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Contribution from the Department of Chemistry,
University of Canterbury, Christchurch, New Zealand

Optically Active *cis*-Dianiono(tetraamine)chromium(III) Complexes. 5. The Absolute Configuration of (−)-*cis*-(*RRRR*)-$[CrCl_2(cyclam)]ClO_4$

DONALD A. HOUSE* and VICKIE McKEE

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The title complex, (−)-*cis*-$[CrCl_2(cyclam)]ClO_4$, crystallizes in the orthorhombic space group $P2_12_12$ with a = 10.097 (8) Å, b = 13.747 (7) Å, c = 6.349 (8) Å, V = 881.4 (9) Å^3, and Z = 2. A single-crystal X-ray structure shows the absolute configuration at the coordinated *s*-NH sites to be *RRRR*, and the chirality of the chelate rings can be described as Λ_{en} or Δ_{tn}. The circular dichroism spectra of the (−)-dichloro complex indicate a Δ absolute configuration with the 6-membered rings dominant. The (−)-dichloro complex was derived from (−)-$Cr(ox)(cyclam)^+$ by reaction with 12 M HCl, and the circular dichroism spectra of the (−)-oxalato complex indicate a Λ configuration with the 5-membered rings dominant. Thus the apparent (−)-oxalato → (−)-dichloro "inversion" is attributed to a change in ring-pair dominance.

Introduction

Inert transition-metal complexes of the tetradentate macrocyclic ligand cyclam[1a] provide a variety of possible stereochemical isomers. Both cis (folded) and trans (planar) ligand conformations have been observed, and in both forms, several different *s*-NH proton configurations are possible.[1b] The cis isomers, and some of the trans, are potentially optically active, but in the cis isomers, the conventional Λ or Δ assignment is not defined as there are equal numbers (albeit nonequivalent) of skewed chelate ring pairs. Nevertheless, it is still possible to describe enantiomeric forms in terms of the *s*-NH configurations (*R* or *S*) (Figure 1). Much work has been done using Co(III)[2] as a central metal, and a single-crystal structure of (±)-*cis*-$CoCl_2(cyclam)^+$ shows[3] this to have the (*RRRR*,*SSSS*) configuration with the "planar" *s*-NH protons remote from the coordinated aniono ligands (Figure 1, I). This is also the configuration found in the single-crystal structure of (±)-$Co(en)(cyclam)^{3+}$.[4] Isomerization of this form (with retention of the *s*-NH configuration) leads to the (*RRRR*,*SSSS*)-trans complex (Figure 1, II). This has been achieved for Co(III) with both racemic[5] $Co(CO_3)(cyclam)^+$ and chiral[6] $Co(ox)(cyclam)^+$, to give the so-called "labile" trans isomer.[5] Isomerization of the cis-(*RSRS*,*SRSR*) form (Figure 1, V) would give one of the three possible meso-trans isomers, and the third cis isomer (*RRRS*,*SSSR*) should isomerize to give a racemic trans form. None of these four last forms appear to have been characterized for the $CoX_2(cyclam)^+$ system although, for the trans complexes at least, molecular mechanics calculations[1b,3] give strain energy values of the same order as that for the known trans-(*RRRR*,*SSSS*) configuration. Of the final two meso forms, trans-(*RSSR*) is the most stable *trans*-$CoCl_2(cyclam)^+$ isomer,[1b,7] and it has no cis analogue as it has no fold axis.

Rather less work has been described for Cr(III) complexes of cyclam, although both cis and trans forms are known[8–14] and the trans isomer is believed to have the *RSSR* configuration.[12–14] In this paper we describe the preparation and resolution of $[Cr(ox)(cyclam)]ClO_4$, the conversion of (−)-$Cr(ox)(cyclam)^+$ to (−)-*cis*-$CrCl_2(cyclam)^+$, and a single-crystal X-ray structure for (−)-*cis*-(*RRRR*)-$[CrCl_2(cyclam)]ClO_4$.

Experimental Section

Cyclam was prepared with use of the method of Barefield et al.,[15a] and a *cis*-/*trans*-$[CrCl_2(cyclam)]Cl$ mixture (~80% cis) was obtained by reacting $CrCl_3{\cdot}6H_2O$, dehydrated in DMF, with the ligand. *trans*-$[CrCl_2(cyclam)]ClO_4$ was separated as described previously,[12] and *cis*-$[CrCl_2(cyclam)]ClO_4$ was obtained from the mother liquor.

CAUTION! Although we have experienced no difficulty with the perchlorate salts described here, these should be treated as potentially explosive and handled accordingly.

(Oxalato)(cyclam)chromium(III) Perchlorate, $[Cr(ox)(cyclam)]ClO_4$. *cis*-$[CrCl_2(cyclam)]ClO_4$ (2.0 g) was dissolved in water (25 mL) containing NaOH (1.0 g) to give a blue-violet solution. Solid $H_2C_2O_4{\cdot}H_2O$ (ca. 1.2 g) was added to the warm solution to pH 3, and the temperature was maintained at 40 °C for ca. 5 min. Solid $NaClO_4{\cdot}H_2O$ (5 g) was then added, and orange crystals deposited from the hot solution. These (1.5 g) were filtered from the ice-cooled solution, washed with isopropyl alcohol and then ether, and air-dried. Anal. Calcd for $CrC_{12}H_{24}N_4ClO_8$: C, 32.77; H, 5.50; N, 12.74. Found: C, 32.81; H, 5.73; N, 12.54. Visible absorption spectrum (0.1 M HCl; λ nm) (ε ($M^{-1}\,cm^{-1}$)): max, 493 (149); min, 420 (22.0); max, 370 (117). Visible absorption spectrum (DMF (90%), 3 M HCl (10%): max, 500 (157); min, 426 (25.7); max, 375 (109).

