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Vibrational Spectra of Metal Cluster Complexes Containing the μ_3 -bridging Sulphur Ligand

A Possible Model for Sulphur Atoms on Metal Surfaces

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Vibrational frequencies of the metal-sulphur stretching modes for a number of metal cluster complexes containing the μ_3 -bridging sulphur atom have been determined and approximate normal-coordinate analyses have been made of selected cluster molecules of this type. A comparison of the sites occupied by the sulphur atom in metal cluster complexes and on metal surfaces reveals a close structural relationship between these environments; this is likely to be manifest in a similarity of the vibrational frequencies associated with the $(\mu_3\text{-S})\text{M}_3$ unit in the two types of system.

A good example of the formal analogy between metal cluster complexes and corresponding species arising from chemisorption on metal surfaces [see, for example, ref. (1)] has been provided by the correlation between the stability of the Co_3S unit in cobalt cluster chemistry and the poisoning by sulphur compounds of the catalytic hydroformylation reaction.² It is of considerable interest to discover whether such an analogy can be fruitfully extended to a correlation of physical properties between sulphur-containing species of the two types. In this paper we provide a comparison of the structural properties of the sulphur atom in metal cluster complexes and as an adsorbate on certain metal surfaces and give an account of the vibrational frequencies associated with, specifically, the μ_3 -sulphur ligand in a number of metal cluster complexes.[†]

The most common sites occupied by sulphur atoms on low-index planes of metals are μ_3 - and μ_4 -bridging, with the local symmetry of the site dependent on the particular crystal face considered. In metal cluster complexes the μ_3 -bridging site appears to predominate, with examples of the μ_4 -bridging sulphur atom being something of a rarity. Structural data from examples of the sulphur atom in both these sites, drawn from metal clusters and surface species, are given in table 1. A striking similarity in the types of coordination geometries is seen. Although there are insufficient data relating to cluster complexes and surface species of the same

[†] A preliminary account of the vibrational spectra of metal cluster complexes containing the $(\mu_3\text{-S})\text{M}_3$ unit (M = first-row transition metal) has appeared.³

TABLE 1.—STRUCTURAL DATA FOR THE SULPHUR ATOM AS A BRIDGING LIGAND IN METAL CLUSTER COMPLEXES AND ON METAL SURFACES^a

	M—M/nm	M—S/nm	M _x ...S/nm ^b	ref.
μ_3-bridging				
C_{3v} symmetry:				
Co ₃ (CO) ₉ (μ_3 -S) ^c	0.2637	0.2139	0.145	4
Ni ₃ (π -C ₅ H ₅) ₃ (μ_3 -S) ₂	0.2801	0.2172	0.145	5
Ni (111)/S	0.252	0.202	0.140	6
Co ₃ (π -C ₅ H ₅) ₃ (μ_3 -S) ₂	0.2691	0.2168	0.151	7
Co ₆ C(CO) ₁₂ (μ_3 -S) ₂	0.2437	0.2194	0.168	8
C_s symmetry:				
Fe ₃ (CO) ₉ (μ_3 -SO)(μ_3 -S) ^d	0.2635	0.2140, 0.2222	0.146	9
Co ₂ Fe(CO) ₉ (μ_3 -S) ^e	0.2554	0.2158	0.157	10
H ₂ Os ₃ (CO) ₉ (μ_3 -S)	0.2764, 0.2915 ^f	0.239	0.172	11
Ir (100)/S	—	—	—	12
Fe ₄ (π -C ₅ H ₅) ₄ (μ_3 -S) ₄ ^g	0.2650, 0.336 ^f	0.225, 0.220 ^f	0.166	13
Fe ₄ (π -C ₅ H ₅) ₄ (μ_3 -S) ₄ ^h	0.2618, 0.336 ^f	0.225, 0.336 ^f	0.166	14
μ_4-bridging				
C_{4v} symmetry:				
Ni (100)/S	0.249	0.219	0.130	6
Rh (100)/S	0.268	0.230	0.130	15
Fe (100)/S	0.286	0.230	0.109	16
C_{2v} symmetry:				
Co ₄ (CO) ₈ (μ_2 -CO) ₂ (μ_4 -S) ₂	0.248, 0.260	0.226	0.137	17
Ni (110)/S ⁱ	0.249, 0.352	0.217, 0.235	0.093	18
Rh (110)/S ⁱ	0.268, 0.380	0.212, 0.2454	0.077	19

