sponding to the N–O stretching, $CH_2$ rocking, and $CH_2$ wagging vibrations, whereas DMEO·2HCl exists in the *trans* form as shown by the $CH_2$ rocking vibration at about 740 cm.$^{-1}$ ($A_u$ mode).[28]

The dihydrochloride of the ligand, DMEO·2HCl, reacts with some metal chlorides to give crystalline compounds of the formula $MX_2$·DMEO·2HCl. We have prepared the Mn(II), Cd(II), and Pd(II) derivatives, but it is to be expected that similar compounds may be formed by other metals. Because of their properties these compounds are formulated as tetrachlorometalates of the diprotonated species [$(CH_3)_2N^+(OH)$-$CH_2CH_2N^+H_3$] and are similar to the tetrahalogen metalates of other organic cations. It may be noticed that these [$H_2$DMEO] salts give anomalous conductivity values in DMF solution. This behavior very likely arises from a partial replacement in solution of one chloride of the tetrachlorometalate ion by an amino or aminooxide group. A similar behavior has been reported for the tetrachloropalladate(II) of diprotonated ethylenediamine and of its methylated analogs.[29]

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# Infrared Spectra from 80 to 2000 Cm.$^{-1}$ of Some Metal–Ammine Complexes

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The infrared spectra of the complexes $[Co(NH_3)_6]X_3$, $[Co(NH_3)_5X]X_2$, and $[M(NH_3)_6]X_2$, where M = Mn, Fe, Co, Ni, Zn, or Cd and X = Cl, Br, or I, have been measured from 80 to 2000 cm.$^{-1}$. The absorption band corresponding to the $N–M^{II}–N$ bending mode was observed at *ca.* 200 cm.$^{-1}$. The Co(III)–halogen stretching vibration in the halopentaammine complexes was observed below 300 cm.$^{-1}$, but no skeletal vibrations were observed in this region in the spectra of hexaammine–Co(III) complexes. Lattice vibrations have been identified in the region 80–155 cm.$^{-1}$ and a possible explanation of the unusual isotopic shifts of these bands is presented.

## Introduction

Although the infrared spectra of numerous metal–ammine complexes have been extensively studied,[2–11] $[Rh(NH_3)_6]Cl_3$ is the only compound for which the far-infrared spectrum (below 300 cm.$^{-1}$) has been reported.[11] The investigation of this region is of particular importance in regard to the long disputed assignment of the skeletal vibrations of these compounds. The lowest frequency band so far observed in the spectra of the hexaammine–metal(II) complexes, at *ca.* 300 cm.$^{-1}$, has been assigned to the M–N stretching mode. On the other hand the band at roughly the same position in the spectra of the complexes of the trivalent metals is now assigned to the N–M–N bending mode[9–11] after being originally assigned to the M–N stretching mode.[5,8] Thus no absorption band is expected below 300 cm.$^{-1}$ in the spectra of the metal(III) complexes, while the N–M–N bending mode of the metal(II) complexes is expected in this region.

We now report the results of a study of the infrared spectra from 80 to 2000 cm.$^{-1}$ of various hexaammine and halopentaammine complexes of cobalt(III) and the series of metal(II) complexes $[M(NH_3)_6]X_2$ where M = Mn, Fe, Co, Ni, Zn, or Cd and X = Cl, Br, or I. The latter three series are particularly well suited to an attempt to correlate the vibration frequencies with some physical property related to the bond strength.

## Experimental

All compounds were prepared by standard methods. $[Ni(ND_3)_6]Cl_2$ was prepared by the reaction of gaseous $ND_3$ with solid $NiCl_2$. $[Co(ND_3)_6]Cl_3$ and $[Co(ND_3)_5Cl]Cl_2$ were prepared by dissolving the corresponding light ammonia complexes in $D_2O$ followed by removal of the water by freeze drying. The process was repeated three times. For the second compound the solid was heated at 80° under vacuum to convert $[Co(ND_3)_5D_2O]Cl_3$ into $[Co(ND_3)_5Cl]Cl_2$. Deuteration was found to be about 90% complete, as judged by the relative intensities of the N–H and N–D stretching bands.

