Inorganica Chimica Acta, 20 (1976) 11–18

Vibrational Spectra and Structure of $K_2Zn(NH_2)_4$ and $Rb_2Zn(NH_2)_4$ Amides

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Received February 9, 1976

The infrared and Raman spectra of polycrystalline samples of $K_2Zn(NH_2)_4$, $K_2Zn(ND_2)_4$, $Rb_2Zn(NH_2)_4$ and $Rb_2Zn(ND_2)_4$ have been investigated at room and liquid nitrogen temperature in the 4000 to 100 cm^{-1} range. An assignment of the observed bands is given. There are at least four different N–H distances in $RbZn(NH_2)_4$ probably related to a distorted tetrahedron $Zn(NH_2)_4$. The Zn–N stretching vibrations occur in the 430 to 370 cm^{-1} range and are not much coupled with NH_2 vibrations. The Zn–N stretch force constant has been determined to be about 1.20 md/Å. A general correlation between the NH stretching frequency and metal–nitrogen stretching force constant for a number of inorganic amides is discussed.

Introduction

As a part of general investigation of structure and metal–ligand interactions of inorganic amides[1–5] we have become interested in amidozincate of potassium (AZP) and rubidium (AZR). In this paper we report the infrared and Raman spectra of polycrystalline compounds $K_2Zn(NH_2)_4$, $K_2Zn(ND_2)_4$, $Rb_2Zn(NH_2)_4$ and $Rb_2Zn(ND_2)_4$ at different temperatures. No previous spectroscopic work on these compounds has been published.

Experimental

The compounds were prepared by a method already described for the preparation of $MBe(NH_2)_3$ compounds[6]. The deuterated derivatives were obtained in the same way using ND_3.

The infrared spectra of polycrystalline samples were examined as emulsions in Nujol or Fluorolube at 300 and 100 K on a Perkin–Elmer 180 spectrometer using CsI windows. The far infrared measurements were carried out on a Beckman IR 11 instrument using polyethylene windows. Raman spectra of samples sealed in glass tubes were recorded on a Coderg PHO double monochromator using a Coherent Radiation Laboratory argon-ion laser (5145 and 4880 Å lines) as exciting source. A liquid nitrogen cold cell was used for measurements at 100 K.

Results and Discussion

Crystal Structure and Symmetry Considerations

The structure of AZR has been determined by X-ray diffraction[6]. The crystal is monoclinic and belongs to the $P2_1/C$ (C_{2h}^5) space group with four $Rb_2Zn(NH_2)_4$ formula units per unit cell. The Rb^+ and $Zn(NH_2)_4^{2-}$ ions are in general position. The structure of AZP is being studied; the crystal is triclinic with two formula units per unit cell. The $P\bar{1}$ (C_i^1) space group can be established from our spectroscopic results since there is a general non-coincidence of infrared and Raman frequencies.

In the case of AZR, 177 optically active vibrations ($\vec{k} = 0$) are expected. The intramolecular forces (Zn–N and N–H) being much stronger than the intermolecular forces we can distinguish 132 internal and 45 external vibrations. The former are represented by $33\ A_g + 33\ B_g + 33\ A_u + 33\ B_u$: each of the 33 intramolecular vibrations of an isolated $Zn(NH_2)_4^{2-}$ ion thus splits into four components two infrared and two Raman active. The lattice vibrations are represented by $12\ A_g + 12\ B_g + 11\ A_u + 10\ B_u$ and can also be approximately divided into 12 rotational and 33 translational vibrations.

In the case of AZP 66 internal ($33\ A_g + 33\ A_u$) and 21 external ($12\ A_g + 9\ A_u$) are expected. Each of the intramolecular vibrations splits into two components, one infrared and one Raman active.

However, in both cases a classification of intramolecular vibrations of an isolated $Zn(NH_2)_4^{2-}$ anion appears to be useful. The complex $Zn(NH_2)_4^{2-}$ ions occupy general positions in AZP and AZR crystals. They can be considered as distorted tetrahedrons with Zn–N distances ranging from 2.00 to 2.04 Å. All the 33 intramolecular vibrations are infrared and Raman active and can be described approximately in terms of group frequencies as follows: each NH_2 group gives rise to six vibrations, usually denoted as antisymmetric and symmetric stretching, scissoring, wagging, twisting and rocking modes; the remaining nine vibrations correspond to skeletal, four stretching and five bending, motions.

