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Chromium(III) Complexes of the Linear Tetraamine 1,4,8,11-Tetraazaundecane (entnen). Synthesis, Configurational Assignments, Optical Activity and Hydrolysis Kinetics

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The synthesis and resolution of cis-β-*(RR,SS)-Cr(ox)(entnen)*$^+$ *is described and from these, racemic or chiral* cis-α-*CrXY(entnen)*$^{n+}$ *can be prepared. (X = Y = Cl*$^-$*; NCS*$^-$*; CF*$_3$*CO*$_2^-$*; OH*$_2$*: X = Cl, Y = OH*$_2$*). The previously known* trans-*CrCl*$_2$*(entnen)*$^+$ *is assigned to the (RS)-*sec*-NH configuration. Kinetic parameters for the acid hydrolysis of the first chloro ligand from* cis-α-*CrCl*$_2$*(entnen)*$^+$ *are* k_H *(298.2) (0.1 M HNO*$_3$*) = 4.12 × 10*$^{-4}$ *s*$^{-1}$*,* E_a *= 74.2 kJ mol*$^{-1}$*,* $\Delta S^{\#} = -69$ *J K*$^{-1}$ *mol*$^{-1}$*. For base hydrolysis, corresponding data for* trans-*(RS)-CrX*$_2$*(entnen)*$^+$ *are X = Cl,* k_{OH} *(298.2) (0.1 M NaCl) = 0.28 M*$^{-1}$ *s*$^{-1}$*,* E_a *= 97.9,* $\Delta S^{\#} = +65$*; X = Br,* k_{OH} *(298.2) (0.1 M NaCl) = 91.8 M*$^{-1}$ *s*$^{-1}$*,* E_a *= 114,* $\Delta S^{\#} = +167$*; and for* cis-α-*CrCl*$_2$*(entnen)*$^+$*,* k_{OH} *(298.2) (0.1 M NaCl) = 0.52 M*$^{-1}$ *s*$^{-1}$*.*

Introduction

Transition metal complexes of the linear tetraamine ligand entnen can potentially adopt several isomeric configurations (Fig. 1)* [1, 2]. The synthesis of unspecified *cis* and *trans*-dihalo isomers for Cr(III) has previously been described [3–5] but only for *trans*-R,S-CrX_2(entnen)$^+$ (X = F [6], NCS [7]) has the *sec*-NH isomeric configuration been confirmed by single crystal X-ray methods.

In this paper we describe our attempts to extend the available information on Cr(III) entnen complexes.

Experimental

The free amine was prepared by the method of Brubaker and Schaefer [8]. In our hands, the yield

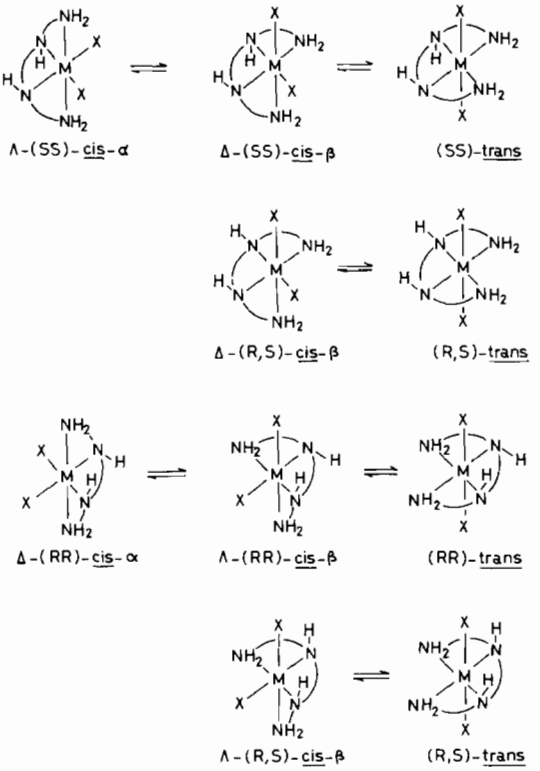

Fig. 1. Interconfigurational relationships for the CrX_2-(entnen)$^{n+}$ system.

*Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tn = NH_2-$(CH_2)_3NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, entnen = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, tnentn = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, cyclam = 1,4,8,11-tetraazacyclotetradecane, teta = C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, ox = oxalate, DMF = dimethylformamide, (+)-H_2BzOT = (−)-dibenzoyltartaric acid, (+)-BCS = (+)-α-bromocamphor-π-sulphonate, TFA = $CF_3CO_2^-$.

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TABLE I. Analytical Data.

	F.W.	Calcd					Found				
		Cr	Cl	C	H	N	Cr	Cl	C	H	N
[Cr(ox)(entnen)]ClO_4	$CrC_9H_{20}N_4ClO_8$	399.73	13.01		27.04	5.04	14.02	13.13		27.18	5.38	13.98
cis-[$CrCl_2$(entnen)]ClO_4	$CrC_7H_{20}N_4Cl_3O_4$	382.61	13.59	18.53	21.97	5.27	14.64	13.22	18.51	21.91	5.41	14.68
t-[$CrCl_2$(entnen)]ClO_4	$CrC_7H_{20}N_4Cl_3O_4$	382.61			21.97	5.27	14.64			22.32	5.53	13.92
t-[$CrBr_2$(entnen)]ClO_4	$CrC_7H_{20}N_4ClBr_2O_4$	471.53			17.83	4.27	11.88			17.91	4.40	11.81
c-[$Cr(NCS)_2$(entnen)]NCS	$CrC_{10}H_{20}N_7S_3$	386.51			31.08	5.22	25.37			31.00	5.24	25.27
[Cr(ox)(entnen)]$BCS \cdot H_2O$	$CrC_{19}H_{36}N_4BrSO_9$	628.49	8.27					8.34				
c-[$Cr(TFA)_2$(entnen)]$ClO_4 \cdot H_2O$	$CrC_{11}H_{22}N_4F_6ClO_5$	555.75			23.77	3.98	10.08			24.05	3.61	10.17

of amine was *ca.* 50% (100 g en and 48 g 1,3-dibromopropane giving 20 g of ligand) and this is probably the experience of others [3, 5, 9, 10] as yields have not previously been reported. *trans*-(R,S)-[CrF_2(entnen)]ClO_4 was prepared as described previously [5].

