Mixed Copper/Iron Clusters. The Preparation and Structure of the Large Planar Cluster Anions, $Cu_3Fe_3(CO)_{12}{}^{3-}$ and $Cu_5Fe_4(CO)_{16}{}^{3-}$

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Abstract: The reaction of a copper(I) halide with $Fe(CO)_4{}^{2-}$ in a 1:1 molar ratio yields the six-atom mixed copper/iron cluster anion $Cu_3Fe_3(CO)_{12}{}^{3-}$. Further addition of CuBr results in the conversion to a novel $Cu_5Fe_4(CO)_{16}{}^{3-}$ anion and ultimately to the $Cu_6Fe_4(CO)_{16}{}^{2-}$ species. The structure of the $Cu_3Fe_3(CO)_{12}{}^{3-}$ anion as its $(C_2H_5)_4N^+$ salt was determined by X-ray methods. Crystals were monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell with dimensions $a = 12.946$ (3) Å, $b = 18.894$ (4) Å, $c = 19.031$ (6) Å, $\beta = 93.91$ (2)°. The metal atoms and the carbonyl atoms were located by direct methods, and the remaining non-hydrogen atoms were located by alternate applications of difference Fourier and least-squares refinement techniques. The structure was refined to $R = 0.060$, $R_w = 0.071$ for 3291 observed reflections. The structure consists of a planar triangular close-packed array of metal atoms in which a triangular Cu_3 core is bridged on all three edges by an $Fe(CO)_4$ group. The structure of the $Cu_5Fe_4(CO)_{16}{}^{3-}$ anion was also solved as its $(C_2H_5)_4N^+$ salt. This complex crystallizes in the tetragonal space group $P4_2/mnn$ with $a = b = 13.553$ (3) Å and $c = 14.650$ (2) Å with $Z = 2$. All non-hydrogen atoms were located by direct methods and a refinement with anisotropic temperature factors led to values of R and R_w of 0.043 and 0.041, respectively, for 534 observed reflections. The structure of this complex is also planar with the metal atoms arranged in the form of a rhombus with $Fe(CO)_4$ groups located on each corner and the remaining positions filled with Cu atoms.

The reaction of phosphine-substituted copper(I) halides with the $Fe(CO)_4{}^{2-}$ anion has resulted in the synthesis of some interesting new mixed Cu/Fe complexes.[1] Depending on the nature of the phosphine ligands and the reaction conditions, one can obtain either a linear Cu–Fe–Cu triatomic complex or the novel $Cu_6Fe_4(CO)_{16}{}^{2-}$ cluster anion. The formation of the 10-metal atom cluster from mononuclear species takes place under very mild conditions suggesting that the reaction might proceed through a number of lower nuclearity complexes. This possibility prompted us to investigate these reactions in more detail. One facet of this was to study the reaction of unsubstituted copper(I) halides with $Fe(CO)_4{}^{2-}$ to determine if the presence of phosphine ligands was necessary for the formation of the large cluster anion. Very little work appears to have been conducted in this area although Hieber was able to prepare a complex with the composition $(NH_3)_4Cu_2Fe(CO)_4$ by adding CuCl to a solution of $Fe(CO)_5$ in concentrated aqueous NH_3.[2] Some related work on reactions of the $Co(CO)_4{}^-$ anion with Cu(I) halides has resulted in the formation of a trinuclear $Cu[Co(CO)_4]_2{}^-$ anion[3] and the interesting $[Cu\text{-}Co(CO)_4]_4$ eight-memberd ring complex.[4]

Results and Discussion

When an equimolar amount of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane is added to suspension of CuBr in THF, a smooth reaction takes place ultimately resulting in the isolation of a complex with the composition $NaCuFe(CO)_4\cdot(dioxane)_2$. Simple metathesis reactions with tetraalkylammonium halides can be used to convert the solvated sodium salt to the tetraalkylammonium derivatives which are somewhat air sensitive but otherwise stable yellow crystalline solids. The infrared spectra of these salts in solution display two strong broad bands in the CO stretching region at approximately 1930 and 1800 cm⁻¹.[1] The spectra are similar to those observed for the $Cu_6Fe_4(CO)_{16}{}^{2-}$ salts ($\nu_{CO} \sim 1970$, 1870 cm⁻¹) except for the shift to lower frequencies but are clearly not the type of spectra that would be predicted for simple $CuFe(CO)_4{}^-$ salts.

An X-ray crystal structure of the tetraethylammonium salt was carried out which revealed the anion to be a trimer, $Cu_3Fe_3(CO)_{12}{}^{3-}$. The six metal atoms are coplanar and arranged in the form of a triangle (see Figure 1 for an ORTEP view). The three copper atoms form an equilateral triangle and each edge is bridged by an $Fe(CO)_4$ group. The average Cu–Cu bond distance (2.60 Å) and Cu–Fe bond distance (2.42 Å) (Table I) are somewhat shorter than those observed in the $Cu_6Fe_4(CO)_{16}{}^{2-}$ cluster anion. The arrangement of the carbonyl groups about the iron atoms is intermediate between the "trigonal-bipyramidal" arrangement found for the $Cu_6Fe_4(CO)_{16}{}^{2-}$ anion and the flattened tetrahedral geometry characteristic of the $\{[(C_6H_5)_3P]_2Cu\}_2Fe(CO)_4$ complex. In each case three of the CO groups on each iron show a significant semibridging interaction with a copper atom. The overall structure of the $Cu_3Fe_3(CO)_{12}{}^{3-}$ species is very nearly identical with one of the large triangular faces of the $Cu_6Fe_4(CO)_{16}{}^{2-}$ cluster. This type of close-packed planar array of metal atoms is quite unusual for a six-atom transition-metal carbonyl cluster although a planar Os_6 complex[5] and the nearly planar Pt_3Fe_3[6] and Pt_3Ir_3 clusters[7] with similar triangular structures have been synthesized. With an electron count of 84, the $Cu_3Fe_3(CO)_{12}{}^{3-}$ complex is short of the 90 electrons predicted for a complex with this geometry such as $Os_6(CO)_{21}$, where the metal uses all nine valence orbitals for bonding.[8] In other cases, the metals may utilize only eight valence orbitals and clusters with lower electron counts such as the 86 electron $Pt_3Fe_3(CO)_{15}{}^{2-}$ anion can be rationalized.[9] Similar arguments can be made for the $Cu_3Fe_3(CO)_{12}{}^{3-}$ cluster. In the case of the Pt_3Fe_3 cluster the additional molecular orbital introduced by the three edge-bridging groups is occupied.[10] This antibonding orbital is presumably vacant in the 84-electron Cu_3Fe_3 cluster maximizing the Cu–Cu bonding interactions.