^a Bond lengths have been averaged where small distortions from "ideal" symmetry occur in the crystal; ^b M_x...S (x = 3 or 4) represents the separation of the S atom from the plane of the metal atoms; ^c two non-equivalent sets of molecules; ^d "open" triangle with only two Fe—Fe bonds; ^e averaged structure due to disorder; ^f two such bond lengths; ^g orthorhombic form; ^h monoclinic form; ⁱ the sulphur atom is five-coordinate, with the shortest bond to the central metal atom of the layer below and the longer bonds (four) to the metal atoms of the top layer.

metal to allow detailed conclusions to be drawn, it would appear at least possible from the data available that the sulphur atom resides generally closer to the plane of the metal atoms on surfaces, compared with cluster molecules. A second difference between the two types of species which could be of some importance concerns the interaction of the adsorbed sulphur atom with layers of metal atoms below the top layer. This situation is believed to occur on certain (110) planes where, in fact, the metal-sulphur distance may be shorter to the second layer of metal atoms than to the top.¹⁹

The structural analogy suggested here might be expected to extend to the metal-sulphur vibrations of the sulphur atom in the two types of environment. In this context it is important in the present study to attempt to assign the symmetry species of the various observed ν (M—S) absorptions in order to be of value when the selection rule appropriate to metal surface spectroscopy must be applied. In

electron energy-loss spectroscopy (EELS), appreciable excitation of a vibrational mode will usually only occur when the dipole moment change is perpendicular to the metal surface. Thus, for a symmetrically μ_3 -bridging S atom on a metal surface, only the symmetric (a_1) metal-sulphur stretching mode is expected to be EEL-active.

In this paper we will also give the results of some approximate normal-coordinate analyses in which we treat the $(\mu_3\text{-S})\text{M}_3$ unit as the vibrating unit. Recent calculations of this type, applied to metal carbonyl clusters²⁰ and to clusters incorporating organic ligands,²¹⁻²³ have yielded metal-metal bond stretching force constants which should provide a basis for comparison in assessing the effects of coordination of the sulphur atom to the metal framework.

EXPERIMENTAL

The metal cluster complexes were prepared by reported methods, as referenced individually in the text. Infrared spectra were measured, at 300 K and *ca.* 90 K, using Perkin-Elmer 325 and Beckman-R.I.I.C IR-720M spectrophotometers, the samples being in the form of KBr discs and nujol mulls, respectively. Raman spectra of polycrystalline samples were obtained with a Spex 1401 monochromator, with exciting radiation of wavelength 647.1 nm from a Spectra-Physics type 126 Ar⁺-Kr⁺ laser.

Normal-coordinate calculations were carried out using Schachtschneider's computer programs GMAT and FPERT.²⁴

RESULTS AND DISCUSSION

In an earlier paper it was shown that,³ by making certain assumptions, a simple expression could be derived for the ratio of the symmetric and antisymmetric metal-sulphur stretching frequencies, involving only the atomic masses and the acute angle, β , between the M-S bonds and the threefold axis of the regular pyramidal $(\mu_3\text{-S})\text{M}_3$ unit, *viz.*

$$\nu_{\text{MS}}^{\text{sym}} = [(1 + 3m_{\text{M}} \cos^2 \beta / m_{\text{S}})(k_{\text{r}} / m_{\text{M}})]^{1/2} / 2\pi c \quad (1)$$

$$\nu_{\text{MS}}^{\text{asym}} = [(1 + 3m_{\text{M}} \sin^2 \beta / 2m_{\text{S}})(k_{\text{r}} / m_{\text{M}})]^{1/2} / 2\pi c \quad (2)$$

where m_{M} and m_{S} are the masses of the metal and sulphur atoms, respectively, k_{r} is the metal-sulphur bond stretching force constant and c is the speed of light. The ratio of the frequencies is then given by

$$\nu_{\text{MS}}^{\text{sym}} / \nu_{\text{MS}}^{\text{asym}} = [(1 + 3m_{\text{M}} \cos^2 \beta / m_{\text{S}}) / (1 + 3m_{\text{M}} \sin^2 \beta / 2m_{\text{S}})]^{1/2}. \quad (3)$$