Analytical data are presented in Table I. **CAUTION**: Although we have had no difficulty with the perchlorate salts of the complexes described in this paper, these should be treated as potentially explosive compounds.

Direct Synthesis of cis- *and* trans-*Dichloro(1,4,8,11-tetraazaundecane)chromium(III) Perchlorate, [$CrCl_2$(entnen)]ClO_4*

Hydrated chromium(III) chloride, $CrCl_3 \cdot 6H_2O$ (8.3 g) was dissolved in DMF (60 ml) and the solution heated to boiling with continuous (magnetic) stirring. Boiling was continued until the volume was reduced to 40 ml and the now violet solution was cooled to about 100 °C. 5 ml of 1,4,8,11-tetraazaundecane was carefully added and the temperature again raised to boiling. Violet crystals of the *cis-/trans*-dichloro chloride isomeric mixture deposited and vigorous stirring was required to prevent 'bumping'. After 5 min boiling, the reaction mixture was allowed to cool to room temperature, the product removed by filtration and washed with 2-propanol and then ether. The yield of crude air dried material was 8.5 g (86%).

2 g of the crude mixture was dissolved in 60 ml of 0.1 *M* HCl and warmed at 80 °C until all the solid had dissolved (*ca.* 5 min). $HClO_4$ (5 ml, 60%) was then added and the resulting green crystals (1.0 g, 40%) of *trans*-[$CrCl_2$(entnen)]ClO_4 that deposited from the cooled, red coloured solution were collected by filtration and washed and dried as above. An equal volume of 12 *M* HCl was added to the aqueous mother liquor which was heated to 80 °C for 15 min. Violet crystals of *cis*-[$CrCl_2$(entnen)]ClO_4 (0.8 g) deposited from the cooled solution overnight. These were collected, washed and dried as above. The *trans*-isomer is assigned to the R,S-configuration and the *cis*- form, to the *cis*-α-RR,SS- (see Discussion).

Indirect Synthesis of trans-*R,S-[$CrCl_2$(entnen)]ClO_4*

trans-R,S-[CrF_2(entnen)]ClO_4 [5, 6] (2.0 g) was suspended in 12 *M* HCl (30 ml) and warmed at 40 °C for 5 min until dissolved. $HClO_4$ (5 ml, 60%) was then added and the reaction mixture was heated on a steam bath (~80 °C) for 1–2 hrs, during which time green crystals (1.5 g) of *trans*-R,S-[$CrCl_2$(entnen)]ClO_4 deposited. These were collected by filtration from the room temperature solution and washed and dried as previously. The IR spectrum of this material was identical to that of the *trans*-isomer prepared in the direct synthesis. This perchlorate salt is only sparingly soluble in water but may be recrys-

tallised from DMF. The perchlorate salt (1 g) was dissolved in 30 ml of 60 °C DMF and 20 ml of 0.1 *M* $HClO_4$ containing 5 g of dissolved $NaClO_4 \cdot H_2O$ was added. The product that deposited was recovered from the ice cooled solution as described above with an almost quantitative yield.

cis-Oxalato(1,4,8,11-tetraazaundecane)chromium(III) Bromide and Perchlorate, cis-*[Cr(ox)(entnen)] ClO_4*

$Na_2Cr_2O_7 \cdot 2H_2O$ (7.0 g) was added in small portions to a slurry of oxalic acid dihydrate (21 g) in water (150 ml). (Care, vigorous CO_2 evolution). The now warm solution was heated on a steam bath for 15 min until all CO_2 evolution ceased, before adding entnen (8.7 g). Steam bath heating was continued for *ca.* 2 hr and NaBr (20 g) was added to the now orange coloured solution. Orange crystals contaminated with sodium oxalate deposited from the ice cooled solution. One recrystallisation from the minimum amount of 60 °C water containing excess NaBr gave 7.5 g of the orange bromide salt of sufficient purity for subsequent resolution. The water insoluble perchlorate salt (3.5 g) was isolated from the mother liquor by the addition of excess $NaClO_4 \cdot H_2O$. The *cis*-β-RR,SS- configuration is assigned to this complex (see Discussion).

Resolution of (±)-cis-β-RR,SS-[Cr(ox)(entnen)]Br

The once recrystallised bromide salt (2.0 g) was dissolved in H_2O (50 ml) at 45 °C and NH_4[(+)BCS]* (2.0 g) was added. A crystalline precipitate (3.0 g of the BCS salt, 30% optically pure Λ) formed immediately and this was filtered from the warm solution and washed with isopropanol and then ether. $NaClO_4 \cdot H_2O$ (5 g) was added to the 45 °C aqueous mother liquor to precipitate 1.2 g of the perchlorate salt (50% optically pure Δ) which was washed and dried as above. The optically impure (+)-BCS salt (3.0 g) was dissolved in 150 ml of 80 °C water and allowed to cool slowly overnight. 0.8 g of optically pure (+)-Λ-*cis*-β-(RR)-[Cr(ox)(entnen)] [(+)BCS] was collected ($[\Delta\epsilon]_{480}$ = +0.91 M^{-1} cm^{-1}, H_2O). Addition of $NaClO_4 \cdot H_2O$ to the mother liquor gave 1.3 g of the racemic perchlorate salt.

The less soluble (+)-BCS enantiomer is a distinct rose red colour, whereas the racemic (+)-BCS salt is orange.

