89. Base Hydrolysis of Pentaaminecobalt(III) Complexes: The $[CoX(dien)(dapo)]^{n+}$ System

Part 1

Syntheses, Structures, Configuration, and Spectroscopy

by **Peter Comba**[a])*, **Donald A. House**[b]), **W. Gregory Jackson**[d])*, **Werner Marty**[c])[1]),
Helen Stoeckli-Evans[c]), and **Luc Zipper**[a])

[a]) Institut für Anorganische Chemie, Universität Basel, CH-4056 Basel
[b]) Department of Chemistry, University of Canterbury, Christchurch, New Zealand
[c]) Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel
[d]) Chemistry Department, University College (N.S.W.), Australian Defence Force Academy,
Campbell, A.C.T., Australia 2600

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Oxygenation of aqueous solutions of Co^{III} in presence of stoichiometric amounts of *N*-(2-aminoethyl)ethane-1,2-diamine (dien) and 1,3-diaminopropan-2-ol (dapo) produces μ-peroxocobalt(III) dimers. Acid cleavage (HCl) yields *mer-exo*(H)-, *mer-endo*(H)-, *unsym-fac-exo*(OH)-, and *unsym-fac-endo*(OH)-$[CoCl(dien)(dapo)]^{2+}$ (**A**–**D** (X = Cl), resp.) and *unsym-fac*-$[Co\text{-}(dien)(dapo\text{-}N,N',O)]^{3+}$ (**G**). Isomer separation was achieved by fractional crystallization as $ZnCl_4^{2-}$ and ClO_4^- salts and by ion-exchange chromatography. The corresponding bromo, azido, nitrito-*O*, nitro-*N*, thiocyanato, hydroxo, and aqua complexes were also synthesized. Optically resolved samples were prepared for chiral compounds, and the complexes were structurally characterized by X-ray analyses ($\vec{\Lambda}(-)_{436(CD)}$-**A** ($X = N_3$), $\vec{\Lambda}(-)_{436(CD)}$-**B** ($X = N_3$), $\vec{\Delta}(+)_{436(CD)}$-**B** ($X = N_3$)), by their chiroptical properties, and by ^{13}C-NMR spectroscopy supported by ^1H-NMR, IR, CD, and UV/VIS spectroscopy. $\vec{\Lambda}(-)_{436(CD)}$-*mer-exo*(H)-$[Co(N_3)(dien)(dapo)]$(hydrogen di-*O*-benzoyl-L-tartrate)$_2 \cdot 4\ H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$, $a = 7.676(1)$ Å, $b = 19.457(1)$ Å, $c = 34.702(2)$ Å. $\vec{\Lambda}(-)_{436(CD)}$-*mer-endo*(H)-$[Co(N_3)(dien)(dapo)]$(hydrogen di-*O*-benzoyl-L-tartrate)$_2 \cdot 2.75\ H_2O$ crystallizes in the triclinic space group $P1$, $a = 8.062(3)$ Å $b = 10.296(1)$ Å, $c = 15.056(2)$ Å, $\alpha = 80.55(1)°$, $\beta = 85.18(2)°$, $\gamma = 89.10(2)°$. $\vec{\Delta}(+)_{436(CD)}$-*mer-endo*(H)-$[Co(N_3)(dien)(dapo)]$(hydrogen di-*O*-benzoyl-L-tartrate)$_2 \cdot 5.75\ H_2O$ crystallizes in the triclinic space group $P1$, $a = 7.742(1)$ Å, $b = 10.014(1)$ Å, $c = 18.045(2)$ Å, $\alpha = 99.57(1)°$, $\beta = 92.87(1)°$, $\gamma = 102.56(1)°$. The absolute configurations of the three cations were determined unambiguously. Interconversions of the various isomers and derivatives and structural, configurational, and spectroscopic aspects are discussed in detail.

Introduction. – Base hydrolizes of aminecobalt(III) complexes were and still are the object of extensive studies [1]. One of the most prominent features is the acceleration of hydrolysis by OH^- which amounts to a factor of up to *ca.* 10^{10}, and this is generally attributed to a deprotonation of a coordinated amine in a rapid preequilibrium [1] [2]. However, the exact origins of the acceleration and the geometric and electronic structures of the intermediates of the substitution reaction are still rather contentious.

The system $[CoX(dien)(dapo)]^{n+}$ (see **A**–**F**)[2]) was designed for a number of reasons: *i*) There are various isomers in this system, and the expected differences in

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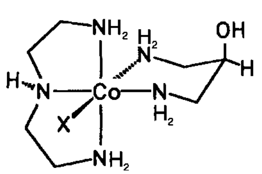
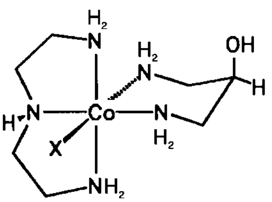
[1]) Deceased on September 20th, 1986.

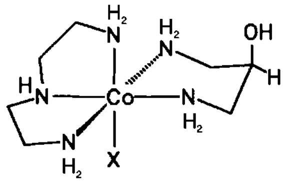
[2]) Abbreviations: dien = *N*-2(-aminoethyl)ethane-1,2-diamine; dapo = 1,3-diaminopropan-2-ol; dpt = N^1-(2-aminopropyl)propane-1,2-diamine; tn = propane-1,3-diamine; en = ethane-1,2-diamine; the configurational prefixes of the isomers of $[CoX(dien)(dapo]^{n+}$ are as defined in *Formulae* **A**–**F**.



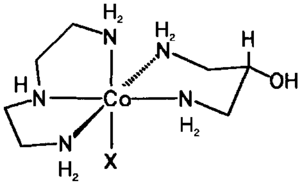
A *mer-exo* (H)



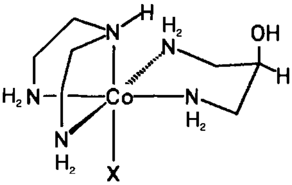
B *mer-endo* (H)



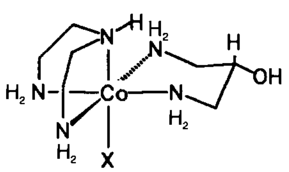
C *unsym-fac-exo* (OH)



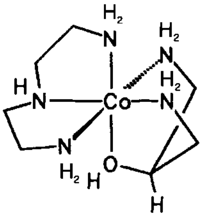
D *unsym-fac-endo* (OH)



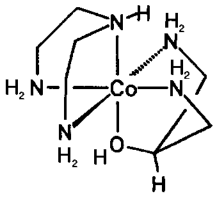
E *sym-fac-exo* (OH)



F *sym-fac-endo* (OH)



G *unsym-fac-NN'O*



H *sym-fac-NN'O*

reactivities (based on the known reactivities for similar systems [3]) might be related to subtle configurational changes. *ii*) The chirality of the *mer*-isomers **A** and **B** together with the meridional arrangement of the tridentate ligand are the basis for probing the geometry of the pentacoordinated intermediate by the steric course of the base hydrolysis (*Scheme*). *iii*) The fact that two epimers of the *mer*-isomer exist (*mer-exo*(H)-isomer **A** and *mer-endo*(H)-isomer **B**) might help to analyze the site of deprotonation and the stage of back-protonation. *iv*) The reactivity of the *mer*-isomers in aqueous base is expected to be quite high [3] [4][3]), and the pentacoordinated intermediate (if formed) might be of increased life-time and selectivity.

Some aspects of the base hydrolysis of *mer-exo*(H)-$[CoCl(dien)(dapo)]^{2+}$ (**A**, X = Cl) were briefly discussed in a preliminary publication [6]. In this paper, we are presenting the

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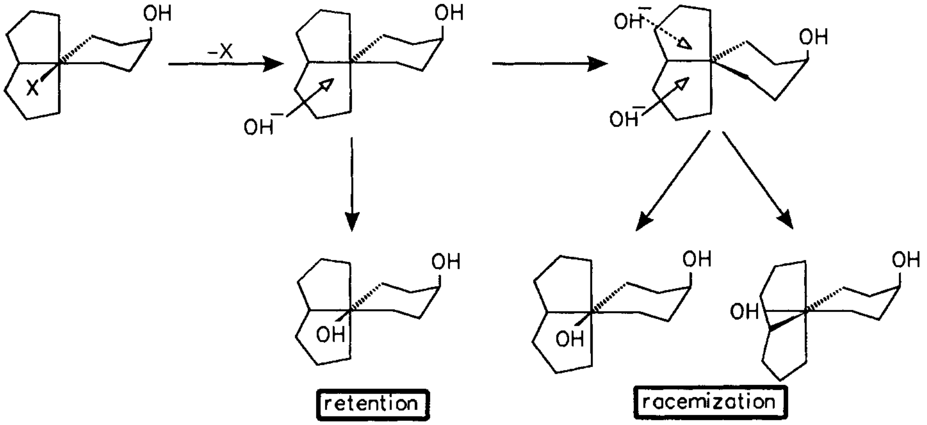
[3]) Note, that the reasons given in [4] for the high reactivity of the structurally similar *mer*-$[CoX(dien)(tn)]^{n+}$ ion might not be generally applicable, and that they might only be coincidental with our results [5].

Scheme



syntheses, chiroptical properties, and spectral and structural characterization of a range of isomers and derivatives. A thorough analysis of the mechanism of base-catalyzed substitution of *mer-exo*(H)-, *mer-endo*(H), *unsym-fac-exo*(OH)-, and *unsym-fac-endo* (OH)[CoCl(dien)(dapo)]$^{2+}$ (**A**–**D**, X = Cl) [7] and of the *mer-exo*(H)- and mer-*endo*(H)-hydroxo and -aqua complexes **A** and **B** (X = OH and H_2O, resp.), respectively, [8] is given in the following papers.

Experimental. – 1. *General.* All commercial reagents (*puriss. p.a.* or similar purities) were used as purchased. H_2O was deionized (syntheses) or doubly distilled (spectroscopy). Ion-exchange resins used were *Dowex 50WX2 p.a.* (200–400 mesh) and *SP Sephadex* C-25. pH Values: *Metrohm-605* pH meter with an *Orion 81025* combined glass electrode (1M $NaClO_4$), calibrated by titrations of standard HCl and NaOH *Titrisol* (*Merck*) solns. (I = 1.0M, $NaClO_4$). Optical rotations: *Perkin-Elmer-241* spectropolarimeter. UV/VIS Spectra: *Uvikon-810* and *-820*, *Cary-14*, and *Unicam-SP1800* instruments; at 25.0 ± 0.1°. CD Spectra: *Jasco-J-500C* instrument; at 25.0 ± 0.1°. IR Spectra: KBr or CsBr discs; *Perkin-Elmer-521* or *Beckmann-IR-4250* instrument; from 4000 to 200 cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-WP-200*, *Bruker-HX-90*, *Bruker-HX-90E*, or *Varian-XL300* instruments; at 25°. Microanalyses were performed by the Mikrolabor at ETH, Zürich, and by *Ciba-Geigy AG*, Basel.

2. *Syntheses. Salts of* mer-exo*(H)-[CoCl(dien)(en)]*$^{2+}$ [9] [10], sym-fac-*[CoCl(dien)(en)]*$^{2+}$ [9], mer-exo*(H)-[CoCl(dien)(tn)]*$^{2+}$ [11], mer-exo*(H)-[CoCl(dpt)(en)]*$^{2+}$ [9], and mer-exo*(H)-[CoCl(dpt)(tn)]*$^{2+}$ [11] were prepared by published methods.

