Vibrational Spectra of Nitrogen-15-substituted Hexa-amminenickel(II) Chloride, Hexa-amminecobalt(III) Chloride, and Tetra-amminezinc(II) Iodide

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I.r. spectra of $[Ni(^{15}NH_3)_6]Cl_2$ and $[Co(^{15}NH_3)_6]Cl_3$ and Raman and i.r. spectra of $[Zn(^{15}NH_3)_4]I_2$ are reported and compared with the spectra of the normal ammines. The $^{14}N-^{15}N$ isotope shifts can be used to solve some assignment problems. Reliable skeletal force constants have been calculated by use of the nitrogen isotope shifts as additional data.

IN the course of our work on vibrational spectra and bond properties of transition-metal complexes we recorded recently i.r. spectra of hexa-ammine-chromium(III), -cobalt(III), and -nickel(II) and tetra-ammine-copper(II), -zinc(II), and -palladium(II) with ^2H and ^{50}Cr, ^{53}Cr, ^{58}Ni, ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{68}Zn, ^{104}Pd, and ^{110}Pd isotope substitution.[1,2] In this paper we present spectra of some ^{15}N-labelled ammine complexes. The $^{14}N-^{15}N$

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[1] A. Müller, K. H. Schmidt, and G. Vandrish, *Spectrochim. Acta*, 1974, **A30**, 651.

[2] K. H. Schmidt and A. Müller, *J. Mol. Structure*, 1974, **22**, 343.

isotope shifts are used as additional data for force-constant calculations.

EXPERIMENTAL

The salts $[Ni(NH_3)_6]Cl_2$, $[Co(NH_3)_6]Cl_3$, and $[Zn(NH_3)_4]I_2$ were prepared by standard methods (*cf.* refs. 3 and 4), the ^{15}N labelled complexes by using 95% isotopically enriched $[^{15}NH_4]Cl$ (Rohstoff-Einfuhr GmbH, Düsseldorf) in milligram quantities. I.r. spectra of Nujol mulls were recorded on a Perkin-Elmer IR 180 spectrometer, Raman spectra on a Coderg PHO spectrometer using a Kr^+ laser from Spectra-Physics (excitation line 6 471 Å). The instruments were calibrated with water vapour and krypton plasma lines, respectively.

TABLE 1

I.r. spectra (cm^{-1}) of $[^{58}Ni(NH_3)_6]Cl_2$,[a] $[Ni(^{15}NH_3)_6]Cl_2$, $[Co(NH_3)_6]Cl_3$,[b] and $[Co(^{15}NH_3)_6]Cl_3$

	$[^{58}Ni(NH_3)_6]Cl_2$	$[Ni(^{15}NH_3)_6]Cl_2$	$\Delta\nu$	$[Co(NH_3)_6]Cl_3$	$[Co(^{15}NH_3)_6]Cl_3$	$\Delta\nu$
$\nu_{asym}(NH)(F_{1u})$	3 345s ± 2	3 340 ± 1	5 ± 3	3 240s ± 5	3 230 ± 5	10 ± 10
$\nu_{sym}(NH)(F_{1u})$	3 190w ± 5	*ca.* 3 185	?	3 160s ± 3	3 155 ± 3	5 ± 6
$\delta_{asym}(HNH)(F_{1u})$	1 607m ± 1	1 605 ± 1	2 ± 2	1 619m ± 3	1 618 ± 2	1 ± 5
$\delta_{sym}(HNH)(F_{1u})$	1 176vs ± 1	1 174 ± 1	2 ± 2	1 328.5s ± 1	1 323.5 ± 1	5 ± 2
$\rho_r(NH_3)(F_{1u})$	685s ± 1	683 ± 1	2 ± 2	831s ± 1	829 ± 1	2 ± 2
$\nu_{asym}(MN)(F_{1u})$	335.2m ± 0.3	327.5 ± 0.3	7.7 ± 0.6	498vw ± 0.5 477vw ± 0.5 449vw ± 0.5	488.5 ± 1 468 ± 1 438 ± 1	9.5 ± 1.5 (14)[c] 9 ± 1.5 11 ± 1.5 (12.5)[c]
$\delta_{asym}(NMN)(F_{1u})$	217m, br ± 1	214 ± 1	3 ± 2 (4.2)[d]	331s ± 1	326 ± 1	5 ± 2 (5.8)[d,e]
Lattice	115m ± 2			154s ± 2		

[a] *Cf.* ref. 1; the frequencies in the region 3 500—500 cm^{-1} were redetermined with higher accuracy, the band at 1 186 cm^{-1} reported in ref. 1 being due to a misprint. [b] *Cf.* ref. 2. [c] Calculated under the assumption that the corresponding band is due to a Raman-active mode (see text). [d] Calculated on the point-mass model and using the Teller–Redlich rule for F_{1u}. [e] The average value of the $\nu_{asym}(CoN)$ triplet was considered.

