Inorganica Chimica Acta, *195* (1992) 187–191

Preparation and characterization of two geometrical isomers of the aqua(ethylenediamine-*N*,*N*,*N*′-tri-3-propionatopropionic acid)chromium(III) complex: X-ray structure of *cis-eq*-$[Cr(Hedtp)(H_2O)]\cdot 5H_2O$

Narumi Sakagami and Sumio Kaizaki*
Department of Chemistry, Faculty of Science, Osaka University, Osaka 560 (Japan)

(Received January 16, 1992)

Abstract

Two geometrical isomers for $[Cr(Hedtp)(H_2O)]$ (Hedtp = ethylenediamine-*N*,*N*,*N*′-tri-3-propionatepropionic acid) were obtained from the most stable diastereoisomer of $[Cr(edtp)]^-$ (edtp = ethylenediamine-*N*,*N*,*N*′,*N*′-tetra-3-propionate) by passing through a column of cation-exchange resin in the H^+ form. The geometrical structure of one isomer (**H-1**) was found to be *cis-eq* by using the X-ray diffraction method. Crystal data for *cis-eq*-$[Cr(Hedtp)(H_2O]\cdot 5H_2O$ are monoclinic with space group $P2_1/c$: $a = 9.796(6)$, $b = 15.195(6)$, $c = 14.825(2)$ Å, $\beta = 94.70(4)°$ and $Z = 4$. The geometrical structure of another isomer (**H-2**) was assigned to *trans-eq* on the basis of the ^2H NMR and the magnetic circular dichroism (MCD) spectra.

Introduction

It has been reported that there are three diastereoisomers for $[Cr(edtp)]^-$ (edtp = ethylenediamine-*N*,*N*,*N*′,*N*′-tetra-3-propionate) and its analogues [1]. In aqueous (or weakly acid) solution, two of the isomers (**I** and **II**) decompose with a C–N bond cleavage in the 3-propionato chelate at the R (out-of-plane) ring into the diamine-*N*,*N*,*N*′-tri-3-propionato complex and 3-hydroxypropionic acid. The other isomer (**III**) is stable in acidic solution; it causes neither decomposition with a C–N bond cleavage, nor dissociation in the carboxylates to form the pentadentate edtp complex in contrast to the case of the edta (ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate) type complexes [2]. Radanovic *et al.* have mentioned that for the most stable isomer of $[Cr(edtp)]^-$ (**E-III**) the edtp ligand behaved as a hexadentate even when the lithium salt was converted into the acid form [3].

We recently obtained two isomers with one uncoordinated protonated 3-propionate from the **E-III** by using column chromatography. This paper reports the preparation and characterization of the first example of the geometrical isomers of the chromium(III) complex with a pentadentate edtp ligand, $[Cr(Hedtp)(H_2O)]$.

Experimental

Preparation of the complexes

The preparation and isolation of $[Cr(edtp)]^-$ (or $[Cr(edtp\text{-}d)]^-$ with deuteriated 2-methylene of 3-propionates) isomers were described previously [1]. The most stable isomer **E-III** (or **E-III-d**) was passed through a 4×20 cm column of Dowex 50W-X4 (200–400 mesh) cation-exchange resin in the H^+ form. By elution with water, three bands (red purple, bluish purple and violet) were obtained. The first eluate was identified with **E-III** (or **E-III-d**) by the absorption spectrum. The second and third eluates (**H-1** and **H-2** or **H-1-d** and **H-2-d**, respectively) were evaporated to dryness. Powders of each complex were obtained by adding acetone to the aqueous solution.

Anal. Calc. for $[Cr(Hedtp)(H_2O)]\cdot 2.5H_2O$ (**H-1**): C, 36.53; H, 6.13; N, 6.08. Found: C, 36.41; H, 6.14; N, 6.15%. Calc. for $[Cr(Hedtp)(H_2O]\cdot 2.5H_2O$ (**H-2**): C, 36.53; H, 6.13; N, 6.08. Found: C, 36.19; H, 6.12; N, 6.10%.

X-ray study of H-1

All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation and the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation by VAX computer at the

---

*Author to whom correspondence should be addressed.

