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MÖSSBAUER STUDY OF SOME Fe-CONTAINING M_6 AND M_5 CLUSTERS

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Summary

Isomer shift (δ) and quadrupole splitting ($\triangle$) parameters have been assigned to the iron sites in $[FeRh_5(CO)_{16}]^-$, *trans*- and *cis*-$[Fe_2Rh_4(CO)_{16}]^{2-}$, $[Fe_3Rh_3(CO)_{17}]^{3-}$, $[FeRh_4(CO)_{15}]^{2-}$, $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd or Pt) from ^{57}Fe Mössbauer spectra recorded at 78 K. The data for the *closo* compounds $[FeRh_5(CO)_{16}]^-$ and $[Fe_2Rh_4(CO)_{16}]^{2-}$ are compared with those for $[Fe_6(CO)_{16}C]^{2-}$. In $[Fe_3Rh_3(CO)_{17}]^{3-}$, the three major Fe sites were identified. For both $[Fe_4M(CO)_{16}]^{2-}$ compounds two isomers were shown to be present in the solid state.

Introduction

We previously noted that the Mössbauer spectrum of the *closo* cluster $[Fe_6(CO)_{16}C]^{2-}$ showed only one doublet (δ 0.23, Δ 0.56 mm s^{-1}) with peak width (Γ 0.25 mm s^{-1}) which was very close to the natural line width of Mössbauer spectra [1]. This was remarkable because the structure of $[Fe_6(CO)_{16}C]^{2-}$ is known to contain four distinctly different Fe-carbonyl ligand arrangements [2], which would have been expected to have been observed separately, i.e. two $Fe(CO)_2{}^tCO^{br}$(sym.), two $Fe(CO)_2{}^t(CO)^{br}$ (unsym.), one $Fe(CO)_3{}^t$, and one $Fe(CO)_2{}^t(CO)_2{}^{br}$(unsym.). Similar sites in Fe_5 [1], Fe_4 [3], and Fe_3 clusters [4] could in general be observed separately. The present study seeks to investigate M_6 and M_5 clusters further by considering the spectra of some compounds which are *closo* on a polyhedral skeletal electron count but which do not contain an interstitial ligand, namely $[FeRh_5(CO)_{16}]^-$ and $[Fe_2Rh_4(CO)_{16}]^{2-}$ [5]. We also consider some compounds with unusual structures such as $[Fe_3Rh_3(CO)_{17}]^{3-}$, which has a *nido* electron count [6], and $[FeRh_4(CO)_{15}]^{2-}$, which has an *arachno* count but a closed trigonal bipyramidal structure [5]. Finally some unusual compounds which contain planar metal skeletons, $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd or Pt) [7] and $[Fe_3Pt_3(CO)_{15}]^{2-}$ [8] are discussed.

Experimental

The compounds $[FeRh_5(CO)_{16}]^-$, $[Fe_2Rh_4(CO)_{16}]^{2-}$, $[FeRh_4(CO)_{15}]^{2-}$ [5], $[Fe_3Rh_3(CO)_{17}]^{3-}$ [6], $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd or Pt) [7], and $[Fe_3Pt_3(CO)_{15}]^{2-}$ [8] were prepared by published methods. Except for $[FeRh_4(CO)_{15}]^{2-}$, the structures of these compounds had been established by single crystal X-ray diffraction studies [5–8].

Mössbauer spectra of polycrystalline samples were recorded at 78 K on an apparatus previously described [9]. In the case of $[Fe_4M(CO)_{16}]^{2-}$ the spectra of a polycrystalline sample were recorded at 78, 100, 180 and 276 K by use of an Oxford Instruments CF 100 variable temperature cryostat. Similarly, spectra of $[Fe_4Pt(CO)_{16}]^{2-}$ were recorded at 78, 215 and 290 K. The spectrum of a single crystal of $[Fe_4Pd(CO)_{16}]^{2-}$ was recorded at 78 K. Isomer shift values are reported relative to sodium nitroprusside as standard.