The structural relationship between the $Cu_3Fe_3(CO)_{12}{}^{3-}$ and $Cu_6Fe_4(CO)_{16}{}^{2-}$ complexes suggested that there may be a chemical relationship between these species also. Of particular interest was the possibility that the $Cu_3Fe_3(CO)_{12}{}^{3-}$ anion could serve as a building block for the formation of the larger cluster. We have found that the addition of 3 equiv of CuBr or CuCl and 1 equiv

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Table I. Bond Distances and Angles for Anion Atoms in $[(C_2H_5)_4N]_3Cu_3Fe_3(CO)_{12}$[a,b]

Bond Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Cu(1)	Cu(2)	2.613 (2)	Cu(2)	C(11)	2.44 (1)	Fe(3)	C(12)	1.74 (1)
Cu(1)	Cu(3)	2.582 (2)	Cu(3)	C(4)	2.23 (1)	Fe(3)	C(12)	1.75 (1)
Cu(1)	Fe(2)	2.409 (2)	Cu(3)	C(6)	2.43 (1)	C(1)	O(1)	1.15 (1)
Cu(1)	Fe(3)	2.421 (2)	Cu(3)	C(8)	2.25 (1)	C(2)	O(2)	1.18 (1)
Cu(2)	Cu(3)	2.610 (2)	Fe(1)	C(1)	1.74 (1)	C(3)	O(3)	1.17 (1)
Cu(2)	Fe(1)	2.415 (2)	Fe(1)	C(2)	1.75 (1)	C(4)	O(4)	1.16 (1)
Cu(2)	Fe(3)	2.404 (2)	Fe(1)	C(3)	1.74 (1)	C(5)	O(5)	1.18 (1)
Cu(3)	Fe(1)	2.437 (2)	Fe(1)	C(4)	1.79 (1)	C(6)	O(6)	1.20 (1)
Cu(3)	Fe(2)	2.442 (2)	Fe(2)	C(5)	1.71 (1)	C(7)	O(7)	1.20 (1)
Cu(1)	C(7)	2.20 (1)	Fe(2)	C(6)	1.73 (1)	C(8)	O(8)	1.17 (1)
Cu(1)	C(9)	2.36 (1)	Fe(2)	C(7)	1.72 (1)	C(9)	O(9)	1.14 (1)
Cu(1)	C(10)	2.33 (1)	Fe(2)	C(8)	1.75 (1)	C(10)	O(10)	1.14 (1)
Cu(2)	C(2)	2.27 (1)	Fe(3)	C(9)	1.78 (1)	C(11)	O(11)	1.16 (1)
Cu(2)	C(3)	2.30 (1)	Fe(3)	C(10)	1.78 (1)	C(12)	O(12)	1.16 (1)

Bond Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cu(2)	Cu(1)	Cu(3)	60.30 (5)	Cu(3)	Fe(1)	C(1)	160.6 (3)	Cu(1)	Fe(3)	C(9)	66.4 (3)
Cu(2)	Cu(1)	Fe(2)	118.77 (7)	Cu(3)	Fe(1)	C(2)	91.3 (4)	Cu(1)	Fe(3)	C(10)	65.3 (3)
Cu(2)	Cu(1)	Fe(3)	56.90 (5)	Cu(3)	Fe(1)	C(3)	86.5 (4)	Cu(1)	Fe(3)	C(11)	117.6 (4)
Cu(3)	Cu(1)	Fe(2)	58.47 (5)	Cu(3)	Fe(1)	C(4)	61.3 (3)	Cu(1)	Fe(3)	C(12)	135.2 (3)
Cu(3)	Cu(1)	Fe(3)	117.18 (7)	C(1)	Fe(1)	C(2)	102.0 (5)	Cu(2)	Fe(3)	C(9)	79.6 (3)
Fe(2)	Cu(1)	Fe(3)	175.23 (7)	C(1)	Fe(1)	C(3)	97.5 (5)	Cu(2)	Fe(3)	C(10)	82.8 (4)
Cu(1)	Cu(2)	Cu(3)	59.25 (4)	C(1)	Fe(1)	C(4)	100.0 (5)	Cu(2)	Fe(3)	C(11)	176.3 (4)
Cu(1)	Cu(2)	Fe(1)	117.12 (7)	C(2)	Fe(1)	C(3)	124.0 (5)	Cu(2)	Fe(3)	C(12)	69.8 (3)
Cu(1)	Cu(2)	Fe(3)	57.52 (5)	C(2)	Fe(1)	C(4)	113.5 (5)	C(9)	Fe(3)	C(10)	131.7 (5)
Cu(3)	Cu(2)	Fe(1)	57.87 (5)	C(3)	Fe(1)	C(4)	113.9 (5)	C(9)	Fe(3)	C(11)	99.8 (5)
Cu(3)	Cu(2)	Fe(3)	116.76 (7)	Cu(1)	Fe(2)	Cu(3)	64.30 (5)	C(9)	Fe(3)	C(12)	110.1 (5)
Fe(1)	Cu(2)	Fe(3)	174.26 (7)	Cu(1)	Fe(2)	C(5)	153.6 (4)	C(10)	Fe(3)	C(11)	100.2 (5)
Cu(1)	Cu(3)	Cu(2)	60.44 (5)	Cu(1)	Fe(2)	C(6)	80.1 (3)	C(10)	Fe(3)	C(12)	105.2 (4)
Cu(1)	Cu(3)	Fe(1)	117.49 (6)	Cu(1)	Fe(2)	C(7)	61.7 (4)	C(11)	Fe(3)	C(12)	107.1 (5)
Cu(1)	Cu(3)	Fe(2)	57.22 (5)	Cu(1)	Fe(2)	C(8)	101.3 (3)	Fe(1)	C(1)	O(1)	179 (1)
Cu(2)	Cu(3)	Fe(1)	57.06 (5)	Cu(3)	Fe(2)	C(5)	140.1 (4)	Fe(1)	C(2)	O(2)	172 (1)
Cu(2)	Cu(3)	Fe(2)	117.66 (7)	Cu(3)	Fe(2)	C(6)	68.8 (3)	Fe(1)	C(3)	O(3)	174 (1)
Fe(1)	Cu(3)	Fe(2)	174.53 (8)	Cu(3)	Fe(2)	C(7)	121.9 (3)	Fe(1)	C(4)	O(4)	169 (1)
Cu(2)	Fe(1)	Cu(3)	65.07 (5)	Cu(3)	Fe(2)	C(8)	62.3 (3)	Fe(2)	C(5)	O(5)	178 (1)
Cu(1)	Fe(2)	Cu(3)	64.30 (5)	C(5)	Fe(2)	C(6)	98.7 (5)	Fe(2)	C(6)	O(6)	173.7 (9)
Cu(1)	Fe(3)	Cu(2)	65.58 (5)	C(5)	Fe(2)	C(7)	97.6 (5)	Fe(2)	C(7)	O(7)	170.1 (9)
Cu(2)	Fe(1)	Cu(3)	65.07 (5)	C(5)	Fe(2)	C(8)	101.1 (5)	Fe(2)	C(8)	O(8)	170.9 (9)
Cu(2)	Fe(1)	C(1)	133.7 (4)	C(6)	Fe(2)	C(7)	119.2 (5)	Fe(3)	C(9)	O(9)	173 (1)
Cu(2)	Fe(1)	C(2)	63.8 (3)	C(6)	Fe(2)	C(8)	123.8 (5)	Fe(3)	C(10)	O(10)	173 (1)
Cu(2)	Fe(1)	C(3)	64.9 (3)	C(7)	Fe(2)	C(8)	109.5 (5)	Fe(3)	C(11)	O(11)	179 (1)
Cu(2)	Fe(1)	C(4)	126.2 (4)	Cu(1)	Fe(3)	Cu(2)	65.58 (5)	Fe(3)	C(12)	O(12)	174 (1)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

of $Na_2Fe(CO)_4$ to a solution of $Na_3Cu_3Fe_3(CO)_{12}$ does indeed lead to the formation of $Na_2Cu_6Fe_4(CO)_{16}$ in nearly quantitative yields (eq 1). Although this reaction appears to be a rational

$$Na_3Cu_3Fe_3(CO)_{12} + 3CuCl + Na_2Fe(CO)_4 \rightarrow Na_2Cu_6Fe_4(CO)_{16} + 3NaCl \quad (1)$$

synthesis of the larger cluster from the smaller one, a closer examination revealed that the process taking place is probably not so simple. We have found that the addition of CuBr or CuCl alone is sufficient to convert the Cu_3Fe_3 complex to the Cu_6Fe_4 cluster. If 1.5 equiv of CuBr or CuCl is added to a solution of $Na_3Cu_3Fe_3(CO)_{12}$ in THF, the conversion to $Na_2Cu_6Fe_4(CO)_{16}$ is rapid and quantitative (eq 2). In order for this reaction to take

$$4Na_3Cu_3Fe_3(CO)_{12} + 6CuCl \rightarrow 3Na_2Cu_6Fe_4(CO)_{16} + 6NaCl \quad (2)$$

place, some dissociation of the Cu_3Fe_3 complex, or some species derived from it, must occur since it is the only iron-containing species present and the formation of the Cu_6Fe_4 complex requires an additional iron atom. In this case it is clear that at least some of the Cu_3Fe_3 cluster must undergo partial or total fragmentation and that the Cu_6Fe_4 cluster is formed either completely from the new fragments or by the addition of the new fragments to undissociated Cu_3Fe_3 complex. The mechanism of this transformation is not known at this time. An examination of the NMR[9] and infrared spectra of both the Cu_3Fe_3 and Cu_6Fe_4 complexes indicates only one detectable species in solution. No detectable concentrations of $Fe(CO)_4^{2-}$ or other carbonyl species can be seen, although this does not rule out equilibria in which small concentrations of other species are formed.

