High-pressure studies of zinc halido complexes of dithiodipyridine

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 $(ZnCl_2 \cdot 2, 2' \cdot DTDP)$ or $(ZnCl_2 \cdot 4, 4' \cdot DTDP)$: C, 33.68%; N, 7.86%; H, 2.26%; S, 17.96%. Found for $(ZnCl_2 \cdot 2, 2' \cdot DTDP)$: C, 33.60%; N, 7.81%; H, 2,18%; Found for $(ZnCl_2 \cdot 4, 4' \cdot DTDP)$: C, 33.85%; N, 7.83%; H, 2.24%; Calc. for $(ZnBr_2 \cdot 2, 2' - DTDP)$ or $(ZnBr_2 \cdot 4, 4' - DTDP)$: C, 26.95%; N, 6.29%; H, 1.80%; S, 14.38%; Found for $(ZnBr_2 \cdot 4, 4' - DTDP)$: C, 26.89%; N, 6.26%; H, 1.82%; S, 14.23%; Found for $(ZnBr_2 \cdot 4, 4' - DTDP)$: C, 27.22%; N, 6.33%; H, 1.85%; S, 14.44%. Calc. for $(ZnI_2 \cdot 2, 2' - DTDP)$ or $(ZnI_2 \cdot 4, 4' - DTDP)$: C, 22.26%; N, 5.19%; H, 1.48%. Found for $(ZnI_2 \cdot 2, 2' - DTDP)$: C, 22.10%; N, 4.97%; H, 1.46%; Found for $ZnI_2 \cdot 4, 4' - DTDP$: 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 $6 \times$ 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 $4000-650 \text{ cm}^{-1}$ confirmed the analytical results showing no water absorptions in the complexes. The carbonnitrogen 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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