ReH$_2$(NO)(PPh$_3$)$_3$, 58694-74-9; [ReF(CO)(NO)(PPh$_3$)$_3$]ClO$_4$, 83095-56-1; [ReF(CO)(NO)(PPh$_3$)$_3$]ClO$_4$·xC$_6$H$_{12}$·yCH$_2$Cl$_2$, 83095-57-2; ReCl$_2$(NO)(PPh$_3$)$_2$, 53435-83-9; benzoylhydrazine, 613-94-5; deuterium, 7782-39-0.

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Structure and Synthesis of Isomers of Novel Binuclear Cobalt(III)–Phenyl Phosphate Complexes

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The reaction between *cis*-[Co(en)$_2$Cl$_2$]ClO$_4$ and silver phenyl phosphate in anhydrous dimethyl sulfoxide yielded the dimeric cation {[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ as the major product. An X-ray structure determination of the meso diastereomer as the triflate salt monohydrate showed that it consisted of two bis(ethylenediamine)cobalt(III) moieties bridged by two phosphate ester groups; the two cobalt atoms and two bridging ligands define an eight-membered ring. Crystals were of space group *P*2$_1$/*c* with *a* = 9.454 (5) Å, *b* = 28.683 (14) Å, *c* = 7.487 (4) Å, β = 97.21 (8)°, and *Z* = 4, *R* being 0.060 for 1675 reflections with *I* > 2.5σ(*I*). The racemic diastereomer has been resolved, and the corresponding rotatory dispersion and circular dichroism spectra are discussed.

Introduction

Polynuclear metal complexes play a significant role in enhancing the rate of hydrolysis of biologically important phosphate compounds.[2–4] For example, the rate of hydrolysis of ATP is accelerated 60-fold in the presence of Cu(II) and this has been attributed to the formation of dimeric [((ATP)CuOH)$_2$]$^{6-}$.[2] Furthermore, the hydrolysis of pyrophosphate to orthophosphate is increased by 10^5 times at pH 7 in the presence of [Co(1,3-diaminopropane)$_2$(OH)(OH$_2$)]$^{2+}$.[4] ^{31}P NMR studies indicate that the catalytically active species is a polynuclear complex containing one pyrophosphate moiety coordinated to three Co(III) centers.

As part of a continuing study into the promotion of phosphate ester hydrolysis by metal ions we now report the synthesis and characterization of a new type of Co(III) dimer containing two bridging phosphate ester moieties.[5]

Experimental Section

Reagents and Instrumentation. Analytical grade reagents were used throughout except where otherwise specified. Dimethyl sulfoxide (Mallinckrodt, AR) was dried over 4A molecular sieves. Laboratory reagent grade sulfolane (tetramethylenesulfone) was predried by passage through a column of 4A molecular sieves and then distilled from calcium hydride before use. Nitronium tetrafluoroborate (NO$_2$BF$_4$) was obtained from Pfaltz and Bauer.

^{1}H NMR spectra were recorded with a JEOL JNM-MH-100 (Minimar) spectrometer. Chemical shifts are quoted as downfield relative to NaTPS [sodium 3-(trimethylsilyl)propanesulfonate] in D$_2$O solution. For the ^{31}P NMR studies, JEOL JNM-FX-100 (^{31}P probe) or JEOL JNM-FX-90 (multiprobe) spectrometers operating at 40.32 and 36.20 MHz, respectively, with internal D$_2$O lock were used. All spectra were proton decoupled. ^{31}P chemical shifts are reported relative to external 85% H$_3$PO$_4$ with increasing values toward low field. ^{13}C{^{1}H}

NMR spectra were recorded at 15.04 MHz with a JEOL FX-60Q spectrometer with chemical shift values quoted relative to 1,4-dioxane (internal reference). An autobalancing resistance bridge (Genrad 1657 RLC Digibridge) was used in conjunction with a Phillips PW 9512/00 dipping electrode for all conductance measurements. A Knauer Dampforuck-Osmometer was used for the determination of molecular weights in aqueous solution. The machine was calibrated with sodium chloride solutions (at 37 °C).

Rotatory dispersion (RD) spectra were obtained with 1-dm cells in a Perkin-Elmer P22 spectropolarimeter. Molecular rotations [M] are recorded in units of deg M^{-1} m^{-1}. Circular dichroism (CD) spectra were recorded on a Jasco UV/5 ORD instrument fitted with a Sproul Scientific SS20 CD modification. The $\Delta\epsilon$ values for the CD spectra are quoted in units of M^{-1} cm^{-1}. The instrument was calibrated against a solution of (+)$_D$-[Co(en)$_3$]$_2$Cl$_6$·NaCl·6H$_2$O ($\Delta\epsilon$ = 1.80 at 484 nm).[6] A Pharmacia K 50/100 chromatography column was used for the resolution of the dimeric complexes into their optical isomers.

Synthesis of the Meso and Racemic Diastereomers of {[Co(en)$_2$-(μ-O$_3$POC$_6$H$_5$)]$_2$}X$_2$ (X = Cl$^-$, CF$_3$SO$_3$$^-$). *cis*-[Co(en)$_2Cl_2$]ClO$_4$ (20 g) was dissolved in vigorously stirred Me$_2$SO (100 mL, 4A molecular-sieve dried) at 80 °C (the flask contained several small glass beads to assist in the fragmentation of the starting materials). Powdered anhydrous Ag$_2$O$_3$POC$_6$H$_5$ (24 g) was added in 2-g lots over a period of 5 min. Stirring was continued for a further 70 min at 80 °C, after which time the mixture was allowed to cool to room temperature. The mixture was then poured into ice-cold water (300 mL). Sodium iodide solution was added to ensure that all residual Ag$^+$ had precipitated. The silver salts were removed, and the filtrate was diluted to 15 L. The reaction products were sorbed on Sephadex C-25 resin (Na$^+$ form, 12 × 8.5 cm). Elution with 0.2 M NaCl gave rise to several bands. The first two (blue and red, respectively) were minor ones and were discarded. The third (major) band was intense red-violet and contained the desired product. Evaporation of this fraction to 250 mL resulted in the formation of red-violet crystals of the chloride salt. After the solution was cooled at 0 °C for 4 h, the product was collected and washed with ice-cold LiCl solution (20 ml, 3 M), methanol (20 mL), and diethyl ether (4 × 10 mL). It was then dried in air (yield 18 g). Anal. Calcd for {[Co(C$_4$H$_{16}$N$_4$)(μ-O$_3$POC$_6$H$_5$)]$_2$}Cl$_2$·2H$_2$O: C, 30.36; H, 5.60; N, 14.16. Found: C, 30.7; H, 5.5; N, 14.1. The ^{1}H NMR spectrum of a saturated solution of the chloride salt of the complex in 1 mL of D$_2$O containing one drop of concentrated DCl gave the following chemical shifts in ppm (relative peak areas and multiplicities in parentheses). Ethylenediamine: CH$_2$, 2.29 (4, br); CH$_2$, 2.76 (4, br); NH$_2$ 3.48 and 3.90 (total 4, overlapping br); NH$_2$

