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High-Pressure Effect on Far-Infrared Spectra. I. Symmetric and Antisymmetric Metal-Halogen Stretching Vibrations¹

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The effect of high pressure (*ca.* 50,000 atm) upon the symmetric and antisymmetric metal-halogen stretching modes for coordination compounds has been measured for four types of symmetries and for both chloro and bromo derivatives. In all of the compounds examined, the peak positions are relatively insensitive to pressure, while the intensity of the symmetric peak is decreased to a much greater extent than that of the antisymmetric mode. It is, therefore, concluded that this technique can be used as a tool in distinguishing the symmetric and antisymmetric metal-halogen stretching modes. An example of the application of this technique to band assignment is given.

Introduction

The effect of high pressure (*ca.* 50,000 atm) on infrared spectra has been limited predominantly to organic compounds^{3,4} and to frequencies above 350 cm⁻¹, although a recent report⁵ gives results below 200 cm⁻¹. Previously^{6,7} we have shown that spectral measurements at high pressures can be made to frequencies of *ca.* 100 cm⁻¹ and serve as a useful tool to distinguish lattice modes which shift position with pressure and internal modes which do not shift appreciably.

Many coordination compounds have bands in the frequency region that our technique has opened. The bonding between metal and ligand may partake of both ionic and covalent character and thus offers an interesting area for pressure measurements. In this paper the results of pressure on the metal-halogen bands are reported for four different ligand configurations about the central metal: trigonal pyramidal (MX₃⁻), square planar (PtX₂Y₂), tetrahedral (CoX₂Y₂), and trigonal bipyramidal (ZnX₂Y₃), where X = Cl or Br and Y = ligand other than halogen. The metal-halogen modes were chosen for investigation because of their high intensity and because previous assignments of these bands have been made.

Experimental Section

The high-pressure cell using opposed diamond anvils was obtained from High Pressure Diamond Optics, McLean, Va., and has been described previously³ as has the modification of the 6× beam condenser used with the Perkin-Elmer Model 301 far-infrared spectrophotometer.⁸ The recorder of the spectro-

photometer was modified to give a 2×, 5×, 10×, and 20× scale expansion,⁸ which allows for less attenuation of the reference beam to match the approximately 7% transmission through the diamond cell; consequently, narrower slit widths, approximating those of normal runs, can be used.

The [(C₆H₅)₄As][SnCl₃] and [(C₆H₅)₄As][GeCl₃] samples were furnished by Shriver.⁹ The other compounds were prepared by readily available techniques.¹⁰⁻¹⁴ The analytical results are given in Table I.

The spectra were recorded on solid material between the two diamond anvils after the pressure had been cycled several times to minimize abnormal pressure gradients.¹⁵ The spectra were run several times at each pressure to ensure that pressure equilibrium was obtained. In all cases the spectral changes were reversible with pressure. The series were run as a function of decreasing pressure to minimize the effect of extrusion of sample between the diamond anvils. Very often the spectrum of the solid gave slightly different peak locations and intensity patterns than that of a mull.

Results and Discussion

A. Metal Chloride Complexes. 1. Norbornadienedichloroplatinum(II), (C₇H₅)PtCl₂.—The preparation of this compound is given by Alexander, *et al.*,^{14a} and X-ray analysis of the analogous Pd compound^{14b} indicates that the two C=C bonds of the norbornadiene (NBD) molecule and the two chlorine atoms form a square-planar skeleton of the *cis*-[PtX₂Y₂] type. The strong spectral bands at 341 and 322 cm⁻¹ have been assigned¹⁰ to the antisymmetric and symmetric Pt-Cl stretching modes of the *cis*-PtCl₂ group. The effect of pressure upon these bands is shown in Figure 1. Although the intensity of both bands is decreased by pressure, that of the symmetric mode at 322 cm⁻¹ is decreased relative to that of the antisymmetric mode at 341 cm⁻¹, while the peak positions hardly change (see figure caption for exact peak locations).

