The Metal–Nitride Stretching Vibrations in [M₄(μ₄-N)(CO)₁₂(μ-H)] (M = Ru, Os) and Related Clusters

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The i.r. spectra of the clusters [M₄(μ₄-N)(CO)₁₂(μ-L)] (M = Ru, L = H, NCO, NO; M = Os, L = H) and [Ru₄(μ₄-N)(CO)₁₁(μ-H)₃] have been measured, and the vibrational modes involving the semi-interstitial nitride ligand are assigned; the use of these compounds as models for atomic nitrogen chemisorbed on (110) surfaces of f.c.c. metals is discussed.

There have been several reported vibrational studies of metal–carbide stretching modes in metal clusters containing interstitial or semi-interstitial carbide ligands, and recent work in these laboratories has shown that the frequencies of these modes depend very closely on the geometry of the cluster core.[1] In particular, the frequencies in pentanuclear metal-carbido clusters show a close correlation with M–C–M bond angles. To date, only one report of metal–nitride stretching frequencies (ν_{MN}) has appeared in the literature,[2] for the clusters [M₆N(CO)₁₅]⁻ (M = Co, Rh) where the nitride ligand occupies a trigonal-prismatic interstitial site.

We now report the frequencies for the ν_{MN} modes in the clusters [M₄N(CO)₁₂(μ-L)] (M = Os, L = H;[3] M = Ru, L = H,[4] NCO,[5] NO[5]) and [Ru₄N(CO)₁₁(μ-H)₃],[3] in which semi-interstitial nitride ligands are co-ordinated over a tetrametal 'butterfly' framework. The structures of the [M₄N(CO)₁₂(μ-L)] clusters are shown schematically in Figure 1, together with the normal ν_{MN} vibrational modes expected under the idealised C_{2v} symmetry of the clusters. In Figure 1, x and y denote the bond distances between the nitride and the 'wing-tip' and 'hinge' metal atoms, respectively; α and β denote the angles subtended at the nitride by the two 'wing-tip' atoms and by the two 'hinge' atoms, respectively. the structure of the trihydridoruthenium cluster can be derived from that of [Ru₄N(CO)₁₂(μ-H)] by the formal replacement of one of the carbonyl ligands bonded to a 'hinge' ruthenium atom by two hydrides bridging between that 'hinge' atom and the two 'wing-tip' atoms. Since the symmetry of this cluster is reduced from C_{2v} to C_s, the a₁, b₁, and b₂ modes are of a′, a″, and a′ symmetries, respectively; this is unlikely to affect significantly the forms of the ν_{MN} modes. Table 1 lists

structural parameters for the ruthenium clusters; no structural data are available for the osmium cluster.

Figure 2 shows the i.r. spectrum of [Ru₄N(CO)₁₂(μ-H)] measured at liquid nitrogen temperature. The band at 681 cm⁻¹ is assigned to the out-of-plane rock (γ_{Ru_2H}) of the hydride ligand, on the basis of the significant sharpening it undergoes on cooling, and its frequency, which is characteristic of hydrides bridging Ru–Ru bonds.[6] Hydride rocking modes in the other clusters are assigned on similar grounds. The very strong bands in the 600—500 cm⁻¹ region of the spectrum result from RuCO deformation modes, and those in the 470—400 cm⁻¹ region from RuC stretching modes. The remaining three bands, labelled N in Figure 2, are assigned to the three ν_{RuN} modes. Table 2 lists the observed frequencies and assignments for bands in the 900—590 cm⁻¹ region for the clusters studied.