[CoCl(dien)(dapo)](ZnCl$_4$) (Isomer Mixture). A precooled (–5°) aq. soln. (240 ml) of dien (63 g, 0.612 mol) and dapo (55.2 g, 0.612 mol) was added slowly to an aq. soln. (300 ml, –10°) of $CoCl_2 \cdot 6\,H_2O$ = (145.8 g, 0.612 mol). O_2 was bubbled through this thermostated (–5°) soln. for 1 h. A soln. of $ZnCl_2$ (120 g, 0.82 mol) in 10M HCl (540 ml) was then added dropwise (*ca.* 3 h) with vigorous stirring and cooling. The brown soln. of complexes was allowed to stand at r.t. overnight. After removal of the green crystalline μ-superoxido complex (see below; 16.4 g, 0.017 mol), the soln. deposited red and violet pentaaminecobalt(III) complexes within 1–7 days. The various crops were recrystallized from a minimum amount of cold H_2O (0°) with addition of $ZnCl_2$ (0.67 g/g complex) and 10M HCl (3.35 ml/g complex). The various fractions were washed with EtOH and Et_2O and dried under vacuum. This fractional-crystallization procedure yielded 4 different isomers, *viz.* salts of *mer-exo*(H)-, *unsym-fac-exo*(OH)-, *unsym-fac-endo*(OH)-[CoCl(dien)(dapo)]$^{2+}$ (**A**, **C**, and **D**, resp.; X = Cl) and *unsym-fac*-[Co(dien)(dapo-*N*,*N'*,O)]$^{3+}$ (**G**)[4]). The first fractions, after removal of the green μ-superoxido complex, contained largely red salt of

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[4]) In the strict sense, *unsym-fac*-[Co(dien)(dapo-*N*,*N'*,*O*)]$^{3+}$ (**G**) is not an isomer unless it is isolated as the mixed chloride tetrachlorozincate salt as was the case in our experiments.

A, then violet salt of **C**, with some red-violet salt of **D** in later fractions, and finally orange salt of **G**. The isomer proportion at −5° was **A** 30% (**B** *ca.* 1%), **C** 25%, **D** 25%, and **G** 20% (^{13}C-NMR). On reaction at −10°, the yield of **A** was increased from 15 to 20% (yield based on mol $CoCl_2$). With ClO_4^- as anion, the separation of **A**, C, and **D** was improved: ClO_4^- crystallized **A** selectively and rapidly. The **D** species crystallized selectively and slowly when mixed with C. Also, from mixtures **C**/**D**, **D** crystallized selectively as rose-red plates.

unsym-fac-endo*(OH)*,unsym-fac-endo*(OH)-{[Co(dien)(dapo)]$_2$[μ-(O$_2$)]} Cl(ZnCl$_4$)$_2$* (*μ*-Superoxido Complex). The green precipitate of *μ*-superoxido complex was recrystallized from a minimum volume of H_2O by filtration and addition of $^1/_5$ volume of freshly filtered 2M Li_2ZnCl_4. Fine deep-green needles deposited readily which were washed with a little Li_2ZnCl_4 soln., MeOH, and then Et_2O and dried in air. The *μ*-superoxido complex was characterized by microanalysis and a frozen-solution EPR spectrum. Anal. calc. for $C_{14}H_{46}Cl_9Co_2N_{10}O_4Zn_2$: C 17.1, H 4.7, Cl 32.4, N 14.2; found: C 16.9, H 5.7, Cl 29.5, N 14.5.

unsym-fac-endo*(OH)*,unsym-fac-endo*(OH)-{[Co(dien)(dapo)]$_2$[μ-(O$_2$)]}(ZnCl$_4$)$_2$* (*μ*-Peroxo Complex). The *μ*-superoxido complex (2.0 g, 2 mmol) was dissolved in H_2O (25 ml) and then treated with a slight molar excess of HI (1.21 g, 8 mmol) in H_2O (5 ml). The soln. rapidly became brown, with some deposition of solid I_2. This was filtered, and $^1/_5$ volume of 2M Li_2ZnCl_4 was added, followed by acetone to the point of cloudinesss. On cooling (0°) and scratching, olive-brown fibrous needles deposited. These were washed with acetone and Et_2O, dried in air, and recrystallized from H_2O/Li_2ZnCl_4/acetone with essentially quantitative recovery: 1.6 g (83%). The *μ*-peroxo complex was characterized by microanalysis, NMR, and UV/VIS (charge-transfer bands). Anal. calc. for $C_{14}H_{46}Cl_8Co_2N_{10}O_4Zn_2$: C 17.7, H 4.9, Cl 29.8, N 14.7; found: C 17.9, H 5.6, Cl 28.3, N 13.8.

mer-exo*(H)-[CoCl(dien)(dapo)](ZnCl$_4$)* (**A**($ZnCl_4$), X = Cl). The isomeric purity was checked by ^{1}H-NMR or by chromatography on *Dowex 50WX2* (NH_4^+ form), as described for the azido analogues. The *mer-endo*(H)-isomer **B** was eluted well in front of the *mer-exo*(H)-species **A** in both cases. Anal. calc. for $C_7H_{23}Cl_5CoN_5O_4Zn$: C 17.0, H 4.7, Cl 35.8, N 14.2; found: C 17.5, H 4.6, Cl 36.0, N 14.0.

Alternatively, **A**(ClO_4)$_2$ (X = Cl) was prepared from 1.0 g (2 mmol) of *unsym-fac-exo*(OH)-[CoCl(dien)(dapo)]($ZnCl_4$) (**C**($ZnCl_4$), X = Cl) which was dissolved in 0.1M NaOH (100 ml). The purple isomer smoothly hydrolyzed to the red hydroxo species, and after 5 min, 11M HCl (100 ml) was added and the mixture heated to 90° for 25 min. After evaporation to 25 ml, 11.7M $HClO_4$ (8 ml) was added and the mixture cooled to 2° for 2 h. The red crystals of **A**(ClO_4)$_2$ (X = Cl) which had deposited were washed with EtOH and Et_2O and air-dried: 0.15 g (15%). Some of the more soluble *unsym-fac-endo* (OH)-isomer **D** precipitated much later in low yield.

Essentially the same procedure was used to produce **A**(ClO_4)$_2$ (X = Cl) from the *unsym-fac-endo* (OH)-isomer **D**. However, the initial base-hydrolysis step is much faster [7], and a reaction time of 1 min was sufficient. The final yield of **A**(ClO_4)$_2$ (X = Cl) was low (*ca.* 8%), and since **D** (X = Cl) is not readily available, this is not a viable source for **A** (X = Cl).

mer-endo*(H)-[CoCl(dien)(dapo)](ZnCl$_4$)* (**B**($ZnCl_4$), X = Cl). To 1M HCl (20 ml), 1.50 g (3.0 mmol) of *mer-endo*(H)-[Co(N_3)(dien)(dapo)]($ZnCl_4$) (**B**($ZnCl_4$), X = N_3, see below) were added. On careful addition of $NaNO_2$ (0.35 g; 4.5 mmol), all dissolved to yield the respective aqua species (liberation of N_2 and N_2O). Then 10M HCl (50 ml) was added and the mixture heated to 90° for 15 min. On cooling and addition of H_2ZnCl_4 (15 ml), deep-pink **B**($ZnCl_4$) (X = Cl) crystallized essentially quantitatively (1.45 g). This material was recrystallized from a minimum volume of H_2O (pH 3), using $^1/_4$ volume of H_2ZnCl_4 (or $HClO_4$, producing the corresponding perchlorate salt): 1.3 g (88%) of chromatographically homogeneous, *viz. exo*-free, **B**($ZnCl_4$) (X = Cl). Anal. calc. for $C_7H_{23}Cl_5CoN_5OZn$: C 17.0, H 4.7, N 14.2; found: C 17.0, H 4.7, N 14.9.

mer-exo*(H)- and* mer-endo*(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$ Salts* **A** *and* **B** (X = N_3), *resp.* **A**(ClO_4)$_2$ (X = Cl; 12.9 g, 26.5 mmol) was added in small portions to a stirred soln. of 2,2′,2″-nitrilotris(ethanol) (1.35 g, 13.3 mmol) in H_2O (40 ml). The color immediately turned deep red (1 min, 20°). NaN_3 (5.2 g; sufficient to yield a 2M soln.) was then added. After further 3 min, a soln. of Li_2ZnCl_4 (14 g of $ZnCl_2$ and 11.6 g of LiCl in 20 ml of H_2O) was added to the clear soln., resulting in the nearly quantitative deposition of [Co(N_3)(dien)(dapo)]($ZnCl_4$) after 1 h at 0°. The crystals were washed with EtOH and Et_2O and vacuum-dried: 13.0 g (98%) of **A**($ZnCl_4$)/**B**($ZnCl_4$) (X = N_3) 7:3, free of starting chloro complex (^{13}C-NMR).

Fractional crystallization of **A**($ZnCl_4$)/**B**(ZnCl) (X = N_3; 20 g) from H_2O, using Li_2ZnCl_4 (pH 2, HCl) as the precipitant yielded the brown-maroon *mer-exo*(H)-[Co(N_3)(dien)(dapo)]-*mer-endo*(H)-[Co(N_3)(dien)(dapo)]($ZnCl_4$)$_2$ double salt as the less soluble component (11.3 g, 55%), and the purple **A**($ZnCl_4$) (X = N_3; 7.0 g, 34%) as the more soluble fraction. The less-soluble material was shown to be a genuine double salt by analysis of a large single crystal (^{13}C-NMR and chromatography showed 50% of each epimer). Such a phenomenon is not especially unusual in coordination chemistry.

Fractional crystallization of **A**($ZnCl_4$)/**B**($ZnCl_4$) (X = N_3) using $NaClO_4$ as precipitant yielded pure **A**(ClO_4)$_2$ (X = N_3; 10.6 g, 52%). Subsequent addition of Li_2ZnCl_4 precipitated the double salt (8.5 g, 41%).

The mixture of diastereoisomeric pairs of enantiomers may also be separated by fractional crystallization with $[Sb((+)\text{-tart})]_2^{2-}$ (successive separation of all four isomers in two steps). The detailed procedures are given below.

A more efficient separation was chromatography: **A**($ZnCl_4$)/**B**($ZnCl_4$) (X = N_3) *ca.* 7:3 (20 g, 0.04 mol) was dissolved in H_2O (1 l, pH 3) and submitted to cation exchange (*Dowex 50WX2*, 200–400 mesh, NH_4^+ form; 30 × 6 cm). After washing with H_2O (1 l), elution with 1M NH_4Cl (pH 3–4) easily separated the faster moving **B** from **A**. Subsequently, **A** was eluted with 1.5–2M NH_4Cl. Each band was then freeze-dried or evaporated (< 30°) to a small volume, and the precipitated NH_4Cl was removed by filtration. This procedure was repeated twice, and the final syrups were treated with ¼ volume of conc. aq. Li_2ZnCl_4 soln. and kept at 0° for 2 h to provide essentially quantitative precipitation of the individual isomers. The crystals were washed with EtOH and Et_2O and air-dried. Each isomer was recrystallized using Li_2ZnCl_4 as precipitant. The crystallized azido species had not mutarotated during workup (ion-exchange chromatography as described above), and they were free of starting chloro complex as shown by nitrosation to the aqua species (see later) followed by chromatography (unreacted chloro complex elutes well in front of the aqua ion on *SP Sephadex C-25* using 1M $NaClO_4$ (pH 2) as eluant).

The above procedure yielded 12.0 g (86% (58% total yield)) of purple **A**($ZnCl_4$) (X = N_3). Anal. calc. for $C_7H_{23}Cl_4CoN_8OZn$: C 16.8, H 4.6, N 22.4; found: C 16.6, H 4.5, N 22.1.