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(5) The kinetics and mechanism of base hydrolysis of the nitrophenyl phosphate analogue of the dimeric species reported in this paper will be presented in a contemporary publication.

5.65 (3, br); NH$_2$, 6.68 (1, br). Aromatic H: complex multiplet centered at 7.28 (5). ^{31}P NMR data: three singlets at 14.43, 14.63, and 14.68 ppm in D$_2$O. Visible spectrum: ϵ_{509}(max) = 205 and ϵ_{372}(max) = 135 in water.

The product from above (12 g) was dissolved in a minimum volume of hot water (60 °C) and filtered. Sodium triflate (10 g) was added with rapid stirring, and red-violet microcrystals were deposited slowly. The solution was cooled to 4 °C and allowed to stand overnight. The product was collected and washed with ice-cold 2 M sodium triflate solution (2 × 4 mL), ether/methanol mixture (4:1 v/v, 20 mL), and ether (15 mL) and finally dried in vacuo over P$_2$O$_5$ for 3 days. Anal. Calcd for {[Co(C$_4$H$_{16}$N$_4$)O$_3$POC$_6$H$_5$]$_2$}(CF$_3$SO$_3$)$_2$·2H$_2$O: C, 25.49; H, 4.47; N, 10.81; P, 5.98; Co, 11.37; F, 11.00. Found: C, 25.7; H, 4.4; N, 11.0; P, 6.0; Co, 11.1; F, 11.0.

Separation of the Meso and Racemic Diastereomers of Bis(μ-phenyl phosphato)bis[bis(ethylenediamine)cobalt(III)] Chloride, {[Co(en)$_2$-(μ-O$_3$POC$_6$H$_5$)]$_2$}Cl$_2$. The chloride salt of the complex (9 g) was dissolved in water (450 mL), and the solution was filtered. Sodium perchlorate solution (450 mL, 0.8 M) was then added dropwise to the stirred filtrated over a period of 1 h. During this time red-violet crystals were deposited which were collected after 15 h at 25 °C (the filtrate from this step was retained) and washed with methanol and ether (5.5 g). The solid was then suspended in water (1000 mL) and converted in situ to the more soluble chloride form by adding Dowex AG1-X8 (Cl$^-$ form) resin with vigorous stirring until dissolution of the complex occurred. The resin was removed and washed with water until the effluent was clear. The filtrate and washings were combined and diluted to 200 mL. Sodium perchlorate solution (200 mL, 0.4 M) was then added dropwise, with stirring, over a period of 30 min, and the solution was cooled in an ice bath for 4 h. The product was collected as described above and the filtrate retained for further processing. The 0.4 M NaClO$_4$ recrystallization was repeated once more to yield the pure meso diastereomer, which was collected and washed with ice-cold 2 M NaClO$_4$, methanol, and ether and then dried in vacuo over P$_2$O$_5$ (5 g). Anal. Calcd for {[Co(C$_4$H$_{16}$N$_4$)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}(ClO$_4$)$_2$·2H$_2$O: C, 25.63; H, 4.95; N, 11.96; P, 6.61; Co, 12.57; Cl, 7.57. Found: C, 25.5; H, 4.6; N, 12.1; P, 6.0; Co, 12.2; Cl, 7.8. The ^{1}H NMR spectrum of a saturated solution of the chloride salt of the complex in 1 mL of D$_2$O containing one drop of concentrated DCl gave the following chemical shifts in ppm (relative peak areas and multiplicities in parentheses). Ethylenediamine: CH$_2$, 2.25 (4, br); CH$_2$, 2.68 (4, br); NH$_2$, 3.58 (2, br); NH$_2$, 4.14 (2, br); NH$_2$, 5.85 (3, br); NH$_2$, 6.64 (1, br). Aromatic H: complex multiplet centered at 7.20 (5). The ^{13}C NMR chemical shifts (in ppm) in D$_2$O relative to 1,4-dioxane are as follows. Ethylenediamine carbons: CH$_2$, −21.10 (s); CH$_2$, −23.74 (s). Aromatic carbons: C$_1$, 85.26 (d, $^2J_{POC}$ = 6.7 Hz); C$_{2,6}$, 54.83 (d, $^3J_{POCC}$ = 3.8 Hz); C$_{3,5}$, 63.20 (s); C$_4$, 58.15 (s). ^{31}P NMR data: 14.68 ppm (s) in D$_2$O. Visible spectrum: ϵ_{509}(max) = 208, ϵ_{430}(min) = 34, and ϵ_{370}(max) = 153 in water.

