Novel Diastereoisomers of Ethylenediaminetetrapropionatochromate(III). Part 1. Preparation and Characterization

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Hexadentate ethylenediaminetetraacetato-like chromate(III) complexes were prepared with ethylenediamine-*N,N,N',N'*-tetrapropionate (edtp), (*S*)-propane-1,2-diamine-*N,N,N',N'*-tetrapropionate [(*S*)-pdtp] and (1*S*,2*S*)-*trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetrapropionate [(*SS*)-cydtp] ligands. For each complex, QAE-Sephadex column chromatography demonstrated three isomers, which were characterized by ^{2}H NMR and circular dichroism (CD) spectra to be novel diastereoisomers arising from a pairwise combination of two chiral ethylenic *gauche* conformations at the six-membered propionate rings. Two of the diastereoisomers were found to undergo thermal hydrolysis with anomalous carbon–nitrogen bond cleavage in aqueous solution to give diaminetripropionato complexes and 3-hydroxypropionic acid.

There have been a number of investigations on the hexadentate edta (ethylenediaminetetraacetate) type chromate(III) complexes with five-membered acetato and/or six-membered propionato chelate rings.[1–4] The strained five-membered acetate chelates force the edta ligand to adopt a pentadentate co-ordination to chromium(III) in acidic solution.[1] As the number of the six-membered chelate rings increases, however, the ligands tend to favour hexadentate co-ordination[2] and it is possible to form geometrical isomers with both five- and six-membered rings because of less-strained six-membered ring chelation.[3,4] There is also the possibility of conversion between the enantiomeric ethylenic *gauche* conformations of the propionate chelates, which may lead to the formation of diastereoisomers with respect to the six-membered chelate conformations. Although such diastereoisomers are expected to give invaluable information on the stability and stereochemistry of the six-membered propionate chelate conformations, they have never been taken into consideration in the course of studies on the edta-type complexes.

This paper deals with the preparation and characterization of the unprecedented diastereoisomers of ethylenediamine-*N,N,N',N'*-tetratetrapropionatochromate(III), [Cr(edtp)]$^-$, (*S*)-propane-1,2-diamine-*N,N,N',N'*-tetrapropionatochromate(III), [Cr{(*S*)-pdtp}]$^-$, and (1*S*,2*S*)-*trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetrapropionatochromate(III), [Cr{(*SS*)-cydtp}]$^-$. For two of the three diastereoisomers, anomalous facile carbon–nitrogen bond cleavage was found to occur in one of the four β-alaninato rings and was examined by ^{2}H NMR and circular dichroism (CD) spectroscopy. Preliminary results of this study have been communicated.[5]

Experimental

The ligands H$_4$edtp, [^{2}H$_4$]H$_4$edtp, (*S*)-H$_4$pdtp and (*SS*)-H$_4$cydtp were prepared by using similar methods to those for analogous ligands.[3]

Preparation of the Complexes.—[Cr(edtp)]$^-$ *and* [Cr([^{2}H$_4$]edtp)]$^-$. To a cold solution of ethylenediamine (31 g, 0.5 mol) was added dropwise a solution of acrylonitrile (64 g, 1.2 mol) with stirring below 40 °C. The mixture was heated at 80 °C for 2 h then allowed to stand overnight at room temperature. It was concentrated under reduced pressure and filtered. The yellow filtrate (0.03 mol) was added to a solution of LiOH or LiOD [lithium (1.0 g, 0.14 mol) in 20 cm^3 of water or D$_2$O] and refluxed at 80–90 °C until no ammonia gas was detected. After cooling to room temperature, the solution was adjusted to pH *ca.* 1 with concentrated HCl solution and kept in a refrigerator overnight. The white powder deposited was collected and washed with cold water and methanol. This compound was identified as H$_2$eddp·2HCl (eddp = ethylenediamine-*N,N'*-dipropionate) or [^{2}H$_4$]H$_2$eddp·2HCl in which the 2-methylene group of the propionate is partially deuteriated (86%), according to ^{1}H NMR spectroscopy.

The compound thus prepared (4.5 g, 0.0163 mol) was dissolved in water (10 cm^3) and neutralized to pH 7 with 2 mol dm^{-3} NaOH solution (8.2 cm^3). A cooled mixture of 3-chloropropionic acid (4.2 g, 0.039 mol) and 2 mol dm^{-3} NaOH solution (19.5 cm^3) was added. More 2 mol dm^{-3} NaOH solution (19.5 cm^3) was added with stirring at 70 °C at pH 10–11. The reaction solution was heated at 85 °C for 2 h and the pH adjusted to *ca.* 9. This solution was assumed to contain 0.0163 mol of H$_4$edtp or [^{2}H$_4$]H$_4$edtp.