The bromide salt can also be resolved with (+)-H_2BzOT* using the method previously described for similar Cr(III) oxalato tetraamine complexes [1, 11]. In this case the Δ-*cis*-β-(SS)- is the less soluble diastereoisomeride ($[\Delta\epsilon]_{480}$ = −0.90 M^{-1} cm^{-1}).

Indirect Synthesis of (±) or (+)-cis-[$CrCl_2$(entnen)]-ClO_4

(a) [Cr(ox)(entnen)] ClO_4 (3.5 g) was warmed at 40 °C in 15 ml of 12 *M* HCl with the initial orange colour changing to violet (15–30 min, the reaction is complete in 4 hr at room temperature, Fig. 2) $HClO_4$ (5 ml, 60%) was then added, and 2.0 g *cis*-[$CrCl_2$(entnen)] ClO_4, identical to that produced in the direct synthesis, was collected after overnight cooling.

(b) [Cr(ox)(entnen)] ClO_4 (0.5 g) was slurried with $SOCl_2$ (10 ml) plus 3–4 drops of water at room temperature for 6 hr (care HCl fumes). Occasional addition of water or $SOCl_2$ was necessary due to evaporation. Methanol (15 ml) was added dropwise (care, violent reaction), followed by $HClO_4$ (3 ml, 60%). The violet crystals (0.45 g, 84%) were collected one hour later from the ice-cooled solution. This material was identical to that produced by method (a) or the direct synthesis. (+)-Δ-*cis*-α-*(RR)*-[$CrCl_2$-(entnen)] ClO_4 can be obtained from (+)-Λ-*cis*-β-(RR)-[Cr(ox)(entnen)] [(+)BCS] using method (b).

cis-Diisothiocyanato(1,4,8,11-tetraazaundecane)chromium(III) Thiocyanate. Racemic or chiral cis-*[Cr(NCS)$_2$(entnen)]NCS*

2.0 g of *cis*-[$CrCl_2$(entnen)] ClO_4 were dissolved in 50 ml of 60 °C 1 *M* acetic acid (20 min) and 10 g of (NH_4)NCS was added. The solution was heated at 80 °C for 4 hours before collecting 1.0 g of the orange crystalline product. This was washed with 2-propanol and then ether and air dried. The salt is readily soluble in acetone and methanol.

A similar reaction with Λ(−)-cis-α-(SS)-[$CrCl_2$-(entnen)] ClO_4 gave Λ-*cis*-α-(SS)-[Cr(NCS)$_2$(entnen)]-NCS. ($[\Delta\epsilon]_{530}$, 50% acetone/0.1 *M* HCl = +0.083 M^{-1} cm^{-1}).

(±)-cis-α-(RR,SS)-Trifluoroacetato(1,4,8,11-tetraazaundecane)chromium(III) Perchlorate, Monohydrate. [Cr(TFA)$_2$(entnen)] $ClO_4 \cdot H_2O$

2.0 g of *cis*-α-RR,SS-[$CrCl_2$(entnen)] ClO_4 was refluxed with 2 *M* trifluoro acetic acid (50 ml) for four hours to give an orange product (1.7 g) which crystallised on cooling at −5 °C overnight. The solid is soluble in most alcohols and was washed with ether.

Kinetics

Methods used to determine the rates of acid hydrolysis of the first chloro ligand from *cis*-α-$CrCl_2$-(entnen)$^+$ and the rates of base hydrolysis of the first halo ligand from *cis*-α-$CrCl_2$(entnen)$^+$, trans-(R,S)-$CrCl_2$(entnen)$^+$, *trans*-(R,S)-$CrBr_2$(entnen)$^+$ and *trans*-$CrCl_2$(cyclam)$^+$ have been adequately described in previous publications [1, 12, 13].

The perchlorate salt of *cis*-α-$CrCl_2$(entnen)$^+$ was sufficiently soluble in the reaction media used (0.1 *M*

*See footnote on p. 1.

TABLE II. CD Spectral Parameters for Some Λ-*cis*-(SS)-$[CrXY(entnen)]^{n+}$ Complexes.

XY	Solvent	λ (nm), Δε (M^{-1} cm^{-1})								$[M]_{589}$ (° M^{-1} m^{-1})
(+)-β-ox	1 *M* HCl	482	394	366	344	435	420	383	346	+260
		(+0.910)	(0)	(−0.142)	(0)					
(−)-α-Cl_2	12 *M* HCl	550	490	475	450	435	420	383	346	−265
		(−0.190)	(0)	(+0.020)	(0)	(−0.016)	(0)	(+0.113)	(0)	
	DMF	570	550	520	445			386	345	−188
		(+0.094)	(0)	(−0.177)	(0)			(+0.181)	(0)	
(−)-α-(Cl)(OH_2)	0.1 *M*	545	525	485	422	380	350			−425
	HNO_3	(−0.236)	(−0.217)	(−0.326)	(0)	(+0.127)	(0)			
(−)-α-$(OH_2)_2$	0.8 *M*	522	492	460	402	375	300			−334
	$HClO_4$ + Hg^{2+}	(−0.426)	(0)	(+0.485)	(0)	(−0.135)	0			
α-$(TFA)_2$	MeOH	505	445	400sh		370				[a]
		(+0.082)	(0)	(−0.03)		(−0.06)				
α-$(NCS)_2$	50% acetone	530	490	450sh		380				[a]
	0.1 *M* HCl	(+0.083)	(0)	(−0.072)		(−0.216)				

[a]Not measured.

