Spectrochemistry of Solutions. Part II.[1] Raman Spectra of Aqueous and Liquid Ammonia Solutions of Metal Salts †

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The Raman spectra of salts of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Al, Ga, In, Zn, Hg, Pb, and Ag have been recorded in liquid ammonia. From trends in the frequency of the symmetric metal–ligand stretching vibration, it is deduced that the co-ordination number of Li^+, Be^{2+}, Zn^{2+}, Hg^{2+}, and Ag^+ is four, and that of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ga^{3+}, In^{3+}, and Pb^{2+} is six. The co-ordination numbers of Zn^{2+} and Ag^+ are thus not the same in liquid ammonia as they are in water. The vibrational spectrum of the solvent and of nitrate anions in liquid ammonia are briefly discussed.

THE structure of molecules and ions in solution is poorly understood in comparison with the structure of species in the solid and gaseous states. This is because structural information on solutions must be obtained by relatively indirect means. For example, thermodynamic studies yield information concerning bulk properties and it is difficult to extrapolate from these to molecular properties, as shown by the widely varying estimates of co-ordination number obtained by such means.[2] Spectroscopic studies yield information concerning the energy levels in molecules and ions, and these energy levels may be sensitive to the type and structure of solvation. Hence spectroscopic techniques of the e.s.r., n.m.r., i.r., and Raman variety will give us the most useful information. Accordingly we have initiated an extended study of the spectrochemical properties of solutions. We have chosen to start with liquid ammonia because of its ability to dissolve many salts, most of which are also soluble in water. Hence we shall be able to compare the properties of aqueous and ammonia

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† No reprints available.

[1] Part I, P. Gans and J. B. Gill, *J. Phys.* (*E*), 1976, in the press.

[2] J. F. Hinton and E. S. Amis, *Chem. Rev.*, 1971, **71**, 627.

solutions and from each gain further insight into the other.

This paper presents the results of a general survey of metal salts dissolved in liquid ammonia, which has already appeared in preliminary form.[3] We concentrate mainly on the structure of the cationic species. Subsequent papers in the series will report: the results of a detailed study of alkali-metal nitrate solutions and ion-pair formation therein; an examination of the equilibria of cyano-complexes of silver in liquid ammonia; and a survey of the spectra of anions, considering some anions in detail, and presenting direct evidence for various types of ion association in liquid ammonia. Much of the experimental work for these papers is already completed. We then intend to transfer our attention to other solvents.

When this work was begun the Raman spectrum of liquid ammonia as a function of temperature [4,5] and pressure [5] had been studied in the N–H stretching region. The Rayleigh scattering of liquid ammonia was briefly illustrated.[6] Solutions of various nitrates were cursorily examined [7] and the Raman spectrum of the germyl ion, $[GeH_3]^-$, and liquid ammonia were reported.[8] Some i.r. studies have also appeared.[9] References to more recent work are given below.

EXPERIMENTAL

All salts were thoroughly dried and recrystallised several times from pure anhydrous ammonia before spectroscopic examination of their solutions. The salts sodium nitrate, sodium iodide, potassium nitrate, rubidium iodide, caesium iodide, lead nitrate, and silver nitrate (all of analytical grade) were first dried *in vacuo* over P_4O_{10} for up to 2 weeks before recrystallisation. Silver iodide, freshly precipitated from dilute aqueous solutions of KI and $Ag[NO_3]$, was dried for 7 d *in vacuo* over P_4O_{10} and then recrystallised three times from liquid ammonia.

Magnesium, calcium, and cadmium nitrates were obtained in a fairly dry state by drying *in vacuo* over P_4O_{10} for 3 d at room temperature followed by 3 weeks at 60 °C. The product at this stage contained basic material which was removed by filtration of the solutions in liquid ammonia prior to two further recrystallisations. Zinc and mercury(II) nitrates were treated in an analogous manner, except that at the first filtration stage cloudy filtrates were produced. The formation of these amido-species was repressed by the addition of a trace amount of ammonium nitrate which clarified the solutions in the two subsequent crystallisations. Strontium nitrate was dehydrated by heating the crystals for 1 h at 70 °C followed by a further period of 4 h at 110 °C before recrystallisations from liquid ammonia. Magnesium perchlorate was dehydrated and purified by recrystallising three times from liquid ammonia the contents of a freshly opened bottle of anhydrone.

Lithium nitrate forms a Divers-type solution in liquid ammonia and cannot be satisfactorily recrystallised. The salt (*ca.* 10 g) was melted and held *in vacuo* at 250 °C for 2 h. An apparatus was designed to allow filtration of the melt through a glass sinter (porosity 2) when inverted. The cooled solidified filtrate was used in the preparation of sample solutions.

It had originally been intended to prepare the solution of beryllium nitrate in liquid ammonia by the electrolysis of the ammonium salt (2 mol dm^{-3}) using a beryllium metal anode and a platinum cathode. This proved to be impossible due to decomposition at the anode, of either the solvent or the nitrate ion, at voltages greater than 2.5 V. Ammonium iodide solutions electrolyse satisfactorily up to a voltage of 8.1 V. Using a current of 40 mA at 7.5 V (area of Be anode, 0.95 cm^2), a solution of ammonium iodide (2 mol dm^{-3}) in liquid ammonia was electrolysed at −40 °C in an H-shaped apparatus in which the anode and cathode compartments were separated by a sinter in the cross-arm. A solution of beryllium iodide (analysis 0.3 mol dm^{-3}) was obtained against a background of $[NH_4]I$ in the anode compartment after 16 h. A small portion of the solution was filtered through a sinter (porosity 3) directly into a sample tube and sealed for spectroscopic examination.

