cating that no

2,2'-DTDP, res containing isotopic zinc

nCl2 · (2,2'-DTDP)

Assignments

Ligand and ligand induced

 ν Zn—Clasym + ligand ν Zn—Cl_{sym}

Ligand vZn—N Ligand, δZn —Cl and lattice vibrations

Br₂ · (2,2'-DTDP)

Assignments

Ligand and ligand

vZnBr_{asym} vZn—N vZn—Br_{sym}

Ligand and lattice

vw), 487(s, sp), 438(w),), 115(vvw), 100(vvw),

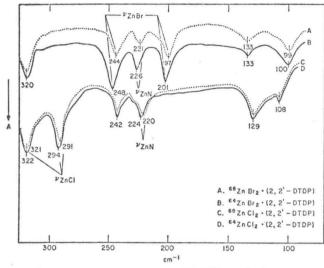


Fig. 1. Infrared spectra in the region $350-150 \, \mathrm{cm^{-1}}$ for the isotopic $\mathrm{ZnCl_2} \cdot (2,2'\text{-DTDP})$ and $\mathrm{ZnBr_2} \cdot (2,2'\text{-DTDP})$ complexes.

For the ZnCl₂·(2,2'-DTDP) complex it may be observed that the absorption at 293 cm⁻¹ is metal-sensitive and halogen-sensitive (disappears in ZnBr₀·(2,2'-DTDP)). Therefore, the absorption must be associated with a zinc-chlorine stretching mode. Its frequency position is normal for a terminal zine-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 halogeninsensitive. 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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