600. *The Infrared Spectra of Some Metal Ammines and Deuteroammines.*

By D. B. Powell and N. Sheppard.

Infrared spectra have been obtained of a representative series of metal–ammonia co-ordination complexes (metal ammines), and of several of the corresponding trideuteroammines. These enable clear-cut vibrational assignments to be made for all of the main bands observed in the spectra of the ammines between 4000 and 700 cm.$^{-1}$. In particular those that usually occur in the vicinity of 800 cm.$^{-1}$ are shown to represent rocking modes of the co-ordinated ammonia molecules. Extra bands not observed before have been found in several cases near 500 cm.$^{-1}$; these represent bond-stretching frequencies of the metal–nitrogen skeleton.

There is a general correlation between the stability of the ammines and the frequencies of certain of the NH_3 angle-deformation vibrations and νM–N vibrations.

Some years ago Duval, Duval, and Lecomte [1] studied the infrared spectra of a number of metal–ammonia co-ordination complexes (metal ammines). They reported absorption bands in the regions of 1500,* 1200,* and 800 cm.$^{-1}$. They considered that the first two represent the frequencies of the internal asymmetrical and symmetrical angle deformation vibrations of the ammonia molecules as modified by co-ordination with the metal atom [$\delta_{as}(NH_3)$ and $\delta_s(NH_3)$ respectively]; the corresponding absorption bands of ammonia itself occur near 1628 and 950 cm.$^{-1}$ in the gaseous state and at 1646 and 1060 cm.$^{-1}$ in the crystalline solid state.[2] These assignments of the ammine bands are agreed as correct by most subsequent workers in the field [3, 4, 5] and are confirmed by the present work. Hill and Rosenberg [6] recently suggested that the bands at *ca.* 1300 cm.$^{-1}$ are to be assigned to the stretching vibrations of the metal–nitrogen bonds (νM–N). However the present results show that the νM–N frequencies occur at much lower values.

Lecomte and his colleagues [1] pointed out that the bands at *ca.* 800 cm.$^{-1}$ might be assigned either to another angle deformation mode of the NH_3 group [presumably the "external" M–NH_3 rocking vibration $\delta_r(NH_3)$] or alternatively to a bond-stretching vibration (νM–N) of the heavy-atom skeleton. In the literature to date no agreed assignment of these bands has been reached although subsequent workers have usually chosen one or other of the above alternatives.

As Duval, Duval, and Lecomte [1] originally pointed out, the best way to distinguish between these alternative possibilities is to study the spectra of the corresponding complexes with ND_3 ligands. If the band at *ca.* 800 cm.$^{-1}$ represents the NH_3 rocking mode it should be lowered in frequency by a factor approaching $1/\sqrt{2}$ in the spectra of the deuteroammines; if it is a νM–N frequency it should be little changed. The spectra of a number of ammines and deuteroammines have therefore now been studied between 3500 and 450 cm.$^{-1}$. They show clearly that the bands at *ca.* 800 cm.$^{-1}$ are to be assigned to NH_3 rocking modes. This is in agreement with the very recent conclusions of Mizushima, Nakagawa, and Quagliano [7] which were based on calculations of the likely rocking frequencies of co-ordinated NH_3 groups. The same authors also made some preliminary deuteration experiments with $[Co(NH_3)_6]Cl_3$ and showed that the band at *ca.* 800 cm.$^{-1}$ is shifted. However, they made no measurements in the lower-frequency potassium bromide

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* The more extensive range of compounds studied since shows that better mean positions of these bands would be 1600 and 1300 cm.$^{-1}$ respectively.

