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VIBRATIONAL SPECTRA AND FORCE CONSTANTS OF PURE AMMINE COMPLEXES

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A. INTRODUCTION

Ammine complexes, especially transition metal ammine complexes, are among the best known complex compounds. The vibrational spectra are now generally well understood and the controversies concerning the assignment of bands in the region around 800 cm^{-1} as well as in the range 500—300 cm^{-1}

have been resolved (see for example refs. 1—6). Recently some assignment problems also have been solved with the help of isotopic data. Force constant calculations for ammine complexes have been based mainly upon IR frequencies and the Urey—Bradley potential function. For many complexes a comparison of the results reported in the literature reveals large discrepancies (cf. ref. 4). Only in recent years has it been possible to obtain reliable force constants by using metal isotope, $^{14}N/^{15}N$, and H/D shifts.

It is the aim of the present paper to give a critical review of vibrational spectroscopic data and force constants for ammine complexes containing only ammonia ligands in the first coordination sphere. Isotopic data, solid state and outer-ion effects, lattice vibrations, and vibronic spectra will also be considered. Metal—nitrogen stretching force constants determined by using appropriate models will be correlated with bond lengths, stability constants, ligand field stabilization energies, and total bond energies.

B. SYMMETRY AND NORMAL MODES OF THE COMPLEX IONS

Many compounds with six NH_3 ligands coordinated to a central atom have cubic structures (cf. ref. 7), and the site symmetries of the complex ions in the crystal are the same as those for the free ions. The $[M(NH_3)_6]^{n+}$ ions have O_h symmetry if one assumes weak libration of the NH_3 ligands around the M—N axes. There is some evidence from incoherent inelastic neutron scattering experiments that these librations occur in compounds with weak hydrogen bonding (see Section F). If one fixes the NH_3 groups at special positions, the symmetry of the complex ion is reduced. The highest possible symmetry for any rigid configuration is D_{3d}. In this case two opposite ammine groups are in the staggered position. The distributions of the 69 vibrational modes of $[M(NH_3)_6]^{n+}$ ions among the species of the point groups O_h and D_{3d} are given in Table 1.

In the case of a tetracoordinated complex with a tetrahedral framework it is possible to treat the whole complex with rigid NH_3 ligands according to a model of T_d symmetry (staggered configuration). The 45 normal modes are classified as given in Table 1.

The NH_3 groups at fixed positions necessarily violate the D_{4h} symmetry of tetracoordinated complexes with a square-planar framework. If two opposite ammine groups are assumed to be in the staggered position, the symmetry of the whole complex ion is C_{4h}; if they are in the eclipsed position, the symmetry is C_{4v}. Table 1 shows the distribution of the vibrational modes among the species of D_{4h} (assuming weak libration) and C_{4h}. Linear diammine complexes have D_{3h} symmetry if one assumes rotating ammine groups. If the ligands are rigid, the highest symmetry is D_{3d} (Table 1).

Since nearly all authors describe the vibrational spectra of hexammine complexes in terms of octahedral symmetry, of square-planar tetrammine complexes in terms of D_{4h} symmetry, and of linear diammine complexes with the nomenclature for D_{3h}, we will refer only to these point groups when we dis-

TABLE 1

Distribution of the vibrational modes of ammine complex ions among the species of the point groups O_h, D_{3d}, T_d, D_{4h}, C_{4h}, D_{3h}, D_{3d}

	Total	Framework (P.M.M.)[a]	ν_s(NH)	ν_{as}(NH)	δ_s(HNH)	δ_{as}(HNH)	$\rho_r(NH_3)$	$\tau(NH_3)$	ν(MN)	δ(NMN)
$[M(NH_3)_6]^{n+}$ (O_h)										
A_{1g} (R)	3	1	1		1				1	
A_{1u} (—)	1							1		
E_g (R)	3	1	1		1				1	
E_u (—)	1							1		
F_{1g} (—)	4			1		1	1	1		
F_{1u} (IR)	7	2	1	1	1	1	1		1	1
F_{2g} (R)	4	1		1		1	1			1
F_{2u} (—)	4	1		1		1	1			1
$[M(NH_3)_6]^{n+}$ (D_{3d})										
A_{1g} (R)	7		1	1	1	1	1		1	1
A_{1u} (—)	5			1		1	1	1		1
A_{2g} (—)	4			1		1	1	1		
A_{2u} (IR)	7		1	1	1	1	1		1	1
E_g (R)	11		1	2	1	2	2	1	1	1
E_u (IR)	12		1	2	1	2	2	1	1	2
$[M(NH_3)_4]^{n+}$ (T_d)										
A_1 (R)	3	1	1		1				1	
A_2 (—)	1							1		
E (R)	4	1		1		1	1			1
F_1 (—)	4			1		1	1	1		
F_2 (R,IR)	7	2	1	1	1	1	1		1	1
$[M(NH_3)_4]^{n+}$ (D_{4h})										
A_{1g} (R)	3	1	1		1				1	
A_{1u} (—)	1							1		
A_{2g} (—)	3			1		1	1			
A_{2u} (IR)	4	1		1		1	1			1
B_{1g} (R)	3	1	1		1				1	
B_{1u} (—)	1							1		
B_{2g} (R)	4	1		1		1	1			1
B_{2u} (—)	4	1		1		1	1			1
E_g (R)	4			1		1	1	1		
E_u (IR)	7	2	1	1	1	1	1		1	1

TABLE 1 (continued)

	Total	Framework (P.M.M.)[a]	ν_s(NH)	ν_{as}(NH)	δ_s(HNH)	δ_{as}(HNH)	ρ_r(NH$_3$)	τ(NH$_3$)	ν(MN)	δ(NMN)
$[M(NH_3)_4]^{n+}$ (C_{4h})										
A_g (R)	6		1	1	1	1	1		1	
A_u (IR)	5			1		1	1	1		1
B_g (R)	7		1	1	1	1	1		1	1
B_u (—)	5			1		1	1	1		1
E_g (R)	4			1		1	1	1		
E_u (IR)	7		1	1	1	1	1		1	1
$[M(NH_3)_2]^{n+}$ (D_{3h})										
A_1' (R)	3	1	1		1				1	
A_1'' (—)	1							1		
A_2'' (IR)	3	1	1		1				1	
E'(R,IR)	4	1		1		1	1			1
E'' (R)	3			1		1	1			
$[M(NH_3)_2]^{n+}$ (D_{3d})										
A_{1g} (R)	3		1		1				1	
A_{1u} (—)	1							1		
A_{2u}(IR)	3		1		1				1	
E_g (R)	3			1		1	1			
E_u (IR)	4			1		1	1			1

[a] Point mass model.

cuss the spectra. The designation of the vibrational modes given in Table 1 and used throughout the paper follows the conventional pattern (cf. ref. 3); δ_{as} is equivalent to δ_d (or δ_e), $\tau(NH_3)$ designates a torsional mode of two ammine groups. The discussion of the spectra in the next two sections (C and D) includes only internal vibrations of the complex ions. External vibrations will be treated in Section F.

C. VIBRATIONAL SPECTRA OF AMMINE COMPLEXES OF MAIN GROUP METAL IONS

(i) Alkali metal ions

The dissolution of alkali and alkaline-earth iodide and bromide in liquid ammonia is characterized by the variation of thermodynamic properties of the solvent, which indicates strong solvent—solution interactions (cf. ref. 8). Vibrational spectroscopic investigations showed the formation of ammine complexes in these solutions [9,10]. Leonard et al. [9] obtained the IR and Raman spectra of a sodium iodide solution in NH_3 and assigned the bands to the vibrational modes of the complex ion $[Na(NH_3)_4]^+$ as follows: δ_{as}(HNH): 1525, δ_s(HNH): 1105, $\rho_r(NH_3)$: ~500 cm^{-1}(all IR), ν(NaN): 435, δ(NNaN): 103 cm^{-1}(Raman). The authors mentioned that the presence of other ionic species such as $[Na(NH_3)_3]^+$ and $[Na(NH_3)_2]^+$ cannot be completely eliminated. In our opinion it is not clear whether all measured bands are really due to the tetrammine sodium ion. Compared to other ammine complexes the NH_3 rocking and the skeletal deformation frequencies are unusually low, especially when considering the relatively high frequency of the metal—nitrogen stretching vibration.

Several phase diagrams for alkali halide and ammonia mixtures (for literature citations see refs. 11 and 12) revealed the formation of ammoniates crystallizing at low temperatures. The structures of NaX, 5 1/7 NH_3 (X = Cl,Br) are known [13]. The crystals contain $[Na(NH_3)_5]^+$ and $[Na(NH_3)_6]^+$ units in the ratio of seven to one. For pentacoordinated Na^+, the Na—N distances vary between 2.47 and 2.53 Å, whereas the distances in the hexammine complex are equal (2.61 Å). Régis et al. [11] investigated the IR and Raman spectra of NaBr, 5 1/7 NH_3; NaBr, 5 1/7 ND_3; and NaI, 5 1/7 NH_3 at liquid nitrogen temperature. By comparison of the spectra they concluded that the iodide is isomorphous to the chloride and bromide. IR bands in the region 460—260 cm^{-1} (H/D frequency ratio: 1.12 compared to $(\mu_{NH_3}/\mu_{ND_3})^{1/2} = 1.08$) due to sodium nitrogen stretching vibrations are split into several components. This splitting was explained by the existence of different Na—N distances in the $[Na(NH_3)_5]^+$ complexes. The Raman bands occurring between 492 and 353 cm^{-1} were not assigned to Na—N stretching but to $\tau(NH_3)$ modes, since ν_H/ν_D was found to be ~1.33. A large number of IR bands between 1000 and 500 cm^{-1} were tentatively attributed to rocking vibrations; bands occurring in the region 1174—1040 cm^{-1} were assigned to δ_s(HNH), those around 1635 cm^{-1}

to δ_{as}(HNH). The bands in the region of the N—H stretching vibrations were interpreted by taking into consideration the influence of hydrogen bonding with the anions on the orientation of the ammonia ligands.

Régis and Corset [12] reported the vibrational spectra of $^{7}LiNO_3$, 2 NH_3; $^{6}LiNO_3$, 2 NH_3; $^{7}LiNO_3$, 2 ND_3; $^{7}LiNO_3$, 4 NH_3; $^{6}LiNO_3$, 4 NH_3; $^{7}LiNO_3$, 4 ND_3 at −180°C. Most of the features of the spectra could be correlated with the existence of complex ions $[Li(NH_3)_n]^+$ with different Li—N distances in the crystalline structure. Bands in the region 570—460 were assigned to Li—N stretching vibrations.

(ii) Alkaline-earth metal ions

The IR spectra of $[Be(NH_3)_4]Cl_2$ and $[Be(ND_3)_4]Cl_2$ have been determined by Grigor'ev et al. [14—16], who also reported those of the nitrate and the perchlorate [16,17]. The tetrammine beryllium complex was assumed to have a tetrahedral structure. From a comparison of the spectra it was concluded that beryllium fluoride ammine should be formulated as $[Be(NH_3)_4][BeF_4]$ [15]. In the Raman spectrum of $[Be(NH_3)_4]Cl_2$, Grigor'ev and Sipachev [14] observed a line at 488 cm^{-1} which they assigned to the totally symmetric Be—N stretching vibration. A band occurring at 493 cm^{-1} in the IR spectrum was also assigned to this mode. Because of the fact that a very intense and broad band at ~900 cm^{-1} in the IR spectra of tetrammine beryllium chloride, nitrate, and perchlorate has a ν_H/ν_D ratio of about 1.1, it was assigned to ν_{as}(BeN)(F_2). In our opinion this assignment is incorrect. On the one hand, symmetric and antisymmetric M—N stretching frequencies of tetrahedral ammine complexes should not differ so much; on the other hand a ν(MN) band at ~900 cm^{-1} indicates an unreasonably high bond order.

Grigor'ev et al. [16,17] were the first to report the IR spectra of normal and fully deuterated hexammine magnesium chloride and nitrate. Recently, Plus made an extensive investigation of the IR [18—20] and Raman [20] spectra of $[Mg(NH_3)_6]Cl_2$ and $[Mg(ND_3)_6]Cl_2$. His data which are listed in Tables 2 and 3 differ somewhat from those of the former authors. Since many bands are doubled, dissymmetric or present shoulders, Plus [20] concluded that the H atoms are at fixed positions. He assumed D_{3d} symmetry for the whole complex ion.

To our knowledge, the only vibrational spectroscopic data of $[Ca(NH_3)_6]Cl_2$ and $[Sr(NH_3)_6]Cl_2$ were determined by Sipachev and Grigor'ev [16] (Table 2). These authors measured the IR spectra down to 400 cm^{-1}. The rocking frequencies were used to estimate the metal—nitrogen stretching force constant (Simple Valence Force Field). From these f(MN) data (Section H(iii)) we calculated ν_{as}(CaN) and ν_{as}(SrN) as given in Table 2.

(iii) Group IIIA metal ions

Ammonia adducts of the type $BX_3 \cdot NH_3$ and $AlX_3 \cdot NH_3$ (X = halide) will not be considered here. The IR spectra of $[Al(NH_3)_6]Cl_3$, $[Al(ND_3)_6]Cl_3$,

TABLE 2

Infrared spectra of octahedral hexammine complexes (cm^{-1}) (unless otherwise stated: frequencies due to F_{1u} vibrations)

	$\nu_{as}(NH)$		$\nu_s(NH)$	$\delta_{as}(HNH)$	$\delta_s(HNH)$	$\rho_r(NH_3)$	$\nu_{as}(MN)$	$\delta_{as}(NMN)$
$[Mg(NH_3)_6]Cl_2$ [a]	3353		3210	1603	1170	660	363	198
$[Mg(ND_3)_6]Cl_2$ [a]	2503		2340	1175	897	512	343	185
$[Ca(NH_3)_6]Cl_2$ [b]		3314		1590	1145	520	(274) [c]	
$[Sr(NH_3)_6]Cl_2$ [b]		3320		1596	1113	470	(247) [c]	
$[Al(NH_3)_6]Cl_3$		3180 [b]		1611 [b]	1357 [b] 1339 [b]	791 [b]	502 [d]	293 [d]
$[Al(ND_3)_6]Cl_3$		2300 [b]		1171 [b]	1033 [b]	632 [b]	462 [d]	
$[Y(NH_3)_6]Cl_3$	3290 [b]		3194 [b]	1605 [b]	1224 [b]	620 [b]	400 [d]	
$[Y(ND_3)_6]Cl_3$	2470 [b]		2380 [b]	1176 [b]	937 [b]	471 [b]		
$[V(NH_3)_6]Cl_2$ [c,f]	(3310)		(3206)	(1605)	(1243)	(713)	(429) (390) (386)	
$[Cr(NH_3)_6]Cl_3$ [g]	3257	3185	3130	1630	1307	748	495 473 456	
$[Cr(ND_3)_6]Cl_3$ [g]	2415	2347	2283	1171	1007	603	455 435 424	
$[^{50}Cr(NH_3)_6](NO_3)_3$ [h] $[^{53}Cr(NH_3)_6](NO_3)_3$ [h]	3310	3250	3190	1627	1290	770	471.0 467.0	270 267
$[Mn(NH_3)_6]Cl_2$	~3340 [i]		3160 [i]	1608 [i]	1146 [i]	592 [i]	502 [j]	165 [j]
$[Fe(NH_3)_6]Cl_2$	3335 [i]		3175 [i]	1596 [i]	1156 [i]	633 [i]	315 [j]	170 [j]
$[Ru(NH_3)_6]Cl_2$ [k]	3300		3195	1610	1220	769	(437) [f]	
$[Ru(NH_3)_6]Cl_3$ [l]		3077		1618	1368 1342	788	463	283 263
$[Ru(ND_3)_6]Cl_3$ [l]	2424		2342	1198	1076 1011	611	417	
$[Os(NH_3)_6]OsBr_6$ [l]		3125		1595	1339	818	452	256
$[Os(ND_3)_6]OsBr_6$ [l]		2320		1147	1027	621	410	
$[Os(^{15}NH_3)_6]OsBr_6$ [l]							440	
$[Co(NH_3)_6]Cl_2$	3330 [m]		3250 [m]	1602 [n]	1163 [n]	654 [n]	325 [j]	192 [j]

Table 2 (continued)

	ν_{as}(NH)		ν_s(NH)	δ_{as}(HNH)	δ_s(HNH)	ρ_r(NH$_3$)	ν_{as}(MN)	δ_{as}(NMN)
$[Co(NH_3)_6]Cl_3$ [o]	3240		3160	1619	1328.5	831	498 477 449	331
$[Co(ND_3)_6]Cl_3$ [h]	2440		2300	1165	1020	667	462 441.5 415.5	294
$[Co(^{15}NH_3)_6]Cl_3$ [o]	3230		3155	1618	1323.5	829	488.5 468 438	326
$[Rh(NH_3)_6]Cl_3$ [l]		3200		1618	1352 1318	845	472	302 287
$[Rh(ND_3)_6]Cl_3$ [l]	2410		2326	1151	1035 1018	658	433	278 256
$[Ir(NH_3)_6]Cl_3$ [i]		3155		1587	1350 1323	857	475	279 264
$[Ir(ND_3)_6]Cl_3$ [l]	2398		2326	1161	1053 1033	662	440	255 236
$[Ni(NH_3)_6]Cl_2$						684 [l]	334.5 [j]	215 [j]
$[^{58}Ni(NH_3)_6]Cl_2$	3345 [o]		3190 [o]	1607 [o]	1176 [o]	685 [o]	335.2 [o,p]	217 [o,p]
$[^{62}Ni(NH_3)_6]Cl_2$						682 [p]	333 [p]	214 [p]
$[Ni(ND_3)_6]Cl_2$ [p]	2498		2350	1159	896	620	315.5	206
$[Ni(^{15}NH_3)_6]Cl_2$ [o]	3340		~3185	1605	1174	683	327.5	214
$[Pt(NH_3)_6]Cl_4$ [q]	3150		3050	1565	1370	960	564 (A_{1g}) 530 516 (F_{1u})	318
$[Zn(NH_3)_6]Cl_2$	3350 [f]		3220 [i]	1596 [n]	1146 [n]	645 [n]	300 [n]	
$[Cd(NH_3)_6]Cl_2$				1585 [n]	1091 [n]	613 [n]	298 [n]	

[a] Ref. 20; [b] ref. 16; [c] calculated from estimated force constant [16]; [d] ref. 17; [e] ref. 21; [f] Uncertain, see text; [g] ref. 26; [h] ref. 37; [i] this work; [j] ref. 44; [k] ref. 46; [l] ref. 47; [m] ref. 28; [n] ref. 43; [o] ref. 65; [p] ref. 84; [q] ref. 101.

