Vibrational Studies of Interstitial Hydrogen in Metal Carbonyl Clusters

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A low-temperature vibrational study of the interstitial hydride clusters $[Co_6(CO)_{15}H]^-$, $[Ni_{12}(CO)_{21}H]^{3-}$, and $[Ni_{12}(CO)_{21}H_2]^{2-}$ has enabled the ν(M–H) modes to be assigned. The salts of $[Co_6(CO)_{15}H]^-$ show the presence of two ν(Co–H) vibration modes at 1 086 and 949 cm^{-1}, which may be attributed either to different restoring forces, or to the presence of two $[Co_6(CO)_{15}H]^-$ isomers differing in the co-ordination of the hydrogen atom, *e.g.* μ_6-interstitial *versus* μ- or μ_3-external co-ordination. This study has also provided evidence for the occurrence in the solid state of an unexpectedly ready deprotonation of the cluster $[Co_6(CO)_{15}H]^-$, presumably due to interaction with traces of CO_3^{2-} present in the alkali halide support. The clusters $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2 or 3), in contrast, show only a broad absorption in the region 650–700 cm^{-1} which has been assigned to different ν(Ni–H) modes according to the different position of the interstitial H with respect to the Ni_6 cage. The low value of their frequency partially reflects the larger dimensions of the Ni_6 cavity of $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$, with respect to the Co_6 cavity of $[Co_6(CO)_{15}H]^-$, but probably indicates an increasing similarity of higher nuclearity hydride clusters to bulk metal hydrides.

Transition metal clusters containing interstitial hydride atoms form a yet restricted class of compounds. So far, there are known five interstitial hydride clusters characterized by single-crystal neutron diffraction studies, *viz.* $[Co_6(CO)_{15}H]^-$,[1] $[Ru_6(CO)_{18}H]^-$,[2] $[Nb_6I_{11}H]$,[3] $[Ni_{12}(CO)_{21}H]^{3-}$,[4] and $[Ni_{12}(CO)_{21}H_2]^{2-}$,[4] and all of them interstitially lodge hydrogen in a more or less regular octahedral cavity. Interstitial co-ordination of hydrogen, either in tetrahedral, square-pyramidal, or octahedral cavities, has been indirectly inferred or suggested in several other hydride clusters by *X*-ray and/or n.m.r. studies, *viz.* $[Os_{10}C(CO)_{24}H]^-$,[5] $[Os_{10}(CO)_{24}H_4]$,[6] $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n = 2, 3, or 4),[7,8] $[Rh_{14}(CO)_{25}H]^-$,[9] and $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ (n = 2 or 3).[10] Moreover, n.m.r. studies have also shown the dynamic behaviour of hydrogen within the metal frame of the cluster.[11,12] Therefore this unique class of clusters seems to be the most reliable molecular model of interstitial metal hydrides, as far as structural and bonding effects of incapsulation of a hydrogen atom in a metal cavity or mobility of hydrogen within a metal lattice are concerned.[13,14]

Vibrational spectroscopy could play a major role in evaluating the importance of the M–H interactions. Although the absorptions related to the M–H modes are difficult to detect, this problem can be probably tackled by low-temperature vibrational studies, since it has been shown that both i.r. and Raman ν(M–H) bands significantly gain sharpness and intensity on lowering the temperature.[15] Since on increasing the cluster size characterization or even detection of hydrogen seems to become progressively more difficult,[16] vibrational spectroscopy could also provide an additional analytical tool.

We here report a low-temperature vibrational spectroscopic study of $[Ni_{12}(CO)_{21}H_2]^{2-}$ [Figure 1(*a*)], $[Ni_{12}(CO)_{21}H]^{3-}$ [Figure 1(*b*)], and $[Co_6(CO)_{15}H]^-$ [Figure 1(*c*)], which enabled us to assign the vibrational modes of their interstitial hydride atoms. Prior to this work only a vibrational study of $[Ru_6(CO)_{18}H]^-$,[17] and neutron inelastic scattering investigations of $[Co_6(CO)_{15}H]^-$ [18] and $[Nb_6I_{11}H]$,[3] which are relevant to the present results, have been reported.

