# Novel Diastereoisomers of Ethylenediaminetetrapropionatochromate(III) Part 2.[1] X-Ray Structures of Diaminetripropionato Complexes†

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The crystal structures of the complexes [Cr{(*S*)-pdtrp}($H_2O$)] **1** [(*S*)-pdtrp = (*S*)-propane-1,2-diamine-*N,N,N′*-tripropionate] and [Cr{(*SS*)-cydtrp}($H_2O$)] **2** [(*SS*)-cydtrp = (1*S*,2*S*)-*trans*-cyclohexane-1,2-diamine-*N,N,N′*-tripropionate] were determined by X-ray diffraction methods: **1**, monoclinic, space group $P2_1$, $a$ = 13.474(9), $b$ = 9.867(3), $c$ = 14.506(5) Å, β = 105.85(3)° and $Z$ = 4; **2**, triclinic, space group $P1$, $a$ = 13.938(7), $b$ = 14.016(6), $c$ = 13.901(4) Å, α = 106.24(3), β = 112.50(3), γ = 73.21(4)° and $Z$ = 4. The two complexes have the same geometrical structure, *trans*-equatorial, where two propionato chelates attached to the tertiary amine are co-ordinated meridionally. This structure substantiates that the anomalous C–N bond rupture observed in the two of the three diastereoisomers of [Cr(edtp)]$^-$ (edtp = ethylenediamine-*N,N,N′,N′*-tetrapropionate) type complexes occurs at the R (relaxed) out-of-plane ring, not at the G (girdling) in-plane ring.

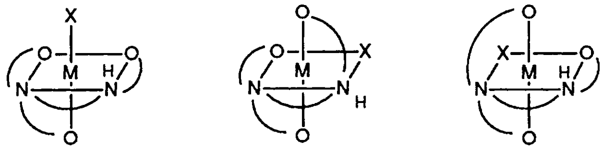
Three diastereoisomers for [Cr(edtp)]$^-$ (edtp = ethylenediaminetetrapropionate), [Cr{(*S*)-pdtp}]$^-$ [(*S*)-pdtp = (*S*)-propane-1,2-diaminetetrapropionate] and [Cr{(*SS*)-cydtp}]$^-$ [(*SS*)-cydtp = (1*S*,2*S*)-*trans*-cyclohexane-1,2-diaminetetrapropionate] have been found, which arise from a pairwise combination of the chiral conformations of the two out-of-plane propionate rings.[1,2] Two of them decompose in aqueous solution to form 3-hydroxypropionic acid and the complexes [Cr(edtrp)($H_2O$)] (edtrp = ethylenediaminetripropionate), [Cr{(*S*)-pdtrp}($H_2O$)] [(*S*)-pdtrp = (*S*)-propane-1,2-diaminetripropionate] and [Cr{(*SS*)-cydtrp}($H_2O$)] [(*SS*)-cydtrp = (1*S*,2*S*)-*trans*-cyclohexane-1,2-diaminetripropionate].[1,2] This decomposition is accompanied by unprecedented C–N bond cleavage. For the elucidation of this bond cleavage it is important to assign the diaminetripropionato complexes to one of three possible geometrical isomers; *cis*-polar, *cis*-equatorial and *trans*-equatorial with respect to the co-ordination site of the monodentate ligand (X) as shown in Fig. 1. However, the geometrical structure of this type of complexes could not be determined by $^2H$ NMR and/or CD spectroscopy.

We report here the X-ray structures for [Cr{(*S*)-pdtrp}($H_2O$)]·$4H_2O$ and [Cr{(*SS*)-cydtrp}($H_2O$)]·$4.5H_2O$, and examine the decomposition reaction and CD spectra in connection with the geometrical structure of the edtrp-type complexes.

## Experimental

The complexes were prepared as previously described.[1] Crystals suitable for the X-ray analyses were grown from water–acetone solutions.

*Spectral Measurements.*—The CD spectra were measured with a JASCO J-500C spectropolarimeter. The solid-state CD spectra were obtained by the Nujol mull method[3] with use of the above spectropolarimeter. Magnetic circular dichroism (MCD) spectra were recorded in a magnetic field of 1.5 T by the same spectropolarimeter as for the CD measurement at room temperature.



*cis*-polar *cis*-equatorial *trans*-equatorial

**Fig. 1** Three possible geometrical isomers of [MX(edtrp)] type complexes

**Table 1** Crystallographic data for [Cr{(*S*)-pdtrp}($H_2O$)]·$4H_2O$ **1** and [Cr{(*SS*)-cydtrp}($H_2O$)]·$4.5H_2O$ **2**

| | **1** | **2** |
|---|---|---|
| Formula | $C_{12}H_{21}N_2O_7Cr·4H_2O$ | $C_{15}H_{25}CrN_2O_7·4.5H_2O$ |
| $M$ | 429.36 | 478.44 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1$ | $P1$ |
| $a$/Å | 13.474(9) | 13.938(7) |
| $b$/Å | 9.867(3) | 14.016(6) |
| $c$/Å | 14.506(5) | 13.901(4) |
| α/° | 90.0 | 106.24(3) |
| β/° | 105.85(3) | 112.50(3) |
| γ/° | 90.0 | 73.21(4) |
| $U$/Å$^3$ | 1855(3) | 2357(2) |
| $Z$ | 4 | 4 |
| $D_m$/g cm$^{-3}$ | 1.27 | 1.33 |
| $D_c$/g cm$^{-3}$ | 1.28 | 1.339 |
| μ(Mo-Kα)/cm$^{-1}$ | 6.76 | 5.26 |
| $F$(000) | 748 | 988 |

*X-Ray Crystallography.*—Crystallographic data for [Cr{(*S*)-pdtrp}($H_2O$)]·$4H_2O$ **1** and [Cr{(*SS*)-cydtrp}($H_2O$)]·$4.5H_2O$ **2** are given in Table 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[4] on a VAX computer at the X-ray diffraction service of the department of chemistry of Osaka University.

