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Infrared Spectra of Metallic Complexes. I. The Effect of Coördination on the Infrared Spectra of Ammine, Rhodanato and Azido Complexes

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The effect of coördination on the infrared spectra of ammine, rhodanato and azido complexes has been studied, considering the effect of the outer-ions. It has been noticed that the shift of the rocking vibration of coördinated ammonia in ammine complexes gives a measure of these effects. The CN and NN stretching frequencies of the rhodanato and azido groups, respectively, have been compared in Cr^{3+} and Co^{3+} complexes, and the results correlated to their stabilities.

Introduction

Studies of infrared spectra of the ligands in metallic complexes have provided useful information on the nature of the metal–ligand bond and the stability of the complex. For example, Sen, *et al.*,[1] have found that, in bis-(glycino)-copper complex, the metal–oxygen bond is essentially ionic, whereas the metal–nitrogen bond is covalent. Bellamy and Branch[2] have found a linear relation between the stability constants and the carbonyl stretching frequencies of a number of metal–salicylaldehydes. More recently, Svatos, *et al.*,[3] have shown that the effects of coördination, hydrogen bonding, configuration of the complex and the solvent result in a decrease in the N–H stretching frequencies.

Among these factors, the effect of coördination is chemically most interesting since it depends upon the strength of the metal–ligand bond. In order to examine the effect of coördination in the crystalline state, the effect of the outer-ions must be considered. Moreover, coördination affects not only the stretching vibration but also the bending modes of the ligands. In the present paper, the effects of coördination on the infrared absorption of the ligands such as ammonia, rhodanato and azido ions have been studied, taking the effect of outer-ions into consideration.

Experimental

Preparation.—The compounds used in this investigation were prepared by the usual methods.[4]

Absorption Measurements.—The infrared spectra were obtained by a Hilger H800 double beam infrared spectrometer using a sodium chloride prism. The Nujol mull technique was employed.

Results and Discussion

I. **Ammine Complexes.**—In ammine complexes, coördination occurs between the metal and the nitrogen atom of ammonia, but the vibrations of ammonia in ammine complex ions are perturbed not only by coördination but also by the outer-ion. Table I gives the frequencies of the absorption bands of $[Co(NH_3)_6]X_3$ ($X = ClO_4^-, NO_3^-, I^-, Br^-, Cl^-$). It is well known that the perchlorate ion has no tendency to form a hydrogen bond of the N–H. . . . . .X type; therefore, the observed shift of N–H stretching frequencies of the perchlorate compared with those of free ammonia must be largely due to the effect of coördination.

TABLE I

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

$[Co(NH_3)_6]X_3$, X =	N–H str.	De-gen. bend.	Sym. de-form.	Rock-ing
Cl^-	*ca.* 3070[a]	1603	1325	818
Br^-	*ca.* 3120[a]	1578	1318	797
I^-	*ca.* 3150[a]	1590	1323	792
NO_3^-	3290, 3200	1618	. .[b]	. .[b]
ClO_4^-	3320, 3240	1630	1352	803
$[Cr(NH_3)_6](ClO_4)_3$	3330, 3280	1622	1334	718
$[Ni(NH_3)_6](ClO_4)_2$	3397, (3312)	1618	1236	(620)
NH_4^+	3138, 3041	1710	1403	. .
NH_3	3414, 3336	1628	950	. .

[a] Broad band. [b] Hidden by the absorption of NO_3^- ion.

The other salts give lower N–H stretching frequencies than the perchlorate, showing the presence of the effect of hydrogen bonding.[5] Although X-ray data are not available for these salts, the N–H. . . . . Cl distance in *trans*-$[Co\ en_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ is known to be 2.91 Å.[6], which is fairly short for this type of hydrogen bonding. It is expected that the N–H. . . . .X distance decreases in the order of I^-, Br^- and Cl^- salts, resulting in a decrease of the N–H stretching frequencies. However, the broadness of the bands in these salts makes it difficult to compare the shifts quantitatively.

