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Kinetics of Aquation and Base Hydrolysis of Some *cis*- and *trans*-Dichloro(1,4,7,10-tetraazatetradecane)chromium(III) Cations. The $CrCl_2(3,2,3\text{-tet})^+$ System

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The synthesis of *cis*-β-(*RR*,*SS*)-[Cr(ox)(3,2,3-tet)]ClO_4, $\Delta(-)_{589}$-*cis*-β-(*RR*)-[Cr(ox)(3,2,3-tet)][hydrogen dibenzoyl-(+)-tartrate], *cis*-β-(*RR*,*SS*)-[$CrCl_2$(3,2,3-tet)]ClO_4, $\Delta(-)_{589}$-*cis*-β-(*RR*)-[$CrCl_2$(3,2,3-tet)]ClO_4, *trans*-(*RR*,*SS*)-[$CrCl_2$(3,2,3-tet)]NO_3, $(-)_{589}$-*trans*-(*RR*)-[$CrCl_2$(3,2,3-tet)]ClO_4, *trans*-(*RR*,*SS*)-[Cr(NCS)$_2$(3,2,3-tet)]NCS, and $(-)_{589}$-*trans*-(*RR*)-[Cr(NCS)$_2$(3,2,3-tet)][hydrogen dibenzoyl-(+)-tartrate] (3,2,3-tet = 1,5,8,12-tetraazatetradecane) is described. Conformational assignments have been made on the basis of chiral interconversions, $\Delta(-)_{589}$-*cis*-β-(*RR*)-Cr(ox)(3,2,3-tet)$^+$ → $\Delta(-)_{589}$-*cis*-β-(*RR*)-$CrCl_2$(3,2,3-tet)$^+$ → $(-)_{589}$-*trans*-(*RR*)-$CrCl_2$(3,2,3-tet)$^+$, in acidic solution. The rates of loss of the first chloro ligand from the racemic dichloro cations have been measured in both acidic and basic solutions. The kinetic parameters at 298.2 K are as follows: k_H(trans-(*RR*,*SS*)) = 1.06×10^{-6} s^{-1} (0.1 M HNO_3), E_a = 94.7 kJ mol^{-1}, and $\Delta S^* = -50$ J K^{-1} mol^{-1}; k_H(cis-β-(*RR*,*SS*)) = 1.02×10^{-4} s^{-1} (0.1 M HNO_3), E_a = 88.7 kJ mol^{-1}, and $\Delta S^* = -32$ J K^{-1}; k_{OH}(trans) = 5.76×10^{-1} M^{-1} s^{-1} (μ = 0.1 M, NaCl), E_a = 87.7 kJ mol^{-1}, and $\Delta S^* = +36$ J K^{-1} mol^{-1}; k_{OH}(cis-β) = 11.2 M^{-1} s^{-1} (μ = 0.1 M, NaCl). For the loss of the second chloro ligand, the kinetic parameters (298.2 K) are K_{OH}(trans) = 8.81×10^{-3} M^{-1} s^{-1} (μ = 0.1 M, NaCl), E_a = 97.3 kJ mol^{-1}, and $\Delta S^* = +34$ J K^{-1} mol^{-1} and k_{OH}(cis-β) = 4.0×10^{-2} M^{-1} s^{-1} (μ = 0.1 M, NaCl). $(-)_{589}$-*trans*-(*RR*)-$CrCl_2$(3,2,3-tet)$^+$ racemizes in basic solution about 10 times faster than loss of the first chloro ligand, and at 298.2 K, k_{rac} = 5.93 M^{-1} s^{-1}, E_a = 88.7 kJ mol^{-1}, and $\Delta S^* = +59$ J K^{-1} mol^{-1}.

Introduction

Linear quadridentate polyamine ligands provide a rich field of geometric and conformational isomers in octahedral transition-metal complexes. Much of the recent research has focused on Co(III) as the central metal, and there are numerous studies relating to the $CoX_2(2,2,2\text{-tet})^+$,[1-5] $CoX_2(2,3,2\text{-tet})^+$,[3-12] and $CoX_2(3,2,3\text{-tet})^+$[3-5,13-18] systems. The stereomobility exhibited by these complexes can sometimes limit the range of accessible isomers; for example, the cis configuration for $CoX_2(3,2,3\text{-tet})^+$ is difficult to stabilize with X = Cl.[14]

The less stereomobile Cr(III) complexes have received much less systematic investigation, and although the $CrX_2(2,2,2\text{-tet})^+$ system has been well studied,[19-25] there still remains some stereochemical problems.[24,26] Several *cis*- and *trans*-$CrX_2(2,3,2\text{-tet})^+$ complexes have been prepared,[6,27,28] but only in the case of the *trans*-(*R*,*S*)-difluoro[28] complex is there any certainty as to the ligand conformation. In the 3,2,3-tet system, only the *trans*-(*RR*,*SS*)-dichloro complex has previously been described.[14,15]

In this paper we describe the synthesis, isomeric interconversions, and hydrolysis rates of some *cis*- and *trans*-$CrX_2(3,2,3\text{-tet})^+$ complexes.

Experimental Section

The anhydrous ligand, 1,5,8,12-tetraazatetradecane[29] (3,2,3-tet), was purchased from Fluka and the resolving agent, dibenzoyl-*d*-tartaric acid monohydrate (H_2BzOT) from Aldrich. All other chemicals were of the best reagent grade available.

Caution. Although we have experienced no difficulty with the perchlorate salts described, these should be regarded as potentially explosive and handled accordingly.

ΔΛ-*cis*-β-(*RR*,*SS*)-(Oxalato)(1,5,8,12-tetraazatetradecane)chromium(III) Perchlorate Monohydrate, [Cr(ox)(3,2,3-tet)]ClO_4·H_2O. Oxalic acid dihydrate (22 g) was slurried in water (150 mL), and $Na_2Cr_2O_7$·$2H_2O$ (7.4 g) was added in small portions (care, CO_2 evolution). The now warm solution was heated on a steam bath for a further 10–15 min (until all CO_2 evolution ceased), and 3,2,3-tet (8.5 mL) was added. Heating was continued until a red-orange color developed (1–2 h), and $NaClO_4$·H_2O (20 g) was added. Orange crystals (occasionally contaminated with $Na_2C_2O_4$) deposited from the hot solution, and these were collected by filtration, washed successively with ice water, ethanol, and ether, and air-dried. Further crystal crops were obtained by continued heating of the mother liquor, with the volume maintained at 120 mL by occasional addition of water. The crude product was recrystallized from water (50 mL (80 °C) g^{-1}) by addition of $NaClO_4$·H_2O (5 g g^{-1}). The total yield of recrystallized material was 9 g (75%). Anal. Calcd for [Cr(ox)-

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(29) Abbreviations used: en = $NH_2(CH_2)_2NH_2$; (*RS*)-pn = (±)-$NH_2CH(CH_3)CH_2NH_2$; tn = $NH_2(CH_2)_3NH_2$; 2,2,2-tet = trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$; 3,2,3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$; cyclam = 1,4,8,11-tetraazacyclotetradecane; teta = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; ox = $C_2O_4^{2-}$, DMF = dimethylformamide, (+)-H_2BzOT = (+)-dibenzoyltartaric acid. The Chemical Abstracts name for 3,2,3-tet is *N,N''*-1,2-ethanediylbis(1,3-propanediamine).

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(3,2,3-tet)]$ClO_4 \cdot H_2O$, $CrC_{10}H_{24}N_4O_9Cl$: Cr, 11.9; C, 27.8; H, 5.6; N, 13.0. Found: Cr, 12.0; C, 27.9; H, 5.9; N, 12.8.

Resolution of ΔΛ-*cis*-β-(*RR*,*SS*)-[Cr(ox)(3,2,3-tet)]$ClO_4 \cdot H_2O$. The racemic perchlorate (2 g) was dissolved in sodium formate–formic acid buffer (50 mL, 1 M, pH 3.7) and water (25 mL) at 60 °C. Dibenzoyl-*d*-tartaric acid monohydrate (H_2BzOT) (2 g) was suspended in water (50 mL, 60 °C), and LiOH (ca. 0.7 g) was added until all the solid had dissolved. The warm solution was filtered and the pH adjusted to <8 with formic acid. The solution containing the resolving agent was added to the solution of the racemate (both at 60 °C) and allowed to cool slowly to room temperature (1–2 h). The less soluble diastereoisomer $(-)_{589}$-[Cr(ox)(3,2,3-tet)][HBzOT]$\cdot H_2O$ crystallized as pink rosettes (1 g). These were collected, washed successively with propan-2-ol and ether, and air-dried. Anal. Calcd for [Cr(ox)-(3,2,3-tet)][HBzOT]$\cdot H_2O$, $CrC_{28}H_{37}N_4O_{13}$: Cr, 7.5. Found: Cr, 7.6.