Band Assignment

NH (ND) stretching vibrations

The infrared and Raman NH and ND stretching regions of amides are shown in Figures 1 and 2. In the case of AZR, we have also studied isotopically mixed crystal containing about 10% of deuterium with respect to hydrogen, where the dominant species is H_7D (67%); no ND coupling is thus expected. The NH and ND frequencies of NH_2, NHD and ND_2 groups and their assignment are given in Tables I and II for AZR and AZP rcspcctively.

AZR: The factor group vibrational analysis shows that 16 infrared and 16 Raman active NH (ND) stretching vibrations are expected. The observed spectra of AZR are indeed rather complex, particularly at low temperature: there are 10 Raman and 9 infrared ND (8 Raman and 9 infrared NH) stretching bands in the spectra of $Rb_2Zn(ND_2)_4$ [$Rb_2Zn(NH_2)_4$].

The spectrum of an isotopically mixed crystal is considerably simplified. There are four bands at 2445, 2432, 2405 and 2397 cm^{-1} corresponding to the decoupled ND stretching vibrations of NHD groups. These frequency splittings are larger than the intermolecular coupling and they indicate that there are at least four different N–D distances. In fact the angular distortion of Zn–N_4 tetrahedron as shown by X-ray diffraction may be responsible for the non equivalency of the ND bands.

The interpretation of the $Rb_2Zn(ND_2)_4$ spectrum can now be undertaken. The corresponding Raman spectrum contains four groups of bands: two doublets and two triplets. Assuming that each uncoupled νND vibration couples intramolecularly we obtain four ν_a–$\nu_s$$ND_2$ doublets while the two additional bands with but little splitting must be due to some intermolecular coupling. This is confirmed by the fact that the intramolecular coupling is much stronger than the intermolecular one shown by the frequency differences: $\nu_a-\nu_s(ND_2) > \nu_a-\nu_s(NH_2)$ (Table I) or in other terms the ν_aNH_2/ν_aND_2 ratio is always lower (1.34) than the ν_sNH_2/ν_sND_2 ratio (1.36). The infrared spectrum is sufficiently similar in order to give an analogous assignment. The ν_a–ν_s difference for intramolecular infrared and Raman coupling is remarkably constant (73 to 82 cm^{-1}) for the ND_2 group while the intermolecular coupling does not exceed 4 cm^{-1} for g–g components (all Raman active) and varies from 4 to 10 cm^{-1} for g–u components (Raman and infrared). The fact that there is almost no coincidence between