[1] Duval, Duval, and Lecomte, *Compt. rend.*, 1947, **224**, 1632.
[2] Reding and Hornig, *J. Chem. Phys.*, 1951, **19**, 594.
[3] Faust and Quagliano, *J. Amer. Chem. Soc.*, 1954, **76**, 5346.
[4] Merritt and Wiberley, *J. Phys. Chem.*, 1955, **59**, 55.
[5] Kobayashi and Fujita, *J. Chem. Phys.*, 1955, **23**, 1354.
[6] Hill and Rosenberg, *ibid.*, 1954, **22**, 148.
[7] Mizushima, Nakagawa, and Quagliano, *J. Chem. Phys.*, 1955, **23**, 1367; Nakagawa and Mizushima, *Bull. Chem. Soc. Japan*, 1955, **28**, 589.

region of the spectrum to observe the new band and hence the degree of the isotopic shift was undetermined. Such measurements have been carried out in the present study. In the course of the work additional bands were observed near 500 cm.$^{-1}$ in several cases which are undoubtedly due to the νM–N vibrations.

EXPERIMENTAL

Preparation of Ammines.—$[Co(NH_3)_6]Cl_3$: this was prepared by oxidation of an ammoniacal cobalt chloride solution by a stream of air, in the presence of active carbon, as described by Bjerrum and McReynolds.[8]

$[Co(NH_3)_5Cl]Cl_2$: ammoniacal cobalt chloride was oxidised with a stream of air by Sörensen's method, described by King.[9]

trans-$[Pd(NH_3)_2Cl_2]$: palladous chloride was dissolved in just sufficient dilute hydrochloric acid to prevent hydrolysis ; excess of concentrated ammonia was added until the solution became pale yellow and the dichlorodiammine was precipitated by addition of dilute hydrochloric acid.[10]

$[Pd(NH_3)_4]Cl_2,H_2O$: *trans*-$[Pd(NH_3)_2Cl_2]$ was dissolved in excess of concentrated aqueous ammonia and ammonium chloride. The solution was then allowed to crystallise.[11]

$[Pt(NH_3)_4]Cl_2$: this was prepared by dissolving the " green salt " $[Pt(NH_3)_4]PtCl_4$ in excess of aqueous ammonia and precipitating the tetrammine with alcohol–acetone. The preparation is described in detail by Keller.[12]

trans-$[Pt(NH_3)_2Cl_2]$: the tetrammine described above was heated in an oil-bath at 250° for 20 min. The product was extracted with hot water, and the crystals which separated on cooling were recrystallised from water as recommended by Biltz.[13]

$[Cu(NH_3)_4]SO_4,H_2O$: this was precipitated from ammoniacal cupric sulphate solution by the addition of alcohol.[14]

$[Ag(NH_3)_2]_2SO_4$: silver nitrate was evaporated with dilute sulphuric acid, and while still hot the silver sulphate formed was dissolved in concentrated aqueous ammonia and allowed to crystallise.[15]

$[Co(NH_3)_6]Cl_2$: this was prepared by adding a concentrated solution of cobalt chloride to aqueous ammonia. The precipitate was dissolved by warming, and the solution allowed to crystallise. Air was excluded throughout the preparation.[16]

The corresponding deuteroammines were prepared by two methods. The compounds $[Co(NH_3)_6]Cl_3$ and $[Pd(NH_3)_2Cl_2]$ were refluxed repeatedly with successive small amounts of pure D_2O, the excess being removed by heating gently on an electric hot-plate. All operations including the preparation of samples for infrared examination were handled by the usual " dry box " procedure. Both $[Cu(NH_3)_4]SO_4,H_2O$ and $[Ag(NH_3)_2]_2SO_4$ were too sensitive to hydrolysis for this method to be used, and so were treated with successive small amounts of D_2O, some of the solvent being removed at each stage by storage over active alumina ; no attempt was made to isolate these ammines in the solid state, the spectra being investigated in D_2O solution.

Determination of Spectra.—Most of the infrared spectra were obtained with a Hilger D 209 double-beam spectrometer, modified to provide a focus in the sample beam. Spectra were obtained with rock-salt and potassium bromide prisms from 1650 to 450 cm.$^{-1}$. A few of the spectra of the ammines were taken from 4000 to 700 cm.$^{-1}$ on a Perkin-Elmer 21 double-beam instrument.