A mixture of the above reaction solution (0.014 mol, 220 cm^3) and CrCl$_3$·6H$_2$O (3.7 g, 0.014 mol) was heated at 85 °C for 2 h together with a small amount of CrSO$_4$·5H$_2$O. The colour changed from green to red-violet. The solution was poured onto a column (4 x 60 cm) of QAE-Sephadex C-25 anion exchanger in the chloride form. After the column was washed with water, the charged complexes were eluted with 0.02 mol dm^{-3} NaCl solution at 4 °C. Three bands, E-I, E-II and E-III (E-I-d, E-II-d and E-III-d for the [^{2}H$_4$]edtp), were successively eluted. Each eluate was evaporated to dryness at 20–25 °C using a vacuum rotatory evaporator. The complexes were extracted with methanol so that sodium chloride was removed and then dissolved in water. Red-purple powders were obtained by adding acetone to the aqueous solution. The sodium salts from bands E-I and E-II were converted into the potassium salts using a Dowex 50W-X8 cation-exchange resin in the potassium form. The formed ratios of E-I : E-II : E-III and E-I-d : E-II-d : E-III-d formed were found to be 1 : 1 : 40 and 4 : 1 : 7, respectively.

[Cr{(*S*)-pdtp}]$^-$. A mixture of (*S*)-propane-1,2-diamine-di-L-tartrate (8.21 g, 0.02 mol) and calcium hydroxide (3.26 g, 0.044 mol) in water (10 cm^3) was heated at 40 °C with stirring overnight. After cooling to room temperature, the suspension was filtered to remove calcium tartrate. To the filtrate was added a cooled mixture of 3-chloropropionic acid

Table 1 Analytical data (%) for the $[Cr(edtp)]^-$ and $[Cr(edtrp)(H_2O)]$ type complexes

	C		H (D)*		N	
Complex	Found	Calc.	Found	Calc.	Found	Calc.
$K[Cr(edtp)]\cdot 4H_2O$ (E-I)	33.65	33.15	5.45	5.55	5.30	5.50
$Na[Cr(edtp)]\cdot 4H_2O$ (E-II)	34.20	34.00	5.75	5.65	5.70	5.55
$K[Cr(edtp)]\cdot 3H_2O$ (E-III)	35.15	34.35	5.50	5.35	5.85	5.70
$K[Cr([^2H_4]edtp)]\cdot 2CH_3OH\cdot 2.5H_2O$ (E-I-d)	35.00	35.10	5.20 (1.25)	5.45 (1.25)	5.10	5.10
$Na[Cr([^2H_4]edtp)]\cdot 3.5H_2O$ (E-II-d)	34.90	34.65	4.90 (1.45)	4.85 (1.40)	5.90	5.75
$K[Cr([^2H_4]edtp)]\cdot CH_3OH\cdot 3H_2O$ (E-III-d)	35.05	34.35	5.20 (1.25)	5.10 (1.30)	5.35	5.35
$Li[Cr\{(S)\text{-pdtp}\}]\cdot 4H_2O\cdot C_3H_6O\cdot 0.5LiCl$ (P-I)	38.20	38.00	6.35	6.40	4.95	4.95
$K[Cr\{(S)\text{-pdtp}\}]\cdot 3H_2O$ (P-II)	36.65	35.95	6.30	6.20	5.15	5.10
$Li[Cr\{(S)\text{-pdtp}\}]\cdot 5H_2O\cdot 0.5CH_3OH$ (P-III)	35.45	35.55	6.50	6.55	5.35	5.35
$K[Cr\{(SS)\text{-cydtp}\}]\cdot 4H_2O$ (C-I)	38.75	38.50	6.45	6.10	5.00	5.00
$K[Cr\{(SS)\text{-cydtp}\}]\cdot 5H_2O$ (C-II)	37.50	37.30	6.15	6.25	4.85	4.85
$K[Cr\{(SS)\text{-cydtp}\}]\cdot 5H_2O\cdot KCl$ (C-III)	32.95	33.05	5.40	5.55	4.25	4.30
$[Cr(edtrp)(H_2O)]\cdot 3H_2O$	33.15	33.25	6.35	6.35	6.95	7.05
$[Cr([^2H_4]edtrp)(H_2O)]\cdot 3H_2O$	33.35	33.10	5.55 (1.35)	5.40 (1.30)	6.90	7.00
$[Cr\{(S)\text{-pdtrp}\}(H_2O)]\cdot 4H_2O$	33.60	33.55	6.75	6.80	6.50	6.50
$[Cr\{(SS)\text{-cydtrp}\}(H_2O)]\cdot 4.5H_2O$	36.70	36.95	7.10	7.25	5.80	5.75

* The extent of deuteriation is 43%.