Aluminium iodide, prepared by direct combination of the elements,[10] was recrystallised three times from liquid ammonia. Initial ammoniation of the iodide was carried out very slowly by passing over it nitrogen gas saturated with ammonia vapour at −65 °C. Failure to do this carefully resulted in the evolution of much heat and the decomposition of the iodide. The solution used for spectroscopic examination was almost saturated at −33 °C (0.3 mol dm^{-3}, 0.121 kg dm^{-3}). Gallium iodide was prepared by heating gallium metal (2.55 g) and iodine (15.1 g) under reflux in dried freshly distilled carbon disulphide (250 cm^3) for 5 d until all metal had dissolved.[11] After removal of the bulk of the solvent, the residual slurry of crystals (50 cm^3) was filtered under dry oxygen-free nitrogen and washed with sodium-dried light petroleum (b.p. 60—80 °C), yield 9.6 g. The product was recrystallised three times from liquid ammonia, the first ammoniation being carried out as for AlI_3 to prevent excessive evolution of heat during ammoniation. After a third recrystallisation, the product was dissolved in liquid ammonia and a small volume filtered directly into the sample tube before sealing to produce a solution which was *ca.* 0.3 mol dm^{-3} in GaI_3 at −33 °C.

Tetra-amminezinc(II) tetrafluoroborate was prepared from aqueous solution.[12] The first solution prepared in liquid ammonia was turbid, *cf.* $Zn[NO_3]_2$, but the amido-formation was repressed by the addition of a trace of $[NH_4][NO_3]$ during the first recrystallisation. Three recrystallisations were carried out.

Large single crystals (0.5—1.0 cm^3) were selected from a freshly opened bottle of anhydrous indium nitrate and immediately dissolved in liquid ammonia. Turbidity due to amide formation was repressed by addition of a few crystals of $[NH_4][NO_3]$ during the first of three recrystallisations.

Tetra-amminesilver(I) perchlorate was prepared by recrystallising silver perchlorate twice from 0.880 s.g. aqueous ammonia, and twice from liquid ammonia at 240 K. The

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[3] P. Gans and J. B. Gill, *J.C.S. Chem. Comm.*, 1973, 914.

[4] B. Bettignies and F. Wallart, *Compt. rend.*, 1970, **B271**, 640.

[5] C. A. Plint, R. M. B. Small, and H. L. Welsh, *Canad. J. Phys.*, 1954, **32**, 653.

[6] J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.*, 1971, **54**, 3846.

[7] M. G. Costeanu, *Compt. rend.*, 1936, **202**, 1432.

[8] T. Birchall and I. Drummond, *J. Chem. Soc.* (*A*), 1970, 1850.

[9] J. Corset, P. V. Huong, and J. Lascombe, *Spectrochim. Acta*, 1968, **24A**, 1385, 2045.

[10] G. W. Watt and J. L. Hall, *Inorg. Synth.*, 1953, **4**, 117.

[11] F. Kutek, *Coll. Czech. Chem. Comm.*, 1966, **31**, 1875.

[12] E. Wilke-Dörfurt and G. Balz, *Z. anorg. Chem.*, 1927, **159**, 197.

product loses ammonia rapidly when exposed to air (Found: Ag, 39.0. $H_{12}AgClN_4O_4$ requires Ag, 39.1%).

Pure anhydrous ammonia was obtained by distilling anhydrous liquid ammonia from its cylinder into a second stock cylinder containing sodium amide. The ammonia used in the experimental work was then distilled from this cylinder, passed through a glass-wool filter, and condensed on to the solid samples.

