Preparation and Ligand Field Absorption Spectra of $[CrF_2(O\text{-}O)_2]^{3-}$ and $[CrF_2(O\text{-}O)(en)]^-$ Type Complexes

Sumio KAIZAKI,* Mieko AKAHO(nee ASADA), Yasuyo MORITA, and Kuniko UNO
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

(Received December 15, 1980)

Two geometrical isomeric pairs of $[CrF_2(O\text{-}O)_2]^{3-}$ and either one of two possible geometrical isomers of $[CrF_2(O\text{-}O)(en)]^-$, where O–O denotes oxalate and malonate anions, were newly prepared and characterized by means of the spectral and chromatographic elution behaviors. It was found that $[CrF_2(ox)(en)]^-$ and $[CrF_2(mal)(en)]^-$ obtained take *cis* and *trans* forms, respectively. The ligand field absorption spectra of the present complexes were compared with one another, and with those of the corresponding aqua complexes of the same type. On the basis of the analyses of the absorption spectra in terms of the angular overlap model, the AOM parameters (e_σ and e_π) for the ligands concerned were estimated, and their transferability assumption and the anisotropic π interactions of Cr–O bonding with respect to the chelate plane of the dicarboxylate ligands were discussed.

There have been spectral as well as preparative studies on difluorochromium(III) complexes like *trans*-$[CrF_2(H_2O)_4]^+$ and *trans*-$[CrF_2(N)_4]^+$ type complexes.[1–4] Such complexes exhibit characteristic spectral pattern in the ligand field band region: significant splitting of the second band, which facilitates the application of the angular overlap model (AOM). These studies have been mainly concerned with linearly ligating ligands[5] such as saturated amines and halide ions, and with nonlinear ligators such as pyridine, but not with dicarboxylate chelates in which Cr–O bonding may be formed with different π-interactions vertical and parallel to the chelate planes besides with the σ-interactions.[5] The estimates of the AOM parameters for the dicarboxylate ligands provide a valuable clue to test the assumption of parameter transferability from one complex to another and to clarify the anisotropy of the Cr–O π-interactions with respect to the chelate planes. For this purpose, such high symmetry complexes as *trans*-$[CrF_2(O\text{-}O)_2]^{3-}$ and *trans*-$[CrF_2(O\text{-}O)(en)]^-$ with dicarboxylates are considered to be suitable as a simple model case, because their ligand field spectra are expected to give splitting patterns as observed for those of *trans*-difluoro chromium(III) complexes with aqua and/or ethylenediamine ligands. However, there has been known no such mixed difluorochromium(III) complex with dicarboxylates.

The present paper deals with the preparation and characterization of two geometrical isomers, *cis*- and *trans*-$[CrF_2(O\text{-}O)_2]^{3-}$, where O–O denotes oxalate and malonate ions, and those of *cis*-$[CrF_2(ox)(en)]^-$ and *trans*-$[CrF_2(mal)(en)]^-$. The spectral behavior in the ligand field band region of these complexes is explored in connection with that of the corresponding aqua complexes, $[CrF_2(H_2O)_4]^+$, $[CrF_2(en)(H_2O)_2]^+$, and $[Cr(ox)_2(H_2O)_2]^-$, and analyzed in terms of the AOM.