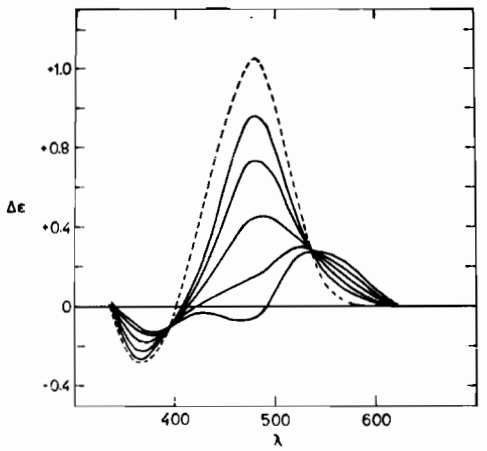

Fig. 2. CD spectral scans with time for the inversion reaction: Λ-*cis*-β-(RR)-Cr(ox)(entnen)$^+$ → Δ-*cis*-α-(RR)-$CrCl_2$(entnen)$^+$ in 12 *M* HCl at room temperature. The dashed curve corresponds to Λ-*cis*-β-Cr(ox)(entnen)$^+$ in 0.1 *M* HCl. Reading downwards at 500 nm (solid lines) the times are 0, 29, 75, 143 and 334 min.

HNO_3 or 0.1 *M* NaCl) but the perchlorate salts of the other complexes were first dissolved in the minimum amount (<1 ml) of dimethylformamide before adding the appropriate reaction medium. Controls showed that rate constant obtained was independent of the amount of DMF used under the experimental conditions.

Results

Dichloro-, difluoro- and oxalato- entnen complexes of chromium(III) have been synthesised using standard procedures [1, 5, 14, 15] and the aniono ligands can be replaced by aquation-anation methods in aqueous acidic solution without extensive Cr—N bond rupture [16].

Cr(ox)(entnen)$^+$ has been resolved with (+)BCS^- or (+)$HBzOT^-$ anions to give the Λ- and Δ-isomers as the less soluble salts, respectively (Fig. 2). The Λ isomer is characterised by a strong positive circular dichroism at 480 nm [11] (Table II) but it is not possible to assign which of the two alternative configurations (*cis*-α-(SS)- or *cis*-β-(RR)-) are adopted (Fig. 1). Treatment of Λ-(+)-Cr(ox)(entnen)$^+$ with 12 *M* HCl (or $SOCl_2/H_2O$) results in conversion to the dichloro, with inversion of configuration (Fig. 2). Thus this system probably follows the course established for Λ-*cis*-β-(SS)-Cr(ox)(trien)$^+$ [17, 18] *viz.*:

$$\Lambda\text{-}cis\text{-}\beta\text{-(RR)-Cr(ox)(entnen)}^+ \xrightarrow{12\,M\ HCl} \Delta\text{-}cis\text{-}\alpha\text{-(RR)-}CrCl_2\text{(entnen)}^+$$

and the chiral or racemic *cis*-α-dichloro have been isolated as the perchlorate salts.

The direct addition of entnen to $CrCl_3 \cdot 6H_2O$, dehydrated in boiling DMF, gives a *cis*- plus *trans*-dichloro mixture with at least 40% *trans* isomer in the purple $[CrCl_2(entnen)]Cl \cdot H_2O$ product. The *cis*- and *trans*- dichloro complexes are readily separated as the perchlorate salts and the *cis*-α-isomer so formed is identical to that produced by the removal of oxalate from Cr(ox)(entnen)$^+$ using either $SOCl_2/H_2O$ [17] or 12 *M* HCl. We suspect that previous preparations [3, 7] of the *cis*-complex have been considerably contaminated with the *trans*- isomer, as the molar extinction coefficients measured for purified *cis*-α-$CrCl_2$(entnen)$^+$ (Table III) are considerably greater than those reported earlier [3].

TABLE III. Visible Absorption Spectral Parameters for some *cis*-$CrXY(N_4)^{n+}$ Complexes.

N_4	X	Y	Solvent	λ_{max}	λ_{min}	λ_{max}	Note
$(en)_2$	Cl	Cl	0.1 *M* HCl	528 (70.6)[b]	456 (20.7)	402 (68.5)	a
α-(RR,SS)-trien	Cl	Cl	0.1 *M* HCl	535 (95.5)	455 (28.5)	396 (86.7)	c,d
β-(RR,SS)-tnentn	Cl	Cl	0.1 *M* HNO_3	526 (63)	459 (20)	404 (65)	e
(?)-entnen	Cl	Cl	1.5 *M* $HClO_4$	527 (78)		404 (76)	f
α-(RR,SS)-entnen	Cl	Cl	0.1 *M* HNO_3	526 (99)	455 (29)	402 (91)	g
$(en)_2$	OH_2	Cl	0.1 *M* HCl	512 (73.5)	440 (21.9)	387 (60.0)	h
α-(RR,SS)-trien	OH_2	Cl	1.5 *M* $HClO_2$	515 (83.5)	440 (25.7)	385 (56.2)	d
β-(RR,SS)-tnentn	OH_2	Cl	0.1 *M* HNO_3	503 (65)	435 (22)	385 (51)	e
α-(RR,SS)-entnen	OH_2	Cl	0.1 *M* HNO_3	509 (94)	447 (26)	386 (75)	g
$(en)_2$	OH_2	OH_2	H^+	484 (67.0)	417 (17)	367 (42.5)	i
α-(RR,SS)-trien	OH_2	OH_2	3 *M* $HClO_4$	497 (72)	420 (22)	372 (36)	d
β-(RR,SS)-trien	OH_2	OH_2	Hg^{2+}/HNO_3	503 (65)	435 (22)	385 (51)	e
α-(RR,SS)-entnen	OH_2	OH_2		483 (82)	415 (25)	366 (56)	g
$(en)_2$	NCS	NCS	0.1 *M* $HClO_4$	485 (127)	418 (35.6)	372 (83.6)	j
α-(RR,SS)-trien	NCS	NCS	0.1 *M* HCl	488 (157)	420 (36.9)	372 (86.7)	c
α-(RR,SS)-entnen	NCS	NCS	50% acetone 0.1 *M* HCl	490 (136)	421 (38.1)	376 (84.3)	g
trans-(RS)-entnen	NCS	NCS	H_2O	485 (92.7)		362 (69.5)	k
$(en)_2$	ox		1.0 *M* H^+	496 (91)	426 (19)	372 (85)	l
β-(RR,SS)-trien	ox		2 *M* HNO_3	495 (147)	420 (337)	370 (104)	m
β-(RR,SS)-tnentn	ox		0.1 *M* HCl	493 (103)	413 (17)	370 (100)	e
β-(RR,SS)-entnen	ox		H_2O	491 (111)	420 (20)	369 (97)	g
α-(RR,SS)-entnen	TFA	TFA	50% $MeOH/H_2O$	486 (86.0)	416 (23.3)	370 (60.0)	g

