

The Structure of a Tetranuclear Metal Cluster with a Four-Coordinate Carbide Carbon Atom: Bis(benzyltrimethylammonium) μ_4 -Carbido-dodecacarbonyl-tetrahydro-tetraferate

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Abstract. $[\text{N}(\text{CH}_3)_3\text{CH}_2\text{C}_6\text{H}_5]_2[\text{Fe}_4(\mu_4\text{-C})(\text{CO})_{12}]$, orthorhombic, $P2_12_12_1$, $a = 11.184$ (1), $b = 17.554$ (3), $c = 18.373$ (3) Å, $V = 3607$ Å³, $Z = 4$. Data were collected on an automated four-circle diffractometer (Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.64$ mm⁻¹) at 295 K using a variable θ - 2θ scan. The structure was solved by direct methods using *MULTAN* and refined by least squares to $R(F) = 0.052$ for the 5215 reflections with $|F_o| \geq 5\sigma(F_o)$. The metal cluster has approximate C_{2v} symmetry with the carbide C atom located directly on a stretched edge of an otherwise tetrahedral Fe_4 group at 1.784 (7) and 1.820 (7) Å from the two Fe atoms between which it is interposed, and at 1.941 (7) and 1.980 (7) Å from the other two Fe atoms.

Introduction. The study was undertaken in preparation of a possible electron density study of this complex which exhibits bonding between a single C atom and a metal cluster, and serves as a model for a carbide C atom on a metal surface. Crystals were kindly supplied by M. A. Beno and J. M. Williams of Argonne National Laboratory. The nature of the counterion was unknown at the time of the analysis and was determined in the course of the structure analysis.

The crystal used for data collection has approximate dimensions of $0.21 \times 0.26 \times 0.29$ mm and showed the form $\{011\}$ and the faces $(11\bar{1})$ and $(\bar{1}\bar{1}1)$; $D_x = 1.61$, $D_m = 1.5$ Mg m⁻³.

Data were collected at 295 K by the θ - 2θ technique on a CAD-4 automated diffractometer. Background was corrected for by a modified Lehmann-Larsen technique as described elsewhere (Blessing, Coppens & Becker, 1974). The intensities of three standards were monitored at regular intervals and showed no deviations larger than 2.4%, the average deviation being 0.7%. 11 405 independent intensity measurements were made and reflections with identical indices were averaged yielding 11 123 observations. 6575 observations with $|F_{\text{obs}}^2| \geq \sigma(F_{\text{obs}}^2)$ were used in the least-squares refinement. The positions of the four Fe atoms and the carbide C atom were determined with *MULTAN*, while the remaining atoms were located

from subsequently calculated difference maps. The structure was refined using the program *LINEX77*, including an isotropic-extinction parameter (Becker & Coppens, 1975); the largest reduction in intensity due to extinction was 21%. Final R factors are $R(F) = 8.5\%$, $R_w(F) = 5.9\%$ for all reflections and $R(F) = 5.2\%$, $R_w(F) = 5.2\%$ for 5215 reflections with $|F_o| \geq 5\sigma(F_o)$ with weights $w = 1/\sigma^2(F_o)$, where $\sigma^2(F_o)$ is derived from the expressions $\sigma^2(F_o^2) = 0.01F_o^2 + \sigma^2$ (counting) and $\sigma^2(F_o) = [(F_o^2)^2 + \sigma^2(F_o^2)/2]^{1/2} - |F_o^2|$. Final positional and thermal parameters are given in Table 1.* The final R factors for the rejected enantiomorphic structure are $R(F) = 8.9\%$, $R_w(F) = 6.3\%$ for all reflections and $R(F) = 5.6\%$ and $R_w(F) = 5.7\%$ for reflections with $|F_o| \geq 5\sigma(F_o)$.

