The Crystal Water Affecting the $^2E_g \rightarrow {^4A_{2g}}$ Relaxation in Tris(oxalato)chromate(III) Complexes

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The measurements of absorption and luminescence spectra and luminescence decay are carried out on pure crystals of $Na_3[Cr(ox)_3]\cdot xH_2O$ ($ox^{2-}=C_2O_4^{2-}$) (x=5 or 4) and $Li_3[Cr(ox)_3]\cdot yH_2O$ (y=6 or 5). In sodium salt, dehydration of one crystal water (x=4) causes the luminescence intensity to be about thirty times larger and the lifetime to be about thirty times longer than those of the most hydrated crystal (x=5) while the opposite trend is obtained in lithium salt. However, in both salts, no change of the position of luminescence maximum is observed by the dehydration of one crystal water from the most hydrated crystals. Comparing these results with X-ray crystallographic analyses shows that a crystal water located near the oxalato-oxygen atom, which is coordinated to Cr^{3+} ion, affects the $^2E_g \rightarrow {^4A_{2g}}$ (all in O_h notation) relaxation of $[Cr(ox)_3]^{3-}$ complexes in the pure crystal.

The relaxation from excited states of transition metal ion complexes has been studied over three decades, and Cr(III) complexes have been the center of studies in the series of the first transition-metal complexes.

A great many papers on the luminescence and relaxation processes of Cr(III) compound have been published since L. S. Forster and K. DeArmond first reported it in 1961.[1] A large number of results were summarized in many reviews.[2–17] Recently, L. S. Forster has published a review about luminescence spectra and relaxation processes of various Cr(III) complexes for up-to-date data.[17] Most of studies are carried out in solution while the studies in crystal are not often done.

The studies about the effect of environment around Cr^{3+} ion on the luminescence and relaxation have mainly been performed by changing the first (inner) coordination sphere which is obtained by varying ligands. From these works, some generalizations have been proposed:[18–22] (1) The reason why either only fluorescence, only phosphorescence or both of them are caused has been revealed.[7,19] (2) The results obtained by systematic change of ligands have indicated that the stretching vibrations of O–H and N–H act as accepting modes.[23–32] (3) C. D. Flint et al. have studied the relation between the complex distortion and the relative intensity of the 0–0 and vibronic bands in crystal.[8,33–40]

The effect of the second (outer) coordination sphere which is located outside of the first coordination sphere has been studied by varying either the host, Cr^{3+} concentration and the number of crystal water in crystal[23,41–49] or the solvent and media (fluid, glass or crystal)[38,50–58] while the ligands are kept intact. However, the accurate position of molecules and ions in the second coordination sphere and the accurate geometry of Cr(III) complexes could not be determined in fluid and glassy solution. In the experiments with doped crystal, the position of the crystal waters and counter ions and the conformation of Cr(III) complexes are assumed to be the same structure of host complexes or of the pure crystal. However, the crystal structure around Cr(III) complexes should not be completely identical with host complex or the pure crystal. Therefore, a pure crystal needs to be employed in order to clear the effect of the second coordination sphere on the relaxation processes.

In this paper, we report the effect of the crystal water molecules in the second coordination sphere around tris(oxalato)chromate(III) complexes ($[Cr(ox)_3]^{3-}$) upon the $^2E_g \rightarrow {^4A_{2g}}$ relaxation processes. The results of thermogravimetric (TG) analysis, the position of the crystal water molecules and the geometry of Cr(III) complexes determined by X-ray crystallographic analyses, luminescence spectra and lifetime and absorption spectra of the pure crystals make clear that a crystal water molecule located near the oxalato-oxygen atom, which is coordinated to Cr^{3+} ion, greatly affects the relaxation processes in the pure crystal of this complex.

Experimental

Samples. $K_3[Cr(ox)_3]\cdot 3H_2O$,[60] $Na_3[Cr(ox)_3]\cdot 5H_2O$,[60] and $Li_3[Cr(ox)_3]\cdot 6H_2O$[61] were prepared according to the literature. All compounds were purified by recrystallization from aqueous solutions a minimum of three times. The compounds were identified by luminescence and absorption spectra, molar extinction coefficient and elemental analysis. The values of molar extinction coefficient were within ±5% of the literature's values.[62] Crystal waters were characterized by the thermogravimetric (TG) analysis with Shimadzu TGA-50 under nitrogen. Heating rate was set at 2 [K min^{-1}].

For absorption and emission measurements, the most hydrated crystals were dispersed in poly (methyl metacrylate) (PMMA) film in order to prevent crystal water from dehydrating.