[a]D. J. MacDonald and G. S. Garner, *J. Am. Chem. Soc., 83,* 4152 (1961). [b]Numbers in parenthesis are the molar extinction coefficients, M^{-1} cm^{-1}. [c]D. A. House and C. S. Garner, *J. Am. Chem. Soc., 88,* 2156 (1966). [d]C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta, 1,* 17 (1967). [e]Ref. [1]. [f]Ref. [3]. [g]This research. [h]D. A. House and C. S. Garner, *J. Inorg. Nucl. Chem., 28,* 904 (1966). [i]F. Woldbye, *Acta Chem. Scand., 12,* 1079 (1958). [j]D. A. House, *J. Inorg. Nucl. Chem., 35,* 3103 (1973). [k]Ref. [7]. [l]R. Davies and R. B. Jordan, *Inorg. Chem., 10,* 2432 (1971). [m]J. Veigel, *Inorg. Chem., 7,* 69 (1968). The oxalato complex is now assigned to the *cis*-β-(RR,SS)- configuration.

It is interesting to note that the analogous *cis*-$CoCl_2(entnen)^+$ complex has been, with good reason, tentatively assigned to the β-(RR,SS)- configuration [19]. The *trans*-dichloro isomer isolated from the direct synthesis is identical to that produced by treatment of *trans*-(RS)-$[CrF_2(entnen)]ClO_4$ [6] with 12 *M* HCl and is thus assigned to the (RS)-configuration (Fig. 1).

In dilute aqueous acidic media, Λ-*cis*-α-(SS)-$CrCl_2$-$(entnen)^+$ aquates to form Λ-*cis*-α-(SS)-$CrCl(OH)_2$-

TABLE IV. Pseudo-first-order Rate Constants for the First Step in the Acid Hydrolysis of *cis*-α-$CrCl_2(entnen)^+$ in 0.1 *M* HNO_3.

T °C	K	$10^4 k_H$[a] (s^{-1})	$10^4 k_H$(calc)[b] (s^{-1})
27.9	301.1	5.83 ± 0.07	5.51
		5.40 ± 0.06	
		5.59 ± 0.11	
31.2	304.4	6.95 ± 0.07	7.60
		7.52 ± 0.07	
36.2	309.4	12.9 ± 0.2	12.2
		12.1 ± 0.1	
39.4	312.6	17.0 ± 0.2	16.4
		16.8 ± 0.5	
42.2	315.6	22.8 ± 0.4	21.5
		19.9 ± 0.5	
46.1	319.3	27.7 ± 0.2	29.9
		27.3 ± 0.3	
49.3	311.5	41.5 ± 0.5	39.4
		42.0 ± 0.6	

[a]Determined spectrophotometrically by fixed wavelength techniques at 490 nm. Isosbestic points at 518, 447 and 388 nm. [b]Calculated from the activation parameters cited in Table VI.

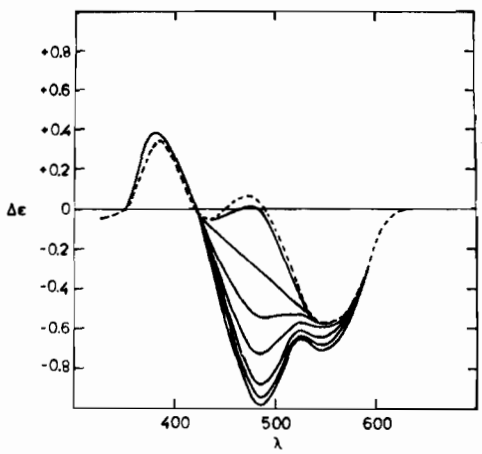

Fig. 3. CD spectral scans (×3) with time for the reaction: Λ-*cis*-α-$CrCl_2(entnen)^+ \rightarrow$ Λ-*cis*-α-$CrCl(entnen)(OH_2)^{2+} + Cl^-$ in 0.1 *M* HNO_3 at room temperature (*ca.* 22 °C). The dashed line corresponds to Λ-*cis*-α-$CrCl_2(entnen)^+$ in 12 *M* HCl. Reading downwards at 500 nm (solid line) the times are 0, 9, 21, 36, 58 and 86 min. The final solid line corresponds to Λ-*cis*-α-$CrCl(entnen)(OH_2)^{2+}$ in 0.1 *M* HNO_3.