Samples were prepared for examination by the usual methods, these depending on the nature of the ammine and the spectral region to be examined. For the cobalt, platinum, and palladium ammines and deuteroammines, the potassium bromide disc and Nujol mull methods were used. In the case of the copper and silver ammines the potassium bromide reacted with the compounds and so either a Nujol mull, or a concentrated aqueous solution between silver chloride plates, was used.

The aqueous solutions had several disadvantages as they absorbed too strongly in the

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[8] *Inorg. Synth.*, 1946, **2**, 216.
[9] King, *Inorg. Preparations*, 1936, 103.
[10] Mellor, " Inorganic and Theoretical Chemistry," Longmans, London, 1936, Vol. XV, p. 664.
[11] *Op. cit.*, p. 667.
[12] Keller, *Inorg. Synth.*, 1946, **2**, 250.
[13] Biltz, reported by Mellor, *op. cit.*, 1937, Vol. XVI, p. 261.
[14] King, *Inorg. Preparations*, 1936, 103.
[15] *Idem, ibid.*, p. 102.
[16] *Op. cit.*, 1935, Vol. XIV, p. 630.

potassium bromide region, also in the rock-salt region at frequencies greater than 1500 cm.$^{-1}$. It was essential to obtain these spectra where possible for comparison with those of the deuteroammines which were not separated from D_2O solution for determination of the infrared spectra.

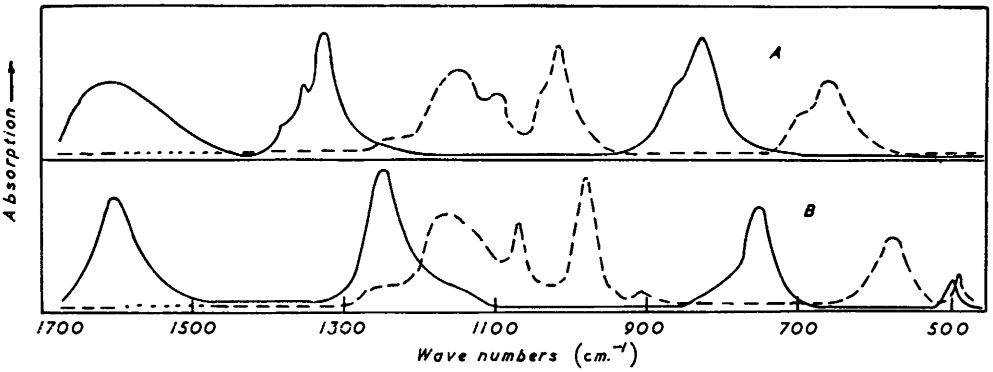
For detection of the weak bands, later assigned to skeletal stretching frequencies of the M–N bond, it was necessary to prepare extremely concentrated Nujol mulls. It was not possible to use the potassium bromide disc method for this purpose, as a sufficiently transparent disc could not be obtained having the required concentration of ammine.

Typical spectra obtained for the ammines and deuteroammines are shown in the Figure, and the main bands observed are listed in Table 1.

DISCUSSION

Spectroscopic Assignments.—The spectra of the ammines and deuteroammines are relatively simple (see Figure) and the analogous absorption bands in the spectra of the ammines of different ions, or of ammines and deuteroammines of the same ion, are readily picked out. These are listed in the same columns of Table 1. This contains the frequencies of all the absorption bands of appreciable strength. At the foot of the Table are listed the vibrational assignments that are discussed below.

Infrared spectra of typical ammines and deuteroammines in the region 1700—450 *cm.*$^{-1}$.



Solid lines, ammines. Broken lines, deuteroammines. A, $[Co(NH_3)_6]Cl_3$. *B,* $[Pd(NH_3)_2Cl_2]$.

The absorption bands near 1600, 1300, and 800 cm.$^{-1}$ in the spectra of the cobalt and palladium ammines are all well shifted to lower frequencies in the spectra of the deuteroammines, showing that they are each to be assigned to angle deformation modes of vibration involving N–H (N–D) bonds. As discussed above, the first two correspond to the asymmetrical and the symmetrical NH_3 deformation modes, and the bands at *ca.* 800 cm.$^{-1}$ are now clearly shown to represent the M–NH_3 rocking vibrations, $\delta_r(NH_3)$.

