The Vibrational Structure of Electronic Transitions for Some Complex Ions
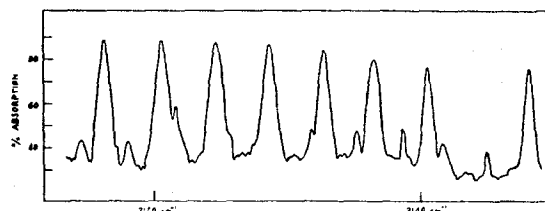
Melvin L. Schultz

The grating used was an echelette replica of 2887 lines per inch, ruled for the region 9 to 12 mu and employed in the second order. Readings of percent absorption were made at intervals of 5 seconds of arc, equivalent to about 0.13 cm^{-1}. The slit width was equivalent to 0.22 cm^{-1}.

Measurements are soon to be made on the overtone band and a complete report will be made at a later date.

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FOR several compounds of some of the transition elements, absorption spectra consisting of groups of approximately equidistant bands have been reported. The positions of the bands and the intervals between them depend only upon the metal ion and upon the identity of the complex of which the metal ion is a part. These spectra may be interpreted as originating in electronic transitions in which the vibrational structure characteristic of the complex ion present is resolved. The experimental basis for this interpretation is summarized in the following paragraphs.

Dreisch and Trommer[1] have found in dilute aqueous solutions of CoCl$_2$, CoBr$_2$ and CoI$_2$ an absorption band at 1.23μ consisting of six maxima with an average separation of 248 cm^{-1}. This band may be attributed to the Co(OH$_2$)$_6^{++}$ ion. In aqueous solutions of NiCl$_2$, NiSO$_4$ and Ni(NO$_3$)$_2$ they have found at 1.17μ a band characteristic of the Ni(OH$_2$)$_6^{++}$ ion. This band is resolved into four maxima with a separation of 264 cm^{-1}. In ammoniacal solutions of Ni(NH$_3$)$_6$Cl$_2$ the band is shifted to 0.940μ and the separation becomes 390 cm^{-1}, the number of maxima remaining the same. For solutions of a number of ferrous salts, Dreisch and Kallscheuer[2] have reported a series of twelve or thirteen bands extending from about 0.7μ to about 1.27μ. The intervals separating the five bands of highest frequency vary considerably from salt to salt. The separations of the next seven bands are approximately the same for all of the salts measured. This constant separation, 324 cm^{-1}, is then characteristic of the Fe(OH$_2$)$_6^{++}$ ion.

The absorption spectra, measured at liquid air temperatures, of solid hydrates of some of the above salts have been reported.[3] These spectra consist of many bands, from about 20 cm^{-1} to about 150 cm^{-1} in width, extending throughout the visible region. Analysis indicates that these spectra may, in part, be interpreted in the same manner as those from the solutions. With CoCl$_2 \cdot 6H_2O$, the average wave number difference for twelve pairs of bands is 226 cm^{-1}. With CoBr$_2 \cdot 6H_2O$, the difference for ten pairs of bands is 220 cm^{-1}. For NiCl$_2 \cdot 6H_2O$, the difference for nine pairs of bands is 237 cm^{-1}. For Co(OH$_2$)$_6^{++}$, in passing from solution to the crystal, there is a decrease of 25 cm^{-1} in the separation of the vibrational bands. For Ni(OH$_2$)$_6^{++}$, there is a corresponding decrease of 27 cm^{-1}.

The interpretation presented here is consistent with the information obtained from the Raman effect of amino complex ions.[4] Cu(NH$_3$)$_4^{++}$, Zn(NH$_3$)$_6^{++}$, and Cd(NH$_3$)$_6^{++}$ give Raman displacements of the same order of magnitude as the separations of the vibrational levels of Ni(NH$_3$)$_6^{++}$ and the aquo complexes (see Table I). If one makes the

TABLE I.

Complex ion	Vibration frequency cm^{-1}	Force constant dynes/cm
Cu(NH$_3$)$_4^{++}$ (solution)	415 (Raman)	1.16 × 10^5
Cd(NH$_3$)$_6^{++}$ (solution)	340 (Raman)	0.85
Zn(NH$_3$)$_6^{++}$ (solution)	423 (Raman)	1.22
Ni(NH$_3$)$_6^{++}$ (solution)	390 (Absorption)	1.01
Ni(OH$_2$)$_6^{++}$ (solution)	264 (Absorption)	0.52
Ni(OH$_2$)$_6^{++}$ (crystal)	237 (Absorption)	0.42
Co(OH$_2$)$_6^{++}$ (solution)	248 (Absorption)	0.46
Co(OH$_2$)$_6^{++}$ (crystal)	223 (Absorption)	0.37
Fe(OH$_2$)$_6^{++}$ (solution)	324 (Absorption)	0.77

approximation that the vibration of the complex ion may be represented by a simple harmonic oscillator, the force constant of the bond between the central metal ion and the coordinated group may be estimated from the vibration frequency. The values so obtained are listed in the table.

Some evidence for anharmonicity is obtained from a series of five bands for solid CoCl$_2 \cdot 6H_2O$.[3] The wave numbers of these bands may be represented with an accuracy of one wave number by:

$$\nu = 24504 + 222n - 1.6n^2 \quad (n = 0, \cdots, 4).$$

From the constants of this equation, the heat of dissociation of Co(OH$_2$)$_6^{++}$ in crystals of CoCl$_2 \cdot 6H_2O$ is estimated to be 22,000 cal. The heat of the reaction:

$$CoX_2 \cdot 6H_2O(s) \rightarrow CoX_2(s) + 6H_2O(l)$$
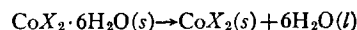
determined from thermochemical data (I.C.T.) is 21,300 cal. for $X = $ Cl, 19,800 cal. for $X = $ Br, and 16,700 cal. for $X = $ NO$_3$. The decrease in the thermochemical value for the bromide as compared with the chloride parallels the decrease in the average separations of the vibrational levels, 226 cm^{-1} for the chloride as compared with 220 cm^{-1} for the bromide. The nitrate has not yet been studied spectroscopically.

[1] Th. Dreisch and W. Trommer, Zeits. f. physik. Chemie B37, 37 (1937).
[2] Th. Dreisch and O. Kallscheuer, Zeits. f. physik. Chemie B45, 19 (1939).
[3] Gieleszen, Ann. d. Physik [5] 22, 537 (1935).
[4] I. Damaschun, Zeits. f. physik. Chemie B16, 81 (1932).