$(entnen)^{2+}$ (Fig. 3) and the spectrophotometrically determined pseudo-first-order rate constants for this reaction are reported in Table IV. Addition of Hg^{2+}/H^+ to Λ-*cis*-α-(SS)-$CrCl_2(entnen)^+$ considerably accelerates the loss of the first chloro ligand and loss

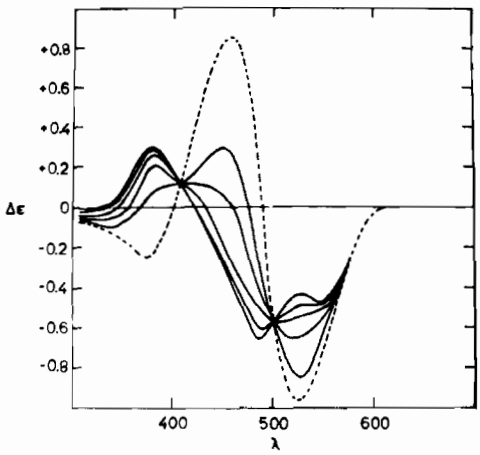

Fig. 4. CD spectral scans (×2) with time for the Hg^{2+}-assisted chloride release reaction: Λ-*cis*-α-$CrCl(entnen)(OH_2)^{2+} \rightarrow$ Λ-*cis*-α-$Cr(entnen)(OH_2)_2^{3+}$ at room temperature. (Hg^{2+} = 2.09 × 10^{-2} *M*, $HClO_4$ = 0.97 *M*, arbitrary time intervals over four hours.) The dashed curve corresponds Λ-*cis*-α-$Cr(entnen)(OH_2)_2^{3+}$.

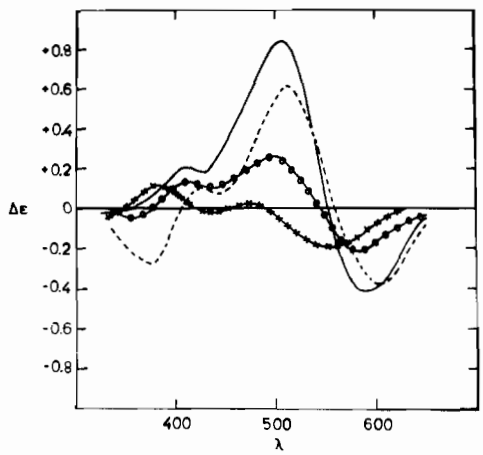

Fig. 5. CD spectra of some Λ-$CrCl_2(N_4)^+$ complexes. N_4 = *cis*-β-tnentn (——); *cis*-α-trien (---- x½); $(en)_2$ (–O–O–O–); *cis*-α-entnen (–X–X–X–).

of the second chloro ligand proceeds more slowly to give Λ-*cis*-α-(SS)-$Cr(OH_2)_2(entnen)^{3+}$ (Fig. 4). The retention of configuration throughout this dichloro → chloroaqua → diaqua sequence has been established by comparison of the circular dichroism spectra of the products with those of analogous Cr(III) complexes of known configuration (Figs. 5, 6) [1, 20]. The rate of acid hydrolysis of *trans*-(RS)-$CrCl_2$-$(entnen)^+$ has been measured previously [4].

In basic media, both *cis*- and *trans*-$CrCl_2(entnen)^+$ lose one and then two chloro ligands at rates proportional to $[OH^-]$. For the *cis*-isomer, there is, how-

TABLE V. Observed and Calculated Rate Constants for the Base Hydrolysis of some *cis*- and *trans*-$CrX_2(N_4)^+$ Complexes (μ = 0.1 *M*, NaCl).[a]

T °C [K]	pH	$10^5[OH^-]$[b] (*M*)	$10^3 k_{obs}$ (s^{-1})	k_{OH} (M^{-1} s^{-1})	k_{OH}(calc)[c] (M^{-1} s^{-1})
	trans-(RS)-$CrBr_2$(entnen)$^+$				
25.0 [298.2]	9.25	2.32	2.10	90.5	91.8
	9.25	2.32	2.13	91.8	
	9.35	2.92	2.60	89.0	
29.8 [303.0]	8.80	1.23	2.31	187	190
	8.90	1.54	2.88	187	
34.9 [308.1]	8.25	0.486	2.02	415	403
	8.25	0.486	1.93	396	
	8.35	0.612	2.56	419	
	8.35	0.612	2.48	406	
39.9 [313.1]	7.85	0.273	2.22	814	821
	7.85	0.273	2.20	806	
	trans-(RS)-$CrCl_2$(entnen)$^+$				
14.5 [287.7]		200[d]	1.34	0.0672	0.0667
		400[d]	2.53	0.0632	
19.5 [292.7]		200[d]	2.82	0.141	0.134
		200[d]	2.70	0.135	
25.2 [298.4]	10.55	46.3	0.135	0.292	0.289
25.5 [298.7]	10.55	46.3	0.139	0.300	0.301
29.8 [303.0]	10.50	61.4	0.325	0.530	0.527
34.9 [308.1]	10.50	86.5	0.848	0.980	1.00
	trans-(RSSR)-$CrCl_2$(cyclam)$^+$				
25.0 [298.2]	9.50	4.13	1.65	40.2	40.0
	9.50	4.13	1.65	40.2	
29.8 [303.0]	9.20	3.08	2.31	75.0	75.9
34.9 [308.1]	8.65	1.22	1.78	146	147
39.9 [313.1]	8.15	0.545	1.50	276	274
	cis-α-$CrCl_2$(entnen)$^+$ [e]				
25.0 [298.2]	9.06	1.50	0.270		
	9.75	7.35	0.299		
	9.76	7.52	0.297		
	10.06	15.0	0.351		
			0.309		
	10.55	46.3	0.516		
			0.500		

[a]Determined using a pH-stat except where noted. The instrument was calibrated using 0.01 *M* borax solution with pH = 9.180, 9.139, 9.102 and 9.068 at 25, 30, 35 and 40 °C respectively. [b]log $[OH^-]$ = pK_{wc} − pH + 0.105 where pK_{wc} = 13.779, 13.607, 13.458 and 13.309 at 25, 30, 35 and 40 °C, respectively. [c]Calculated from the activation parameters cited in Table VII. [d]Determined spectrophotometrically, monitoring the reaction at 530 nm. Isosbestic points at 555 and 458 nm. [e]The plot of k_{obs} *vs.* $[OH^-]$ is linear with the slope giving k_{OH} (298.2; μ = 0.1, NaCl) = 0.52 M^{-1} s^{-1} and intercept giving k_H = 2.65 × 10^{-4} s^{-1} (*cf.* k_H = 4.12 × 10^{-4} s^{-1} from the data in Table IV.