The absolute configuration was determined on the basis of the absolute configuration of the chiral carbon(s) in the diamine chelates of the starting materials: *S* for the pdtrp and *S*,*S* for the cydtrp.

*Structural determination.* A red stick crystal (0.1 × 0.15 ×

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv

**Table 2** Fractional coordinates for complex **1** [a]

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cr(A)[b] | 0.7098(1) | 0.1668 | 0.2832(1) |
| Cr(B) | 0.1957(1) | 0.1808(2) | 0.2734(1) |
| O(1A) | 0.6333(5) | 0.3344(9) | 0.2677(5) |
| O(2A) | 0.5499(7) | 0.518(1) | 0.1992(6) |
| O(3A) | 0.8317(5) | 0.262(1) | 0.3570(5) |
| O(4A) | 0.9968(5) | 0.315(1) | 0.4074(6) |
| O(5A) | 0.5837(5) | 0.083(1) | 0.2069(5) |
| O(6A) | 0.4738(6) | −0.0593(9) | 0.1184(6) |
| O(7A) | 0.6730(5) | 0.1249(8) | 0.4054(5) |
| O(1B) | 0.1297(5) | 0.002(1) | 0.2611(5) |
| O(2B) | 0.0468(7) | −0.175(1) | 0.1905(7) |
| O(3B) | 0.0610(5) | 0.253(1) | 0.2090(5) |
| O(4B) | −0.0660(5) | 0.395(1) | 0.1510(6) |
| O(5B) | 0.3237(5) | 0.0932(9) | 0.3419(5) |
| O(6B) | 0.4862(5) | 0.046(1) | 0.3946(6) |
| O(7B) | 0.1701(5) | 0.2200(8) | 0.3996(5) |
| N(1A) | 0.7576(6) | 0.199(1) | 0.1622(5) |
| N(2A) | 0.7907(6) | −0.014(1) | 0.2930(6) |
| N(1B) | 0.2344(6) | 0.160(1) | 0.1459(6) |
| N(2B) | 0.2700(6) | 0.364(1) | 0.2804(6) |
| C(1A) | 0.6842(8) | 0.279(1) | 0.0871(8) |
| C(2A) | 0.6671(9) | 0.419(1) | 0.1231(8) |
| C(3A) | 0.6134(8) | 0.422(2) | 0.204(1) |
| C(4A) | 0.8701(8) | −0.022(1) | 0.3887(7) |
| C(5A) | 0.9561(8) | 0.078(1) | 0.4047(9) |
| C(6A) | 0.928(1) | 0.230(2) | 0.3893(9) |
| C(7A) | 0.7219(9) | −0.1328(1) | 0.292(1) |
| C(8A) | 0.6348(8) | −0.151(1) | 0.2025(9) |
| C(9A) | 0.558(1) | −0.035(1) | 0.1725(8) |
| C(10A) | 0.7818(8) | 0.065(1) | 0.1259(7) |
| C(11A) | 0.8391(8) | −0.020(1) | 0.2109(8) |
| C(12A) | 0.841(1) | 0.077(2) | 0.0517(8) |
| C(1B) | 0.244(1) | 0.015(1) | 0.121(1) |
| C(2B) | 0.142(1) | −0.059(2) | 0.106(1) |
| C(3B) | 0.1043(9) | −0.078(1) | 0.1906(9) |
| C(4B) | 0.1973(8) | 0.478(1) | 0.2823(9) |
| C(5B) | 0.1025(8) | 0.487(1) | 0.201(1) |
| C(6B) | 0.0266(9) | 0.372(1) | 0.1875(8) |
| C(7B) | 0.3533(7) | 0.375(1) | 0.3696(8) |
| C(8B) | 0.442(1) | 0.278(2) | 0.383(1) |
| C(9B) | 0.4163(8) | 0.130(1) | 0.3736(7) |
| C(10B) | 0.3288(8) | 0.242(1) | 0.1531(8) |
| C(11B) | 0.3125(7) | 0.379(1) | 0.1973(8) |
| C(12B) | 0.355(1) | 0.261(2) | 0.0594(9) |

[a] Standard deviations in the least significant figures are given in parentheses. [b] The *y* coordinate of Cr(A) is fixed.

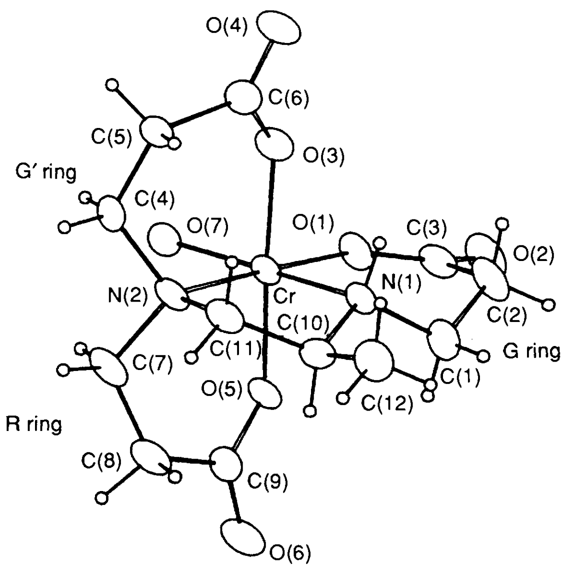


**Fig. 2** Molecular structure of complex **1** (fragment A), *trans*-equatorial [Λ(G)δ(G′)λ(R); ob$_2$]. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are represented as spheres of arbitrary radius

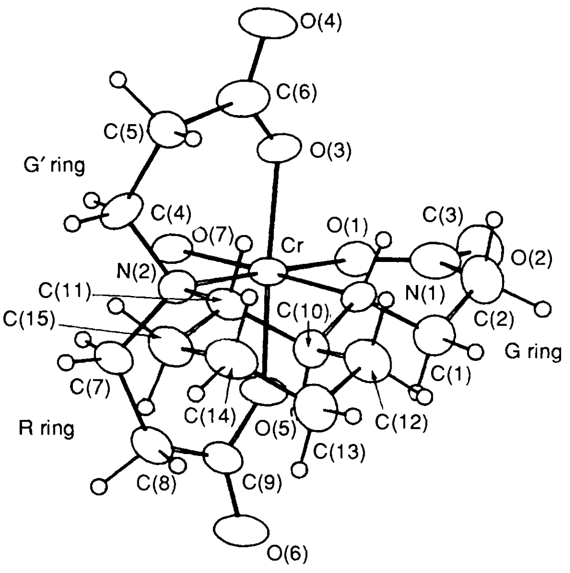


**Fig. 3** Molecular structure of complex **2** (fragment A), *trans*-equatorial [Λ(G)δ(G′)λ(R); ob$_2$]. Other details as in Fig. 2

