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### Vibrational Spectra and Normal Coordinate Analysis of Diamminediiodidezinc(II) with $^{15}\text{N}$ and $^2\text{H}$ Isotopic Substitution.

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**VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS  
OF DIAMMINEDIODIDEZINC(II) WITH  $^{15}\text{N}$  AND  $^2\text{H}$  ISOTOPIC  
SUBSTITUTION.**

**Key words:** IR, Raman spectra. Diamminediiodidezinc (II) isotopic complexes. Force constants.

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**ABSTRACT:** The Raman and IR. spectra of solid diamminediiodidezinc (II) with  $^{15}\text{N}$  and  $^2\text{H}$  isotopic substitution have been measured. The spectra have been interpreted assuming  $\text{C}_{2v}$  symmetry for the  $\text{Zn}(\text{NH}_3)_2\text{I}_2$  complex structure . The skeletal stretching metal-ligand modes  $\nu_s(\text{ZnN})$ ,  $\nu_{as}(\text{ZnN})$ ,  $\nu_s(\text{ZnI})$ ,  $\nu_{as}(\text{ZnI})$  as well as the three bending modes  $\delta(\text{NZnN})$ ,  $\delta(\text{IZnI})$  and  $\delta(\text{IZnN})$  were assigned by comparison with the spectra of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  and  $\text{Zn}(\text{NH}_3)_2\text{Br}_2$  , and by the

observed isotopic shifts of the frequencies. A normal coordinate analysis for the whole complex was carried out using the Local Symmetry Force Field Model.

## INTRODUCTION

The IR, and Raman spectra of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  and  $\text{Zn}(\text{NH}_3)_2\text{Br}_2$  with  $^{15}\text{N}$  and  $^2\text{H}$  isotopic substitution have previously been reported by Téllez et al., [1,2]. In this work the IR., and Raman spectra of the solid state of  $\text{Zn}(\text{NH}_3)_2\text{I}_2$  with  $^{15}\text{N}$  and  $^2\text{H}$  isotopic substitution are presented.

The normal coordinate analysis (NCA) for  $\text{Zn}(\text{NH}_3)_2\text{I}_2$ , based on a General Valence Force Field (GVFF) , using the H/D isotopic observed frequencies, has been reported only for a reduced model [3,4] using the point mass model restriction [5]. We confirm the trend for the  $f_{\text{ZnN}}$  force constants reported by Perchard e Novak [3].

The purpose of this work is to report the IR. and Raman spectra of the diamminediiodidezinc (II)  $^{15}\text{N}$  labeled complex, to determine also the potential field for the whole complex without the restriction of considering the  $\text{NH}_3$  ligand as point mass of 17 or 18 daltons, and to complete the vibrational study of the complexes  $\text{Zn}(\text{NH}_3)_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) with  $^{14}\text{N}/^{15}\text{N}$  and H/D isotopic substitution.

## EXPERIMENTAL

The complexes  $\text{Zn}(\text{NH}_3)_2\text{I}_2$  ,  $\text{Zn}({^{15}\text{NH}_3})_2\text{I}_2$  and  $\text{Zn}(\text{ND}_3)_2\text{I}_2$  , were prepared in mg quantities according the reaction in ethanol solution: $\text{ZnI}_2 + 2\text{NH}_3(\text{g}) \rightarrow \text{Zn}(\text{NH}_3)_2\text{I}_2(\text{s})$ .The following reagents were obtained commercially: methyl-d<sub>3</sub> alcohol-d, 99.8%D; ammonium- $^{15}\text{N}$  Chloride, 98%  $^{15}\text{N}$ ; ammonium-d<sub>4</sub> deuterioxide, 99 +atom%D from Aldrich.  $\text{ZnI}_2$  from Merck.

