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Claudio A. Téllez^a; Dilson N. Ishikawa^b; Jacobo Gómez Lara^c

^a Departamento de Química. Lab. Espectroscopia Vibracional, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ, Brasil ^b Departamento de Química, Fundação Universidade Estadual de Londrina -FUEL, Londrina, Paraná, Pr. Brasil ^c Departamento de Química Inorgânica, Instituto de Química, Coyoacán, México, D.F.

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

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

Claudio A. Téllez S.^{*1}, Dilson N. Ishikawa² and Jacobo Gómez Lara³.

¹Departamento de Química . Lab. Espectroscopia Vibracional. Pontificia Universidade Católica do Rio de Janeiro. PUC/Rio. R. Marquês de S. Vicente 225, Gávea. Cep: 22453-900 Rio de Janeiro-RJ. Brasil .

²Departamento de Química. Fundação Universidade Estadual de Londrina - FUEL. Londrina. Paraná - Pr. Brasil.

³Instituto de Química. Departamento de Química Inorgánica. Universidad Nacional Autónoma de México. UNAM . Circuito Exterior, Ciudad Universitaria. Coyoacán, 04510-México. D.F.

ABSTRACT: The Raman and IR. spectra of solid diamminediiodidezinc (II) with ^{15}N and ^2H isotopic substitution have been measured. The spectra have been interpreted assuming 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}N and ^2H 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}N and ^2H 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_{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}N labeled complex, to determine also the potential field for the whole complex without the restriction of considering the 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_3 alcohol- d , 99.8%D; ammonium- ^{15}N Chloride, 98% ^{15}N ; ammonium- d , deuterioxide, 99 +atom%D from Aldrich. ZnI_2 from Merck.

The infrared spectra from 4000 to 200 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 Ar⁺ laser and with a NICOLET 900-FT Raman spectrometer using the 1064 nm (9394 cm⁻¹) from a Neodymium YVO₄ (Nd:YVO₄) excitation laser. The deuterated samples suffer rapid exchange with hydrogen atoms.

RESULTS AND DISCUSSIONS

Vibrational irreducible representations: Assuming C_{2v} symmetry for the tetrahedral structure of Zn(NH₃)₂I₂, the 3n-6= 27 vibrational modes after discarding the torsional frequencies can be distributed among the symmetry species: $\Gamma_{\text{vib}} = 9a_1(\text{IR,R}) + 4a_2(\text{R}) + 7b_1(\text{IR,R}) + 5b_2(\text{IR,R})$.

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 $\nu_s(\text{NH})$ stretching, as well as the bending $\delta_{\text{as}}(\text{HNN})$, $\delta_s(\text{HNN})$ 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 NH₃/ND₃ ligands absorption's in the ir. spectra for Zn(NH₃)₂Cl₂/Zn(ND₃)₂Cl₂ [1], Zn(NH₃)₂Br₂/Zn(ND₃)₂Br₂ [2] and Zn(NH₃)₂I₂/Zn(ND₃)₂I₂ show a lowering of the frequencies by deuterations of the order of 23%. A shift of 15cm⁻¹ was found between the $\rho(\text{NH}_3)$ modes of the Zn(NH₃)₂Cl₂ and Zn(NH₃)₂I₂ complexes.

Metal - nitrogen stretching vibrations

According the assumed C_{2v} symmetry for the Zn(NH₃)₂I₂ structure, the metal-nitrogen stretching vibrations (a₁ and b₁) 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 cm⁻¹ for the Zn(NH₃)₂I₂, Zn(¹⁵NH₃)₂I₂ and Zn(ND₃)₂I₂ complexes, respectively. The symmetrical a₁ modes were observed in the Raman spectra as shifts of mean intensities at 424.0m 418.0, and at 398.0 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 cm⁻¹ for

Table 1. Observed frequencies (cm⁻¹) and approximate assignments for Zn(NH₃)₂I₂ with ¹⁴N/¹⁵N and H/D isotopic substitution.

Zn(NH ₃) ₂ I ₂	Zn(¹⁵ NH ₃) ₂ I ₂	Zn(ND ₃) ₂ I ₂	
<i>Infrared</i>			
3317.0	3310.0	2418.0	ν _{as} (NH/ND)
3236.0	3233.0	2356.0	ν _s (NH/ND)
1611.0	1594.0	1159.0	δ _{as} (HNH/DND)
1242.0	1232.0	958.0	δ _s (HNH/DND)
676.0	676.0	571.0	ρ(NH ₃ /ND ₃)
646.0	647.0	541.0	ρ(NH ₃ /ND ₃)
-----	-----	493.0	ρ(NH ₃ /ND ₃)
425.0	391.0	380.0	ν _s (ZnN)
406.0	-----	-----	ν _{as} (ZnN)
177.0	175.0	176.0	ν _{as} (ZnI)
162.0	161.0	161.0	ν _s (ZnI)
124.0	121.0	121.0	δ(ZZnN)
74.0	73.0	73.0	δ(ZZnN)
<i>Raman</i>			
3312.0	3307.0	2418.0	ν _{as} (NH/ND)
3233.0	3233.0	2356.0	ν _s (NH/ND)
3148.0			1598.0x2 = 3196.0
	3145.0		1593.0x2 = 3186.0
		2378.0	1167+1164 = 2331
		2305.0	1159.0x2 = 2318.0
1598.0	1593.0	1167.0	δ _{as} (HNH/DND)
1248.0	1245.0	-----	δ _s (HNH/DND)
1238.0	1234.0	960.0	δ _s (HNH/DND)
678.0	680.0	512.0	ρ(NH ₃ /ND ₃)
615.0	612.0	475.0	ρ(NH ₃ /ND ₃)
424.0	418.0	398.0	ν _s (ZnN)
412.0	400.0	382.0	ν _{as} (ZnN)
173.0	173.0	173.0	ν _{as} (ZnI)
157.0	155.0	158.0	ν _s (NZnI)
106.0	-----	-----	δ(NZnI)
67.0	67.0	70.0	δ(NZnI)
55.0	53.0	53.0	δ(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 cm^{-1}).