0.4 mm) of complex **1** was loaded into a glass capillary. Data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ of 50.1°. Of the 3058 reflections collected, 2930 were unique. Three representative reflections were monitored every 100 and their intensities showed no decay. The structure was solved by direct methods. Two crystallographically independent molecules were partially revealed. The remaining atoms in these molecules and solvent molecules were found in the Fourier-difference map. The positional and thermal parameters were refined by block-diagonal least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were introduced in calculated positions, and their isotropic thermal parameters were refined. The final cycle of refinement was based on 2180 observed reflections [$I > 2\sigma(I)$]. The absolute configuration was confirmed by the anomalous dispersion method; the *R* value for the (*S*)-pdtrp complex was 0.046 and $R' = 0.057$ [for the (*R*)-pdtrp complex: $R = 0.049$ and $R' = 0.060$], where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o) + 0.0078F_o^2]$. The final difference electron-density map was fairly clean (largest peak 0.45 e Å$^{-3}$).

A red stick crystal (0.1 × 0.15 × 1.0 mm) of complex **2** was loaded into a glass capillary. The same scan techniques as employed for **1** were used except that the maximum 2θ was 55.2°. Of the 11 356 reflections, 10 906 were unique. Four crystallographically independent molecules were revealed by the direct method. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for those of water molecules were introduced in calculated positions and were not refined. The final cycle of block-diagonal least-squares refinement was based on 6596 observed reflections [$I > 3\sigma(I)$]. The absolute configuration was confirmed by the anomalous