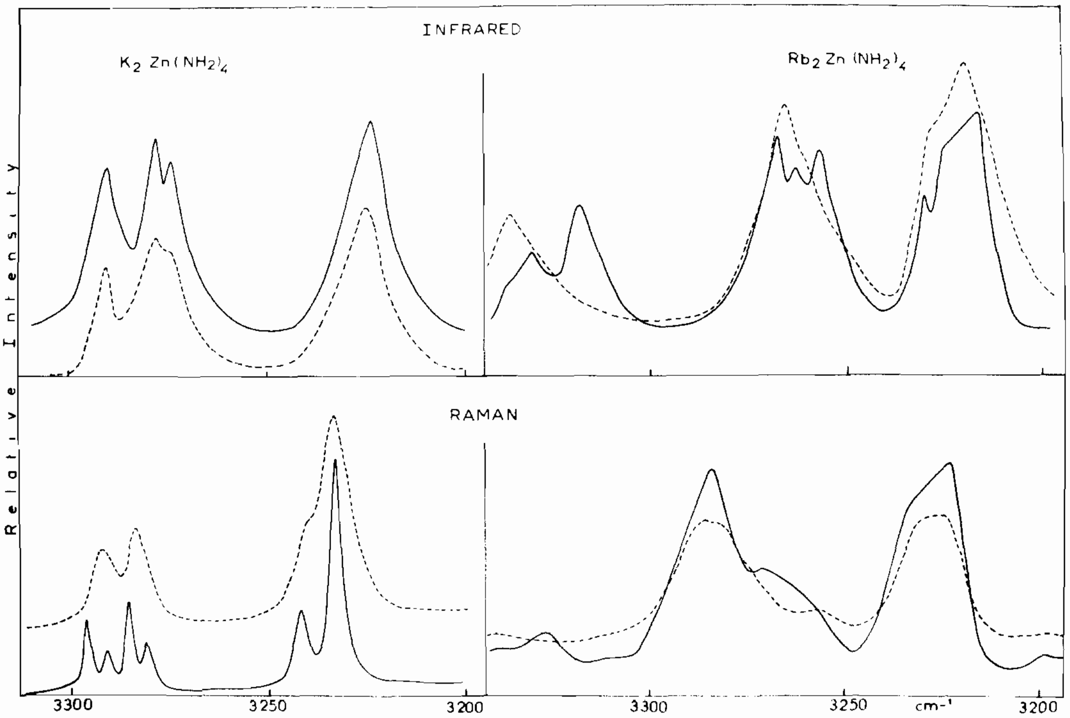

Figure 1. The infrared and Raman NH stretching region of $K_2Zn(NH_2)_4$ and $Rb_2Zn(NH_2)_4$. Solid and dotted lines correspond to the liquid nitrogen and room temperature spectrum respectively.

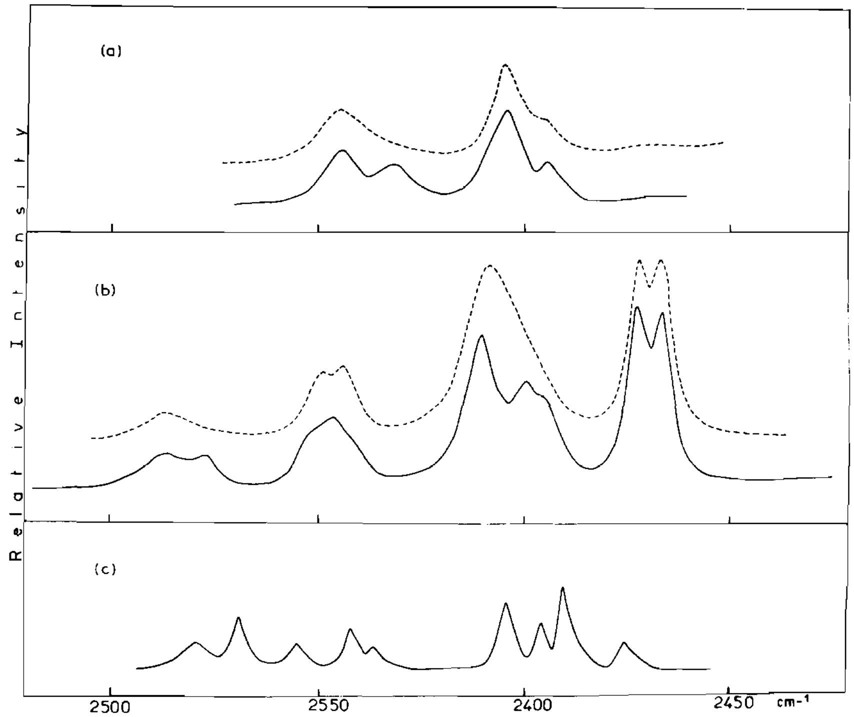

Figure 2. The Raman and infrared ND stretching region of $Rb_2Zn(ND_2)_4$; (a) Raman spectrum of an isotopically diluted AZR crystal containing a D/H ratio of about 10%; (b) Raman spectrum of $Rb_2Zn(ND_2)_4$; (c) infrared spectrum of $Rb_2Zn(ND_2)_4$. Solid and dotted lines correspond to the liquid nitrogen and room temperature spectrum respectively.

the infrared and Raman ND stretching frequencies justifies the factor group analysis rather than the isolated ion approach (Table I). Finally a comparison with $NaGa(NH_2)_4$ must be pointed out: the crystalline structure is the same as that of $Rb_2Zn(NH_2)_4$ while the NH stretching frequencies occur in a much narrower range between 3277 and 3357 cm^{-1}[4] compared to 3338–3216 cm^{-1} range of AZR. The N–H distances are expected thus to be much more similar in the former in spite of the reported widely different Ga–N distances[4].