Besides the N–H stretching modes, all the ammine complexes show three bands at *ca.* 1600, 1320 and 800 cm.$^{-1}$ which were recently assigned by Mizushima, *et al.*,[7] to degenerate deformation, symmetric deformation and rocking vibration of the coördinated ammonia, respectively. As is shown in Table I, the band near 800 cm.$^{-1}$ is most sensitive to the kind of outer-ions present, shifting progressively to higher frequency in the order of I^-, Br^- and Cl^- salts. Hill and Rosenberg[8] also found the same trend for many pentammine complexes. Although Hill and Rosenberg and the present authors[9] attributed this band to the skeletal vibration of the octahedral complex, the present result is more consistent with the assignment of Mizushima, *et al.*, since the rocking vibration

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[1] D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 211 (1955).

[2] L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).

[3] G. F. Svatos, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 6159 (1955).

[4] For example, see J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, Vol. II (1946).

[5] K. Nakamoto, M. Margoshes and R. E. Rundle, THIS JOURNAL, **77**, 6480 (1955).

[6] A. Nakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **25**, 331 (1952).

[7] S. Mizushima, I. Nakagawa and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

[8] D. G. Hill and A. F. Rosenberg, *ibid.*, **22**, 148 (1954).

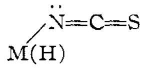
[9] M. Kobayashi and J. Fujita, *ibid.*, **23**, 1354 (1955).

should be expected to go to higher frequency as the hydrogen bonding becomes stronger. Thus, from the observation of the rocking mode, we conclude that the hydrogen bond between the N-H bond and the outer-ion becomes stronger in the order of I^-, Br^- and Cl^- salts. Although the rocking vibration of the NO_3 salt is overlapped by the NO_3^- absorption, the N-H stretching frequencies suggest that the strength of the hydrogen bond in this salt is between the perchlorate and the iodide ion.

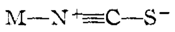
In Table I, frequencies of the N—H vibrations of $[M(NH_3)_6](ClO_4)_{3,2}$ (M = Co^{3+}, Cr^{3+} and Ni^{2+}) are compared with those of NH_3 and NH_4^+ ion. It is clear that the N-H stretching vibrations are shifted to lower frequency in the order of NH_3, $[Ni(NH_3)_6]^{2+}$, $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$ and NH_4^+ ion. As stated before, the effect of hydrogen bonding is negligibly small for the perchlorates. Therefore we conclude that the effect of coördination or the strength of the M-N bond increases in the above order. This result is in good accord with the stabilities of these complex ions.

On the other hand, the three bending modes are shifted to higher frequency in the order of Ni^{2+}, Cr^{3+} and Co^{3+} complexes. The rocking mode near 800 cm.$^{-1}$ shows a most remarkable shift among the three bending modes. It is anticipated theoretically[10] that an increase of the strength of the M-N bond results in an increase of the bending force constants, especially that of the rocking mode. Thus the N-H stretching as well as the NH_3 rocking mode leads us to the conclusion that the effect of coördination increases in the order of Ni^{2+}, Cr^{3+} and Co^{3+} salts.

II. Rhodanato Complexes.—According to the structural analysis, the N-C distance in HNCS molecule (1.22 Å.)[11] is longer than that of the rhodanato groups in $NH_4[Cr(NH_3)_2(NCS)_4]\cdot H_2O$ (1.14 Å.),[12] whereas the C-S distance in the former (1.56 Å.) is shorter than that of the latter (1.80 Å.). Moreover the HNCS molecule is bent (<HNC = 136°) while the Cr-N-C-S bond in the complex is linear. These facts suggest that the electronic structures of the rhodanato groups in the two compounds may be expressed by the following formulas, respectively.



a



$M—N^+≡C—S^-$

b

Conforming to the expectation from the above structures, the CN stretching frequencies of the rhodanato complexes are generally higher than that of HNCS molecule, as is shown in Table II.

It is expected that the M-N bond of (b) is more ionic than that of (a), since the nitrogen in (b) (sp hybridization) is more electronegative than that of (a) (sp^2 hybridization). An increase in the CN stretching frequency of the rhodanato complexes therefore can be interpreted as an increase in ionic character of an M-N bond. Table II indicates that the Co^{3+} complexes always show higher frequencies than the corresponding Cr^{3+} complexes, and we conclude that the M-N bond of the former is more ionic than that of the latter. This result agrees with the chemical fact that Co^{3+} complexes which coördinate more than two rhodanato groups are not known, whereas the Cr^{3+} rhodanato complexes are abundant.