The infrared spectra from 4000 to 200  $\text{cm}^{-1}$  were recorded with a NICOLET 60 SXR FTIR spectrophotometer as CsI pellet. The far infrared were recorded on a NICOLET 740 FT-IR, in this case the samples were mixed and fused with polyethylene powder. The Raman spectra were run on a Jarrel-Ash 25-

300 spectrometer using the 514.5 nm radiation from an  $\text{Ar}^+$  laser and with a NICOLET 900-FT Raman spectrometer using the 1064 nm (9394  $\text{cm}^{-1}$ ) from a Neodymium YVO<sub>4</sub> (Nd:YVO<sub>4</sub>) excitation laser. The deuterated samples suffer rapid exchange with hydrogen atoms.

## RESULTS AND DISCUSSIONS

**Vibrational irreducible representations:** Assuming C<sub>2v</sub> symmetry for the tetrahedral structure of Zn(NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub>, the 3n-6= 27 vibrational modes after discarding the torsional frequencies can be distributed among the symmetry species:  $\Gamma_{\text{vib}} = 9a_1(\text{IR}, \text{R}) + 4a_2(\text{R}) + 7b_1(\text{IR}, \text{R}) + 5b_2(\text{IR}, \text{R})$ .

The observed ir absorption's bands and the Raman shifts with the approximate assignments are given in Table 1.

### Bands assignments

The  $\nu(\text{NH})_{\text{as}}$  and  $\nu_{\text{s}}(\text{NH})$  stretching, as well as the bending  $\delta_{\text{as}}(\text{HNH})$ ,  $\delta_{\text{s}}(\text{HNH})$  and the  $\rho(\text{NH}_3)$  rocking vibrations are considered to be characteristic for the ammin complexes [6]. The values for the quotient  $\nu(\text{H})/\nu(\text{D})$  calculated for the NH<sub>3</sub>/ND<sub>3</sub> ligands absorption's in the ir. spectra for Zn(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/Zn(ND<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> [1], Zn(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>/Zn(ND<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> [2] and Zn(NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub>/Zn(ND<sub>3</sub>)<sub>2</sub>I<sub>2</sub> show a lowering of the frequencies by deuterations of the order of 23%. A shift of 15  $\text{cm}^{-1}$  was found between the  $\rho(\text{NH}_3)$  modes of the Zn(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and Zn(NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub> complexes.

### Metal - nitrogen stretching vibrations

According the assumed C<sub>2v</sub> symmetry for the Zn(NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub> structure, the metal-nitrogen stretching vibrations (  $a_1$  and  $b_1$  ) should be infrared and Raman active. The  $\nu_{\text{as}}(\text{ZnN})(b_1)$  modes were observed in the infrared spectra at 406.0, 391., and 380.0  $\text{cm}^{-1}$  for the Zn(NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub> , Zn(<sup>15</sup>NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub> and Zn(ND<sub>3</sub>)<sub>2</sub>I<sub>2</sub> complexes,respectively. The symmetrical  $a_1$  modes were observed in the Raman spectra as shifts of mean intensities at 424.0m 418.0, and at 398.0  $\text{cm}^{-1}$  for the three isotopomers, respectively. The  $\nu_{\text{as}}(\text{ZnN})(b_1)$  were also observed in the Raman spectra as Raman shifts of low intensities at 412.0, 400.0, and at 382.0  $\text{cm}^{-1}$  for

**Table 1. Observed frequencies (cm<sup>-1</sup>) and approximate assignments for Zn(NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub> with <sup>14</sup>N/<sup>15</sup>N and H/D isotopic substitution.**

