

Resonance Phosphorescence,¹ Raman Scattering, and Decomposition of Hexaamminechromium(III) Salts Utilizing He-Ne Laser Excitation⁸

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Abstract: He-Ne laser excitation (632.8 nm) of $\text{Cr}(\text{NH}_3)_6^{3+}$ in a conventional Raman experiment produces both a Raman spectrum and a resonance-phosphorescence spectrum containing Stokes and anti-Stokes vibronic components. The frequencies of all vibrations of the CrN_6 octahedron are measured and assigned, including the infrared- and Raman-forbidden but vibronically allowed bending mode of T_{2u} symmetry (ν_6). A general valence-force-field analysis of $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ yields values of f_r , the metal-ligand stretching force constant, of 1.60 and 1.72 mdyne/Å, respectively. The laser-Raman spectrum of $\text{Cr}(\text{NH}_3)_6\text{Cl}^{2+}$ is also reported. The 0-0 band of the (${}^4A_{2g} \rightarrow {}^2E_g$) electronic transition of $\text{Cr}(\text{NH}_3)_6^{3+}$ is located, and the vibronic components of this transition are completely assigned for both emission and absorption spectra. The phosphorescence spectrum of $\text{Cr}(\text{ND}_3)_6^{3+}$ in D_2O is also reported and the shifts on deuteration are consistent with the vibronic assignments. Decomposition of the salts upon laser irradiation is observed, and, for the solid materials, this results in the formation of complexes in which the counteranion has replaced one or more ammine groups, while the previously observed green photoaquation product⁴ forms in solution.

The substantial interest in the electronic spectra and photochemistry of chromium(III) complexes is reflected in the number of excellent recent reviews and general articles devoted, at least in part, to these subjects.⁵⁻¹⁰ The suggestion by Plane and Hunt¹¹ and, independently, by Schläfer¹² of the involvement of the lowest lying doublet in photochemical racemizations and substitutions of octahedral Cr(III) complexes, though controversial,^{4,5,18} has focused attention on this state. The position of the 2E_g state has been established for a number of chromium complexes on the basis of their absorption or emission spectra,^{12,14-18} and in $\text{Cr}(\text{NH}_3)_6^{3+}$ the absorption at *ca.* 15,000 cm^{-1} has been attributed to a spin- and parity-forbidden transition

from the ${}^4A_{2g}$ ground state to (${}^2E_g, {}^2T_{1g}$), the latter states being degenerate in first-order crystal-field theory. In $\text{Cr}(\text{NH}_3)_6^{3+}$, this intercombination band is relatively intense, clearly separated from the more intense spin-allowed transitions, and it exhibits a well-defined vibronic structure that has been carefully studied in absorption by Adamson and Dunn.¹⁹ They conclude that a band measured at 15,175 cm^{-1} is probably a vibronic origin (*i.e.*, a transition from a ground state with an antisymmetric vibration excited to the zero level of an upper electronic state). Also, sizable shifts of peaks at 15,975 and 15,905 cm^{-1} on deuteration were taken to indicate that they should be associated with levels involving vibrational modes that are principally those of the ammonia ligands, likely rocking modes, but more complete assignments were not attempted. Porter and Schläfer¹⁸ recorded the Stokes phosphorescence spectrum of $\text{Cr}(\text{NH}_3)_6^{3+}$ in rigid glass at liquid-air temperatures using mercury-arc excitation, and a maximum at 15,120 cm^{-1} is assigned as the 0-0 band of (${}^2E_g \rightarrow {}^4A_{2g}$). Although the structural detail of their photographic study is somewhat less than that we report below, it did enable a comparison between available infrared data (above 700 cm^{-1}) and ground-state vibrational frequencies derived from phosphorescence measurements. Employing He-Ne laser excitation (632.8 nm), we were able to obtain well-resolved spectra containing both Stokes and anti-Stokes vibronic components of the ${}^2E_g \rightarrow {}^4A_{2g}$ emission for hexaamminechromium(III) in the solid state and in aqueous solution. Mirror symmetry relations between these components permit an unambiguous selection of the 0-0 transition, and *all* vibronic bands can be correlated with normal modes of the ground and excited states. A comparison of frequencies of ground- and excited-state vibrations is made, and, to our knowledge, this is the first time that such a complete and relatively definitive assignment of a vibronic system of a transi-

(1) This phenomenon may be better characterized as simply resonance radiation rather than resonance phosphorescence, since only one excited electronic state of the complex is involved in the absorption and emission processes (see text);² however, the term phosphorescence is retained because it is employed in earlier luminescence studies of this system, and because the transition in question is both spin and parity forbidden.

(2) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience, New York, N. Y., 1949, p. 2.

(3) Presented in part at the 5th Middle Atlantic Regional Meeting of the American Chemical Society, Newark, Del., April 1970.

(4) M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63**, 327 (1959); *Inorg. Chem.*, **3**, 231 (1964).

(5) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **69**, 541 (1969).

(6) D. Valentine, Jr., *Advan. Photochem.*, **6**, 123 (1968).

(7) H. L. Schläfer, *Z. Chem.*, **10**, 9 (1970); *J. Phys. Chem.*, **69**, 2201 (1965).

(8) C. Furlani, *Coord. Chem. Rev.*, **1**, 51 (1967).

(9) F. D. Camassei and L. S. Förster, *J. Chem. Phys.*, **50**, 2603 (1969).

(10) J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144, 3155 (1967); *Coord. Chem. Rev.*, **4**, 73 (1969).

