The influence of molecular shape upon the internal field is evident in the values of β in Table I and the points in Fig. 1. For the roughly spherical molecules of the substituted methanes, the effect of the internal field is greater than that calculated by means of the Powles equation, a discrepancy which would be still greater if the correction for the effect of viscosity were not omitted. The flattening of the sphere to the roughly oblate spheroidal form of the substituted benzene and pyridine molecules reduces the effects of the field to amounts close to those calculated by means of the Powles equation, an apparent exception being 2,6-dimethylpyridine, the points for which lie close to the O'Dwyer and Sack curve. Elongation of the flattened structure as in the quinoline, isoquinoline and substituted naphthalene molecules reduces the effects of the field below those calculated by the Powles equation. That the decrease in field effect is not merely the result of increase in molecular volume is shown by the fact that pyridine and the monomethyl and monohalogenated pyridines and benzenes have about the same molar volumes as the tetrasubstituted methanes under consideration. The strong local fields of the highly polar cyanide and nitro groups raise the effects of field well above those calculated by the Powles equation for nitrobenzene and benzonitrile, but the effect is much smaller in the case of the larger 1-nitronaphthalene.

It is evident that the macroscopic dielectric relaxation time of a polar liquid is usually greater than the molecular relaxation time but not nearly as much greater as is indicated by calculation based on the Lorentz internal field. The Powles equation and the identical first approximation obtained by O'Dwyer and Sack seems to be the best approximation for the calculation of the molecular relaxation time from the macroscopic, but it is a very rough approximation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes.[1a,b] XII. The Characteristic NH_3 Deformation Vibrations of Solid Inorganic Complexes

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The infrared spectra of a number of solid metal ammine complexes have been investigated. It has been possible to determine the three deformation vibrations of the ligated molecules in these complexes. The NH_3 degenerate deformation is observed in the region of 1650–1560 cm.$^{-1}$; the NH_3 symmetric deformation in the region of 1350–1150 cm.$^{-1}$; and the NH_3 rocking frequency in the region of 950–650 cm.$^{-1}$. Each of these absorption bands has a characteristic absorption profile. A theoretical explanation for the range of these deformation frequencies is presented.

Introduction

Infrared spectra of solid ammine coördination compounds of the transition metals have been subject to several investigations.[3–7] The comparative ease of preparation and the wide diversity of substituents possible in this series have emphasized the importance of a definite characterization of the absorption bands, which may be attributed to the NH_3 grouping upon complex formation.

Mizushima, Nakagawa and Quagliano have recently characterized the deformation vibrations of coördinated ammonia molecules in Co(III) ammines.[8] Using a Urey–Bradley type potential function, the frequencies of the degenerate and symmetric deformations and the rocking vibrations have been calculated for the $Co(NH_3)_6^{+++}$ ion. These calculated values were shown to be in good agreement with frequencies observed for a number of Co(III) ammines containing coördinated ammonia molecules and, furthermore, the values calculated for the deuterated hexammine cobalt(III) chloride, using the same set of force constants, agreed with the observed frequencies.

The infrared spectra of a number of ammines have now been obtained to determine the effect of the nature and the oxidation state of the central metal atom on the frequencies of the three characteristic deformation vibrations of the coördinated ammonia molecules.

Experimental

Preparation of Compounds.—The compounds listed in Table I were prepared by methods similar to those given in the references in the last column. Most of the compounds were dried by heating under reduced pressure in an Abderhalden apparatus for several hours at 110°. All other compounds listed in Table II were supplied by Dr. D. N. Sen.[9]

Absorption Measurements.—Spectra were obtained by means of a Perkin–Elmer Infrared Spectrophotometer Model 21 with a sodium chloride prism. Preparation of the potassium bromide disks was carried out according to the procedure of Stimson and O'Donnell[10] as described in a previous article.[4]

The frequency values for the NH_3 deformation vibrations are listed in Table II.

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[1] (a) Paper XI in series, *Spectrochim. Acta.* in press. (b) Abstracted from the Ph.D. theses of G. F. Svatos, 1954, and D. M. Sweeny, 1955. Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame. Presented before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb., 1955.