It was further shown that, since β is usually $< 54^\circ$ [at which value of β the right-hand side in eqn (3) is unity], we would generally expect to observe $\nu_{\text{MS}}^{\text{sym}}$ at higher frequency than $\nu_{\text{MS}}^{\text{asym}}$. This conclusion is in agreement with the normal-coordinate analyses reported here for selected cluster molecules and we shall not describe detailed assignments here for the simple case of single, undistorted $(\mu_3\text{-S})\text{M}_3$ cluster units. Rather, we will consider the more complicated cases in which the cluster molecule contains more than one unit of this type and cases where the symmetry of the unit is reduced.

METAL CLUSTERS CONTAINING TWO EQUIVALENT $\mu_3\text{-S}$ LIGANDS

Several metal cluster complexes have been characterised structurally in which two multiply-bridging sulphur atoms are associated with the same face, or different

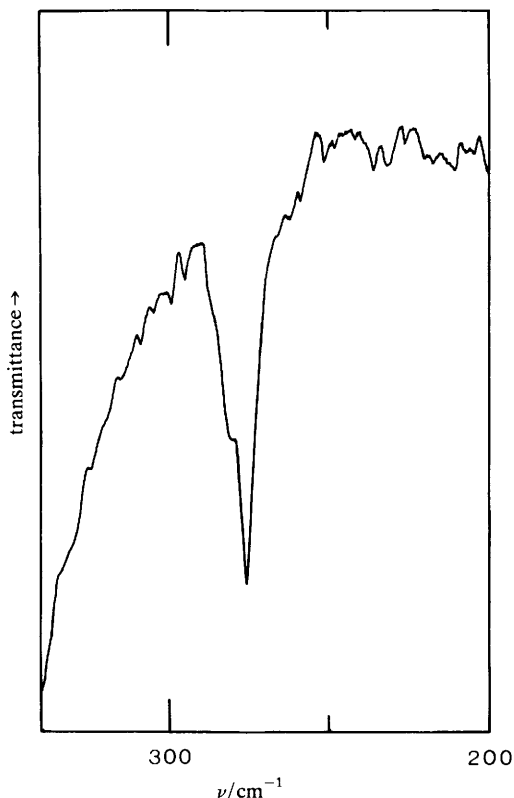


FIG. 1.—350–200 cm^{-1} region of the infrared spectrum of $\text{Ni}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$, at 90 K.

faces, of the metal atom framework.* Coupling of the motions of the sulphur atoms, if it should occur, will obviously cause considerable modification of the observed vibrational frequencies. We consider here two examples of this type of cluster molecule: $\text{Ni}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$ ⁵ and $\text{Co}_6\text{C}(\text{CO})_{12}(\mu_3\text{-S})_2$.⁸

As shown in fig. 1, the metal–sulphur stretching region of the infrared spectrum of $\text{Ni}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$ contains two absorptions, at 282 and 277 cm^{-1} , which have been assigned to ν_{NiS} .³ The closeness of these frequencies, in contrast to the *ca.* $\nu_{\text{NiS}}^{\text{sym}}/\nu_{\text{NiS}}^{\text{asym}} = 1.17\text{--}55 \text{ cm}^{-1}$ splitting predicted by eqn (3) on the basis of uncoupled metal–sulphur vibrations, has been taken to be indicative of coupling between the motions of the sulphur atoms.³ This suggestion is investigated below by means of an approximate normal-coordinate analysis. Note that this cluster molecule contains an unusually short intramolecular S···S distance of 0.290(2) nm.⁵

A different situation seems likely to occur in the case of the hexanuclear cluster $\text{Co}_6\text{C}(\text{CO})_{12}(\mu_3\text{-S})_2$. This cluster molecule possesses a trigonal prismatic metal skeleton, with a sulphur atom capping each triangular face.⁸ Two absorptions, at 309 and 239 cm^{-1} , in the infrared spectrum of this complex²⁵ have been assigned

