Metal−Metal and Metal−Ligand Vibrational Interaction in Compounds of the Fe₃EE′(CO)₉ (E, E′ = S, Se, Te) Series and the Low-Frequency Vibrational Spectra of Co₂FeS(CO)₉ and Os₃S₂(CO)₉

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The infrared and Raman spectra of the title compounds in the ca. 400−150 cm⁻¹ region are reported. For the first time, detailed assignments are given for all of the features in this region for the first series of compounds. An attempt is made to extend to all of the modes the plastic cluster model of vibrational analysis, which is normally applied only to ν(M−M) vibrations. While mixing occurs between ν(Fe−Fe) and ν(Fe−E), species containing Te posed particular problems; the reasons for this are discussed and give new insights into the plastic cluster model itself.

Introduction

Transition metal species containing sulfur ligands are of considerable current interest in fields as diverse as bioinorganic chemistry, catalysis, and molecular electronics.[1] Vibrational spectroscopy is a potentially valuable tool in all of these areas but suffers from the disadvantage that the relevant modes fall in relatively low frequency regions where many other modes are also active. Although contemporary tabulations contain typical frequencies for M−S stretching modes,[2] these are not usually sufficient to enable unambiguous interpretations, although significant insights have been gained. It seems to us that there is a real need for analyses admitting of conclusions of some reliability, for such analyses would be of value in the more difficult areas indicated above. In the present communication we give what we believe to be a reasonable interpretation of the low-frequency vibrational spectra of a set of M₃S₂ molecules. Species based on a M₃E unit (M = transition metal; E = chalcogen) have posed a number of vibrational problems, not all of which have been solved, and exhibited interesting phenomena the understanding of which has proved important to an understanding of their vibrational characteristics. So, a remarkable splitting and infrared/Raman exclusion in the low-frequency spectra of the D_{3h} species Co₆(CO)₁₂E₂ (E = S, Se) was found to be the result of the intermolecular packing in the crystal and not intramolecular in origin, although this would be the most evident area of explanation.[3] Then, again, the species Fe₃(CO)₉E₂ (E = S, Se, Te) show an apparent resonance Raman effect in their low-frequency spectra; although relative band intensities change with change in excitation wavelength, to date no rationale has been suggested.[4] These complexities are in contrast to the relatively straightforward analysis suggested by the literature, at least for the ν(M−M) modes. It has been found that the ν(M−M) regions of cluster species are usually explicable to a good first approximation by the Quicksall and Spiro model, an approach which has been termed "the plastic cluster model" (PCM).[5] This is a remarkably simple analysis; it assumes that the stretching of one metal−metal bond has no electronic effect on adjacent metal−metal bonds: that the corresponding interaction constants are negligibly small. All vibrational couplings between the motions of different metal atoms are G-matrix determined. That is, they are determined by the requirement that the motions included in the analysis, collectively, are free of any resultant angular and linear momentum. The PCM has many attractions. The G-matrices are geometry and mass determined; the only ambiguity arises from the mass of the metal atoms: should the mass of groups rigidly attached to a metal atom be added to its mass? The usual answer is "no", thereby, incidentally, avoiding uncertainties in the purely geometric quantities involved in the G-matrix: it contains no parameters. The F-matrix contains only one parameter (if all of the metal atoms are identical), leading to problems which are overdetermined. That reasonable results are obtained is therefore gratifying.[6]

In the present paper we investigate in some detail six iron complexes, Fe₃(CO)₉E₂ (E₂ = S₂, Se₂, and Te₂) and Fe₃(CO)₉-EE′ (E ≠ E′ = S, Se, and Te), a mixed-metal species, Co₂FeS-(CO)₉, and three osmium complexes, Os₃(CO)₈LS₂. Chart 1

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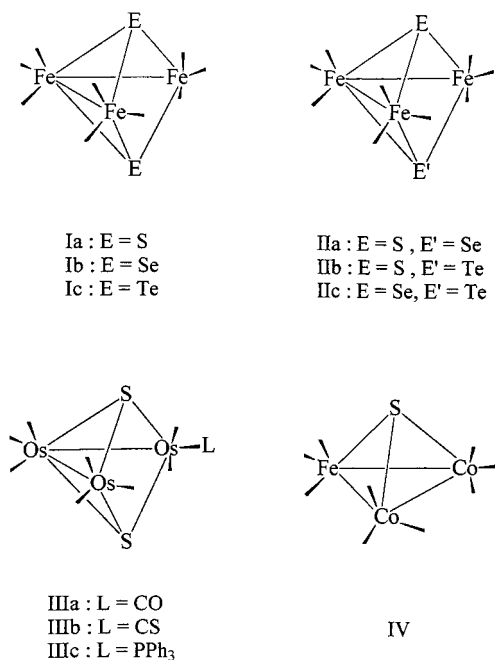§ Università del Piemonte Orientale "A. Avogadro".
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Chart 1

Ia : E = S
Ib : E = Se
Ic : E = Te

IIa : E = S , E′ = Se
IIb : E = S , E′ = Te
IIc : E = Se, E′ = Te

IIIa : L = CO
IIIb : L = CS
IIIc : L = PPh$_3$

IV

Figure 1. Infrared (upper, polyethylene disk) and Raman (lower, crystals) spectra of Fe$_3$(CO)$_9$S$_2$ (**Ia**).