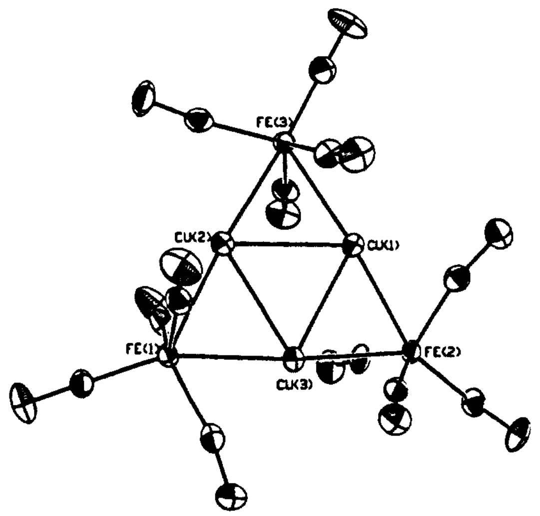

Figure 1. An ORTEP drawing of the $Cu_3Fe_3(CO)_{12}^{3-}$ anion viewed perpendicular to the plane containing the six metal atoms. Only the metal atoms are labeled for clarity.

Table II. Bond Distances and Angles for Anion Atoms in $[(C_2H_5)_4N]_3Cu_5Fe_4(CO)_{16}$^{a,b}

Bond Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Cu(1)	Cu(2)	2.527 (2)	Cu(1)	Fe(1)	2.426 (3)
Cu(1)	Cu(1″)^{c}	2.691 (4)	Cu(1)	Fe(2)	2.394 (3)
			Cu(2)	Fe(1)	2.491 (3)
Fe(1)	C(1)	1.73 (2)			
Fe(1)	C(2)	1.82 (2)	O(1)	C(1)	1.19 (2)
Fe(2)	C(3)	1.75 (2)	O(2)	C(2)	1.13 (2)
Fe(2)	C(4)	1.79 (2)	O(3)	C(3)	1.14 (2)
			O(4)	C(4)	1.16 (2)

Bond Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cu(2)	Cu(1)	Fe(1)	60.4 (1)	Cu(1)	Cu(2)	Fe(1)	57.8 (1)
Cu(2)	Cu(1)	Fe(2)	113.6 (1)	Cu(1)	Cu(2)	Cu(1′)^{c}	180.0 (–)^{d}
Fe(1)	Cu(1)	Fe(2)	174.0 (1)	Fe(1)	Cu(2)	Cu(1′)^{c}	122.2 (1)
Cu(2)	Cu(1)	Cu(1″)^{c}	57.8 (1)	Cu(1)	Cu(2)	Cu(1″)^{c}	64.4 (1)
Fe(1)	Cu(1)	Cu(1″)^{c}	118.2 (1)	Cu(1′)	Cu(2)	Cu(1″)^{c}	115.6 (1)
Fe(2)	Cu(1)	Cu(1″)^{c}	55.8 (1)	Fe(1)	Cu(2)	Fe(1′)^{c}	180.0 (–)^{d}
Cu(1)	Fe(1)	Cu(2)	61.8 (1)	Cu(1)	Fe(2)	C(3)	160.0 (6)
Cu(1)	Fe(1)	C(1)	168.2 (6)	Cu(1)	Fe(2)	C(4)	70.6 (4)
Cu(2)	Fe(1)	C(1)	129.9 (6)	C(3)	Fe(2)	C(4)	103.6 (3)
Cu(1)	Fe(1)	C(2)	80.2 (4)	Cu(1)	Fe(2)	Cu(1″)^{c}	68.4 (1)
Cu(2)	Fe(1)	C(2)	68.8 (2)	C(3)	Fe(2)	Cu(1″)^{c}	91.6 (5)
C(1)	Fe(1)	C(2)	103.4 (4)	C(3)	Fe(2)	C(3″)^{c}	108.3 (11)
Cu(1)	Fe(1)	Cu(1‴)^{c}	123.6 (1)	C(4)	Fe(2)	C(4‴)^{c}	132.8 (10)
C(1)	Fe(1)	Cu(1‴)^{c}	68.1 (6)				
C(1)	Fe(1)	C(1‴)^{c}	100.1 (11)	Fe(1)	C(1)	O(1)	173 (2)
C(2)	Fe(1)	C(2‴)^{c}	137.6 (4)	Fe(1)	C(2)	O(2)	172 (1)
				Fe(2)	C(3)	O(3)	178 (2)
				Fe(2)	C(4)	O(4)	173 (1)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with figure 3. [c] Primed atoms are related to nonprimed atoms by the symmetry operations listed in the figure caption for figure 3. [d] This is a symmetry-required value and is therefore listed without an estimated standard deviation.

An examination of the infrared spectra of solutions of $Na_3Cu_3Fe_3(CO)_{12}$ with added CuBr (Figure 2) shows that there is at least one intermediate species formed in the conversion to the Cu_6Fe_4 cluster. If one adds less than 0.75 equiv of CuBr to a solution of $Na_3Cu_3Fe_3(CO)_{12}$, two sets of peaks are observed in the infrared spectra, one set correpontding to the $Cu_3Fe_3(CO)_{12}^{3-}$ anion and another set with peaks at approximately 1950 and 1850 cm^{-1}. At a ratio of 0.75 equiv of CuBr to 1 equiv of $Na_3Cu_3Fe_3(CO)_{12}$, which corresponds to a composition $Na_3Cu_5Fe_4(CO)_{16}$, only the 1950- and 1850-cm^{-1} bands are observed. At ratios between 0.75:1 and 1.5:1 two sets of peaks are again seen corresponding to a mixture of the $Na_3Cu_5Fe_4(CO)_{16}$ and $Na_2Cu_6Fe_4(CO)_{16}$ complexes. The intermediate $Cu_5Fe_4(CO)_{16}^{3-}$ complex was isolated as a solvated sodium salt and converted to the tetraethylammonium derivative. The compositions of both were verified by elemental analyses.

The $Cu_5Fe_4(CO)_{16}^{3-}$ anion has a very unusual composition and although a few nine-atom carbonyl clusters are known, none of the observed arrangements for nine-atom clusters seemed to be likely possibilities for the structure of this compound.[12] An X-ray diffraction study of the tetraethylammonium salt showed the metal atoms to be arranged in a nearly perfect 3 × 3 rhombus with $Fe(CO)_4$ groups occupying the four corners and copper atoms located in the remaining positions (see Figure 3). The metal atoms thus form a small section of a close-packed surface. To the best of our knowledge this is the largest planar carbonyl cluster which has been synthesized. As can be readily seen, there are two different types of iron atoms and copper atoms in the cluster, the central Cu atom having six nearest neighbors in the plane. The central Cu atom is 2.53 Å from the edge lying Cu atoms whereas the edge lying coppers are 2.69 Å from the copper atom on an adjacent edge. The two Fe atoms which define the short diagonal of the rhombus bridge three coppers and are located 2.43 Å from the copper atoms on the edge and 2.49 Å from the central copper atom. The remaining two iron atoms bridge two coppers with a Fe–Cu distance of 2.39 Å. The average metal–metal distances (see Table II) are thus similar to those observed in the Cu_3Fe_3 and Cu_6Fe_4 cluster anions (see Table III).