The single crystals of $Na_3[Cr(ox)_3]\cdot 5H_2O$ and $Li_3[Cr(ox)_3]\cdot 6H_2O$ were obtained by slow evaporation from aqueous solution. X-ray crystallographic analyses were carried out at room temperature. The structure of these complexes is published elsewhere.[63]

The partially dehydrated crystals, $Na_3[Cr(ox)_3]\cdot 4H_2O$ and $Li_3[Cr(ox)_3]\cdot 5H_2O$, were obtained by keeping the most hydrated crystals in P_2O_5 and silica gel desiccator, respectively. The number of crystal water was analyzed by the thermogravimetry. For each salt, the TG analysis was reiterated with the partially dehydrated crystals which were obtained by the same procedure. The errors were within a few per cent.

Further dehydrated crystals, $Na_3[Cr(ox)_3]\cdot x_1H_2O$ ($x_1<4$) and $Li_3[Cr(ox)_3]\cdot 3H_2O$, were obtained by stopping a raise in temperature in the middle of TG analysis.

Measurements. Luminescence spectra were measured on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier. The samples were set into 3 ϕ quartz tube and immersed directly in the coolant (liquid nitrogen) and were excited at 420 nm. The samples were prepared with the same procedure at least five times, and the luminescence spectra of the most hydrated and partially dehydrated crystals were found to be reproducible.

Relative intensity of luminescence was determined with physically mixing $[Cr(en)_3](ClO_4)_3$ (en=1,2-diaminoethane) as inner-standard sample into $M_3[Cr(ox)_3]\cdot xH_2O$. In this system, no intermolecular energy transfer is observed. The relative intensity were reproducible within 10% in spite of changing the mix ratio and sample amount.

Luminescence decay was recorded on an oscillograph (Lecroy, model 9450) following excitation with the second harmonics (532 nm, FWHM 5 ns) of a Nd: YAG laser (Spectron, model SL 401). The lifetimes were determined by a semi-logarithmic plot of the decay curve. The lifetime of the most hydrated and partially dehydrated crystals were reproducible within 1.5% and 10%, respectively (five runs).

In the measurement of luminescence spectra and decay curve, powder crystal was employed as samples.

Absorption spectra of powder samples at 77 K were measured by means of opal glass method[64] on a Shimadzu MPS-50S using PMMA film dispersed sample immersed directly in the coolant (liquid nitrogen).

Results and Discussion

Luminescence Spectra of $[Cr(ox)_3]^{3-}$ in Various Circumstances. Figure 1 shows the luminescence spectra of $M_3[Cr(ox)_3]$ ($M=Li^+, Na^+, K^+$) in a rigid ethanol-water glass and powder sample at 77 K, and the absorption spectra of these complexes in powder at 77 K. The luminescence is assigned to phosphorescence from the lowest excited state ^2E_g to the ground state $^4A_{2g}$ (all in O_h notation).[4] Luminescence spectra and lifetimes are independent of the counter cation in a rigid solution at 77 K, while changing the counter cation in powder samples with the most hydrated crystals gives a very different luminescence spectra, intensity and lifetimes. The luminescence of lithium salt is very strong, in contrast, that of sodium salt is very weak. In the potassium salt, emission can not be observed. The spectrum of sodium salt is very broad because the luminescence is so weak that the resolution of the spectrometer can not be set high. In Fig. 1, the resolution of the apparatus for measurement of the luminescence is shown by separation of two vertical lines. The ^2E_g state of nonluminescent potassium salt is estimated at the position of absorption maximum since phosphorescence from ^2E_g state of Cr(III) complexes is hardly shifted relative to the absorption band;[3] no Stokes-shift. In fact, the position of emission maximum is corresponded with that of absorption maximum in lithium and sodium salts as shown in Fig. 1. A basin (14.4×10^3 cm^{-1}) on the top of the absorption maximum in lithium salt results from the luminescence of Cr(III) complex.

