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SYNTHESIS OF HETERONUCLEAR CARBONYL-CARBIDE CLUSTERS OF TRANSITION METALS VIA VERTEX REPLACEMENT IN A METAL POLYHEDRON. X-RAY CRYSTAL STRUCTURES OF THE BIMETALLIC TETRAGONAL-PYRAMIDAL $[Fe_4CoC(CO)_{14}]^-$ AND THE TRIMETALLIC OCTAHEDRAL $Fe_4CoRhC(CO)_{16}$ CLUSTERS *

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Summary

The successive degradation of the *closo*-octahedral iron carbonyl clusters with an interstitial C atom and addition of the metal carbonyl unit of different metal atoms to the resultant nido-tetragonal-pyramidal clusters lead to replacement at the vertex of octahedrons resulting in the bimetallic $[Fe_5CoC(CO)_{16}]^-$ (I) and $[Fe_4CoC(CO)_{14}]^-$ (II) anions as well as trimetallic $Fe_4CoRhC(CO)_{16}$ (III) and $[Fe_4CoPdC(CO)_{15}]^-$ (IV) clusters. An X-ray investigation of II and III revealed the nido-tetragonal-pyramidal cluster structure in II with the Co atom in the basal face and in III the octahedral cluster structure with a cis-arrangement of the Co and Rh heteroatoms. The Co atom in II and the Co and Rh atoms in III are disordered over the pairs of stereochemically equivalent vertices of the metal polyhedron inside the ordered ligand polyhedron.

Introduction

The easy degradation of the octahedral transition metal carbonyl clusters with an interstitial non-metal atom in solution under action of various factors (heating, oxidation, etc.) together with the possible subsequent addition of a lacking vertex to the *nido*-cluster formed by this procedure provides a route to the synthesis of heteronuclear clusters via vertex replacement in the metal polyhedron [1,2]. At

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present a number of bimetallic clusters with an interstitial carbon atom has been prepared by this method [1–5]. In particular, pyrolysis of the hexanuclear carbide-carbonyl $[Fe_6C(CO)_{16}]^{2-}$ cluster in diglyme leads to the pentanuclear dianion $[Fe_5C(CO)_{14}]^{2-}$ [2,3,], and this tetragonal-pyramidal cluster may be easily restored to an octahedron by treatment with some coordinatively unsaturated organometallics or complexes with readily dissociating ligands [3,4].

By the reaction of $[Fe_5C(CO)_{14}]^{2-}$ with $Co_2(CO)_8$ we have obtained the hexanuclear anion $[Fe_5CoC(CO)_{16}]^-$ (I), whose thermolysis in diglyme again leads to degradation of the metal framework and transformation to the pentanuclear anion $[Fe_4CoC(CO)_{14}]^-$ (II). The sequence of transformations corresponds to eq. 1.

$$[Fe_6C(CO)_{16}]^{2-} \xrightarrow[-Fe(CO)_5]{\Delta} [Fe_5C(CO)_{14}]^{2-} \xrightarrow{Co_2(CO)_8}$$

$$\underset{(I)}{[Fe_5CoC(CO)_{16}]^-} \xrightarrow[-Fe(CO)_5]{\Delta} \underset{(II)}{[Fe_4CoC(CO)_{14}]^-} \qquad (1)$$

An alternative way to II is direct interaction between $[Fe_6C(CO)_{16}]^{2-}$ and $CoCl_2$. This reaction is evidently more complicated and includes all the above-mentioned stages: (a) thermal degradation of the initial cluster (facilitated by the parallel reduction of $CoCl_2$), (b) Co addition at the vacant vertex site in the intermediate pentanuclear cluster and (c) thermolysis of the hexanuclear iron-cobalt monoanion.

The heterometallic cluster II can undergo further addition at the lacking vertex producing clusters with three different metal atoms in the octahedron. Thus, the reaction of II and $[Rh(CO)_2Cl]_2$ gives the neutral cluster $Fe_4CoRhC(CO)_{16}$ (III):

$$\underset{(II)}{[Fe_4CoC(CO)_{14}]^-} \xrightarrow{[Rh(CO)_2Cl]_2} \underset{(III)}{Fe_4CoRhC(CO)_{16}}$$

Similarly, II with $[(\eta^3\text{-}C_3H_5)PdCl]_2$ forms the Fe,Co,Pd cluster:

$$\underset{(II)}{[Fe_4CoC(CO)_{14}]^-} \xrightarrow{(C_3H_5)PdCl_2} \underset{(IV)}{[Fe_4CoPdC(CO)_{15}]^-}$$

Successive replacement of two Fe atoms by Co and Rh (Pd) atoms in the octahedron is accomplished in accordance with Wade's rule [6].

The structure of polyheteronuclear clusters is evidently controlled by the location of the most labile vertex in the monosubstituted octahedron. The removal of trans or cis vertices therefore creates a possibility of preparation for clusters with isomeric metal frameworks.

In continuation of our investigation of heteronuclear clusters, we now report a new synthetic route to octahedral clusters with two or three "hetero" vertices. The structures of the key pentanuclear product of vertex abstraction II and trimetallic *closo*-octahedral cluster III were established by X-ray studies.