The separation produced 5.25 g (88% (26% total yield)) of the purple **B**($ZnCl_4$) (X = N_3). Anal. calc. for $C_7H_{23}Cl_4CoN_8OZn$: C 16.8, H 4.6, N 22.4; found: C 16.8, H 4.5, N 22.3.

mer-exo*(H)-[CoBr(dien)(dapo)](ZnBr₄)* (**A**($ZnBr_4$), X = Br). Pure **A**($ZnCl_4$) (X = Cl) (10 g, 0.02 mol) and $AgNO_3$ (17.16 g, 0.10 mol) were dissolved in the minimum amount of H_2O and stirred at r.t. in the dark for 3 days. After removal of the AgCl precipitate, 48% HBr soln. (157 ml) and $ZnBr_2$ (30 g, 0.13 mol) were added. The soln. was then slowly reduced in volume in a desiccator over H_2SO_4 in the refrigerator. The first 3 fractions collected within 3 days contained pure **A**($ZnBr_4$) (X = Br; 5.35 g, 37%). Anal. calc. for $C_7H_{23}Br_5CoN_5OZn$: C 11.7, H 3.2, Br 55.7, N 9.8; found: C 11.9, H 3.1, Br 55.5, N 9.9.

mer-exo*(H)-[Co(ONO)(dien)(dapo)](ZnCl₄)* (**A**($ZnCl_4$), X = ONO). **A**(ClO_4)$_2$ (X = N_3; 3.0 g, 6.0 mmol) was dissolved in 0.5M $HClO_4$ (60 ml) while stirring at 0°. Solid $NaNO_2$ (1.38 g, 20 mmol) was added portionwise over 1 min, during which time the aqua complex was generated and N_2 and N_2O liberated; quickly thereafter, the aqua complex nitrosated to give the nitrito-*O* complex. After 3 min, Li_2ZnCl_4 soln. (5 ml) was added, followed by acetone (50 ml) and, slowly and carefully, i-PrOH (300 ml). Crystals deposited during the last stage. After 30 min at 0°, the product was collected, washed with i-PrOH and Et_2O, air-dried, and recrystallized twice from cold H_2O by the addition of i-PrOH at 0°: 2.8 g (93%) of **A**($ZnCl_4$) (X = ONO). The product can be stored in the dark at −15° for several weeks without detectable isomerization to the nitro-*N* form. Anal. calc. for $C_7H_{23}Cl_4CoN_6O_3Zn$: C 16.6, H 4.6, Cl 28.1, N 16.6; found: C 16.9, H 4.7, Cl 28.0, N 16.5.

If **A**($ZnCl_4$) (X = N_3) was used as starting material, a little **A**($ZnCl_4$) (X = Cl) resulted from capture of free Cl^- during the nitrosation of the azido species. **A**($ZnCl_4$) (X = Cl) is very much less soluble than **A**($ZnCl_4$) (X = ONO) and is removed by filtration after waiting 1 h at 0° prior to the addition of acetone and i-PrOH.

Alternatively, pure **A**($ZnCl_4$) (X = ONO) may be prepared by direct nitrosation of the recrystallized aqua complex (below), using the same quantities of materials as above but replacing the azido species by the aqua one.

The recrystallized **A**($ZnCl_4$) (X = ONO) was tested for the presence of chloro and nitro-*N* complexes by reaction with 1M HCl (pure nitrito-*O* complex yields the aqua ion quantitatively, while the nitro-*N* and chloro species remain unchanged). The mixture was then reacted with a few mg of NaN_3 to destroy liberated HNO_2, and the VIS spectrum was recorded and compared with that for authentic **A** (X = H_2O). A similarly treated sample, after dilution and sorption on *SP Sephadex-C25*, was eluted with 1M $NaClO_4$ (pH 2).

Recrystallization of **A**($ZnCl_4$) (X = ONO) from cold H_2O by addition of $NaClO_4$ very slowly yielded **A**(ClO_4)$_2$ (X = ONO), but contaminated with increasing amounts (after each recrystallization) of the nitro-*N* species (^{13}C-NMR).

mer-endo*(H)-[Co(ONO)(dien)(dapo)](ZnCl₄)* (**B**($ZnCl_4$), X = ONO) was prepared exactly as described for **A**($ZnCl_4$) (X = ONO), using the respective *mer-endo*(H)-reactants. **B**($ZnCl_4$) (X = ONO) always contained $\leqslant$ 3% of *mer-endo*(H)-nitrito-*N* complex. Anal. calc. for $C_7H_{23}Cl_4CoN_6O_3Zn$: C 16.6, H 4.6, Cl 28.1, N 16.6; found: C 16.8, H 4.6, Cl 27.9, N 17.0.

mer-exo*(H)-[Co(NO₂)(dien)(dapo)](ClO₄)₂* (**A**(ClO_4)$_2$, X = NO_2). **A**($ZnCl_4$) (X = ONO) (0.5 g, 1 mmol) was dissolved in H_2O (20 ml; pH 2.5, $HClO_4$) at *ca.* 70°, and the soln. was maintained at 70° for 20 min. A soln. of H_2ZnCl_4 (5 ml) was then added, followed by i-PrOH (100 ml). On cooling and standing, yellow crystals of **A**($ZnCl_4$) (X = NO_2) deposited: 0.45 g (90%). The product was recrystallized from 0.01M HCl using i-PrOH as precipitant. **A**(ClO_4)$_2$ (X = NO_2) was readily obtained by metathesis using $NaClO_4$. Anal. calc. for $C_7H_{23}Cl_2CoN_6O_{11}$: C 17.9, H 4.7, Cl 14.3, N 16.9; found: C 18.0, H 4.8, Cl 14.5, N 16.8.

Purity was confirmed by reaction of the samples with 1M HCl (1 min), followed by chromatography on *SP Sephadex-C25* with 1M $NaClO_4$ (pH 2).

mer-endo*(H)-[Co(NO_2)(dien)(dapo)](ClO_4)$_2$* (**B**(ClO_4)$_2$, X = NO_2). The synthesis followed that of **A**(ClO_4)$_2$ (X = NO_2), and the samples were checked for isomeric purity in the same way. Anal. calc. for $C_7H_{23}Cl_2CoN_6O_{11}$: C 17.9, H 4.7, Cl 14.3, N 16.9; found: C 18.0, H 4.3, Cl 14.1, N 16.9.

mer-exo*(H)-[Co(H_2O)(dien)(dapo)]Cl_3 · H_2O.* (**A**Cl_3 · H_2O, X = H_2O). *Method 1:* **A**($ZnCl_4$)(X = N_3; 1.5 g, 3.0 mmol) was dissolved in 0.5M $HClO_4$ (20 ml). The addition of $NaNO_2$ (0.3 g, 4.3 mmol) effected the rapid and complete conversion to the aqua ion. Then 5M HCl (25 ml) was added, followed by careful addition of acetone (350 ml), resulting in the crystallization of the aqua complex as the chloride monohydrate salt. The product was recrystallized twice from 0.1M HCl, using acetone as the precipitant: 0.90 g (76%) of **A**Cl_3 · H_2O (X = H_2O). In the first recrystallization, a trace of *mer-exo*(H)-chloro complex deposited first; this was removed by filtration, and the orange aqua species was then crystallized with addition of acetone. When the **A**(ClO_4)$_2$ (X = N_3) was used as starting material, the product was free from chloro impurities, confirming that the source of the chloro complex was capture of Cl^- during the synthesis.

Method 2: **A**($ZnCl_4$) (X = ONO; 1.5 g, 3.0 mmol) was dissolved in 5M HCl (25 ml) at 0°. A few mg of NaN_3 were added to destroy liberated HNO_2, and the soln. was carefully diluted with cold acetone (400 ml). On scratching, orange crystals deposited, essentially quantitatively (1.1 g, 93%). This product was recrystallized as above. Anal. calc. for $C_7H_{27}Cl_3CoN_5O_3$: C 21.3, H 6.9, Cl 27.0, N 17.8; found: C 21.2, H 7.3, Cl 26.5, N 17.5.

mer-endo*(H)-[Co(H_2O)(dien)(dapo)]Cl_3 · 1.5H_2O* (**B**Cl_3 · 1.5H_2O, X = H_2O). The syntheses closely followed those described for **A**Cl_3 · H_2O (X = H_2O). The product consistently crystallized more slowly but more completely than its *mer-exo*(H)-counterpart. Anal. calc. for $C_7H_{28}Cl_3CoN_5O_{3.5}$: C 20.8, H 7.0, Cl 26.4, N 17.4; found: C 20.7, H 7.1, Cl 26.1, N 17.0.

The complexes **A** (X = H_2O) and **B** (X = H_2O) were characterized by their ^{13}C-NMR spectra (D_2O/DCl) and their chromatographic behaviour (*Dowex 50WX2*, 2M, $NaClO_4$ (pH 2); 2 well separated bands, **B** (X = H_2O) eluting first). Reaction of either of the aqua salts with 1M NaN_3 (pH *ca.* 3) at 25° for 10 min resulted in **A**/**B** (X = N_3) 7:3 (UV/VIS: ε_{512}(max) 341; chromatography).

mer-exo*(H)-[Co(NCS)(dien)(dapo)]Cl_2* (**A**Cl_2, X = NCS). **A**Cl_3 · H_2O (X = H_2O) (1.0 g, 2.6 mmol) was dissolved in H_2O (50 ml) containing $HClO_4$ or CF_3COOH (pH *ca.* 2). NaNCS (2 g, 0.025 mol) was added (first the aqua complex crystallized as the thiocyanate salt, but this dissolved and reacted on heating) and the mixture heated on a steam bath until it was deep red (*ca.* 5 min). It was cooled, diluted with H_2O (300 ml), and submitted to *Dowex 50WX2* (H^+ form). Elution with 1M HCl gave **A**Cl_2 (X = NCS). No **B**Cl_2 (X = NCS) was detected (the two epimers would separate under these conditions, with **B**Cl_2 eluting in front of **A**Cl_2). Crystals of **A**Cl_2 (X = NCS) were obtained on evaporation (< 40°) and recrystallized from a minimum volume of acidified H_2O, using aq. NaNCS or H_2ZnCl_4 soln. as precipitant to afford **A**$(NCS)_2$ or **A**($ZnCl_4$) (X = NCS), resp.

mer-endo*(H)-[Co(NCS)(dien)(dapo)]Cl_2* (**B**Cl_2, X = NCS). The procedure followed exactly that given above, using the *mer-endo*(H)-aqua complex. The crystallized **B**Cl_2 (X = NCS) proved chromatographically pure.

unsym-fac-exo*(OH)-[CoCl(dien)(dapo)]($ZnCl_4$)* (**C**($ZnCl_4$), X = Cl) was obtained directly from the Co^{II}/ligand/O_2 synthesis as described above[5]). Anal. calc. for $C_7H_{23}Cl_5CoN_5OZn$: C 17.0, H 4.7, Cl 35.8, N 14.2; found: C 17.2, H 4.6, Cl 36.0, N 13.9.

unsym-fac-*[Co(dien)(dapo-*N,N′,O*)](Cl)($ZnCl_4$)* (**G**(Cl)($ZnCl_4$)) was obtained directly from the Co^{II}/ligand/O_2 synthesis as described above[6]). Anal. calc. for $C_7H_{23}Cl_5CoN_5OZn$: C 17.0, H 4.7, Cl 35.8, N 14.2; found: C 17.1, H 4.6, Cl 36.0, N 14.0.

unsym-fac-endo*(OH)-[CoCl(dien)(dapo)] Salts* **D** (X = Cl). These salts were obtained directly from the Co^{II}/ligand/O_2 synthesis as described above or from either the μ-superoxido or μ-peroxo precursors. The procedure using the superoxido complex (reduced to the peroxo complex *in situ* using I^-) is more convenient: The superoxido complex (10.0 g, 0.01 mol) in H_2O (100 ml) was treated with NaI (5.0 g, 0.03 mol) and, after 1 min, with 37% HCl soln. (130 ml). The mixture was evaporated (70°; the liberated I_2 was sublimed under these conditions, and the aqua complex derived from the cleaved peroxo species was partly anated to yield the **D** (X = Cl) ion). The reaction was completed by heating the residue in a small volume of H_2O/HCl (25 ml of H_2O/50 ml of 37% HCl soln.) on a steam bath for 30 min. Finally, the addition of ¼ volume of 70% $HClO_4$ soln. or 3M H_2ZnCl_4 resulted

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[5]) This isomer may be prepared in yields of up to 20% when the oxygenation of cobalt(II) in presence of the ligands is performed at r.t. and the resulting solution of peroxo complex is heated for *ca.* 1 h at 80° after treatment with $ZnCl_2$ and HCl.