The mother liquor was warmed to 60 °C, and $NaClO_4 \cdot H_2O$ (10 g) was added. Orange crystals of $(+)_{589}$-[Cr(ox)(3,2,3-tet)]ClO_4 (89% optically pure based on data from the $(-)_{589}$ isomer) were collected from the cooled solution. The $[HBzOT]^-$ salt (1 g) was ground with $NaClO_4 \cdot H_2O$ (3 g) and water (2 mL) to a thin paste, slurried with methanol (15 mL), and filtered. The orange solid that remained was recrystallized from water as for the racemate to give an 84% yield of $(-)_{589}$-[Cr(ox)(3,2,3-tet)]ClO_4. Anal. Calcd: Cr, 12.6. Found: Cr, 12.8.

ΔΛ-*cis*-β-(*RR*,*SS*)-Dichloro(1,5,8,12-tetraazatetradecane)chromium(III) Perchlorate, *cis*-β-[$CrCl_2$(3,2,3-tet)]ClO_4. The racemic oxalato perchlorate (2 g) was gently warmed in HCl (15 mL, 12 M, 30 °C), and the initial orange solution slowly turned violet (15–20 min). The warm solution was filtered, and $HClO_4$ (8 mL, 70%) was added to the filtrate cooled in an ice bath. After 2 h, the violet crystals (1.6 g, 85%) that deposited were collected by filtration, washed with propan-2-ol and then ether, and air-dried. Anal. Calcd for [$CrCl_2$(3,2,3-tet)]ClO_4, $CrC_8H_{22}N_4O_4Cl_3$: Cr, 13.1; C, 24.2; H, 5.6; N, 14.1, Cl(non-perchlorate); 17.9. Found: Cr, 13.0; C, 24.5; H, 5.9; N, 14.0; Cl, 17.3.

$(-)_{589}$-*cis*-β-(*RR*)-[$CrCl_2$(3,2,3-tet)]ClO_4. $(-)_{589}$-*cis*-β-(*RR*)-[Cr(ox)(3,2,3-tet)]ClO_4 (1 g) was stirred with thionyl chloride (15 mL) and 3 drops of water (care, HCl fumes) for 24 h. Occasional addition of $SOCl_2$ and water was necessary due to evaporation. Propan-2-ol (10 mL) was added dropwise (care, HCl fumes) followed by $HClO_4$ (5 mL, 70%) and the mixture left to stand at room temperature for 30 min, during which time violet crystals deposited. The product was collected and recrystallized from HCl (8 mL, 6 M, 30 °C) by the addition of $HClO_4$ (3 mL, 70%). The recrystallized material (0.64 g, 64%) was collected and washed as for the racemate. Anal. Calcd for [$CrCl_2$(3,2,3-tet)]ClO_4: Cr, 13.1. Found: Cr, 13.2.

***trans*-(*RR*,*SS*)-Dichloro(1,5,8,12-tetraazatetradecane)chromium(III) Nitrate, *trans*-[$CrCl_2$(3,2,3-tet)]NO_3.** The chloride and perchlorate salts of this cation have been prepared previously by a different route.[14] $CrCl_3 \cdot 6H_2O$ (13.3 g) was added to dimethylformamide (DMF, 150 mL) in a dry conical flask and the mixture boiled until 30 mL of DMF had evaporated (ca. 30 min). The violet solution was cooled to 120 °C, and 3,2,3-tet (9 mL) was added (care, temperature increase) to the well-stirred solution. Green crystals of the presumed chloride salt deposited almost immediately, but the mixture was digested at 120 °C for a further 30 min to complete the reaction (care, bumping may occur). The product (16 g) was collected by filtration from the cooled solution, washed with propan-2-ol and ether, and air-dried. This material was dissolved in HCl (3 M, 450 mL) by warming to 60 °C and $NaNO_3$ (15 g) added. Green crystals of the nitrate salt (16 g, 89%) deposited from the ice-cooled solution, and these were washed and dried as above. Anal. Calcd for [$CrCl_2$(3,2,3-tet)]NO_3, $CrC_8H_{22}N_5O_3Cl_2$: Cr, 14.5; C, 26.7; H, 6.1; N, 19.5; Cl, 19.8. Found: Cr, 14.1; C, 27.1; H, 6.6; N, 19.2; Cl, 20.0.

The much less water soluble perchlorate salt can be obtained from the chloride or nitrate salts by metathesis. Anal. Calcd for [$CrCl_2$(3,2,3-tet)]ClO_4: Cl(non-perchlorate), 17.9. Found: Cl, 17.4.

$(-)_{589}$-*trans*-(*RR*)-[$CrCl_2$(3,2,3-tet)]ClO_4. $(-)_{589}$-*cis*-β-(*RR*)-[Cr(ox)(3,2,3-tet)]ClO_4 (1 g) was heated with HCl (6 M, 30 mL) in a boiling tube in a beaker of boiling water. After about 1 h $HClO_4$ (4 mL, 70%) was added and heating was continued for a further 5–6 h, during which time green crystals (85% yield) of the desired product deposited. These were collected by filtration, washed with propan-2-ol and ether, and air-dried. Anal. Calcd for [$CrCl_2$(3,2,3-tet)]ClO_4: Cr, 13.1. Found: Cr, 13.1.

***trans*-(*RR*,*SS*)-Bis(isothiocyanato)(1,5,8,12-tetraazatetradecane)chromium(III) Thiocyanate, *trans*-[$Cr(NCS)_2$(3,2,3-tet)]NCS.** $Cr(NO_3)_3 \cdot 9H_2O$ (10 g) was dissolved in absolute ethanol (150 mL), and potassium thiocyanate (14.6 g) was added. The mixture was warmed and 40 °C until all the KNCS had dissolved and white crystals of KNO_3 deposited from the violet solution. This was removed by filtration from the cooled solution, washed with a little absolute ethanol, and discarded. The combined filtrate and washings, together with 3,2,3-tet (4.4 mL) were refluxed for 5–6 h (an initial violet precipitate dissolved during the refluxing). The now orange-red solution was evaporated on a steam bath, and the desired orange product crystallized as the volume decreased. A further crystal crop was obtained by adding sodium acetate (10 g) to the mother liquor with continued heating. The combined products were recrystallized from water (450 mL, 80 °C) by the addition of KNCS (15 g); yield 9 g, 60%. Anal. Calcd for [$Cr(NCS)_2$(3,2,3-tet)]NCS, $CrC_{11}H_{22}N_7S_3$: Cr, 13.0; C, 33.0; H, 5.5; N, 24.6. Found: Cr, 13.0; C, 33.3; H, 5.8; N, 24.5.

Resolution of *trans*-(*RR*,*SS*)-[$Cr(NCS)_2$(3,2,3-tet)]NCS. The procedure outlined for the *cis*-β-(*RR*,*SS*)-oxalato complex was followed on a half-scale. The less soluble $(-)_{589}$-*trans*-(*RR*)-[$Cr(NCS)_2$-(3,2,3-tet)][HBzOT] crystallized as orange rosettes over a period of 5 days at room temperature in an open beaker. Chiroptical parameters (determined as described under Ion-Exchange Procedures) are listed in Table I. The *RR* configuration was established by warming the solid with 6 M HCl containing a few drops of 30% H_2O_2 and 3 M $HClO_4$. Green crystals of $(-)_{589}$-*trans*-(*RR*)-[$CrCl_2$(3,2,3-tet)]ClO_4 slowly deposited.

Ion-Exchange Procedures. About 100 mg of the $HBzOT^-$ salts of $(-)_{589}$-Cr(ox)(3,2,3-tet)$^+$ or $(-)_{589}$-*trans*-$Cr(NCS)_2$(3,2,3-tet)$^+$ was dissolved in DMF (5 mL) and HCl (3 M, 2 mL). These solutions were diluted to 50 mL with water and the cations adsorbed on a 1 × 10 cm column of Zerolit 225 SRC6 (52–100 mesh, 2% DVB) cation-exchange resin prewashed with 50 mL of 1 M HCl and 3 bed-volumes of water, and the complex cations were eluted with 1 M HCl. The first 10 mL of effluent was discarded, and the cations were completely removed from the column by the next 50 mL. ORD, CD, and visible absorption spectra were recorded as quickly as possible, and complex concentrations were estimated from the absorption spectral parameters of the racemates (Table II).

Kinetics. Spectrophotometrically determined rate constants were determined with use of either spectral scans or fixed-wavelength techniques. For the base hydrolysis studies, $[OH^-]$ was >10[complex] to ensure pseudo-first-order conditions.