0020-1693/92/$5.00

X-ray diffraction service of the Department of Chemistry of Osaka University.

Crystals of the **H-1** isomer suitable for the X-ray analysis were grown in water–acetone solution. A red purple crystal (0.15×0.10×0.10 mm) was loaded into a glass capillary. The data were collected at 23±1 °C using the ω–2θ scan technique to a maximum 2θ value of 45.1°. Of the 2766 reflections which were collected 2561 were unique. The intensities of three representative reflections which were measured after every 100 reflections declined by −4.90%. A linear correction factor was applied to the data to account for this phenomena.

The structure was solved by direct methods. The difference-Fourier map revealed five water molecules of crystallization in the crystal of **H-1**. The positional and thermal parameters were refined by the block-diagonal least-squares refinement. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the difference-Fourier map, and their isotropic thermal parameters were refined. The final cycle of block-diagonal least-squares refinement was based on 1390 observed reflections ($I > 2\sigma(I)$). The final R value was 0.040 and $R_w = 0.040$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.33 and −0.37 e/Å^3, respectively.

Crystallographic data and fractional coordinates of non-hydrogen atoms for the **H-1** are given in Tables 1 and 2.

Measurements

Absorption spectra were measured by a Shimadzu UV-2100 spectrophotometer. IR spectra were obtained by a Shimadzu IR-385 spectrophotometer using KBr disks. The ^{2}H NMR spectra were measured on a Jeol JNM-GSX270 spectrometer. The magnetic circular dichroism (MCD) spectra were recorded in a magnetic field of 1.5 T ($1T = 1\times10^4$ G) with a JASCO J-500C spectropolarimeter at room temperature.

TABLE 1. Crystallographic data of *cis-eq*-[Cr(Hedtp)(H_2O)]·5H_2O (**H-1**)

Formula	$C_{14}H_{23}O_9N_2Cr \cdot 5H_2O$
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.796(6)
b (Å)	15.195(6)
c (Å)	14.825(2)
β (°)	94.70(4)
Z	4
D_{calc} (g cm^{-3})	1.526
Crystal size (mm)	0.15×0.10×0.10
μ(Mo Kα) (cm^{-1})	5.74
No. unique reflections	2561
No. observed reflections	1390
R^a	0.040
R_w^b	0.040

$^aR = \Sigma \| F_o\| - |F_c\| / \Sigma |F_o|$. $^bR_w = [(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2}$; $w = 1/\sigma^2(F_o) + 0.0078 F_o^2]$.

TABLE 2. Fractional coordinates of *cis-eq*-[Cr(Hedtp)(H_2O)]·5H_2O (**H-1**)

Atom	x	y	z
Cr	0.3329(1)	0.12408(8)	0.68705(8)
O(1)	0.4771(4)	0.2116(3)	0.6972(3)
O(2)	0.6872(5)	0.2590(3)	0.7329(3)
O(3)	0.4671(5)	0.0310(3)	0.6760(3)
O(4)	0.5704(6)	−0.0945(3)	0.6951(4)
O(5)	0.1915(4)	0.0345(3)	0.6652(3)
O(6)	−0.0017(5)	−0.0255(3)	0.6107(3)
O(7)	0.0578(6)	0.5236(3)	0.6279(4)
O(8)	0.2284(5)	0.4609(3)	0.5620(3)
O(9)	0.3332(4)	0.1460(3)	0.5523(3)
N(1)	0.3469(5)	0.1065(3)	0.8267(4)
N(2)	0.1784(5)	0.2209(3)	0.7067(4)
C(1)	0.4694(7)	0.1470(5)	0.8783(5)
C(2)	0.6000(7)	0.1546(5)	0.8318(5)
C(3)	0.5887(7)	0.2121(5)	0.7496(5)
C(4)	0.3383(8)	0.0106(4)	0.8472(5)
C(5)	0.4586(8)	−0.0434(5)	0.8201(5)
C(6)	0.4997(7)	−0.0359(5)	0.7241(5)
C(7)	0.0337(7)	0.1903(5)	0.6845(5)
C(8)	0.0159(7)	0.1306(5)	0.6022(5)
C(9)	0.0697(7)	0.0399(5)	0.6262(5)
C(10)	0.2025(7)	0.3022(4)	0.6532(5)
C(11)	0.1210(7)	0.3830(5)	0.6769(5)
C(12)	0.1431(7)	0.4586(5)	0.6148(5)
C(13)	0.2217(7)	0.1523(5)	0.8558(5)
C(14)	0.2007(7)	0.2383(4)	0.8058(5)
O(W1)	0.5845(5)	0.1342(4)	0.4846(4)
O(W2)	0.2732(5)	0.0150(3)	0.4374(3)
O(W3)	0.0648(5)	0.6646(3)	0.5265(4)
O(W4)	0.1100(5)	0.8083(3)	0.6341(4)
O(W5)	0.7058(6)	0.2944(4)	0.5543(4)

