Anomalous Facile Carbon–Nitrogen Bond Cleavage in Novel Diastereoisomers of the Ethylenediaminetetra-3-propionatochromate(III) Ion

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Diastereoisomers of three ethylenediaminetetra-3-propionatochromate(III) ions and the (*S*)-propane-1,2-diamine analogues, have been synthesized and characterized by ^{2}H n.m.r. and circular dichroism (c.d.) spectroscopy; a facile C–N bond cleavage occurs during decomposition on heating at 60 °C, and this process was followed by spectroscopy.

It has been reported that the thermal decomposition of edta-like (H_4edta = ethylenediaminetetra-acetic acid) Mn^{III} and Co^{III} complexes to form diamine-*N*,*N*,*N*′-triacetato and/or diamine-*N*,*N*′-diacetato complexes involves decarboxylation of the edta-like ligand, the redox reaction in the complexes bringing about the C–N bond cleavage.[1,2] However, there has been no report of studies on thermal hydrolytic activation of the C–N bond in reduction inert edta-like Cr^{III} complexes by steric effects. We report here an anomalous facile carbon–nitrogen bond cleavage in one of the four β-alaninate arms of the novel diastereoisomers of the ethylenediaminetetra-3-propionatochromate(III) ion, $[Cr(edtp)]^-$, and the (*S*)-propane-1,2-diamine analogue, $[Cr\{(S)\text{-pdtp}\}]^-$.

The ligands H_4edtp and (*S*)-propane-1,2-diaminetetra-3-propionic acid [H_4(*S*)-pdtp] were prepared by the alkylation of ethylenediamine-*N*,*N*′-di-3-propionate and (*S*)-propane-1,2-diamine with 3-chloropropionate, respectively, using a

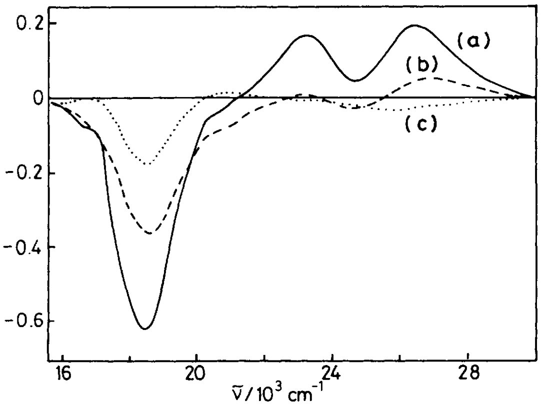

Figure 1. C.d. spectra of three diastereoisomers of $[Cr\{(S)\text{-pdtp}\}]^-$: (a) P-I; (b) P-II; (c) P-III in aqueous solution.

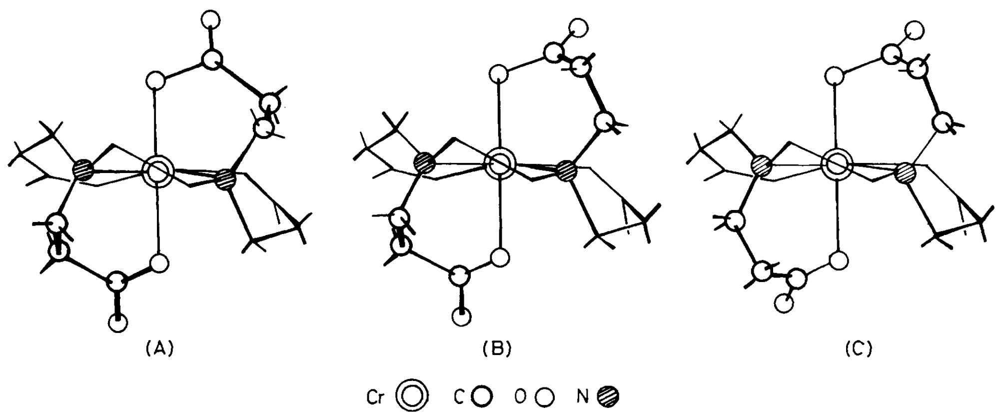

Figure 2. Proposed structure for the three diastereoisomers of edtp or (*S*)-pdtp complexes: (A) lel$_2$ Λ(δδ); (B) lelob Λ(δλ); (C) ob$_2$ Λ(λλ). Only Cr, C, O, and N atoms in the R rings are shown for clarity.

method described for the preparation of the analogous ligands.[3] The edtp or (*S*)-pdtp complex was synthesized by heating an equimolar mixture of $CrCl_3 \cdot 6H_2O$ and the reaction solution of the ligand for *ca.* 2 h. Column chromatography (QAE–Sephadex) of the resulting red–purple solution using NaCl solution (0.02 M) as eluant at 4 °C, gave three bands (E-I, E-II, and E-III for the edtp complex, and P-I, P-II, and P-III for the (*S*)-pdtp complex in elution order).† The chromatographic behaviour, u.v.–visible, and i.r. spectra as well as chemical analyses‡ indicated that the isolated complexes corresponded to isomers with the same chemical composition ($[Cr(edtp)]^-$ or $[Cr\{(S)\text{-pdtp}\}]^-$), the compounds correspond to bands P-I, P-II, and P-III having the same structure as those corresponding to E-I, E-II, and E-III, respectively.§

