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Absorption Spectra of ^2E States of Some Chromium(III) Complexes Revealed by Flash Method

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Excited states of some chromium(III) complexes were studied by a flash technique at −196°C. Transient species with strong absorption bands in visible and near UV regions were observed to decay at the same rate as their phosphorescence for $Cr^{III}(acac)_3$, $K_3[Cr^{III}(NCS)_6]$, $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, and $Cr^{III}(exan)_3$. They are therefore ^2E states (phosphorescent states). A strong absorption band for $Cr^{III}(acac)_3$ is assigned to a charge transfer transition from ^2E state based on the intensity and energy of the transition. A transition to localized excited states in ligand with a small extinction coefficient was observed in near infrared region for $Cr^{III}(acac)_3$.

It is known that triplet excited states of organic compounds play important roles in photochemical reactions.1) Triplet excited states have often been confirmed in rigid media at low temperature by their phosphorescence and ESR signals.2) However, they are scarcely observed in fluid media at room temperature, at which photochemical reactions usually take place. Absorption spectra of triplet excited states are observed with less difficulty by means of flash technique even in a condition where neither phosphorescence nor ESR signals were detected.3)

Among coordination compounds of transition metals, many chromium(III) complexes are known to emit phosphorescence in rigid solvents4); the most prominent example is ruby laser.5) The phosphorescent state has been assigned to ^2E state.6) Although no phosphorescence has been observed for the complexes in fluid media at room temperature, ^2E states are believed to have a significant part in photoreactions.7) Direct observation of these states is desirable for a precise discussion of the mechanism of the photochemical reactions of the complexes. These states are expected to be detected as absorption spectra in fluid media by means of flash technique.

For this purpose, it is desirable to examine favorable complexes which have high extinction coefficients in the excited states. Absorption bands due to *d–d* transition from ^2E state will be weak since such transitions are all parity-forbidden. It is hard

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1) T. Ohno, S. Kato and M. Koizumi, This Bulletin, **39**, 232, (1966).

2) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York (1966).

3) G. Porter and M. W. Windsor, *Discuss. Faraday Soc.*, **17**, 178 (1954).

4) G. B. Porter and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.*, **68**, 316 (1964).

5) T. H. Maiman, R. H. Hoskins, I. J. D'Haenens, C. K. Asawa and V. Eutuhov, *Phys. Rev.*, **123**, 1151 (1961).

6) G. B. Porter and H. L. Schläfer, *Z. Physik. Chem., N. F.*, **40**, 280 (1964).

7) H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **11**, 65 (1957). M. R. Edelson and R. A. Plane, *Inorg. Chem.*, **3**, 231 (1964).

to analyze such weak bands because the measurements will be seriously interferred by the absorption of the ground state unchanged after flash irradiation. For this reason $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, $K_3[Cr^{III}(NCS)_6]$, $Cr^{III}(acac)_3$,*1 and $Cr^{III}(exan)_3$,*2 were examined, the ${}^2E$ states of which were expected to show intense charge transfer absorptions in visble or near UV regions. In the present investigation, identification of transient absorption bands for these complexes was made, and the decay of the absorption bands was compared with that of their phosphorescence.

Experimental

Chromium(III) Complexes. They were prepared by the usual methods. Preparation of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]\cdot 3/2H_2O$, $K_3[Cr^{III}(NCS)_6]\cdot 4H_2O$, $Cr^{III}(acac)_3$, and $Cr^{III}(exan)_3$ was based on the method by Dakin, Repsler, Cooperstein, and Dubsky respectively.[8]

Solvents. Ethanol was dried over calcium oxide, followed by refluxing with silver nitrate and distillation. Ether was dried over calcium chloride and distilled over metallic sodium. Isopentane was distilled over metallic sodium.

Polymer Rods doped with Chromium(III) Complexes. Methyl methacrylate monomer solution of a chromium(III) complex was polymerized in a glass tube at 40°C for three days using azobis-butyronitrile. The polymer rod thus prepared was cut in a length of 10 cm and polished at the ends with a fine emery. The polymer rods were clear and had no serious stria.