Results and discussion

Closo-M_6 clusters without interstitial atoms

The X-ray crystallographic analysis of the $[N(PPh_3)_2]^+$ salt of $[FeRh_5(CO)_{16}]^-$ [5] showed that the compound is isostructural (Fig. 1) with the isoelectronic $[Rh_6(CO)_{16}]$. Each metal atom has two terminal and two triply-bridging CO ligands. In the $FeRh_5$ cluster the metal atoms are disordered and the unique iron atom is mainly distributed in two mutually *trans* positions (ca. 40% each). However, since all sites are stereochemically identical, the Mössbauer spectrum shows a simple doublet with parameters δ 0.34; Δ 1.32, and Γ 0.27 mm s^{-1}. Clearly the $Fe(CO)_2{}^t(CO)_2{}^{tbr}$ site in this compound is not in the same kind of electronic environment as the iron sites in $[Fe_6(CO)_{16}C]^{2-}$.

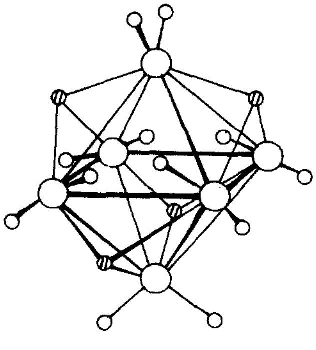

Fig. 1. Molecular structure of $[Fe_nRh_{(6-n)}(CO)_{16}]^{n-}$ (n = 0, 1, 2).

In the carbide the Fe–C bond defines the major symmetry axis of the iron sites to which the carbonyl ligands contribute a small (low symmetry) perturbation. Whereas in the $[FeRh_5(CO)_{16}]^-$ cluster the carbonyl ligands represent the principal influence on site symmetry, hence the different Δ values. The more asymmetric electric field gradient in $[FeRh_5(CO)_{16}]^-$ is reflected in the large increase in Δ (1.32 compared to 0.56 mm s^{-1}). The value of 1.32 mm s^{-1} may be compared with that reported for the $Fe(CO)_2{}^t(CO)_2{}^{br}$ site in $[FeRu_2(CO)_{10}(PPh_3)_2]$ (0.95 mm s^{-1}) [10]. The difference in δ values (0.34 compared to 0.23 mm s^{-1} in $[Fe_6(CO)_{16}C]^{2-}$) indicates more $4s$ electron density on the iron atoms in the carbide, probably as a result of the enhanced involvement of the hybrid ($4s$, $4p_z$, $3d_{z^2}$) orbital in $Fe–C_{(carbide)}$ bonding.