Small amounts of the complex were added to the appropriate solvent (preheated to the desired temperature) in a 1.00-cm spectrophotometer cell, and spectral scans were recorded to establish the position of isosbestic points and to determine the most appropriate wavelength for kinetic studies. Temperature control (±0.01 °C) was maintained on both sample and reference cell holders by circulating water from a thermostated water bath.

Pseudo-first-order rate constants (k) were calculated from the variation of absorbance with time trace with the expression

$$kt = \ln \frac{A_\infty - A_0}{A_\infty - A_t}$$

where A_0, A_∞, and A_t are the observed absorbance data at time zero, at the end of the reaction (8–10 half-lives), and at time = t (s). For reactions in basic solution, the second-order rate constant, k_{OH}, was calculated with the relationship

$$k_{OH} = k[OH^-]^{-1}$$

Pseudo-first-order rate constants were also obtained from the uptake of OH^- (0.1 M) with time with use of a pH stat. The set pH was converted to $[OH^-]$ by using the expression $-\log [OH^-] = pK_{wc} + \log \gamma_\pm$ – set pH, where $\log \gamma_\pm = 0.105$ for $\mu = 0.1$ M (NaCl) and $pK_{wc} = 13.779$ at 25.0 °C. The pH meter was calibrated with 0.01 M borax solution (pH 9.18 at 25.0 °C).

Instrumentation. Visible absorption spectra were measured with a Varian Superscan recording spectrophotometer and the ORD and CD spectra with a JASCO ORD/CD-5 recording spectropolarimeter. Infrared spectra were measured in Nujol mulls with a Shimadzu IR spectrometer. Halide concentrations were determined by potentiometric titration using a Radiometer TTTlc automatic titrator. This same instrument was used in the pH stat mode for some of the base hydrolysis studies. C, H, and N determinations were performed by

Table I. Chiroptical Parameters for Some Optically Active $CrX_2(N_4)^{n+}$ Complexes

complex	solvent	λ, nm										ref
		CD Spectra[a,b]										
$\Delta(-)_{589}$-Cr(ox)$(en)_2^+$	1 M HCl	480 (−2.12)	392 (0)	365 (+0.16)	345 (0)	330 (−0.07)						*c*
$\Delta(-)_{589}$-β-(*RR*)-Cr(ox)(3,2,3-tet)$^+$	1 M HCl	472 (−1.00)	370 sh (−0.06)	330 (0)								*d*
$\Delta(-)_{589}$-*cis*-$CrCl_2(en)_2^+$	0.8 M $HClO_4$	580 (−0.442)	544 (0)	501 (+0.515)	440 (+0.192)	412 (+0.256)	377 (0)	356 (−0.096)				*e*
$\Delta(-)_{589}$-*cis*-β-(*RR*)-$CrCl_2$(3,2,3-tet)$^+$	3 M HCl	583 (−0.404)	552 (0)	506 (+0.838)	430 (+0.281)	406 (+0.20)						*d*
$\Delta(-)_{589}$-*cis*-Cr$(en)_2(OH_2)_2^{3+}$	1.5 M $HClO_4$	528 (+0.170)	505 (0)	464 (−0.562)	373 (0)	360 (+0.02)	340 (0)	330 (−0.007)				*e*
$\Delta(-)_{589}$-*cis*-β-(*RR*)-Cr(3,2,3-tet)-$(OH_2)_2^{3+}$	1.0 M HNO_3 + Hg^{2+}	540 (+0.721)	511 (0)	472 (−1.64)	404 (0)	366 (+0.182)						*d*
$(-)_{589}$-*trans*-(*RR*)-$CrCl_2$(3,2,3-tet)$^+$	3 M HCl	590 (−0.107)	528 (−0.017)	457 (−0.167)	424 (−0.117)	368 (−0.191)	303 (0)					*d, f*
$(-)_{589}$-*trans*-(*RR*)-Cr$(NCS)_2$(3,2,3-tet)	1 M HCl	428 (−0.223)	472 (−0.218)	452 (−0.228)	402 (−0.060)	366 (−0.144)						*d*
$(?)_{589}$-*trans*-(*RR*)- + $(+)_{589}$-*cis*-β-(*RR*)-Cr(3,2,3-tet)$(OH_2)_2^{3+}$ mixture	0.8 M HNO_3 + Hg^{2+}	534 (+0.397)	506 (0)	468 (−0.923)								*d*
		ORD Spectra[a,g]										
$\Delta(-)_{589}$-Cr(ox)$(en)_2^+$	1 M HCl	589 (−1230)	525 (−3190)	488 (0)	445 (+4370)	390 sh (+3000)	353 (+2000)	320 sh (+2640)				*c*
$\Delta(-)_{589}$-β-(*RR*)-Cr(ox)(3,2,3-tet)$^+$	1 M HCl	589 (−472)	507 (−1372)	478 (0)	440 (+2078)	370 (+1387)						*d*
$\Delta(-)_{589}$-*cis*-$CrCl_2(en)_2^+$	0.8 M $HClO_4$	638 (+435)	605 (0)	589 (−680)	548 (−2300)	500 (0)	472 (+612)	436 (+235)	392 (+1265)	352 (+432)		*e*
$\Delta(-)_{589}$-*cis*-β-(*RR*)-$CrCl_2$(3,2,3-tet)$^+$	3 M HCl	625 (+125)	608 (0)	589 (−601)	546 (−2337)	502 (0)	464 (+1190)	420 (+877)	370 (+1070)			*d*
$\Delta(-)_{589}$-*cis*-Cr$(en)_2(OH_2)_2^{3+}$	1.5 M $HClO_4$	589 (−24)	503 (−1460)	468 (0)	435 (+986)	400 sh (+752)	351 (+414)	310 sh (+566)				*e*
$\Delta(+)_{589}$-*cis*-β-(*RR*)-Cr(3,2,3-tet)-$(OH_2)_2^{3+}$	1.0 M HNO_3 + Hg^{2+}	589 (+424)	580 (+429)	562 (0)	507 (−4290)	472 (0)	437 (+2680)					*d*
$(-)_{589}$-*trans*-(*RR*)-$CrCl_2$(3,2,3-tet)$^+$	3 M HCl	630 (−300)	589 (−31)	584 (0)	570 (+32)	551 (0)	494 (−260)	460 (0)	434 (+124)	410 (+78)	346 (+626)	308 (+442)	*d*
$(-)_{589}$-*trans*-(*RR*)-Cr$(NCS)_2$(3,2,3-tet)$^+$	1 M HCl	589 (−170)	526 (−377)	514 (−368)	517 (−375)	470 sh (−290)	466 (0)	426 (+434)	388 (+196)			*d*
$(?)_{589}$-*trans*-(*RR*)- + $(+)_{589}$-*cis*-β-(*RR*)-Cr(3,2,3-tet)$(OH_2)_2^{3+}$ mixture	0.82 M HNO_3 + Hg^{2+}	589 (+126)	570 (+176)	554 (0)	503 (−2310)	468 (0)	437 (+1305)					*d*

[a] Wavelengths (nm) of extrema and crossover points. [b] $[\Delta\epsilon]_\lambda$ (M^{-1} cm^{-1}) in parentheses. [c] House, D. A. *Inorg. Chim. Acta* **1982**, *60*, 143. [d] This research. [e] Kindred, I. J.; House, D. A. *J. Inorg. Nucl. Chem.* 1975, *37*, 1359. [f] Bosnich, B.; Harrowfield, J. MacB. *Inorg. Chem.* 1975, *14*, 828. [g] $[M]_\lambda$ (deg M^{-1} m^{-1}) in parentheses.