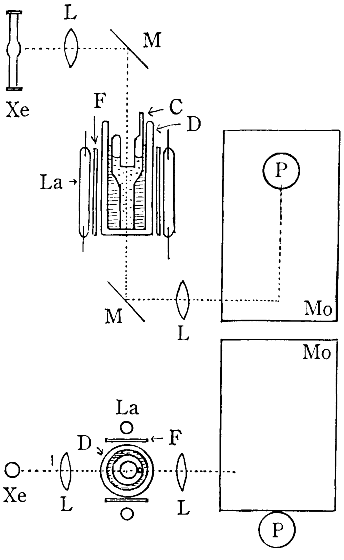

Fig. 1. Schematic diagram of the optical system of the flash apparatus.
Xe: 150 W xenon lamp (Ushio UXL-150), L: lenz, M: mirror, C: quartz cell, D: Dewar's vessel, F: cut-off filter (Toshiba Co), La: flash lamp, P: photomultiplier (1P-28 or 7102), Mo: monochrometer (Nalumi RM-23)

Measurements. A schematic diagram of the optical system is shown in Fig. 1. The output of the photomultiplier was recorded by a Hitachi synchroscope V-116. Two flash lamps were connected in series to a 4μF capacitor and fired at 10 kV. Cut-off filter transmitted light of wave numbers lower than 27 kK. A photomultiplier IP-28 (Hamamatsu TV Co.) was used for higher wave numbers, and a photomultiplier 7102 (Hamamatsu TV Co.) for lower wave numbers than 16 kK.

A quartz cell, 8 mm in inner diameter and 10 cm in optical path, was placed in a quartz Dewar vessel filled with liquid nitrogen. The polymer rod was placed in a coolant without cover.

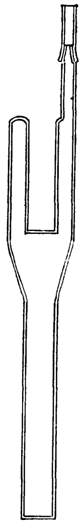

Fig. 2. Cross section of the quartz cell.

Results

When $Cr^{III}(acac)_3$, $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, $K_3[Cr^{III}(NCS)_6]$, and $Cr^{III}(exan)_3$ were irradiated with flash light in EPA or rigid polymethyl methacrylate at −196°C, transient absorption spectra were observed without any permanent change. The spectra shown in Fig. 3 were constructed from the absorbances measured on the oscillograms obtained for different wave numbers of monitoring light, 20 μsec after the triggering of the photolysis flash. A typical oscillogram is shown in Fig. 4.

In Fig. 3, ΔA in the ordinate is the transient increase in absorbance caused by flash irradiation. ΔA is expressed as follows,

$$\Delta A = (\varepsilon_T C_T + \varepsilon_G \Delta C_G) l \qquad (1)$$

where ε_T and ε_G represent the molar extinction coefficients of the transient species and the complex in the ground state, respectively, C_T the concentration of the transient species, ΔC_G the transient decrease in the concentration of the ground state and l the optical path length. In order to obtain the