The interpretation of the Mössbauer spectrum of $[Fe_2Rh_4(CO)_{16}]^{2-}$ is rather complex. An X-ray crystallographic study has shown that the basic structure is like that of the isoelectronic $[Rh_6(CO)_{16}]$ and $[FeRh_5(CO)_{16}]^-$ (Fig. 1) but the iron atoms are disordered in such a way that there is occupancy of all metal positions (occupancy fraction ranging 20 to 50%), with a slight preference for two mutually *trans* sites. Since all sites have the same $M(CO)_2{}^t(CO)_2{}^{tbr}$ environments, one would expect a simple doublet in the Mössbauer spectrum with parameters very close to those in $[FeRh_5(CO)_{16}]^-$. The actual spectrum shows two doublets with the intensity ratio 3/1. The large (outer) doublet has δ 0.32, Δ 1.30 mm s^{-1} and the smaller (inner) doublet has δ 0.40, Δ 0.53 mm s^{-1}. Obviously the larger doublet has the isomer shift and quadrupole splitting parameters expected on the basis of these for $[FeRh_5(CO)_{16}]^-$ but the other site is problematic. Although the solid state structure of $[Fe_2Rh_4(CO)_{16}]^{2-}$ showed occupancy of Fe atoms in all sites, the ^{103}Rh NMR spectrum in acetone showed both *cis*-Fe_2 and *trans*-Fe_2 isomers existing in a 1/3 ratio. It seems possible that in the solid state sample this ratio is retained, and that this feature is the source of the different signals in the Mössbauer spectrum. The indirect evidence from ^{103}Rh NMR clearly suggests that the Fe atoms in the *trans*- and *cis*-compounds are in different electronic environments. In the *trans*-compound only one signal is observed for the Rh atoms ($\delta(^{103}Rh)$ -408.9 ppm) but in the *cis*-compound there are two signals ($\delta(^{103}Rh)$ -408.7 and -452.7 ppm; note $\delta(^{103}Rh)$ in $[Rh_6(CO)_{11}]$ -426 ppm). It is tempting to assign the Mössbauer parameters δ 0.40 ppm, Δ 0.53 mm s^{-1} to the Fe sites in the *cis*-compound but it is difficult to rationalise the effects which are responsible for the substantial increase in δ and decrease in Δ compared to the *trans*-compound. It is known that the reactivity and/or instability of Fe-substituted derivatives of $[Rh_6(CO)_{16}]$ increases with increasing Fe content [5], and this has been associated with the increase in the number of the weaker Fe–Fe at the expense of the stronger Rh–Fe or Rh–Rh bonds. If in general this signifies that the metal–metal cluster bonding has become less important in the *cis*-Fe_2Rh_4 compound compared to the *trans* isomer, then the *cis*-Fe atoms will be in a more "isolated" (ML_n) environment. In the present case the $Fe(CO)_4$ unit will probably become more like a tetrahedral $Fe(CO)_4$ site, i.e. will approach a more cubic symmetry and hence the asymmetry parameter η will tend more towards zero. Interestingly, the parameters for the *cis*-Fe sites (δ 0.40, Δ 0.53 mm s^{-1}) are very close to those for $[Fe_2(CO)_9]$ and $[Fe_2(H)(CO)_8]^-$ (δ 0.36 and 0.26, Δ 0.42 and 0.50 mm s^{-1}, respectively [4]). In the binuclear complexes the iron atoms could be said to have approximately octahedral (cubic) symmetry and the small electric field gradient that they experience lies along the "trigonal" axis of the molecules. In the $[Fe_2Rh_4(CO)_{16}]^{2-}$ cluster the $\{Rh_4(CO)_n\}$-unit could be said to be acting as a bridging ligand similar in effect to the bridging CO or H^- ligands in the binuclear compounds.

$[Fe_3Rh_3(CO)_{17}]^{3-}$ and $[FeRh_4(CO)_{15}]^{2-}$, two clusters with unusual structures

The electronically *nido*-$[Fe_3Rh_3(CO)_{17}]^{3-}$ cluster has two unusual features in the solid state [6]. First, it exists in a trigonal bipyramidal structure with an iron carbonyl unit pendant from an axial metal atom (Fig. 2). Second, although the pendant iron site and the axial iron site have occupancy factors of 1.0, there is some disorder in the other sites. Refinement showed the equatorial iron site in Fig. 2 to have an occupancy of 0.89 with remaining 0.11 fraction located randomly in the other three metal sites (Rh in Fig. 2). All isomers have the same number of Fe–Fe, Rh–Fe and Rh–Rh bonds, i.e. 1, 6, and 3, respectively. It has been suggested that this unusual structure owes some of its stability to the involvement of many of the CO ligands as bridging ligands [6]. This enables the relatively high negative charge to be accommodated better in the present structure than in a less CO-bridged octahedral or raft structure. From the X-ray analysis it would be expected that three "major" sites $Fe(CO)_3{}^t(CO)_2{}^{br}$, $Fe(CO)_3{}^t(CO)^{br}$, and $Fe(CO)_2{}^t(CO)_2{}^{br}$ with occupancy factors of 1.0, 1.0, and 0.89 would be observed in the Mössbauer spectrum but that the three "minor" sites with the total occupancy factor 0.11, i.e. two $Fe(CO)^t(CO)_2{}^{br}$ sites and one $Fe(CO)_3{}^{br}$, would probably not be clearly located. Throughout our previous work on iron carbonyl clusters [1,3,10,12] we have found that the variation in δ values (0.23 to 0.38 mm s^{-1}) is remarkably small. Using this information and the relative site occupancy factors, we were able to identify three pairs of doublets corresponding to the three major sites (Fig. 3).