Figure 2. See Figure 1; Fe$_3$(CO)$_9$Se$_2$ (**Ib**).

contains the labels for those compounds that we will discuss in the text, and L is defined. Of interest is the fact that these molecules do not have a basic metallic D_{3h} symmetry; the three metal atoms are not at the corners of an equilateral triangle: two of the metals are not bonded to each other, and so the structure is butterfly-like.[7] Many of these molecules also, of course, contain an EE′ unit (where E can be identical to E′), and it is here that our present interest in the molecules originates. Whereas the S atom is lighter than Fe, Se is heavier and Te much heavier. So, a problem which a study of these molecules addresses is that of the extent to which it remains a valid approximation to separate out the Fe$_3$ motions from those of the E$_2$ in a relatively low symmetry environment.

Experimental Section

The compounds **Ia**, **Ib**, **Ic**,[8] **IIa**, **IIb, IIc**,[9] and **IV**[10] were prepared according to literature methods. The Os complexes were kindly supplied by Prof. B. F. G. Johnson (University of Cambridge).

The mid-infrared spectra were recorded as KBr pellets on a FTIR Bruker Equinox 55 spectrophotometer; the far-IR spectra were recorded as PET pellets on an IFS 113 FTIR Bruker spectrophotometer.

The samples for the Raman spectra were prepared by sealing crystals of the complexes in a glass capillary under argon. The spectra were recorded by a Bruker RFS 100 with Nd^{3+}:YAG laser and Ge-diode detector (laser power 20−100 mW, resolution 4 cm^{-1}). Because the photodecomposition of the samples under the laser light is a real risk, a standard procedure for running the Raman spectra has been adopted. It consists of recording several scan packets (say, 10) of several scans each (say, 50). The spectra of each packet were compared: their common pattern excludes any decomposition of the sample.

The force fields of the Fe$_3$EE′ systems E, E′ = S, Se, Te were studied by use of the CLIMAX[11] program, one that allows rapid iterative calculations. The program employs the methodology of Wilson, Decius,
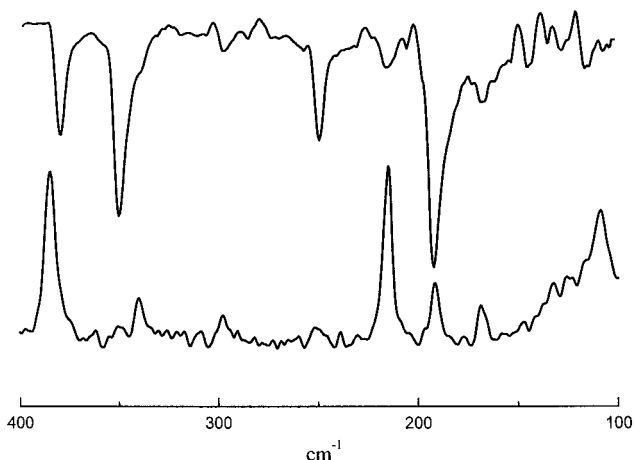
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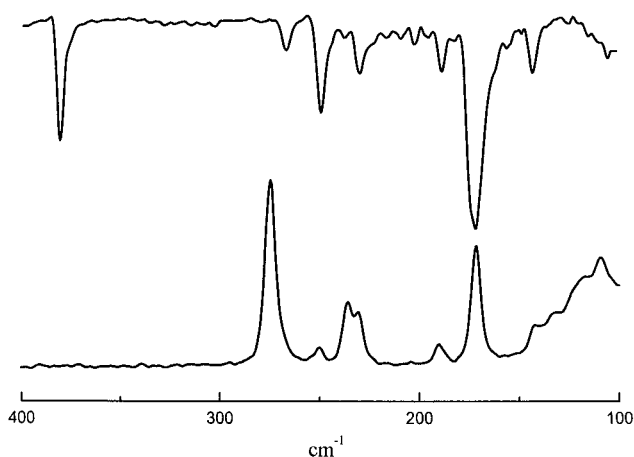
and Cross, and, most important for us, both input and output are expressed in terms of symmetry coordinates. In the program, the geometry of the molecule is expressed in terms of the Cartesian coordinates, the z axis being taken as coincident with the principal molecular rotational axis. Symmetry was introduced in the definition of the U-matrix (symmetry coordinates expressed in term of internal coordinates). The eigenvalues of the output enable comparison with the assignments made below.

Results

The infrared and Raman spectra of the title compounds in the frequency range 400−120 cm^{-1} are given in Figures 1 (**Ia**), 2 (**Ib**), and 3 (**Ic**) and in figures reported in the Supporting Information for the complexes **IIa−c**. The region above ca. 350 cm^{-1} up to about 600 cm^{-1} (not reported in the figures) is essentially the same for all. There is the same pattern of infrared-active bands at nearly the same frequencies for all of the species, but the Raman is weak or silent, except for features assigned as ν(Fe−S) (see below). The infrared peaks are clearly CO in origin and significantly show no sensitivity to the nature of the E groups. As our interest in the present work concerns the interaction between the E- and Fe$_3$-derived modes, we shall not concern ourselves further with these carbonyl features.

It is convenient first to review the spectra of another species, the complex **IV,** with a local C_s symmetry of the core. In contrast to the above complexes, it has a single E group, a

(11) Kearley G. J. *J. Chem. Soc., Faraday Trans. 2* **1986**, *8*, 41; *Nucl. Instrum. Methods Phys. Res.* **1995**, *A345*, 53.