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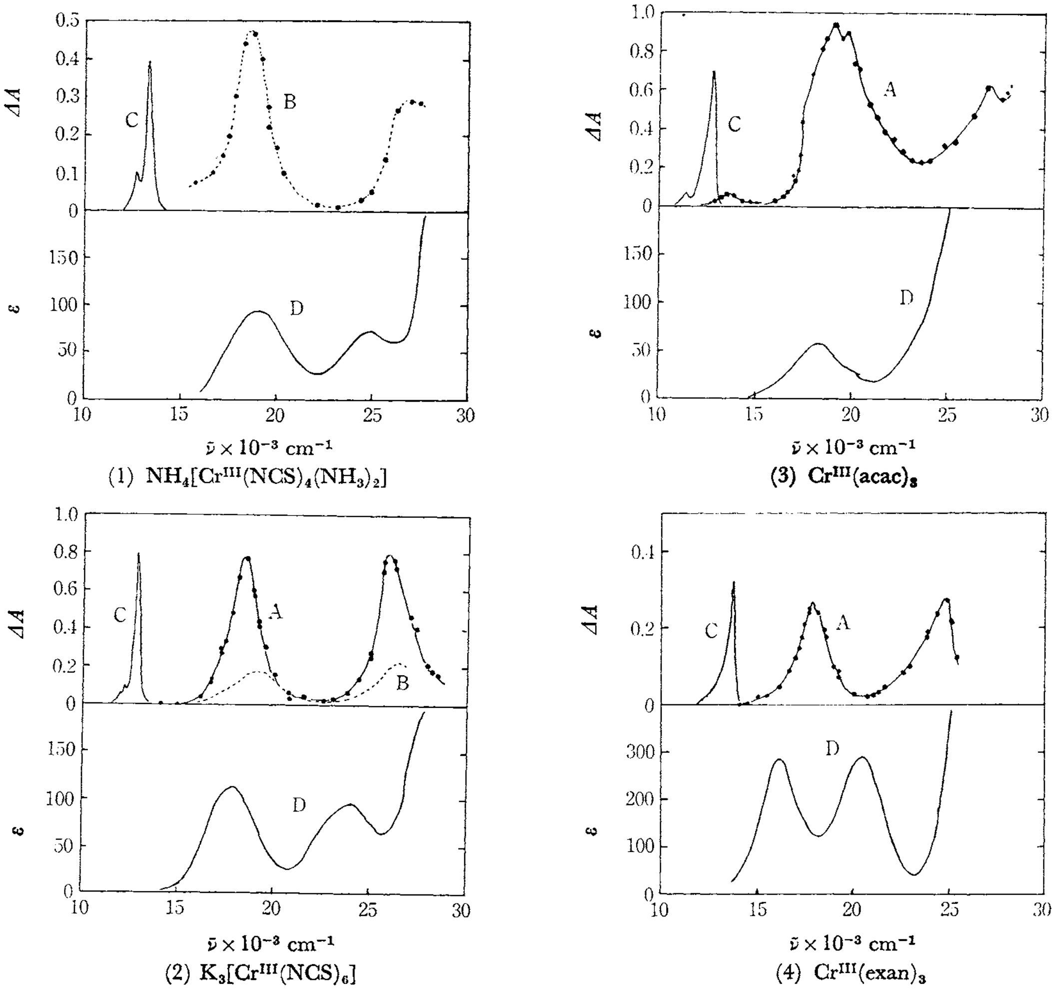
*1 acac: acetylacetonate ion.

*2 exan: ethylxanthogenate ion.

[8] Y. Shimura, "Jikken Kagaku Koza," Vol. 11, Maruzen, Tokyo (1957), pp. 58—60.



(1) $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$

(3) $Cr^{III}(acac)_3$

(2) $K_3[Cr^{III}(NCS)_6]$

(4) $Cr^{III}(exan)_3$

Fig. 3. Absorption spectra of the transient species and the ground states and phosphorescence spectra. A: absorption spectrum of the transient in EPA, B: absorption spectrum of the transient in polymethyl methacrylate, C: phosphorescence spectrum, D: absorption spectrum of the ground state in ethanol.

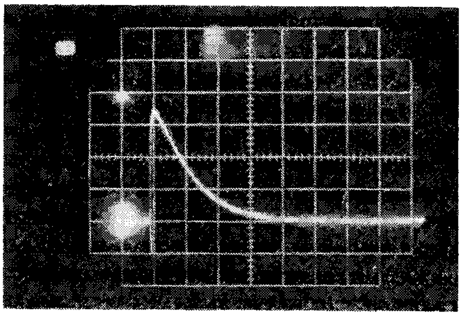


Fig. 4. A typical oscillogram of the decay curve of transient absorption.
$Cr^{III}(acac)_3$: 5×10^{-4}M in EPA. Point upper left is 0% transmission, straight line at bottom 100% transmission, and one division 5 msec. Monitoring light is 18.5 kK.

true absorption spectrum of the transient species, a correction must be made for the term $\varepsilon_G \Delta C_G$. Although the number of molecules in the ground state transiently consumed by light absorption is difficult to estimate, it cannot exceed the number of photons absorbed by the sample. The number was measured by using the aqueous solution of the same complex as an actinometer, the quantum yield of which is known to be 0.28. The highest value of $-\Delta C_G$ thus obtained was 4.3×10^{-5} mol/*l* for $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ in polymer. It follows that the correction to obtain true absorbance of the transient species is estimated to be 0.04 in the *d–d* bands at the largest. In the region of wave numbers lower than 15 kK, there is practically no absorption of the ground state to be corrected.