TABLE 2

Raman and i.r. spectra (cm^{-1}) of $[Zn(NH_3)_4]I_2$ and $[Zn(^{15}NH_3)_4]I_2$

	Raman[a]			I.r.[a]		
	$[Zn(NH_3)_4]I_2$	$[Zn(^{15}NH_3)_4]I_2$	$\Delta\nu$	$[Zn(NH_3)_4]I_2$[b]	$[Zn(^{15}NH_3)_4]I_2$	$\Delta\nu$
$\nu_{asym}(NH)(E, F_2)$	3 290vw ± 3	3 290 ± 3	?	3 288s ± 2	3 286 ± 2	2 ± 4
$\nu_{sym}(NH)(A_1)$	3 234.5s ± 0.3	3 231.5 ± 0.5	3 ± 0.8	3 227w ± 3	3 225 ± 3	2 ± 6
$\nu_{sym}(NH)(F_2)$	3 197vw ± 5	3 197 ± 2	?	3 177w ± 3	3 176 ± 3	1 ± 6
$2\delta_{asym}(HNH)$?	3 151.2m ± 0.3	3 147 ± 1	4.2 ± 1.3	3 145w ± 3	3 143 ± 3	2 ± 6
$\delta_{asym}(HNH)(F_1)$?	1 730vw ± 2	*ca.* 1 730	?	1 700vw ± 5	1 700 ± 5	?
$\delta_{asym}(HNH)(E, F_2)$	1 615w ± 3 1 600m ± 2	1 615 ± 2 1 595 ± 2	? 5 ± 4	1 596m ± 1	1 596 ± 1	?
$\delta_{sym}(HNH)(A_1, F_2)$	1 256m ± 1 1 242m ± 1	1 247 ± 1 1 234 ± 1	9 ± 2 8 ± 2	1 255m ± 1 1 239.5vs ± 0.5	1 250.5 ± 0.5 1 234.6 ± 0.5	4.5 ± 1.5 4.9 ± 1
$\rho_r(NH_3)(E,F_1,F_2)$	688m ± 2 611w ± 1	675 ± 2 605 ± 2	13 ± 4 6 ± 3	690vs ± 0.5 610(sh) ± 5	684 ± 1 610 ± 5	6 ± 1.5 ?
$\nu_{sym}(ZnN)(A_1)$	431.2s ± 0.3	419.5 ± 0.3	11.7 ± 0.6			
$\nu_{asym}(ZnN)(F_2)$	411.5m ± 0.3	401.3 ± 0.3	10.2 ± 0.6	428.5m ± 0.3 423.0m—w ± 0.5 409.7m ± 0.3	418.5 ± 0.3 *ca.* 414 400.1 ± 0.5	10 ± 0.6 ? 9.6 ± 0.6
$\delta_{sym}(NZnN)(E)$	156.5m ± 1			160m ± 2	160 ± 2	?
$\delta_{asym}(NZnN)(F_2)$				146m—w ± 2	146 ± 2	?
Lattice	94m ± 2			70m ± 2		

[a] For further details see text. [b] *Cf.* ref. 1; the N–H stretching frequencies reported therein were recorded for CsI pellets.