(11) R. A. Plane and J. D. Hunt, *J. Amer. Chem. Soc.*, **79**, 3343 (1957).

(12) H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **11**, 1125 (1957).

(13) A. W. Adamson, *Advan. Chem. Ser.*, No. 49, 237 (1965).

(14) G. B. Porter and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **37**, 109 (1963); **38**, 227 (1963).

(15) C. D. Flint, *Chem. Phys. Lett.*, **2**, 661 (1968).

(16) C. D. Flint, *J. Chem. Phys.*, **52**, 168 (1970).

(17) R. Dingle, *ibid.*, **50**, 1952 (1969).

(18) G. B. Porter and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **40**, 280 (1964).

(19) A. Adamson and T. M. Dunn, *J. Mol. Spectrosc.*, **18**, 83 (1965).

tion-metal complex has been possible. The assignment is thoroughly consistent with the previously reported absorption spectrum, including the isotopic shifts observed on deuteration,¹⁹ and with the laser-excited spectrum of $\text{Cr}(\text{ND}_3)_6^{3+}$ in D_2O , which we also report below.

Because the laser-excited spectra are recorded using a conventional Raman spectrometer, they contain lines attributable to Raman shifts of $\text{Cr}(\text{NH}_3)_6^{3+}$ in addition to the phosphorescent transitions. The two phenomena may be experimentally discriminated, since the positions of the vibronic maxima are markedly sensitive to environmental effects, while the frequencies of Raman lines of the CrN_6 skeleton are invariant. The infrared spectrum of hexaamminechromium(III) has been measured,^{20,21} but our investigation furnishes the first complete Raman spectrum of this material. Three of the six fundamentals are Raman-active [$\nu_1(\text{A}_{1g})$, $\nu_2(\text{E}_g)$, and $\nu_5(\text{T}_{2g})$], two are infrared active [$\nu_3(\text{T}_{1u})$ and $\nu_4(\text{T}_{1u})$], and $\nu_6(\text{T}_{2u})$, which is infrared- and Raman-forbidden, is vibronically allowed and its frequency may be assigned from the phosphorescence data. A normal-coordinate analysis employing a general valence force field²² is in good agreement with experimental data, and it is interesting to compare this analysis with an identical treatment of the $\text{Co}(\text{NH}_3)_6^{3+}$ ion and with an earlier modified Urey-Bradley analysis based on infrared frequencies exclusively.^{20,23}

The laser radiation resulted in decomposition of both the solid salts and aqueous $\text{Cr}(\text{NH}_3)_6^{3+}$. Quantitative measurements on photoaquations of solutions of chromium(III)-ammine complexes have been reported by Edelson and Plane,⁴ but solid-state photolytic investigations are rare.^{24,25} Stenbridge and Wendlandt²⁴ concluded that irradiation of solid $[\text{Cr}(\text{en})_3]\text{X}_3$ produced $[\text{Cr}(\text{en})_2\text{X}]\text{X}$,²⁶ and the solid-state reactions of the hexaammine compounds appear to be similar, with the replacement of one or more ammine groups in the first coordination sphere by anions.

While this paper was in preparation, two articles appeared that bear on some of the questions discussed. In a terse note, Flint²⁷ provided the mercury-arc-excited emission spectrum of solid $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$ and suggested some of the vibronic assignments made below. Because the Raman data were not available to him, rigorous assignment was precluded, and the physical implications of the study were not explored. On the other hand, Siebert and Eysel²⁸ reported partial laser-Raman data for a solution of $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ and for the hexachlorothallate(III) and pentachlorocuprate(II) salts of this cation, but the accompanying phosphorescence spectrum was neither shown nor discussed.

Experimental Section

Syntheses. $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$ was prepared according to a standard literature procedure.^{29a} The bromide and perchlorate

(20) T. Shimanouchi and I. Nakagawa, *Inorg. Chem.*, **3**, 1805 (1964).

(21) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

(22) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, Appendix II.

(23) J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Part A*, **24**, 819 (1968).

(24) C. H. Stenbridge and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **27**, 29 (1965).

(25) S. E. Beacon, *Nature (London)*, **183**, 38 (1959).

(26) en = ethylenediamine, X = Cl, Br, NCS.

(27) C. D. Flint, *J. Mol. Spectrosc.*, **22**, 514 (1969).

(28) H. Siebert and H. H. Eysel, *J. Mol. Structure*, **4**, 29 (1969).

salts were obtained by addition of a concentrated solution of the corresponding acid to a saturated solution of $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$, with subsequent dissolution and recrystallization with concentrated acid. Sulfate and chloride derivatives were prepared from $\text{Cr}(\text{NH}_3)_6\text{Br}_3$ by crushing a mixture of this compound with a large excess of moist Ag_2O . The mixture was dissolved in water, and the excess Ag_2O was removed by filtration. Concentrated HCl or H_2SO_4 was added to the solution until a precipitate of the desired salt formed, and recrystallization followed. The chloride formed only with difficulty, and it was generally necessary to add ethanol equivalent to 50% solution volume and to cool in order to promote crystallization. Purity checks utilized the infrared spectra. The deuterated analog, $\text{Cr}(\text{ND}_3)_6(\text{NO}_3)_3$, was synthesized by the method outlined for $\text{Cr}(\text{ND}_3)_6\text{Cl}_3$ in which the proto compound is recrystallized from D_2O under vacuum.^{29b} The resulting crystalline material was dried over CaCl_2 *in vacuo*. The $\text{Cr}(\text{ND}_3)_6(\text{NO}_3)_3$ was dissolved in D_2O for spectral analyses.