The three filtrate solutions from above were combined and allowed to stand at room temperature (25 °C) for 2 days. The crystals that deposited during this time were removed by filtration, and the filtrate was reduced in volume until further crystallizatin commenced. The volume was then reduced by half and the solution cooled to 4 °C overnight. The product was collected and washed with ice-cold 3 M NaClO$_4$, ether/methanol mixture (4:1 v/v), and ether. The red-violet crystals were then converted to the more soluble chloride form in 100 mL of water by using the anion-exchange resin procedure described above. Sodium perchlorate solution (100 mL, 0.8 M) was added dropwise, with stirring. When the solution was cooled to 0 °C for 30 min, some crystals were deposited and these were collected by filtration. The filtrate was reduced in volume to yield the pure racemic diastereomer, which was collected and washed with ice-cold 3 M NaClO$_4$, ether/methanol (4:1 v/v), and ether and then dried in vacuo over P$_2$O$_5$ for 18 h (yield 3.5 g). Anal. Calcd for {[Co-(C$_4$H$_{16}$N$_4$)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}(ClO$_4$)$_2$·2H$_2$O: C, 25.63; H, 4.95; N, 11.96; P, 6.61; Co, 12.57; Cl, 7.57. Found: C, 26.0; H, 5.0; N, 12.0; P, 6.5; Co, 12.7; Cl, 7.6. The ^{1}H NMR spectrum of a saturated solution of the chloride salt of the complex in 1 mL of D$_2$O containing one drop of concentrated DCl gave the following chemical shifts in ppm (relative peak areas and multiplicities in parentheses). Ethylenediamine: CH$_2$, 2.20 (4, br); CH$_2$, 2.70 (4, br); NH$_2$, 3.67 (2, br); NH$_2$, 4.16 (2, br); NH$_2$, 5.90 (3, br); NH$_2$, 6.62 (1, br). Aromatic H: complex multiplet centered at 7.20 (5). The ^{13}C NMR assignments are as follows (shifts in ppm, in D$_2$O relative to 1,4-dioxane). Ethylenediamine: CH$_2$, −21.25 (s); CH$_2$, −22.95 (s); CH$_2$, −23.34

(s). Aromatic carbons: C$_1$, two sets of overlapping doublets at 85.63 (d, $^2J_{POC}$ = 6.7 Hz) and 85.45 (d, $^2J_{POC}$ = 6.7 Hz); C$_{2,6}$, two sets of overlapping doublets at 54.22 (d, $^3J_{POCC}$ = 4.1 Hz) and 54.08 (d, $^3J_{POCC}$ = 4.1 Hz); C$_{3,5}$, two singlets at 63.27 and 63.22; C$_4$, two singlets at 57.86 and 57.78. ^{31}P NMR data: two singlets at 14.63 and 14.43 ppm in D$_2$O. Visible spectrum: ϵ_{509}(max) = 236, ϵ_{428}(min) = 33, ϵ_{369}(max) = 164 in water.

Resolution of rac-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$. The racemic diastereomer was resolved by ascending cation-exchange chromatography. A total of 1.6 g of complex was sorbed on the bottom of a column of Sephadex C-25 resin (75 × 5 cm) that had been previously equilibrated with 0.1 M (+)$_D$-sodium antimonyl tartrate solution. The resultant band was eluted upward by pumping more of antimonyl tartrate solution (2.8 mL/min) into the base of the column. Three passes through the column were required in order to obtain good separation of the enantiomers. The first band to be eluted was the (+)$_D$ isomer. It is noted that extensive decomposition of the dimeric complex occurs under these conditions (presumably catalyzed by the antimonyl tartrate). However, the decomposition product has a 1+ charge and can easily be separated from the 2+ dimer. Antimonyl tartrate was removed from the solutions of the enantiomers by adsorbing the respective complex cations on a short column of Sephadex C-25 (Na$^+$ form) resin, washing the resin bed with water, and then eluting with 0.2 M NaClO$_4$. The optical isomers were crystallized by reducing the volume of the eluate to ca. 15 mL and adding solid NaClO$_4$ to produce a final concentration of ca. 8.0 M. The resulting solutions were kept at 0 °C for 4 days. The products were then collected by filtration and washed with an ether/methanol mixture (6:1 v/v) to remove residual sodium perchlorate solution. Because of the extreme solubilities of the enantiomers and the high concentration of NaClO$_4$ that was required to precipitate them, some residual NaClO$_4$ was always present in the final product. Thus the elemental analyses were not satisfactory, although the element ratios were correct. The concentrations of the solutions used for the rotatory dispersion (RD) and circular dichroism (CD) measurements were determined by atomic absorption and visible (with use of the extinction coefficient for the racemic mixture) spectrophotometry. Rotatory dispersion: [M]$_{589}$ = +1300; [M]$_{548}$(max) = +3300; [M]$_{460}$(min) = −3440; [M]$_{589}$ = −1360; [M]$_{548}$(min) = −3440; [M]$_{460}$(max) = +3460. Circular dichroism: $\Delta\epsilon_{586}$(max) = +0.67; $\Delta\epsilon_{496}$(min) = −1.27 (for the (−)$_D$ enantiomer).

Conductivity Measurements. The electrolyte types for the complexes were determined by the method of Feltham and Hayter.[7] The Onsager equation representing conductivity as a function of equivalent concentration is commonly written in the form $\Lambda_e = \Lambda_0 - Bc^{1/2}$. Since B is a function of the charge on the complex cation, comparison of the slope of the Λ_e vs. $c^{1/2}$ plot with complexes of known ionic type will establish the electrolyte type of the unknown complex.

The conductivities of the metal complexes were measured at 25 ± 0.2 °C over an equivalent concentration range of 2 × 10^{-3} to 10^{-2} M. The standards used for comparison were [Co(en)$_2$CO$_3$]ClO$_4$ (1:1), [Co(en)$_2$(glycinate)](ClO$_4$)$_2$ (1:2), and [Co(en)$_3$](ClO$_4$)$_3$ (1:3).

Molecular Weight Determination by Vapor Pressure Osmometry. Water was used as the solvent for the present determinations since the metal complexes were not sufficiently soluble in suitable organic solvents. Sodium chloride was selected as the reference compound, and all measurements were made at 37 °C. The molecular weights of a number of known complexes representing 1:1, 1:2, and 1:3 electrolytes were measured in order to confirm that the technique provided satisfactory results in aqueous solution. One nonelectrolyte was also tested ([Co(en)$_2$PO$_4$]). The optimum concentration for the complexes was found to lie between 10 and 20 mg/mL (ca. 3 × 10^{-2} M). At higher concentrations ion-pairing effects became significant for the 1:2 and 1:3 electrolytes, and at lower concentrations machine sensitivity was the limiting factor. The molecular weights obtained were reproducible to within ±7%.