In the present study the weaker infrared absorption bands near 500 cm.$^{-1}$ have been observed for the first time. It is clear that they represent vibration frequencies of the heavy-atom skeleton as they are almost unaffected when the hydrogen atoms are replaced by deuterium. There can be no doubt that these represent the infrared-active νM–N bond stretching modes. In several cases frequencies have been observed in the Raman spectra of certain ammines in the same region [17, 18, 19] (see Table 1). For the tetramminoplatinum ion Mathieu [18] observed Raman lines at 538 (polarised) and 526 cm.$^{-1}$ (depolarised). Together with the infrared band at 511 cm.$^{-1}$, these provide just the right number of frequencies for assignment to the νPt–N stretching modes. If the ion is assumed to have an effectively D_{4h} planar structure for the heavy atoms, two Raman active frequencies of symmetries A_{1g} and B_{2g} (the former polarised and the latter depolarised) and one E_u infrared-active mode are expected to occur. The fact that the 538 cm.$^{-1}$ Raman line is polarised shows directly that it is a νPt–N frequency, as none of the angle-deformation vibrations of

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[17] Bose and Datta, *Nature*, 1931, **128**, 725.
[18] Mathieu, *Chim. phys.*, 1939, **36**, 308.
[19] Joos and Damashun, *Z. Physik*, 1931, **32**, 553.

TABLE 1. *The infrared and Raman frequencies of some ammines and deuteroammines and their assignment to fundamental modes of vibration of the complexes.*

Formula	Method	Observed infrared frequencies					Raman frequencies*
$[Co(NH_3)_6]Cl_3$	KBr, N	3230, 3170, (3130)	1615 (bd)	(1352), 1329	(862), 830	—	575, 483
$[Co(ND_3)_6]Cl_3$	KBr	N.I.	1155, 1088 [a]	1016	665	N.I.	N.I.
$[Co(NH_3)_5Cl]Cl_2$	N	(3220), 3140	1575 (bd)	1305, (1272)	845	493	575
$[Co(ND_3)_5Cl]Cl_2$	N	N.I.	N.I.	N.I.	N.I.	487	N.I.
$[Co(NH_3)_6]Cl_2$	N	3340 (3180)	1600 (bd)	1165	670	N.I.	N.I.
$[Pd(NH_3)_4]Cl_2,H_2O$	N	(3520), 3250, 3150	1595 (bd)	(1300), 1283	842, 800	498	N.I.
trans-$[Pd(NH_3)_2Cl_2]$ [b]	N	3320, 3230, 3170	1605	1246	752	496	N.I.
trans-$[Pd(NH_3)_2Cl_2]$ [c]	KBr	N.I.	1615	1266	753	N.I.	N.I.
trans-$[Pd(ND_3)_2Cl_2]$ [c]	KBr	N.I.	1165, 1068 [a]	978	580	493	N.I.
$[Pt(NH_3)_4]Cl_2$	N	(3520),[e] 3240, 3150	1587 (bd)	(1340), 1326	892, 841	511 (bd),	538 (p), 526 (dp), 270 (dp)
trans-$[Pt(NH_3)_2Cl_2]$	N	3270, 3170	1638, 1538	(1305), 1288	828	507	N.I.
$[Cu(NH_3)_4]SO_4,H_2O$ [d]	N	3320, (3250), 3170	(1678),[e] 1643	1287	(783), 733 (bd)	—	410
	H_2O	N.I.	H_2O	1280	H_2O	H_2O	N.I.
$[Cu(ND_3)_4]SO_4,D_2O$ [d]	D_2O	N.I.	D_2O	982	D_2O	N.I.	N.I.
$[Ag(NH_3)_2]_2SO_4$ [d]	N	3290, 3230, 3140	1640, 1600	1190	741	—	N.I.
	H_2O	N.I.	H_2O	1220	H_2O	H_2O	N.I.
$[Ag(ND_3)_2]_2SO_4$ [d]	D_2O	N.I.	D_2O	950	D_2O	N.I.	N.I.
Vibrational assignments	—	$\nu(NH)$	$\delta_{as}(NH_3)$	$\delta_s(NH_3)$	$\delta_r(NH_3)$	νM–N	—

