

N(5) et ce groupe méthyle pourrait exercer une influence sur les positions du groupe nitrate autour de N(1).

Dans l'environnement de l'atome d'uranium, les six atomes d'oxygène équatoriaux forment un hexagone très déformé et non plan, les cotes par rapport au plan perpendiculaire à l'uranyle étant respectivement pour la séquence O(2), O(22'), O(22), O(2'), O(12), O(12') de -0,08, +0,08, -0,08, +0,08, +0,31 et -0,31 Å, le plus grand écart à la planéité étant apporté par le groupe nitrate autour de N(1). Dans chacun des groupes nitrate, les trois distances N—O diffèrent peu des valeurs généralement observées dans l'ion NO₃⁻: ceci semble en faveur d'un caractère ionique relativement important de la liaison métal—nitrate que suggère également la longueur des liaisons U—O(12) et U—O(22): 2,526 et 2,564 Å.

L'arrangement des molécules est réalisé par l'axe hélicoïdal 4₃, il n'y a aucun contact intermoléculaire inférieur à 3,13 Å.

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The Structure of Tricarbonyl{C,13,14,C-η-(2RS,5SR,8SR,13RS,14SR)-8-methyl-13,14-dimethylene-9-oxatetracyclo[6.2.2.2^{2,5}.0^{1,6}]}tetradeca-3,6-diene-11,11,12,12-tetracarbonitrile}iron(0), [Fe(C₂₀H₁₄N₄O)(CO)₃]

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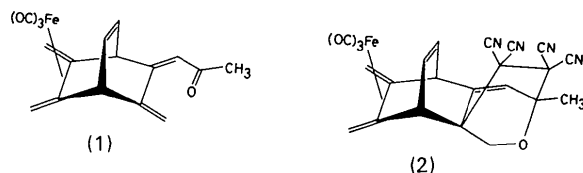
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Abstract. $M_r = 466.2$, monoclinic, $P2_1/c$, $a = 8.635$ (5), $b = 12.868$ (8), $c = 18.897$ (7) Å, $\beta = 96.64$ (5)°, $V = 2086$ (3) Å³, $Z = 4$, $D_m = 1.46$, $D_x = 1.48$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 7.7$ cm⁻¹, $F(000) = 952$, $T = 298$ K, $R = 0.039$ for 1627 [$I > 3\sigma(I)$] reflections. The molecules are discrete monomeric units. The coordination polyhedron of the Fe atom is tetragonal pyramidal with one apical and two basal carbonyl groups [Fe—CO(apical) = 1.760 (5); Fe—CO(basal) = 1.772 (6), 1.780 (5) Å]. The fourth and fifth sites are occupied by the midpoints of the two outer C=C bonds of the diene system [Fe—C distances 2.057 (4)–2.111 (5) Å]. The relative positions of the

8-methyl and 11,11,12,12-tetracarbonitrile groups in the title product result from a selective *exo*-facial addition of tetracyanoethylene to the heterotriene and cyclization of the latter.

Introduction. The Diels–Alder addition of tetracyanoethylene (TCE) to tricarbonyl[C,7,8,C-η-(1RS,4RS,7SR,8RS)-(methyl 3,7,8-trimethylenebicyclo[2.2.2]-oct-5-en-2-ylidene ketone)]iron (1) (Roulet, Tagliaferri, Vogel & Chapuis, 1981) leads with high selectivity to the title product (2), among four possible isomers. The absence of absorption in the $\nu(\text{C}=\text{O})$ region of the infrared spectrum of (2) suggested

that cyclization of the heterotriene moiety of (1) had occurred. As cyclization of such 1-acylbutadiene derivatives is very rare, we report here a structural characterization of the title complex.



Experimental. A solution of (1) (0.11 g) and TCE (0.5 g) in acetone (10 cm³) was stirred at 323 K for 4 d under Ar. Column chromatography followed by high performance liquid chromatography (HPLC) (30 × 0.8 cm column, 10 μm SiO₂, hexane/AcOEt 9:1, 3 cm³ min⁻¹) and recrystallization from hexane/AcOEt gave (2) with 80% selectivity.