Resolution. $[Cr(ox)(cyclam)]ClO_4$ (2.0 g) was dissolved in 150 mL of $NaHCO_2/HCO_2H$ buffer (1 M in each component, pH ~3.7) at 80 °C. (2*R*,3*R*)-Dibenzoyltartaric acid (derived from (+)-tartaric acid) (3.0 g) was suspended in warm water (50 mL) and solid LiOH added in small portions until all the acid had dissolved. The final pH of this solution should be less than 8, and excess LiOH can be neutralized with formic acid. The solution of the resolving agent was added to that of the Cr(III) complex (both at 80 °C) and the mixture allowed to cool to 40 °C. Crystal needles of the less soluble diastereoisomer began to form, and the temperature was maintained at 40 °C for 10 min before filtering ca. 1 g of the dibenzoyltartrate salt. The solubility difference between the two diastereoisomers is not great, and subsequent crops give only partially resolved mixtures. Racemic or partially resolved $[Cr(ox)(cyclam)]ClO_4$ can be recovered from the mother liquor by addition of $NaClO_4{\cdot}H_2O$. The composition of the dibenzoyltartrate salt was not established, but orange needles of (−)-$[Cr(ox)(cyclam)]ClO_4$ can be obtained by adding $NaClO_4{\cdot}H_2O$ to a hot (80 °C) aqueous solution of the less soluble diastereoisomer. ORD spectra of (−)-$[Cr(ox)(cyclam)]ClO_4$ (H_2O; λ (nm), [M] (deg $M^{-1}\,m^{-1}$)): 589, −155; 540, 0; 510, +606; 484, 0; 470, −209; 452, 0;

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(1) (a) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, entnen = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, tnentn = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, cyclam = 1,4,8,11-tetraazacyclotetradecane, DMF = dimethylformamide, ox = $C_2O_4^{2-}$, EDTA = ethylenediaminetetraacetate ion. The sign of optical rotation is given in parentheses with the wavelength as a subscript, e.g. $(+)_{465}$. Where no subscript is indicated, 589 nm is assumed. A similar convention is adopted for circular dichroism, using braces, e.g. $\{-\}_{456}$. (b) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 4029.

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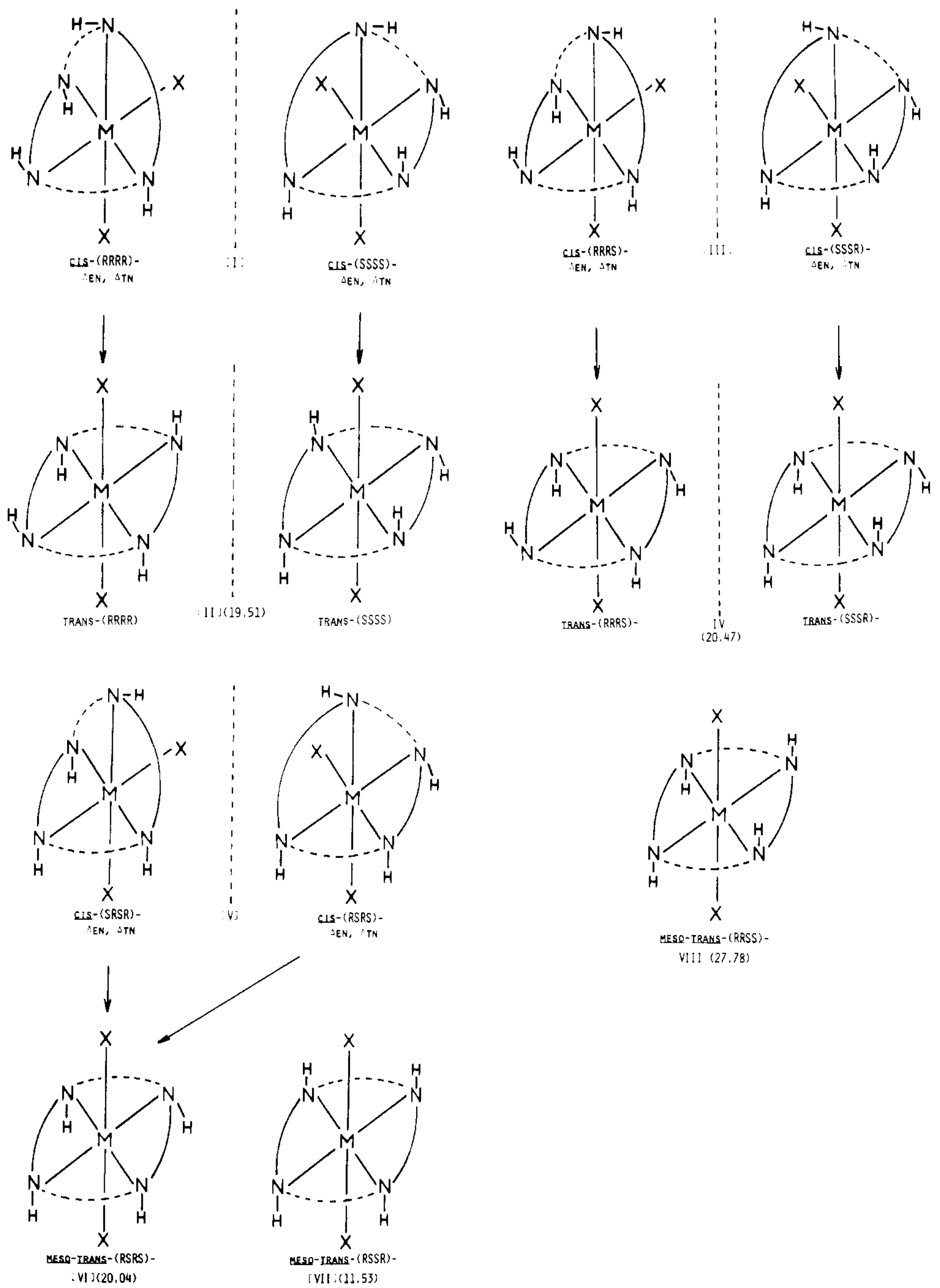