AZP: Sixteen NH stretching frequencies are expected for this triclinic crystal containing two formula units per unit cell. Six infrared and six Raman bands have been observed in the low temperature spectra (Figure 1) and the fact that their frequencies do not coincide shows that the space group must be $P\bar{1}$. The spectral pattern, identical for the deuterated derivative, is much simpler than that of AZR. The ν_a and $\nu_sNH_2(ND_2)$ stretching vibrations can be assigned in a straightforward manner using the isotopic frequency ratio criterion (Table II). The intramolecular splitting (ν_a–ν_s) of about 54 cm^{-1} is a little weaker than that of AZR but anyway much stronger than the u–g intermolecular one which varies between 5 and 8 cm^{-1}. The NH stretching frequencies are spread out in a relatively narrow range of 70 cm^{-1} which could imply a higher symmetry of the $Zn(NH_2)_4^{2-}$ anion. In fact, assuming a S_4 point group for the latter each of the ν_aNH_2 and ν_sNH_2 vibrations is expected to split into three components of A, B and E species, much in the same way as those of $NaGa(NH_2)_4$ crystal[4]. The observed spectrum is rather close to this expectation.

NH bending and Zn–N skeletal vibrations

The NH_2 deformation vibrations can be identified as deuteration sensitive bands with isotopic frequency ratio varying between 1.30 and 1.36 (Table III). The NH_2 scissoring modes gives rise to a group of bands, strong in infrared but weak in Raman, in the 1600–1500 cm^{-1} range like many other inorganic amides[1–5]. The spread-out of the δNH_2 frequencies is larger for AZR than for AZP similarly as observed for the corresponding NH_2 stretching frequencies. The 1640 cm^{-1} medium–strong absorption band, on the other hand, has no Raman counterpart and is believed to be a combination band since its frequency appears too high for a δNH_2 fundamental.

The "external" deformation vibrations of NH_2 groups occur in the 1300 to 500 cm^{-1} range and we cannot distinguish between the usually denoted wagging, twisting and rocking NH_2 modes. There are two

TABLE I. Infrared and Raman NH and ND Stretching Frequencies of $Rb_2Zn(NH_2)_4$, $Rb_2Zn(ND_2)_4$ and Partially Deuterated AZR at 100 K.

Raman		IR	Raman	IR	$\nu NH/\nu ND$	Assignment
NDH	ND_2	ND_2	NH_2	NH_2		
	2487		3338		1.342	
						$\nu_a ND_2$ (NH_2)
		1479		3335 3330	1.343	
2445						νND
	2410		3270		1.357	$\nu_s ND_2$ (NH_2)
		2405		3265	1.357	
	2477		3325		1.342	$\nu_a ND_2$ (NH_2)
		2467		3318	1.345	
2432						νND
	2400 2396		3260		1.358	
						$\nu_s ND_2$ (NH_2)
		2396 2389		3257	1.359	
		2455				$\nu_a ND_2$ (NH_2)
	2450		3300		1.345	
2405						νND
	2373		3234		1.365	$\nu_s ND_2$ (NH_2)
		2373		3233 3225	1.363	
	2446 2442		3285		1.345	
						$\nu_a ND_2$ (NH_2)
		2442 2437		3278	1.345	
2397						νND
	2367		3222		1.361	$\nu_s ND_2$ (NH_2)
				3216		

TABLE II. Infrared and Raman NH and ND Stretching Frequencies of $K_2Zn(NH_2)_4$ and $K_2Zn(ND_2)_4$ at 100 K.

$K_2Zn(NH_2)_4$		$K_2Zn(ND_2)_4$	$\nu NH/\nu ND$	Assignment	
Raman	IR	Raman			
3295 m		2453 m	1.34	Ag	
					$\nu_a NH_2$
	3287 ms			Au	
3290 w		2451 w	1.34	Ag	
					$\nu_a NH_2$
				Au	
3285 m		2446 m	1.34	Ag	
					$\nu_a NH_2$
	3278 ms			Au	
3280 w		2442 w	1.34	Ag	
					$\nu_a NH_2$
	3272 ms			Au	
3241 m		2377 m	1.36	Ag	$\nu_s NH_2$
3231 s		2371 s	1.36	Ag	
	3226 s				$\nu_s NH_2$

TABLE III. Infrared and Raman Spectra of $Rb_2Zn(NH_2)_4$, $Rb_2Zn(ND_2)_4$, $K_2Zn(NH_2)_4$ and $K_2Zn(ND_2)_4$ at 100 K.