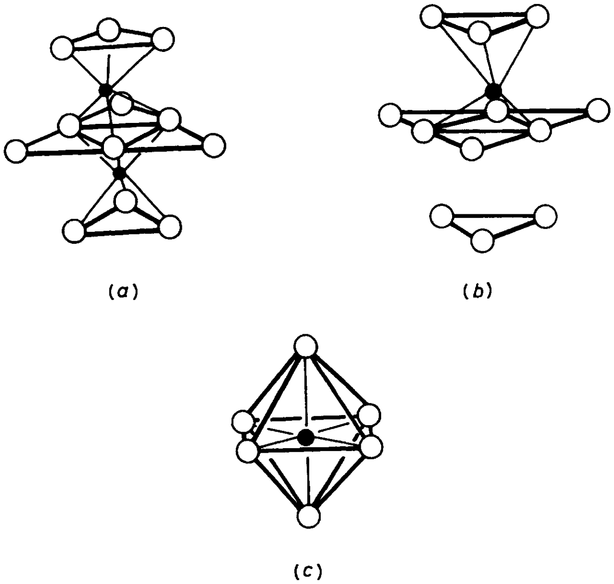

Figure 1. Schematic representations of the core structures of (*a*) $[Ni_{12}(CO)_{21}H_2]^{2-}$, (*b*) $[Ni_{12}(CO)_{21}H]^{3-}$, and (*c*) $[Co_6(CO)_{15}H]^-$: (○) metal atoms, (●) hydrogen atoms

Experimental

The $[NMe_4]_2[Ni_{12}(CO)_{21}H_2]$, $[NMe_4]_3[Ni_{12}(CO)_{21}H]$, and $K[Co_6(CO)_{15}H]$ compounds have been prepared according to the known procedures.[1,19] The corresponding deuteriated samples (isotopic labelling ⩾ 90%) have been analogously obtained by performing their synthesis in D_2O with deuteriated acid.

