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LETTER

High-pressure vibrational spectroscopic study of cesium decachloroborate, $Cs_2[B_{10}Cl_{10}]$

Yining Huang and Ian S. Butler*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Que., H3A 2K6 (Canada)

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The vibrational spectra of the icosahedral caged borane derivatives, $Cs_2[B_{12}H_{12}]$ [1] and $B_{10}C_2H_{12}$ [2], have been investigated under high external pressures. In both cases, a pressure-induced phase transition was detected at moderate pressures (*c.* 10 kbar). We now report here the results of a similar high-pressure vibrational spectroscopic study of the related boron cage compound, $Cs_2[B_{10}Cl_{10}]$. Some limited vibrational assignments have been proposed for this decachloroborate anion on the basis of room-temperature IR and Raman data [3].

Experimental

Crystalline $Cs_2[B_{10}Cl_{10}]$ was a generous gift from Dr W. H. Knoth (Dupont Corp.). Complete experimental results for the high-pressure IR and Raman measurements have been described elsewhere [4].

Results and discussion

The effect of increasing pressure on the internal vibrational modes of $Cs_2[B_{10}Cl_{10}]$ was monitored in the IR above 400 cm^{-1} and in the Raman below 400 cm^{-1} for pressures up to 50 and 70 kbar, respectively. The pressure dependences of the observed IR and Raman peaks are plotted in Figs. 1 and 2, respectively. The relevant $d\nu/dP$ and $d\ln\nu/dP$ values are listed in Table 1. The absence of any breaks in the slopes of the ν versus P plots indicates that there are no pressure-induced phase transitions throughout the pressure range studied.

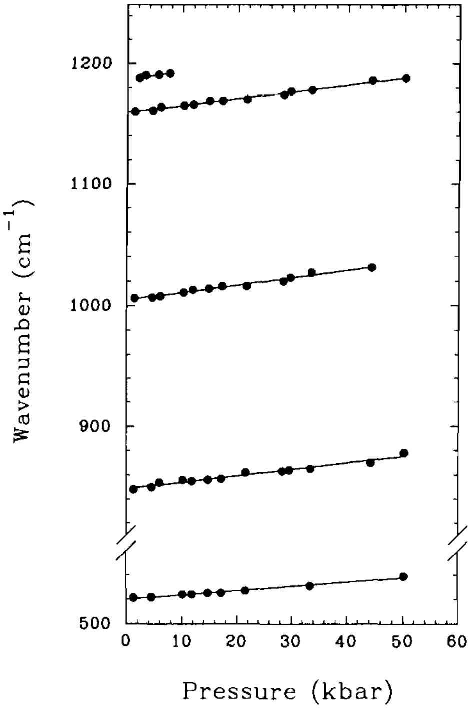

Fig. 1. Pressure dependences of the observed IR modes of $Cs_2[B_{10}Cl_{10}]$.

The pressure dependences and the relative pressure dependences of the B–Cl stretching modes are smaller than those of the B–H vibrations in $Cs_2[B_{12}H_{12}]$ [1]. Since the B–Cl stretching force constant [5] and the B–Cl bond distance [6] are generally smaller and longer than the corresponding values for the B–H bond, the B–Cl bond would be expected to be more easily shortened under the influence of pressure than is the B–H bond. Consequently, a larger pressure dependence would be anticipated for the B–Cl stretching mode. Experimentally, the opposite is observed. This situation might be due to the stronger interactions between either the anion cages within the unit cell or the individual chlorine atoms and the cesium ions because of the larger electronegativity of chlorine. Both types of interaction would certainly be strongly affected by pressure and, consequently, they 'buffer' the effect of pressure on the B–Cl bonds. Another possible reason for the minimal effect of pressure on the B–Cl stretching modes is the much smaller vibrational amplitudes of the B–Cl stretches compared to those of the B–H stretches.

The pressure dependences of the B–B stretching modes are comparable to those for the C–C stretching vibrations of many rigid caged hydrocarbons [7], although it should be mentioned that these B–B modes are probably mixed with the B–Cl vibrations. The symmetric B–B cage breathing mode (ν_2) assigned to the 305 cm^{-1} peak at ambient conditions has a par-

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*Author to whom correspondence should be addressed.