Spectra. Infrared spectra were obtained on a Perkin-Elmer Model 621 grating infrared spectrometer that had been frequency calibrated using known polystyrene and water-vapor bands, and the accuracy is $\pm 2 \text{ cm}^{-1}$. The spectra were measured as Nujol mulls on CsI plates and as KBr or CsI pellets.

The (combination) Raman-emission spectra were measured with a module instrument which employed dc amplification and consisted of a Spex Model 1400-II double-monochromator spectrometer, a Spectra-Physics Model 112 He-Ne laser, and an ITT FW-130 photomultiplier. Although the measurements were made at a variety of slit widths corresponding to resolutions from 10 to 2.5 cm^{-1} , further resolution of the broad bands was not achieved, and the frequency placement is accurate to only $\pm 10 \text{ cm}^{-1}$, except for the 0-0 band, for which an accuracy of $\pm 5 \text{ cm}^{-1}$ is probable. The instrument was calibrated using certain neon lines and known frequencies of chloroform, carbon tetrachloride, and benzene. The solid-state spectra were obtained from pressed polycrystalline pellets of the pure material mounted on a goniometer head at an angle of 20° to the incident laser beam. Light scattered or emitted at an angle of 90° to the excitation beam was collected and analyzed. Solution data were recorded for 1-ml samples of concentrated aqueous solutions, and the angle between the incident and analyzed light is again 90° , as in the usual laser-Raman experimental arrangement. Depolarization measurements employed a Polaroid analyzer placed between the sample and the spectrometer and rotated so as to pass a single polarized component, which was then scrambled.

Results

Resonance-Phosphorescence Spectra. The laser-excited spectrum of crystalline $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$ between 14,300 and $15,600 \text{ cm}^{-1}$ is shown in Figure 1. The He-Ne laser excitation frequency is $15,802 \text{ cm}^{-1}$, and intense Rayleigh radiation partially obscured the region $15,875$ – $15,725 \text{ cm}^{-1}$. Very weak emission bands are found close to the Rayleigh line at 15,894 and $15,962 \text{ cm}^{-1}$, and these are tabulated along with other emission frequencies of the perchlorate salt in Table I. The weak features at 14,867 and $15,432 \text{ cm}^{-1}$ correspond to shifts of 935 and 460 cm^{-1} from the incident frequency, and they are ascribed to the Raman-active perchlorate and Cr-N symmetric stretching modes, respectively (*vide infra*), and are not included in Table I. To facilitate comparison, the bands are numbered as in the paper by Adamson and Dunn,¹⁹ with the primed numbers assigned to Stokes emission and the unprimed numbers given to the anti-Stokes components. A mirror symmetry of the system about the sharp line at $15,223 \text{ cm}^{-1}$ is obvious, and its assignment as the 0-0 transition is straightforward. The frequency of the 0-0 band is sensitive to environmental effects, and this is illustrated in Table II, where the 0-0 frequencies for the solids and for an aqueous solution of $\text{Cr}(\text{NH}_3)_6^{3+}$ are given. The phosphorescent system shifts with the 0-0 band, but

(29) (a) A. L. Oppegard and J. C. Bailar, Jr., *Inorg. Syn.*, **3**, 153 (1950); (b) "Gmelin's Handbuch der Anorganischen Chemie," Vol. 52C, Verlag Chemie, Berlin, 1924, p 36.

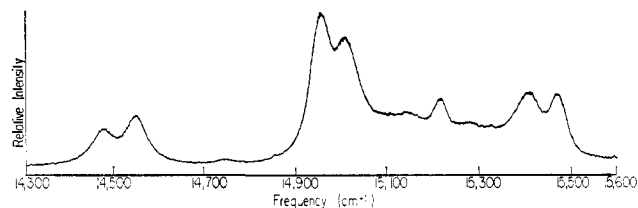


Figure 1. Laser-excited spectrum of crystalline $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$.

the frequency differences ($\omega - \omega_{00}$) given in Table I are maintained for all the solid materials within experimental error.

Table I. Emission Spectrum of Solid $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$ [${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$] System^{a,b}

No.	ω	$ \omega - \omega_{00} $	Assignment
7	15,962	739	(0-0) + (T_{1u} NH_3 rock)*
6	15,894	671	(0-0) + (T_{2u} NH_3 rock)*
4	15,478	255	(0-0) + $\nu_4^*(\text{T}_{1u})$
3	15,414	191	(0-0) + $\nu_6^*(\text{T}_{2u})$
9	15,289	66	(0-0) + $\nu_5^*(\text{T}_{2g}) - \nu_6(\text{T}_{2u})$
2	15,223	0	(0-0)
9'	15,153	70	(0-0) - $\nu_5(\text{T}_{2g}) + \nu_6^*(\text{T}_{2u})$
3'	15,016	207	(0-0) - $\nu_6(\text{T}_{2u})$
4'	14,963	260	(0-0) - $\nu_4(\text{T}_{1u})$
5'	14,757	466	(0-0) - $\nu_3(\text{T}_{1u})$
6'	14,555	668	(0-0) - T_{2u} NH_3 rock
7'	14,483	740	(0-0) - T_{1u} NH_3 rock

^a All frequencies in this and subsequent tables are in cm^{-1} .