Zn(NH <sub>3</sub> ) <sub>2</sub> I <sub>2</sub>	Zn( <sup>15</sup> NH <sub>3</sub> ) <sub>2</sub> I <sub>2</sub>	Zn(ND <sub>3</sub> ) <sub>2</sub> I <sub>2</sub>	
<i>Infrared</i>			
3317.0	3310.0	2418.0	$\nu_{as}$ (NH/ND)
3236.0	3233.0	2356.0	$\nu_s$ (NH/ND)
1611.0	1594.0	1159.0	$\delta_{as}$ (HNH/DND)
1242.0	1232.0	958.0	$\delta_s$ (HNH/DND)
676.0	676.0	571.0	$\rho$ (NH <sub>3</sub> /ND <sub>3</sub> )
646.0	647.0	541.0	$\rho$ (NH <sub>3</sub> /ND <sub>3</sub> )
-----	-----	493.0	$\rho$ (NH <sub>3</sub> /ND <sub>3</sub> )
425.0	391.0	380.0	$\nu_s$ (ZnN)
406.0	-----	-----	$\nu_{as}$ (ZnN)
177.0	175.0	176.0	$\nu_{as}$ (ZnI)
162.0	161.0	161.0	$\nu_s$ (ZnI)
124.0	121.0	121.0	$\delta$ (IZnN)
74.0	73.0	73.0	$\delta$ (IZnN)
<i>Raman</i>			
3312.0	3307.0	2418.0	$\nu_{as}$ (NH/ND)
3233.0	3233.0	2356.0	$\nu_s$ (NH/ND)
3148.0	3145.0	1598.0x2 = 3196.0	
		1593.0x2 = 3186.0	
		2378.0	1167+1164 = 2331
		2305.0	1159.0x2 = 2318.0
1598.0	1593.0	1167.0	$\delta_{as}$ (HNH/DND)
1248.0	1245.0	-----	$\delta_s$ (HNH/DND)
1238.0	1234.0	960.0	$\delta_s$ (HNH/DND)
678.0	680.0	512.0	$\rho$ (NH <sub>3</sub> /ND <sub>3</sub> )
615.0	612.0	475.0	$\rho$ (NH <sub>3</sub> /ND <sub>3</sub> )
424.0	418.0	398.0	$\nu_s$ (ZnN)
412.0	400.0	382.0	$\nu_{as}$ (ZnN)
173.0	173.0	173.0	$\nu_{as}$ (ZnI)
157.0	155.0	158.0	$\nu_s$ (NZnI)
106.0	-----	-----	$\delta$ (NZnI)
67.0	67.0	70.0	$\delta$ (NZnI)
55.0	53.0	53.0	$\delta$ (NZnI)

**Table 2. X-Zn-N angle deformations for the  $\text{Zn}(\text{NH}_3)_2\text{X}_2$  complexes (X = Cl, Br, I) ( frequencies in  $\text{cm}^{-1}$ ).**

	$\delta(\text{NZnX})(\text{a}_1)$	$\delta(\text{NZnX})(\text{a}_1)$	$\delta(\text{NZnX})(\text{a}_2)$	$\delta(\text{NZnX})(\text{b}_1)$	$\delta(\text{NZnX})(\text{b}_2)$	Ref.
$\text{Zn}(\text{NH}_2)_2\text{Cl}_2$	157.0 (R)	117.0 (R)	(142) <sup>*</sup>	225.0 (IR)	98.0 (R)	3
$\text{Zn}({}^{15}\text{NH}_3)_2\text{Cl}_2$	154.0 (R)	117.0 (R)	-----	-----	-----	3
$\text{Zn}(\text{ND}_3)_2\text{Cl}_2$	152.0 (R)	116.0 (R)	134.0 (R)	220.0 (IR)	98.0 (R)	3
$\text{Zn}(\text{NH}_3)_2\text{Br}_2$	153.0 (R)	71.0 (R)	137.0 (R)	133.0 (IR)	82.0 (IR)	4
$\text{Zn}({}^{15}\text{NH}_3)_2\text{Br}_2$	148.0 (R)	70.0 (R)	134.0 (R)	132.0 (IR)	81.0 (IR)	4
$\text{Zn}(\text{ND}_3)_2\text{Br}_2$	138.0 (R)	70.0 (R)	128.0 (R)	124.0 (IR)	82.0 (IR)	4
$\text{Zn}(\text{NH}_3)_2\text{I}_2$	111.0 (R)	55.0 (R)	130.0 <sup>*</sup>	124.0 (IR)	74.0 (IR)	
$\text{Zn}({}^{15}\text{NH}_3)_2\text{I}_2$	111.0 (R)	53.0 (R)	126.0 <sup>*</sup>	121.0 (IR)	73.0 (IR)	
$\text{Zn}(\text{ND}_3)_2\text{I}_2$	100.0 (R)	53.0 (R)	118.0 <sup>*</sup>	121.0 (IR)	73.0 (IR)	

