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Preparation of μ-Cyano Dinuclear Chromium(III) Complexes $M^I[F(en\ or\ tn)_2Cr(NC)Cr(CN)_5]$ from the Doubly Complexed Salts of the Form $M^I[CrF(H_2O)(en\ or\ tn)_2][Cr(Cn)_6]$

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Preparation of the μ-cyano dinuclear complexes $M^I[F(en\ or\ tn)_2Cr(NC)Cr(CN)_5]\cdot nH_2O$ from the double complexes $M^I[CrF(H_2O)(en\ or\ tn)_2][Cr(CN)_6]\cdot nH_2O$ was carried out both in the solid state and in solution, where M^I is Li^+, Na^+, K^+, or Rb^+ ion; en and tn stand for 1,2-ethanediamine and 1,3-propanediamine, respectively. The desired μ-cyano dinuclear complexes were successfully obtained in solution, but the mixture of di- and trinuclear complexes was formed along with unknown polymeric species in the solid state. The electronic spectra of the dinuclear complexes exhibited a small but clear band due to spin-forbidden transition ($^4A_{2g}\rightarrow{}^2E_g$). Magnetic moments of the dinuclear complexes were 3.4—3.5 μ_B at ambient temperatures and 2.2—2.4 μ_B at 80 K, which are substantially smaller than the spin-only value (3.87 B.M.). The J values for the dinuclear complexes were estimated to be -19—-20 cm^{-1}, indicating that an antiferromagnetic superexchange interaction is exerted between two chromium(III) ions through μ-CN group, but the magnitude of the interaction is smaller than that of the μ-oxo complexes ($J=-450$ cm^{-1}) and comparable to that of the μ-hydroxo complexes ($J=-23$ cm^{-1}) reported previously.

Several magnetic studies have declared that a superexchange interaction is exerted in the dinuclear chromium(III) complexes containing μ-hydroxo,[1—10] μ-oxo,[1,11—15] and μ-alkoxo[16,17] groups: e.g., $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Br_5$[5,6] and $[(NH_3)_5Cr(O)Cr(NH_3)_5]Br_4$[11] give the magnetic moments of 3.44 (294.5 K) and 1.29 μ_B (294.7 K) respectively, which are considerably lower magnetic moments than that expected from the spin-only value for the chromium(III) ion. The J values for the μ-hydroxo[5,6] and μ-oxo[11] complexes have been evaluated as -23 and -450 cm^{-1}, respectively. Earnshaw and Lewis[1] have pointed out from magnetic studies on the analogues of the above dinuclear complexes that the degree of metal-metal interaction depends upon the nature of the bridging group and markedly upon the M-L-M′ bond angle: The greater the bonding ability of the bridging groups and the larger the M-L-M′ bond angle is, the stronger the metal-metal interaction becomes (M and M′ are the same or different metal ions, and L is the bridging ligand). From this point of view, the dinuclear chromium(III) complexes containing a single μ-cyano group are another interesting candidates for examining magnetic interaction between two metal ions because Cr(III)-CN-Cr(III) is linear. Unfortunately, although polymeric μ-cyano complexes have been reported,[18,19] any dinuclear chromium(III) complex with a single μ-cyano group has not been known except for $K[F(en)_2Cr(NC)Cr(CN)_5]$ reported by Ribas et al.[20,21] Very recently, we derived the same complex from $K[CrF(H_2O)(en)_2][Cr(CN)_6]$ in solution, and found that our complex exhibits astonishingly different physicochemical properties from that reported previously.[20,21] For example, the magnetic moments of our complex were 3.40 μ_B at 300 K and 2.22 μ_B at 80 K, whereas those of the previous complex were 3.79 μ_B at 293.5 K and 3.51 μ_B at 77 K.[20] Thus, we suspected that the previous complex is not a dinuclear complex, but simply a doubly complexed salt $K[CrF(H_2O)(en)_2][Cr(CN)_6]$.

Therefore, the present paper was undertaken (1) to prepare a series of the dinuclear chromium(III) complexes with a single μ-cyano group $M^I[F(en\ or\ tn)_2Cr(NC)Cr(CN)_5]$ from the double complexes $M^I[CrF(H_2O)(en\ or\ tn)_2][Cr(CN)_6]$, where M^I is Li^+, Na^+, K^+, or Rb^+; en and tn stand for 1,2-ethanediamine and 1,3-propanediamine, respectively, and (2) to examine physicochemical properties of the complexes especially from the view point of a superexchange interaction exerted between two chromium(III) ions through a μ-cyano group.