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TABLE I

ANALYSIS OF COMPOUNDS

Compound	Component analyzed	% Calcd.	% Found	Ref.
$[Co(NH_3)_6]Cl_3$	NH_3	38.20	37.94	10
$[Co(NH_3)_6]Cl_2$	NH_3	44.04	43.71	11
$[Ag(NH_3)_2]_2SO_4$	NH_3	17.93	17.58	11
$[Cu(NH_3)_4]SO_4 \cdot H_2O$	NH_3	27.72	27.34	11
$[Ni(NH_3)_6]Cl_2$	NH_3	44.08	43.83	11
$[Cr(NH_3)_6]Cl_3$	NH_3	39.22	38.77	11
$[Cr(NH_3)_5Cl]Cl_2$	NH_3	34.96	34.58	11
$[Co(NH_3)_5Br]Br_2$	NH_3	22.18	22.06	12
$[Co(NH_3)_5NO_2]Cl_2$	NH_3	32.62	32.38	13
$[Co(NH_3)_5NO_3]Cl_2$	NH_3	30.74	30.64	14
$[Co(NH_3)_5H_2O]Cl_3$	NH_3	31.71	31.58	11
$[Co(NH_3)_4(H_2O)_2]Cl_3$	NH_3	25.28	24.99	15
trans-$[Co(NH_3)_4(NO_2)_2]Cl$	NH_3	26.76	26.71	11
$[Co(NH_3)_3(NO_2)_3]$	NH_3	20.60	20.57	11
$[Co(NH_3)_5Cl]Br_2$	NH_3	25.09	25.20	16
$[Co(NH_3)_5ONO]Cl_2$	NH_3	32.62	32.75	13
$[Co(NH_3)_5SO_4]Cl$	NH_3	30.98	30.98	17
$[Co(NH_3)_5CO_3]NO_3 \cdot {}^1/_2H_2O$	NH_3	26.40	26.11	18
$[Co(NH_3)_5OH]Br_2 \cdot H_2O$	NH_3	25.12	25.10	19
$[Co(NH_3)_5C_2O_4]Br \cdot HBr$	NH_3	21.67	21.76	20
$[Co(NH_3)_4CO_3]Cl$	NH_3	30.62	30.35	21
$K[Co(NH_3)_2(NO_2)_4]$[22]	NH_3	10.77	11.19	11

TABLE II

DEFORMATION FREQUENCIES IN CM.$^{-1}$ FOR METAL AMMINE COMPLEXES

	Compound	Degenerate	Symmetric	Rocking
1	$[Ag(NH_3)_2]_2SO_4$	1650	1215	738
2	$[Co(NH_3)_6]Cl_2$	1610	1158	650
3	$[Ni(NH_3)_6]Cl_2$	1610	1175	678
4	$[Cu(NH_3)_4]SO_4 \cdot H_2O$	1615	1285	732
5	$[Cr(NH_3)_6]Cl_3$	1620	1314	757
6	$[Pd(NH_3)_4]Cl_2$	1610	1304	827
7	$[Co(NH_3)_6]Cl_3$	1620	1325	827
8	$[Pt(NH_3)_4]Cl_2$	1570	1350	850
9	$[Pt(NH_3)_5Cl]Cl_3$	1560	1355	935
10	$[Cr(NH_3)_5Cl]Cl_2$	1600	1290	724
11	$[Cr(NH_3)_5NO_2]Cl_2$	1620	1305	768
12	*trans*-$[Pt(NH_3)_2Cl_2]$	1605	1295	815
13	*trans*-$[Pd(NH_3)_2Cl_2]$	1614	1250	756
14	$[Co(NH_3)_5NO_2]Cl_2$	1595	1315	850
15	*trans*-$[Co(NH_3)_4(NO_2)_2]Cl$	1620	1300	840
16	$[Co(NH_3)_3(NO_2)_3]$	1630	1290	815
17	$K[Co(NH_3)_2(NO_2)_4]$	1630	1265	790
18	$[Co(NH_3)_5Cl]Br_2$	1600	1310	840
19	$[Co(NH_3)_5Br]Br_2$	1590	1312	832
20	$[Co(NH_3)_5OH]Br_2$	1620	1303	806
21	$[Co(NH_3)_5ONO]Cl_2$	1620	1320	845
22	$[Co(NH_3)_5H_2O]Cl_3$	1620	1325	835
23	*cis*-$[Co(NH_3)_4(H_2O)_2]Cl_3$	1620	1320	850
24	$[Co(NH_3)_5CO_3]NO_3$	1603	1305	830
25	$[Co(NH_3)_4CO_3]Cl$	1600	1280	850
26	$[Co(NH_3)_5NO_3]Cl_2$	1600	1315	855
27	$[Co(NH_3)_5SO_4]Cl$	1615	1315	830
28	$[Co(NH_3)_5(C_2O_4)]Br \cdot HBr$	1625	1310	835