For the same concentrated solutions of $Cr^{III}(acac)_3$ and $K_3[Cr^{III}(NCS)_6]$ with that of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, the highest values of $-\Delta C_G$ are similar to that of the last, because both solutions of the complexes have very similar absorption spectra to that of the last in visible regions. Over

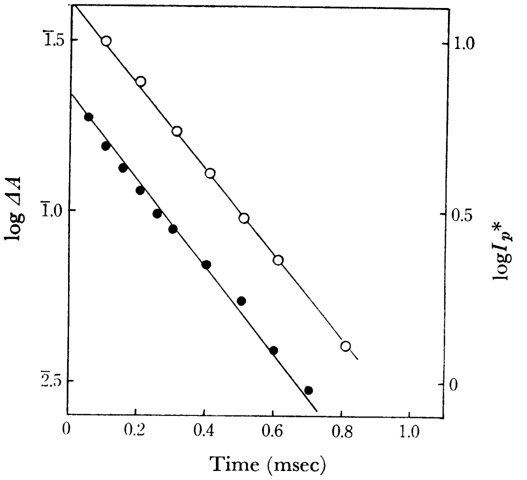


Fig. 5. Decays of the transient absorption and the phosphorescence of 5×10^{-4}M $Cr^{III}(acac)_3$ in EPA at −196°C.
—○—: transient absorption at 21.3 kK
—●—: phosphorescence at 12.8 kK
* I_p=intensity of phosphorescence

27 kK in the case of $Cr^{III}(acac)_3$, the largest correction (0.14) appears. Even this largest possible value is less than one fifth of the observed absorbance change. Thus the ΔA spectra in Fig. 3 can be regarded as the spectra of the transient species without correction.

The general features of transient spectra resemble each other, although peaks in UV regions for some complexes are obscure on account of the interference of the intense charge transfer absorption of the ground states. A weak absorption band appears in near IR regions only for $Cr^{III}(acac)_3$. For other complexes, no such band was detected even in the conditions of higher flash energy.

TABLE 1. LIFE-TIME OF THE TRASIENT SPECIES AT −196°C

Complex	Solvent	Life-time (msec)	
		Absorption	Phosphorescence
$Cr^{III}(acac)_3$	EPA	0.33	0.36 0.42*
$Cr^{III}(acac)_3$	polymer	0.44	0.44
$Cr^{III}(exan)_3$	EPA	0.28	0.31
$K_3[Cr^{III}(NCS)_6]$	EPA	10.1	9.6 2.38*
$K_3[Cr^{III}(NCS)_6]$	polymer	3.1	2.6
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	polymer	0.16	0.16 0.31*

* measured by L. S. Forster at −140——150°C in ethylene glycol and water (2 : 1) except for $Cr^{III}(acac)_3$ in EPA at −188°C.[9]

The transient absorption decayed in a first order process (Fig. 5), and the decay constant for each complex was independent of the monitoring wave number. This result proves that the whole spectrum is due to a single transient species.

Phosphorescence also decayed in a first order process (Fig. 5). The rate constants are represented in Table 1 with those for the transient absorptions. The coincidence between the life-time of the transient absorption and that of the phosphorescence for each complex indicates that both measurements were made for the same species in different ways.

Molar extinction coefficients of the transient species can be calculated from the absorbances and the numbers of photon absorbed, if the quantum yields of the species are known.

The values ε' in Table 2 are calculated on a tentative assumption that the quantum yields are equal to unity. A discussion for ε will be given.

TABLE 2. LIFE-TIME OF THE TRANSIENT SPECIES AT −196°C

Complex	Solvent	Peak kK cm^{-1}	ε'	ε
			10^3 l/mol·cm	
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	polymer	18.6	1.1	3.8
		27	0.8	2.8
$K_3[Cr^{III}(NCS)_6]$	EPA	18.6	1.8	3.8
		26	1.9	4.0
$Cr^{III}(acac)_3$	EPA	13.5	0.2	0.3
		18.5	2.2	3.3
		27	1.4	2.1

Discussion

1) Origin on the Transient Spectra. It is established that the phosphorescence states of trivalent chromium complexes in rigid media are ^2E states. The good agreement of the life-time of the transient spectrum with that of the phosphorescence for each complex may lead to the conclusion that the spectrum is due to the ^2E state. The life-time obtained in the present investigation is comparable with the values measured by Forster at −140——150°C as seen in Table 1.

2) Assignments of the Transient Absorption Bands. The extinction coefficients of the transient species ^2E estimated by assuming that the quantum yields Φ_E of the doublet states are unity, are the lowest possible values. These values are high to attribute the transient absorption bands to the *d-d* transition from ^2E state because they are parity-forbidden. The most probable assignments are charge transfer transitions as expected at the beginning.