Figure 1. Selected optical and geometric isomers for $MX_2(cyclam)^{n+}$. Numbers in parentheses are the calculated[3] strain energies (kcal mol^{-1}). The cis isomers considered here are restricted to those with the same exo configuration at the folded N atoms.[27] Dashed lines represent the tn component (six-membered rings) of the macrocycle.

428, +451; 400, +242; 350, +1075. Complex ion concentrations were estimated from the visible absorption spectral parameters.

(−)-*cis*-Dichloro(cyclam)chromium(III) Perchlorate, (−)-*cis*-[$CrCl_2$(cyclam)]ClO_4. The less soluble dibenzoyltartrate salt of (−)-Cr(ox)(cyclam)$^+$ (1 g) was suspended in methanol (20 mL), and 10 mL of 12 M HCl was added. When the mixture was heated to almost boiling, the color slowly changed from orange to violet (30 min). $HClO_4$ (5 mL, 60%) was then added, and the violet solution was heated on a steam bath to remove most of the methanol. Violet crystals (contaminated with some dibenzoyltartaric acid) deposited, and these were collected from the ice-cooled solution. The crude material was recrystallized from 3 M HCl (10 mL, 40 °C) by the addition of 12 M HCl (5 mL) and 60% $HClO_4$ (5 mL) with an overall yield of 0.4 g. ORD spectrum (3 M HCl; λ (nm), [M] (deg M^{-1} m^{-1}): 625, +148; 605, 0; 589, −432; 548, −1630; 500, 0; 475, +568; 433, +222; 395, +494; 310, +74.

Figure 2 shows the changes in the CD spectrum with time for the reaction of (−)-[Cr(ox)(cyclam)]ClO_4 (12 mM) in HCl (12 M) to give (−)-$CrCl_2$(cyclam)$^+$.

The following cations were derived from (−)-*cis*-[$CrCl_2$(cyclam)]ClO_4. In all cases, the complex ion concentration was estimated from the visible absorption spectral parameters.[8]

(i) (+)-*cis*-CrCl(cyclam)(OH_2)$^{2+}$. A small quantity (50 mg/50 mL) of the (−)-dichloro complex was heated (42.0 °C) in 0.1 M HNO_3. Samples were removed from time to time, and the CD spectrum was recorded. Isorotatory points were observed at 580, 506, and 410 nm (Figure 4) corresponding to the isosbestic points at 520, 444, and 389 nm for the dichloro–chloroaqua conversion.[9] After 6 h, the now pink solution of mainly *cis*-CrCl(cyclam)(OH_2)$^{2+}$ had the following spectral parameters. Visible absorption spectrum (λ (nm), ε (M^{-1} cm^{-1}): max, 510 (118); min, 440 (31.7); max, 390 (97.7) (cf. *cis*-CrCl(en)$_2$(OH_2)$^{2+}$ (0.1 M HCl): max, 512 (73.5); min, 440 (21.9); max, 387 (60.0)[9a]). ORD spectrum (λ (nm), [M] (deg M^{-1} m^{-1}): 600, +406; 589, +355; 574, 0; 520, −2790; 481, 0; 440, +1500; 310, 0.

The half-life for the reaction, estimated from the CD spectral scans, gives a value of k_H 1.3 × 10^{-4} s^{-1} at 42.0 °C in acceptable agreement with the value of k_H = 1.6 × 10^{-4} s^{-1} calculated from the activation parameters determined spectrophotometrically.[9]

(ii) (+)-*cis*-Cr(cyclam)(OH$_2$)$_2$$^{3+}$. (−)-*cis*-CrCl$_2$(cyclam)]ClO$_4$ (2 mg/2 mL) was dissolved in 0.83 M HNO$_3$ containing 5.74 × 10^{-2} M Hg^{2+} at room temperature. The initial CD spectral parameters corresponded to those obtained for (+)-*cis*-CrCl(cyclam)(OH$_2$)$^{2+}$ above, and loss of the second chloro ligand occurred over several hours, with considerable increase in CD intensity. Isorotatory points were observed at 562, 490, and 405 nm (Figure 5). (The spectrophotometrically determined isosbestic points are at 497, 428, and 375 nm.)[9] The final visible absorption spectrum (after 3 days at room temperature) corresponded to *cis*-Cr(cyclam)(OH$_2$)$_2$$^{3+}$.[8] ORD spectrum (λ (nm), [M] (deg M^{-1} m^{-1}): 589, +750; 570, +900; 449, 0; 503, −7400; 468, 0; 447, +3700; 375 sh, +1500; 350, 0.

(iii) (−)-*cis*-Cr(OH)$_2$(cyclam)$^+$. (−)-*cis*-[CrCl$_2$(cyclam)]ClO$_4$ (2 mg/2 mL) was dissolved in 0.1 M NaOH at room temperature and the solution left for 5 min to ensure complete base hydrolysis.[9] The CD spectrum of this now blue-violet solution was unchanged after 1 h. Visible absorption spectrum (λ (nm) (ε (M^{-1} cm^{-1})): max, 546 (92.3); min, 440 (17.7); max, 370 (73.8) (cf. max, 547 (84); max, 370 (66)[8]). ORD spectrum (λ (nm), [M] (deg M^{-1} m^{-1}): 622, −642; 589, −562; 525 sh, −193; 505, 0; 460, +650; 400 sh, +497; 358, 0. Acidification of this solution gave (+)-Cr(cyclam)(OH$_2$)$_2$$^{3+}$, with spectral parameters identical in all respects with those of the diaqua complex produced by the Hg^{2+}-assisted chloride release in acid solution.