Table 2 Absorption spectral data* for $[Cr(edtp)]^-$ and related complexes

Isomer	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
E-I	542.0	178.7	401.8	67.1
E-II	528.3	181.2	400.0	63.5
E-III	539.0	196.5	398.3	71.1
P-I	541.0	169.1	404.0	63.0
P-II	531.3	184.8	399.6	64.3
P-II	539.3	189.9	398.4	67.0
C-I	539.8	162.2	404.0	61.7
C-II	524.0	173.8	399.0	57.5
C-III	537.0	185.2	398.6	65.2

* In aqueous solution.

(10.4 g, 0.096 mol) and 2 mol dm^{-3} NaOH solution (48 cm^3). The yield of (S)-H_4pdtp in the reaction solution was regarded as almost 100%. Subsequent procedures were the same as that for $[Cr(edtp)]^-$ with exception that the reaction time was 1 h. QAE-Sephadex C-25 column chromatography gave three successive bands, P-I, P-II and P-III. The resulting sodium salts were converted into the lithium salts for P-I and P-III and into the potassium salt for P-II by using Dowex 50W-X8 cation-exchange resins. The ratio of P-I:P-II:P-III formed was 8:5:8.

$[Cr\{(SS)\text{-cydtp}\}]^-$. (1*S*,2*S*)-*trans*-Cyclohexane-1,2-diamine dihydrochloride (0.935 g, 0.005 mol) in water (4 cm^3) was neutralized by 2 mol dm^{-3} NaOH solution. To this solution was added a cooled mixture of 3-bromopropionic acid (4.0 g, 0.026 mol) and 2 mol dm^{-3} NaOH solution (13 cm^3) in water. The yield of (SS)-H_4cydtp in the reaction solution was regarded as 50%. Subsequent procedures were carried out as for $[Cr\{(S)\text{-pdtp}\}]^-$. The QAE-Sephadex column gave six bands by using 0.02 mol dm^{-3} KCl solution as the eluent, the first, second and fifth being in trace amounts. The three major bands (third, fourth and sixth) are denoted as C-I, C-II and C-III in elution order; formation ratio 2:2:1.

Diaminetripropionate complexes. When the reaction solution of $[Cr(edtp)]^-$ (or $[Cr\{(S)\text{-pdtp}\}]^-$ or $[Cr\{(SS)\text{-cydtp}\}]^-$) was poured onto a column of QAE-Sephadex C-25 anion exchanger a portion was not adsorbed. This red solution was concentrated and passed through a column of Dowex 50W-X8 cation-exchange resin in the H^+ form. After washing with water a neutral complex was obtained. The elemental analysis (Table 1) shows that this complex contains pentadentate ethylenediamine- [or (*S*)-propanediamine- or (*SS*)-cyclohexanediamine-*N*,*N*,*N*′-tripropionate] [edtrp^{3-}, (*S*)-pdtrp^{3-} or (*SS*)-cydtrp^{3-}, respectively] together with one water molecule.

Attempted Optical Resolution of Band E-III.—An aqueous solution of compound E-III (5 mg) was poured onto a column (1 x 50 cm) of QAE-TOYO PEARL 50 anion exchanger derived from Toyopearl HW50S (TOSO Co.)[6] and eluted with a 30% MeOH solution of 0.02 mol dm^{-3} sodium $(+)_{589}$-tartratoantimonate(III). The sign of the major CD component in the first spin-allowed transition region near 540 nm was positive and negative for the first and the last fractions of the eluate.

Spectral Measurements.—Absorption spectra were measured by a Shimadzu UV-240 and/or UV-3100 spectrophotometer, CD spectra with a JASCO MOE-1 spectropolarimeter, IR spectra with a Shimadzu IR-385 spectrometer, and ^1H, ^2H and ^{13}C NMR spectra on a JEOL GX-270 spectrometer.

Results and Discussion

Characterization of Complexes.—Satisfactory elemental analyses were obtained for the isolated complexes as shown in Table 1. The chromatographic behaviour and elemental analyses indicate that the complexes correspond to isomers with the same chemical composition. For the three isomers of each complex the ligand-field absorption spectra show a similar trend, as shown in Table 2. Thus, the absorption band maxima shift to longer wavelengths in the order of isomers II, III and I for the first band, and of III, II and I for the second band. The intensity of the first band increases in the order I, II and III, whereas that of the second increases in the order II, I and III, with the exception of the (*S*)-pdtp complex. No shift to lower energy is observed with increasing pH (*ca.* 10) for these absorption spectra. Only one strong IR band near 1600 cm^{-1} due to the asymmetric stretching vibration of the co-ordinated carboxylates is observed for each isomer of the complexes. These observations indicate that all carboxylate groups of the three diaminetetrapropionato complexes are co-ordinated to one Cr^{III}.

