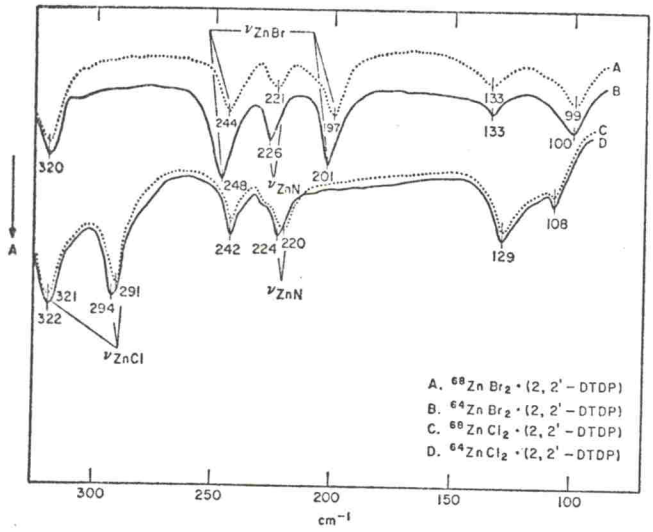

Fig. 1. Infrared spectra in the region 350–150 cm^{-1} for the isotopic $ZnCl_2 \cdot (2,2'\text{-DTDP})$ and $ZnBr_2 \cdot (2,2'\text{-DTDP})$ complexes.

For the $ZnCl_2 \cdot (2,2'\text{-DTDP})$ complex it may be observed that the absorption at 293 cm^{-1} is metal-sensitive and halogen-sensitive (disappears in $ZnBr_2 \cdot (2,2'\text{-DTDP})$). Therefore, the absorption must be associated with a zinc-chlorine stretching mode. Its frequency position is normal for a terminal zinc–chlorine stretching mode associated with a tetrahedral environment for the zinc atom [28–35]. The selection rules predict a symmetrical and an asymmetric vibration in molecules of this type. A second zinc–chlorine stretching vibration in complexes of this stereochemistry has been assigned in related complexes in the region of 310–330 cm^{-1}. A band was observed at 320 cm^{-1} in both the chloride and bromide complexes, and was found to be only slightly metal-sensitive. A ligand band was observed at 345 cm^{-1}, and thus the band at 320 cm^{-1} may involve both a ligand mode and the other zinc–chlorine stretching mode. The absorption at 222 cm^{-1} is metal-sensitive and halogen-insensitive. Thus, this band must involve the zinc–nitrogen stretching mode. Pressure sensitivities allow us to determine the nature of the two zinc–chlorine stretching modes. Under pressure, the absorption at 293 cm^{-1} shows a significant decrease in peak intensity relative to the band at 320 cm^{-1}. From previous high-pressure studies we have determined that the symmetrical metal–halogen stretching vibration is more

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