N.I., not investigated in this region. N, Nujol mull. KBr, potassium bromide disc. H_2O or D_2O, spectra determined in solution of these solvents. (bd), broad band. (p), polarised line. (dp), depolarised line.

Frequencies in parentheses denote bands which are shoulders on neighbouring strong bands or are of subsidiary intensity. *a*, Possibly due to ND_2H groups. *b*, Yellow powder. *c*, Red crystals. *d*, These spectra showed extra bands in the vicinity of 1100 and 600 cm.$^{-1}$, due to SO_4^{2-} ions. *e*, Absorption in this region may be partly due to water of crystallisation.

* See refs. 17—19.

TABLE 2. *The ratios* νH : νD *for the analogous bands in the spectra of the ammines and deuteroammines and of methyl bromide and trideuteromethyl bromide.*

Vibration	Cobaltic hexammine	*trans*-Palladium dichlorodiammine *	Methyl bromide
$\delta_{as}(NH_3)$ or $\delta_{as}(CH_3)$	1·395	1·386	1·372
$\delta_s(NH_3)$ or $\delta_s(CH_3)$	1·305	1·295	1·322
$\delta_r(NH_3)$ or $\delta_r(CH_3)$	1·248	1·298	1·328
νM–N or νC–Br	—	1·006	1·059

* During the reaction of the yellow $Pd(NH_3)_2Cl_2$ with D_2O a change in appearance to reddish crystals was noted. A sample of the ammine treated with water under the same conditions gave similar crystals. The crystals seem to be the second crystalline form of this compound noted by Mann, Crowfoot, Gattiker, and Wooster (*J.*, 1935, 1642). Spectra for both forms are given in Table 1, but the frequency ratios in Table 2 are calculated for the reddish crystals in each case.

TABLE 3. *Comparison of vibration frequencies and stabilities of ammines.*

		$[Co(NH_3)_6]^{3+}$	$[Ag(NH_3)_2]^+$	$[Cu(NH_3)_4]^{2+}$	*$[Zn(NH_3)_4]^{2+}$
log $k_{av.}$ + log 55		7·6	5·3	5·0	4·1
Vibration frequencies	$\delta_s(NH_3)$	1329	1190	1287	1260
	$\delta_r(NH_3)$	830	741	733	N.I.
νM–N (Raman)		575	410 (for chloride)	419 (for chloride)	418 (for hexammine)

		*$[Cd(NH_3)_4]^{2+}$	$[Ni(NH_3)_6]^{2+}$	$[Co(NH_3)_6]^{2+}$
log $k_{av.}$ + log 55		3·6	3·2	2·6
Vibration frequencies	$\delta_s(NH_3)$	1205, 1130	1172 †	1165
	$\delta_r(NH_3)$	N.I.	682 †	670
νM–N (Raman)		340 (for hexammine)	N.I.	N.I.

* These spectra were not examined in detail. † Given by Kobayashi and Fujita.[5]

N.I. = not investigated.

the heavy-atom skeleton can belong to the completely symmetrical symmetry class. The depolarised Raman line at 270 cm.$^{-1}$ is probably one of these angle-deformation vibration frequencies.