The doublet with δ 0.29, Δ 1.71 mm s^{-1} is assigned to the pendant $Fe(CO)_3{}^t(CO)_2{}^{br}$ group. The X-ray analysis showed the overall geometry of this site to be somewhat like that in $Fe(CO)_5$ (δ 0.30, Δ 2.57 mm s^{-1} [4]) and the $Fe(CO)_3{}^t(CO)_2{}^{br}$ sites in the $[Fe_3(CO)_{12}]$ (δ 0.32, Δ 1.11 mm s^{-1}). The $Fe(CO)_2{}^t(CO)_2{}^{br}$ site is assigned δ 0.31 and Δ 1.14 mm s^{-1}. The Δ value lies within the range expected by comparison with similar sites in $[FeRu_2(CO)_{10}(PPh_3)_2]$ (0.95) [10] and $[FeRh_5(CO)_{16}]^-$ (1.32). The apical iron site is assigned parameters δ

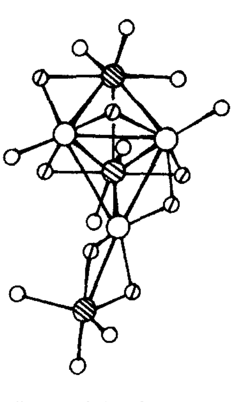

Fig. 2. Molecular structure of $[Fe_3Rh_3(CO)_{17}]^{3-}$.

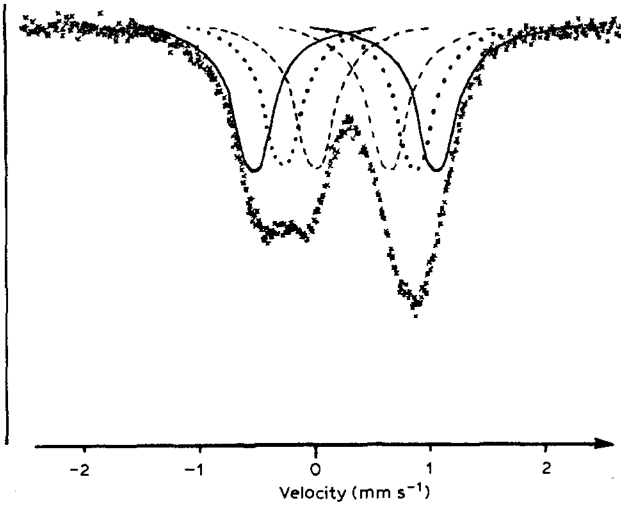

Fig. 3. Mössbauer spectrum of $[Fe_3Rh_3(CO)_{17}]^{3-}$.

0.34, Δ 0.64 mm s^{-1} which are close to those for the analogous $Fe(CO)_3{}^t(CO)^{br}$ site in $[Fe_3Ni(CO)_{12}]^{2-}$ (δ 0.32, Δ 0.62 mm s^{-1}) [12].

The M_5 cluster $[FeRh_4(CO)_{15}]^{2-}$ has an electron count which, if Wade's rules were obeyed, would imply a structure based on a pentagonal bipyramid with two vertices removed. Instead, the structure indicated by multinuclear NMR spectroscopy is a trigonal bipyramid with the iron atom in an axial position bonded to two bridging and three terminal CO ligands [5] (Fig. 4). Although all the CO ligands except those bridging the Rh_3-equatorial triangle are migratory at 65°C, there was no evidence for metal rearrangements at this temperature. The Mössbauer spectrum showed a simple doublet with parameters (δ 0.31, Δ 0.57 mm s^{-1}) close to those for the sites in $[Fe_6(CO)_{16}C]^{2-}$. This is consistent with the $Fe(CO)_3{}^t(CO)_2{}^{br}$ unit having a high degree of "completeness" which it presumably would not have if the cluster structure were based on an open *arachno* system. As has been pointed out previously [5], the geometry about the Fe atom in crystalline $[FeRh_4(CO)_{15}]^{2-}$ is most probably like that for the Ru atom in $[RuIr_4(CO)_{15}]^{2-}$. Here the five CO