TABLE II

THE CN STRETCHING FREQUENCIES OF RHODANATO COMPLEXES

Compound	ν (cm.$^{-1}$)
$[Cr(NH_3)_5NCS](NO_3)_2$	2084
$[Co(NH_3)_5NCS](NO_3)_2$	2114
trans-$[Cr\ en_2(NCS)_2]Cl\cdot H_2O$	2088
trans-$[Co\ en_2(NCS)_2]Cl\cdot H_2O$	2122
$M[Cr(NH_3)_2(NCS)_4]$	
M = cholin^{+a}	2083 (sharp)
NH_4^+	2050 ~ 2120 (broad)
Ba^{2+}	2000 ~ 2130 (broad)
Hg^{2+}	2073 ~ 2098, 2160
$[Co(NH_3)_4NO_2NCS]X$	
X = Cl^-	2115
$Cl^-\cdot AgNO_3$	2183
$Cl^-\cdot HgCl_2$	2179
HNCS^b	1963

^{a} $(CH_3)_3N^+CH_2CH_2OH$. ^{b} G. Herzberg and C. Reid, *Disc. Faraday Soc.*, 9, 92 (1950).

It is apparent that the interaction between the sulfur atom of the coördinated rhodanato group and the outer-ion is also favorable to the (b) structure. The outer-ions such as Hg^{2+} and Ag^+, which have a strong tendency to cause interaction with sulfur, therefore shift the CN stretching vibration further to a higher frequency. As is shown in Table II, the CN stretching frequency of $[Co(NH_3)_4NO_2NCS]Cl$ is lower than those of the corresponding $Cl^-\cdot AgNO_3$ and $Cl^-\cdot HgCl_2$ salts.

The complexes of $M[Cr(NH_3)_2(NCS)_4]$ type are expected to yield more complicated spectra, since the stoichiometric ratio of NCS^- and M^+ is not 1 : 1 and some of the rhodanato groups will probably be free from the interaction with the outer-ions. The NH_4^+ and Ba^{2+} salts give broad bands near 2080 cm.$^{-1}$ which may be a superposition of the CN stretching bands of bonded and free rhodanato groups. It is interesting to note that the cholin's salt gives a sharp band at 2083 cm.$^{-1}$. This fact may be due to the following reason; in cholin's ion, the effective charge is small because the positive charge on the central nitrogen atom is screened by the bulky aliphatic groups. Thus the interaction between the rhodanato groups and the cholin's ion is negligibly small. The Hg^{2+} salt which has a strong tendency to form the Hg-S bond shows an additional band at 2160 cm.$^{-1}$, well separated from the band at 2098 ~ 2073 cm.$^{-1}$. From the above discussion, it is reasonable to assign the former band to the rhodanato group bonded with Hg^{2+} ion, and the latter to the rhodanato groups free from such an interaction.

III. Azido Complexes.—It is well known that the structure of the azido group is symmetrical in ionic crystals such as NH_4N_3 (a), while it is anti-

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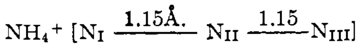
[10] I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 589 (1955).

[11] C. I. Beard and B. P. Dailey, *J. Chem. Phys.*, **18**, 1437 (1950).

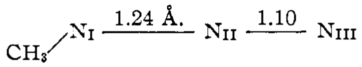
[12] Y. Saito and Y. Takeuchi, presented before the symposium of metallic complexes, October 29, 1955, Osaka, Japan.

symmetrical in molecular crystals such as CH_3N_3 **(b).**[13]



$$NH_4^+ [N_I \overset{1.15\text{Å.}}{\text{——}} N_{II} \overset{1.15}{\text{——}} N_{III}]$$

a



b

Thus one expects that the asymmetrical N_3 stretching frequency is higher in covalent molecules than in ionic crystals, since the N_{II}–N_{III} distance of the former is shorter. As is shown in Table III, the observed results are in good accord with the above expectation.

