are of three different types, namely, *terminal bidentate*, *bridging*, and *terminal and bridging*, the last via a tricoordinate oxygen atom. Similar types of arrangements are encountered with other uranium complexes, such as carboxylates and carbonates. The carbamato, carboxylato, and carbonato complexes may in fact be regarded as belonging to the general class of coordination compounds containing the ligating group O_2CX ($X = NR_2$, R, and O). As to type (b), significantly different values are observed for the two U–O bond distances, the mean values within the four ligands being 2.325 (5) and 2.366 (7) Å. The pertinent data are in Table VI. Arrangements of types (b) and (c) are found in uranium(IV) acetate,[15] with U–O bond distances considerably longer than in our diethylcarbamato complexes. On the other hand, arrangement of type (a) is found in both the uranylcarbonato[16] and the uranylacetato[17] derivatives and the U–O bond distances observed (2.44–2.46 and 2.49 (1) Å, respectively) compare quite well with the corresponding mean value (2.431 (11) Å) observed for ligand (5) in our diethylcarbamato complex.

As far as the C–O bond distances are concerned, they are not significantly different (see Table IV) within the six ligands of our carbamato complex, the overall mean value being 1.263 (8) Å. If we now consider that the C–O distances reported[13] for $W(NMe_2)_3(O_2CNMe_2)_3$ are 1.30 (1) and 1.24 (1) Å (the carbamato group is monodentate and the longer C–O distance is to the uranium-bonded oxygen atom), we in fact verify that our mean value is almost exactly between them, as expected.

Concerning the U_4O_2 fragment, it is to be noted that tricoordinate oxygen atoms bonded to three metal atoms are rather rare among nonbinary metal oxides. Of the known

Table IV. Geometrical Parameters

(a) Uranium Geometry[a] (Å)

U(1)–O(11)	2.379 (12)	U(2)–O(21)	2.336 (12)
U(1)–O(12)	2.329 (13)	U(2)–O(22)	2.374 (13)
U(1)–O(13)	2.320 (11)	U(2)–O(23′)	2.348 (12)
U(1)–O(14)	2.313 (14)	U(2)–O(24′)	2.364 (13)
U(1)–O(16)	2.682 (7)	U(2)–O(16)	2.485 (9)
U(1)–O(26)	2.360 (9)	U(2)–O(15)	2.442 (11)
U(1)–O	2.239 (7)	U(2)–O(25)	2.419 (10)
U(1)–O′	2.294 (7)	U(2)–O′	2.147 (7)

(b) Bond Angles around the Oxygen Atoms[a] (deg)

U(1)–O(11)–C(11)	140.5 (12)	U(2)–O(21)–C(11)	131.6 (10)
U(1)–O(12)–C(12)	137.7 (13)	U(2)–O(22)–C(12)	134.8 (13)
U(1)–O(13)–C(13)	137.3 (11)	U(2′)–O(23)–C(13)	133.7 (12)
U(1)–O(14)–C(14)	139.3 (13)	U(2′)–O(24)–C(14)	135.8 (13)
U(1)–O(16)–C(16)	86.2 (5)	U(2)–O(15)–C(15)	92.6 (6)
U(1)–O(26)–C(16)	102.7 (6)	U(2)–O(25)–C(15)	91.9 (6)
U(1)–O–U(1′)	109.4 (1)	U(2)–O(16)–C(16)	168 (4)
U(1)–O–U(2′)	133.0 (1)	U(2′)–O–U(1′)	116.5 (1)

(c) Geometry of the Ligands

	Ligand					
	(1)	(2)	(3)	(4)	(5)	(6)
(i) Bond Lengths, Å						
C(1)–O(1)	1.272 (16)	1.278 (19)	1.268 (15)	1.306 (21)	1.205 (24)	1.303 (18)
C(1)–O(2)	1.268 (15)	1.260 (19)	1.244 (19)	1.223 (17)	1.275 (23)	1.248 (16)
C(1)–N	1.34 (2)	1.34 (3)	1.36 (2)	1.36 (3)	1.41 (2)	1.32 (2)
N–C(2)	1.44 (2)	1.46 (3)	1.49 (3)	1.74 (4)	1.47 (3)	1.47 (2)
N–C(4)	1.48 (2)	1.46 (3)	1.52 (3)	1.49 (3)	1.48 (3)	1.46 (2)
C(2)–C(3)	1.47 (3)	1.33 (5)	1.35 (4)	1.23 (6)	1.30 (5)	1.50 (4)
C(4)–C(5)	1.45 (3)	1.43 (4)	1.30 (5)	1.37 (4)	1.37 (5)	1.48 (4)
(ii) Bond Angles, Deg						
O(1)–C(1)–O(2)	124.9 (6)	124.5 (7)	124.2 (6)	125.3 (7)	121.0 (7)	119.0 (5)
O(1)–C(1)–N	118.0 (6)	117.0 (8)	116.7 (6)	114.0 (9)	123.8 (7)	119.4 (6)
O(2)–C(1)–N	117.1 (6)	118.4 (8)	119.0 (7)	120.7 (8)	115.2 (7)	121.6 (6)
C(1)–N–C(2)	121.0 (8)	121.6 (12)	121.7 (9)	121.1 (9)	115.4 (8)	121.1 (6)
C(1)–N–C(4)	121.5 (7)	121.0 (11)	120.8 (9)	117.5 (10)	120.3 (9)	118.8 (6)
C(2)–N–C(4)	117.4 (7)	116.6 (10)	117.0 (9)	117.7 (10)	123.7 (11)	120.1 (7)
N–C(2)–C(3)	112.6 (9)	99.2 (16)	111.5 (13)	79.2 (16)	115.0 (16)	114.1 (9)
N–C(4)–C(5)	111.9 (9)	109.7 (12)	104.8 (13)	108.6 (12)	111.3 (16)	114.8 (10)
(iii) Torsional Angles, Deg						
C(2)–N–C(4)–C(5)	88.7	−75.1	−95.3	−73.8	81.9	−97.3
C(3)–C(2)–N–C(4)	85.5	−95.6	−85.8	−102.3	−91.5	82.5

[a] The second digit in the O and C atoms numbering system denotes ligand (1)–(6).

cases, three contain a tricoordinate oxygen atom which is not coplanar[18–20] with the three metal atoms. Three other cases are known for which coplanarity has been found for the M_3O system (M = Cr,[21] Ru,[22] Fe[23]).

Among the well-established binary metal oxides is the rutile structure[24] in which a substantially coplanar μ_3-OTi_3 system is present.

In our compound the U_4O_2 system can be regarded as two U_3O triangles joined by a common edge. The deviation of the oxygen atoms from the plane of the three related uranium atoms is 0.135 Å (see Table V) to be compared with the 0.06 Å deviation found[22b] for the central oxygen atom in the Ru_3O system. Moreover the coordination of each oxygen atom to its three related uranium atoms is slightly asymmetrical, the U–O distances ranging from 2.147 (7) to 2.294 (7) Å, see Table IV. In UO_2, which has been reported to have the fluorite-type of structure, the U–O bond distance is 2.37 Å.[25] The shorter U–O distance found for the diethylcarbamato complex and the substantial planarity of the U_3O system both suggest that a considerable degree of π bonding is involved.

The infrared spectrum of the tetrameric complex is substantially identical with that of the diethylcarbamato complex $U(O_2CNEt_2)_4$.[2] Both in the solid state and in toluene solution, no bands attributable to the U–O stretching vibrations of the U_4O_2 system could be detected down to 250 cm^{-1}. The U–O stretching vibration of uranyl complexes is usually found[27,28] at about 900 cm^{-1}. The U–O asymmetric stretching vibration of the U_3O system is expected to be at considerably lower wavenumber values and it may be covered by ligand vibrations.

With reference to Table IV, it may be noted that the NEt_2 groups, particularly in the ligands (2)–(5), display an unusual geometry with generally short C–C bond distances, one N–C distance, i.e., N(4)–C(24), 1.74 (4) Å, being, on the contrary, unusually long. Moreover, there is a tendency for the N–C–C bond angles to decrease from the tetrahedral value. Similar findings have been reported[29] for bis(diethyldithiocarbamato)oxovanadium(IV). These effects are almost certainly to be attributed to both thermal motion and disorder in the peripheral regions of the molecule, as indicated by the high values of the coefficients of the thermal parameters found for the ethyl carbon atoms (see Table II). This is substantiated by the observation that ligands (1) and (6), which display the closest intra- and intermolecular contacts, show lower apparent thermal vibrations and smaller deviations from the expected usual geometry. It is to be noted that the ethyl groups in our diethylcarbamato derivative are on opposite sides of the O_2CN plane for ligands (1)–(4), while ligands (5) and (6) have the ethyl groups on the same side of this plane, as indicated by the values of the torsional angles reported in Table IV. In Figure 4, ligands (6) and (1) are shown.