Raman bands (cm^{-1}) for metal salt solutions in liquid ammonia

Salt	Concentration [a]	T/K	ν_{sym} (M–NH_3)	Nitrate ν_4	Nitrate ν_1	Nitrate ν_3	Nitrate $2\nu_2$	Ammonia ν_2	Ammonia ν_4	Ammonia N–H stretching			Others
$Li[NO_3]$	1 : 60	223	249	708	1 044	1 360	1 662	*b*	1 640	3 213	3 300	3 380	
$Na[NO_3]$	1 : 20	233	*c*	710	1 044	1 355, 1 380 (sh)	1 662	*b*	1 650				
NaI	1 : 10	293	*c*	*d*	*d*	*d*	*d*	1 100	1 645				450 (sh),
$K[NO_3]$	1 : 70	293	*c*	712	1 044	1 385, 1 351		*b*					
RbI	1 : 7.5	293	*c*	*d*	*d*	*d*	*d*	1 100	1 645	3 215	3 295	3 372	325
CsI	1 : 12	293	*c*	*d*	*d*	*d*	*d*	1 085	1 645				300 (sh)
BeI_2	1 : 130	242	485	*d*	*d*	*d*	*d*	1 120	1 650	3 210	3 290	3 360	350 (sh)
$Mg[NO_3]_2$	1 : 100	233	329	710	1 047	1 350 (sh), 1 370	1 660	*b*	1 640	3 200	3 300	3 370	
$Mg[ClO_4]_2$	1 : 26	233	330	*d*	*d*	*d*	*d*	1 075	1 640				$[ClO_4]^-$: 467, 630, 939p
$Ca[NO_3]_2$	1 : 20	233	265	708	1 044	1 361	1 661	*b*	1 635	3 215	3 300	3 380	3 180 (sh), $[^{18}ONO_2]^-$: 1027
$Sr[NO_3]_2$	1 : 150	233	250	708	1 045	1 370	1 661	*b*	1 637	3 215	3 300	3 380	
AlI_3	1 : 160	235	*c*	*d*	*d*	*d*	*d*	1 060	1 640	3 210	3 300	3 380	265 (sh)
GaI_3	1 : 100	243	477	*d*	*d*	*d*	*d*	1 050					
$In[NO_3]_3$	1 : 45	233	440	711	1 044	1 377, 1 350	1 663	*b*	1 635	3 215	3 302	3 382	215 (sh), $[^{18}ONO_2]^-$: 1 029
$Zn[NO_3]_2$	1 : 40	293	437	711	1 045								
$Zn[NO_3]_2$	1 : 40	233	438	709	1 045	1 370, 1 350 (sh)	1 664	*b*	1 640	3 212	3 300	3 382	358p
$Zn[BF_4]_2$	1 : 40	293	440	*d*	*d*	*d*	*d*	1 055[e]	1 640				$[BF_4]^-$: 769p, 355, 525
$Zn[BF_4]_2$	1 : 40	213	435	*d*	*d*	*d*	*d*	1 060[e]					
$Cd[NO_3]_2$	1 : 60	233	342	710	1 045	1 370, 1 352	1 662	*b*	1 640	3 210	3 299	3 389	*ca.* 240
$Hg[NO_3]_2$	1 : 21	233	415	710	1 046	1 375, 1 345	1 662	*b*	1 640	3 225	3 305	3 390	1 240p?, 3 180 (sh)
$Pb[NO_3]_2$	1 : 40	233	315	709	1 046	1 370, 1 350 (sh)	1 660	*b*	1 640	3 210	3 300	3 383	$[^{18}ONO_2]^-$: 1 025, 1 130p, 3 165 (sh)
$Ag[NO_3]$	1 : 100	233	263	710	1 046	1 368	1 661	*b*	1 640	3 205	3 300	3 380	
AgI	1 : 20	243	260	*d*	*d*	*d*	*d*	1 080	1 640	3 214	3 294	3 388	

sh = shoulder, p = polarised.

[a] Expressed as the ratio moles of solute metal ion : moles of ammonia. [b] Obscured. [c] Not observed. [d] Not present. [e] Partially obscured by $[BF_4]^-$ band.

All recrystallisations were carried out under an atmosphere of ammonia gas in apparatus which incorporated standard techniques for the handling of air- and moisture-sensitive compounds. The filtrations were effected by inversion of the apparatus and a range of filters of various porosities was available. Sample solutions for spectroscopic examination were prepared by dissolving a weighed quantity of the recrystallised salt in either a known volume or a known weight of solution using standard vacuum-line techniques. In the former case the solutions were transferred at *ca.* −50 °C to a 10 × 5 × 45 mm fluorimeter cell mounted in the cryostat and attached to the line. In the latter case, solutions (*ca.* 1 cm^3) were sealed into ampoules of standard Pyrex glass tubing (5-mm internal diameter, 9-mm outside diameter). The use of recrystallised salts in the preparation of the ammonia solutions gave very clear solutions and eliminated the need for filtration before the Raman spectrum was recorded. Aqueous solutions were prepared by standard techniques but were always put through a Millipore filter to clarify them.

Raman emission was analysed using a Coderg PHO spectrophotometer with d.c. amplification and a cooled photomultiplier. On this instrument the laser beam (Ar^+ or He–Ne), and the emergent Raman beam at right angles to it, lie in the horizontal plane with the sample held vertically. The samples run at low temperatures were housed in a specially constructed top-loading cryostat.[1] Frequency calibration was against indene, neon, or plasma lines.

RESULTS

A typical spectrum of a metal nitrate in liquid ammonia is shown in Figure 1. Because the low-frequency band lies in the foot of the Rayleigh wing, its depolarisation ratio cannot be measured directly, although this is very small (Figure 1). Observed Raman bands for metal salt solutions are in the Table, and the observed M–NH_3 stretching bands are given in Figure 2. Attempts to locate a polarised low-frequency band in ammonia solutions of salts of K^+, Rb^+, Cs^+, and Al^{3+} were not successful.

A number of spectra of aqueous solutions were also recorded. The polarised low-frequency bands observed are also given in Figure 2. Suitable bands were not observed in the spectra of aqueous solutions of Ag^+, Ca^{2+},

Sr^{2+}, Ba^{2+}, Pb^{2+}, Tl^{+} or with any of the alkali-metal ions. Further details concerning the aqueous spectra are not given here, as they accord well with published data,[13,14] with minor differences.

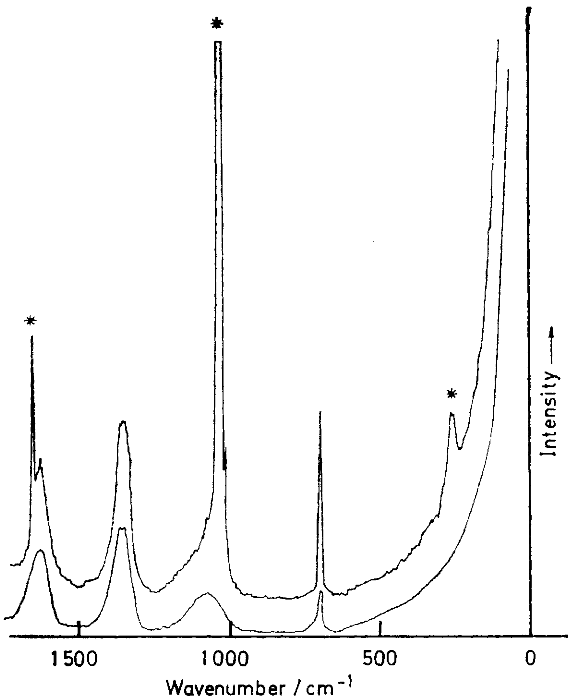

FIGURE 1 Raman spectrum of $Ca[NO_3]_2$ in liquid ammonia at 215 K. The bands marked with an asterisk are polarised. The lower curve shows the perpendicularly polarised spectrum