TABLE VI. Activation Parameters for the Acid Hydrolysis of some *cis*- and *trans*-$CrX_2(N_4)^+$ Complexes at 298.2 K.

N_4	X	k_H (s^{-1})	E_a (kJ mol^{-1})	$S^{\#}$ (JK mol^{-1})	Note
		trans-$CrX_2(N_4)^+$			
$(en)_2$	Cl	2.25×10^{-5}	97	−17	a
	Br	3.26×10^{-4}	94	−4	a
$(tn)_2$	Cl	2.08×10^{-5}	103	+1	b
	Br	3.62×10^{-4}	96	+2	b
RS-entnen	Cl	3.23×10^{-6}	107	0	c
	Br	4.27×10^{-5}	100	+1	d
RR,SS-tnentn	Cl	1.06×10^{-6}	95	−50	e
	Br	1.02×10^{-5}	94	−35	d
RSSR-tet*a*	Cl	1.26×10^{-5}	93	−37	f
	Br	1.70×10^{-3}	74	−58	d
		cis-$CrX_2(N_4)^+$			
$(NH_3)_4$	Cl	2.12×10^{-4}	89.7	−14	g
$(en)_2$	Cl	3.3×10^{-4}	89	−24	h
α-trien	Cl	1.9×10^{-4}	89	−27	i
α-entnen	Cl	4.12×10^{-4}	74.2 ± 1.7	−69 ± 3	j,k
β-RR,SS-(tnentn)	Cl	1.02×10^{-4}	88.7	−32	e
RRRR,SSSS-cyclam	Cl	2.5×10^{-5}	96	−21	l

[a]D. A. House and C. S. Garner, *Trans. Met. Chem., 6,* 59 (1970), Table 23. [b]M. C. Couldwell and D. A. House, *Inorg. Chem., 11,* 2024 (1972). [c]C. Kutal and A. W. Adamson, *J. Am. Chem. Soc., 93,* 5581 (1971). [d]D. A. House and O. Nor, *Inorg. Chim. Acta, 72,* 195 (1983). [e]D. Yang and D. A. House, *Inorg. Chem., 21,* 2999 (1982). [f]D. A. House and D. Yang, *Inorg. Chim. Acta, 64,* L167 (1982). [g]L. Mønsted and O. Mønsted, *Acta Chem. Scand., 32A,* 917 (1978). [h]J. Selbin and J. C. Bailar, *J. Am. Chem. Soc., 79,* 4285 (1975). [i]C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta, 1,* 17 (1967). [j]This research. [k]B. Bosnich, R. D. Gillard, E. D. MacKenzie and G. A. Webb, *J. Chem. Soc., A,* 1331 (1966). [l]E. Campi, J. Ferguson and M. L. Tobe, *Inorg. Chem., 9,* 1781 (1970).

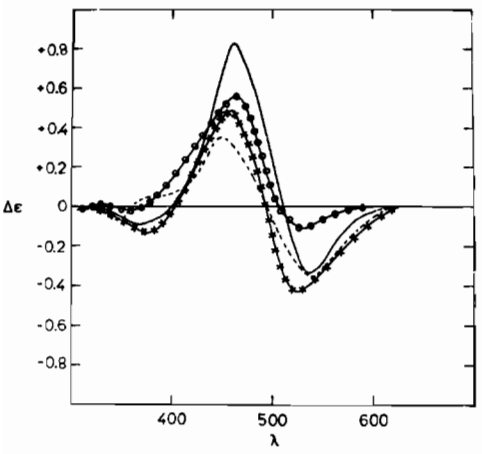

Fig. 6. CD spectra of some Λ-$Cr(N_4)(OH_2)_2^{3+}$ complexes. N_4 = *cis*-β-tnentn (—— X½); *cis*-α-trien (- - - -); $(en)_2$ (–O–O–O–O–); *cis*-α-entnen (–X–X–X–).

ever, concurrent background aquation and some evidence of isomerisation to the *trans*- form.

The rates of base hydrolysis for (±)-*cis*-α-(RR,SS)-$CrCl_2(entnen)^+$ and *trans*-(RS)-$CrCl_2(entnen)^+$ were measured using a pH-stat. For the *cis*- isomer in the pH range 9–10.5 at 298.2 K, the uptake of OH^- corresponded to the loss of one chloro ligand, and a plot of k_{obs} *vs.* $[OH^-]$ was linear with an intercept corresponding to the background aquation rate at that temperature (Table V). From the slope of this plot we estimate k_{OH} (298.2) = 0.52 M^{-1} s^{-1} and this is compared with similar data for analogous *cis*-$CrCl_2(N_4)^+$ complexes in Table VI. In 0.1 *M* NaOH, both chloro ligands are lost (*ca.* 15 min at room temperature) from *cis*-α-$CrCl_2(entnen)^+$ to give (presumably) *cis*-α-$Cr(OH)_2(entnen)^+$ as acidification gives *cis*-α-$Cr(OH_2)_2(entnen)^{3+}$, but if this solution is heated and then re-anated with 12 *M* HCl a *trans*-(RS)-dichloro/*cis*-α-dichloro mixture is obtained. This suggests that in basic solution some *cis*-α → (*cis*-β) →

TABLE VII. Activation Parameters for the Base Hydrolysis of some *cis*- and *trans*-$CrX_2(N_4)^+$ Complexes at 298.2 K (μ = 0.1 *M*, NaCl).