Experimental

Preparation of the Complexes. *(1)* cis- *and* trans-$[CrF_2(O\text{-}O)_2]^{3-}$: Five grams of *cis*-$K[Cr(ox)_2(H_2O)_2]\cdot 3H_2O$ and 0.86 g of potassium fluoride were dissolved in 300 cm³ of water in a polyethylene beaker. After the solution was heated at 60 °C on a water bath for about 6 h, the color of the solution changed from red violet to dark green. By adding the resultant solution to a large amount of methanol, pale green precipitate was obtained. An aqueous solution of this precipitate was poured onto a column (4×60 cm) of anion exchanger (QAE-Sephadex A-25), and the column was swept with water. When the adsorbed band was eluted with a 0.1 mol dm^{-3} sodium chloride solution, the column gave five bands. Of these bands, the four faster eluted bands (B-I, B-II, B-III, and B-IV) were found to be the complexes containing fluoride, oxalate ion, and water as ligands by the qualitative analyses in terms of zirconium alizarin paper tests for fluoride and potassium permanganate tests for oxalate, and by the fact that their first d-d absorption bands are shifted to the lower frequency by increasing in pH (*ca.* 10) of the eluate with a 0.1 mol dm^{-3} sodium hydroxide solution. Taking into account of these facts and the position of the first absorption band as well as the chromatographic elution behavior, three faster eluted bands (B-I, B-II, and B-III) may be three possible geometrical isomers of $[CrF_2(ox)(H_2O)_2]^-$ and two later eluted bands (B-IV and B-V) two possible isomers of $[CrF_3(ox)(H_2O)]^{2-}$ or $[CrF(ox)_2(H_2O)]^{2-}$. But their characterization was not attempted. When the fifth band(B-V) was eluted with a sodium chloride solution (0.2 mol dm^{-3} in the early stage of elution, and then 0.25 and 0.3 mol dm^{-3} successively in the later stage), three bands (B-V′, B-VI, and B-VII) were separated. The slowest eluate (B-VII) was confirmed to be tris(oxalato)chromate(III) ion from the absorption measurement. The remaining two bands (B-V′ and B-VI) were found to be complex ions containing only fluoride and oxalate ions as ligands, because the first d-d absorption band of these eluates shows no shift with increase in pH and the qualitative analyses indicate the presence of fluoride and oxalate ions in the complexes. The yield of the B-VI band was much smaller than that of the B-V′ one. After dilution with water, each eluate was loaded again on each column of QAE-Sephadex A-25. Each adsorbed band was eluted with a 1 mol dm^{-3} sodium chloride solution. To each eluate was added a large excess of barium perchlorate. Then green fine powder was obtained. Each barium salt was converted to methylammonium salt by a batchwise method with a cation exchange resin of $CH_3NH_3^+$ form (Dowex 50w×8) in water. The resultant green solutions were separately condensed by a vacuum rotatory evaporator at about 30 °C. By adding acetone and ethanol to each condensed solution, green solid was crystallized. Each green powder was recrystallized from water and acetone. Found for the B-VI: C, 23.21; H, 5.02; N, 11.60%. Calcd for $(CH_3NH_3)_3[CrF_2(ox)_2]$: C, 22.84; H, 5.05; N, 11.24%. Found for the B-V′: C, 21.41; H, 4.33; N, 7.65%. Calcd for $(CH_3NH_3)_3[CrF_2(ox)_2]\cdot C_3H_6O\cdot 2.25NaCl$ (C_3H_6O= acetone): C, 21.71; H, 4.38; N, 7.62%.

(2) cis- *and* trans-$[CrF_2(mal)_2]^{3-}$ *Complexes*: After dissolving

3.8 g of *cis*-K[Cr(mal)$_2$(H$_2$O)$_2$]·3H$_2$O and 1.2 g of potassium fluoride in 100 cm^3 of water in a polyethlene beaker, the solution was heated at 60 °C on a water bath for about 4 h. The resulting green solution was added to a large amount of methanol. Then pale green precipitate was obtained. An aqueous solution of this precipitate was poured onto a column (4×60 cm) of QAE-Sephadex A-25. After washing the column with water, the adsorbed band was eluted with a sodium chloride solution (0.1 mol dm^{-3} in the early stage of elution, and then 0.2 and 0.3 mol dm^{-3} successively in the later stage). The column gave eleven bands. From the elution behavior and the absorption spectral change with increase in pH, the b-I—b-VIII bands were found to be univalent or bivalent complex anions containing H$_2$O, F$^-$, and mal^{2-} as ligands. The slowest eluted band (b-XI) was confirmed to be [Cr(mal)$_3$]$^{3-}$ from the absorption measurements. The two remaining eluates (b-IX and b-X) were found to be the complexes with· only fluoride and malonate ions but not with water. After dilution of these eluates with water, they were reloaded on short columns of QAE-Sephadex A-25. After each column was washed well with a 0.01 mol dm^{-3} lithium chloride solution, each band was eluted with a 1.0 mol dm^{-3} lithium chloride solution. To the condensed solutions was added ethanol and acetone; then lithium salts being precipitated. Each green powder was recrystallized from water and acetone. Found for the b-IX: C, 19.41; H, 2.55%. Calcd for Li$_3$[CrF$_2$(mal)$_2$]·2.5H$_2$O: C, 20.02; H, 2.52%. Found for the b-X: C, 16.72; H, 2.20%. Calcd for Li$_3$[CrF$_2$(mal)$_2$]·3H$_2$O·1.5LiCl: C, 16.66; H, 2.33%.

