Raman Spectra and Structure of Dihydridotetracarbonyl Derivatives of Iron, Ruthenium, and Osmium

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Summary Raman spectra have been obtained at *ca.* 90 K for the complexes $[H_2M(CO)_4]$ (M = Fe, Ru or Os); shifts due to ν(M–H) vibrations are very intense, contrasting with the weakness of corresponding i.r. absorptions, and are consistent with a *cis*-configuration in the solid state for all three molecules which persists into the liquid phase for M = Os.

The structural properties of the unsubstituted, mononuclear transition-metal hydridocarbonyls[1] (those of Mn, Tc, Re, Fe, Ru, Os, and Co) have been uncertain for a long time, especially because of their very low thermal stability (except for Mn, Re and Os) and the extremely feeble i.r. absorption due to metal–hydrogen stretching vibrations in these complexes, resulting in doubt as to the mode of bonding of the hydrogen atoms. Raman spectroscopy provides definitive confirmation of earlier, often tentative conclusions regarding this problem.

The Raman spectra of the complexes $[H_2M(CO)_4]$ (M = Fe[2], Ru[3], or Os[4]) obtained† following direct deposition of samples on a brass wedge cooled (liquid N_2) to *ca.* 90 K, are shown in the Figure. This strikingly illustrates the extreme prominence of Raman shifts below 2000 cm^{-1}, which are assigned to ν(M–H) vibrations, in direct contrast to the very low intensities of corresponding i.r. bands.[2–4] Owing to the unexpectedly[4] high thermal stability of $[H_2Os(CO)_4]$, it is also possible to record its Raman spectrum in the liquid phase at 295 K; ν/cm^{-1}, 1940 (dpol)s, 1970 (pol)vs, 2039 (dpol)m,sh, 2063 (dpol?)s, and 2140 (pol)vs.‡ The depolarization ratios establish that the symmetric Os–H stretching mode is that at higher energy, and it is the antisymmetric component which appears weakly in the i.r.[4]

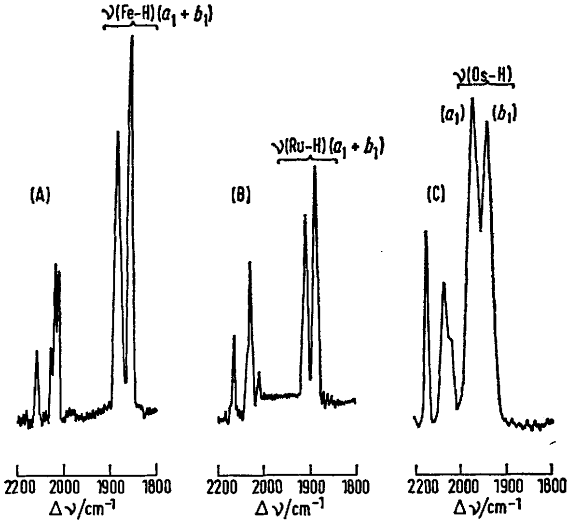

Figure. Raman spectra (1800—2200 Δ cm^{-1}) at *ca.* 90 K for $[H_2M(CO)_4]$: (A) M = Fe; (B) Ru; (C) Os.

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† Reproducibly, from 488·0 nm at 3 mW (focussed) or 22 mW (unfocussed) laser power; under these conditions no discolouration of the (white) solid sample films could be detected.

‡ depol = depolarized, pol = polarized.

(1942 cm^{-1}). The very close resemblance between the liquid data and the spectrum at 90 K [Figure, (C)] indicates that the latter may be interpreted on the basis of molecular symmetry predictions and that solid-state splitting of fundamentals can be neglected. In view of the overall similarity of their Raman spectra, a *cis*-configuration in the solid state can be deduced for all three (Fe, Ru, Os) molecules, since for each 2 Raman shifts attributable to ν(M–H) modes are observed (a_1 and b_1 of C_{2v}; the alternative *trans*-geometry is D_{4h} with only a_{1g} Raman-active) together with 3 or 4 (rather than 2) Raman-active ν(CO) modes. (Existence of *cis-trans*-isomer mixtures at 90 K cannot be completely ruled out but appears to be unlikely owing to the absence of further unexplained Raman shifts and the equivalence between solid and liquid data for M = Os).

The positions of the Raman bands due to ν(M–H) demonstrates the invalidity of some earlier conclusions based on i.r. data. Thus it becomes obvious that for each molecule only one such fundamental (either a_1 or b_1) has been located in the i.r., not both as has been suggested.[2–4] For [$H_2Ru(CO)_4$] the Raman shifts due to ν(Ru–H) are at 1916 and 1897 cm^{-1} so that the weak i.r. band[3] at 1980 cm^{-1} is not likely to arise from Ru–H stretching. The relative positions of the ν(M–H) fundamentals follow an interesting trend, increasing monotonically along the series Fe<Ru<Os (despite increasing mass of the metal atom). This is consistent with increasing stretching force-constant $k_{\text{M–H}}$, may imply increasing bond-dissociation energy $\overline{D}$(M–H), and may correlate with the remarkable change in thermal stability[4] between M = Fe or Ru and M = Os. It can also be associated with a similar, though much less pronounced effect for[5] [$Cl_2M(CO)_4$], where ν(M–Cl) vibrations are of near equal energy for M = Fe or Os.

We thank the N. Ireland Department of Education for financial support (G.F.B.) and Dr. Peter Goggin, University of Bristol, for measuring the Raman spectrum of the liquid osmium compound.

(*Received*, 24*th January* 1975; *Com.* 082.)

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