N_4	X	k_H (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	Note
		trans-$CrX_2(N_4)^+$			
$(en)_2$	Cl	3.62×10^{-2}	98.3	+49	a
	Br	6.4 [a]	123	+175	b
(RS)-(entnen)	Cl	2.82×10^{-1}	97.9 ± 1.2	+65 ± 3	c
	Br	9.18×10^{1}	114 ± 0.9	+167 ± 2	c
(RR,SS)-(tnentn)	Cl	5.8×10^{-1}	87.7 ± 1.2	+36 ± 3	d
	Br	8.09×10^{1}	127	+211	a
(RSSR)-cyclam	Cl	4.00×10^{1} [e]	100 ± 0.5	+113 ± 2	c
	Br [f]	1.4×10^{2}	123	+200	a
(RSSR)-tet*a*	Cl	1.45×10^{2}	116	79	g
	Br [h]				c
		cis-$CrX_2(N_4)^+$			
$(en)_2$	Cl	2.7×10^{-2}			i
α-(entnen)	Cl	5.2×10^{-1}			c
β-(tnentn)	Cl	1.12×10^{1}			d
cyclam	Cl	8.6 (299.5 K, μ = 0.74 *M*)			e

[a] D. A. House and O. Nor, *Inorg. Chim. Acta, 70,* 13 (1983). [b] M. S. Nozari and J. A. McLean, Jr., in 'Coordination Chemistry Papers in Honour of John C. Bailar, Jr., Plenum Press (1969). [c] This research. [d] D. Yang and D. A. House, *Inorg. Chem., 21,* 2999 (1982). [e] E. Campi, J. Ferguson and M. L. Tobe, *Inorg. Chem., 9,* 1781 (1970) give k_{OH} (299.5, μ = 0.1 *M*, $NaNO_3$) = 1.6 M^{-1} s^{-1}. [f] These values were determined from two temperatures only and are subject to considerable uncertainty. [g] D. A. House and R. W. Hay, *Inorg. Chim. Acta, 54,* L145 (1981). [h] Complicated by rapid background aquation: k_H (298.2) = 1.70×10^{-3} s^{-1} ($t_{1/2}$ ~ 7 min), D. A. House and O. Nor, *Inorg. Chim. Acta, 72,* 195 (1983). [i] R. G. Pearson, R. A. Munson and F. Basolo, *J. Am. Chem. Soc., 80,* 504 (1958).

trans-(RS)- isomerisation occurs via proton inversion.

The rate of loss of the first chloride ligand from *trans*-(RS)-$CrCl_2$(entnen)$^+$ in basic solution was measured in the [OH^-] range 4.0×10^{-2}–4.6×10^{-4} *M*, over a 20 K temperature range, using both pH-stat and spectrophotometric techniques. Although the two methods were applied in different temperature ranges, the linearity of the Arrhenius plot for all data (Table V) was most satisfactory. The rate of loss of the second chloro ligand (from *trans*-CrCl(OH)(entnen)$^+$) is only about 20 times slower than that of the first and analysis of the pH-stat data was complicated by 'drifting infinities'. This problem was overcome in the spectrophotometric work by following the extent of reaction at 530 nm, an isosbestic point for the second hydrolysis step.

Base hydrolysis of *trans*-(RS)-$CrBr_2$(entnen)$^+$ proceeded with the consumption of two moles of OH^-/mole of complex to form *trans*-$Cr(OH)_2$-(entnen)$^+$. This behaviour is similar to that observed for other *trans*-dibromo chromium(III) tetraamines [12] and indicates that the *trans*-CrBr(OH)(entnen)$^+$ is more labile than the original dibromo, with the loss of the first bromo ligand being rate determining. The bromo/chloro base hydrolysis rate ratio in these Cr(III) entnen complexes follows the pattern observed for other analogous tetraamines [12].

We also report here our data (Table V) for the activation parameters (Table VII) for the base hydrolysis of *trans*-(RSSR)-$CrCl_2$(cyclam)$^+$. We do not agree with a previous spectrophotometric estimate [21] of k_{OH} (299.5) = 1.6 M^{-1} s^{-1}, our value being approximately 25 times greater.

Orange crystals of *cis*-α-[Cr(NCS)$_2$(entnen)]-NCS were isolated by prolonged heating (80 °C, 4 hours) of an acetic acid solution of *cis*-α-[$Cr(Cl)_2$-(entnen)]ClO_4 with excess NH_4NCS. Orange-red crystals of *cis*-α-[CrCl(NCS)(entnen)]NCS (?) can be isolated as an intermediate but were not further characterised. This reaction proceeds with retention of configuration as a similar reaction with the Λ-dichloro gives the Λ-diisothiocyanato.

While this work was in progress a report by Macke *et al.* [7] appeared, which seemed to be at variance with this observation, as the diisothiocyanate com-

TABLE VIII. Stereochemistry of $CrCl_2(N_4)^+$ Complexes Formed by Reaction of $CrCl_3 \cdot 6H_2O$ and (N_4) in Dipolar Aprotic Solvents.

N_4	Solvent	*cis*-	*trans*-	Note
trien	DMSO	α-(RR,SS)-(100%)	0%	a
entnen)	DMF	α-(RR,SS)-(60%)	(RS)-40%	b
tnentn	DMF	0%[c]	(RR,SS)-100%	d
cyclam	DMF	(RRRR,SSSS)-(?)-(90%)	(RSSR)-10%	e
tet*a*	DMF	0%	(RSSR)-100%	f
tet*b*	DMF	(RRRR,SSSS)-100%	0%	f,g

[a]Ref. [15]. [b]This research, see also Refs. [3, 4, 7]. [c]Some violet solid is observed at low temperatures. [d]Ref. [1]. [e]D. A. House, unpublished research, see also Refs. [21, 25]. [f]M. Akbar Ali, D. A. House and R. S. Hay, unpublished research, see also Refs. [26, 27]. [g]E. Bang, J. Eriksen, L. Mønsted and O. Mønsted, *Proc. Int. Conf. