Metal–Metal Stretching Frequencies

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IN view of the current interest in compounds containing metal–metal bonds, we have studied the far-infrared spectra of a number of binuclear metal–metal compounds, in which one of the metals is tin, and have arrived at an assignment, based on frequencies and on comparison with analogous molecules, for the tin–metal stretching vibration. These are given in Table 1.

Only in those compounds containing the tin–tin bond did we experience any difficulty in detecting

TABLE 1

Metal-metal stretching frequencies

Compound	State	M–M	cm.$^{-1}$	Ref.
$\mathrm{Ph_3Sn{-}SnEt_3}$	Liquid	Sn–Sn	208	a
$\mathrm{Et_3Sn{-}SnBu_3}$	Liquid	Sn–Sn	199	a
$\mathrm{Ph_3Sn{-}SnMe_3}$	Solid	Sn–Sn	194	a
$\mathrm{Me_3Sn{-}GePh_3}$	Solid	Sn–Ge	225	
$\mathrm{Et_3Sn{-}GePh_3}$	Solid	Sn–Ge	230	
$\mathrm{Ph_3Sn{-}GeBu_3}$	Liquid	Sn–Ge	235	
$\mathrm{Me_3Sn{-}Mn(CO)_5}$	Liquid	Sn–Mn	182	b
$\mathrm{Ph_3Sn{-}Mn(CO)_5}$	Solid	Sn–Mn	174	b
$\mathrm{Me_3Sn{-}Mo(CO)_3C_5H_5}$	Solid	Sn–Mo	172	
$\mathrm{Ph_3Sn{-}Mo(CO)_3C_5H_5}$	Solid	Sn–Mo	169	
$\mathrm{Me_3Sn{-}Fe(CO)_2C_5H_5}$	Liquid	Sn–Fe	185	
$\mathrm{Ph_3Sn{-}Fe(CO)_2C_5H_5}$	Solid	Sn–Fe	174	
$\mathrm{Me_3Sn{-}Co(CO)_4}$	Solid	Sn–Co	176	

[a] The Raman spectra of: $\mathrm{Ph_6Sn_2}$ gives ν(Sn–Sn) 208 cm.$^{-1}$ (ref. 1); $\mathrm{Sn(SnPh_3)_4}$ gives ν(Sn–Sn) 207 cm.$^{-1}$ (ref. 1); $\mathrm{Me_6Sn_2}$ gives ν(Sn–Sn) 190 cm.$^{-1}$ (ref. 2).

[b] The Raman spectra of: $\mathrm{Me_3Sn{-}Mn(CO)_5}$ gives ν(Mn–Sn) 179 cm.$^{-1}$ (ref. 3); $\mathrm{Ph_3Sn{-}Mn(CO)_5}$ gives ν(Mn–Sn) 174 cm.$^{-1}$ (ref. 1).

ν(Sn–Sn),* whilst in the heteronuclear metal–metal compounds, the band that we have assigned as belonging mainly to ν(M–M′) has invariably been of medium, and in some cases, even of strong intensity. From our experience, contrary to what was intimated by Gager, Lewis, and Ware[1] in their rather pessimistic generalization of the suitability of far-infrared spectroscopy for the detection of ν(M–M′), we have found that this technique can be used quite successfully for the evaluation of ν(M–M′) where one of the metals is tin and the other, a transition metal.

The assignment of bands in the i.r. spectra of molecules as complex as these is a somewhat hazardous operation; the bands assigned to ν(M–M′) may well include contributions from other modes, either implicitly, through coupling with modes of the same symmetry, or by accidental degeneracy with modes of different symmetry. The most one can say is that the band assigned to ν(M–M′) probably includes the main contribution of ν(M–M′).

We have also studied the far-infrared spectra of a number of halogen-containing tin–manganese compounds. The values for ν(Sn–Mn) in these compounds are given in Table 2.

The variation of ν(Sn–Mn), as iodine is replaced successively by bromine and chlorine, probably arises as a result of the change in effective mass of the tin atom rather than a change in the polarity of the tin–manganese bond. The carbonyl region would appear to be consistent with these findings,[4] in that no change in frequency for the monosubstituted compounds is observed for any of the three i.r.-active carbonyl stretching modes, although all are higher than in trimethyltin-manganese pentacarbonyl. At the same time, successive replacement of the methyls with chlorine substantially shifts the carbonyl stretching modes to higher frequencies.[5]

TABLE 2

Compound	ν(Mn–Sn) cm.$^{-1}$
$\mathrm{Me_2ISn{\cdot}Mn(CO)_5}$	179
$\mathrm{Me_2BrSn{\cdot}Mn(CO)_5}$	191
$\mathrm{Me_2ClSn{\cdot}Mn(CO)_5}$	197
$\mathrm{MeCl_2Sn{\cdot}Mn(CO)_5}$	201
$\mathrm{Cl_3Sn{\cdot}Mn(CO)_5}$	201

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* A far-infrared study of a series of substituted digermanes would indicate ν(Ge–Ge) to be extremely weak.

[1] H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Comm.*, 1966, 616.
[2] M. P. Brown, E. Cartmell, and G. W. A. Fowles, *J. Chem. Soc.*, 1960, 506.
[3] V. Maroni, private communication.
[4] M. R. Booth, private communication.
[5] H. C. Clark, M. R. Booth, and N. A. D. Carey, to be published.