Experimental

Preparation of the Starting Materials for Obtaining Double Complexes. $K_3[Cr(CN)_6]$[22] and *trans*-$[CrF(H_2O)(en)_2](ClO_4)_2$[23a] were prepared by the same methods as those described in the literature.

trans-$[CrF(H_2O)(tn)_2](ClO_4)_2$ was obtained from *trans*-$[CrF_2(py)_4]ClO_4$ (py: pyridine)[24] as follows: *trans*-$[CrF_2(py)_4]ClO_4$ (20 mmol) and 1,3-propanediamine (40 mmol) were dissolved in 2-methoxyethanol (80 cm^3). The solution was refluxed for 1 h and cooled to room temperature. Products thus obtained were collected by filtration, washed with ethanol and ether, and air-dried. Purification of the products was carried out by dissolving them in water and adding a mixture of ethanol and ether (1 : 1) to the solution.

Preparation of Double Complexes. *trans*-$K[CrF(H_2O)(en\ or\ tn)_2][Cr(CN)_6]\cdot H_2O$. *trans*-$[CrF(H_2O)(en\ or\ tn)_2](ClO_4)_2$ (25 mmol) was dissolved in ice-cooled water (100 cm^3), to which $K_3[Cr(CN)_6]$ (25 mmol) was added with stirring. After several minutes, the $KClO_4$ which formed was removed by filtration. To the filtrate was added ethanol (100 cm^3) to give products, which were collected by filtration, washed with ethanol and ether, and air-dried. The products were purified by dissolving them in a minimum amount of ice-cooled

Table 1. Analytical Data and Molar Conductivities (Λ) of the Double and the Dinuclear Complexes Obtained

Complex	C(%) Found	C(%) Calcd	H(%) Found	H(%) Calcd	N(%) Found	N(%) Calcd	Λ/Ω^{-1} cm^2 cm^{-1}
Double complexes							
trans-$Li[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot2H_2O$	26.05	26.09	4.89	4.38	30.36	30.43	285
trans-$Na[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	26.29	26.21	4.53	4.40	30.65	30.56	272
trans-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	25.84	25.32	4.05	4.25	29.82	29.52	282
trans-$Rb[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	23.21	23.06	3.92	3.87	27.01	26.89	311
trans-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$	28.71	28.68	4.85	4.81	27.76	27.88	341
Dinuclear complexes							
$Li[F(en)_2Cr(NC)Cr(CN)_5]\cdot4.5H_2O$	24.61	24.65	5.19	5.17	28.93	28.74	95
$Na[F(en)_2Cr(NC)Cr(CN)_5]\cdot1.5H_2O$	26.85	26.73	4.37	4.26	31.31	31.17	123
$K[F(en)_2Cr(NC)Cr(CN)_5]\cdot1.5H_2O$	25.92	25.83	4.21	4.11	30.26	30.12	130
$Rb[F(en)_2Cr(NC)Cr(CN)_5]\cdot1.5H_2O$	23.49	23.47	3.88	3.74	27.38	27.37	112
$K[F(tn)_2Cr(NC)Cr(CN)_5]\cdot1.5H_2O$	29.38	29.21	4.66	4.70	28.56	28.38	102

water and adding ethanol to the solution.

***trans*-$Li[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot2H_2O$ and *trans*-$Na[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$.** $K_3[Cr(CN)_6]$ (25 mmol) was dissolved in a minimum amount of water (100 cm^3) and thereto excess $LiClO_4$ or $NaClO_4$ (125 mmol) was added. The solution was stirred for 5 min. The $KClO_4$ thus formed was filtered off. To the filtrate, *tans*-$[CrF(H_2O)(en)_2](ClO_4)_2$ (25 mmol) was added. The solution was once filtered and thereto ethanol (100 cm^3) was added with stirring to produce precipitates. The precipitates were collected by filtration, washed with ethanol and acetone, and air-dried. Purification was carried out in a manner similar to that of *trans*-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$.