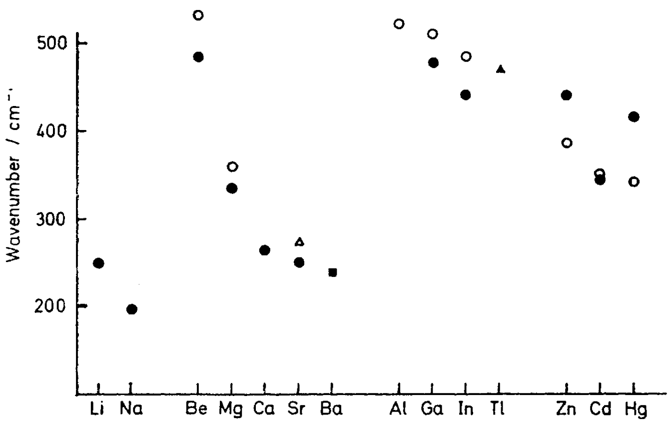

FIGURE 2 Raman-active $M–NH_3$ (●) and $M–OH_2$ (○) stretching vibrations. (■), $\nu_{sym}(Ba–NH_3)$;[17] (△), $\nu_{sym}(Sr–OH_2)$;[30] (▲), $\nu_{sym}(Tl^{III}–OH_2)$[13]

Spectra of Ag^{+}, Zn^{2+}, Cd^{2+}, and Cu^{2+} were also recorded in solution in 0.880 s.g. aqueous ammonia.

DISCUSSION

Ammonia.—Previous investigations of the spectra of liquid ammonia and its solutions were concentrated almost entirely in the N–H stretching region.[4,5,15-20] This region is complicated by Fermi resonance and another process whose nature is controversial, which result in an envelope which must be resolved into four rather than the expected two bands of A_1 and E symmetry. We observed an additional band at *ca.* 3 180 cm^{-1} in the spectra of solutions of Ca^{2+}, Mg^{2+}, and Pb^{2+}, which is presumably to be assigned to metal-co-ordinated ammonia N–H stretching vibrations.

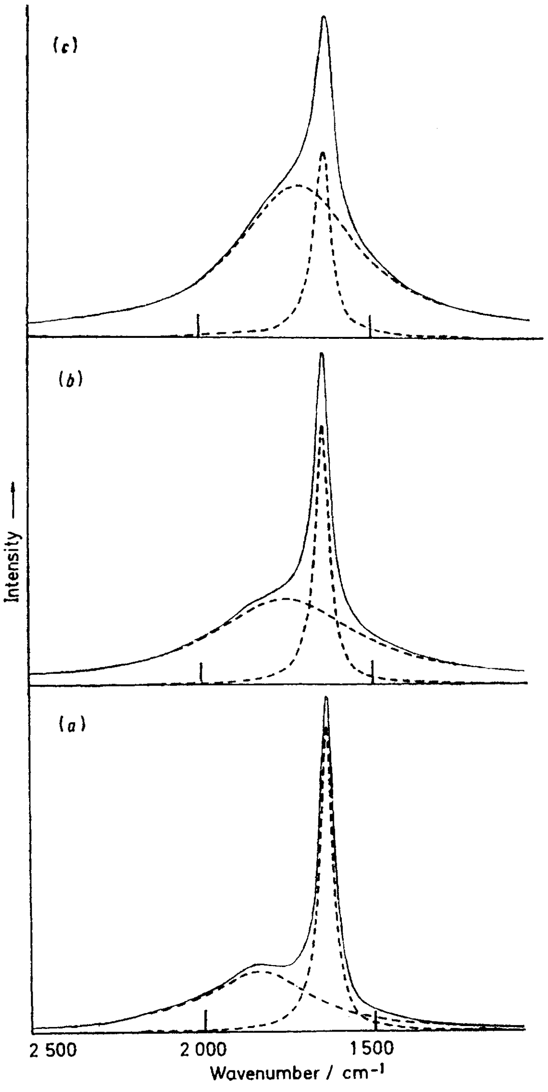

FIGURE 3 Raman spectrum of liquid ammonia at 196 (*a*), 232 (*b*), and 293 K (*c*). The envelope has been resolved into components having Lorenzian shape. Both bands are depolarised

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[13] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 768.

[14] D. J. Gardiner, R. E. Hester, and E. Mayer, *J. Mol. Structure*, 1974, **22**, 327.

[15] M. Buback, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 1230.

[16] M. Schwartz and C. H. Wang, *J. Chem. Phys.*, 1973, **10**, 5258.

[17] K. R. Plowman and J. J. Lagowski, *J. Phys. Chem.*, 1974, **78**, 143.

[18] A. T. Lemley, J. H. Roberts, K. R. Plowman, and J. J. Lagowski, *J. Phys. Chem.*, 1973, **77**, 2185.

[19] D. J. Gardiner, R. E. Hester, and W. E. L. Grossman, *J. Raman Spectroscopy*, 1973, **1**, 87.

[20] D. J. Gardiner, R. E. Hester, and W. E. L. Grossman, *J. Chem. Phys.*, 1973, **59**, 175.