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TABLE I

INFRARED ABSORPTION FREQUENCIES (CM.$^{-1}$) OF AMMINE COMPLEXES

| Compound | $NH_3$ degen. deform. | $NH_3$ sym. deform. | $NH_3$ rocking | M–N str. | N–M–N deform. | M–X str. | Lattice vibr. |
|---|---|---|---|---|---|---|---|
| $[Mn(NH_3)_6]Cl_2$ | 1592 m | 1134 vs | 617 vs | 307 s | *a* | | *a* |
| $[Fe(NH_3)_6]Cl_2$ | 1597 m | 1151 vs | 641 vs | 321 s | *a* | | *a* |
| $[Co(NH_3)_6]Cl_2$ | 1602 m | 1163 vs | 654 vs | 327 s | 192 s | | 113 s |
| $[Ni(NH_3)_6]Cl_2$ | 1607 m | 1175 vs | 680 vs | 334 s | 215 s | | 115 s |
| $[Zn(NH_3)_6]Cl_2$ | 1596 m | 1145 vs | 645 vs | 300 s | *a* | | *a* |
| $[Cd(NH_3)_6]Cl_2$ | 1585 m | 1091 vs | 613 vs | 298 s | *a* | | *a* |
| $[Mn(NH_3)_6]Br_2$ | 1589 m | 1145 vs | 606 vs | 299 s | *a* | | *a* |
| $[Fe(NH_3)_6]Br_2$ | 1595 m | 1159 vs | 625 vs | 315 s | *a* | | *a* |
| $[Co(NH_3)_6]Br_2$ | 1600 m | 1174 vs | 647 vs | 318 s | *a* | | *a* |
| $[Ni(NH_3)_6]Br_2$ | 1603 m | 1188 vs | 672 vs | 327 s | 217 s | | 90 s |
| $[Zn(NH_3)_6]Br_2$ | 1592 m | 1156 vs | 636 vs | 294 s | *a* | | *a* |
| $[Cd(NH_3)_6]Br_2$ | 1578 m | 1099 vs | 594 vs | 291 s | *a* | | *a* |
| $[Mn(NH_3)_6]I_2$ | 1582 m | 1155 vs | 592 vs | 295 s | *a* | | *a* |
| $[Fe(NH_3)_6]I_2$ | 1592 m | 1182 vs | 617 vs | 306 s | *a* | | *a* |
| $[Co(NH_3)_6]I_2$ | 1595 m | 1189 vs | 626 vs | 312 s | *a* | | *a* |
| $[Ni(NH_3)_6]I_2$ | 1597 m | 1205 vs | 654 vs | 322 s | 216 s | | 81 s |
| $[Zn(NH_3)_6]I_2$ | 1594 m | 1179 vs | 621 vs | 282 s | *a* | | *a* |
| $[Cd(NH_3)_6]I_2$ | 1567 m | 1123 vs | 585 vs | 277 s | *a* | | *a* |
| $[Co(NH_3)_6]Cl_3$ | 1610 m | 1330 vs | 830 s | 499 vw, 476 vw, 449 vw | 332 s | | 155 s |
| $[Co(NH_3)_6]Br_3$ | 1605 m | 1320 vs | 820 s | 496 vw, 474 vw, 444 vw | 322 s | | 118 s |
| $[Co(NH_3)_6]I_3$ | 1595 m | 1320 vs | 803 s | 464[b] | 319 s | | 99 s |
| $[Co(NH_3)_5Cl]Cl_2$ | 1570 m | 1315 vs | 849 m | 498 m, 490 m, 466 w | 331 s | 284 s | 143 s |
| $[Co(NH_3)_5Br]Br_2$ | 1600 m | 1310 vs | 830 m | 493 w, 480 m, 455 w | 322 s | 205 s | 120 s |
| $[Co(NH_3)_5I]I_2$ | 1602 m | 1310 vs | 810 m | 480 vw, 464 w, 422 w | 314 s | 164 s | 108 s |
| $[Ni(ND_3)_6Cl_2$ | 1170 m | 896 vs | 517 s | 318 s | 206 s | | 108 s |
| $[Co(ND_3)_6]Cl_3$ | 1158 m | 1020 vs | 662 m | 465,[c] 446,[c] 419[c] | 296 s | | 153 s |
| $[Co(ND_3)_5Cl]Cl_2$ | 1152 m | 1010 vs | 670 m | 452 m, 425 w | 299 s | 274 s | 149 s |
| $[Zn(NH_3)_4]Cl_2$ | 1610 m | 1255 sh<br>1215 s | 702 s | 437 w | *a* | | *a* |

[a] Not investigated. [b] From ref. 10. [c] From ref. 9b.