2. 2,2',2''-Terpyridinedichlorozinc(II), (terpy)ZnCl₂.

(8) G. Mack, Argonne National Laboratory, devised and installed this modification.

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) Argonne National Laboratory; (b) Illinois Institute of Technology.

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(5) C. C. Bradley, H. A. Gebbie, A. C. Gilby, V. V. Kechin, and J. H. King, *Nature*, **211**, 839 (1966).

(6) J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nucl. Letters*, **2**, 269 (1966).

(7) S. S. Mitra, C. Postmus, and J. R. Ferraro, *Phys. Rev. Letters*, **12**, 455 (1967).

TABLE I
 ANALYTICAL RESULTS^a

	% C		% H		% N		% X ^b		Prepn ref
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
(NBD)PtCl ₂	23.45	23.72	2.27	2.31			19.85	20.40	10, 14a
(NBD)PtBr ₂	18.75	19.46	1.79	1.72			35.8	35.5	10, 14a
(α -pic) ₂ CoCl ₂	45.59	44.73	4.46	4.43	8.86	8.67	22.43	22.39	11
(α -pic) ₂ CoBr ₂	35.58	35.51	3.48	3.48	6.92	6.92	39.46	39.49	11
(terpy)ZnCl ₂	48.75	48.53	3.00	3.05	11.37	11.37	19.19	19.20	12
(terpy)ZnBr ₂	39.29	39.46	2.42	2.47	9.17	9.23	34.86	34.98	12
(py) ₂ CoBr ₂	31.85	31.61	2.67	2.68	7.43	7.32	42.40	41.90	13

^a Microanalysis performed by Micro-Tech Laboratories, Skokie, Ill. ^b X = Cl or Br; halogen analyses by micro- or macrotechniques.

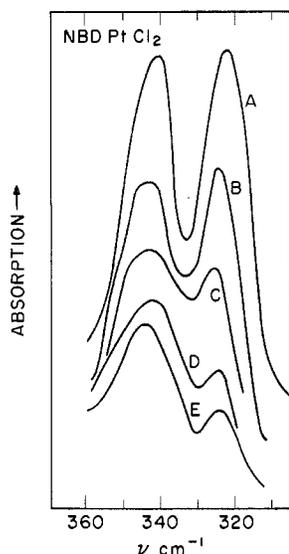


Figure 1.—Pt-Cl stretching bands as a function of pressure in (NBD)PtCl₂, a square-planar structure. Curves are displaced vertically: (A) atmospheric pressure (341, 322 cm⁻¹); (B) 6000 atm (345, 325 cm⁻¹); (C) 12,000 atm (343, 326 cm⁻¹); (D) 18,000 atm (343, 326 cm⁻¹); (E) 24,000 atm (345, 325 cm⁻¹).

—X-Ray analysis of this compound indicates a trigonal-bipyramidal structure with the Cl atoms occupying two equatorial positions.^{16,17} Coates and Ridley¹⁸ report the Zn-Cl stretching bands of this compound at 288 and 279 cm⁻¹. Postmus, *et al.*,¹² have assigned them to 287 and 278 cm⁻¹ for mull spectra. Figure 2 shows the effect of pressure upon these two bands. As the pressure is increased, the symmetric band at 274 cm⁻¹ in the solid decreases in intensity relative to the antisymmetric band, at 290 cm⁻¹ in the solid. At the highest pressure the symmetric mode is seen as only a very weak peak on the lower frequency side of the antisymmetric band. It should also be noted that no appreciable change in peak position occurs. A mull spectrum of this compound shows the symmetric band as a lower intensity, resolvable shoulder on the antisymmetric band.¹²

3. Bis(α -picoline)dichlorocobalt(II), (C₆H₇N)₂CoCl₂.

—This compound is known to be monomeric and tetrahedral.^{11,19} The Co-Cl stretching modes of this com-