***trans*-$Rb[CrF(H_2O)en_2][Cr(CN)_6]\cdot H_2O$.** $K_3[Cr(CN)_6]$ (25 mmol) was added to a solution of *trans*-$[CrF(H_2O)(en)_2](ClO_4)_2$ (25 mmol) in ice-cooled water (100 cm^3). The solution was allowed to stand for several minutes to precipitate $KClO_4$. After the $KClO_4$ was removed out by filtration, RbCl (50 mmol) was added to the filtrate. To the resulting solution, ethanol (100 cm^3) was added with stirring to produce precipitates. The precipitates were collected by filtration, washed with ethanol and acetone, and air-dried. Purfication was carried out by the same method as that of *trans*-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$.

Preparation of Dinuclear Complexes from Double Complexes in Water. The double complexes *trans*-$M^I[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot nH_2O$ (M^I: Li^+, Na^+, K^+, or Rb^+) (5.0 g) were dissolved in a minimum amount of water (10 cm^3) and the resulting solution was warmed for 30 min at 45—50 °C. The solution was once filtered and the filtrate was cooled at 0 °C to produce crude dinuclear complexes. The crude complexes were recrystallized from water. $K[F(tn)_2Cr(NC)Cr(CN)_5]\cdot1.5H_2O$ was similarly prepared except that *trans*-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$ was used in place of $M[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot nH_2O$.

The double complexes are in general pink in color, while the dinuclear complexes are orange. The analytical data of the complexes obtained are summarized in Table 1 together with the molar conductivities measured in water of the complexes.

Spectral Measurements. The IR spectra of samples were measured by a KBr-disk method with a Jasco Model A-3 infrared spectrophotometer. Visible and UV spectra in water were measured with a Jasco UVIDEC-505 UV/VIS recording digital spectrophotometer. The spectra in the solid state were measured by a diffuse reflectance methed with a Jasco UVIDEC-410 UV/VIS spectrophotometer equipped with a Jasco Model TIS-241 reflectance attachment.

Molar Conductivity Measurements. Molar conductivities of the complexes were measured in water at 25 °C on a Toa CM-20S conductivity meter at a concentration of 10^{-3} mol dm^{-3}.

Magnetic Measurements. The effective magnetic moments of samples were evaluated from magnetic susceptibilities measured by Gouy method at room temperature. $Hg[Co(NCS)_4]$ was employed as a susceptibility standard in all cases. Variable-temperature(78—300 K) magnetic susceptibilities were monitored on a Shimadzu torsion magnetometer MB-2 which was calibrated with $Hg[Co(NCS)_4]$. Diamagnetic correction was made by using Pascal's constants.

TG and DTA Measurements. The TG and DTA measurements for samples were carried out with a Seiko TA Station SSC 5000 system under a constant flow of nitrogen (100 cm^3 min^{-1}), sample weight being in the range of 10—20 mg. Heating rate was 2.0 °C min^{-1}. Heating processes were also observed by using a Chyo 100-L thermobalance.

Results

For clarification of the following discussion, the double complexes *trans*-$M^I[CrF(H_2O)(en\text{ or }tn)_2][Cr(CN)_6]$ and the dinuclear complexes $M^I[F(en\text{ or }tn)_2Cr(NC)Cr(CN)_5]$will be simply abbreviated as M(en or tn)[Cr][Cr] and M(en or tn)[Cr–Cr]. The first and second products stand for the products formed at the temperature of the first and second plateaus during the thermal reactions of the double complexes, respectively.

Molar Conductivities. The values for molar conductivities of the complexes are given in the last column of Table 1. The values of the double and the dinuclear comlexes are in the range of 272—341 and 95—130 Ω^{-1}cm^2 mol^{-1}, indicating that the double and the dinuclear complexes are 2:1 and 1:1 electrolytes, respectively.[25)]