TABLE 3

Raman spectra of octahedral hexammine complexes (cm^{-1})

	ν_{as}(NH)	ν_s(NH)	δ_{as}(HNH)	δ_s(HNH)	$\rho_r(NH_3)$	ν(MN)	δ(NMN)
$[Mg(NH_3)_6]Cl_2$ [a]	3359 ~3300 (F_{2g})	3258 (A_{1g}) 3168 (E_g)	1568 (F_{2g})	1229 (A_{1g}) 1142 (E_g)	650 (F_{2g})	335 (A_{1g}) 243 (E_g)	188 (F_{2g})
$[Mg(ND_3)_6]Cl_2$ [a]	2504 2466 (F_{2g})	2367 (A_{1g}) 2320 (E_g)	1153 (F_{2g})	936 (A_{1g}) 876 (E_g)	491 (F_{2g})	312 (A_{1g}) 227 (E_g)	176 (F_{2g})
$[Al(NH_3)_6](NO_3)_3$						470 (A_{1g}) [b]	
$[Cr(NH_3)_6]^{3+}$ [c,d]						465 (A_{1g}) 412 (E_g)	260 (F_{2g})
$[Mn(NH_3)_6]^{2+}$						330 (A_{1g}) [c,e]	
$[Ru(NH_3)_6]^{3+}$ [c,f]						500 (A_{1g}) 475 (E_g)	248 (F_{2g})
$[Ru(ND_3)_6]^{3+}$ [c,f]						466 (A_{1g}) 430 (E_g)	228 (F_{2g})
$[Co(NH_3)_6]^{2+}$ [c,e]						357 (A_{1g}) ~255 (E_g)	
$[Co(NH_3)_6]^{3+}$ [c,g]				1417 (A_{1g}) 1335 (E_g)	833 (F_{2g})	490 (A_{1g}) 440 (E_g)	317 (F_{2g})
$[Co(ND_3)]^{3+}$ [c,g]				1068 (A_{1g}) 1019 (E_g)	644 (F_{2g})	460 (A_{1g}) 407 (E_g)	278 (F_{2g})
$[Co(NH_3)_6]Cl_3$ [g]		3190 (A_{1g},E_g)		1303 1328 (E_g)	830 (F_{2g})	500 (A_{1g}) 490 (F_{1u}) 445 (E_g)	330 (F_{1u}) 308 (F_{2g})
$[Co(ND_3)_6]Cl_3$ [g]		2370 (A_{1g},E_g)		1061 (A_{1g}) 1005 (E_g)	646 (F_{2g})	464 (A_{1g}) 410 (E_g)	281 (F_{2g})
$[Rh(NH_3)_6]^{3+}$ [c,h]		3140 (A_{1g},E_g)		~1330 (E_g)		516 (A_{1g}) 480 (E_g)	240 (F_{2g})
$[Rh(ND_3)_6]^{3+}$ [c,f]						489 (A_{1g}) 455 (E_g)	220 (F_{2g})
$[Ir(NH_3)_6]^{3+}$ [c,f]						527 (A_{1g}) 500 (E_g)	262 (F_{2g})
$[Ir(ND_3)_6]^{3+}$ [c,f]						498 (A_{1g}) 471 (E_g)	245 (F_{2g})

TABLE 3 (continued)

	ν_{as}(NH)	ν_s(NH)	δ_{as}(HNH)	δ_s(HNH)	ρ_r(NH$_3$)	ν(MN)	δ(NMN)
$[\mathrm{Ni(NH_3)_6}]^{2+}$ [c]	(3320) [i,j]					370 (A_{1g}) [k]	235 (F_{2g}) [k]
	(3210) [i,j]					265 (E_g) [l]	
$[\mathrm{Pt(NH_3)_6}]^{4+}$ [c,m]						569 (A_{1g})	
						545 (E_g)	
$[\mathrm{Pt(NH_3)_6}]\mathrm{Cl_4}$ [n]						$\left.\begin{array}{l}562\\570\end{array}\right\}(A_{1g})$	288 (F_{2g})
						$\left.\begin{array}{l}544\\532\end{array}\right\}(E_g)$	
$[\mathrm{Cd(NH_3)_6}]^{2+}$ [c]	(3372) [j,o]					342 (A_{1g}) [c]	
	(3287) [j,o]						

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[a] Ref. 20; [b] ref. 17; [c] aqueous solution; [d] ref. 34; [e] ref. 44; [f] ref. 47; [g] ref. 32; [h] refs. 27, 80; [i] ref. 27; [j] uncertain; [k] ref. 84; [l] refs. 44, 65; [m] ref. 102; [n] ref. 101; [o] ref. 85.

$[Al(NH_3)_6](NO_3)_3$, and $[Al(ND_3)_6](NO_3)_3$ were reported in refs. 16 and 17; $\nu_s(AlN)(A_{1g})$ was determined from the Raman spectrum of solid $[Al(NH_3)_6]Cl_3$ [17]. The data for normal and deuterated hexammine aluminium chloride can be taken from Tables 2 and 3. The vibrational spectra of ammine complexes of zinc, cadmium, and mercury with closed *d* shells will be presented in Section D(vii).

D. VIBRATIONAL SPECTRA OF AMMINE COMPLEXES OF TRANSITION METAL IONS

(i) Group IIIB—VB metal ions

Vibrational spectra of $[Sc(NH_3)_6]^{3+}$ are not yet known. Grigor'ev et al. [16, 17] determined the IR spectra of normal and deuterated $[Sc(NH_3)_5Cl]Cl_2$. By analogy with the skeletal IR and Raman data of $[Al(NH_3)_6]Cl_3$ and $[Al(NH_3)_5Cl]Cl_2$, $\nu_s(ScN)(A_{1g})$ and $\nu_{as}(ScN)(F_{1u})$ were estimated as 410—380 cm^{-1} and 431 cm^{-1}, respectively. The IR spectra of $[Y(NH_3)_6]Cl_3$ and $[Y(ND_3)_6]Cl_3$ were reported [16,17], (Table 2). $\nu_s(YN)(A_{1g}) \sim 350$ cm^{-1} was estimated from the $\nu_s(YO)(A_{1g})/\nu_{as}(YO)(F_{1u})$ ratio of $[Y(H_2O)_6]^{3+}$.

Behrens and Lutz [21] reported IR data for $[V(NH_3)_6]Cl_2$ (Table 2). Three bands at ~400 cm^{-1} were assigned to $\nu(VN)$. We expect the IR active stretching vibration for hexammines with divalent central atoms to be at much lower wavenumbers.

(ii) Group VIB—VIIB metal ions

Infrared spectra of $[Cr(NH_3)_6]Cl_3$ have been reported several times [22—34] and that of $[Cr(ND_3)_6]Cl_3$ by Tanaka et al. [26]. The site symmetry of the complex ion in the crystal is C_s or C_1 (cf. ref. 32), and hence all degeneracies are removed in the solid state. Most authors found three bands in the region of the N—H stretching vibrations. The triplet was not attributed to site symmetry splitting, but to Fermi resonance of one N—H stretching mode with $2\delta_{as}$(HNH) (cf. ref. 27). Splitting of bands pertaining to δ_s(HNH) and $\rho_r(NH_3)$ were observed by Siebert and Eysel [32] (see also ref. 25). Two IR bands in the region of the metal—nitrogen stretching vibrations were reported [31] and three bands in refs. 25 and 26 (Table 2) and ref. 32. Blyholder and Vergez [25] pointed out that two of the bands may be due to interactions of the complex with its lattice. Tanaka et al. [26] stated that the main cause for the splitting is the formation of hydrogen bonds. Swaddle et al. [33] concluded that two weak bands arise from the activation of the IR inactive mode A_{1g} owing to the monoclinic environment. In their opinion, the duality of the non-degenerate mode may reflect at least two different site-types of $[Cr(NH_3)_6]^{3+}$ in the unit cell. Siebert and Eysel [32] did not observe a band at ~495 cm^{-1}, but they found a shoulder on the lower frequency side of the band at ~470 cm^{-1} and an additional band at 417 cm^{-1}. They assigned the doublet to ν_{as}-

(CrN)(F_{1u}) and the latter band to an E_g mode. Allen and Hush [31] reported a threefold splitting of a band in the region of δ_{as}(NCrN)(F_{1u}); the other authors found only a single band.

The IR spectra of $[Cr(NH_3)_6]Br_3$ and $[Cr(NH_3)_6]I_3$ which show similar band splittings as the spectrum of the chloride have been given [26,27,32]. None of the bands in the spectrum of the perchlorate is split [26,27,33,35] (cubic crystal structure [36]), the same is also true for the pentachlorocuprate [31—33]. Unlike Tanaka et al. [26] and the present authors [37], Siebert and Eysel [32] observed a splitting of some bands in the IR spectrum of $[Cr(NH_3)_6](NO_3)_3$, the structure of which is not yet known. The spectra of $[^{50}Cr(NH_3)_6](NO_3)_3$ and $[^{53}Cr(NH_3)_6](NO_3)_3$ have been reported in ref. 37 (Table 2).

Infrared data (partly rudimentary) of $[Cr(NH_3)_6]^{3+}$ with the following anions have also been reported: $TlBr_6^{3-}$ [32], SiF_6^{2-}, BF_4^-, PF_6^- [27], MnF_6^{3-} [38], MnO_4^-, ReO_4^-, CrO_4^{2-} [39], OsO_3N^- [40].

The Raman spectra (He—Ne excitation, 6328 Å) of some hexammine chromium (III) salts and of the normal and fully deuterated complex in aqueous solution are partly superimposed by a phosphorescence spectrum (for further details see Section G). Siebert and Eysel [32] found one polarized and one depolarized line (ν_s(CrN)(A_{1g}), ν(CrN)(E_g)) in the Raman spectrum of $[Cr(NH_3)_6]^{3+}$ (aq.). Besides these lines, Long and Penrose [34] observed an additional depolarized line which was assigned to δ(NCrN)(F_{2g}) (Table 3). The position of two IR and Raman forbidden but vibronically allowed modes ($\rho_r(NH_3)$(F_{2u}), δ(NCrN)(F_{2u})) could be determined from the vibrational structure of the $^2E_g \leftrightarrow A_{2g}$ transition [34,41] (Table 11). Some Raman lines of solid $[Cr(NH_3)_6]CuCl_5$ have been reported [32,33]. The latter reference contains also data for the sulfate, the former for the tetrabromothallate. Some Raman lines of the nitrate in the region of the N—H stretching vibrations are given in ref. 34.

There is some evidence for the existence of ammine molybdenum complexes. Opalovskii and Blokhina [42] investigated the reaction of MoF_6 with liquid ammonia. They stated that the spectrum of a compound formulated as $MoF_5(NH_3)_4$ indicates that the ammine ligands are in the inner coordination sphere. In our opinion it is doubtful whether such Mo^V complexes exist.

Sacconi et al. [43] determined the IR spectra of hexammine manganese (II) chloride, bromide, and iodide. They did not report the vibrational frequencies due to the N—H stretching vibrations and to δ_{as}(NMnN)(F_{1u}). The data for $[Mn(NH_3)_6]Cl_2$ obtained by us (Table 2, for the skeletal frequencies see also ref. 44) differ somewhat from theirs. In the Raman spectrum of $[Mn(NH_3)_6]^{2+}$ in aqueous solution we observed one line [44] which could be unequivocally assigned to ν_s(MnN)(A_{1g}) from depolarization measurements (Table 3).

(iii) Iron, ruthenium, osmium

The IR spectra of $[Fe(NH_3)_6]Cl_2$, Br_2, and I_2 have been reported [43] and also the skeletal data of the chloride salt [44]. As in the case of the manganese complex our data given in Table 2 differ a bit from those in ref. 43. Though the Raman spectrum of $[Fe(NH_3)_6]^{2+}$ in aqueous solution could not be obtained by us, the value for $\nu_s(FeN)(A_{1g})$ = 344 cm^{-1} could be determined quite accurately by graphical interpolation [44]. To our knowledge, no reliable vibrational spectroscopic information of the well known $[Fe(NH_3)_6]^{3+}$ complex is known.

Infrared spectra of hexammine ruthenium (II) chloride, bromide, iodide, and tetrafluoroborate have been reported by Allen and Senoff [45], that of the chloride also by Fairey and Irving [46]. Whereas the latter authors found a band at 437 cm^{-1} which they assigned to $\nu_{as}(RuN)$, Allen and Senoff were not able to detect any band in this region. As in the case of $[V(NH_3)_6]^{2+}$ we expect this mode to be at much lower wavenumbers.

Griffith [47], Vogt et al. [48] as well as Allen et al. [31,45] determined the IR spectrum of $[Ru(NH_3)_6]Cl_3$; Allen also reported data for the pentachlorocuprate [31], bromide, iodide, and tetrafluoroborate [45]. IR data for $[Ru(ND_3)_6]Cl_3$ have been given [45,47]. Allen and Senoff [45] found that the ammonia symmetric deformation and the antisymmetric Ru—N stretching bands, respectively, occur as multiplets. Griffith [47] observed one polarized and two depolarized lines in the Raman spectra of $[Ru(NH_3)_6]^{3+}$ and $[Ru(ND_3)_6]^{3+}$ in H_2O and D_2O, respectively (Table 3). The IR spectra of normal and deuterated $[Os(NH_3)_6]$ $[OsBr_6]$ as well as $\nu_{as}(OsN)$ for $[Os(^{15}NH_3)_6]$ $[OsBr_6]$ have also been reported [47]. Bottomley and Tong [49] measured the IR spectra of the bromide and iodide. Without mentioning the frequencies, they stated that the spectra are similar to those of the ruthenium compound, but with ammonia vibrations approximately 25 cm^{-1} higher in energy.

(iv) Cobalt, rhodium, iridium

Müller, Christophliemk, and Tossidis [50] reported the IR spectrum of $[Co(NH_3)_4](ReO_4)_2$ (Table 4). In the Raman spectrum of this compound they observed a single line (apart from lines pertaining to the anion) which they assigned to $\nu_s(CoN)(A_1)$ (Table 5). Two IR bands of weak intensity (1410 and ~3200 cm^{-1}) were assigned to $2\rho_r(NH_3)$ and $2\delta_{as}(HNH)$, respectively.

Infrared data for $[Co(NH_3)_6]Cl_2$ have been given [22,23,28,29,43,44,51—53]. Different numbers of bands in the region of the N—H stretching vibrations were reported in the literature. The discrepancies may be explained by the fact that for all ammine metal chlorides $\nu(NH)$ bands are very broad. Whereas the frequencies of the bands due to $\delta_s(HNH)$ and $\delta_{as}(HNH)$ given in the literature do not differ essentially, the $\rho_r(NH_3)$ frequencies vary between 634 cm^{-1} [28,51] and 670 cm^{-1} [52], and the $\nu_{as}(CoN)$ data between 318 cm^{-1} [28,51] and 328 cm^{-1} [53]. Our own measurements revealed bands at 655 and 325 cm^{-1}.

The IR spectra of the bromide and iodide have been reported [43,51,53]. The disagreement mentioned above occurs also for these compounds. Patil and Secco [54] determined the IR spectrum of $[Co(NH_3)_6]F_2$. Because of the

TABLE 4

Infrared spectra of tetrahedral tetrammine complexes (cm^{-1}) (unless otherwise stated: frequencies due to F_2 vibrations)

	$\nu_{as}(NH)$	$\nu_s(NH)$	$\delta_{as}(HNH)$	$\delta_s(HNH)$	$\rho_r(NH_3)$	$\nu_{as}(MN)$	$\delta(NMN)$
$[Be(NH_3)_4]Cl_2$ [a]	(3290) [b] (3140) [b]		(1608) [b—d]	(1305) [b—d]	(625) [b—d]	(493) [e]	(290) [c]
$[Be(ND_3)_4]Cl_2$ [a]	(2460) [b] (2315) [b]		(1176) [b—d]	(1012) [b—d]	(520) [b—d]		(278) [c]
$[Co(NH_3)_4](ReO_4)_2$ [f]	3340	3260	1610	1240	693	430	~195
$[Zn(NH_3)_4]I_2$ [g]	3288 (E,F_2)	3227 (A_1) 3177 (F_2)	1700 $(F_1$?) 1596 (E,F_2)	1255 1239.5 (A_1, F_2)	690 610 (E,F_1, F_2)	428.5 423.0 409.7 (F_2)	160 146 (E,F_2)
$[Zn(^{15}NH_3)_4]I_2$ [g]	3286 (E,F_2)	3226 (A_1) 3176 (F_2)	1700 $(F_1$?) 1596 (E,F_2)	1250.5 1234.6 (A_1, F_2)	684 610 (E,F_1, F_2)	418.5 ~414 400.1 (F_2)	160 146 (E,F_2)
$[Cd(NH_3)_4](ReO_4)_2$	3354 [h]	3267 [h]	1617 [h]	1175.5 [h]	670 [h]	369.5 [i]	166 [h], 160 [h]
$[Cd(^{15}NH_3)_4](ReO_4)_2$ [j]	3342	3260	1612	1169	667	360.5	160.5, 153.5

[a] Uncertain (see text); [b] ref. 15; [c] ref. 14; [d] ref. 16; [e] Grigor'ev and Sipachev [14] assigned this band to $\nu_s(BeN)$ (A_1) and a band at 914 cm^{-1} to $\nu_{as}(BeN)$ (F_2)(see text); [f] ref. 50; [g] ref. 65; [h] this work; [i] ref. 44; [j] ref. 115.

TABLE 5

Raman spectra of tetrahedral tetrammine complexes (cm^{-1})

	ν_{as}(NH)	ν_s(NH)	δ_{as}(HNH)	δ_s(HNH)	ρ_r(NH$_3$)	ν(MN)	δ(NMN)
$[Be(NH_3)_4]Cl_2$						488 (A_1) [a]	
$[Co(NH_3)_4](ReO_4)_2$						~405 (A_1) [b]	
$[Zn(NH_3)_4]^{2+}$ [c]	(3268) [d]	(3193) [d]				427 (A_1) [e,f]	
$[Zn(NH_3)_4]I_2$ [g]	3290 (E,F_2)	3234.5 (A_1) 3197 (F_2)	1730 (F_1 ?) 1615, 1600 (E,F_2)	1256, 1242 (A_1,F_2)	688, 611 (E,F_1, F_2)	431.2 (A_1) 411.5 (F_2)	156.5 (E,F_2)
$[Zn(^{15}NH_3)_4]I_2$ [g]	3290 (E,F_2)	3231.5 (A_1) 3197 (F_2)	~1730 (F_1 ?) 1615, 1595 (E,F_2)	1247, 1234 (A_1,F_2)	675, 605 (E,F_1, F_2)	419.5 (A_1) 401.3 (F_2)	
$[^{64}Zn(NH_3)_4]I_2$ [e]						432 (A_1) 412 (F_2)	156 (E,F_2)
$[^{68}Zn(NH_3)_4]I_2$ [e]						431.6 (A_1) 410 (F_2)	155 (E,F_2)
$[Zn(ND_3)_4]I_2$ [c]	2375 (E,F_2)	2366 (A_1) 2307 (F_2)	1166 (E,F_2)	964 (A_1) 956 (F_2)	525 (E,F_2)	400 (A_1) 385 (F_2)	
$[Cd(NH_3)_4](ReO_4)_2$ [h]						386	~170

[a] Ref. 14; [b] ref. 50; [c] aqueous solution; [d] uncertain, Damaschun [85] attributed these lines to $[Zn(NH_3)_6]^{2+}$; [e] ref. 112; [f] ref. 114; [g] ref. 65; [h] ref. 44.

presence of a band at 400 cm^{-1} which was assigned to a metal—fluorine stretching mode, it seems doubtful whether the given formulation is correct.

The present authors [44] determined one polarized and one depolarized line due to $\nu_s(CoN)(A_{1g})$ and $\nu(CoN)(E_g)$ in the Raman spectrum of $[Co(NH_3)_6]^{2+}$ (aq.). Reliable solid state Raman spectra are not yet known. The frequencies reported recently by Grzybek et al. [53] seem to be incorrect. Their skeletal data correspond approximately to those for hexammine cobalt(III).