these isotopomers. In the ir spectrum of  $\text{Zn}(\text{NH}_3)_2\text{I}_2$ , the  $\nu_s(\text{ZnN})$  stretching mode was also observed at  $425.0 \text{ cm}^{-1}$  ( sample in nujol suspension).

#### Metal-halogen stretching vibrations

The Raman shifts found at  $173.0 \text{ cm}^{-1}$  in the spectra of the three isotopic substituted complexes, were assigned to the  $\nu_{as}(\text{ZnI})$ . In the ir spectra the  $\nu_{as}(\text{ZnI})$  stretching mode were found at  $177.0$ ,  $175.0$  and at  $176.0 \text{ cm}^{-1}$  for  $\text{Zn}(\text{NH}_3)_2\text{I}_2$ ,  $\text{Zn}({}^{15}\text{NH}_3)_2\text{I}_2$  and  $\text{Zn}(\text{ND}_3)_2\text{I}_2$ , respectively. Symmetrical  $\nu_s(\text{ZnI})$  stretching modes were assigned in the ir spectra to the following frequencies:  $162.0$ ,  $161.0$ , and  $161.0 \text{ cm}^{-1}$  for these complexes. The Raman shifts at  $157.0$ ,  $155.0$  and at  $158.0 \text{ cm}^{-1}$

were assigned to the  $\nu_s(\text{ZnI})$  stretching mode for the three zincdiammine complexes.

#### Normal coordinate analysis (NCA)

The following geometrical parameters for a tetrahedral coordination of the Zn(II) ions by two ammonia and two iodide were used:  $d(\text{Zn-N}) = 2.10\text{\AA}$  [5],  $d(\text{Zn-I}) = 2.53\text{\AA}$  (assumed),  $d(\text{N-H}) = 1.0\text{\AA}$ , and tetrahedral angles around the nitrogen atoms were assumed. Excluding torsional coordinates, 28 internal valence coordinates were used to describe the normal modes and the symmetry coordinates using projection operators were constructed. The approach in the NCA is based on the Cyvin's assumption that vibrational modes may be separated into ligand vibrations, ligand- framework vibrations and skeletal vibrations [8,9,10]. For a least square refinement of the force constants a modified general valence force field (MGVFF) potential function was used, and for the iterative autoconsistence method [11] a general force field was used. In the MGVFF the force constants were adjusted to give the best frequency fit. In both procedures, the initial force constants concerning to the ligand have been transferred from the values given by Cyvin et al.[10] The ligand framework initial coupling force constant was obtained from the relation  $F_{ii} = \lambda_i/G_{ii}$ , where  $\lambda_i = 0.589141(\omega_i/1000)^2$  and the framework force constants were based on the point mass model approximation. Table 3. shows the symmetry force constants obtained by the least square refinement (upper values over the diagonal)[12] and those obtained by the iterative autoconsistency method (lower values of the diagonal)[11], where the reliability of the force constant results given by this method has been tested previously in series of polyatomic molecules[13]. Table 3 shows also, that there are no significant differences between the force constants obtained by the two methods.

The principal valence force constant determined in this study for the zincdiamminediiodide isotopomers are listed in Table 4 together with the values obtained for the diamminedichloridezinc (II) and -dibromidezinc (II) complexes [1,2].