^b Excited-state fundamentals are marked with an asterisk throughout this paper.

Table II. Frequencies of 0-0 Transitions

Compound	ω_{00}
$\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$	15,223
$\text{Cr}(\text{NH}_3)_6^{3+}$ (aqueous)	15,212
$\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$	15,190
$[\text{Cr}(\text{NH}_3)_6]_2(\text{SO}_4)_3$	15,185
$\text{Cr}(\text{NH}_3)_6\text{Cl}_3$	15,144
$\text{Cr}(\text{NH}_3)_6\text{Br}_3$	15,129

The mirror symmetry apparent in the emission spectra can be rationalized only in terms of transitions between vibrational levels of a single excited state and those of the ground state. At 2.5-cm^{-1} resolution, no splitting of the 0-0 or other bands is observed, or expected, since the separation between Kramer's doublets must be small if it exists. In first-order crystal-field theory, the two lowest doublet states, ${}^2\text{E}_g$ and ${}^2\text{T}_{1g}$, are degenerate and lie at an energy of $9B + 3C$ (B and C are the Racah electron repulsion parameters) above the ${}^4\text{A}_{2g}$ ground state.³⁰ Configuration interaction can be important in the spin-forbidden states, however. When this is taken into account, the ${}^2\text{E}_g$ lies lowest (at $9B + 3C - 90B^2/10Dq$), while the energy of ${}^2\text{T}_{1g}$ state is $9B + 3C - 24B^2/10Dq$. The phosphorescent system therefore most probably arises from the ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ transition. A discussion of selection rules for an intercombination band is properly couched in extended group notation, and in octahedral symmetry, both ${}^4\text{A}_{2g}$ and ${}^2\text{E}_g$ transform as $\text{G}_{3/2g}$.³¹ In a purely octahedral

(30) C. K. Jørgenson, *Advan. Chem. Phys.*, **5**, 88 (1962).

(31) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," 2nd ed, Van Nostrand, Princeton, N. J., 1950.

field, the 0-0 transition is electric-dipole and electric-quadrupole forbidden but may be magnetic-dipole allowed. Vibronically, transitions involving single quanta of vibrations of T_{1u} or T_{2u} symmetry are allowed. Fundamentals of T_{1u} symmetry are infrared allowed, and modes of this symmetry have been observed at 745, 470, and 270 cm^{-1} , assigned as the NH_3 rocking mode and the CrN_6 skeletal asymmetric stretch and bend, respectively.^{20,21} Emission bands 7', 5', and 4' are correlated with transitions from the zero level of the excited state to T_{1u} vibrationally excited levels of the ground state. Vibrations of T_{2u} symmetry are both infrared and Raman forbidden, but an NH_3 rock and a CrN_6 skeletal bend of this symmetry are contained among the normal modes of $\text{Cr}(\text{NH}_3)_6^{3+}$. They would be expected to be similar in energy to the corresponding T_{1u} modes, and bands 6' and 4', which are separated from the 0-0 band by 668 and 207 cm^{-1} , respectively, are attributed to T_{2u} modes on this basis. The assignment of the very weak 9' line to a transition from a vibrationally excited (ν_6) level of ${}^2\text{E}_g$ to the $\nu_5(\text{T}_{2g}$ - CrN_6 bend—Raman active) vibrational level of ${}^4\text{A}_{2g}$ is permitted by vibronic selection rules. The 70-cm^{-1} value for ($\omega_9 - \omega_{00}$), when incorporated with the frequency for ν_6 from band 3 gives $\nu_6 = 261\text{ cm}^{-1}$ compared to the directly measured Raman shift at 260 cm^{-1} (*vide infra*). The origin of line 9 in a vibrationally excited ${}^2\text{E}_g$ state is also consistent with an intensity temperature dependence that differs from that of the other bands.²⁷ One may confidently assign bands 2-9 on the basis of the pairwise nearly identical frequency separations of the Stokes and anti-Stokes phosphorescence from the 0-0 band.

The laser-stimulated emission spectrum of an aqueous solution of $\text{Cr}(\text{NH}_3)_6^{3+}$ is compared with the absorption spectrum obtained by Adamson and Dunn¹⁹ in Table III. The absorption system is assigned under the assumption that the mirror symmetry evident in the spectrum of the perchlorate solid is maintained in the aqueous environment. Although the discrepancy between the positions of bands 4, 3, 2, and (1-3) in emission and absorption is *ca.* 40 cm^{-1} , the values of ($\omega - \omega_{00}$) are in reasonable agreement, and it is felt that the absolute frequency differential between the two sets of measurements reflects a constant experimental error. Since an independent emission study placed the 0-0 band in solid $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$ at $15,228\text{ cm}^{-1}$ ²⁷ *vs.* $15,223\text{ cm}^{-1}$ in our study (Table I), we feel that the value of $15,212\text{ cm}^{-1}$ may be somewhat more accurate for the 0-0 frequency in solution. Band 8, which is apparently too weak to be discriminated in emission, is ascribed to a transition involving an NH_3 deformation which appears at 1310 cm^{-1} in the infrared spectrum of solid $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$.^{20,21}

The absorption¹⁹ and laser-stimulated emission spectra of $\text{Cr}(\text{ND}_3)_6^{3+}$ in D_2O solution are also contained in Table III. The shifts accompanying deuteration are completely consistent with the assignments in Tables I and III. In particular, the vibronic components that exhibit the greatest isotopic sensitivity are those localized on the ammine ligands (bands 8, 7, 6, 6', and 7'), while smaller shifts are measured for lines involving CrN_6 skeletal modes. The relatively large shift in bands 1 (band 3' in emission), 4', and 5' may be explained by an 18-cm^{-1} increase in the energy of the 0-0

