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The $^2E \leftrightarrow {}^4A_2$ Transition in Tetragonal Cr^{3+} Complexes*

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The $^2E \leftrightarrow {}^4A_2$ absorption and emission spectra of $[Cr(NH_3)_5(NO_3)](NO_3)_2$, $[Cr(NH_3)_5(NO_2)]\cdot(NO_3)_2$, and $[Cr(NH_3)_5(H_2O)](NO_3)_3$ microcrystals have been recorded at 77 °K. Tetragonal ^2E splittings are 209, 188 and 87 cm^{-1}, respectively. An analysis of the limited vibronic structure has been made and compared to the results for the parent "octahedral" complex, $[Cr(NH_3)_6](NO_3)_3$. Vibrations of approximately 270 and 700 cm^{-1} are prominent.

Die $^2E \leftrightarrow {}^4A_2$ Absorptions- und Emissionsspektren von $[Cr(NH_3)_5(NO_3)](NO_3)_2$-, $[Cr(NH_3)_5(NO_2)](NO_3)_2$- und $[Cr(NH_3)_5(H_2O)](NO_3)_3$-Mikrokristallen werden für 77° angegeben. Die tetragonalen ^2E Aufspaltungen sind 209, 188 bzw. 87 cm^{-1}. Eine Analyse der begrenzten vibronischen Struktur wurde vorgenommen und mit den Resultaten für den oktaedrischen Stammkomplex, $[Cr(NH_3)_6](NO_3)_3$ verglichen. Schwingungen von etwa 270 und 700 cm^{-1} treten besonders hervor.

Les spectres d'émission et d'absorption $^2E \leftrightarrow {}^4A_2$ de microcristaux de $[Cr(NH_3)_5(NO_3)](NO_3)_2$, $[Cr(NH_3)_5(NO_2)](NO_3)_2$ et $[Cr(NH_3)_5(H_2O)](NO_3)_3$ ont été enregistrés à 77° K. Les écartements tétragonaux ^2E sont respectivement 209, 188 et 87 cm^{-1}. Une analyse de la structure vibronique limitée a été effectuée et comparée aux résultats pour le complexe «octaédral» parent $[Cr(NH_3)_6](NO_3)_3$. Les vibrations au voisinage de 270 et 700 cm^{-1} émergent.

The $^2E \leftrightarrow {}^4A_2$ transition has been observed in absorption and emission from a large number of Cr^{3+} systems [1]. The $0-0$ transition (R line) is split into two components ($0-0_1$ and $0-0_2$) when the site symmetry is reduced from O_h, due to the partial removal of the ^2E degeneracy. In most cases studied to date, the distortions have been essentially trigonal and the ^2E splittings typically range from 5–60 cm^{-1} [1]. When a well-defined molecular complex, e.g., $[Cr(H_2O)_6^{3+}]$ is incorporated into a crystal lattice, it has been possible in several instances to assign much of the vibronic structure to intramolecular modes [2–5]. In each of these trigonal systems, the vibrational intervals were nearly the same in both the ground ($^4A_2$) and excited (^2E) states, as expected for an intraconfigurational (t_2^3) transition. The intensity distributions were sometimes quite different, the absorption and emission spectra were not good "mirror images" [4, 6].

In contrast to the rather large number of ^2E splittings in trigonal fields that have been identified, only one example of a tetragonal splitting appears to have been reported, *viz.*, $Cr^{3+}:MgO$ [7]. Although most of the Cr^{3+} ions in this crystal are in cubic environments, some are in C_{4v} sites produced by the cation vacancies that result when Mg^{+2} is replaced by Cr^{3+}. In these tetragonal sites the ^2E splitting is 94 cm^{-1}.

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* This contribution is dedicated to the memory of Prof. Hans-Ludwig Schläfer, a stimulating colleague and valued friend.

The absorption and emission spectra of another tetragonal [D_{4h}] complex, *trans* $K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$, have been recorded [8]. Although considerable structure is present in these spectra, the second ^2E component was not assigned.

