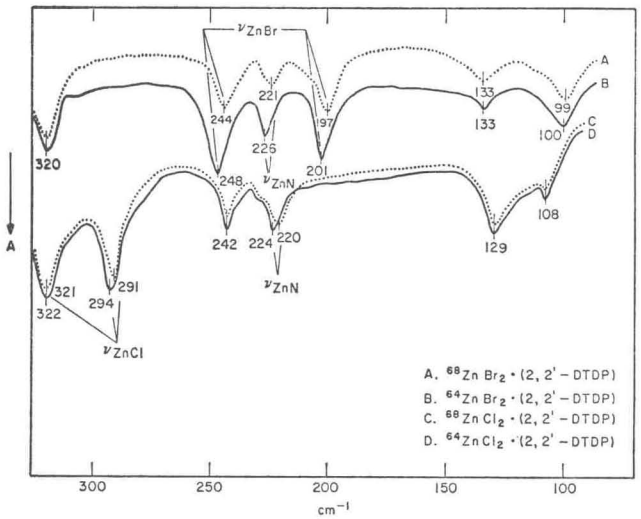

Fig. 1. Infrared spectra in the region 350–150 cm^{-1} for the isotopic $ZnCl_2$ · (2,2′-DTDP) and $ZnBr_2$ · (2,2′-DTDP) complexes.

For the $ZnCl_2$·(2,2′-DTDP) complex it may be observed that the absorption at 293 cm^{-1} is metal-sensitive and halogen-sensitive (disappears in $ZnBr_2$·(2,2′-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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pressure-sensitive to a lowering of peak intensity than the asymmetric metal–halogen stretching mode [36]. Therefore, to assign the 293 cm^{-1} band as the $\nu_{ZnCl_{sym}}$ mode is reasonable. The band at 222 cm^{-1} is not significantly changed with pressure. The absorption at 108 cm^{-1} in the chloride may be associated with a lattice mode, since it is found at lower frequency in the bromides. Band assignments for $ZnCl_2$·(2,2′-DTDP) are shown in Table 1.

For the $ZnBr_2$·(2,2′-DTDP) complex the absorptions at 247 and 200 cm^{-1} are metal-sensitive and halogen-sensitive (disappearing in ZnI_2·(2,2′-DTDP(indicating that the absorptions are associated with zinc-bromine stretching modes. The frequency positions are normal for terminal zinc–bromine stretching vibrations associated with a tetrahedral environment for the zinc atom [28–34]. The 223 cm^{-1} vibration is metal-sensitive and halogen-insensitive, and probably is the metal–nitrogen stretching vibration. Pressure studies show that the 200 cm^{-1} band decreases in peak intensity with pressure relative to the 247 cm^{-1} band, and must be the $\nu_{ZnBr_{sym}}$ vibration. The 223 cm^{-1} absorption is slightly affected by pressure. Table 2 includes the assignments for $ZnBr_2$·(2,2′-DTDP).

B. *Raman studies.* Raman scattering spectra of the 2,2′-DTDP complexes, obtained from pellets of powders, demonstrated a high degree of coincidences with infrared frequency positions, eliminating any possible centrosymmetric configuration for the complexes (see Table 3). The Raman bands were observed to be not as sensitive to metal isotopic shifts as were the i.r. absorptions.

III. *Complexes with* 4,4′-DTDP

A. *Infrared studies.* The mid-i.r. studies from 4000–650 cm^{-1} gave results very similar to those obtained for 2,2′-DTDP, indicating that bonding occurred to the nitrogen atom of the ligand. Figure 2 shows the spectra of the isotopic zinc halide complexes from 325 to 100 cm^{-1}. Tables 4 and 5 record the low-frequency data for

Table 3. Observed Raman frequencies for various DTDP complexes

		$\Delta\nu(cm^{-1})$ (550–80)	
$^{NA}ZnCl_2$ · (2,2′-DTDP)	$^{NA}ZnBr_2$ · (2,2′-DTDP)	$^{NA}ZnCl_2$ · (4,4′-DTDP)	$^{NA}ZnBr_2$ · (4,4′-DTDP)
528(m)	526(s)	548(m)	546(s)
486(vw)	497(w)		505(vw)
	488(m)		493(vw)
430(m)	431(m)	465(vvw)	466(m)
291(m)	320(m)	440(m)	446(w)
240(w)	237(m)		385(vw)
226(w)	226(m)		363(vw)
	199(s)	300(vs)	299(vw)
	171(m)		285(m)
161(w)	155(m)	255(w)	255(m)
130(w)	127(s)	235(w)	230(vw)
118(sh)	118(m)	205(m)	215(m)
101(w)	101(m)	197(vw)	190(s)
85(vw)	91(m)		162(w)
	79(w)	146(vw)	137(sh)
		112(m)	

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