Table III. Emission and Absorption Spectra of $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{ND}_3)_6^{3+}$ in H_2O and D_2O , Respectively

Band no.	$\text{Cr}(\text{NH}_3)_6^{3+}$				$\Delta\omega$ - (D-H) ^b	$\text{Cr}(\text{ND}_3)_6^{3+}$				Assignment
	ω absorp- tion ^a	$ \omega - \omega_{00} $	ω emis- sion	$ \omega - \omega_{00} $		ω absorp- tion	$ \omega - \omega_{00} $	ω emis- sion	$ \omega - \omega_{00} $	
8	16,525	1350			(-80)	16,445	1260			(0-0) + $\delta_3(\text{NH}_3)^*$ or $\delta_3(\text{ND}_3)^*$
7	15,975	800			(-165)	15,810	625			(0-0) + T _{1u} NH ₃ (ND ₃) rock*
6	15,905	730			(-175)	15,730	545			(0-0) + T _{2u} NH ₃ (ND ₃) rock*
5	15,650	475			(-10)	15,640	455			(0-0) + ν_3^*
4	15,430	255	15,474	262	-10 (-20)	15,410	225	15,461	231	(0-0) + ν_4^*
3	15,380	205	15,396	184	+6 (-10)	15,370	185	15,402	172	(0-0) + ν_6^*
2	15,175	0	15,212	0	+18 (+10)	15,185	0	15,230	0	(0-0)
1	14,990	185			(+40)	15,030	155			Hot band [(0-0) - ν_6]
3'			15,022	190	+36			15,058	172	
4'			14,958	254	+48			15,006	224	(0-0) - ν_4
5'			14,751	461	+48			14,799	431	(0-0) - ν_3
6'			14,488	724	+196			14,684	544	(0-0) - T _{2u} NH ₃ (ND ₃) rock
7'			14,415	797	+197			14,612	618	(0-0) - T _{1u} NH ₃ (ND ₃) rock

^a The absorption data are from ref 19 and are for solutions at ambient temperature: private communication, Professor T. M. Dunn, University of Michigan. ^b Frequency differences in parentheses in this column are taken from ref 19.

transition accompanied by 18, 30, and 30 cm^{-1} decreases in the frequencies of ν_6 , ν_4 , and ν_3 , respectively.

Vibrational Spectra and Normal Coordinate Analyses.

The Raman spectrum of $\text{Cr}(\text{NH}_3)_6^{3+}$ is given in Table IV along with infrared fundamentals.^{20,21} The Raman-

Table IV. Raman and Infrared Spectra of Crystalline $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$

Raman	Infrared	Assignment
3315 (w, sh) ^{a,b}		
3260 (mw)	3260	Asym NH str
3190 (mw)	3205	Sym NH str
3115 (vw)		
	1600	NH ₃ deg def
	1310	NH ₃ sym def
	745	NH ₃ rock
	470	$\nu_3(\text{CrN}_6)$
465 (m (p))		$\nu_1(\text{CrN}_6)$
412 (w (dp))		$\nu_2(\text{CrN}_6)$
	270	$\nu_4(\text{CrN}_6)$
260 (w (dp))		$\nu_5(\text{CrN}_6)$

^a m, medium; w, weak; v, very; p, polarized; dp, depolarized.

^b Raman NH stretching frequencies from $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$. Polarization measurements on aqueous solution.

active modes can be distinguished from emission lines, since they do not shift (within experimental error) with anion variation. Also, the emission-free, laser-Raman spectrum of $[\text{Cr}(\text{NH}_3)_6\text{Cl}]\text{Cl}_2$ contains peaks at 463, 413, and 251 cm^{-1} that correspond to ν_1 , ν_2 , and ν_3 of hexaamminechromium(III), in addition to lines at 506, 436, and 301 cm^{-1} . Polarization measurements on the aqueous solution of $\text{Cr}(\text{NH}_3)_6\text{Br}_3$ confirm that the 460- cm^{-1} band is fully polarized ($\rho \approx 0$) and correctly assigned as a mode of A₁ symmetry. Contemporary measurements accorded values of $\nu_1 = 462$ and $\nu_2 = 412$ cm^{-1} , but were unable to discriminate ν_5 .²⁸

Since, to our knowledge, only for neutral fluoride complexes³²⁻³⁴ have vibrational data as complete as those above been available for octahedral transition-metal complexes, a normal-coordinate analysis of $\text{Cr}(\text{NH}_3)_6^{3+}$ seemed valuable. The results obtained from such an analysis based on a generalized valence

(32) H. H. Claassen, H. Selig, and J. G. Malm, *J. Chem. Phys.*, **38**, 1470 (1963).

(33) B. Weinstock, H. H. Claassen, and J. G. Malm, *ibid.*, **32**, 181 (1960).

(34) H. H. Claassen and H. Selig, *Israel J. Chem.*, 499 (1969).

