Metal–isotopic substitution and high-pressure studies of zinc halide complexes of dithiodipyridine*

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Abstract—New zinc halide complexes of dithiodipyridine were prepared and investigated by spectroscopic techniques. Band assignments in the far-i.r. region were made utilizing sensitivity techniques. By noting the sensitivity to cation-isotopic changes, anion changes, and pressure effects, assignments of metal–ligand vibrations were possible. From these assignments, structural inferences relative to these complexes were made.

INTRODUCTION

DITHIODIPYRIDINE (DTDP) exists in two isomers, 2,2′-dithiodipyridine (2,2′-DTDP) and 4,4′-dithiodipyridine (4,4′-DTDP). The structure of these isomers is illustrated as follows:
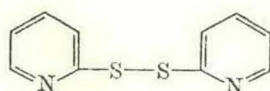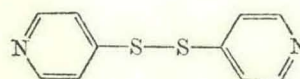
2,2′–dithiodipyridine   4,4′–dithiodipyridine

Recently, the use of these compounds as complexing agents for transition metals has been demonstrated [1]. These ligands have two nitrogen and two sulfur atoms, all possible ligand atom sites for complexation. Since zinc(II) tends to form complexes in which bonding is to the sulfur atoms rather than the nitrogen atoms [2–10], it was of interest to determine its behavior with dithiodipyridine. Thus, the zinc halide complexes of 2,2′-DTDP and 4,4′-DTDP have been prepared for the first time. These

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complexes were studied by i.r. and Raman techniques. By the use of the high-pressure technique and by metal–isotopic substitution, it was possible to make assignments for the metal–ligand vibrations in these molecules, and to draw some structural inferences for the complexes. The nature of these complexes (high degree of insolubility in common solvents, amorphous powders) precluded using other structural tools.

The use of high-pressure techniques for the study of inorganic and coordination compounds in the far-i.r. region has recently been explored. Such studies have helped in assigning metal–ligand vibrations. Several reviews have been written on the subject [11–15]. The availability of stable metal isotopes has added an additional technique to study the metal–ligand vibrations [16–22]. The combination of the two techniques constitutes a powerful tool in making more definitive assignments for the metal–ligand vibrations in coordination compounds. Such a combination of techniques was utilized in the present study.

EXPERIMENTAL METHOD

A. *Preparation*

The complexes containing natural abundance zinc were prepared by dissolving 1 mole of the zinc halide in warm 95% ethanol, and slowly adding with stirring to a warm ethanol solution containing 1 mole of the ligand. For the 2,2′-dithiodipyridine complexes, a precipitate formed slowly with stirring, while for the 4,4′-dithiopyridine complexes precipitates formed immediately. The solids were filtered, washed with ethanol and dried by suction, and were obtained as white to creamy powders. The 2,2′-DTDP complexes were somewhat soluble in ethanol, while the 4,4′-DTDP complexes were insoluble in most common solvents.

The complexes containing the zinc isotopes were prepared similarly. However, since the zinc isotopes of mass 64 and 68 were obtained as the zinc oxide, it was necessary to convert them to the halides using hydrochloric and hydrobromic acid. The syntheses of the complexes containing these isotopes were made on a mg scale. The i.r. spectrum of the compound containing the metal isotope was compared with

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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 $(ZnCl_2 \cdot 2,2'\text{-DTDP})$ or $(ZnCl_2 \cdot 4,4'\text{-DTDP})$: C, 33.68%; N, 7.86%; H, 2.26%; S, 17.96%. Found for $(ZnCl_2 \cdot 2,2'\text{-DTDP})$: C, 33.60%; N, 7.81%; H, 2,18%; Found for $(ZnCl_2 \cdot 4,4'\text{-DTDP})$: C, 33.85%; N, 7.83%; H, 2.24%; Calc. for $(ZnBr_2 \cdot 2,2'\text{-DTDP})$ or $(ZnBr_2 \cdot 4,4'\text{-DTDP})$: C, 26.95%; N, 6.29%; H, 1.80%; S, 14.38%; Found for $(ZnBr_2 \cdot 2,2'\text{-DTDP})$: C, 26.89%; N, 6.26%; H, 1.82%; S, 14.23%; Found for $(ZnBr_2 \cdot 4,4'\text{-DTDP})$: C, 27.22%; N, 6.33%; H, 1.85%; S, 14.44%. Calc. for $(ZnI_2 \cdot 2,2'\text{-DTDP})$ or $(ZnI_2 \cdot 4,4'\text{-DTDP})$: C, 22.26%; N, 5.19%; H, 1.48%. Found for $(ZnI_2 \cdot 2,2'\text{-DTDP})$: C, 22.10%; N, 4.97%; H, 1.46%; Found for $ZnI_2 \cdot 4,4'\text{-DTDP}$: 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 $6 \times$ 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