Instrumentation. ORD and CD spectra were measured with a JASVO ORD/CD/UV-5 recording spectropolarimeter and the visible absorption spectra with a Varian Super Scan recording spectrophotometer. IR spectra were measured in KBr disks with a Pye Unicam SP3-300. Microanalytical data for C, H, and N were determined by Professor A. D. Campbell, Department of Chemistry, University of Otago, Dunedin, New Zealand.

Crystal data for (−)-*cis*-(*RRRR*)-[CrCl$_2$(cyclam)]ClO$_4$: empirical formula CrC$_{10}$H$_{24}$N$_4$Cl$_3$O$_4$; formula weight 422.68; orthorhombic, space group $P2_12_12$; a = 10.097 (8), b = 13.747 (7), c = 6.349 (8) Å; V = 881.4 (9) Å^3; Z = 2; λ(Mo Kα) = 0.71069 Å; μ = 11.1 cm^{-1}; ρ(calcd) = 1.59 g cm^{-3}; index ranges h (0–13), k (0–17), l (0–8); 811 reflections with $I > 3[\sigma(I)]$; R = 0.0534; R_w = 0.0568.

A dark red, irregularly shaped crystal of approximate dimensions 0.25 × 0.25 × 0.375 mm was used for the structure determination. Intensity data were collected at room temperature on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo Kα radiation. The cell parameters were determined by least-squares refinement using 25 accurately centered reflections (25° < 2θ < 35°). A total of 954 reflections were collected with use of the θ–2θ scan technique (3° < 2θ < 50°) and variable scan rate (3.91–29.3° min^{-1}). Crystal stability was monitored by recording 3 standard reflections every 50 reflections, and no significant variation was observed. Data reduction gave 942 unique reflections of which 811, having $I > 3[\sigma(I)]$, were used for subsequent structural analysis. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scan data was applied. (Transmission factors varied from 0.376 to 0.409.) Systematic absences uniquely specified the space group as $P2_12_12$.

Solution and Refinement. The Cr and Cl (ClO$_4$) atoms were located from Patterson calculations and the remaining 14 non-hydrogen atoms located from difference Fourier maps. Blocked-cascade least-squares refinement resulted in a conventional R value of 0.0769. The ClO$_4$$^-$ anion showed 2-fold disorder about the Cl atom and was refined with 50% occupancy of each orientation. Hydrogen atoms were included at calculated positions by using the riding model with a common isotropic thermal parameter (C–H, N–H = 0.96 Å), and the structure was further refined with all the non-hydrogen atoms given anisotropic thermal parameters. The refinement converged with R = 0.0534, R_w = 0.0548 for the (*RRRR*) enantiomer. Least-squares refinement for the (*SSSS*) enantiomer gave R = 0.0550, R_w = 0.0568, confirming that the (−)$_{589}$ cation has the (*RRRR*) configuration at the 99.5% confidence limit.[15b] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.0024F_o^2]^{-1}$. All the programs used for data reduction and structure solution are included in the SHELXTL (Version 3.0) program package. Final atom positions are given in Table I.

Results and Discussion

Samples of (±)-*cis*-[CrCl$_2$(cyclam)]ClO$_4$ obtained via the direct synthesis of cyclam with CrCl$_3$·6H$_2$O dehydrated in DMF[8-13] and via the HCl decomposition of (±)-[Cr(ox)(cyclam)]ClO$_4$ were identical (IR). These racemic *cis*-Cr^{III} cyclam complexes are assigned to the (*RRRR*,*SSSS*) configuration (Figure 1, I) on the basis of the following crystal structure, and we note that (±)-*cis*-[CoCl$_2$(cyclam)]ClO$_4$ is also reported to have a similar configuration.[3]

Table I. Atom Coordinates (× 10^4) for (−)-*cis*-(*RRRR*)-[CrCl$_2$(cyclam)]ClO$_4$

atom	x	y	z
Cr	0	0	520 (2)
Cl(1)	503 (2)	1127 (2)	−2105 (3)
N(1)	1963 (6)	−446 (4)	836 (10)
C(2) (tn)	2239 (8)	−1514 (7)	1012 (17)
C(1) (tn)	1524 (11)	−2009 (6)	2803 (15)
C(3) (en)	2567 (6)	88 (7)	2633 (12)
C(4) (en)	2021 (8)	1105 (7)	2649 (14)
N(2)	556 (6)	1034 (4)	2731 (10)
C(5) (tn)	−22 (12)	2024 (5)	2638 (12)
Cl(2) (ClO$_4$$^-$)	5000	0	−2644 (4)
O(1)	4929 (17)	719 (8)	5573 (18)
O(2)	4671 (14)	663 (11)	9228 (23)
O(3)	−6127 (12)	−621 (10)	7080 (31)
O(4)	6191 (13)	−411 (13)	7428 (32)

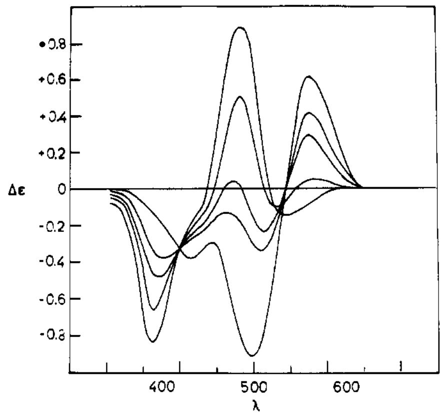

Figure 2. Changes in the CD spectra (×2) with time for $\{+\}_{482}$-(*RRRR*)-Λ_{en}-Cr(ox)(cyclam)$^+$ in 12 M HCl to give $\{-\}_{500}$-(*RRRR*)-Δ_{tn}-*cis*-CrCl$_2$(cyclam)$^+$ at room temperature. Reading downwards at 500 nm, the times are 0, 117, 243, 323, and 563 min.