Other evidence for co-ordinated ammonia was lacking in this region, but there was usually a large excess of unco-ordinated ammonia present to mask the bands due to the complex cation. Even in many concentrated systems, such as $Li[NO_3]\cdot 2.9NH_3$ in which all the ammonia is almost certainly co-ordinated, there is little shift of the major frequencies.[20]

Our results are entirely concordant with the underlying four-band hypothesis for the N–H stretching region. However, since there is little direct evidence for extensive hydrogen bonding, for example in the 1 375 cm^{-1} region of the spectrum of the nitrate ion (see below), we are inclined towards Buback's explanation [15] in terms of the symmetric and antisymmetric components of the overtone of an ammonia deformation mode (ν_4) resulting in the two extra components, through Fermi resonance. However, the dilution experiments [19] strongly suggest a solvent association link. It could be that ν_4 is association sensitive.

In fact the ν_4 region of pure ammonia is more complex than has been appreciated, as suggested by Figure 3. The very broad feature we observed at *ca.* 1 750 cm^{-1} has not previously been recognised. Its integrated intensity is, at 293 K, more than five times as large as the intensity of the narrow band normally assigned to ν_4, although the relative proportion decreases with temperature. We did not study this band in the salt solutions. The assignment of the broad band is a matter for speculation. This band could originate from associated solvent molecules, and, if this is the case, its overtone might be in Fermi resonance with N–H stretching vibrations.

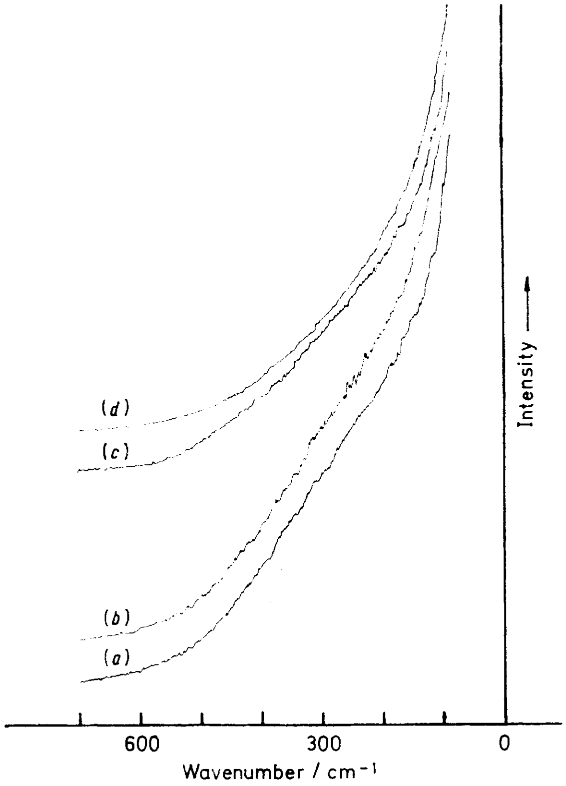

FIGURE 4 Rayleigh wing (unpolarised) of pure ammonia at 196 (*a*), 212 (*b*), 232 (*c*), and 293 K (*d*). The spectra have been shifted on the vertical scale for the sake of clarity

The symmetric ammonia deformation (ν_2) shifted from 1 050 cm^{-1} at 293 K to 1 075 cm^{-1} at 196 K in pure ammonia. This also suggests that the ammonia deformation modes are sensitive to the molecular environment and, perhaps, to the state of aggregation of the liquid.

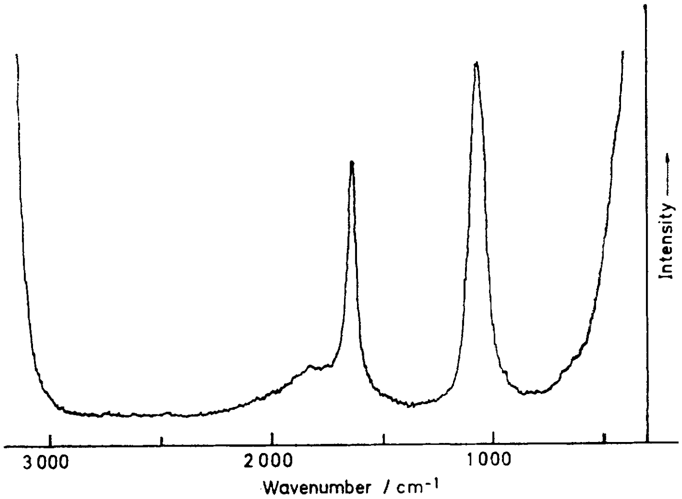

FIGURE 5 Raman spectrum of liquid ammonia at 196 K between 400 and 3 000 cm^{-1}

At low frequencies we find an extensive Rayleigh wing as noted previously.[6] However the 'band' which we previously reported [3] to be at *ca.* 240 cm^{-1} seems to have been a grating ghost as the spectra obtained subsequently using new gratings (Figure 4) did not show it. It is nevertheless difficult to observe weak features below *ca.* 200 cm^{-1} because of the extent of the Rayleigh wing. This is seen clearly in the context of a complete spectrum of liquid ammonia (Figure 5). The low-frequency 'librational' features which are so clearly visible in the Raman spectra of water [21] are thus not to be seen in ammonia. This is another reason why we do not believe that hydrogen bonding is extensive in ammonia.[22]

Various iodides caused a depolarised 'bulge' to appear in this region (Figure 6). This 'bulge' was noticeable only in the very concentrated solutions (solutions perhaps more aptly described as molten ammoniates) but did not usually occur with other anions. It was also observed that the 'broad' ammonia band moved to lower frequencies in these solutions. A band at *ca.* 1 200 cm^{-1}, perhaps polarised, appeared in the spectra of solutions of Hg^{2+} and Pb^{2+}. This is the only additional band to the solvent and anion bands, apart from the low-frequency band which forms the major part of this discussion.