[6]) A higher yield of this species can be obtained if the oxygenation of the cobalt(II)/ligand mixture is performed at r.t., and if the peroxo complex/HCl/$ZnCl_2$ mixture is heated to 80° until the effervescence of O_2 has ceased.

in the crystallization of rose-red **D**(ClO_4)$_2$ and **D**($ZnCl_4$) (X = Cl), resp. The product was recrystallized from a minimum volume of H_2O using the respective precipitants. Yield of **D**($ZnCl_4$) (X = Cl), 8.6 g (85%). Anal. calc. for $C_7H_{23}Cl_5CoN_5OZn$: C 17.0, H 4.7, Cl 35.8, N 14.2; found: C 17.0, H 4.5, Cl 35.4, N 14.0.

unsym-fac-exo*(OH)-[CoBr(dien)(dapo)](ZnBr$_4$)* (**C**($ZnBr_4$), X = Br). **C**($ZnCl_4$) (X = Cl; 5 g, 0.01 mol) was dissolved in the minimum amount of H_2O. Then, $AgNO_3$ (8.58 g, 0.05 mol) was added and the mixture stirred at r.t. in the dark for 6 days. After removal of AgCl, 48% HBr soln. (100 ml) and $ZnBr_2$ (15 g, 0.07 mol) were added. The soln. was reduced to *ca.* ½ volume at 40° and reduced pressure. Violet crystals (1.73 g, 24.12%) were filtered off after one day. Anal. calc. for $C_7H_{23}Br_5CoN_5OZn$: C 11.7, H 3.2, N 9.8; found: C 11.8, H 3.2, N 9.5.

unsym-fac-exo*(OH)-[Co(N$_3$)(dien)(dapo)](ZnCl$_4$)* (**C**($ZnCl_4$), X = N_3). **C**($ZnCl_4$) (X = Cl; 5 g, 0.01 mol) was dissolved in the minimum amount of H_2O containing NaN_3 (1.5 g, 0.02 mol). After 3 weeks in the dark at r.t., violet crystals were filtered off and recrystallized once from H_2O by addition of LiCl and $ZnCl_2$: 0.43 g (8.58%). Anal. calc. for $C_7H_{23}Cl_4CoN_8OZn$: C 16.8, H 4.6, N 22.4; found: C 16.4, H 4.5, N 21.9.

mer-exo*(H)-[CoCl(dpt)(dapo)](ZnCl$_4$)*. To an aq. soln. (50 ml) of $CoCl_2 \cdot 6\ H_2O$ (24.3 g, 0.102 mol) was added an aq. soln. of dpt (13.38 g, 0.102 mol) and dapo (9.2 g, 0.102 mol). O_2 was bubbled through the well stirred and cooled (0°) soln. for 1 h. Subsequently, $ZnCl_2$ (50 g, 0.31 mol) and 10M HCl (85 ml) were added at 0°. After 2 days (r.t.), the mauve crystalline product which had deposited was recrystallized once from a minimum amount of cold H_2O by addition of $ZnCl_2$ (2 g, 0.015 mol) and 10M HCl (10.05 ml): 1.2 g (2.25%). Anal. calc. for $C_9H_{27}Cl_5CoN_5OZn$: C 20.7, H 5.2, N 13.4; found: C 20.6, H 5.1, N 13.3.

3. *Optically Active Compounds.* Some of the chiral complexes described above were obtained in (at least partly) optically resolved forms from their recemic mixtures by fractional crystallization of diastereoisomeric salts with chiral anions. The procedures are given below. However, at least for the complexes **A** and **B**, it proved to be more convenient to prepare optically pure samples from optically pure precursors (usually the respective azido complexes). Spectral data of all (at least partly) resolved species are given below (*Table 5*).

Resolution of mer-exo*(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$* (**A**, X = N_3). To racemic **A**($ZnCl_4$) (X = N_3; 2.13 g, 4.3 mmol) in H_2O (25 ml) was added $Na_2[Sb((+)\text{-tart})]_2$ (1.44 g, 2.3 mmol) and the resultant mixture filtered. On standing at 0° overnight, purple needles of the diastereoisomer deposited. They were washed with EtOH and Et_2O and air-dried. To the filtrate was added ¼ volume of Li_2ZnCl_4 containing a trace of H_2ZnCl_4; purple crystals deposited essentially quantitatively on ice-cooling for 1 h. The diastereoisomer was ground as a thin paste with cold Li_2ZnCl_4 soln. to yield the $ZnCl_4^{2-}$ salt which was recrystallized from H_2O using Li_2ZnCl_4 as precipitant. Then the crude enantiomer derived from the less soluble diastereoisomer, as well as the crude enantiomer obtained from the original filtrate were enriched in optical purity as follows: Sufficient H_2O was added to dissolve approximately half of the material, and the suspension was filtered. The solid was retained, and to the filtrate was added ¼ volume of 2M $LiZnCl_4$, and crystals readily deposited. This procedure was repeated twice to provide optically pure samples of the more soluble active forms in *ca.* 10% yield for each (based on total Co). The retained solids were combined to give two lots of partly active materials, one lot derived from the original diastereoisomer and the other from the original filtrate. The extraction procedure described above could be repeated on these recovered solids to afford a little more of each of the optically pure enantiomers. The enantiomer derived from the less soluble diastereoisomer from the $[Sb((+)\text{-tart})]_2^{2-}$ resolution is $\vec{\Lambda}(-)_{436(CD)}$-*mer-exo*(H)-[Co($N_3$)(dien)(dapo)]($ZnCl_4$) ($\vec{\Lambda}(-)_{436(CD)}$-**A**($ZnCl_4$), X = N_3).

Resolution of mer-endo*(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$* (**B**, X = N_3). Di-*O*-benzoyl-L-tartaric acid (1.15 g, 3.4 mmol) was suspended in H_2O (8 ml) and treated with 2.0M NaOH (1.53 ml). The formed sodium salt went into soln. on addition of acetone (8 ml). This mixture was added dropwise with stirring to a soln. of **B**($ZnCl_4$) (X = N_3; 1.53 g, 3.1 mmol) in H_2O (25 ml), and crystals deposited readily. A little acetone was added to slow the crystallization. The mixture was left overnight at 0°, and purple needles of the bis(hydrogen di-*O*-benzoyl-L-tartrate) diastereoisomer which had deposited were washed with i-PrOH and Et_2O and air-dried. To the filtrate was added ¼ volume of 2M Li_2ZnCl_4, and after 1 h at 0°, the purple crystals (nearly quant. precipitation) were filtered, washed, and dried. The diastereoisomer was converted to the $ZnCl_4^{2-}$ salt by triturating with 2M Li_2ZnCl_4. The crude material obtained from the diastereoisomer, and its crude enantiomer from the filtrate, were each purified by the same extraction procedures as described above for isomer **A** (X = N_3). Optically pure materials were obtained in moderate to low yields (*ca.* 10% of total Co for each enantiomer) after 3 such extraction/crystallization procedures. The enantiomer derived from the less soluble diastereoisomer from the hydrogen di-*O*-benzoyl-L-tartrate resolution is $\vec{\Lambda}(-)_{436(CD)}$-*mer-endo*(H)-[Co($N_3$)(dien)(dapo)]($ZnCl_4$) ($\vec{\Lambda}(-)_{436(CD)}$-**B**($ZnCl_4$), X = N_3).

Resolution of mer-exo*(H)-[CoCl(dien)(dapo)]$^{2+}$* (**A**, X = Cl). Racemic **A**($ZnCl_4$) (X = Cl; 13.2 g, 0.027 mol) was dissolved in aq. 0.24M LiCl (123 ml) at 0°. A soln. of sodium arsenyl-L-tartrate (12.7 g, 0.027 *mol) in* H_2O (42 ml) was added to the above soln. The precipitate formed (15.6 g) was filtered immediately, washed with EtOH and Et_2O, and air-dried. The less soluble diastereoisomeric salt was recrystallized from aq. 1.92M LiCl (500 ml) at 0° by addition of sodium arsenyl-L-tartrate (3.6 g, 0.0075 mol) in H_2O (12 ml). After one night at −15°, red crystals (5.25 g) were collected, washed with EtOH and Et_2O, and air-dried. The arsenyl-L-tartrate salt was dissolved in 0.1M HCl (35 ml). Addition of 10M HCl (15 ml) and $ZnCl_2$ (6 g, 0.044 mol) provoked precipitation of the $ZnCl_4^{2-}$ salt (4.05 g). When the whole procedure was repeated, 2.25 g (33%) of optically pure $\vec{\Lambda}(+)_{436(\mathrm{CD})}$-*mer-exo*(H)-[CoCl (dien)(dapo)]($ZnCl_4$) ($\vec{\Lambda}(+)_{436(\mathrm{CD})}$-**A**($ZnCl_4$), X = Cl) were isolated. The more soluble diastereoisomeric arsenyl-L-tartrate salt was isolated from the mother liquor and converted to the $ZnCl_4^{2-}$ salt. It was further purified by applying the essentially identical procedure using sodium arsenyl-D-tartrate.

Resolution of mer-exo*(H)-[CoBr(dien)(dapo)]*$^{2+}$ (**A**, X = Br). Racemic **A**($ZnBr_4$) (X = Br; 10.0 g, 0.014 mol) was dissolved in aq. 0.24M LiCl (80 ml) at 0°. Sodium arsenyl-L-tartrate (6.59 g, 0.014 mol) in H_2O (22 ml) was added. The precipitate (12.3 g) was washed with EtOH and Et_2O and air-dried. The arsenyl-L-tartrate salt obtained was recrystallized from 1.92M LiCl (380 ml) at 0° by addition of sodium L-tartrate (1.9 g, 0.004 mol) in H_2O (6.3 ml). After one night at −15°, the precipitate (4.8 g) was collected, washed with EtOH and Et_2O and air-dried. The recrystallized arsenyl-L-tartrate salt was dissolved in the minimum amount of 0.1M HBr. On addition of 48% HBR soln. (14.5 ml) and $ZnBr_2$ (6.8 g, 0.03 mol), the salt of optically active **A** (X = Br) precipitated (2.82 g, 28%).

Resolution of unsym-fac-exo*(OH)-[CoCl(dien)(dapo)]*$^{2+}$ (**C**, X = Cl). Racemic **C**Cl_2 (X = Cl; 17.0 g, 0.047 mol) was dissolved in H_2O (20 ml, 30°). Sodium arsenyl-L-tartrate (11.55 g, 0.024 mol) in H_2O (15 ml; 30°) was added dropwise. The precipitate, collected after 30 min at r.t., was washed with EtOH and Et_2O and air-dried: 9.73 g (48%). The arsenyl-L-tartrate salt of the resolved cation was transformed into the chloride salt by passing an aq. soln. of the complex through *a Dowex 50WX2* column (H^+ form), washing it with 1M NaCl, eluting the optically active cation with 3M HCl, and precipitating it as the $ZnCl_4^{2-}$ salt using $ZnCl_2$.

