[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Infrared Absorption Studies of Inorganic Coördination Complexes. XIII. Hexamminecobalt(II) Halides and Diamminemercury(II) Halides[1a,b]

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The infrared absorption spectra of Co(II) ammine halides have been measured, and the three characteristic deformation bands at approximately 1600, 1170 and 630 cm.$^{-1}$ have been observed. These bands have been assigned to the degenerate deformation, symmetric deformation and rocking vibrations of the NH_3 ligand, respectively, by the approximate calculation of the normal vibrations with a potential function of the Urey–Bradley type. Differences in the infrared frequencies between the Co(II) and Co(III) complexes are explained in terms of the force constants involved in each of these deformation vibrations. The normal vibration calculation of the $Hg(NH_3)_2^{++}$ ion is made as a nine-body problem.

Introduction

Hexammine complexes of Co(II) differ appreciably from those of Co(III). The halides of the former dissociate reversibly into the metal halide and ammonia; those of the latter dissociate irreversibly, only at higher temperatures, to give some free nitrogen and hydrogen halide.[2] The Co(II) complexes have a magnetic moment of 5.04 Bohr magnetons,[3a] indicating three unpaired electrons, with an "outer" orbital configuration, 4s4p^{3}4d^2. The Co(III) complexes are diamagnetic,[3b,4] and have an "inner" orbital configuration, 3d^{2}4s4p^3.

Infrared absorption studies have been reported on hexamminecobalt (III) salts, and the characteristic NH_3 deformation frequencies have been assigned.[5] A similar study of hexamminecobalt(II) chloride, bromide and iodide is reported in this paper, together with a comparison of the absorption frequencies of Co(II) and Co(III) ammine complexes. A nine-body treatment of the vibrations of the $Hg(NH_3)_2^{++}$ ion is also reported, giving an example of a more exact calculation of the normal vibrations of a simpler ammine complex.

Experimental

Preparation of Complexes.—The hexamminecobalt(II) halides were prepared, under air-free conditions, from ammoniacal solutions of the corresponding simple salts.[6,7] Prolonged cooling of the hexamminecobalt(II) iodide in a salt–ice-bath was necessary for appreciable crystallization. The salts $CoBr_2 \cdot 6H_2O$ and $CoI_2 \cdot 6H_2O$ were made from cobalt(II) carbonate and the appropriate halogen acid,[8] the hydriodic acid having been previously regenerated by treatment with hypophosphorous acid.[9]

The hexamminecobalt(III) halides were prepared in the following ways: the chloride, by air-oxidation of $CoCl_2$ in the presence of NH_4Cl, NH_3 and activated charcoal[10a]; the bromide, by oxidation of $CoBr_2$ by 30% H_2O_2 with added NH_4Br and NH_3;[10b] and the iodide, by treatment of $[Co(NH_3)_6]Cl_3$ with HI.[11] Analysis for cobalt was carried out by cathodic electrodeposition.[12] Diamminemercury(II) chloride and bromide were prepared by adding the simple salts to liquid ammonia, evaporating nearly to dryness, filtering and washing the product three times with absolute alcohol.[13]

Anal. Calcd. for $[Co(NH_3)_6]Cl_2$: Co, 25.40. Found: Co, 25.41. Calcd. for $[Co(NH_3)_6]Br_2$: Co, 18.35. Found: Co, 18.23. Calcd. for $[Co(NH_3)_6]I_2$: Co, 14.20. Found: Co, 13.85. Calcd. for $[Co(NH_3)_6]Cl_3$: Co, 22.05. Found: Co, 22.07. Calcd. for $[Co(NH_3)_6]Br_3$: Co, 14.73. Found: Co, 14.70. Calcd. for $[Co(NH_3)_6]I_3$: Co, 10.87. Found: Co, 10.85.

Absorption Measurements.—The infrared spectra were obtained by means of a model 21 Perkin–Elmer recording infrared spectrophotometer, with sodium chloride and cesium bromide prisms. The media employed were Nujol mulls and potassium bromide disks.[14]

Results

Table I lists the absorption frequencies of the hexamminecobalt(II) and (III) halides studied and the calculated deformation frequencies of $[Co(NH_3)_6]^{++}$ and $[Co(NH_3)_6]^{+++}$. Figure 1 shows the spectra of the hexamminecobalt(II) and hexamminecobalt(III) chlorides. The frequency values, relative intensities and profiles of the corresponding Co(II) and Co(III) bromides and iodides are almost identical with the chlorides.