* See, for example, $\text{Ni}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$, ref. (5); $\text{Co}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$, ref. (7); $\text{Co}_6\text{C}(\text{CO})_{12}(\mu_3\text{-S})_2$, ref. (8); $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-S})_2$, ref. (17).

to cobalt-sulphur stretching modes.³ When the observed frequency ratio, $\nu_{\text{CoS}}^{\text{sym}}/\nu_{\text{CoS}}^{\text{asym}} = 1.29$, is used in eqn(3) a value for the angle β of 44° is obtained. This estimate may be compared with the experimentally determined value of 40° .⁸ The agreement between calculated and observed angles is reasonable, with the discrepancy being in the same direction as found previously³ in calculations of this type. We thus conclude that the motions of the two sulphur atoms in this cluster are uncoupled, as might perhaps be expected in view of the large non-bonded $\text{S} \cdots \text{S}$ separation of 0.604 nm.⁸

METAL CLUSTERS CONTAINING $(\mu_3\text{-S})\text{M}_3$ UNITS OF LOW SYMMETRY

The regular pyramidal geometry of the $(\mu_3\text{-S})\text{M}_3$ unit is frequently distorted* for either electronic reasons, such as in certain "open" triangular iron clusters,³ or as a result of a chemical distinction between the metal atoms, as in a heteronuclear cluster. When the symmetry is lowered from C_{3v} for either reason, the degeneracy of the antisymmetric M—S stretching mode is removed and three absorptions will be expected in the infrared spectrum.

The infrared spectrum of the paramagnetic complex $\text{Co}_3(\text{CO})_9(\mu_3\text{-S})$ has been shown to contain two bands due to Co—S stretching modes, 342 cm^{-1} (a_1) and 316 cm^{-1} (e).³ When an iron atom is substituted for one of the cobalt atoms to give the diamagnetic complex $\text{Co}_2\text{Fe}(\text{CO})_9(\mu_3\text{-S})$, a splitting of the antisymmetric metal-sulphur stretching mode is expected and indeed three such bands are observed, at 357, 324 and 319 cm^{-1} . In agreement with the known structure of this complex¹⁰ the spectral evidence suggests that the geometric distortion of the cluster from regular pyramidal is slight. The force constants in these two cluster molecules will be discussed below.

A more severe distortion of the $(\mu_3\text{-S})\text{M}_3$ unit occurs in the cluster $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$. A recent combined X-ray and neutron diffraction crystal structure determination of this complex¹¹ revealed that the Os_3 triangle is close to isosceles, with Os—Os bond lengths of 0.2764 and 0.2915 nm (mean of two bonds). The metal-sulphur stretching regions of the infrared and Raman spectra of $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$, at *ca.* 90 K, are shown in fig. 2. The most probable assignment of the Os—S stretching modes is to the group of three bands in the $330\text{--}280\text{ cm}^{-1}$ regions of the spectra. A group of three bands of very similar appearance is also observed in the spectra of the analogous ruthenium complex,²⁶ suggesting that these cluster species are isostructural. Three bands are again found in this region of the infrared spectrum of the third member of this series of complexes, $\text{H}_2\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})$,²⁷ but in this case a rather different pattern of absorption is observed (fig. 3). The presence of the close doublet at 338 and 332 cm^{-1} seems to suggest that the distortion from C_{3v} symmetry is appreciably less in the iron complex than is the case in the Ru and Os analogues. Vibrational frequencies of the metal-sulphur and metal-metal stretching modes of these complexes are given in table 2.

Assignments of metal-sulphur stretching modes in a number of other metal cluster complexes containing the C_s -type $(\mu_3\text{-S})\text{M}_3$ arrangement have been made and are given in table 3.

* We ignore here small departures from C_{3v} symmetry which commonly arise from "crystal packing" effects.