Table II. Visible Absorption Spectral Parameters for Some $Cr(X)_2(3,2,3\text{-tet})^{n+}$ Complexes

complex	solvent	λ, nm (ε, M^{-1} cm^{-1})						
cis-β-(*RR,SS*)-Cr(ox)(3,2,3-tet)$^+$	0.1 M HCl	493 (102)	413 (17)	370 (100)	328 (20)			
cis-β-(*RR,SS*)-$CrCl_2$(3,2,3-tet)$^+$	0.1 M HNO_3	526 (63)	459 (20)	404 (65)	341 (3)			
cis-β-(*RR,SS*)-CrCl(3,2,3-tet)-$(OH_2)^{2+}$	0.1 M HNO_3[a]	503 (65)	435 (22)	385 (51)	336 (11)			
cis-β-(*RR,SS*)-Cr(3,2,3-tet)-$(OH_2)_2^{3+}$	0.1 M HNO_3 + Hg^{2+} [b,d]	490 (59)	424 (23)	376 (45)	346 (29)			
cis-β-(*RR,SS*)-$Cr(OH)_2$(3,2,3-tet)$^+$	0.1 M NaOH	525 (59)	441 (17)	377 (47)				
trans-(*RR,SS*)-$Cr(NCS)_2$-(3,2,3-tet)$^+$	3 M HCl	487 (97)	410 (31)	366 (83)	356 (81)			
trans-(*RR,SS*)-$CrCl_2$(3,2,3-tet)$^+$	3 M HCl	584 (23)	524 (7)	466 sh (40)	452 (45)	432 (43)	413 (44)	328 (4)
trans-(*RR,SS*)-Cr(3,2,3-tet)-$(OH_2)_2^{3+}$	0.9 M HNO_3[c]	530 sh (18)	443 (51)	407 (34)	370 (48)	342 (37)		
trans-(*RR,SS*)- + *cis*-β-(*RR,SS*)-Cr(3,2,3-tet)$(OH_2)_2^{3+}$ mixture (15% cis)	1.0 M HNO_3 + Hg^{2+}	465 (47)	418 (32)	374 (49)	345 (32)			
trans-(*RR,SS*)-$Cr(OH)_2$(3,2,3-tet)$^+$	0.1 M NaOH	489 (41)	435 (28)	395 (32)				

[a] Spectrum 2 h (8 half-lives) after the *cis*-dichloro complex was dissolved in 40 °C 0.1 M HNO_3. [b] Spectrum 24 h after mixing. [c] *trans*-Dichloro complex, with 0.1 M NaOH (2 h) followed by acidification with 1.0 M HNO_3. [d] Identical results were obtained by treating the *cis*-dichloro complex as in footnote *c*.

the microanalytical service of the University of Otago, Dunedin, New Zealand. The method used for Cr analysis has been previously described.[21]

Results

Configurational Assignments. A linear tetraamine ligand can adopt two configurations in a cis complex that have the trivial cis-α and cis-β nomenclature[1,21] (Figure 1). For a cis-α geometry, the positions of the asymmetric *sec*-NH protons are regarded as fixed and point away from the bent C–N–C angle. Thus for 3,2,3-tet and 2,2,2-tet the Λ-cis-α configuration has necessarily the *RR* configuration at the *sec*-NH positions.[3-5,14,30] (Note that for 2,3,2-tet, the exactly similar configuration is assigned the *SS* configuration.[4]) For a cis-β geometry, one *sec*-NH proton is fixed, but the other (at the "planar" *sec*-NH position) can adopt one of two alternate configurations, i.e., Λ-cis-β-(*SS*) or Λ-cis-β-(*R,S*).

The constraints on the system are such that cis-α to cis-β conversion (or vice versa) will result in a geometric inversion (Δ-α ⇄ Λ-β)[26] (Figure 1), but only a proton inversion will lead to the cis-β-(*R,S*) configuration.

In trans complexes of this type, there are again two possible configurations, the (*RR,SS*)-racemic and the (*R,S*)-meso arrangements. In the absence of proton inversions, Λ-cis-β-(*S,S*) will isomerize to trans-(*SS*) and Λ-cis-(*R,S*)-β to trans-(*R,S*). Figure 1 outlines the interconversions (both geometric and chiral) that are possible for 2,2,2-tet and 3,2,3-tet in the absence of proton inversions. The important feature to note is that Λ-cis-(*RR*)-α will isomerize to the trans-(*RR*), while Λ-cis-(*SS*)-β will produce the enantomeric trans-(*SS*). This allows a method of assigning the α or β configurations to a cis complex, providing the isomerizations can be performed and no proton inversions are involved. $Cr(ox)(3,2,3\text{-tet})^+$ must necessarily have a cis configuration, and this complex has been resolved with the hydrogen dibenzoyl-(+)-tartrate anion.[4] The least soluble diatereoisomer has a large negative CD at 470 nm (Table I) and, by comparison with the $Cr(ox)(en)_2^+$ system[31] and the analogous Co(III) complex,[4] is assigned the Δ absolute configuration.

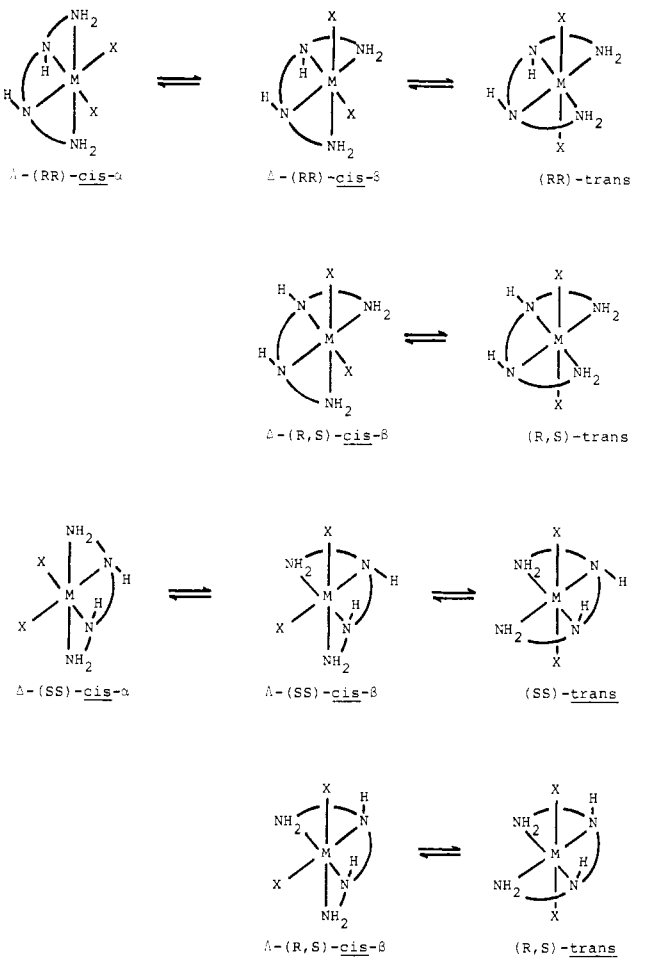

Figure 1. Interconfigurational relationships for a linear quadridentate polyamine ligand in an octahedral transition-metal complex. The *RS* assignments of the *sec*-NH protons are appropriate for 2,2,2-tet and 3,2,3-tet, but for 2,3,2-tet, with entirely equivalent topology, the assignments will be reversed.

It is, however, not possible from the CD spectrum to assign the cis-α or cis-β configuration. (There are, for example, only minor differences in the CD spectra of *cis*-α- and *cis*-β-Co(ox)(2,2,2-tet)$^+$.[4]) Reaction of $\Delta(-)_{589}$-Cr(ox)(3,2,3-tet)$^+$ with

(30) Cragel, J.; Brubaker, G. R. *Inorg. Chem.* **1972**, *11*, 303.
(31) Garner, C. S.; House, D. A. *Transition Met. Chem. (N.Y.)* **1970**, *6*, 59 (Tables 14-16).
(32) Kindred, I. J.; House, D. A. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1359.

Table III. Pseudo-First-Order Rate Constants (k_H) for the First Step in the Acid Hydrolysis of $[CrCl_2(3,2,3\text{-tet})]ClO_4$ in 0.1 M HNO_3

(±)-cis-β-(*RR,SS*)			(±)-trans-(*RR,SS*)		
T, °C [K]	10^4k_H,[a] s^{-1}	10^4k_H(calcd),[b] s^{-1}	*T*, °C [K]	10^4k_H,[c] s^{-1}	10^4k_H(calcd),[b] s^{-1}
44.7 [317.9]	9.16 ± 0.3	9.40	70.0 [343.2]	1.63	1.60
	9.16 ± 0.26			1.53	
	9.25 ± 0.23		73.8 [347.0]	2.31	2.30
	9.78 ± 0.15[d]			2.28	
47.3 [320.5]	12.0 ± 0.3	12.3	76.9 [350.1]	3.14	3.07
	12.2 ± 0.4			3.14	
	12.2 ± 0.3		79.9 [353.1]	4.11	4.05
49.2 [322.4]	14.7 ± 0.5	15.0		3.96	
	14.9 ± 0.9		82.1 [355.3]	5.03	4.95
	15.2 ± 1.0			4.98	
51.1 [324.3]	19.4 ± 0.9	18.2	85.8 [359.0]	6.68	6.89
	19.2 ± 1.0			6.89	
53.2 [326.4]	23.8 ± 1.3	22.5			
	22.6 ± 1.4				
55.2 [328.4]	27.1 ± 2.1	27.5			
	27.9 ± 0.9				
58.1 [331.3]	35.2 ± 1.5	36.5			
	35.2 ± 1.1				

[a] Spectrophotometrically determined by fixed-wavelength techniques at 370 nm, unless otherwise stated. [b] Calculated from the activation parameters cited in Table VIII. [c] Titrimetrically determined. An error of ±5% is estimated for each determination. [d] Monitored at 480 nm.