Low-frequency νM–N bands were observed in the infrared spectra in all cases studied in the potassium bromide region except for the cobalt hexammine and the copper and silver ammines. In the last cases the corresponding Raman lines occur near 400 cm.$^{-1}$, and the infrared bands are therefore probably beyond the range of the potassium bromide prism used. The absence of a band in the spectrum of the cobalt hexammine is more surprising as, by analogy with the Raman data, one νM–N frequency which is infrared-active would have been expected in the region of 500 cm.$^{-1}$. The pentamminocobalt chloride does however show an infrared band in the expected region.*

The assignment of the various ammine frequencies is obvious on the basis of the qualitative frequency shifts occurring on deuteration. However, it is of interest to compare quantitatively the ratio of the frequencies observed for normal and deutero-derivatives, with those obtained for related vibrations of CH_3X and CD_3X compounds (X denotes a heavy atom). The available data [20] for CH_3Br and CD_3Br have been chosen for this purpose, and the appropriate ratios are listed in Table 2. It is seen that there is a very close correspondence between the magnitudes of the νH : νD ratios for the bands that have been assigned to analogous $\delta(NH_3)$ and $\delta(CH_3)$ vibrations.

An interesting feature of the spectra of the platinum and palladium tetrammines is the doubling of the $\delta_r(NH_3)$ frequency, which is not observed with the dichlorodiammines. It is very probable that the two frequencies found for the tetrammines are due to in-plane and out-of-plane rocking vibrations.

Variation in Molecular Vibration Frequencies with Stabilities of Ammines.—Kobayashi and Fujita [5] have suggested that there is a relation between the stability of cobaltic, chromic, and nickelous hexammines and the frequencies of their N–H vibrations.

Table 3 contains figures for $\delta_s(NH_3)$ and $\delta_r(NH_3)$ frequencies for the wider range of ammines now examined, with the corresponding values for $\log k_{\text{average}} + \log 55$ (where k_{average} is the average value of the stability constant for the substitution of one NH_3 molecule in aqueous solution). $\text{Log } k_{\text{average}} + \log 55$ is taken as a measure of stability, as it is proportional to the free energy of formation of the ammines in aqueous solution. The values given are from Bjerrum's table of collected data.[21] It is observed that the vibration frequencies and stabilities in general show a similar trend, but if these vibration frequencies are plotted against corresponding values for $\log k_{\text{average}} + \log 55$ deviations from a smooth curve are found, particularly with $\delta_s(NH_3)$ frequencies. This is not surprising since the N–H vibrations are only indirectly related to the strength of the M–N bond, and also the stability constants concern the formation of the ammine from the hydrated ion, and not directly the bond strength. Further, the data are obtained from ammine complexes of various shapes, and it is expected that this factor has some effect on the observed frequencies.

It might be expected that there would be a more direct correlation between stability and the νM–N frequencies. Moreover, although as yet insufficient infrared data are available, the more numerous Raman data [22] do show the same trend as is shown by the $\delta(NH_3)$ frequencies (Table 3). It is to be expected that the strongest Raman lines in the νM–N region will represent the symmetrical "breathing" frequencies of the ions, and these are dependent on the M–N force constant only, and not on the mass of the central atom. In selecting from Raman data for the cobalt ammine it has been assumed that the higher-frequency line represents the breathing frequency, by analogy with the platinum tetrammine discussed in the previous section.

It is noteworthy that the $\delta(NH_3)$ frequencies for the dichlorodiammines of palladium and platinum differ considerably from those of the corresponding tetrammines (see Table 1), although the stabilities of the simple and mixed complexes are apparently similar.

* [*Added*, 17.6.56.] Further work has revealed a weak absorption band centred at 502 cm.$^{-1}$ in the spectrum of cobaltic hexammine chloride.

[20] Noether, *J. Chem. Phys.*, 1942, **10**, 664.

[21] Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

[22] Hibben, "The Raman Effect and its Chemical Application," Reinhold, New York, 1939, p. 462.

However the corresponding νM–N frequencies observed in the infrared spectra do not vary to nearly the same extent. It may be concluded that the $\delta(NH_3)$ frequencies are particularly sensitive to the substitution of neighbouring ammonia ligands by chlorine; this effect is not unexpected.

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SIR JOHN CASS COLLEGE, JEWRY STREET, LONDON.
DEPARTMENT OF COLLOID SCIENCE,
THE UNIVERSITY, CAMBRIDGE.

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