Unlike the Co(III) system, the reactions of the less stereomobile *cis*-CrCl$_2$(cyclam)$^+$ proceed with retention of geometric configuration in acid conditions[8,9a] and *trans*-(*RRRR*,*SSSS*)-Cr^{III}cyclam complexes have not yet been characterized. However, in basic media, some cis → trans isomerization,[10] accompanied by proton inversion, occurs to give the trans-(*RSSR*) form.

Conversion of (±)-*cis*-CrCl$_2$(cyclam)$^+$ to (±)-Cr(ox)(cyclam)$^+$ proceeds smoothly in good yield, and the resulting oxalato complex can be resolved with use of the (2*R*,3*R*)-dibenzoyltartrate anion, by following the procedure described previously for the resolution of other Cr(ox)(N$_4$)$^+$ complexes.[16-19] An aqueous solution of the Cr(ox)(cyclam)$^+$ cation from the less soluble diastereoisomer has a negative rotation at 589 nm. The circular dichroism spectra (Figures 2 and 3) are quite solvent dependent and are not immediately related to those of other Cr(ox)(N$_4$)$^+$ complexes, which have only a single dominant band at about 480 nm (positive for a Λ configuration).[16-20] It is, nevertheless, enantiomeric with the $\{-\}_{494}$-Co(ox)(cyclam)$^+$ cation isolated from the less soluble (−)$_{546}$-Co(EDTA)$^-$ diastereoisomer[6] and could be assigned to the Λ configuration on the basis of CD spectral comparisons

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Table II. CD Spectral Parameters

	λ, nm (Δε, M^{-1} cm^{-1})							ref
Λ-(+)-$Cr(ox)(en)_2^+$ [a]			480 (+2.12)	392 (0)	365 (−0.16)	345 (0)	330 (+0.07)		16
Λ-(+)-$Cr(ox)(tn)_2^+$ [a]			478 (+1.51)	393 (0)	362 (−0.11)				16
(−)-$Cr(ox)(cyclam)^+$ [a]	530 (−0.181)	502 (0)	482 (+0.175)	455 (0)	435 (−0.122)	415 (−0.097)	368 (−0.258)	310 (0)	this work
(−)-$Cr(ox)(cyclam)^+$ [b]	533 (−0.425)	509 (0)	480 (+0.620)	415 (0)	365 (−0.193)	310 (0)			this work
Λ-(+)-$CrCl_2(en)_2^+$ [c]	580 (−0.442)	544 (0)	501 (+0.515)	440 (+0.192)	412 (+0.256)	377 (0)	356 (−0.096)		20
Λ-(+)-$CrCl_2(tn)_2^+$ [d]	590 (−0.36)	550 (0)	511 (+0.33)	450 (+0.08)	419 (+0.10)	395 (0)	370 (−0.01)		e
(−)-$CrCl_2(cyclam)^+$ [f]	582 (+0.278)	550 (0)	502 (−0.525)	440 (−0.142)	410 (−0.179)	350 (0)			this work
Λ-(+)-$CrCl(en)_2(OH_2)^{2+}$ [g]	570 (−0.208)	536 (0)	484 (+0.475)	406 sh (+0.171)	350 (0)				20
(+)-$CrCl(cyclam)(OH_2)^{2+}$ [h]	550 (+0.457)	520 (0)	477 (−1.01)	385 (0)	358 (+0.071)				this work
Λ-(+)-$Cr(en)_2(OH_2)_2^{3+}$ [i]	528 (−0.170)	505 (0)	464 (+0.562)	373 (0)	360 (−0.020)	340 (0)	330 (+0.007)	315 (0)	20
(+)-$Cr(cyclam)(OH_2)_2^{3+}$ [j]	530 (+1.42)	500 (0)	465 (−2.33)	400 (0)	355 (+0.47)				this work
Λ-(+)-$Cr(OH)_2(en)_2^+$ [k]	552 (+0.498)	501 (0)	468 (−0.193)	435 (−0.165)	428 (−0.170)	368 (0)	358 (+0.080)		20
(−)-$Cr(OH)_2(cyclam)^+$ [k]	550 sh (−0.290)	495 (−0.361)	400 (0)	360 (+0.108)	315 (0)				this work

[a] 1 M HCl. [b] DMF (90%), 3 M HCl (10%). [c] 0.8 M $HClO_4$. [d] 12 M HCl. [e] Pedersen, E. *Acta Chem. Scand.* **1970**, *24*, 3362. [f] 3 M HCl. [g] 0.8 M $HClO_4$. [h] 0.1 M HNO_3. [i] 1.5 M $HClO_4$. [j] 0.83 M HNO_3 containing 5.74×10^{-2} M Hg^{2+}. [k] 0.1 M NaOH.

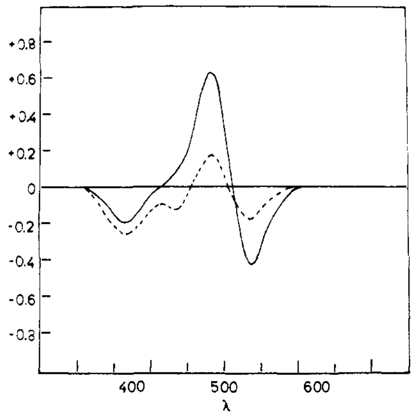

Figure 3. CD spectra of (−)-$Cr(ox)(cyclam)^+$ in 0.1 M HCl (- - -) and 90% DMF, 10% 3 M HCl (—) at room temperature.

Table III. Selected Bond Lengths (A) and Angles (deg) in (−)-*cis*-(*RRRR*)-$[CrCl_2(cyclam)]ClO_4$

Bond Lengths

Cr-Cl(1)	2.331 (2)	N(1)-C(3) (en)	1.487 (10)
Cr-N(1)	2.084 (6)	C(3)-C(4) (en)	1.502 (13)
N(1)-C(2) (tn)	1.499 (11)	C(4)-N(2) (en)	1.483 (10)
C(2)-C(1) (tn)	1.510 (15)	Cr-N(2)	2.076 (6)
C(1)-C(5′) (tn)	1.520 (17)	N(2)-C(5) (tn)	1.482 (9)
Cl(2)-O(1)	1.505 (12)	Cl(2)-O(3)	1.433 (13)
Cl(2)-O(2)	1.534 (15)	Cl(2)-O(4)	1.330 (14)

Bond Angles

N(1)-Cr-N(1′)	169.0 (4)	Cl(1)-Cr-N(2)	88.2 (2)
Cl(1)-Cr-N(2′)	176.1 (2)	Cl(1)-Cr-N(1)	93.3 (2)
N(1)-Cr-N(2)	83.0 (2)	Cl(1)-Cr-Cl(1′)	88.7 (1)
N(1)-Cr-Cl(1′)	94.6 (2)	N(2)-Cr-N(1′)	89.5 (2)
N(2)-Cr-N(2′)	94.9 (3)		
O(1)-Cl(2)-O(3)	105.2 (9)	O(2)-Cl(2)-O(4)	115.0 (10)
O(2)-Cl(2)-O(3)	106.1 (9)	O(3)-Cl(2)-O(4)	118.0 (9)
O(1)-Cl(2)-O(4)	110.3 (11)	O(1)-Cl(2)-O(2)	100.5 (7)
Cr-N(1)-C(2) (tn)	118.1 (5)	Cr-N(1)-C(3) (en)	110.5 (7)
N(1)-C(2)-C(1) (tn)	114.3 (8)	N(1)-C(3)-C(4) (en)	108.3 (6)
C(2)-C(1)-C(5′) (tn)	115.5 (8)	C(3)-C(4)-N(2) (en)	107.8 (7)
C(1)-C(5′)-N(2′) (tn)	112.4 (7)	C(4)-N(2)-C(5)	109.4 (7)
Cr-N(2)-C(5) (tn)	119.7 (5)	Cr-N(2)-C(4) (en)	106.9 (5)

Dihedral Angles

Cr-N(1)-C(2)-C(1) (tn)	−56.7
N(1)-C(2)-C(1)-C(5′) (tn)	64.7
C(2)-C(1)-C(5′)-N(2′) (tn)	−64.5
C(1)-C(5′)-N(2′)-Cr (tn)	58.5
Cr-N(1)-C(3)-C(4) (en)	−36.7
N(1)-C(3)-C(4)-N(2) (en)	55.6[a]
C(3)-C(4)-N(2)-Cr (en)	−46.1

[a] The theoretical value for an unstrained dihedral angle in a chelated $-NH(CH_2)_2NH-$ residue is ±48.8°.

with Λ-(+)-$Cr(ox)(en)_2^+$[16] (both having a strong positive CD at 480 nm) or from the Δ assignment to the enantiometric Co(III) analogue.[6]

Conversion of (−)-$Cr(ox)(cyclam)^+$ to (−)-$CrCl_2(cyclam)^+$ (Figure 2) is readily achieved in 12 M HCl, and from this, (+)-*cis*-$CrCl(cyclam)(OH_2)^{2+}$ (Figure 4), (+)-*cis*-$Cr(cyclam)(OH_2)_2^{3+}$ (Figure 5), and (−)-*cis*-$Cr(OH)_2(cyclam)^+$ can be obtained in solution, with retention of both geometric and optical configuration. The CD spectra of these *cis*-CrXY-$(cyclam)^{n+}$ cations (Figures 2, 4, and 5) derived from the less soluble dibenzoyltartrate salt of Λ-(−)-$Cr(ox)(cyclam)^+$ are very similar to those of the Δ-*cis*-$CrXY(en)_2^{n+}$ analogues[20] (Table II). A configurational inversion from the oxalato to the dichloro complex in acidic solution is unlikely for a cis cyclam structure (whereas it is possible for a cis-$\beta \rightleftharpoons$ cis-α configuration change in linear tetraamines[17-19]), and the apparent inversion (Figure 2) could result from a change in ring-pair dominance.

In order to establish the dominant ring pair in at least one of these complexes, a single-crystal X-ray structure of (−)-*cis*-$[CrCl_2(cyclam)]ClO_4$ was undertaken. The structure consists of discrete $CrCl_2(cyclam)^+$ cations and ClO_4^- anions, with the anion showing 2-fold disorder. Figure 6 shows a perspective view of the cation and the numbering scheme adopted.

