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Fluxional Behaviour of the Binary Carbonyls. A Comparison of the Isoelectronic and Isostructural Tetranuclear Clusters: $Co_4(CO)_{12}$, $HFeCo_3(CO)_{12}$ and $[FeCo_3(CO)_{12}]^-$

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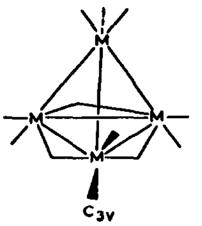
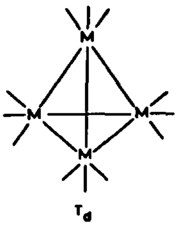
The ^{13}C NMR spectra of ^{13}CO enriched samples of the cluster molecules $HFeCo_3(CO)_{12}$ and $[FeCo_3(CO)_{12}]^-$ have been recorded over a wide temperature range. In the low temperature limiting spectra of these species four resonances of equal intensity were observed, in each case consistent with their proposed molecular geometries. As the temperature is raised two distinct fluxional processes are observed. The first corresponds to interconversion of the nine CO-ligands about the Co_3 basal plane and the second to total scrambling over the $FeCo_3$ tetrahedron.

Introduction

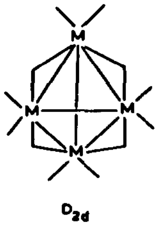
For $M_4(CO)_{12}$ tetrahedral species, the determination of the solid state structures have shown that the cobalt and rhodium compounds have C_{3v} symmetry [1, 2] with both terminal and edge-bridging carbonyl groups, whereas the iridium compound has Td symmetry with all terminal carbonyl groups [2].



C_{3v}



T_d



D_{2d}

It was Cotton who first suggested that intramolecular carbonyl exchange can be a facile process in these molecules [3] and suggested that amongst the mechanisms leading to the total equivalence of the carbonyl ligands, the rapid interconversion between the C_{3v} and Td forms appears to be the simplest and most likely [4]. While in $Ir_4(CO)_{12}$ (Td symmetry) all the carbonyls are equivalent even in the absence of any fluxional process, $Rh_4(CO)_{12}$ shows a low temperature ^{13}C NMR limiting spectrum completely consistent with its C_{3v}-solid state structure [5]. At +50 °C the fast exchange limit is reached and $^{103}Rh-^{13}C$ coupling unequivocally establishes an *intramolecular* delocalized migration of carbonyl ligands over the four metal atoms.

The solution structure of $Co_4(CO)_{12}$ has been a long-standing problem, although a complete analysis of the IR spectrum [6] and the observation in the ^{59}Co NMR spectrum [7] of two resonances with relative intensities 1:3 agree with the C_{3v} solid-state structure, since the low temperature limiting ^{13}C NMR spectrum [7–9] is anomalous. Three equally intense peaks consistent with a D_{2d} structure were observed by different groups. It was suggested that the quadrupole moment of the ^{59}Co nuclei might perturb the relative intensities of the carbonyl absorptions. Further insight into the nature of this problem came from the recording of the fast-exchange spectrum in viscous solution [9], since to fit the chemical shift value of the average peak (at +61 °C) one of the cobalt-terminal carbonyl resonances should weight twice the other resonances. This observation is consistent with an accidental degeneracy of two

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terminal resonances, but the anomalous intensity ratio observed in the low temperature spectrum remained a problem. Eventually this problem was resolved by means of High-Field ^{17}O NMR spectroscopy [10]. The advantages of such measurements in dynamic NMR studies of carbonyl complexes containing quadrupolar metals have already been stressed [11]. Four resonances of equal intensities are present in the ^{17}O NMR spectrum (at -25 °C) of $Co_4(CO)_{12}$; these broaden and eventually merge into a single peak as the temperature is raised. Similarly to the $Co_4(CO)_{12}$ case, the ^{17}O NMR study [10] of $HFeCo_3(CO)_{12}$ gave results conflicting with those obtained from a previous ^{13}C NMR study [9]. Also in this case only the ^{17}O NMR study is in agreement with the structure inferred from the neutron diffraction study of $HFeCo_3(CO)_9[P(OMe)_3]_3$ [12]. However, the differences in the ^{13}C and ^{17}O spectral features are apparently beyond the anomalies that can be expected from quadrupolar metal effect. This prompted us to repeat the ^{13}C NMR study of the mixed metal cluster, together with that of its conjugate anion $[FeCo_3(CO)_{12}]^-$.