Discussion. Fig. 1 shows the numbering scheme of the atoms, while the bond lengths in the Fe_4C cluster are given in Fig. 2. Other bond lengths and angles are listed in Tables 2 and 3. Three other relevant structure determinations have been completed. The first two by Beno, Williams, Tachikawa & Muetterties (1980, 1981) are an X-ray and a neutron study of the neutral diprotonated cluster in which one H atom bridges the tetrahedron edge opposite the C atom, while the second H atom is attached to the C and one of the Fe atoms. The third structure determination of a monohydrate of the tetraammonium zinc salt of the dianion was performed at the same time as the present work was in progress (Davis, Beno, Williams, Zimmie, Tachikawa & Muetterties, 1981). The cluster in the tetraammonium zinc salt has a crystallographic mirror plane unlike the structure reported here. Comparison of the bond lengths (Table 2) shows small differences between the two dianions especially with regard to the Fe-Fe distances which differ by about 0.03 Å. The Fe(1)-C(1)-Fe(4) angle is found to be 176.3 (4)°

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36134 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates (×10⁴, for Fe ×10⁵) and equivalent isotropic parameters (Å² × 10³, for Fe × 10⁴)

	x	y	z	U _{eq} †
Fe(1)	14965 (8)	2599 (6)	-31330 (6)	369 (6)
Fe(2)	34108 (9)	-5947 (6)	-33206 (5)	343 (6)
Fe(3)	31286 (9)	936 (6)	-21213 (5)	352 (7)
Fe(4)	46567 (8)	6522 (6)	-30890 (5)	336 (6)
C(1)	3050 (6)	486 (3)	-3107 (3)	31 (3)
C(11)	1201 (6)	487 (4)	-4064 (5)	44 (5)
O(11)	1019 (5)	633 (4)	-4654 (3)	68 (4)
C(12)	779 (7)	994 (5)	-2667 (4)	49 (5)
O(12)	300 (6)	1484 (4)	-2352 (4)	76 (5)
C(13)	406 (7)	-474 (5)	-2994 (5)	51 (5)
O(13)	302 (6)	4058 (4)	-2076 (4)	79 (5)
C(21)	3269 (6)	-632 (4)	-4270 (4)	37 (4)
O(21)	3186 (5)	-685 (4)	-4897 (3)	68 (5)
C(22)	4820 (8)	-1013 (4)	-3248 (5)	51 (6)
O(22)	5740 (5)	-1350 (3)	-3225 (4)	69 (5)
C(23)	2593 (7)	-1413 (5)	-3026 (4)	50 (6)
O(23)	2104 (6)	-1957 (3)	-2864 (3)	75 (5)
C(31)	3000 (7)	942 (5)	-1625 (4)	44 (5)
O(31)	2935 (6)	1517 (4)	-1306 (3)	70 (4)
C(32)	1989 (7)	-430 (4)	-1685 (4)	44 (5)
O(32)	1252 (5)	-743 (4)	-1360 (3)	68 (5)
C(33)	4356 (7)	-365 (5)	-1708 (4)	50 (6)
O(33)	5131 (6)	-695 (4)	-1430 (3)	86 (6)
C(41)	4879 (7)	940 (4)	-4007 (5)	45 (6)
O(41)	4985 (6)	1140 (4)	-4599 (3)	70 (5)
C(42)	4866 (6)	1547 (5)	-2690 (4)	55 (5)
O(42)	5031 (6)	2141 (4)	-2431 (4)	80 (5)
C(43)	3866 (7)	-4731 (5)	-2143 (4)	49 (5)
O(43)	2934 (4)	5051 (3)	-2287 (3)	67 (5)
C(51)	3082 (9)	-3967 (5)	-4015 (5)	60 (6)
C(52)	1911 (10)	-4137 (5)	-3793 (6)	72 (7)
C(53)	1052 (9)	-4357 (6)	-4310 (7)	79 (10)
C(54)	3646 (9)	4394 (6)	-47 (7)	78 (10)
C(55)	2482 (10)	4211 (5)	-265 (5)	74 (9)
C(56)	3406 (8)	-3984 (4)	-4761 (4)	54 (6)
C(57)	4646 (7)	-3816 (4)	-4993 (5)	48 (6)
N(58)	145 (6)	2966 (4)	-160 (4)	48 (4)
C(59)	4660 (8)	-2485 (5)	-4483 (4)	52 (5)
C(510)	951 (9)	2694 (6)	-760 (5)	68 (8)
C(511)	1149 (8)	-2091 (5)	-4594 (6)	66 (7)
C(61)	2664 (9)	-2312 (5)	-407 (5)	64 (8)
C(62)	2752 (10)	-2450 (6)	-1159 (5)	69 (8)
C(63)	2287 (8)	-3119 (6)	-1457 (5)	55 (6)
C(64)	1739 (8)	-3644 (6)	-1000 (5)	64 (7)
C(65)	1631 (7)	-3509 (5)	-256 (5)	56 (6)
C(66)	2885 (8)	2847 (5)	-4952 (5)	55 (6)
C(67)	3005 (7)	2692 (5)	-4142 (4)	51 (6)
N(68)	1973 (5)	3011 (3)	-3688 (3)	38 (3)
C(69)	1861 (7)	3862 (4)	-3775 (4)	32 (5)
C(610)	2244 (8)	2818 (5)	-2908 (4)	55 (6)
C(611)	808 (7)	2654 (4)	-3898 (5)	47 (5)

