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An Interesting Feature in Vibrational Spectra of Dicarba-closo-dodecaboran(12)yl Derivatives of Non-transition Metals

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It is well known that the frequencies of non-transition metal–carbon bond stretching vibrations (ν_{M-C}) including those of Hg–C and Tl–C bonds lie in the region 400–600 cm^{-1} [1, 2]. However, Raman spectra of bis(dicarba-closo-dodecaboran(12)yl-1)-mercury and bis(dicarba-closo-dodecaboran(12)yl-1)-thallium chloride* exhibit no lines in this region but strong polarized lines between 130 and 180 cm^{-1} are observed instead, which were not present in the spectra of original carboranes. These low values of ν_{M-C} could have been explained by a low value of K_{M-C} force constant, if it had not been known that the M–C bond in C-carboranyl derivatives of Hg and Tl is stronger than that for corresponding alkyl derivatives [4, 5]. So it is to be concluded that during the vibration with the frequency ~150 cm^{-1} not simply metal–carbon bond stretching occurs, but the carborane nucleus behaves as a rigid body pseudo-atom, the vibration having metal–carborane stretching character. Indeed, if one calculates the vibrations of a linear three-mass model "carborane–

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*For brevity in the following text we shall use, as is often done [3], the trivial name "carborane" instead of "dicarba-closo-dodecaborane(12)".

TABLE. The Frequencies of the Metal–Carborane Stretching Vibrations in Raman Spectra[a] of Carboranyl Derivatives of Non-transition Metals.

Compound[b]	Position of Substituent in Carborane Nucleus	$\nu_{M\text{-}Carb}$ in cm^{-1}
$(1,2\text{-}B_{10}H_{10}C_2H)_2Hg$	C(1)	141s, 161s (in solid)
$(1,7\text{-}B_{10}H_{10}C_2H)_2Hg$	C(1)	154s (in solid)
$(1,12\text{-}B_{10}H_{10}C_2H)_2Hg$	C(1)	155s, 175w (in solid)
$(1,2\text{-}C_2H_2B_{10}H_9)_2Hg$	B(9)	136s, 143sh (in solid) 140s (in acetone solution)
$(1,7\text{-}C_2H_2B_{10}H_9)_2Hg$	B(9)	129s, 148s, 165w (in solid) 138s (in benzene and acetone sol.)
$(1,12\text{-}C_2H_2B_{10}H_9)_2Hg$	B(2)	132s, 148s, 168w (in solid) 138s (in acetone solution)
$(1,2\text{-}C_2H_2B_{10}H_9)HgCl$	B(9)	158w, 173s (in solid)
$(1,7\text{-}C_2H_2B_{10}H_9)HgCl$	B(9)	150w, 173s (in solid)
$(1,12\text{-}C_2H_2B_{10}H_9)HgCl$	B(2)	176s (in solid)
$(1,2\text{-}C_2H_2B_{10}H_9)HgBr$	B(9)	149s, 157s, 162s (in solid)
$(1,7\text{-}C_2H_2B_{10}H_9)HgBr$	B(9)	144w, 158s (in solid)
$(1,2\text{-}B_{10}H_{10}C_2H)HgMe$	C(1)	176s, 555s (in solid)
$(1,2\text{-}C_2H_2B_{10}H_9)HgEt$	B(9)	165s, 486s (in solid)
$(1,7\text{-}C_2H_2B_{10}H_9)HgEt$	B(9)	166s, 486s (in solid)
$(1,2\text{-}B_{10}H_{10}C_2H)TlCl$	C(1)	144s, 186w (in solid)
$(1,2\text{-}C_2H_2B_{10}H_9)_2TlCl$	B(9)	142s (in solid)
$(1,7\text{-}C_2H_2B_{10}H_9)AsCl_2$	B(9)	239m (in benzene solution)
$(1,7\text{-}C_2H_2B_{10}H_9)SbCl_2$	B(9)	195m (in solid)

[a] Raman spectra were obtained using a Jobin-Ivon HG 2S spectrometer equipped with Ar$^+$ laser CR-8. [b] The preparation and physical constants of the compounds studied are given in the following papers: for carboranes containing C–Hg bonds [4], B–Hg bonds [6], C–Tl bonds [5], B–As and B–Sb bonds [7].

metal–carborane", taking into account the whole mass of the carborane nucleus and assuming the force constant K_{M-C} equal to that in alkyl derivatives [1], then frequencies are obtained which are close to the observed ones. For B-mercurated carboranes the frequency of the metal–carborane stretching vibration changes only by 10–15 cm^{-1} in comparison with C-mercurated isomers.

Sometimes the ν_{M-Carb} Raman line is split into two or three components due to crystal lattice effects, because only one line is observed in solution spectra. If one of the substituents attached to a metal atom (Hg or Tl) is a carborane nucleus and the second an alkyl group (see Table), two strong polarized lines are observed in Raman spectra: one in the low frequency region corresponding to the metal–carborane stretching and the other one in the usual region (~500 cm^{-1}) corresponding to ν_{M-C} of metal–alkyl bonds.

In the spectra of carboranyl derivatives of As and Sb of the type $C_2H_2B_{10}H_9MCl_2'$ the ν_{M-Cl} stretchings are more intense in Raman than ν_{M-Carb}, the latter being easily identified as a polarized line of medium intensity whose frequency lies in the region of 180–250 cm^{-1}, its value depending on the mass of the element M.

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