The macrocycle is folded diagonally at N(1) and N(1′) and coordinated to four adjacent sites of the Cr atom, the two Cl^- ligands occupying the remaining sites. The folded macrocycle has C_2 symmetry, with a 2-fold axis passing through the Cr

Table IV. CD Spectral Parameters for Some Δ-(−)-Cr(ox)(N_4)$^+$ Systems[a]

N_4	no. of rings[b] 5	no. of rings[b] 6	λ, nm (Δε, M^{-1} cm^{-1})					ref
$(en)_2$	2	0	480 (−2.12)	392 (0)	365 (+0.16)	345 (0)	330 (−0.07)	16
$(tn)_2$	0	2	478 (−1.51)	393 (0)	362 (+0.11)			16
cis-β-(*SS*)-(entnen)[c]	2	1	482 (−0.91)	394 (0)	366 (+0.142)	344 (0)		19
cis-β-(*RR*)-(trien)[d]	3	0	482 (−1.91)	395 (0)	358 (+0.23)			17
cis-β-(*RR*)-(tnentn)	1	2	472 (−1.00)		370 sh (−0.06)	330 (0)		18

[a] 1 M H^+ except where noted. [b] Number of 5- or 6-membered rings. [c] These three following linear tetraamine complexes all have the same *s*-NH stereochemistry. The apparent change in NH assignment is an artifact of the nomenclature used.[21] [d] 10% DMF, 90% H_2O.

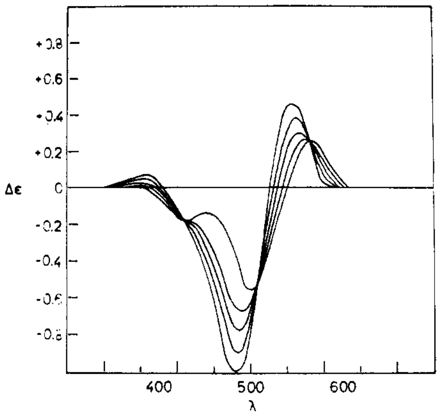

Figure 4. Changes in the CD spectra with time for {−}$_{500}$-(*RRRR*)-*cis*-$CrCl_2$(cyclam)$^+$ in 0.1 M HNO_3 to give {−}$_{475}$-(*RRRR*)-*cis*-CrCl(cyclam)$(OH_2)^{2+}$ at 42.0 °C. Reading downwards at 475 nm, the times are 0, 35, 90, 190, and 370 min.

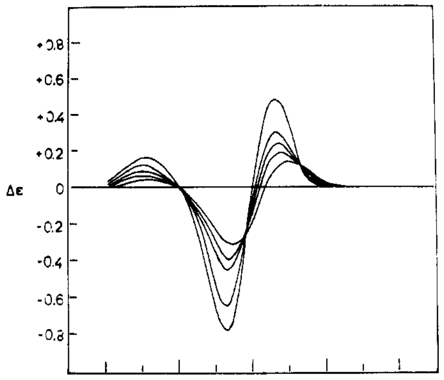

Figure 5. Changes in the CD spectrum ($X^1/_3$) with time for {−}$_{475}$-(*RRRR*)-*cis*-CrCl(cyclam)$(OH_2)^{2+}$ in 0.82 M HNO_3 containing 5.74 × 10^{-2} M Hg^{2+} to give {−}$_{465}$-(*RRRR*)-*cis*-Cr(cyclam)$(OH_2)_2{}^{3+}$ at room temperature. Reading downwards at 465 nm, the times are 0, 99, 249, and 469 min and complete reaction.

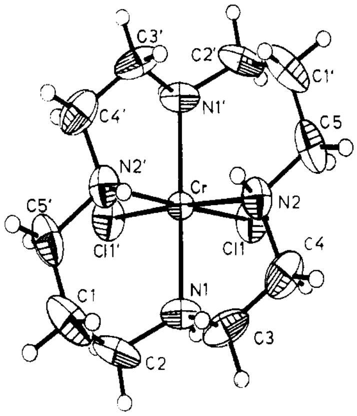

Figure 6. General view of the $(-)_{589}$-*cis*-δδ*cc*-Λ_{en},Δ_{tn}-(*RRRR*)-$CrCl_2$(cyclam)$^+$ cation showing the atom-numbering scheme.

atom and bisecting the C(1)–C(5′) and C(1′)–C(5) bonds. Thus the halves of the folded ligand are equivalent. Bond lengths and angles for half of the molecule are listed in Table III.

In terms of helicity of the four *s*-NH centers, the structure shown in Figure 6 has the (*RRRR*) designation, based on the sequence rules of Cahn, Ingold, andd Prelog[21] (NH < $NHCH_2CH_2CH_2$ < $NHCH_2CH_2NH$ < NHCr). In addition, the cation shown in Figure 6 can be described as Λ_{en} or Δ_{tn} with respect to the pairs of 5- or 6-membered chelate rings.[22] Both en rings adopt a δ configuration,[22] and the tn rings, the chair (*c*) form. Thus the dichloro cation derived from the less soluble dibenzoyltartrate oxalato enantiomer (Figure 6) can be described as $(-)_{589}$-*cis*-δδ*cc*-Λ_{en},Δ_{tn}-(*RRRR*)-$CrCl_2$(cyclam)$^+$. Consequently, the parent oxalato complex probably has a similar configuration as removal of the oxalato ligand in concentrated hydrochloric acid is expected to be stereospecific.

Thus we propose that in the chiral *cis*-(*RRRR*)-CrXY-(cyclam)$^{n+}$ complexes (X, Y = monodentate ligands) it is the 6-membered chelate rings that dominate the CD intensity (Δ_{tn}), whereas in the chiral *cis*-(*RRRR*)-Cr(AA)(cyclam)$^{n+}$ complexes (AA = bidentate ligand) the CD intensity arises from the 5-membered ring systems (Λ_{en}).