The observed bands can be assigned to specific ν_{MN} modes by a simple consideration of the cluster geometries. On inspection of Table 1, it can be seen that for the clusters [Ru₄N(CO)₁₂(μ-L)], the ('wing-tip'–nitride–'wing-tip') geometries are similar for these three clusters, suggesting that the b₁ modes might occur at similar frequencies. In addition, $x <$ y, so the ('wing-tip'–nitride) bonding might be expected to be stronger (presumably as the result of π-bonding[7]), and α ~180° so that the two bonds are nearly colinear. Thus, it follows that the b₁ mode is likely to occur at higher frequency than the other two modes. From Table 2, the ν_{MN} band at highest frequency is at very similar frequencies in the three clusters, and can be assigned to the b₁ mode. In the trihydridoruthenium cluster, x is significantly longer than in the other ruthenium clusters; the corresponding band is shifted to lower frequency, supporting the assignment.
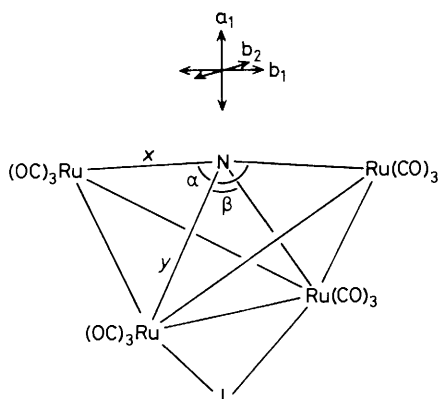

Figure 1. Schematic structure of the clusters [Ru₄(μ₄-N)(CO)₁₂(μ-L)] (L = H, NCO, NO), defining the geometrical parameters used in this work, and showing the approximate forms of the metal–nitride stretching modes.
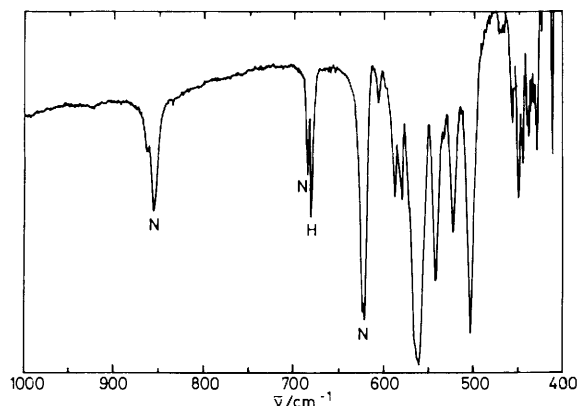

Figure 2. I.r. spectrum of [Ru₄N(CO)₁₂(μ-H)] in CsI disc in the 1000—400 cm⁻¹ region, measured at *ca.* 95 K. Bonds marked N are assigned to the metal–nitride stretching modes; that marked H to the hydride out-of-plane rock (γ_{RuH}).

The other two bands are equally readily assignable. Down the series $[Ru_4N(CO)_{12}(\mu\text{-}L)]$ (L = H, NCO, NO) the angle β shows a steady increase: 83°,[4] 97°,[5] and 106°,[5] respectively. It is reasonable to suppose that as β increases, the b_2 mode would increase in frequency (for β = 180° it becomes degenerate with the high-frequency b_1 mode) whereas the a_1 mode would become less bond-stretching and more angle-bending in nature and so be predicted to move to lower frequency. Table 2 shows that of the other two bands, one increases in frequency down the series (L = H, NCO, NO) while the other decreases, as predicted. Hence the three ν_{RuN} modes can be assigned as in Table 2, in the frequency order $b_1 > b_2 > a_1$.

The frequencies for the osmium cluster are similar to those of the corresponding ruthenium cluster and are assigned similarly. It is interesting to note that, relative to the carbonyl modes below 600 cm⁻¹ and the hydride rocking mode, the osmium–nitride modes are much weaker than the corresponding ruthenium–nitride modes.

From Table 2 it can be seen that in several of the clusters,

the metal–nitride bands show splitting into two or three components, as do some of the hydride rocking bands. This results from the presence of inequivalent molecules in the crystal, rather than from factor-group coupling. The isocyanate cluster has only one molecule per asymmetric unit in the crystal[5], and all modes appear as sharp, single bands in the i.r. spectrum, even though a factor-group analysis ($P2_1/a$, $Z = 4$) predicts two i.r.-active factor-group modes to be derived from each molecular mode. The nitrosyl cluster, on the other hand, has two independent molecules per asymmetric unit ($P\bar{1}$, $Z = 4$),[5] and most of the bands in the spectrum of this cluster are split into doublets.

