tion of K_{11} from $\bar{\epsilon}_1$ than what the wave lengths 370–400 mμ offered.

Acknowledgment.—This work was supported by the United States Atomic Energy Commission through contract AT(11-1)-687.

DEPARTMENT OF CHEMISTRY
OHIO UNIVERSITY
ATHENS, OHIO
JAMES YINGPEH TONG

RECEIVED JULY 6, 1964

Infrared Spectra and Force Constants of Ammine Complexes

Sir:

Watt and Klett suggested that the nature of Co–N stretching and deformation modes of cobalt–ammine complex ions remains to be resolved.[1] Recently we have extensively measured the far-infrared spectra down to 80 cm.$^{-1}$ for various metal–ammine complexes. We have made a normal coordinate analysis of the infrared-active species where the vibrations in the NH_3 ligand as well as those for the skeletal part are taken into consideration and obtained the force constants associated with the metal–ligand bonds and those for the ligand vibration.[2]

The results are summarized in Table I. With regard to $[Co(NH_3)_6]^{3+}$ we reported three bands, at 503, 492(?), and 464 cm.$^{-1}$, in the region from 500 to 450 cm.$^{-1}$ in the previous paper.[3] However, it was found that the band at 464 cm.$^{-1}$ is due to the stray light and is not a real band.[4] The band at 503 cm.$^{-1}$ is definitely a real one, although it is very weak.[4] The metal–nitrogen stretching bands for Co(III), Pt(II), and Pd(II) are very weak, that for Cr(III) moderately weak, that for Cu(II) medium, and those for Ni(II) and Co(II) fairly strong. The values of the metal–nitrogen force constants vary in the order Pt(II) > Pd(II) > Co(III) > Cr(III) > Cu(II) > Ni(II) > Co(II). The intensity for the metal–nitrogen stretching vibrations increases as the value of the force constants decreases. This trend is plausible, because the ionic character of the metal–nitrogen bond seems to increase as the force constant decreases, causing a larger transition moment ($\partial\mu/\partial r$).

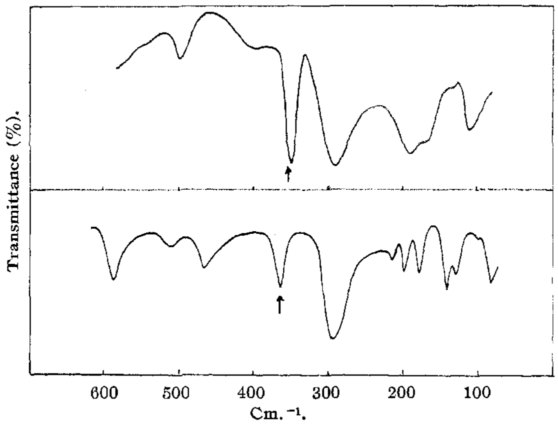

Fig. 1.—The far-infrared spectra of *trans*-$[CoCl_2(NH_3)_4]Cl$ (upper curve) and *trans*-$[CoCl_2(en)_2]Br$ (lower curve).