**Table 3. Symmetry force constants obtained using the least squares refinement and the iterative autoconsistency method .**

Species	Symmetry coordinates												Species	Symmetry coordinates											
a <sub>1</sub>	<u>6.019</u>	-0.310	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	a <sub>2</sub>	<u>6.019</u>	-0.310	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	6.067	<u>0.571</u>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		5.785	<u>0.571</u>	-0.049	0.000									
	-0.342	0.571	<u>6.063</u>	-0.222	0.000	0.000	0.000	0.000	0.000	0.000	0.000		-0.315	0.594	<u>0.222</u>	0.139									
	0.000	0.000	6.143	<u>0.397</u>	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.000	0.000	0.235	<u>0.623</u>									
	0.000	0.000	-0.204	0.393	<u>0.267</u>	0.000	0.000	0.000	0.000	0.000	0.000		0.000	0.000	0.006	0.498									
	0.000	0.000	0.000	0.000	0.264	<u>1.374</u>	-0.016	0.007	0.093																
	0.000	0.000	0.000	0.000	0.000	1.399	<u>0.903</u>	0.141	0.010																
	0.000	0.000	0.000	0.000	0.000	-0.021	0.908	<u>0.376</u>	0.069																
	0.000	0.000	0.000	0.000	0.000	0.004	0.136	0.369	<u>0.192</u>																
	0.000	0.000	0.000	0.000	0.000	-0.005	0.019	0.070	0.193																
b <sub>1</sub>	<u>6.019</u>	-0.310	0.000	0.000	0.000	0.000	0.000	0.000	b <sub>2</sub>	<u>6.019</u>	-0.310	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
	6.073	<u>0.571</u>	0.000	0.000	0.000	0.000	0.000	0.000		6.082	<u>0.571</u>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000			
	-0.344	0.568	<u>6.063</u>	-0.222	0.000	0.000	0.000			-0.360	0.570	<u>0.250</u>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
	0.000	0.000	6.146	<u>0.397</u>	0.000	0.000	0.000			0.000	0.000	0.254	<u>0.655</u>	-0.050											
	0.000	0.000	-0.201	0.396	<u>0.249</u>	0.000	0.000			0.000	0.000	0.000	0.658	<u>0.152</u>											
	0.000	0.000	0.000	0.000	0.254	<u>1.208</u>	0.028			0.000	0.000	0.000	-0.042	0.140											
	0.000	0.000	0.000	0.000	0.000	1.236	<u>0.506</u>																		
	0.000	0.000	0.000	0.000	0.000	0.027	0.516																		

The units are : stretching force constants in mdynÅ<sup>-1</sup> , bending and bending interaction force constants are in mdynÅ and mdyn, respectively.