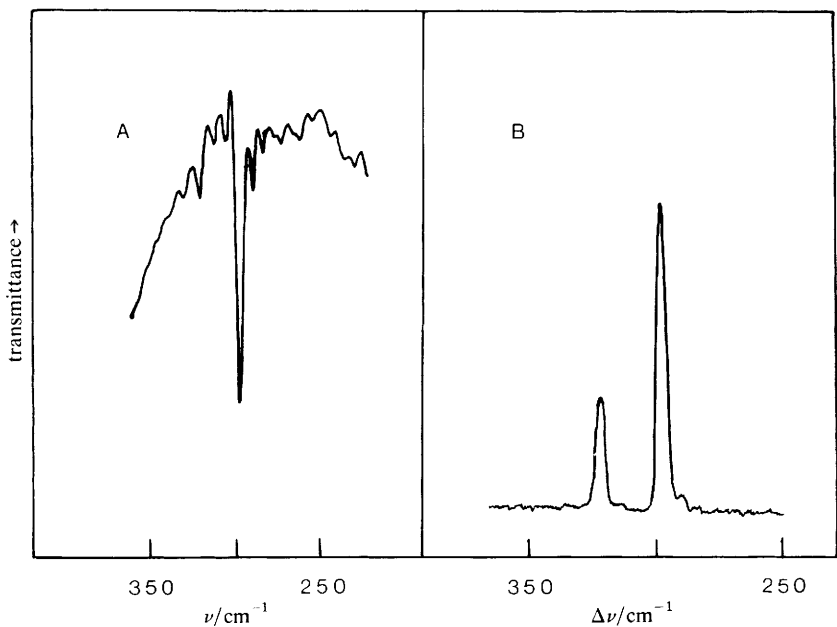


FIG. 2.—400–200 cm^{-1} regions of the infrared (A) and Raman (B) spectra of $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$, at 90 K.

TABLE 2.—LOW-FREQUENCY VIBRATIONS (cm^{-1}) OF THE METAL CLUSTER COMPLEXES $\text{H}_2\text{M}_3(\text{CO})_9(\mu_3\text{-S})$, $\text{M} = \text{Fe}, \text{Ru}$ AND Os^a

mode	$\text{H}_2\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})$	$\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-S})$	$\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$
$\nu_{\text{MS}}^{\text{sym}}$	368 (w)	326 (w)	322 (w)
$\nu_{\text{MS}}^{\text{asym } b}$	338 (w)	303 (w)	298 (ms)
	332	291 (w)	291 (w)
$\nu_{\text{MM}}^{\text{sym}}$	230 (w, br)	203 (w)	172 (w)
$\nu_{\text{MM}}^{\text{asym } b}$	194 (w)	172 (w)	144 (w)
		123 (w)	94 (w)

^a Abbreviations: w, weak; m, medium; s, strong; br, broad. ^b The modes labelled “asym” are those derived from the degenerate, antisymmetric mode of the undistorted (C_{3v}) ($\mu_3\text{-S}$) M_3 unit.

TABLE 3.—METAL-SULPHUR STRETCHING FREQUENCIES (cm^{-1}) IN SOME METAL CLUSTER COMPLEXES OF LOW SYMMETRY

complex	
$\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})(\mu_3\text{-SO})^a$	350, 339, 323, 273, 255, 238
$\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})_2^a$	354, 302, 283, 272, 254
$\text{HFe}_2\text{Co}(\text{CO})_9(\mu_3\text{-S})$	338, 320, 308
$\text{HFe}_3(\text{CO})_8(\text{NO})(\mu_3\text{-S})$	360, 335, 315
$\text{Fe}_2\text{Co}(\text{CO})_8(\text{NO})(\mu_3\text{-S})$	357, 327, 319

^a Ref. (3).

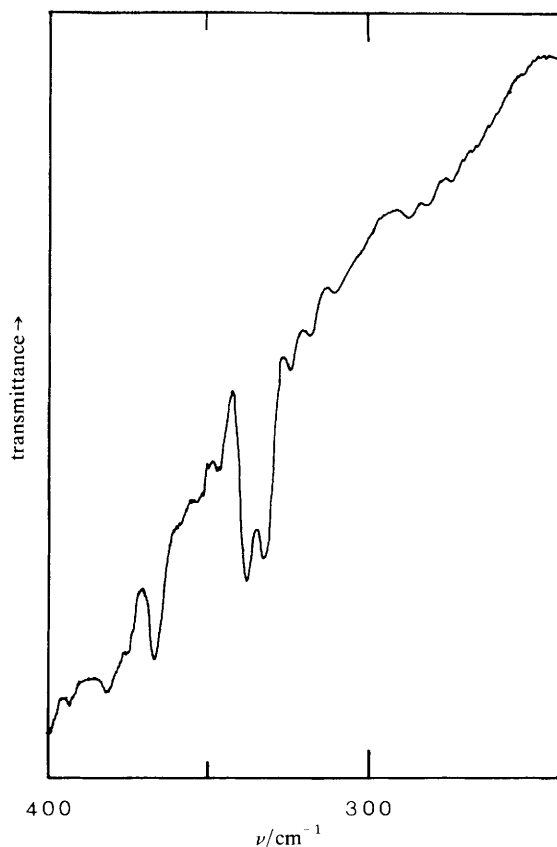


FIG. 3.—400–240 cm^{-1} region of the infrared spectrum of $\text{H}_2\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})$, at 90 K.

NORMAL-COORDINATE ANALYSES OF SIMPLE $(\mu_3\text{-S})\text{M}_3$ SYSTEMS

In addition to the two absorptions in the far-infrared spectrum of $\text{Co}_3(\text{CO})_9(\mu_3\text{-S})$ previously assigned to the cobalt–sulphur stretching modes, two further absorptions at lower frequency, 188 and 129 cm^{-1} , are observed and may be assigned to the symmetric and antisymmetric cobalt–cobalt stretching modes, respectively. An approximate normal-coordinate analysis was performed in which the carbonyl ligands were ignored.^{20–23} Good agreement between observed and calculated frequencies could be obtained by refinement of a force field containing three force constants: k_{CoS} , the primary Co–S bond stretching force constant, f_{CoS} , the force constant associated with the stretching of different Co–S bonds, and k_{CoCo} , the primary Co–Co bond stretching force constant. Details of the final calculated force field are given in table 4. The value of k_{CoCo} calculated here, 48 N m^{-1} , is the lowest reported for this type of bond to date [*cf.* 54 and 94 N m^{-1} in $\text{Co}_4(\text{CO})_{12}$ ²⁰ and $110 \pm 5 \text{ N m}^{-1}$ in a number of $(\mu_3\text{-CY})\text{Co}_3(\text{CO})_9$ complexes²³] and thus is consistent with the rather long Co–Co bond determined in this complex (mean 0.2637 nm^4).

Force constants derived in this way, with the neglect of the relatively light carbonyl ligands, have been shown to display an internal consistency,^{20–23} although,

TABLE 4.—APPROXIMATE NORMAL-COORDINATE ANALYSIS OF THE $\text{Co}_3(\text{CO})_9(\mu_3\text{-S})$ CLUSTER

mode	$\nu_{\text{obs}}/\text{cm}^{-1}$	$\nu_{\text{calc}}/\text{cm}^{-1}$	$\epsilon^a/\text{cm}^{-1}$
$\left. \begin{array}{l} \nu_{\text{CoS}}^{\text{sym}} \\ \nu_{\text{CoCo}}^{\text{sym}} \end{array} \right\} a_1$	342 186	342 182	0 4
$\left. \begin{array}{l} \nu_{\text{CoS}}^{\text{asym}} \\ \nu_{\text{CoCo}}^{\text{asym}} \end{array} \right\} e$	316 129	316 134	0 -5
force constants: ^b			
$k_{\text{CoS}} = 127(3) \text{ N m}^{-1}$			
$k_{\text{CoCo}} = 48(3) \text{ N m}^{-1}$			
$f_{\text{CoS}} = -13(2) \text{ N m}^{-1}$			

^a $\epsilon = \nu_{\text{obs}} - \nu_{\text{calc}}$. ^b The estimated standard errors in the least significant figures are given in parentheses.