Forster *et al.* reported the phosphorescence quantum yields (Φ_P), the natural life-times (τ_0), and the actual life-times (τ) of some chromium complexes. Employing these values, Φ_Es of NH_4-

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[9] K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964); D. C. Bhatnagar and L. S. Forster, *ibid.*, **21**, 1803, (1965); K. DeArmond and L. S. Forster, *ibid.*, **19**, 1687, (1963).

$[Cr^{III}(NCS)_4(NH_3)_2]$, $Cr^{III}(acac)_3$, and $K_3[Cr^{III}(NCS)_6]$ are calculated by the following equation to be 0.29, 0.67, and 0.47, respectively.

$$\Phi_E = \frac{\tau_0}{\tau} \times \Phi_P \qquad (2)$$

The extinction coefficients corrected on the basis of these values are given in the last column of Table 1.

Barrunum assigned the electronic spectrum of $Cr^{III}(acac)_3$ by comparing it with many acetylacetonate complexes.[10] Hanazaki and Nagakura calculated completely the energy levels of the same complexes, using "composite molecule method" and obtained assigments similar to Barrunum's[10]. In Fig. 6 solid lines show the energy levels observed in the absorption spectrum of the complex and assigned by Hanazaki and Nagakura. The levels of doublet states represented by broken lines are calculated by the method presented by Tanabe and Sugano[12] using parameters, $Dq=1.78$, $B=0.57$, and $C=4\times B=2.28$ kK.

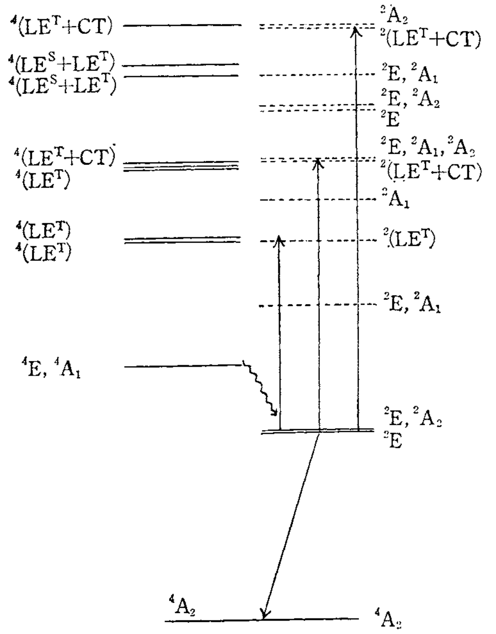

Fig. 6. Energy levels of $Cr^{III}(acac)_3$.
Solid line shows energy level of the quartet state, broken line a calculated energy level of the doublet state, and solid arrow the transition observed in this work.
LE^T: triplet state on localized excitation in ligand
LE^S: singlet state on localized excitation in ligand
CT: charge transfer excited state

Quartet charge transfer states are located 30.1 and 39.2 kK above the ground $^4A_2$ state. The energy levels of the doublet charge transfer states may not be much apart from that of the corresponding quartet state. Since ^2E state is 12.8 kK higher than the ground state, the energy differences between the doublet charge transfer states and ^2E state are 17.3 and 26.3 kK, which agree with the wave numbers of the peaks of the transient absorption spectrum.

The weak band at 13 kK for $Cr^{III}(acac)_3$ might be due to a *d-d* transition from ^2E state considered from the magnitude of the extinction coefficient. The energy level of $^2A_1$ state is calculated to be 14.95 kK above ^2E state, which is only 1.5 kK greater than the observed value. However, it is difficult to explain why similar bands in near IR regions were not observed for other compounds.

Another possible assignment of this band is the charge transfer transition to $^2(LE^T)$ state, which is inferred to be located 13 kK higher than ^2E state as seen in Fig. 6. This assignment is more plausible because the transition to $^4(LE^T)$ state appears in the spectrum of the ground state only for $Cr^{III}(acac)_3$ among all compounds examined.

The authors are grateful to Dr. Ichiro Hanazaki for his help to assign the transitions from ^2E state of $Cr^{III}(acac)_3$. A financial support from Fuji Photo Film Co., Ltd. is acknowledged.

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[10] D. W. Barrunum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

[11] I. Hanazaki and S. Nagakura, to be published in *J. Chem. Phys.*

[12] Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 753 (1954).