The most numerous IR investigations of ammine complexes were made for $[Co(NH_3)_6]Cl_3$ (cf. refs. 22—24, 27—29, 31—33, 35, 37, 43, 44, 51, 52, 55—66). For discussions of the controversies appearing in the literature concerning the location of $\nu(CoN)$ the reader is referred to refs. 2 and 3. Whereas some authors observed only one band at ~500 cm^{-1} [27—29,31,59], Nakamoto et al. [60] (cf. ref. 3), Sacconi et al. [43], Siebert and Eysel [32], Swaddle et al. [33], as well as the present authors [37,65] determined three bands at 498, 477, and 449 cm^{-1}. As in the case of $[Cr(NH_3)_6]Cl_3$, the site symmetry of the complex ion in the crystal is C_s or C_1 [67]. This is also true for the bromide, but not for the cubic iodide, where the site symmetry of $[Co(NH_3)_6]^{3+}$ is the same as that for the free ion. In this case only one band at 464 cm^{-1} was observed [68], for contrary statements see refs. 32, 69. Several authors assumed the three bands between 450 and 500 cm^{-1} for $[Co(NH_3)_6]Cl_3$ to be the components of the threefold degenerate $\nu_{as}(CoN)(F_{1u})$ mode (cf. literature citations in ref. 33). Sacconi et al. [43] stated that it is not possible to establish whether the triplet arises from the splitting of the F_{1u} mode or from the activation of other normally inactive modes. Siebert and Eysel [32] excluded the first possibility. In their opinion, the frequency differences are too great. They assigned the bands as follows: 497 and 477 cm^{-1}: $\nu_{as}(CoN)(F_{1u})$, 448 cm^{-1}: $\nu(CoN)(E_g)$. On the other hand Swaddle et al. [33] made the following assignment: 499 and 476 cm^{-1}: $\nu_s(CoN)(A_{1g})$ (cf. $[Cr(NH_3)_6]Cl_3$), 449 cm^{-1}: $\nu(CoN)(E_g)$. The bands at 499 and 449 cm^{-1} agree well with the Raman frequencies of $[Co(NH_3)_6]^{3+}$ (aq.) (494 cm^{-1}(p): $\nu_s(CoN)(A_{1g})$, 442 cm^{-1}(dp): $\nu(CoN)(E_g)$). In our opinion, the coincidence may be accidental and is not unequivocal proof of the correct assignment of the three bands in the IR spectrum of $[Co(NH_3)_6]Cl_3$. One would expect that at least one of the three bands represents the IR active mode $\nu_{as}(CoN)(F_{1u})$. The transition moment of this mode should be greater than the moments of the IR inactive modes $\nu_s(CoN)(A_{1g})$ and $\nu(CoN)(E_g)$. Recently we have reported the IR spectrum of $[Co(NH_3)_6]Cl_3$, $[Co(ND_3)_6]Cl_3$, and $[Co(^{15}NH_3)_6]Cl_3$ (Table 2) [37,65]. Figure 1 shows that all three bands under consideration for the three compounds have nearly equal intensities and shapes. The H/D and the $^{14}N/^{15}N$ isotope shifts, respectively, are equal within the error limits. If one tentatively assigns the IR bands of $[Co(NH_3)_6]Cl_3$ at 498 and 449 cm^{-1} to the Raman active A_{1g} and E_g modes, the isotope shifts of these bands can be calculated on the basis of the Point Mass Model (Section H(iii)). It has been shown [65] that measured and calculated $^{14}N/^{15}N$ shifts of the lower frequency band agree approximately within the error limits, whereas the calculated shift of the

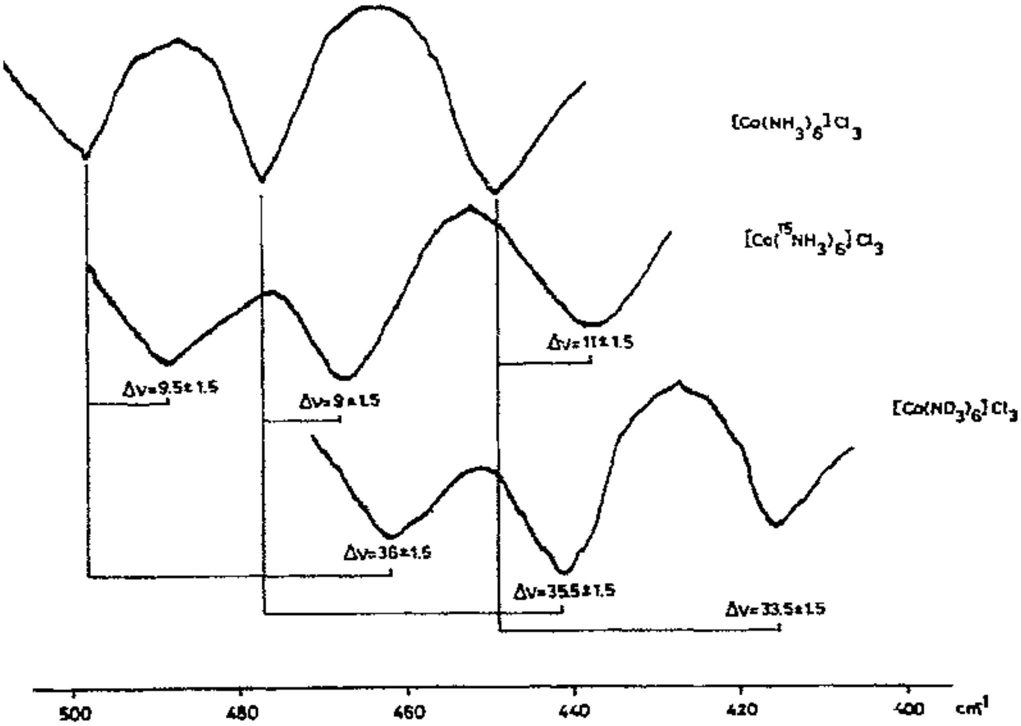

Fig. 1. IR spectra of $[Co(NH_3)_6]Cl_3$, $[Co(^{15}NH_3)_6]Cl_3$ and $[Co(ND_3)_6]Cl_3$ in the range 500—400 cm^{-1}.

higher frequency band is clearly greater than the measured one. Similar relations, though less unequivocal, hold for the H/D shifts [37]. All facts strongly support the assignment of the triplet to components of $\nu_{as}(CoN)(F_{1u})$.

IR spectroscopic information for $[Co(ND_3)_6]Cl_3$ may also be found in refs. 28, 29, 32, 43, 52, 58—60 and 64, data for $[Co(NH_3)_6]Br_3$ in refs. 27, 30, 32, 35, 43, 51, 56, 57, 68 and 70, for $[Co(NH_3)_6]I_3$ in refs. 27, 32, 35, 43, 51, 56, 57, 64, 68 and 71 for the nitrate in refs. 32, 35, 64 and 72, for $CuCl_5^{3-}$ in refs. 31, 32, 61, 63 and 73, for ClO_4^- in refs. 27, 35 and 64, for $InCl_6^{3-}$, $PbCl_6^{2-}$, $BiCl_6^{3-}$ and $TlCl_6^{3-}$ (only $\delta_{as}(NCoN)(F_{1u})$ [70]; $SbCl_6^{3-}$ [70,74]; $TlBr_6^{3-}$ [32]; F^-, SiF_6^{2-}, BF_4^-, PF_6^-, [27]; MnO_4^- [39,75]; ReO_4^- [39]; $C_2O_4^{2-}$ [22]; MnF_6^{3-} [38]; $CdCl_5^{3-}$ [73]; $Co(CN)_6^{3-}$ [76]; OsO_3N^- ($\rho_r(NH_3)$) [40]; $ZnCl_4(Cl)$ [73]. Viltange [62] reported the IR spectra of hexammine cobalt (III) with 25 different anions (incorrect assignment of $\nu_{as}(CoN)$). Infrared data for $[Co(ND_3)_6]^{3+}$ with Br^-, I^-, NO_3^-, $TlBr_6^{3-}$ and $CuCl_5^{3-}$ as anions have been given in refs. 32, 64 and 72.

The IR intensity of bands due to $\nu_{as}(CoN)$ in hexammine cobalt (III) salts is remarkably low. Shimanouchi and Nakagawa [28] tried to explain this fact by the following consideration: They found for a series of ammine complexes that the intensity of $\nu_{as}(MN)$ increases as the M—N stretching force constant decreases. According to ref. 28, this may be due to an increase in ionic character of the M—N bond, causing a larger transition moment. On the other hand, compounds like $[Co(NH_3)_5Cl]Cl_2$ present intense IR bands due to cobalt—nitrogen stretching modes (cf. refs. 3, 28, 30, 60), whereas the properties of the Co—N bonds are similar as those of $[Co(NH_3)_6]^{3+}$. It should be emphasized that the factors governing the intensity of a band are more complex than a simple change in the ionic character. Terrasse et al. [27] stated that the intensity of the bands under consideration is strongly dependent on the anion. They explained the intensity differences in terms of different dipole effects on the N—H bonds by the anions. The experimental results given in ref. 27 could be only partly confirmed by Siebert and Eysel [32].

Raman spectra of $[Co(NH_3)_6]^{3+}$ in aqueous solution have been reported by Bose and Datta [77], Haas and Hall [78], Krauzman [79], Siebert and Eysel [32] as well as by Swaddle et al. [33], those of $[Co(ND_3)_6]^{3+}$ in D_2O can be found in refs. 32, 78. The early data given [77] turned out to be incorrect. References 78 and 79 reported two lines due to $\nu_s(CoN)(A_{1g})$ and $\nu(CoN)(E_g)$, respectively; the position of $\delta(NCoN)(F_{2g})$ is reported in refs. 32 and 33, which also include some ammonia stretching [33] and deformation modes [32,33], and $\rho_r(NH_3)(F_{2g})$ [32]. Solid state Raman spectra of the chloride, bromide, and iodide are also given in these references [32,33]. Reference 32 contains Raman data for the normal and deuterated complex with the following anions: Cl^-, Br^-, I^-, NO_3^-, $TlBr_6^{3-}$ and $CuCl_5^{3-}$. Barrowcliffe et al. [70] determined the low frequency range of the Raman spectra of hexammine cobalt(III) with Br^-, $InCl_6^{3-}$, $BiCl_6^{3-}$, $SbCl_6^{3-}$ and $TlCl_6^{3-}$ as anions. For incoherent inelastic neutron scattering data (I.I.N.S.) of $[Co(NH_3)_6]I_2$, $[Co(NH_3)_6]Cl_3$, and $[Co(NH_3)_6]I_3$ see Section F.

Infrared frequencies for $[Rh(NH_3)_6]Cl_3$ have been listed [27,31] (skeletal vibrations), [47,80] and those for the deuterated compound in ref. 47. In the region >800 cm^{-1} the reported data differ considerably: Griffith [47] found a single band in the region of the N—H stretching vibrations (3200 cm^{-1}), Poulet and Mathieu [80] (see also ref. 27) determined two bands at 3140 and 3230 cm^{-1}. Whereas these authors assigned one band to $\delta_s(HNH)$ (1320 cm^{-1}), Griffith [47] reported a doublet (1352 and 1318 cm^{-1}). According to Griffith, $\delta_{as}(HNH)$ and $\rho_r(NH_3)$ absorb at 1618 and 845 cm^{-1}, respectively; according to Poulet and Mathieu at 1550 and 830 cm^{-1}. In the $\delta_{as}(NRhN)$ range, one band is reported [27,80], whereas in ref. 47 it is stated as a doublet and in ref. 31 as a triplet. IR spectra of the fluoride, iodide, and perchlorate can be found in ref. 27, that of the pentachlorocuprate in ref. 31, and that of the hexafluoromanganate (III) in ref. 38.

The first Raman spectra of $[Rh(NH_3)_6]^{3+}$ in aqueous solution were obtained by Mathieu [81,82]. Two weak lines at 560 and 390 cm^{-1} [81] turned out to be incorrect. The position of $\nu_s(RhN)(A_{1g})$, $\nu(RhN)(E_g)$, and $\delta(NRhN)(F_{2g})$ previously [82] reported at 500, 475, and 270 cm^{-1}, was later on [27,80] corrected to 515, 480 and 240 cm^{-1}. This is in excellent agreement with the data of Griffith [47], who also determined the Raman spectrum of $[Rh(ND_3)_6]^{3+}$ in D_2O (Table 3).

Only one vibrational spectroscopic investigation of $[Ir(NH_3)_6]^{3+}$ has been given in the literature: the IR spectra of normal and deuterated $[Ir(NH_3)_6]Cl_3$ and the Raman spectra of the ions in H_2O and D_2O have been presented [47].

(v) Nickel, palladium, platinum

Infrared spectra of $[Ni(NH_3)_6]Cl_2$ have been given [22—25,27—30,43,44,53, 65,83,84]. Apart from the position of bands in the region of the N—H stretching vibrations (Section D(ii)) the literature data are quite conformable. Blyholder and Vergez [25] observed an intense band at 460 cm^{-1} which could not be confirmed by other workers. The present authors reported the IR spectra of $[^{58}Ni(NH_3)_6]Cl_2$, $[^{62}Ni(NH_3)_6]Cl_2$, $[Ni(ND_3)_6]Cl_2$, and $[Ni(^{15}NH_3)_6]Cl_2$ [65,84] (Table 2); for the deuterated compound see also Sacconi et al. [43].

IR data for the hexammine nickel complex with the anions Br^-, I^-, BF_4^-, ClO_4^-, PF_6^- have been given [27,53] with ClO_4^- and SiF_6^{2-} in refs. 35 and 27 respectively. Müller et al. [39] observed the IR spectra of 11 oxo- and thio-metallates. Viltange [83] reported the spectra of the complexes with the following anions: Cl^-, Br^-, ClO_3^-, BrO_3^-, ClO_4^-, NO_3^-, SO_4^{2-}, $S_2O_8^{2-}$, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, SCN^-. As in the case of $[Co(NH_3)_6]F_2$, Patil and Secco [54] assigned one band in the IR spectrum of $[Ni(NH_3)_6]F_2$ to an M—F stretching mode (cf. Section D(iv)).

In the Raman spectrum of $[Ni(NH_3)_6]^{2+}$ in aqueous solution, Damaschun [85] observed no lines in the region of the Ni—N stretching vibrations. She determined two lines at 3374 and 3286 cm^{-1} which are slightly displaced with regard to the N—H stretching modes of free ammonia. Terrasse et al. [27] found two lines at 3320 and 3210 cm^{-1} in this region. Moreover, they observed a line at 370 cm^{-1} which was later on confirmed by us [84]. From measurements of the degree of depolarization we assigned this line to $\nu_s(NiN)(A_{1g})$. A careful reinvestigation of the Raman spectrum revealed two additional lines at ~265 and 235 cm^{-1} which we attributed to $\nu(NiN)(E_g)$ and $\delta(NNiN)(F_{2g})$, respectively [44,65,84]. The solid state Raman data for various hexammine nickel(II) salts reported recently by Grzybek et al. [53] do not seem reliable. In the Raman spectrum of $[Ni(NH_3)_6]Cl_2$ they reported three lines below 500 cm^{-1} which they assigned as follows: 490 cm^{-1}: $\nu_s(NiN)(A_{1g})$, 441 cm^{-1}: $\nu(NiN)(E_g)$, 378 cm^{-1}: $\delta(NNiN)(F_{2g})$. In our opinion it is impossible that the symmetric M—N stretching mode of a hexammine complex with divalent central atom occurs at such high wavenumbers (~160 cm^{-1} higher than the antisymmetric stretching mode). I.I.N.S. data for $[Ni(NH_3)_6]I_2$ will be reported in Section F.

The IR data for tetrammine palladium (II) chloride (monohydrate) with a square-planar PdN_4 structure have been reported [23,28,29,37,52,86—91]. The present authors determined the infrared spectra of $[^{104}Pd(NH_3)_4]Cl_2 \cdot H_2O$ and $[^{110}Pd(NH_3)_4]Cl_2 \cdot H_2O$ (ref. 37, Table 6). The IR active in-plane and out-of-plane

TABLE 6

Infrared spectra of square-planar tetrammine complexes (cm^{-1}) (A_{2u},E_u species)

	$\nu_{as}(NH)$ (A_{2u},E_u)	$\nu_s(NH)$ (E_u)	$\delta_{as}(HNH)$ (A_{2u},E_u)	$\delta_s(HNH)$ (E_u)	$\rho_r(NH_3)$ (A_{2u},E_u)	$\nu_{as}(MN)$ (E_u)	$\delta(NMN)$ (A_{2u},E_u)
$[Pd(NH_3)_4]Cl_2 \cdot H_2O$	3270 [b]	3170 [b]	1630 [b]	1279 [b]	849 [b] 802 [b]	494 [a]	291 (E_u) [a] 237 (A_{2u}) [a]
$[^{104}Pd(NH_3)_4]Cl_2 \cdot H_2O$						496 [b]	291 (E_u) [b] 237.5 (A_{2u}) [b]
$[^{110}Pd(NH_3)_4]Cl_2 \cdot H_2O$						492 [b]	290.6 (E_u) [b] 236 (A_{2u}) [b]
$[Pt(NH_3)_4]Cl_2$	3250 [c]	3140 [c]	1560 [c]	1325 [c]	888 [c] 842 [c]	510 [d]	297 (E_u) [d] 235 (A_{2u}) [d]
$[Cu(NH_3)_4]SO_4 \cdot H_2O$	3327 [e] 3253 [e]	3169 [e]	1669 [e] 1639 [c]	~1300 [e] 1282.5 [e]	735 [e]	425.5 [a]	256 (E_u) [a] 226 (A_{2u}) [a]
$[^{63}Cu(NH_3)_4]SO_4 \cdot H_2O$						426 [b]	256 (E_u) [b] 226.5 (A_{2u}) [b]
$[^{65}Cu(NH_3)_4]SO_4 \cdot H_2O$						424 [b]	255 (E_u) [b] 226 (A_{2u}) [b]
$[Cu(ND_3)_4]SO_4 \cdot D_2O$ [b]	2465 2360	2320	1225 1195	975	555	407.5	235.5 (E_u) 216.5 (A_{2u})
$[Cu(^{15}NH_3)_4]SO_4 \cdot H_2O$ [e]	3318 3245	3166	1667 1636.5	~1300 1277	732	418.3	250 (E_u) 222.5 (A_{2u})

[a] Ref. 44; [b] ref. 37; [c] ref. 95; [d] ref. 91; [e] ref. 92.

NPdN deformation vibrations have been assigned in a different manner: Whereas Perry et al. [30] attributed a band at 160 cm^{-1} to the out-of-plane deformation mode, Hiraishi et al. [91] assigned a band at much higher wavenumber (232 cm^{-1}) to $\delta(NPdN)(A_{2u})$. According to Perry et al. [90], $\delta(NPdN)(E_u)$ should lie at 245 cm^{-1}, according to Hiraishi et al. [91] at 295 cm^{-1}. We could not ascertain a band at 245 cm^{-1} in the infrared spectrum of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$. For $[Cu(NH_3)_4]SO_4 \cdot H_2O$, we solved the assignment problem by the comparison of measured and calculated H/D and $^{14}N/^{15}N$ shifts of the vibrational frequencies [37,92] (see below). The relation $\delta(NMN)(E_u) > \delta(NMN)(A_{2u})$ should also be valid for the tetrammine palladium (cf. ref. 37) and platinum complexes.

Powell and Sheppard [52] observed a doubling of the $\rho_r(NH_3)$ frequency and stated that this may be due to in-plane and out-of-plane rocking vibrations. Perry et al. [90] pointed at that the $\delta_s(HNH)$ and $\nu_{as}(PdN)$ fundamentals are split into various components. In their opinion, some of these bands must be ascribed to coupling between molecules in the unit cell. Some weak bands in the spectrum were assigned to overtones and combination tones. The splittings mentioned above were not reported by other authors. Infrared data for $[Pd(NH_3)_4]Br_2$ are given in refs. 87, 88 and 90, those for $[Pd(NH_3)_4][PdCl_4]$ in refs. 87, 91 and 93 and for $[Pd(NH_3)_4][PtCl_4]$ in ref. 94. Hiraishi et al. [91] studied the FIR spectrum of tetrachloropalladate at liquid nitrogen temperature, Hendra [89] determined three lines in the solid state Raman spectrum of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ (Table 7). Numerous workers reported the infrared spectrum of $[Pt(NH_3)_4]Cl_2$ (H_2O) [23,28,29,52,58,86,88,89,91,95,96]. As in the case of the corresponding palladium salt, different assignments for the E_u and A_{2u} skeletal deformation modes occur in the literature. We favour the assignment given in Table 6. Several authors reported a doublet in the region of $\rho_r(NH_3)$ (cf. $[Pd(NH_3)_4]Cl_2 \cdot H_2O$).