Experimental

$[Fe_5C(CO)_{14}]^{2-}$, $[Fe_6C(CO)_{16}]^{2-}$, $[Rh(CO)_2Cl]_2$ and $[(C_3H_5)PdCl]_2$ were obtained by the known methods. Commercial iron pentacarbonyl and cobalt chloride hexahydrate were used without further purification. Tetrahydrofuran (THF) and diglyme were purified by distillation with sodium benzophenone ketyl. All other solvents were of grades "chemically pure" or "spectroscopically pure". All manipulations in the preparation and purification of clusters were carried out under argon. IR spectra were measured on "Specord IR-75" spectrometer.

Synthesis of $Et_4N[Fe_5CoC(CO)_{16}]$ (I). $Fe(CO)_5$ (0.4 ml, 3 mmol) in 50 ml of diglyme was treated with sodium amalgam. The diglyme solution was mixed with 1.2 ml (9 mmol) of $Fe(CO)_5$ in a four-necked flask and stirred at 150–160°C until appearance of the stable dark brown colour of the solution (usually after 5–6 h). The solution was cooled to 20°C, 1.5 g (5.5 mmol) of $Co_2(CO)_8$ was added and the mixture was stirred for 1.5 h at 50°C. After cooling the dark purple solution was filtered and the threefold excess of hexane was added. The solution was decanted, the dark oily residue washed with 50 ml of hexane and extracted with 150 ml of water. The aqueous extract was mixed with the solution of 6 g Et_4NCl in 100 ml of water. The deep purple precipitate was filtered off, washed with water (3 times with 30 ml) and dried in vacuo at 20°C, yield 50%. Cluster I was recrystallized from CH_2Cl_2. Found: C, 32.22; H, 2.76; N, 1.81; Co, 6.92; Fe, 29.53. $Fe_5CoC_{25}H_{20}NO_{16}$ calcd.: C, 32.29; H, 2.14; N, 1.50; Co, 6.35; Fe, 30.13%. IR (THF, ν(CO) cm^{-1}): 2064 vw, 2002 vs 1984 m, sh, 1940 w, sh, 1226 w, broad.

Thermolysis of $Et_4N[Fe_5CoC(CO)_{16}]$. Of the initial cluster (0.5 g, 0.54 mmol) was stirred for 2 h at 100°C in diglyme (30 ml). The colour of the solution changed from dark claret to brown-red. After cooling to 10°C the solution was mixed with a fivefold excess of hexane. The precipitate was filtered off and washed with hexane. $Et_4N[Fe_4CoC(CO)_{14}]$ was recrystallized from $CH_2Cl_2/CHCl_3$ (2/1), yield 80%. Found: C, 33.65; H, 2.38; N, 1.58; Co, 6.93; Fe, 26.93. $C_{23}H_{20}Fe_4CoNO_{14}$ calcd.: C, 33.61; H, 2.45; N, 1.71; Co, 7.23; Fe, 27.48%. IR (THF, ν(CO) cm^{-1}): 2062 vw, 2016 s, 2000 vs, 1962 m, sh, 1982 w, sh, 1828 w.

Reaction of $(Et_4N)_2[Fe_6C(CO)_{16}]$ with $CoCl_2 \cdot 6H_2O$. Cobalt chloride hexahydrate (0.45 g, 1.9 mmol) was added to $(Et_4N)_2[Fe_6C(CO)_{16}]$ (1 g, 0.95 mmol) in diglyme (60 ml). The mixture was stirred for 7 h at 95°C, the colour gradually changed from dark claret to red-brown. The mixture was cooled to ca. 20°C, mixed with a fivefold excess of hexane, the precipitate was filtered off and washed with hexane. $Et_4N[Fe_4CoC(CO)_{14}]$ was recrystallized from $CH_2Cl_2/CHCl_3$ (2/1), yield ca. 70%.

Reaction of $Et_4N[Fe_4CoC(CO)_{14}]$ with $[Rh(CO)_2Cl]_2$. Equimolar quantities of reactants, 0.2 g and 0.095 g (0.24 mmol), respectively, were dissolved in CH_2Cl_2 (15 ml) and left for 12 h at 20°C. The solvent was removed in vacuo and the residue was extracted with pentane. From the pentane solution, concentrated in vacuo, black needle-like crystals of $Fe_4CoRhC(CO)_{16}$ were grown at −20°C. Yield 0.08 g (40%). Found: C, 23.88; Co, 6.43; Rh, 12.30; Fe, 25.90. $C_{17}Fe_4CoRhO_{16}$ calcd.: C, 24.11; Co, 6.97; Rh, 12.17; Fe, 26.47%. IR (hexane, ν(CO) cm^{-1}): 2098 vs, 2060 s, 2044 vs, 2030 s, 2022 m, 1995 w, 1982 w, 1955 w, sh, 1890 w, sh.