Thermal Reactions of the Double Complexes in the Solid State. The thermal reactions of the double complexes were observed in the solid state by means of TG and DTA methods. As an example, Fig. 1 shows the TG and DTA curves of *trans*-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$ and *trans*-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$. The TG curve of the complex K(en)[Cr][Cr] shows two steps of the mass losses at 25—162 °C. The first mass loss starts at about 25 °C endothermically. Then, a break point appears at about 52 °C, after which a smooth plateau is obtained at 52—110 °C. The second mass loss takes place at 110—162 °C, the second plateau being obtained at 162—210 °C. The first and second mass losses correspond to the losses of one mole of lattice water (Found: 3.8%; Calcd: 3.8%), and one mole of coordinated water (Found: 3.7%; Calcd: 3.8%). The original pink color remained unchanged at the first plateau and changed to orange at the second plateau. Similar TG and DTA patterns can be seen for the complex K(tn)[Cr][Cr]. The complex turned in color from the original pink to orange at the second plateau. The color change is due to the formation of the dinuclear complex K(en or tn)[Cr–Cr] along with minor polynuclear species as mentioned later. Table 2 lists up the temperatures and enthalpy changes (ΔH) for the evolution of lattice and coordinated waters of the double complexes. The ΔH's for the evolution of coordinated waters are greater than those for those of lattice water for all the double complexes.

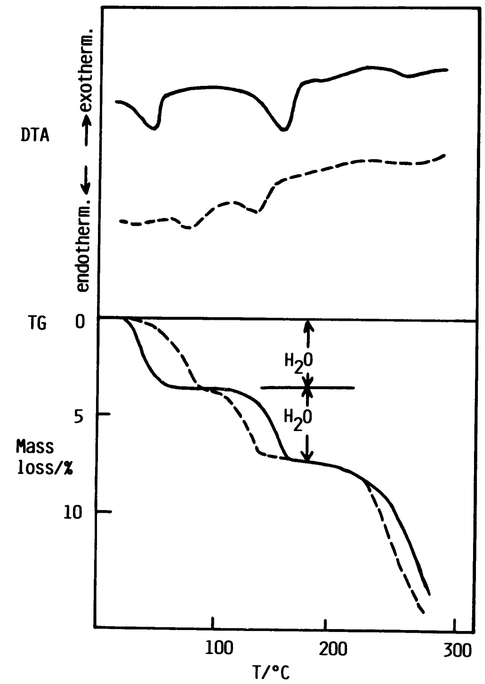

Fig. 1. TG and DTA curves of *trans*-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$ (——) and *trans*-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$ (------).

IR Spectra. Table 3 summarizes the IR data due to CN stretching vibration. As seen from the table, all the double complexes give a single peak at 2130—2138 cm^{-1}, which is assignable to the terminal CN stretching vibration of $[Cr(CN)_6]^{3-}$ (2135 cm^{-1}). On the other hand, the dinuclear complexes indicate two peaks at 2130—2138 and 2160—2170 cm^{-1}; the former is due to the terminal CN stretching and the latter is attributable to the bridging CN stretching vibration.[26] The first products show only terminal-CN stretching band, whereas the second products, both terminal- and bridging-CN stretching bands.

Electronic Spectra. The electronic spectral data of the double and the dinuclear complexes in water are listed in Table 4 together with those of the reference complexes *trans*-$[CrF(H_2O)(\text{en or tn})_2](ClO_4)_2$ and $K_3[Cr(CN)_6]$. On the other hand, the electronic spectral data in the solid state are summarized in Table 5 which also includes the data of the second products obtained by heating the double complexes M(en or tn)[Cr][Cr]. Figure 2 shows the electronic spectra in water of *trans*-$[CrF(H_2O)(en)_2](ClO_4)_2$, $K_3[Cr(CN)_6]$, the double complex K(en)[Cr][Cr] and the dinuclear complex K(en)[Cr–Cr]. The spectrum of the double complex K(en)[Cr][Cr] exhibits four bands at 505, 451, 376, and 307 nm. The bands at 505 and 451 nm are due to the components of the first band of the cationic moiety *trans*-$[CrF(H_2O)(en)_2]^{2+}$. The band at 376 nm may be the mixture of the second band (370 nm) of *trans*-$[CrF(H_2O)(en)_2]^{2+}$ and the first band (377 nm) of $[Cr(CN)_6]^{3-}$. The last band at 307 nm is assignable to the second band of $[Cr(CN)_6]^{3-}$. On the other hand, in the spectrum of the dinuclear complex K(en)[Cr–Cr], three bands can be seen at 677, 492, and 372 nm; the small but clear band at 677 nm ($\varepsilon = \approx 5$) comes from spin-forbidden transition ($^4A_{2g} \rightarrow$