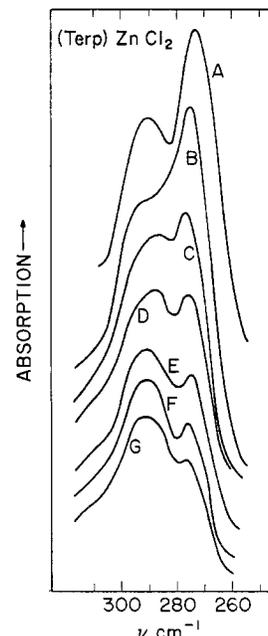


Figure 2.—Zn-Cl stretching bands as a function of pressure in (terp)ZnCl₂, a trigonal-bipyramidal structure. Curves are displaced vertically: (A) atmospheric pressure (290, 274 cm⁻¹); (B) 12,000 atm (291 sh, 276 cm⁻¹); (C) 18,000 atm (289, 277 cm⁻¹); (D) 24,000 atm (288, 277 cm⁻¹); (E) 30,000 atm (291, 275 cm⁻¹); (F) 36,000 atm (291, 276 cm⁻¹); (G) 42,000 atm (291, 278 cm⁻¹).

ound are reported at 351, 313 cm⁻¹,¹⁹ and at 334, 306 cm⁻¹.¹¹ As is shown in Figure 3, we observe two strong bands at 335 and 309 cm⁻¹, in agreement with Gill and Kingdon¹¹ and therefore conclude the spectrum of ref 19 is in error. As pressure is increased, the intensity of the symmetric Co-Cl band (309 cm⁻¹) decreases relative to that of the antisymmetric band (335 cm⁻¹) while the peak positions hardly change.

4. Tetraphenylarsenic Trichlorostannate(II), [(C₆H₅)₄As][SnCl₃].—The preparation, spectra, and assignments of this compound, a pyramidal structure, are given by Shriver and Johnson.⁹ The 289-cm⁻¹ band has been assigned to the symmetric Sn-Cl stretching mode and the 252-cm⁻¹ band to the doubly degenerate antisymmetric mode. Raman studies on the SnCl₃⁻ species give the symmetric mode at 297 cm⁻¹ and the antisymmetric at 256 cm⁻¹.²⁰ The effect of pressure on the infrared spectrum is shown in Figure 4. It should be noted that the symmetric mode (290 cm⁻¹) is at higher frequencies than the antisymmetric (254

(16) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

(17) F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, **20**, 924 (1966), referred to by C. M. Harris, T. N. Lockyer, and N. C. Stephenson, *Australian J. Chem.*, **19**, 1741 (1966).

(18) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).

(19) J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1305 (1965).

(20) L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 407 (1962).

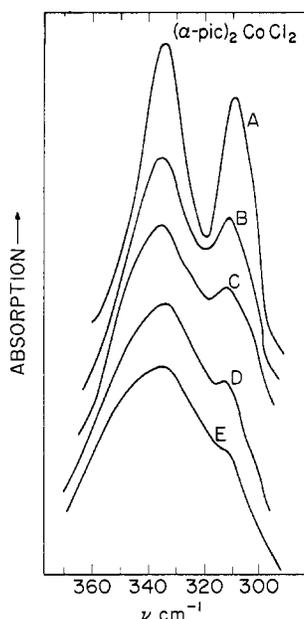


Figure 3.—Co-Cl stretching bands as a function of pressure in $(\alpha\text{-pic})_2\text{CoCl}_2$, a tetrahedral structure. Curves are displaced vertically: (A) atmospheric pressure (335, 309 cm^{-1}); (B) 12,000 atm (335, 313 cm^{-1}); (C) 18,000 atm (334, 314 cm^{-1}); (D) 24,000 atm (334, 313 cm^{-1}); (E) 36,000 atm (336, 312 (sh) cm^{-1}).

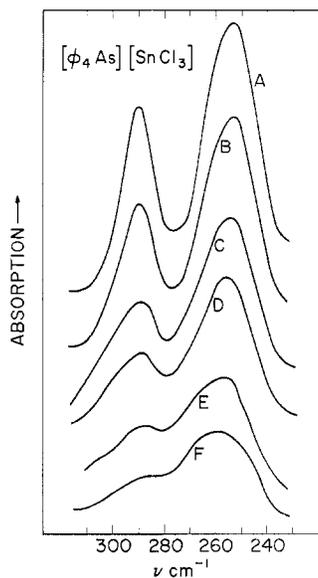


Figure 4.—Sn-Cl stretching bands as a function of pressure in $[(\text{C}_6\text{H}_5)_4\text{As}][\text{SnCl}_3]$, a trigonal-pyramid structure. Curves are displaced vertically: (A) atmospheric pressure (290, 254 cm^{-1}); (B) 1500 atm (290, 254 cm^{-1}); (C) 7500 atm (290, 255 cm^{-1}); (D) 10,500 atm (289, 256 cm^{-1}); (E) 19,500 atm (289, 257 cm^{-1}); (F) 25,500 atm (. . . , 259 cm^{-1}).

cm^{-1}), in contrast to the compounds previously discussed, and that its intensity is decreased relative to that of the antisymmetric mode until at the highest pressure it is only a shoulder. Again, no appreciable shift of peak location occurs. A mull spectrum gives an indication of a shoulder on the low-frequency side of the antisymmetric mode which cannot be seen for the solid in the pressure cell. Under nonequilibrium pressure conditions (immediately after a large change in

pressure) two peaks can be seen in the 250-cm^{-1} region, but as pressure equilibrium is obtained with time, a broad single peak emerges.

5. Tetraphenylarsenic Trichlorogermanate(II), $[(\text{C}_6\text{H}_5)_4\text{As}][\text{GeCl}_3]$.—The assignment of the 322-cm^{-1} band as the symmetrical Ge-Cl stretching mode and of the 273-cm^{-1} band as the doubly degenerate anti-symmetric Ge-Cl stretching mode has been made by Shriver and Johnson.⁹ As in the tin compound, the higher frequency band is the symmetric mode. The decrease in intensity of this band relative to that of the antisymmetric with increasing pressure is shown in Figure 5.

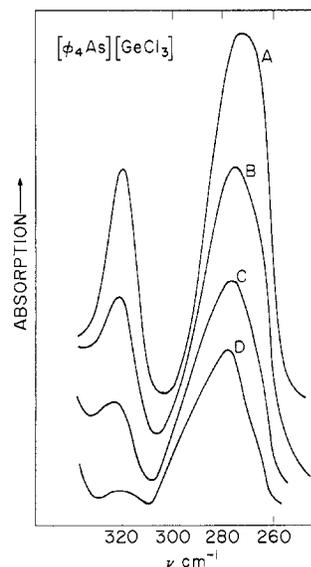


Figure 5.—Ge-Cl stretching bands for $[(\text{C}_6\text{H}_5)_4\text{As}][\text{GeCl}_3]$, a trigonal-pyramid structure. Curves are displaced vertically: (A) atmospheric pressure (320, 272 cm^{-1}); (B) 4600 atm (322, 275 cm^{-1}); (C) 10,800 atm (324, 278 cm^{-1}); (D) 17,000 atm (322, 278 cm^{-1}).

We have studied the antisymmetric and symmetric metal chloride stretching bands of several other complexes. For potassium acetylacetonatodichloroplatinum(II) monohydrate, $\text{K}[\text{Pt}(\text{acac})\text{Cl}_2]\cdot\text{H}_2\text{O}$, the symmetric band (326 cm^{-1}) decreases relative to the antisymmetric (338 cm^{-1}).²¹ For bis(pyridine)dichlorozinc, $(\text{py})_2\text{ZnCl}_2$, the symmetric band (293 cm^{-1}) decreases relative to that of the antisymmetric band (326 cm^{-1}).¹² In some compounds it was impossible to resolve the M-X peaks, e.g., for *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ ²² and dichloroethylenediaminepalladium(II). For dichloro-(2,2'-bipyridine)palladium(II) the symmetric band (346 cm^{-1}) was shifted into the region of the antisymmetric band (358 cm^{-1}) making the interpretation difficult.

B. Metal Bromide Complexes.—Bromide complexes of Co(II) and Zn(II) containing pyridine and its analogs have overlapping spectral regions of M-Br and M-N stretching bands. Unequivocal assignments are difficult to make, and conflicting assignments by

(21) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

(22) K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, *ibid.*, **4**, 36 (1965).

different investigators occur. It is, therefore, of particular interest to apply high-pressure techniques to solve conflicting assignments. Before discussing the M-Br and M-N assignments, it is necessary to show that M-Br bands and M-N show the same pressure effect as demonstrated above for M-Cl.

1. **Norbornadienedibromoplatinum(II)**, $(C_7H_8)PtBr_2$.—The structure of this compound is similar to that of the analogous chloro complex.^{14a} The symmetric and antisymmetric Pt-Br bands in $(NBD)PtBr_2$ have been assigned at 223 (sh) and 218 cm^{-1} , respectively,¹⁰ and no interfering bands as M-N occur in this region. The effect of pressure upon these bands is shown in Figure 6. Again, the symmetric mode at 218 cm^{-1} loses its intensity more rapidly than the antisymmetric mode at 223 cm^{-1} , and no appreciable change of peak location occurs. It should be mentioned that the spectrum of the solid at 1 atm with the high-pressure cell gives better resolution of these bands than that of a mull where the 223- cm^{-1} band appears only as a shoulder on the high-frequency side of the symmetric mode.

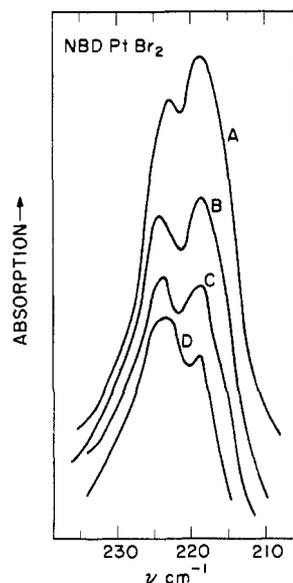


Figure 6.—Pt-Br stretching bands as a function of pressure in $(NBD)PtBr_2$, a square-planar structure. Curves are displaced vertically: (A) atmospheric pressure (223, 218 cm^{-1}); (B) 3000 atm (224, 218 cm^{-1}); (C) 6000 atm (225, 218 cm^{-1}); (D) 9000 atm (224, 219 cm^{-1}).

2. **2,2',2''-Terpyridinedibromozinc(II)**, $(terpy)ZnBr_2$.—The structure of this compound is similar to that (trigonal bipyramid) of the chloro compound.¹⁶ The assignments of the 243- cm^{-1} band to Zn-N and of the 222- (sh) and 213- cm^{-1} bands to Zn-Br stretching vibrations have been made.¹² The effect of pressure on the Zn-Br stretching bands is shown in Figure 7. At low pressure the band is definitely asymmetric with a pronounced shoulder at *ca.* 220 cm^{-1} (antisymmetric) on the main peak at 213 cm^{-1} (symmetric). As pressure is applied, the peak at 213 cm^{-1} decreases in intensity and shifts to a slightly higher frequency. At 9000 atm the 222- cm^{-1} band is the more intense

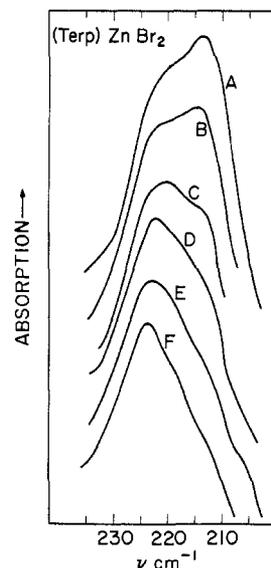


Figure 7.—Zn-Br stretching bands as a function of pressure in $(terpy)ZnBr_2$, a trigonal-bipyramid structure. Curves are displaced vertically: (A) atmospheric pressure; (B) 3000 atm; (C) 6000 atm; (D) 9000 atm; (E) 12,000 atm; (F) 15,000 atm.

with the symmetric band appearing only as a weak shoulder on the low-frequency side. As the pressure is increased further, the intensity of the symmetric mode continues to decrease.

3. **Bis(pyridine)dibromocobalt(II)**, $(C_5H_5N)_2CoBr_2$.—This compound is known to be tetrahedral and monomeric^{13,19} in contrast to the polymeric nature of the stable form of the corresponding chloride. Curve A of Figure 8 shows the mull spectrum we obtain which differs from that reported in the literature by showing a shoulder at 280 cm^{-1} on the main peak at 277 cm^{-1} . We assign both of these peaks to Co-Br stretching modes, the 280 cm^{-1} to the antisymmetric and the 277 cm^{-1} to the symmetric mode. The remaining two peaks are assigned to Co-N stretching modes, the 253 cm^{-1} to the antisymmetric and the 244 cm^{-1} to the symmetric mode. A summary of previous assignments for Co-Br complexes is given in Table II.

The effect of pressure upon these bands is shown in curves B-E of Figure 8. At 1 atm pressure for the solid, the symmetric Co-Br band (276 cm^{-1}) is much more intense than the antisymmetric (280 cm^{-1}). As pressure is increased, the intensity of the symmetric band decreases (approximately of equal intensity at 4600 atm). At higher pressures the peaks cannot be resolved, probably owing to pressure broadening of the two closely spaced Co-Br bands. The decrease in intensity of the 277- cm^{-1} band relative to that of the 280- cm^{-1} band confirms the above assignments.

The effect of pressure upon the Co-N bands is to decrease the intensity of the symmetric mode, 244 cm^{-1} (and shift it slightly, ~ 4 cm^{-1}), relative to that of the antisymmetric mode at 253 cm^{-1} . It should be noted that the decrease in intensity of two different types of bands (*e.g.*, M-Br and M-N) in the same compound need not necessarily occur to the same extent for a given pressure.

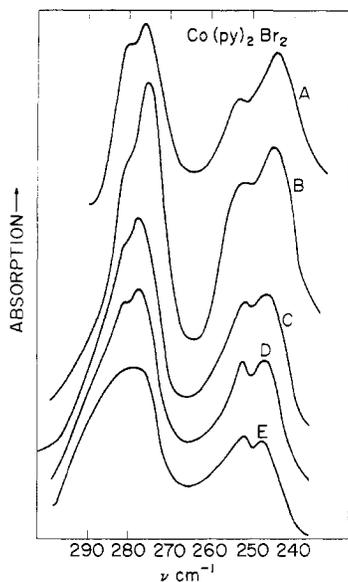


Figure 8.—Co-Br and Co-N stretching bands for $\text{Co}(\text{py})_2\text{Br}_2$, a tetrahedral structure. Curves are displaced vertically. Bands near 280 cm^{-1} are Co-Br; those at 250 cm^{-1} are Co-N: (A) Nujol mull spectrum taken between high-density polyethylene windows (280 sh , 277 , 253 , 244 cm^{-1}); (B-F) spectra are of the solid material held between diamond anvils; (B) atmospheric pressure ($280\text{ sh}?$, 276 , 253 , 244 cm^{-1}); (C) 1500 atm (281 sh , 278 , 252 , 246 cm^{-1}); (D) 4600 atm (281 , 278 , 253 , 247 cm^{-1}); (E) 7700 atm (252 b , 253 , 248 cm^{-1}).

	Co-Br	Co-N	Ref
$\text{Co}(\text{py})_2\text{Br}_2$	274, 242 274	250 sh	13 19; also bands at 254, 249, and 239 cm^{-1} not assigned
$\text{Co}(\alpha\text{-pic})_2\text{Br}_2$	280 sh, 277 s 267	253 sh, 244 s	This work 19; band at 234 cm^{-1} not as- signed
	263, 244 263 s	237, 222 244 s, 237 s	11 This work; band at 220 cm^{-1} (vw) not assigned (see text)

4. **Bis(α -picoline)dibromocobalt(II), $(\text{C}_6\text{H}_7\text{N})_2\text{CoBr}_2$.**—Although our mull spectrum of $\text{Co}(\alpha\text{-pic})_2\text{Br}_2$ agrees in peak location with that reported by Gill and Kingdon,¹¹ we differ in assignments (see Table II). In view of the small separation (3 cm^{-1}) of the Co-Br bands in the pyridine complex (see above), only a small separation in the α -picoline compound is expected, not 20 cm^{-1} as assigned by Gill and Kingdon.¹¹ We therefore assign only the 263-cm^{-1} band to Co-Br in the picoline complex; the lack of splitting may be due to many factors, it has been observed previously that M-Cl bands may split but the M-Br bands of analogous compounds do not show a separation.¹³ The remaining two intense bands, 253 and 244 cm^{-1} , are assigned to the antisymmetric and symmetric Co-N stretching modes, respectively. The band reported at 222 cm^{-1} by Gill and Kingdon¹¹ we observe at 220 cm^{-1} in a mull spectrum as only a very, very weak band (Gill and Kingdon

do not report intensities) and we make no attempt to assign it.

The effect of pressure upon the 263 -, 244 -, and 237-cm^{-1} bands is shown in Figure 9. The intensity of the 237-cm^{-1} band is extremely sensitive to pressure, indicating it is a symmetric mode—in this case the Co-N symmetric stretch. The relative intensities of the 263 - and 244-cm^{-1} bands remain essentially constant (aside from an initial decrease of the 244-cm^{-1} band due to the decrease of the overlapping 237-cm^{-1} band), indicating that the 244-cm^{-1} band is *not* the symmetric Co-Br stretch as previously assigned. As the pressure is increased with a subsequent decrease in intensity of the 263 - and 244-cm^{-1} peaks, two additional peaks emerge, 276 and 251 cm^{-1} , the intensities of which are not decreased as rapidly with pressure. No assignment of these peaks is apparent. The pressure measurements corroborate the empirical assignments given above and refute the previous assignments of Gill and Kingdon.¹¹

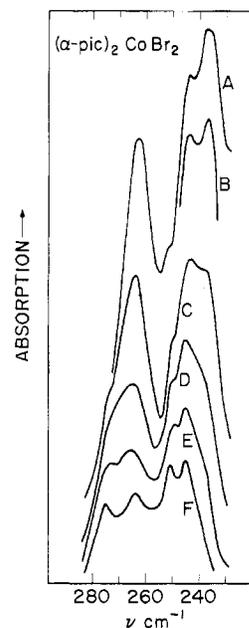


Figure 9.—Co-Br and Co-N stretching bands as a function of pressure in $(\alpha\text{-pic})_2\text{CoBr}_2$, a tetrahedral structure. Curves are displaced vertically: (A) atmospheric pressure (263 , 252 sh , 244 , 236 cm^{-1}); (B) 900 atm (263 omitted, 244 , 237 cm^{-1}); (C) 1500 atm (275 sh , 264 , 250 sh , 245 , 239 sh cm^{-1}); (D) 4500 atm (\dots , 264 , 250 sh , 245 , 240 sh cm^{-1}); (E) 7500 atm (273 sh , 265 , 250 , 245 , 240 sh? cm^{-1}); (F) $10,500\text{ atm}$ (276 , 263 , 251 , 245 , $\dots\text{ cm}^{-1}$).

Conclusion

Thus far, the distinctions of the antisymmetric and symmetric modes have been made experimentally by polarized light studies of infrared dichroism²³ and depolarization studies of Raman lines.²³ Theoretical normal coordinate analysis can predict the frequency order of these two modes.²³ As shown above, pressure measurements are also useful in distinguishing these two modes, since the intensity of the symmetric mode

(23) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 1.

is more suppressed by increasing pressure than that of the antisymmetric mode regardless of the type of vibration (M-Cl, M-Br, M-N), central metal ion, molecular structure, or the relative position of the frequencies of the two modes. Although the most extensive work has been done on the M-Cl stretching modes, the M-Br and M-N we have investigated follow the same pattern and indicate the general applicability of the technique.