Table V. Vibrational Analyses (MVFF)

	$\text{Cr}(\text{NH}_3)_6^{3+}$			$\text{Co}(\text{NH}_3)_6^{3+}$		
	Obsd	Calcd		Obsd	Calcd	
ν_1	465	465	$f_r = 1.60^{a,b}$	490	490	$f_r = 1.72$
ν_2	412	416	$f_{rr'} = 0.28$	441	444	$f_{rr'} = 0.40$
ν_3	470	464	$f_{r\alpha} = 0.07$	464	468	$f_{r\alpha} = 0.07$
ν_4	270	270	$f_{\alpha} = 0.21$	318	315	$f_{\alpha} = 0.31$
ν_5	260	260	$f_{\alpha\alpha'} = 0.02$	330	328	$f_{\alpha\alpha'} = 0.02$
ν_6	206	206	$f_{\alpha\alpha} = 0.00$	[240] ^c	249	$f_{\alpha\alpha} = 0.00$

^a Frequencies in cm^{-1} ; force constants in $\text{mdyn}/\text{\AA}$. ^b The force constants are associated with: f_r , the M-N stretch; f_{α} , N-M-N bend; $f_{r\alpha}$, the interaction between a bond stretch and bend having a bond in common; $f_{rr'}$, the interaction between two bond stretches on the same straight line, while f_{rr} denotes a similar interaction between perpendicular bonds; $f_{\alpha\alpha'}$ denotes interaction between two bends in the same plane, while $f_{\alpha\alpha}$ denotes a similar interaction between perpendicular bends. ^c This is an estimate based on the observation of a crudely similar mode in crystal-field-distorted $\text{Co}(\text{NH}_3)_6^{3+}$ at 233 cm^{-1} . (A report of the Raman and infrared spectra of $\text{Co}(\text{NH}_3)_6^{3+}$ has been published in conjunction with a study of pentachloro complexes of Cu(II) and Cd(II): T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, **9**, 459 (1970). A thorough study of the vibrational spectra of Co(III) hexaammine, pentaammines, and tetraammines is forthcoming: T. V. Long, J. Zinich, and T. M. Loehr, submitted for publication.)

force field²² are contained in Table V. The calculations were carried out on a desk calculator, and the results are intended to be only qualitatively instructive. A previous analysis employing a modified Urey-Bradley force field and infrared data alone^{20,21} suggested that there is little coupling between modes of the CrN_6 skeleton and ammine vibrations, and we treat the NH_3 ligand as a single atom of mass 17.03 amu. Interestingly, an attempted fit using a Urey-Bradley field was unsuccessful, largely because it appeared impossible to simultaneously obtain reasonable values of (ν_1 , ν_2 , ν_5 , ν_6) and (ν_3 , ν_4) using only the three force constants K , H , and F . Of course, a good fit to the data is facilitated when one uses seven force constants (although one, $f_{\alpha\alpha'}$, is taken to be zero) to calculate six vibrational frequencies. The frequencies of ν_1 and ν_2 are used to establish a value for $f_{rr'}$ and f_{α} is chosen so as to fit ν_6 with the separation between ν_5 - ν_6 yielding $f_{\alpha\alpha}$. The constant $f_{r\alpha}$ is arbitrarily assigned the small value 0.05 $\text{mdyn}/\text{\AA}$, and f_r and f_{rr} are produced in a trial-and-error calculation of ν_1 , ν_2 , ν_3 , and ν_4 . Since f_{rr} , $f_{r\alpha}$, $f_{\alpha\alpha'}$, and $f_{\alpha\alpha}$ are either quite small or vanishing (and do not sensitively affect the analysis), these constants

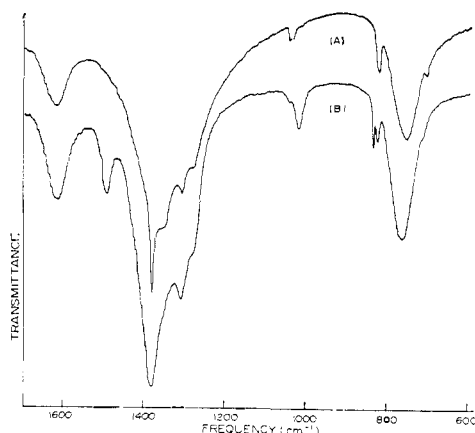


Figure 2. Partial infrared spectra (1700–600 cm^{-1}) of (A) $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$ and (B) the photodecomposition product.

are transferred to the $\text{Co}(\text{NH}_3)_6^{3+}$ case, and only f_r , f_α , and $f_{rr'}$ are manipulated in obtaining the calculated frequencies for the cobalt complex in Table V.

Laser-Stimulated Photodecomposition. The incident laser radiation resulted in the decomposition of the complex in both solution and crystalline states. In aqueous solution, a green precipitate forms after moderate periods of irradiation (*ca.* 1 hr) that appears to be identical with the polynuclear species reported by Edelson and Plane⁴ as the eventual product of photoaquation and subsequent hydrolytic polymerization of $\text{Cr}(\text{NH}_3)_6^{3+}$.³⁵ Decomposition of the solid salts occurs at the spot where the laser beam is focused, with a reddish material produced initially. Because only micro amounts of the decomposition product were obtained, we attempted characterization on the basis of its infrared spectrum. The decomposed material was scraped from the surface of the pellet of the pure material, and infrared spectra were obtained from mulls or from KBr or CsI pellets. The infrared spectra of $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$ and its decomposition product are displayed in Figure 2. The significant spectral differences lie in new nitrate absorptions that appear in the decomposed material at 839, 1020, and 1493 cm^{-1} and the absence of an absorption at 1035 cm^{-1} in this substance. The spectrum of the decomposition product resembles (in the region 2000–600 cm^{-1}) that of $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$,³⁶ and a formulation $[\text{Cr}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ or $[\text{Cr}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$ seems likely.