Table 2. Temperatures and Enthalpy Changes (ΔH) for the Evolution of Lattice and Coordinated Waters of the Double Complexes *trans*-$M^I[CrF(H_2O)(\text{en or tn})_2][Cr(CN)_6]\cdot nH_2O$

Complex	Lattice water		Coordinated water	
	Temperature/°C	ΔH/kJ mol^{-1}	Temperature/°C	ΔH/kJ mol^{-1}
trans-$Li[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$	40—116	40.7	116—166	51.5
trans-$Na[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	20— 70	41.1	115—165	52.7
trans-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	25— 52	38.6	130—162	73.7
trans-$Rb[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	40— 90	43.0	117—150	55.4
trans-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$	30— 90	51.8	95—146	68.2

Table 3. IR Spectral Data (cm^{-1}) Due to the CN-Stretching Vibration (ν_{CN})

Compound[a]	Terminal-CN bands	Bridging-CN bands
$K_3[Cr(CN)_6]$	2135	—
trans-$Li[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$	2138	—
first product	2138	—
second product	2138	2167
$Li[F(en)_2Cr(NC)Cr(CN)_5]\cdot 4.5H_2O$	2138	2166
trans-$Na[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	2133	—
first product	2135	—
second product	2133	2162
$Na[F(en)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	2133	2160
trans-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	2130	—
first product	2130	—
second product	2130	2165
$K[F(en)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	2130	2165
trans-$Rb[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$	2130	—
first product	2130	—
second product	2128	2162
$Rb[F(en)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	2130	2170
trans-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$	2134	—
first product	2134	—
second product	2134	2165
$K[F(tn)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	2132	2166

a) The first and second products are the products obtained at the first and second plateaus during the thermal reactions of the double complexes, respectively.

Table 4. Electronic Spectral Data in Water

Complex	λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})[a]				
Reference complex					
trans-$[CrF(H_2O)(en)_2](ClO_4)_2$[23a)]		520(24.2)	458(25.6)	370(31.2)	
trans-$[CrF(H_2O)(tn)_2](ClO_4)_2$[23b)]		533(20.9)	460(22.4)	375(37.8)	
$K_3[Cr(CN)_6]$[22)]				377(85.9)	307(59.5)
Double complex					
trans-$Li[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$		515sh(28)	452sh(32)	377(121)	307(77)
trans-$Na[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$		513sh(39)	451sh(41)	377(135)	307(94)
trans-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$		505sh(33)	451sh(37)	376(128)	307(82)
trans-$Rb[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$		510sh(31)	450sh(36)	377(129)	307(86)
trans-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$		530sh(27)	453sh(30)	376(128)	307(66)
Dinuclear complex					
$Li[F(en)_2Cr(CN)Cr(CN)_5]\cdot 4.5H_2O$	677(≈5)[b)]	490(50)		370(155)	
$Na[F(en)_2Cr(CN)Cr(CN)_5]\cdot 1.5H_2O$	677(≈5)[b)]	490(46)		371(150)	
$K[F(en)_2Cr(CN)Cr(CN)_5]\cdot 1.5H_2O$	677(≈5)[b)]	492(46)		372(147)	
$Rb[F(en)_2Cr(CN)Cr(CN)_5]\cdot 1.5H_2O$	677(≈5)[b)]	491(49)		371(156)	
$K[F(tn)_2Cr(CN)Cr(CN)_5]\cdot 1.5H_2O$	677(≈5)[b)]	499(43)		370(154)	

a) Measured in water. b) Spin-forbidden transition ($^4A_{2g}\rightarrow{}^2E_g$).

^2E_g).[27–29)] Other two bands at 492 and 372 may be due to spin-allowed transition $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$, respectively.