Three (*S*)-pdtp isomers giving a negative major c.d. component in the first ligand field d–d transition near 19 000 cm^{-1} (Figure 1) are formed stereospecifically adopting a Λ(ΛΔΛ) absolute configuration.¶ The observation that the c.d. spectrum of P-II is intermediate or average in pattern and intensity between that of P-I and P-III (Figure 1) suggests that these isomers are diastereoisomers arising from a pairwise combination of two chiral conformations at the 3-propionate rings, *i.e.*, δδ, δλ, λλ conformation for the Λ(ΛΔΛ) configuration. In accordance with this c.d. consideration, the ^{2}H n.m.r. spectra of the deuteriated edtp complexes show that the E-II-d (deuteriated) isomer has C_1 symmetry and that E-III-d and E-I-d have C_2 symmetry. In comparison with ^{2}H n.m.r. spectra of the edtp complex and *trans*-(O_6)-propane-1,3-diamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionatochromate(III), $[Cr(1,3\text{-pddda})]^-$, in which the 2-methylene groups of the 3-propionate units are deuteriated, and in which these are co-ordinated in the form of the R(relaxed) out-of-plane ring at *trans*-axial sites,[3]‖ it is plausible that E-III has the δδ and λλ conformation, respectively, with respect to the ethylenic C–C *gauche* conformation of 3-propionates in the R rings for the Λ and Δ configurations. Thus, this leads to the assignment that P-I(E-I) and P-II(E-II) take the λλ and λδ conformation for the Λ configuration, respectively, in the 3-propionates of the R rings as predicted by the c.d. results. From a geometrical viewpoint, the Λ(δδ) P-III, Λ(δλ) P-II, and Λ(λλ) P-I diastereoisomers (and their enantiomers) are denoted as the lel$_2$, lelob, and ob$_2$ forms, respectively,** as shown in Figure 2.

On heating aqueous solutions of these diastereoisomers at 60 °C for 24 h, it was found that E-I-d and E-II-d give the same ^{2}H n.m.r. spectrum and that the c.d. spectrum of P-I coincided with that of P-II in aqueous solution, whereas no spectral change was observed for E-III-d and P-III. From the heat-treated solution of E-I-d and E-II-d or P-I and P-II, a neutral complex with an ethylenediaminetri-3-propionate (edtrp) or (*S*)-propane-1,2-diaminetri-3-propionate [(*S*)-pdtrp] ligand, $[Cr(edtrp)(H_2O) \cdot 3H_2O$ or $[Cr\{(S)\text{-pdtrp}\}] \cdot 4H_2O$, was obtained along with 3-hydroxypropionate as a major product.†† This fact proves the occurrence of hydrolytic thermolysis of a C–N bond in the β-alaninate R ring with the ob form. The half-life for the pseudo first order decomposition reaction monitored by ^{2}H n.m.r. signals or c.d. spectra was several hours at 60 °C for the E-I-d and E-II-d or

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† The formation ratio for these bands depended on the concentration of the reaction solution and/or the deuteriation of the ligands used.

‡ Satisfactory elemental analyses obtained for E-I, E-III, P-I—P-III, and deuteriated complexes. Pure E-II could not be isolated, but its properties were analogous to those of E-II-d. Selected spectroscopic data: u.v.–visible [λ_{max}/nm(ε/l mol^{-1} cm^{-1})]: E-I, 541.9(178.7), 401.8(67.1); E-II, 528.3(181.2), 400(63.5); E-III, 539.1(196.5), 398.3(71.1); P-I, 541.4(169.1), 404.0(63.0); P-II, 531.3(184.8), 399.6(64.3); P-III, 539.3(189.9), 398.4(67.0). No shift to lower energy was observed with increasing pH (*ca.* 10) for these spectra. Only one strong i.r. band (*ca.* 1600 cm^{-1}) due to asymmetric stretching vibration of co-ordinated carboxylates was observed.

§ The c.d. spectrum of P-III is almost identical with that of $(-)_D[Cr(edtp)]^-$ obtained by Radanović *et al.*[4]

¶ This is supported by the fact that the corresponding isomers of (1*S*,2*S*)-*trans*-cyclohexane-1,2-diaminetetra-3-propionatochromate(III) give the same c.d. pattern as those of the (*S*)-pdtp isomers, disregarding any possibility of the formation of the Δ(ΔΛΔ) diastereoisomer with an axially oriented methyl group as found for the (*S*)-pdta Co^{III} complex.[5]

‖ ^{2}H N.m.r. δ 59.0, 30.0, 19.5, 13.6 (E-III-d); 54.7, 38.5, 27.0, 21.0, 18.0, 10.7 (E-II-d); 51.0, 29.6, 25.5(sh) (E-I-d).

** For the lel form, the ethylenic C–C bond of the 3-propionate is parallel with the C_2 axis bisecting the N–Cr–N angle, while the ob one has the C–C bond oblique to the C_2 axis.

†† Satisfactory elemental analyses obtained for the edtrp and pdtrp complexes.

P-I and P-II.‡‡ This is extraordinarily short compared with the known shortest half-life of *ca.* 90 days at 60 °C for carbon–carbon cleavage in highly-branched ethane derivatives,[6] even on considering the C–N bond to be weaker than the C–C bond.

It is likely that non-bonding interactions between the 3-propionate in the R ring and the chelates in the G and/or diamine backbone rings give rise to unusually strained but rigid conformations which are sufficiently stable to be isolated but relax after dissociation of the C–N bond; neither goes from the strained ob state to the strain-free lel one, nor brings about Cr–O bond rupture, and of course does not reduce Cr^{III} to Cr^{II} with the decarboxylation. Thus the unprecedented facile C–N bond cleavage or bond activation in the ob β-alaninate ring can be considered to be attributed to steric acceleration.[7] Further elucidation of the modified lability of such ring conformations should lead to a deeper understanding of the fundamental principles governing the stereochemistry in these systems, but this must await *X*-ray crystallographic studies which will soon be in progress.

Received, 28th September 1987; Com. 1407

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‡‡ On heating the E-I and E-II or P-I and P-II isomers in D_2O at 60 °C for 24 h, signal intensities in the ^1H and ^{13}C n.m.r. spectra identical with those of 3-hydroxypropionate were found to increase with time.