We now add to the meager literature describing tetragonal effects on the ^2E state by presenting the absorption and emission spectra of microcrystalline $[Cr(NH_3)_5(H_2O)](NO_3)_3$, $[Cr(NH_3)_5(NO_3)](NO_3)_2$, and $[Cr(NH_3)_5(NO_2)] \cdot (NO_3)_2$ and comparing these with the spectra of $[Cr(NH_3)_6](NO_3)_3$.

Results

In order to minimize spurious emissions, it is desirable to incorporate the complex of interest in a transparent host. The Al^{3+} analogs, which are quite satisfactory for trigonal complexes, have not been prepared for these tetragonal complexes. The only hosts that we were able to obtain were the corresponding Co^{3+} systems. Unfortunately, the host absorption masks the Cr^{3+} absorption in the mixed crystals and energy transfer from Co^{3+} to Cr^{3+} is so inefficient that no $^2E \rightarrow {}^4A_2$ emission was detectable. Consequently, it was necessary to utilize pure Cr^{3+} compounds for both the absorption and emission studies. Under these conditions, energy migration between Cr^{3+} centers is rapid and the excitation is easily trapped in defect and impurity centers [9, 10]. In addition, photodecomposition was observed in $[Cr(NH_3)_6](NO_3)_3$ and $[Cr(NH_3)_6]Cl_3$. We have reduced interference from impurities and defects by several procedures. To decrease the irradiation time and eliminate photodecomposition, the spectra were recorded quickly with a photoelectric instrument (20 cm^{-1} slit width). These spectra were compared with those obtained photographically at higher resolution (4 cm^{-1}). Photoproduced lines were identified in this manner. Examination of the photoelectric emission spectrum as a function of temperature permitted the identification of impurity (defect?) lines. The impurity and genuine line intensities should have a different temperature dependence. These are denoted by an asterisk in Figs. 6 and 8. We believe that all features assigned in Figs. 1–8 arise from the species of interest.

$[Cr(NH_3)_6](NO_3)_3$

Our crystal spectra (Figs. 1–2) are in good agreement with the room temperature solution absorption and low temperature glass emission spectra of $[Cr(NH_3)_6^{3+}]$ [11, 12]. The $0-0$ transition (unsplit) is located at 15,209 cm^{-1} in the crystal and 15,225 cm^{-1} in an ethylene glycol-water (2 : 1 *v*/*v*) glass at 77 °K. Direct measurement of the $^2E \leftarrow {}^4A_2$ absorption in solution has been made in Prof. Schläfer's laboratory and $f = 4.7 \times 10^{-7}$ [13]. Since the $0-0$ transition accounts for roughly 5% of the total emission intensity, $f_{0-0} \cong 2 \times 10^{-8}$, rather large for a magnetic dipole transition. It is probable that the $0-0$ transition contains a large electric dipole component indicating the absence of an inversion center at the Cr^{3+} site.

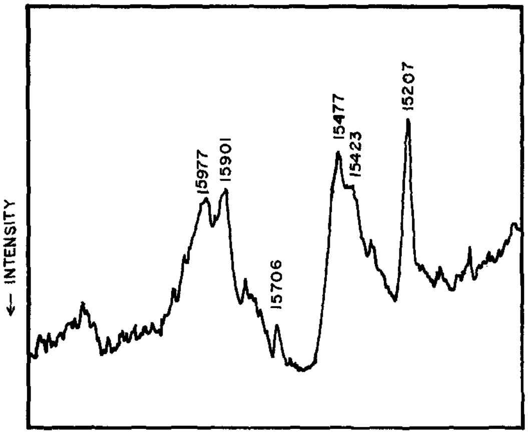

Fig. 1. Absorption spectrum of $[Cr(NH_3)_6](NO_3)_3$ at 77 °K

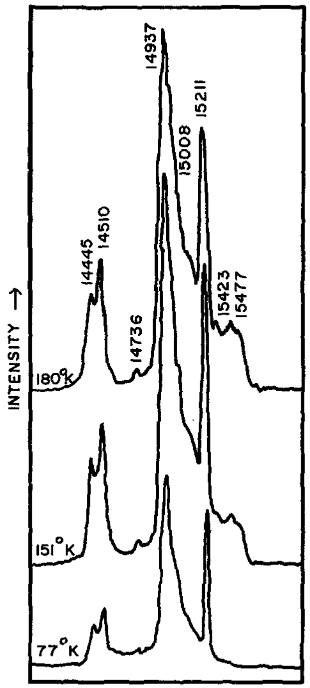

Fig. 2. Emission spectra of $[Cr(NH_3)_6](NO_3)_3$ at several temperatures. The sensitivity was increased above 77 °K

The intrinsic line widths and resolution attainable in this work preclude the detection of splittings $< 10\ \mathrm{cm}^{-1}$. Hence, exchange couplings [2], if present are ignored in the analysis. Indeed, the emission spectra from microcrystals and glassy solutions are nearly identical.