The i.r. spectra were run on a 580B Perkin-Elmer grating

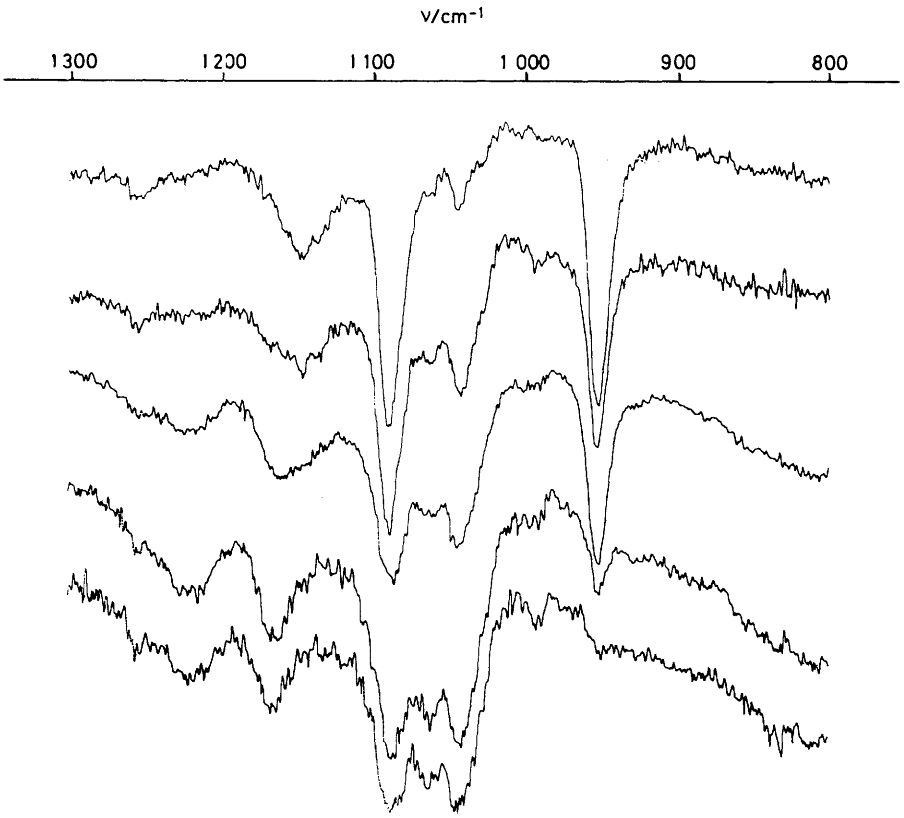

Figure 2. Series of subsequent i.r. spectra of the same sample of K$[Co_6(CO)_{15}H]$ in CsI discs at *ca.* 110 K

Table 1. Comparison between the non-cluster absorptions (cm^{-1}) of $[Co_6(CO)_{15}H]^-$ on alkali halide discs and some typical modes of HCO_3^- and XHX^- (X = Br or I) systems

$[Co_6(CO)_{15}H]^-$	HCO_3^-	XHX^-
1 710m	1 600—1 700 $\nu_{asym.}$(CO)	1 650 $\nu_{asym.}$(I–H)
ca. 1 480s, vbr	1 350—1 400 $\nu_{sym.}$(CO)	1 420—1 540 $\nu_{asym.}$(Br–H)
ca. 1 390s, vbr		
1 130w		1 165 δ(X–H–X)
1 062w	1 000—1 050 ν(C–OH)	
1 040w	950—1 000 γ(OH)	

spectrophotometer and elaborated, when necessary, on the 1500 Data Station with the PE580 software provided.

Owing to the great sensitivity of the compounds to aerial oxidation, all the samples were carefully prepared in a deaerated glove-box filled with dry nitrogen. The spectra were recorded at room temperature and at low temperature (*ca.* 110 K) in a special i.r. cell cooled by liquid nitrogen: the increase of sharpness and intensity of the bands from the hydrogen modes by lowering the temperature allowed them to be magnified by means of difference spectra.

Series of spectra on the same sample of $[Co_6(CO)_{15}H]^-$ were performed as follows. Initially, the complex and the substrate were separately ground and mechanically mixed. After having prepared the disc and run the spectra, the sample was accurately ground and pressed again several times, each time recording the new spectrum. Typical spectra are shown in Figures 2 and 3. In the ν(Co–H) region (Figure 2) each spectrum is the difference between the spectrum at low temperature and that at room temperature. The relative intensity of the carbonyl bands indicates a negligible decomposition of the complex during the entire manipulation.

Results

$[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (*n* = 2 *or* 3) *Systems*.—The Ni–H stretching modes appear as a weak and broad absorption at *ca.* 667 cm^{-1} for $[Ni_{12}(CO)_{21}H_2]^{2-}$ and as a sharper band at 684 cm^{-1} for $[Ni_{12}(CO)_{21}H]^{3-}$: both gain intensity on lowering the temperature. The assignment is supported by the disappearance of the bands in the spectra of the deuterium-labelled derivatives. The Ni–D stretching modes are expected in the 470—500 cm^{-1} region, but the presence of stronger Ni–CO stretching and bending modes does not allow an unambiguous assignment, even if a careful spectra subtraction is carried out.

