The Infrared Spectra of Trimetal Carbonyl Species in Frozen Gas Matrices at 20°K

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Summary I.r. spectra of $Os_3(CO)_{12}$, $Ru_3(CO)_{10}(NO)_2$, and $Fe_3(CO)_{12}$ in solution and in low-temperature matrices show that the structures of $Fe_3(CO)_{12}$ in solution and matrix are different and the spectrum of molecular $Fe_3(CO)_{12}$ (C_{2v} structure) is reported for the first time.

A LOW-PRESSURE stream of metal carbonyl can be co-condensed at a low temperature (20°K) with a large excess of an inert gas (*e.g.* argon or nitrogen) to give a matrix, from which a vibrational spectrum of the carbonyl molecule can be obtained, free from the intermolecular coupling effects found in solids. This technique[1] is particularly valuable for compounds of low vapour-pressure whose vibrational spectrum cannot be obtained in the gas phase.

The Figure and Table summarize some results, selected from a large number of our observations on trimetal dodecacarbonyls and related species in solution and in various gas matrices. These results are significant in several respects.

(i) The i.r. spectrum of $Os_3(CO)_{12}$ in a nitrogen matrix over the C–O stretch region shows a pattern, identical to the solution spectrum, but with narrower half-widths and slight frequency shifts. This indicates the same structure for $Os_3(CO)_{12}$ in solution and matrix, presumably the unbridged D_{3h} structure found in the solid.[2] It is worth mentioning that only four i.r. bands are predicted in this case, whether or not there is intramolecular coupling. (With some highly symmetrical molecules we do observe splitting of bands in some matrices; this we believe is due to slight molecular distortion and details will be presented elsewhere.[3])

(ii) The solution and matrix spectra of $Ru_3(CO)_{10}(NO)_2$[4] are almost identical. This molecule almost certainly has a C_{2v} structure,[4,5] analogous to $Fe_3(CO)_{12}$, with bridging NO groups in place of the CO bridges. Seven terminal carbonyl bands are predicted for this structure, in the absence of intramolecular coupling. There are eight bands in the matrix spectrum, which seems to be *some* evidence for intramolecular coupling.

(iii) The spectrum of $Fe_3(CO)_{12}$ in an argon matrix is very different from that in solution. The matrix spectrum cannot be interpreted as a highly resolved solution spectrum but it is very similar to both the argon matrix and solution spectra of $Ru_3(CO)_{10}(NO)_2$—note in particular the weak high-frequency band at 2110 cm^{-1}, which is not observed even in extremely concentrated solutions of $Fe_3(CO)_{12}$.[5] These spectra strongly suggest that in argon (but not *necessarily* in the gas phase) $Fe_3(CO)_{12}$ has the doubly bridged structure[5] found in the solid,[6] and that $Fe_3(CO)_{12}$ and $Ru_3(CO)_{10}(NO)_2$ have closely related structures. Since the solid-state spectrum[7] is complicated by intermolecular coupling, the matrix spectrum in the Figure shows, for the first time, the vibrational bands of 'free' $Fe_3(CO)_{12}$ in the C_{2v} form. In view of the correspondence between solution and matrix spectra of $Os_3(CO)_{12}$ or $Ru_3(CO)_{10}(NO)_2$, it would appear that the solution structure of $Fe_3(CO)_{12}$ is different from the structure found in the solid and matrix. As yet there is no additional evidence to support or refute the symmetrical solution structure suggested by Wei and Dahl,[6] but we are currently