X-ray Structure Determination. Rod-shaped crystals of mes-{[Co(en)(μ-O$_3$POC$_6$H$_5$)]$_2$}(CF$_3$SO$_3$)$_2$·2H$_2$O were obtained from aqueous solution; crystal parameters are listed in Table I Intensity data were collected on a Stoe Weissenberg diffractometer with Mo Kα radiation and fitted with a graphite monochromator, for the levels 0kl to 8kl in 0° < 2θ < 45°, with use of the ω-scan technique. Lorentz,

(6) Sample supplied by C. J. Hawkins, University of Queensland.
(7) Feltham, R. D. *Inorg. Chem.* **1964**, *3*, 1038–1039. Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587–4591.

Table I. Crystal Data for
meso- {[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}(CF$_3$SO$_3$)$_2$·2H$_2$O

formula	C$_{22}$H$_{46}$N$_8$O$_{16}$F$_6$P$_2$S$_2$Co$_2$	space group	P2$_1$/c
mol wt	1036.36	a	9.454 (5) Å
Z	4	b	28.683 (14) Å
ρ_{obsd}	1.71 g/cm^3	c	7.487 (4) Å
ρ_{calcd}	1.709 g/cm^3	β	97.21 (8)°
μ, Mo Kα	10.57 cm^{-1}	V	2014.2 Å^3
F(000)	1064	λ	0.7107 Å

polarization, and absorption corrections[8] were applied to give 1675 nonzero structure factors with $I < 2.5\sigma(I)$. Maximum and minimum transmission factors were 0.91 and 0.85.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques.[8] All atoms of the cation were incorporated, and the phenyl ring was treated as a rigid group with only isotropic thermal parameters. All other non-hydrogen atoms were treated anisotropically. The hydrogens of the water molecule were not found; the others were placed at their calculated positions (C–H = 1.00, N–H = 0.91 Å), and their thermal parameters were refined coupled together by chemical type. Individual layer scale factors were adjusted during the isotropic phase of the refinement when all atoms were placed. The weighting scheme was refined[8] and converged at $w = 2.62/(\sigma^2(F) + 0.000514F^2)$. The final R was 0.0598 on F for 1675 nonzero reflections. The largest residuals, 0.9 e/Å^3, in the final difference map are located in bonds of the phenyl group, which was only refined isotropically.

All scattering factors [Co$^+$ for Co(III)] were taken from ref 9. Atomic positional and thermal parameters are given in Table II. The hydrogen atom parameters together with a list of observed and calculated structure factors have been deposited as supplementary material.

Results and Discussion

The reaction between cis-[Co(en)$_2$Cl$_2$]ClO$_4$ and silver phenyl phosphate in dimethyl sulfoxide led to isolation of a product of empirical composition [Co(en)$_2$O$_3$POC$_6$H$_5$]ClO$_4$. Fractional crystallization of this product yielded two isomers which gave different ^{31}P NMR spectra (Figure 1). Conductivity measurements indicated that both products were 1:2 electrolytes, and molecular weight determinations by vapor pressure osmometry showed that their molecular weights were twice that expected for a monomeric formulation.

The structure of the triflate salt of the less soluble isomer was obtained by X-ray diffraction, and the structure of the complex cation is given in Figure 2. The cation is a dimer consisting of two bis(ethylenediamine)cobalt(III) moieties bridged by two phenyl phosphato groups. The two metal atoms and two bridging ligands define an unusual eight-membered ring system.

The dimer is centered on a crystallographic center of symmetry which relates the two cobalt centers as enantiomorphs ($\Delta\Delta$ or $\Lambda\Lambda$). The bond lengths (Table III) are normal for a CoN$_4$O$_2$ cation with Co–N lengths (average 1.949 Å) shorter than those found in CoN$_6$ complexes (1.974 Å).[10] The absolute configurations of the ethylenediamine rings are opposite to each other. The ring adjacent to the phenyl ether group has the ob configuration and the other one the lel configuration. The lel[2] and lel,ob Co(en)$_2$ configurations in complexes of type [Co(en)$_2$XY]$^+$ are known to be similar in energy, and the conformation adopted depends on crystal forces.[11] In this case the lel[2] configuration would cause a close contact with
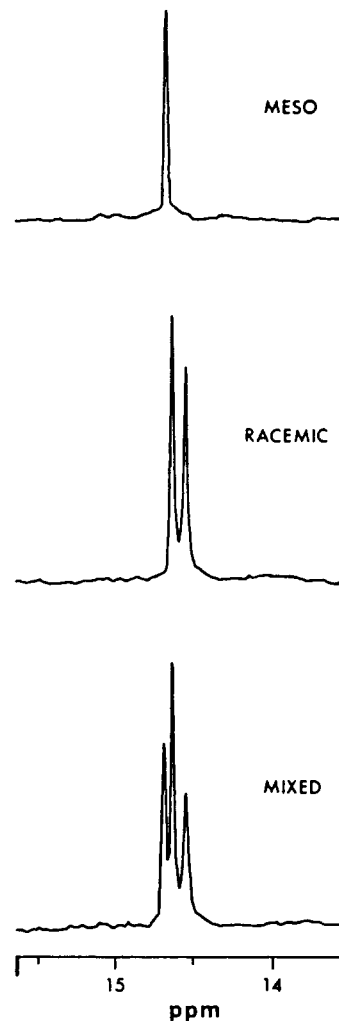

Figure 1. ^{31}P{^{1}H} NMR spectra of the meso, racemic, and mixed diastereomers of {[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ in D$_2$O.
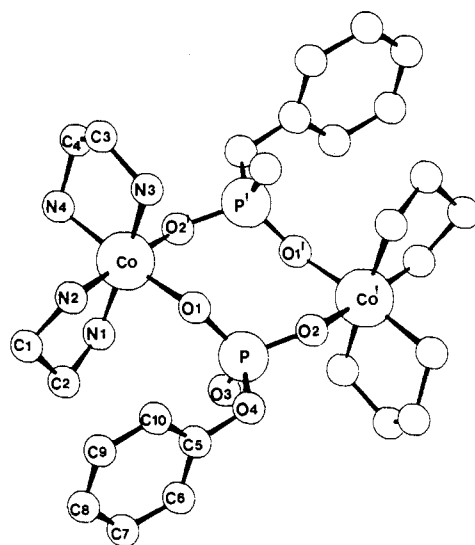
Figure 2. X-ray crystal structure of the dimeric cation meso-{[Co-(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$.