Infrared		Raman		Infrared	Raman		ν/ν'[b]	Assignment
AZR	AZP	AZR	AZP	AZR-d_8	AZR-d_8	AZP-d_8[a]		
1640 m	1643 m							Combination
1572 s	1575 s		1587 w	1156 s	1158 w		1.36	
1550 s	1565 sh		1584 w	1140 s			1.36	NH_2 Scissoring
1545 sh			1548 w	1135 s				
1532 sh								
1527 s				1122 s			1.36	
1310 m	1320 ms			975 mw			1.35	
1260 m	1260 ms			930 mw			1.35	NH_2 External Deformation
1190 w				890 w			1.34	
1100 w	1110 w							
1010 w	1025 w			770 w			1.31	
885 w	885 w							
800 sh	790 sh		739 w					
685 s	675 s	708 w	681 wm	530 s	526 w	509 w	1.30 (1.34)	
655 s			645 wm	500 s		482 mw	1.31 (1.34)	NH_2 External Deformation
615 s	625 s	630 w	625 wm	470 sh	482 w	460 mw	1.31 (1.36)	
578 s	590 s		611 mw	444 m			1.31	
540 s				400 s			1.35	
		427 s	427 s		406 ms	402 ms	1.05 (1.06)	
			400 s			387 s	(1.03)	
						374 s		Zn–N Stretch
380 s	385 s	380 s	377 m	370 s	370 ms	363 s	1.03 (1.03)	
			361 m					
345 sh								
310 ms	305 ms		301 m	305 m		297 m	1.02 (1.05)	
			270 w			250 w	(1.08)	
243 ms	245 ms		241 w	225 s			1.08 (1.08)	Zn–N Bend
	203 s		210 m			194 m	(1.08)	
			179 w					
						159 w		
						139 w		

[a] Low frequencies at 120 (w), 107 (w), 95 (m), 87 (w), 72 (ms), 62 (w) are due to external vibrations which are not specifically assigned. [b] Isotopic frequency ratio for infrared frequencies of AZR. Values between parenthesis correspond to Raman frequencies of AZP.

groups of such bands in both AZR and AZP spectra (Figure 3). The first one (1300–1000 cm^{-1}), observed in the infrared spectra, only has surprisingly high frequencies for NH_2 external fundamentals, the intensity of the 1300 and 1260 cm^{-1} absorptions, however, being considerable. The second group is observed in the 900 to 500 cm^{-1} region and contains strong infrared bands with the Raman counterparts and their frequencies are similar to those of other inorganic amides[1–5].

The Zn–N stretching vibrations correspond to the strongest Raman bands in the 430 to 360 cm^{-1} region. They shift but little on deuteration as expected yielding isotopic frequency ratios between 1.03 and 1.05. The infrared Zn–N stretching bands are also strong but there is no counterpart of the strong Raman band at 427 cm^{-1}. The latter may thus be assigned to a totally symmetric stretching vibration of a more or less distorted ZnN_4 tetrahedron assuming either T_d or S_4 point group symmetry.

The last group of bands, between 310 and 200 cm^{-1}, are doubtless due to Zn–N skeletal bending modes since their isotopic ratios are also low (Table III). In the AZP spectra which appear better resolved than those of AZR three infrared and four Raman bands are observed in this region. This can be compared with the three infrared (2B + E) and four Raman active (A + 2B + E) Zn–N bending vibrations expected for an isolated $Zn(NH_2)^{2-}$ ion of S_4 symmetry[4].

A few frequencies lower than 200 cm^{-1} are attributed to the lattice vibrations involving motions of cations