The present oxalato and malonato complexes were also prepared from [CrF$_2$(H$_2$O)$_4$]NO$_3$, which was obtained by evaporating the reaction mixture of Cr(NO$_3$)$_3$·9H$_2$O with 40% hydrofluoric acid and formaldehyde.[2a]

(3) [CrF$_2$(en)(H$_2$O)$_2$]Br: This complex was used as a starting complex for the preparation of [CrF$_2$(O–O)(en)]$^-$ type complexes. The preparation of this complex was performed by the similar method to that of [CrF$_2$(pn)(H$_2$O)$_2$]-Br[7] except that ethylenediamine(en) was used instead of 1,2-propanediamine(pn). Found: C, 9.14; H, 4.67; N, 10.46%. Calcd for [CrF$_2$(en)(H$_2$O)$_2$]Br: C, 9.03; H, 4.55; N, 10.53%.

(4) [CrF$_2$(ox)(en)]$^-$: A solution containing 1.0 g of [CrF$_2$(en)(H$_2$O)$_2$]Br and 0.7 g of potassium oxalate monohydrate was heated at 60 °C on a water bath for 2.5 h. After cooling the reaction mixture, the solution was added to a large amount of methanol to form violet precipitate. This solid was filtered and dissolved again in a small amount of water. The resultant solution was poured onto a column of anion exchange resin (Dowex 1×8, Cl$^-$ form). The adsorbed band was washed with water and then eluted with a 0.05 mol dm^{-3} sodium chloride solution. The column gave three bands. The third eluate was confirmed to be [Cr(ox)$_2$(en)]$^-$ by the absorption measurement. The second band was proved to contain fluoride and oxalate ions but not water as ligands by means of the qualitative analyses for these ions and by the fact of no shift of the first band with increase in pH. This eluate was concentrated at about 25 °C by a vacuum rotatory evaporator. By adding methanol to the condensed solution, red violet crystals were obtained. Recrystallization was carried out from water and methanol several times. Found: C, 16.28; H, 3.48; N, 8.62%. Calcd for Na[CrF$_2$(ox)(en)]·0.75 H$_2$O·0.5 CH$_3$OH·0.6 NaCl: C, 16.60; H, 3.56; N, 8.60%.

(5) [CrF$_2$(mal)(en)]$^-$: This complex was prepared by the similar method to that of the corresponding oxalato complex as described in *(4)* except that potassium malonate was used in place of potassium oxalate. The sodium salt obtained was converted to lithium salt with a cation exchange resin (Dowex 50×8, Li$^+$ form) by a batchwise method. After concentrating the solution by a vacuum rotatory evapolator, red violet crystals were obtained by adding methanol and then cooling. Recrystallization was carried out from water and methanol. Found: C, 19.75; H, 4.97; N, 9.21%. Calcd for Li[CrF$_2$(mal)(en)]·2.5H$_2$O: C, 20.06; H, 5.00; N, 9.28%.

Measurements. Absorption spectra were obtained on a Shimadzu UV-200S spectrophotometer. Diffuse reflectance spectrum was measured by a Hitachi EPS-3T spectrophotometer with a reflectometer. CD curves were recorded on a JASCO MOE-1 spectropolarimeter, and infrared spectra on a JASCO DS-402G spectrophotometer.

Calculations. Computer programs for the calculations of the transition energies of the d-d bands and for the Gaussian analyses of the observed curves were based on the programs (AOM/2 and LGNCD) already obtained. The calculations were carried out by a FACOM 230-28 at the Nara Women's University.

Results and Discussion

Characterization. *1) [CrF$_2$(O–O)$_2$]$^{3-}$ Complexes*: In view of the chromatographic elution behavior and the absorption spectra as well as the elemental analyses for each pair of the oxalato (B-V′ and B-VI) and the malonato (b-IX and b-X) complexes, each of them corresponds to the geometrical isomeric pair with the same chemical composition. The first absorption bands of [CrF$_2$(O–O)$_2$]$^{3-}$ are observed near the positions predicted by the average of environment.[8] In such cases, it is empirically expected[9] that the first absorption band of *trans*-[CrF$_2$(O–O)$_2$]$^{3-}$ locates at the lower frequency side than that of *cis*-[CrF$_2$(O–O)$_2$]$^{3-}$, because the ligand fluoride lies below the ligands oxalate and malonate in the spectrochemical series.[8] Since the B-V′ isomer of the present oxalato complexes gives the first band at the lower frequency side than the B-VI one as shown in Fig. 1, the former and the latter isomers may be assigned to *trans* and *cis* forms, respectively. This assignment is confirmed by the fact that the elution order of the ion exchange chromatography agrees with that generally recognized for *cis* and *trans* geometrical