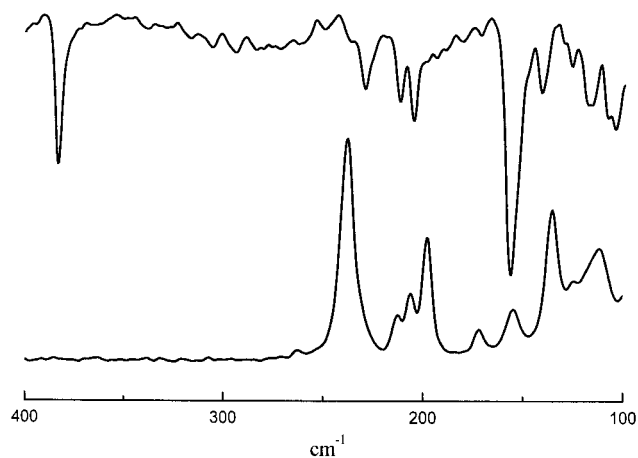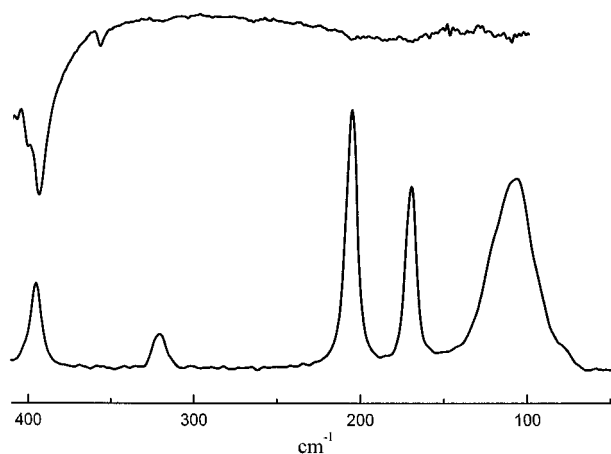**Figure 3.** See Figure 1; Fe₃(CO)₉Te₂ (**Ic**).

Figure 4. See Figure 1; Co₂Fe (CO)₉S (**IV**).

Table 1. Band Assignments for Co₂FeS(CO)₉ (**IV**) (Idealized Symmetry C_s) in the Low-Frequency Region

type of vibration	symmetry	frequency	
		R	IR
ν(M−S)	A′	395 m	394 m
δ(Co₂Fe−S)	A″		356 w
δ(Co₂Fe −S)	A′	321 m	
ν(M−M)	A′	205 s	
ν(M−M)	A″	170 s	

unique S atom, and, consequently, very simple spectra (Figure 4 and Table 1). The importance of the data for this compound is that they serve to define, at least for complexes containing a bridging S atom, the spectral regions of the most important vibrational modes. At first sight, the δ(M₃−S) modes show remarkably high frequencies (at ca. 340−350 cm⁻¹), but, as will become evident, this pattern is common throughout the species that we discuss. The metal core stretching modes give rise to two strong Raman bands at 205 cm⁻¹ (totally symmetric stretching) and at 170 cm⁻¹ (asymmetric stretching). The allocation of these spectral regions leads us smoothly to assignments for all of the E₂ and E,E′ species.

(a) The (Fe−E) Stretching Modes. The absence of any bands in the **Ib** spectra above 275 cm⁻¹ suggests that all bands in the ca. 100 cm⁻¹ region above this and which occur only for S-containing compounds are Fe−S in origin, just as the absence of bands in the **Ic** spectra above 238 cm⁻¹ points to those features which are Se-associated **Ib**. The 386 cm⁻¹ strong Raman band in the **Ia** spectrum is ν(Fe−S)ₛᵧₘ, and the medium band at 350 cm⁻¹ in the infrared is ν(Fe−S)ₐₛᵧₘ. Of these, there

is no evident infrared activity associated with the strong Raman feature (the band at 380 cm⁻¹ evident in Figure 1 is a CO feature), although there is a weak Raman counterpart of the strong infrared. The 36 cm⁻¹ separation between symmetric and antisymmetric combinations shows that coupling occurs between the Fe−S stretching motions of the two S atoms in this molecule.

With the ν(Fe−S) pattern established for **Ia**, the ν(Fe−Se) for **Ib** and the ν(Fe−Te) for **Ic** become reasonably clear (Table 2). Further clarity is shown by the mixed chalcogenide species. So, we can assign the coincident infrared and Raman peaks at 370 cm⁻¹ in the spectra of **IIa** to ν(Fe−S), as it lies at essentially the arithmetic mean frequency of the two peaks for **Ia**. Likewise, in **IIb** ν(Fe−S) is at 367 cm⁻¹. A Raman peak at 265 cm⁻¹ in **IIa** lies at the mean of the two Fe−Se features in the Se₂ compound; in **IIc** there is a corresponding peak at 265 cm⁻¹. Their assignment to ν(Fe−Se) seems reasonable. Essentially the same pattern holds for the Te compounds, although the interleaving−and, as will be seen, mixing−with Fe−Fe modes are problems. In the spectra of **Ic** there is a Raman peak ν(Fe−Te) at 238 cm⁻¹, which has counterparts at 235 and 227 cm⁻¹ in **IIb** and **IIc**, respectively. If the B₁ mode for **Ic** is assigned to that at 229 cm⁻¹ (infrared), then the mean of the two ν(Fe−Te) peaks in this compound is 233 cm⁻¹, close to the ν(Fe−Te) frequency observed in **IIb** and **IIc**, so the assignment to the two ν(Fe−Te) seems clear. In general, then, it is possible to assign the ν(Fe−E) modes, with some considerable confidence (Table 3), at least to a first, rather good, approximation.