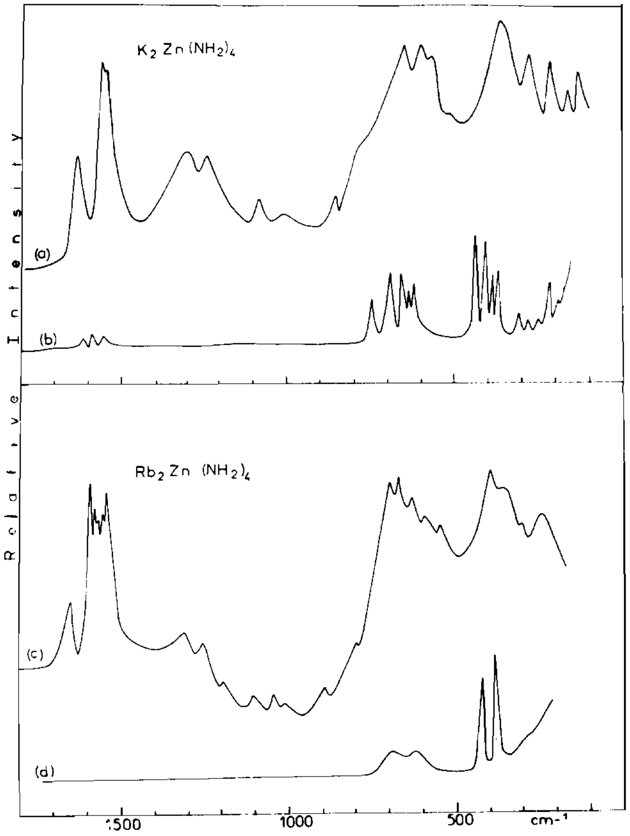

Figure 3. Infrared [(a) and (c)] and Raman [(b) and (d)] spectra of $K_2Zn(NH_2)_4$ and $Rb_2Zn(NH_2)_4$ in the 1800 to 100 cm^{-1} region.

and anions as a whole, however, without any specific assignment.

Zn–N and N–H Stretching Force Constants

The assignment of the bands given above shows that there is but little coupling between the skeletal and NH_2 vibrations unlike in the case of $RbBe(NH_2)_3$ compound where some of these modes are heavily mixed[5]. We can thus evaluate the force constants of an isolated ZnN_4 skeleton assuming a T_d point group symmetry. The following frequencies (average infrared and Raman frequencies) have been used in our calculation: $\nu_1(A) = 427$ cm^{-1}, $\nu_2(E) = 295$ cm^{-1}, $\nu_3(F_2) = 380$ cm^{-1} and $\nu_4(F_3) = 250$ cm^{-1} and the following force constants* have been obtained: $f_r = 1.20$ md/Å; $f_{rr} = 0.17$ md/Å and $f_\alpha = 0.23$ md/Å neglecting $f_{r\alpha}$ and $f_{\alpha\alpha}$ force constants. The Zn–N stretching force constants can be compared to those of $Zn(NH_3)_2X_2$ ammonia complexes where $f_r = 1.42$, 1.38 and 1.28 md/Å for X = Cl, Br and I respectively[7] and to those of $(Zn(NH_3)_4)I_2$ where $f_r = 1.50$ md/Å[8].

The force constants of the NH_2 group were calculated assuming an isolated NH_2 group and taking average ν_aNH_2, ν_sNH_2 and δNH_2 frequencies of 3300, 3240 and 1556 cm^{-1} for AZR and 3287, 3236 and 1563 cm^{-1} for AZP. The following force constants have been determined: $f_r = 5.95$, $f_{rr} = 0.10$ and $f_\alpha = 0.665$ md/Å for AZR and $f_r = 5.82$, $f_{rr} = 0.06$ and $f_\alpha = 0.676$ md/Å for AZP. The difference of about 0.13 md/Å of the NH stretching force constants is significant and probably due to an intermolecular effect such as different crystal packing or different cation rather than to a different Zn–N interaction since the Zn–N stretching frequencies are almost the same for the two amides.

Correlation between Metal–Nitrogen and N–H Stretching Force Constants of Inorganic Amides

Hagenmuller *et al.*[12] have already shown that the NH stretching frequency (or the corresponding force constant) increases with the increasing polarising

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* f_r: Zn–N stretching force constant; f_α: N–Zn–N bending force constant; f_{rr}: Zn–N stretching interaction force constant; $f_{r\alpha}$: stretching–bending interaction force constant; $f_{\alpha\alpha}$: bending interaction force constant.

TABLE IV. Metal–Nitrogen and N–H Stretching Frequencies and Force Constants of Some Inorganic Amides.

Compound	Bond	fM–N (md/Å)	νM–N[a] (cm^{-1})	νNH[b] (cm^{-1})	$\Delta\nu$[c] (cm^{-1})	Ref.
$Sr(NH_2)_2$	Sr–N	0.29	200	3236	92	(2)
$NaNH_2$	Na–N	0.34	260	3231	49	(1)
$LiNH_2$	Li–N	0.73	445	3285	55	(1)
α-$Ca(NH_2)_2$	Ca–N	0.72	350	3259	62	(9)
$K_2Zn(NH_2)_4$	Zn–N	1.20	403	3261	69	Present work
$Rb_2Zn(NH_2)_4$		1.20	403	3262	122	
$Mg(NH_2)_2$	Mg–N	1.35	510	3294	53	(10)
$Na_2Mg(NH_2)_4$	Mg–N	1.93	609	3293	103	(11)
$Rb_2Mg(NH_2)_4$		2.07	630	3303	89	
$NaGa(NH_2)_4$	Ga–N	2.11	550	3318	70	(4)
$NaAl(NH_2)_4$	Al–N	2.52	680	3348	76	(3)
$KAl(NH_2)_4$		2.58	688	3369	101	(3)
$LiAl(NH_2)_4$		2.39	663	3351	111	(3)
$RbBe(NH_2)_3$	Be–N	2.63	830	3360	130	(5)
$KBe(NH_2)_3$		2.63	830	3373	109	(5)

[a] Average metal–ligand stretching frequency. [b] Average NH stretching frequency. [c] Maximum splitting between the highest and the lowest NH stretching frequency.