TABLE I
OBSERVED AND CALCULATED FREQUENCIES (CM.$^{-1}$) OF METAL–AMMINE COMPLEX IONS

		ν_1 $\nu(NH)_a$	ν_2 $\nu(NH)_s$	ν_3 $\delta(NH_3)_d$	ν_4 $\delta(NH_3)_s$	ν_5 $\delta(NH_3)_r$	ν_6 $\nu(MN)$	ν_7 $\delta(NMN)$	$K(MN)$, mdynes/Å.	$H(HNM)$, mdynes/Å.
$[Pt(NH_3)_4]Cl_2$	Calcd. E_u	3231	3155	1619	1344	846	509	295	1.92	0.180
	Obsd.	3236	3156	1563	1325	842	510	297		
$[Pd(NH_3)_4]Cl_2$	Calcd. E_u	3240	3164	1613	1304	774	493	296	1.71	0.150
	Obsd.	3268	3142	1601	1285	797	491	295		
$[Co(NH_3)_6]Cl_3$	Calcd. F_{1u}	3240	3164	1615	1323	830	501	328	1.05	0.169
	Obsd.	3240	3170	~1600	1325	820	503	325		
$[Co(ND_3)_6]Cl_3$	Calcd. F_{1u}	2396	2265	1165	1009	661	454	291	1.05	0.169
	Obsd.	2450		1155	1016	665	...	310		
$[Cr(NH_3)_6]Cl_3$	Calcd. F_{1u}	3268	3191	1612	1292	759	474	267	0.94	0.123
	Obsd.	3260	3205 (3140)	1600	1310	745	470	...		
$[Cu(NH_3)_4]SO_4$	Calcd. E_u	3310	3231	1610	1251	708	419	249	0.84	0.107
	Obsd.	3270		1610	$\left\{\begin{matrix}1270\\1240\end{matrix}\right\}$	713	420	~250		
$[Ni(NH_3)_6]Cl_2$	Calcd. F_{1u}	3393	3310	1606	1197	672	335	214	0.34	0.095
	Obsd.	3370 b		1610	1175	678	330	~215		
$[Co(NH_3)_6]Cl_2$	Calcd. F_{1u}	3338	3258	1605	1171	625	323	184	0.33	0.065
	Obsd.	3330	3250	1605	1160	634	318	...		

We have made the calculation of the normal modes of vibration (the elements of the L-matrix) and the per cent potential energy distributions among the symmetry coordinates (PED, the diagonal elements of the matrix $LFL\Lambda^{-1}$, $F_{ii}L_{i\lambda}^2/\lambda$). The results for the $[Co(NH_3)_6]^{3+}$ ion are given in Table II as an example.

---

[1] G. W. Watt and D. S. Klett, *Inorg. Chem.*, **3**, 782 (1964).

[2] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, to be published; J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *ibid.*, to be published.

[3] T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).

[4] In $[CoX(NH_3)_5]^{2+}$ and *trans*-$[CoX_2(NH_3)_4]^+$ ions, where one or two NH_3 ligands are substituted by halogens, the bands observed in the region 500–450 cm.$^{-1}$ enhance their intensities, and these bands are primarily assigned to metal–ligand stretching vibrations.[2,3] For $[Co(NH_3)_6]Br_3$ we have made very careful measurements using two different instruments and we could not regard the band at 464 cm.$^{-1}$ as a real band.

The results for the other metals are more or less alike, but these are not given to save space. Table II shows that the ligand vibrations (NH_3 stretching and deformation vibrations) are pure vibrational modes corresponding to the symmetry coordinates. The Co–N stretching and NCoN deformation modes (ν_6 and ν_7) are coupled with each other moderately but they are not coupled with the ligand vibrations. When we look at the results of Table I, NH_3 rocking frequencies change considerably with metal ions. This arises mainly from the change of the angle deformation force constants H(HNM), which are also listed in Table I, but not from the coupling of NH_3 rocking and M–N stretching modes.

TABLE II

PER CENT POTENTIAL ENERGY DISTRIBUTIONS (PED) FOR $[Co(NH_3)_6]^{3+}$ (F_{1u} SPECIES)[a]

Symmetry coordinates	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
S_1 NH_3 asym. str.	100						
S_2 NH_3 sym. str.		100		1−			
S_3 NH_3 deg. def.			94+		5−		
S_4 NH_3 sym. def.				100+			
S_5 NH_3 rocking			3+		90+	5−	2+
S_6 M–N str.					1+	71+	28+
S_7 NMN def.					7−	29−	64+

[a] Only the relative signs for the L-matrix are given.