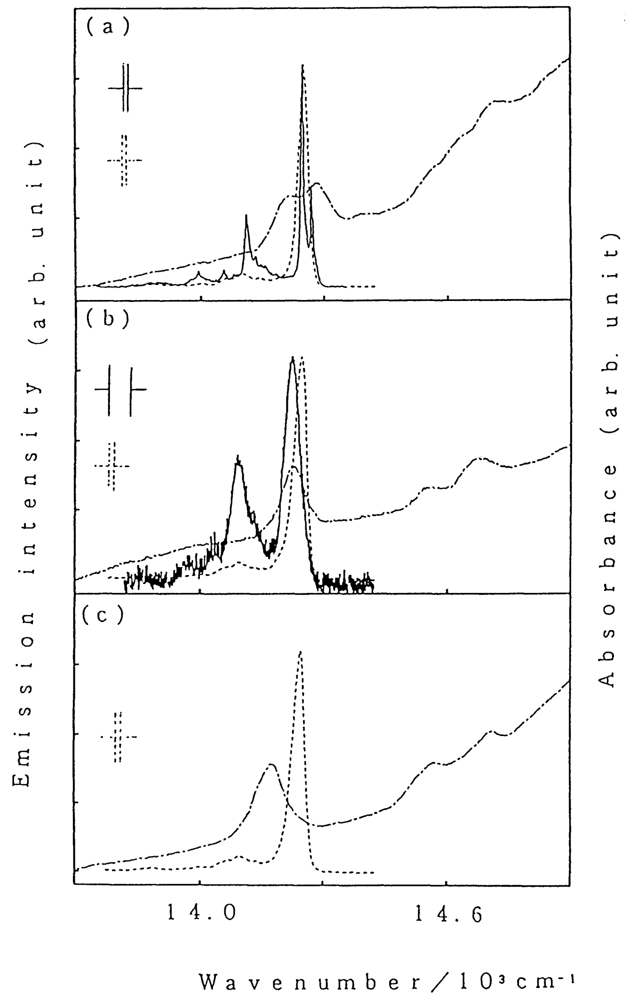

Fig. 1. Luminescence and absorption spectra of $[Cr(ox)_3]^{3-}$ at 77 K, (a) $Li_3[Cr(ox)_3]\cdot 6H_2O$, (b) $Na_3[Cr(ox)_3]\cdot 5H_2O$, (c) $K_3[Cr(ox)_3]\cdot 3H_2O$: luminescence of powder crystal (——): luminescence of $EtOH-H_2O$ (1 : 1, v/v) rigid solution (------); absorption of powder crystal (—·—). Separation of two vertical lines shows the resolution of apparatus for measurement of luminescence.

As the counter cation becomes bigger, the ^2E_g state shifts to lower energy. In general, the shift of ^2E_g energy, which is independent of 10Dq according to ligand field theory, is interpreted as either nephelauxetic effect[17,65,66] or complex distortion.[67] In this case, the shift is not induced by the nephelauxetic effect but by the complex distortion, because every complex has the same ligands and the distance between Cr^{3+} ion and inner oxygen atoms, which are coordinated to Cr^{3+} ion, of ligands is almost the same.[59,63]

The Relation between Complex Distortion and ^2E_g State. Since the average values of the Cr–O bond length (1.975 Å) is constant in $Li_3[Cr(ox)_3]\cdot 6H_2O$,[63]

$Na_3[Cr(ox)_3]\cdot 5H_2O$,[63] and $K_3[Cr(ox)_3]\cdot 3H_2O$,[59] the distortion of $[Cr(ox)_3]^{3-}$ complex from octahedron is given by the bite angle ($90-2\alpha$) and twist angle (β) (see Fig. 2). Three bite angles in one complex are almost constant: lithium salt is 82.72° (α=3.64°), sodium is 82.58° (α=3.71°) and potassium is 82.24° (α=3.88°). Here, θ is defined as the angle between the vector of direction of trigonal axis ($\vec{T}$) and the vertical vector to the plane of oxalato molecule ($\vec{n}$): $\theta=\cos^{-1}(\vec{T}\cdot\vec{n}/|\vec{T}|\cdot|\vec{n}|)$ (see Fig. 3). θ is obtained as a function of β. If the geometry of complex is regular octahedron, then the θ value is 54.74°. The θ values of lithium, sodium, and potassium salts are evaluated at 56.61°, 58.03°, and 59.44°, respectively. Therefore, trigonal distortion from octahedron is bigger in order of lithium salt< sodium salt<potassium salt and the complexes are not "pressed" but "stretched" (see Fig. 4). From α and θ value, the β values of lithium, sodium and potassium salts can be estimated at 1.88°, 3. 30°, and 4.71°, respectively. The value of 4.71° (potassium salt) is in good agreement with the value estimated by P. E. Hoggard (4.75°).[67] Table 1 shows the α, θ, and β values of lithium, sodium, and potassium salts.

L. G. Vanquickenborne and A. Ceulemans,[68] P. E. Hoggard[67] and M. A. Atanasov et al.[69] have pointed out that the energy level for each excited state of Cr(III) complexes depends on the complex distortion and that the energy gap between ^2E_g and $^4A_{2g}$ becomes smaller as the distortion from octahedron is bigger.[67] This view corresponds with our absorption results of the most hydrated complexes.

Luminescence intensity and lifetime have been also considered to depend on the complex distortion such as ^2E_g position.[17,70–73] However, our luminescence results indicate that the complex geometry does not greatly affect the relaxation processes in this pure crystal as follows.