X-ray structural study of II and III

The $[Fe_4CoC(CO)_{14}]^-$ cluster was investigated in the form of its tetraethylammonium salt. X-ray studies of II and III were carried out with a Syntex $P2_1$ diffractometer (see Table 1). Atomic coordinates and thermal parameters are listed in Tables 2 (cluster II) and 3 (cluster III). Both structures were solved by the MULTAN programme and refined by full-matrix least squares in anisotropic approximation (Et groups in Et_4N^+ cation of II in isotropic approximation),

TABLE 1

CRYSTAL DATA FOR II AND III

	$Et_4N[Fe_4CoC(CO)_{14}]$ (II)	$Fe_4CoRhC(CO)_{16}$ (III)
a, Å	11.971(16)	8.946(5)
b, Å	14.007(16)	9.659(5)
c, Å	17.704(16)	15.445(7)
α, °	90	83.10(4)
β, °	90	87.22(4)
γ, °	90	63.23(4)
Space group	$Pnmn$	$P\bar{1}$
Z	4	2
T (°C)	−120	−120
Radiation	Mo-K_α	Mo-K_α
Scan	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$, °	50	54
Total reflections	1426	5127
Observed reflections ($I > 2\sigma(I)$)	1311	4481
Number of reflections in the final refinement	1255	3013
R	0.041	0.047
R_w	0.047	0.060

hydrogen atoms not found and absorption was neglected. Comparison of the thermal parameters of metal atoms in the cluster frameworks revealed the Co atom in II and the Co and Rh atoms in III disordered over stereochemically equivalent vertices of the metal polyhedrons. Taking into account this disorder mixed scattering factors were used.

On the basis of the refinement of the structures of II and III in anisotropic (metal atoms) or isotropic approximation the choice was made between two stoichiometries of II: $Et_4N[Fe_3Co_2C(CO)_{14}]$ (which contradicted Wade's rule [6]) and $Et_4N[Fe_4CoC(CO)_{14}]$ (which corresponded to this rule), in favour of the latter, and the heteroatoms were located in metal polyhedra. In II the Co atom was found to be disordered presumably over two M(2) and M(2′) positions (see Fig. 1). This structure is in agreement with the crystal structure of an isomorphous Rh analogue $Et_4N[Fe_4RhC(CO)_{14}]$, earlier investigated by Muetterties and co-workers [7]. As in the latter case, in crystals of II the Et_4N^+ cation is disordered with equal weights over two positions with $2/m$ crystallographic symmetry. Accordingly, each Et group in the cation also is disordered over two symmetry related positions (by m or i operations). Due to this disorder, the geometrical parameters of the Et_4N^+ cation are of low accuracy.

The lowest value of the discrepancy factor in III was found for disordering of the Rh atom over the M(1) and M(2) vertices with populations of 0.4 and 0.6, respectively, and of the Co atom over two *cis*-vertices M(3) and M(5) (their relative populations were not determined because of closeness of Co and Fe scattering factors). The same disorder is retained also in the corresponding non-centrisymmetric space group (Pn2n for II, P1 for III), confirming the correctness of choice of the centric space groups for II and III. Finally $R = 0.041$, $R_w = 0.047$ for II (1255

(Continued on p. 282)

TABLE 2

ATOM COORDINATES IN II ($\times 10^4$, for metal atoms $\times 10^5$) AND THEIR THERMAL PARAMETERS IN THE FORM $T = \exp[-1/4(B_{11}a^{*2}h^2 + \ldots + 2B_{23}b^*c^*kl)]$; M(2) = 1/2Fe + 1/2 Co

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	6047(13)	0	15739(8)	0.78(6)	1.82(7)	1.10(6)	0	-0.03(6)	0
Fe(2)	-6946(9)	-9060(8)	24785(6)	0.49(4)	2.13(5)	1.83(4)	-0.60(5)	0.30(4)	0.17(5)
Fe(3)	14975(9)	9432(9)	26806(6)	1.27(4)	2.39(5)	1.82(4)	-0.52(5)	-0.02(4)	-0.65(5)
O(1)	-1250(7)	0	508(5)	1.0(4)	10.9(8)	1.9(4)	0	-0.4(3)	0
O(2)	1793(10)	1512(8)	787(4)	15.9(9)	13.4(8)	2.6(3)	-12.8(7)	-1.2(4)	1.5(4)
O(3)	-1425(5)	-2350(4)	1395(3)	3.2(3)	3.2(3)	3.1(3)	-1.0(3)	-0.3(3)	-0.8(2)
O(4)	-1538(6)	-1777(5)	3867(3)	5.2(4)	6.5(5)	3.0(3)	-2.6(4)	0.6(3)	1.6(3)
O(5)	-2896(7)	0	2145(5)	1.3(4)	3.5(4)	3.3(4)	0	-0.2(3)	0
O(6)	1009(5)	2951(5)	2357(5)	2.5(3)	2.3(3)	10.5(5)	0.3(3)	-0.8(3)	-1.9(4)
O(7)	1754(6)	1181(6)	4311(3)	6.4(4)	8.0(5)	2.1(3)	-3.5(4)	-0.0(3)	-2.0(3)
O(8)	3841(5)	1114(5)	2206(4)	1.5(2)	4.5(4)	6.0(4)	-0.4(3)	0.7(3)	-1.3(3)
N(1) [a]	0	1/2	0	0.7(6)	6.0(9)	1.9(6)	0	-0.1(5)	0
N(2) [a]	0	1/2	1/2	2.4(7)	4.3(9)	2.0(6)	0	-0.7(6)	0
C_{in}	410(9)	0	2678(6)	1.0(4)	2.3(5)	1.3(5)	0	-0.3(4)	0
C(1)	-557(10)	0	944(6)	1.4(5)	5.5(8)	1.2(5)	0	0.8(4)	0
C(2)	1335(9)	936(9)	1135(5)	5.6(6)	8.1(7)	1.4(3)	-4.6(6)	0.3(4)	-0.6(5)
C(3)	-1155(7)	-1787(6)	1821(5)	1.7(4)	2.3(4)	2.3(4)	0.0(3)	0.7(3)	0.7(3)
C(4)	-1223(7)	-1439(6)	3321(5)	1.9(4)	2.9(4)	2.9(4)	-1.1(4)	-0.4(3)	0.3(4)
C(5)	-1962(11)	0	2291(6)	3.0(6)	3.8(7)	1.7(5)	0	0.7(5)	0
C(6)	1119(7)	2152(7)	2480(6)	1.5(3)	3.2(5)	5.4(5)	0.3(3)	-1.2(4)	-1.4(5)
C(7)	1673(8)	1108(7)	3677(5)	3.0(5)	4.1(6)	4.1(5)	-2.6(4)	-0.4(4)	-1.1(4)
C(8)	2935(7)	1042(6)	2410(4)	2.4(4)	2.0(4)	2.5(3)	0.0(3)	-0.6(3)	-0.9(3)
C(1')	309(22)	1/2	-869(14)	3.0(5) [b]					
C(2')	-830(19)	5340(15)	-1313(12)	5.8(6)					
C(3')	787(26)	4171(24)	-131(17)	8.4(8)					
C(4')	655(20)	3269(16)	183(12)	5.1(5)					
C(5')	1152(41)	1/2	332(26)	9(1)					
C(6')	1048(13)	4280(11)	5089(8)	1.6(3)					
C(7')	-64(14)	4525(11)	5736(9)	2.1(3)					
C(8')	1112(9)	3646(8)	4384(6)	4.8(2)					