Fig. 1. Absorption curves of (a) *cis*-[CrF$_2$(ox)$_2$]$^{3-}$ (——), (b) *trans*-[CrF$_2$(ox)$_2$]$^{3-}$ (----) (left side ordinate), (c) *cis*-[CrF$_2$(mal)$_2$]$^{3-}$ (——), and (d) *trans*-[CrF$_2$(mal)$_2$]$^{3-}$ (----) (right side ordinate) in water.

isomers of $[MX_2L_4]$ type complexes,[10] and also supported by the fact that the B-VI (*cis*) isomer is found to have larger molar absorption coefficients of the d-d bands than the B-V′ (*trans*) one (Fig. 1) as noticed in the cases of $[Cr(CN)_2(en)_2]^+$[11] and $[Cr(NCS)_2(en)_2]^+$.[12] Further, the validity of this assignment is justified by the CD behavior in the first band region of these complexes in solutions containing chiral environmental substances as is applied to the structural assignments of $[SnCl_2(acac)_2]$ and the related complexes in *d*-malic acid systems.[13] That is, when the complexes at about 5×10^{-3} mol dm^{-3} in a mixture of water and acetone (1 : 1) containing *d*-cinchonine hydrochloride (15×10^{-3} mol dm^{-3}) were allowed to stand for about half an hour, the intensity of the CD extremum of the B-VI isomer in this region ($\Delta\varepsilon=+0.02$ mol^{-1} dm^{-3} cm^{-1} at 17750 cm^{-1}) is found to be much larger than that of the B-V′ isomer and to be as large as that of $[Cr(ox)_3]^{3-}$ in the analogous condition.[14] Since most bis(oxalato)-chromate(III) complexes are found to undergo rapid racemization,[15] the present complexes are expected to exhibit the CD associated with the enrichment of one enantiomer in terms of the so-called Pfeiffer effect. Thus, it appears that the B-VI isomer is a racemic mixture consisting of enantiomers with configurational chirality due to *cis* arrangement of two fluoride ions, and that the B-V′ isomer takes achiral configuration owing to *trans* coordination of two fluoride ions.

The corresponding malonato complexes show somewhat different spectral behavior from the oxalato complexes; the first absorption band of the faster eluted b-IX isomer was observed at a slightly higher frequency than that of the slower eluted b-X isomer. As shown in Fig. 1, the difference between the first band position of the b-IX isomer and that of the b-X one is too small to offer an any reliable clue for the assignment of the geometrical structures. The elution behavior on the column chromatography and the absorption intensities of the d-d bands seem to be more reliable for the structural assignments. As shown in Fig. 1, on the basis of these criterions, the b-IX and b-X isomers are to be assigned to *trans* and *cis* forms, respectively. This assignment is also supported by the CD behavior in a mixture of water and acetone containing *d*-cinchonine hydrochloride as in the case of the corresponding oxalato complexes. That is, the b-X (*cis*) isomer in such a solution gives a much stronger CD peak ($\Delta\varepsilon=+0.01$ mol^{-1} dm^3 cm^{-1} at 16880 cm^{-1}), probably due to the Pfeiffer effect, than the b-IX (*trans*) isomer. The infrared spectra of the malonato complexes may provide another clue for the assignment of the geometrical structure. Three infrared bands are observed at 1620, 1695, and 1720 cm^{-1} for the b-X isomer and only one at 1615 cm^{-1} for the b-IX isomer in the region of C=O asymmetric stretching as is observed for the corresponding diaquabis(malonato)chromate(III) complexes; *i.e.*, three components for the *cis*-isomer and one component for the *trans*-isomer. Such a difference in the number of the observed bands between the geometrical isomers of the malonato complexes may be mainly ascribed to the difference in symmetry of the complexes. Thus, these infrared spectral behavior of the malonato complexes confirms the assignment on the basis of the chromatographic elution orders, the molar absorption coefficients, and the Pfeiffer CD.