The magnetic susceptibility of the tetrameric compound was found to correspond to a magnetic moment at room tem-

Table V. Selected Least-Squares Planes Calculations in the Form $Ax + By + Cz = D$, Where x, y, and z Are the Atomic Fractional Coordinates: O(1), O(2), C(1), and N Atoms

Plane	Atoms in plane	Plane	Atoms in plane
(1)	Ligand (1)	(5)	Ligand (5)
(2)	Ligand (2)	(6)	Ligand (6)
(3)	Ligand (3)	(7)	U(1), U(2), U(1′), U(2′)
(4)	Ligand (4)		

	Plane						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
				Parameters from Equation of Plane			
A	−5.137	−4.173	−4.174	11.423	−4.289	−1.076	−0.300
B	−2.984	−4.613	6.166	1.387	−9.530	7.793	8.379
C	12.085	12.211	7.629	1.749	6.704	4.690	3.456
D	1.545	1.997	−0.406	−1.200	1.513	0.631	0.0
				Deviation of Atoms from Planes, Å			
O(1)	0.001	−0.002	0.006	0.004	0.002	−0.001	
O(2)	0.001	0.002	0.006	0.005	0.002	−0.001	
C(1)	−0.001	0.006	−0.017	−0.013	−0.006	0.003	
N	0.0	−0.002	0.005	0.004	0.002	−0.001	
C(2)	−0.061	−0.356	−0.013	−0.594	−0.098	−0.059	
C(3)	1.256	0.864	1.234	0.622	−1.303	−1.439	
C(4)	−0.039	0.112	0.233	0.057	−0.081	0.012	
C(5)	−1.400	−1.191	−0.962	−1.216	−1.386	−1.309	
U(1)	0.125	−0.324	1.198	0.401		−0.429	0.0
U(1′)							0.0
U(2)	−0.252	−0.466			−0.538	−0.516	0.0
U(2′)			0.168	−0.484			0.0
O							0.135

Angles between Planes, Deg

(1)–(7)	72.5	(2)–(7)	78.7	(3)–(7)	25.4
(4)–(7)	42.8	(5)–(7)	50.7	(6)–(7)	6.4
(1)–(2)	7.1	(3)–(4)	60.2		

Table VI. Uranium–Oxygen Bond Distances (Å) in Some Uranium Complexes[a]

Compd	(a)	(b)	(c)	Ref
$U_4O_2(O_2CNEt_2)_{12}$	2.431 (11)	2.325 (5), 2.366 (7)[b]	2.360–2.682	This work
$U(O_2CMe)_4$		2.49–2.55	2.50–2.80	15
$UO_2(CO_3)_3{}^{4-}$	2.44–2.46			16
$UO_2(O_2CMe)_3{}^-$	2.49 (1)			17

[a] (a), (b), and (c) denote the different types of molecular arrangements of the ligand groups, as specified in Figure 3. Mean values of bond distances (Å) are indicated for types (a) and (b) of the diethylcarbamato ligands. The standard deviation of the mean s has been calculated as $s^2 = \Sigma_1{}^n(x_i - \bar{x})^2/(n-1)n$, $\bar{x}$ being the mean of the x_i values and n their number. [b] Two different mean values are reported corresponding to the longer and shorter bond distances.

perature ($\mu_{\text{eff}} = 2.76\ \mu_B$) typical of most uranium(IV) complexes of f^2 electronic configuration. No important spin coupling takes place at room temperature, contrary to what one might expect, due to the proximity of the uranium atoms in the molecule. However, it should be recalled that uranium dioxide has been reported to have a magnetic moment[30] at room temperature ($\mu_{\text{eff}} = 3.03\ \mu_B$) very similar to our value, despite the fact that extensive U–O–U interactions also exist in this compound. It is also worth mentioning that spin pairing in the dimeric diethylamido derivative of uranium(IV) was not observed[31] down to 4.2 K.