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

2,2'-DTDP	$^{NA}ZnCl_2 \cdot (2,2'$-DTDP)	$^{64}ZnCl_2 \cdot (2,2'$-DTDP)	$^{68}ZnCl_2 \cdot (2,2'$-DTDP)	$\tilde{\nu}(^{64}Zn) - \tilde{\nu}(^{68}Zn)$	Assignments
	648(m, sp)	648	648	0	
	648(m, sp)	641	641	0	
622(s, p)					
	499(m, sp)	500	501	−1	Ligand and ligand
	487(m, sp)	488	487	1	induced
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}	νZn—Cl$_{asym}$ + ligand
	293(vs)	294	291	3	νZn—Cl$_{sym}$
254(vvw)					
	242(m)	242	242	0}	Ligand
	231(m)	231	231	0	
	222(m)	224	220	4	νZn—N
158(w)	158(m)	—	—	—	Ligand, δZn—Cl and
	130(s), 121(sh)	130	129	1	lattice vibrations
	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 $ZnBr_2 \cdot (2,2'$-DTDP)

2,2'-DTDP	$^{NA}ZnBr_2 \cdot (2,2'$-DTDP)*	$^{64}ZnBr_2 \cdot (2,2'$-DTDP)	$^{68}ZnBr_2 \cdot (2,2'$-DTDP)	$\tilde{\nu}(^{64}Zn) - \tilde{\nu}(^{68}Zn)$	Assignments
	646(m, sp)	646	646	0	
	639(m, sp)				
622(s, sp)					
	499(m, sp)	501	500	1	
	486(m, sp)	488	488	0	Ligand and ligand
471(m, sp)					induced
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	νZnBr$_{asym}$
	223(s)	226	221	5	νZn—N
	200(s)	201	197	4	νZn—Br$_{sym}$
158(w)	152(vw)	—	—	—	
	133(vw), 120(vw)	133	133	0	Ligand and lattice
	113(vw)	—	—	—	vibrations
	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.

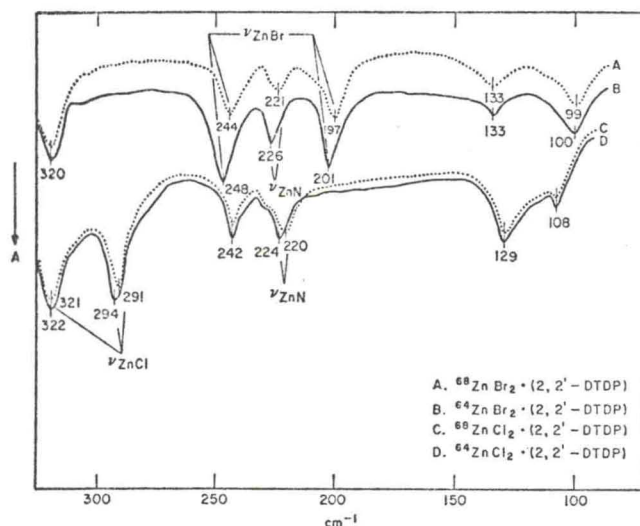[27] P. C. H. MITCHELL and R. J. P. WILLIAMS, *J. Chem. Soc.* 1912 (1960).

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· 2,2'-DTDP,
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isotopic zinc

nCl$_2$ · (2,2'-DTDP)

Assignments

Ligand and ligand
induced

νZn—Cl$_{asym}$ + ligand
νZn—Cl$_{sym}$

Ligand
νZn—N

Ligand, δZn—Cl and
lattice vibrations

Br$_2$ · (2,2'-DTDP)