2) $[CrF_2(O-O)(en)]^-$ Complexes: For each of the oxalato and malonato complexes of this type, only one of two possible geometrical isomers could be isolated. The d-d absorption spectrum of the oxalato complex is symmetrical in shape and shows no splitting, whereas that of the malonato complex is of asymmetric shape and exhibits a shoulder at the higher frequency side for the first band and at the lower frequency side for the second band, as shown in Fig. 2. According to the Yamatera's rule,[16] it is suggested that the oxalato and malonato complexes take *cis* and *trans* forms, respectively. That is, it is predicted that the orbitally doubly degenerate and nondegenerate components of the $^4T_{2g}$ splitting states locate at 17390 and 19720 cm^{-1}, respectively, by using $10Dq(en)=21900$ cm^{-1}, $10Dq(F^-)=15050$ cm^{-1}, and $10Dq(mal^{2-})=17670$ cm^{-1}. These predicted transition energies lie close to the peaks and near the shoulder observed for $[CrF_2(mal)(en)]^-$. For the *cis* form, three splitting components are predicted to locate at 19100, 18100, and 17390 cm^{-1}. This splitting interval and the positions obtained may account for the observed symmetric pattern and the maximum of the first band for the oxalato complex (Fig. 2). In addition, this assignment may be confirmed by the solvent effect on the absorption spectra of these complexes. The second absorption band of *trans*-$[CrF_2(en)_2]^+$ in *N*-methylformamide (nmf) is more distinctly resolved into two components than that in water, and the corresponding *cis*-isomer gives almost unaltered behavior in these solvents. The present oxalato and malonato complexes exhibit the similar spectral behavior in water and nmf. The second band of the *trans*-difluoro malonato complex in nmf is more remarkably split than that in water, while that of the *cis*-difluoro oxalato complex remains unchanged.

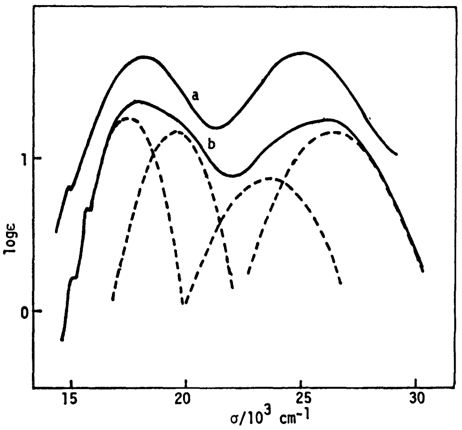

Fig. 2. Absorption curves of (a) *cis*-$[CrF_2(ox)(en)]^+$ and (b) *trans*-$[CrF_2(mal)(en)]^+$ in water, and the resolved curves of the latter complex (----) using the Gaussian analysis.

Assuming that $[CrF_2(en)(H_2O)_2]^+$ takes *trans*(F) form as mentioned below, the formation of the malonato complex seems to take place with retention of configuration, but the oxalato complex may be formed with conversion to *cis* configuration.

Ligand Field Absorption Bands. In spite of the fact that the ligand malonate lies at the higher position than the ligand fluoride in the spectrochemical series as in the case of the ligand oxalate,[8)] the first absorption band of *trans*-$[CrF_2(mal)_2]^{3-}$ locates at the higher frequency side than that of the *cis* one; *i.e.*, contrary to the empirical prediction,[9)] which is valid for the corresponding oxalato complexes as mentioned before. It is noted that the ligand field band of the malonato complexes behaves unlike that of the oxalato complexes to some significant degree. Such a difference in the ligand field band between the malonato and oxalato complexes is not observed for the absorption spectra of $[Cr(O\text{-}O)_n(en)_{3-n}]^{3-2n}$ type complexes; *e.g.*, the first band being observed at 20170 cm^{-1} for both $[Cr(ox)(en)_2]^+$ and $[Cr(mal)en)_2]^+$, at 18830 cm^{-1} for both $[Cr(ox)_2(en)]^-$ and $[Cr(mal)_2(en)]^-$, and at 17500 and 17670 cm^{-1} for $[Cr(ox)_3]^{3-}$ and $[Cr(mal)_3]^{3-}$, respectively. It is interesting to note that both the first and the second bands of the present dicarboxylato complexes are compared with those of the corresponding aqua complexes of the same types; *i.e.*, $[CrF_2(H_2O)_4]^+$, $[CrF_2(en)(H_2O)_2]^+$, and $[Cr(ox)_2(H_2O)_2]^-$. The absorption spectrum of *trans*-$[CrF_2(H_2O)_4]^+$ reported by Chia and King[1)] shows a large splitting in the second absorption band region as in Fig. 3. *trans*-Diaquabis (oxalato)chromate(III) complex also gives a splitting pattern for both the first and second bands, which is revealed with the aid of the Gaussian analysis of the diffuse reflectance spectrum (Fig. 3) as well as by the low-temperature single-crystal polarized spectral study.[17)] Since the ligand field strength of the fluoride ligand is weaker than that of the aqua ligand,[8)] it is anticipated that the splitting of the d-d absorption spectra for the present newly prepared *trans*-difluorobis(dicarboxylato) complexes is larger, at least in the first band region, than that for the diaqua complexes. Contrary to this expectation, however, both the present *trans*-difluoro complexes show the symmetrical shape and no splitting in their absorption spectra as in Fig. 1. The analogous situation is observed in the case of *trans*-$[CrF_2(O)_2(en)]$ type complexes. While the second absorption band of the malonato complex, *trans*-$[CrF_2(mal)(en)]^-$, is split similarly to that of *trans*(F)-$[CrF_2(en)(H_2O_2)]^+$, the first band exhibits a shoulder at the higher frequency side for the malonato complex, but not for the aqua complex as in Figs. 2—3.