Metal–Solvent Stretching Modes.—A sharp polarised

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[21] G. E. Walrafen in 'Water. A Comprehensive Treatise,' ed. F. Franks, Plenum Press, New York, 1972.

[22] J. B. Gill, *J. Chem. Educ.*, 1970, **47**, 619.

band in the 200—500 cm^{-1} region is assigned to the totally symmetric vibration of the complex cation $[M(NH_3)_x]^{n+}$. From the trends in frequency of this band (Figure 2), and by arguments of analogy, we deduce the co-ordination number, *x*, of the metal cation. We shall show that co-ordination numbers of cations in ammonia are the same as in water except for Zn^{2+} and Ag^+.

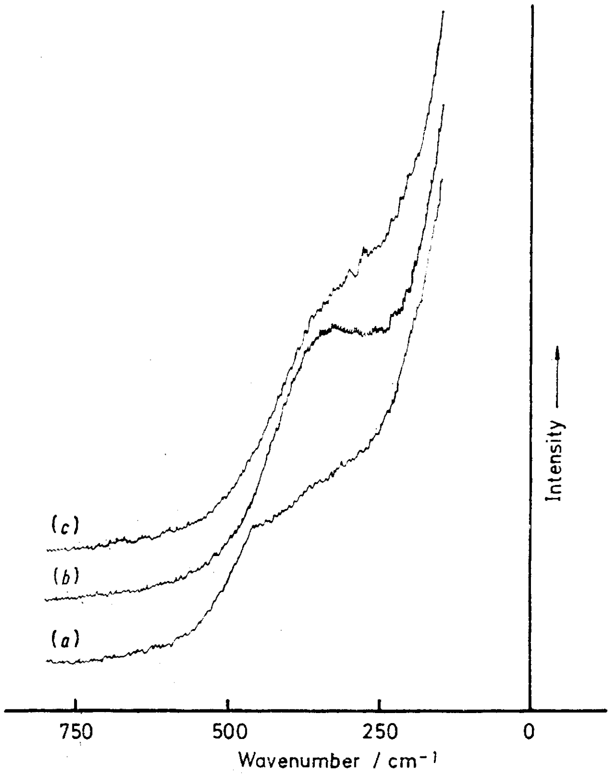

FIGURE 6 Low-frequency Raman spectra of NaI (*a*), RbI (*b*), and CsI (*c*) in liquid ammonia at 293 K. For details of concentrations see the Table

The frequency of the totally symmetric vibration, $\nu_{sym}(M-NH_3)$, is independent of the mass of the metal ion which is stationary during the vibration. Variations in the frequency of $\nu_{sym}(M-NH_3)$ therefore result from changes in the intrinsic resistance of the metal–ammonia bond to deformation, *i.e.* period changes, or from changes in co-ordination number.[23] An example of a periodic change is shown in Group 3 with the ions Al^{3+}, Ga^{3+}, In^{3+}, and Tl^{3+}. (The band at *ca.* 470 cm^{-1} in aqueous solution was wrongly attributed [13] to the ion Tl^+; a solution of pure $Tl[NO_3]$ shows no such feature.) In water $\nu_{sym}(M-OH_2)$ decreases gradually with increasing atomic number, which is the normal periodic trend. A co-ordination number of six has been established by n.m.r. methods for Al^{3+}, Ga^{3+}, and In^{3+} in water.[24] The intensity of $\nu_{sym}(M-OH_2)$ also increases dramatically in the order Al < Ga < In [25] < Tl.

In ammonia the data are less extensive. The Al^{3+} ion has a co-ordination number of six from n.m.r. data,[26] but we were unable to locate $\nu_{sym}(Al-NH_3)$ for two reasons: the most soluble compound AlI_3 gives a maximum concentration of 0.3 mol dm^{-3} at 233 K, which in Raman terms is not particularly concentrated; and, by analogy with the aqua-system, $\nu_{sym}(Al-NH_3)$ is expected to be relatively weak. For Ga^{3+} and In^{3+}, $\nu_{sym}(M-NH_3)$ is at *ca.* 60 cm^{-1} lower than $\nu_{sym}(M-OH_2)$ in both cases. Since (*i*) in water Ga^{3+} and In^{3+} have the same co-ordination number as has Al^{3+}, *viz.* six, (*ii*) Al^{3+} is also six-co-ordinate in ammonia, and (*iii*) $\nu_{sym}(M-NH_3)$ is at *ca.* 60 cm^{-1} lower than $\nu_{sym}(M-OH_2)$ for both Ga^{3+} and In^{3+}, we propose that Ga^{3+} and In^{3+} have the same co-ordination number in ammonia, and that its value is six.