Results and discussion

Infrared (IR) and absorption (AB) spectra

The analytical data show that the two complexes (**H-1** and **H-2**) newly obtained from **E-III** by chromatography have the same composition as the acid form of the edtp complex, H[Cr(edtp)]·$n$$H_2O$ (see 'Experimental'). Radanovic *et al.* reported that the acid form of **E-III** exhibits only one strong IR band (*c.* 1600 cm^{-1}) corresponding to the coordinated carboxylates [3]. As shown in Fig. 1, however, the present **H-1** and **H-2** complexes have another IR band at 1700 cm^{-1}, indicating that both complexes have a protonated carboxylate group.

Table 3 shows the absorption data in H_2O and 0.04 M (1 M = 1 mol dm^{-3}) NaOH solution. The shift to the lower energy with increasing pH indicates that each complex has one water ligand. That is, **H-1** and **H-2** are geometrical isomers which can be represented as [Cr(Hedtp)(H_2O)] where one of four 3-propionate

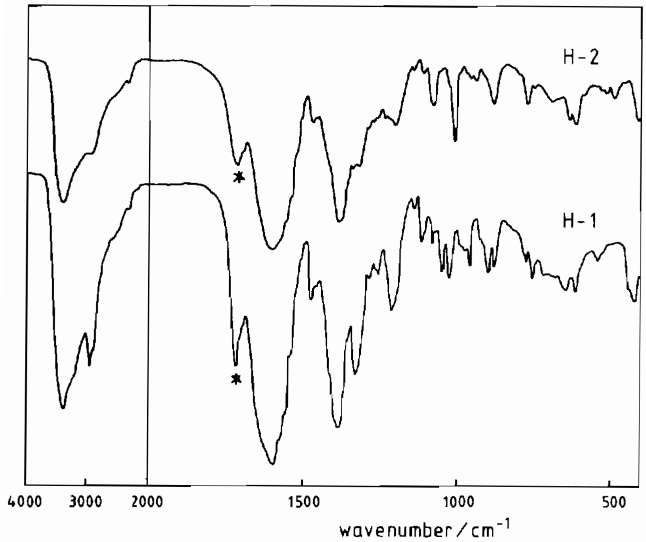


Fig. 1. IR spectra for the two [Cr(Hedtp)(H_2O)] complexes: **H-1** (lower); **H-2** (upper). Asterisked peaks indicate the bands corresponding to the uncoordinated carboxylates (—COOH).

groups is protonated and the edtp ligand acts as a pentadentate Hedtp^{3-}. Only one isomer has been obtained for the analogous chromium(III) complexes; *cis-eq* for [Cr(Hedta)(H_2O] [4], *trans-eq* for [Cr{(*S*)-pdtrp}(H_2O)] ((*S*)-pdtrp = (*S*)-propane-1,2-diamine-*N*,*N*,*N*′-tri-3-propionate) and [Cr{(*S*,*S*)-cydtrp}(H_2O)] ((*S*,*S*)-cydtrp = (1*S*, 2*S*)-*trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*′-tri-3-propionate) [5]. Thus, this is the first example of a chromium(III) complex with a pentadentate edta type ligand which has more than one geometrical isomer.