(b) The (Fe₃−E) Deformation Modes. We start with the assignment of the four (Fe₃−S) deformation modes in **Ia**, where the sulfurs move over the Fe₃ triangle. A comparison with the spectra of another compound which is not featured in our initial list, **IIIa**,[12] proves very useful. **Ia** and **IIIa** are isostructural: so, the different mass of the Os compared to Fe means that the modes involving the metal cluster are moved to lower frequencies, but the (M₃−S) deformation modes are expected to have very similar frequencies. In fact, the two spectra are very similar (cf. Figure 1 and Figure 5). Additionally, the shift of the metal cluster modes for **IIIa** to lower frequencies allows the spectra of the Os compound to reveal all of the peaks belonging to the four metal−sulfur deformation modes. Clearly, the deformation motions of the sulfur atoms are both highly anisotropic and highly coupled: the spectral pattern seems that of a pair of pairs.[13]

In any of the E₂ compounds the four deformation motions involving the E atoms will fall into two pairs; one pair will be symmetric and the other antisymmetric with respect to reflection in the plane of the metal triangle. That is, the pairs are (A₁ + B₂) and (A₂ + B₁); we associate this pair of pairs with the "pair of pairs" pattern seen in the spectra. It should be possible to determine which pair is which because the A₂ mode has no infrared activity. The spectra of **IIIa** provide this information

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(12) We have also recorded the infrared and Raman spectra of two other Os₃S₂ complexes (**IIIb** and **IIIc**). Their molecular symmetry is lowered to C_s because of the CO substitution, but this is without evident effect on the spectral region under study, and the C_{2v} idealized symmetry of the cores determines the spectra. The spectral patterns observed are essentially identical to those of the parent complex **IIIa** (see Table 1). All of the comments we make relevant to the spectra of the complex **IIIa** can be extended to, and supported by, the vibrational characteristics of complexes **IIIb** and **IIIc**.

(13) The spectra of **IV** show that there is an anisotropy of motion of the S on the surface of the M triangle but, because the splitting is so much smaller when there is only one S atom in a molecule, the major origin of the frequency splitting of the deformation modes in **Ia** must lie in a coupling between the motion of the sulfurs on opposite faces of the metal triangle.

Table 2. Band Assignments for M$_3$E$_2$ Species (Idealized Symmetry C_{2v}) in the Low-Frequency Region

type of vibration	symmetry	Ia R	Ia IR	Ib R	Ib IR	Ic R	Ic IR	IIIa R	IIIa IR	IIIb R	IIIb IR	IIIc R	IIIc IR
ν(M−E)$_{sym}$	A$_1$	386 s		275 s		238 s		380 m	380 w	382 m	380 w	380 m	380 w
ν(M−E)$_{asym}$	B$_1$	350 w	350 m	250 w	250 mw		229 m	364 w	360 mw	355 w	355 w	360 w	360 w
δ(M$_3$−E)	A$_2$	340 m		236 m		172 mw		350 w		345 w		345 w	345 vw
δ(M$_3$−E)	B$_1$	298 m	298 w	230 m	230 w	156 mw	156 s	340 w	340 w	338 m		340 w	340vw
δ(M$_3$−E)	B$_2$	251 mw	250 m	190 w	189 w	212 m	212 m	274 w	280 w	275 w		275 w	280 vw
δ(M$_3$−E)	A$_1$	216 s	ca. 218 w br			206 m	204 m	240 mw	240 w	238 m	240 vw	235 w	235 vw
ν(M−M)	A$_1$	216 s	ca. 218 w br	230 m		198 ms		170 s		170 s		165 s	170 w
ν(M−M)	B$_2$	192 m	195 m	190 w	189 w		156 s	145 m sh	145 ms	ca. 140 w sh	145 w	ca. 145 w sh	150 m
ν(M···M)	A$_1$	168 m	ca. 165 w br	172 m	170 ms			ca. 110 vs br		ca. 100 vs br		ca. 100 vs br	

Table 3. Band Assignments for Fe$_3$EE′ Species (Idealized Symmetry C_s) in the Low-Frequency Region

type of vibration[a]	symmetry	IIa R	IIa IR	IIb R	IIb IR	IIc R	IIc IR
ν(Fe−E)$_{sym}$	A′	370 s	ca. 370 w	367 m	366 w	265 s	ca. 260 vw
ν(Fe−E′)$_{asym}$	A′	265 vs	ca. 260 w br	235 vs		227 s	ca. 230 vw
δ(Fe$_3$−E)	A″	284 mw		282 mw	282 w	ca. 220 w sh	218 w
δ(Fe$_3$−E)	A′	250 m		266 m			
δ(Fe$_3$−E′)	A″	182 m	183 m	ca. 175 m sh	173 w		
δ(Fe$_3$−E′)	A′			166 s	166 w		
ν(Fe−Fe)	A′	208 m		216 m		211 s	
ν(Fe−Fe)	A″	191 s		193 mw	ca. 190 vw	180 m	
ν(Fe···Fe)	A′			166 s	166 w	163 m	164 w