Some bands in the IR spectra of the iodide and tetrachloropalladate were reported in refs. 96 and 94, respectively. The IR spectra of $[Pt(NH_3)_4][Pt(SCN)_4]$ and $[Pt(NH_3)_4][Pt(CN)_4]$ are reported [93,97]. The spectrum of Magnus Green Salt, (MGS) $[Pt(NH_3)_4][PtCl_4]$ has been given several times [91,93–95,98]. Hiraishi et al. [91] investigated the FIR spectrum of MGS at ambient and liquid nitrogen temperature. They found inter alia that a band at ~200 cm^{-1} increased substantially in intensity upon cooling with liquid nitrogen. The same effect was observed for $[Pd(NH_3)_4][PdCl_4]$ and $[Pt(NH_3)_4][PtBr_4]$. From the fact that the spectral change occurs only in the infrared spectra of MGS type complexes, Hiraishi et al. suggested to assign this band to the antisymmetric stretching vibration of the Pt—Pt—Pt chain (A_{2u} species) of the salts. This lattice mode band is normally expected to be below 100 cm^{-1} (cf. Section F), but it was suggested that the metal—metal interaction (the Pt—Pt distance is 3.25 Å [99]) gives high Pt—Pt stretching frequencies.

Adams and Hall [98] who determined the symmetry species of the skeletal vibrations of MGS from experiments with oriented single crystals (IR and Raman measurements at ambient and liquid nitrogen temperature) placed the A_{2u} lattice mode of the cation—anion chain at 81 cm^{-1} and not at 201 cm^{-1}.

TABLE 7

Raman spectra of square-planar tetrammine complexes (cm^{-1})

	ν_{as}(NH)	ν_s(NH)	δ_{as}(HNH)	δ_s(HNH)	$\rho_r(NH_3)$	$\nu(MN)$	$\delta(NMN)$
$[Pd(NH_3)_4]Cl_2 \cdot H_2O$ [a]						510 (A_{1g}) 468 (B_{1g})	305 (B_{2g})
$[Pt(NH_3)_4]^{2+}$ [b,c]		3315 (A_{1g})	1647			538 (A_{1g}) 526 (B_{1g})	270 (B_{2g})
$[Pt(NH_3)_4]Cl_2 \cdot H_2O$ [d]	3295 (B_{2g},E_g)	3145 (A_{1g},B_{1g})	1610 (B_{2g},E_g)	1365 (A_{1g},B_{1g})		524 (A_{1g}) 508 (B_{1g})	265 (B_{2g})
$[Cu(NH_3)_4]^{2+}$ [b,e]						420 (A_{1g}) 376 (B_{1g})	

[a] Ref. 69; [b] aqueous solution; [c] ref. 82; [d] ref. 95; [e] ref. 37.

They attributed the latter band to a NH_3 torsional motion. Fishman and Interrante [100] obtained the absorption spectra of normal and fully deuterated MGS in the near infrared region and found 6 bands between 6400 and 4050 cm^{-1} with fractional shifts (ν_H/ν_D) close to $\sqrt{2}$, which they attributed to overtones and combinations of the ammonia fundamentals of the $[Pt(NH_3)_4]^{2+}$ complex ion. A band at 3140 cm^{-1} was assigned to a N—H stretching mode. Raman frequencies of $[Pt(NH_3)_4]^{2+}$ in aqueous solution were determined by Mathieu [82] (Table 7) (c.f. ref. 81). Single crystal Raman data of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ can be found in ref. 95.

Hiraishi et al. [91] as well as Nolan and James [101] reported the IR spectrum of hexammine platinum(IV) chloride and of the corresponding monohydrate. Bands due to $\delta_{as}(HNH)$, $\delta_s(HNH)$, and $\rho_r(NH_3)$ in the spectrum of the hydrate showed splittings which are probably due to a loss of degeneracy caused by different symmetries in the solid state [101].

In the region of the Pt—N stretching vibrations, Hiraishi et al. [91] observed three bands at 602, 583, and 536 cm^{-1} in the IR spectrum of the hydrate; in that of the anhydrous compound the highest frequency band (possibly caused by crystalline water) was missing. The band at 583 cm^{-1} was assigned to a combination tone ($F_{1u} \times F_{2g}$, cf. ref. 101), and the lowest band to $\nu_{as}(PtN)(F_{1u})$. Nolan and James [101] found three bands at 564, 530, and 516 (sh) cm^{-1} in the IR spectra of both compounds. According to them, the band at 564 cm^{-1} is possibly due to the Raman active mode $\nu_s(PtN)(A_{1g})$. The band at 530^{-1} and the shoulder at 516 cm^{-1} were attributed to $\nu_{as}(PtN)(F_{1u})$. In the spectrum of $[Pt(NH_3)_6](SO_4)_2 \cdot H_2O$, Hiraishi et al. [91] determined a single band at 531 cm^{-1} and assigned it to $\nu_{as}(PtN)$. (The reference to a band at 521 cm^{-1} in the text [91] is possibly due to a misprint.)

The Raman spectrum of $[Pt(NH_3)_6]^{4+}$ in aqueous solution was reported by Clegg and Hall [102] (Table 3), that of $[Pt(NH_3)_6]Cl_4 \cdot H_2O$ and of the anhydrous compound (Table 3) by Nolan and James [101], who stated that the two A_{1g} lines may be due to different sites occupied by the complex ion or to coupling between A_{1g} modes of different $M(NH_3)_6$ units caused by the low symmetry in the solid state. A weak line at 603 cm^{-1} was not assigned.

(vi) Group IB metal ions

IR data of $[Cu(NH_3)_4]SO_4 \cdot H_2O$ have been given [22,23,28—30,44,52]; those of the chloride may be taken from [58]. Powell and Sheppard [52] as well as Goulden and Manning [103] found a band due to $\delta_s(HNH)$ at 1280 and 1270 cm^{-1}, respectively, in the IR spectrum of $[Cu(NH_3)_4]^{2+}$ in aqueous solution. The former authors determined the position of $\delta_s(DND)$ of $[Cu(ND_3)_4]^{2+}$ in D_2O at 982 cm^{-1}. The IR spectra of ^{63}Cu, ^{65}Cu, and ^{15}N labelled $[Cu(NH_3)_4]SO_4 \cdot H_2O$ and of $[Cu(ND_3)_4]SO_4 \cdot D_2O$ were reported by us [37,92] (Table 6). The site symmetry of the $[Cu(NH_3)_4]^{2+}$ ion in the crystal is C_s (cf. ref. 7), i.e. the degeneracy of the E_u modes is removed. As can be seen from Table 6, $\nu_{as}(NH)$, $\delta_{as}(HNH)$, and $\delta_s(HNH)$ show splittings, which may be either due to site-symmetry interactions or to the activation of IR inactive modes. In the region of the antisymmetric N—H stretching and HNH bending vibrations bands due to lattice water vibrations are also expected (cf. ref. 52). Since all bands in these regions show $^{14}N/^{15}N$ isotope shifts, the possibility of assigning some of the bands to water modes can be excluded with great confidence [92]. The splittings mentioned above were not noted in refs. 22, 23 and 58. Whereas in refs. 22, 23, 37, 52 and 92 three bands in the region of the N—H stretching vibrations were found, only one broad band is seen elsewhere [28,29,58]. Some IR frequencies reported by Shimanouchi and Nakagawa [28,29] (δ_{as}(HNH): 1610; δ_s(HNH): 1270, 1240; $\rho_r(NH_3)$: 713 cm^{-1}) differ considerably from the data of most other workers. The problem to distinguish between the IR active in-plane and out-of-plane NCuN deformation vibrations has recently [37,92] been solved by the comparison of measured and calculated H/D and $^{14}N/^{15}N$ shifts on the basis of the Point Mass Model.

Müller et al. [104] determined the IR spectra of tetrammine copper permanganate, perrhenate, chromate, molybdate, and tungstate. A crystal structure of $[Cu(NH_3)_6]Cl_2$ and $[Cu(NH_3)_6]Br_2$ revealed that the hexammine copper ion is not octahedral but shows strong tetragonal distortion (4 short Cu—N bond lengths with 2.11 Å and two long bond lengths with 2.59 Å) [105]. The IR data for $[Cu(NH_3)_6]F_2$ given by Patil and Secco [54] seem to be doubtful (c.f. Section D(iv)).

Damaschun [85] (see also Joos and Damaschun [106]) was the first to determine the Raman spectrum of $[Cu(NH_3)_4]^{2+}$. An aqueous solution of the sulfate shows a line at 410 cm^{-1}, whilst the chloride shows a line at 419 cm^{-1}. These were confirmed by us [37]. In addition to this line at 420 cm^{-1} (unequivocally assigned as $\nu_s(CuN)(A_{1g})$ from measurements of the degree of depolarization), we observed a very weak line at 375 cm^{-1}, which we attributed to $\nu(CuN)(B_{1g})$.

Corey and Wyckoff [107] determined linear coordination of Ag^+ to two ammonia molecules in $[Ag(NH_3)_2]_2SO_4$. Infrared spectra of this compound have been listed [22,23,52,58,108]. Powell and Sheppard [52] reported the position of δ_s(HNH) and δ_s(DND) in the IR spectrum of $[Ag(NH_3)_2]^+$ in H_2O and of $[Ag(ND_3)_2]^+$ in D_2O, respectively. IR data for the nitrate and the perchlorate were reported by Miles et al. [109]. Geddes and Bottger [108] investigated the spectra of the normal and fully deuterated sulfate and nitrate. Table 8 contains the sulfate data (bands below 400 cm^{-1} have been measured at 143 K). The site symmetry of the $[Ag(NH_3)_2]^+$ ion in crystalline $[Ag(NH_3)_2]_2SO_4$ is C_2. As can be seen from the table, all of the type E' bands appear as doublets and the IR forbidden $\delta_s(HNH)(A_1')$ and $\nu_s(AgN)(A_1')$ bands are strong enough to be resolved. One band at 265 cm^{-1} in the spectrum of the deuterated sulfate was tentatively assigned to $\tau(NH_3)$ [108]. Geddes and Bottger [108] attributed a doublet at 221, 211 cm^{-1} ($[Ag(NH_3)_2]_2SO_4$) and 206, 192 cm^{-1} ($[Ag(ND_3)_2]_2SO_4$) to $\delta(NAgN)(E')$. This assignment was supported by the occurence of a band at 184 cm^{-1} in the IR spectra of the ni-

TABLE 8

Infrared spectra of linear diammine complexes (cm^{-1})

	$\nu_{as}(NH)$	$\nu_s(NH)$	$\delta_{as}(HNH)$	$\delta_s(HNH)$	$\rho_r(NH_3)$	$\nu(MN)$	$\delta(NMN)$
$[Ag(NH_3)_2]_2SO_4$ [a]	3320 3230 (E')	3150 (A_2'')	1642 1626 (E')	1236 (A_2'') 1222 (A_1')	740 703 (E')	476 (A_2'') 400 (A_1')	221 211 (E')
$[Ag(ND_3)_2]_2SO_4$ [a]	2460 2380 (E')	2290 (A_2'')	1196 1185 (E')	937 (A_2'') 930 (A_1')	548 517 (E')	449 (A_2'') 376 (A_1')	206 192 (E')
$[Hg(NH_3)_2]Cl_2$	3265 [b]	3197 [b]	1605 (E') [c]	1268 (A_2'') [c]	719 (E') [c]	513 (A_2'') [c]	

[a] Ref. 108; [b] ref. 109; [c] ref. 51.

TABLE 9

Raman spectra of linear diammine complexes (cm^{-1})

	$\nu_{as}(NH)$	$\nu_s(NH)$	$\delta_{as}(HNH)$	$\delta_s(HNH)$	$\rho_r(NH_3)$	$\nu(MN)$	$\delta(NMN)$
$[Ag(NH_3)_2]^+$ [a,b]	3373	3287 (A_1')	1668 (A_1') 1624	1224 (A_1')		372 (A_1')	
$[Hg(NH_3)_2]Cl_2$ [b]	3280	3218	1665 1610	1293		412	

[a] Aqueous solution (nitrate); [b] ref. 109.

trate in dimethylformamide and dimethylsulphoxide [108]. The solid state IR spectra of the normal and deuterated nitrate show a pattern similar to those of the sulfate, but some bands occur at considerably lower wavenumbers, e.g. $\rho_r(NH_3)(E')$: 660, 610 cm^{-1}, $\nu_s(AgN)(A_1')$: 386 cm^{-1}, $\delta(NAgN)(E')$: 208, 176 cm^{-1} ($[Ag(NH_3)_2]NO_3$). Bands at 3230 and 2350 cm^{-1} in the spectra of the normal and deuterated nitrate, respectively, were assigned to an overtone of $\delta_{as}(HNH)(E')$ enhanced by Fermi resonance [109]. Contrary to Geddes and Bottger [108], Miles et al. [109] found no clear feature in the IR spectrum of $[Ag(NH_3)_2]NO_3$ which could be assigned to $\nu_{as}(AgN)(E')$. A very broad band at ~430 cm^{-1}) tentatively attributed to this vibration is much lower in frequency than the band found by the former authors (470 cm^{-1}).

Raman spectra of saturated aqueous solutions of $[Ag(NH_3)_2]ClO_4$ and $[Ag(NH_3)_2]NO_3$ have been determined by Miles et al. [109] (Table 9). The line at ~370 cm^{-1} ($\nu_s(AgN)(A_1')$) was found to be only very weakly polarized. According to Miles et al. this is probably a result of strong hydrogen bonding between the ammine groups and the solvent cage. Geddes and Bottger [108] stated that the value of 410 cm^{-1} quoted by Powell and Sheppard [52] for $\nu_s(AgN)$ was apparently a misquote.

To our knowledge, vibrational spectroscopic data of ammine gold complexes have not yet been reported (for the electronic spectrum of $[Au(NH_3)_4]^{3+}$ see for example, ref. 110).

(vii) Group IIB metal ions

IR data of tetrammine zinc chloride and iodide with tetrahedral ZnN_4 framework have been reported in refs. 43 and 58, respectively. The present authors [65] determined the IR spectra of $[Zn(NH_3)_4]I_2$ and $[Zn(^{15}NH_3)_4]I_2$ (Table 4) (see also ref. 84). Baran [111] obtained the spectrum of $[Zn(NH_3)_4][PtCl_4]$, Müller et al. [104] those of the permanganate, perrhenate, chromate, and tungstate. $\rho_r(NH_3)$ of the osmiate was given in ref. 40.

The Raman spectra of $[^{64}Zn(NH_3)_4]I_2$, $[^{68}Zn(NH_3)_4]I_2$, and $[Zn(ND_3)_4]I_2$ were determined by Nakamoto et al. [112] (see also ref. 113), those of $[Zn(NH_3)_4]I_2$ and $[Zn(^{15}NH_3)_4]I_2$ by us [65] (cf. ref. 84). We found agreement with the data reported in [112] but also several additional lines. Some of these lines are observable in the figure presented in their publication but have not been listed. The totally symmetric zinc—nitrogen stretching frequency of $[Zn(NH_3)_4]^{2+}$ in aqueous solution has also been determined [112—114]. Damaschun [85] (cf. ref. 106) erroneously assigned this frequency to $\nu_s(ZnN)$ of the hexammine complex which does not exist in aqueous solution.

The crystal structure of tetrammine zinc iodide is not yet known, but it seems likely that the site symmetry of the complex ion in the crystal is low, since the solid state Raman and IR spectra are rather complicated. The Raman as well as the IR spectra of normal and ^{15}N labelled tetrammine zinc iodide present four bands in the region of the N—H stretching vibrations [65]. By intensity considerations and by inspection of the analytical expressions for the F and G matrix elements three bands were assigned as given in Tables 4 and 5.

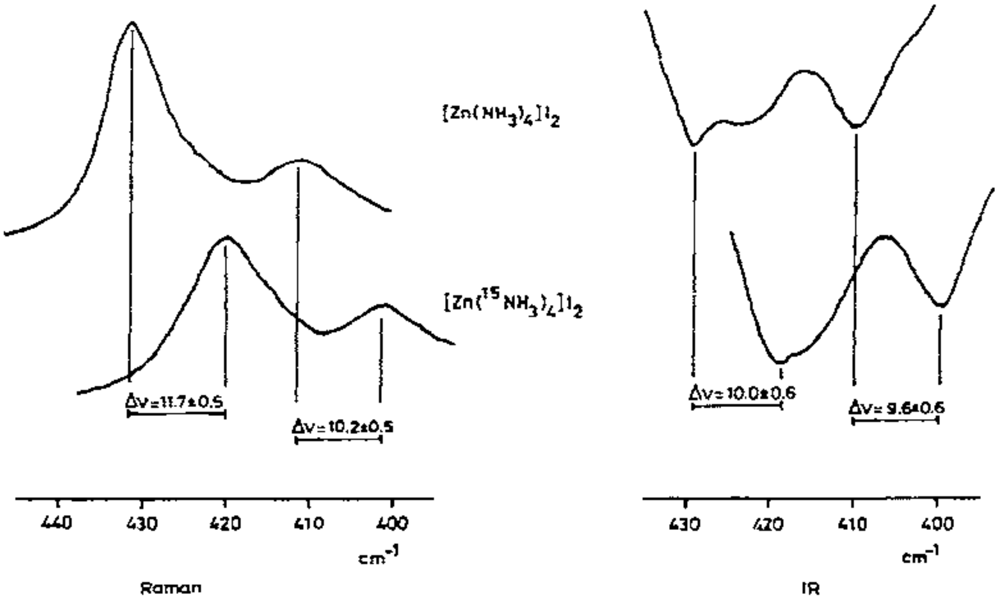

Fig. 2. Raman and IR spectra of [Zn(NH$_3$)$_4$]I$_2$ and [Zn(^{15}NH$_3$)$_4$]I$_2$ in the range 440—400 cm^{-1}.

A Raman line at 3151.2 cm^{-1} and an IR band at 3145 cm^{-1} ([Zn(NH$_3$)$_4$]I$_2$) are possibly overtones of δ_{as}(HNH). It is interesting to note that the very similar ^{14}N/^{15}N isotope shifts of the Raman doublet at ~1250 cm^{-1} are clearly different from those of the IR doublet in this region. Thus the Raman and IR bands do not belong to the same species.

Figure 2 shows the Raman and IR spectra of [Zn(NH$_3$)$_4$]I$_2$ and [Zn(^{15}NH$_3$)$_4$]I$_2$ in the region of the metal—nitrogen stretching vibrations. From the relative intensities of the two Raman lines it is clear that the higher frequency Raman line corresponds to ν_s(ZnN)(A_1) (cf. [Zn(NH$_3$)$_4$]$^{2+}$ in aqueous solution), and the lower frequency line to ν_{as}(ZnN)(F_2). The isotope shifts of the two bands differ by ~1.5 cm^{-1}. By applying the Point Mass Model, one can calculate the ^{14}N/^{15}N isotope shift of ν_s(ZnN)(A_1). The result (11.6 cm^{-1}) is in excellent agreement with the measured value 11.7 cm^{-1}. Instead of one single band, the IR spectra clearly show three bands in this region. From the isotope shifts it seems likely that these bands can be assigned to the components of the threefold degenerate ν_{as}(ZnN)(F_2) mode.

Terrasse et al. [27] reported the IR spectra of the hexammine zinc ion with the following anions: Cl$^-$, ClO$_4^-$, SiF$_6^{2-}$, BF$_4^-$, PF$_6^-$; Sacconi et al. [43] determined those of the chloride, bromide, and iodide. While for [Zn(NH$_3$)$_6$]Cl$_2$ the bands due to δ_{as}(HNH) and ρ_r(NH$_3$) are nearly the same in both references, the ν_{as}(ZnN) and δ_s(HNH) frequencies given in ref. 27 are approximately 100 cm^{-1} higher than those reported in ref 43. Sacconi et al. [43] pointed out that the values in ref. 27 appear to be contradictory in that the former bands correspond to bands of the tetrammine complex whereas the latter bands are due to those of the hexammine complex. A reinvestigation of the IR spectrum of hexammine zinc chloride accomplished by us confirmed the data reported in ref. 43. The IR data of $[Zn(NH_3)_6]F_2$ (also those of $[Cd(NH_3)_6]F_2$) [54] are questionable (see Section D(iv)).