$[Co_6(CO)_{15}H]^-$ *System*.—The spectrum of the cobalt cluster shows different patterns, strongly depending on the nature of the support and on the preparation of the sample. As

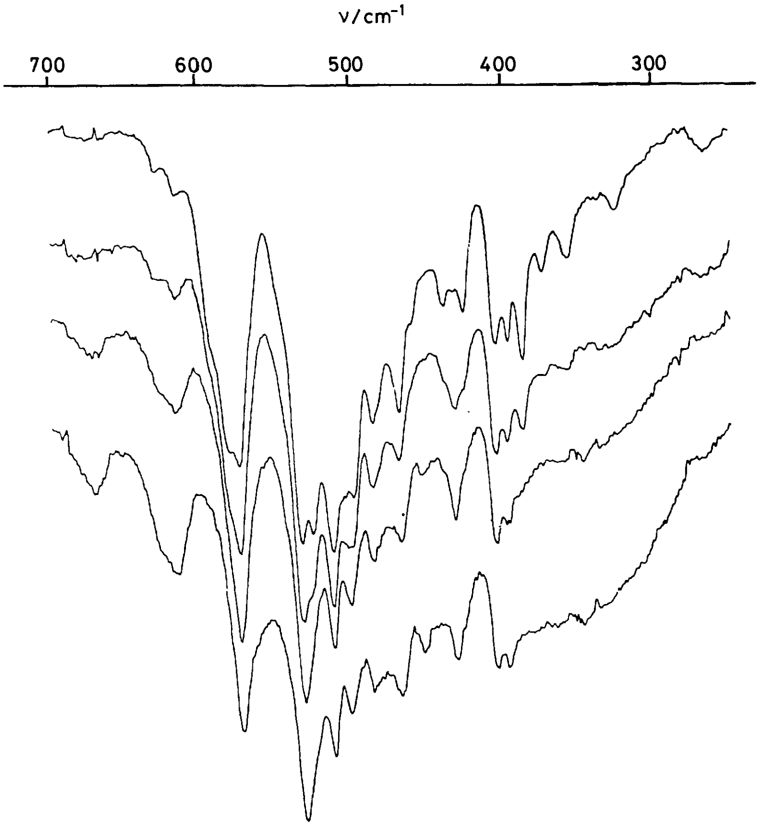

Figure 3. Series of subsequent spectra of the same sample of $K[Co_6(CO)_{15}H]$ as in Figure 2 in CsI discs at *ca.* 110 K in the CO deformation region

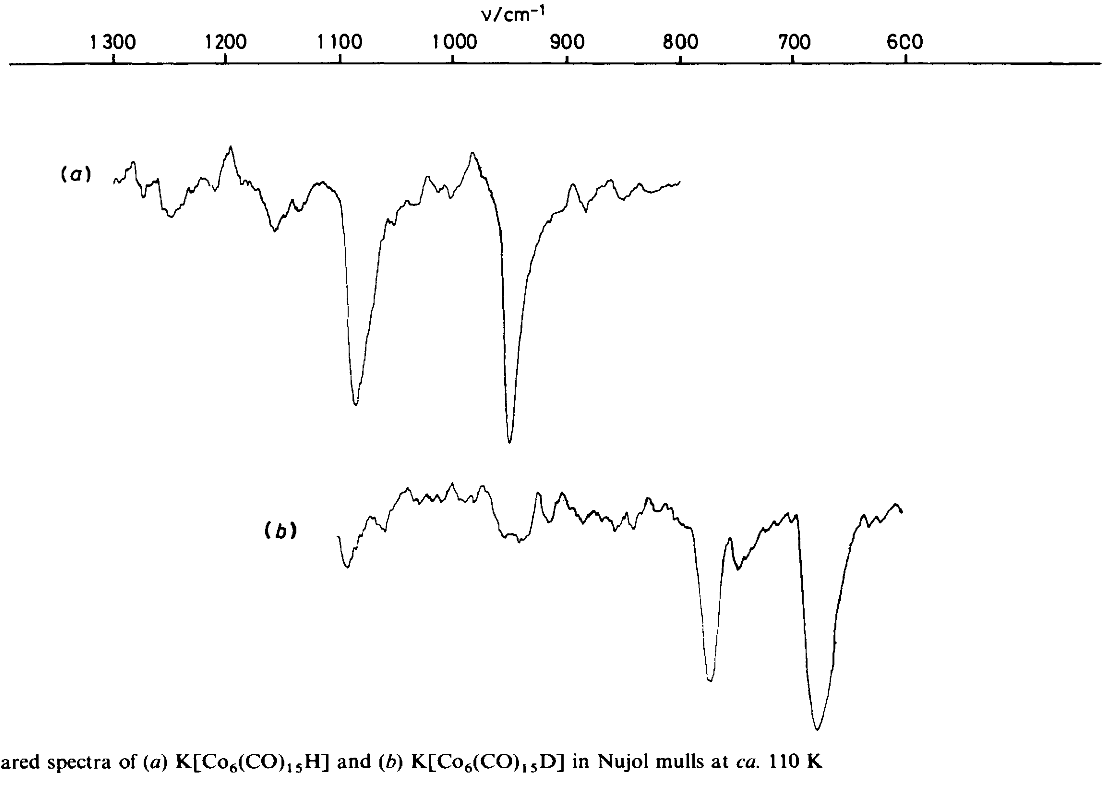

Figure 4. Infrared spectra of (*a*) $K[Co_6(CO)_{15}H]$ and (*b*) $K[Co_6(CO)_{15}D]$ in Nujol mulls at *ca.* 110 K

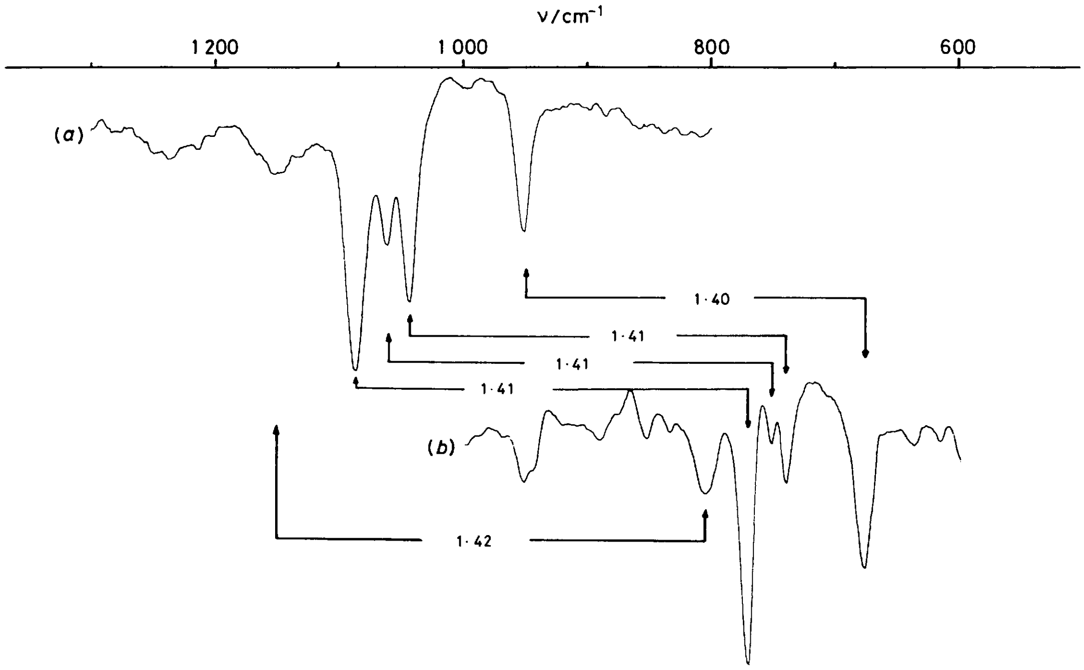

Figure 5. Infrared spectra of (*a*) K[$Co_6(CO)_{15}H$] and (*b*) K[$Co_6(CO)_{15}D$] in CsI discs at *ca.* 110 K, showing the one-to-one correspondence between the absorptions and the (ν_H/ν_D) values