The asymmetrical N_3 stretching frequencies of Cr^{3+} and Co^{3+} azido complexes are also given in Table III. The Cr^{3+} complexes always show higher frequencies than the corresponding Co^{3+} complexes. This fact suggests that the M–N bond of the latter is more ionic than that of the former and agrees with the observation that the aqueous solution of the Co^{3+} azido complex is more easily aquotized than that of the corresponding Cr^{3+} complex.

TABLE III

THE NN STRETCHING FREQUENCIES OF AZIDO COMPOUNDS (CM.$^{-1}$)

	Asym. str.
NH_4N_3[a]	2050(solid)
	2030(solid)
HN_3[b]	2140(gas)
	2169(solid)
CH_3N_3[c]	2143(gas)
$[Cr(NH_3)_5N_3]I_2$	2094
$[Co(NH_3)_5N_3]I_2$	2047
$[Cr(NH_3)_3(N_3)_3]$	2072
$[Co(NH_3)_3(N_3)_3]$	2017

[a] D. A. Dows, E. Whittle and C. C. Pimental, *J. Chem. Phys.*, **23**, 1475 (1955). [b] D. A. Dows and C. C. Pimental, *ibid.*, **23**, 1258 (1955). [c] E. H. Eyster and R. H. Gillet, *ibid.*, **8**, 369 (1940).

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(13) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 200.

[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

High Temperature Reaction Kinetics of the System H_2–HI–I_2[1]

BY WENDELL M. GRAVEN[2]

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An investigation of the kinetics of the reactions which comprise the equilibrium 2HI = $H_2 + I_2$ has been conducted within the temperature interval of 600–775°. With the use of a flow system both forward and reverse reactions have been examined under conditions such that the extent of reaction ranged from 3 to 95% of its equilibrium value. Five to 24-fold variations in the reactant and product concentrations have provided kinetic information in substantial agreement with extrapolations of data obtained at lower temperatures. The following second-order rate constants have been calculated for decomposition of hydrogen iodide and combination of hydrogen and iodine, respectively, $k_1 = 3.59 \times 10^{12} \exp(-49200/RT)$ and $k_2 = 1.23 \times 10^{12} \exp(-41000/RT)$ l. mole^{-1} sec.$^{-1}$.

Introduction

Bodenstein's investigation of the hydrogen iodide synthesis and decomposition[3a–d] was the first comprehensive study of the kinetics of gaseous processes. This system has remained the best example of bimolecular gas phase reactions, having withstood tests of the influence of moisture,[4,5] glass surface[6] and extended concentration range.[7] It has been re-examined in conjunction with studies of the analogous reactions of deuterium iodide.[8–12]

Lewis, in his introduction to the collision theory of reaction rates,[13] noted that at high temperature the normally bimolecular hydrogen iodide decomposition could be superseded by a unimolecular process. His choice of a unimolecular rate constant with an activation energy of 66 kcal. led him to predict that in the neighborhood of 1200°K. the observed reaction rate expression would be no longer exactly second order in hydrogen iodide.

Recently, Benson[14] has revived the hypothesis that at high temperature the reactions are more complex. His calculations lead him to postulate that above 600°K. free radical processes contribute, and above 900°K. predominate in the over-all synthesis of hydrogen iodide.

In view of the above conclusions it becomes worthwhile to report the results of an examination of these reactions within the temperature interval of 600–775°.

The purpose of this investigation was to examine the kinetics of the decomposition and synthesis of hydrogen iodide at as high a temperature as possible

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[1] This research was supported in whole or in part by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

[2] University of Oregon, Eugene, Oregon.

[3] (a) M. Bodenstein, *Ber.*, **26**, 2603 (1893); (b) *Z. physik. Chem.*, **13**, 56 (1894); (c) **22**, 1 (1897); (d) **29**, 295 (1899).

[4] B. Lewis and E. Rideal, THIS JOURNAL, **48**, 2553 (1926).

[5] M. Bodenstein and W. Jost, *ibid.*, **49**, 1416 (1927).

[6] H. A. Taylor, *J. Phys. Chem.*, **28**, 984 (1924).

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[11] A. Taylor and R. Crist, THIS JOURNAL, **63**, 1377 (1941).

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[14] S. Benson and R. Srinivasan, *J. Chem. Phys.*, **23**, 200 (1955).