[a] **IIa**: E = S, E′ = Se. **IIb**: E = S, E′ = Te. **IIc**: E = Se, E′ = Te.
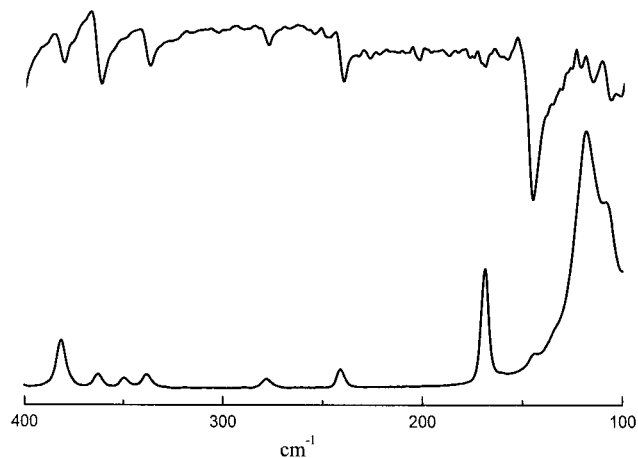
Figure 5. See Figure 1; Os$_3$(CO)$_9$S$_2$ (**IIIa**).

since of the four peaks in the Raman only three are seen in the infrared; the A$_2$ is the highest frequency mode. It follows that the most probable frequency order is A$_2$ > B$_1$ ≫ B$_2$ > A$_1$ (although the B$_2$ and A$_1$ could be reversed). On this basis, the assignment for **Ia** of the two Raman peaks at 340 (A$_2$) and 298 cm^{-1} (B$_1$) as members of the first set of deformations is clear. For the second set, one member is the 251 cm^{-1} peak and we have little doubt that the other is contained within the strong 216 cm^{-1} peak. Averaging all of the deformation frequencies we obtain a value of 276 cm^{-1}. In **IIb**, peaks which can only be δ(Fe$_3$−S) occur at 282 and 266 cm^{-1}, an average of 274 cm^{-1}. The coincidence of these averages is surely significant. In **IIa**, one δ(Fe$_3$−S) peak is at 284 cm^{-1} and the other surely within the medium 250 cm^{-1} feature, an average of approximately 267 cm^{-1}, very close to that previously found. The conclusion is detailed in Tables 2 and 3. It is to be expected that the above frequency sequence holds, mutatis mutandis, for all of the species considered in this paper. Given it, it is

concluded that in the EE′ compounds the frequency sequence is A″ > A′ for each of the δ(Fe−E) and δ(Fe−E′) modes.

A complicating feature, particularly for the species containing Te, is the proximity of ν(Fe−Fe) features to the chalcogenide deformation modes and with which mixing involving A$_1$ and B$_2$ deformation modes can occur: we shall return later to this point.

(c) The (Fe−Fe) Stretching Modes. The assignment of the ν(Fe−Fe) features in **Ia** is straightforward. The totally symmetric mode is at 216 cm^{-1} (Raman strong, infrared weak), and the antisymmetric at 192 cm^{-1} (Raman weak, infrared medium), the infrared and Raman coinciding in both cases. From the antisymmetric mode it is clear that the individual ν(Fe−Fe) vectors have significant dipolar activity, and so it is reasonable to attribute the infrared intensity at 216 cm^{-1} to this activity.

Turning to the other compounds, we search for the presence of these ν(Fe−Fe) modes. They are present in **IIb** (at 216 and 193 cm^{-1}) and, probably, in **Ic** (at 198 and 156 cm^{-1}). For the Se-containing species the nearest assignments (all Raman-based) that one could make are **IIa** (208 cm^{-1} and 191 cm^{-1}, but with an inverted Raman intensity pattern), **Ib** (230 cm^{-1}, 190 cm^{-1}), and **IIc** (211 cm^{-1}, 180 cm^{-1}). Only the latter follows the expected pattern, but even here, there is a problem in that the lower frequency band is much weaker than the corresponding feature in **Ia**. Our general conclusion is that there is mixing between the ν(Fe−Fe) and ν(Fe−Se) modes. This is expected to be greatest for the case of E = Se (where the two sets of modes fall in the same frequency range) but less for E = S (where the deformations are largely at a higher frequency) and E = Te (where the deformations are at a lower frequency). There is a different line of argument leading to the same conclusion. Consider the position of the strongest Raman-active mode in this frequency region. This is at 216 cm^{-1} in **Ia**, at 191 cm^{-1} in **IIa**, and at 172 cm^{-1} in **Ib**. The arithmetic mean of 216 and 172 cm^{-1} is 194 cm^{-1}; that is, the Raman intensity (which the

spectrum of **Ia** shows is largely ν(Fe−Fe) in origin) moves approximately linearly with the Se content of the species, although there is no reason to expect that the frequency of the ν(Fe−Fe) mode will vary in this way. The unavoidable conclusion is that there is extensive mixing between ν(Fe−Se) and ν(Fe−Fe).

