



Fig. 2. Infrared spectra in the region 350–150  $\text{cm}^{-1}$  for the isotopic  $\text{ZnCl}_2 \cdot (4,4'\text{-DTDP})$  and  $\text{ZnBr}_2 \cdot (4,4'\text{-DTDP})$  complexes.

Table 4. Observed frequencies ( $\text{cm}^{-1}$ ), isotopic shifts, and band assignments for  $\text{ZnCl}_2 \cdot (4,4'\text{-DTDP})$

4,4'-DTDP	$^{64}\text{ZnCl}_2 \cdot (4,4'\text{-DTDP})$	$^{64}\text{ZnCl}_2 \cdot (4,4'\text{-DTDP})$	$^{68}\text{ZnCl}_2 \cdot (4,4'\text{-DTDP})$	$\bar{\nu}(^{64}\text{Zn}) - \bar{\nu}(^{68}\text{Zn})$	Assignments
533(s, sp)	551(vvw)	549	549	0	Ligand and ligand induced
500(sh)	499(s, sp)	498	498	0	
488(s, sp)	486(s, sp)	485	486	-1	
438(m)	446(w)	445	445	0	
414(m)	409(vvw)	409	409	0	
379(w)	363(vw)	363	363	0	
343(vw)	341(s)	340	335	5	
281(vvw)	299(s)	299	296	3	$\nu\text{ZnCl}_{\text{sym}}$
	256(m)	256	256	0	Ligand induced
	235(w)	234	234	0	
		227	227	0	
183(vvw)	213(m)	213	211	2	$\nu\text{Zn-N}$
	199(vvw)	198	198	0	Ligand
	170(m)	170	168	2	
	154(vvw, br)				
	113(m)	114	112	2	Lattice

Abbreviations: s = strong; sp = sharp; m = medium; w = weak; v = very; sh = shoulder; br = broad.

4,4' DTDP,  $^{64}\text{ZnCl}_2 \cdot (4,4'\text{-DTDP})$ ,  $^{64}\text{ZnBr}_2 \cdot (4,4'\text{-DTDP})$ , and for the zinc complexes containing the zinc isotopes of mass 64 and 68.

For the  $\text{ZnCl}_2 \cdot (4,4'\text{-DTDP})$  complex it was observed that the 341 and 299  $\text{cm}^{-1}$  absorptions are metal and halogen sensitive. For the  $\text{ZnBr}_2 \cdot (4,4'\text{-DTDP})$  complex the 264  $\text{cm}^{-1}$  absorption is also metal- and halogen-sensitive. Thus, these bands may be assigned as metal-halogen stretching vibrations. These vibrations occur in a region normal for terminal zinc-halogen stretching modes associated with a tetrahedral environment for the zinc atom [28]. The band at  $\sim 212 \text{ cm}^{-1}$  in both the chloride and bromide is sensitive only to metal and may be assigned as the metal-nitrogen stretching vibration.

Table 5. Observed frequencies ( $\text{cm}^{-1}$ ), isotopic shifts, and band assignments for  $\text{ZnBr}_2 \cdot (4,4'\text{-DTDP})$ 

4,4'-DTDP	$^{64}\text{ZnBr}_2 \cdot (4,4'\text{-DTDP})$	$^{64}\text{ZnBr}_2 \cdot (4,4'\text{-DTDP})$	$^{68}\text{ZnBr}_2 \cdot (4,4'\text{-DTDP})$	$\bar{\nu}(^{64}\text{Zn}) - \bar{\nu}(^{68}\text{Zn})$	Assignments	
533(s, sp)	550(vw)	547	547	0	Ligand and ligand induced	
500(sp)	499(s, sp)	498	497	1		
488(s, sp)	486(s, sp)	484	484	0		
438(m)	446(m)	445	445	0		
414(m)	409(vw)	409	409	0		
379(w)	389(vvw)	386	386	0		
343(vw)	363(vw)	363	363	0		
281(vvw)		284	284	0		
	264(s)	267	261	6		$\nu\text{ZnBr}$
		261(sh)				
	233(vvw)	233	233	0	Ligand induced	
	212(s)	212	210	2	$\nu\text{ZnN}$	
183(vvw)	192(vvw)	192	192	0	Ligand	
	167(m)	168	166	2		
	103(w, br)	104	104	0	Lattice	
	92(w, br)	92	92	0		

Abbreviations: s = strong; sp = sharp; m = medium; w = weak; v = very; sh = shoulder; br = broad.

The observed i.r. frequencies for the  $^{64}\text{ZnI}_2(4,4'\text{-DTDP})$  complex from 650–80  $\text{cm}^{-1}$  are 548(vvw), 498(s, sp), 485(s, sp), 446(m), 408(vvw), 385(vvw), 362(vvw), 282(vvw), 261(vvw), 243(m), 223(m), 204(m), 173(m), 163(w), 104(vvw). No band assignments were made for this compound since no isotopic studies were conducted for it.

High-pressure studies of the 341 and 299  $\text{cm}^{-1}$  bands in the chloride indicate that the 299  $\text{cm}^{-1}$  band is more intensity sensitive to pressure than the 341  $\text{cm}^{-1}$  band, and is the most intense of the Raman bands, and therefore, may be assigned as the  $\nu_{\text{ZnCl}_2\text{sym}}$  mode. The mode at 113  $\text{cm}^{-1}$  in the chloride shifts to lower frequency in the bromide and may be assigned as a lattice mode. Other assignments are listed in Tables 3 and 4.

**B. Raman studies.** Raman scattering spectra of the 4,4'-DTDP complexes, obtained from pellets of powders, showed a lack of coincidence with infrared frequency position indicating a possible centrosymmetric configuration existing for the complexes (see Table 3).

### III. Stereochemistry of complexes

The spectroscopic results indicate a high degree of asymmetry in the 2,2'-DTDP complexes. The local environment around the central zinc atom is tetrahedral, as indicated by the position of the zinc-halogen stretching vibrations. Only nitrogen atoms of the ligand are involved in the bonding to zinc. Since one ligand molecule is coordinated per molecule of zinc halide, the ligand could be bidentate (2 nitrogen atoms of a ligand molecule linked to a zinc atom), but this would involve a strained, seven-membered ring which is unlikely. Additionally, such a structure is monomeric and would confer a higher degree of solubility on the complex than is observed. A twisted, polymeric structure of bridging 2,2'-DTDP molecules, held together by zinc halide molecules, is plausible.

The 4,4'-DTDP complexes appear to demonstrate a lack of coincidences between i.r. and Raman frequencies, and thus the complexes are judged to possess a higher degree of symmetry than the 2,2'-DTDP complexes. The local symmetry is tetrahedral and is determined from the far i.r. data. The stoichiometry involves one ligand molecule per molecule of zinc halide, and a linear, polymeric structure involving bridged 4,4'-DTDP molecules, held together by zinc halide molecules, is plausible.