Figure 3 illustrates the electronic spectra in the solid state of the double complex K(en)[Cr][Cr], of the dinuclear complex K(en)[Cr–Cr], and of the second product obtained by heating the double complex K(en)[Cr][Cr]. The spectrum of the double complex gives five bands at 665, 520, 460 (sh), 380, and 307 nm (Table 5). The bands at 520 and 460 nm are due to the components of the first band of *trans*-$[CrF(H_2O)(en)_2]^{2+}$; the band at 380 nm is assignable to the mixture of the second band of *trans*-$[CrF(H_2O)(en)_2]^{2+}$ plus the first band of $[Cr(CN)_6]^{3-}$; and the band at 307 nm is the second band of $[Cr(CN)_6]^{3-}$. A tiny band can be seen at 665 nm, which may be due to spin-forbidden transition. The spectrum of the second product obtained by heating the double complex

Table 5. Electronic Spectral Data in the Solid State

Compound	λ_{max}/nm					
trans-Li[CrF(H_2O)(en)$_2$][Cr(CN)$_6$]·2H_2O	*665w	520		456	374	307
Second product[a]	*677w		490		374	
Li[F(en)$_2$Cr(NC)Cr(CN)$_5$]·4.5H_2O	*677s		494		374	
trans-Na[CrF(H_2O)(en)$_2$][Cr(CN)$_6$]·H_2O	*665w	520		460sh	379	309
Second product[b]	*677w		488		378	
Na[F(en)$_2$Cr(NC)Cr(CN)$_5$]·1.5H_2O	*677s		497		380	
trans-K[CrF(H_2O)(en)$_2$][Cr(CN)$_6$]·H_2O	*665w	520		460sh	380	307
Second product[c]	*677w		490		378	
K[F(en)$_2$Cr(NC)Cr(CN)$_5$]·1.5H_2O	*675s		490		370	
trans-Rb[CrF(H_2O)(en)$_2$][Cr(CN)$_6$]·H_2O	*665w	525		460sh	380	310
Second product[d]	*677w		490		378	
Rb[F(en)$_2$Cr(NC)Cr(CN)$_5$]·1.5H_2O	*680s		500		380	
trans-K[CrF(H_2O)(tn)$_2$][Cr(CN)$_6$]·H_2O	*668w	530	470		378	309
Second product[e]	*676w		499		374	
K[F(en)$_2$Cr(NC)Cr(CN)$_5$]·1.5H_2O	*678s		500		374	

* Spin-forbidden transition ($^4A_{2g} \rightarrow {}^2E_g$): w=week, s=strong. a to e): The products obtained by heating the corresponding double complexes in air bath for 2 h: a) at 175 °C, b) at 175 °C, c) at 165 °C, d) at 165 °C, and e) at 150 °C.

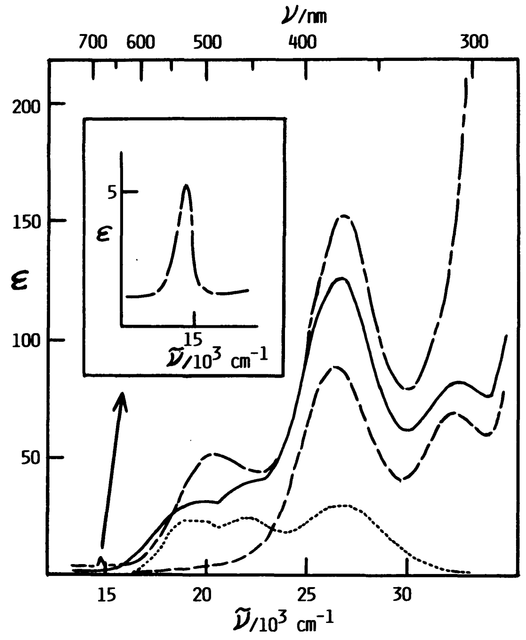

Fig. 2. Electronic spectra in water of *trans*-[CrF(H_2O)(en)$_2$](ClO$_4$)$_2$ (------), K$_3$[Cr(CN)$_6$] (– – – –), *trans*-K[CrF(H_2O)(en)$_2$][Cr(CN)$_6$]·H_2O (———), and K[F(en)$_2$Cr(NC)Cr(CN)$_5$]·1.5H_2O (— — —).