In view of the absorption spectra and CD patterns of the

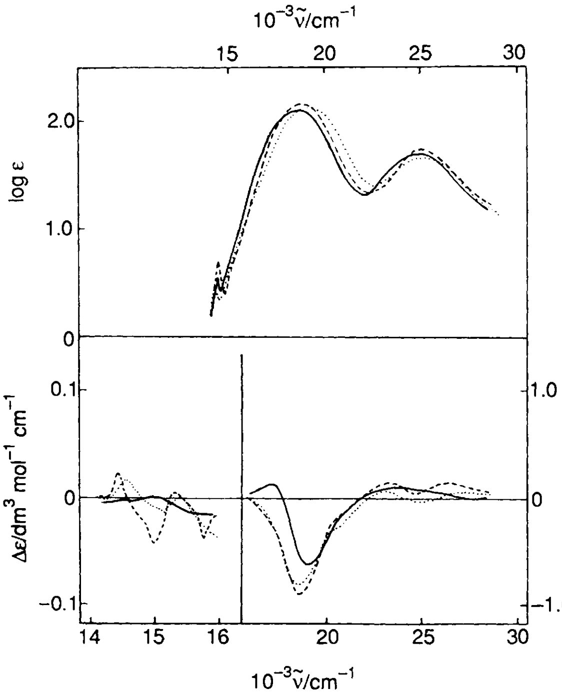

Fig. 1 Absorption (upper) and CD (lower) spectra for three diastereoisomers of $[Cr\{(S)\text{-pdtp}\}]^-$ in H_2O: P-I (——), P-II (· · ·), and P-III (- - -)

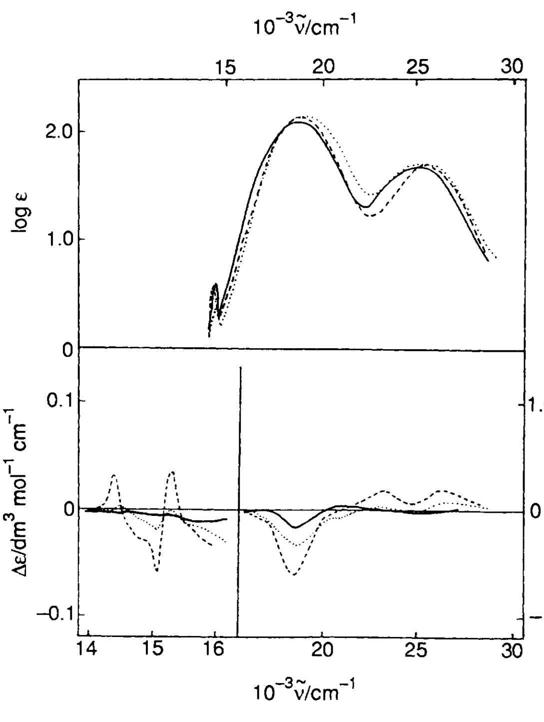

Fig. 2 Absorption (upper) and CD (lower) spectra for three diastereoisomers of $[Cr\{(SS)\text{-cydtp}\}]^-$ in H_2O: C-I (——), C-II (· · ·), and C-III (- - -)

P-III and C-III as well as the partially resolved E-III isomer (the later fraction eluted), it is evident that the III isomers correspond to that reported for Λ-$(-)_{589}[Cr(edtp)]^-$.[4]

Three (*S*)-pdtp isomers giving a negative major CD component in the first ligand-field d–d transition near 19 000 cm^{-1} as shown in Fig. 1 are formed stereospecifically and adopt a Λ(ΛΔΛ) absolute configuration owing to the preference for the equatorial orientation of the methyl group with respect to the diamine ring. This is supported by the fact that the corresponding isomers of the (*SS*)-cydtp complex give almost the same CD pattern as those of the (*S*)-pdtp isomers (Fig. 2), disregarding any possibility of the formation of the Δ(ΔΛΔ) diastereomer with an axially oriented methyl group as found for the (*S*)-propane-1,2-diaminetetraacetatocobaltate(III) complex.[7]