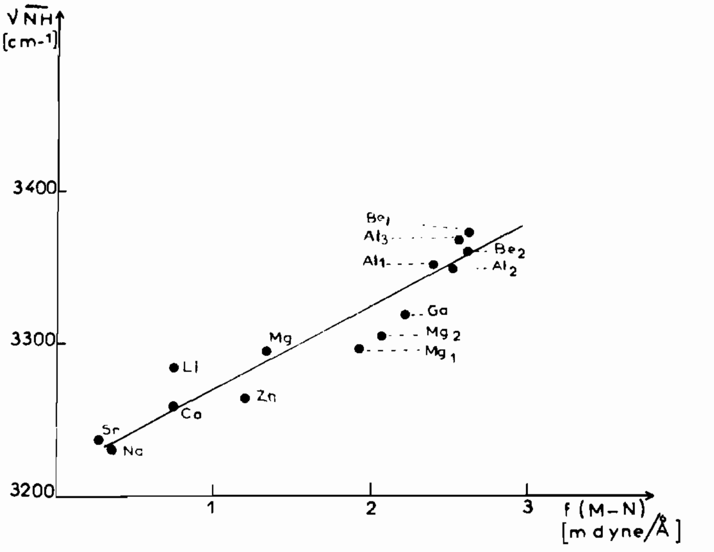

Figure 4. Relationship between the average N–H stretching frequency and metal nitrogen force constant for 15 inorganic amides. Al_1, Al_2 and Al_3 correspond to $NaAl(NH_2)_4$, $KAl(NH_2)_4$ and $LiAl(NH_2)_4$ respectively. Mg_1 and Mg_2 correspond to $Na_2Mg(NH_2)_4$ and $KMg(NH_2)_4$ respectively.

power (Ze/r^2) of the nitrogen bonded metal ion. We have accumulated some spectroscopic data on inorganic amides and it appeared interesting to correlate the NH stretching frequencies and metal–nitrogen force constants. The results are shown in Table IV [where the average NH stretching frequencies are compared to metal–nitrogen stretching frequencies and force constants]; some metal–nitrogen stretching force constants have been determined previously (f Ga–N (4) and f Be–N (5)) or in this work (f Zn–N) using Wilson's method. The other values given in Table IV are calculated in a very approximative manner using a diatomic molecule model consisting of a metal atom and NH_2 group: $K = 4\pi^2c^2\bar{\nu}^2\mu$ where $\bar{\nu}$ is the average metal–nitrogen stretching frequency and the reduced mass ($\mu = \frac{m_M\, m_{NH_2}}{m_M + m_{NH_2}}$.) A comparison with more rigorous calculations shows that the error probably does not exceed 5 to 10%. A diatomic model approach for Ga–N stretching force constant gives 2.05 instead of 2.11

md/Å, for Be–N 2.5 instead of 2.63 md/Å and for Zn–N 1.09 instead of 1.20 md/Å.

The relationship νNH–f_{M-N} is illustrated in Figure 4: the points follow roughly a straight line indicating a variation of 55 cm^{-1} of the NH stretching frequency while the M–N stretching force constant increases by 1 md/Å. This trend, *i.e* an increase of the NH stretching frequency with increasing force or covalency of the metal–nitrogen bond is expected. Alternative formulation of the observed trend is that the stretching frequency decrease is proportional to the charge density increase on the nitrogen atom. Finally, it should be pointed out that these inorganic amides are well suited for correlations with metal–ligand interaction since there is no hydrogen bonding between the NH_2 groups and the environment. The intermolecular effects, however, exist as shown by different splitting of the NH stretching frequencies ($\Delta\nu$ in Table IV) and non-equivalent NH_2 groups. They may be at least partially responsible for the dispersion of the points of Figure 4.

Acknowledgments

The authors are indebted to Dr. Palvadeau and Mr Leroy for experimental help.

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