(d) The Mixed Modes. The mixing of the modes, as illustrated above, is largely present in the Te-containing complexes. The deformation modes of **Ic** seem to follow a pattern different from that previously described. Assigning them to features which are relatively weak in the Raman (strong Raman bands normally being associated with M−M modes), then we consider those at 212, 206, and 172 cm^{-1}. Of these, only the latter is without infrared counterpart and so must be assigned to the A_2 mode. This is an entirely reasonable frequency: the same mode for **Ia** has frequency 340 cm^{-1} and for **Ib** 235 cm^{-1}. Presumably its B_1 counterpart is located at ca. 156 cm^{-1}. If this analysis is correct, it leads to an inescapable conclusion: that for **Ic** the A_1 and B_1 deformations are at a *higher* frequency than the A_2 and the B_2. Further, they are at higher frequencies than are the bands of the same symmetries assigned to ν(Fe−Fe) modes. Two comments are immediately relevant. First, the assignment of ν(Fe−Fe) modes in **Ic** was based on Raman band intensities and so may be questionable. Second, the frequencies just assigned to the A_1 and B_1 δ(Fe$_3$−Te) modes are quite close to those of the A_1 and B_1 ν(Fe−Fe) modes of **Ia**; those features assigned to the A_1 and B_1 ν(Fe−Fe) modes of the Te$_2$ compound are at significantly lower frequencies. The conclusion is the presence of an extensive mixing between δ(Fe$_3$−Te) and ν(Fe−Fe) so that any unique assignment to either one or the other is somewhat arbitrary. In this case, it is not reasonable to expect that either the frequency or intensity patterns set by other members of the series under consideration in this paper will be followed. That this conclusion is basically correct is supported by the communality of the NCA's which we have carried out and in which the above frequency pattern for the "δ(Fe$_3$−Te)" and "ν(Fe−Fe)" modes is well reproduced. Further evidence supporting this general conclusion is provided by the spectra of **IIb** and **Ic** in this region, where, as has been noted above, only the latter shows an assignment/intensity problem. Recall that in the E$_2$ species there is a strong cross-Fe$_3$ plane coupling of the motions of the E atoms which leads to a much larger splitting of the deformation modes than in the EE′ compounds. So, although in **Ic** the highest frequency deformations fall very close to the ν(Fe−Fe), in the TeE′ they do not. That is, if significant coupling occurs between ν(Fe−Fe) and δ(Fe$_3$Te) in **Ic**, it will not in the TeE. It is then understandable that the observed assignment/intensity anomalies should occur only for the former.

(e) The (Fe···Fe) Stretching Mode. In that it has in large measure been accounted for in the above discussion, it is helpful to return to the spectrum of **Ia**, that shown in Figure 1. In fact, only one peak remains unassigned, that at 168 cm^{-1} (Raman; 165 cm^{-1} infrared). It cannot, directly at least, involve the S atoms because all of the modes of these have been accounted for. It cannot involve the COs because the feature is too variable in the spectra of the other species. There seems to be only one possible assignment to a ν(Fe···Fe) between the two formally nonbonded iron atoms. We recall that, had the system been that of an equilateral triangle of metal atoms, then there would have been three ν(Fe−Fe) modes to consider, and, so far, we have met only two. The third, if it is apparent, will surely be at a lower frequency as, indeed, is the mode under consideration. If this assignment is correct, we must expect that in the Os$_3$S$_2$

case a counterpart will be evident. Indeed, there is a fairly strong low-frequency peak in the Raman of this compound which presumably is this counterpart. This assignment must be expected to contribute to the spectra of all of the species under discussion. However, for most of the other species the fact that this mode is of A_1 symmetry will mean that it may be influenced by the couplings involving this symmetry which have been discussed above.

Discussion

The above assignments provide a rather complete qualitative understanding of the low-frequency spectra of the title compounds. Is it possible to obtain at least an approximate quantitative interpretation which enables the understanding of the spectra of those species in which mixing occurs? The frequent and successful use of linear interpolations gives hope that the answer is in the affirmative.

(a) The Plastic Cluster Model. We have first applied the PCM to the problem. The main problem to be addressed is the way that the E atoms are treated. According to the general tenet of the PCM, they have been treated in a manner almost equivalent to the way that the metal atoms are covered: that is, we use a correct G-matrix but an approximate F. As evident from the above discussion, two ν(Fe−Fe) force constants are needed, including one associated with the two nonbonded metal atoms. For the E$_2$ complexes, G-matrix coupling alone will not give the observed large interaction between the deformation modes. We have therefore made a systematic study of the effect of the introduction of different relevant coupling constants; a coupling between ν(Fe−E) on either side of the metal triangle, a coupling between ν(Fe−E) on the same side of the metal triangle, and finally, a coupling between ν(Fe−E) and ν(Fe−Fe). In these analyses, the E$_2$ species behave differently from the EE′. For the former, the only interaction constant with a nonzero value is that between ν(Fe−E) and ν(Fe−Fe), whereas for the latter the nonzero constant is that between the two ν(Fe−E) with the same E atom. All of the others, in particular the cross-metal-triangle ν(Fe−E)−ν(Fe−E) coupling constants, are negligible. Moreover, the EE′ complexes require, of course, two different iron−chalcogen stretching force constants. The interested reader can find the detailed calculation in the Supporting Information.

This extension of the PCM includes therefore a maximum of six unknowns. Because there are at least seven or eight observed frequencies for all of the molecules, the problems are all overdetermined.[14] This model, in which no account was taken of the CO groups, gives rise to reasonable frequency fits which conformed to our assignments for **Ia, Ib,** and **IIa**. However, for the other complexes the agreement between the calculation and our assignments was quite poor. As any other reasonable set of force and interaction constants produces similar results and as we have considerable faith in our assignments, we discarded this model and undertook a search for a model which gives acceptable fits for all of the species studied.

(b) The Heavy Atom Model. We proceed using the recognition that it is the heaviest of the chalcogenides which gives the worst fit in the above analysis. In such a case one would normally consider other heavy atoms in the system and the way that they have been treated. In fact, such heavy units are the Fe(CO)$_3$ groups, whose mass of ca. 140 can be compared with

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(14) In this, as in all of the calculations that are presented in this paper, we have required that the system be overdetermined; that is, the number of experimental data should exceed the number of force and interaction constants.

the mass of Te of ca. 127. In the PCM all carbonyl groups are ignored; they merely ride on the motion of the metals. Of course, it is the mass of the bare metal that is used in the G-matrix, but this difference with the real mass must surely be compensated by the force constant values that result. In our systems the real masses are used for the chalcogenides but unreal masses are used for the metals. As seen above, it seems that this problem is minimal until the mass of one of the atoms in the system approximates that of the real mass of a group which has been given an unreal mass.

If this is the origin of the difficulty with the Te system, the way forward is obvious: the mass of the $Fe(CO)_3$ group should be used in place of that of the Fe. Unfortunately, placing this mass in the most obvious position, at the center of mass of the $Fe(CO)_3$ group, removes from the PCM the simplicity, which is one of its attractions. However, we studied this alternative, the so-called HAM, the "heavy" atom model. While it is possible to obtain good fits for all of the species using this model, we have been unable to find a unique force field which both gives acceptable frequency fits and agreement with our assignments for all of the species. The species with heavy chalcogenides, again, produces the greatest problems. Nonetheless, we believe that this model could be developed to be of value in the future, in the resolution of problems resulting from the low-frequency vibrations of the carbonyl groups (vide infra). Details of this model are given in the Supporting Information.

(c) The Center-of-Gravity Model. The best fit has been obtained by another model, which we call CGM, the center-of-gravity model. In this model, the carbonyl groups are combined together and placed as a single pseudoatom approximately at the center of gravity of the molecule (actually, on the E−E′ axis and in the plane defined by the three metal atoms). This is the place where, rather accurately, their combined center of mass falls. This pseudoatom is then treated in exactly the same way as a real atom in order that it perturb the system appropriately. In this way it is possible to include the bulk translatory motions of the carbonyl ligands (spanning $A_1 + B_1 + B_2$) while retaining metal-only masses for the metal atoms. With this development, it seems likely that the metal−metal force constants that result will be more meaningful than those derived from the simple PCM. Noteworthy is the absence of A_2 from the above list; this means that the assignment of this deformation mode assumes the role of a marker: interactions with the center-of-gravity atom can move the other deformation frequencies, but not this one.

As far as the force field is concerned, the CGM has to be handled rather differently from the other two models. Again, there are two ν(Fe−Fe) force constants, but now the stretching motion of the E atoms is represented as a stretch from the center of gravity atom, denoted G and hence ν(E−G), along with an interaction between these two modes, one on either side of the metal triangle. The ν(E−G) motion does not cover any sideways motion of the E atom, and so it is necessary to introduce a deformation force constant δ(Fe₃−E). In order to introduce the possibility of further asymmetry into the motion (one is already implicit in the G-matrix), we have included an interaction constant between the δ(Fe₃−E). A total of six unknowns results for both the E₂ and EE′ systems, again overdetermined problems. The above description is diagrammatically given in Figure 6. In order that the two models which seek to account for the presence of the CO groups may be compared directly, they should contain the same number of unknowns; this requirement is satisfied by the HAM and CGM.
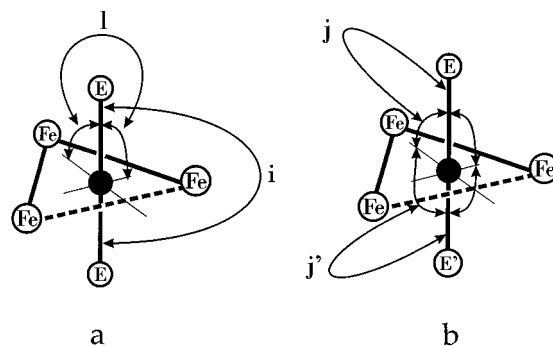
The results from CGM are good for all of the species and

Figure 6. Force and (shown in the diagrams) interaction constants involving the added atoms used for the systems Fe₃(CO)₉E₂ (a) and Fe₃(CO)₉EE′ (b) in the center of gravity model (CGM) (see also Table 4).

