

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'-dithiodipyridine 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

- [11] J. R. FERRARO, *Anal. Chem.* **40**, 24A (1968).
- [12] J. R. FERRARO, in: *Modern Classics in Analytical Chemistry* (Edited by A. L. BELBY). Am. Chem. Soc., Washington, D.C. (1970).
- [13] J. R. FERRARO, in: *Far Infrared Properties of Solids* (Edited by S. S. MITRA and S. NUDELMAN). Plenum, New York (1970).
- [14] J. R. FERRARO, in: *Spectroscopy in Inorganic Chemistry*, Vol. II (Edited by C. N. R. RAO and J. R. FERRARO). Academic Press, New York (1971).
- [15] J. R. FERRARO, *Low Frequency Vibrations in Inorganic and Coordination Compounds*. Plenum, New York (1971).
- [16] K. NAKAMOTO, K. SHOBATAKE and B. HUTCHINSON, *Chem. Commun.* 1451 (1969).
- [17] P. TARTE and J. PREUDHOMME, *Spectrochim. Acta* **26A**, 2207 (1970).
- [18] K. SHOBATAKE and K. NAKAMOTO, *J. Am. Chem. Soc.* **92**, 3332, 3339 (1970).
- [19] B. HUTCHINSON, J. TAKEMOTO and K. NAKAMOTO, *J. Am. Chem. Soc.* **92**, 3335 (1970).
- [20] J. T. WANG, C. UDOVICH, K. NAKAMOTO, A. QUATTROCHI and J. R. FERRARO, *Inorg. Chem.* **9**, 2675 (1970).
- [21] J. R. FERRARO, K. NAKAMOTO, C. UDOVICH and A. QUATTROCHI, *Appl. Spectry* **24**, 606 (1970).
- [22] N. OHKAKU and K. NAKAMOTO, *Inorg. Chem.* **10**, 798 (1971).