With regard to the Co–X stretching mode of the halogenoammine complexes, we should revise our previous assignment, as Watt and Klett pointed out. The far-infrared spectrum of $[CoCl_2(NH_3)_4]^+$ is shown in Fig. 1, compared with $[CoCl_2(en)_2]^+$. By this comparison we can reasonably assign the sharp band at 353 cm.$^{-1}$ to the Co–Cl stretching mode. The observed and calculated frequencies are shown in Table III. The broad strong band at 290 cm.$^{-1}$ of similar feature to the 325 cm.$^{-1}$ band of $[Co(NH_3)_6]^{3+}$ is assigned to NCoN deformation vibration of E_u species. The calculated value of this vibration by using the same value of the force constant H(NMN) is in good agreement with the observed value. In $[CoCl_2(en)_2]^+$, the broad band near 290 cm.$^{-1}$ is assigned to the skeletal deformation mode similar to that for $[CoCl_2(NH_3)_4]^+$, which is also supported by a normal coordinate analysis.[5] If we assign the 290 cm.$^{-1}$ band to a Co–Cl stretching mode, we should assign the 353 cm.$^{-1}$ band to a NCoN deformation mode. This is unreasonable, because the band feature is quite different from the NCoN vibration band for $[Co(NH_3)_6]^{3+}$, and also the observed frequency deviates from the calculated one. K(Co–N) is assumed to be the same as in $[Co(NH_3)_6]^{3+}$ and K(Co–Cl) is calculated to be .00 mdyne/1Å. A normal coordinate analysis has also been done for $[CoX(NH_3)_5]^{2+}$. For $[CoCl(NH_3)_5]^{2+}$, the 457 cm.$^{-1}$ band is assigned to the antiphase (Co–N, Co–Cl) stretching mode of A_1 species and the doublet (487 and 479 cm.$^{-1}$) is assigned to the Co–N stretching mode of E species.

TABLE III

OBSERVED AND CALCULATED FREQUENCIES OF $[CoCl_2(NH_3)_4]^+$

$[D_{4h}]$		Calcd.	Obsd.	Vib. mode
A_{2u}	ν_1	3239	3253	$\nu(NH)_a$
	ν_2	1616	1585	$\delta(NH_3)_d$
	ν_3	829	815	$\delta(NH_3)_r$
	ν_4	347	353	ν(MX)
	ν_5	186	186	δ(NMX)
E_u	ν_6	3240	3252	$\nu(NH)_a$
	ν_7	3164	3161	$\nu(NH)_s$
	ν_8	1617	1585	$\delta(NH_3)_d$
	ν_9	1339	1300	$\delta(NH_3)_s$
	ν_{10}	833	815	$\delta(NH_3)_r$
	ν_{11}	485	501	ν(MN)
	ν_{12}	311	290	δ(NMN)
	ν_{13}	127	(167)	δ(NMX)

---

(5) I. Nakagawa and T. Shimanouchi, to be published (Eighth International Conference on Coordination Chemistry, Vienna, 1964).

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF TOKYO
HONOGO, TOKYO, JAPAN

TAKEHIKO SHIMANOUCHI
ICHIRO NAKAGAWA

RECEIVED JULY 9, 1964

Book Review

Organoboron Chemistry. Volume 1. Boron–Oxygen and Boron–Sulfur Compounds. By HOWARD STEINBERG. Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y. 1964. xxxii + 950 pp. 16 × 23.5 cm. Price, $33.

This book, which is one of three volumes planned by Dr. Steinberg, deals with organic compounds having boron–oxygen and boron–sulfur linkages. The next two volumes will deal with boron–nitrogen, boron–phosphorus, and boron–carbon compounds. The arrangement of material follows a detailed outline; the same outline is given in the Table of Contents (which alone encompasses 24 pages!). The research results reported in over a thousand publications are mentioned. There are 21 chapters and each is ended with a list of references and of compounds (including what physical properties are available). For example, Chapter 15, which deals with "Coordination Compounds Derived from Polyhydric Alcohols and Phenols," has about 55 pages of text, 45 pages of tables, and 169 references.

This book clearly demonstrates the large amount of available qualitative data on boron–oxygen compounds containing organic groups. Unfortunately the available amount of quantitative data, such as structures, rates, and equilibrium constants, lags far behind. The material in Chapter 21 ("Hydrolytic Stability") exemplifies the type of data that we need more of.

The author has done a monumental (and, I believe, successful) job in bringing together the data on these compounds into one volume, and the resulting encyclopedic nature is useful to those interested in this field. Nevertheless, the strengths of the book are also the weaknesses; for example, several types of synthetic methods for the preparation of a class of compounds are listed, yet rarely does the reader get any feel for the preferred method.