$$\dagger U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

compared with 177.6 (5)° in the tetraammonium zinc salt and 170.5 (1), 170.8 (1)° for the two independent clusters in the unit cell of the neutral complex. The C atom is displaced slightly outward from the center of the tetrahedron.

The apical Fe—C distances in the dianion average 1.80 Å, which is significantly shorter than the H-

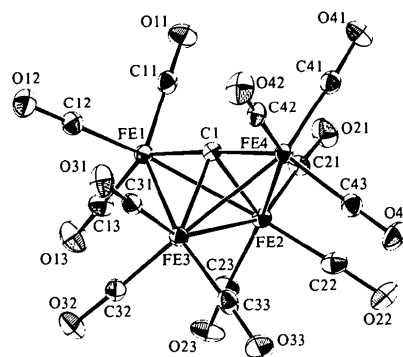


Fig. 1. ORTEP drawing (Johnson, 1965) of [Fe₄(μ₄-C)(CO)₁₂]²⁻ with 20% probability ellipsoids, indicating numbering of atoms.

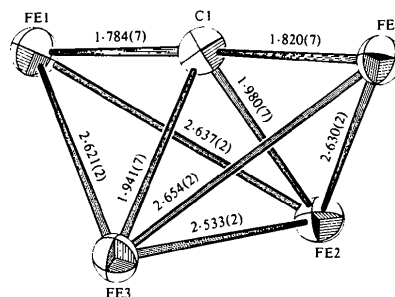


Fig. 2. As Fig. 1 for the Fe₄C group, indicating bond lengths (Å).

Table 2. Comparison of bond lengths (Å) in the Fe₄C group

	(I)*	(II)*	(III)*†
Fe(1)—Fe(2)	2.637 (2)	2.637 (1)	2.6188 (9)
Fe(1)—Fe(3)	2.621 (2)	—	2.6130 (9)
Fe(4)—Fe(2)	2.630 (2)	2.653 (1)	2.6317 (8)
Fe(4)—Fe(3)	2.654 (2)	—	2.6305 (9)
Fe(2)—Fe(3)	2.533 (2)	2.534 (1)	2.6039 (8)
Fe(1)—C(1)	1.784 (7)	1.810 (7)	1.924 (5)
Fe(4)—C(1)	1.820 (7)	1.786 (7)	1.825 (5)
Fe(2)—C(1)	1.980 (7)	1.969 (5)	1.944 (5)
Fe(3)—C(1)	1.941 (7)	—	1.952 (5)

* (I) Present study; (II) Davis *et al.* (1981); (III) Beno, Williams, Tachikawa & Muettterties (1981).

† Average over two independent molecules.

bridged Fe—C distance in the methyldyne cluster and about equal to the non-bridged Fe—C distance in the latter cluster. Similarly, the Fe—Fe distance along the tetrahedral edge opposite the C atom (2.53 Å) is considerably shorter than the H-bridged distance in the neutral species (2.60 Å). All other Fe—Fe distances are very similar.