where corresponding values are available from complete normal-coordinate analyses, the absolute values may be up to *ca.* 10% in error. The internal consistency is of interest in the present work in so far as we would like to discern possible trends in the values of metal-sulphur and metal-metal stretching force constants. There has been some discussion in the literature concerning the effect of the unpaired electron in the $\text{Co}_3(\text{CO})_9(\mu_3\text{-S})$ cluster upon its structure and bonding.^{2,4,10} The most obvious manifestation of the unpaired electron lies in the long Co—Co bonds which exist in this cluster molecule. To assess the effect upon the strength of these bonds we have also determined an approximate force field for the related species $\text{Co}_2\text{Fe}(\text{CO})_9(\mu_3\text{-S})$, which has one less electron. The force field required to reproduce the observed vibrational frequencies adequately contained four force constants, the three described above for $\text{Co}_3(\text{CO})_9(\mu_3\text{-S})$ and k_{CoFe} , the cobalt-iron stretching force constant. Initial refinement of independent cobalt-sulphur and iron-sulphur stretching force constants resulted in almost equal values (within 1–2%) and a single k_{MS} was thus utilised. Observed and calculated frequencies and the final force constant values are given in table 5, with the corresponding values from $\text{Co}_3(\text{CO})_9(\mu_3\text{-S})$. It is seen that, whilst the value of k_{CoS} is little different in the two cluster molecules, the Co—Co stretching force constant increases markedly when the unpaired electron is removed. It is also pertinent to note the similarity between the values of f_{CoS} in the two force fields, *ca.* -10% of k_{CoS} .

It is of interest to compare the values of the force constants determined in this way with those which are given by eqn (1) and (2) in order to gauge the level of approximation inherent in these expressions. For $\text{Co}_3(\text{CO})_9(\mu_3\text{-S})$, values of 110 and 145 N m^{-1} are obtained for k_{CoS} from eqn (1) and (2), respectively, compared with the value of 127 N m^{-1} derived in the force constant refinement. The agreement from the two calculations is encouraging and lends some validity to the neglect of interaction between the metal-sulphur and metal-metal stretching modes assumed in the derivation of the simplified vibration equations.

The two infrared-active nickel-sulphur stretching modes of $\text{Ni}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$, symmetry species a_2'' and e' , have been assigned to bands at 282 and 277 cm^{-1} .³ Additionally, a band at 138 cm^{-1} in the far-infrared spectrum of this complex is

TABLE 5.—APPROXIMATE NORMAL-COORDINATE ANALYSIS OF THE $\text{Co}_2\text{Fe}(\text{CO})_9(\mu_3\text{-S})$ CLUSTER

mode	$\nu_{\text{obs}}/\text{cm}^{-1}$	$\nu_{\text{calc}}/\text{cm}^{-1}$	$\epsilon^a/\text{cm}^{-1}$
$\left. \begin{array}{l} \nu_{\text{MS}}^{\text{sym}} \\ \nu_{\text{MS}}^{\text{asym}} \end{array} \right\} a'$	357	356	1
	324	324	0
$\left. \begin{array}{l} \nu_{\text{CoCo}} \\ \nu_{\text{CoFe}}^{\text{sym}} \end{array} \right\}$	206	214	-8
	169	160	9
$\left. \begin{array}{l} \nu_{\text{MS}}^{\text{asym}} \\ \nu_{\text{CoFe}}^{\text{asym}} \end{array} \right\} a''$	319	319	0
	^b	148	—
force constants:			
$k_{\text{CoCo}} = 77(3) \text{ N m}^{-1}$			
$k_{\text{CoFe}} = 57(3) \text{ N m}^{-1}$			
$k_{\text{MS}}^c = 134(3) \text{ N m}^{-1}$			
$f_{\text{MS}}^c = -16(2) \text{ N m}^{-1}$			

^a $\epsilon = \nu_{\text{obs}} - \nu_{\text{calc}}$. ^b Not observed. ^c See text.

a probable candidate for assignment to the antisymmetric Ni—Ni stretching mode. With the three fundamental frequencies of the $\text{Ni}_3(\mu_3\text{-S})_2$ unit presently available,* a simple valence force field was calculated. The results of this calculation are shown in table 6. The assignment of the two infrared-active Ni—S stretching modes, with the a_2'' component at higher frequency than the e' component, is arbitrary, being that suggested by the SVFF treatment. This procedure supports the coupling scheme suggested earlier³ and it is interesting to note that the estimated “uncoupled” frequencies from this calculation (that is, the mean frequency of the a_1' and a_2'' components and of the e' and e'' components) gives an “uncoupled” frequency ratio $\nu_{\text{NiS}}^{\text{sym}}/\nu_{\text{NiS}}^{\text{asym}}$ of 1.21, in reasonable agreement with the estimate of 1.17 calculated above from eqn (3).