**Table 3** Fractional coordinates for complex **2**[a]

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Cr(A) | 0.4939(2) | 0.5163(2) | 1.0138(2) | C(11A) | 0.543(1) | 0.466(1) | 0.820(1) |
| Cr(B) | 1.0053(2) | 0.5167(2) | 1.0107(2) | C(12A) | 0.657(2) | 0.295(1) | 0.812(2) |
| Cr(C)[b] | 1 | 1 | 1 | C(13A) | 0.701(2) | 0.316(2) | 0.741(2) |
| Cr(D) | 0.9992(3) | 0.9941(2) | 0.4833(2) | C(14A) | 0.620(2) | 0.388(2) | 0.674(2) |
| O(1A) | 0.500(1) | 0.4665(9) | 1.134(1) | C(15A) | 0.582(2) | 0.488(1) | 0.739(2) |
| O(2A) | 0.519(1) | 0.367(1) | 1.237(1) | C(1B) | 0.983(1) | 0.376(1) | 0.801(1) |
| O(3A) | 0.3582(8) | 0.4759(7) | 0.9408(9) | C(2B) | 0.924(1) | 0.463(1) | 0.746(1) |
| O(4A) | 0.199(1) | 0.462(1) | 0.824(1) | C(3B) | 0.855(1) | 0.553(1) | 0.800(1) |
| O(5A) | 0.6286(8) | 0.5565(9) | 1.099(1) | C(4B) | 1.204(1) | 0.525(1) | 1.195(1) |
| O(6A) | 0.783(1) | 0.599(1) | 1.153(1) | C(5B) | 1.250(1) | 0.572(1) | 1.144(1) |
| O(7A) | 0.4163(8) | 0.6561(8) | 1.064(1) | C(6B) | 1.176(1) | 0.6292(9) | 1.058(1) |
| O(1B) | 0.8823(8) | 0.5748(7) | 0.8996(7) | C(7B) | 1.101(1) | 0.416(1) | 1.195(1) |
| O(2B) | 0.775(1) | 0.602(1) | 0.742(1) | C(8B) | 1.031(1) | 0.334(1) | 1.142(1) |
| O(3B) | 1.0806(7) | 0.6130(6) | 1.0085(8) | C(9B) | 0.933(1) | 0.353(1) | 1.052(1) |
| O(4B) | 1.2070(8) | 0.6922(7) | 1.0347(9) | C(10B) | 1.132(1) | 0.319(1) | 0.955(1) |
| O(5B) | 0.9181(7) | 0.4281(7) | 1.0080(8) | C(11B) | 1.203(1) | 0.363(1) | 1.063(1) |
| O(6B) | 0.8698(8) | 0.2980(7) | 1.022(1) | C(12B) | 1.198(1) | 0.244(1) | 0.894(1) |
| O(7B) | 0.9534(8) | 0.6190(6) | 1.1250(8) | C(13B) | 1.269(2) | 0.164(1) | 0.957(2) |
| O(1C) | 1.1114(8) | 1.0606(7) | 1.1133(7) | C(14B) | 1.341(1) | 0.206(1) | 1.063(2) |
| O(2C) | 1.273(1) | 1.0786(9) | 1.2174(9) | C(15B) | 1.279(1) | 0.280(1) | 1.129(1) |
| O(3C) | 1.0011(8) | 0.9230(7) | 1.0999(7) | C(1C) | 1.202(1) | 0.906(1) | 0.963(1) |
| O(4C) | 0.976(1) | 0.8108(7) | 1.1655(8) | C(2C) | 1.262(1) | 0.934(1) | 1.078(1) |
| O(5C) | 1.0043(8) | 1.0832(6) | 0.9130(7) | C(3C) | 1.215(1) | 1.031(1) | 1.143(1) |
| O(6C) | 0.987(1) | 1.1398(8) | 0.7705(8) | C(4C) | 0.807(1) | 0.912(1) | 0.917(1) |
| O(7C) | 0.8905(7) | 1.1149(6) | 1.0465(7) | C(5C) | 0.858(1) | 0.836(1) | 0.995(1) |
| O(1D) | 0.889(1) | 0.933(1) | 0.4807(9) | C(6C) | 0.951(1) | 0.857(1) | 1.092(1) |
| O(2D) | 0.787(1) | 0.822(1) | 0.442(1) | C(7C) | 0.812(1) | 1.009(1) | 0.806(1) |
| O(3D) | 0.9026(9) | 1.0386(9) | 0.3490(8) | C(8C) | 0.864(1) | 1.043(1) | 0.748(1) |
| O(4D) | 0.836(1) | 1.099(1) | 0.202(1) | C(9C) | 0.956(1) | 1.092(1) | 0.812(1) |
| O(5D) | 1.084(1) | 0.9464(8) | 0.6131(8) | C(10C) | 1.056(1) | 0.843(1) | 0.826(1) |
| O(6D) | 1.226(1) | 0.890(1) | 0.737(1) | C(11C) | 0.934(1) | 0.834(1) | 0.818(1) |
| O(7D) | 0.939(1) | 1.1246(8) | 0.5670(8) | C(12C) | 1.101(1) | 0.744(1) | 0.777(1) |
| N(1A) | 0.570(1) | 0.378(1) | 0.953(1) | C(13C) | 1.035(1) | 0.711(1) | 0.663(1) |
| N(2A) | 0.496(1) | 0.5560(9) | 0.882(1) | C(14C) | 0.929(2) | 0.696(1) | 0.660(1) |
| N(1B) | 1.0650(9) | 0.4053(8) | 0.9021(9) | C(15C) | 0.866(1) | 0.794(1) | 0.708(1) |
| N(2B) | 1.138(1) | 0.4471(8) | 1.1224(9) | C(1D) | 1.049(2) | 0.771(1) | 0.416(2) |
| N(1C) | 1.1022(9) | 0.8795(8) | 0.9432(8) | C(2D) | 0.934(2) | 0.765(2) | 0.376(2) |
| N(2C) | 0.8802(9) | 0.9323(8) | 0.8755(9) | C(3D) | 0.866(2) | 0.845(1) | 0.438(1) |
| N(1D) | 1.065(1) | 0.864(1) | 0.400(1) | C(4D) | 1.074(1) | 1.146(1) | 0.432(1) |
| N(2D) | 1.120(1) | 1.053(1) | 0.482(1) | C(5D) | 1.004(1) | 1.132(1) | 0.317(1) |
| C(1A) | 0.643(2) | 0.324(2) | 1.036(2) | C(6D) | 0.909(1) | 1.091(1) | 0.290(1) |
| C(2A) | 0.589(2) | 0.297(2) | 1.094(2) | C(7D) | 1.182(1) | 1.090(1) | 0.593(1) |
| C(3A) | 0.531(1) | 0.386(2) | 1.161(2) | C(8D) | 1.240(2) | 1.014(1) | 0.663(1) |
| C(4A) | 0.384(1) | 0.596(1) | 0.819(1) | C(9D) | 1.180(2) | 0.949(1) | 0.673(1) |
| C(5A) | 0.309(1) | 0.525(1) | 0.774(1) | C(10D) | 1.146(1) | 0.869(1) | 0.426(1) |
| C(6A) | 0.287(1) | 0.486(1) | 0.851(1) | C(11D) | 1.182(1) | 0.973(1) | 0.419(1) |
| C(7A) | 0.553(1) | 0.642(1) | 0.915(1) | C(12D) | 1.233(1) | 0.783(1) | 0.355(1) |
| C(8A) | 0.668(1) | 0.621(1) | 0.981(2) | C(13D) | 1.348(2) | 0.794(2) | 0.380(2) |
| C(9A) | 0.696(1) | 0.591(1) | 1.084(1) | C(14D) | 1.345(2) | 0.904(1) | 0.369(2) |
| C(10A) | 0.621(1) | 0.393(1) | 0.883(1) | C(15D) | 1.289(2) | 0.989(1) | 0.436(2) |

[a] Standard deviations in the least significant figures are given in parentheses. [b] The fractional coordinates of Cr(C) are fixed.

dispersion method. The final *R* value for the (*SS*)-cydtrp complex was 0.079 and $R' = 0.111$ [for the (*RR*)-cydtrp complex: $R = 0.087$ and $R' = 0.116$]. The maximum and minimum peaks on the final Fourier difference map corresponded to 2.04 and $-1.01$ e Å$^{-3}$, respectively.

Fractional coordinates of non-hydrogen atoms for complexes **1** and **2** except for the water molecules of crystallization are given in Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

*Molecular Structure.*—The molecular structures of complexes **1** and **2** are given in Figs. 2 and 3. Each chromium atom is co-ordinated by a pentadentate (*S*)-pdtrp or (*SS*)-cydtrp ligand and a water molecule, producing an octahedral *cis*-$CrN_2O_4$ geometry. The bond distances and angles (Tables 4 and 5) of these complexes are comparable with the corresponding ones of analogous complexes.[5–9] The mean Cr–$OH_2$ [O(7)] bond distance [2.002(7) for **1**, 2.02(1) Å for **2**] is a little longer than the other Cr–O (carboxylate) distances in conformity with the Cr–O bond distances found in [Cr(Hedta)($H_2O$)].[5] The geometrical structures of these complexes are *trans*-equatorial where two propionato chelate rings attached to the tertiary amine of the (*S*)-pdtrp or (*SS*)-cydtrp are co-ordinated meridionally, as shown in Figs. 2 and 3. The *trans*-equatorial isomers of cobalt(III) edtra (ethylenediaminetriacetate) type complexes were characterized only by absorption, CD and NMR spectra;[10,11] the *cis*-equatorial structure alone has been determined by X-ray diffraction methods.[12] Thus, this is the first X-ray determination of the *trans*-equatorial structure of the pentadentate edtra-type complexes.