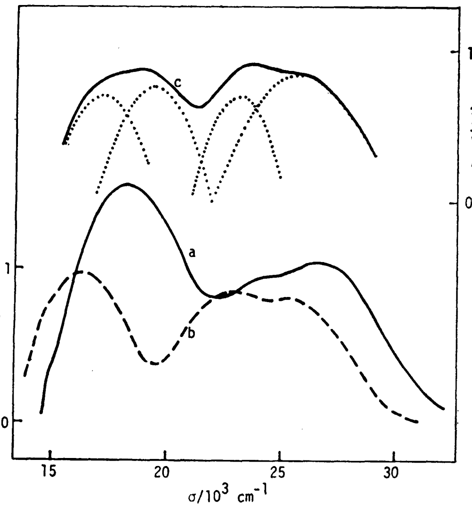

Fig. 3. Absorption curves of (a) *trans*(F)-$[CrF_2(en)(H_2O)_2]^+$ (——) and (b) *trans*-$[CrF_2(H_2O)_4]^+$ (----) (from Ref. 1) in water; diffuse reflectance spectrum of (c)*trans*-$K[Cr(ox)_2(H_2O)_2]\cdot 3H_2O$ (——) (right side ordinate) and its resolved curves using the Gaussian analysis (······).

In order to examine the different nature of Cr-ligand bonding, an attempt to estimate the angular overlap parameters is made by fitting the calculated transition energies to the observed positions of the d-d bands in terms of the angular overlap model on the assumption of orthoaxial ligation.[4)] The theoretical calculations are carried out by diagonalizing full energy matrix incorporating all configurational interactions for the d^3 configuration.[18)] The results are summarized in Tables 1 and 2 together with the AOM (e_σ and e_π) and Racah (B) parameter values as well as the assignments of the transition states. By using the AOM parameters for the fluoride and aqua ligands transferred from *trans*-$[CrF_2(N)_4]^+$ type and ammineaquachromium(III) complexes, $[Cr(NH_3)_n(H_2O)_{6-n}]^{3+}$,[3—4)] the calculated positions of the ligand field bands for *trans*-$[CrF_2(H_2O)_4]^+$ and $[CrF_2(en)(H_2O)_2]^+$ (assumed *trans*(F) form) correspond fairly well to those of the observed ones, except that the rather large splitting of the first band is reproduced despite of the observed symmetrical envelope of this band (Fig. 1 and Table 1). Among several attempts to estimate the AOM parameters for *trans*-$[CrF_2(H_2O)_4]^+$,[19—20)] the parameter values estimated by Keeton *et al.*[19)] are close to the present values. Similar calculations are carried out for *trans*-$[Cr(ox)_2(H_2O)_2]^-$, *trans*-$[CrF_2(mal)(en)]^-$, and *trans*-$[CrF_2(O\text{-}O)_2]^{3-}$, assuming that the π orbitals vertical to

TABLE 1. OBSERVED AND CALCULATED TRANSITION ENERGIES OF *trans*-$[CrF_2(H_2O)_4]^+$ AND *trans*-(F)-$[CrF_2(en)(H_2O)_2]^+$ COMPLEXES

trans-$[CrF_2(H_2O)_4]^+$		*trans*(F)-$[CrF_2(en)(H_2O)_2]^+$	
Obsd	Calcd (Assign)$^{b)}$	Obsd	Calcd(Assign)$^{b)}$
16.33$^{a)}$	16.09$^{a)}$(^4E)	18.42$^{a)}$	17.09$^{a)}$(^4E)
	17.20($^4B_2$)		19.10($^4B_2$)
22.70	22.68(^4E)	24.10	23.81(^4E)
25.50	25.47($^4A_2$)	26.81	26.92($^4A_2$)
37.00	35.98($^4A_2$)	38.30	37.78($^4A_2$)
	37.47(^4E)		39.92(^4E)
$e_\sigma(F)=7.43^{a)}$		$e_\sigma(F)=7.43^{a)}$	
$e_\pi(F)=1.78$		$e_\pi(F)=1.78$	
$e_\sigma(H_2O)=6.50$		$e_\sigma(H_2O)=6.50$	
$e_\pi(H_2O)=0.575$		$e_\pi(H_2O)=0.575$	
$B=0.73$		$e_\sigma(en)=7.00$	
		$B=0.71$	

a) Wavenumbers are given in 1000 cm^{-1}. b) Assignments are made according to the results of the theoretical calculations.