The CD spectrum in the spin-forbidden as well as the spin-allowed region of the P-II(C-II) isomers is intermediate or average in pattern and intensity between those of the P-I(C-I) and P-III(C-III) isomers. This suggests that the relation $\Delta\varepsilon(\text{II}) = \frac{1}{2}[\Delta\varepsilon(\text{I}) + \Delta\varepsilon(\text{III})]$ holds approximately. The construction of molecular models suggests that the propionate chelates are interconvertible between δ and λ propionate ethylenic *gauche* conformations in the R (relaxed) out-of-plane ring, but that the propionate chelates at the G (girdling) in-plane rings are forced stereospecifically to adopt λ conformations for the Λ(ΛΔΛ) configuration. The X-ray analysis of Λ-$(-)_{589}Li[Cr(edtp)]\cdot 3H_2O^{4b}$ reveals that both the two ethylenic *gauche* conformations in the R rings are δ for the Λ configuration. According to the additivity of the CD contributions from the configurational [Δε(Λ)] and conformational chiralities {Δε[δ(R)] or Δε[λ(R)] and Δε[λ(G)] and Δε[δ-(diamine)] due to the chiral ethylenic *gauche* conformations in the propionate chelates of the R and G rings and the diamine chelates of the (*S*)-propanediamine and (*S*,*S*)-cyclohexanediamine backbone, respectively}, the CD curves for the three diastereoisomers can be expressed by equations (1)–(3). Assuming $\Delta\varepsilon[\delta(\text{R})] = -\Delta\varepsilon[\lambda(\text{R})]$, the observed relation for

$$\Delta\varepsilon(\text{I}) = \Delta\varepsilon(\Lambda) + 2\Delta\varepsilon[\lambda(\text{R})] + \Delta\varepsilon[\lambda(\text{G})] + \Delta\varepsilon[\delta(\text{diamine})] \quad (1)$$

$$\Delta\varepsilon(\text{II}) = \Delta\varepsilon(\Lambda) + \Delta\varepsilon[\delta(\text{R})] + \Delta\varepsilon[\lambda(\text{R})] + \Delta\varepsilon[\lambda(\text{G})] + \Delta\varepsilon[\delta(\text{diamine})] \quad (2)$$

$$\Delta\varepsilon(\text{III}) = \Delta\varepsilon(\Lambda) + 2\Delta\varepsilon[\delta(\text{R})] + \Delta\varepsilon[\lambda(\text{G})] + \Delta\varepsilon[\delta(\text{diamine})] \quad (3)$$

the CD curves of P-I(C-I), P-II(C-II) and P-III(C-III) is reproduced. Therefore, the three isomers obtained are considered to correspond to the diastereoisomers arising from a pairwise combination of two conformations at the propionate arms of the R rings, *i.e.* Λ(δδ), Λ(δλ), Λ(λλ). From a geometrical viewpoint, the Λ(δδ), Λ(δλ) and Λ(λλ) diastereoisomers and their enantiomers are denoted as the lel_2, lelob, and ob_2 forms, respectively. For the lel form, the ethylenic C–C bond of the propionate is parallel with the C_2 axis bisecting the N–Cr–N angle, while the ob form has this bond oblique to the C_2 axis as shown in Fig. 3.

The ^2H NMR spectra of the $[^2H_4]$edtp complexes are in accord with the CD interpretation. Since the E-I-d, E-II-d and E-III-d isomers give three, six and four NMR signals, respectively, as shown in Fig. 4, it is suggested that E-II-d has C_1 symmetry and E-I-d and E-III-d have C_2 symmetry. The ^2H NMR signal at δ 11.2 of the E-III-d isomer may be ascribed to the 2-methylenes of the lel propionate arms at the R ring in comparison with those[3] of the three isomers [*trans*(O_5), *trans*(O_5O_6), and *trans*(O_6)] of propane-1,3-diamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionatochromate(III), where O_5 and O_6 refer to the five- and six-membered N–O rings, respectively and the 2-methylenes of the propionate are deuteriated. The corresponding signal is observed at δ 8 for the E-II-d isomer which has one R(lel) propionate arm. For E-I-d with two R(ob) propionate arms there is no signal around δ 10. These facts lend support to the assignment of the three isomers to the lel_2, lelob and ob_2 conformational isomers as shown in Fig. 3. These three diastereoisomers are stable enough to be isolated, since the propionate chelate conformations at the R ring are rigid; there is no puckering or no conformational inversion between the ob