In Group 2A, Mg^{2+} has a co-ordination number of six in water,[24] and a corresponding $\nu_{sym}(M-OH_2)$ band at 358 cm^{-1} (360,[13] 357 cm^{-1} [27,28]). In ammonia, n.m.r. work [29] gave a co-ordination number of six to Mg^{2+}, and $\nu_{sym}(Mg-NH_3)$ at 330 cm^{-1} is some 25 cm^{-1} less than the corresponding value in aqueous solution. It follows by analogy with Group 3 that Ca^{2+} and Sr^{2+} are also six-co-ordinate in ammonia, although corresponding $\nu_{sym}(M-OH_2)$ bands could not be observed. A single-crystal study [30] gave $Sr-OH_2$ (terminal) at 275 cm^{-1}. Plowman and Lagowski [17] observed $\nu_{sym}(M-NH_3)$ at 215 (Ba^{2+}), 240 (Sr^{2+}), 264 (Ca^{2+}), and 328 cm^{-1} (Mg^{2+}). These values, obtained with solutions of the perchlorate salts at 293 K, are in excellent agreement with ours. Their value for Ba^{2+} indicates that a co-ordination number of six is appropriate. The Be^{2+} ion has a co-ordination number of four in water,[24] and $\nu_{sym}(Be-OH_2)$ is at 532 cm^{-1}.[14] In ammonia, $\nu_{sym}(M-NH_3)$ is found at 485 cm^{-1}, some 45 cm^{-1} less than the aqueous value. The difference between the bands of Be^{2+} and Mg^{2+} is 170 cm^{-1} in water and 155 cm^{-1} in ammonia. These findings are fully consistent with Be^{2+} having the anticipated co-ordination number of four in ammonia. To summarise for Group 2A, $\nu_{sym}(M-NH_3)$ follows the trend $Be^{2+} \gg Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, with a smooth decrease along the heavier six-co-ordinate ions.

In Group 1A we presume Li^+ is four-co-ordinate [$\nu_{sym}(Li-NH_3)$ at 240 cm^{-1}].[17] The decrease in frequency relative to four-co-ordinate Be^{2+} is consistent with the decrease in oxidation state.[23] We confirm that $Na[ClO_4]$ gives a band at 194 cm^{-1},[17] but we consider that this is insufficient evidence from which to deduce a co-ordination number for Na^+. Values for the other alkali metals are needed here but will be difficult to obtain

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[23] P. Gans, ' Vibrating Molecules,' Chapman and Hall, London, 1971, ch. 8.

[24] A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *J. Chem. Phys.*, 1968, **48**, 3705.

[25] R. E. Hester and W. E. L. Grossman, *Spectrochim. Acta*, 1967, **A23**, 1945.

[26] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1967, **89**, 3065.

[27] T. G. Chang and D. E. Irish, *J. Phys. Chem.*, 1973, **77**, 52.

[28] M. Peleg, *J. Phys. Chem.*, 1972, **76**, 1019.

[29] L. W. Harrison and T. J. Swift, *J. Amer. Chem. Soc.*, 1970, **92**, 1963.

[30] D. M. Adams and W. R. Trumble, *J.C.S. Faraday II*, 1974, 1967.

because of their low frequency and the mainly ionic character of the M–NH_3 bond.

We conclude that Ag^+ is four-co-ordinate for the following reasons. The band at *ca.* 370 cm^{-1} observed [31] as ν_{sym}(Ag–NH_3) of the ion $[Ag(NH_3)_2]^+$ is not visible in liquid-ammonia solution; a new band at *ca.* 290 cm^{-1} is just discernible in the Rayleigh wing. The decrease in frequency would be consistent with a change of co-ordination number from two to four. Although there is no evidence for the formation of tetra-ammine silver complexes in aqueous solution, we have synthesised an unstable compound having the formula $Ag(NH_3)_4ClO_4$, by recrystallising $[Ag(NH_3)_2][ClO_4]$ from liquid ammonia. We note an early report that solid $Ag[ClO_4]$ absorbs ammonia gas up to the stoicheiometry $Ag[ClO_4]\cdot 3NH_3$ at 288 K,[32] and point to the analogous situation in pyridine where an unstable compound $[Ag(py)_4][ClO_4]$ is formed.[33] Surprisingly, AgI in ammonia at 223 K was reported by Linhard [34] as early as 1936 to give Raman bands at 192 and 150 cm^{-1}! The formation of $[Ag(NH_3)_4]^+$ sheds some light on the received explanation of a very well known and elementary phenomenon, the solubility of silver halides in ammoniacal solutions. We suggest that two different reactions take place, and that the

$$AgX \xrightarrow{NH_3(aq)} [Ag(NH_3)_2]^+ \quad (X = Cl \text{ or } Br) \qquad (1)$$

$$AgI \xrightarrow{NH_3(l)} [Ag(NH_3)_4]^+ \qquad (2)$$

solubility of AgI in ammonia is a result, not just of the greater concentration of ammonia ligand, but of the fact that a different reaction takes place when compared to strong aqueous ammonia.

The situation in Group 2B is complex. At first sight it seems that ν_{sym}(M–OH_2) follows a regular trend Zn^{2+} [25] > Cd^{2+} [35,36] > Hg^{2+}.[37] However, the band intensity for mercury is acid sensitive [38] and would therefore seem to originate from a hydrolysed species rather than a simple aqua-ion. For Zn^{2+}, the value for aqueous solution (386 cm^{-1}) is almost identical with that for the solid complex $[Zn(OH_2)_6][SiF_6]$ (388 cm^{-1}); [39] it is thus very probable that both Zn^{2+} and Cd^{2+} are six-co-ordinate in water, although there is no direct evidence such as n.m.r. concerning the co-ordination number in the aqua-ions.