As shown in Figs. 2 and 3, two out-of-plane propionate rings

**Table 4** Bond distances (Å) for complexes **1** and **2** (average)

| | **1** | **2** | | **1** | **2** |
|---|---|---|---|---|---|
| Cr–O(1) | 1.946(7) | 1.95(1) | Cr–O(3) | 1.939(6) | 1.96(1) |
| Cr–O(5) | 1.943(6) | 1.94(1) | Cr–O(7) | 2.002(7) | 2.02(1) |
| Cr–N(1) | 2.059(8) | 2.05(1) | Cr–N(2) | 2.065(9) | 2.09(2) |
| O(1)–C(3) | 1.26(2) | 1.26(2) | O(2)–C(3) | 1.26(1) | 1.23(3) |
| O(3)–C(6) | 1.29(1) | 1.28(2) | O(4)–C(6) | 1.24(1) | 1.26(2) |
| O(5)–C(9) | 1.27(1) | 1.29(2) | O(6)–C(9) | 1.23(1) | 1.24(3) |
| N(1)–C(1) | 1.49(1) | 1.46(3) | N(1)–C(10) | 1.49(1) | 1.51(2) |
| N(2)–C(4) | 1.51(1) | 1.50(2) | N(2)–C(7) | 1.48(1) | 1.50(2) |
| N(2)–C(11) | 1.49(1) | 1.50(2) | C(1)–C(2) | 1.54(2) | 1.49(3) |
| C(2)–C(3) | 1.50(2) | 1.55(3) | C(4)–C(5) | 1.50(1) | 1.51(3) |
| C(5)–C(6) | 1.53(2) | 1.49(3) | C(7)–C(8) | 1.51(1) | 1.51(2) |
| C(8)–C(9) | 1.52(2) | 1.48(3) | C(10)–C(11) | 1.54(1) | 1.51(2) |
| C(10)–C(12) | 1.53(2) | 1.51(2) | C(12)–C(13) | | 1.51(3) |
| C(13)–C(14) | | 1.53(3) | C(14)–C(15) | | 1.50(3) |
| C(15)–C(11) | | 1.53(3) | | | |

**Table 5** Selected bond angles (°) for complexes **1** and **2** (average)

| | **1** | **2** | | **1** | **2** |
|---|---|---|---|---|---|
| O(1)–Cr–O(3) | 88.1(3) | 87.9(6) | O(1)–Cr–O(5) | 87.3(3) | 87.4(5) |
| O(1)–Cr–O(7) | 92.5(3) | 90.4(5) | O(1)–Cr–N(1) | 93.0(3) | 93.1(5) |
| O(1)–Cr–N(2) | 176.9(3) | 176.9(5) | O(3)–Cr–O(5) | 175.1(3) | 175.0(5) |
| O(3)–Cr–O(7) | 89.7(3) | 89.6(4) | O(3)–Cr–N(1) | 90.5(3) | 90.9(5) |
| O(3)–Cr–N(2) | 93.3(3) | 92.5(5) | O(5)–Cr–O(7) | 89.9(3) | 89.1(4) |
| O(5)–Cr–N(1) | 90.5(3) | 90.8(5) | O(5)–Cr–N(2) | 91.5(3) | 92.3(6) |
| O(7)–Cr–N(1) | 174.2(3) | 176.3(5) | O(7)–Cr–N(2) | 90.3(3) | 92.7(5) |
| N(1)–Cr–N(2) | 84.3(3) | 83.8(5) | Cr–N(1)–C(1) | 113.2(6) | 113(1) |
| Cr–N(1)–C(10) | 107.9(6) | 108(1) | Cr–N(2)–C(4) | 110.3(6) | 110(1) |
| Cr–N(2)–C(7) | 111.0(6) | 109(1) | Cr–N(2)–C(11) | 111.0(7) | 108(1) |
| C(1)–N(1)–C(10) | 112.9(8) | 114(1) | C(4)–N(2)–C(7) | 104.6(7) | 105(1) |
| C(4)–N(2)–C(11) | 110.9(8) | 111(1) | C(7)–N(2)–C(11) | 110.7(8) | 115(1) |
| O(1)–C(3)–O(2) | 123(1) | 122(2) | C(3)–C(6)–O(4) | 121(1) | 120(2) |
| O(5)–C(9)–O(6) | 121(1) | 122(2) | O(1)–C(3)–C(2) | 122(1) | 119(2) |
| O(3)–C(6)–C(5) | 119.3(9) | 120(1) | O(5)–C(9)–C(8) | 120.2(8) | 119(2) |
| O(2)–C(3)–C(2) | 115.7(9) | 118(2) | O(4)–C(6)–C(5) | 120(1) | 119(2) |
| O(6)–C(9)–C(8) | 119(1) | 120(2) | C(1)–C(2)–C(3) | 116(1) | 117(2) |
| C(4)–C(5)–C(6) | 117.4(9) | 118(1) | C(7)–C(8)–C(9) | 116.3(9) | 119(2) |
| C(11)–C(10)–N(1) | 107.6(8) | 107(1) | C(12)–C(10)–N(1) | 113.6(9) | 113(1) |
| C(10)–C(11)–N(2) | 112.3(8) | 112(1) | C(11)–C(10)–C(12) | 111.1(9) | 111(1) |
| C(15)–C(11)–N(2) | | 115(1) | C(10)–C(11)–C(15) | | 114(1) |
| C(11)–C(15)–C(14) | | 110(2) | C(15)–C(14)–C(13) | | 113(2) |
| C(14)–C(13)–C(12) | | 111(2) | C(10)–C(12)–C(13) | | 111(2) |