RESULTS AND DISCUSSION

Vibrational Spectra.—Our i.r. data for $[Ni(^{15}NH_3)_6]Cl_2$ and $[Co(^{15}NH_3)_6]Cl_3$ are given in Table 1; for comparison, the frequencies of $[^{58}Ni(NH_3)_6]Cl_2$ and $[Co(NH_3)_6]Cl_3$ are also reported. As has been observed by many authors, three bands occur in the region of the anti-symmetric Co–N stretching vibration. Whereas some workers assumed these bands to be components of the three-fold degenerate F_{1u} vibration, split due to the monoclinic environment, others stated that some bands arise from the activation of i.r.-inactive modes (for further details see refs. 2, 5, and 6). All three bands of normal and ^{15}N-labelled $[Co(NH_3)_6]Cl_3$ had nearly equal intensities and shapes. The ^{14}N–^{15}N isotope shifts were equal within the error limits. This is also true for the ^1H–^2H shifts.[2] If one tentatively assigns the i.r. bands of $[Co(NH_3)_6]Cl_3$ at 498 and 449 cm^{-1} to Raman-active A_{1g} and E_g modes, respectively, the isotope shifts of these bands can be calculated on the basis of the point-mass model. As can be seen from Table 1, measured and calculated ^{14}N–^{15}N shifts of the lower-frequency band agree approximately within the error limit, whereas the calculated shift of the higher-frequency band is clearly larger than the measured one. Similar relations, though less unequivocal, hold for the ^1H–^2H shifts.[2] All facts

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[4] K. Nakamoto, J. Takemoto, and T. L. Chow, *Appl. Spectroscopy*, 1971, **25**, 352.

[5] H. Siebert and H. H. Eysel, *J. Mol. Structure*, 1969, **4**, 29.

[6] T. W. Swaddle, P. J. Craig, and P. M. Boorman, *Spectrochim. Acta*, 1970, **A26**, 1559.

strongly support the assignment of the triplet to the components of ν_{asym} (CoN)(F_{1u}).

Our i.r. and Raman data for solid $[Zn(NH_3)_4]I_2$ and $[Zn(^{15}NH_3)_4]I_2$ are in Table 2. (In the following discussion we refer to the frequencies of the former complex.) As can be seen from the Table, four Raman and i.r. bands occur in the region of the N–H stretching vibrations. By intensity considerations one can assign the most intense Raman band at 3 234.5 cm^{-1} to ν_{sym} (NH)(A_1) and the most intense i.r. band at 3 288 cm^{-1} to ν_{asym} (NH)(F_2). The former band possibly corresponds to the weak i.r. band at 3 227 cm^{-1} (activated because of low site symmetry) and the latter to the weak Raman band at 3 290 cm^{-1}. Analytical expressions for the F and G matrix elements [7] indicate that ν_{sym}(NH) in A_1 and F_2 as well as ν_{asym}(NH) in E and F_2 should lie very close together. Thus we have assigned the Raman band at 3 197 cm^{-1} and the i.r. band at 3 177 cm^{-1} to ν_{sym}(NH)(F_2). The two antisymmetric N–H stretching frequencies may be accidentally degenerate in the Raman spectrum. The lowest-lying bands are possibly overtones of δ_{asym}(HNH) modes increased in intensity by Fermi resonance. One of the weak bands may also be due to the Raman- and i.r.-forbidden ν_{asym}(NH)(F_1) mode. Whereas the Raman and i.r. bands at *ca.* 1 600 cm^{-1} can be assigned to δ_{asym}(HNH) in E or F_2, the very weak bands at *ca.* 1 700 cm^{-1} may belong to the inactive F_1 deformation mode (*cf.* ref. 8). In the region of the δ_{sym}(HNH) modes both Raman and i.r. spectra showed a doublet. Since the isotope shifts of the Raman bands are clearly different from those of the i.r. bands, they cannot belong to the same species. The Raman doublet may be assigned to an A_1 and the i.r. doublet to a F_2 vibration.

In the region of the rocking vibrations, two Raman and i.r. bands occurred. The ^{14}N–^{15}N shifts of the Raman bands were different, as were the shifts of the Raman and i.r. bands at approximately the same wavenumber. We suggest the following assignment: 688 (Raman) (E mode); 690 cm^{-1} (i.r.) (F_2 mode); and 611 (Raman) and 610 cm^{-1} (i.r.) (F_1 mode). From the relative intensities of the two Raman bands at *ca.* 420 cm^{-1} it is clear that the higher-frequency band corresponds to ν_{sym}(ZnN)(A_1) and the lower to ν_{asym}(ZnN)(F_2). The ^{14}N–^{15}N shifts of the two bands differed by *ca.* 1.5 cm^{-1}. The i.r. spectrum showed three bands in this region. If one compares the shifts of the i.r. bands with those of the Raman it seems likely that the i.r. triplet can be assigned to the components of the i.r.-active antisymmetric stretching vibration.