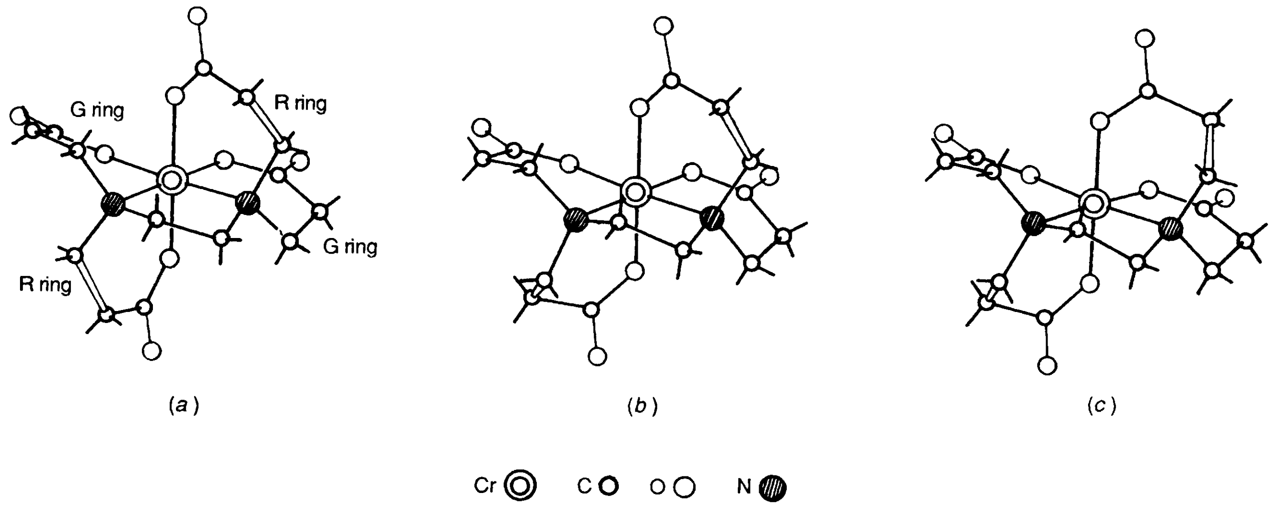

Fig. 3 Proposed structure for three diastereoisomers of the edtp complex: (*a*) E-I, $\Lambda[\lambda(R)\lambda(R), ob_2]$; (*b*) E-II, $\Lambda[\delta(R)\lambda(R)$, lelob]; (*c*) E-III, $\Lambda[\delta(R)\delta(R), lel_2]$. The double lines represent the C–C bonds of the propionato chelates of the R ring

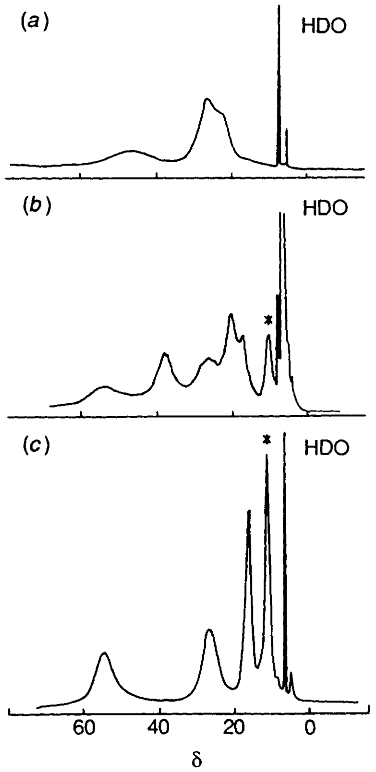

Fig. 4 The ^2H NMR spectra for three diastereoisomers of $[Cr([^2H_4]$-edtp)]$^-$ in H_2O: (*a*) E-I-d, (*b*) E-II-d, and (*c*) E-III-d. Asterisks indicate the signals due to the propionates in the R(lel) rings

and the lel state. To our knowledge, these diastereoisomers are the first example of this type of conformational isomerism.