**Table 4. Valence force constants for  $Zn(NH_3)_2X_2$  (X = Cl, Br, I) complexes.**

	$Zn(NH_3)_2Cl_2$		$Zn(NH_3)_2Br_2$		$Zn(NH_3)_2I_2$	
force constant	(I)	(II)	(I)	(II)	(I)	(II)
$f_r = f_{NH}$	$6.14 \pm 0.12$	$6.11 \pm 0.03$	$6.11 \pm 0.11$	$6.05 \pm 0.03$	$6.11 \pm 0.10$	$6.04 \pm 0.03$
$f_{RN} = f_{ZnN}$	$1.54 \pm 0.02$	$1.38 \pm 0.41$	$1.42 \pm 0.05$	$1.38 \pm 0.05$	$1.32 \pm 0.05$	$1.29 \pm 0.05$
$f_{R} = f_{ZnX}$	$1.12 \pm 0.04$	$1.15 \pm 0.06$	$0.98 \pm 0.04$	$0.98 \pm 0.05$	$0.78 \pm 0.05$	$0.78 \pm 0.06$
$f_{rr} = f_{NH/NH}$	$0.04 \pm 0.00$	$0.05 \pm 0.00$	$0.04 \pm 0.11$	$0.02 \pm 0.03$	$0.07 \pm 0.10$	$0.02 \pm 0.03$
$f_{RR} = f_{ZnN/ZnN}$	$-0.05 \pm 0.00$	$0.05 \pm 0.00$	$0.10 \pm 0.05$	$0.08 \pm 0.05$	$0.08 \pm 0.05$	$0.08 \pm 0.05$
$f_{RN} = f_{ZnX/ZnX}$	$0.16 \pm 0.01$	$0.19 \pm 0.01$	$0.17 \pm 0.04$	$0.17 \pm 0.05$	$0.13 \pm 0.05$	$0.12 \pm 0.06$
$f_{\alpha} - f_{\alpha\alpha} = f_{HHH}$	$0.57 \pm 0.10$	$0.56 \pm 0.01$	$0.56 \pm 0.10$	$0.56 \pm 0.01$	$0.57 \pm 0.04$	$0.57 \pm 0.01$
$f_{\beta} - f_{\beta\beta} = f_{(NH_3)_p}$	$0.25 \pm 0.01$	$0.26 \pm 0.01$	$0.26 \pm 0.01$	$0.26 \pm 0.01$	$0.26 \pm 0.03$	$0.27 \pm 0.01$

F(I) ; Iterative autoconsistency set of force constants . F(II): obtained by least square refinement.

The units are  $mdyn\text{\AA}^{-1}$ .

The following trends were observed in the internal (valence) force constants: The value Zn-N stretching force constant  $f_r$  increases from  $Zn(NH_3)_2I_2$  to  $Zn(NH_3)_2Cl_2$ . The same trend was observed for the values of the Zn-X (X = Cl,Br, I) stretching force constant  $f_R$  . The above trends are in agreement with the empirical rule that the substitution of an atom or a group by a more electronegative one leads to an increase of all stretching force constants. The constant  $f_r$  corresponding to the N-H stretching, is smaller in the complex than in  $NH_3(g)$ . The weakness of the N-H bond is due to the coordination of the  $Zn^{+2}$  cation with the  $NH_3$  ligands, as it has been pointed out by Cyvin et al. [10].

### X-Zn-N deformations

For the diammine Pt(II) and Pd(II) square planar  $M(NH_3)_2X_2$  - type complexes, the skeletal bending modes were assigned between  $263\text{ cm}^{-1}$  to  $100\text{ cm}^{-1}$  [4,6]. For the linear diammine complex  $[Ag(NH_3)_2]_2SO_4$ , bending modes were found at  $221\text{ cm}^{-1}$  [7]. For  $Zn(NH_3)_2Cl_2$  and  $Zn(ND_3)_2Cl_2$ , the ir spectra show very weak and poorly resolved bands at  $225\text{ cm}^{-1}$  and nearly to  $220\text{ cm}^{-1}$ , these bands were tentatively assigned to the  $\delta(ClZnN)(b_1)$  vibrational modes. The Raman shifts at: 157, 154 and  $152\text{ cm}^{-1}$  in the  $Zn(NH_3)_2Cl_2$ ,  $Zn(^{15}NH_3)_2Cl_2$  and  $Zn(ND_3)_2Cl_2$  isotopomers, were assigned to the  $\delta(NZnN/ClZnCl)(a_1)$  modes [1]. For the  $Zn(NH_3)_2Br_2$  complexes, two  $\delta(NZnN/BrZnBr)(a_1)$  modes were expected below  $200\text{ cm}^{-1}$ . The Raman shifts at: 153, 148 and  $138\text{ cm}^{-1}$ , and at: 71, 70 and  $71\text{ cm}^{-1}$  were assigned to these bending vibrations. For these some zincdiamminedibromide isotopomers, only one  $\delta(BrZnN)(a_2)$  mode expected in the Raman spectra and its appears at 137, 134 and  $128\text{ cm}^{-1}$  for the three isotopomers. Also, in the ir spectra the bands at 133, 132 and  $124\text{ cm}^{-1}$  were assigned to the  $\delta(NZnBr)(b_1)$  vibrational modes, and the bands at 82, 81 and  $82\text{ cm}^{-1}$  were assigned to the  $\delta(NZnBr)(b_2)$  vibrational modes [1,2]. The tentative assignments for the N-Zn-Br deformations in the zincdiamminediiodide complexes were made by comparison of the ir and Raman spectra of the zincdiamminedichloride and zincdiamminedibromide complexes. The frequencies and assignments for the X-Zn-N angle deformations are given in Table 2. In the Raman spectra plasma bands appears also at  $118\text{ cm}^{-1}$  and at  $73.0\text{ cm}^{-1}$ . Fig.1. shows the  $\nu_{as}(ZnN)$  and  $\nu_s(ZnN)$  Raman shifts for the three isotopomers of the zincdiamminediiodide complex. and illustrate the Raman spectra of the low region between  $250 - 50\text{ cm}^{-1}$  in which appears the metal - halogen stretching and the  $\delta(XZnN)$  vibrational modes.