Force Constants.—If one considers the NH_3 ligands as point masses, as has been done by several authors, the order of the secular equations is reduced to $n = 1$ and 2. It is well known that the latter equations can only be solved by help of additional information. We have shown for a number of ammine complexes [1,2] that reasonable skeletal force constants for the F_{1u}, F_2, or E_u eigenvalue problems can be calculated by using the metal isotope or the ^1H–^2H shift of ν_{asym}(MN). Table 3 contains the F_{1u} skeletal force constants of hexa-amminenickel(II) and -cobalt(III) as well as the F_2 force constants of tetra-amminezinc(II) obtained with the aid of the ^{14}N–^{15}N shifts of ν_{asym}(MN) in Tables 1 and 2. The given error limits arise from the maximum measurement uncertainty of $\Delta\nu_{asym}$(MN). In the case of the cobalt complex, no error limits are mentioned since the average values of the triplets were used. The inner force constants f(MN), which are very useful for understanding the nature of the metal–ligand bonding, are also included in the Table. Comparison of the ^{14}N–^{15}N data with the force-constant sets determined by using metal-isotope and ^1H–^2H shifts as additional data (Table 3) reveals excellent agreement. This conformity can be taken as unequivocal proof of the applicability of the point-mass model in conjunction with accurately determined isotope shifts.

TABLE 3

Skeletal force constants (mdyn $Å^{-1}$) of $[Ni(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, and $[Zn(NH_3)_4]^{2+}$

Additional data	$f_{33}(F_{1u})(O_h)$ $(F_2)(T_d)$	$f_{34}(F_{1u})(O_h)$ $(F_2)(T_d)$	$f_{44}(F_{1u})(O_h)$ $(F_2)(T_d)$	f(MN)
(*a*) $[Ni(NH_3)_6]^{2+}$				
$\Delta\nu_3(^{58}Ni–^{62}Ni)$ [a]	0.87 ± 0.02	0.18 ± 0.03	0.15 ± 0.01	0.90 [b]
$\Delta\nu_3(^1H–^2H)$ [a]	0.85 ± 0.01	0.16 ± 0.02	$0.14 \pm 0.00_5$	0.89 [b]
$\Delta\nu_3(^{14}N–^{15}N)$	0.88 ± 0.02	0.20 ± 0.03	0.15 ± 0.01	0.90 [b]
(*b*) $[Co(NH_3)_6]^{3+}$				
$\Delta\nu_3(^1H–^2H)$ [c]	1.77	0.53	0.41	1.97 [d]
$\Delta\nu_3(^{14}N–^{15}N)$ [c]	1.72	0.33	0.33	1.92 [d]
(*c*) $[Zn(NH_3)_4]^{2+}$				
$\Delta\nu_3(^{64}Zn–^{68}Zn)$ [a,e]	1.39 ± 0.03	0.19 ± 0.07	0.10 ± 0.02	1.51 [f]
$\Delta\nu_3(^1H–^2H)$ [a,e]	1.37 ± 0.02	0.16 ± 0.03	0.09 ± 0.01	1.50 [f]
$\Delta\nu_3(^{14}N–^{15}N)$ [e]	1.41 ± 0.02	0.27 ± 0.08	0.12 ± 0.03	1.52 [f]

[a] *Cf.* ref. 1. [b] Determined from the symmetry force constants and from the following Raman wavenumbers of $[Ni(NH_3)_6]^{2+}$ in aqueous solution: $\nu_{sym}(NiN)(A_{1g})$ 370 cm^{-1} (ref. 1) and ν (NiN)(E_g) 265 cm^{-1} (this work). [c] Average value of the triplet band. [d] Determined by using $\nu_{sym}(CoN)(A_{1g})$ and $\nu(CoN)(E_g)$ from ref. 6 {Raman spectrum of $[Co(NH_3)_6]^{3+}$ in aqueous solution}. [e] Raman frequencies. [f] Determined by using $\nu_{sym}(ZnN)(A_{1g})$ from ref. 4 {Raman spectrum of solid $[^{64}Zn(NH_3)_4]I_2$}.

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