CD in the d–d Transitions.—The CD spectra corresponding to the first and second absorption bands of the P-III and C-III isomers are almost identical with that for the E-III isomer reported by Radanovic and co-workers[4] except for the intensities and the two weak negative components near 20 000 cm^{-1}. This CD pattern is also similar to that of $(-)_{589}$-*trans*(O_5)-ethylenediamine-*N,N′*-diacetate-*N,N′*-dipropionatochromate(III).[2] For the former edtp-type complexes, the lowest-frequency positive CD component in the first spin-allowed band region disappears, which has been used as a criterion to determine the absolute configuration for the edta-type complexes.[2] However, in the lower-frequency spin-forbidden transition region for the P-III and C-III isomers a positive CD peak is observed near 14 300 cm^{-1}. The corresponding peak for $(+)_{589}[Cr(edtp)]^-$ could not be measured by Radanovic *et al.*[4a] This positive peak and a positive peak near 15 200 cm^{-1} correspond in position and intensity to those assignable to the $^2A_1$ (or $^2A_1 + {}^2B_1$) $[^2E_g(O_h)]$ and $^2A_2$ $[^2T_{1g}(O_h)]$ states for the ethylenediaminediacetatedipropionato, [*S,S*]-ethylenediamine-*N,N′*-disuccinato and (2*S*,4*S*)-pentane-2,4-diamine-*N,N,N′,N′*-tetraacetato complexes.[2b] It is predicted theoretically that these CD components attain their rotational strengths solely from those of the tetragonal split $^4E[^4T_{2g}(O_h)]$ component.[8] This indicates the existence of the lowest-frequency positive CD component which cannot be observed only because of masking or cancelling by the nearby intense negative component. In view of the CD behaviour in the spin-forbidden and spin-allowed band region of the edta or edtp type complexes, it can be proposed that the signs of the CD components of the $^2A_1$ (or $^2A_1 + {}^2B_1$) $[^2E_g(O_h)]$ and $^2A_2$ $[^2T_{1g}(O_h)]$ states near 14 800 and 15 300 cm^{-1}, respectively, in the spin-forbidden transitions are correlated to the absolute configuration; the complexes giving the positive signs for both components adopt a $\Lambda(\Lambda\Delta\Lambda)$ configuration. On the other hand, the P-II and C-II isomers give also only one negative CD component in the first spin-allowed transitions similar to the P-III and C-III complexes. The CD patterns of their spin-forbidden transitions are much different in intensity and position from those of the P-III and C-III isomers as shown in Figs. 1 and 2. This difference in CD behaviour in the spin-forbidden and -allowed transition regions is also observed for the P-I and C-I isomers. The lowest-frequency positive CD component at 16 000 cm^{-1} appears for C-I. The fact that the CD curve of P-I almost coincides with the baseline around 16 000 cm^{-1} suggests that a positive component grows in comparison with the CD spectra of P-II and P-III. In spite of the existence or indication of the lowest-frequency positive CD component near 16 000 cm^{-1} in the spin-allowed transitions, the CD signs of the spin-forbidden transitions of the P-I and C-I isomers are always negative. This situation cannot be accounted for by means of the conventional theoretical approach.[2b,8] Such a remarkable difference in the CD behaviour in the spin-forbidden transitions between the P-I(C-I) or P-II(C-II) and P-III(C-III) isomers may result from a change in the π interaction between the Cr $d_\pi(t_{2g})$ and oxygen (carboxylato) p_π orbitals on going from the ob [P-I(C-I)] to the lel [P-II(C-II) or P-III(C-III)] propionato ring conformation as revealed previously from the sensitivity of the chiroptical spectra in the spin-forbidden transitions of the edta-type complexes.[1]

Carbon–Nitrogen Bond Cleavage.—When aqueous solutions of the three $[Cr([^2H_4]edtp)]^-$ isomers were heated, ^2H NMR spectra of two isomers (E-I-d and E-II-d) changed with time and finally gave the same spectrum (Fig. 5). A similar tendency was observed for the CD spectra of P-I, P-II and C-I, C-II, respectively (Fig. 6). No spectral change occurred for E-III-d, P-III and C-III. QAE Sephadex anion-exchange column chromatography for the heat-treated solutions of E-I-d and E-II-d (P-I and P-II; C-I and C-II) was found to give small amounts of the I, II and III isomers as well as a large amount of a neutral complex. The latter was confirmed to be the same diaminetripropionato complex as that obtained from the reaction solution in the preparation of the complexes (see Experimental section) by means of absorption (Table 3) and/or CD or ^2H NMR spectra. Along with these diaminetripropionato complexes, 3-hydroxypropionic acid is detected in the heated solution by ^1H and ^{13}C NMR spectra. On heating the E-I and E-II or P-I and P-II isomers in D_2O at 60 °C for 24 h, the intensities of the ^1H and ^{13}C NMR signals at δ 2.4, 3.7 and 40, 60, 180, respectively, which are identical with those of 3-hydroxypropionate, were found to increase with time. These facts indicate that the major products of this reaction are the diaminetripropionato complex and 3-hydroxypropionic acid. Therefore, the reaction proceeds as in equation (4). That is,

$$\begin{aligned} \text{I (or II)} \longrightarrow\ & \text{diaminetripropionato complex} \\ & + \text{3-hydroxypropionic acid} \\ & + \text{I, II, III (trace)} \qquad (4) \end{aligned}$$