Barrow et al. [58] determined the IR spectrum of $[Cd(NH_3)_4]Cl_2$, Müller et al. [104] those of $[Cd(NH_3)_4](MnO_4)_2$ and $[Cd(NH_3)_4](ReO_4)_2$. Our recent data for $[Cd(NH_3)_4](ReO_4)_2$ and $[Cd(^{15}NH_3)_4](ReO_4)_2$ [115] are given in Table 4. Additional bands at 3184 cm^{-1} and 3176 cm^{-1} (^{15}N compound), respectively, may be due to 2 δ_{as}(HNH). IR data for $[Cd(NH_3)_4]$ $[PtCl_4]$ are given [111]. The ammonia rocking frequency for $[Cd(NH_3)_4]$ $(OsO_3N)_2$ can be found [40].

Recently [44] we reported the solid state Raman spectrum of $[Cd(NH_3)_4]$-$(ReO_4)_2$. In addition to lines corresponding to the anion, we observed one intense line at 386 cm^{-1} and a very weak shoulder at about 170 cm^{-1}, which we assigned as shown in Table 5. Plane [114] reported a line at 350 cm^{-1} in the spectrum of an ammoniacal solution of cadmium chloride, which he mistakenly attributed to $[Cd(NH_3)_4]^{2+}$ (see below).

The IR spectra of hexammine cadmium salts containing the same anions as the corresponding zinc compounds are reported [27,43]. A similar disagreement as in the case of $[Zn(NH_3)_6]Cl_2$ exists over the frequencies of $[Cd(NH_3)_6]$-Cl_2 (cf. ref. 43). Raman data of $[Cd(NH_3)_6]^{2+}$ in aqueous solution have been determined in [85,106] and [114]. Our determination of a fully polarized line at 342 cm^{-1} ($\nu_s(CdN)(A_{1g})$) [44] confirmed previous work. We could also find the corresponding line (341 cm^{-1}) in the low temperature Raman spectrum (173 K) of $[Cd(NH_3)_6]Cl_2$ (this work).

In $[Hg(NH_3)_2]Cl_2$ and $[Hg(NH_3)_2]Br_2$, the N—Hg—N atoms lie on a straight line (d(HgN): 2.05 Å (chloride), 2.11 Å (bromide), while 4 halide ions are in the equatorial position [116,117]. Several authors regarded these compounds to contain quasi-isolated $[Hg(NH_3)_2]^{2+}$ ions. There is some justification for this approach, because the mercury—halogen distances (2.99 Å for $[Hg(NH_3)_2]Br_2$) are much larger than the sum of the covalent radii.

The IR spectra have been studied by several authors [51,58,93,109,118]; a bent diammine structure is assumed in ref. 58. Bertin et al. [51] (see also Clark and Williams [93]) reported a band at 513 cm^{-1} (chloride) which they assigned to ν_{as}(HgN). Miles et al. [109] could not with confidence make any assignment of a band due to this vibration. A poorly resolved band at ~217 cm^{-1} (chloride) and <200 cm^{-1} (bromide), tentatively assigned to ν(HgCl) and ν(HgBr), respectively, was given in ref. 93. The solid state Raman spectra were reported in ref. 109 (for the chloride see Table 9). According to Miles et al. [109], the increase of 33 cm^{-1} for ν_s(HgN) in going from the bromide to the chloride indicates some interaction between the mercury ion and the halide ions.

No reliable data for $[Hg(NH_3)_4]^{2+}$ are available. The frequencies reported in the literature (cf. refs. 58 and 114) possibly pertain to the diammine complex (for the existence of $[Hg(NH_3)_4]^{2+}$ in aqueous solution see for example ref. 119).

E. CORRELATIONS BETWEEN THE VIBRATIONAL SPECTROSCOPIC DATA

Table 10 contains the frequency ranges for the vibrational modes of the compounds listed in Table 2—9. In cases where single bands (especially Raman lines) for some compounds lie outside the given ranges, we have specified them in footnotes. The uncertain data of $[V(NH_3)_6]Cl_2$ and $[Be(NH_3)_4]Cl_2$ are not considered in the table.

As is to be expected, the metal—nitrogen stretching vibrations for hexammine complexes of divalent metals occur in a lower frequency range than those for the corresponding complexes of trivalent metals and for $[Pt(NH_3)_6]^{4+}$. The totally symmetric M—N stretching frequencies for most hexammine complexes (exceptions: $[Mg(NH_3)_6]^{2+}$, $[Al(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$) are higher than the other two stretching frequencies. It is interesting to note that $\nu(MN)(E_g)$ is lower than $\nu_{as}(MN)(F_{1u})$ in the case of the first transition series trivalent and divalent hexammines and also for $[Mg(NH_3)_6]^{2+}$ and $[Al(NH_3)_6]^{3+}$, whereas it occurs between $\nu_s(MN)(A_{1g})$ and $\nu_{as}(MN)(F_{1u})$ in the case of hexammine complexes of trivalent metal ions belonging to the second and third transition series as well as of hexammine platinum(IV) (cf. ref. 44). While the frequency ratios $\nu_s(MN)(A_{1g})/\nu_{as}(MN)(F_{1u})$ are nearly constant for all hexammines, the values for $\nu_s(MN)(A_{1g})/\nu(MN)(E_g)$ and $\nu(MN)(E_g)/\nu_{as}(MN)(F_{1u})$ differ more. If one compares the M—N stretching frequencies for the tetrahedral and square-planar tetrammine complexes of divalent metal ions and of $[Ag(NH_3)_2]^+$ and $[Hg(NH_3)_2]^{2+}$, it turns out that they occur approximately in the same range as the stretching vibrations for the hexammines of trivalent metal ions.

It has been stated in several publications [3,16,23—25,35,43,47,51,52,71, 86,120,121] that the NH_3 rocking frequency is very sensitive to the nature of the metal ion. Some authors (cf. refs. 16 and 23) postulated a linear relation between $\rho_r(NH_3)$ and $\nu_{as}(MN)(F_{1u})$; for an opposite statement see Griffith [47]. This author found that both $\nu_s(MN)(A_{1g})$ and $\nu(MN)(E_g)$ for hexammine ruthenium(III), iridium, and rhodium decrease in the same sequence as $\rho_r(NH_3)$. A comparison of the data collected in Tables 2—9 reveals that high metal—nitrogen stretching frequencies generally imply high rocking frequencies (cf. the frequency ranges in Table 10), but a direct connection does not exist. The nature of the metal ions is also reflected considerably in the values of the symmetric ammonia deformation frequencies, whereas bands due to $\delta_{as}(HNH)$ occur for all ammine complexes around 1600 cm^{-1} within a rather narrow range (Table 10) (cf. refs. 23, 71, 120). Wilmshurst [122] has shown that there is a linear relationship between the squares of the symmetric NH_3 deformation and rocking frequencies in a series of ammine complexes and the electronegativity of the metal. Grinberg and Varshavskii [123] explained the sensitivity of the $\delta_s(HNH)$ frequencies by periodic changes in the character of the orbital occupied by the unshared electron pair of the nitrogen atom during changes of

TABLE 10

Frequency ranges of the vibrational modes (cm^{-1}) (single bands outside the given ranges are specified in footnotes)

	$[M(NH_3)_6]^{2+}$ (O_h)	$[M(NH_3)_6]^{3+}$ (O_h)	$[M(NH_3)_6]^{4+}$ (O_h) [a]	$[M(NH_3)_4]^{2+}$ (T_d)	$[M(NH_3)_4]^{2+}$ (D_{4h})	$[M(NH_3)_2]^{n+}$ $n = 1,2$ (D_{3h})
$\nu(NH)$	3360—3160	3290—3125	3150—3050	3355—3175	3330—3140	3320—3150
$\delta_{as}(HNH)$	1610—1585 [b]	1630—1585	1565	1620—1595 [h]	1640—1560 [j]	1660—1610
$\delta_s(HNH)$	1180—1090 [c]	1370—1300 [f]	1370	1260—1175	1325—1280 [k]	1295—1220
$\rho_r(NH_3)$	685—470 [d]	860—745 [g]	950	695—670 [i]	890—735	740—700
$\nu(MN)$	370—240	530—400	564—516	435—370	525—375	515—370
$\delta(NMN)$	215—165 [e]	330—240	318—288	195—145	300—225	220—210

[a] $[Pt(NH_3)_6]^{4+}$; [b] M = Mg: 1568 (F_{2g}) (Raman); [c] M = Mg: 1229 (A_{1g}) (Raman), M = Ru;1220 (F_{1u}) (IR); [d] M = Ru: 769 (F_{1u}) (IR); [e] M = Ni: 235 (F_{2g}) (Raman); [f] M = Y: 1224 (F_{1u}) (IR); [g] M = Y: 620 (F_{1u}) (IR); [h] M = Zn: 1700 (F_1(?)) (IR), 1730 (F_1(?)) (Raman); [i] M = Zn: 610, 611 (IR, Raman); [j] M = Cu: 1669 (IR); [k] M = Pt: 1365 cm^{-1} (Raman).

HNH angles (for correlations between the NH_3 rocking and M—N stretching frequencies and stability constants as well as ligand field stabilization energies see Section I).

A greater formal charge on the metal ion strengthens the M—N bonds and weakens the N—H bonds. Hence the N—H stretching frequencies for ammine complexes of trivalent metal ions should occur at lower wavenumbers than those for complexes of divalent ions. This effect is not clearly to be seen from the frequencies of the chlorides given in the tables, since bands due to N—H stretching modes are usually very broad and cannot be determined accurately. Especially in the case of the halides the bands are not readily resolved. This may partly be attributed to hydrogen bonding between the ammonia—hydrogen atoms and the outer ion. Replacing a halide ion by a complex anion (e.g. ClO_4^-) renders the bands well resolvable in many cases makes the above mentioned effect detectable (for discussions see refs. 3 and 35).

It is well known that the vibrational frequencies of ammine complexes are not only sensitive to changes in the metal ions but also to changes in the anions. The shifts of the N—H stretching modes to higher and of the $\rho_r(NH_3)$ and ν(MN) modes to lower wavenumbers on going from the chloride to the iodide salt of a given complex have been explained with decreasing hydrogen honding [3,26,27,35,43,121]. The rocking modes turned out to he most sensitive to the kind of the outer ions present. Müller et al. [39,104,121] made a systematical investigation on the dependency of the frequencies due to $\rho_r(NH_3)$ upon the nature of the anion. They stated among other things that the rocking frequency increases with increasing charge of the anion (e.g. MnO_4^- to CrO_4^{2-}) and is nearly constant for complexes with anions of approximately equal size and equal charge (e.g. MnO_4^- and I^-). Wieghardt and Siebert [124] showed that for some cubic hexammine metal hexafluorometallates(III) the position of $\rho_r(NH_3)$ can be correlated to the lattice constants.

F. LATTICE VIBRATIONS

(i) IR and Raman spectra

The Bravais unit cell for compounds of the type $[M(NH_3)_6]X_2$ crystallizing in the space group $O_h^5 — Fm3m$ ($z = 4$) contains one complex ion $[M(NH_3)_6]^{2+}$ and two outer ions (X^-). A factor group analysis (cf. ref. 20) reveals 4 external vibrations, which are distributed among the species of O_h as follows:

$$\begin{aligned}\Gamma_{\text{external}} = {} & F_{1g} \text{ (IR and Raman inactive rotatory mode)}\\ & +2F_{1u} \text{ (acoustic mode + IR active translatory mode)}\\ & +F_{2g} \text{ (Raman active translatory mode).}\end{aligned}$$

A strong absorption band between 125 and 80 cm^{-1} in the infrared spectra of hexammine magnesium [20], cobalt(II) [43,53], and nickel [30,43,53,125] salts has been assigned to the IR active optical translatory mode (F_{1u}) of the complex ions against the halide ions. The frequency of this band decreases markedly with increasing atomic weight of the halogen (cf. for example $[Ni(NH_3)_6]Cl_2$: 115 cm^{-1}; $[Ni(NH_3)_6]I_2$: 81 cm^{-1} [43,53]).

Plus [20] assigned a line at 158 cm^{-1} in the Raman spectra of $[Mg(NH_3)_6]Cl_2$ and $[Mg(ND_3)_6]Cl_2$ to the F_{2g} translatory mode. By using the measured F_{1u} lattice frequencies (IR) for $[Co(NH_3)_6]X_2$ and $[Ni(NH_3)_6]X_2$ (X = Cl, Br, I) and a lattice dynamics model based on electrostatic interactions between punctiform ions, Grzybek et al. [53] calculated the frequencies of the Raman active F_{2g} lattice mode. According to these authors, this vibration should appear around 95 cm^{-1} for the chlorides, 65 cm^{-1} for the bromides, and 50 cm^{-1} for the iodides.

Nakagawa and Shimanouchi [125] pointed out that bands due to two F_{1u} translatory modes should occur in the IR spectra of compounds of the type $[M(NH_3)_6]X_3$ (space group O_h^5), since in this case two kinds of halide ions (X_1, X_2) exist in the Bravais unit cell, while for compounds of the type $[M(NH_3)_6]X_2$ only one kind of X exists. In the lattice mode which should occur at higher wavenumbers, the X_1 and X_2 ions displace in the same direction causing a large transition moment, whereas in the mode which is to be expected at lower wavenumbers the X_1 and X_2 ions displace in opposite directions, and accordingly the transition moment may be very small. For $[Co(NH_3)_6]X_3$ (X = F, Cl, Br, I) only one strong band in the range 160—100 cm^{-1} was observed (see also refs. 30, 33 and 43) which was attributed to the higher frequency lattice vibration. Apart from very doubtful bands at ~85 and ~55 cm^{-1} in the spectra of the chloride and iodide, respectively, the lower frequency band could not be determined by these authors. In addition to the intense band mentioned above, Baranovskii and Mazo [64] found a band of weak intensity between 77 and 75 cm^{-1} in the FIR spectra of normal and fully deuterated hexammine cobalt(III) chloride and iodide as well as of $[Co(NH_3)_6](ClO_4)_3$, which may be due to the second F_{1u} mode. Raman lines due to F_{2g} lattice modes of hexammine cobalt(III) salts have not yet been reported.

For $[Mg(NH_3)_6]Cl_2$, the bands due to the lattice modes undergo almost no (2 cm^{-1}, F_{1u} mode) or no displacement (F_{2g} mode) on deuteration [20]. The same is true for the two F_{1u} lattice bands in the IR spectra of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]I_3$ (refs. 43 and 64), whereas in the case of $[Ni(NH_3)_6]Cl_2$, the F_{1u} lattice band shows a distinct shift to lower wavenumbers (7 cm^{-1}) [43]. It is interesting to note that Sacconi et al. [43] observed a lattice frequency increase by 6 cm^{-1} for $[Co(NH_3)_5Cl]Cl_2$/$[Co(ND_3)_5Cl]Cl_2$. According to them, this phenomenon may be explained by contraction of the crystal lattice (decrease of the N—Cl distance) as a result of deuteration. The N—Cl distance should be practically unchanged in $[Co(NH_3)_6]Cl_3$ and should increase in $[Ni(NH_3)_6]Cl_2$. Contrary to ref. 43, Baranovskii and Mazo [64] found no lattice band shifts for $[Co(NH_3)_5Cl]Cl_2$.

Nakagawa [76] reported some results of a factor group analysis for $[Co(NH_3)_6][Co(CN)_6]$ (space group $C_{3i}^2 - R\overline{3}$). He stated that two translational lattice modes (A_u, E_u) should occur in the IR spectrum. At least one out of 4 IR bands between 169 and 94 cm^{-1} should be due to a lattice vibration. A factor group analysis for $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ was made by Poulet et al. [95]. None of the bands in the IR spectrum was attributed to a lattice mode. Hiraishi et al. [91] assigned an IR band at 122 cm^{-1} to a lattice vibration, whereas the former authors stated that this band (118 cm^{-1}) [95] is possibly due to an internal vibration or to a combination of lattice vibrations.

Magnus Green Salt ($[Pt(NH_3)_4][PtCl_4]$) crystallizes in the space group D_{4h}^6 — $P4/mnc$ ($z = 2$) [99]. According to the results of a factor group analysis (hydrogen atoms neglected) [91,98], the 16 external vibrations are classified as follows:

$\Gamma_{external}$ = $2A_{1g}$(Raman active rotatory modes) + $2A_{1u}$(IR and Raman inactive translatory modes) + $2A_{2g}$(inactive rotatory modes) + $2A_{2u}$(acoustic mode + IR active translatory mode) + $4E_g$(Raman active rotatory modes) + $4E_u$(acoustic mode + 3 IR active translatory modes).

Adams and Hall [98] assigned an IR band at 81 cm^{-1} to the A_{2u} translatory mode (for a different assignment see ref. 91) and a band at 71 cm^{-1} to one of three predicted E_u translatory modes (see also ref. 91). Their single crystal Raman experiments indicated that the four E_g rotatory lattice modes are either not higher than 30 cm^{-1} or vanishingly weak. Similarly, they found no evidence for the two A_{1g} rotatory modes predicted. Hiraishi et al. [91] attributed three bands at 102, 94 and 87 cm^{-1} in the IR spectrum of $[Pd(NH_3)_4][PdCl_4]$ and two bands in the spectra of $[Pt(NH_3)_4][PtBr_4]$ (95, 62 cm^{-1}) and $[Pd(NH_3)_4][PdBr_4]$ (90, 76 cm^{-1}) to E_u translatory vibrations. Geddes and Bottger [108] attributed 6 bands in the low-temperature (143 K) IR spectrum of $[Ag(NH_3)_2]_2SO_4$ as well as 5 bands in the spectra of $[Ag(ND_3)_2]_2SO_4$, $[Ag(NH_3)_2]NO_3$ and $[Ag(ND_3)_2]NO_3$ to lattice vibrations. These bands appear to be of translational origin, since no significant H/D frequency shift was observed. Two bands at 161 and 139 cm^{-1} in the spectrum of $[Ag(ND_3)_2]_2SO_4$ were tentatively assigned to lattice combination and overtones, respectively. For several other compounds, IR and Raman bands due to lattice vibrations have been reported without detailed discussion, for example, for $[Cr(NH_3)_6]Cl_3$, $[Cu(NH_3)_4]SO_4 \cdot H_2O$ [30], $[Zn(NH_3)_4]I_2$ [65,112] and $[Pt(NH_3)_6]Cl_4$ [101].

(ii) Neutron incoherent inelastic scattering

Janik et al. [126] determined the incoherent inelastic neutron scattering (I.I.N.S.) of the complex compounds $[Co(NH_3)_6]I_2$ and $[Ni(NH_3)_6]I_2$. Measurements were made on a time-of-flight spectrometer at 113 K. In the phonon density plots calculated from the scattered neutron intensity plots the following peaks below 300 cm^{-1} were obtained: 43, 72, 110, 152, 184 cm^{-1} ($[Co(NH_3)_6]I_2$); 80, 105, 142, 200 cm^{-1} ($[Ni(NH_3)_6]I_2$). (In an earlier work, Jakób et al. [127] measured the I.I.N.S. of $[Co(NH_3)_6]I_3$, $[Co(NH_3)_6]Cl_3$, and $[Co(NH_3)_6]I_2$. By comparison with the vibrational spectroscopic data of SeF_6, they interpreted the peaks as being caused by internal vibrations of the CoN_6 skeleton. In our opinion, this assignment is incorrect in most cases; for example, peaks in the ranges 880—700 cm^{-1} and 530—410 cm^{-1} cannot be due to metal—nitrogen stretching and skeletal deformation vibrations, respectively.)

The I.I.N.S. peaks at 184 cm^{-1} ($[Co(NH_3)_6]I_2$) and 200 cm^{-1} ($[Ni(NH_3)_6]I_2$) occur at similar wavenumbers as the bands due to $\delta_{as}(NMN)(F_{1u})$ in the IR spectra (188 and 216 cm^{-1}, respectively [53,43]). This is also true for the I.I.N.S. peaks at 72 cm^{-1} ($[Co(NH_3)_6]I_2$), 80 cm^{-1} ($[Ni(NH_3)_6]I_2$) and the translatory IR lattice bands (F_{1u}) at 77 and 81 cm^{-1}, respectively [43,53]. On the basis of the agreement with the IR data, Janik et al. [126] assigned the peaks at 184 and 200 cm^{-1} to skeletal deformation modes, whilst they did not attribute the peaks at 72 and 80 cm^{-1} to translatory lattice modes, but to NH_3 torsional modes. This assignment was made on grounds of the fact that van Kempen et al. [128] obtained rotational barriers from the specific heat anomaly below 1 K which led to the determination of torsional frequencies at 81 cm^{-1} ($[Co(NH_3)_6]I_2$) and 79 cm^{-1} ($[Ni(NH_3)_6]I_2$). According to ref. 126, there is a temptation to consider the IR and calorimetry data as being based on the same physical phenomenon. In the opinion of Janik et al., the coincidence is completely fortuitous. The rather indistinct I.I.N.S. peaks at 152 and 142 cm^{-1}, respectively, were attributed to an overtone of the NH_3 torsional mode, and the peaks at 110 and 105 cm^{-1}, respectively, to the optic translatory vibration. It was postulated that the translatory frequency shifts to higher wavenumbers if the temperature decreases from room temperature (IR data) to 113 K (I.I.N.S. measurements). No assignment was given for the I.I.N.S. peak at 43 cm^{-1} ($[Co(NH_3)_6]I_2$).

In a recent publication, Janik et al. [129a] determined the rotational barriers for some hexammine nickel salts by applying an IR band profile method (cf. ref. 129b and literature therein). Because of the disagreement between the activation energy for $[Ni(NH_3)_6]I_2$ obtained by them (0.91 kcal mol^{-1}) and that of van Kempen et al. [128] (0.50 kcal mol^{-1}), they pointed out that the selection of an I.I.N.S. peak at 80 cm^{-1} as NH_3 torsion, which led to a rotational barrier of ~0.50 kcal mol^{-1}, may be erroneous. According to ref. 129, this peak should correspond rather to the translatory lattice mode, opening the possibility that either the peak at 105 or that at 142 cm^{-1} given in ref. 126 could correspond to $\tau(NH_3)$, leading to barrier values closer to 0.91 kcal mol^{-1}.

It should be mentioned for the completeness that Leech et al. [130] studied the temperature dependence (90 K—470 K) of the IR band contours for *trans*-$Pd(NH_3)_2X_2$ (X=Cl, I). According to these authors it seems probable that in $Pd(NH_3)_2I_2$ the NH_3 groups are rotating with gradually decreasing freedom from higher to lower temperatures, whereas it appears that with $Pd(NH_3)_2Cl_2$ the ammonia groups are not rotating appreciably at room temperature and below, but that they begin to rotate with limited freedom at temperatures above this. The barriers to internal rotation for $Pd(NH_3)_2I_2$ were determined as follows: 210 cm^{-1} (90 K), 255 cm^{-1} (298 K), 210 cm^{-1} (470 K) ($\hat{=}$0.60, 0.73, 0.60 kcal mol^{-1}).

G. VIBRONIC SPECTRA

Wentworth [131] investigated the vibronic structure of the Laporte forbidden $^1T_{1g} \leftarrow {}^1A_{1g}$ absorption band in the near UV polarized crystal spectrum of $[Co(NH_3)_6][Co(CN)_6]$ and also of the deuterated compound at 80 K and explained it in terms of a uniquantal progression of a CoN_6 vibration at 420 cm^{-1} and its combination with a vibration at 390 cm^{-1}. Deuteration lowers these bands to 380 and 340 cm^{-1}, respectively. Yeranos [132] pointed out that one should expect progressions due to the CoN_6 skeletal modes of F_{1u} and F_{2u} symmetry and to combination tones whose direct product includes the F_{1u} and/or F_{2u} species. His assignment ($\nu_{as}(CoN)(F_{1u})^* \cong 420$ cm^{-1}, $\nu_s(CoN)(A_{1g})^* \cong 390^{-1}$) appears to be doubtful, if one compares the excited state frequencies with the IR and Raman ground-state data given in Tables 2 and 3.

Seven F_{1u} and four F_{2u} vibrational modes can act as vibronic origins for the $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^2E_g \leftarrow {}^4A_{2g}$ transitions of $[Cr(NH_3)_6]^{3+}$ [133]. Whereas the absorption band due to the former transition is not resolved, the structure of the latter has been investigated by several authors in absorption and emission. Porter and Schläfer [134] determined the phosphorescence spectrum of $[Cr(NH_3)_6]^{3+}$ in rigid glass at −195°C using a high-pressure mercury arc lamp as exciting light. Some vibronic bands corresponding to transitions from the zero level of the lowest doublet state ^2E_g to vibrational levels of the quartet ground state ($^4A_{2g}$) were detected and tentatively assigned by comparison with IR bands. Adamson and Dunn [135] examined the vibrational structure of the $^2E_g \leftarrow {}^4A_{2g}$ absorption band for the normal and fully deuterated hexammine chromium ion. They found marked isotope shift in at least two bands, which they correlated to ammonia deformation and rocking vibrations. More complete assignments of all bands reported in ref. 135 were given later [34]. Eysel [136] investigated the absorption and emission spectra of a series of hexammine chromium salts. For $[Cr(NH_3)_6][TlCl_6]$, a detailed assignment of the bands due to F_{1u} and F_{2u} fundamentals (and also some combination tones) coupled with the electronic transition $^2E_g \longleftrightarrow {}^4A_{2g}$ was reported. Whereas the assignment for the fundamentals was confirmed in later publications [34,41a], that for some combination tones was found to be inconsistent with the vibronic selection rules [41a].

Flint [137] obtained the luminescence spectrum of normal and deuterated $[Cr(NH_3)_6](ClO_4)_3$ and gave some preliminary assignments. Later on, Flint and Greenough [41a] reported more detailed spectra of the former compound, of $[Cr(NH_3)_6]PF_6$ and their deuterated analogues at room temperature and at 80 K; in some cases also at 4 K. Nine bands ($7F_{1u}$, $2F_{2u}$) correlated with transitions from the zero level of the excited state to F_{1u} and F_{2u} vibrationally excited levels of the ground state and five bands ($3F_{1u}$, $2F_{2u}$) due to transitions from excited vibrational levels of the ^2E_g state to the ground state were observed (Table 11). Most combination bands could be assigned as transitions involving one quantum of a F_{1u} or F_{2u} mode and one quantum of $\nu(CrN)(E_g)$

or δ_s(HNH)(E_g). The frequencies for these modes derived from combinations are 422 and 1324 cm^{-1}, respectively ([Cr(NH$_3$)$_6$](ClO$_4$)$_3$). According to Flint and Greenough [41a], the appearence of the combinations may be due to a Jahn—Teller effect in the $^4T_{2g}$ state.

Employing He/Ne laser excitation (6328 Å) in a Raman experiment, Long and Penrose [34] obtained phosphorescence spectra of [Cr(NH$_3$)$_6$]$^{3+}$ and [Cr(ND$_3$)$_6$]$^{3+}$ in aqueous solution (Table 11) and of solid [Cr(NH$_3$)$_6$](ClO$_4$)$_3$. For the latter compound, their results are essentially identical to those reported in refs. 41a and 137. The absorption data of Adamson and Dunn [135] with the assignment of Long and Penrose [34] are also given in Table 11. A comparison of ground-state and excited state vibronic frequencies with the IR and Raman data presented in Tables 2 and 3 reveals that the shapes of the potential surfaces of the ^2E_g and $^4A_{2g}$ states do not differ much [34]. As can be seen from the table, the differences in the vibronic frequencies ρ_r(NH$_3$)(F_{1u}) and ρ_r(NH$_3$)(F_{2u}), respectively, obtained from the emission spectra of [Cr-

TABLE 11

Electronic ground state and excited state (*) fundamentals of [Cr(NH$_3$)$_6$]$^{3+}$ ([Cr(ND$_3$)$_6$]$^{2+}$ in brackets) determined from the vibronic system of the $^2E_g \longleftrightarrow {}^4A_{2g}$ transition in emission and absorption (cm^{-1})

	Emission		Absorption
	[Cr(NH$_3$)$_6$](ClO$_4$)$_3$ cryst. [a]	[Cr(NH$_3$)$_6$]$^{3+}$ aqueous solution [b]	[Cr(NH$_3$)$_6$]$^{3+}$, aqueous solution [c]
δ_s(HNH) (F_{1u}) *			1350 (1260)
ρ_r(NH$_3$) (F_{1u}) *	740 (625)		800 (625)
ρ_r(NH$_3$) (F_{2u}) *	664 (517)		730 (545)
ν_{as}(CrN) (F_{1u}) *	466 (438)		475 (455)
δ(NCrN) (F_{1u}) *	252 (242)	262 (231)	255 (225)
δ(NCrN) (F_{2u}) *	191 (194)	184 (172)	205 (185)
δ(NCrN) (F_{2u})	212 (190)	190 (172)	
δ(NCrN) (F_{1u})	264 (237)	254 (224)	
ν_{as}(CrN) (F_{1u})	476 (429)	461 (431)	
ρ_r(NH$_3$) (F_{2u})	670 (509)	724 (544)	
ρ_r(NH$_3$) (F_{1u})	741 (591)	797 (618)	
δ_s(HNH) (F_{1u})	1340 (1071)		
δ_{as}(HNH) (F_{1u})	1623 (1184)		
ν_s(NH) (F_{1u})	3270 (2399)		
ν_{as}(NH) (F_{1u})	3335 (2478)		

[a] Ref. 41a, positions of the zero phonon lines for [Cr(NH$_3$)$_6$](ClO$_4$)$_3$: 15,232 cm^{-1} (295 K), 15,221 cm^{-1} (80 K); [Cr(ND$_3$)$_6$](ClO$_4$)$_3$: 15,243 cm^{-1} (295 K), 15,232 cm^{-1} (80 K); Stokes lines measured at 80 K, anti-Stokes lines at 295 K. [b] Ref. 34, O—O transition: 15,212 cm^{-1} ([Cr(NH$_3$)$_6$]$^{3+}$), 15,230 cm^{-1} ([Cr(ND$_3$)$_6$]$^{3+}$). [c] Lines: ref. 135, assignment: ref. 34; O—O transition: 15,175 cm^{-1} ([Cr(NH$_3$)$_6$]$^{3+}$), 15,185 cm^{-1} ([Cr(ND$_3$)$_6$]$^{3+}$).

$(NH_3)_6](ClO_4)_3$ and of $[Cr(NH_3)_6]^{3+}$ (aq.) are rather large. The same is also true if one compares $\rho_r(NH_3)(F_{1u})^*$ and $\rho_r(NH_3)(F_{2u})^*$, respectively, for $[Cr(NH_3)_6](ClO_4)_3$ in emission and $[Cr(NH_3)_6]^{3+}$ in absorption. The H/D shifts, too, differ much in many cases. Because of possible systematic errors a reinvestigation of the system seems desirable.

Recently, Flint et al. [41b] reported the $^2E_g \longleftrightarrow {^4A_{2g}}$ transition of $[Cr(NH_3)_6]CdCl_5$, $[Cr(ND_3)_6]CdCl_5$, $[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(NH_3)_6](N_3)_3$ in emission and absorption. The vibronic spectra showed splittings which were interpreted in terms of the non-cubic environments of the hexammine chromium ion.

H. FORCE CONSTANTS

(i) General remarks

As can be seen from the first column of Table 1, the determination of force constants for octahedral hexammine and tetrahedral and square-planar tetrammine complexes requires the solution of third, fourth and seventh order inverse eigen-value problems. If one assumes a rigid configuration of the ammonia groups in hexammine complexes, even eleventh and twelfth order secular equations occur. It is well known that the determination of exact force constants corresponding to species with more than one vibration is not possible, if besides the vibrational frequencies appropriate additional data are not available. In the case of ammine complex ions, the isotope shifts of the vibrational frequencies are the only additional data obtainable for determining the force field. Even by using complete IR and Raman data sets and all possible isotope shifts of the vibrational frequencies as additional data, the eigen-value problems remain underdetermined. In order to overcome the difficulties, approximation methods and/or simplified models have been used.

(ii) Urey—Bradley Force Field

The large majority of normal coordinate analyses reported in the literature has been based on the Urey—Bradley Force Field (U.B.F.F.) [138,139]. Preliminary U.B.F.F. calculations in which only that part of the potential function was considered which is directly related to the ammonia deformation vibrations $\delta_{as}(HNH)$, $\delta_s(HNH)$, $\rho_r(NH_3)$ can be found in refs. 51, 71 and 120 ($[Co(NH_3)_6]^{3+}$), [51] ($[Co(NH_3)_6]^{2+}$), [86] ($[Pd(NH_3)_4]^{2+}$, $[Pt(NH_3)_4]^{2+}$).

Nakagawa et al. [29] (see also ref. 28) calculated the internal U.B. force constants (and also some diagonal symmetry force constants) for $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Pd(NH_3)_4]^{2+}$, $[Pt(NH_3)_4]^{2+}$, and $[Cu(NH_3)_4]^{2+}$ on the basis of seven IR active frequencies for each complex (F_{1u} and E_u species, respectively). In subsequent publications [30,91] the corresponding data for $[Hg(NH_3)_2]^{2+}$ and $[Pt(NH_3)_6]^{4+}$ were also given. The values for the deformation constant H(HNH) were transferred from that determined for NH_3, ND_3, NH_4^+, and ND_4^+ [120]. The repulsion constants $F(H \cdots H)$ and $F(H \cdots M)$ were assumed to be 0.06 and 0.10 mdyn $Å^{-1}$, respectively, for all the complex ions, and the $F(N \cdots N)$ data were estimated (0.03—0.05 mdyn $Å^{-1}$) from the interaction force between Ar atoms using a Lennard—Jones potential function. All other force constants were adjusted by a trial and error method. The authors found that the metal—nitrogen stretching force constants $F(MN)$ vary in the order [28—30,91]:

$$\begin{array}{lllllllll} Pt^{IV} > & Hg^{II} > & Pt^{II} > & Pd^{II} > & Co^{III} > & Cr^{III} > & Cu^{II} > & Ni^{II} > & Co^{II} \\ 2.13 & 2.05 & 1.92 & 1.71 & 1.05 & 0.94 & 0.84 & 0.34 & 0.33 \text{ mdyn } Å^{-1}, \end{array}$$

showing that the covalent degree of the M—N bonds decreases from $[Pt(NH_3)_6]^{4+}$ to $[Co(NH_3)_6]^{2+}$. The same relationships hold for the diagonal symmetry force constant data which mainly determine $\nu_{as}(MN)(F_{1u}$ or $E_u)$. (These force constants were considered to be physically more significant than the inner U.B. force constants $K(MN)$, when the nature of chemical bonding in the complexes is discussed [30].) Nakagawa et al. [29] noted that the values of $H(HNM)$, $F_{diagonal}(\rho_r(NH_3))$ and $F_{diagonal}(\delta_s(HNH))$ vary in a similar manner. Some irregularities were explained by the statement that the ligand vibrations are more or less affected by the outer ion through hydrogen bonding. As is to be expected, the nitrogen—hydrogen stretching force constant $K(NH)$ increases from $[Pt(NH_3)_6]^{4+}$ (5.20 mdyn $Å^{-1}$) [91] to $[Co(NH_3)_6]^{2+}$ (6.00 mdyn $Å^{-1}$) [28].

When the force constant data determined for $[Co(NH_3)_6]^{3+}$ [28,29] were transferred to halogenoammine complexes of the type $[Co(NH_3)_5X]^{2+}$ and $[Co(NH_3)_4X_2]^+$, complex values resulted [30]. It was found that a value of ~0.25 mdyn $Å^{-1}$ for $F(N \cdots N)$ is needed in order to obtain real solutions. By using these values, Nakagawa and Shimanouchi recalculated the force constants for $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$. The new $K(MN)$ values (Cr^{III}: 0.84, Co^{III}: 1.05, Co^{II}: 0.10, Ni^{II}: 0.16, Cu^{II}: 0.76 mdyn $Å^{-1}$) differ considerably from those determined earlier. This is also true for $F_{diagonal}(\nu_{as}(MN))$ and $H(HNM)$. From a normal coordinate analysis for $[Co(NH_3)_6]^{3+}$ and $[Ni(NH_3)_6]^{2+}$ which also considered the IR active translatory lattice vibrations (chlorides, bromides, and iodides), Nakagawa and Shimanouchi [125] obtained force constants which are very close to those given [28,29]. The authors pointed out that the metal—nitrogen stretching force constants may be almost accurately obtained without the introduction of lattice modes, whereas the deformation constants $H(HNM)$ and $H(NMN)$ are modified showing that $\rho_r(NH_3)$ and $\delta_{as}(NMN)$ are somewhat affected by the outer ion. Similar results were obtained by a normal coordinate treatment of the optically active crystal vibrations for $[Co(NH_3)_6][Co(CN)_6]$ [76].

Terrasse et al. [27] reported a normal coordinate analysis for the IR and Raman active species of $[Rh(NH_3)_6]^{3+}$ on the basis of 7 IR and 5 Raman frequencies. Poulet et al. [95] made a similar calculation for the in-plane vibrations of $[Pt(NH_3)_4]^{2+}$ by using 7 IR and 8 Raman frequencies. The force constants $H(HNH)$, $H(HNM)$, $F(H \cdots H)$, $F(N \cdots H)$ and the intermolecular tension were transferred from [120]; K(NH) was arbitrarily estimated as 5.4 ([Rh(NH_3)$_6$]$^{3+}$) and 5.6 mdyn Å^{-1} ([Pt(NH_3)$_4$]$^{2+}$). The skeletal force constants K(MN), H(NMN), and F(N ⋯ N) were obtained as follows: 1.6, 0.085, 0.1 mdyn Å^{-1} ([Rh(NH_3)$_6$]$^{3+}$) and 2.1, 0.19, 0.09 mdyn Å^{-1} ([Pt(NH_3)$_4$]$^{2+}$).

Miles et al. [109] determined the U.B. force constants for the diammine silver (I) and mercury(II) ions by using IR and Raman data. Different force constant sets were given for [Hg(NH_3)$_2$]Cl_2 and [Hg(NH_3)$_2$]Br_2. Their F(HgN) values (0.85 mdyn Å^{-1} for the chloride and 0.53 mdyn Å^{-1} for the bromide) are considerably lower than those reported earlier [30] (2.05 mdyn Å^{-1}, see above). K(AgN) was obtained as 0.31 mdyn Å^{-1}.

Nakamoto et al. [112] reported the force constants of [Zn(NH_3)$_4$]$^{2+}$ calculated on the basis of Raman data for [^{64}Zn(NH_3)$_4$]$^{2+}$, [^{68}Zn(NH_3)$_4$]$^{2+}$, and [Zn(ND_3)$_4$]$^{2+}$. All vibrations for the whole complex except two torsional modes were considered. The best agreement between observed and calculated frequencies was obtained with K(NH): 5.66, K(ZnN): 0.54, H(HNH): 0.43, H(ZnNH): 0.048, H(NMN): 0.018, F(H ⋯ H): 0.09, F(Zn ⋯ H): 0.24, F(N ⋯ N): 0.19 mdyn Å^{-1}.