D_m by flotation in aqueous ZnI₂ solutions. Crystal 0.40 × 0.24 × 0.12 mm mounted on Syntex P2₁ diffractometer. Nb-filtered Mo Kα radiation; unit-cell dimensions from exact goniometer settings of 15 reflections, 15 ≤ 2θ ≤ 30°; θ–2θ scans, background from scan profile interpretation (Blessing, Coppens & Becker, 1974; Schwarzenbach, 1977); [(sinθ)/λ]_{max} = 0.54 Å⁻¹; 2725 unique reflections; 1627 with *I* > 3σ(*I*), 0 ≤ *h* ≤ 9, 0 ≤ *k* ≤ 13, -20 ≤ *l* ≤ 19; 3 intensity standards checked every 70 reflections showed no decay over 95 h of X-ray exposure; Lorentz, polarization and absorption corrections applied, transmission factors 0.84–0.93; structure solved by direct methods (Main *et al.*, 1980), 9 of 14 H atoms found in difference Fourier map, positions of remaining 5 H atoms calculated; coordinates, anisotropic temperature factors and scale factor refined for heavier atoms; H atoms refined isotropically; *R* = 0.039, *wR* = 0.033, *w* = 1/σ²(|*F_o*|); *S* = 2.16; max. and min. Δρ in final difference Fourier map 0.41 and -0.38 e Å⁻³, respectively; max. Δ/σ in final least-squares cycle 0.45; atomic scattering factors and *f*', *f*'' values from *International Tables for X-ray Crystallography* (1974). All calculations performed with XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on a Cyber 170–855 computer.

Discussion. The positional parameters and equivalent isotropic thermal parameters are given in Table 1,* while selected interatomic distances and angles are listed in Table 2. Fig. 1 depicts the molecule and defines the atomic labelling scheme.

* Lists of structure amplitudes, anisotropic thermal parameters and atomic parameters for the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42053 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *List of atomic parameters*

The equivalent isotropic thermal parameter is defined by $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> (Å ²)
Fe	0.66507 (8)	0.23225 (5)	0.50907 (3)	0.0487 (2)
C(1)	1.2356 (5)	0.0853 (3)	0.7330 (2)	0.037 (2)
C(2)	1.2204 (5)	0.1165 (3)	0.6553 (2)	0.038 (2)
C(3)	1.1058 (5)	0.1794 (3)	0.6344 (2)	0.030 (2)
C(4)	1.0389 (5)	0.2187 (3)	0.5616 (2)	0.037 (2)
C(5)	1.0254 (5)	0.3348 (3)	0.5684 (2)	0.041 (2)
C(6)	0.9404 (5)	0.3655 (4)	0.6174 (2)	0.039 (2)
C(7)	0.8748 (5)	0.2793 (4)	0.6587 (2)	0.037 (2)
C(8)	1.0147 (4)	0.2127 (3)	0.6934 (2)	0.029 (1)
C(9)	0.9630 (5)	0.1155 (3)	0.7312 (2)	0.039 (2)
O(10)	1.0906 (3)	0.0467 (2)	0.7510 (1)	0.041 (1)
C(11)	1.2636 (5)	0.1864 (3)	0.7802 (2)	0.035 (2)
C(12)	1.1319 (4)	0.2700 (3)	0.7511 (2)	0.032 (2)
C(13)	0.8757 (5)	0.1700 (3)	0.5538 (2)	0.034 (2)
C(14)	0.7871 (5)	0.2033 (3)	0.6071 (2)	0.034 (2)
C(15)	1.3568 (8)	0.0040 (5)	0.7534 (4)	0.057 (3)
C(16)	0.8082 (6)	0.1006 (4)	0.5016 (3)	0.049 (2)
C(17)	0.6344 (6)	0.1630 (5)	0.6057 (3)	0.049 (2)
C(18)	0.5107 (6)	0.1680 (4)	0.4579 (3)	0.062 (2)
C(19)	0.7486 (6)	0.3070 (4)	0.4439 (2)	0.059 (2)
C(20)	0.5696 (6)	0.3442 (4)	0.5372 (3)	0.064 (2)
C(21)	1.4233 (5)	0.2260 (3)	0.7772 (2)	0.038 (2)
C(22)	1.2486 (5)	0.1581 (3)	0.8556 (2)	0.043 (2)
C(23)	1.2081 (5)	0.3621 (4)	0.7224 (2)	0.040 (2)
C(24)	1.0487 (5)	0.3120 (3)	0.8094 (2)	0.041 (2)
O(1)	0.4126 (4)	0.1230 (3)	0.4254 (2)	0.093 (2)
O(2)	0.8014 (4)	0.3585 (3)	0.4030 (2)	0.086 (2)
O(3)	0.5074 (5)	0.0862 (3)	0.0588 (2)	0.096 (2)
N(1)	1.5484 (4)	0.2511 (3)	0.7741 (2)	0.057 (2)
N(2)	1.2382 (5)	0.1372 (3)	0.9129 (2)	0.069 (2)
N(3)	1.2740 (5)	0.4333 (3)	0.7066 (2)	0.063 (2)
N(4)	0.9857 (5)	0.3448 (3)	0.8532 (2)	0.076 (2)