Molecular structure of the H-1 isomer

The molecular structure of [Cr(Hedtp)(H_2O)]·5H_2O (**H-1**) is given in Fig. 2. The chromium is coordinated by a pentadentate Hedtp ligand and an aqua molecule, producing an octahedral *cis*-CrN_2O_4 geometry. This isomer has the same *cis-eq* configuration as [Cr(Hedta)(H_2O)] in which one of the 3-propionates at the G (in-plane) ring is dissociated. Bond distances and angles of the chelates are almost the same as the corresponding ones of (+)-(+)$_{589}$-LiΔ(λλ)-[Cr(edtp)]·3H_2O (**E-III**) and the related chromium(III) complexes [4–8] as in Tables 4 and 5. The bond distance between the chromium and the nitrogen of the tertiary amine containing the protonated carboxylate group (Cr–N(2)) is lengthened in comparison with the usual Cr–N distances as found in [Cr(Hedta)(H_2O)] [4]. The ethylenic gauche conformations for both two 3-propionato chelates at the R ring are δ when the absolute configuration of the complex is Λ as shown in Fig. 2. These conformations are also described as lel$_2$ form in which the ethylenic C–C bonds of 3-propionato chelates are parallel to the pseudo C_2 axis bisecting the N–Cr–N angle. The six-membered 3-propionato chelates at the G and R ring take an asymmetric envelope and a skew-boat conformation, respectively. The ethylenediamine backbone takes the usual *gauche* conformation, while the corresponding one of the diaminetripropionato complexes [5] with *trans-eq* configuration takes an asymmetric envelope conformation. Accordingly, the conformations of the diamine and 3-propionato chelates of the **H-1** are almost identical with those of **E-III** except for one uncoordinated protonated 3-propionate at the G ring.

^2H NMR and magnetic circular dichroism (MCD) spectra

The ^2H NMR spectra of [Cr(Hedtp)(H_2O)] isomers and related complexes are shown in Fig. 3. The similarity in the spectral patterns of **H-1-d** and the **E-III-d** (Fig. 3(a) and (c)) indicates that the structures of these complexes are similar not only in solid state but also in solution. It is noted that the peak at +57 ppm for the **E-III-d** is shifted to the upfield by about 10 ppm for the **H-1-d**. This fact indicates that the peak around +50 ppm corresponds to the signal of the 3-propionate group at the G ring in accordance with that proposed for the deuteriated 1,3-propanediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionato complex ([Cr(1,3-pddda-6-d)]$^-$) [8]. One sharp peak at +7 ppm is due to the deuteriated 2-methylene of the uncoordinated protonated 3-propionate.

The ^2H NMR spectrum of **H-2-d** is different from that of **E-III-d**. However, it is almost identical with that of *trans-eq*-[Cr(edtrp-d)(H_2O)] as shown in Fig.

TABLE 3. Absorption data of the [Cr(Hedtp)(H_2O)] isomers

Isomer	Solvent	λ_{max} (nm)	ϵ (mol^{-1} dm^3 cm^{-1})	λ_{max} (nm)	ϵ (mol^{-1} dm^3 cm^{-1})
H-1	a	549.5	121.0	395.5	49.9
	b	579.2	90.2	415.6	49.8
H-2	a	546.0	172.9	402.0	65.3
	b	567.6	125.0	414.2	60.4

[a] In aqueous solution. [b] In 0.04 M NaOH aqueous solution.

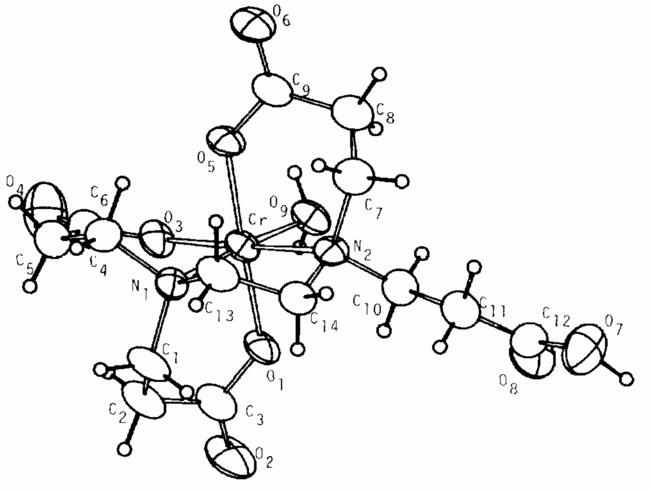


Fig. 2. Molecular structure of complex **H-1**.