the phenyl group which is relieved in the observed lel,ob configuration. The torsion angles for the C–C bonds in the lel and ob chelate rings are –47.6 and 46°, respectively. The bridging behavior of the phosphate ester group was unexpected since the only other structurally known cobalt phosphate complex, [Co(en)$_2$PO$_4$]·2.5H$_2$O, has bidentate phosphate coordination.[12,13] Only one other coordination complex,

(8) Program SHELX by G. M. Sheldrick, Cambridge, England, 1976.
(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.
(10) Butler, K. R.; Snow, M. R. *J. Chem. Soc., Dalton Trans.* **1976**, 259–262.
(11) Gollogly, J. R.; Hawkins, C. J.; Beattie, J. K. *Inorg. Chem.* **1971**, *10*, 317–323. See for nomenclature: *Inorg. Chem.* **1970**, *9*, 1.

Table II. Final Least-Squares Parameters for [Co(en)₂O₃POC₆H₅]CF₃SO₃·H₂O (×10⁴)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	3635 (1)	4529 (0)	7184 (1)	282 (7)	292 (6)	193 (6)	74 (6)	64 (5)	−76 (6)
S	−337 (3)	3680 (1)	258 (5)	477 (20)	570 (15)	988 (27)	−127 (18)	334 (18)	−116 (16)
P	5356 (2)	4463 (1)	3795 (3)	292 (13)	316 (13)	193 (12)	25 (10)	59 (10)	−12 (11)
F(1)	861 (13)	2889 (3)	−162 (18)	1558 (111)	844 (62)	2548 (147)	−249 (74)	−82 (98)	504 (74)
F(2)	−105 (23)	3158 (4)	−2433 (18)	4275 (263)	1305 (88)	1410 (100)	−572 (82)	333 (143)	−374 (129)
F(3)	−1320 (14)	2867 (4)	−580 (25)	1661 (116)	1042 (74)	4593 (237)	−755 (106)	1161 (132)	−1049 (86)
O(1)	4024 (6)	4450 (2)	4743 (7)	312 (34)	443 (35)	210 (31)	15 (26)	95 (26)	−72 (30)
O(2)	5353 (6)	4876 (2)	2491 (6)	324 (36)	242 (29)	203 (30)	44 (23)	44 (27)	−92 (27)
O(3)	6708 (6)	4389 (2)	5013 (7)	317 (37)	386 (33)	236 (34)	39 (26)	58 (28)	−46 (29)
O(4)	5116 (7)	4039 (2)	2319 (7)	554 (42)	268 (29)	226 (32)	27 (25)	119 (31)	−21 (30)
O(5)	906 (8)	3902 (2)	−23 (11)	658 (58)	585 (46)	986 (64)	43 (44)	318 (49)	−269 (44)
O(6)	−231 (18)	3528 (4)	2156 (16)	3019 (195)	1547 (105)	1323 (101)	−212 (87)	1502 (123)	−556 (123)
O(7)	−1575 (11)	3869 (4)	−328 (28)	549 (80)	740 (71)	5516 (293)	−426 (116)	−231 (119)	198 (61)
O(8)	9699 (8)	902 (2)	55 (10)	549 (48)	627 (43)	664 (49)	−10 (39)	−48 (40)	138 (40)
N(1)	5363 (8)	4196 (2)	8180 (9)	310 (43)	435 (43)	193 (38)	3 (33)	65 (34)	−68 (37)
N(2)	2746 (8)	3915 (2)	6952 (9)	366 (45)	278 (38)	294 (41)	−18 (33)	42 (37)	−26 (36)
N(3)	1846 (7)	4828 (2)	6234 (8)	303 (42)	368 (41)	243 (41)	−1 (32)	75 (34)	−63 (35)
N(4)	3040 (8)	4639 (2)	9533 (9)	355 (45)	365 (40)	305 (42)	37 (33)	115 (36)	−69 (37)
C(1)	3645 (10)	3565 (3)	8087 (13)	399 (62)	350 (50)	459 (59)	14 (45)	84 (50)	−84 (46)
C(2)	5190 (10)	3685 (3)	7942 (13)	380 (61)	418 (54)	401 (60)	24 (46)	79 (49)	30 (48)
C(3)	985 (9)	4940 (3)	7703 (11)	318 (58)	331 (48)	417 (55)	−43 (44)	136 (48)	21 (41)
C(4)	2003 (10)	5021 (3)	9372 (11)	365 (60)	491 (55)	313 (57)	−32 (48)	66 (46)	25 (49)
C(5)	4990 (6)	3587 (2)	2925 (8)	343 (22)					
C(6)	6208 (6)	3322 (2)	3462 (8)	496 (27)					
C(7)	6080 (6)	2875 (2)	4152 (8)	750 (36)					
C(8)	4733 (6)	2691 (2)	4305 (8)	689 (34)					
C(9)	3515 (6)	2956 (2)	3768 (8)	620 (31)					
C(10)	3644 (6)	3402 (2)	3078 (8)	451 (25)					
C(11)	−310 (20)	3104 (5)	−76 (27)	960 (130)	660 (97)	1321 (155)	−33 (97)	355 (118)	−81 (94)

Table III. Bond Lengths (Å) for
meso-{[Co(en)₂(μ-O₃POC₆H₅)]₂}(CF₃SO₃)₂·2H₂O^a

Covalent Bonds

Co–O(1)	1.922 (5)	N(2)–C(1)	1.506 (11)
Co–O(2)	1.956 (5)	N(3)–C(3)	1.483 (9)
Co–N(1)	1.958 (7)	N(4)–C(4)	1.465 (11)
Co–N(2)	1.951 (6)	O(4)–C(5)′	1.384 (6)
Co–N(3)	1.949 (7)	O(5)–S	1.377 (7)
Co–N(4)	1.938 (7)	O(6)–S	1.478 (12)
P–O(1)	1.521 (6)	O(7)–S	1.313 (11)
P–O(2)	1.534 (5)	C(11)–F(1)	1.298 (19)
P–O(3)	1.489 (6)	C(11)–F(2)	1.299 (18)
P–O(4)	1.640 (6)	C(11)–F(3)	1.194 (17)
N(1)–C(2)	1.483 (10)	C(11)–S	1.822 (15)