**Table 6** Selected torsion angles (°) for complexes **1** and **2** (average)*

| | **1** | **2** | | **1** | **2** |
|---|---|---|---|---|---|
| Cr–N(1)–C(1)–C(2) | 61.9(9) | 63.2(4) | N(1)–C(1)–C(2)–C(3) | −66.0(1) | −66.5(3) |
| Cr(1)–C(2)–C(3)–O(1) | −31.5(1) | −30.0(2) | C(2)–C(3)–O(1)–Cr | 1.5(9) | 2.5(1) |
| Cr–N(2)–C(4)–C(5) | −63.0(9) | −62.6(4) | N(2)–C(4)–C(5)–C(6) | 58.5(1) | 59.2(4) |
| C(4)–C(5)–C(6)–O(3) | 20.0(2) | 21.7(1) | C(5)–C(6)–O(3)–Cr | −6.5(1) | −2.8(1) |
| Cr–N(2)–C(7)–C(8) | 64.5(9) | 63.5(4) | N(2)–C(7)–C(8)–C(9) | −56.5(1) | −57.4(3) |
| C(7)–C(8)–C(9)–O(5) | −14.0(2) | −14.3(1) | C(8)–C(9)–O(5)–Cr | 12.0(2) | 12.1(1) |
| N(1)–Cr–N(2)–C(4) | 121.7(6) | 123.1(4) | N(1)–Cr–N(2)–C(7) | —122.9(7) | −122.6(4) |
| N(1)–Cr–N(2)–C(11) | −0.5(5) | 2.6(1) | N(1)–C(10)–C(11)–N(2) | 45.1(9) | 50.3(3) |
| N(2)–Cr–N(1)–C(10) | 25.0(6) | 24.1(2) | N(2)–Cr–N(1)–C(1) | 150.7(7) | 150.4(2) |
| Cr–N(1)–C(10)–C(11) | −43.5(8) | −45.8(3) | Cr–N(2)–C(11)–C(10) | −24.0(9) | −29.5(2) |

* The sign is positive if when looking from atom 2 to 3 a clockwise motion of atom 1 would superimpose it on atom 4; atoms are numbered successively as 1–4 from the left to the right.

with the tertiary amine on the same and opposite side with respect to the axially oriented proton of the secondary amine are denoted as the G′ and R ring, respectively. The G ring is the in-plane propionate ring attached to the secondary amine as usual. The six-membered propionato chelates at the G, G′ and R rings adopt an asymmetric envelope-like conformation. The ethylenic *gauche* conformations for the three propionato chelates are λ, δ and λ at the G, G′ and R ring, respectively. From a geometrical point of view, the last two conformations are described as the $ob_2$ form in which the ethylenic C–C bonds of the propionate rings are oblique to the pseudo-$C_2$ axis bisecting the N–Cr–N angle.

The absolute configurations of the co-ordinated asymmetric nitrogen for the secondary amine are found to be *R* for both complexes. The methyl group of the propanediamine backbone of the (*S*)-pdtrp complex adopts stereospecifically an equatorial orientation and is connected with the ethylenic carbon on the side of the secondary amine. It is to be noted that the propanediamine and cyclohexanediamine backbones adopt an asymmetric envelope δ conformation distorted from the usual ethylenic *gauche* conformation. That is, the torsion angles N(1)–Cr–N(2)–C(11) and N(2)–Cr–N(1)–C(10) are very different; the former angles are −0.5(5) and 2.6(1)° and the latter 25.0(6) and 24.1(2)° for the (*S*)-pdtrp and the (*SS*)-cydtrp complexes, respectively, as shown in Table 6, in contrast to both the torsion angles (*ca.* 15°) for *rac*-[Cr(cydta)]$^-$ (cydta = *trans*-cyclohexane-1,2-diaminetetraacetate) and related complexes.[6–8] The torsion angles N(1)–C(10)–C(11)–N(2) are much smaller than those of the usual five-membered diamine chelates (*ca.* 60°) as shown in Table 6. Moreover, the sums of the diamine ring internal bond angles are much larger compared with those of the other complexes as seen in Table 7. These facts reveal that the diamine chelates are more planar for both the present complexes than those in the edta (ethylenediaminetetraacetate) type complexes.

The sums of the G′ and R ring internal bond angles are larger than those of the G ring (Table 7); the former rings are flatter than the latter and the R and G rings of the edtp and related complexes.[7–9] The angle C(4)–N(2)–C(7) is bisected by the N(1)–Cr–N(2) plane. The torsion angles N(1)–Cr–N(2)–C(4) and N(1)–Cr–N(2)–C(7) are almost equal for both the (*S*)-pdtrp and the (*SS*)-cydtrp complexes. The chelate conformations at the G′ and R ring are almost enantiomeric, especially around the Cr–N–C–C moieties, but with considerable discrepancy around the carboxyl groups as seen from the torsion angles in Table 6. The latter variability may be due to the hydrogen bonding between the complexes in the crystal structures.

In the crystal structure of complex **1** the two independent molecules of the (*S*)-pdtrp complex have intermolecular hydrogen bonding between the aqua [O(7)] and unco-ordinated carboxylate oxygen atoms, O(7A)···O(6B) (2.60 Å), as shown in Fig. 4(*a*). In the crystal structure of **2** similar types of hydrogen bonding are found for O(7A)···O(6B) (2.60), O(4B)···O(7C) (2.68) and O(7C)···O(6D) (2.65 Å) between four independent molecules of the (*SS*)-cydtrp complex as shown in Fig. 4(*b*). The relative arrangement of a pair of the (*SS*)-cydtrp complexes (A and B) in the unit cell is similar to that of an A and B pair of the (*S*)-pdtrp complex as well as that of a C and D pair of the (*SS*)-cydtrp complex.

