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Multinuclear NMR Studies on Mixed Copper/Iron Carbonyl Clusters

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^{63}Cu, ^{13}C, and ^{17}O NMR spectra of the mixed clusters $Na_3[Cu_3Fe_3(CO)_{12}]$, $Na_3[Cu_5Fe_4(CO)_{16}]$, $Na_2[Cu_6Fe_4(CO)_{16}]$ are reported. The ^{63}Cu resonances are at significantly higher field than those found for Cu(I) mononuclear complexes and are much sharper than those previously reported. In all cases, ^{13}C and ^{17}O NMR spectra are consistent with complete carbonyl fluxionality at room temperature, but it has been possible to partially stop this carbonyl exchange in $[Cu_5Fe_4(CO)_{16}]^{3-}$ at low temperature (−90 °C).

The recent synthesis of a novel series of mixed-metal clusters containing copper,[1] viz., $Na_3[Cu_3Fe_3(CO)_{12}]$, $Na_3[Cu_5Fe_4(CO)_{16}]$, and $Na_2[Cu_6Fe_4(CO)_{16}]$ is an exciting new development in cluster chemistry. Their structures are shown in Figure 1, and their interesting structural properties and chemical behavior, particularly their ready interconversion, prompted us to measure their multinuclear (^{63}Cu, ^{13}C, ^{17}O) NMR spectra. [The NMR measurements were carried out on a Bruker WH 200 spectrometer using a broad-band tuneable VSP probe; saturated solutions (ca. 0.3 M) in oxygen-free acetone-d_6 were contained in a 10-mm tube. ^{63}Cu resonances were obtained using a carrier frequency of 52.9386 MHz, pulse width of 5 μs, and pulse delay of 0.3 s with a sweep width of 80 KHz. ^{63}Cu chemical shifts are related to a saturated solution of $[Cu(NCCH_3)_4][BF_4]$ in acetonitrile as external reference. $\delta(^{13}CO)$ is referenced to Me_4Si and $\delta(^{17}O)$ is related to the ^{17}O resonance in acetone and referenced to D_2O by using the relationship:[6] $\delta(D_2{}^{17}O) = \delta(Me_2C^{17}O) + 569.$] ^{63}Cu resonances have previously been observed for mononuclear Cu(I) complexes,[2-4] but the present work provides the first report of the direct observation of ^{63}Cu resonances in clusters, (Figure 2).

The X-ray crystallographic structures of $Na_3[Cu_3Fe_3(CO)_{12}]$ and $Na_2[Cu_6Fe_4(CO)_{16}]$ consist of a Cu_3 triangle with each edge occupied by an $Fe(CO)_4$ group and a Cu_6 octahedron with four face-bridging $Fe(CO)_4$ groups, respectively (see Figure 1). As a result, all the copper atoms are equivalent in each compound and a single resonance is expected and found (Table I). The structure of $Na_3[Cu_5Fe_4(CO)_{16}]$ shows that there are four equivalent peripheral copper atoms with a unique interstitial copper atom. However, in this case we could only observe the resonance due to the peripheral atoms and their was no other signal over ±10 000 ppm at room or low (−90 °C) temperatures. Related difficulties have been experienced in attempts to directly observed ^{103}Rh resonances due to interstitial rhodium atoms in $[Rh_{13}(CO)_{24}H_n]^{(5-n)-}$ (n = 1–4) and $[Rh_{14}(CO)_{25}H_x]^{(4-x)-}$ (x = 0, 1),[5] although they were clearly observed by indirect, $^1H\{^{103}Rh\}$, measurements, and it seems probable that related effects could account for our nonobservance of interstitial copper resonances.

Table I. Room-Temperature ^{63}Cu NMR Data of Mixed Copper/Iron Clusters in Acetone

	$\delta(^{63}Cu)$	linewidth/Hz
$Na_3[Cu_3Fe_3(CO)_{12}]$	−2411.0	30
$Na_3[Cu_5Fe_4(CO)_{16}]$	−2410.4	25
$Na_2[Cu_6Fe_4(CO)_{16}]$	−2410.0	20

Table II. Room-Temperature ^{13}C and ^{17}O NMR Data of Mixed Copper/Iron Clusters in Acetone

	$\delta(^{13}CO)$	$\delta(C^{17}O)$
$Na_3[Cu_3Fe_3(CO)_{12}]$	222.5	354.5
$Na_3[Cu_5Fe_4(CO)_{16}]$	217.4	364.2
$Na_2[Cu_6Fe_4(CO)_{16}]$	214.1	374.8

The copper resonances in all three clusters occur at significantly lower frequency than those observed for Cu(I) complexes,[3,4] and, since the resonance frequency of other first-row metals always shifts to lower frequency with decreasing oxidation state, the shift of ca. −2400 ppm, for the present clusters suggests that the copper atoms are in an oxidation state which is formally much less than one.