TABLE 6.—APPROXIMATE NORMAL-COORDINATE ANALYSIS OF THE $\text{Ni}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$ CLUSTER^a

mode	$\nu_{\text{obs}}/\text{cm}^{-1}$	$\nu_{\text{calc}}/\text{cm}^{-1}$	$\epsilon^b/\text{cm}^{-1}$
$\left. \begin{array}{l} \nu_{\text{NiS}}^{\text{sym}} \\ \nu_{\text{NiNi}}^{\text{sym}} \end{array} \right\} a_1'$	—	336	—
	—	170	—
$\nu_{\text{NiS}}^{\text{sym}} a_2''$	282	287	-5
$\left. \begin{array}{l} \nu_{\text{NiS}}^{\text{asym}} \\ \nu_{\text{NiNi}}^{\text{asym}} \end{array} \right\} e'$	277	270	7
	136	138	-2
$\nu_{\text{NiS}}^{\text{asym}} e''$	—	244	—
force constants:			
$k_{\text{NiS}} = 85(4) \text{ N m}^{-1}$			
$k_{\text{NiNi}} = 62(8) \text{ N m}^{-1}$			

^a Infrared-active frequencies only. ^b $\epsilon = \nu_{\text{obs}} - \nu_{\text{calc}}$.

* Attempts to obtain a Raman spectrum of $\text{Ni}_3(\pi\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})_2$ have thus far proved unsuccessful, due to decomposition of the intensely-coloured complex in the laser radiation.

SULPHUR ATOMS ADSORBED ON METAL SURFACES

As discussed in the Introduction, several instances of μ_3 - and μ_4 -bridging sulphur atoms adsorbed on metal surfaces have been reported. Unfortunately, vibrational spectroscopy (in this case EELS) has been applied to these systems far less frequently than has LEED analysis and the only vibrational frequency for the sulphur atom in this type of environment appears to have been determined by Andersson,²⁸ who measured the EEL spectrum of sulphur on Ni (100). In that study an electron-loss at 363 cm^{-1} was reported, corresponding to the symmetric Ni—S stretching mode of the μ_4 -bridging S atom.⁶ This frequency falls in the range suggested by us for the $\nu_{\text{MS}}^{\text{sym}}$ mode of the μ_3 -bridging sulphur atom ($370\text{--}320\text{ cm}^{-1}$); it may well be that this mode is of comparable frequency in the μ_3 - and μ_4 -bridging environments.

The measurement of EEL spectra of sulphur adsorbed on the (111) planes of metal single crystals would clearly be of considerable interest for comparison with the analogous metal cluster species; in particular, the determination of $\nu_{\text{MS}}^{\text{sym}}$ for S on Ni (111), Pd (111) and Pt (111) would be expected to permit a reasonable comparison with the frequencies reported here for the triply-bridging sulphur ligand in cluster complexes involving metals from the three transition series.

SUMMARY

The symmetric M—S stretching mode of the μ_3 -bridging sulphur ligand in metal cluster complexes falls in the relatively narrow frequency range $370\text{--}320\text{ cm}^{-1}$. This is the vibrational mode of major interest when the analogous metal surface species are considered; when available, EELS data for this type of system might be expected to permit an assessment of the validity of the close analogy between the two types of system implied by the available structural data.

In relation to the spectroscopic diagnosis of the triply-bridging sulphur ligand in metal cluster complexes, the usefulness suggested by the narrow frequency range of $\nu_{\text{MS}}^{\text{sym}}$ is largely negated by the low intensity displayed by these modes in the infrared, and Raman, spectrum.

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