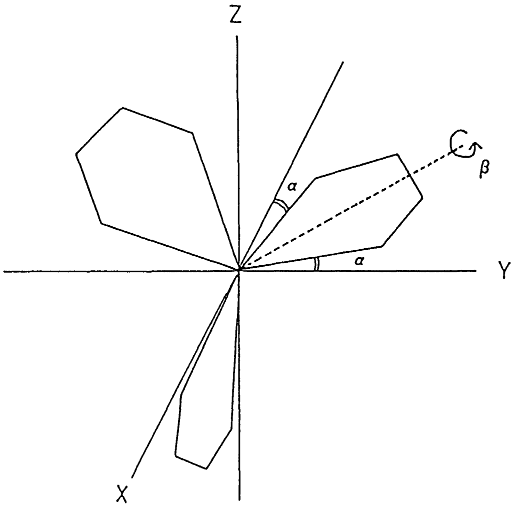

Fig. 2. Structural angles for symmetrically coordinated tris-bidentate complexes.

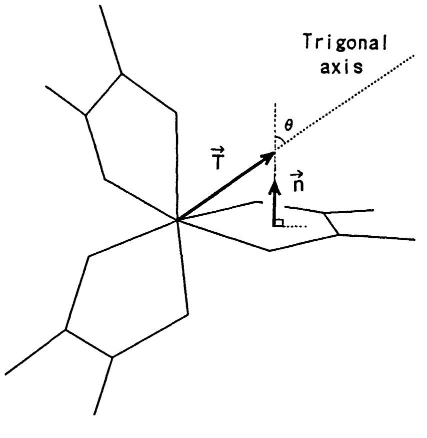

Fig. 3. The vector of direction of trigonal axis ($\vec{T}$) and the vertical vector to the plane of oxalato molecule ($\vec{n}$).

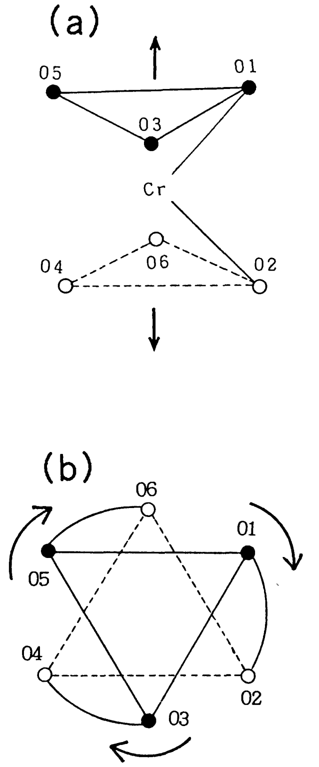

Fig. 4. The distortion of $M_3[Cr(ox)_3]$ complexes ($M=Li^+$, Na^+, and K^+) from octahedron: (a) stretch, (b) rotation.

Table 1. The Average Values of Structural Angles of $M_3[Cr(ox)_3]$ in Crystal[a]

M^+	α/°	θ/°	β/°
Li^+	3.64	56.61	1.88
Na^+	3.71	58.03	3.30
K^+	3.88	59.44	4.71

a) The average value of Cr–O bond length (1.975 Å) is constant in lithium, sodium, and potassium salts.