Resolution of unsym-fac-exo*(H)-[CoBr(dien)(dapo)]*$^{2+}$ (**C**, X = Br). Racemic **C**Br_2 (X = Br; 15.7 g, 0.032 mol) was dissolved in H_2O (30 ml; pH 3 ($HClO_4$)). An aq. soln. (25 ml) of sodium arsenyl-L-tartrate (7.79 g, 0.016 mol) was added. After 12 h at 0°, the precipitate formed was washed with EtOH and Et_2O and air-dried: 4.58 g (24%). The arsenyl-L-tartrate salt of the optically active species was transformed into the $ZnBr_4^{2-}$ salt by passing an aq. soln. of the complex through a *Dowex 50WX2* column, washing it with 1M NaCl, eluting the resolved cation with 3M HBr, and precipitating it from the eluent with $ZnBr_2$.

Resolution of unsym-fac-*[Co(dien)(dapo-*N,N′,O*)]*$^{3+}$ (**G**). Racemic **G**Cl($ZnCl_4$) (15.0 g, 0.041 mol) was dissolved in 1% aq. LiCl soln. (20 ml). An aq. soln. (15 ml) of sodium arsenyl-L-tartrate (11.1 g, 0.021 mol) was added dropwise. The precipitate, collected after 20 min at 0°, was washed with EtOH and Et_2O and air-dried. The arsenyl-L-tartrate salt of the resolved cation was transfered into the chloride salt by passing an aq. soln. of the complex through a *Dowex 50WX2* column (H^+ form), washing it with 1M NaCl, eluting the optically active cation with 3M HCl, and precipitating it as the $ZnCl_4^{2-}$ salt using $ZnCl_2$.

4. *Crystal Structures.* Preliminary *Weissenberg* and precession photographs served to determine the space groups of the three complexes. Crystal data, X-ray data collection, and refinement details are given in *Table 1*. The SHELX-76 program system [12] was used to solve the three structures by *Patterson* and *Fourier* methods. Complex neutral-atom scattering factors not given in SHELX [12] were taken from [13].

Tables of observed and calculated structure factors, final anisotropic thermal parameters for the cations and anions, final positional and equivalent isotropic thermal parameters for the anions, H-atom positions in the cations and anions, torsion angles in the five and six-membered chelate rings in the cations, and nonbonded distances O···O and O···N > 3.3 Å are available on request (ordering information is given on any current masthead page), and the relevant data are deposited with the *Cambridge Crystallographic Data Center.*

$\vec{\Lambda}(-)_{436(CD)}$-mer-exo*(H)-[Co(N*$_3$*)(dien)(dapo)](hydrogen di-*O*-benzoyl-*L*-tartrate)*$_2$$\cdot 4H_2O$ ($\vec{\Lambda}(-)_{436(\mathrm{CD})}$-**A**((Bz)$_2$-L-tart(H))$_2\cdot 4H_2O$, X = N_3). Intensity data were measured on a *Stoe-Siemens-AED2* four-circle diffractometer (graphite monochromated MoK_α radiation) at r.t. The crystal was sealed in a *Lindemann* glass capillary. Accurate cell parameters were obtained from ±ω values of 31 reflections (15° < 2θ < 30°). There was no significant intensity variation for 3 standard reflections measured every h. No absorption or extinction corrections were applied. The majority of H-atoms were introduced in idealized positions, in both the cation and the anion (C–H 1.08 Å, N–H 1.01 Å, H–X–H 109.5°), with overall isotropic thermal parameters (U_{iso} refined NH and NH_2 type 0.0937; CH_2 type 0.0286; benzene type 0.0727). It was not possible to locate the hydroxy H-atom on O(1) in the cation, however, those of the COOH functions in both anions could be located and refined isotropically. Four H_2O molecules and their H-atoms were located from difference maps.

$\vec{\Lambda}(-)_{436(CD)}$-mer-endo*(H)-[Co(N*$_3$*)(dien)(dapo)](hydrogen di-*O*-benzoyl-*L*-tartrate)*$_2$$\cdot 2.75H_2O$ ($\vec{\Lambda}(-)_{436(\mathrm{CD})}$-**B**((Bz)$_2$-L-tart(H))$_2\cdot 2.75H_2O$, X = N_3). Intensity data were measured on an *Enraf-Nonius-CAD4* diffractometer (graphite monochromated MoK_α radiation) at r.t. The crystal was studied in air and not sealed in a *Lindemann* glass tube. Accurate cell parameters were obtained by least-squares refinement of the 2θ values of 14 intense reflections (18° < 2θ < 34°). For 4 standard reflections measured every h, a significant intensity decrease

Table 1. *Crystal Data for Optical Isomers of* mer-exo*(H)- and* mer-endo*(H)-[Co(N_3)(dien)(dapo)](hydrogen di-*O*-benzoyl-*L*-tartrate)$_2$·*n*H_2O* ($\vec{\Lambda}$-**A**($(Bz)_2$-L-tart(H))$_2$, $\vec{\Lambda}$-**B**($(Bz)_2$-L-tart(H))$_2$, and $\vec{\Delta}$-**B**($(Bz)_2$-L-tart(H))$_2$) (X = N_3), resp.

	$\vec{\Lambda}(-)_{436(CD)}$-**A**($(Bz)_2$-L-tart(H))$_2$·$4H_2O$ (X = N_3)	$\vec{\Lambda}(-)_{436(CD)}$-**B**($(Bz)_2$-L-tart(H))$_2$·$2.75H_2O$ (X = N_3)	$\vec{\Delta}(+)_{436(CD)}$-**B**($(Bz)_2$-L-tart(H))$_2$·$5.75H_2O$ (X = N_3)
Formula	$C_{43}H_{57}N_8O_{21}Co$	$C_{43}H_{54}N_8O_{19.5}Co$	$C_{43}H_{60.5}N_8O_{22.75}Co$
Mol. wt.	1080.9	1053.9	1112.4
Space group	orthorhombic $P2_12_12_1$	triclinic $P1$	triclinic $P1$
a [Å]	7.676(1)	8.062(3)	7.742(1)
b [Å]	19.457(1)	10.296(1)	10.014(1)
c [Å]	34.702(2)	15.056(2)	18.045(2)
α [deg]	90	80.55(1)	99.57(1)
β [deg]	90	85.18(2)	92.87(1)
γ [deg]	90	89.10(2)	102.56(1)
V [Å^3]	5182.8	1228.4	1341.1
Z	4	1	1
$d_{exper.}$ [g·cm^{-3}]	1.38(1)	1.43(1)	1.38(1)
	by flotation in CCl_4 and benzene		
$d_{calc.}$ [g·cm^{-3}]	1.385	1.419	1.377
Crystal colour, habit	red needles	red rods	red rods
Crystal dimensions [mm]	0.11 × 0.19 × 0.38	0.1 × 0.3 × 0.3	0.19 × 0.42 × 0.46
Radiation	Mo$K\alpha$, λ = 0.71073	Mo$K\alpha$, λ = 0.71069	Mo$K\alpha$, λ = 0.71073
Data collection	ω–θ scans	ω scans	ω–θ scans
Index limits	h 0–20, k 0–20, l 0–37	h ± 8, k ± 11, l 0–16	h ± 10, k ± 13, l 0–23
θ limits [deg]	$2.5 < \theta < 22.5$	$0 < \theta < 23$	$2.5 < \theta < 27.5$
No. of unique reflections	3722	3921	5633
No. of reflections used	2555 ($F_o > 3\sigma(F_o)$)[a]	3770 ($F_o > 4\sigma(F_o)$)[a]	5526 ($F_o > 5\sigma(F_o)$)[a]
Abs. coeff. (μ_λ) [cm^{-1}]	0.92	3.86	3.59
Refinement method	blocked full-matrix least-squares		
No. of reflections/ no. of parameters	3.8	5.5	7.6
Final R value	0.050	0.035	0.032
Weighted final R_w[b])	0.041	0.037	0.035
g	3.65×10^{-4}	1.53×10^{-3}	9.29×10^{-4}
Non H-atom param. shift/e.s.d. in last cycle of refinement	2.5 (max); < 0.3 (av.)	1.10 (max); < 0.3 (av.)	0.62 (max); < 0.3 (av.)
Residual density in final difference map [eÅ^{-3}]	0.28 (max); −0.29 (min)	0.36 (max); −0.22 (min)	0.32 (max); −0.17 (min)

[a]) 9, 7, and 8 reflections, respectively, (probably suffering from extinction) were also removed.

[b]) $R_w = \Sigma\sqrt{w}\,||F_o| - |F_c||/\Sigma\sqrt{w}\,|F_o|$, $w^{-1} = \sigma^2(F_o) + g(F_o^2)$

was observed. At 12% intensity decrease, the crystal was replaced. Three crystals of similar size were necessary for a full data collection. No absorption or extinction corrections were applied. The majority of H-atoms were included in idealized positions (overall refined U_{iso} NH and NH_2 type 0.065; CH_2 type 0.0507; benzene type 0.0881). The hydroxy H-atom on O(1) in the cation and the H-atom of the COOH function in one anion were located from difference maps and refined isotropically. Five H_2O molecules were located from difference maps. Only site O(W1) was fully occupied, the remainder were disordered and only partially occupied. No H_2O-molecule H-atoms were located.

$\vec{\Delta}(+)_{436(CD)}$-mer-endo*(H)-[Co($N_3$)(dien)(dapo)](hydrogen di-*O*-benzoyl-*L*-tartrate)$_2$·5.75H_2O* ($\vec{\Delta}(-)_{436(CD)}$-**B**($(Bz)_2$-L-tart(H))$_2$·$5.75H_2O$, X = N_3). Intensity data were measured on a *Stoe-Siemens-AED2* four-circle diffractometer as described above. The crystal was sealed in a *Lindemann* glass capillary. Accurate cell parameters were obtained from the ±ω values of 29 reflections ($20° < 2\theta < 38°$). There was no significant intensity variation for 4 standard reflections measured every h. No absorption or extinction corrections were applied. In the cation, a certain number of H-atoms could be located from difference maps and were refined isotropically. The remaining H-atoms in both the cation and the anions were included in idealized positions (overall U_{iso} refined NH_2 type 0.105; CH_2 type 0.0337; benzene type 0.0831). The hydroxy H-atom on O(1) in the cation and one COOH-function H-atom were located from difference maps and refined isotropically. Seven H_2O-molecule sites were located from difference maps. Only waters O(W1) to O(W4) were fully occupied sites, the remainder were disordered and partially occupied. A limited number of H_2O-molecule H-atoms were located.