As to mode of formation of the tetrameric complex, the U_4O_2 system could originate from the uranium chloride used for the synthesis. The chloride had in fact been prepared by chlorination of uranium oxides with either hexachloropropene or CCl_4. Although the presence of partially chlorinated oxides could not be excluded, this explanation is in contrast with the observation that no secondary products of a similar type had been observed in the preparation of $U(S_2CNEt_2)_4$.[2] That the starting UCl_4 was not responsible for the formation of the μ_3-oxo species was definitely established by carrying out the carbonatation of UCl_4–Et_2NH, using UCl_4 prepared from uranium metal and chlorine. Under these conditions, formation of the tetrameric species was also observed. One way of formation is possibly the hydrolysis of the U–diethylcarbamato bond, in agreement with the observation[2] that the dialkylcarbamato group is readily attacked by electrophilic reagents, such as protons. It is not excluded, however, that other reaction pathways are also operating simultaneously towards the formation of this apparently stable molecular arrangement and work is now in progress aimed at optimizing the yields of the tetranuclear species and at establishing the origin of the central core oxygen atoms in this molecule conclusively.[32]

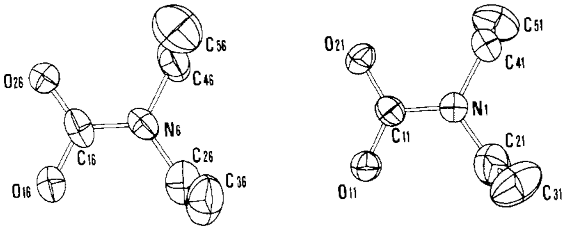


Figure 4. View of the diethylcarbamato groups, showing the orientation of the ethyl groups with respect to the O_2CN plane in ligand (6), left, and ligand (1).

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Registry No. $U_4O_2(O_2CNEt_2)_{12}$, 64957-25-1.

Supplementary Material Available: A listing of crystal structure amplitudes (28 pages). Ordering information is given on any current masthead page.

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Notes

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Structure of Bis(acetylacetonato)(nitro)(2-aminopyrimidine)cobalt(III)

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Relatively few pyrimidine complexes have been studied crystallographically.[1] Substituted pyrimidines are typically expected to form less stable complexes than those formed by purines.[2] We recently reported[3] an extensive series of stability constant data (in Me_2SO) for the reaction

$$[(Me_2SO)Co^{III}(acac)_2(NO_2)] + B \rightleftharpoons [BCo^{III}(acac)_2(NO_2)] + Me_2SO$$

where B = a number of purine and pyrimidine derivatives and acac = acetylacetonate. The purine complexes were typically more stable than the pyrimidine complexes, and we were successful in obtaining the structure of the bis(acetylacetonato)(nitro)(deoxyadenosine)cobalt(III) complex.[3] The absence of any crystallographic data on a cobalt(III)–pyrimidine complex prompted us to pursue the preparation and crystallographic investigation of the title complex.

Experimental Section

The combination of aqueous solutions of 2-aminopyrimidine (0.5 mmol) and $Na[Co(acac)_2(NO_2)_2]$[4] (0.5 mmol) afforded a brown precipitate which was filtered and air-dried. The crystals, obtained by recrystallizing this product from a 1:1:1 by volume mixture of C_3H_7OH–THF–H_2O, belong to the monoclinic system, space group $P2_1$ or $P2_1/m$, with a = 8.769 (4) Å, b = 13.899 (7) Å, c = 7.238 (4) Å, β = 94.39 (4)°, V = 879.6 Å^3, D_{measd} = 1.48 (1) g gm^{-3}, and D_{calcd} = 1.50 g cm^{-3} for two molecules of $C_{14}H_{19}N_4O_6Co$ per unit cell.