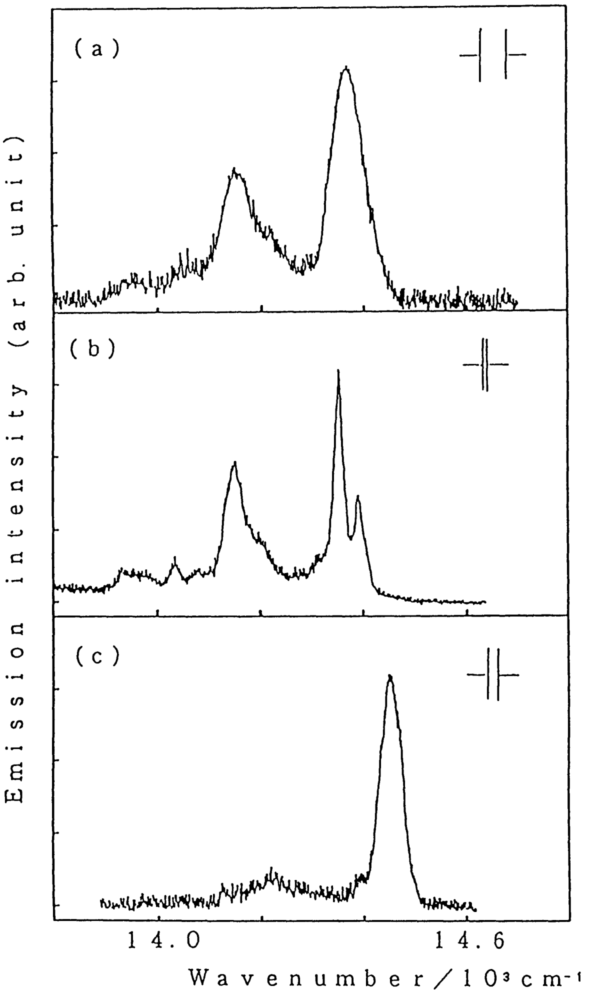

Fig. 5. Luminescence spectra of $Na_3[Cr(ox)_3]\cdot xH_2O$ powder crystal at 77 K: (a) the most hydrated crystal ($x=5$); (b) mono-dehydrated crystal ($x=4$); (c) further dehydrated crystal ($x<4$). Separation of two vertical lines shows the resolution of apparatus.

Luminescence Spectra and Lifetime of $Na_3[Cr(ox)_3]\cdot xH_2O$ in Pure Crystal. Figure 5 shows the luminescence spectra of $Na_3[Cr(ox)_3]\cdot xH_2O$ ($x=5$, 4, $x<4$) at 77 K. The luminescence of $Na_3[Cr(ox)_3]\cdot 5H_2O$, which is the most hydrated crystal, is very weak. The luminescence decay was single exponential, and lifetime can be evaluated as 70 ns. In contrast, $Na_3[Cr(ox)_3]\cdot 4H_2O$, which is obtained by dehydration of one crystal water from $Na_3[Cr(ox)_3]\cdot 5H_2O$, gives a very strong luminescence while the position of luminescence maximum of $Na_3[Cr(ox)_3]\cdot 4H_2O$ is the same as that of $Na_3[Cr(ox)_3]\cdot 5H_2O$. This result suggests that $[Cr(ox)_3]^{3-}$ in $Na_3[Cr(ox)_3]\cdot 4H_2O$ has the same molecular geometry in the first coordination sphere as $Na_3[Cr(ox)_3]\cdot 5H_2O$. It should be noted that the decay curve for the mono-dehydrated crystal can be analysed by double exponents having life times of 1.90 μs and 5.12 μs. Luminescence intensity and lifetime of sodium salt are listed in Table 2.

Recently, L. S. Forster et al. have proposed that nonexponential decay of Cr(III) phosphorescence is due to reverse intersystem crossing pathways ($^2E_g \rightarrow {}^4T_{2g}$) in the rigid glass solution.[74] Lifetime reduction arises from reverse intersystem crossing. On the contrary, in our experiment, lifetime of the mono-dehydrated crystal is longer than that of the most hydrated crystal whose phosphorescence decay is a single exponential. Thus, another reason must be provided.

Table 2. Lifetimes and Relative Luminescence Intensity of the Most Hydrated Crystal and the Mono-dehydrated Crystal for Lithium and Sodium Salts

Compound	Lifetime/ns	Relative intensity
$Li_3[Cr(ox)_3]\cdot 6H_2O$	2830	62±3
$Li_3[Cr(ox)_3]\cdot 5H_2O$	40—1700[a)]	3.5±0.3
$Na_3[Cr(ox)_3]\cdot 5H_2O$	70	1.0
$Na_3[Cr(ox)_3]\cdot 4H_2O$	1900, 5120	30±2

a) Multiexponential decay.

Table 3. Thermogravimetric Analysis Data of the Most Hydrated Crystal of $M_3[Cr(ox)_3]$ ($M=Li^+$, Na^+)

Compound	Dissociation range of water by TG/°C	Mass loss/%	
		Found	Calcd
$Li_3[Cr(ox)_3]\cdot 6H_2O$	23.0— 50.0	3.7	4.05
	50.0— 93.0	8.0	8.10
	93.0—200.0	11.6	12.15
$Na_3[Cr(ox)_3]\cdot 5H_2O$	51.0— 70.0	3.7	3.79
	70.0— 90.0	15.2	15.17

Further dehydration of crystal waters results in the shift of luminescence maximum to high energy about 80 cm^{-1}. The shift indicates that the molecular geometry of the first coordination sphere is changed by the dehydration.

The dehydration of one crystal water molecule causes the luminescence intensity to be about thirty times larger and the lifetime to be about thirty times longer than those of the most hydrated crystal (see Table 2), however both complexes have the same geometry. These facts imply that the most-loosely packed water molecule affects the $^2E_g \rightarrow {}^4A_{2g}$ relaxation processes whereas the distortion of the first coordination sphere does not in this crystal.

