Spectrochimica Acta, Vol. 28A, pp. 817 to 824, Pergamon Press 1972. Printed in Northern Ireland

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

JOHN R. FERRARO,[†] B. MURRAY, A. QUATTROCHI[‡] and C. A. LUCHETTI§ Argonne National Laboratory, Argonne, Illinois 60439

(Received 18 June 1971)

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



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

1 Present address: U.S. Tobacco Co., 4325 N. Fifth, Chicago, Illinois.

§ CSUI Honors Program Student from Emmanuel College, Boston, Massachusetts, Fall 1970.

817

^{*} Based on work performed under the auspices of the U.S. Atomic Energy Commission.

^{*} Person to whom correspondence should be addressed.

J. R. FERRARO, B. B. MURRAY and N. J. WIECKOWICZ, J. Inorg. Nucl. Chem., to be published.

^[2] R. B. PENLAND, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, J. Am. Chem. Soc. 79, 1575 (1957).

^[3] A. YAMAGUCHI, R. B. PENLAND, S. MIZUSHIMA, T. J. LANE, C. CURRAN and J. V. QUAGLIANO, J. Am. Chem. Soc. 80, 527 (1958).

^[4] R. A. BAILEY and T. R. PETERSON, Can. J. Chem. 45, 1135 (1967).

^[5] K. SWAMINATHAN and H. M. N. H. IRVING, J. Inorg. Nucl. Chem. 26, 1291 (1964).

^[6] C. D. FLINT and M. GOODGAME, J. Chem. Soc. A 744 (1966).

^[7] P. J. HENDRA and Z. JOVIĆ, J. Chem. Soc. A 735 (1967).

^[8] D. M. ADAMS and J. B. CORNELL, J. Chem. Soc. A 884 (1967).

^[9] T. J. LANE, A. YAMAGUCHI, J. V. QUAGLIANO, J. A. RYAN and S. MIZUSHIMA, J. Am. Chem. Soc. 81, 3824 (1959).

^[10] A. YAMAGUCHI, T. MIYAZAWA, T. SHIMANOUCHI and S. MIZUSHIMA, Spectrochim. Acta 10, 170 (1957).