Table III. Summary of Important Bond Distances in Cu–Fe Clusters

complex	Cu–Cu distance, Å	Cu–Fe distance, Å	shortest Cu–C distance, Å
$[(Ph_3P)_2Cu]_2Fe(CO)_4$		2.509	2.24
$Cu_3Fe_3(CO)_{12}^{2-}$	2.602	2.421	2.20
$Cu_5Fe_4(CO)_{16}^{3-}$	2.527	2.426	2.40
	2.691	2.491	
		2.394	
$Cu_6Fe_4(CO)_{16}^{2-}$	2.616	2.466	2.26

The arrangement of the carbonyl groups around the iron atoms is quite different from that found in the Cu_6Fe_4 cluster anion. In the Cu_5Fe_4 cluster anion, two of the carbonyls on each of the irons lie in the plane of the metal atoms. The other two carbonyls are bent over the metal-containing plane, one above and one below. These two carbonyl groups and the iron atom to which they are attached lie in a plane which also contains the central copper atom and the iron atom with its two carbonyl groups on the opposite corner of the rhombus. These two planes are perpendicular to the metal-containing plane. The $Fe(CO)_4$ groups therefore appear as somewhat flattened tetrahedra similar to that seen in the Cu_2Fe complex.[1] Although there seems to be some interaction between the carbonyl groups and the copper atoms, it is apparently somewhat weaker than in the other three Cu–Fe complexes, assuming that the Cu–C distances are a good indicator of the strength of this interaction. The closest Cu–C distance for the copper atoms lying on the edge is 2.40 Å while the shortest Cu–C distance for the central copper atom is even longer at 2.50 Å both considerably longer than those observed in the other Cu–Fe clusters.

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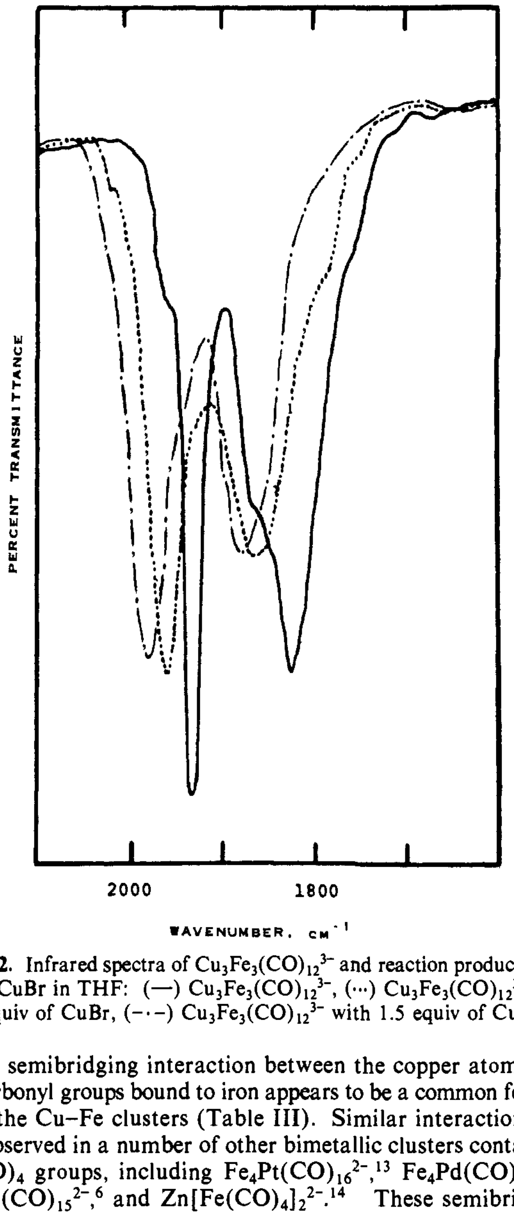
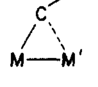


Figure 2. Infrared spectra of $Cu_3Fe_3(CO)_{12}^{3-}$ and reaction products with added CuBr in THF: (—) $Cu_3Fe_3(CO)_{12}^{3-}$, (···) $Cu_3Fe_3(CO)_{12}^{3-}$ with 0.75 equiv of CuBr, (-·-) $Cu_3Fe_3(CO)_{12}^{3-}$ with 1.5 equiv of CuBr.

The semibridging interaction between the copper atoms and the carbonyl groups bound to iron appears to be a common feature in all the Cu–Fe clusters (Table III). Similar interactions are also observed in a number of other bimetallic clusters containing $Fe(CO)_4$ groups, including $Fe_4Pt(CO)_{16}^{2-}$,[13] $Fe_4Pd(CO)_{16}^{2-}$,[13] $Fe_3Pt_3(CO)_{15}^{2-}$,[6] and $Zn[Fe(CO)_4]_2^{2-}$.[14] These semibridging carbonyl groups bear a superficial resemblance to the "classical" linear semibridging carbonyls first studied by Curtis.[15] In both cases the M–CO angles are nearly linear and the M–M–C angles are quite small, leading to short M′–C distances.



Although there are structural similarities, the nature of the bonding of the CO semibridges in these compounds must be different. A theoretical study by Hall[16] has shown that the CO semibridge in the dimolybdenum compounds can be regarded as an acid–base interaction between the CO π^* as an acceptor and the Mo–Mo π-bond as the donor. Such interactions are not likely in the Cu–Fe and other related M–Fe complexes. In a recent survey Crabtree[17] has suggested that semibridging carbonyls in these type of compounds can best be regarded as terminal CO's which happen to have small M′–M–C angles and that the relatively short M′–C distances do not necessarily indicate a significant bridging interaction.

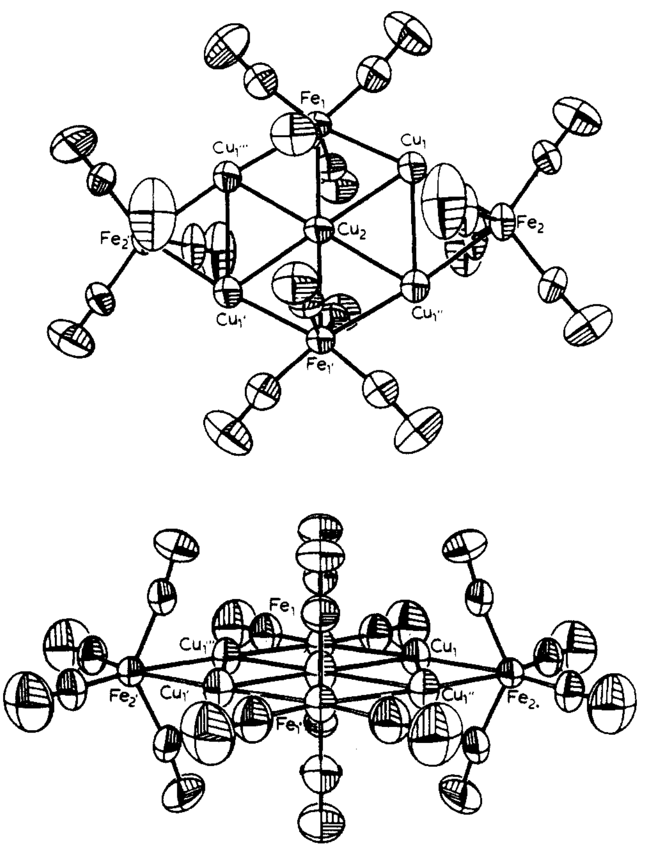


Figure 3. A perspective ORTEP drawing of the $Cu_5Fe_4(CO)_{16}^{3-}$ anion in crystalline $[(C_2H_5)_4N]_3(Cu_5Fe_4(CO)_{16})$ with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density viewed (a, top) perpendicular to and (b, bottom) nearly parallel to the lane of 9 metals. Primed atoms are related to nonprimed atoms by the symmetry operation $-x,-y,-z$, doubly primed atoms are related to nonprimed atoms by the symmetry operation y,x,z, and triply primed atoms are related to nonprimed atoms by the symmetry operation $-y,-x,-z$, where the fractional atomic coordinates are those given in Table VI.