The Role of the Crystal Water on the $^2E_g \rightarrow {}^4A_{2g}$ Relaxation in Sodium Salt. Sodium salt usually has five crystal water molecules. The result of TG analysis is summarized in Table 3. One crystal water molecule is removed at 50 °C and another four water molecules at 70 °C.

Table 4 cites the crystal data of $Na_3[Cr(ox)_3]\cdot 5H_2O$ and $Li_3[Cr(ox)_3]\cdot 6H_2O$.[63] On the basis of X-ray analysis of $Na_3[Cr(ox)_3]\cdot 5H_2O$, the four crystal waters (O_w 1—4) are bound to counter cations (Na^+), while the other one crystal water (O_w 5) is not bound. Moreover, this one crystal water (O_w 5) is to be disordered over two possible sites (A, B) with occupancy ratios A/B ca. 6 : 4. Therefore, the most-loosely bound crystal water, which

Table 4. Crystal Data of $Na_3[Cr(ox)_3]\cdot 5H_2O$ and $Li_3[Cr(ox)_3]\cdot 6H_2O$

	$Na_3[Cr(ox)_3]\cdot 5H_2O$	$Li_3[Cr(ox)_3]\cdot 6H_2O$
Crystal system	Monoclinic	Triclinic
a/Å	17.360	9.321
b/Å	12.576	11.947
c/Å	15.227	8.066
α/°	90.00	104.86
β/°	100.37	109.44
γ/°	90.00	91.79
Z	8	2
Space group	$C2/c$	$P\bar{1}$
R/%	5.53	3.20

Table 5. Distances between O_w 5 and an Oxygen Atom in $Na_3[Cr(ox)_3]\cdot 5H_2O$

Site-A		Site-B	
Atom	Distance/Å	Atom	Distance/Å
O_w 5–O 3	2.840	O_w 5*–O 3	2.759
O_w 5–O_w 1	2.865	O_w 5*–O_w 1	2.787
O_w 5–O_w 4	2.903	O_w 5*–O_w 4	3.018

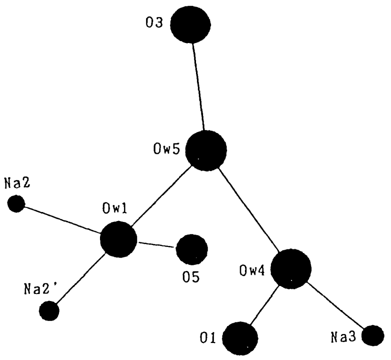

Fig. 6. Structure around the most-loosely packed water, O_w 5, in $Na_3[Cr(ox)_3]\cdot 5H_2O$ (site-A).

is dehydrated at lower temperature, is assigned to the crystal water O_w 5.

In sodium salt, O_w 5 and /or O_w 5* (*; site-B) greatly affects the relaxation processes from ^2E_g because the dehydration of O_w 5 causes an increase in luminescence intensity and lifetime without deforming complex geometry. At site-A, O_w 5 is surrounded by O_w 1, O_w 4, and O 3 which is an oxygen atom, coordinated to Cr^{3+} ion, of oxalato molecule (an inner oxygen atom) (see Fig. 6). At site-B, O_w 5* is also surrounded by O_w 1, O_w 4, and inner oxygen atom O 3. The distances between these oxygen atoms and the oxygen atom O_w 5 are summarized in Table 5. The distance between O_w 5 and O 3 is shorter than others. It suggests that the water molecules located near inner oxygen atoms become good quenchers, because mono-dehydration of the most hydrated complexes causes a stronger emission.

Table 6 gives the distances between crystal water molecules and inner oxygen atoms in lithium, sodium and potassium salts. In $Na_3[Cr(ox)_3]\cdot 5H_2O$, the water molecules located near the inner oxygen atoms are O_w 5, O_w 1, and O_w 4. O_w 5 is the water molecule which is the closest to inner oxygen atoms at both site-A (2.840 Å) and site-B (2.759 Å).

Therefore, $Na_3[Cr(ox)_3]\cdot 5H_2O$ emits very weakly since the crystal water molecule (O_w 5) is located very near the inner oxygen atom and acts as an good quencher.

After the dehydration of O_w 5 and/or O_w 5*, O_w 1, O_w 4, and O 3 atom should be scarcely moved at site-A and site-B in sodium salt, because O_w 1 and O_w 4 are tightly bound to counter cations (Na^+) and O 3 is coordinated to Cr^{3+} ion. This supports the fact that there is no change of "the first coordination sphere" around Cr^{3+} ion when O_w 5 is dehydrated; i.e. the complex geometry and ligand field around Cr^{3+} ion are not changed. Therefore, in mono-dehydrated compound, the luminescence becomes very strong since an water molecule is no longer located very near an inner oxygen atom.