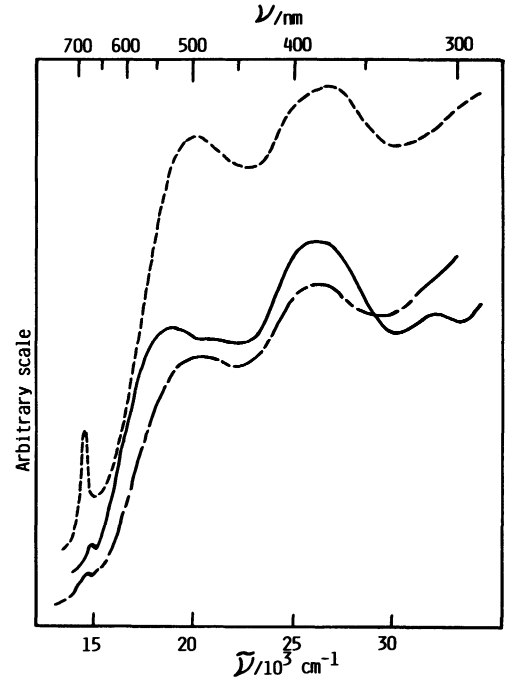

Fig. 3. Electronic spectra in the solid state of *trans*-K[CrF(H_2O)(en)$_2$][Cr(CN)$_6$]·H_2O (———), the product obtained by heating the double complex (— — —), and K[F(en)$_2$Cr(CN)Cr(CN)$_5$]·1.5H_2) (-----).

K(en)[Cr][Cr] is very similar to that of the dinuclear complex, but the spin-forbidden band at 677 nm is much smaller than that of the dinuclear complex. This implies that the product contains some species other than the dinuclear species (vide infra).

Magnetic Properties. Table 6 summarizes the effective magnetic moments (μ_{eff}) of the double complexes, of the second products obtained by heating the double complexes, and of the dinuclear complexes. As seen from the table, the μ_{eff}'s per a Cr(III) ion of all the double complexes are 3.81—3.89 B.M. at ambient temperatures, whereas those of the second products obtained by heating the double complexes are 3.40—3.67 B.M., and those of the dinuclear complexes are 3.31—3.47 B.M. In both cases of the second products and of the dinuclear complexes, the μ_{eff}'s are obviously reduced from the spin-only value and so it is

Table 6. Effective Magnetic Moment μ_{eff}, per a Chromium(III) Ion of Double Complexes, of Their Second Products by Heating Double Complexes, and of Dinuclear Complexes

Complex	μ_{eff}/B.M.	Temp/K
Double complex		
trans-$Li[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$	3.89	290
Second product[a]	3.42	289
trans-$Na[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$	3.81	298
Second product[b]	3.41	290
trans-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$	3.85	295
Second product[c]	3.43	300
	2.96	80
trans-$Rb[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$	3.89	292
Second product[d]	3.49	298
trans-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot 2H_2O$	3.84	289
Second product[e]	3.40	290
Dinuclear complex		
$Li[F(en)_2Cr(NC)Cr(CN)_5]\cdot 4.5H_2O$	3.47	290
$Na[F(en)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	3.31	286
$K[F(en)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	3.40	300
	2.22	80
$Rb[F(en)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	3.45	300
	2.28	80
$K[F(tn)_2Cr(NC)Cr(CN)_5]\cdot 1.5H_2O$	3.43	300
	2.44	80

a) Obtained by heating *trans*-$Li[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2H_2O$ at 175 °C for 2 h. b) Obtained by heating *trans*-$Na[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot 2.5H_2O$ at 175 °C for 2 h. c) Obtained by heating *trans*-$K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$ at 165 °C for 2 h. d) Obtained by heating *trans*-$Rb[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$ at 165 °C for 2 h. e) Obtained by heating *trans*-$K[CrF(H_2O)(tn)_2][Cr(CN)_6]\cdot H_2O$ at 150 °C for 2 h.

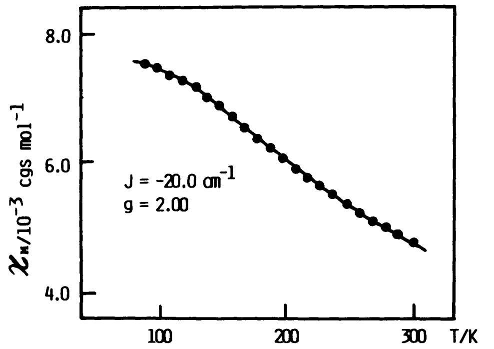

Fig. 4. Temperature dependence of magnetic susceptibilities of $K[F(en)_2Cr(CN)Cr(CN)_5]\cdot 1.5H_2O$.

conceivable that certain metal-metal interaction is exerted through the CN bridge.