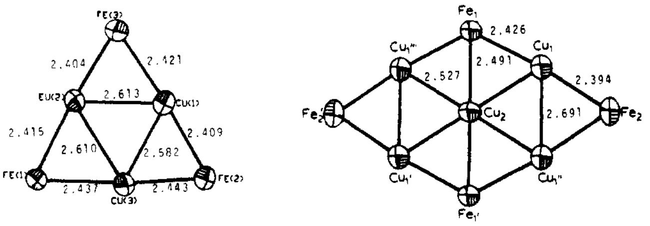


Figure 4. ORTEP drawing of the metal framework of the Cu_3Fe_3 and Cu_5Fe_4 clusters showing the metal–metal distances.

By using the procedures for determining electron counts in condensed polyhedra outlined by Mingos,[18] the electron count of 122 for the $Cu_5Fe_4(CO)_{16}^{3-}$ cluster can easily be predicted. The Cu_5Fe_4 species can be visualized as two Cu_3Fe_3 units sharing an edge with a $(OC)_4FeCuFe(CO)_4^{3-}$ fragment common to both triangular units. The total electron count for the Cu_5Fe_4 cluster should then be (2 × 84) − 46 or 122 as is observed.

Although the Cu_3Fe_3 and the Cu_5Fe_4 cluster anions are structurally related (see Figure 4), there is no way that the Cu_3Fe_3 species can be converted to the Cu_5Fe_4 complex by the reaction of CuBr or CuCl without some prior dissociation of the Cu_3Fe_3 cluster, or a derivative thereof, to provide the additional Fe required. In the subsequent step, the conversion of the Cu_5Fe_4 to

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(14) Sosinsky, B. A.; Shong, R. G.; Fitzgerald, B. J.; Norem, N.; O'Rourke, C. *Inorg. Chem.* **1983**, *22*, 3124.

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(16) Morris-Sherwood, B. J.; Powell, C. B.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 5079.

(17) Crabtree, R. H.; Lavin, M., in press.

(18) Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1983**, 706.

(19) Mehrotra, P. K.; Hoffman, R. *Inorg. Chem.* **1978**, *17*, 2188.

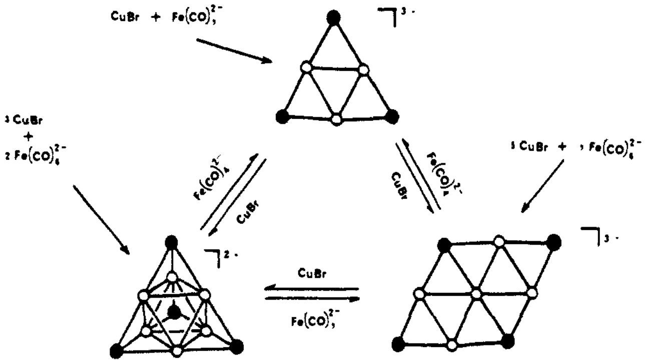

Figure 5. Reaction scheme showing the formation and interconversion of the $Cu_3Fe_3(CO)_{12}^{3-}$, $Cu_5Fe_4(CO)_{16}^{3-}$, and $Cu_6Fe_4(CO)_{16}^{2-}$ cluster anions. The open circles represent Cu atoms and the closed circles represent $Fe(CO)_4$ groups.

the Cu_6Fe_4 complex, no dissociation is necessary. If one folds the Cu_5Fe_4 complex along the short diagonal containing atoms Fe(1), Cu(2), and Fe(1′), the resulting butterfly structure is very similar to the metal atom arrangement in the Cu_6Fe_4 cluster anion except for a vacancy in one of the Cu positions. The addition of a Cu(I) species can then fill the vacant site, closing the butterfly and forming the Cu_6Fe_4 tetracapped octahedron or ν_2 tetrahedron. Although a mechanism of this type is appealing, there is not sufficient evidence to determine if the reaction proceeds in this straightforward manner or whether a more complicated process involving the dissociation of the Cu_5Fe_4 species is taking place.

Since the formation of the $Cu_3Fe_3(CO)_{12}^{3-}$ cluster from $Fe(CO)_4^{2-}$ and copper(I) halides and its subsequent conversion to the larger clusters takes place under similar conditions, it should be possible to form the Cu_5Fe_4 and the Cu_6Fe_4 clusters directly from $Fe(CO)_4^{2-}$ and a copper(I) halide. This has been confirmed and synthetic routes producing nearly quanlitative yields of any of the three cluster anions are available. In the case of the $Cu_6Fe_4(CO)_6^{2-}$ anion, this direct synthesis is important since the anion was previously available only as a salt of a phosphine-substituted copper(I) cation. Cations of this type introduce various complications and are detrimental to a number of studies we wished to carry out on the anion.

Just as the two larger copper-rich cluster anions can be formed by the reaction of $Cu_3Fe(CO)_{12}^{3-}$ with a copper(I) species, the reaction of the larger clusters with $Fe(CO)_4^{2-}$ will result in the formation of the more iron-rich clusters. Thus $Cu_6Fe_4(CO)_{16}^{2-}$ and $Fe(CO)_4^{2-}$ react to form $Cu_5Fe_4(CO)_{12}^{3-}$ and ultimately $Cu_3Fe_3(CO)_{12}^{3-}$. (The formation and interconversion of the three species are shown in Figure 5.) The relative ease with which these reactions take place may be due to the relatively weak bonding holding the clusters together and to the open nature of the structures. The bonding contributions due to copper–copper interactions would be expected to be small,[10] and the long Cu–C distances indicate only weak semibridging interactions. A study of space-filling drawings of these clusters show that the copper atoms are highly exposed and easily accessible to attack (see Figure 5). Although these cluster anions are quite stable in solution with no detectable dissociation taking place, they can undergo complete structural rearrangements under surprisingly mild conditions. This type of behavior should lead to some interesting new synthetic chemistry although the products formed may be very unpredictable.

Experimental Section

All syntheses and manipulations were carried out under a nitrogen atmosphere unless specified. Solvents were dried prior to use by standard procedures. Reagents were obtained from commercial sources or synthesized by well-known procedures. The $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane which was purchased from Alfa Products often contained excess dioxane solvent, and the quantities employed were based on the actual analysis of each sample. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Elemental analyses were carried out by the Analytical Division, Exxon Research and Engineering Co., and Galbraith Microanalytical Laboratories.

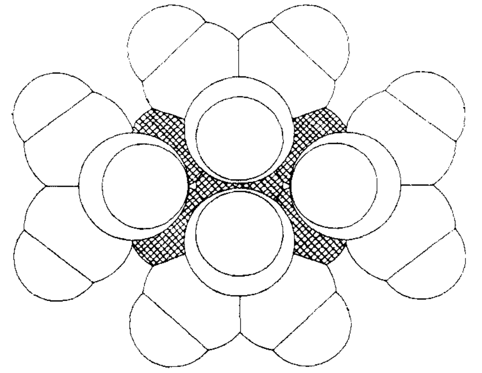

Figure 6. Space-filling drawing of the $Cu_5Fe_4(CO)_{16}^{3-}$ cluster anion viewed perpendicular to the plane of the metal atoms. Copper atoms are shaded. Radii used in drawing: C, 1.77; O, 1.40; Fe, 1.40; Cu, 1.40 Å.