The frequencies of ν_{sym}(M–NH_3) observed in liquid ammonia are very similar to those found in 0.880 s.g. aqueous ammonia (Zn 431, Cd 342 cm^{-1}). In view of the known aqueous chemistry, this gives Zn^{2+} a co-ordination number of four and Cd^{2+} a co-ordination number of six. Support for this assignment is provided in the zinc case by the Raman spectra of four-co-ordinate complexes of ^{64}Zn and ^{68}Zn $[Zn(NH_3)_4]I_2$ [ν_{sym}(Zn–NH_3) at 432.0 and 431.5 cm^{-1}].[40] If we assign to Hg^{2+} a co-ordination number of four, then the Raman-active vibrations of the Group 2 ions are all at slightly higher frequency than the corresponding i.r.-active vibration: $[Zn(NH_3)_4]Cl_2$, 437; [41] $[Cd(NH_3)_6]Cl_2$, 298; [41] $[Hg(NH_3)_4][ClO_4]_2$, 408 cm^{-1}.[42] The small decrease in frequency from Zn^{2+} to Hg^{2+} is consistent with their both having the same co-ordination number.

Comparing aqueous and ammonia solutions, it will be seen that in all cases (Be^{2+}, Mg^{2+}, Cd^{2+}, Ga^{3+}, and In^{3+}) ν_{sym}(M–OH_2) lies at a higher frequency than ν_{sym}(M–NH_3), with the single exception of Zn^{2+}. This is evidence that the co-ordination number of Zn^{2+} is different in the two solvents, and is surprising in view of the fact that zinc hexa-ammines can be crystallised from liquid ammonia (as chloride, bromide, or iodide) and give i.r. M–NH_3 stretching frequencies almost equal to those of the corresponding cadmium compounds,[41] implying not greatly different bond strengths.

At low temperatures a new, additional, polarised band appears at 358 cm^{-1} in the spectra of $Zn[NO_3]_2$ in ammonia. This new band is not present in the spectrum of $Zn[BF_4]_2$ under similar conditions and is therefore assigned as a Zn–ONO_2 stretching vibration, rather than ν_{sym}(Zn–NH_3) in $[Zn(NH_3)_6]^{2+}$ as suggested earlier.[37] There is supporting evidence for nitrato-complex formation in the $\nu_{sym}(NO_3^-)$ band which is broader than normal.

The Pb^{2+} ion is assigned a co-ordination number of six by comparison with Cd^{2+}.

Conclusions.—The co-ordination number in liquid ammonia of the ions Li^+, Ag^+, Be^{2+}, Zn^{2+}, and Hg^{2+} is four, whereas for Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Ga^{3+}, and In^{3+} it is six. Thus, the only differences between ammonia and water appear with Ag^+ and Zn^{2+}. The co-ordination around Ag^+ in water appears to be linear,[43] but the evidence is rather indirect. A consequence of the change in disposition and number of solvent ligands is that the chemistry of Ag^+ in liquid ammonia may be profoundly different relative to its aqueous chemistry. For example, $[Ag(CN)_2]^-$ is much less stable in ammonia than in water. There is no evidence for the existence of $[Ag(NH_3)_4]^+$ ions in an aqueous environment, but four-co-ordinate *N*-donor complexes such as $[Ag(py)_4]^+$ are known.[33]

The ν_{sym}(M–NH_3) band is usually found at lower frequency than ν_{sym}(M–OH_2). This is also true of ν_{asym}(M–NH_3) compared to ν_{asym}(M–OH_2) in the few cases

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where a direct comparison is possible (Ni^{2+}, Mn^{2+}, and Fe^{2+}).[44]

Nitrate Spectra.—We conclude this survey with a brief discussion of the spectral features due to nitrate anions. Our work on the alkali-metal nitrates (Part III [45]) shows that the extent of contact ion-pair formation is very temperature sensitive. Therefore it is not wise to compare these results, which were mostly obtained at 233 K, with results for aqueous solutions obtained at 293 K.

In all cases the nitrate ion gave rise to single bands at *ca.* 710 (ν_4), 1 044 (ν_1, p), and 1 662 cm^{-1} ($2\nu_2$, p). The ν_1 band was particularly sharp (width at half height, $w_{\frac{1}{2}}$, 2—3 cm^{-1}) in all spectra, so that the $[^{18}ONO_2]^-$ satellite could be easily observed at *ca.* 1 027 cm^{-1} (see Figure 1) even at the natural abundance of ^{18}O (0.204 atom %, 0.612 molecule %). The fact that ν_4 does not show obvious fine structure is indicative that there is little contact ion pairing.[27,35,37] The $2\nu_2$ band was strikingly apparent, being similar in height to the ν_4 band. It has previously been observed in aqueous solution,[27,46] although it appears as a broad feature. In both cases there is overlap with a solvent-deformation mode, but in ammonia this is much broader than $2\nu_2$ which consequently appears to 'sit' on the solvent band.

The ν_3 (asymmetric N–O stretching) region shows the greatest difference from the aqueous analogue. It is much less broad; $w_{\frac{1}{2}}$ is of the order of 60 cm^{-1}. There is evidence for at least two underlying features at *ca.* 1 370 and 1 350 cm^{-1} in most spectra, but detailed examination of the alkali-metal nitrates has revealed more fine structure. It is widely believed that in aqueous solution hydrogen bonding is the origin of the complexity of the ν_3 envelope, its main function being to lift the degeneracy of the vibration. The results in ammonia are consistent with there being much less hydrogen bonding. Complex formation would be evidenced by a band at *ca.* 1 400 cm^{-1}, and the absence of such a feature is consistent with the indication, from ν_4, that little complex formation (contact ion pairing) takes place under our experimental conditions. This is unexpected, since ammonia has a much lower dielectric constant than water, but may be due to the low temperatures employed. It is particularly obvious with ions such as Ca^{2+} and In^{3+} which form contact ion pairs with ease in water at ambient temperatures.

We thank M. Griffin for the preparation of tetra-amminesilver perchlorate.

[5/1765 *Received*, 15*th September*, 1975]

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