[a] Nitrogen atom disordered between two positions. [b] Disordered carbon atoms of Et groups with isotropic B_{iso}.

TABLE 3

ATOM COORDINATES IN III ($\times 10^4$, for M $\times 10^5$) AND THEIR THERMAL PARAMETERS IN THE FORM $T = \exp[-1/4(B_{11}a^{\star 2}h^2 + \ldots + 2B_{23}b^\star c^\star kl)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M(1)	27011(9)	36918(8)	73813(5)	3.08(3)	1.20(3)	2.53(3)	−1.42(3)	0.85(3)	−0.61(2)
M(2)	25369(10)	16694(9)	62673(6)	2.42(4)	2.02(4)	3.61(4)	−1.64(3)	1.74(3)	−1.85(3)
M(3)	36931(11)	6344(10)	79519(6)	0.58(4)	0.77(4)	2.25(4)	−0.12(3)	−0.15(3)	−0.54(3)
M(4)	7497(12)	28738(11)	85232(6)	1.10(4)	0.98(4)	1.57(4)	−0.52(3)	0.29(3)	−0.44(3)
M(5)	−3276(12)	38384(10)	69178(7)	1.15(4)	0.56(4)	2.02(4)	−0.32(3)	−0.23(3)	0.04(3)
M(6)	8532(11)	7480(10)	75145(7)	1.02(4)	0.61(4)	2.09(5)	−0.55(3)	−0.05(3)	−0.18(3)
O(1)	3450(8)	5265(8)	8699(4)	4.7(3)	5.0(3)	4.1(3)	−3.5(3)	1.4(3)	−1.8(3)
O(2)	4691(7)	4665(6)	6073(4)	2.6(2)	2.4(2)	3.2(3)	−1.2(2)	0.8(2)	−0.6(2)
O(3)	−266(6)	6889(6)	6661(4)	1.9(2)	1.1(2)	6.5(4)	−0.7(2)	−0.2(2)	0.7(2)
O(4)	4399(9)	2583(7)	4880(4)	5.6(4)	4.1(3)	5.1(4)	−3.6(3)	2.4(3)	−2.1(3)
O(5)	1675(8)	121(7)	5006(4)	4.0(3)	4.2(3)	4.1(3)	−2.5(3)	0.4(2)	−1.1(3)
O(6)	6022(6)	−1139(6)	6617(4)	1.4(2)	2.6(3)	4.3(3)	0.7(2)	0.4(2)	−1.5(2)
O(7)	6456(7)	1196(8)	8478(4)	3.3(3)	6.3(4)	4.3(3)	−3.9(3)	−0.8(2)	0.7(3)
O(8)	4725(7)	−2326(7)	9057(4)	3.7(3)	2.8(3)	4.7(3)	−1.9(2)	−1.0(2)	0.6(2)
O(9)	2922(7)	1321(7)	10063(4)	2.4(2)	3.6(3)	2.2(2)	−0.9(2)	−0.3(2)	−0.5(2)
O(10)	−2327(7)	2996(7)	9365(4)	2.2(2)	4.0(3)	3.9(3)	−1.7(2)	1.1(2)	−0.7(2)
O(11)	−419(8)	6025(7)	9016(4)	4.3(3)	2.8(3)	5.4(4)	−1.8(2)	2.4(3)	−2.7(3)
O(12)	−3745(7)	5536(7)	7545(4)	1.7(2)	4.5(3)	4.6(3)	−1.1(2)	0.1(2)	−0.2(3)