TABLE 4. Bond distances (Å) of *cis-eq*-[Cr(Hedtp)(H_2O)]·$5H_2O$ (**H-1**)

Cr–O(1)	1.938(5)	Cr–O(3)	1.947(5)
Cr–O(5)	1.950(5)	Cr–O(9)	2.025(5)
Cr–N(1)	2.081(5)	Cr–N(2)	2.147(5)
O(1)–C(3)	1.287(8)	O(2)–C(3)	1.240(9)
O(3)–C(6)	1.268(8)	O(4)–C(6)	1.228(9)
O(5)–C(9)	1.284(8)	O(6)–C(9)	1.225(8)
O(7)–C(12)	1.320(9)	O(8)–C(12)	1.192(9)
N(1)–C(1)	1.502(9)	N(1)–C(4)	1.492(9)
N(1)–C(13)	1.504(9)	N(2)–C(7)	1.503(9)
N(2)–C(10)	1.497(9)	N(2)–C(14)	1.491(9)
C(1)–C(2)	1.51(1)	C(2)–C(3)	1.50(1)
C(4)–C(5)	1.52(1)	C(5)–C(6)	1.51(1)
C(7)–C(8)	1.52(1)	C(8)–C(9)	1.51(1)
C(10)–C(11)	1.52(1)	C(11)–C(12)	1.50(1)
C(13)–C(14)	1.51(1)		

3(b) and (d), except for one signal near +10 ppm assignable to the uncoordinated protonated 3-propionate. Moreover, the MCD spectrum of the **H-2** shows the same pattern as that of *trans-eq*-[Cr(*rac*-pdtrp)(H_2O)] and -[Cr(edtrp)(H_2O)] in the spin-forbidden transitions as shown in Fig. 4. From these observations, the geometrical structure of **H-2** is assigned to *trans-eq*.

Reaction of the isomers

Though the two Hedtp isomers are stable in basic solution (pH 9–10), they gradually revert to **E-III** in aqueous (or acidic) solution. These rechelation reactions to **E-III** were followed by measuring the absorption spectra for **H-1** and **H-2** successively. As shown in Fig. 5, the spectra of both the complexes were changing with time and finally identified with that of **E-III**. Two isosbestic points are observed in the spectra of **H-1** and the half lifetime of the reaction is about 30 min. In the case of **H-2**, however, there is no isosbestic point in the spectra and the reaction rate is slower than that of the **H-1** isomer; the half lifetime is estimated to be more than 240 min.

TABLE 5. Bond angles (°) of *cis-eq*-[Cr(Hedtp)(H_2O)]·$5H_2O$ (**H-1**)