we suspect a chemical interaction between the complex and the support (see below), the real spectrum of the unreacted complex may be that obtained with the most inactive substrate, *i.e.* Nujol. The spectrum (Figure 4) shows in the 1 300—800 cm^{-1} region at low temperature two medium-intensity bands at 1 086 and 949 cm^{-1} which can be unambiguously assigned to the Co–H stretching modes, because of the clear shift in the spectra of the deuteriated derivatives at 772 and 677 cm^{-1} (ν_H/ν_D = 1.41). A series of subsequent spectra of the same sample on CsI pellets are given in Figure 2, recorded according to the procedure reported in the Experimental section. The repeated grinding and pressing processes cause the appearance of new bands, which gradually gain intensity, and the disappearance of the old ones. By extrapolating, it is possible to identify two bands, at 1 089 and 951 cm^{-1}, as genuine Co–H stretching frequencies of the starting material, strictly related to those found in Nujol mulls. Different alkali halide substrates (KBr or NaCl matrices) have similar qualitative effects on the spectra. The deuterium-labelled cluster shows exactly the same band pattern with a one-to-one correspondence with the bands of the hydride cluster and frequency ratios close to the expected values (Figure 5).

Table 2. Vibrational and structural data for interstitial hydrogen in metal clusters and in bulk metals

System	ν(M–H)/ cm^{-1}	F.c./ N m^{-1}	*d*(M–H)$_{av.}$/ nm	*d*(M–M)$_{av.}$/ nm	Ref.
[$Co_6(CO)_{15}H$]$^-$	949 1 086	27 35	0.182	0.256	*
[$Ru_6(CO)_{18}H$]$^-$	825	21	0.203	0.287	17
[$Ni_{12}(CO)_{21}H$]$^{3-}$	684	23	0.172 0.222	0.270	*
[$Ni_{12}(CO)_{21}H_2$]$^{2-}$	667	21 5	0.184 0.203	0.270	*
[$Nb_6I_{11}H$]	*ca.* 1 090		0.209	0.291	3
α-PdH	549		0.195	0.276	27
β-PdH	460		0.201	0.285	27
$NiH_{0.75}$	710		0.186	0.263	28

* This work.

Discussion

An interstitial H atom occupying an octahedral cavity in a metal cluster is expected to have three vibrational degrees of freedom belonging to the same i.r.-active species, T_{1u}, and should give rise to a single band, unless the distortion of the metal octahedron is so large substantially to remove the degeneracy of the mode. Other effects (low molecular symmetry due to the ligands, crystal site effects) do not seem to be important on modifying the symmetry of the vibrations of the interstitial atoms.[20,21]

As schematically shown in Figure 1(*a*) and (*b*), hydrogen atoms in the two Ni_{12} clusters are located in considerably distorted octahedral cavities and asymmetrically displaced from the centre, so that the Ni–H distances for the central Ni_3 triangle are significantly shorter than those for the outer Ni_3 triangles.[4] As a consequence the T_{1u} mode is expected to be split into *A* and *E* modes, according to the local idealized symmetry (C_{3v} for $Ni_{12}H$, D_{3h} for $Ni_{12}H_2$). Taking into account also a probable weak coupling between the motions of the two hydrogen atoms of [$Ni_{12}(CO)_{21}H_2$]$^{2-}$, four ν(Ni–H) bands are expected with a range of 20—30 cm^{-1}: the complex indeed shows a weak and broad band at 667 cm^{-1}. A simple calculation in which the Ni_6H system is considered to be a distorted octahedron with three strong and three weak Ni–H interactions gives satisfactory agreement with the observed frequency [the calculated values, ignoring the coupling, are 673 (A_1) and 662 cm^{-1} (*E*), using the force constant (f.c.) values reported in Table 2].