Luminescence Spectra and Lifetime of $Li_3[Cr(ox)_3]\cdot yH_2O$ in Pure Crystal. Figure 7 shows luminescence spectra of $Li_3[Cr(ox)_3]\cdot yH_2O$ (y=6, 5, 3). The most hydrated crystal of lithium salt, $Li_3[Cr(ox)_3]\cdot 6H_2O$, emits very strong luminescence. The luminescence decay curve is single exponential, and lifetime is evaluated as 2.83 μs. Mono-dehydrated powder crystal, $Li_3[Cr(ox)_3]\cdot 5H_2O$, shows weak emission. This characteristic is opposite to the case of sodium salt, while the position of emission peak is not changed by mono-dehydration similar to the case of sodium salt. Further the dehydrated crystal, $Li_3[Cr(ox)_3]\cdot 3H_2O$, emits strongly, and the luminescence peak is blue-shifted about 60 cm^{-1}. This blue-shift is due to the rearrangement of the first coordination

Table 6. Distances between Water Molecule and Inner Oxygen Atom in the Most Hydrated Crystal

Lithium salt		Sodium salt		Potassium salt	
Atom	Distance/Å	Atom	Distance/Å	Atom	Distance/Å
O_w 5–O 5	2.866	O_w 5–O 3	2.840	O_w 3–O 6	2.780
O_w 4–O 2	2.875	O_w 5*–O 3	2.759	O_w 3*–O 3	2.777
O_w 3–O 3	2.876	O_w 4–O 1	2.869	O_w 3*–O 4	2.793
O_w 2–O 2	2.943	O_w 1–O 5	2.987	O_w 1–O 5	2.753

*; site-B.

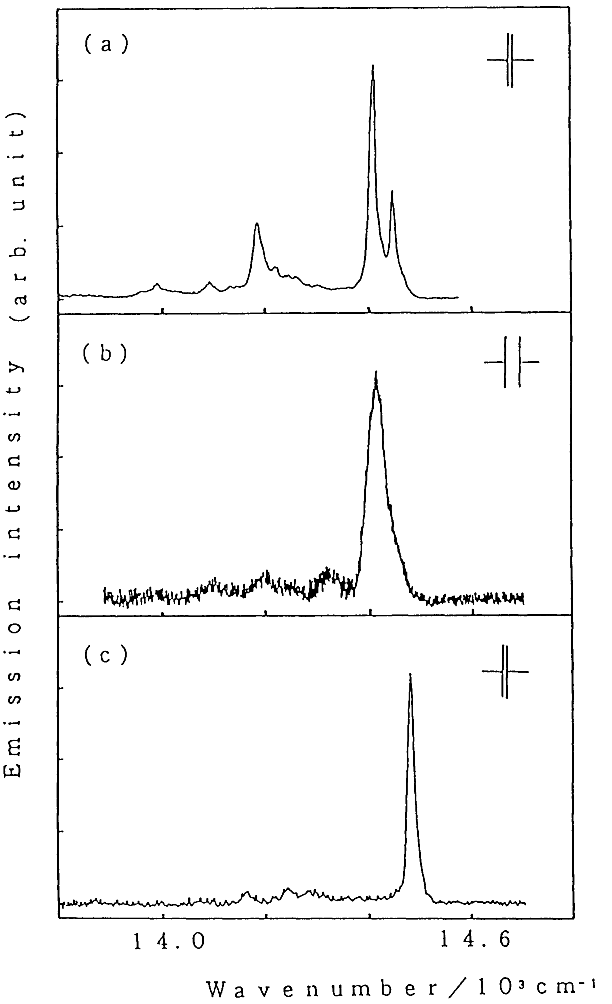

Fig. 7. Luminescence spectra of $Li_3[Cr(ox)_3]\cdot yH_2O$ powder crystal at 77 K: (a) the most hydrated crystal (y=6); (b) mono-dehydrated crystal (y=5); (c) further dehydrated crystal (y=3). Separation of two vertical lines shows the resolution of apparatus.

sphere around Cr^{3+} ion.

The Role of the Crystal Water on the $^2E_g \rightarrow ^4A_{2g}$ Relaxation in Lithium Salt. From TG analysis (see Table 3), the six water molecules in lithium salts are classified as three kinds of crystal water. One water molecule is the most subject to dehydration and removed at 23 °C. Another two waters are lost at 50 °C and last three at 93 °C.

The result of X-ray analysis of $Li_3[Cr(ox)_3]\cdot 6H_2O$ indicates that four crystal waters (O_w 1—3, 6) are tightly bound to counter cations (Li^+) while another two water molecules (O_w 4 and O_w 5) are not.