TABLE 2. OBSERVED AND CALCULATED TRANSITION ENERGIES OF *trans*-$[CrF_2(mal)(en)]^-$ AND *trans*-$[CrX_2(O\text{–}O)_2]^{-3}$ TYPE COMPLEXES

trans-$K[Cr(ox)_2(H_2O)_2]\cdot 3H_2O$		*trans*-$[CrF_2(mal)(en)]^-$			*trans*$[CrF_2(O\text{–}O)_2]^{3-}$		
Obsd[a]	Calcd (Assign)[b]	Obsd[a]	Calcd I	II (Assign)[b]	Obsd(ox)	Obsd(mal)	Calcd(Assign)[b]
17.20[c]	17.12[c](^4E)	17.46[c]	17.22[c]	17.05[c](^4E)	16.80[c]	17.05[c]	16.33[c](^4E)
19.44	19.05($^4B_2$)	19.50	19.50	19.20($^4A_2$)			17.40($^4B_2$)
23.13	23.81(^4E)	23.60	23.42	22.95(^4E)	23.90	23.90	23.09(^4E)
25.85	25.75($^4A_2$)	26.40	26.53	27.07($^4A_2$)			24.83($^4A_2$)
	37.60($^4A_2$)	38.30	37.42	36.98($^4A_2$)	37.50	37.50	36.32($^4A_2$)
	39.32(^4E)		39.81	39.69(^4E)			37.48(^4E)
	$e_\sigma(H_2O)=6.50$[c]		$e_\sigma(F)=7.00$[c]	7.43[c]			$e_\sigma(F)=6.20$[c]
	$e_\pi(H_2O)=0.575$		$e_\pi(F)=1.25$	1.78			$e_\pi(F)=0.825$
	$e_\sigma(O)$[d]$=6.35$		$e_\sigma(O)$[d]$=6.35$	5.80			$e_\sigma(O)$[d]$=5.80$
	$e_{\pi\perp}(O)$[d]$=0.50$		$e_{\pi\perp}(O)$[d]$=0.50$	0.00			$e_{\pi\perp}(O)$[d]$=0.00$
	$B=0.66$		$e_\sigma(en)=6.65$	7.00			$B=0.71$
			$B=0.63$	0.63			

a) The positions are obtained by the Gaussian analyses as shown in Figs. 2—3. b) Assignments are made according to the of the theoretical calculations. c) Wavenumbers are given in 1000 cm^{-1}. d) The parameter values for the dicarboxylate ligands; the same transition energies are obtained for the oxalato and malonato complexes owing to the assumption of orthoaxial ligation.

chelate planes participate predominately in the Cr–O π-interactions: $e_{\pi//} \gg e_{\pi\perp}$.[5],† Using the AOM parameter values for the aqua ligand from *trans*-$[CrF_2(H_2O)_4]^+$ and *trans*-(F)-$[CrF_2(en)(H_2O)_2]^+$, the reproduction of both the first and the second bands of *trans*-$[Cr(ox)_2(H_2O)_2]^-$ results in the estimation of the $e_\sigma(O)$ and $e_{\pi\perp}(O)$ values for the dicarboxylates as in Table 2. In addition, use of the transferred parameter values for the dicarboxylate ligand in calculating the transition energies for *trans*-$[CrF_2(mal)(en)]^-$ leads to the reproduction of four gaussian-analyzed band positions of this complex, though the values for the fluoride and ethylenediamine ligands used in this case are estimated to be smaller than those from the aqua complex, *trans*(F)-$[CrF_2(en)(H_2O)_2]^+$, as shown in Calcd I of Table 2. The parameter values obtained for the dicarboxylates agree fairly well with those estimated by the less sophisticated analyses for the ligand field bands of oxalato Cr(III) complexes.[21] On the other hand, use of the parameters for the fluoride and ethylenediamine ligands transferred from the aqua complex requires a significant decrease in the $e_\sigma(O)$ and $e_{\pi\perp}(O)$ values for the dicarboxylate ligand (Calcd II of Table 2), in order to account for the four observed bands of *trans*-$[CrF_2(mal)(en)]^-$. The similar situation may be also encountered for $[CrF_2(O\text{–}O)_2]^{3-}$ type complexes. That is, the reproduction of the small splitting expected from the symmetrical shape of the first and the second bands of *trans*-$[CrF_2(O\text{–}O)_2]^{3-}$ results in the unlikely decrease in the AOM parameters for the fluoride and dicarboxylate ligands as is tentatively estimated (Table 2). By comparing the present parameter values which are not always the best fit ones for the ligands of the complexes concerned, it is difficult to extract some quantitative information about the bonding nature of Cr and ligator. Within the framework of the AOM, however, it is concluded that the anisotropic Cr–O π-interactions in the dicarboxylato complexes play an important role in the splitting of the ligand field band for *trans*-$[Cr(ox)_2(H_2O)_2]^-$ and *trans*-$[CrF_2(mal)(en)]^-$, and that both the σ and π antibonding interactions between Cr and ligators in the fluoro complexes with the dicarboxylate ligands become weaker than those in the aqua complexes with the fluoride or dicarboxylate ligands.