In the $Ni_{12}H$ complex the hydrogen atom is much more displaced from the centre of the Ni_6 cavity, so it may be regarded as triply bridging to the inside Ni_3 triangle. The ν(Ni–H) absorption at 684 cm^{-1} could be assigned to the *E* mode solely; consequently the frequency of the A_1 mode, which can be calculated at *ca.* 480 cm^{-1}, would be obscured by the carbonyl absorptions.

A schematic representation of the structure of the anion $[Co_6(CO)_{15}H]^-$, derived from single-crystal neutron diffraction studies,[1] is given in Figure 1(*c*). Although the Co_6 octahedron is more accurately described as having a C_{2v} symmetry, splitting of the T_{1u} ν(Co–H) mode is not expected since departures from O_h symmetry are only due to minor deformations (see below). Indeed, inelastic neutron-scattering spectroscopy on pure $K[Co_6(CO)_{15}H]$ revealed a unique very broad band at 1 056 cm^{-1}, assigned to the ν(Co–H) mode,[18] although the poor resolution (*ca.* 106 cm^{-1}) prevented observation of the fine details of the spectrum.

In contrast to the above expectations, the i.r. spectra of $K[Co_6(CO)_{15}H]$ show two intriguing features. First of all, the ν(Co–H) modes give rise to two well separated absorptions, instead of the expected one (Figure 4). Secondly, new hydrogen absorptions appear in the spectra recorded in alkali halide pellets (Figure 2), which progressively gain intensity by repeated grinding of the pellet and pressing (see Experimental section). These new bands are due to hydrogen modes of new chemical species formed in the pellet, as suggested by identical behaviour of the deuteriated samples (Figure 5). A close inspection of the spectra of the above series of subsequent samples in the CO deformation region (Figure 3) concomitantly shows a systematic change of the absorption bands which, even if it cannot be rationalized because of the enormous complexity of the pattern in this region, is suggestive of a systematic change of the arrangement of the co-ordinated CO groups.

On the basis of chemical behaviour of $[Co_6(CO)_{15}H]^-$, it seems reasonable to suggest that the matrix is able to abstract hydrogen from the cluster, either as H^+ or H^-. Abstraction of H^+ could generate '*in situ*' a $[Co_6(CO)_{15}]^{2-}$ moiety,[22] whereas abstraction of H^- could be compensated by closer interaction of the resulting $Co_6(CO)_{15}$ moiety with halide ions. Although $[Co_6(CO)_{15}X]^-$ species (X = halide) have never been reported, the corresponding $[Rh_6(CO)_{15}X]^-$ species are known.[23] A direct consequence of hydrogen abstraction would be a change in the ligand arrangement around the cluster. For instance, the dianion $[Co_6(CO)_{15}]^{2-}$, which is readily obtained by deprotonation of $[Co_6(CO)_{15}H]^-$ in polar organic solvents,[1] shows a greatly different co-ordination of the CO groups around the Co_6 core.[22]

Some reasonable assignments of the additional hydrogen modes developing on employing alkali halide matrices are given in Table 1. The most probable one concerns HCO_3^-,[24] which could originate from H^+ abstraction due to a trace impurity of CO_3^{2-} present in the substrate and/or deriving from absorption of atmospheric CO_2 or aereal oxidation of the metal carbonyl. Thus, although we cannot exclude the alternative formation of hydride dihalide species XHX^-,[25] or substitutional and/or interstitial hydrides in the alkali halide lattices,[26] the similarity of the frequency and intensity of the new bands for all the substrates (NaCl, KBr, or CsI) strongly suggests the presence of a common chemical species, which conceivably is HCO_3^-.

The problem concerning the presence of two ν(Co–H) bands attributable to $[Co_6(CO)_{15}H]^-$ also in the most inert substrates is even more intriguing. Two sharp bands separated by *ca.* 40 cm^{-1} appeared to be due to the motion of H in the octahedral cavity of $[Ru_6(CO)_{18}H]^-$ and were explained by the occurrence of the Fermi resonance of an overtone or a combination mode with ν(Ru–H).[17] We cannot invoke the same effect because the shift between the two absorptions is too large (*ca.* 140 cm^{-1}) to be a consequence of vibrational perturbation and the spectrum of $[Co_6(CO)_{15}D]^-$ shows two similar bands with the frequencies lowered by a factor of 1.4.