Possible Hydrogen Bonds

N(1)···O(3)	2.881	N(4)···O(5)^{III}	2.968
O(8)···O(3)^{II}	2.945	O(8)···O(6)^{IV}	2.725
N(1)···O(4)^{III}	3.169	N(1)···O(7)^V	3.117
N(4)···O(4)^{III}	3.184	N(2)···O(8)^{VII}	3.092
N(2)···O(5)^{III}	3.024	N(3)···O(8)^{VII}	2.971

Symmetry Operations

I	$1-x, 1-y, 1-z$	V	$1-x, \frac{1}{2}-y, z-\frac{1}{2}$
II	$x, \frac{1}{2}-y, z-\frac{1}{2}$	VI	$1+x, y, 1+z$
III	$x, y, z+1$	VII	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
IV	$1-x, \frac{1}{2}-y, z-\frac{1}{2}$	VIII	$x-1, \frac{1}{2}-y, \frac{1}{2}+z$

^a The numbers in parentheses are the estimated standard deviations in the least significant digits quoted.

Table IV. Bond Angles (Deg) for
meso-{[Co(en)₂(μ-O₃POC₆H₅)]₂}(CF₃SO₃)₂·2H₂O^a

N(1)–Co–N(2)	85.6 (3)	O(3)–P–O(4)	110.0 (3)
N(2)–Co–N(4)	93.2 (3)	P–O(4)–C(5)	119.0 (4)
O(1)–Co–O(2)′	94.1 (2)	Co–O(1)–P	135.2 (4)
O(1)–Co–N(1)	93.1 (3)	Co′–O(2)′–P	129.2 (4)
O(1)–Co–N(2)	86.6 (3)	C(11)–S–O(5)	107.5 (6)
O(1)–Co–N(3)	88.1 (2)	C(11)–S–O(6)	97.6 (8)
O(1)–Co–N(4)	173.6 (3)	C(11)–S–O(7)	107.0 (9)
O(2)–Co′–N(1)′	90.4 (3)	S–C(11)–F(1)	110.0 (1.3)
O(2)–Co′–N(2)′	175.9 (3)	S–C(11)–F(2)	113.3 (2.0)
O(2)–Co′–N(3)′	92.8 (3)	S–C(11)–F(3)	114.6 (1.3)
O(2)–Co′–N(4)′	86.5 (3)	F(1)–C(11)–F(2)	99.5 (1.5)
O(1)–P–O(2)	112.4 (3)	F(1)–C(11)–F(3)	110.5 (1.5)
O(1)–P–O(3)	114.1 (3)	F(2)–C(11)–F(3)	113.3 (2.0)
O(1)–P–O(4)	104.1 (3)	O(5)–S–O(6)	109.1 (7)
O(2)–P–O(3)	115.6 (3)	O(5)–S–O(7)	120.0 (7)
O(2)–P–O(4)	98.9 (3)	O(6)–S–O(7)	113.1 (1.0)

^a The numbers in parentheses are the estimated standard deviations in the least significant digits quoted.

and a further one of the same type with dichloro phosphate.[18] In the ternary complexes bis(μ-uridine 5′-monophosphate)-bis[aquo(2,2′-dipyridylamine)copper(II)] pentahydrate[16] and bis(μ-guanosine 3′-monophosphate)bis[aquo(1,10-

^a The numbers in parentheses are the estimated standard deviations in the least significant digits quoted.

[aquo(cytidine 5′-monophosphate)cadmium(II)]·1.5H₂O, in the Cambridge data file displays the bidentate coordination mode.[14] The same file, however, has six entries of phosphate ester complexes exhibiting the bridging coordination mode[15–17]

(12) Anderson, B.; Milburn, R. M.; Harrowfield, J. M.; Robertson, G. B.; Sargeson, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 2652–2661.

(13) Two complexes containing μ-phosphato ligands have been reported. They are the (μ-amido)(μ-phosphato)bis[bis(ethylenediamine)cobalt-(III)](2+) (Garbett, K.; Gillard, R. D. *J. Chem. Soc. A* **1968**, 1725–1735) and (μ-amido)(μ-phosphato)bis[tetraamminecobalt-(III)](2+) (Edwards, J. D.; Foong, S. W.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1973**, 829–838) cations. They were characterized by spectroscopic and analytical methods.

(14) Shiba, J. K.; Bau, R. *Inorg. Chem.* **1978**, *17*, 3484–3488.

(15) Diaquobis(α-aminoethylmethylphosphoric acid)manganese(II) bromide dihydrate: Glowiak, R.; Sawka-Dobrawalska, W. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2648–2650. Aquo(cytidine 5′-monophosphate)cadmium(II) hydrate: Goodgame, D. M. L.; Jeeves, I.; Reynolds, C. D.; Skapski, A. C. *Biochem. J.* **1975**, *151*, 467–468. Sodium tetramethylammonium pentamolybdobis(ethylammonium phosphate) pentahydrate and ammonium pentamolybdobis(methyl phosphate) pentahydrate: Stalick, J. K.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 1577–1584.

(16) Fischer, B. E.; Bau, R. *Inorg. Chem.* **1978**, *17*, 27–34.

(17) Ya Wei, C.; Fischer, B. E.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1978**, 1053–1055. We are grateful to the reviewers for bringing to our attention three other eight-membered ring structures of this same type. Published coordinates are not available for these, but they appear to have the same flexible structure: Aoki, K. *J. Am. Chem. Soc.* **1978**, *100*, 7106. Akoki, K. *J. Chem. Soc., Chem. Commun.* **1979**, 589. Gellert, R. W.; Fischer, B. E.; Bau, R. *Biochem. Biophys. Res. Commun.* **1979**, *88*, 1443.

