Vibrational Frequencies Associated with the μ_3-Bridging Sulphur Ligand in Some Cluster Complexes of First-row Metals

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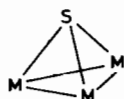
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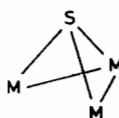
Vibrational frequencies of the μ_3-bridging sulphur atom in a number of first-row metal cluster complexes have been determined by infrared spectroscopy. The metal–sulphur stretching modes have frequencies in the 350–200 cm^{-1} spectra region for the sulphur ligand in these complexes. The infrared absorptions associated with these modes are of generally low intensity.

Introduction

In this paper we give a brief account of the vibrational frequencies associated with the μ_3-bridging sulphur atom in some first-row metal cluster complexes. This grouping has obvious importance in the context of catalysis, in view of the effectiveness of sulphur as a catalyst poison, especially since there is evidence to suggest that atomic S is chemisorbed on the Ni (111) crystal face as a μ_3-bridging species [1]. Two types of ligand environment are considered here for the μ_3-S grouping; these are represented schematically as I and II:

The type I grouping, typified by $Co_3(CO)_9S$, approximates to local C_{3v} symmetry at the S atom, whilst type II is encountered in the tri-iron clusters $Fe_3(CO)_9S(SO)$, $Fe_3(CO)_9S_2$ and $Fe_4(\pi-C_5H_5)_4S_4$ and has local C_s symmetry.

Experimental

Complexes

$Co_3(CO)_9S$ [2], $Co_3(\pi-C_5H_5)_3S(CS)$ [3], $Ni_3(\pi-C_5H_5)_3S_2$ [4], $Fe_3(CO)_9S(SO)$ [5], $Fe_3(CO)_9S_2$ [6] and $Fe_4(\pi-C_5H_5)_4S_4$ [7] were prepared by reported methods.

Spectra

Infrared spectra of the complexes were measured, as Nujol mulls at 300 K and 95 K, using Beckman-R.I.I.C. IR-720M Fourier-transform and Perkin-Elmer 325 spectrophotometers in the far-infrared (500–100 cm^{-1}) and mid-infrared (1000–250 cm^{-1}), respectively. The vibrational frequencies assigned to metal–sulphur stretching modes in spectra of the complexes studied are given in Table I, along with the few tentative assignments which have been previously proposed for these modes. The absorptions noted are of generally low intensity; preliminary Raman measurements on less highly coloured metal cluster complexes suggest that the intensity displayed by these modes in the Raman effect is also low [8].

Discussion

Interpretation of the observed spectra is not straightforward as a consequence of coupling of the motions of more than one sulphur atom within the cluster unit, or the presence of non-equivalent sets of cluster molecules in the unit cell or low symmetry of the cluster molecule in the crystal. We shall discuss the spectra of the two types of complex separately.

TABLE I. Vibrational Frequencies of the μ_3-Bridging Sulphur Ligand in Some First-row Metal Cluster Complexes.

Complex	Type[e]	ν_{MS}/cm^{-1}
$Co_3(CO)_9S^a$	I	342, 316
$Co_3(\pi\text{-}C_5H_5)_3S(CS)$	I	334,[f] 296
$Co_3(\pi\text{-}C_5H_5)_3S(CO)^b$	I	305
$Ni_3(\pi\text{-}C_5H_5)_3S_2$	I	282, 277
$Co_3(\pi\text{-}C_5H_5)_3S_2{}^b$	I	272, 265
$Co_6(CO)_{12}C(S)_2{}^c$	I	309, 239
$Fe_3(CO)_9S(SO)$	II	350, 339, 323, 273, 255, 238
$Fe_3(CO)_9S_2$	II	354, 302, 283, 272, 254
$Fe_4(\pi\text{-}C_5H_5)_4S_4$	II	346, 310, 296, 252

[a]Unit cell contains two non-equivalent sets of molecules [10].   [b]Taken from ref. 12.   [c]Taken from ref. 14.   [d]Crystallises in orthorhombic and monoclinic forms [7, 13].   [e]See text.   [f]An alternative assignment for this absorption is discussed in the text.

Type I Complexes

It is informative to consider the vibration equations for a regular, C_{3v}, arrangement of the M_3S unit (see, for example, ref. 9) and make the assumption that the M–S and M–M stretching modes are sufficiently separated in frequency to be considered independent. We have,

$$\nu_{MS}^{sym} = [(1 + 3m_M\cos^2\beta/m_S)(k_r/m_M)]^{1/2}/2\pi c \quad (1)$$

$$\nu_{MS}^{asym} = [(1 + 3m_M\sin^2\beta/2m_S)(k_r/m_M)]^{1/2}/2\pi c \quad (2)$$

where β is the acute angle between the threefold axis and each M–S vector, m_M and m_S are the masses of the metal and sulphur atoms, respectively, c is the speed of light and k_r is the metal–sulphur bond stretching force constant. The ratio of the frequencies is then given by

$$\nu_{MS}^{sym}/\nu_{MS}^{asym} = [(1 + 3m_M\cos^2\beta/m_S)/$$
$$(1 + 3m_M\sin^2\beta/2m_S)]^{1/2} \quad (3)$$

Although this treatment represents a gross simplification of the vibrations of the M_3S unit, there is reason to suppose that it is nevertheless meaningful as a guide to assignment of the observed absorption frequencies [8]. It follows from eqn. 3 that, for β <54° as is usually the case, the symmetric should occur at a higher frequency than the antisymmetric M–S stretching mode.

