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 $ZnCl_2 \cdot (2,2'\text{-DTDP})$ are shown in Table 1.

For the $ZnBr_2 \cdot (2,2'\text{-DTDP})$ complex the absorptions at 247 and 200 cm^{-1} are metal-sensitive and halogen-sensitive (disappearing in $ZnI_2 \cdot (2,2'\text{-DTDP}($ 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 $ZnBr_2 \cdot (2,2'\text{-DTDP})$.

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)

$^{NA}ZnCl_2 \cdot (2,2'\text{-DTDP})$	$^{NA}ZnBr_2 \cdot (2,2'\text{-DTDP})$	$^{NA}ZnCl_2 \cdot (4,4'\text{-DTDP})$	$^{NA}ZnBr_2 \cdot (4,4'\text{-DTDP})$
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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