O(1)–Cr–O(3)	90.7(2)	O(1)–Cr–O(5)	174.7(2)
O(1)–Cr–O(9)	84.5(2)	O(1)–Cr–N(1)	91.3(2)
O(1)–Cr–N(2)	92.1(2)	O(3)–Cr–O(5)	87.4(2)
O(3)–Cr–O(9)	88.9(2)	O(3)–Cr–N(1)	90.0(2)
O(3)–Cr–N(2)	175.8(2)	O(5)–Cr–O(9)	90.5(2)
O(5)–Cr–N(1)	93.6(2)	O(5)–Cr–N(2)	90.1(2)
O(9)–Cr–N(1)	175.6(2)	O(9)–Cr–N(2)	94.5(2)
N(1)–Cr–N(2)	86.7(2)	Cr–O(1)–C(3)	128.9(4)
Cr–O(3)–C(6)	132.5(5)	Cr–O(5)–C(9)	130.6(4)
Cr–N(1)–C(1)	116.0(4)	Cr–N(1)–C(4)	109.1(4)
Cr–N(1)–C(13)	103.7(4)	Cr–N(2)–C(7)	114.9(4)
Cr–N(2)–C(10)	110.5(4)	Cr–N(2)–C(14)	102.0(4)
C(1)–N(1)–C(4)	110.7(5)	C(1)–N(1)–C(13)	107.5(5)
C(4)–N(1)–C(13)	109.5(5)	C(7)–N(2)–C(10)	109.0(5)
C(7)–N(2)–C(14)	109.3(5)	C(10)–N(2)–C(14)	111.1(5)
O(1)–C(3)–O(2)	121.3(6)	O(3)–C(6)–O(4)	120.5(7)
O(5)–C(9)–O(6)	121.9(6)	O(7)–C(12)–O(8)	124.1(7)
O(1)–C(3)–C(2)	119.4(6)	O(3)–C(6)–C(5)	121.0(6)
O(5)–C(9)–C(8)	117.2(6)	O(7)–C(12)–C(11)	111.0(6)
O(2)–C(3)–C(2)	119.4(6)	O(4)–C(6)–C(5)	118.4(6)
O(6)–C(9)–C(8)	120.9(6)	O(8)–C(12)–C(11)	124.9(7)
C(1)–C(2)–C(3)	114.1(6)	C(4)–C(5)–C(6)	118.7(6)
C(7)–C(8)–C(9)	110.0(6)	C(10)–C(11)–C(12)	111.8(6)
N(1)–C(1)–C(2)	118.2(6)	N(1)–C(4)–C(5)	114.6(6)
N(2)–C(7)–C(8)	113.9(6)	N(2)–C(10)–C(11)	115.7(6)
N(1)–C(13)–C(14)	110.0(6)	N(2)–C(14)–C(13)	109.5(5)

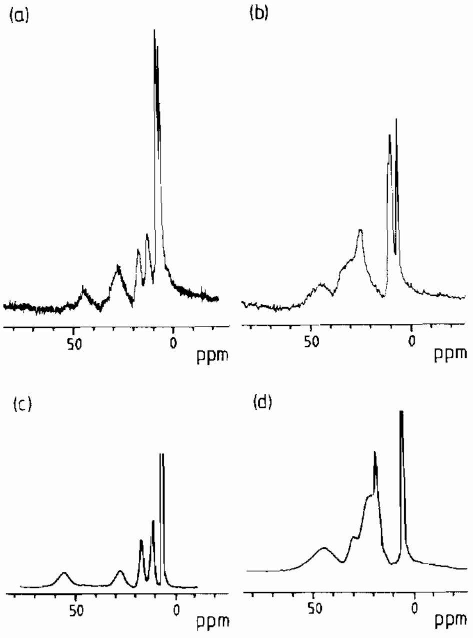


Fig. 3. ^2H NMR spectra of [Cr(Hedtp-d)(H_2O)] isomers and related complexes in 0.04 M NaOH solution: (a) **H-1-d**; (b) **H-2-d**; (c) **E-III-d**; (d) [Cr(edtrp-d)(H_2O)].

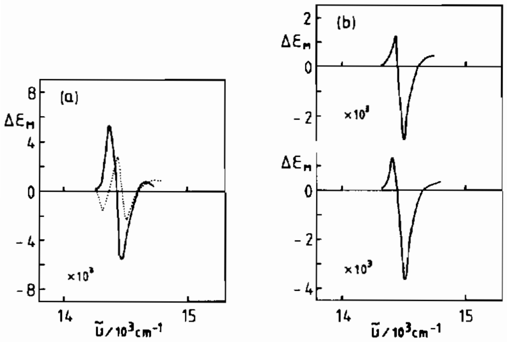


Fig. 4. Magnetic circular dichroism (MCD) spectra of the **H-1** and **H-2**: (a) **H-1-d** (···); **H-2-d** (——); (b) [Cr(edtrp)(H_2O)] (upper); [Cr(*rac*-pdtrp)(H_2O)] (lower).