thermal hydrolysis with C–N bond cleavage may occur in the β-alaninate R ring having the ob form. The half-life for the pseudo-first-order decomposition reaction monitored by ^2H NMR or CD spectra was several hours at 60 °C for the I and II isomers. This is extraordinarily short compared with the shortest half-life known for carbon–carbon cleavage in highly branched ethane derivatives,[9,10] even when considering the C–N to be weaker than the C–C bond. Similar C–N bond cleavage is observed for cobalt(III) edta-like complexes which give diaminetriacetato and/or diamine-*N*,*N*′-diacetato complexes upon thermal decomposition and redox reaction.[11,12] However, redox reaction never occurs with the inert chromium(III) complexes. It has been proposed[5] that the facile C–N bond cleavage in the ob β-alaninate ring might arise from the difference in steric strain between the lel and ob conformations. Preliminary experiments show that this reaction is affected by the proton concentration, but never occurs in aprotic solvents such as dimethylformamide. Thus the solvent also plays an important role in the C–N bond cleavage.

Table 3 Absorption spectral data* for the diaminetripropionatochromium(III) complexes

Complex	λ_{max}/nm	ε/dm³ mol⁻¹ cm⁻¹	λ_{max}/nm	ε/dm³ mol⁻¹ cm⁻¹
edtrp	532.6	190.9	395.8	63.4
pdtrp	533.7	177.8	397.4	63.1
cydtrp	532.8	174.4	395.4	61.3

* In aqueous solution.

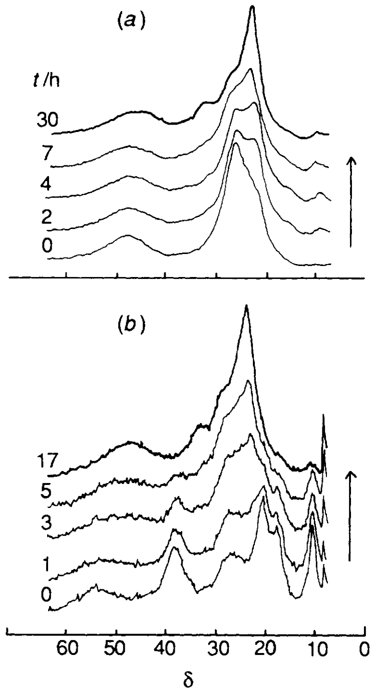

Fig. 5 The ^2H NMR spectral changes for the $[^2H_4]$edtp complexes [(*a*) E-I-d, (*b*) E-II-d] in water at 60 °C

For the elucidation of the C–N bond cleavage reaction it is necessary quantitatively to examine the lability of the two diastereoisomers (I and II) in protic and aprotic solvents and to determine the geometrical structure of the diaminetripropionato complex, $[Cr(edtrp)(H_2O)]$, and its analogues. The X-ray structures of $[Cr\{(S)\text{-pdtrp}\}(H_2O)]\cdot4H_2O$ and $[Cr\{(SS)\text{-cydtrp}\}(H_2O)]\cdot4.5H_2O$ are reported in the following paper,[13] and a kinetic study of the acid hydrolysis and C–N bond rupture is in progress.

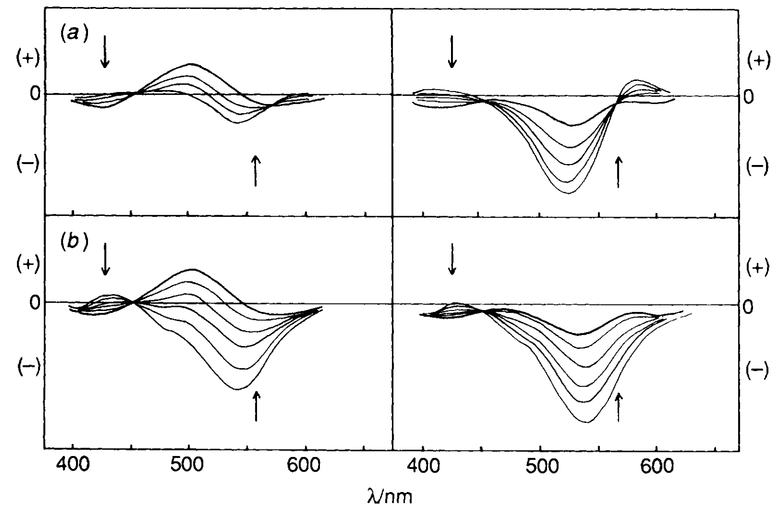

Fig. 6 The CD spectral changes for the (*S*)-pdtp [left: (*a*) P-I, (*b*) P-II] and the (*SS*)-cydtp [right: (*a*) C-I, (*b*) C-II] isomers

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