These clusters can be considered as models for atomic nitrogen chemisorbed on a (110) surface of a f.c.c. metal single crystal, occupying the 'long bridged' site. In such a site, the adsorbate is bonded between two metal atoms in adjacent ridges on the surface, and probably also interacting with two metal atoms in the trough between the ridges; these atoms correspond to the 'wing-tip' atoms and the 'hinge' atoms, respectively, in the cluster. For such a surface species, it is the

Table 1. $Ru_4(\mu_4\text{-}N)$ geometries.[a]

	Ref.	$x/\text{Å}$	$\alpha/°$	$y/\text{Å}$	$\beta/°$
$[Ru_4N(CO)_{11}\{P(OMe)_3\}(\mu\text{-}H)]$[b]	4	(1.913) (1.941)	173	2.110	83
$[Ru_4N(CO)_{12}(\mu\text{-}NCO)]$	5	1.902	175	2.132	97
$[Ru_4N(CO)_{12}(\mu\text{-}NO)]$	5	1.901	173	2.164	106
$[Ru_4N(CO)_{11}(\mu\text{-}H)_3]$	3	1.960	174	(2.017) (2.097)	86

[a] x, y, α, and β are defined as in Figure 1. For each cluster, mean values are given for chemically equivalent parameters. [b] The structure of the unsubstituted cluster $[Ru_4N(CO)_{12}(\mu\text{-}H)]$ has not been determined, but the structure of the Ru_4N core should not be significantly different from that of the phosphite derivative.

Table 2. I.r. assignments in the 900—590 cm⁻¹ region.[a]

	ν_{MN}			γ_{M_2H}	δ_{MNO}
	b_1	b_2	a_1		
$[Ru_4N(CO)_{12}(\mu\text{-}H)]$	{863(mw)} {856(ms)}	685(m)	{623(vs)} {621(vs)}	681(ms)	—
$[Ru_4N(CO)_{12}(\mu\text{-}NCO)]$	863(s)	706(mw)	595(vs)	—	—
$[Ru_4N(CO)_{12}(\mu\text{-}NO)]$	{863(ms)} {859(mw,sh)}	{740(w,sh)} {734(w)}	591(vs)	—	{753(s)} {748(ms)}
				{697(m)} {695(m)}	
$[Ru_4N(CO)_{11}(\mu\text{-}H)_3]$	787(m)	676(m)	633(s)	680(vs)	—
				{656(ms)} {655(m)}	
$[Os_4N(CO)_{12}(\mu\text{-}H)]$	{860(mw)} {855(vw)} {849(mw)}	{733(vw)} {722(vw)}	{642(mw)} {640(w)} {634(m)}	{700(m)} {697(s)} {690(w)}	

[a] Frequencies in cm⁻¹; spectra measured at *ca.* 95 K. Multiple bands resulting from the same molecular mode are bracketed together: s = strong; m = medium; w = weak; sh = shoulder; v = very.

totally symmetric a_1 ν_{MN} mode which is observable by electron energy loss spectroscopy (e.e.l.s.). Canning has attributed a vibration at 411 cm^{-1} in the e.e.l. spectrum of a nitrided Ni(110) surface to such a vibrational mode.[8] Low energy electron diffraction of this overlayer indicated a p(2 × 3) structure, previously observed in studies of N_2[9] and N_2^+ [10] adsorption on the same surface. In these studies, models were proposed in which nitrogen atoms occupied rectangular 'four-fold' sites[10] or replaced some of the ridge and trough nickel atoms in a reconstructed surface.[9] In neither case was the 'long bridge' site proposed, in agreement with the present work; the frequency of the surface vibration (411 cm^{-1}) is very different from the a_1 frequencies observed for these clusters (*ca.* 600 cm^{-1}).

If a N/M(110) system could be identified in which the nitrogen occupied the 'long-bridge' site, this would provide a useful test of the cluster-surface analogy.

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