Results. – *Syntheses and Optical Resolution.* Oxygenation of cobalt(II) chloride in presence of equimolar amouts of dien and dapo[2]) in aqueous solution at low temperature, followed by HCl cleavage of the resulting peroxo and superoxido compounds, led to a mixture of various isomers of $[CoCl(dien)(dapo)]^{2+}$ and [Co(dien)(dapo-*N*,*N'*,*O*)]$^{3+}$. The isomers were separated by fractional crystallization as the $ZnCl_4^{2-}$ salts, and the yield of the different species was strongly dependent on the temperature during the oxygenation and cleavage processes (and possibly on the H^+ concentration and the time used for crystallization): *mer-exo*(H)-$[CoCl(dien)(dapo)]^{2+}$ (**A**, X = Cl) 15–21%, *unsym-fac-exo*(OH)-$[CoCl(dien)(dapo)]^{2+}$ (**C**, X = Cl) 5–20%, *unsym-fac-endo*(OH)-$[CoCl(dien)(dapo)]^{2+}$ (**D**, X = Cl) *ca.* 0.1%, and *unsym-fac*-[Co(dien)(dapo-*N*,*N'*,*O*)]$^{3+}$ (**G**) 7–20%. The main goal was to synthesize the *mer*-isomers of the complexes, and the synthesis was not optimized for the other isomers. Clearly, the isomer ratio reported is not of thermodynamically equilibrated solutions. Also, no special effort was taken to isolate the missing isomers of the series, *viz.* the two *sym-fac*-isomers **E** and **F** and the *sym-fac*-species **H** containing tridentate dapo. The *mer-endo*(H)-$[CoCl(dien)(dapo)]^{2+}$ (**B**, X = Cl) species may be isolated in very small amounts from the above reaction mixture. However, **B** (X = Cl) is more conveniently prepared from the corresponding azido complex **B** (X = N_3) which results from anation of the *mer*-hydroxo complex or which arises from azide competition during base hydrolysis: 7:3 mixtures of the *mer*-exo-(H)- and *mer-endo*(H)-epimers **A** and **B** (X = N_3), respectively, are obtained in either case, and were readily separated [7]. The yield of complex **D** (X = Cl) from the oxygenation reaction is also quite poor, but **D** (X = Cl) is prepared in relatively high yield by direct cleavage of the superoxido precursor after first reducing it to the peroxo ion with I^-. The bromo, azido, nitrito-*O*, nitro-*N*, thiocyanato, aqua, and hydroxo derivatives of the complexes described are prepared by conventional substitution processes, and other pentaaminecobalt(III) complexes, studied for comparison, are prepared by published methods or modifications thereof. Optically active compounds are resolved by taking advantage of the solubility difference of salts of the enantiomers with optically pure anions (di-*O*-benzoyl-L-tartrate, L-tartrate, arsenyl-L-tartrate, antimonyl-L-tartrate). To obtain optically pure complexes, recrystallizations are repeated until a constant ellipticity of the products is achieved. Optical purity of the *mer*-chloro species is established by a stereochemical cycle using chemical correlations between resolved species [7] and by X-ray crystallography of salts with optically pure counterions.

Spectroscopy. The configurations of the various isomers of $[CoXL^3L^2]^{n+}$, where X = Cl^-, Br^-, N_3^-, OH^-, ONO^-, NO_2^-, and OH_2, L^3 = dien and dpt, and L^2 = en, tn, and dapo[2]), are most conveniently determined by ^{13}C-NMR spectroscopy. Owing to the different site symmetries, the expected number of ^{13}C-NMR signals are different for *mer*-, *sym-fac*- and *unsym-fac*-isomers, *viz.* there are symmetry-equivalent atoms for the *mer*- and *sym-fac*-isomers. This is not strictly true for the *mer*-isomers of $[CoXL^3(dapo)]^{n+}$, (L^3 = dien or dpt), where the presence of the OH substituent in the six-membered chelate

Table 2. *^{13}C-NMR Chemical Shifts* (at 50.32 and 75.48 MHz; δ in ppm; *vs.* internal dioxane (67.4 ppm)) *of the Various Isomers of [CoXL^{3}L^2]$^{n+}$ in D$_2$O*

	C(6)[a]	C(1), C(4)[a]	C(2), C(3)[a]	C(5)[a]	C(7)[a]
mer-exo(H)-[CoCl(dien)(dapo)]$^{2+}$ (**A**, X = Cl)[b]	64.0	48.3, 48.2	50.9, 51.1	43.4 43.3[d] 43.2[e]	43.6
mer-endo(H)-[CoCl(dien)(dapo)]$^{2+}$ (**B**, X = Cl)[b]	63.9	47.8, 47.4	50.2, 50.0	43.1 43.0[d] 42.9[e]	43.5
mer-exo(H)-[CoBr(dien)(dapo)]$^{2+}$ (**A**, X = Br)[c]	63.8	48.2, 48.1	52.1, 52.0	43.2	43.5
mer-endo(H)-[CoBr(dien)(dapo)]$^{2+}$ (**B**, X = Br)[c]	63.2	47.2, 47.1	51.3, 51.1	43.0	43.1
mer-exo(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$ (**A**, X = N$_3$)[b]	64.5	48.2, 48.1	50.3, 50.0	43.7	44.3
mer-endo(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$ (**B**, X = N$_3$)[b]	64.2	47.4, 47.2	49.9, 49.8	43.5	44.1
mer-exo(H)-[Co(ONO)(dien)(dapo)]$^{2+}$ (**A**, X = ONO)[b]	64.4	48.6, 48.5	49.7, 49.4 49.5, 49.3[f]	43.7 43.6[d] 43.5[e]	44.5
mer-endo(H)-[Co(ONO)(dien)(dapo)]$^{2+}$ (**B**, X = ONO)[b]	64.3	47.5, 47.2	50.4, 50.3	43.4	44.2
mer-exo(H)-[Co(NO$_2$)(dien)(dapo)]$^{2+}$ (**A**, X = NO$_2$)[b]	64.2	48.3, 48.0	51.0, 50.5	43.8	44.1
mer-endo(H)-[Co(NO$_2$)(dien)(dapo)]$^{2+}$ (**B**, X = NO$_2$)[b]	64.3	47.8, 47.4	50.6, 50.3	43.7	44.5
mer-exo(H)-[Co(OH)(dien)(dapo)]$^{2+}$ (**A**, X = OH)[b]	65.1	47.8, 47.7	49.5, 49.3	44.9	45.1
mer-endo(H)-[Co(OH)(dien)(dapo)]$^{2+}$ (**B**, X = OH)[b]	65.0	46.7, 46.4	50.1, 50.0	43.8	43.8
mer-exo(H)-[Co(H$_2$O)(dien)(dapo)]$^{3+}$ (**A**, X = H$_2$O)[b]	63.8	48.5, 48.3	50.6, 50.4 50.5, 50.3[f]	43.1 43.0[d] 42.9[e]	44.2
mer-endo(H)-[Co(H$_2$O)(dien)(dapo)]$^{3+}$ (**B**, X = H$_2$O)[b]	63.8	48.3, 47.9	50.6, 50.3 50.5, 50.2[f]	43.1 43.0[d] 42.9[e]	44.1
unsym-fac-exo(OH)-[CoCl(dien)(dapo)]$^{2+}$ (**C**, X = Cl)[b]	64.5	45.0, 44.7	55.7, 55.0	42.7	43.0
unsym-fac-endo(OH)-[CoCl(dien)(dapo)]$^{2+}$ (**D**, X = Cl)[b]	65.1	45.1, 44.2	55.8, 53.7	43.5	43.8
unsym-fac-exo(OH)-[CoBr(dien)(dapo)]$^{2+}$ (**C**, X = Br)[b]	64.5	45.2, 44.1	56.2, 55.7	42.9	43.4
unsym-fac-exo(OH)-[Co(N$_3$)(dien)(dapo)]$^{2+}$ (**C**, X = N$_3$)[b]	64.4	44.4, 44.2	54.8, 54.3	42.8	43.2
unsym-fac-[Co(dien)(dapo-*N*,*N'*,*O*)]$^{3+}$ (**G**)[b]	78.2	45.7, 43.8	55.2, 53.0	45.6	45.6
unsym-fac-[Co(dien)(dapo-*N*,*N'*,*O*)]$^{2+}$[b]	77.3	44.4, 42.9	53.9, 52.3	47.2	47.9
Peroxo dimer[b]	65.1	42.7, 42.7	54.2, 51.0	43.8	44.9
mer-exo(H)-[CoCl(dpt)(dapo)]$^{2+}$[c]	64.4	40.2, 39.5, 25.8[g], 25.7[g]	51.9, 51.6	41.6	42.5
mer-exo(H)-[CoCl(dpt)(tn)]$^{2+}$[c]	25.6	39.9, 25.4[b]	51.6	37.7	39.3
mer-exo(H)-[CoCl(dpt)(en)]$^{2+}$[c]	–	38.9, 25.2[b]	52.4	44.5	45.7
mer-exo(H)-[CoCl(dien)(tn)]$^{2+}$[c]	25.9	48.2	50.8	39.5	39.8
sym-fac-[CoCl(dien)(en)]$^{2+}$[c]	–	45.8	55.6	44.0	

[a] For atom numbering, see *Figure*. [b] 75.48 MHz. [c] 50.32 MHz. [d] Monodeuterated at N(4). [e] Dideuterated at N(4). [f] Deuterated at N(2). [g] Central methylene C-atom of dpt.

ring of the diamine ligand has an influence on its conformational equilibrium position, resulting in a small splitting of all the otherwise pairwise isochronous C-atoms of the tridentate ligand. Spectral data are given in *Table 2*. From ^{13}C-NMR spectra of *unsym-fac-endo*(OH),*unsym-fac-endo*(OH)-{[Co(dien)(dapo)]$_2$(μ-O$_2$)}$^{4+}$ (μ-peroxo complex) it follows that it is either the pure *meso-* or pure *rac*-isomer, as must be the μ-superoxido ion from which it is derived.

At 200 MHz, the ^{1}H-NMR spectra of the various isomers of [CoX(dien)(dapo)]$^{n+}$ have a poorly resolved *m* for the CH$_2$ protons in the region of 2–3.5 ppm. The well-resolved *nonuplet* of the single proton of the tertiary C-atom of dapo (C(6) in *Fig.*) appears, as expected, at the low-field and of the CH_2 region (*ca.* 3.5 ppm). In general, the ^{1}H-NMR spectra are too complex to be of diagnostic value for the characterization of the various isomers. However, of importance for proton-exchange studies [7] is the analysis of the ^{1}H-NMR signals of the NH and NH_2 protons. Their assignment to the different sites is by their integrals (a/b/c/d/e 1:2:2:2:2) and the expected relative proton-exchange rates. The assignments are also confirmed by ^{13}C-NMR studies of H-exchange, reported elsewhere [7]. The secondary-amine proton NH of the *mer*-isomers and the NH_2 group *trans* to the leaving group X have the highest exchange rates. As expected, NH appears at the lowest field and NH_2 *trans* to X at the highest field (see *Table 3*).

Table 3. *^{1}H-NMR Assignments of the NH and NH_2 Protons* (at 200 MHz, in D_2O/D_2SO_4 (pD *ca.* 3); δ rel. to internal DSS or TSP (0 ppm)) *of $[CoX(dien)(dapo)]^{n+}$ Isomers*

	NH(2)[a]) δ [ppm]	$NH_2(4)$[a]) δ [ppm]	$NH_2(1)$, $NH_2(3)$, $NH_2(5)$[a])[b]) δ [ppm]
mer-exo(H)-$[CoCl(dien)(dapo)]^{2+}$ (**A**, X = Cl)	6.80	4.09	5.21 (4.60), 5.09, 4.93
mer-endo(H)-$[CoCl(dien)(dapo)]^{2+}$ (**B**, X = Cl)	7.21	4.19	5.28 (4.70), 5.10, 4.98
mer-exo(H)-$[CoBr(dien)(dapo)]^{2+}$ (**A**, X = Br)	6.61	[c])	[c])
mer-exo(H)-$[Co(N_3)(dien)(dapo)]^{2+}$ (**A**, X = N_3)	6.48	4.09	5.09 (4.19), 4.68, 4.48
mer-endo(H)-$[Co(N_3)(dien)(dapo)]^{2+}$ (**B**, X = N_3)	6.78	3.68	5.08 (4.25), 4.68, 4.48
unsym-fac-exo(OH)-$[CoCl(dien)(dapo)]^{2+}$ (**C**, X = Cl)	6.64	[c])	[c])
unsym-fac-endo(OH)-$[CoCl(dien)(dapo)]^{2+}$ (**D**, X = Cl)	6.91	[c])	[c])
unsym-fac-exo(OH)-$[CoBr(dien)(dapo)]^{2+}$ (**C**, X = Br)	6.58	[c])	[c])
unsym-fac-exo(OH)-$[Co(N_3)(dien)(dapo)]^{2+}$ (**C**, X = N_3)	6.31	[c])	[c])
unsym-fac-$[Co(dien)(dapo\text{-}N,N',O)]^{3+}$ (**G**)	7.32	[c])	[c])

[a]) For atom numbering, see *Figure*. [b]) NH_2 protons *cis* to the leaving group are not assigned individually. [c]) Not resolved.