(18) Danielsen, J.; Rasmussen, S. E. *Acta Chem. Scand.* **1963**, *17*, 1971–1979.

Table V. Comparison of Phosphate Bond Angles (Deg) in Cyclohexylammonium Phenyl Hydrogen Phosphate[22] and *meso*-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}(CF$_3$SO$_3$)$_2$

angle	dimer	PO$_2$(OH)(OC$_6$H$_5$)$^-$
O(1)–P–O(2)	112.4 (3)	103.9
O(1)–P–O(3)	114.1 (3)	109.4
O(1)–P–O(4)	104.1 (3)	106.4
O(2)–P–O(3)	115.6 (3)	118.4
O(2)–P–O(4)	98.9 (3)	106.9
O(3)–P–O(4)	110.0 (3)	119.9

phenanthroline)copper(II)] heptahydrate[17] the two copper atoms are bridged by the two phosphate groups of the nucleoside moieties. In both of these cases an eight-membered ring is defined by the metal atoms and bridging ligands. Thus it appears that the bridging coordination mode is preferred by phosphate esters. However, there are cases in which no coordination of the phosphate moiety to the metal ion occurs; for example, (inosine 5′-monophosphate)pentaaquonickel(II) dihydrate[19] and sodium bis(inosine 5′-monophosphate)(diethylenetriamine)copper(II) decahydrate.[20] There is also an example, the (cytidine 5′-monophosphate)platinum dimer, in which only one metal–phosphate bond is formed.[21]

The eight-membered ring formed by the two phosphates and cobalt atoms in the present structure is distinctly nonplanar. The ring has the CoCo′ inversion symmetry and a pseudo mirror plane containing PP′ which is perpendicular to CoCo′. The displacements from the CoCo′ plane are as follows: Co, 0.00; O and O′$_2$, –0.29; P, 0.46 Å. Planes were calculated through all the structures with the same eight-membered ring structure,[16,17] but no general pattern of distortion of these nonplanar rings could be seen. The ring appears to be very flexible with the phosphorus atoms ranging from 0.2 to over 1.0 Å from the MOO planes and with the angle between these planes lying between 0 and 165°.

The crystal structure of *meso*-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}(CF$_3$SO$_3$)$_2$ is the first to be reported for a cobalt(III) complex which contains a μ-phosphato or a μ-phosphato ester ligand, and the bond angles around the phosphorus tetrahedron (Table IV) are therefore of some considerable interest. The O(1)–P–O(2), O(1)–P–O(3), O(1)–P–O(4), O(2)–P–O(3), O(2)–P–O(4), and O(3)–P–O(4) angles in the dimer are compared with the corresponding angles in uncomplexed phenyl hydrogen phosphate (cyclohexylammonium salt)[22] in Table V. It is apparent that the geometry about the phosphorus atoms in the dimer is considerably distorted relative to that observed for the free phenyl phosphate moiety. This may be a reflection of the geometric constraint that is imposed by the eight-membered ring.

Binuclear complexes of the present type can exist in two diastereomeric forms: the meso ($\Delta\Lambda$ and $\Lambda\Delta$) form (**1**) and the racemic ($\Delta\Delta$ and $\Lambda\Lambda$) form (**2**). The latter can potentially
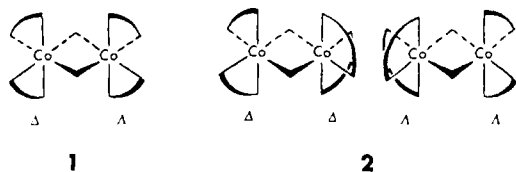
be resolved into its optical enantiomers. Since the crystal structure of the less soluble complex shows that it is the meso diastereomer, this implies that the more soluble form is the
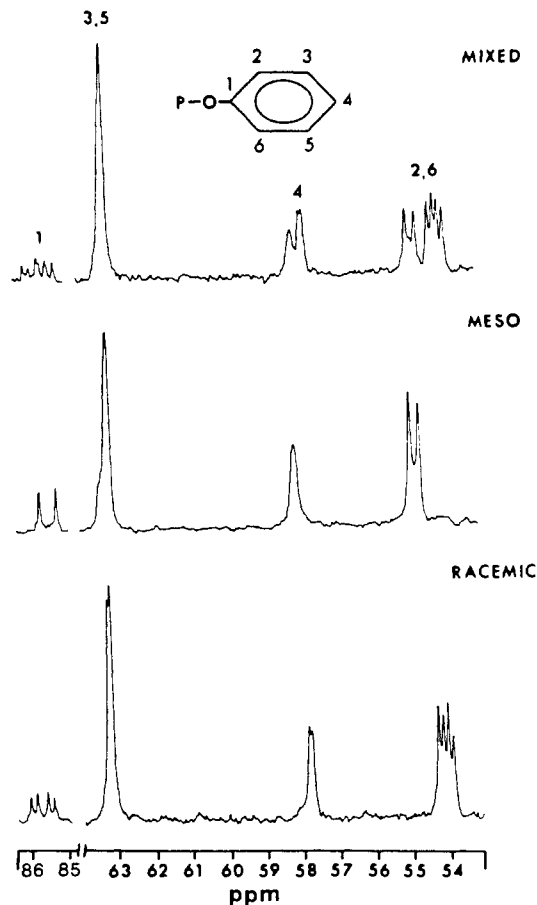

Figure 3. ^{13}C{^{1}H} NMR spectra of the aromatic diastereomers of {[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ in D$_2$O.
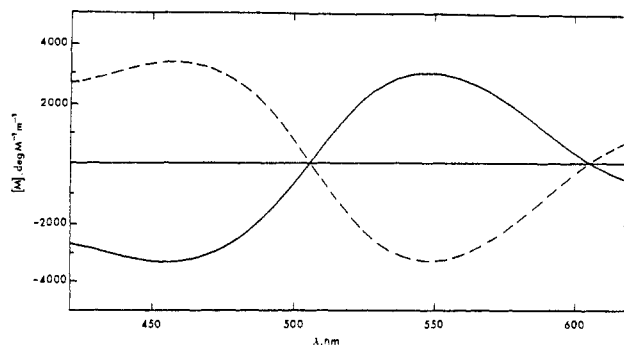
Figure 4. Rotatory dispersion spectra for (+)$_D$-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ (—) and (–)$_D$-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ (- - -) in water at 25 °C.

