The Infrared Spectra of Trimetallic Carbonyls in Solution

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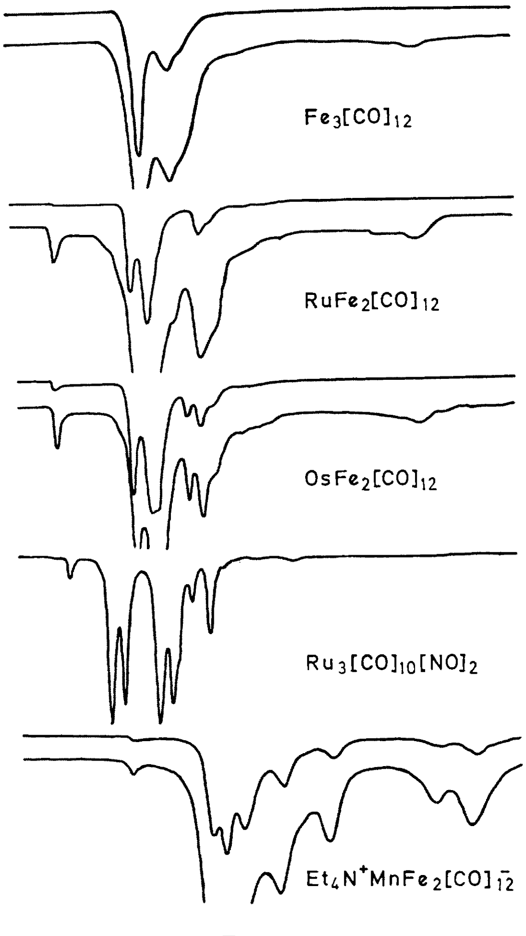
Summary Comparison of the solution and matrix i.r. spectra of $Fe_3(CO)_{12}$ with the solution i.r. spectra of related trimetallic species provides strong supporting evidence for a previous suggestion that the structure of $Fe_3(CO)_{12}$ in solution is different from that in the solid state.

ALTHOUGH the molecular structure of tri-iron dodecacarbonyl in the crystalline state has finally been determined,[1] some doubt still exists as to its structure in solution. The unusually simple i.r. spectrum of $Fe_3(CO)_{12}$ in solution in nonpolar solvents has led to the suggestion[1] that the molecule in solution may have a C_{3v} type structure with three bridging carbonyl groups, one on each edge of the Fe_3 triangle. For a molecule of this symmetry, five terminal and two bridging carbonyl absorptions are allowed.

It is often true, however, that the i.r. spectra of polynuclear carbonyl complexes in the carbonyl region show fewer bands than expected according to group theory.[2] The simple solution spectrum of $Fe_3(CO)_{12}$ does not therefore, by itself, militate against the solid-state structure being retained in solution. For this reason, it was of interest to compare the solution i.r. spectrum of $Fe_3(CO)_{12}$ with those of other related trimetallic carbonyl complexes which may be presumed to have C_{2v} symmetry. The synthesis by us of the new complex $OsFe_2(CO)_{12}$† [formed in low yield on u.v. irradiation of a mixture of $Os_3(CO)_{12}$ and $Fe(CO)_5$ in acetone solution] has allowed comparison of the i.r. spectrum of $Fe_3(CO)_{12}$ with the spectra of the complete series of related carbonyls $MFe_2(CO)_{12}$ (M=Ru, Os, Mn^-, Tc^-, Re^-).

A comparison of the solution i.r. spectra of the trimetallic carbonyls (Figure, Table) shows that the spectra of $RuFe_2(CO)_{12}$, $OsFe_2(CO)_{12}$, $MnFe_2(CO)_{12}^-$, $TcFe_2(CO)_{12}^-$, $ReFe_2(CO)_{12}^-$, and $Ru_3(CO)_{10}(NO)_2$ are all similar and, in particular, show a weak absorption in the terminal carbonyl region approximately 65 cm^{-1} higher in frequency than the several other strong terminal absorptions. Only $Fe_3(CO)_{12}$ itself fails to show this band, suggesting that it has a structure different from that of the other species. This argument is reinforced by an examination of the i.r. spectra taken for $Fe_3(CO)_{12}$ and for $Os_3(CO)_{12}$ in an argon matrix at 20°K.[3] For $Os_3(CO)_{12}$, the i.r. spectra in solution and in the matrix are very similar showing that there is no reason to expect differences in matrix and solution spectra if there is no difference in molecular structure in the two phases. In contrast, the i.r. spectra of $Fe_3(CO)_{12}$ in solution and in the matrix are different and, furthermore, the matrix spectrum of $Fe_3(CO)_{12}$ is very similar to those of the other trinuclear carbonyls $MFe_2(CO)_{12}$ in solution.

We may therefore conclude that the difference between the solution i.r. spectra of $Fe_3(CO)_{12}$ and the related trinuclear carbonyls is indeed due to a difference in molecular structure and, although the structures of the species cannot be assigned unequivocally from i.r. data, the evidence is consistent with a C_{3v} molecular symmetry for $Fe_3(CO)_{12}$ and a C_{2v} symmetry for the other species. Indeed for $Ru_3(CO)_{10}(NO)_2$, the i.r. spectrum clearly indicates the presence of bridging NO groups[4] and the absence of bridging CO groups; it is therefore difficult to conceive of a structure other than one analogous to that found for $Fe_3(CO)_{12}$ in the solid state and having C_{2v} symmetry.



FIGURE

Solution i.r. spectra of trimetallic carbonyl complexes in the carbonyl region

Compound	Solvent	ν_{CO} cm^{-1}
$Fe_3(CO)_{12}$[a]	n-Hexane	2046s, 2023m, 2013sh, 1867vw, 1835w .
$RuFe_2(CO)_{12}$[a]	n-Hexane	2115w, 2052s, 2040s, 2021sh, 2000m, 1989sh, 1860vw, 1828w
$OsFe_2(CO)_{12}$[a]	n-Hexane	2117w, 2055s, 2041s, 2036s, 2013m, 2001m, 1990sh, 1860vw, 1827vw
Et_4N^+ $MnFe_2(CO)_{12}^-$ [a]	THF	2063w, 1999s, 1990s, 1972s, 1944m, 1903w, 1827w, 1785w
Et_4N^+ $TcFe_2(CO)_{12}^-$ [b]	THF	2077w, 2008m, 1987s, 1943m, 1903w, 1814w, 1783w
Et_4N^+ $ReFe_2(CO)_{12}^-$ [c]	THF	2075w, 2006m, 1991s, 1946m, 1903w, 1814w, 1785w
$Ru_3(CO)_{10}(NO)_2$ [d]	n-Hexane	2110w, 2077s, 2068s, 2061sh, 2039s, 2030s, 2026sh, 2015w, 2000m

[a] This work.
[b] M. W. Lindauer, G. O. Evans, and R. K. Sheline, *Inorg. Chem.*, 1968, **7**, 1249.
[c] G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Comm.*, 1967, 186.
[d] J. Norton, D. Valentine, and J. P. Collman, *J. Amer. Chem. Soc.*, 1969, **91**, 7537.

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† Characterised by its mass spectrum.

[1] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 1351.
[2] See, for example, the spectrum of $Ru_2Fe(CO)_{12}$ in J. Knight and M. J. Mays, *Chem. and Ind.*, 1968, 1159.
[3] Following communication.
[4] R. C. Elder, F. A. Cotton, and R. A. Schunn, *J. Amer. Chem. Soc.*, 1969, **89**, 3645.