Assuming a single oscillator for the Zn-N bonds in the zincdiamminedihalogenides complexes, the Zn-N and Zn-X bond order can be calculated by the Gordy's equation [14]:

$$f = 1.67N_{ZnN}(X_{Zn}X_N/d^2)^{3/4} + 0.30,$$

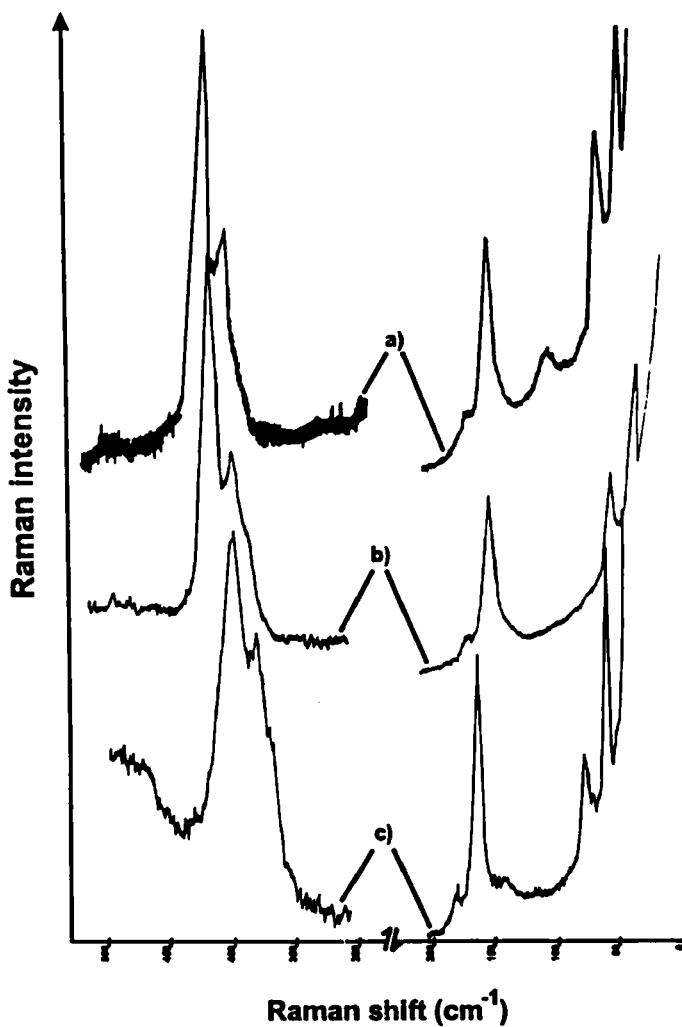


Fig. 1. Metal ligand Raman stretching and bending bands: a)  $\text{Zn}(\text{NH}_3)_2\text{I}_2$ , b)  $\text{Zn}({^{15}\text{NH}_3})_2\text{I}_2$ , c)  $\text{Zn}(\text{ND}_3)_2\text{I}_2$ .