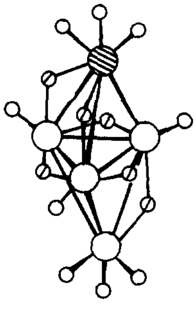

Fig. 4. Molecular structure of $[FeRh_4(CO)_{15}]^{2-}$.

ligands and the unbridged Ru–Ir bond form a regular octahedral architecture around the Ru atom. Hence, on the basis of this observation, we would expect a low Δ value because of the local pseudo-octahedral environment even though there is no interstitial atom to provide "complete" cluster bonding of the $Fe(CO)_3{}^t(CO)_2{}^{br}$ unit such as is found in $[Fe_6(CO)_{16}C]^{2-}$.

Clusters with planar metal skeletons

Both $[Fe_3Pt_3(CO)_{15}]^{2-}$ (Fig. 5) [8], and $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd or Pt) (Fig. 6) [7] have been studied by single crystal X-ray techniques. The structures are raft-like and contain essentially planar metal arrangements with $Fe(CO)_4$ units. To a first approximation all the iron carbonyl units could be described as $Fe(CO)_4{}^t$ sites but there is clear evidence of semi-bridging between one CO per iron and the central metal atoms in $[Fe_4M(CO)_{16}]^{2-}$. These bridges are alternatively above and below the Fe_4M-plane (Fig. 6). In the case of $[Fe_3Pt_3(CO)_{15}]^{2-}$ the metal skeleton is twisted slightly out of plane so that the iron atoms are displaced by amounts ranging from 0.1 to 0.6 Å from the plane containing the Pt_3 triangle (Fig. 5), and some CO ligands are bent towards the Pt atoms. The bonding abilities of $M(CO)_4$ units and their possible interactions with p_z and d_{z^2} orbitals on the Pd or Pt atoms have been discussed in detail elsewhere [13].

The gross geometry around the iron atoms in $[Fe_3Pt_3(CO)_{15}]^{2-}$ is approximately octahedral but the PtFePt angle is ca. 63°. In view of this the Mössbauer spectrum would be expected to show a simple doublet with a Δ value similar to those found for $Fe(CO)_4{}^t$ sites $[Fe_3(CO)_{12}]$ (0.08 mm s^{-1}) or $[Fe_3(H)(CO)_{11}]^-$ (0.16 mm s^{-1}) [10]. The actual value of 0.26 mm s^{-1} can be accounted for in terms of the slightly greater overall distortion from octahedral geometry in the Fe_3Pt_3 compound.

The isomer shift (δ 0.21 mm s^{-1}) is lower than those for $[Fe_3(CO)_{12}]$ and $[Fe_3(H)(CO)_{11}]^-$ (0.36 and 0.32 mm s^{-1}, respectively). This could be due to an increase in the amount of negative charge localised on the Fe atoms in $[Fe_3Pt_3(CO)_{15}]^{2-}$.

It is of interest to compare the structure of $[Fe_3Pt_3(CO)_{15}]^{2-}$ with those of $[Rh_6(CO)_{16}]$, $[FeRh_5(CO)_{16}]^-$, and $[Fe_2Rh_4(CO)_{16}]^{2-}$ and $[Fe_3Rh_3(CO)_{17}]^{3-}$. The first four compounds are all strictly "*closo*" 86-electron clusters which do not contain interstitial ligands. However platinum rarely behaves in metal clusters as a normal metal, and often prefers planar coordination or the formation of highly nucleated clusters such as $[Pt_{26}(CO)_{32}]^{2-}$ or $[Pt_{38}(CO)_{44}(H)_2]^{2-}$ [14]. In the Fe_3Pt_3 compound the structure is apparently determined less by metal–metal cluster

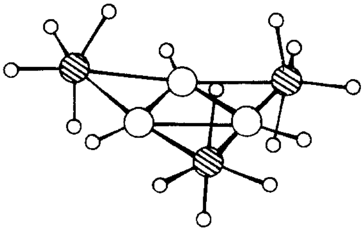

Fig. 5. Molecular structure of $[Fe_3Pt_3(CO)_{15}]^{2-}$.