$SOCl_2$ and a little water,[24] followed by methanol, gives crystals of $\Delta(-)_{589}$-$[CrCl_2(3,2,3\text{-tet})]Cl$ with retained absolute configuration again by comparison with *cis*-$CrCl_2(en)_2^+$ and the analogous Co(III) trien complexes.[1] The same reaction occurs in solution with 12 M HCl. Thus both the oxalato and dichloro complexes must be either cis-α or cis-β as isomerization would lead to inversion. Such an inversion has already been observed in the $Cr(ox)(2,2,2\text{-tet})^+$ system.[26] Treatment of either Δ-$(-)_{589}$-$Cr(ox)(3,2,3\text{-tet})^+$ or $\Delta(-)_{589}$-*cis*-$CrCl_2(3,2,3\text{-tet})^+$ with hot 6 M HCl containing a little $HClO_4$ gives crystals of $(-)_{589}$-*trans*-$[CrCl_2(3,2,3\text{-tet})]ClO_4$, which has been assigned[14,15] to the *RR* configuration by comparison with the analogous Co(III) complex.[12,13,16,17] Thus this sequence of interconversions establishes that both the racemic oxalato and racemic dichloro have the ΔΛ-cis-β-(*RR,SS*) configuration.

Acid Hydrolysis Kinetics. The violet (Table II) *cis*-β-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ cation slowly hydrolyzes the acid solution to give *cis*-β-(*RR,SS*)-$CrCl(3,2,3\text{-tet})(OH_2)^{2+}$ with no evidence for isomerization or Cr–N bond rupture.[23] Spectral scans for this process show sharp isosbestic points at 520, 445, and 390 nm, and the spectrophotometrically determined pseudo-first-order rate constants for this process (0.1 M HNO_3) are presented in Table III. No attempt was made to determine the rate of loss of the second chloro ligand, but addition of Hg^{2+} to acidic (HNO_3) solutions of the dichloro complex gave a spectrum characteristic of a *cis*-diaqua species, presumably *cis*-β-(*RR,SS*)-$Cr(3,2,3\text{-tet})(OH_2)_2^{3+}$ (Table II). For this Hg^{2+}-assisted second hydrolysis step, isosbestic points were observed at 478, 422, and 370 nm. The green *trans*-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ cation is rather inert toward acid hydrolysis, and temperatures in excess of 70 °C were required to obtain a measurable rate. In this case, the rate of loss of the first chloro ligand was determined titrimetrically (Table III). Isosbestic points at 568, 435, and 456 nm were maintained for about 3 half-lives, that is, until the loss of the second chloro ligand became evident. At the high temperature required, the second hydrolysis step appears to be complicated by isomerization and/or Cr–N bond rupture (*trans*-$CrCl_2(cyclam)^+$ behaves similarly[33]). In the presence of Hg^{2+}, the loss of the second chloro ligand holds good isosbestic points at 560, 440, and 388 nm to give a final spectrum (Table II) corresponding to a *cis*-β-diaqua/*trans*-diaqua mixture of about 15% cis-β. This isomerization proceeds with retention of *sec*-NH proton configuration, as there is a dramatic increase in the CD intensity for the diaqua product mixture when the reaction is performed with $(-)_{589}$-*trans*-(*RR*)-$CrCl_2(3,2,3\text{-tet})^+$ in 0.82 M HNO_3 containing 5.7×10^{-2} M Hg^{2+} (Table I).

(33) Campi, E.; Ferguson, J.; Tobe, M. L. *Inorg. Chem.* **1970**, *9*, 1781.

Table IV. Observed and Calculated Rate Constants for the Base Hydrolysis of *cis*-β-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ (μ = 0.1 M, NaCl)

cis-β-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ [a]

pH[b]	$10^5 \times [OH^-]$,[c] M	10^4k_{obsd},[d] s^{-1}	k_{OH}(calcd),[e] $M^{-1}\ s^{-1}$
9.08	1.57	2.22 ± 0.05	11.2
		2.49 ± 0.05	
		2.28 ± 0.04	
9.57	4.85	6.42 ± 0.14	
9.58	4.97	7.68 ± 0.12	
9.78	7.87	10.0 ± 0.24	
		9.34 ± 0.31	

cis-β-(*RR,SS*)-$Cr(OH)(Cl)(3,2,3\text{-tet})^+$ [f]

$[OH^-]$, M	10^3k_{obsd},[d] s^{-1}	10^2k_{OH},[g] $M^{-1}\ s^{-1}$
0.101[h]	4.25 ± 0.26	4.23 ± 0.26
	3.94 ± 0.21	3.91 ± 0.21
	4.00 ± 0.54	3.98 ± 0.54
	4.02 ± 0.25	4.00 ± 0.25
0.101[i]	3.98 ± 0.30	3.96 ± 0.38
	4.04 ± 0.50	4.00 ± 0.48
	4.08 ± 0.37	4.06 ± 0.37
	3.90 ± 0.28	3.88 ± 0.28
		av 4.00 ± 0.11

[a] Determined by pH stat; T = 25.0 °C (298.2 K). [b] Set pH. [c] Calculated with methods outlined in the Experimental Section. [d] Observed pseudo-first-order rate constant. [e] Calculated from the slope of the linear $[OH^-]$ vs. k_{obsd} plot. [f] Determined spectrophotometrically, isosbestic points at 515, 467, and 350 nm; T = 25.0 °C (298.2 K). [g] $k_{OH} = k_{obsd}[OH^-]^{-1}$. [h] Fixed wavelength at 570 nm. [i] Fixed wavelength at 440 nm.

Base Hydrolysis Kinetics. The first hydrolysis step for *cis*-β-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ was measured in basic solution with a pH stat (μ = 0.1 M NaCl) (Table IV). The rate constants for the two steps shown in eq 1 and 2 are well

$$cis\text{-}\beta\text{-}CrCl_2(3,2,3\text{-tet})^+ + OH^- \xrightarrow{k_{OH'}} CrCl(OH)(3,2,3\text{-tet})^+ \quad (1)$$

$$CrCl(OH)(3,2,3\text{-tet})^+ + OH^- \xrightarrow{k_{OH''}} cis\text{-}\beta\text{-}Cr(OH)_2(3,2,3\text{-tet})^+ \quad (2)$$

Table V. Spectrophotometrically Determined Rate Constants for the Base Hydrolysis of *trans*-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ at $\mu = 0.1$ M (NaCl)[a]

T, °C [K]	$[OH^-]$,[b] mM	$10^3 k_{obsd}$,[c] s^{-1}	$10k_{OH}$,[d] M^{-1} s^{-1}	$10k_{OH}$(calcd),[e] M^{-1} s^{-1}
28.1 [301.3]	5	3.76 ± 0.2	7.52 ± 0.4	8.29
	10	8.36 ± 0.2	8.36 ± 0.2	
24.4 [297.6]	5	2.79 ± 0.05	5.58 ± 0.1	5.56
		2.60 ± 0.05	5.20 ± 0.1	
		2.83 ± 0.1	5.66 ± 0.2	
	10	5.52 ± 0.1	5.52 ± 0.1	
	20	11.4 ± 0.2	5.85 ± 0.1	
		11.7 ± 0.4	5.70 ± 0.2	
	10[f]		6.97 ± 0.4	
	20[g]		6.85 ± 0.4	
			6.65 ± 0.2	
21.8 [295.0]	5	1.96 ± 0.08	3.92 ± 0.2	3.92
	10	3.99 ± 0.1	3.99 ± 0.1	
	20	8.56 ± 0.2	4.28 ± 0.1	
18.0 [291.2]	5	1.12 ± 0.04	2.42 ± 0.08	2.46
	10	2.39 ± 0.05	2.39 ± 0.05	
	20	5.13 ± 0.3	2.56 ± 0.15	
14.2 [287.4]	10	1.52 ± 0.05	1.52 ± 0.05	1.52
	20	3.14 ± 0.1	1.57 ± 0.05	
10.3 [283.5]	20	1.79 ± 0.07	0.90 ± 0.14	0.92
	20	1.86 ± 0.05	0.93 ± 0.1	
	20	1.76 ± 0.05	0.88 ± 0.1	

[a] Complex concentration ca. 0.5 mM. Rate data for loss of first chloro ligand are given, with the reaction monitored at 530 nm. [b] Prepared by dilution of 0.1 M NaOH with 0.1 M NaCl. [c] Observed pseudo-first-order rate constant. [d] $k_{OH} = k_{obsd}[OH^-]^{-1}$. [e] k_{OH} calculated from the activation parameters cited in Table IX. [f] $\mu = 0.01$ M. [g] $\mu = 0.02$ M.