	$\delta(\text{NZnX})(a_1)$	$\delta(\text{NZnX})(a_1)$	$\delta(\text{NZnX})(a_2)$	$\delta(\text{NZnX})(b_1)$	$\delta(\text{NZnX})(b_2)$	Ref.
$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$	157.0 (R)	117.0 (R)	(142) [*]	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 [*]	124.0 (IR)	74.0 (IR)	
$\text{Zn}(^{15}\text{NH}_3)_2\text{I}_2$	111.0 (R)	53.0 (R)	126.0 [*]	121.0 (IR)	73.0 (IR)	
$\text{Zn}(\text{ND}_3)_2\text{I}_2$	100.0 (R)	53.0 (R)	118.0 [*]	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 cm^{-1} (sample in nujol suspension).

Metal-halogen stretching vibrations

The Raman shifts found at 173.0 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 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 cm^{-1} for these complexes. The Raman shifts at 157.0 , 155.0 and at 158.0 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 ₁	<u>6.019</u>	-0.310	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	a ₂	<u>6.019</u>	-0.310	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	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	-0.315	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	0.235	<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	0.006	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 ₁	<u>6.019</u>	-0.310	0.000	0.000	0.000	0.000	0.000				b ₂	<u>6.019</u>	-0.310	0.000	0.000
	6.073	<u>0.571</u>	0.000	0.000	0.000	0.000	0.000				6.082	<u>0.571</u>	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	6.146	<u>0.397</u>	0.000	0.000	0.000				0.000	0.000	0.254	<u>0.655</u>	
	0.000	0.000	-0.201	0.396	<u>0.249</u>	0.000	0.000				0.000	0.000	0.000	0.658	
	0.000	0.000	0.000	0.000	0.254	<u>1.208</u>	0.028				0.000	0.000	0.000	-0.042	
	0.000	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⁻¹ , bending and bending interaction force constants are in mdynÅ and mdyn, respectively.

Table 4. Valence force constants for $\text{Zn}(\text{NH}_3)_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes.

	$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$		$\text{Zn}(\text{NH}_3)_2\text{Br}_2$		$\text{Zn}(\text{NH}_3)_2\text{I}_2$	
force constant	(I)	(II)	(I)	(II)	(I)	(II)
$f_r = f_{\text{NH}}$	6.14 ± 0.12	6.11 ± 0.03	6.11 ± 0.11	6.05 ± 0.03	6.11 ± 0.10	6.04 ± 0.03
$f_R = f_{\text{ZnN}}$	1.54 ± 0.02	1.38 ± 0.41	1.42 ± 0.05	1.38 ± 0.05	1.32 ± 0.05	1.29 ± 0.05
$f_R = f_{\text{ZnX}}$	1.12 ± 0.04	1.15 ± 0.06	0.98 ± 0.04	0.98 ± 0.05	0.78 ± 0.05	0.78 ± 0.06
$f_{rr} = f_{\text{NH/NH}}$	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.11	0.02 ± 0.03	0.07 ± 0.10	0.02 ± 0.03
$f_{RR} = f_{\text{ZnN/ZnN}}$	-0.05 ± 0.00	0.05 ± 0.00	0.10 ± 0.05	0.08 ± 0.05	0.08 ± 0.05	0.08 ± 0.05
$f_{RR} = f_{\text{ZnX/ZnX}}$	0.16 ± 0.01	0.19 ± 0.01	0.17 ± 0.04	0.17 ± 0.05	0.13 ± 0.05	0.12 ± 0.06
$f_{\alpha} - f_{\alpha\alpha} = f_{\text{H/NH}}$	0.57 ± 0.10	0.56 ± 0.01	0.56 ± 0.10	0.56 ± 0.01	0.57 ± 0.04	0.57 ± 0.01
$f_{\beta} - f_{\beta\beta} = f(\text{NH}_3)_p$	0.25 ± 0.01	0.26 ± 0.01	0.26 ± 0.01	0.26 ± 0.01	0.26 ± 0.03	0.27 ± 0.01