Table IV. Crystal Data and Summary of Data Collection and Structure Refinement

compound	$[(C_2H_5)_4N]_3Cu_3$-$Fe_3(CO)_{12}$	$[(C_2H_5)_4N]_3Cu_5$-$Fe_4(CO)_{16}$
form wt	1085.0	1380.0
crystal system	monoclinic	tetragonal
space group	$P2_1/n$	$P4_2/mnn$
cell constants		
a, Å	12.946 (3)	13.553 (3)
b, Å	18.894 (4)	13.553 (3)
c, Å	19.031 (6)	14.650 (2)
α, deg	90.00	90.00
β, deg	93.91 (2)	90.00
γ, deg	90.00	90.00
cell volume, Å^3	4644.2 (7)	2961 (1)
Z	4	2
ρ(calcd), g/cm^3	1.55	1.703
crystal size, mm	0.20 × 0.25 × 0.30	0.20 × 0.20 × 0.90
radiation	Mo $K\alpha$	Mo $K\alpha$
scan technique	$\omega - 2\theta$	ω
scan range, deg	1.00	1.00
2θ limits, deg	5–50	3.00–45.8
independent reflectns collected	8219	1034
no. of independent data	3291	534
parameters refined	440	115
R^a	0.060	0.043
$R_w{}^b$	0.071	0.041
goodness of fit[c]	1.78	1.86
largest peak, e/Å^3	0.76	0.36

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|^2/\sum w|F_o|\}^{1/2}$. [c] $GOF = \{\sum w(|F_o| - |F_c|^2/(NO - NV)\}^{1/2}$.

$Na_3Cu_3Fe_3(CO)_{12}\cdot$6Dioxane. To a suspension of 1.66 g (11.6 mmol) of CuBr in 175 mL of THF was added 12.1 mmol of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane, and the mixture was stirred at room temperature for 16 h. The mixture was then filtered, and the clear yellow filtrate was reduced in volume to 15 mL on a rotary evaporator. Hexane (2 mL) was added and the solution was allowed to stand overnight during which time a mass of yellow crystals had formed which were collected on a filter. The filtrate was evaporated to dryness, yielding additional product. The total yield was 4.8 g. Anal. Calcd for $Na_3Cu_3Fe_3C_{36}H_{48}O_{24}$: C, 33.47; H, 3.74; Cu, 14.75; Fe, 12.97. Found: C, 33.24; H, 3.96; Cu, 14.46; Fe, 13.11. $\nu_{(CO)}$ (Nujol) 1925, 1800 cm^{-1}.

$[(C_2H_5)_4N]_3Cu_3Fe_3(CO)_{12}$. To a solution of 2.86 mmol of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane in 100 mL of THF was added 0.41 g (2.86 mmol) of CuBr. The mixture was stirred for 6 h and then filtered. $(C_2H_5)_4NCl$ (0.48 g, 2.93 mmol) was then added to the clear yellow filtrate which was stirred for 16 h and again filtered, yielding 1.09 g yellow solids. The solid material was extracted with four 15-mL portions of acetone. To the combined acetone extracts 50 mL of diethyl ether was added, and the resulting mixture was allowed to slowly evaporate overnight in a drybox. Approximately 0.75 g of yellow crystals were obtained. Anal. Calcd for $C_{36}H_{60}N_3Cu_3Fe_3O_{12}$: C, 39.85; H, 5.57; N, 3.87; Cu, 17.57; Fe, 15.44. Found: C, 39.70; H, 5.61; N, 3.96; Cu, 17.20; Fe, 15.44. $\nu_{(CO)}$ (Nujol) 1911, 1830, 1780 cm^{-1}.

Preparation of $Na_2Cu_6Fe_4(CO)_{16}\cdot$3THF. From $Na_3Cu_3Fe_3(CO)_{12}$. A solution of Cu(CO)Cl was prepared by passing CO through a suspenson of 0.48 g (4.8 mmol) of CuCl in THF. After the solution was stirred an

Table V. Table of Positional Parameters and Their Estimated Standard Deviations for $[(C_2H_5)_4N]_3Cu_3Fe_3(CO)_{12}$[a]

anion					cation				
atom	*x*	*y*	*z*	*B* (Å²)	atom	*x*	*y*	*z*	*B* (Å²)
Cu(1)	0.0110 (1)	0.19879 (8)	0.78365 (8)	4.73 (4)	N(1)	0.0305 (7)	0.1626 (5)	0.3856 (5)	4.8 (3)
Cu(2)	−0.0390 (1)	0.33263 (8)	0.78852 (8)	4.64 (4)	C(17)	0.010 (1)	0.0992 (8)	0.4350 (8)	7.3 (4)
Cu(3)	0.0147 (1)	0.27553 (8)	0.67159 (8)	4.61 (4)	C(18)	0.088 (1)	0.0379 (7)	0.4213 (9)	7.9 (5)
Fe(1)	−0.0307 (1)	0.40017 (9)	0.68130 (9)	3.70 (4)	C(19)	−0.051 (1)	0.2156 (8)	0.4050 (9)	8.0 (5)
Fe(2)	0.0618 (1)	0.15034 (9)	0.67413 (9)	3.82 (4)	C(20)	−0.047 (1)	0.2858 (8)	0.3584 (9)	8.3 (5)
Fe(3)	−0.0358 (1)	0.25704 (9)	0.89026 (9)	3.62 (4)	C(21)	0.140 (1)	0.1912 (8)	0.3942 (9)	8.5 (5)
C(1)	−0.0441 (9)	0.4896 (7)	0.6611 (7)	4.7 (3)	C(22)	0.168 (1)	0.2186 (8)	0.4734 (8)	7.6 (4)
C(2)	−0.155 (1)	0.3784 (7)	0.7056 (7)	4.9 (3)	C(23)	0.018 (1)	0.1406 (9)	0.3079 (8)	8.3 (5)
C(3)	0.077 (1)	0.4075 (7)	0.7406 (7)	5.3 (3)	C(24)	−0.100 (1)	0.112 (1)	0.289 (1)	10.3 (5)
C(4)	−0.003 (1)	0.3661 (7)	0.5970 (7)	5.3 (3)	N(2)	0.2722 (7)	0.5156 (5)	0.5423 (5)	4.2 (2)*
C(5)	0.1209 (9)	0.0887 (7)	0.6243 (7)	5.0 (3)	C(25)	0.322 (2)	0.543 (1)	0.610 (1)	4.0 (5)*
C(6)	0.1680 (9)	0.2032 (7)	0.6965 (7)	5.0 (3)	C(258)	0.182 (2)	0.534 (2)	0.592 (2)	7.4 (8)*
C(7)	0.0181 (9)	0.0932 (7)	0.7359 (6)	5.0 (3)	C(26)	0.233 (1)	0.5601 (8)	0.6658 (8)	6.6 (4)*
C(8)	−0.0416 (9)	0.1763 (6)	0.6162 (6)	4.2 (3)	C(27)	0.364 (2)	0.501 (1)	0.491 (1)	3.9 (5)*
C(9)	0.099 (1)	0.2617 (7)	0.8770 (6)	5.1 (3)	C(278)	0.277 (2)	0.982 (2)	0.023 (2)	6.7 (7)*
C(10)	−0.1406 (9)	0.2147 (7)	0.8413 (6)	5.0 (3)	C(28)	0.184 (1)	0.9689 (8)	0.0805 (8)	7.3 (4)*
C(11)	−0.031 (1)	0.2071 (7)	0.9673 (7)	5.5 (4)	C(29)	0.199 (2)	0.452 (1)	0.548 (1)	3.7 (5)*
C(12)	−0.082 (1)	0.3408 (7)	0.9109 (6)	5.0 (3)	C(298)	0.348 (2)	0.462 (2)	0.582 (2)	6.6 (7)*
O(1)	−0.0532 (8)	0.5486 (5)	0.6463 (6)	7.7 (3)	C(30)	0.271 (1)	0.3902 (9)	0.5947 (9)	8.5 (5)*
O(2)	−0.2430 (7)	0.3688 (6)	0.7159 (5)	8.2 (3)	C(31)	0.199 (2)	0.575 (1)	0.504 (1)	3.5 (5)*
O(3)	0.1515 (8)	0.4181 (6)	0.7778 (6)	10.3 (3)	C(318)	0.342 (2)	0.578 (2)	0.528 (1)	6.3 (7)*
O(4)	0.0093 (9)	0.3545 (5)	0.5382 (5)	8.1 (3)	C(32)	0.237 (1)	0.1412 (8)	0.0100 (8)	7.4 (4)*
O(5)	0.1619 (8)	0.0453 (5)	0.5917 (5)	7.5 (3)	N(3)	0.6005 (8)	0.1122 (6)	0.6232 (6)	5.9 (3)*
O(6)	0.2473 (7)	0.2353 (5)	0.7085 (5)	7.1 (3)	C(33)	0.708 (2)	0.099 (1)	0.672 (1)	12.4 (7)*
O(7)	−0.0094 (7)	0.0456 (5)	0.7716 (5)	6.8 (3)	C(34)	0.726 (1)	0.035 (1)	0.699 (1)	11.0 (6)*
O(8)	−0.1099 (7)	0.1847 (5)	0.5735 (5)	6.3 (3)	C(35)	0.599 (2)	0.189 (1)	0.595 (1)	15.9 (9)*
O(9)	0.1864 (6)	0.2665 (5)	0.8750 (5)	6.8 (3)	Cn(36)	0.583 (2)	0.235 (1)	0.664 (1)	15.2 (8)*
O(10)	−0.2132 (7)	0.1899 (6)	0.8150 (5)	7.2 (3)	C(37)	0.596 (2)	0.067 (1)	0.554 (1)	12.9 (7)*
O(11)	−0.0288 (8)	0.1733 (6)	1.0181 (5)	9.4 (3)	C(38)	0.671 (2)	0.081 (1)	0.503 (1)	10.6 (6)*
O(12)	−0.1143 (8)	0.3939 (5)	0.9306 (5)	7.3 (3)	C(39)	0.512 (2)	0.086 (1)	0.663 (1)	12.7 (7)*
					C(40)	0.406 (2)	0.096 (1)	0.632 (1)	11.6 (6)*