All of several crystals, examined by both photographic and diffractometer methods, showed split peaks. These results plus our subsequent analysis (vide infra) indicate that a twin plane exists parallel to (010). For data collection we chose what we considered our best crystal, although it clearly had split peaks and marginal scattering power. A total of 4469 reflections (the $+h$-hemisphere to 55° in 2θ(Mo K$\bar{\alpha}$), graphite-monochromatized radiation) were surveyed on a Syntex P$\bar{1}$ automated diffractometer; of these, 2605 had $I > \sigma(I)$ and were subsequently employed. The data were corrected for Lorentz, polarization, and absorption effects. The crystal was a plate with perpendicular distances between faces as follows: (001)–(00$\bar{1}$) 0.07 mm, (110)–($\bar{1}\bar{1}$0) 0.21 mm, ($\bar{1}$10)–(1$\bar{1}$0) 0.21 mm. The calculated transmission factors ranged from 0.80 to 0.93 (μ(Mo K$\bar{\alpha}$) = 10.38 cm^{-1}). The corrected data were then symmetry averaged (R = 0.053) to yield a final set of 1462 independent data. Observational variances were based on counting statistics plus a term $(0.04I)^2$. An approximate absolute scale was determined by the method of Wilson.[5]

The complete structure was deduced from a three-dimensional Patterson synthesis. Refinement was initiated in the space group $P2_1/m$ which requires that the complex has mirror symmetry with the mirror plane populated by Co, the NO_2 group, and the 2-aminopyrimidine ring. Four cycles of isotropic refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, plus two cycles of anisotropic refinement reduced the R value $(\sum||F_o| - |F_c||/\sum|F_o|)$ to 0.16. It was then evident that several atoms (NO_2 group, acac methyl carbons, and the NH_2 nitrogen) had anomalously large B_{22} components. After pseudosymmetry problems for the reduced-symmetry space group $P2_1$ proved insurmountable, we continued our refinement in $P2_1/m$ with the knowledge that the mirror plane is a consequence of twinning and not intrinsic to the molecule, although the complex has approximate mirror symmetry.

Likely positions for all of the hydrogen atoms in the structure were obtained via a difference Fourier synthesis. Three further cycles of anisotropic refinement, with the hydrogen atoms accounted for but not refined, produced convergence (all shift/error less than 0.7) and a final R value of 0.149. The final weighted R value $[(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}]$ and goodness-of-fit $[(\sum(|F_o| - |F_c|)^2/(NO - NV))^{1/2}$, where NO = 1462 data and NV = 130 variables] were 0.102 and 2.6, respectively. A final difference Fourier map showed no features exceeding +0.7 or −0.6 e/Å^3. Final positional and thermal parameters for the nonhydrogen atoms are given in Table I. The hydrogen atom parameters, selected intramolecular dimensions, and a final list of observed and calculated structure factors have been deposited. Scattering factor tables for the nonhydrogen atoms[6] and the hydrogen atoms[7] were taken from common sources.

Discussion

A stereoview of the bis(acetylacetonato)(nitro)(2-aminopyrimidine)cobalt(III) complex is shown in Figure 1, while the crystal packing is illustrated in the [010] projection of Figure 2. The cobalt(III) center is six-coordinate, with the two acac ligands occupying the four coordination sites in the equatorial plane and the N-bonded nitro group and the N(3)-bonded 2-aminopyrimidine ligand in axial positions. The geometrical parameters in the primary coordination sphere are presented in Table II. As in the deoxyadenosine[3] and triacanthine[8] complexes of this system, the exocyclic amino group ($N(2)H_2$) forms a bifurcated hydrogen bond to two of the oxygen atoms (O(10) and its mirror image) of the acac ligands (Figure 1 and Table II). This favorable interligand hydrogen bonding and the absence of any repulsive forces confirm our original interpretation[3] of the relatively large (27 M^{-1}) formation constant for this pyrimidine complex. As is found in many metal–purine complexes which form interligand hydrogen bonds,[9,10] the exterior angles at the coordinated N(3) atom are dissymmetric, with the exocyclic Co–N(3)–C(2) angle (126.3 (6)°) being some 6° larger than the Co–N(3)–C(4) angle (120.1 (7)°). This dissymmetry is presumedly in response to the geometrical requirements of the formation of the interligand hydrogen bonding.[9,10]

The required coplanarity of the nitro group and the 2-aminopyrimidine ligand is a consequence of twinning in the crystal. However, we note that the dihedral angle between the plane of the nitro group and the nine-atom framework of the deoxyadenosine ligand in its complex[3] is only 5 (1)°, so that approximate coplanarity of these two ligands is not unexpected.

The parameters in the nitro group are anomalous, owing to the large thermal ellipsoids assumed by this group. The geometry found in the 2-aminopyrimidine ligand is reasonably

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