The assignment of the absolute configuration of *cis*-Co-(AA)(cyclam)$^{n+}$ (AA = ox,[6] en[23]) complexes has previously been made on the basis that the helicity of the two five-membered chelate rings should dominate, as the CD intensity of bis- or tris(ethylenediamine) complexes is generally greater than that of the trimethylenediamine analogues. This procedure is supported by the observation that there is a progressive decrease in CD intensity as more 6-membered rings are introduced in the $M(en)_x(tn)_{3-x}{}^{3+}$ (M = Co,[24] Cr[25]) series. However, the factors influencing the CD intensity in *linked* 5- and 6-membered chelate rings are not well understood,[26] and the pattern of CD intensity for Δ-*cis*-β-Cr(ox)(tetraamine)$^+$ complexes (Table IV) hardly supports the above assumptions.

Nevertheless, our empirical proposal agrees with the previous assignments made for chiral *cis*-Co(AA)(cyclam)$^{n+}$ complexes (AA = bidentate ligand) based on the 5-membered ring pair dominance, but the proposal that the CD intensity of chiral *cis*-CoXY(cyclam)$^{n+}$ (X, Y = monodentate ligands)

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will be dominated by the 6-membered ring pair awaits confirmation.

There still remain some assignments in the literature that require modification. The absolute configuration of the Co(en)(cyclam)$^{3+}$ enantiomer presented by Lai and Poon[4] (Figure 2) should be (*SSSS*), and the chirality defined by the 5-membered chelate rings in isomer I (Figure 3 of ref 6) should be Λ.

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Registry No. [Cr(ox)(cyclam)]ClO$_4$, 93110-52-2; *cis*-[CrCl$_2$(cyclam)]ClO$_4$, 27435-97-8; (−)-[Cr(ox)(cyclam)]ClO$_4$, 93219-75-1; (−)-*cis*-[CrCl$_2$(cyclam)]ClO$_4$, 93219-77-3; (+)-*cis*-CrCl(cyclam)(OH$_2$)$^{2+}$, 93220-77-0; (+)-*cis*-Cr(cyclam)(OH$_2$)$_2$$^{3+}$, 93219-78-4; (−)-*cis*-Cr(OH)$_2$(cyclam)$^+$, 93110-53-3.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic temperature factors, coordinates of hydrogen atoms, and calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department,
University of Canterbury, Christchurch, New Zealand

X-ray Crystal and Molecular Structures of Related Octahedral Magnesium Tetraphenylporphyrin Complexes

V. McKEE, CHIN CHOON ONG, and G. A. RODLEY*

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The crystal and molecular structures are reported for the magnesium tetraphenylporphyrin complexes, MgTPP(1-methylimidazole)$_2$ MgTPP(4-picoline)$_2$, and MgTPP(piperidine)$_2$. MgTPP(1-methylimidazole)$_2$ crystallizes in the tetragonal space group $P4_2/n$ with 4 molecules per unit cell of dimensions $a = 20.764$ (5) Å, $c = 9.659$ (3) Å. MgTPP(4-picoline)$_2$ and MgTPP(piperidine)$_2$ are isostructural. These two compounds crystallize in the triclinic space group $P\bar{1}$ with 1 molecule in unit cells of dimensions $a = 10.146$ (2), 9.944 (3) Å, $b = 11.210$ (2), 11.436 (3) Å, $c = 11.643$ (3), 11.914 (3) Å, $\alpha = 65.63$ (2), 101.78 (2)°, $\beta = 76.32$, 104.59 (2)°, and $\gamma = 67.42$ (1), 115.60 (2)°, respectively. As observed for related complexes the binding in the axial, octahedral positions is weak. The Mg–N axial bond distances are long, varying from 2.297 (8) Å (1-methylimidazole) to 2.386 (2) and 2.419 (3) Å (4-picoline and piperidine, respectively). Corresponding values for isostructural low-spin Fe(II) 1-methylimidazole and piperidine complexes are significantly shorter, indicating that an absence of t$_{2g}$ electrons for Mg(II) limits the binding of axial ligands to porphyrin systems to a significant extent. The stronger binding of 1-methylimidazole, compared with piperidine, for both Mg(II) and Fe(II) complexes indicates that an electronic effect as well as a smaller steric interaction favors the axial coordination of this ligand.

Introduction

The crystal and molecular structures of metalloporphyrins have been of considerable interest because of their relevance to the structure and function of biological compounds.[1] The majority of these metalloporphyrin structures consist of elements in the first-row transition series, particularly iron.[2] However, the structures of magnesium porphyrins are also of interest because of their relationship to chlorophyll, as highlighted in a recent report.[3]

Most X-ray structural studies of magnesium macrocyclic tetrapyrrole complexes are those of five-coordinated entities. In these cases the magnesium atom is displaced out of the mean plane of the four chelating nitrogen atoms toward the axial ligands, by values ranging from 0.27 to 0.496 Å.[3-9] Equilibrium studies of Mg porphyrins with nitrogenous bases also indicate that five-coordination is the preferred coordination state of Mg. However, under suitable conditions, six-coordination can be realized[10-13] as shown in particular by X-ray structural results.

Although the first attempt to determine the crystal structure of a six-coordinated complex, (Mg etioporphyrin)(py)$_2$ (py = pyridine), was limited by a high degree of disorder, it did reveal the existence of long Mg–N axial ligand bonds.[14-16] More recently, a complete structure determination of six-coordinated MgOEP(py)$_2$ (OEP = octaethylporphyrin) confirmed this result.[17] In this paper, we report details of the crystal and molecular structures of three related six-coordinated MgTPP (TPP = tetraphenylporphyrin) complexes, MgTPP(1-MeIm)$_2$

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