^{63}Cu is a quadrupolar nucleus (spin $^3/_2$, quadrupolar moment -0.16×10^{-28} m^2), but the linewidths reported in Table I are quite small and significantly less than those previously reported.[3,4] The quadrupolar contribution is however important in these clusters since, on lowering the temperature, an increase in linewidth is observed due to an increased correlation time; other mechanisms proposed for Cu(I) relaxation[4] require an opposite behavior. As a result, the small linewidths observed for these clusters suggest a small electric field gradient which seems to be becoming a common feature in clusters.[4]

Although the ^{63}Cu resonances in all three clusters are remarkably close, this cannot be attributable to a common species in solution arising from a common decomposition since the ^{13}C and ^{17}O NMR together with the IR spectra of all three clusters are significantly different. It therefore suggests that the electronic environments of the copper atoms are similar which is consistent with their ready interconvertability.

The ^{13}C and ^{17}O NMR data, which was obtained on nonenriched samples at room temperature, are summarized in Table II. The ^{17}O linewidths are 7–10 Hz, which is usual for metal carbonyls, and, in all cases, there is complete carbonyl fluxionality at room temperature. The

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(1) Doyle, G.; Eriksen, K. A.; Van Engen, D., in press.

(2) Harris, R. K., Mann, B. E., Eds. "NMR and the Periodic Table"; Academic Press: London, 1978.

(3) Brevard, C.; Granger, P. "Handbook of High Resolution NMR"; Wiley-Interscience: New York, 1981.

(4) Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125.

(5) Heaton, B. T.; Seregni, C.; Strona, L.; Goodfellow, R. J.; Martinengo, S. *J. Chem. Soc., Dalton Trans.*, submitted for publication.

(6) Kintzinger J. P. *NMR; Basic Princ. Prog.* **1981**, *17*, 1.

0276-7333/85/2304-1224$01.50/0

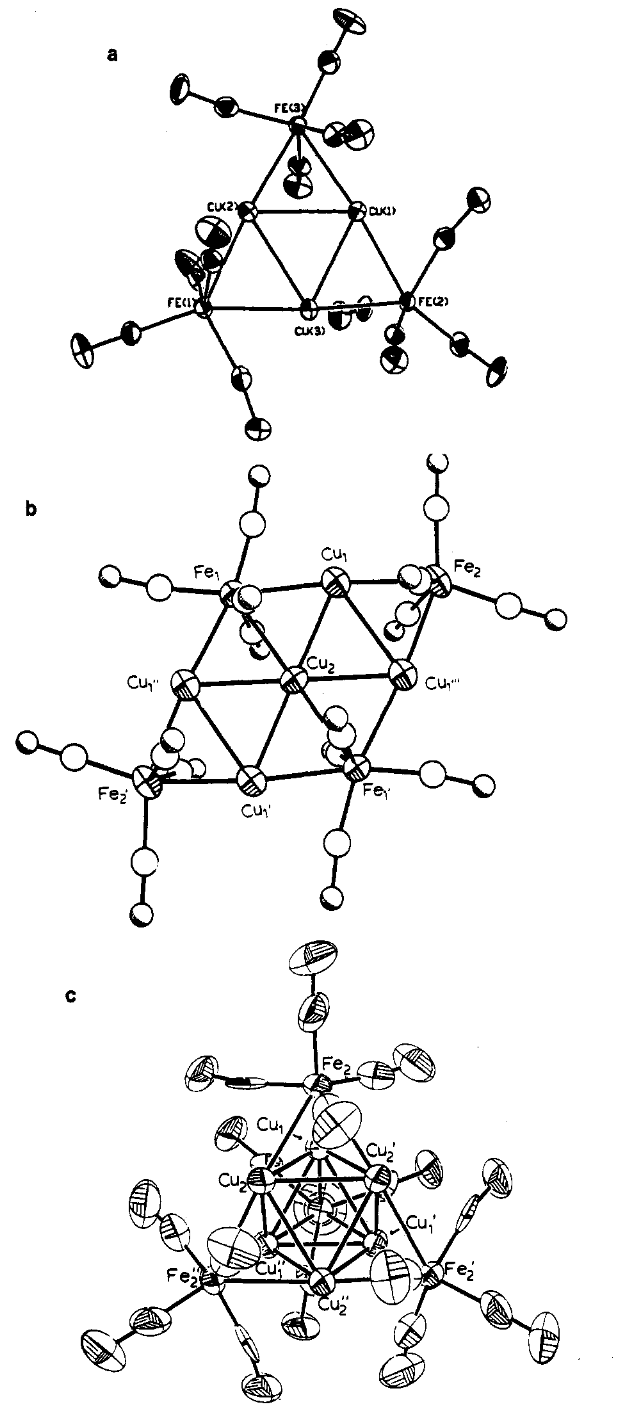

Figure 1. ORTEP figures of (a) $[Cu_3Fe_3(CO)_{12}]^{3-}$, (b) $[Cu_5Fe_4(CO)_{16}]^{3-}$, and (c) $[Cu_6Fe_4(CO)_{16}]^{2-}$.

