the great activation energy barriers are overcome. The possibility that an argon–oxygen compound could also be formed without recourse to the fluorides cannot be ruled out, and from the foregoing one can conclude that species like $HArO_4^-$ and ArO_4 have a fair chance of being about as stable as, respectively, the known $HXeO_4^-$ ion and xenon tetroxide (XeO_4).[16]

(16) H. Selig, H. H. Claassen, C. L. Chernick, J. G. Malm, and J. L. Huston, *Science*, **143**, 1322 (1964).

CHEMISTRY DEPARTMENT
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA
RICARDO FERREIRA

RECEIVED JULY 27, 1964

Chromium(VI) Species and Spectra in Acidic Solutions

Sir:

The first dissociation equilibrium quotient of H_2CrO_4, K_{11}, was first determined[1] from the apparent absorptivities[2] ($\tilde{\epsilon}_1$) of monomeric Cr(VI), determined at different hydrogen ion concentrations, (H^+), in the investigation of dimerization of Cr(VI) in acidic solutions.

$$K_{11} = (HCrO_4^-)(H^+)/(H_2CrO_4) \qquad (1)$$

$$\tilde{\epsilon}_1 = \frac{\epsilon_{11}(HCrO_4^-) + \epsilon_{12}(H_2CrO_4)}{(HCrO_4^-) + (H_2CrO_4)} = [\epsilon_{11}K_{11} + \epsilon_{12}(H^+)]/[K_{11} + (H^+)] \qquad (2)$$

where ϵ_{11} and ϵ_{12} are the molar absorptivities of $HCrO_4^-$ and H_2CrO_4, respectively. Since the ratios $\tilde{\epsilon}_1/\epsilon_{11}$ at 25.0° in 1 M $HClO_4$, the most acidic solutions used, were only 0.922, 0.915, 0.909, and 0.911 at wave lengths 370, 380, 390, and 400 mμ, respectively, K_{11} was not determined with great precision. It was found that with the K_{11} value of 1.21 moles l.$^{-1}$ determined in this manner, it was necessary to postulate the existence of $HCr_2O_7^-$ in order to account for the dependence of the gross dimerization quotient, K', on (H^+), where

$$K' = (\text{total dimers})/(\text{total monomers})^2 \qquad (3)$$

The apparent absorptivities of dimeric Cr(VI), $\tilde{\epsilon}_2$, which were determined with less accuracy than $\tilde{\epsilon}_1$, did not show sufficient change with (H^+) to offer spectral evidence at these wave lengths for the existence of $HCr_2O_7^-$.

There is an alternate interpretation of the earlier data. If one assumes that in solutions of (H^+) 1 M or less, the only dimer present was $Cr_2O_7^{2-}$, one can calculate K_{11} from K', (H^+), and K_d since

$$K_{11} = (H^+)/[(K_d/K')^{1/2} - 1] \qquad (4)$$

where

$$K_d = (Cr_2O_7^{2-})/(HCrO_4^-)^2 \qquad (5)$$

The K_{11} values at 25.0° in solutions of unit ionic strength calculated using $K_d = 98$ are given in Table I.

TABLE I

K_{11} CALCULATED FROM K' WITH EQ. 4 AND K_d = 98

(H^+), M	Av. K'	K_{11}
0.277	86	4.10
0.416	81	4.16
0.693	72	4.16
1.000	64	4.21

The average K_{11} is 4.16 (standard deviation σ = 0.05). Since at the same (H^+), the ratio $(K_d/K')^{1/2}$ differs from unity more than the ratios $\tilde{\epsilon}_1/\epsilon_{11}$ do, the calculation of K_{11} from K' is probably much more reliable than that from $\tilde{\epsilon}_1$ if the assumption made concerning the dimeric Cr(VI) species is valid. Until other experimental evidence shows otherwise, this interpretation is as good as, if not better than, our previous one. The values of ϵ_{12} calculated from $\tilde{\epsilon}_1$ using the new value of K_{11} are 589 (σ = 76), 405 (σ = 43), 250 (σ = 22), and 155 (σ = 18) M^{-1} cm.$^{-1}$ at 370, 380, 390, and 400 mμ, respectively.