Discussion

The previous calculation[8] of normal frequencies for the NH_3 ligand was based on the following potential function

$$V = \Sigma \frac{1}{2}K_i(\Delta r_i)^2 + \Sigma \frac{1}{2}H_{ij}r_i^0r_j^0\,(\Delta\alpha_{ij})^2 + \Sigma \frac{1}{2}F_{ij}(\Delta q_{ij})^2 + \text{linear terms}$$

where r_i and r_j are bond lengths with equilibrium values r_i^0 and r_j^0; α_{ij} bond angles and q_{ij} distances between non-bonded atoms. In addition K, H and F represent stretching, bending and repulsive force constants, respectively.

The deformation frequencies depend on the bending force constants H(HNH) and H(HNM), and the repulsive force constants, $F(H\cdot\cdot\cdot H)$ and $F(H\cdot\cdot\cdot M)$, where M denotes the central metal. Of these constants H(HNH) and $F(\cdot\cdot\cdot H)$ are the same as those used for the calculation of the vibrations of ammonia (NH_3), ammonium ion (NH_4^+), and the deuterated products (ND_3 and ND_4^+).[23] Therefore, these two constants have the same value throughout the series, whereas the remaining two, H(HNM) and $F(H\cdot\cdot\cdot M)$, depend considerably on the nature of the central metal, M.

The calculation showed that the degenerate deformation frequency depends on H(HNH) and $F(H\cdot\cdot\cdot H)$, the rocking frequency on H(HNM) and $F(H\cdot\cdot\cdot M)$, and the symmetric deformation frequency on all four constants. It follows from these relationships that the difference in the nature of the central metal atom should be reflected very strongly in the value of the rocking frequency considerably in the symmetric deformation frequency and little in the degenerate deformation frequency.

The frequencies of the deformation vibrations fall in characteristic regions of the spectra for all metal–ammine complexes reported. The degenerate deformation appears between 1650 and 1560 cm.$^{-1}$, the symmetric deformation between 1350 and 1150 cm.$^{-1}$ and the rocking vibration between 950 and 650 cm.$^{-1}$. The absorption profiles of the deformation are also quite characteristic. The degenerate deformation is broad and of moderate intensity, the symmetric deformation is quite sharp and very intense, and the rocking vibration band is very broad and intense.[24]

The effects of the nature and oxidation state of the central metal atom on the deformation frequencies are revealed by the data in Table II. It is evident that the rocking frequency decreases

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in the following order: Pt(IV) > Pt(II) > Co(III) > Pd(II) > Cr(III) > Cu(II) > Ni(II) > Co(II). Univalent silver is somewhat out of line, the ammonia ligands in $[Ag(NH_3)_2]^+$ having a rocking frequency slightly greater than that in $[Cu(NH_3)_4]^{++}$. The presence of rocking frequencies in the spectra of the hexammine Ni(II) and Co(II) complex ions indicates that the nitrogen-to-metal bonds have covalent character; the relatively low frequencies along with the paramagnetism of these complexes indicate sp^3d^2 outer orbital type bonds.

The rocking frequencies show a large variation and are thus very sensitive to the nature and oxidation state of the central metal ion. This is understandable from the above discussion of the nature of the rocking vibration.