One of the authors (S.K.) wishes to express his thanks to Professor Yoichi Shimura of Osaka University for his kind guidance and valuable discussions throughout this work and also for making the circular dichroism and infrared spectra available for the present work. Grateful acknowledgement is made to Dr. Kiyoshi Isobe of Osaka City University for his aid in obtaining the elemental analyses of the fluoro complexes. The authors also wish to thank Dr. Takashi Komorita, Osaka University, for his generous offer of the LGNCD and AOM/2 computer programs.

References

1) T. Y. Chan and E. L. King, *Discuss. Faraday Soc.*, **29**, 109 (1966); E. L. King, private communication for the absorption data.

2) J. Glerup, J. Josephsen, K. Michelsen, E. Pedersen, and C. E. Schäffer, *Acta Chem. Scand.*, **24**, 247 (1970); b) J. Glerup and C. E. Schäffer, *Inorg. Chem.*, **15**, 1408 (1976).

3) T. J. Barton and R. C. Slade, *J. Chem. Soc., Dalton Trans.*, **1975**, 651.

4) J. Glerup, O. Mønsted, and C. E. Schäffer, *Inorg. Chem.*, **15**, 1399 (1976); **17**, 3153 (1978).

5) C. E. Schäffer, *Proc. R. Soc. London, Ser. A*, **297**, 96 (1967); C. K. Jørgensen, "Modern Aspects of Ligand Field Theory," North-Holland Publishing Company, Amsterdam (1971), Chap. 17.

6) C. E. Schäffer, *Pure Appl. Chem.*, **24**, 361 (1970).

7) J. W. Vaughn and J. Marzowski, *Inorg. Chem.*, **12**, 2346 (1973).

8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford (1962).

9) Y. Shimura, *Bull. Chem. Soc. Jpn.*, **25**, 49 (1952); R. G.

---

† In this case, $\Delta(10Dq)$ equals to $3e_\sigma - 2e_{\pi\perp} - 2e_{\pi//} \simeq 3e_\sigma - 2e_{\pi\perp}$.

Wilkins and J. G. Williams, "Modern Coordination Chemistry," ed by J. Lewis and R. G. Wilkins, Interscience Publications, New York (1960), p. 190.

10) L. F. Druding, *Coord. Chem. Rev.*, **3**, 409 (1968).

11) S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 902 (1975).

12) W. A. Baker and M. G. Phillips, *Inorg. Chem.*, **5**, 1042 (1966).

13) V. Doron and W. Durham, *Inorg. Nucl. Chem. Lett.*, **6**, 285 (1970).

14) K. Miyoshi, Y. Kuroda, J. Takeda, H. Yoneda, and I. Takagi, *Inorg. Chem.*, **18**, 1425 (1979).

15) S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **42**, 988 (1969); G. L. Welch and R. E. Hamm, *Inorg. Chem.*, **2**, 295 (1963).

16) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

17) R. Dingle, *Acta Chem. Scand.*, **22**, 2219 (1968).

18) J. R. Perumareddi, *Coord. Chem. Rev.*, **4**, 73 (1969).

19) M. Keeton, B. Fa-Chun, and A. B. P. Lever, *Can. J. Chem.*, **49**, 192 (1971).

20) D. S. McClure, *Adv. Chem. Coord. Compounds*, **6**, 498 (1961); A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968); L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 839 (1969); H. U. Rahman, *Physica*, **53**, 256 (1971).

21) S. Bunel, C. Ibarra, and L. Adan, *J. Inorg. Nucl. Chem.*, **31**, 3203 (1969).