O_w 4 is surrounded by O_w 1, O_w 2, O_w 5, and an inner oxygen atom O 2 under distorted tetrahedral (Td) geometry, while O_w 5 is in Td geometry of neighboring molecules, O_w 3, O_w 3′, O_w 4, and inner oxygen atom O 5. Thus, the most-loosely bound water molecule is assigned to O_w 4 in $Li_3[Cr(ox)_3]\cdot 6H_2O$ because it suggests that O_w 5 is hydrogen-bonded to the neighboring molecules more rigidly than O_w 4.

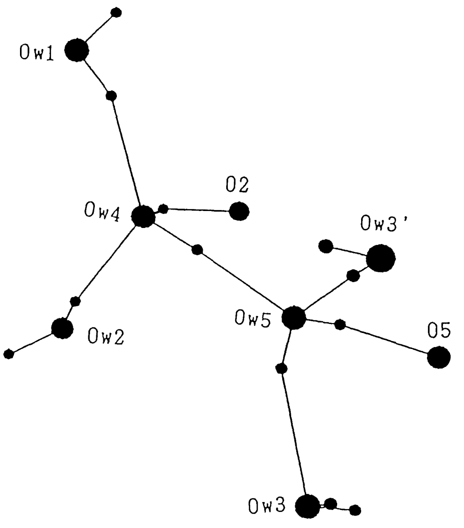

Fig. 8. Structure around the most-loosely packed water, O_w 4, in Li_3 $[Cr(ox)_3]\cdot 6H_2O$, where small circules indicate hydrogen atoms of crystal waters.

The distances between water molecules and their neighboring inner oxygen atoms are 2.866 Å (O_w 5–O 5), 2.875 Å (O_w 4–O 2), 2.876 Å (O_w 3–O 3) and 2.943 Å (O_w 2–O 2), respectively (Table 4). No water molecule is placed at a short distance from the inner oxygen atoms such as O_w 5 in the sodium salt (site-A 2.840 Å, site-B 2.759 Å). Therefore, $Li_3[Cr(ox)_3]\cdot 6H_2O$ emits very strongly. This situation is similar to that of $Na_3[Cr(ox)_3]\cdot 4H_2O$.

In lithium salt, the most-loosely bound water molecule, O_w 4, is surrounded by O_w 1, O_w 2, O_w 5, and an inner oxygen atom O 2. This is shown in Fig. 8. O_w 5 is in almost tetrahedron. On dehydration of O_w 4, O_w 5 which is not bound to counter cation (Li^+) should be moved toward O 5 because O_w 5 is hydrogen-bonded to O_w 4 and O 5, and O_w 4 is located opposite of O 5. Mono-dehydration results in a shortened distance between O 5 and O_w 5. Therefore, O_w 5 reduces emission intensity in mono-dehydrated compound.

Concluding Remarks

The results from luminescence and absorption spectra, TG and X-ray crystallographic analyses and luminescence lifetimes show that the relaxation processes from ^2E_g state in the crystals of $[Cr(ox)_3]^{3-}$ complexes are affected by the specific water molecules which are located near the oxygen atoms, coordinated to Cr^{3+} ion, of oxalato molecules. From the present work, it is suggested that the water molecules within 2.80 Å, which is double length of Pauling's ionic radius of oxygen ion (1.40 Å), from inner oxygen atoms ((O_w–O)<2.80 Å) are good quenchers; while the water molecules outside 2.87 Å from the inner oxygen atoms scarcely affect the relaxation processes. Based on this view, no luminescence of $K_3[Cr(ox)_3]\cdot 3H_2O$ results because two crystal water molecules exist very near the inner oxygen atoms as shown in Table 6.

Since the water molecules are hydrogen-bonded to inner oxygen atoms, O–H stretching vibration of crystal water molecule should be an effective accepting mode. This inference needs to be demonstrated through deuteration of the crystal water. Unfortunately, the most-loosely packed water molecule which greatly affects the relaxation processes is very rapidly exchanged for water molecules in atmosphere. Thus, the deuterated effects can not be reported in this paper.

The results that complex distortion enhances nonradiative decay have been reported.[17,70–73] Certainly, our results appear to follow the "distortion rule" about the most hydrated crystals of lithium, sodium and potassium salt as shown in Fig. 1. According to the results of mono-dehydration, however, the crystal waters affect the relaxation processes more greatly than the complex distortion.

In $[Cr(ox)_3]^{3-}$ complexes, there is no correlation between Cr–Cr distance and luminescence intensity, since the Cr–Cr distances are 6.734, 6.596, and 6.975 Å in lithium, sodium, and potassium salts, respectively, however, luminescence intensity in the salts is in the order of lithium salt>sodium salt>potassium salt.

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