Recently, some of us put forward an alternative explanation of the carbonyl scrambling paths observed in C_{3v} tetrahedral $M_4(CO)_{12}$ clusters [13a], on the basis of a single process well defined in terms of molecular geometry. The initial icosahedral arrangement of ligands (corresponding to C_{3v} ground-state geometry) is considered to undergo rearrangement *via* a cubo-octahedral transition state (corresponding to Td intermediate geometry). The different patterns of carbonyl scrambling arise as a consequence of the geometrical disposition of the metal-atom tetrahedron within the ligand polyhedral envelope. Furthermore, in some of these systems rotation of triangular faces in the cubo-octahedral intermediate occurs. This approach appears to be general and applies not only to $M_4(CO)_{12}$ compounds but also to $Fe_3(CO)_{11}L$ complexes [13b]. This approach may be extended to the title anion, but the presence of the hydride ligand does not allow a simple extension to the $HFeCo_3(CO)_{12}$ case, despite the overall C_{3v} symmetry.

Experimental

Preparation of Complexes

$HFeCo_3(CO)_{12}$

$HFeCo_3(CO)_{12}$ was prepared by the method described in the literature [14]. Purity was checked by IR and ms spectroscopy. We have repeated the enrichment procedure followed in our earlier work [9] by stirring 50 mg of the compound dissolved in $CDCl_3$ for four days in a sealed 10 mm tube at room temperature in the presence of <1 atmosphere of 90% enriched ^{13}CO. The low temperature ^{13}C NMR limiting spectrum of this sample was identical to that previously reported. The solvent was removed under reduced pressure from the recorded solution, and IR monitoring showed that the residue contained $Co_2(CO)_8$ and $HFeCo_3(CO)_{12}$. Thus we feel that in the above experimental conditions $HFeCo_3(CO)_{12}$ has undergone a partial declusterification to $Fe(CO)_5$ and $Co_2(CO)_8$ not dissimilar to that reported by U.V. irradiation in CO atmosphere [15]. The chemical shifts at 210.2 and 203.1 ppm are similar to those reported for $Fe(CO)_5$ [16] and $Co_2(CO)_8$ [17]. By repeating the enrichment in preparative scale (200 mg of $HFeCo_3(CO)_{12}$ in a sealed ampoule) and by separation of the residue on SiO_2 column, eluent $CHCl_3$, we were able to obtain a sample of enriched (30%) $HFeCo_3(CO)_{12}$ whose purity was confirmed by ms.

$[FeCo_3(CO)_{12}]^-$

The method reported by Chini [14] was slightly modified. A mixture of $Co_2(CO)_8$ and $Fe(CO)_5$ (molar ratio 1:0.8) was refluxed for 6 hours in acetone under N_2. After filtration, the solvent was removed under reduced pressure; the residue was washed three times using warm cyclohexane to eliminate any trace of $Co_4(CO)_{12}$. The black residue showed an IR spectrum (acetone, νCO, cm^{-1}: 2062w, 2006vs, 1969m, 1932m, 1813m) very similar to that reported for $[Et_4N][FeCo_3(CO)_{12}]$ [14]. The enrichment was achieved by stirring a solution of the compound in acetone in a sealed ampoule for five days at +40 °C in the presence of <1 atmosphere of ^{13}CO. Further purification on a SiO_2 column using methanol as eluent was carried out before running the spectra.

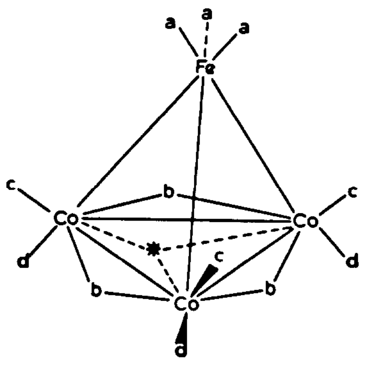
General

^{13}C NMR spectra were recorded on a Bruker WH-400 for $HFeCo_3(CO)_{12}$ and on a Jeol-PFT-100 for $[FeCo_3(CO)_{12}]^-$ operating at 100.5 and 25.1 MHz respectively. All chemical shifts are reported downfield positive with respect to $SiMe_4$. The solvent, $CDCl_3$ for $HFeCo_3(CO)_{12}$ and CD_3OD for $[FeCo_3(CO)_{12}]^-$, were purchased from C.E.A. and distilled immediately prior to use. Solutions were sealed *in vacuo* in 10 mm tubes together with $SiMe_4$ as an internal standard.

