the compound containing the metal in natural abundance to determine if the complex had formed.

B. *Materials*

The natural abundance zinc halide hydrates used were C.P. grade. The isotopes were obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee, in the form of oxide. The ligands were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

C. *Analyses*

The analyses for carbon, nitrogen, and hydrogen were made at Argonne National Laboratory, using micro-analytical techniques. The elemental analysis follow: Anal. Calc. for ($ZnCl_2$·2,2′-DTDP) or ($ZnCl_2$·4,4′-DTDP): C, 33.68%; N, 7.86%; H, 2.26%; S, 17.96%. Found for ($ZnCl_2$·2,2′-DTDP): C, 33.60%; N, 7.81%; H, 2,18%; Found for ($ZnCl_2$·4,4′-DTDP): C, 33.85%; N, 7.83%; H, 2.24%; Calc. for ($ZnBr_2$·2,2′-DTDP) or ($ZnBr_2$·4,4′-DTDP): C, 26·95%; N, 6.29%; H, 1.80%; S, 14.38%; Found for ($ZnBr_2$·2,2′-DTDP): C, 26.89%; N, 6.26%; H, 1.82%; S, 14.23%; Found for ($ZnBr_2$·4,4′-DTDP): C, 27·22%; N, 6·33%; H, 1.85%; S, 14.44%. Calc. for (ZnI_2·2,2′-DTDP) or (ZnI_2·4,4′-DTDP): C, 22.26%; N, 5.19%; H, 1.48%. Found for (ZnI_2·2,2′-DTDP): C, 22.10%; N, 4.97%; H, 1.46%; Found for ZnI_2·4,4′-DTDP: C, 22·48%; N, 4.92%; H, 1·54%.

D. *Infrared and Raman measurements*

Infrared measurements from 4000–650 cm^{-1} were made with KBr disks of the solids using a Beckman IR-12. Measurements in the region from 650–80 cm^{-1} were obtained with a Beckman IR-11 or a Perkin–Elmer Model No. 301, using polyethylene disks. High-pressure measurements in the far i.r. (up to ~24 kbar), were obtained with an opposed diamond-anvil cell using the Model 301 equipped with a 6× beam condenser. The techniques used and the method of pressure calibration have been previously reported [23, 24]. The Raman spectra were obtained on the powdered solids using a Cary 81 spectrophotometer with a helium–neon laser.

Results and Discussion

I. *Complexes with* 2,2′-DTDP

A. *Infrared studies.* The mid-i.r. spectra from 4000–650 cm^{-1} confirmed the analytical results showing no water absorptions in the complexes. The carbon–nitrogen ring vibration at about ~1570 cm^{-1} in 2,2′-DTDP shifted toward higher frequencies in the complexes, and the results were indicative of bonding occurring to the nitrogen atom of the ligand [25, 26]. Little change occurred in the C—S stretching

[23] J. R. Ferraro, S. S. Mitra and C. Postmus, *Inorg. Nucl. Chem. Letters* **2,** 269 (1966); **4,** 55 (1968).
[24] L. J. Basile, C. Postmus and J. R. Ferraro, *Spectry Letters* **1,** 189 (1968).
[25] J. R. Ferraro, J. Zipper and W. Wozniak, *Appl. Spectry* **23,** 160 (1969).
[26] J. R. Ferraro and K. C. Davis, *Inorg. Chim. Acta* **3,** 685 (1969).

vibration region at 700–800 cm^{-1} from the uncomplexed ligand, indicating that no bonding occurred to the sulfur atom [27].

Tables 1 and 2 tabulate the low-frequency absorptions for 2,2′-DTDP, $^{NA}ZnCl_2$·(2,2′-DTDP), $^{NA}ZnBr_2$·(2,2′-DTDP), and for the zinc complexes containing the zinc isotopes of mass 64 and 68. Figure 1 depicts the spectra of isotopic zinc halide complexes from 325–100 cm^{-1}.

Table 1. Observed frequencies (cm^{-1}), isotopic shifts, and band assignments for $ZnCl_2$ · (2,2′-DTDP)

2,2′-DTDP	$^{NA}ZnCl_2$·(2,2′-DTDP)	$^{64}ZnCl_2$·(2,2′-DTDP)	$^{68}ZnCl_2$·(2,2′-DTDP)	$\tilde{\nu}(^{64}Zn) - \tilde{\nu}(^{68}Zn)$	Assignments
	648(m, sp)	648	648	0	Ligand and ligand induced
	648(m, sp)	641	641	0	
622(s, p)					
	499(m, sp)	500	501	−1	
	487(m, sp)	488	487	1	
471(m, sp)					
429(m, sp)	429(m, sp)	429	429	0	
	417(s, sp)	417	417	0	
402(sh)					
345(s, sp)	345(w)				
	321(vs)	322	321	1	$\nu Zn—Cl_{asym}$ + ligand
	293(vs)	294	291	3	$\nu Zn—Cl_{sym}$
254(vvw)					
	242(m)	242	242	0	Ligand
	231(m)	231	231	0	
	222(m)	224	220	4	$\nu Zn—N$
158(w)	158(m)			—	Ligand, $\delta Zn—Cl$ and lattice vibrations
	130(s), 121(sh)	130	129	1	
	108(m)	108	108	0	

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

Table 2. Observed frequencies (cm^{-1}), isotopic shifts, and band assignments for $ZnBr_2$ · (2,2′-DTDP)

2,2′-DTDP	$^{NA}ZnBr_2$·(2,2′-DTDP)*	$^{64}ZnBr_2$·(2,2′-DTDP)	$^{68}ZnBr_2$·(2,2′-DTDP)	$\tilde{\nu}(^{64}Zn) - \tilde{\nu}(^{68}Zn)$	Assignments
	646(m, sp)	646	646	0	Ligand and ligand induced
	639(m, sp)				
622(s, sp)					
	499(m, sp)	501	500	1	
	486(m, sp)	488	488	0	
471(m, sp)					
429(m, sp)	429(m, sp)	429	429	0	
	417(s, sp)	418	417	1	
402(sh), 345(s, sp)					
	320(m)	320	320	0	
254(vvw)					
	247(vs)	248	244	4	$\nu ZnBr_{asym}$
	223(s)	226	221	5	$\nu Zn—N$
	200(s)	201	197	4	$\nu Zn—Br_{sym}$
158(w)	152(vw)	—	—	—	Ligand and lattice vibrations
	133(vw), 120(vw)	133	133	0	
	113(vw)	—	—		
	98(m)	100	99	1	

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

* The observed i.r. frequencies for the $^{NA}ZnI_2$(2,2′-DTDP) complex from 650–80 cm^{-1} are 648(m), 528(vvw), 487(s, sp), 438(w), 433(w), 421(s, sp), 417(s, sp), 348(w), 314(s), 240(m), 231(m), 213(m), 194(s), 185(s), 162(m), 140(vw), 115(vvw), 100(vvw), 84(m). No band assignments were made for this compound since no isotopic studies were conducted for it.

[27] P. C. H. MITCHELL and R. J. P. WILLIAMS, *J. Chem. Soc.* 1912 (1960).