The dihedral angle δ between the two Fe-atom planes sharing the Fe—Fe edge opposite the C atom is 102.4° in this study, compared with 101.5° in the structure determined by Beno *et al.* (1980, 1981) and 110.6° in

Table 3. Bond angles (°) in the Fe₄C group (present study)

Fe(2)—Fe(1)—Fe(3)	57.59 (4)	C(1)—Fe(1)—Fe(2)	48.6 (2)
Fe(2)—Fe(4)—Fe(3)	57.29 (4)	C(1)—Fe(1)—Fe(3)	47.8 (2)
	<57.44>	C(1)—Fe(4)—Fe(2)	48.8 (2)
Fe(2)—Fe(1)—Fe(4)	46.77 (4)	C(1)—Fe(4)—Fe(3)	47.0 (2)
Fe(3)—Fe(1)—Fe(4)	47.32 (3)		<48.0>
Fe(2)—Fe(4)—Fe(1)	46.94 (3)	C(1)—Fe(2)—Fe(1)	42.6 (2)
Fe(3)—Fe(4)—Fe(1)	46.57 (3)	C(1)—Fe(2)—Fe(4)	43.7 (2)
	<46.90>	C(1)—Fe(3)—Fe(1)	42.9 (2)
Fe(1)—Fe(2)—Fe(3)	60.90 (4)	C(1)—Fe(3)—Fe(4)	43.3 (2)
Fe(4)—Fe(2)—Fe(3)	61.84 (4)		<43.1>
Fe(1)—Fe(3)—Fe(2)	61.51 (4)	C(1)—Fe(2)—Fe(3)	49.1 (2)
Fe(4)—Fe(3)—Fe(2)	60.87 (4)	C(1)—Fe(3)—Fe(2)	50.4 (2)
	<61.28>		<49.8>
Fe(1)—Fe(2)—Fe(4)	86.30 (5)	Fe(1)—C(1)—Fe(4)	176.3 (4)
Fe(1)—Fe(3)—Fe(4)	86.11 (5)		
	<86.21>	Fe(2)—C(1)—Fe(3)	80.5 (3)
		Fe(1)—C(1)—Fe(2)	88.8 (3)
		Fe(1)—C(1)—Fe(3)	89.4 (3)
		Fe(4)—C(1)—Fe(2)	87.5 (3)
		Fe(4)—C(1)—Fe(3)	89.7 (3)
			<88.8>

the neutral species. We thus conclude that the two anions are very similar, the largest differences being observed in the Fe—Fe distances.

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trans-Tetraaquabis(nicotinamide)cobalt(II) Dichloride Dihydrate

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Abstract. [Co(H₂O)₄(C₆H₆N₂O)₂]₂Cl₂·2H₂O, C₁₂H₂₀CoN₄O₆²⁺·2Cl⁻·2H₂O, *M_r* = 482.18, monoclinic, *P*2₁/*n*, *a* = 11.0895 (2), *b* = 13.2582 (3), *c* = 7.1124 (1) Å, β = 101.35 (1)°, *Z* = 2, *D_c* = 1.562 Mg m⁻³, μ(Mo Kα) = 1.140 mm⁻¹, *F*(000) = 498, final *R* = 0.041 for 2116 observed reflexions. The structure consists of *trans*-tetraaquabis(nicotinamide)cobalt(II) cations, chloride anions and water molecules forming a three-dimensional network. Hydrogen bonds are responsible for the structure building. The Co atom is at the center of a distorted octahedron with the four water molecules in equatorial positions. The nicotinamide

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molecules coordinate to Co through the N atoms of the pyridine rings which adopt an eclipsed configuration.

Introduction. The title compound has been used as starting material for the synthesis of a new Co complex containing nicotinamide and glutathione as ligands (Silió, 1978). This new compound presents a high biological activity as a glucose tolerance factor (GTF) and it has been postulated that its specific action is to facilitate the physiological action of insulin so that animals deprived of a GTF develop insulin-resistant diabetes (Silió, 1979).