[a] Asterisked atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)*[*a***2**B*(1,1) + *b***2**B*(2,2) + *c***2**B*(3,3) + *ab*(cos γ)**B*(1,2) + *ac*(cos β)*(1,3) + *bc*(cos α)**B*(2,3)].

Table VI. $[(C_2H_5)_4N]_3Cu_5Fe_4(CO)_{16}$; Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom[b]	point symmetry	*x*	*y*	*z*	*B* (Å²)[c]
Cu(1)	*m*	0.0414 (2)	0.1818 (1)	0.0000[d]	4.5 (1)
Cu(2)	*mmm*	0.0000[d]	0.00000[d]	0.0000[d]	4.7 (1)
Fe(1)	*mm*	−0.1300 (2)	0.1300 (2)	0.0000[d]	3.7 (1)
Fe(2)	*mm*	0.2149 (2)	0.2149 (2)	0.0000[d]	3.8 (1)
O(1)	*m*	−0.3450 (8)	0.1222 (10)	0.0000[d]	9.6 (6)
O(2)	*m*	−0.0823 (6)	0.0823 (6)	−0.1922 (9)	6.1 (3)
O(2)	*m*	0.4256 (9)	0.1833 (10)	0.0000[d]	9.2 (6)
O(4)	*m*	0.1599 (7)	0.1599 (7)	−0.1875 (8)	10.4 (4)
C(1)	*m*	−0.2570 (14)	0.1187 (12)	0.0000[d]	5.7 (6)
C(2)	*m*	−0.0957 (8)	0.0957 (8)	−0.1157 (13)	4.5 (4)
C(3)	*m*	0.3425 (11)	0.1943 (12)	0.0000[d]	4.8 (6)
C(4)	*m*	0.1774 (8)	0.1774 (8)	−0.1120 (12)	5.9 (4)
			Cations		
N(A)[e]	*mmm*	0.0000[d]	0.0000[d]	0.5000[d]	5.2 (7)
C(A1)[e]	1	0.0884 (22)	−0.0024 (22)	0.4401 (23)	12.5 (14)
C(A2)	*m*	0.0969 (14)	0.0969 (14)	0.3801 (18)	14.4 (9)
N(B)[e]	4	0.5000[d]	0.0000[d]	−0.2500[d]	4.4 (4)
C(B1)[e]	1	0.4640 (17)	0.0832 (15)	−0.1828 (14)	4.9 (8)
C(B2)	1	0.4185 (10)	0.1710 (9)	−0.2467 (10)	9.0 (6)
C(B3)[e]	1	0.4293 (22)	−0.0475 (24)	−0.1782 (18)	7.0 (13)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] This is one-third of the trace of the orthogonalized B_{ij} tensor. [d] This is a symmetry required value and is therefore listed without an estimated standard deviation. [e] The two crystallographically independent $(C_2H_5)_4N^+$ cations are both disordered such that two independent tetrahedral arrangements of the α-methylene carbons appear to exist. The nitrogen atom of cation A occupies a crystallographic *mmm* site at 0,0,$^1/_2$ while that of cation B occupies a $\bar{4}$ site at $^1/_2$,0,−$^1/_2$. The occupancy of carbon C(A1) was fixed at 0.50; the occupancies of atoms C(B1) and C(B3) refined to final values of 0.56 and 0.44, respectively.

additional 30 min, 1.29 g (1.7 mmol) of $Na_3Cu_3Fe_3(CO)_{12}$ was added which after another 30 min was followed by 0.34 g (1.6 mmol) of $Na_2Fe(CO)_4$. The mixture was stirred for 16 h under CO and then filtered. The filtrate was evaporated to dryness, giving 1.30 g of a bright yellow solid. Anal. Calcd for $C_{28}H_{24}Cu_6Fe_4Na_2O_{19}$: Cu, 28.99; Fe, 16.99; Na, 3.50. Found: Cu, 28.69; Fe, 17.01; Na, 3.24. $\nu_{(CO)}$ (Nujol) 1970, 1873 cm^{-1}.

From CuBr and $Na_2Fe(CO)_4\cdot{}^3/_2$Dioxane. To a suspension of 1.43 g (10 mmol) of CuBr in 150 mL of THF, 6.7 mmol of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane was added and the mixture was stirred at room temperature for 20 h. The mixture was then filtered and the yellow filtrate was evaporated to approximately 25 mL, and 100 mL of hexane was then added. The yellow precipitate was collected on a filter and dried under nitrogen. The dried solid appeared to contain a small amount of residual dioxane but was otherwise identical with that prepared from $Na_3Cu_3Fe_3(CO)_{12}$.

$Na_3Cu_5Fe_4(CO)_{16}\cdot4$Dioxane. To a suspension of 2.86 g (20 mmol) of CuBr in 200 mL of THF, 16 mmol of solid $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane was added, and the mixture was stirred for 16 h at room temperature. The solution was then filtered, giving 2.1 g of grey solid NaBr and a clear yellow filtrate. The filtrate was evaporated to dryness, giving 5.5 g of a bright yellow solid. Anal. Calcd for $C_{32}H_{32}Cu_5Fe_4Na_3O_{24}$: C, 27.25; H, 2.28; Cu, 22.52; Fe, 15.84; Na, 4.88. Found: C, 27.09; H, 2.12; Cu, 22.46; Fe, 15.30; Na, 5.06. $\nu_{(CO)}$ (Nujol) 1950, 1850 cm^{-1}.