Results and Discussion

$HFeCo_3(CO)_{12}$

The low temperature ^{13}C NMR limiting spectrum of $HFeCo_3(CO)_{12}$ (see Experimental Section) is fully consistent with its ^{17}O NMR spectrum [10] and with the solid state structure inferred from that of $HFeCo_3(CO)_9[P(OMe)_3]_3$.



✱ = H for the hydrido complex
✱ = ⊖ for the anion complex

Four resonances of almost equal intensities are observed at 231.7, 208.2, 194.8 and 191.0 ppm in the low temperature ^{13}C NMR limiting spectrum (−63 °C). Three of them are significantly broader than that at 208.2, thus the latter is assigned to the terminal carbonyls bound to the non-quadrupolar iron atom *a*. Among the remaining resonances the downfield one is attributed to the bridging carbonyls *b* and the others to the terminal COs bound to the cobalt atoms *c*, *d*. By comparing the ^{13}C- and ^{17}O-NMR spectra an inversion in the chemical shift order between resonances attributed to terminal carbonyls is clear. On raising the temperature to −40 °C the broadening of the *b*, *c* and *d* resonances occurs while that at 208.2 (*a*) remains sharp. At higher temperature the spectral features are similar to those observed in the ^{17}O NMR study [10].

$[FeCo_3(CO)_{12}]^-$

The redox condensation of $Fe(CO)_5$ and $Co_2(CO)_8$ has been reported to give the first mixed metal carbonyl, the anion $[FeCo_3(CO)_{12}]^-$, which is believed to be isostructural with $Co_4(CO)_{12}$ [14]. Accordingly, four resonances of equal intensities are expected for the COs in the low temperature ^{13}C NMR limiting spectrum. This is observed at −98 °C at 247.5, 217.4, 205.2 and 201.5 ppm (Fig. 1).

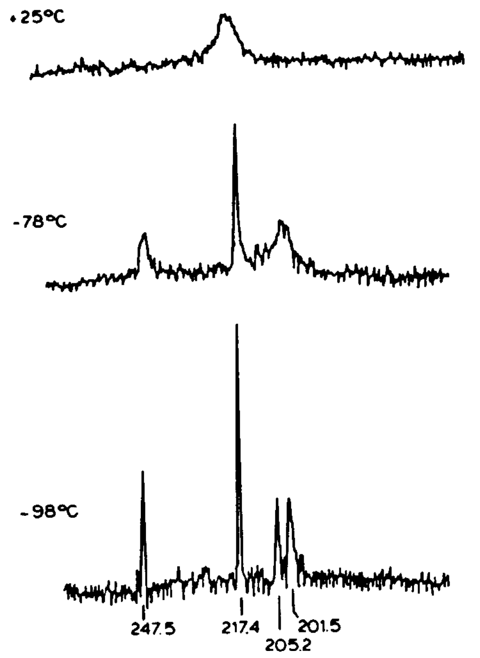


Fig. 1. VT ^{13}C NMR spectra of $[FeCo_3(CO)_{12}]^-$ in CD_3OD.

The resonances are assigned as for the hydrido parent compound; the observed downfield shift of all the resonances is a consequence of the negative charge [18].

On raising the temperature to −78 °C the broadening of *b*, *c* and *d* resonances occurs much faster than that of *a*. A further increase in the temperature causes the collapse of all the resonances, which merge in a single peak observed in the room temperature spectrum at 218.5 ppm. The chemical shift is in good accord with the weighted average or the resonances observed in the −98 °C spectrum (217.9 ppm). We interpret these results as evidence of the exchange of the COs in two steps. The lower energy process involves only the COs bound to the cobalt atoms, in the higher energy process all the COs are engaged. The broadening of the resonances of the cobalt bonded COs in the −98, −78 °C interval is mainly ascribed to the COs exchange rather than to the progressively inefficient quadrupolar relaxation [19] of the cobalt nuclei, since this kind of broadening is not substantial in this range of temperature for $Co_4(CO)_{12}$ [9], $FeCo_2(CO)_9S$ [20] and $FeCo_2(CO)_9(C_2Et_2)$ [21]. We point out that the VT ^{17}O NMR spectra of $HFeCo_3(CO)_{12}$ has revealed [10] two steps, very close in activation energy for the scrambling of the COs bound to cobalt atoms. The lower step is consistent with the merry-go-round process [4], the slightly higher one consistent with rotation of $Co(CO)_3$ faces, giving respectively a 6:3:3 and 9:3 patterns. In the VT ^{13}C NMR spectra, although recorded at the same field, these two processes are undistinguishable. The same considerations might hold for $[FeCo_3(CO)_{12}]^-$.

Alternatively the absence of the face bridging hydride might effectively lower the activation energy of triangular rotation. The preferential site of the negative charge in $[FeCo_3(CO)_{12}]^-$ can be ascertained by comparing the $\delta(^{13}C)$ of the carbonyl ligands in $HFeCo_3(CO)_{12}$ and $[FeCo_3(CO)_{12}]^-$, since more downfield shifts of the carbonyls are observed for higher electron density. This is consistent with a reduction in the CO bond order as a result

TABLE I. Comparison between $\delta(^{13}CO)$ in $HFeCo_3(CO)_{12}$ and $[FeCo_3(CO)_{12}]^-$.

Carbonyl	Hydrido parent	Anion	Δ/ppm
b	231.7	247.5	15.8
a	208.2	217.4	9.2
c,d	194.8	205.2	10.5
	191.0	201.5	

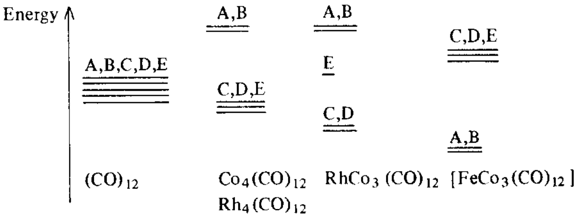
of increasing dative d_π–π^* bonding and is in agreement with the shift of νCO to lower frequencies [18].

The data reported in Table I indicate that the $Co_3(CO)_9$ moiety, mainly through the bridging carbonyls, is the fragment of the cluster in which the electron density is preferentially localized. This is in agreement with the observations reported for the *isobal* $Co_3(CO)_9CY$ compounds [22], in which the $Co_3(CO)_9$ fragment acts as the electron reservoir of the whole cluster.

Fluxional Behaviour of $[FeCo_3(CO)_{12}]^-$ in the Tetrahedral $M_4(CO)_{12}$ Series

The dynamics of tetrahedral $M_4(CO)_{12}$ clusters having C_{3v} symmetry is accounted for by the rearrangement of the initial icosahedral of COs ligands *via* a cubo-octahedral transition-state. There are two sets of degenerated modes of this distortion [13a]. Modes A and B consist in a cyclic permutation of the six ligands in the equatorial plane (merry-go-round process). Modes CDE result in the formation of ligand bridges about faces of the M_4 tetrahedron, that were not originally the bridged one. Consideration of the entity of the distortion during such processes leads to the conclusion that for homometallic $M_4(CO)_{12}$, modes C–E occur at lower energy than AB ones. The former set results in the exchange of all the ligand over the four metals as found for $Rh_4(CO)_{12}$ [5] and $Co_4(CO)_{12}$ [10].

For heterometallic $M_3M'(CO)_{12}$ species the above degeneracy may be further lifted depending on the position of the heterometal. In the complex $RhCo_3(CO)_{12}$ the heterometal occupies a basal position in the tetrahedron [23, 24]. Modes C, D will have lower activation energy than E, because they result in the formation of isomers with the Rh atom in the basal plane (ground-state structure) instead of a less stable isomer with Rh apical, as produced by mode E. Modes A, B (again degenerate) are expected to have higher activation energies because of breaking of a stable Rh–CO terminal bond. This order of processes finely matches the experimental results [24]. The title anion has the heterometal in the apical position. Thus, the degeneracy is not removed with respect to $M_4(CO)_{12}$. In this case, however, the AB modes are expected to occur at lower activation energy than C–E modes because the former set results in formation of an isomer with Fe in the apical position (ground-state structure) instead of less stable isomers with the iron atom occupying a basal position (as in C–E modes). A, B modes associated with triangular face rotation of $Co(CO)_3$ units fully explain the experimentally observed 9:3 relationship. This mechanism has been proved to be operative in $Rh_4(CO)_8[P(OPh)_3]_4$ [25]. At higher temperature C–E modes account for the total carbonyl scrambling.



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