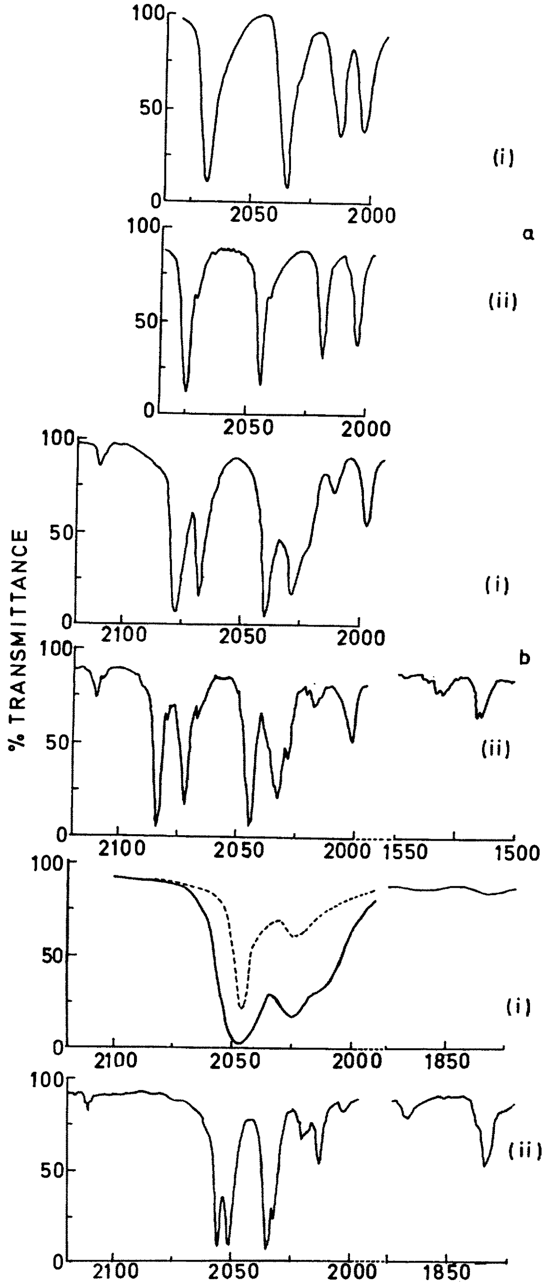

FIGURE. *Infrared spectra* a (i) $Os_3(CO)_{12}$ *in cyclohexane solution*; a (ii) $Os_3(CO)_{12}$ *in nitrogen matrix at* 20°K; b (i) $Ru_3(CO)_{10}(NO)_2$ *in n-hexane solution*; b (ii) $Ru_3(CO)_{10}(NO)_2$ *in argon matrix at* 20°K; c (i) $Fe_3(CO)_{12}$ *in n-hexane solution*; c (ii) $Fe_3(CO)_{12}$ *in argon matrix at* 20°K. *Low temperatures were obtained using an Air-Products* AC–2L *Cryotip refrigerator.*

Infrared frequencies of trimetal carbonyl species

Molecule	Solvent/matrix	Frequencies
$Os_3(CO)_{12}$	Cyclohexane[a]	2068s, 2035s, 2014m, 2002m
$Os_3(CO)_{12}$	N_2 matrix[b]	2075s, 2070sh, 2045s, 2041sh, 2018·5m, 2004m
$Ru_3(CO)_{10}(NO)_2$	n-Hexane[c]	2110w, 2077s, 2068s, 2061sh, 2039s, 2030s, 2026sh, 2015w, 2000m, 1524w, 1508m
$Ru_3(CO)_{10}(NO)_2$	Ar matrix[b]	2115w, 2083vs, 2071s, 2066sh, 2044vs, 2033s, 2028m, 2017w, 2001m, 1533w, 1530w, 1516m, 1513m
$Fe_3(CO)_{12}$	n-Hexane[d]	2046s, 2023m, 2013sh, 1867vw, 1835w
$Fe_3(CO)_{12}$	Ar matrix[b]	2110vw, 2056s, 2051s, 2036s, 2032m, 2021w, 2013m, 2003vw, 1871sh, 1867w, 1833ms Also 612sh m, 606m, 580m, 449vw, and many other weaker bands in region 625—400cm^{-1}

[a] Ref. 8; [b] This work; [c] Ref. 4; [d] Ref. 5

engaged in experiments on frozen glasses (i.r. and Mössbauer) which we hope will characterize the solution species.

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