Table VI. Spectrophotometrically Determined Rate Constants for the Base Hydrolysis of *trans*-(*RR,SS*?)-$Cr(OH)(Cl)(3,2,3\text{-tet})^+$ at $\mu = 0.1$ M (NaCl)[a]

T, °C [K]	$[OH^-]$, M	$10^3 k_{obsd}$,[b] s^{-1}	$10^2 k_{OH}$,[c] M^{-1} s^{-1}	$10^2 k_{OH}$(calcd),[d] M^{-1} s^{-1}
26.8 [300.0]	0.1	1.19 ± 0.02	1.19 ± 0.02	1.11
28.3 [301.5]	0.1	1.35 ± 0.03	1.35 ± 0.03	1.35
30.1 [303.3]	0.1	1.71 ± 0.01	1.71 ± 0.01	1.70
33.4 [306.6]	0.1	2.61 ± 0.02	2.61 ± 0.02	2.58
36.1 [309.3]	0.1	3.75 ± 0.04	3.75 ± 0.04	3.60
39.1 [312.3]	0.1	5.56 ± 0.08	5.56 ± 0.08	5.18
	0.075	4.01 ± 0.04	5.34 ± 0.10	
	0.05	2.22 ± 0.04	4.44 ± 0.08	
		2.30 ± 0.09	4.60 ± 0.17	
42.5 [315.7]	0.1	7.03 ± 0.07	7.03 ± 0.07	7.75
	0.075	6.56 ± 0.07	8.74 ± 0.09	
	0.05	3.65 ± 0.01	7.30 ± 0.03	
44.7 [317.9]	0.1	9.12 ± 0.04	9.12 ± 0.04	10.0
	0.075	7.28 ± 0.03	9.71 ± 0.04	
	0.05	5.12 ± 0.03	10.24 ± 0.05	
48.1 [321.3]	0.075	12.4 ± 0.06	16.5 ± 0.08	14.8
	0.05	8.12 ± 0.03	16.2 ± 0.06	

[a] Complex concentration ca. 0.5 mM. The reaction was monitored at 380 nm. [b] Observed pseudo-first-order rate constant. [c] $k_{OH} = k_{obsd}[OH^-]^{-1}$. [d] Calculated from the activation parameters cited in Table IX.

separated, and satisfactory "infinity" data were obtained for the first stage. A linear plot of k_{obsd} vs. $[OH^-]$ was obtained, which, at zero $[OH^-]$, extrapolates to a value of 0.8×10^{-4} s^{-1} at 298.2 K, in approximate agreement with the acid hydrolysis rate constant (Table VIII) at the same temperature. A value of $k_{OH}'(298.2\text{ K}) = 11.2$ M^{-1} s^{-1} was calculated from the slope of the k_{obsd} vs. $[OH^-]$ plot. The second hydrolysis step was determined spectrophotometrically in dilute NaOH ($\mu = 0.1$ M, NaCl) to give a value of $k_{OH}'' = 4.0 \times 10^{-2}$ M^{-1} s^{-1} (Table IV). Acidification of the final solution gave a diaqua species with a spectrum identical with that produced by the Hg^{2+}-assisted aquation of *cis*-β-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$. This suggests that no proton inversion or isomerization occurs during the base hydrolysis process.

The base hydrolysis rates of the *trans*-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ cation are much slower than those of the cis-β-(*RR,SS*) analogue and were measured spectrophotometrically in NaOH solution ($\mu = 0.1$ M). Again the first and second hydrolysis steps are well separated (Table V and VI) by a factor of 65 at 298.2 K. Isosbestic points observed were at 570, 468, and 392 nm and 532, 482, and 348 nm for the first and second base hydrolysis steps, respectively. Acidification of the final solution gave an absorption spectrum expected for a *trans*-diaqua complex (Table II), but this did not change to the equilibrium *cis*-β-diaqua/*trans*-diaqua mixture observed as the final product from the Hg^{2+}-assisted chloride release of the *trans*-dichloro complex. This implies that Hg^{2+} is, in some way, affecting the stereochemistry of the aquation of the *trans*-dichloro complex, a situation previously observed in the Hg^{2+}-assisted aquation of *trans*-(*RR,SS*)-$CoCl_2(2,2,2\text{-tet})^+$.[34] Anation of the *trans*-diaqua complex with 80 °C 6 M HCl containing $HClO_4$ slowly produced the *trans*-(*RR,SS*)-dichloro perchlorate.

(34) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 2172.

Table VII. Spectropolarimetrically Determined Rate Constants for the Racemization of *trans*-(*RR*)-$CrCl_2(3,2,3\text{-tet})^+$ in 0.1 M Borax[a]

T, °C [K]	pH	$10^5[OH^-]$ [b]	$10^4 k_{obsd}$, s^{-1}	k_{OH}, [c] $M^{-1}\ s^{-1}$	k_{OH}(calcd), [d] $M^{-1}\ s^{-1}$
25.0 [298.2]	9.180	1.98	1.19 ± 0.05	6.01	5.93
			1.15 ± 0.15	5.81	
27.7 [300.9]	9.158	2.32	1.89 ± 0.04	8.15	8.18
29.6 [302.8]	9.142	2.60	2.75 ± 0.04	10.6	10.2
31.8 [305.0]	9.125	2.95	3.79 ± 0.06	12.9	13.2

[a] Complex concentration ca. 2 mM in a 5.0-cm cell. The reaction was followed by changes in the CD spectrum at 452 nm. [b] Calculated from the expression $-\log [OH^-] = pK_{wc} + 0.105 - pH$. Values for pK_{wc} were 13.779, 13.658, 13.622, and 13.551 at 25.0, 27.7, 29.6, and 31.8 °C, respectively. [c] $k_{OH} = k_{obsd}[OH^-]^{-1}$. [d] Calculated from the activation parameters $E_a = 88.7 \pm 3.5$ kJ mol^{-1}, $\log PZ = 16.309$, and $\Delta S^{\ddagger}_{298.2} = 59 \pm 7$ J K^{-1} mol^{-1}.

Table VIII. Activation Parameters for the Acid Hydrolysis of Some $CrCl_2(N_4)^+$ Complexes at 298.2 K[a]

N_4	k_H, s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	ref
	trans-$CrCl_2(N_4)^+$			
$(NH_3)_4$	4.5×10^{-5}	91	−25	*b, r*
$(en)_2$	2.2×10^{-5}	97	−17	*c*
$[(R,S)\text{-pn}]_2$	$\sim 3 \times 10^{-5}$			*d*
(en)(tn)	1.93×10^{-5}	98	−15	*e*
$(tn)_2$	2.08×10^{-5}	103	+1	*f, g*
(*R,S*?)-(2,3,2-tet)	3.23×10^{-6}	107	0	*h*
(*RR,SS*)-(3,2,3-tet)	1.06×10^{-6}	94.7 ± 1.3	−50 ± 3	*i*
(*R,S,S,R*?)-(cyclam)	2×10^{-8}	116	−8	*j*
(*R,S,S,R*?)-(tet*a*)	1.26×10^{-5}	92.6 ± 2.4	−37 ± 5	*k*
	cis-$CrCl_2(N_4)^+$			
$(NH_3)_4$	2.12×10^{-4}	89.7	−14	*r*
$(en)_2$	3.3×10^{-4}	89	−24	*l*
$[(R,S)\text{-pn}]_2$	3.5×10^{-4}			*m*
α-(2,2,2-tet)	1.9×10^{-4}	89	−27	*n*
β?-(2,2,2-tet)	3.13×10^{-2} (0 °C)			*o*
	6.4×10^{-3} (0 °C)			
β?-(2,3,2-tet)	4.12×10^{-4}	74.2 ± 1.7	−69 ± 3	*p, q*
β-(*RR,SS*)-(3,2,3-tet)	1.02×10^{-4}	88.7 ± 1.6	−32 ± 3	*i*
cyclam	2.5×10^{-5}	96	−21	*j*

[a] A question mark indicates uncertainty in geometric configuration. [b] Hoppenjans, J. B.; Hunt, J. B.; Gregoire, C. R. *Inorg. Chem.* **1968**, *7*, 2506. [c] MacDonald, D. J.; Garner, C. S. *J. Inorg. Nucl. Chem.* **1961**, *18*, 219. [d] Barona, R. R.; McLean, J. A. *Inorg. Chem.* **1971**, *10*, 286. The value was estimated from data at 35 °C with use of the activation parameters for *trans*-$CrCl_2(en)_2^+$. [e] Couldwell, M. C.; House, D. A.; Powell, H. K. J. *Ibid.* **1973**, *12*, 627. [f] Couldwell, M. C.; House, D. A. *Ibid.* **1972**, *11*, 2024. [g] Couldwell, M. C.; House, D. A. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 947. [h] Kutal, C.; Adamson, A. W. *Inorg. Chem.* **1973**, *12*, 1990. [i] This research. [j] Campi, E.; Ferguson, J.; Tobe, M. L. *Inorg. Chem.* **1970**, *9*, 1781. [k] Yang, D.; House, D. A. *Inorg. Chim. Acta* **1982**, *64*, L167. [l] Selbin, J.; Bailar, J. C. *J. Am. Chem. Soc.* **1957**, *79*, 4285. [m] Esparza, M.; Garner, C. S. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2377. [n] Hsu, C. Y.; Garner, C. S. *Inorg. Chim. Acta* **1967**, *1*, 17. [o] Fordyce, W. A.; Sheridan, P. S.; Zinato, E.; Riccieri, P.; Adamson, A. W. *Inorg. Chem.* **1977**, *16*, 1154. [p] Yang, D.; House, D. A., unpublished research. [q] Bosnich, B.; Gillard, R. D.; MacKenzie, E. D.; Webb, G. A. *J. Chem. Soc. A* **1966**, 1331. [r] Monsted, L.; Monsted, O. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 917.