The Interconversion of the $Cu_3Fe_3(CO)_{12}^{3-}$, $Cu_5Fe_4(CO)_{16}^{3-}$, and $Cu_6Fe_4(CO)_{16}^{2-}$ Anions. Starting with the appropriate sodium salt in THF, it is possible to convert either of the three cluster anons to another by the addition of CuBr or $Na_2Fe(CO)_4 \cdot {}^3/_2$dioxane. To a solution containing 0.76 g (1.0 mmol) of $Na_2Cu_3Fe_3(CO)_{12}$ in 50 mL of THF was added 0.11 g (0.75 mmol) of CuBr. The mixture was stirred for 2 h at room temperature and then filtered to remove the NaBr. An infrared spectra of the clear yellow filtrate showed only two CO stretching bands at 1950 and 1850 cm^{-1} attributed to the $Cu_5Fe_4(CO)_{16}^{3-}$ anion. The solvated sodium salt $Na_3Cu_5Fe_4(CO)_{16} \cdot 4THF$ was obtained quantitatively upon evaporation of the solvent. Similarly, if the original solution of the $Na_3Cu_3Fe_3(CO)_{12}$ complex is treated with 0.22 g (1.5 mmol) of CuBr then the $Cu_6Fe_4(CO)_{16}^{2-}$ anion is obtained. The reaction of a solution of 1.06 g (1.0 mmol) of $Na_3Cu_5Fe_4(CO)_{16}$ in 50 mL of THF with 1.4 g (1.0 mmol) of CuBr under identical conditions also gives quantitative yields of the $Cu_6Fe_4(CO)_{16} \cdot 3THF$ by solvent evaporation after filtration. The reaction of 2.2 g (2.0 mmol) of $Na_2Cu_6Fe_4(CO)_{16}$ in 100 mL of THF with 1.6 mmol of $Na_2Fe(CO)_4$ for 2 h at room temperature gives quantitative yields of $Na_3Cu_5Fe_4(CO)_{16} \cdot 4THF$. Treatment of 2.2 g (2.0 mmol) of $Na_2Cu_6Fe_4(CO)_{16}$ with 4.0 mmol of $Na_2Fe(CO)_4$ or 2.1 g (2.0 mmol) of $Na_3Cu_5Fe_4(CO)_{16}$ with 2.0 mmol of $Na_2Fe(CO)_4$ in 100 mL of THF gives $Na_3Cu_3Fe_3(CO)_{12} \cdot 6THF$ under identical conditions.

Preparation of $[(C_2H_5)_4N]_3Cu_5Fe_4(CO)_{16}$. A solution of $Na_3Cu_3Fe_3(CO)_{12}$ was prepared containing approximately 1 g of the complex in 75 mL of THF. To this solution was added 0.12 g (0.84 mmol) of CuBr, and the mixture was stirred for 6 h at room temperature. The solution was filtered, 0.28 g (1.70 mmol) of $(C_2H_5)_4NCl$ was added to the filtrate, and the resulting mixture was stirred for 16 h. The solid material was collected on a glass frit and dried. The dried solid was washed with 50 mL of acetone in four portions, and the acetone washes were combined and evaporated to approximately 25 mL. Toluene (25 mL) was then added, and after 24 h 0.25 g of yellow crystals formed which were collected on a filter. An additional 0.27 g of yellow powder was obtained by evaporation of the mixed solvent. Anal. Calcd for $C_{40}H_{60}N_3Cu_5Fe_4O_{16}$: C, 34.07; H, 4.29; N, 2.98; Cu, 22.53, Fe, 15.84. Found: C, 34.11; H, 4.53; N, 2.89; Cu, 22.17; Fe, 16.14. $\nu_{(CO)}$ 1950, 1850 cm^{-1}.

X-ray Data for $[(C_2H_5)_4N]_3Cu_3Fe_3(CO)_{12}$. A crystal was mounted in a glass capillary first sealed with wax and then epoxy. Lattice parameters (shown in Table IV) were determined by a least-squares fit of 25 diffractometer measured 2θ values. All unique diffractometer maxima with $5° \leq 2\theta \leq 50°$ were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a variable speed, $\omega - 2\theta$ scan technique. The space group was uniquely determined to be $P2_1/n$ by observation of the following systematic absenses: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$. A density of 1.55 g/cm^3 was calculated for $Z = 12$ and a molecular weight of 362 g ($CuFeC_{12}H_{20}NO_4$). Three check reflections, monitored periodically during data collection, indicated there was a total loss of intensity of 8.4%. The decay of intensity was linear with time and the data were corrected accordingly (program DECAY). Psi scan data indicated absorption effects to be negligible (maximum variation ± 2%). Of the 8219 unique data measured, 3291 were considered observed [$|F_o|^2 \geq 2\sigma(F_o^2)$].

An initial phasing model was developed by using direct methods. A weighted E-synthesis corresponding to the most consistent set of phases revealed the location of 3 copper atoms and 3 iron atoms. The remaining non-hydrogen atoms were located by alternate applications of difference fourier and least-squares refinement techniques. Of the three independent tetraethylammonium (TEA) cations, only one is completely ordered. In the second, the methylene carbons are disordered between two positions which were entered into refinement with a multiplicity of $^1/_2$. The atoms of the third TEA cation display large thermal vibrations indicating a general disorder of the entire cation. The hydrogen atoms of the TEA cations were not located.

Full-matrix least-squares refinement with anisotropic thermal parameters for Cu, Fe, carbonyl groups and the ordered TEA cation, isotropic thermal parameters for the remaining two TEA cations, and anomalous dispersion corrections for Cu and Fe has given current crystallographic residuals R = 0.060, R_w = 0.071.

The final values of the positional parameters are given in Table V, and thermal parmeters, cation bond distances and angles, and structure factor amplitudes are given as supplementary material.

X-ray Data for $[(C_2H_5)_4N]_3Cu_5Fe_4(CO)_{16}$. The structure of this complex was determined by Crystalytics Co. A yellow crystal of the complex was glued to the inside of a thin-walled glass capillary and sealed under N_2. Lattice parameters (given Table IV) were determined by a least-squares refinement of 15 computer-centered reflections with $\theta < 20°$. Data were collected on a computer-controlled four-circle Nicolet Autodiffractometer with graphite monochromated MoKα radiation using the ω scan technique. A scan range of 1.00° with a ratio of background counting time to net scanning time of 0.50 was used. A total of 17 steps were taken, 13 of which were used in intensity calculations. Background counts were measured at ω settings 1.00° above and below the calculated value for each reflection. The intensities were corrected for Lorentz and polarization effects. The intensity data were corrected empirically for absorption effects using psi scans for 4 reflections having 2θ between 12.8° and 22.0°.

The 19 non-hydrogen atoms were located by using the SHELXT Direct Methods program. The methylenic carbon atoms on the cation are disordered. Variable occupanices of 0.50 for C(A1), 0.56 for C(B1), and 0.44 for C(B3) were found. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to values of R and R_w of 0.043 and 0.041, respectively. There were no peaks in the final difference Fourier above the noise level of 0.36 e$^-$/Å^3. The final values of the positional parameters are given in Table VI. Tables of thermal parameters, cation bond lengths and angles, the structure factor amplitudes are given as supplementary material.

Supplementary Material Available: Tables of thermal parameters, cation bond distances and angles, and structure factor amplitudes for $[(C_2H_5)_4N]_3Cu_3Fe_3(CO)_{12}$ and $[(C_2H_5)_4N]_3Cu_5Fe_4(CO)_{16}$ (26 pages). Ordering information is given on any current masthead page.