O(13)	−1246(8)	4116(8)	5093(4)	4.0(3)	5.4(4)	2.9(3)	−2.4(3)	−0.7(2)	0.9(3)
O(14)	−2318(6)	1518(6)	6648(4)	1.8(2)	2.5(2)	3.4(3)	−1.2(2)	−0.3(2)	−0.5(2)
O(15)	2641(7)	−2306(5)	6857(4)	2.9(3)	0.9(2)	5.6(3)	−0.9(2)	0.6(2)	−1.3(2)
O(16)	173(7)	−796(6)	9134(4)	4.0(3)	3.0(3)	3.0(3)	−2.7(2)	−0.3(2)	1.2(2)
C_{in}	1688(8)	2251(7)	7423(4)	1.4(3)	0.6(3)	2.0(3)	−0.6(2)	0.0(2)	−0.3(2)
C(1)	3099(10)	4709(9)	8182(5)	3.0(4)	1.8(3)	2.4(4)	−0.8(3)	0.7(3)	0.2(3)
C(2)	3926(9)	4279(8)	6553(5)	2.4(3)	0.6(3)	2.5(3)	0.3(3)	−0.7(3)	−0.4(3)
C(3)	198(12)	5590(9)	6823(7)	4.4(5)	1.2(3)	4.9(5)	−0.3(3)	3.1(4)	−0.2(3)
C(4)	3687(11)	2269(9)	5441(6)	3.3(4)	2.2(4)	4.7(5)	−1.6(3)	0.8(3)	−1.9(3)
C(5)	2037(9)	677(9)	5509(5)	2.1(3)	1.5(3)	3.1(4)	−0.4(3)	0.4(3)	−0.2(3)
C(6)	4839(12)	−212(9)	6862(7)	3.7(4)	1.5(4)	7.1(6)	−1.3(3)	2.5(4)	−0.8(4)
C(7)	5331(10)	1079(9)	8248(5)	2.6(4)	3.0(4)	2.5(4)	−2.0(3)	0.2(3)	0.0(3)
C(8)	4327(9)	−1193(9)	8612(5)	2.1(3)	2.1(3)	2.6(4)	−1.3(3)	−0.6(3)	0.2(3)
C(9)	2167(9)	1836(8)	9432(5)	1.5(3)	1.9(3)	2.5(4)	−0.7(3)	0.7(3)	−0.8(3)
C(10)	−1113(9)	2886(8)	9029(5)	2.1(3)	1.8(3)	2.4(3)	−0.8(3)	−0.3(3)	−0.0(3)
C(11)	79(10)	4794(9)	8812(5)	2.3(3)	2.3(4)	3.4(4)	−1.2(3)	1.7(3)	−1.8(3)
C(12)	−2405(9)	4864(9)	7298(5)	1.7(3)	2.4(4)	3.5(4)	−1.2(3)	−0.1(3)	0.1(3)
C(13)	−796(9)	3969(9)	5798(5)	2.0(3)	2.7(4)	2.8(4)	−1.4(3)	0.1(3)	0.3(3)
C(14)	−1119(9)	1324(8)	6985(5)	1.8(3)	0.9(3)	2.4(3)	−0.7(2)	0.3(3)	−0.3(2)
C(15)	1953(9)	−1106(8)	7094(6)	1.7(3)	1.7(3)	3.8(4)	−1.2(3)	0.0(3)	−0.1(3)
C(16)	414(9)	−155(8)	8513(6)	1.7(3)	1.6(3)	3.8(4)	−0.9(3)	−0.8(3)	−0.3(3)

[a] M(1) = 0.6Rh + 0.4Fe, M(2) = 0.4Rh + 0.6Fe, M(3) and M(5) = 0.5Co + 0.5Fe, M(4) and M(6) = Fe.

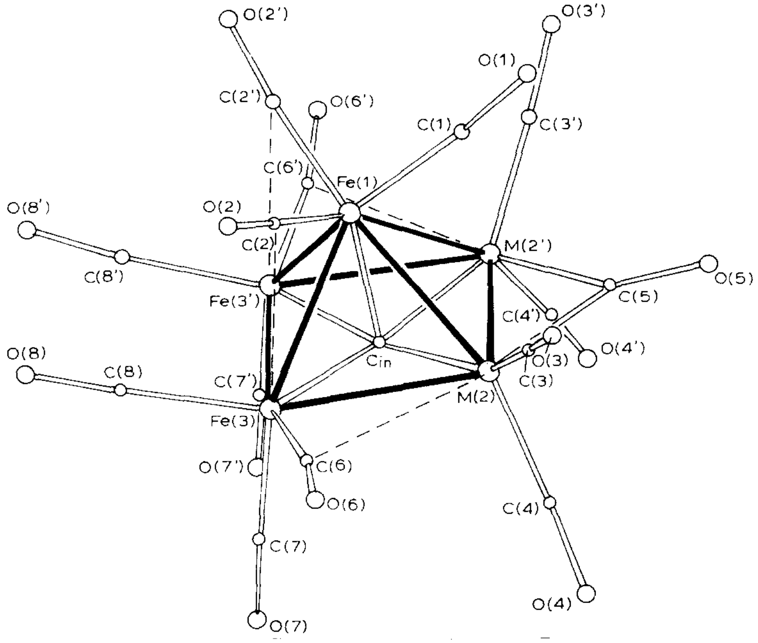

Fig. 1. Structure of II (the Co atom is disordered over M(2) and M(2') positions with equal weights).