The symmetrical bending frequencies of coördinated ammonia molecules show a similar variation with the nature of the N–M bond but the percentage difference in frequency in going from the Co(II) to Pt(IV) ammines is not so great as for the rocking frequencies. Moreover, the degenerate frequencies show little variation with the nature of the N–M bond. These observations are also in accord with the foregoing discussions of the natures of the symmetric and degenerate deformation vibrations.

The neutral $Pt(NH_3)_2Cl_2$ molecule (12) has a lower rocking and a lower symmetric deformation frequency than the $[Pt(NH_3)_4]^{++}$ ion (8) and a similar effect is observed in the Pd(II) compounds (13 and 6). The effect of the charge of the complex itself on the ammonia deformation frequencies is seen also in the series of cobalt(III) ammines (compounds 17, 16, 15 and 14). (The position of the rocking band at 790 cm.$^{-1}$ in compound 17 is not accurately known as the NO_2 group also absorbs strongly in this region). Both the rocking and symmetrical deformation frequencies increase, in general, with increasing positive charge on the complex. This increasing positive charge coincides with increasing number of ammonia molecules in these Co(III) complexes.

The replacement of the carbonate group in the $[Co(NH_3)_5CO_3]^+$ ion (compound 24) by a sulfate group (compound 27) has no effect on the rocking frequency, and replacement by an oxalate group (compound 28) has very little effect on either the rocking or the symmetric deformation frequencies. In the $[Co(NH_3)_5X]^{+2}$ ions (compounds 18 to 21 and 26), an appreciable lowering of the rocking and symmetric deformation frequencies occurs only where X is a hydroxyl group. The replacement of an inner chlorine atom by a nitro group in the $[Cr(NH_3)_5Cl]^{++}$ ion (compounds 10 and 11) results in an appreciable increase in the these deformation frequencies.

The spectra of these metal ammine complexes are being determined in the cesium bromide region in these laboratories to study the nature of the lower frequencies, as reported in a previous paper.[25]

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Synthesis of Certain Ethylenediamineplatinum(II) and (IV) Bromides and Iodides[1]

BY GEORGE W. WATT AND ROBERT E. MCCARLEY

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Methods for the synthesis of ethylenediamine coördination compounds of certain halides of platinum(II) and (IV) in high yield and high purity are described. It is shown that $[Pt(en)Br_2]$ and its isomer $[Pt(en)_2]PtBr_4$ may be separated quantitatively owing to the solubility of the former in liquid ammonia at −33.5°.

In the course of studies on the lower oxidation states of platinum,[2] we have had occasion to prepare numerous ethylenediamine coördination compounds of platinum halides. Although many of the corresponding chlorides have been synthesized and are well characterized, they are not desirable as starting materials for reactions in liquid ammonia owing to their generally low solubility. Accordingly, the necessary bromides and iodides were prepared. The syntheses described below either correspond to compounds not previously reported or represent new and/or improved procedures.

Experimental

Methods.—Platinum, when present as the only nonvolatile component, was determined by ignition to the metal; otherwise, platinum was reduced to the metal with hydrazine, dissolved in aqua regia, and determined spectrophotometrically.[3] Halogens were determined as silver halide; where halogen was covalently bonded in complexes, it was displaced with ethylenediamine prior to precipitation.

All X-ray diffraction patterns were obtained using a Hayes unit, Cu Kα radiation, an Ni filter, a tube voltage of 35 kv., a filament current of 15 ma. and exposure times that varied with the nature of the sample. All of the X-ray diffraction data reported here are assembled in Table I and include only the six most intense lines for each compound for which such data are not already available; more nearly complete data are tabulated elsewhere.[4]

For potentiometric titrations, the potential was measured with a Leeds and Northrup type K potentiometer, a platinum indicator electrode, and a saturated calomel reference electrode.

Materials.—Unless otherwise indicated, all chemicals employed in this work were reagent grade materials that were used without further purification.

Hexabromoplatinic acid was obtained by dissolving finely divided platinum in bromine and concentrated hydrobromic acid followed by boiling to remove excess bromine and acid. Massive platinum was dissolved in aqua regia and the re-

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