^{13}C shifts are typical of iron carbonyls and arise from terminal/bridge exchange with a varying amount of semibridging character.[17] Thus, $\delta(^{13}CO)$ for the trianion $Na_3[Cu_3Fe_3(CO)_{12}]$ is at significantly lower field than $Na_3[Cu_5Fe_4(CO)_{16}]$, consistent with the former having three semibridging carbonyls per $Fe(CO)_4$ group in the solid state compared with two in the latter compound. However, comparing $Na_3[Cu_3Fe_3(CO)_{12}]$ with $Na_2[Cu_6Fe_4(CO)_{16}]$ which both have three semibridging carbonyls in the crystalline state, the change in $\delta(^{13}CO)$ in this case is probably mainly the result of the different ionic charges.

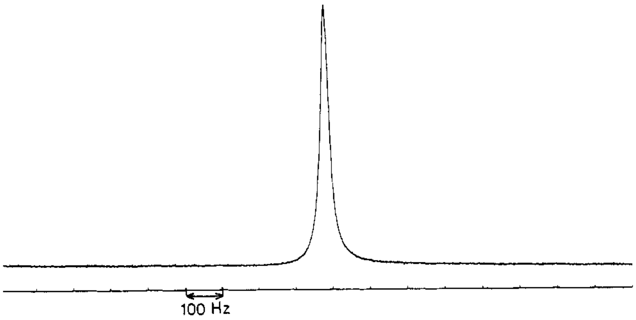

Figure 2. ^{63}Cu NMR spectrum of $Na_3[Cu_3Fe_3(CO)_{12}]$ in acetone solution at room temperature. The spectrum was obtained in 100 scans: sweep width, 2500 Hz; flip angle, 90°; acquisition time, 0.8 s.

Compared to $\delta(^{13}CO)$, there is an opposite variation in oxygen-17 chemical shifts (see Table II). This behavior is quite common in metal carbonyls,[8] and it has been proposed[9] that this reflects a dominant contribution of the Q terms in the Karplus–Pople expression of the paramagnetic contribution to the average shielding constant (eq 1) since it is known that the Q terms are linked with the M–C and C–O bond orders.

$$\sigma_p{}^A = -\frac{e^2\hbar^2}{2m^2c^2\Delta E}\langle r^{-3}\rangle_{2p}[Q_{AA} + \Sigma_{B\neq A}Q_{AB}]$$

In none of the three cases was it possible to observe the low-temperature limiting spectrum. At −90 °C, only a limited broadening of the ^{13}C resonance from $Na_3[Cu_3Fe_3(CO)_{12}]$ was observed and near coalescence of $Na_2[Cu_6Fe_4(CO)_{16}]$. For $Na_3[Cu_5Fe_4(CO)_{16}]$, complete coalescence of the ^{13}C resonance occurred at −60 °C and at −90 °C two two broad resonances are observed at 211.8 and 219.1 ppm. We prefer to attribute these resonances to the terminal and semi-edge-bridging carbonyls, respectively, but it is possible that they could be due to two sets of carbonyls undergoing a localized exchange on the inequivalent iron atoms, Fe_1 and Fe_2. However, this low-temperature spectrum is obviously still not the limiting spectrum since the solid-state structure shows the presence of two sets of semibridging and two sets of terminal carbonyls in the ratio 1:1:1:1 and it is presently impossible to determine whether the carbonyl fluxionality involves a localized exchange on each iron or complete scrambling over the whole metal skeleton since it has not been possible to observe any splitting of the ^{63}Cu resonance arising from $^1J(^{13}C-^{63}Cu)$ even at high ^{13}CO enrichments.

Finally, it is worthwile commenting on the variation of chemical shifts of these clusters with temperature. Despite the much larger range of ^{63}Cu chemical shifts, there is a very small variation with temperature whereas there is a 2–4 ppm difference in $\delta(^{13}CO)$ and $\delta(C^{17}O)$ on going from room to low (−90 °C) temperature. These differences can probably be attributed to interactions with the solvent; the copper nuclei are well shielded by the $Fe(CO)_4$ groups, and so the temperature dependence is not very strong.

Registry No. $Na_3[Cu_3Fe_3(CO)12]$, 96453-18-8; $Na_3[Cu_5Fe_4(CO)16]$, 96453-19-9; $Na_2[Cu_6Fe_4(CO)16]$, 96453-20-2; ^{63}Cu, 14191-84-5.

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(7) Aime, S.; Milone, L.; Sappa, E. *J. Chem. Soc., Dalton Trans.* **1976**, 838.

(8) Hickey, J. P.; Wilkinson, J. R.; Todd, L. J.; *J. Organomet. Chem.* **1979**, *179*, 159.

(9) Buchner, W.; Schenk, W. A. *J. Magn. Reson.* **1982**, *48*, 148.