A recent publication indicates that for material in solution an increase in pressure may change a tetrahedral structure to square planar.²⁴ Since we observe similar changes in band intensities for square-planar structures as for the other structures, it is concluded that a change in structure does not occur.

Whether the observed effect is due to pressure alone or to a combination with shear forces exerted by the anvils is difficult to determine and is immaterial for the purpose of distinguishing experimentally between symmetric and antisymmetric stretching modes. The observed effect cannot be explained by a phase transformation with varying amounts of low- and high-pressure phases (both phases present due to the pressure gradient across the anvils) as the pressure is changed for the following reasons. (1) Whenever two phases are present, they can be observed through a microscope.¹⁵ The Beck line between the phases moves toward the edges of the anvils as the pressure is increased. This type of phenomenon has been looked for but not observed in any of the coordination compounds reported

(24) A. E. Ewald and E. Sinn, *Inorg. Chem.*, **6**, 40 (1967).

in this work. (2) Generally, the pressure range over which both high- and low-pressure phases can be detected spectrophotometrically is more limited than most of the pressure ranges reported in this work.²⁵ Further, the appearance of the high-pressure phase is marked by a discontinuous spectral change at a minimum pressure. All of the changes reported here are continuous from essentially atmospheric pressure. (3) If phase transformation is responsible, it seems unlikely that all of the compounds studied would have a similar high-pressure phase which would alter the intensity pattern in this identical way.

The intensity of an infrared band is related to the change in dipole moment during the vibration.²⁶ For the symmetric vibration a change in molecular volume occurs, while for the antisymmetric the volume remains essentially constant. A closer packing of molecules at high pressures may thus interfere more with the symmetric than with the antisymmetric vibration. It is not possible at this stage, however, to discuss quantitatively the effect of bulk pressure on intramolecular parameters.

Acknowledgments.—We wish to thank Wayne Wozniak, M. J. Grogan, and John Wasson for the preparation of some of the compounds used in this study. We also thank Dr. Shriver for the Sn and Ge compounds and the opportunity to read his manuscript prior to publication.

(25) Unpublished results of lattice vibrations of alkali metal halides.

(26) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 241.

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A Spectrophotometric Study of the Equilibrium Formation of Gaseous Zinc(I) Chloride¹

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The system Zn(g)-ZnCl₂(g) has been studied at equilibrium over the range of 320–950° by means of its electronic spectrum. The absorbance of ZnCl(g) was determined in the presence of various known concentrations of the reactants between 750 and 950° to give $\Delta H^{\circ}_{1125} = 43.9 \pm 0.5$ kcal for the reaction $\text{ZnCl}_2(\text{g}) + \text{Zn}(\text{g}) = 2\text{ZnCl}(\text{g})$. With a statistical value for the entropy change ΔG°_{1125} is 33.4 kcal, and D°_0 is computed to be 2.37 ± 0.03 ev. No other product is detectable in either the electronic or the mass spectrum down to 300°. The latter results are in contrast with the substantial stability of gaseous Zn₂Cl₂ inferred from sublimation experiments.^{2,3} Such a product is shown to give unreasonable thermodynamic data for the dimerization of ZnCl(g) and for the vaporization of the presumed Zn₂Cl₂(l) from liquid ZnCl₂. It is suggested that the sublimation properties of the mixed system are determined more by kinetic factors.

Introduction

In the zinc family the stability of M₂Cl₂ species in condensed halide systems increases markedly and reasonably uniformly from zinc to mercury. The prin-

cipal evidence for Zn₂Cl₂(l) is the Henry's law study of the small (~0.02 mole %) solubility of metal in ZnCl₂(l) at 500°.⁴ The compound Cd₂Cl₂(l) has likewise been considered to be the probable product of the more substantial solution of metal in molten CdCl₂.⁵

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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