racemic diastereomer. Examination of the structure of *meso*-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ (Figure 2) reveals that the two phosphate ester groups are related by an inversion symmetry operation. Therefore there should be only one peak in the ^{31}P{^{1}H} NMR spectrum and one set of resonances in the aromatic region of the ^{13}C{^{1}H} NMR spectrum. This was observed to be the case (Figures 1 and 3). If it is assumed that the orientation of the phenyl groups is the same in the *rac* diastereomer (that is, one above and one below the plane containing the two cobalt atoms), then it is apparent that the two phosphato ester moieties are no longer equivalent. The ester groups would also be inequivalent if both were orientated above the cobalt–cobalt plane. In each of the above cases the two groups would be expected to have slightly different NMR spectra. A doubling of the peaks was observed in the ^{13}C and ^{31}P NMR spectra (Figure 2) of the complex corresponding to the more soluble complex, and therefore this species is

(19) Clark, G. R.; Orbell, J. D. *J. Chem. Soc., Chem. Commun.* **1974**, 139–140.
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(22) Watson, D. G.; Kennard, O. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2358–2364.
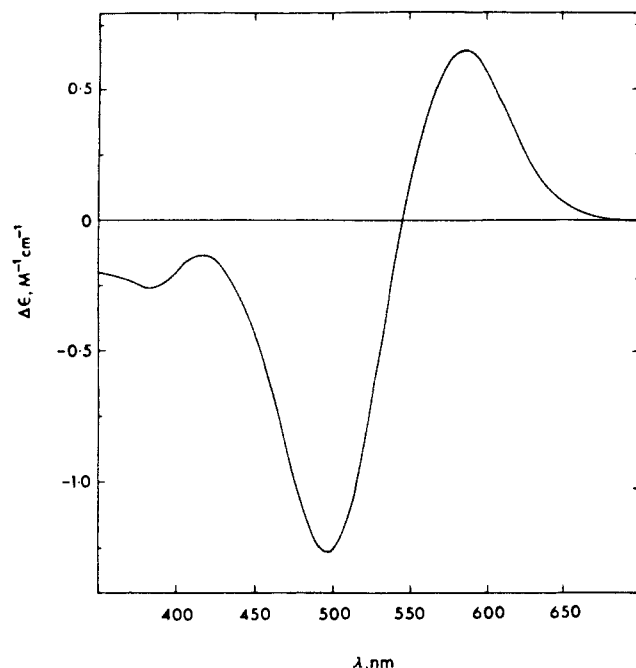
Figure 5. Circular dichroism spectrum of $(-)_D$-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ in water at 25 °C.

assigned as the *rac* diastereomer.

The *rac*-{[Co(en)$_2$(μ-O$_3$POC$_6$H$_5$)]$_2$}$^{2+}$ cation was resolved into its optical enantiomers by cation-exchange chromatography with $(+)_D$-sodium antimonyl tartrate as the eluent; the first band to elute was the $(+)_D$ enantiomer. The rotatory dispersion and circular dichroism (CD) spectra of the enantiomers are illustrated in Figures 4 and 5, respectively. With the assumptions that the absolute configuration of complexes of type [Co(en)$_2$X$_2$]$^+$ can be predicted from their CD spectra[23] and that the CD spectra of bis[bis(ethylenediamine)cobalt-(III)] dimers can be interpreted in terms of the circular dichroism of their individual monomeric units,[24] the basic chromophore in the Λ-phenyl phosphate dimer can thus be considered to be
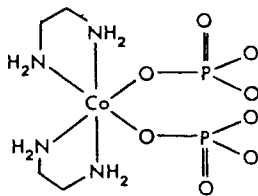
In [Co(en)$_3$]$^{3+}$ the transition of E symmetry dominates the sign of the CD for the first absorption region and the enantiomer which exhibits dominant positive CD in the first absorption region has the Λ absolute configuration.[23] The replacement of one chelate ligand by X$_2$ converts the [CoN$_6$] chromophore into a [CoN$_4$X$_2$] chromophore with C_2 symmetry. In the C_2 ligand field, the first absorption arises from two transitions with B symmetry and one with A symmetry. The A transition arises from the lowering of symmetry of the E transition. The observed CD spectrum is interpreted as an unresolved composite of A$_2$ + B$_2$ (E) and B$_1$ (A$_2$). The former is assumed to preserve the sign of the parent (E) transition and will thus be positive for the Λ absolute configuration. The shifting and splitting of the energy levels depend on the nature of X. The ligand field splitting (Δ) which is induced by X can be used to predict the relative positions of the energy levels for a given transition-metal ion.[23] If Δ_X is greater than Δ_{en}, the prominent diagnostic A$_2$ + B$_2$ band lies on the longer wavelength side in the first ligand field band. If $\Delta_X < \Delta_{en}$, the band is shifted to the shorter wavelength side. The absorption maximum for the phenyl phosphate dimer is at 509 nm while the maximum for [Co(en)$_3$]$^{3+}$ is at 493 nm. Since the geometry about the cobalt octahedron is essentially the same for both species, the spectral evidence stongly implies that $\Delta_X < \Delta_{en}$. Thus the prominent A$_2$ + B$_2$ transition in the CD spectrum should be found to the left of the maximum for the ligand field band. This is observed for $(-)_D$-{[Co-(en)$_2$O$_3$POC$_6$H$_5$]$_2$}$^{2+}$, which has its CD maximum at 496 nm and its ligand field maximum at 509 nm. Therefore the $(-)_D$ enantiomer is tentatively assigned the Δ,Δ absolute configuration about the two cobalt centers since the A$_2$ + B$_2$ transition has a negative sign. This is a reasonable conclusion provided that the dimer exhibits the same CD characteristics as the two pseudomonomer units of which it is composed, and the evidence obtained by other workers from studies on optically active cobalt dimers implies that this assumption is valid.[24]

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