*The* C–N *Bond-cleavage Site.*—It has been reported[1] that two of the three isomers for [Cr(edtp)]$^-$, [Cr{(*S*)-pdtp}]$^-$ and [Cr{(*SS*)-cydtp}]$^-$ decompose with C–N bond cleavage in aqueous solution to form a diaminetripropionato complex and 3-hydroxypropionic acid. If the cleavage occurs at the G ring the geometrical structure of the diaminetripropionato complex is *cis*-equatorial as found for the edtra type complexes.[12] Such bond cleavage at the R ring results in a *cis*-polar structure. The X-ray analyses reveal that the structures of [Cr{(*S*)-pdtrp}(H$_2$O)] and [Cr{(*SS*)-cydtrp}(H$_2$O)] are *trans*-equatorial. The complex [Cr(edtrp)(H$_2$O)] is also considered to have this geometrical structure according to the spectroscopic data. The absorption spectra show similar patterns and that the MCD spectrum in the spin-forbidden transitions of [Cr(edtrp)(H$_2$O)] exhibits a similar pattern to that of *rac*-[Cr(pdtrp)(H$_2$O)]: $\lambda_{ext}(10^3\Delta\varepsilon_M/dm^3\ mol^{-1}\ cm^{-1}\ T^{-1})$: 693 (+1.26), 689 (−3.01) and 471 nm (+1.93) for the edtrp complex: 693 (+2.66), 689 (−3.72) and 471 nm (+1.24) for the pdtrp complex. This means that the C–N bond cleavage of the edtp-type complexes occurs subsequently to the isomerization from the *cis*-equatorial or *cis*-polar to the *trans*-equatorial form. As shown in Scheme 1, the isomerization from the *cis*-polar isomer can occur easily by interchanging the co-ordination sites between one propionate arm of the G ring on the tertiary amine side and the aqua ligand. On the other hand, isomerization from the *cis*-equatorial isomer requires interchange between the co-ordination sites of two propionate arms, followed by inversion from the *S* to the *R* configuration of the co-ordinated asymmetric nitrogen atom of the secondary amine, or by conversion from the δ into the λ diamine conformation. The latter isomerization is impossible for the (*S*)-pdtrp and (*SS*)-cydtrp complexes. Thus, it is apparent that C–N bond cleavage occurs at the R ring as shown in Scheme 1. Further, the fact that the methyl group of the diamine chelate of the (*S*)-pdtrp complex is connected to the ethylenic carbon on the same side as the secondary amine reveals that the C–N bond cleavage occurs stereoselectively at the R ring close to the methyl group of the propanediamine backbone.

**Table 7** Sums of the chelate ring bond angles (°) for Complexes **1** and **2** (average)

| | Diamine | G | G′ | R | Ref. |
|---|---|---|---|---|---|
| **1** | 521.5 | 685.3 | 689.2 | 690.5 | This work |
| **2** | 518.1 | 686.5 | 690.8 | 690.5 | This work |
| **3**[a] | 512.8 | 685.1 | | | 7 |
| **4**[b] | 512.0 | 686.8 | | 687.1 | 8 |
| **5**[c] | | | | 681.2 | 9 |

[a] *trans*(O$_5$)-Λ-(−)$_{589}$Li[CrL$^1$]·5H$_2$O, where L$^1$ = ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionate. [b] Λ-(−)$_{589}$-Li[Cr(edtp)]·3H$_2$O. [c] *trans*(O$_6$)-K[CrL$^2$]·3H$_2$O, where L$^2$ = propane-1,3-diamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionate.

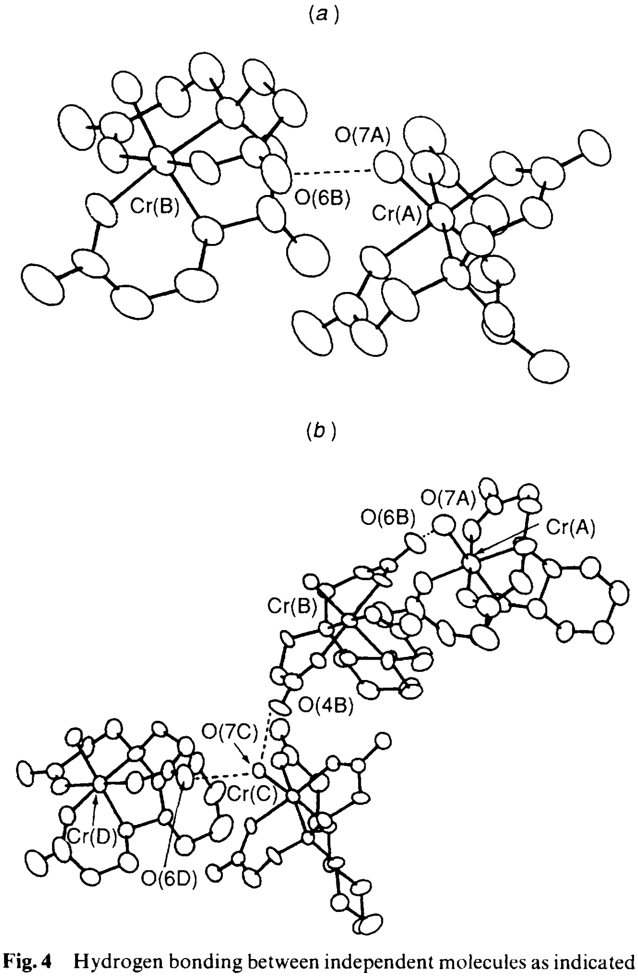
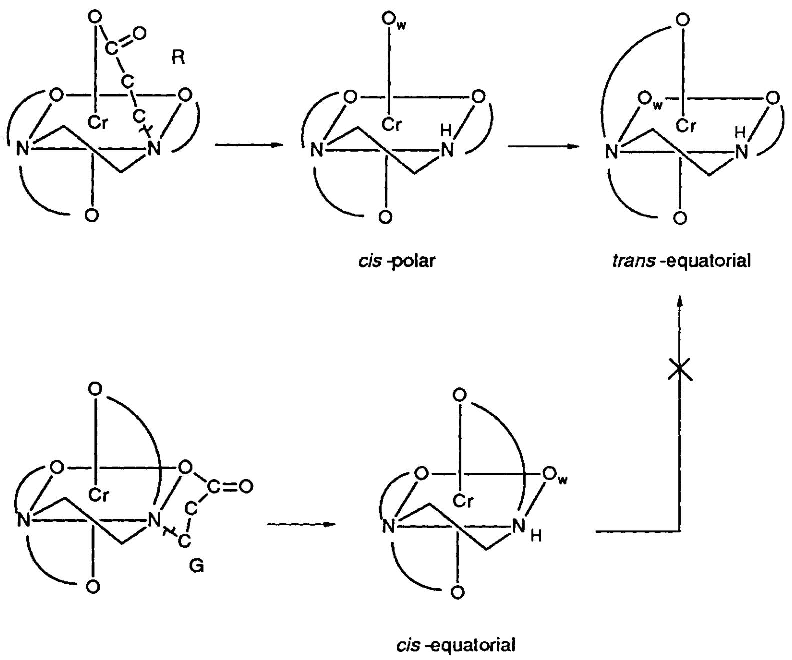