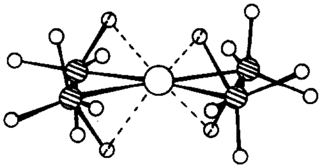

Fig. 6. Molecular structure of $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt).

bonding involving the six centres than by the requirement of the Pt atoms to adopt a planar configuration. The $Fe(CO)_4$ unit, which is isolobal with CH_2, performs a bridging function like CO in $[Pt_3(CO)_6]^{2-}$. In some respects the Fe_3Pt_3 compound could be considered as incorporating some of the effects found for the sequence $[Rh_6(CO)_{16}]$, $[FeRh_5(CO)_{16}]^-$, and $[Fe_2Rh_4(CO)_{16}]^{2-}$ and also indicated by the non-observation of $[Fe_3Rh_3(CO)_{16}]^{3-}$ [5,6]. In the $[Fe_3Rh_3(CO)_{17}]^{3-}$ cluster the failure to incorporate all three iron atoms into the metal cluster framework is important in determining the structure and particularly the formation of the pendant $Fe(CO)_3{}^t(CO)_2{}^{br}$ unit. It is apparent that failure to incorporate the iron atoms into a three dimensional metal framework is even more marked in the Fe_3Pt_3 and Fe_4M compounds.

The published structures of the trimethylbenzylammonium salts of $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd or Pt) show $Fe(CO)_4$ sites which are more distorted than those in $[Fe_3Pt_3(CO)_{15}]^{2-}$ [7]. Since they are all equivalent, one would expect a simple doublet in the Mössbauer spectrum with Δ somewhat greater than 0.26 mm s^{-1}. The spectrum of the Fe_4Pd cluster showed four lines as two pairs whose ratios depended slightly on the sample used; see e.g. Fig. 7a. For the same sample the relative intensities of the lines remained constant over the temperature range 78 to 276 K, which suggested the absence of any isomerisation or phase change on cooling Fig. 7a–c. Closer examination of the analytically pure sample revealed that it contained small microcrystallites or powder and several larger single crystals. It was decided to record the spectrum of a single crystal in case the sample had contained two different (possibly isomeric) but analytically identical compounds. Although the spectrum of the single crystal was of lower quality (because of the lower intensity), it clearly showed only the lines of the inner doublet (δ 0.32, Δ 0.34 mm s^{-1}) (Fig. 7d). To date we have not succeeded in characterising the second component of this mixture (δ 0.31, Δ 1.13 mm s^{-1}) but the Mössbauer parameters suggest a possible $Fe(CO)_3{}^t(CO)_2{}^{br}$ type site. Since the crystal used in the Mössbauer work had a similar morphology to that used for the X-ray analysis we conclude that the Mössbauer results refer to the compound whose structure had been reported [5].

Another aspect of the spectra shown in Fig. 7a–c is noteworthy. There is a distinct change with temperature in the quadrupole splitting of the inner doublet but the outer doublet changes imperceptably. The values (mm s^{-1}) for the inner doublet are 0.31 at 78 K, 0.27 at 180 K, and 0.21 at 276 K. It therefore appears that the weak semi-bridging Pd $\cdots$ OC(Fe) interactions become progressively weaker as the temperature is raised and the $Fe(CO)_4$ site becomes more octahedral. On the other hand if the second component of the polycrystalline sample had contained $Fe(CO)_3{}^t(CO)_2{}^{br}$ sites which were not interacting with Pd, they would not have been as affected by a change in temperature.