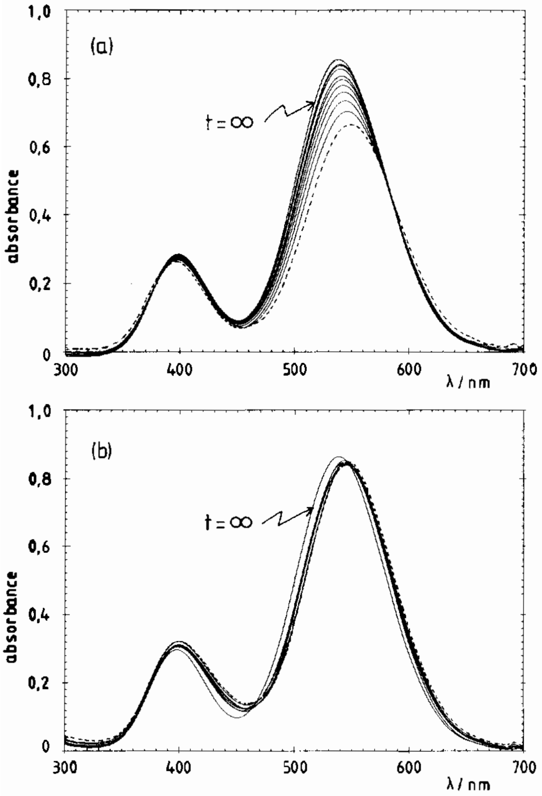
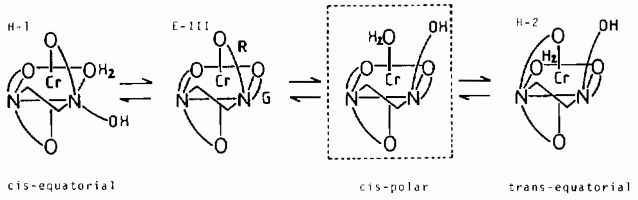


Fig. 5. Absorption spectral change for the **H-1** and **H-2** in H_2O at 50 °C: dashed lines, initial spectra; solid lines, spectra at successive times of 10, 20, 30, 40, 50, 60, 80, 100 and 120 min for **H-1** and 20, 40, 60, 120, 180 and 240 min for **H-2**.

The differences reflect the rechelation reaction path from the isomers to E-III as in Scheme 1. The rechelation from the *cis-eq* as well as the *cis-polar* isomer to E-III may occur easily by interchanging of one uncoordinated 3-propionate and the aqua ligand. On the other hand, the reaction from the *trans-eq* isomer to **E-III** requires interchange among two 3-propionates and the aqua ligand, even in the shortest pathway through the *cis-polar* intermediate as in Scheme 1. Thus, the complicated spectral change observed during the reaction for **H-2** supports the assignment of **H-2** to the *trans-eq* configuration.



Scheme 1.

From the fact that both two isomers revert to **E-III** completely, **H-1** and **H-2** are found to be much more unstable than **E-III** in aqueous (or acidic) solution. This may be the reason why the Hedtp complexes could not be found in the acidic solution of E-III in contrast to the case of [Cr(Hedta)(H_2O)] type complexes [2].

Supplementary material

Tables of thermal parameters, H-atom coordinates, torsion angles, and observed and calculated structure factors can be obtained from the authors on request.

References

1 N. Sakagami, M. Hayashi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, (1992) 285.

2 (a) W. D. Wheeler and J. I. Legg, *Inorg. Chem.*, *24* (1985) 1292; (b) H. Ogino and M. Shimura, *Adv. Inorg. Bioinorg. Mech.*, *4* (1986) 107; (c) S. Kaizaki and H. Mizu-uchi, *Inorg. Chem.*, *25* (1986) 2732.

3 D. J. Radanović, M. I. Djuran, M. M. Djorović and B. E. Douglas, *Inorg. Chim. Acta*, *146* (1988) 199.

4 L. E. Gerdom, N. A. Baenziger and H. M. Goff, *Inorg. Chem.*, *20* (1981) 1606.

5 N. Sakagami and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, (1992) 291.

6 M. Parvez, C. Maricondi, D. J. Radanović, M. I. Djuran and B. E. Douglas, *Inorg. Chim. Acta*, *182* (1991) 177.

7 F. T. Helm, W. H. Watson, D. J. Radanović and B. E. Douglas, *Inorg. Chem.*, *16* (1977) 2351.

8 S. Kaizaki, M. Byakuno, M. Hayashi, J. I. Legg, K. Umakoshi and S. Ooi, *Inorg. Chem.*, *26* (1987) 2395.