Table VI. Infrared Absorption Bands of $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$ and the $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$ Decomposition Product

$[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2^a$	Decomposition product ^b
1495 (s)	1493 (s)
1377 (vs)	1382 (vs)
1330 (sh)	1350 (sh)
1269 (s)	
1052 (w)	1045 (m)
1032 (w)	
1011 (s)	1020 (m)
	839 (vs)
828 (s)	828 (w)
803 (w)	

^a See ref 36. ^b Contaminated with $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$.

(35) J. A. Laswick and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3564 (1959).

(36) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

The two spectra are tabulated in Table VI. Satisfactory spectra could not be obtained below 600 cm^{-1} because of the contamination with $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$ and the weakness of the absorption in that region. Results on the decomposition products from other salts were less definitive.

Discussion

Resonance Phosphorescence Spectra. It is often assumed that the 2E_g and ${}^4A_{2g}$ states of $\text{Cr}(\text{III})$ octahedral complexes have equilibrium configurations at nearly identical internuclear distances and that the shapes of their potential surfaces are not markedly different, since both states derive from a strong-field t_{2g}^3 configuration and differ by but spin pairing in that set of orbitals.^{5,7,18} The comparison made in Table VII

Table VII. Comparison of Ground-State and Excited-State Frequencies in $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$ Solid

Frequency	Ground state (vibronic)	Excited state (vibronic)	Ground state (ir and Raman)
T_{1u} NH_3 rock	740	739	742
T_{2u} NH_3 rock	668	671	Forbidden
ν_3	466	475 ^a	462
ν_4	260	255	256
ν_5	261	273	260 ^b
ν_6	207	191	Forbidden

^a From aqueous absorption spectrum assignment. ^b From $\text{Cr}(\text{NH}_3)_6\text{Br}_3$ spectrum.

between ground-state and excited-state frequencies supports the latter contention, since the vibrational frequencies of the two states are equal within experimental error. Table III shows that this conclusion is also valid for $\text{Cr}(\text{ND}_3)_6^{3+}$. On the basis of the present studies it is not possible to determine whether the 0–0 transition gains its intensity *via* an electric-dipole or a magnetic-dipole mechanism. Our inability to resolve a splitting of this band at moderately narrow slit widths may indicate that at least a significant contribution is derived from magnetic-dipole sources, and the anomalously large magnetic circular dichroism found for $\text{Cr}(\text{III})$ spin-forbidden transitions³⁷ may also originate from this.

Vibrational Spectra and Normal-Coordinate Analyses. The vibrational measurements are important because they represent a complete set of data for the skeletal fundamentals of the $\text{Cr}(\text{NH}_3)_6^{3+}$ octahedron, and, as such, they provide an opportunity for vibrational comparison of this species with $\text{Co}(\text{NH}_3)_6^{3+}$.³⁸ The hexaammines of $\text{Co}(\text{III})$ and $\text{Cr}(\text{III})$ were chosen for study because they are substitutionally inert, and, consequently, the kinetics of their substitution and redox reactions have been avidly explored.^{39,40} The intent of the normal-coordinate analysis is to furnish a basis

(37) A. J. McCaffery, P. J. Stephens, and P. N. Schatz, *Inorg. Chem.*, **6**, 1614 (1967).

(38) A report of the Raman and infrared spectra of $\text{Co}(\text{NH}_3)_6^{3+}$ has been published in conjunction with a study of pentachloro complexes of $\text{Cu}(\text{II})$ and $\text{Cd}(\text{II})$: T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *ibid.*, **9**, 459 (1970). A thorough study of the vibrational spectra of $\text{Co}(\text{III})$ hexaammine, pentaammines, and tetraammines is forthcoming: T. V. Long, J. Zinich, and T. M. Loehr, submitted for publication.

(39) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(40) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1969.

for such a comparison. One result of the analysis is the emphasis on the interaction constant $f_{rr'}$, which reflects the interaction between the stretching of bonds that are trans to each other. It is this interaction that precludes satisfactory agreement between observed and calculated frequencies using a modified Urey-Bradley force field, and one may muse on the possible implications of this result in regard to phenomena which seemingly involve a trans effect.³⁹ Although the remaining interaction constants f_{ra} , f_{rr} , and f_{aa} are nontrivial to the degree that they are required in order to obtain the good fit observed in Table VI, they are small, and physical interpretation of them would be unwise. Values for the constants f_{ra} , f_{rr} , f_{aa} , and $f_{aa'}$ from the chromium calculation are transferred to the cobalt analysis. Only the magnitudes of f_r , f_a , and $f_{rr'}$, to which the analysis is more sensitive, are varied. Significantly larger values are required for $\text{Co}(\text{NH}_3)_6^{3+}$ than for $\text{Cr}(\text{NH}_3)_6^{3+}$, and this may be interpreted as reflecting a somewhat firmer coordination bond in the former complex.²¹ The stretching force constants should be singled out for comment, since reasonable estimates of their magnitudes are required in the Marcus-Hush theory of electron-transfer rates.³⁹⁻⁴² The constants ($f_r = 1.60 \text{ m dyn}/\text{\AA}$, $\text{Cr}(\text{NH}_3)_6^{3+}$ and $f_r = 1.72 \text{ m dyn}/\text{\AA}$, $\text{Co}(\text{NH}_3)_6^{3+}$) diverge widely from the values reported for $K(\text{M}-\text{N})$ from the Urey-Bradley treatment ($K(\text{Cr}-\text{N}) = 0.84 \text{ m dyn}/\text{\AA}$ and $K(\text{Co}-\text{N}) = 1.05 \text{ m dyn}/\text{\AA}$).^{20,21} However, they are remarkably similar to the values of the Urey-Bradley diagonal matrix element of the F_{1u} degenerate stretching coordinate ($F_{\text{dia}}(\text{CrN}) = 1.55 \text{ m dyn}/\text{\AA}$ and $F_{\text{dia}}(\text{CoN}) = 1.75 \text{ m dyn}/\text{\AA}$), whose relation to the strength of the coordinate bond has been argued.^{20,21,23} Also, Block⁴³ calculated a cobalt-nitro-