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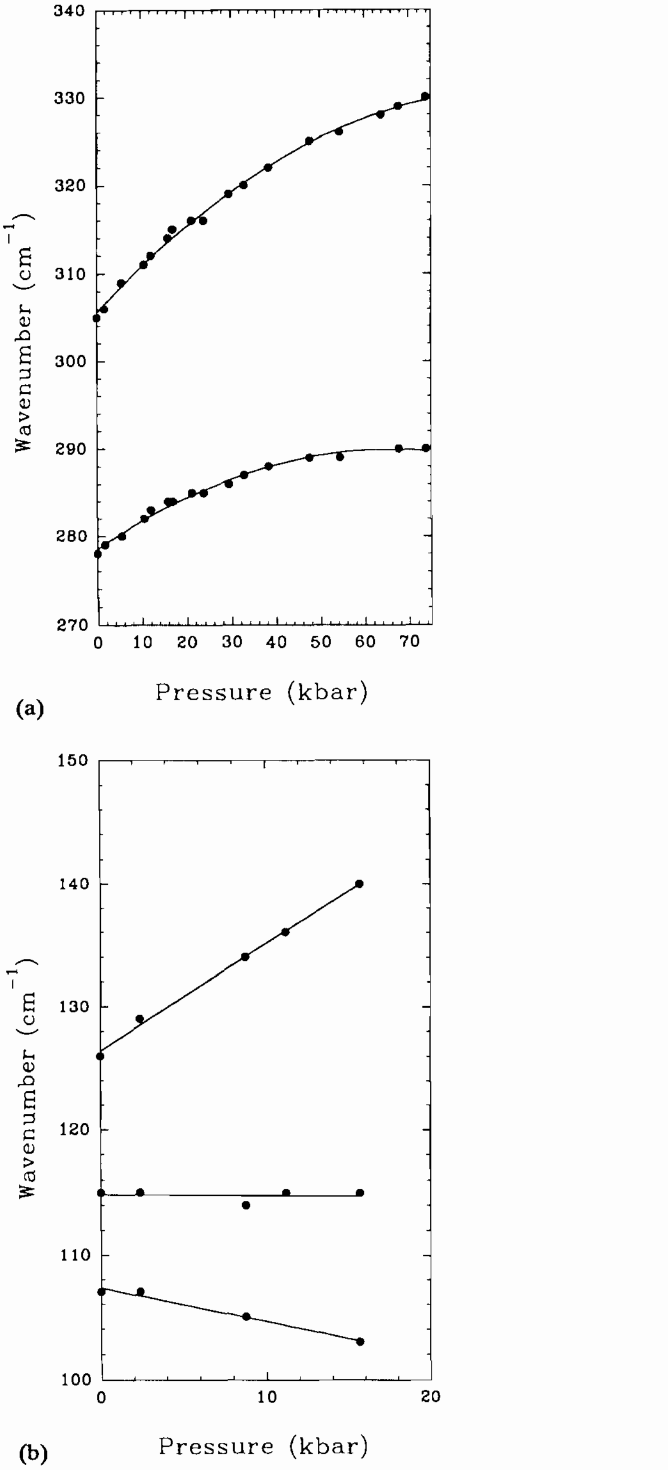

Fig. 2. Pressure dependences of the observed Raman modes of $Cs_2[B_{10}Cl_{10}]$.

TABLE 1. High-pressure vibrational data for $Cs_2[B_{10}Cl_{10}]$

ν (cm^{-1})	$d\nu/dP$ (cm^{-1}/kbar)	$d\ln\nu/dP$ (kbar$^{-1}\times10^4$)	Assignment[a]
1188	0.67	5.6	ν_1, B–Cl cage breath.
1160	0.58	5.0	
1006	0.60	6.0	ν_6, B–Cl str.
848	0.53	6.3	B–B str.
521	0.36	6.9	ν_4, B–B str., B–Cl bend.
305[b]	0.56[c]	18	ν_2, B–B cage breath.
278[d]	0.36[c]	13	ν_8, B–B str., B–Cl def.
126	0.87	69	B–B–B skeletal deformation
115	0.0	0.0	
107	−0.27	−25	

[a] From refs. 3, 5 and 8. [b] Fit of curve: $-0.0029P^2+0.54P+305$. [c] Initial slopes. [d] Fit of curve: $-0.0026P^2+0.35P+278$.

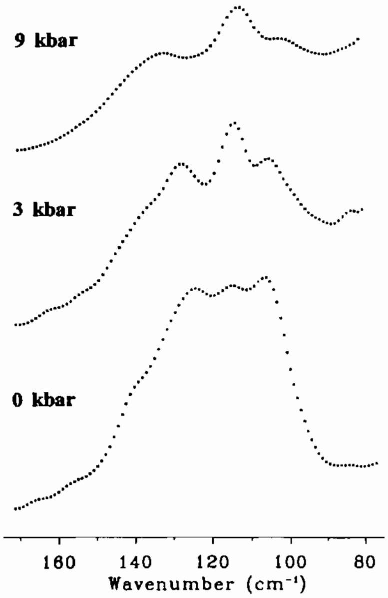

Fig. 3. Raman spectra of $Cs_2[B_{10}Cl_{10}]$ at selected pressures.

ticularly large $d\ln\nu/dP$ value presumably due to the large volume change involved.

The pressure behavior of the three main low-energy Raman bands, initially at 107, 115 and 126 cm^{-1}, is interesting. At ambient conditions, these three bands are extremely broad and overlapped with one other resulting in the ambient spectrum appearing as a very broad envelope. While continuing to remain broad at high pressure, the three bands are better resolved due to their different pressure sensitivities (Fig. 3). Based on the vibrational assignments for the related species $Cs_2[B_{12}Cl_{12}]$ [5,8], these three bands can be assigned as cage deformation modes. These skeletal deformation modes are expected to be quite sensitive to any geometrical or conformational changes since they involve entire cage movements. Many polyhedral boranes are known to undergo intramolecular rearrangement without breaking substituent-B bonds and a number of B_{10} derivatives rearrange in solution at high temperatures [6]. A possible mechanism has been put forward for this intramolecular rearrangement in which the intermediate is probably a distorted B_{10} polyhedron that results from the large amplitudes of the B–B–B deformation vibrations [6]. Although the barriers to the rearrangement of B_{10} polyhedrons are relatively high, the cage is probably not rigid and can be twisted under certain conditions. In the case of $Cs_2[B_{10}Cl_{10}]$, the broadness of these three deformation bands at ambient conditions implies that the cage skeleton of the $[B_{10}Cl_{10}{}^{2-}]$ anion undergoes large amplitude thermal motions. Therefore, the cage skeleton may indeed be distorted by application of external pressures. Under normal circumstances, these three modes should shift to higher energies since compression of the lattice should lead to a more densely packed structure and so to a higher barrier to motion.

The experimental observations were that the 126 cm^{-1} band did shift very quickly to higher energy, while the 115 cm^{-1} band was totally insensitive to pressure, and the 107 cm^{-1} peak moved to lower energy with increasing pressure (Fig. 2 and Table 1). Since no pressure-induced phase transition was observed, it is not possible that the pressure insensitivity of the 115 cm^{-1} band and the negative pressure dependence of the 107 cm^{-1} band are due to coupling with soft modes. These results indicate that the bicapped, square-antiprismatic structure might be gradually distorted by increasing external pressure because distortion of the cage would result in changes in the energies of the deformation modes. For instance, simple stretching of two boron–boron equatorial interactions would lead to some B–B–B angles increasing and other decreasing.

It is also worth mentioning that the ν–P plots of the two Raman bands located at 305 and 278 cm^{-1} begin curving after about 20 kbar. Since these bands mainly involve B–B cage stretching, especially the 305 cm^{-1} band (in-phase cage breathing mode), the non-linearity may be another indication that the $[B_{10}Cl_{10}]^{2-}$ cage is slightly distorted by pressure because the volume change caused by the cage breathing vibration in the distorted cage is smaller than that in the undistorted one.

Acknowledgements

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