## Results and Discussion

The frequencies and relative intensities of the absorption bands are given in Table I.

Absorption bands are assigned as by Barrow, *et al.*,[5] above 300 cm.$^{-1}$ (metal(II) complexes) and Nakamoto, *et al.*[9b] (cobalt(III) complexes). The strong band found in the region 80–155 cm.$^{-1}$ has the following characteristics: (a) The frequency of this band diminishes as, for example, along the series $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]Br_3$, and $[Co(NH_3)_6]I_3$ with increasing atomic weight of the halogen. (b) Isotopic substitution of the hydrogen atoms by deuterium has little effect on this band. This behavior indicates most strongly that this band is not associated with a fundamental skeletal vibration, but with a lattice vibration.

Only the lattice vibration is observed below 300 cm.$^{-1}$ in the spectra of the hexaammine–cobalt(III) complexes, but with the metal(II) complexes another band appears at *ca.* 200 cm.$^{-1}$ which must be the N–M–N bending frequency. The presence of this band is a further indication that the band at lower frequency is associated with vibrations within the lattice. The far-infrared spectra therefore confirm the correctness of the assignments above 300 cm.$^{-1}$ that we have used in this paper.

The compounds $[Co(NH_3)_5X]X_2$ have strong absorption bands at 284, 205, and 164 cm.$^{-1}$ where X = Cl, Br, and I, respectively. The shifts of this frequency on changing the halogen are analogous to the shifts found in other complexes and taken together with the values of the frequency lead to the assignment of the band as the Co–X stretching vibration. Thus, the $F_2$ Co–X stretching frequency was found to be 297, 231, and 192 cm.$^{-1}$ in the tetrahedral ions $CoX_4^{2-}$ (X = Cl, Br, and I).[12] Furthermore Adams, *et al.*,[13] found the $F_{1u}$ Pt–X stretching frequency at 344 cm.$^{-1}$ in $K_2PtCl_6$, 240 cm.$^{-1}$ in $K_2PtBr_6$, and 186 cm.$^{-1}$ in $K_2PtI_6$. The slight shift of the Co–Cl stretching frequency on deuteration of the complex $[Co(NH_3)_5Cl]Cl_2$ ($\nu_H/\nu_D = 1.04$) can be attributed to the coupling of this vibration with other skeletal vibrations.

The number of bands observed requires some comment. All the compounds of the formula $[M(NH_3)_6]X_2$ (except X = Cl; M = Zn, Cd) crystallize in the cubic system and the site symmetry of the complex ion is $O_h$. The site symmetry is also $O_h$ in $[Co(NH_3)_6]I_3$. A single M–N stretching band and a single N–M–N bending band are observed for all these compounds, in agreement with the local site symmetry which allows two $F_{1u}$ skeletal vibrations to be infrared active. In the spectra of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Br_3$, which do not crystallize in the cubic system, three M–N stretching bands are observed, but it is, of course, impossible to establish whether they arise from the splitting of the degenerate $F_{1u}$ mode or from the activation of other normally inactive modes. The N–M–N

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deformation band is not split and so would appear to be insensitive to the site symmetry. Four infrared-active stretching vibrations of the skeleton (three $A_1$, one E) and four deformations (one $A_1$, three E) are expected in the spectrum of the ion $[Co(NH_3)_5X]^{2-}$, which has the symmetry $C_{4v}$. Four stretching vibrations are actually found but only one deformation. Either accidental degeneracy or very weak intensity may be responsible for the latter effect.