(41) R. A. Marcus, *J. Chem. Phys.*, **24**, 966, 979 (1956); **26**, 867 (1957); *Discuss. Faraday Soc.*, **29**, 129 (1960).

(42) N. S. Hush, *Z. Elektrochem.*, **61**, 734 (1957); *J. Chem. Phys.*, **48**, 962 (1968); *Trans. Faraday Soc.*, **57**, 557 (1961).

(43) H. Block, *ibid.*, **55**, 867 (1959).

gen stretching force constant of $2.00 \text{ m dyn}/\text{\AA}$ based on a modified valence-force-field treatment of incomplete vibrational data, but including interaction between skeletal and ligand modes. The values of f_r derived from our analyses do not appear to be aberrational, therefore, and their incorporation in kinetic discussions would be feasible.

Photodecomposition. As discussed above, the laser-stimulated decomposition of $\text{Cr}(\text{NH}_3)_6^{3+}$ in aqueous solution is very likely identical with the stepwise photoaquation previously investigated.⁴ For the reactions of the crystalline materials, it is not possible to distinguish between a photochemical substitution process and thermal decomposition, since local heating from the focused laser beam could occur. However, there is little reason to believe that the solid-state process is not directly analogous to the aqueous solution reaction with photosubstitution by the outer-sphere anion for an ammine ligand. The occurrence of this substitution process in thermal decompositions of chromium(III) amines has been well documented,^{44,45} and a direct photochemical parallel is available in the reaction of crystalline trisethylenediaminechromium(III) salts.²⁴ For $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$, the infrared spectrum of the decomposition product is consistent with the formation of a complex in which a nitrate resides in the first coordination sphere of the Cr(III). Once again, the involvement of the 2E_g state in photosubstitution reactions of Cr(III) is indicated,^{5,11-13,84} since this is the state that is resonance populated by the He-Ne laser radiation.

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(44) W. W. Wendlandt and C. Y. Chou, *J. Inorg. Nucl. Chem.*, **26**, 943 (1964).

(45) N. Tanaka and K. Nagase, *Bull. Chem. Soc. Jap.*, **42**, 2854 (1969).

Autoxidation of a Coordinated Trialkylphosphine¹

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Abstract: That the sole product of the slow but quantitative autoxidation of $\text{CoCl}_2(\text{P}(\text{C}_2\text{H}_5)_3)_2$ in several organic solvents is the phosphine oxide complex $\text{CoCl}_2(\text{OP}(\text{C}_2\text{H}_5)_3)_2$ is proven by mass balance and complete characterization⁴ of the product. In its initial stages, the reaction is first order in oxygen and first order in complex. Azobisisobutyronitrile and hydroquinone have no effect. A dissociation mechanism is precluded since autoxidation of uncoordinated phosphines is a radical process giving mixed $\text{R}_n\text{P}(\text{O})(\text{OR})_{3-n}$ products.⁵ The mechanism may involve the formation and rearrangement of an O_2 adduct of the cobalt complex. During the reaction in solution the redistribution equilibrium $\text{CoCl}_2(\text{P}(\text{C}_2\text{H}_5)_3)_2 + \text{CoCl}_2(\text{OP}(\text{C}_2\text{H}_5)_3)_2 \rightleftharpoons 2\text{CoCl}_2(\text{P}(\text{C}_2\text{H}_5)_3)(\text{OP}(\text{C}_2\text{H}_5)_3)$ is observed, with an equilibrium constant of about ten. Resolution of the components of the transition ${}^4A_2 \rightarrow {}^4T_1(\text{P}) (T_d)$ is partial in the complexes $\text{CoCl}_2\text{L}_2 (C_{2v})$ and complete in the complex $\text{CoCl}_2\text{LL}' (C_1)$.

In the autoxidation of free trialkylphosphines,⁵ intermediate phosphoranyl radicals ROPR_3 can decompose to give phosphine oxides or to give trivalent phosphorus esters ROPR_2 , susceptible to further oxidation.⁶

In this way, a mixture of all the $\text{R}_n\text{PO}(\text{OR})_{3-n}$ products is obtained. In a coordinated phosphine ligand, phosphorus is four coordinate and its lone pair is involved in the σ portion of the coordinate bond. In the autoxidation

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(4) D. D. Schmidt and J. T. Yoke, *Inorg. Chem.*, **9**, 1176 (1970).

(5) S. A. Buckler, *J. Amer. Chem. Soc.*, **84**, 3093 (1962); M. B. Floyd and C. B. Boozer, *ibid.*, **85**, 984 (1963).

(6) C. Walling, *Advan. Chem. Ser.*, No. 75, 170 (1968).