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

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

The following trends were observed in the internal (valence) force constants: The value Zn-N stretching force constant f_R increases from $\text{Zn}(\text{NH}_3)_2\text{I}_2$ to $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$. The same trend was observed for the values of the Zn-X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) 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 $\text{NH}_3(\text{g})$. 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 cm^{-1} to 100 cm^{-1} [4,6]. For the linear diammine complex $[Ag(NH_3)_2]_2SO_4$, bending modes were found at 221 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 cm^{-1} and nearly to 220 cm^{-1} , these bands were tentatively assigned to the $\delta(ClZnN)(b_1)$ vibrational modes. The Raman shifts at: 157 , 154 and 152 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 cm^{-1} . The Raman shifts at: 153 , 148 and 138 cm^{-1} , and at: 71 , 70 and 71 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 it appears at 137 , 134 and 128 cm^{-1} for the three isotopomers. Also, in the ir spectra the bands at 133 , 132 and 124 cm^{-1} were assigned to the $\delta(NZnBr)(b_1)$ vibrational modes, and the bands at 82 , 81 and 82 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 cm^{-1} and at 73.0 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]:

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

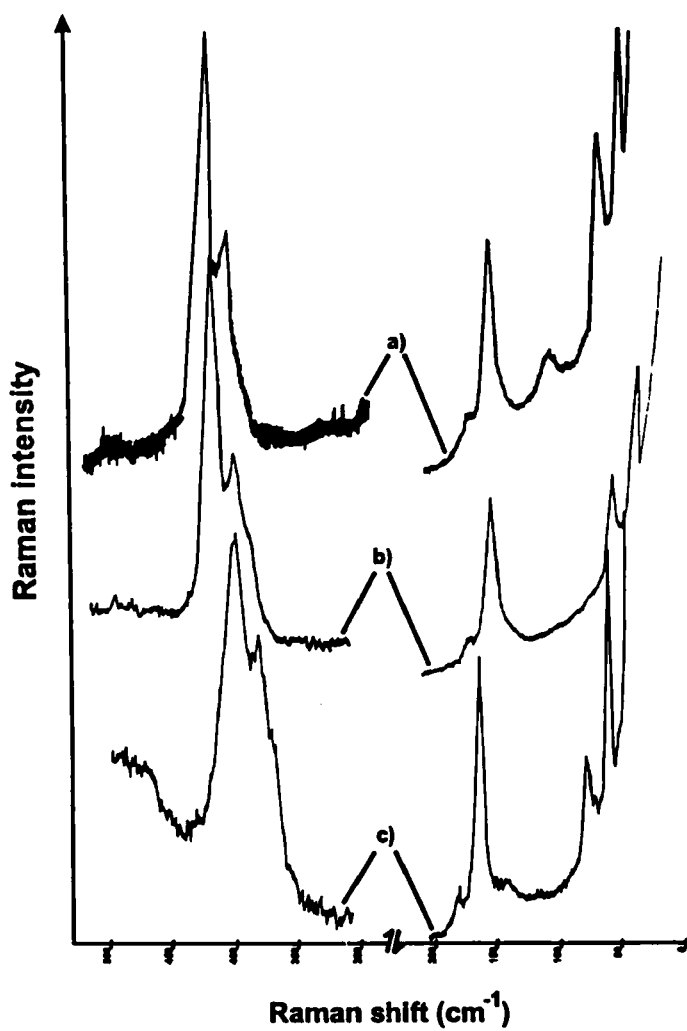


Fig. 1. Metal ligand Raman stretching and bending bands: a) $\text{Zn}(\text{NH}_3)_2\text{I}_2$,
 b) $\text{Zn}({}^{15}\text{NH}_3)_2\text{I}_2$, c) $\text{Zn}(\text{ND}_3)_2\text{I}_2$.

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

Bond Order	$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$	$\text{Zn}(\text{NH}_3)_2\text{Br}_2$	$\text{Zn}(\text{NH}_3)_2\text{I}_2$
$N_{\text{ZnN}}(\text{AR})^{\text{I}}$	0.71	0.60	0.55
$N_{\text{ZnN}}(\text{AR})^{\text{II}}$	0.61	0.58	0.53
$N_{\text{ZnN}}(\text{M})^{\text{I}}$	0.84	0.80	0.73
$N_{\text{ZnN}}(\text{M})^{\text{II}}$	0.73	0.77	0.71
$N_{\text{ZnX}}(\text{AR})^{\text{I}}$	0.53	0.48	0.44
$N_{\text{ZnX}}(\text{AR})^{\text{II}}$	0.55	0.48	0.44
$N_{\text{ZnX}}(\text{M})^{\text{I}}$	0.55	0.52	0.42
$N_{\text{ZnX}}(\text{M})^{\text{II}}$	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 $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$, $\text{Zn}(\text{NH}_3)_2\text{Br}_2$ and $\text{Zn}(\text{NH}_3)_2\text{I}_2$ 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 $\nu_s(\text{ZnI})$ and the $\delta(\text{NZnN}/\text{NZnI})$ modes in the a_1 species.

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