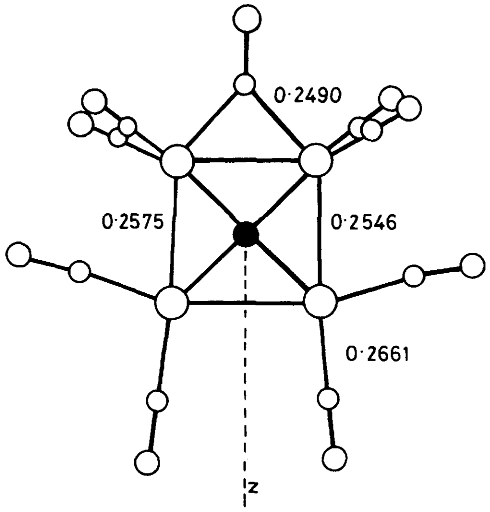

Figure 6. Schematic drawing of the central equatorial plane of $[Co_6(CO)_{15}H]^-$, showing the Co–Co bond distances (nm)

In addition, the geometry of the complex cannot at first sight be responsible for the effect. Although the Co_6 octahedron is slightly distorted, so that its structure is more accurately described as having C_{2v} symmetry, the distortion is too small to justify such a large splitting of the T_{1u} mode. A simple calculation shows that the splitting at least requires either an elongation or a compression of the cluster along the three-fold axis of 9%, whereas the difference between the short CO-bridged and the long unbridged Co–Co distances is $<3\%$. In other words, the splitting effect cannot be ascribed to the values of the *G* matrix elements, but to those of the *F* matrix. Also, a close inspection of the structure shows that in the central equatorial plane the bridged Co–Co bond is shorter than the others, and the opposite one is the longest, and that the carbonyls associated with the long edge are enlarged, as in a 'splayed-out' configuration (Figure 6). This structure is suggestive of a preferential exit of the H from the cluster along the direction (*z* axis in the C_{2v} symmetry) perpendicular to the long Co–Co bond. So the vibration along *z* may be subjected to a lower restoring force than, for instance, along the *x* axis, which maintains H in the cluster and undergoes a strong interaction with Co atoms. The two absorptions might be assigned to different vibration modes with different stretching force constants: a 25% difference can account for the actual T_{1u} mode splitting.

An alternative reasonable interpretation implies that the hydrogen atom, moving from the interstitial position, does not immediately leave the cluster and remains co-ordinated outside the Co_6 core, probably in a doubly- or triply-bridging arrangement. The deprotonation of the cluster can be presented as the simplified equilibria given below, which are shifted to the right

$$[Co_6(CO)_{15}(\mu_6\text{-}H)]^- \rightleftharpoons [Co_6(CO)_{15}(\mu_3\text{-}H)]^- \rightleftharpoons [Co_6(CO)_{15}]^{2-} + H^+(\text{substrate})$$

by the effect of the substrate. So, an absorption, presumably the low-frequency band at 949 cm^{-1}, could be assigned to the vibrational mode of the interstitial hydrogen and the other at 1 086 cm^{-1} to the vibrational modes of the bridging hydrogen.

Vibrational spectroscopic data for hydrogen encapsulated in metal clusters and in the lattices of the metals are collected in Table 2.[27,28] The paucity of the data does not allow any general consideration, but the frequency and force constant values might be approximately related to the average M–H distance: the larger the distance, the weaker is the metal–hydrogen interaction, at least among the metals belonging to the same transition series. The low values of the frequencies for the Ni clusters should only partially reflect the cluster size, but, because of the closeness with those of the metal lattice, they could reflect the greater similarity (or less dissimilarity) of the high-nuclearity clusters with the bulk metals.

Acknowledgements

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