The vibration frequencies of the hexaammine-metal(II) complexes show a steady trend parallel to the Irving–Williams order of stability $Mn < Fe < Co < Ni > Zn > Cd$.[14] The vibrations most sensitive to the nature of the metal are the $NH_3$ symmetric deformation, the $NH_3$ rocking, and the M–N stretching modes. An attempt to correlate quantitatively the vibration frequencies with the stability constants and heats of formation gave no satisfactory results. This failure, moreover, is not due to interfering factors, since all the complexes except $[Zn(NH_3)_6]Cl_2$ and $[Cd(NH_3)_6]Cl_2$ are isomorphous and crystallize in the cubic system, so that the effects of hydrogen bonding and other solid state effects are expected to vary regularly if at all within each series of chlorides, bromides, and iodides.

The effect of hydrogen bonding on the vibration frequencies is interesting. Passing from the chloride to bromide to iodide salts hydrogen bonding decreases and the $NH_3$ degenerate deformation, $NH_3$ rocking, and M–N stretching modes shift to lower frequencies, but the symmetric deformation shifts in the other direction.

Our frequency assignments are sometimes in disagreement with those reported previously. For instance, Mathieu and co-workers[11] report bands at 1595, 1240, 644, and 423 cm.$^{-1}$ in the spectra of the complex $[Zn(NH_3)_6]Cl_2$. While the first and third bands are in excellent agreement with our observations, the second and fourth bands are at *ca.* 100 cm.$^{-1}$ higher than ours and agree well with our frequencies for the complex $[Zn(NH_3)_4]Cl_2$ and those of Barrow, *et al.*,[5] for $[Zn(NH_3)_4]I_2$. The values of Mathieu and co-workers appear to be contradictory in that the $NH_3$ symmetric deformation and the Zn–N stretching bands correspond to the bands of the tetraammine complex whereas the $NH_3$ degenerate deformation and the $NH_3$ rocking bands correspond to those of the hexaammine complex. A similar disagreement exists over the frequencies of $[Cd(NH_3)_6]Cl_2$.

Blyholder and Vergez[15] observed an intense band at 400 cm.$^{-1}$ in the spectrum of $[Ni(NH_3)_6]Cl_2$ and assigned it to the M–N stretching mode. We could not observe any band, not even a weak one, in this region.

Shimanouchi, *et al.*,[10] assigned the 283 cm.$^{-1}$ band in $[Co(NH_3)_5Cl]Br_2$, which we have assigned to the Co–Cl stretching mode, as the N–Co–N, N–Co–Cl deformation. They assign the Co–Cl stretching mode, coupled out of phase with the axial Co–N stretching mode, to the band at 487 cm.$^{-1}$. They also assign the band in the spectrum of $[Co(NH_3)_5Br]Cl_2$ at the same frequency of 487 cm.$^{-1}$ to the out-of-phase coupled Co–Br stretching mode. It would be very surprising if the two vibrations had indeed the same frequency, and furthermore the values are very high compared to the metal–halogen stretching frequencies in other compounds. The assignment of Shimanouchi, *et al.*, has also been recently called into question by other authors.[16]

With regard to the lattice vibrations it is perhaps somewhat surprising that their frequency can rise as a result of deuteration, as with the compound $[Co(NH_3)_5Cl]Cl_2$, but this effect has been clearly observed outside the limits of experimental error. The hydrogen halides also show an increase in the frequency of the translational lattice modes upon deuteration.[17] On the other hand, the vibrational spectrum of the alkali halides shows a shift of the transverse optic modes toward higher frequencies upon lowering the temperature.[18] This shift is due to the contraction of the lattice.

It is well known that the distance between two atoms bound to hydrogen may either increase or decrease upon deuteration.[19] Thus, if the intermolecular distance in the hydrogen halides decreases, as expected,[19] the crystal lattice contracts and the translational lattice frequencies increase.

It seems possible to invoke the same effect to explain our observed shifts of the lattice frequencies of the metal-ammine complexes upon deuteration. In this case also the lattice vibrations appear to be of translational origin, as is shown by the magnitude of the shifts of these frequencies upon substitution of $Cl^-$ by $Br^-$ and by $I^-$. It appears, therefore, that upon deuteration the N–Cl distance decreases in $[Co(NH_3)_5Cl]Cl_2$, is practically unchanged in $[Co(NH_3)_6]Cl_3$, and increases in $[Ni(NH_3)_6]Cl_2$.

No other explanation has been offered for the shift to higher frequency of a lattice vibration as a result of deuteration.

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