Table 4. Values of the Stretching (mdyn Å⁻¹) and of the Bending (mdyn Å⁻¹ rad⁻²) Force Constants and of the Stretching/Stretching (mdyn Å⁻¹), Stretching/Bending (mdyn rad⁻¹), and Bending/Bending (mdyn Å⁻¹ rad⁻²) Interaction Constants Calculated on the Basis of the Center-of-Gravity Model (CGM)

force constant[a]	Ia	Ib	Ic	IIa	IIb	IIc	III
f_ν	2.5	2.9	3.2	2.3	2.3	2.2	2.5
f_ν'				3.0	3.5	3.5	
k_ν	0.64	0.63	0.41	0.65	0.68	0.63	1.3
k_ν'	0.28	0.50	0.45	0	0	0	0.74
f_δ	2.7	2.4	3.4	1.5	1.2	1.4	3.6
f_δ'				1.7	1.3	1.8	
i	0.33	0.65	1.0	b	b	b	0.26
j	b	b	b	0.0	b	0.22	b
j'				b	0.30	b	b
l	1.1	0.70	2.2	b	b	b	−0.81
l'				b	b	b	b

[a] Stretching force constant: f_ν (E−G), f_ν' (E′−G), k_ν (Fe−Fe), k_ν' (Fe···Fe). Bending force constant: f_δ (Fe₃−E), f_δ' (Fe₃−E′). Coupling constant: i (E−G)(E′−G), j (E−G)(Fe₃−E), j' (E′−G)(Fe₃−E′), l (Fe₃−E)(Fe₃−E), l' (Fe₃−E′)(Fe₃−E′). [b] These constants have been set equal to zero, because preliminary calculations indicate that they have very small values.

Table 5. Mean Frequency-Weighted Errors[a] between the Experimental Frequency Values and the Values Calculated by the Different Vibrational Models

complex	PCM	HAM	CGM
Ia	3.9	1.3	0.5
Ib	7.1	7.9	3.1
Ic	11.7	11.3	2.5
IIa	6.2	7.6	0.5
IIb	9.3	15.6	5.8
IIc	8.1	10.1	2.4
IIIa	9.0	9.0	1.8

[a] The error is given by $(1/n)\sum_{m=1}^{n}|[v_{\exp}(m) - v_{\text{calc}}(m)]/v_{\exp}(m)|100$.

are detailed in Tables A and B of the Supporting Information. The force constant values are reported in Table 4.

An indication of the relative success of the CGM can be gained by comparing the errors associated with the best fits to all of the species under study with the different vibrational models (Table 5). Given the simplicity of the CGM, the fits, overall, are quite acceptable. The species which give the worst fits are, first, **IIb**, the species in which the mass imbalances are greatest and in which the models which we have introduced to compensate for the mass of the CO groups would be expected to perform at their worst. The frequencies which are badly calculated are those involving motion of S and Te against the Fe₃, again those which would be expected to be most sensitive

to the approximations. These show errors of 41 and 29 cm^{-1}, respectively. Otherwise, the errors for this compound are entirely acceptable.

For **Ic** it seems clear that the constants obtained indicate that significant coupling occurs between ν(Fe–Fe) and δ(Fe$_3$–Te). In accord with this, our assignment of the 156 cm^{-1} mode as a mixture of ν(Fe–Fe) and δ(Fe$_3$–Te) is supported by the calculation. However, we note a cluster of modes that lie just below the cutoff frequency of the present assignments (135 cm^{-1}). There are other peaks at 124, 112, and 99 cm^{-1}, associated with low-frequency CO–Fe–CO deformation modes. These are close enough to have mixing with the low-frequency G–Te modes of our model, and, if this mixing occurs, these modes, accordingly, will not be properly described. Part of our explanation of the problems with this species is, essentially, that this mixing is real and so the approximation of replacing nine CO groups by a single atom at their center of gravity breaks down when the relative motion of these groups against each other is of a frequency comparable to the frequency of other motions in the molecule.

(d) Conclusion. The above discussion, both of spectra and of calculations, indicates that the assignments which form the body of the present paper form a rather coherent and consistent set. The model which gives the best overall fit is the CGM, which has the advantage of simplicity, and, although it introduces some clearly artificial force constants, it probably leaves "cleaner" metal–metal force constants as a result; and, historically, these are the subject of interest.

Moreover, the validity of the linear interpolations that we have used gives significant light on the PCM and its applications. In particular, it demonstrates that the model is capable of development to include some ligand atoms, at least. However, it is clear that care must be taken not to include such ligands too selectively. For us, it was not possible to include the chalcogenides without including the carbonyls, at least approximately, if a consistent pattern was to emerge. A similar conclusion has recently been reached following a study of some M$_2$ species.[15]

Finally, an important point is the presence of a band that we have suggested be assigned to the stretching mode between the formally nonbonded Fe atoms. This assignment does not require that the two iron atoms are effectively bonded: when they are well separated a cluster deformation occurs, which may alternatively be regarded as responsible for the band. A similar behavior was reported for the [M$_2$Cl$_9$]$^{3-}$ complexes, which show a strong Raman band, formally a ν(M–M). When M = W, the band was calculated to be mainly M–M stretching, whereas, for M = Cr, it mainly involves deformations of Cl–Cr–Cl and Cr–Cl–Cr angles.[16] The key to the interpretation was found to be the value of the M–M distance, which is lower than the sum of the covalent radii in the former case, but much greater in the latter case. In our complexes, the length of the genuine Fe–Fe bonds varies from 2.59 to 2.74 Å whereas the Fe···Fe distance is ca. 3.6 Å,[17] more than twice the van der Waals radius of the iron atom. The conclusion, at the first sight, seems to be that a direct interaction between the two Fe atoms is unlikely; so that in general, the observation of a strong band in the appropriate region of the Raman spectrum is not itself a proof of the existence of a direct M–M bond.

Supporting Information Available: Listing of the figures with the infrared and Raman spectra of Fe$_3$(CO)$_9$EE′ (**IIa**–**c**); the PCM force field and listing of tables containing the experimental and calculated (by the CGM) frequency values of **Ia**–**c** and **IIa**–**c** complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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