Isomerization and Racemization Reactions. Although we have used the sequence shown in eq 3 as a synthetic route, we

$$cis\text{-}\beta\text{-}(RR,SS)\text{-}CrCl_2(3,2,3\text{-tet})^+ \xrightarrow[90\text{–}100\ °C]{HCl/HClO_4} trans\text{-}(RR,SS)\text{-}[CrCl_2(3,2,3\text{-tet})]ClO_4 \quad (3)$$

are unable to pinpoint the precise species involved in this isomerization process. Heating *cis*-β-(*RR,SS*)-Cr(3,2,3-tet)$(OH_2)_2^{3+}$ in 1 M HNO_3 containing 7.44×10^{-2} M Hg^{2+} at 80 °C results in complete decomposition, and changing to 1 M $HClO_4$ containing 2×10^{-2} M Hg^{2+} gives no improvement. It may be that insolubility of the *trans*-dichloro perchlorate salt in $HClO_4$ is the major factor in its isolation. This same problem has been commented on previously[35] with regard to the isomerization of *cis*-$CrCl_2(en)_2^+$ to insoluble *trans*-$[CrCl_2(en)_2]HgCl_3$.[36]

Treatment of $(-)_{589}$-*trans*-(*RR*)-$CrCl_2(3,2,3\text{-tet})^+$ with base results in loss of optical activity at a much greater rate than chloride release. The rate of racemization has been measured spectropolarimetrically in 0.1 M $Na_2B_2O_3 \cdot H_2O$ (pH 9.2) solution at 298.2 K to give a pseudo-first-order rate constant of 1.17×10^{-4} s^{-1} and thus an assumed second-order rate constant of 5.93 M^{-1} s^{-1} (Table VII).

Discussion

Table VIII presents the activation parameters obtained from the literature for the acid hydrolysis of a variety of *cis*- and *trans*-$CrCl_2(N_4)^+$ complexes. There is a growing consensus that the aquation process for haloaminechromium(III) complexes involves a much more associative mechanism than is currently accepted for the analogous cobalt(III) systems.[37] Nevertheless, when rate data are compared within the two systems, care must be taken that the complex stereochemistries are similar. Two structural features have a significant effect on the aquation rates of Co(III) systems: (a) the size of the chelate ring and (b) the conformation of the *sec*-NH protons. We have shown earlier that the "ring size effect", so important in bis(diamine)cobalt(III) chemistry, in negligible in the analogous complexes of Cr(III).[38] The effect of increasing

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Table IX. Activation Parameters for the Base Hydrolysis of Some $CrX_2(N_4)^+$ Complexes at 298.2 K, $\mu = 0.1$ M[a]

N_4	k_{OH}, M^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$, J K^{-1} mol^{-1}	ref
	trans-$CrCl_2(N_4)^+$			
$(en)_2$	3.7×10^{-2}			*b*
(*RR,SS*)-(3,2,3-tet)	5.8×10^{-1}	87.7 ± 1.2	+36 ± 3	*c*
(*R,S,S,R*?)-(cyclam)	1.6 (299.5 K)			*d*
(*R,S,S,R*?)-(tet*a*)	145	116	+179	*e*
	cis-$CrCl_2(N_4)^+$			
$(en)_2$	2.7×10^{-2}			*b*
β-(*RR,SS*)-(3,2,3-tet)	11.2			*c*
cyclam	8.6 (299.5 K, $\mu = 0.74$ M)			*d*
	trans-$CrCl(OH)(N_4)^+$			
$(en)_2$	4×10^{-3}			*f*
(*RR,SS*?)-(3,2,3-tet)	8.81×10^{-3}	97.3 ± 2.5	+33 ± 5	*c*
(*R,S,S,R*?)-(cyclam)	1.1×10^{-2} (299.5 K)			*d*
(*R,S,S,R*?)-(tet*a*)	~100			*e*
	cis-$CrCl(OH)(N_4)^+$			
$(en)_2$	3×10^{-4}			*f*
β-(*RR,SS*?)-(3,2,3-tet)	4.0×10^{-2}			*c*
cyclam	4.6×10^{-2} (298.7 K)	109	+85	*d*

[a] A question mark indicates uncertainty in stereochemical assignment. [b] Pearson, R. G.; Munson, R. A.; Basolo, F. *J. Am. Chem. Soc.* **1958**, *80*, 504. [c] This research. [d] Campi, E.; Ferguson, J.; Tobe, M. L. *Inorg. Chem.* **1970**, *9*, 1781. [e] House, D. A.; Hay, R. W. *Inorg. Chim. Acta* **1981**, *54*, L145. [f] Olson, D. C.; Garner, C. S. *Inorg. Chem.* **1963**, *2*, 415, 558.

the degree of chelation in both *cis*- and *trans*-$CrCl_2(N_4)^+$ systems (Table VIII) causes a decrease in the rate constant, mainly reflected in an increase in activation energy. For example, in the trans systems, the rate order is $(en)_2$ < 2,3,2-tet < 3,2,3-tet < cyclam. Nevertheless, even this trend may be fortuitous as it is not known with any assurance if the *sec*-NH proton configurations are similar in the linear tetraamine cases. Indeed, the evidence available may even suggest a contrary opinion as *trans*-$CrCl_2(3,2,3\text{-tet})^+$ is known to have the *RR,SS* configuration, whereas *trans*-$CrF_2(2,3,2\text{-tet})^+$ has the *R,S* arrangement.[28] We note, however, that the *trans*-$CrCl_2(2,3,2\text{-tet})^+$ salt used in the kinetic studies[27] was not synthesized via the *trans*-difluoro complex. Data from this laboratory[39] indicate that *trans*-$CrCl_2(tet\,a)^+$ (tet*a* = *C-meso*-Me_6cyclam) aquates about 10^3 times faster than *trans*-$CrCl_2(cyclam)^+$.[33] Despite a more associative mechanism, axial methyl acceleration[40,41] could still be the basis for the observed rate difference between *trans*-$CrCl_2(tet\,a)^+$ and *trans*-$CrCl_2(cyclam)^+$, as has been proposed for the Co(III) analogues.[41] However, the *sec*-NH proton conformations for both of these Cr(III) complexes are unknown, and aquation rate differences of this magnitude have been attributed to such conformational changes in Co(III) systems. In this respect we note that the labile[42] *trans*-(*RRRR,SSSS*)-$CoCl_2(cyclam)^+$ aquates 1590 times faster[43] than the trans-(*R,S,S,R*) isomer and *trans*-(*RR,SS*)-$CoCl_2(2,3,2\text{-tet})^+$ aquates 19 times faster[7] than the trans-(*R,S*) form. It is clear that much more information on *sec*-NH proton conformations is necessary in these *trans*-$CrCl_2(N_4)^+$ systems before meaningful structure/reactivity patterns can be established. The situation in the *cis*-$CrCl_2(N_4)^+$ systems (Table IX) is not much better. The strained *cis*-β-$CrCl_2(trien)^+$ cations are very labile,[24] but there is little difference in the aquation rates or activation parameters for *cis*-$CrCl_2(en)^+$, *cis*-α-$CrCl_2(trien)^+$, and *cis*-β-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$. The more associative nature of aquation in Cr(III)–amine complexes is again illustrated by the observation that while *cis*-$CoCl_2(cyclam)^+$ aquates[44] more rapidly than *cis*-$CoCl_2(en)_2^+$ the reverse is true for the Cr(III) pair (Table VIII).