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

A and *B* are the midpoints of bonds C(13)–C(16) and C(14)–C(17), respectively.

Fe–C(13)	2.076 (4)	C(4)–C(13)	1.533 (6)
C(14)	2.057 (4)	C(5)–C(6)	1.308 (6)
C(16)	2.111 (5)	C(6)–C(7)	1.503 (6)
C(17)	2.076 (6)	C(7)–C(8)	1.563 (6)
C(18)	1.760 (5)	C(14)	1.520 (6)
C(19)	1.780 (5)	C(8)–C(9)	1.532 (6)
C(20)	1.772 (6)	C(12)	1.581 (5)
C(1)–C(2)	1.513 (6)	C(9)–O(10)	1.429 (5)
C(11)	1.581 (6)	C(11)–C(12)	1.615 (5)
C(15)	1.498 (8)	C(13)–C(14)	1.401 (6)
O(10)	1.424 (5)	C(16)	1.407 (6)
C(2)–C(3)	1.305 (6)	C(14)–C(17)	1.415 (7)
C(3)–C(4)	1.515 (5)	<C–CN>	1.486 (8)
C(8)	1.500 (6)	<C–N>	1.131 (8)
C(4)–C(5)	1.505 (6)	<C–O>	1.174 (8)
C(1)–C(2)–C(3)	115.9 (4)	C(7)–C(8)–C(12)	115.8 (3)
C(11)–C(12)	107.5 (3)	C(14)–C(13)	112.6 (4)
O(10)–C(9)	113.2 (3)	C(17)	130.0 (4)
C(2)–C(1)–C(11)	108.6 (3)	C(8)–C(7)–C(14)	102.7 (3)
C(15)	114.5 (4)	C(9)–O(10)	111.8 (3)
O(10)	110.2 (3)	C(12)–C(11)	107.1 (3)
C(3)–C(4)	132.7 (4)	C(9)–C(8)–C(12)	104.9 (3)
C(8)	113.3 (3)	C(11)–C(1)–C(15)	111.9 (4)
C(3)–C(4)–C(5)	106.2 (3)	C(13)–C(14)–C(17)	117.4 (4)
C(13)	101.6 (3)	C(14)–C(13)–C(16)	118.8 (4)
C(8)–C(7)	106.9 (3)	O(10)–C(1)–C(11)	103.5 (3)
C(9)	108.6 (3)	C(15)	107.6 (4)
C(12)	107.3 (3)	C(18)–Fe–C(19)	102.4 (2)
C(4)–C(3)–C(8)	113.7 (3)	C(20)	101.4 (2)
C(5)–C(6)	114.6 (4)	C(19)–Fe–C(20)	90.5 (2)
C(13)–C(14)	112.3 (3)	A–Fe–C(18)	108.7 (2)
C(16)	128.9 (4)	A–Fe–C(19)	95.8 (2)
C(5)–C(4)–C(13)	109.5 (3)	A–Fe–B	63.5 (2)
C(6)–C(7)	114.9 (4)	B–Fe–C(18)	115.2 (2)
C(6)–C(7)–C(8)	107.6 (3)	B–Fe–C(20)	91.9 (2)
C(14)	109.4 (3)	<Fe–C–O>	177.1 (7)
C(7)–C(8)–C(9)	113.0 (3)	<C–C–N>	177 (3)

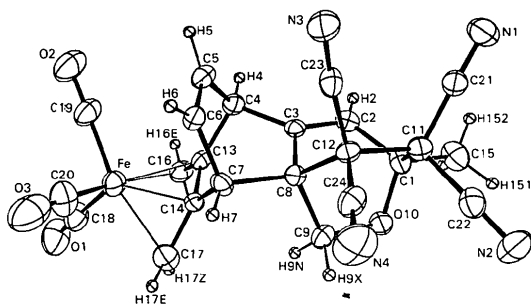


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule with 35% thermal ellipsoids.

The coordination polyhedron of the Fe atom is tetragonal pyramidal. Four coordination sites are occupied by two CO and the midpoints *A* and *B* of the diene bonds C(13)–C(16) and C(14)–C(17), respectively. The fifth site is occupied by the apical C(18)–O(1) group. The apical Fe–CO bond makes an angle of 7 (1)° with the normal to the basal plane defined by *A*–*B*–C(19)–C(20). The diene is perpendicular to the basal plane and the Fe atom lies 0.5 (1) Å over it. The angles subtended at the Fe atom by the coordination polyhedron are listed in Table 2, and are comparable to those already discussed for analogous (exocyclic 1,3-diene)Fe(CO)₃ complexes (Pinkerton, Chapuis, Vogel, Hänisch, Narbel, Boschi & Roulet, 1979). The Fe atom is in an *exo* position with respect to the roof-shaped ligand, indicating that addition under Diels–Alder conditions does not cause epimerization at the

metal atom with respect to precursor (1) whose structure has been determined (Roulet *et al.*, 1981). Cyclization at C(10) is unambiguously confirmed. The position of the carbonitrile groups indicates that the Diels–Alder addition of TCE to (1) takes place with high *exo*-facial selectivity.

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The Structure of Tetramethylammonium μ_3 -Oxo-cyclo-tri- μ -bromo-tri- μ -formato-(*O,O'*)-tris(chloromolybdate)(3 *Mo–Mo*), [N(CH₃)₄][{MoBrCl(CHO₂)₃O}]

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Abstract. $M_r = 859.089$, triclinic, $P\bar{1}$, $a = 6.848$ (1), $b = 11.933$ (1), $c = 13.164$ (1) Å, $\alpha = 100.20$ (1), $\beta = 93.12$ (1), $\gamma = 101.14$ (1)°, $V = 1034.4$ (2) Å³, $Z = 2$, $D_m = 2.72$ (by flotation), $D_x = 2.76$ g cm⁻³, graphite-monochromated Mo $K\alpha$, $\lambda = 0.71073$ Å, μ

$= 79.102$ cm⁻¹, $F(000) = 804$, $T = 295$ K, final $R = 0.030$ for 3514 reflections. The crystal contains discrete cations and anions. The bond lengths and angles of the cation are normal. The mono-oxo-capped trinuclear Mo cluster anion consists of three Br atoms and HCO₂⁻

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