For pentaaminecobalt(III) complexes, two main ligand-field transitions (derived from octahedral $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$ modes) at *ca.* 500 and 350 nm, respectively, are expected in the UV/VIS spectra. For $[CoXL^3L^2]^{n+}$ systems (L^3 = dien, dpt; L^2 = en, tn, dapo), the lower-energy transition is characteristically split by the tetragonal distortion of the chromophore (*Table 4*). The relative intensities of the two components $^1A_2 \leftarrow {}^1A_1$ and $^1E \leftarrow {}^1A_1$ (in C_2 symmetry) might be used to assign the various isomers by UV/VIS spectroscopy, and the observed spectra are consistent with the assignments [9–11]. However, the analysis based on ^{13}C-NMR spectroscopy is more straightforward and less ambiguous. The high-energy transition of the *unsym-fac*-$[Co(dien)(dapo\text{-}N,N',O)]^{3+}$ iso-

Table 4. *UV/VIS Spectra of $[CoXL^3L^2]^{n+}$ Isomers in Aqueous Solution*

	$^1T_{1g} \leftarrow {}^1A_{1g}$ λ [nm] (ε [$l \cdot mol^{-1} \cdot cm^{-1}$])	$^1T_{2g} \leftarrow {}^1A_{1g}$ λ [nm] (ε [$l \cdot mol^{-1} \cdot cm^{-1}$])
mer-exo(H)-$[CoCl(dien)(dapo)]^{2+}$ (**A**, X = Cl))	540 (60.8)[a]), 486 (81.7)	375 (75.2)
mer-endo(H)-$[CoCl(dien)(dapo)]^{2+}$ (**B**, X = Cl)	540 (58.1)[a]), 481 (87.0)	371 (81.1)
mer-exo(H)-$[CoBr(dien)(dapo)]^{2+}$ (**A**, X = Br)	540 (68)[a]), 482 (87)	–
mer-exo(H)-$[Co(N_3)(dien)(dapo)]^{2+}$ (**A**, X = N_3)	510 (356.0)	–
mer-endo(H)-$[Co(N_3)(dien)(dapo)]^{2+}$ (**B**, X = N_3)	515 (304.7)	–
mer-exo(H)-$[Co(NCS)(dien)(dapo)]^{2+}$ (**A**, X = NCS)	484.5 (254.1)	–

Table 4 (cont.)

	$^1T_{1g} \leftarrow {}^1A_{1g}$ λ [nm] (ε [l·mol^{-1}·cm^{-1}])	$^1T_{2g} \leftarrow {}^1A_{1g}$ λ [nm] (ε [l·mol^{-1}·cm^{-1}])
mer-endo(H)-[Co(NCS)(dien)(dapo)]$^{2+}$ (**B**, X = NCS)	485 (191.2)	–
mer-exo(H)-[Co(H_2O)(dien)(dapo)]$^{3+}$ (**A**, X = H_2O)	473 (91.0)	352 (73.9)
mer-endo(H)-[Co(H_2O)(dien)(dapo)]$^{3+}$ (**B**, X = H_2O)	470 (102.1)	336 (77.4)
mer-[Co(OH)(dien)(dapo)]$^{3+}$ (**A**/**B**, X = OH)[b])	490 (105.5)	350 (90.5)
unsym-fac-exo(OH)-[CoCl(dien)(dapo)]$^{2+}$ (**C**, X = Cl)	532.5 (74.6), 480 (58.1)[a])	367.5 (99.1)
unsym-fac-endo(OH)-[CoCl(dien)(dapo)]$^{2+}$ (**D**, X = Cl)	531 (71.8), 470 (50.7)[a])	366 (88.1)
unsym-fac-exo(OH)-[Co(H_2O)(dien)(dapo)]$^{3+}$ (**C**, X = H_2O)	484 (83)	346 (80)
unsym-fac-endo(OH)-[Co(H_2O)(dien)(dapo)]$^{3+}$ (**D**, X = H_2O)	480 (81)	340 (78)
unsym-fac-exo(OH)-[CoBr(dien)(dapo)]$^{2+}$ (**C**, X = Br)	532 (71), 490[a])	370 (96)
unsym-fac-exo(OH)-[Co(N_3)(dien)(dapo)]$^{2+}$ (**C**, X = N_3)	516 (345.5)	–
unsym-fac-[Co(dien)(dapo-*N*,*N*′,*O*)]$^{3+}$ (**G**)	469.5 (57.0)	340 (78.3)
unsym-fac-[Co(dien)(dapo-*N*,*N*′,*O*)]$^{2+}$	480 (74.4)	378 (135.0), 340 (97.4)[a])
mer-exo(H)-[CoCl(dpt)(dapo)]$^{2+}$	520 (67.3)	376 (87)

[a]) Shoulder. [b]) At **A**/**B** equilibrium (9:1); imidazole buffer (I = 1.0M, $NaClO_4$; pH 7.4).

mers **G** is very sensitive to base concentration, consistent with deprotonation of the coordinated OH substituent ($pK_a = 2.74 \pm 0.1$, 25.0°, I = 1.0M ($NaClO_4$; potentiometric and spectrophotometric titration)).

The CD spectra (*Table 5*) show, in the region of the low-energy transition ($^1T_{1g} \leftarrow {}^1A_{1g}$ in O_h) two transitions with opposite sign (see also *Discussion*). The region of the higher-energy transition ($^1T_{2g} \leftarrow {}^1A_{1g}$ in O_h) is very sensitive to the sixth ligand X. The isomers with meridionally coordinated dien or dpt have CD spectra that are phenomenologically

Table 5. *CD Spectra of [CoX(L^3L^2)]$^{n+}$ Isomers in Aqueous Solution*

	λ [nm] (θ_λ [m°·l·mol^{-1} cm^{-1}]					
A (X = Cl)[b])[e])	543[g]) (+530)	506[h])	463[g]) (−760)			
B (X = Cl)[b])[e])	558[g]) (+500)	524[h])	469[g]) (−980)	392[g]) (−290)	363[h])	346[g]) (+160)
A (X = Br)[c])	553[g]) (+410)	513[h])	468[g]) (−620)	405[g]) (−400)		
A (X = N_3)[b])[e])	568[g]) (+220)	546[h])	494[g]) (−1560)	431[h])	393[g]) (+830)	
B (X = N_3)[b])[e])	570[g]) (−170)	545[h])	528[g]) (+140)	518[h])	467[g]) (−1560)	414[h])
A (X = H_2O)[d])[f])	538[g]) (+550)	504[h])	463[g]) (−770)	388[h])	360[g]) (+200)	
B (X = H_2O)[d])[f])	538[g]) (+310)	507[h])	459[g]) (−960)	384[h])	356[g]) (+240)	
C (X = Cl)[d])[f])	552[g]) (−3200)	505[h])	462[g]) (+3340)	395[g]) (+840)	376[h])	350[g]) (−1740)
C (X = Br)[c])	556[g]) (−3850)	516[h])	471[g]) (+4250)	391[h])	364[g]) (−2710)	
G[d])	535[g]) (+150)	512[h])	479[g]) (−300)	380[g]) (−70)	362[h])	340[g]) (+90)
unsym-fac-[Co(dien) (dapo-*N*,*N*′,*O*)]$^{2+}$[d])	492[g]) (+30)	442[h])	420[g]) (−3)	400[h])	364[g]) (−10)	

[a]) The samples ([complex] ≈ 10^{-3} M) were measured at pH *ca.* 3 ($HClO_4$). No other anions were added. In cases where spectra of various salts were studied, the spectra were shown to be independent of the counter-ion. The configuration of the *mer*-isomers **A** and **B** given in this table is $\vec{\Lambda}$. In case of the azido complexes, this was shown by X-ray crystallography. The configuration of other *mer*-complexes is based on chemical conversions of optically pure azido isomers. The configuration of the *fac*-isomers **C** and **G** was not assigned, and the spectra presented correspond to the materials described in the *Exper. Part.* [b]) $ZnCl_4^{2-}$ salt. [c]) $ZnBr_4^{2-}$ salt. [d]) Cl^- salt. [e]) Optically pure (X-ray, stereochemical cycle). [f]) Optically pure (recrystallized to constant ellipticity). [g]) Maximum. [h]) Intercept.

similar to the one of optically pure $[CoX(bamp)(dapo)]^{n+}$ (bamp is meridionally coordinating 2,6-bis(aminomethyl)pyridine) [14]. This is not unexpected since the source of chirality, *viz.* the OH substituent of dapo, responsible for the removal of the time-average mirror plane of the analoguous tn complexes, is the same. The CD intensities of the isomers with facially coordinated dien are $\geqslant 5$ times larger than for the corresponding *mer*-isomers. This might be attributed to configurational effects which clearly are absent in the *mer*-isomers.

IR spectra were used to assign the various isomers of $[CoXL^3L^2]^{n+}$ complexes (L^3 = dien, dpt; L^2 = en, tn) [9–11]. Our IR spectra are qualitatively similar to those reported and are not elaborated upon here.

Crystal Structures. The absolute configurations and the assignments of *exo*(H)- and *endo*(H)-configuration of the secondary-amine proton NH were established by X-ray crystallographic analysis of $\vec{\Lambda}(-)_{436(CD)}$-**A**((Bz)$_2$-L-tart(H))$_2$·4 H_2O (X = N_3), $\vec{\Lambda}(-)_{436(CD)}$-**B**((Bz)$_2$-L-tart(H))$_2$·2.75 H_2O (X = N_3), and $\vec{\Delta}(+)_{436(CD)}$-**B**((Bz)$_2$-L-tart(H))$_2$·5.75 H_2O (X = N_3), obtained by crystallization with chiral anions of known configuration (s. *Exper. Part*). Selected bond distances and angles are listed in *Table 6*. Perspective views of

Table 6. *Selected Bond Lengths* [Å] *and Angles* [°] *of* $\vec{\Lambda}(-)_{436(CD)}$-mer-exo*(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$* ($\vec{\Lambda}(-)_{436(CD)}$-**A**, X = N_3), $\vec{\Lambda}(-)_{436(CD)}$-mer-endo*(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$* ($\vec{\Lambda}(-)_{436(CD)}$-**B**, X = N_3), *and* $\vec{\Delta}(+)_{436(CD)}$-mer-exo*(H)-[Co(N$_3$)(dien)(dapo)]$^{2+}$* ($\vec{\Delta}(+)_{436(CD)}$-**B**, X = N_3)[a])

	($\vec{\Lambda}(-)_{436(CD)}$-**A**, X = N_3)	($\vec{\Lambda}(-)_{436(CD)}$-**B**, X = N_3)	($\vec{\Delta}(+)_{436(CD)}$-**B**, X = N_3)
Co–N(1)	1.976(5)	1.983(4)	1.966(3)
Co–N(2)	1.951(5)	1.936(3)	1.942(3)
Co–N(3)	1.961(6)	1.972(3)	1.972(3)
Co–N(4)	1.989(5)	2.000(3)	1.983(2)
Co–N(5)	1.960(6)	1.986(4)	1.970(3)
Co–N(6)	1.970(6)	1.950(4)	1.962(2)
N(6)–N(7)	1.206(9)	1.195(5)	1.189(4)
N(7)–N(8)	1.141(9)	1.137(6)	1.147(4)
N(1)–Co–N(2)	86.3(2)	84.8(1)	83.6(1)
N(1)–Co–N(3)	169.6(2)	169.8(1)	169.2(1)
N(2)–Co–N(3)	85.3(2)	85.0(1)	83.6(1)
N(2)–Co–N(4)	91.3(2)	92.6(1)	93.3(1)
N(2)–Co–N(5)	178.5(3)	174.4(1)	173.9(1)
N(2)–Co–N(6)	92.1(3)	86.9(1)	85.2(1)
N(4)–Co–N(5)	89.6(2)	92.7(1)	92.3(1)
N(4)–Co–N(6)	173.9(3)	177.0(2)	177.0(1)
N(5)–Co–N(6)	86.9(3)	88.0(2)	89.3(1)
Co–N(1)–C(1)	108.5(4)	108.4(3)	111.4(2)
Co–N(2)–C(2)	108.2(4)	111.3(2)	110.5(2)
Co–N(2)–C(3)	107.6(5)	109.6(2)	110.1(2)
Co–N(3)–C(4)	109.4(4)	109.0(2)	108.3(2)
Co–N(4)–C(5)	119.0(4)	120.1(3)	120.9(2)
Co–N(5)–C(7)	120.1(5)	122.7(3)	120.7(2)
Co–N(6)–N(7)	126.8(5)	121.9(3)	124.2(2)
N(6)–N(7)–N(8)	174.7(8)	176.9(6)	176.4(3)