Assignments

Ligand and ligand
induced

νZnBr$_{asym}$
νZn—N
νZn—Br$_{sym}$

Ligand and lattice
vibrations

vw), 487(s, sp), 438(w),
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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 $ZnCl_2 \cdot (2,2'\text{-DTDP})$ 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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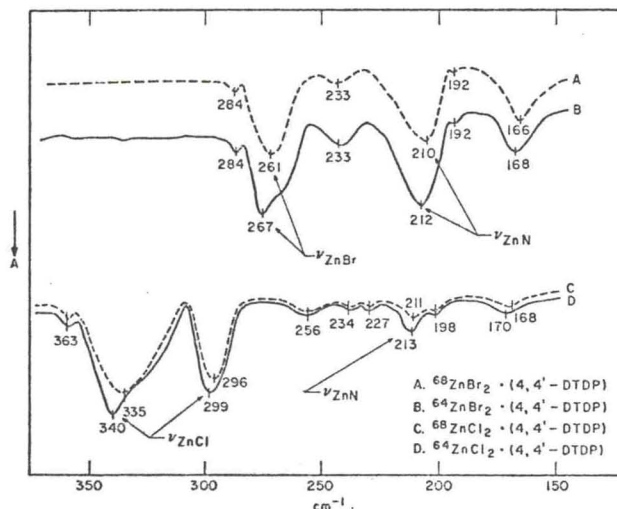
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$r_2 \cdot$ (4,4'-DTDP)

546(s)
505(vw)
493(vw)
466(m)
446(w)
385(vw)
363(vw)
299(vw)
285(m)
255(m)
230(vw)
215(m)
190(s)
162(w)
137(sh)

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

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

4,4'-DTDP	^{NA}ZnCl$_2$·(4,4'-DTDP)	^{64}ZnCl$_2$·(4,4'-DTDP)	^{68}ZnCl$_2$·(4,4'-DTDP)	$\bar{\nu}(^{64}$Zn$) - \bar{\nu}(^{68}$Zn$)$	Assignments
533(s, sp)	551(vvw)	549	549	0	
		536	—	—	
500(sh)	499(s, sp)	498	498	0	Ligand and ligand
488(s, sp)	486(s, sp)	485	486	−1	induced
438(m)	446(x)	445	445	0	
414(m)	409(vvw)	409	409	0	
379(w)	363(vw)	363	363	0	
343(vw)	341(s)	340	335	5	νZnCl$_{asym}$
281(vvw)	299(s)	299	296	3	νZnCl$_{sym}$
	256(m)	256	256	0	
	235(w)	234	234	0	Ligand induced
		227	227	0	
183(vvw)	213(m)	213	211	2	νZn—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, ^{NA}ZnCl$_2$·(4,4'-DTDP), ^{NA}ZnBr$_2$·(4,4' DTDP), and for the zinc complexes containing the zinc isotopes of mass 64 and 68.

For the ZnCl$_2$·(4,4'-DTDP) complex it was observed that the 341 and 299 cm^{-1} absorptions are metal and halogen sensitive. For the ZnBr$_2$·(4,4'-DTDP) complex the 264 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 ~212 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 (cm^{-1}), isotopic shifts, and band assignments for $ZnBr_2 \cdot (4,4'\text{-DTDP})$

4,4'-DTDP	$^{NA}ZnBr_2 \cdot (4,4'\text{-DTDP})$	$^{64}ZnBr_2 \cdot (4,4'\text{-DTDP})$	$^{68}ZnBr_2 \cdot (4,4'\text{-DTDP})$	$\tilde{\nu}(^{64}Zn) - \tilde{\nu}(^{68}Zn)$	Assignments
533(s, sp)	550(vw)	547	547	0	
500(sp)	499(s, sp)	498	497	1	
488(s, sp)	486(s, sp)	484	484	0	
438(m)	446(m)	445	445	0	Ligand and ligand
414(m)	409(vw)	409	409	0	induced
370(w)	389(vvw)	386	386	0	
343(vw)	363(vw)	363	363	0	
281(vvw)		284	284	0	
	264(s)	267	261	6	$\nu ZnBr$
		261(sh)			
	233(vvw)	233	233	0	Ligand induced
	212(s)	212	210	2	νZnN
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 $^{NA}ZnI_2(4,4'\text{-DTDP})$ complex from 650–80 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 cm^{-1} bands in the chloride indicate that the 299 cm^{-1} band is more intensity sensitive to pressure than the 341 cm^{-1} band, and is the most intense of the Raman bands, and therefore, may be assigned as the $\nu_{ZnCl_{sym}}$ mode. The mode at 113 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.