Tetragonal Complexes

Of prime interest here is the evaluation of the ^2E splitting. Although the vibronic structure is more limited in these spectra of the tetragonal complexes than in the $[Cr(NH_3)_6](NO_3)_3$ parent, some of the vibrational frequencies appear

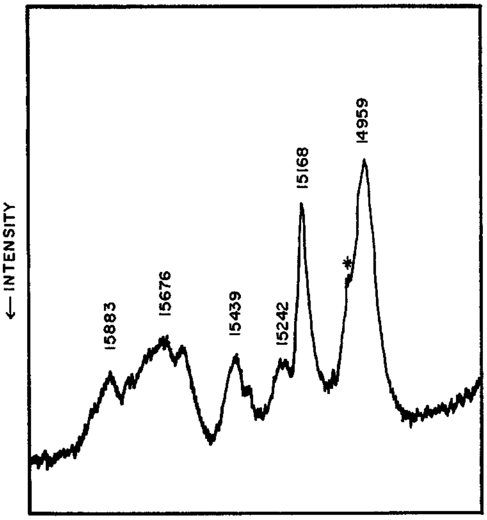

Fig. 3. Absorption spectrum of $[Cr(NH_3)_5(NO_3)](NO_3)_2$ at 77 °K. The feature designated by the asterisk does not appear in all spectra and is probably spurious

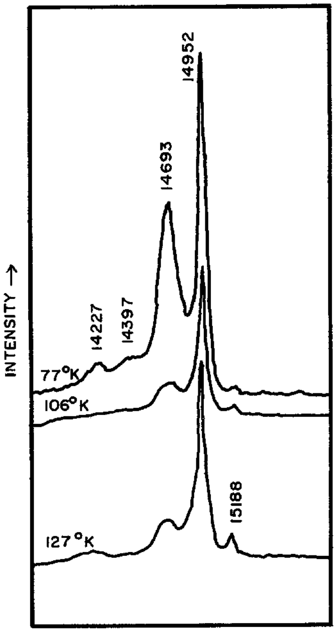

Fig. 4. Emission spectra of $[Cr(NH_3)_5(NO_3)](NO_3)_2$ at several temperatures. The sensitivity was increased above 106 °K