The measurements of the magnetic susceptibilities in the temperature range of 80—300 K, however, indicated different results between the second product and the dinuclear complexes. The results were analyzed with the spin-spin interaction Hamiltonian, $H=-2JS_1\cdot S_2$. The molar susceptibility (χ_M) of an $S_1=S_2=3/2$ exchange coupling dimer is given by the following equation:

$$\chi_M = \frac{N\beta^2 g^2}{3\kappa T}\cdot\frac{3x^{10}+15x^6+42}{x^{12}+3x^{10}+5x^6+7}$$

where $x=\exp(-J/\kappa T)$ and the symbols have their usual meanings. The experimental values are well-interpreted in terms of the above equation as can be seen in Fig. 4. The solid line is a calculated curve by using the following parameters, $J=-20.0\ \mathrm{cm^{-1}}$ and $g=2.00$ for K(en)[Cr–Cr], indicating that an antiferromagnetic interaction is effected in the dinuclear complex. Such antiferromagnetic interaction was also observed in another dinuclear complex: $J=-19.0\ \mathrm{cm^{-1}}$ and $g=2.00$ for Rb(en)[Cr–Cr].

On the other hand, the magnetic properties of second product obtained by heating the double complex K(en)[Cr][Cr] were not explained by the above equation. This may be due to the presence of impure species (vide infra).

Discussion

Preparation of Dinuclear Complexes. Ribas et al. reported that the dinuclear complex $K[F(en)_2Cr(NC)Cr(CN)_5]\cdot 2H_2O$ is obtained by mixing *trans*-$[CrF(H_2O)(en)_2](ClO_4)_2$ with $K_3[Cr(CN)_6]$ in water-ice bath.[20,21] Our reexamination of the procedures always gave the pink double complex $K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$. On the other hand, we obtained the dinuclear complexes M(en or tn)[Cr–Cr] by heating the corresponding double complexes in water at 45—50 °C for about 30 min. Our dinuclear complexes are orange in color and have magnetic moments of 3.4—3.7 μ_B at room temperatures and 2.2—2.4 μ_B at 80 K, whereas the previously reported complex is pink in color and has magnetic moments of 3.79 μ_B at 293.5 K and 3.51 μ_B at 77.0 K. It seems reasonable to consider that the previous complex is not a dinuclear complex, but the double complex $K[CrF(H_2O)(en)_2][Cr(CN)_6]\cdot H_2O$.

Products Obtained by Heating the Double Complexes in the Solid State. The pinkish double complexes M(en or tn)[Cr][Cr], upon heating, evolved first lattice waters and then coordinated waters to convert into orange products (second products). From the results of TG and DTA analyses, the second products are seemingly conceivable to be dinuclear complexes. However, minute examination of the orange products revealed that the products are the mixture of di- and trinuclear complexes along with unknown polymeric species. This suggests that the thermal deaquation-anation of the double complexes in the solid state does not give pure dinuclear complexes.

Configuration of the Dinuclear Complexes. Two geometrical isomers (cis and trans) are possible for the dinuclear complexes $K[CrF(en\ or\ tn)_2Cr(NC)Cr(CN)_5]$ with respect to the positions of F^- ion and $-(NC)Cr(CN)_5$ moiety. It is difficult to accurately decide the geometrical configurations from electronic spectral data because both isomers are expected to give a similar spectrum to each other. In fact, it has been reported that both *cis*- and *trans*-$[CrF(NH_3)(en)_2]^{2+}$ exhibit close band maxima except for ε values because they have the same core ($CrFN_5$) and hence the same symmetry (C_{4v}).[30,31] However, we tentatively conclude that the dinuclear complexes in the present study are trans-configuration provided that trans-to-cis isomerization were not involved in the preparative procedures. Possibility of the isomerization can be completely discarded in the case of the tn complex because $[CrX_2(tn)_2]^+$ has been found to undergo cis-to-trans isomerization, but not trans-to-cis isomerization.[32] Comparison of the λ_{max}'s and ε's in Table 4 implies that both en and tn dinuclear complexes give essentially similar spectra except that the λ_{max}'s of the tn complex appear at longer wavelengths than those of the en complexes, which arises from the difference in ligand field strength of en and tn. Therefore, it seems reasonable to consider that the en dinuclear complexes also have trans-configuration.

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