Recently Haight, *et al.*,[3] reported a value for K_{11} of 6.5 at 25° and unit ionic strength calculated from $\tilde{\epsilon}$ at wave lengths of 260 and 350 mμ. They used a Cr(VI) concentration of 4×10^{-4} g.-atom/l. and assumed that the concentrations of dimeric Cr(VI) were negligible. Their value of K_{11} at unit ionic strength is probably too large since they used in their calculation ϵ_{12} values, calculated from data at ionic strength 3.0, which were smaller than corresponding ϵ_{12} values calculated at ionic strength 1.0.

We have examined the absorption spectra of Cr(VI) at wave lengths 220–365 mμ carefully at much lower Cr(VI) concentrations. The removal of reducing impurities from water used, the preparation of solutions, and the spectrophotometric equipment were similar to those reported earlier,[1] except that the cell thermostating device has been improved. Reagent grade potassium dichromate was recrystallized.

A pair of solutions of unit ionic strength and 4.98×10^{-5} g.-atom/l. in Cr(VI) and 1.002 M and 0.001073 M in $HClO_4$, respectively (the ionic strength of the latter was maintained with $NaClO_4$), was carefully scanned at wave lengths 320–365 mμ at 5-mμ intervals at 25.0°. The ratio of the net absorbance of the more acidic solution to that of the less acidic solution, or approximately $\tilde{\epsilon}_1/\epsilon_{11}$, decreased from 0.99 at 320 mμ to 0.93 at 365 mμ (0.94 at 350 mμ) and all were greater than those reported at wave lengths of 370–400 mμ. A second pair of solutions, similar to the first but containing only 2.00×10^{-5} g.-atom/l. of Cr(VI), was scanned at wave lengths of 220–292 mμ at 2-mμ intervals at 15.0°. The ratio ranged from 0.98 to 0.92 (0.93 at 260 mμ). Therefore, none of the wave lengths in the 220–365 mμ region examined offered a better $\tilde{\epsilon}_1/\epsilon_{11}$ ratio for the determina-

---

(1) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

(2) The symbols of ref. 1 are used in the present report. All concentrations of Cr(VI) species were expressed in g.-atoms/l. and the absorptivities, ϵ, were calculated on that scale. Absorptivities were called extinction coefficients in ref. 1.

(3) G. P. Haight, Jr., D. C. Richardson, and N. Hall, paper presented before the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963; *Inorg. Chem.*, **3**, 1777 (1964).

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]

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	. . .		

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 ($\partial\mu/\partial r$).

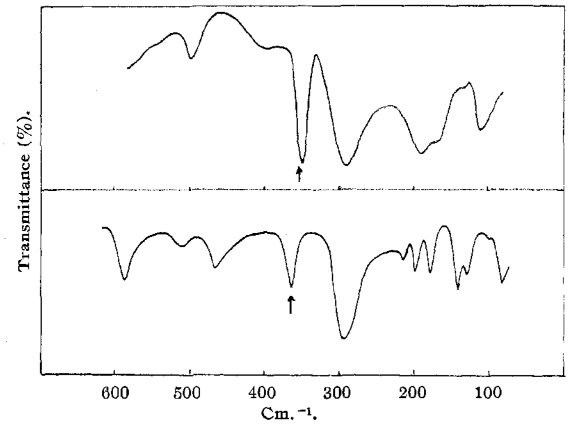

Fig. 1.—The far-infrared spectra of *trans*-$[CoCl_2(NH_3)_4]Cl$ (upper curve) and *trans*-$[CoCl_2(en)_2]Br$ (lower curve).

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.