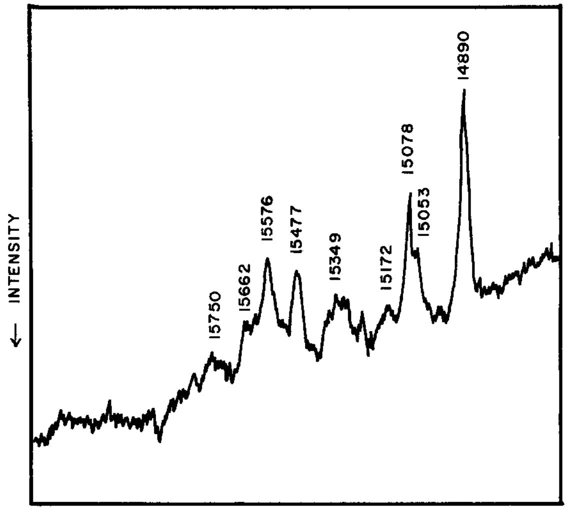

Fig. 5. Absorption spectrum of $[Cr(NH_3)_5(NO_2)](NO_3)_2$ at 77 °K

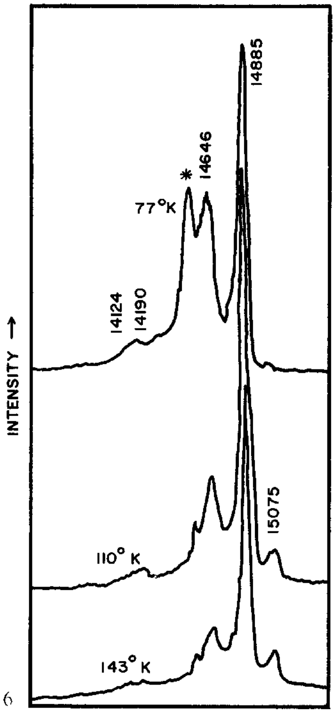

Fig. 6

Fig. 6. Emission spectra of $[Cr(NH_3)_5(NO_2)](NO_3)_2$ at several temperatures. The feature designated by the asterisk disappears at higher-temperatures and is ascribed to an impurity

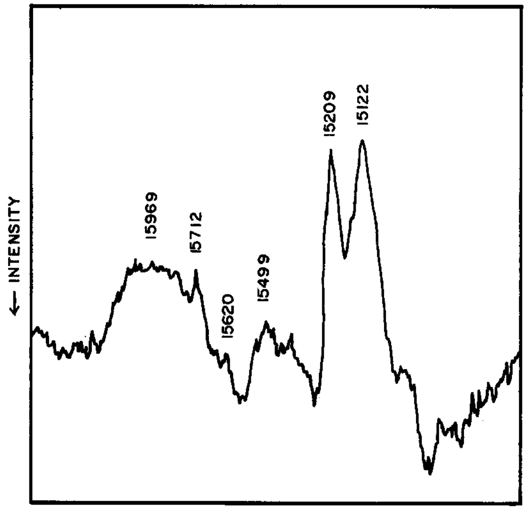

Fig. 7. Absorption spectrum of $[Cr(NH_3)_5(H_2O)](NO_3)_3$ at 77 °K

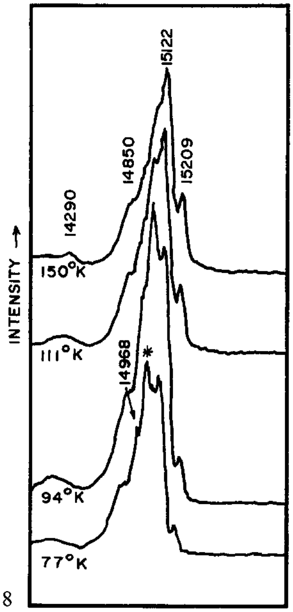

Fig. 8

Fig. 8. Emission spectra of $[Cr(NH_3)_5(H_2O)](NO_3)_3$ at several temperatures. The feature designated by the asterisk disappears at higher-temperatures and is ascribed to an impurity

Table. *Line positions (cm^{-1}) and correlations of vibronic assignments*

$[Cr(NH_3)_6](NO_3)_3$		$[Cr(NH_3)_5(NO_3)](NO_3)_2$		$[Cr(NH_3)_5(NO_2)](NO_3)_2$		$[Cr(NH_3)_5(H_2O)](NO_3)_3$	
Absorption	Emission	Absorption	Emission	Absorption	Emission	Absorption	Emission
	$15477(0-0+266)$						
	$15423(0-0+212)$						
$15207(0-0)$	$15211(0-0)$	$14959(0-0_1)$ $15168(0-0_2)$	$14952(0-0_1)$ $15188(0-0_2)$	$14890(0-0_1)$ $15078(0-0_2)$	$14885(0-0_1)$ $15075(0-0_2)$	$15122(0-0_1)$ $15209(0-0_2)$	$15122(0-0_1)$ $15209(0-0_2)$
$15423(0-0+216)$	$15008(0-0-203)$						
$15477(0-0+270)$	$14937(0-0-274)$	$15242(0-0_1+283)$ $15439(0-0_2+271)$	$14693(0-0_1-259)$	$15172(0-0_1+282)$ $15349(0-0_2+271)$	$14646(0-0_1-239)$	? $(0-0_1+290)$ $15499(0-0_2+290)$	$14850(0-0_1-272)$
$15706(0-0+499)$	$14736(0-0-475)$		$14397(0-0_1-555)$	$15477(0-0_1+587)$ $15662(0-0_2+584)$		$15620(0-0_1+498)$ $15712(0-0_2+503)$	
$15901(0-0+694)$	$14510(0-0-701)$	$15676(0-0_1+717)$ $15883(0-0_2+715)$	$14227(0-0_1-725)$	$15576(0-0_1+686)$ $15750(0-0_2+672)$	$14190(0-0_1-695)$		
$15977(0-0+770)$	$14445(0-0-766)$						