As can be shown by model calculations for a complete ammine metal complex, the skeletal vibrations are only slightly coupled with the ligand vibrations, and the ammonia ligands can approximately be regarded as dynamic units [44] (Point Mass Model (P.M.M.) [68], see also the calculations of the potential energy distribution [28,30,109]). Mizushima et al. [86] calculated the skeletal U.B. force constants of [Pt(NH_3)$_4$]$^{2+}$ on the basis of the P.M.M. Since no low frequency IR data were known at that time, only the Raman frequencies (Mathieu [82]) were used. The force constants K(PtN): 2.804, H(NPtN): 0.147 and F(N ⋯ N): 0.05 mdyn Å^{-1} do not reproduce ν_{as}(PtN) and δ_{as}(NPtN)(E_u) (Table 6). Shimanouchi and Nakagawa [68] obtained the corresponding force constants for [Co(NH_3)$_6$]$^{3+}$ by using the skeletal IR frequencies of [Co(NH_3)$_6$]$^{3+}$, [Co(NH_3)$_5$X]$^{2+}$ and *trans*-[Co(NH_3)$_4$$X_2$]$^{+}$. The Raman frequencies ν_s(CoN)(A_{1g}), ν(CoN)(E_g), and δ(NCoN)(F_{2g}) calculated from K(CoN): 1.07, H(NCoN): 0.29 and F(N ⋯ N): 0.10 mdyn Å^{-1} do not agree with the measured values (Table 3). This is also true for the Raman frequencies calculated from K(CoN): 1.34, H(NCoN): 0.22 and F(N ⋯ N): 0.18 mdyn Å^{-1}, which have been determined by Yeranos [132] on the basis of skeletal IR data for [Co(NH_3)$_6$]$^{3+}$ and [Co(ND_3)$_6$]$^{3+}$.

The U.B.F.F. data for the framework of the following complexes were determined on the basis of IR and Raman data: [Pd(NH_3)$_4$]$^{2+}$ (K: 2.2, H: 0.1, F: 0.2 mdyn Å^{-1}) [89], [Co(NH_3)$_4$]$^{2+}$ (K: 1.19, H: 0.09, F: 0.09 mdyn Å^{-1}) [50], [Zn(NH_3)$_4$]$^{2+}$ (K: 1.10, H: 0.02, F: 0.19 mdyn Å^{-1}) [84], [Ni(NH_3)$_6$]$^{2+}$ (K: 0.46, H: 0.02, F: 0.23 mdyn Å^{-1}) [84].

If one compares the force constants for many complexes reported in the literature, the disagreements are readily apparent (see, for example, the K(MN) values for [Ni(NH_3)$_6$]$^{2+}$ (0.16, 0.34, 0.46 mdyn Å^{-1}), [Pd(NH_3)$_4$]$^{2+}$ (1.71, 2.2 mdyn Å^{-1}) and [Zn(NH_3)$_4$]$^{2+}$ (0.54, 1.10 mdyn Å^{-1})). Some reasons for this fact have been pointed out by the present authors [44,84]:

(a) U.B. force constants determined on the basis of 7 IR active F_{1u}, F_2, and E_u vibrational frequencies, respectively, are not very reliable. On the one hand, additional constraints are necessary, which can be estimated only very arbitrarily, but which have much influence on the final force constants (see, for example, the data reported in ref. 30). On the other hand, the Raman data are disregarded. The calculations do not give reliable M—N stretching force constants if the Raman and IR active metal—nitrogen stretching frequencies differ by more than several wavenumbers. As can be seen from the tables, this applies to many complexes.

(b) The application of simple least-squares procedures including all fundamentals is problematical. One can sometimes obtain force constants which reproduce the measured frequencies but which are not physically meaningful. For example, the analytical expressions for those diagonal force constant matrix elements which mainly determine the M—N stretching vibrations show clearly, how insensitive K(MN) is to these matrix elements because of the presence of other terms comparable in value of K(MN).

(iii) General Valence Force Field

Under the assumption of the Point Mass Model the order of the secular equations is drastically reduced. As can be seen from the second column of Table 1, not more than two skeletal vibrations are involved in one species. The skeletal symmetry force constants of first order secular equations can be calculated directly from the corresponding vibrational frequencies, those of second order equations can be determined from the fundamentals and at least one piece of additional information. These force constants are called pseudo-exact [84]. The concept refers to a force field based on a simplified but physically reasonable model, using so much additional information that it can be determined definitely within the approximation. It has been shown [140] that small isotope shifts can be used to calculate force constants within reliable error limits, even if the shifts can only be measured with relatively low accuracy. A theoretical interpretation of this effect has been given in terms of the Jacobians $\partial(\Delta\lambda_i/\lambda_i)/\partial F_{ij}$ [141,142].

The present authors used the metal isotope, H/D, and $^{14}N/^{15}N$ shifts of the IR bands corresponding to the antisymmetric metal—nitrogen stretching vibrations in the spectra of hexammine chromium, cobalt(III), nickel, of tetrammine palladium, copper, cadmium, and the Raman lines of tetrammine zinc as additional data for force constant calculations on the basis of the P.M.M. [37,65, 84,92,115]. Table 12 contains the skeletal vibrational frequencies of $[Ni(NH_3)_6]^{2+}$, $[^{58}Ni(NH_3)_6]^{2+}$, $[^{62}Ni(NH_3)_6]^{2+}$, $[Ni(^{15}NH_3)_6]^{2+}$, $[Ni(ND_3)_6]^{2+}$ and the pseudo-exact F_{1u} symmetry force constants determined by help of three isotope shifts of ν_{as}(NiN)(F_{1u}) as illustrative examples. The A_{1g}, E_g, and F_{2g} symmetry force constants (calculated from the fundamentals) as well as the inner G.V.F.F. force constant data for f(NiN) are also stated. The table shows that the agreement between the skeletal force constants calculated by using

TABLE 12

Skeletal vibrational frequencies and force constants for $[Ni(NH_3)_6]^{2+}$ (for further details see text)

ν_i(cm^{-1})	$[Ni(NH_3)_6]^{2+}$	$[^{58}Ni(NH_3)_6]^{2+}$	$[^{62}Ni(NH_3)_6]^{2+}$	$[Ni(^{15}NH_3)_6]^{2+}$		$[Ni(ND_3)_6]^{2+}$	
$\nu_1(A_{1g}) = \nu_s$(NiN)	370 ± 1						R
$\nu_2(E_g) = \nu$(NiN)	265 ± 3						R
$\nu_3(F_{1u}) = \nu_{as}$(NiN)	334.5 ± 0.5	335.2 ± 0.3	333.0 ± 0.3	327.5 ± 0.3		315.5 ± 0.3	IR
$\nu_4(F_{1u}) = \delta$(NNiN)	215 ± 1	217 ± 1	214 ± 1	214 ± 1		205 ± 1	IR
$\nu_5(F_{2g}) = \delta$(NNiN)	235 ± 1						R
F_{ij}(mdyn Å^{-1})	$\Delta\nu_3(^{58}Ni/^{62}Ni)$	$\Delta\nu_3(^{14}N/^{15}N)$	$\Delta\nu_3$(H/D)	$L_{34} = 0$	Fadini	UBFF	
$F_{33}(F_{1u})$	0.87 ± 0.02	0.88 ± 0.02	0.85 ± 0.01	0.78	0.81	0.88	
$F_{34}(F_{1u})$	0.18 ± 0.03	0.20 ± 0.03	0.16 ± 0.02	0.10	0.12	0.21	
$F_{44}(F_{1u})$	0.15 ± 0.01	0.15 ± 0.01	0.14 ± 0.00$_5$	0.13	0.14	0.16	
$F_{11}(A_{1g})$			1.37				
$F_{22}(E_g)$			0.71				
$F_{55}(F_{2g})$			0.14				
f(NiN) $= 1/6(F_{11} + 2F_{22} + 3F_{33})$	0.90	0.90	0.89	0.85	0.87	0.91	

different isotopic frequencies is very good. This conformity, which could equally be shown for $[Co(NH_3)_6]^{3+}$, $[Cu(NH_3)_4]^{2+}$ and $[Zn(NH_3)_4]^{2+}$ can be regarded as unequivocal proof of the applicability of the P.M.M. used in conjunction with isotopic data.

For those complexes, for which reliable isotope shifts of the skeletal vibrational frequencies have not yet been determined, supplementary assumptions are necessary to determine the skeletal symmetry force constants of second order secular equations. Reports on approximate G.V.F.F. force constants (P.M.M.) by using IR and Raman data can be found, in ref. 34 for $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$ (f(CrN): 1.60, f(CoN): 1.72 mdyn Å^{-1}, constraint: estimation of the interaction constant $f_{r\alpha}$), in ref. 47 for $[Ru(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$ (f(RuN): 2.07, f(RhN): 2.31, f(IrN): 2.40 mdyn Å^{-1}, simplified valence-force expressions), in ref. 50 for $[Co(NH_3)_4]^{2+}$ (f(CoN): 1.38 mdyn Å^{-1} L matrix approximation method ($L_{ij}(j > i) = 0$) [143—145]; f(CoN): 1.31 mdyn Å^{-1}, Modified Valence Force Field (M.V.F.F.) ($F_{ij}(i \neq j) = 0$), and in refs. 146, 147 for $[Pt(NH_3)_4]^{2+}$ (f(PtN): 2.44 mdyn Å^{-1}, Fadini method [145,148,149]).

The present authors [44] have calculated the skeletal force constants for 19 transition metal ammine complexes on the basis of critically selected spectral data by using different approximation methods. A comparison of the approximate symmetry force constants with the pseudo-exact data did not reveal satisfactory agreement in all cases. On the other hand, the approximation data for the inner G.V.F.F. force constant f(MN), which is very useful for understanding the nature of bonding in complexes, agree well with the pseudo-exact data within an error of 5%. One can assume with some certainty that the inaccuracies in the approximate f(MN) values for those complexes, for which no pseudo-exact data are known, are of comparable order of magnitude. Table 12 shows the force constants for $[Ni(NH_3)_6]^{2+}$, obtained by help of the L matrix approximation, the Fadini method and the U.B.F.F. Table 13 contains the reported [44] f(MN) values (L matrix approximation method). The estimated bond orders according to Siebert [1,150] are given in parentheses. It should be noted that the inner G.V.F.F. force constants f(MN) cannot be directly compared with the inner U.B.F.F. force constants K(MN) given in Section H(ii). The latter constants are generally expected to have lower values.

Some correlations between the metal—nitrogen stretching force constants may be summarized here (cf. ref. 44 for further details): f(MN) for ammine complexes with the same symmetry, with central atoms having the same oxidation state and belonging to the same transition series, do not differ much. f(MN) increases when the charge of the central atom increases (cf. $[Co(NH_3)_6]^{2+}$—$[Co(NH_3)_6]^{3+}$) or when the coordination number decreases (cf. $[Co(NH_3)_6]^{2+}$—$[Co(NH_3)_4]^{2+}$). For ammine complexes of transition metals in the same group, the force constant increases from lighter to heavier atom (cf. $[Co(NH_3)_6]^{3+}$—$[Rh(NH_3)_6]^{3+}$—$[Ir(NH_3)_6]^{3+}$), for nontransition metal complexes, f(MN) decreases (cf. $[Zn(NH_3)_4]^{2+}$—$[Cd(NH_3)_4]^{2+}$). The estimated bond orders for hexammine complexes of divalent metals indicate rather little covalent de-

TABLE 13

G.V.F.F. metal—nitrogen stretching force constants and bond orders [a] of transition metal ammine complexes (X = NH_3) (cf. ref. 44)

	VIa	VIIa	VIII			Ib	IIb
O_h		MnX$_6^{2+}$ 0.6$_7$ (0.3)	FeX$_6^{2+}$ 0.7$_3$ (0.3)	CoX$_6^{2+}$ 0.8$_0$ (0.3)	NiX$_6^{2+}$ 0.85 (0.4)		ZnX$_6^{2+}$ 0.6$_9$ (0.3)
	CrX$_6^{3+}$ 1.66 (0.6)			CoX$_6^{3+}$ 1.86 (0.6)			
T_d				CoX$_4^{2+}$ 1.44 (0.5)			ZnX$_4^{2+}$ 1.43 (0.5)
D_{4h}						CuX$_4^{2+}$ 1.42 (0.5)	
O_h							CdX$_6^{2+}$ 0.7$_3$ (0.4)
			RuX$_6^{3+}$ 2.01(0.8)	RhX$_6^{3+}$ 2.10 (0.8)			
T_d							CdX$_4^{2+}$ 1.24 (0.5)
D_{4h}					PdX$_4^{2+}$ 2.15 (0.8)		
O_h			OsX$_6^{3+}$ 2.1$_3$ (0.9)	IrX$_6^{3+}$ 2.28 (0.9)			
					PtX$_6^{4+}$ 2.75 (1.0)		
D_{4h}					PtX$_4^{2+}$ 2.54 (1.0)		

[a] In brackets.

gree. Hexammine complexes of trivalent and quadrivalent metals belonging to the second and third transition series have nearly pure covalent single bonds. This is also true for tetrammine palladium and platinum.

Block [59] calculated the force constants for the whole ion $[Co(NH_3)_6]^{3+}$ assuming O_h symmetry and employing IR frequencies of the normal and fully deuterated complex as well as (incorrect) Raman data from ref. 77. He used a M.V.F.F., according to ref. 27 with oversimplified F and G matrix elements. f(CoN) was determined as 2.0 mdyn Å^{-1} and f(NH) as 5.2 mdyn Å^{-1}.

Normal coordinate analyses for the complete ions $[Zn(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ (NH_3 groups at special positions) on the basis of a force constant method by Cyvin [151—153] in which special symmetry coordinates for ligand vibrations, ligand—framework couplings, and framework vibrations are used, can be found in refs. 92, 154 and 155. The force constants reproduce satisfactorily the observed frequencies for all the isotopic compounds. The framework force constants fall within the error limits of the pseudo-exact P.M.M. data [37,65,84,92], which confirms their reliability.

The ligand force constants were used to calculate the frequencies of free ammonia [92,154]. As expected, these frequencies turned out to be substantially different from those measured for gaseous NH_3 due to kinematic coupling. This effect was found to be small for the N—H stretching frequencies, but significant for bending. In the case of $[Zn(NH_3)_4]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, the mean amplitudes of vibration were calculated for all types of interatomic distances at different temperatures. The Zn—N and Cu—N mean amplitudes at 298 K were determined as 0.066 Å [154] and 0.056 Å [92].

It should be noted for the sake of completeness that some authors estimated metal—nitrogen stretching force constants from one single frequency (S.V.F.F. - Simple Valence Force Field). Kobayashi and Fujita [24] calculated f(MN) values from IR bands due to $\rho_r(NH_3)$, which they erroneously assigned to ν_{as}(MN). For $[Na(NH_3)_4]^+$ (cf. Section C(i)), Leonard et al. [9] obtained f(NaN) = 1.9 mdyn Å^{-1} from a Raman line at 435 cm^{-1}. For $[Be(NH_3)_4]^{2+}$, $[Al(NH_3)_6]^{3+}$, $[Mg(NH_3)_6]^{2+}$, $[Sc(NH_3)_6]^{3+}$ and $[Y(NH_3)_6]^{3+}$, Grigor'ev et al. [14,17] determined f(MN) = 2.4, 2.2, 1.1, ~1.5, ~1.25 mdyn Å^{-1}, respectively, from ν_s(MN) (Raman) (for the Sc and Y complexes estimated frequencies were used). The metal—nitrogen stretching force constants for $[Ca(NH_3)_6]^{2+}$ and $[Sr(NH_3)_6]^{2+}$ (0.75 and 0.61 mdyn Å^{-1}, respectively) were calculated [16] by using a relation between ammonia rocking and metal—nitrogen stretching frequencies. From the bands due to ν_{as}(AgN) and ν_s(AgN) in the IR spectra of diammine silver sulfate and nitrate, Geddes and Bottger [108] obtained f(AgN) = 1.72 and 1.58 mdyn Å^{-1}, respectively. Plane [114] calculated f(ZnN) = 1.8 mdyn Å^{-1} for $[Zn(NH_3)_4]^{2+}$ from ν_s(ZnN)(A_1). His f(CdN) value of 1.2 mdyn Å^{-1} determined from a Raman line which he mistakenly attributed to ν_s(CdN)(A_1) of $[Cd(NH_3)_4]^{2+}$ (cf. Section D(vii)) applies to $[Cd(NH_3)_6]^{2+}$. f(HgN) = 1.7 mdyn Å^{-1} for $[Hg(NH_3)_4]^{2+}$ was calculated from a Raman line at 350 cm^{-1}. As has already been stated, the assignment of this line is doubtful. Plane also estimated the M—N bond orders from relative Raman intensities of the A_1 modes and by comparison with the data for tetrahedral tetrachloro and tetrabromo complexes of Zn, Cd, Hg, Ga. For [Zn(NH$_3$)$_4$]$^{2+}$ he obtained a bond order of 0.48 (cf. our value reported in Table 13).

By using a simple triatomic model for calculating metal—ligand vibrations, Baylis [156] obtained the metal—nitrogen stretching force constants for [Co-[Co(NH$_3$)$_6$]$^{3+}$, [Co(ND$_3$)$_6$]$^{3+}$: 2.00, [Co(NH$_3$)$_6$]$^{2+}$: 0.84, [Cr(NH$_3$)$_6$]$^{3+}$: 1.72, [Ni(NH$_3$)$_6$]$^{2+}$: 0.88, [Ni(ND$_3$)$_6$]$^{2+}$: 0.93 mdyn Å^{-1}.