unique reflections with $I > 2\sigma(I)$, $0.12 < \sin\theta/\lambda < 0.58$) and $R = 0.047$, $R_w = 0.060$ for III (3013 unique reflections with $I > 5\sigma(I)$, $0.10 < \sin\sigma/\lambda < 0.55$). All calculations were carried out with an Eclipse S/200 computer using the INEXTL [8] programmes.

Structure of II and III

The structure of anion II is shown in Fig. 1, the bond lengths are listed in Table 4. The *nido*-cluster II represents a slightly distorted tetragonal pyramid with the Co atom in the basal plane. The cluster occupies a special position on the crystallographic mirror plane, passing through Fe(1) (apical vertex of the pyramid), C(1),

TABLE 4

BOND LENGTHS d(Å) IN II

Bond	d	Bond	d	Bond	d
Fe(1)–M(2) [a]	2.568(2)	M(2)–C(4)	1.783(8)	O(1)–C(1)	1.13(1)
Fe(1)–Fe(3)	2.594(2)	M(2)–C(5)	2.01(1)	O(2)–C(2)	1.15(2)
Fe(1)–C_{in}	1.97(1)	M(2)–C(6)	2.785(9)	O(3)–C(3)	1.137(9)
Fe(1)–C(1)	1.78(1)	Fe(3)–Fe(3')	2.642(2)	O(4)–C(4)	1.14(1)
Fe(1)–C(2)	1.76(1)	Fe(3)–C_{in}	1.855(7)	O(5)–C(5)	1.15(2)
M(2)–M(2')	2.538(2)	Fe(3)–C(2)	2.743(8)	O(6)–C(6)	1.15(1)
M(2)–Fe(3)	2.649(2)	Fe(3)–C(6)	1.788(9)	O(7)–C(7)	1.13(1)
M(2)–C_{in}	1.866(8)	Fe(3)–C(7)	1.792(9)	O(8)–C(8)	1.149(9)
M(2)–C(3)	1.784(8)	Fe(3)–C(8)	1.792(8)		

[a] See footnote to Table 2.

O(1), C(5), O(5) and C_{in} atoms. The Co atom is disordered by this mirror plane over the M(2) and M(2′) positions with equal weights. The average bond distances Fe–Fe and Fe–(Co,Fe) in II are 2.618 and 2.609 Å, respectively, the M(2)–M(2′) basal edge linking two positions of the Co atom is the shortest (2.538(2) Å) in the polyhedron. The carbide C_{in} atom is displaced from the basal plane of the pyramid to the opposite side from the apical Fe(1) atom by 0.17 Å. Its distances to the vertices of the metal polyhedron are: C_{in}–Fe(1) 1.97(1), C_{in}–Fe(3) 1.855(7), C_{in}–M(2) 1.866(8) Å. The corresponding distances in the earlier investigated octahedral cobalt cluster $[Co_6C(CO)_{14}]^-$ with the interstitial carbide atom are: Co–Co 2.64 Å (averaged over all edges excluding one elongated to 2.96 Å), Co–C_{in} 1.88 (av.) [9]. However, it is noteworthy, that the $[Co_6C(CO)_{14}]^-$ cluster has 87 valence electrons, i.e. according to Wade's rule it is "electron-excessive" and exhibits the substantial distortions in the octahedral moiety, interpreted by the authors [9] as a result of discrepancy between the small size of the cluster cavity and the covalent radius of carbon atom. The geometrical characteristics of the Rh-analog of II, viz. $[Fe_4RhC(CO)_{14}]^-$ (Fe–Fe 2.616, C_{in}–Fe 1.980 (apical) and 1.868 Å (basal), the deviation of C_{in} from the basal plane outwards the apex 0.19 Å) are close to those found in II. In the first structurally studied tetragonal-pyramidal $Fe_5C(CO)_{15}$ cluster the average distances are: Fe–Fe 2.64, C_{in}–Fe 1.96 (apex) and 1.89 Å (base) [10].

Interionic distances in the crystal of II correspond to normal van der Waals radii. The carbonyl ligand envelope of the $Fe_4Co(C)$ polyhedron includes 9 terminal CO groups (av. Fe–C and (Fe,Co)–C distances are 1.78(1) Å), one μ_2-bridging, which lies in the mirror plane (M(2)–C(5) 2.01(1) Å), and four weakly semibridging CO ligands (C(2)O(2), C(6)O(6) and related by the mirror plane), av. Fe–C 1.78(1), Fe(3)–C(2) 2.743(8), M(2)–C(6) 2.785(9) Å; bond angles Fe–C–O of 174(1) and 171.8(8)° are slightly decreased as compared with the values for the terminal CO ligands in II 175.8–178.5°. In accordance with the idea of minimization of interligand repulsion the CO shell is roughly spherical (Fig. 2, the vertices of the ligand polyhedron correspond to positions of carbon atoms in CO's). However, in contrast with more symmetrical cluster frameworks, the ligand envelope does not correspond to any of the most energetically favourable configurations, calculated by Johnson and Benfield [11]. The ligand polyhedron in II may be approximately stratified into layers as 3/7/4 (in terms of ref. 11). The most close configuration has the 15-vertex ligand polyhedron in $Fe_5C(CO)_{15}$ (3/7/5 in the same notation). As in all other

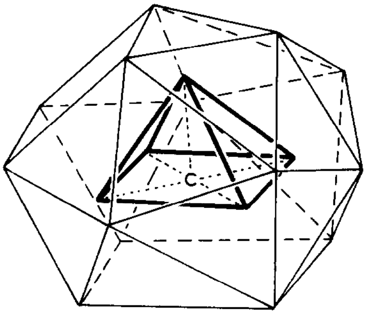

Fig. 2. The ligand polyhedron in II (the vertices correspond to the positions of C atoms of carbonyl ligands).

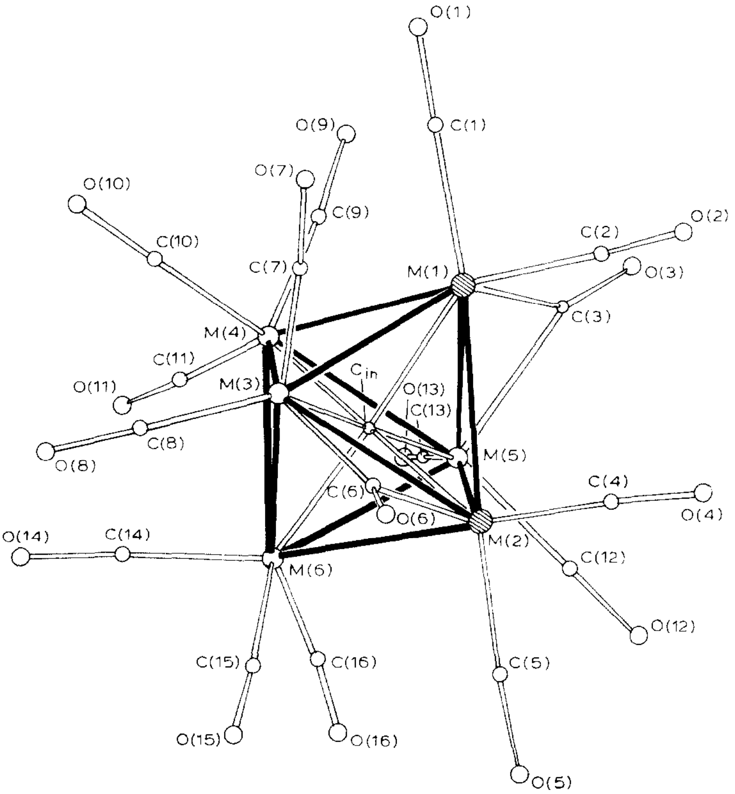

Fig. 3. Molecule II (the Rh atom is disordered over M(1) and M(2) vertices with the 0.6 and 0.4 occupancies, the Co atom is disordered over M(3) and M(5) vertices).

tetragonal-pyramidal clusters, four CO ligands of the "lower" layer (farthest from the apical vertex) enclose a "hole" in the ligand envelope, i.e. the area of weak shielding of the cluster core (Fig. 1, ligands C(4)O(4), C(4′)O(4′), C(7)O(7) and C(7′)O(7′)). This "hole" makes the carbide C_{in} atom accessible to attack by a mononuclear ML_n intermediate with resulting formation of the $MFe_4Co(C)$ octahedron.

The non-charged cluster III (Fig. 3) form molecular crystals with the normal Van der Waals intermolecular interactions. Most important bond lengths in III are listed in Table 5. Both Rh and Co atoms in III are disordered over the M(1), M(2) and M(3), M(5) pairs of vertices, respectively. Thus in III metal heteroatoms are in cis-position to each other in agreement with the preferable cleavage of a *cis*-vertex in monosubstituted octahedron confirmed with the crystal structure of II.

Due to the disordering of metal atoms, the geometrical parameters of the metal polyhedron in III are mainly averaged values. The bond distance M(1)–M(2) (i.e. (Rh,Fe)–(Rh,Fe)) 2.809(1) Å is longer than the length of the basal edge (Rh,Fe)–(Rh,Fe) (2.779(2) Å) in the tetragonal-pyramidal $[Fe_4RhC(CO)_{14}]^-$ cluster [7], but slightly shorter than the Rh–Fe distance (2.823(1) Å) in the disordered octahedral $Fe_5RhC(CO)_{16}^-$ cluster [5]. The average distances C_{in}–(Rh,Fe) 1.959(8),

TABLE 5

BOND LENGTHS d(Å) IN III

Bond	d	Bond	d	Bond	d
M(1)–M(2) [a]	2.809(1)	M(3)–C(6)	1.99(1)	M(6)–C(16)	1.794(8)
M(1)–M(3)	2.716(1)	M(3)–C(7)	1.794(9)	O(1)–C(1)	1.14(1)
M(1)–M(4)	2.719(1)	M(3)–C(8)	1.788(8)	O(2)–C(2)	1.13(1)
M(1)–M(5)	2.773(1)	M(4)–M(5)	2.610(1)	O(3)–C(3)	1.129(9)
M(1)–C_{in}	1.967(7)	M(4)–M(6)	2.690(1)	O(4)–C(4)	1.14(1)
M(1)–C(1)	1.808(8)	M(4)–C_{in}	1.899(7)	O(5)–C(5)	1.13(1)
M(1)–C(2)	1.847(8)	M(4)–C(9)	1.808(8)	O(6)–C(6)	1.12(1)
M(1)–C(3)	2.286(9)	M(4)–C(10)	1.801(9)	O(7)–C(7)	1.14(1)
M(2)–M(3)	2.747(1)	M(4)–C(11)	1.780(8)	O(8)–C(8)	1.136(9)
M(2)–M(5)	2.718(1)	M(5)–M(6)	2.733(1)	O(9)–C(9)	1.139(9)
M(2)–M(6)	2.699(1)	M(5)–C_{in}	1.890(7)	O(10)–C(10)	1.15(1)
M(2)–C_{in}	1.951(7)	M(5)–C(3)	1.938(9)	O(11)–C(11)	1.144(9)
M(2)–C(4)	1.803(9)	M(5)–C(12)	1.776(9)	O(12)–C(12)	1.15(1)
M(2)–C(5)	1.788(8)	M(5)–C(13)	1.776(8)	O(13)–C(13)	1.15(1)
M(2)–C(6)	2.191(9)	M(6)–C_{in}	1.898(7)	O(14)–C(14)	1.14(1)
M(3)–M(4)	2.737(1)	M(6)–C(14)	1.800(8)	O(15)–C(15)	1.138(9)
M(3)–M(6)	2.612(2)	M(6)–C(15)	1.797(8)	O(16)–C(16)	1.14(1)
M(3)–C_{in}	1.907(7)				

[a] See the footnote for Table 3.

C_{in}–(Co,Fe) 1.899(9) and C_{in}–Fe 1.898(7) Å can be compared with the distances C_{in}–(Rh,Fe) 1.94, C_{av}–Fe 1.98 Å (av.) in $[Fe_4RhC(CO)_{14}]^-$ and C_{in}–(Co,Fe) 1.87, C_{in}–Fe 1.97 (av.) Å in II. The length of the M(4)–M(6) edge (2.690(1) Å), corresponding to the Fe–Fe bond, is equal, within accuracy limits, to the average Fe–Fe distance (2.695 Å) in the heteronuclear octahedral $Fe_5RhC(CO)_{16}^-$ cluster [5], and consideraby longer than the average Fe–Fe distance in $[Fe_4RhC(CO)_{14}]^-$

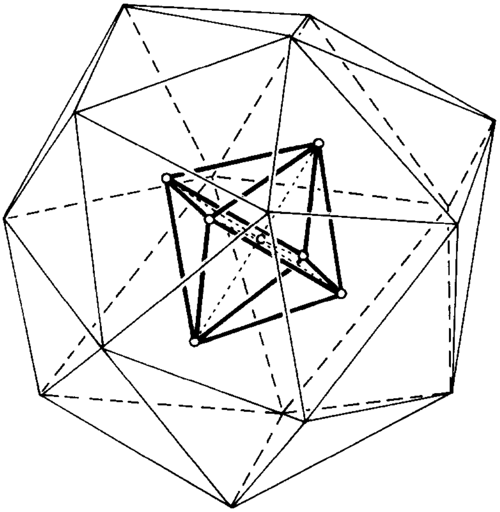

Fig. 4. Ligand polyhedron in III.

(2.616 Å) and in II (2.618 Å). This is probably a result of cluster expansion caused by the interstitial carbon atom (see [12]).

In the molecule III are 14 terminal and two μ_2-CO ligands. A general configuration of the ligand envelope (Fig. 4) corresponds to the minimum of interligand repulsion and (in Johnson and Benfield's notation) may be described as 1/6/3/(3)/3 [11]. The same configuration of the ligand polyhedron exists also in heteronuclear $[Fe_5RhC(CO)_{16}]^-$ (12 terminal and 4 semibridging μ_2-CO groups) and $[FeRh_5(CO)_{16}]^-$ clusters (12 terminal and 4 μ_3-CO groups) [5]. The relative orientation of the cluster core and the ligand shell as well as the character of disordering of metal atoms over octahedral vertices inside the ordered ligand polyhedron are, however, different in all three cases. It is noteworthy, that in the disordered metal clusters considered here, the metal heteroatoms are statistically distributed over the vertices with identical ligand environments.

Finally, it should be stressed that vertex cleavage with subsequent addition in octahedral carbide clusters open a possibility for the construction of multimetallic heteronuclear polyhedra. The next step along this path represents a very promising class of heterometallic clusters with four (or even more) different metal atoms in the octahedron. Among clusters of this type we are especially looking for compounds with an asymmetric metal core, which (with absence of dynamic processes in the metal framework) can exhibit chirality and other related interesting features.

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