In the regions near 3100 and 1600 cm.$^{-1}$, all complexes showed sharper absorption peaks with KBr disks than with Nujol mulls. However, in the spectra of the cobalt(II) complexes, absorption peaks at about 1400, 1250 and 820 cm.$^{-1}$ were ob-

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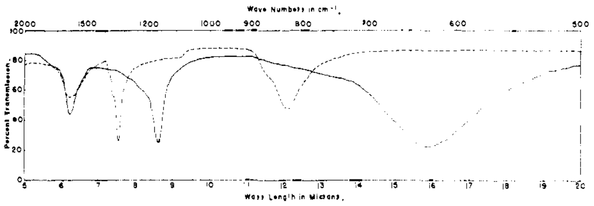

Fig. 1.—Infrared absorption spectra of hexamminecobalt(III) chloride and hexamminecobalt(II) chloride: - - - - -, hexamminecobalt(III) chloride $[Co(NH_3)_6]Cl_3$; ———, hexamminecobalt(II) chloride $[Co(NH_3)_6]Cl_2$.

served only when the KBr technique was employed. These peaks failed to appear in the spectra of these complexes in Nujol mulls or in KBr disks formed at a pressure of only two tons, indicating that these peaks are spurious and attributable to some undefined interaction with KBr at higher pressures.

TABLE I

INFRARED ABSORPTION FREQUENCIES IN CM.$^{-1}$ OF HEXAMMINECOBALT(II) AND (III) HALIDES IN SODIUM CHLORIDE AND CESIUM BROMIDE REGIONS

Co(II)	NH_3 Stretching	NH_3 Deg. def.	NH_3 Sym. def.	NH_3 Rocking	Co–N Stretching
$[Co(NH_3)_6]Cl_2$	3130	1605	1160	634	318
$[Co(NH_3)_6]Br_2$	3080	1590	1165	634	317
$[Co(NH_3)_6]I_2$	3220	1600	1190	622	308
Calculated	..	1579	1198	630	..
Co(III)					
$[Co(NH_3)_6]Cl_3$	3080	1600	1325	827	328
$[Co(NH_3)_6]Br_3$	3090	1590	1322	813	322
$[Co(NH_3)_6]I_3$	3080	1600	1325	808	320
Calculated	..	1579	1340	854	..

Discussion

The deformation frequencies of the coördinated NH_3 group in cobalt(II) ammines have been calculated by a method similar to that reported for the cobalt(III) ammines.[5a,d] The kinetic energy matrix G and the potential energy matrix F are set up according to Wilson's method.[15] Approximate calculations of the deformation frequencies of the NH_3 ligand have been made from the product of the corresponding diagonal terms, because the diagonal terms of the G-matrix containing the reciprocals of hydrogen mass are much greater than the cross terms containing the reciprocals of masses of heavier atoms. In this calculation a potential function of the Urey–Bradley type has been used,[16] which has the form

$$\bar{V} = \sum_{i} 1/2K_i(\Delta r_i)^2 + \sum_{ij} 1/2H_{ij}r_i^0r_j^0(\Delta\alpha_{ij})^2 + \sum_{ij} 1/2F_{ij}(\Delta q_{ij})^2 + \text{linear terms}$$

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, and K, H and F, stretching, bending and repulsive force constants.

Values of the force constants for Co(II) complexes are shown in Table II, together with those used in our previous calculation for Co(III) complexes.[5b] The calculated deformation frequencies are in good agreement with the observed values, as is shown in Table I. It is to be noted that two of these force constants, namely, H(HNH) and F(H· · ·H), used in previous calculations for NH_3, NH_4^+, ND_3 and ND_4^+, also work well in the case of the Co(II) and Co(III) ammine complexes.[5d]

TABLE II

FORCE CONSTANTS IN 10^5 DYNES/CM. AND INTRAMOLECULAR TENSION k IN 10^{-11} DYNES/CM. OF HEXAMMINECOBALT(II) AND (III) HALIDES

	Co(II)	Co(III)
H(HNH)	0.540	0.540
H(HNCo)	.094	.182
F(H...H)	.060	.060
F(H...Co)	0	.100
k	-0.040^a	$-.040^a$

[a] k is the intramolecular tension, which is introduced because of the redundancy condition connecting the internal coördinates (see T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949)).

A comparison of the NH_3 deformation frequencies of the Co(II) and Co(III) complexes shows that the difference in deformation frequencies is smallest in the degenerate vibration and greatest in the rocking motion. This is understandable if one considers the relationship between these vibrations and the force constants. The degenerate vibration is related to the bending force constant, H(HNH), and the repulsive force constant, F(H· · ·H), whereas the rocking motion is related to H(CoNH) and F(Co· · ·H). The symmetric deformation, on the other hand, is related to all four of these force constants. In other words, the potential function requires that the deformation frequency will change least in the degenerate vibration and most in the rocking motion, as is actually the case.