I. CORRELATIONS OF SKELETAL FORCE CONSTANTS WITH OTHER PHYSICAL PROPERTIES

(i) Bond lengths

Table 14 contains the sums of estimated covalent and ionic radii and a compilation of metal—ammonia bond lengths for ammine complexes determined by X-ray diffraction in recent years (for previous literature citations see refs. 7, 157 and 158). Since accurate M—N distances are known for only a few pure metal ammine complexes, the data for complexes containing other ligands besides NH$_3$ are also stated. The bond lengths reported in the table are average values of all metal—nitrogen (ammonia) distances in a given compound (except in cases with a pronounced *trans*-effect where only the *cis* distances have been considered). A comparison of the experimentally determined mean

TABLE 14

Metal—nitrogen bond lengths in ammine complexes (Å)

Metal ion	Sum of covalent radii	Sum of ionic radii	Bond length	Compound	Ref.
V^{V}	1.97	2.30	2.110	NH$_4$[VO(O$_2$)(NH$_3$)]	159
Cr^{III}	1.93	2.40	2.064	[Cr(NH$_3$)$_6$]CuCl$_5$	160, 161
			2.059	[Cr(NH$_3$)$_6$]CuBr$_5$	161
			2.067	[Cr(NH$_3$)$_6$]MnF$_6$	162
			2.073	[Cr(NH$_3$)$_6$]FeF$_6$	162
			2.08	[(NH$_3$)$_5$Cr(OH)Cr(NH$_3$)$_5$]Cl$_5$ · H$_2$O	163
			2.11	[(NH$_3$)$_5$CrOCr(NH$_3$)$_5$]Cl$_4$ · H$_2$O	164
Cr^{IV}	1.93	—	2.113	Cr(O$_2$)$_2$(NH$_3$)$_3$	165
Ru^{II}	2.00	—	2.144	[Ru(NH$_3$)$_6$]I$_2$	166
			2.137	[Ru(NH$_3$)$_6$]Cl$_2$	167
			2.127	[Ru(NH$_3$)$_5$NO$_2$]Cl · H$_2$O	168
			2.10	[Ru(NH$_3$)$_5$N$_2$]Cl$_2$	169
			2.127	[Ru(NH$_3$)$_4$SO$_2$Cl]Cl	48
Ru^{III}	2.00	2.40	2.104	[Ru(NH$_3$)$_6$](BF$_4$)$_3$	166
			2.10	[Ru(NH$_3$)$_5$Cl]Cl$_2$	170
			2.169	[Ru(NH$_3$)$_5$DMSO](PF$_6$)$_2$	171

TABLE 14 (continued)

Metal ion	Sum of covalent radii	Sum of ionic radii	Bond length	Compound	Ref.
			2.09	$[Ru(NH_3)_5NO]Cl_3 \cdot H_2O$	172
			2.137	$[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4 \cdot H_2O$	173
			2.125	$Ru_3O_2(en)_2(NH_3)_{10}Cl_6$	174
Os^{II}	—	—	2.137	$[Os(NH_3)_5N_2]Cl_2$	175
Co^{II}	1.91	2.45	2.114	$[Co(NH_3)_6]Cl_2$	176, 177
Co^{III}	1.91	2.34	1.936	$[Co(NH_3)_6]I_3$	177, cf. 176
			1.968	$[Co(NH_3)_6][ZnCl_4]Cl$	178
			1.96	$[Co(NH_3)_6]Cu_5Cl_{17}$	179
			1.960	$[Co(NH_3)_6]CdCl_5$	180
			1.982	$[Co(NH_3)_6]SbCl_6$	181
			1.990	$[Co(NH_3)_6]Sb_2F_9$	182
			1.972	$[Co(NH_3)_6][Co(CN_6]$	183
			1.947	$[(NH_3)_5CoN_2O_2HCo(NH_3)_5]^{5+}$	184
			1.957	$[Co(NH_3)_5NO_2]Cl_2$	185
			1.978	$[Co(NH_3)_5NO_2]Br_2$	186
			1.981	$[(Co(NH_3)_5NO]Cl_2$	187, cf. 188, 189
			1.966	$[Co(NH_3)_5N_3](N_3)_2$	190
			1.98	$[Co(NH_3)_5N_3]Cl_2$	191
			1.968	$[Co(NH_3)_5Cl]Cl_2$	192
			1.96	$[Co(NH_3)_5CO_3]Br \cdot H_2O$	193
			1.963	$[CH_3CONHCo(NH_3)_5](ClO_4)_2$	194
Rh^{III}	2.00	2.40	2.071	$[RhH(NH_3)_5](ClO_4)_2$	195
			2.056	$[Rh(NH_3)_5Cl]Cl_2$	196
			2.057	$[Rh(NH_3)_5Br]Br_2$	196
			2.072	$[RhEt(NH_3)_5]Br_2$	197
Ir^{III}	2.02	—	2.121	$[Ir(NH_3)_5(SCN)](ClO_4)_2$	198
Ni^{II} (cf. ref. 7)	1.90	2.49	2.10	$Ni(NH_3)(CN)_2 \cdot nH_2O$	199, 200
			2.07	$Ni(NH_3)_4(NO_2)_2$	201, 202
			2.15	$Ni(NH_3)_4(NCS)_2$	202, 203
			2.07	$Ni(NH_3)_3(NCS)_2$	202
Pd^{II}	2.03	2.21	2.11	$Pd(NH_3)SO_3$	204
Pt^{II}	2.05	2.51	2.051	$[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$	205
			2.01	*cis*-$Pt(NH_3)_2Cl_2$	206
			2.05	*trans*-$Pt\ (NH_3)_2Cl_2$	206
Cu^{II}	1.92	2.40	2.032	$[Cu(NH_3)_4]SO_4 \cdot H_2O$	207
			2.015	$[Cu(NH_3)_4]SeO_4$	207
			1.994	$Na_4[Cu(NH_3)_4]Cu(S_2O_3)_2$	208
			2.025	$[Cu(NH_3)_4](CuCl_2)_2 \cdot H_2O$	209
			1.996	$[Cu(NH_3)_4](CuBr_2)_2$	209
			2.14	$[Cu(NH_3)_4](CuI_2)_2$	209
			2.11 (eq.)	$[Cu(NH_3)_4(NH_3)_2]Cl_2$ $[Cu(NH_3)_4(NH_3)_2]Br_2$	105 105
Zn^{II}	2.00	2.45	2.00	$[NH_4)_2[Zn(NH_3)_2(CrO_4)_2]$	210

bond lengths data for hexacoordinated nickel(II) and cobalt(II) complexes with the sums of covalent radii reveals that the d_{MN} values are considerably greater (>10%) than those expected for covalent single bonds. This confirms the statement made on the basis of force constant calculations that the covalent character of the metal—ligand bonds in these complexes is not great. In the case of hexacoordinated Co^{III}, Ru^{III}, Rh^{III}, Ir^{III} and of tetracoordinated Pd^{II} and Pt^{II} complexes with $f(MN)$ values around 2 mdyn $Å^{-1}$ and bond orders between 0.6 and 1, the differences between actual bond lengths and sums of covalent radii are less than 5%.

If one compares the metal—nitrogen stretching force constants of Table 13 with the mean bond lengths in hexacoordinated complexes of central atoms belonging to the same transition series (Co^{II}: 2.114 Å [176,177], Ni^{II}: 2.10 Å [199—203], Cr^{III}: 2.07 Å [160—162], Co^{III}: 1.97 Å [176—183]; and Ru^{III}: 2.10 Å [166,170], Rh^{III}: 2.07 Å [195—197]) it turns out as expected that the force constants increase with decreasing M—N distances, though a direct correlation cannot be established. It must be taken into consideration, however, that for some complexes d_{MN} is strongly dependent on the nature of the anion (or (if present) on other ligands) (Table 14), and hence a comparison of bond lengths in different complexes with different anions (and crystal structures) is problematical.

(ii) Stability constants and ligand field stabilization energies

For each step of the formation of an ammine complex in aqueous solution by the displacement of water molecules by ammonia there is a thermodynamic equilibrium, described by a stability constant K_n, the antilogarithm of which is directly related to the free energy change ΔG_n^0 at the binding of the *n*th ligand. Several authors have tried to correlate stability constants with IR data, especially with $\rho_r(NH_3)$ and $\nu_{as}(MN)$ frequencies (cf. refs. 24, 25, 35, 43 and 52).

We wish now to compare the logarithms of individual stability constants for ammine complexes of divalent metals belonging to the first transition row with the metal—ligand stretching force constants for the hexammines. Figure 3 contains a plot of log K_n and $f(MN)$ versus atomic number. The stability constant data for the cobalt, nickel, copper, and zinc complexes refer to EMF measurements at 30°C of solutions with ionic strengths held constant at 2 mol l^{-1} by addition of NH_4NO_3. log K_1 and log K_1 for the manganese and iron complexes were determined from a hypothesis at temperatures between 20° and 30°C in solutions with ionic strengths of 0.5—5 mol l^{-1}. All stability constants have been collected from refs. 119 and 211.

The ligand field stabilization energies for the high spin hexammines of divalent metals are also given in Fig. 3. For $[Fe(NH_3)_6]^{2+}$, the LFSE has been determined from an estimated value of 10 $Dq = f \cdot g$ by using $g = 12500$ [212]; for $[Co(NH_3)_6]^{2+}$ an approximate 10 Dq value deduced from the $\nu_1(^4T_{2g} \leftarrow {}^4T_{1g})/\nu_3(^4T_{1g}(P) \leftarrow {}^4T_{1g})$ ratio [213] has been used; the effect of configuration inter-

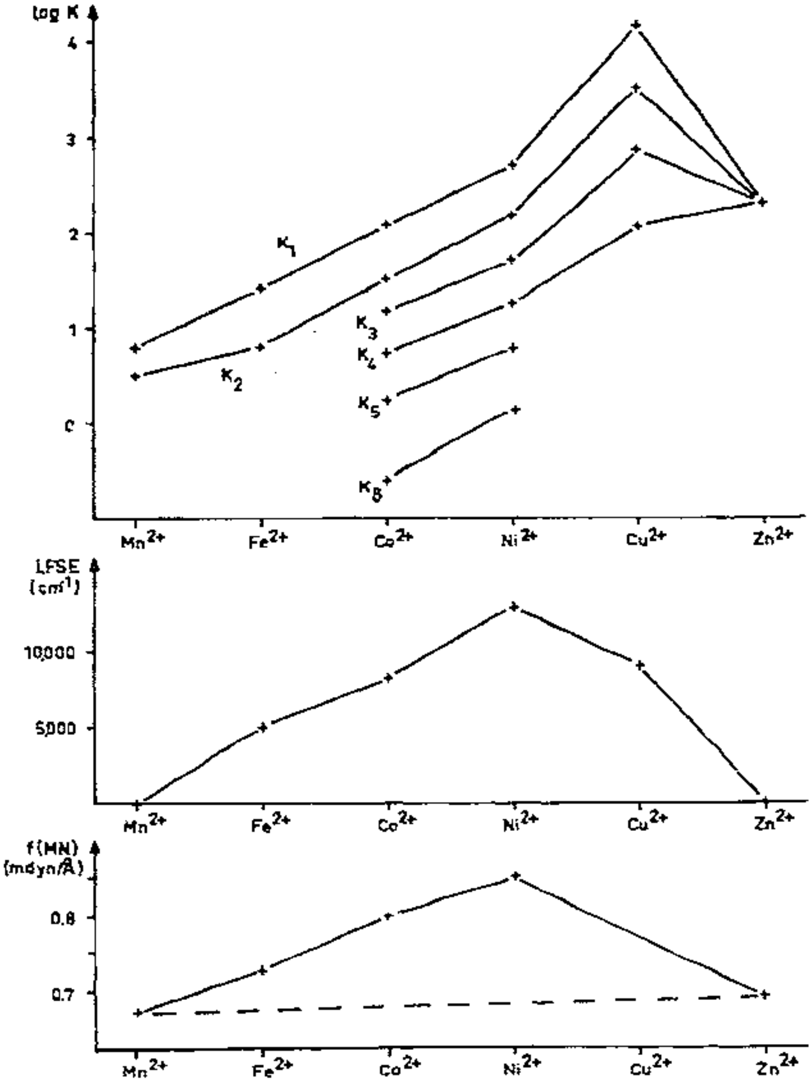

Fig. 3. Plot of the logarithms of individual stability constants for ammine complexes of divalent metal ions belonging to the first transition row, of the ligand field stabilization energies, and of the metal—nitrogen stretching force constants for the hexammines versus atomic number.

action was neglected. The LFSE for $[Ni(NH_3)_6]^{2+}$ has been directly determined from spectroscopic data [213], that for hexacoordinated copper is an idealized value assuming a regular octahedron which does not exist because of strong tetragonal distortion [105]. Ligand field stabilization energies for trivalent low spin complexes are much higher than those given in Fig. 3. For example, the values for $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$ and $[Ir(NH_3)_6]^{3+}$, which can be calculated from spectroscopic data (cf. 213) are 27093 cm^{-1}, 65690 cm^{-1} and 81490 cm^{-1}, respectively.

It is well known that the log K_n values fall in the Irving—Williams series [214] ($Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$). As can be seen from Figure 3, the metal—nitrogen stretching force constants follow the same trend. (This is also true for the frequencies due to $\nu_{as}(MN)(F_{1u})$, cf. refs. 43, 212 and 215.) The evaluation of complexity constants and IR frequencies was explained by help of the ligand field theory which predicts a maximum stabilization for Ni^{2+} and no LFSE for Mn^{2+} and Zn^{2+}. The inconsistency in the case of copper arises from the fact that octahedral hexammine copper does not exist in aqueous solution.

In the terminology of the MO theory, the e_g orbitals are antibonding causing destabilization, whereas the t_{2g} orbitals are nonbonding without effecting the bond strengths. To the first approximation, the LFSE can be defined as the product of the ligand field parameter Δ and the number of vacant positions in antibonding orbitals [216]. Yatsimirskii [217] defined the LFSE as the change in energy on going from a structure with a limitingly uniform distribution of electrons in all the nonbonding and antibonding orbitals to a structure with the actual distribution of the electrons. For octahedral hexammine high spin complexes, he got qualitatively the same relation between electronic configuration and LFSE as that given in Figure 3.

If one compares the ligand field stabilization energies of hexammine iron(II), cobalt(II,III) and Ni(II) with the energies for individual M—N bonds (see next paragraph), it turns out that the LFSE's contribute only 4—9% to the total energy. Bond energies for complexes with much higher LSFE values have not yet been determined, but a comparison of force constants and LFSEs in the series $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$ reveals that the f(MN) values increase by less than 25% on going from Co to Ir, whereas we find a LFSE increase of more than 200%. This shows clearly that even the extremely high ligand field stabilization energies for low-spin hexammine complexes of metals belonging to the second and third transition series are only minor sources of the bond strengths.

According to Bjerrum [218] the logarithm of the mean complexity constant as defined by

$$1/n \sum_n \log K_n$$

is a direct measure of the affinity between ammonia and metal ion in aqueous solution. This expression gives average values per complex-bound group irrespective of the actual number of ligands. For all transition metal ammine complexes, for which logarithms of stability constants have been given [119,211], we have plotted the mean log K_n values versus our f(MN) data [44]. Except for $[Mn(NH_3)_6]^{2+}$, $[Fe(NH_3)_6]^{2+}$ (see above), $[Cr(NH_3)_6]^{3+}$, $[Pd(NH_3)_4]^{2+}$ and $[Pt(NH_3)_4]^{2+}$, the data determined from EMF measurements at 30°C (medium: NH_4NO_3, constant ionic strengths of 2 mol l^{-1} or constant concentrations of the inert salt) have been used. The stability constants for the Pd and Pt complexes refer to constant ionic strengths of 1 mol l^{-1} (media: $NaClO_4$, KNO_3) and to 25 and 18°C, respectively. For $[Cr(NH_3)_6]^{3+}$ only a maximum value of the overall stability constant could be determined (25°C, constant concentration of 4.5 mol l^{-1} NH_4Cl). Strictly speaking, only those mean stability constants can be compared with each other and correlated to other data, which have been determined under the same conditions. In spite of the fact that this is not true for all data used for Fig. 4, one finds a qualitative relation between metal—ligand stretching force constants and logarithms of the mean complexity constants. (Geddes and Bottger [108] reported a similar graph for some complexes by using force constants based on a S.V.F.F.)

(iii) Total bond energies

$\Delta H_f[M(NH_3)_m]^{n+}$ (g) the enthalpy of formation of an ammine complex in

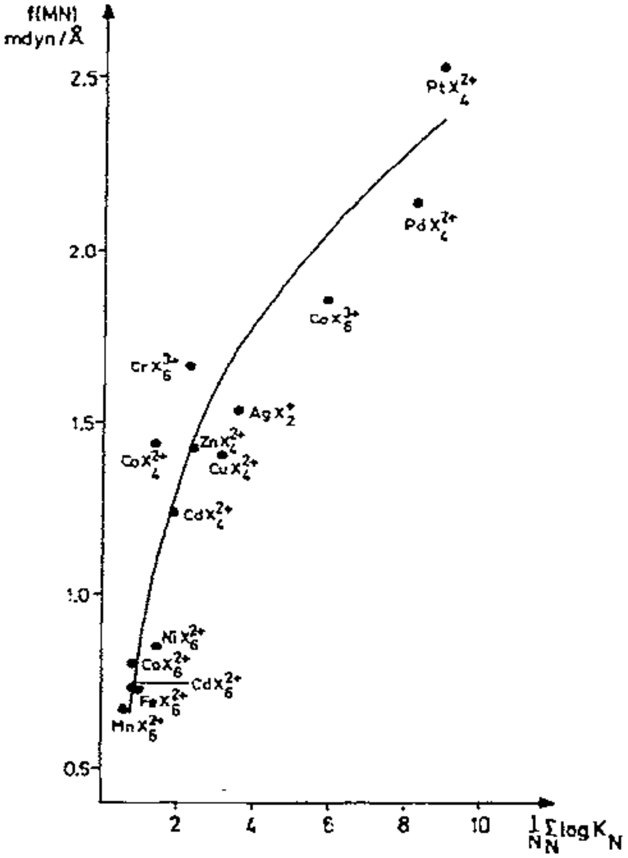

Fig. 4. Plot of the logarithms of the mean complexity constants of ammine complexes against metal—nitrogen stretching force constants ($X = NH_3$).

the gaseous phase, i.e. the energy of the reaction

$$M^{n+}(g) + mNH_3(g) \rightarrow [M(NH_3)_m]^{n+}(g)$$

is equal to m times the M—NH_3 bond energy. The total bond energy can be calculated by a thermodynamic cycle from the standard enthalpies of formation of gaseous ammonia, halide ion, and metal ion in the valence state, from the standard enthalpy of formation of the crystalline complex, and from the pseudo-lattice energy cf. ref. 219. In Fig. 5, we have plotted our metal-nitrogen stretching force constants for the hexammine complexes of divalent metal ions of the first transition series and for $[Co(NH_3)_6]^{3+}$ versus the total bond energies determined originally by Cotton [220] and recalculated by Ashcroft and Mortimer [219] who used some more recent subsidiary data. (Yatsimirskii [217] obtained nearly the same bond energies on the basis of a thermodynamic cycle and by using an appropriate MO method.)

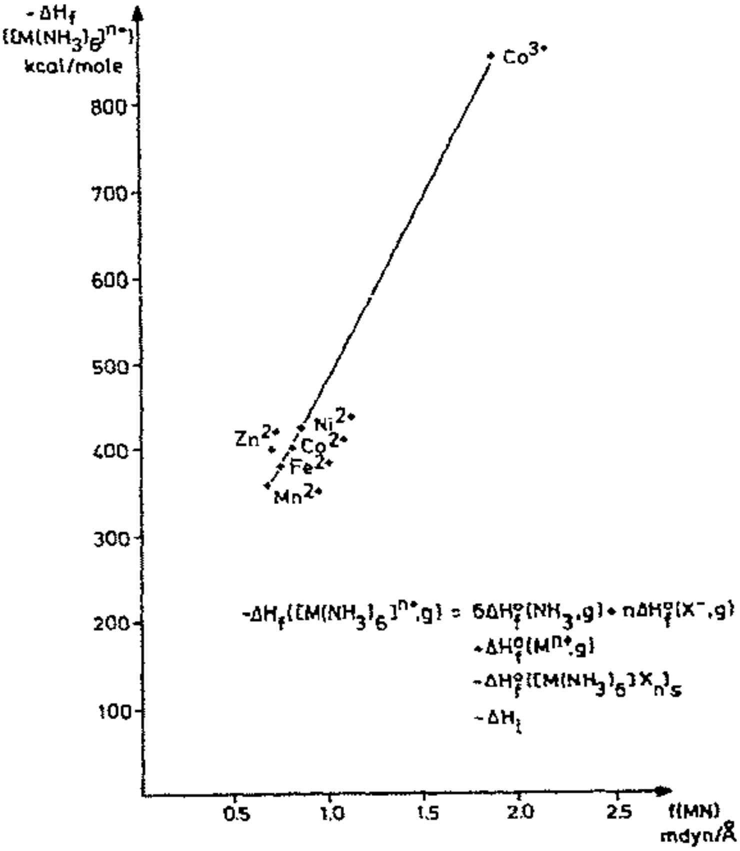

Fig. 5. Plot of metal—nitrogen stretching force constants for hexammine complexes of divalent metal ions of the 1st transition series and for $[Co(NH_3)_6]^{3+}$ versus the total bond energies obtained by a thermodynamic cycle.

Whereas the dissociation energy of a bond is given by the depth of the potential well, the stretching force constant is a measure of the curvature of the potential function near the equilibrium position. Generally one gets linear relations between bond energies and stretching force constants. A view on Fig. 5 shows that this dependency is confirmed, but it must be conceded that only very few data are available and that the reliability of bond energy values as calculated by Cotton is restricted by the simplifications involved in the determination of pseudo-lattice energies. The data for $[Zn(NH_3)_6]^{2+}$ are the only which do not fit the curve. Since this complex is very unstable, the standard enthalpies of formation or the vibrational spectra may need further attention.

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