This approximate treatment may be applied to the $Co_3(CO)_9S$ cluster, where the spectral interpretation is complicated by the presence of two non-equivalent sets of cluster molecules in the unit cell [10]. However, the dimensions of the two types of molecule are very similar; specifically, the two values of β are almost equal (45.2(4)° and 45.7(4)°).

The two absorptions, at 342 cm^{-1} and 316 cm^{-1} Table), are thus assigned to ν_{CoS}^{sym} and ν_{CoS}^{asym}, respectively, on the assumption that the absorptions of the individual sets of cluster molecules cannot be resolved. This interpretation leads to a calculated mean value of β of ca. 51°, compared with the mean value of 45.5° determined by X-ray diffraction [10].

A very similar situation prevails in $Co_3(\pi\text{-}C_5H_5)_3$-S(CS), where two sets of non-equivalent, but structurally similar, cluster molecules are also found in the crystal [11]. Our assignment of the absorptions at 334 cm^{-1} and 296 cm^{-1} to the symmetric and antisymmetric Co–S stretching modes, respectively, leads to a calculated mean value of β of ca. 49°, to be compared with a mean observed value of 42° [11]. Although this assignment seems reasonable the possibility that the band at 334 cm^{-1} arises from a Co–C stretching mode of the μ_3-CS ligand cannot be ruled out entirely, in view of the fact that a single absorption was reported in this region of the spectrum of the analogous complex $Co_3(\pi\text{-}C_5H_5)_3S(CO)$ [12].

The simple vibrational model described by eqns. 1–3 appears to be moderately successful in the treatment of the $Co_3(CO)_9S$ and $Co_3(\pi\text{-}C_5H_5)_3S(CS)$ clusters, in terms of the agreement between the observed and calculated values of the parameter β. It is interesting to note that in each case the calculated β is too great by a few degrees. This is to be expected from the neglect of the lower-frequency metal–metal stretching modes in the model.

The absorptions in the spectrum of $Ni_3(\pi\text{-}C_5H_5)_3$-$S_2$ which are assigned to Ni–S stretching modes are similar to those observed in the infrared spectrum of the analogous cobalt cluster (Table). For uncoupled vibrations of the two sulphur atoms, eqn. 3 would predict a frequency ratio $\nu_{NiS}^{sym}/\nu_{NiS}^{asym}$ of 1.17, using the value of β, 48.1(4)°, determined by X-ray diffraction [4]. Compared with this prediction the rela-
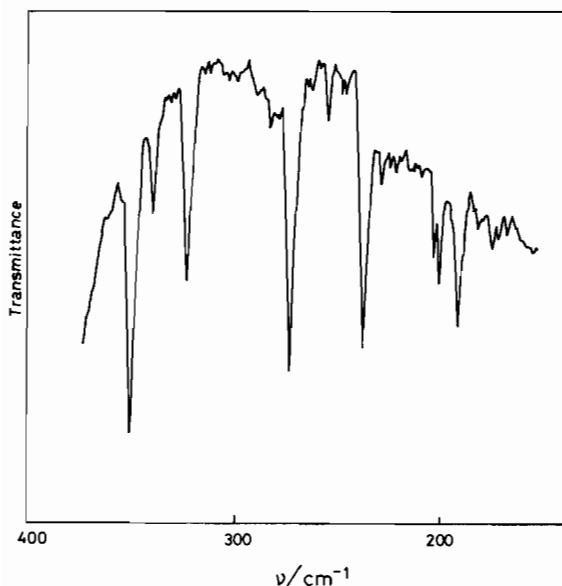
Fig. 1. The far-infrared spectrum of $Fe_3(CO)_9S(SO)$ at 95 K (Nujol mull).

tive closeness of the observed ratio to unity therefore suggests that coupling of these motions does occur and that the two absorptions arise from ν_{NiS}^{sym} (a_2'') and ν_{NiS}^{asym} (e'), in terms of D_{3h} symmetry, the components of a_1' and e'' symmetry being only active in the Raman. A similar interpretation of the infrared spectrum of the cobalt analogue seems reasonable.

Type II Complexes

The infrared spectra of the type II complexes reflect the considerable departure of these clusters from C_{3v} symmetry. This is seen clearly in the spectrum of the complex $Fe_3(CO)_9S(SO)$, which is shown in Fig. 1. Six absorptions are expected from the Fe–S stretching modes of the Fe_3S_2 central unit and these are considered to appear as the series of bands occurring in the 350–230 cm^{-1} region; the only other modes which are expected to absorb in this region are δ_{FeSO}, tentatively assigned to the sharp doublet near 200 cm^{-1}, and the symmetric and antisymmetric Fe–Fe stretching modes, which

are assigned to bands at 229 cm^{-1} and 191 cm^{-1}, respectively. A similar range of frequencies is found for ν_{FeS} in the structurally related complex $Fe_3(CO)_9S_2$ (Table); in this case five infrared-active modes are predicted. The two Fe–Fe stretching modes in this complex occur at 219 cm^{-1} and 195 cm^{-1}.

In $Fe_4(\pi$-$C_5H_5)_4S_4$ the situation is complicated by the two crystal forms in which this complex may crystallise [7, 13]. Spectra of samples from different preparations, and from recrystallisation under different conditions [7], showed variations which were consistent with the co-crystallisation of varying proportions of two phases. The frequencies given in the Table refer to a mixture of the two crystalline forms.

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