The mechanism of base hydrolysis of Cr(III) amine complexes (Table IX) has been the subject of some discussion.[45] Reaction rates can be several orders of magnitude less than those observed for the analogous Co(III) systems, and background solvolysis is often competitive. Thus, if a conjugate base mechanism is operative in Cr(III) systems, either the NH protons must be much less acidic or the derived conjugate base much less labile. The kinetic parameters for the racemization and base hydrolysis of *trans*-(*RR*)-$CrCl_2(3,2,3\text{-tet})^+$ reported here suggest that a conjugate base mechanism is operative, at least for this complex, and that the rate difference between Co(III) and Cr(III) is due to a marked reduction of NH proton acidity for Cr(III) amines. The rate constant for the base hydrolysis of *trans*-(*RR,SS*)-$CrCl_2(3,2,3\text{-tet})^+$ is k_{OH} = 0.58 M^{-1} s^{-1} at 298.2 K (loss of first chloro ligand), and this can be compared with $k_{OH} = 1 \times 10^5$ M^{-1} s^{-1} [46] for the Co(III) analogue. Bosnich et al.[14] have made some qualitative observations on the rate of racemization of *trans*-(*RR*)-$Co(3,2,3\text{-tet})(OH_2)_2^{3+}$, which is complicated by concurrent cis-β-(*RR*) isomerization. The diaqua complex racemizes slowly in acid solution, and there is a dramatic rate increase when the hydroxoaqua complex is present. In comparison, the rate of racemization of $Co(OH)_2(3,2,3\text{-tet})^+$ is again a much slower process, although proton exchange is "instantaneous". Because of the slower rate of base hydrolysis of $(-)_{589}$-*trans*-(*RR*)-$CrCl_2(3,2,3\text{-tet})^+$, as compared to that of the Co(III) analogue,[46] we have been able to measure the rate of racemization of the dichloro complex directly (Table VII) and find this to be about 10 times faster than chloride release but with an identical activation energy. Comparable activation energies for racemization and chloride release are expected if *sec*-NH deprotonation is involved in both processes.

As racemization must proceed via the *R,S* configuration, the possibility that the diaqua complex resulting from acidification of base-hydrolyzed solutions of the *trans*-(*RR,SS*)-dichloro complex may contain some of the *trans*-(*R,S*) isomer

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cannot be excluded, although we have no evidence for it at this stage.

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Registry No. *cis*-β-(*RR*,*SS*)-[Cr(ox)(3,2,3-tet)]ClO_4, 81688-76-8; $\Delta(-)_{589}$-*cis*-β-(*RR*)-[Cr(ox)(3,2,3-tet)][HBzOT], 81739-55-1; $\Lambda(+)_{589}$-*cis*-β-(*SS*)-[Cr(ox)(3,2,3-tet)]ClO_4, 81739-53-9; $\Lambda(-)_{589}$-*cis*-β-(*RR*)-[Cr(ox)(3,2,3-tet)]ClO_4, 81739-56-2; *cis*-β-(*RR*,*SS*)-[$CrCl_2$(3,2,3-tet)]ClO_4, 81738-84-3; $\Delta(-)_{589}$-*cis*-β-(*RR*)-[$CrCl_2$(3,2,3-tet)]ClO_4, 81739-51-7; *trans*-(*RR*,*SS*)-[$CrCl_2$(3,2,3-tet)]NO_3, 81688-78-0; *trans*-(*RR*,*SS*)-[$CrCl_2$(3,2,3-tet)]ClO_4, 81688-79-1; $(-)_{589}$-*trans*-(*RR*)-[$CrCl_2$(3,2,3-tet)]ClO_4, 53625-78-8; *trans*-(*RR*,*SS*)-[$Cr(NCS)_2$(3,2,3-tet)]NCS, 81688-81-5; $(-)_{589}$-*trans*-(*RR*)-[$Cr(NCS)_2$(3,2,3-tet)][HBzOT], 81738-86-5; $\Delta(-)_{589}$-*cis*-β-(*RR*)-[Cr(3,2,3-tet)$(OH_2)_2]^{3+}$, 81739-49-3; *trans*-(*RR*)-[Cr(3,2,3-tet)$(OH_2)_2]^{3+}$, 81739-48-2; *cis*-β-(*RR*,*SS*)-[CrCl(3,2,3-tet)$(OH_2)]^{2+}$, 81688-82-6; *cis*-β-(*RR*,*SS*)-[Cr(3,2,3-tet)$(OH_2)_2]^{3+}$, 81738-87-6; *cis*-β-(*RR*,*SS*)-[Cr$(OH)_2$(3,2,3-tet)]$^+$, 81739-47-1; *trans*-(*RR*,*SS*)-[Cr(3,3,3-tet)$(OH_2)_2]^{3+}$, 81688-29-1; *trans*-(*RR*,*SS*)-[Cr$(OH)_2$(3,2,3-tet)]$^+$, 81688-30-4; *trans*-(*RR*,*SS*)-[Cr(OH)(Cl)(3,2,3-tet)]$^+$, 81688-31-5.

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Proton Association and Metal Stability Constants of 2-Oxalopropionic, α-Ketobutyric, and Acetoacetic Acids

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The proton association constants for the carboxyl protons of 2-oxalopropionic acid (OPA), acetoacetic acid (AAA), and α-ketobutyric acid (AKBA) were determined potentiometrically, and the dissociation constant of the enolic proton of OPA, H_2L, was determined spectrophotometrically. The metal stability constants of AAA and AKBA were calculated for Zn(II), Al(III), and Cu(II) chelates. In all cases complexes having 1:1 molar ratios of ligand to metal ion were formed, and in the aluminum(III) and copper(II) systems 2:1 complexes were also formed. The stability constants of 1:1 OPA chelates of Zn(II), Al(III), and Cu(II) were determined. In addition to 1:1 complexes of OPA, H_2L, formation of a deprotonated species, $MH_{-1}L^-$, was detected for Zn(II) and a 2:1 complex of Al(III), ML_2^-, was detected. The Cu(II) investigation shows the existence of a deprotonated complex, $MH_{-1}L^-$, and of binuclear complexes.

Introduction

Research on the reaction kinetics of α-keto diacids in which the second carboxyl function is located on the β-carbon has been of scientific interest since these substrates are present in biological systems and are subject to enzyme catalysis. The reactions reported to date include spontaneous,[2-10] metal-catalyzed,[7-16] and enzymatic[17,18] decarboxylation, along with the enolization[19-21] dehydration[19,21] and hydration[21] reactions. The substrates that have undergone examination are oxaloacetic acid (OAA), dimethyloxaloacetic acid (DMOAA), fluorooxaloacetic acid (FOAA), and 2-oxalopropionic acid (3-methyl-2-oxobutanedioic acid, OPA).

Initial studies[2,3] on the decarboxylation of OPA, the ketonization of the enolic α-ketobutyric acid intermediate, and the enolization of OPA have been carried out in this laboratory. Sakkab and Martell[2] introduced 2-oxalopropionic acid as a substrate for decarboxylation studies for two reasons. First, the β-protons of OAA in D_2O solutions deuterate while the β-methyl group of OPA provides a direct NMR probe during the decarboxylation process, and second, OPA has the ability to enolize and is thus a better model for OAA than DMOAA. The investigation of the metal-catalyzed decarboxylation is the next step in the ongoing work with OPA, which will eventually culminate in the study of pyridoxamine catalysis. The vitamin B_6-catalyzed systems are of importance since the Schiff bases of OAA and its analogues with pyridoxamine are models for the probable intermediates in the corresponding enzyme-catalyzed biological processes.

The first goal of the present investigation is to determine the stability constants of the metal chelates of OPA with Cu(II), Zn(II), and Al(III) so that when kinetics of the corresponding metal-catalyzed decomposition reactions are examined, rate constants for the decarboxylation of the metal chelates may be calculated. The determination of such rate constants makes possible a quantitative description of the effects of metal ions on decarboxylation. Previous potentiometric studies on oxaloacetic acid have reported 1:1 ligand to metal complexes[12,22-24] along with 2:1 complexes (ML_2)[22,23] and binuclear chelates (M_2L). Kinetic studies[11] of DMOAA inferred the five-membered chelate ring as the active intermediate in decarboxylation with the chelates having six- and seven-membered rings being inactive. Reyes-Zamora and Tsai[25] obtained NMR spectra of europium(III) oxaloacetates and concluded that the five-membered ring is preferably formed with no apparent spectral evidence for formation of the larger chelate rings. Covey and Leussing[14] later agreed that the five-membered species of Zn(II) and OAA is the predominant form in their studies but suggested on the basis of thermodynamic principles that 10–20% of the chelate may exist in the seven-membered ring configuration. The second goal of this investigation is to determine if higher order

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