As shown above, the value of the force constants depends considerably upon the nature of the central metal atom of the complex. Hence it is not surprising that the frequencies of the deformation vibrations of $[Na(NH_3)_4]I$ appear at 1525, 1105 and 500 cm.$^{-1}$.[17]

The observation that the frequencies of the peaks in the 500–900 cm.$^{-1}$ region vary considerably with the nature of the central metal ion might lead one to conclude that these frequencies arise from the nitrogen-to-metal stretching motions, rather than to the NH_3 rocking vibrations. However, we conclude that our assignment is correct for the following reasons: (1) These bands are shifted greatly upon deuteration and, therefore, should arise from hydrogen vibrations. In the case of the Co(III) complexes, the calculated isotopic shifts have been shown to agree, within experimental errors, with the observed values.[5b,18] (2) The calculation of normal vibrations explained above shows that the rocking frequencies can change considerably with the nature of the central metal atom. (3) The coördinated NH_3 group should have three deformation frequencies, by an-

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alogy with the reported CH_3 deformation frequencies in methyl halides.[19] The assignment of the lowest frequency band to a metal-to-nitrogen stretching vibration would leave unassigned one deformation vibration. (4) Finally, if this observed low frequency band were to be assigned to the metal-to-nitrogen stretching frequency, the value of the calculated force constant for cobalt(III) ammines would be about 6×10^5 dynes/cm. However, this value is much greater than would be expected for a stretching frequency involving only a single bond.

In connection with the NH_3 deformation frequencies explained above, we are reporting a nine-body calculation of the vibrations of the $[Hg(NH_3)_2]^{++}$ ion, in order to show a more exact treatment of the vibrational problem of a metal ammine complex. In this complex ion, the N–Hg–N atoms lie on a straight line[20] and, therefore, regardless of the relative positions of internal rotations of the two NH_3 groups with respect to each other, a C_3 axis of symmetry is always present. For this symmetry, the vibrational frequencies are independent of the relative positions of the two NH_3 groups.[20] If free rotation of the two NH_3 groups occurs the point group is D'_{3h}.

We have calculated the normal vibrations of the $[Hg(NH_3)_2]^{++}$ ion using the same force constants as those reported in our calculation of the infinite chain of $[Hg(NH_2)]^{+}$.[21] Table III lists the result of the calculation, together with the experimental values. The agreement between the theoretical and experimental values is satisfactory. In the lower frequency region, we have calculated the Hg–N stretching frequencies and also the N–Hg–N deformation frequencies.

TABLE III

CALCULATED AND OBSERVED FREQUENCIES IN CM.$^{-1}$ OF $Hg(NH_3)_2^{++}$

Symmetry of vibration for $D'_{3}h$.	Type of vibration	Calcd. value	Obsd. values	
A_1	Hg–N stretching	493	$[Hg(NH_3)_2]Cl_2$	$[Hg(NH_3)_2]Br_2$
	NH_3 sym. def.	1281	I.R. inactive	I.R. inactive
$\overline{A}_2$	Hg–N stretching	533	513	499
	NH_3 sym. def.	1282	1268	1245
$\overline{E}$	NH_3 rocking	788		
	NH_3 deg. def.	1577	I.R. inactive	I.R. inactive
E	NH_3 rocking	791	719	697
	NH_3 deg. def.	1577	1605	1595
	N–Hg–N deformation	159	Outside the CsBr region	Outside the CsBr region

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Infrared Absorption Spectra of Inorganic Coördination Complexes. XIV. Infrared Studies of Some Metal Thiourea Complexes[1a]

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Infrared spectra of some metal thiourea complexes have been measured in the 2–35 μ region. The spectra reveal that thiourea forms sulfur-to-metal bonds in all complexes studied. The calculation of the normal vibrations of thiourea is reported. Based on the result of this calculation, the absorption bands observed in the metal thiourea complexes have been assigned.

Introduction

Stable Werner type coördination complexes formed from metal salts with 2, 4 or 6 moles of thiourea are known. However, the inner structures of these complex salts have not been determined.

Crystal structure investigations of thiourea have established the coplanarity of the C, N and S atoms in the molecule.[2] Kumler[3] interpreted the dipole moment of thiourea as indicating a resonance hybrid with 20–30% contribution of highly polar structures and concluded that the structure of thiourea is not essentially different from that of simple thioamides.

The present investigation was undertaken to assign the infrared absorption bands for metal thiourea complexes based on the normal vibration calculation of the thiourea molecule.

Previous studies of some metal–urea complexes[4] have shown that urea forms nitrogen-to-metal bonds with Pt(II) and Pd(II) and oxygen-to-metal bonds with Cr(III), Fe(III), Zn(II) and Cu(II). It is of interest to compare the manner in which urea and thiourea molecules coördinate with metal atoms.

Experimental

Preparation of Compounds.—Dichlorobis-(thiourea)-platinum(II), $[Pt(SC(NH_2)_2)_2Cl_2]$, prepared by the method of Kurnakow,[5] was dried *in vacuo* over phosphorus pentoxide.

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