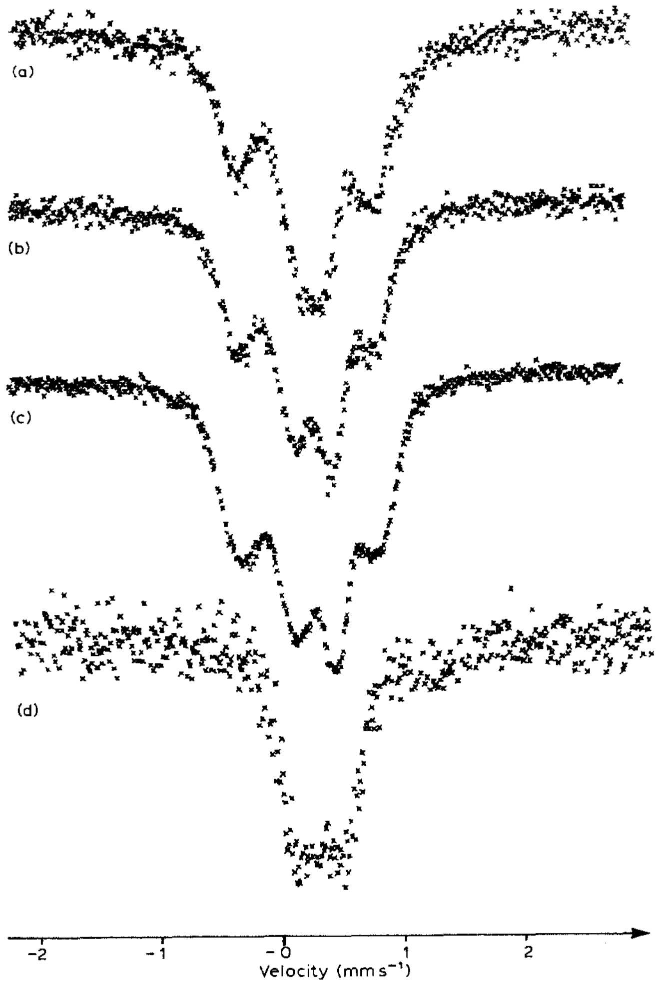

Fig. 7. Mössbauer spectra of polycrystalline samples of $[Fe_4Pd(CO)_{16}]^{2-}$ recorded at (a) 276, (b) 180, (c) 78 K and (d) a single crystal recorded at 78 K.

The spectrum of $[Fe_4Pt(CO)_{16}]^{2-}$ was analogous to that of the palladium compound. The Mössbauer parameters were δ 0.31, Δ 0.48 and δ 0.30, Δ 1.11 mm s^{-1}. The slightly larger values of Δ for the inner doublet compared to the Fe_4Pd compound is understandable in terms of differences in the X-ray structures. In the Fe_4Pt cluster the semi-bridging CO–M interactions are stronger, as shown by the bond lengths $Pt–C_{semi-br}$ 2.285 and $Pd–C_{semi-br}$ 2.371, and $Fe–C_{Pt}$ 1.814 and $Fe–C_{Pd}$ 1.766 Å. Hence there is a greater distortion from octahedral in the Pt case, and this is confirmed by the observation of a 7° dihedral angle between the Fe_2Pt triangles whereas the Fe_4Pd skeleton is planar. A difference in δ values for the inner doublets in the Pt and Pd clusters can be expected if there is a decrease in the negative charge subtended at the Fe sites as has been previously suggested [5]. Both the M_5 clusters show larger δ values than that found in the Fe_3Pt_3 compound. This may be a function of the reduced negative charge per Fe atom in the Fe_4M compounds.

Conclusions

A comparison of the δ and Δ values for the iron sites in $[FeRh_5(CO)_{16}]^-$ and $[Fe_6(CO)_{16}C]^{2-}$ confirms that the $Fe-C_{carbide}$ interaction is a major factor influencing both the electric field gradient and the electron density at the Fe nucleus. The possible effects on the overall cluster bonding of an interstitial ligand have been discussed from a theoretical viewpoint elsewhere [11].

The spectrum of $[Fe_2Rh_4(CO)_{16}]^{2-}$ suggests that the polycrystalline sample contains *cis*- and *trans*-isomers in a 1/3 ratio. The Mössbauer parameters for the *trans*-compound are closely similar to those for $[FeRh_5(CO)_{16}]^-$, but the values for the *cis*-isomer resemble those for $[Fe_2(CO)_9]$. Thus the iron sites in the *cis*-compound appear to resemble the pseudo-octahedral sites in the dinuclear carbonyl.

The unusual compounds $[Fe_3Rh_3(CO)_{17}]^{3-}$ and $[FeRh_4(CO)_{15}]^{2-}$ adopt metal skeletal structures which would not be predicted by Wade's rules. The spectrum of the Fe_3Rh_3 compound contained three doublets which were assigned to the three major types of Fe sites, i.e., $Fe(CO)_3{}^t(CO)_2{}^{br}$, $Fe(CO)_2{}^t(CO)_2{}^{br}$ and $Fe(CO)_3{}^t(CO)^{br}$. The $Fe(CO)_3{}^t(CO)_2{}^{br}$ site in the $FeRh_4$ compound has Mössbauer parameters which are close to those in $[Fe_6(CO)_{16}C]^{2-}$, suggestive of a local iron environment which approaches a pseudo-octahedral geometry.

The $Fe(CO)_4{}^t$ sites in $[Fe_3Pt_3(CO)_{15}]^{2-}$ had a relatively small quadrupole splitting (0.26 mm s^{-1}) which would be expected on the basis of the slightly distorted octahedral geometry. More distorted $Fe(CO)_4{}^t$ units were observed in polycrystalline samples of $[Fe_4M(CO)_{16}]^{2-}$ (Δ 0.34 or 0.48 mm s^{-1} for M = Pd or Pt). However, other sites were also seen in these samples (Δ 1.13 or 1.11 mm s^{-1}, respectively) and these could be associated with CO bridging such as is found at the $Fe(CO)_3{}^t(CO)_2{}^{br}$ sites in $[Fe_3(CO)_{12}]$. The spectrum of a single crystal of $[Fe_4Pd(CO)_{16}]^{2-}$ clearly showed that the polycrystalline data referred to a mixture of isomers, and it is probable that the isomer whose structure had been determined by X-ray crystallograpy was the one with Δ 0.34 mm s^{-1}.

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References

1 R.P. Brint, K. O'Cuill, T.R. Spalding and F.A. Deeney, J. Organomet. Chem., 247 (1983) 61.
2 M.R. Churchill and J. Wormald, J. Chem. Soc., Dalton Trans., (1974) 2410.
3 R.P. Brint, M.P. Collins, T.R. Spalding and F.A. Deeney, J. Organomet. Chem., 258 (1983) C57.
4 N.N. Greenwood and T.C. Gibb, Mössbauer Spectroscopy, Chapman and Hall Ltd., London, 1971.
5 A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni, R.D. Pergola, B.T. Heaton and D.O. Smith, J. Chem. Soc., Chem. Commun., (1982) 886; A. Ceriotti, G. Longoni, R.D. Pergola, B.T. Heaton and D.O. Smith, J. Chem. Soc., Dalton Trans., (1983) 1433; M. Manassero, personal communication.

6 A. Ceriotti, R.D. Pergola, F. Demartin, B.T. Heaton, G. Longoni and M. Manassero, J. Organomet. Chem., 311 (1986) C31.

7 G. Longoni, M. Manassero and M. Sansoni, J. Amer. Chem. Soc., 102 (1980) 3242.

8 G. Longoni, M. Manassero and M. Sansoni, J. Amer. Chem. Soc., 102 (1980) 7942.

9 W.E. Carroll, F.A. Deeney and F.J. Lalor, J. Organomet. Chem., 198 (1980) 189.

10 M.P. Collins, T.R. Spalding, F.A. Deeney, G. Longoni and T. Venalainen, J. Organomet. Chem., 317 (1986) 243.

11 P. Brint, K. O'Cuill and T.R. Spalding, Polyhedron, in press.

12 M.P. Collins, T.R. Spalding and G. Longoni, unpublished results (1986).

13 D.G. Evans and D.M.P. Mingos, Organometallics, 2 (1983) 435.

14 G. Schmid, Structure and Bonding, 63 (1985) 52; D.M.P. Mingos and R.W.M. Wardle, Trans. Met. Chem., 10 (1985) 441.