[a]) Note that the atomic numbering for $\vec{\Delta}(+)_{436(CD)}$-**B** is not the same as that of $\vec{\Lambda}(-)_{436(CD)}$-**B** (see *Fig.*). Therefore, some of the data given in this table are not *directly* comparable. However, this seems to be immaterial since some related bond lengths and angles of $\vec{\Lambda}(-)_{436(CD)}$-**B** and $\vec{\Delta}(+)_{436(CD)}$-**B** are anyway slightly different, and this is not unexpected due to the different environment in the respective crystal lattices.

the cations are shown in the *Figure*. As previously observed for Co^{III} complexes with meridionally coordinated dien [16–19], the main distortion from octahedral geometry around the Co^{III} atom is the *trans* angle of *mer*-dien (N(1)–Co–N(3), average value 170°,

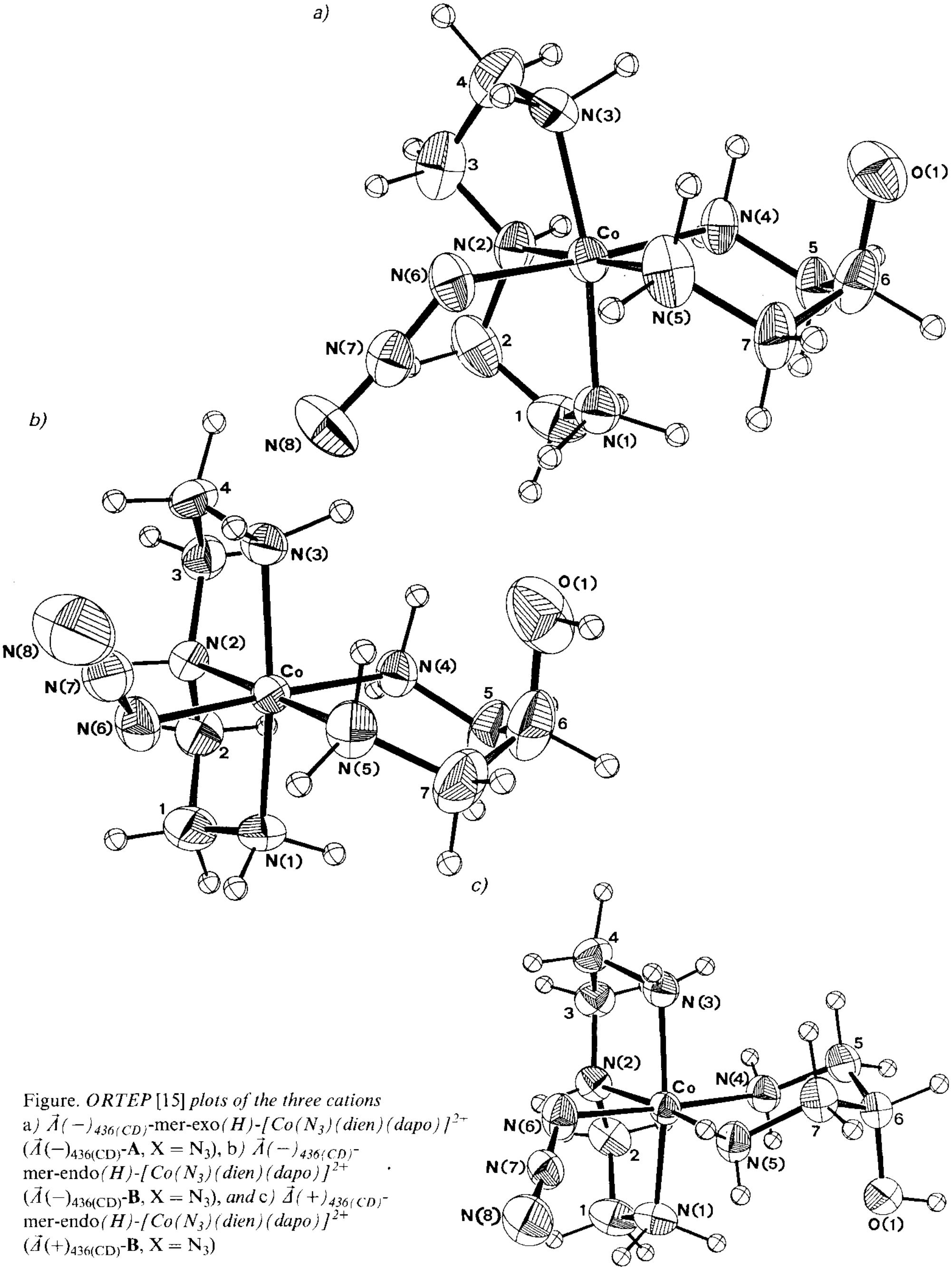

Figure. *ORTEP* [15] *plots of the three cations* a) $\vec{\Lambda}(-)_{436(CD)}$-mer-exo*(H)-[Co(N$_3$)(dien)(dapo)]*$^{2+}$ ($\vec{\Lambda}(-)_{436(CD)}$-**A**, X = N_3), b) $\vec{\Lambda}(-)_{436(CD)}$-mer-endo*(H)-[Co(N$_3$)(dien)(dapo)]*$^{2+}$ ($\vec{\Lambda}(-)_{436(CD)}$-**B**, X = N_3), *and* c) $\vec{\Delta}(+)_{436(CD)}$-mer-endo*(H)-[Co(N$_3$)(dien)(dapo)]*$^{2+}$ ($\vec{\Delta}(+)_{436(CD)}$-**B**, X = N_3)

Table 6). The valence angles around the secondary-amine group NH of dien are also quite strained (C(2)–N(2)–C(3), average value 118°), and this is also consistent with structures of comparable compounds [16–19]. In all three complexes, the six-membered chelate ring of dapo adopts a chair conformation with the OH substituent being axial. This conformation was also observed in a structure of $[Co(N_3)(bamp)(dapo)]^{2+}$ [20].

Discussion. – The complexes *mer-exo*(H)-, *mer-endo*(H)-, *unsym-fac-exo*(OH)-, and *unsym-fac-endo*(OH)-$[CoCl(dien)(dapo)](ZnCl_4)$ (**A**–**D**, X = Cl) and *unsym-fac*-[Co(dien)(dapo-*N*,*N'*,*O*)]Cl$(ZnCl_4)$ (**G**) and some derivatives (bromo, azido, nitrito-*O*, nitro-*N*, thiocyanato, hydroxo, and aqua complexes) were isolated and characterized. Some of the chiral species were obtained in optically resolved forms. The structural assignment of all isomers is based on X-ray crystallography, ^{13}C-NMR spectroscopy, chiroptical properties, and relative reactivities towards base hydrolysis (see also [7] [8]). The symmetries of the *mer*-, *unsym-fac*-, and *sym-fac*-isomers of $[CoXL^3L^2]^{n+}$ (L^3 = dien, dpt; L^2 = en, tn, dapo) and [Co(dien)(dapo-*N*,*N'*,*O*)]$^{2+/3+}$ are reflected in their ^{13}C-NMR spectra. The correctness of the assigned configurations is also supported by the base-hydrolysis reactivity of the various isomers and by the strereochemical changes observed for their base-catalyzed substitution reactions [7] [8]. However, the *exo*(H)- *vs.* *endo*(H)-configuration at the secondary-amine group NH of dien or dpt can not be determined by these means. The main *mer*-isomer resulting from the oxygenation and subsequent HCl cleavage might be assigned to a *mer-exo*(H)-configuration **A**, based on assumed stabilities and in analogy to similar preparative procedures for analogous $[CoXL^3L^2]^{n+}$ complexes (L^3 = dien; L^2 = en, tn) [9–11], [21–23]. Such an assignment, however, would be speculative, although the product mixture is probably at thermodynamic equilibrium with respect to inversion at the secondary-amine group under the basic conditions of the synthesis. Therefore, the structural assignments were confirmed by crystal structure determinations of some selected isomers, in particular of the *mer-exo*(H)- and *mer-endo*(H) species **A** and **B**, respectively.

The configuration of the isomers **C**–**H** with facially coordinated dien is most conveniently described with Δ, Λ standard helicities [24–26]. The chiral isomers (the *sym-fac*-isomers **E**, **F**, and **H** are achiral) have Λ-(*unsym-fac-exo*(OH)-isomer **C**), Λ-(*unsym-fac-endo*(OH)-isomer **D**) and $\vec{\Delta}$ (*unsym-fac-N,N',O*-isomer **G**) configuration[7]). Alternatively, based on the CIP [27] or CAS [28] reference systems, the three species **C**, **D**, and **G** have (*S*), (*S*), and (*R*) or *A*, *A*, and *C* configurations, respectively, consistent with the fact that the three reference systems are equivalent [26]. The assignment of the configuration of the isomers **A** and **B** with meridionally coordinated dien is less trivial since the arrangement of ligand atoms or chelate rings around the cobalt(III) center is in principle not dissymmetrical. As a consequence, the CIP [27], CAS [28], and nonoriented skew lines [24] reference systems do not lead to unambiguous assignments of configuration. For a similar system ($[CoX(bamp)(dapo)]^{n+}$, bamp = 2,6-bis(aminomethyl)pyridine, X = Cl^-, Br^-, N_3^-), the CIP and CAS rules had to be extended to assign the chiral descriptors [14]

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[7]) The reference system based on oriented skew lines is not fully established and well defined yet [25] [26]. For the orientation of the skew lines, we used the same priority rules as in the nonoriented skew line and CIP reference systems. For the *mer*-isomers, the skew lines considered involved the two substituents on which the asymmetry of the complexes is based, *viz.* the leaving group X and the dapo OH substituent. In the *unsym-fac-N,N',O*-isomer only five-membered chelate rings were considered.

[20], and the configurations of the *mer*-isomers **A** and **B** are (*S*) or *A*, accordingly. With the recently proposed reference system of oriented skew lines, the assigned configuration is $\vec{\Lambda}$ (consistent with (*S*) or *A*) [26]. This nomenclature has to be preferred since it is not based, as the CIP and CAS systems are, on elements of chirality, which are not observable quantities and should for various reasons be abandoned [29].

Classically, optical activity of octahedral coordination compounds (*viz.* the observed CD intensity) is attributed to configurational, conformational, and vicinal effects [30]. An unambiguous attribution of the observed CD intensities for the various isomers does not seem to be warranted in the present case. In the *mer*-isomers **A** and **B** of [CoX(dien)(dapo)]$^{n+}$, the chirality arises from the combination of two prostereogenic elements, based on the dapo ligand and the CoX(dien) fragment, respectively. The same prostereogenic ligand-based element is combined with a chiral Co^{III}-center-based fragment in the case of the *fac*-isomers **C**, **D**, and **G**. Therefore, it is not unexpected that the CD intensities of optically pure *unsym-fac*-isomers is much larger than for the *mer*-isomers.

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