in all four complexes (Table). An interval around 270 cm^{-1} is ubiquitous and, with the exception of $[Cr(NH_3)_5(H_2O)](NO_3)_3$, a vibration near 700 cm^{-1} seems to be involved. On the basis of the analysis presented in the table, we assign the following ^2E splittings: $[Cr(NH_3)_5(NO_3)](NO_3)_2$, 209 cm^{-1}; $[Cr(NH_3)_5(NO_2)](NO_3)_2$, 188 cm^{-1}; and $[Cr(NH_3)_5(H_2O)](NO_3)_3$, 87 cm^{-1}.

The ratio of the $0-0$ and vibronic intensities is larger in the tetragonal complexes than in the parent "octahedral" species, as expected for C_{4v} symmetry.

Discussion

A splitting of the broad $^4T_2 \leftarrow {}^4A_2$ absorption band cannot be detected unless the magnitude exceeds 2000 cm^{-1}. In solution, at room temperature, the $^4T_2 \leftarrow {}^4A_2$ spectra of $[Cr(NH_3)_5(NO_2)]^{2+}$, $[Cr(NH_3)_5(NO_3)]^{2+}$ and $[(Cr(NH_3)_5 \cdot (H_2O)]^{3+}$ are more asymmetrical (tailing to the red) than is the corresponding $[Cr(NH_3)_6]^{3+}$ band. We estimate the tetragonal splittings to lie between 1000 and 2000 cm^{-1}. A similar asymmetry is observed in the excitation spectrum ($^4T_2 \leftarrow {}^4A_2$) for the $^2E \rightarrow {}^4A_2$ emission arising from the tetragonal Cr^{3+} sites in Cr^{3+} : MgO [14], where the ^2E splitting is 94 cm^{-1}. The ^2E and $^4T_2$ splittings depend upon the tetragonal parameters, μ and δ in different ways and a simple parallelism between these splittings is not expected. Nonetheless, as a crude estimate, we can say that tetragonal distortions which split $^4T_2$ by 1000–2000 cm^{-1}, produce ^2E splittings in the neighbourhood of 100–200 cm^{-1} in the pentamine complexes.

We can interpret the spectra of Dingle [8] in light of the present results. The ^2E splitting in *trans* $K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ must be at least 131 cm^{-1}. The emission within 130 cm^{-1} of the 0–0 line is probably due to impurities.

In summary, we conclude that the ^2E splittings in tetragonal complexes are rather larger than those commonly encountered in trigonal systems. When allowance is made for the ^2E splitting, the absorption and emission spectra are good mirror images of one another.

Experimental

The compounds were synthesized by published methods: $[Cr(NH_3)_6](NO_3)_3$ [15], $[Cr(NH_3)_5(NO_3)](NO_3)_2$ [16], $[Cr(NH_3)_5(NO_3)](NO_3)_2$ [16], and $[Cr(NH_3)_5(H_2O)](NO_3)_3$ [17].

The powdered samples were mounted in a dewar in direct contact with liquid nitrogen. The temperature dependences of emission spectra were obtained by allowing the liquid nitrogen to evaporate while the spectra were continuously scanned.

The spectra were recorded photographically on Kodak I-N plates with a small grating spectrograph (80 Å/mm) and photoelectrically by means of a Jarrell-Ash 0.75 m instrument equipped with an EMI 9558 B detector (S-20). The spectra were analyzed by reference to the neon spectrum and we believe that the absolute positions of sharp lines are reliable to 6 cm^{-1}. The photographic plates were scanned with a Joyce-Lobel recording microdensitometer and visually with a Nikon Profile Projektor, Model 6C. For uniformity and ease of comparison all of the spectra shown in Figs. 1–8 are photoelectric records, although the line positions were obtained for the most part from the photographic plates.

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