**Fig. 4** Hydrogen bonding between independent molecules as indicated by dashed lines. All hydrogen atoms are omitted for clarity: (*a*) complex **1**; (*b*) **2**

*The* CD *Spectra of the* (*S*)-pdtrp *and* (*SS*)-cydtrp *Complexes.*—The CD spectra for complexes **1** and **2** in aqueous



Scheme 1

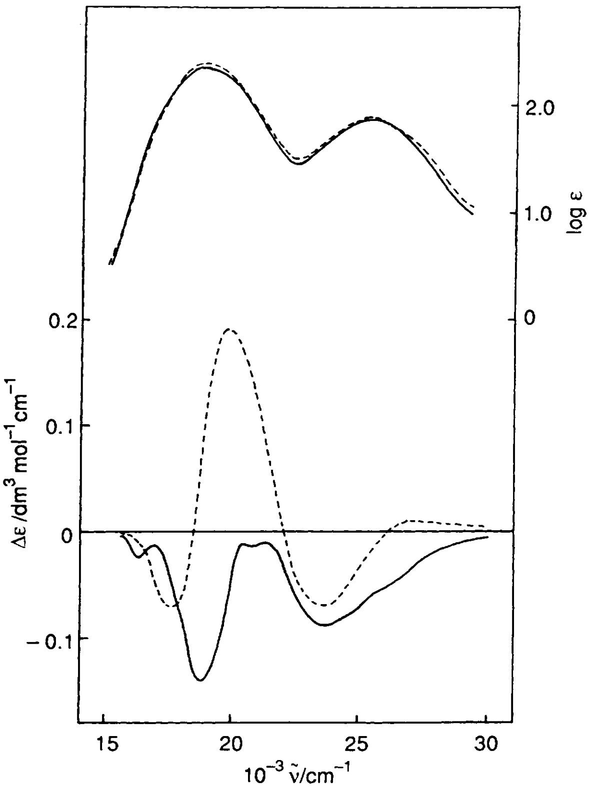


**Fig. 5** Absorption (upper) and CD (lower) spectra of [Cr{(*S*)-pdtrp}($H_2O$)] (– – –) and [Cr{(*SS*)-cydtrp}($H_2O$)] (——) in aqueous solution

solution are shown in Fig. 5. For each complex the same CD pattern is observed in the solid state. Thus there is no puckering or conformational inversion with respect to the ethylenic *gauche* conformations at the two propionato G′ and R rings in solution. The signs of the major CD component in the first band region for **1** and **2** are opposite, though these two complexes have almost the same structure. This is in contrast with the case for *cis*-equatorial [Cr{(*S*)-pdtra}($H_2O$)] and [Cr{(*SS*)-cydtra}($H_2O$)] [(*S*)-pdtra = (*S*)-propane-1,2-diamine-*N*,*N*,*N*′-triacetate, (*SS*)-cydtra = (1*S*,2*S*)-*trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*′-triacetate], where the CD patterns are very similar to each other.[13] In the *trans*-equatorial type complexes there is no net configurational chirality due to pairings of chelates. Since the G′- and R-ring conformations are almost enantiomeric in structural parameters as mentioned above, the contribution to the CD intensity from the G′ and R ring may cancel for each complex. Thus, the asymmetric secondary nitrogens are expected to make major contributions to the CD intensities. The difference in CD between the (*S*)-pdtrp and (*SS*)-cydtrp complexes may arise from the difference in the asymmetric carbon(s). The (*S*)-pdtrp complex has only one chiral carbon, whereas there are two inequivalent chiral carbons in the (*SS*)-cydtrp complex. In the latter complex the two asymmetric carbons contribute to different extents, for the diamine chelates adopt similar asymmetric envelope configurations. The contribution from one carbon close to the tertiary amine is much different from that from the other carbon near the secondary amine which is similar to that in the (*S*)-pdtrp complex. This may result in the difference in the CD signs.

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## References

1 Part 1, N. Sakagami, M. Hayashi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, preceding paper.
2 S. Kaizaki and M. Hayashi, *J. Chem. Soc., Chem. Commun.*, 1988, 613.
3 Y. Taniguchi and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2847.
4 TEXSAN, Molecular Structure Corporation, ver. 5.0, 1989.
5 L. E. Gerdom, N. A. Baenziger and H. M. Goff, *Inorg. Chem.*, 1981, **20**, 1606.
6 S. Kaizaki, M. Hayashi, K. Umakoshi and S. Ooi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3519.
7 F. T. Helm, W. H. Watson, D. J. Radanovic and B. E. Douglas, *Inorg. Chem.*, 1977, **16**, 2351.

8 M. Parvez, C. Maricondi, D. J. Radanovic, M. I. Djuran and B. E. Douglas, *Inorg. Chim. Acta*, 1991, **182**, 177.

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

10 C. W. Maricondi and C. Maricondi, *Inorg. Chem.*, 1974, **13**, 1110.

11 D. E. Bause, C. A. Chang and B. E. Douglas, *J. Coord. Chem.*, 1979, **6**, 211.

12 C. Maricondi, S. Utsuno, D. J. Radanovic, S. R. Trifunovic, J. E. Abola and B. E. Douglas, *Inorg. Chim. Acta*, 1988, **142**, 135; D. J. Radanovic, S. R. Trifunovic, D. E. Bause, C. Maricondi, J. E. Abola and B. E. Douglas, *Inorg. Chem.*, 1987, **26**, 3994; J. D. Bell and G. L. Blackmer, *Inorg. Chem.*, 1973, **12**, 836.

13 S. Kaizaki and H. Mizu-uchi, *Inorg. Chem.*, 1986, **25**, 2732.

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