**Table 5. Bond orders calculated according the Gordy's equation.**

Bond Order	$Zn(NH_3)_2Cl_2$	$Zn(NH_3)_2Br_2$	$Zn(NH_3)_2I_2$
$N_{ZnN}(AR)^I$	0.71	0.60	0.55
$N_{ZnN}(AR)^{II}$	0.61	0.58	0.53
$N_{ZnN}(M)^I$	0.84	0.80	0.73
$N_{ZnN}(M)^{II}$	0.73	0.77	0.71
$N_{ZnX}(AR)^I$	0.53	0.48	0.44
$N_{ZnX}(AR)^{II}$	0.55	0.48	0.44
$N_{ZnX}(M)^I$	0.55	0.52	0.42
$N_{ZnX}(M)^{II}$	0.57	0.52	0.42

where  $f$  is the Zn-N force constant ,  $N$  is the bond order ,  $d$  is the Zn-N bond length and  $X_{ZnN}$  and  $X_N$  are the Zn and N atom electronegativities. Using the Allred and Rochow [15] electronegativities and the Mulliken method [16], we obtained the values given in Table 5 for the bond order of the Zn-N and Zn-X bonds in the  $Zn(NH_3)_2Cl_2$  ,  $Zn(NH_3)_2Br_2$  and  $Zn(NH_3)_2I_2$  complexes.

The values given in Table 5., also reflects the influence of the halogenide ligand on the coordination of the  $Zn^{2+}$  cation.

The potential energy distribution reveals that the vibrational modes pertaining to the ligands and framework coupling are nearly pure ( more than 90%). Coupling higher than 10% was found between the  $\nu_s(ZnI)$  and the  $\delta(NZnN/NZnI)$  modes in the  $a_1$  species.

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**Literature**

1. C.A.Téllez S. and L.D'Avila Cruspeire.,Can.J.Appl.Spectrosc.,**35(5)** (1990) **105.**
2. D.N.Ishikawa and C. A .Téllez S., Vibrational Spectroscopy.,**8** (1994) 87.
3. C.Perchard and A .Novak., Spectrochim.Acta.,**26A**(1970) 871.
4. R.J.H.Clark and C.S.Williams.,J.Chem.Soc.,**A** (1966) 1425.
5. R.Friess.,J.A .Chem.Soc.,**52** (1930) 3083.
6. K.Nakamoto.,Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York,4th ed.,1986.
7. A .L.Geddes and G.L.Bottger.,Inorg.Chem.,**8** (1969) 802.
8. R. Andreassen, S.J.Cyvin and L.H.Lyham.,J.Mol. Struct.,**25** (1975) 155.
9. S.J.Cyvin and L.Lyham., J.Mol.Struct.,**25** (1975) 151.
10. S.J.Cyvin, B.N.Cyvin, R.Andreassen, A.Müller.,J.Mol.Struct.,**25**(1975) 141.
11. Yu.N.Panchenko, G.S.Koptev, N.F.Stepanov and V.M.Tatevskii. Optics and Spectroscopy.,**25**(1968) 350.
12. Y.Hase and O .Sala., Computer Programmes for Normal Coordinate Analysis, Universidade de São Paulo (USP), Brazil,1973.
13. R.Aroca, E.A .Robinson and T.A.Ford., J.Mol.Struct.,**31**(1976)457.

14. W.Gordy.,J.Chem.Phys.,**14**(1946)305.
15. A . L.Allred, E.G.Rochow.,J.Inorg.Nucl.Chem.**5**(1958)264.
16. H.O.Pritchard, H. A.Skinner.,Chem.Revs.**55**(1955)745.

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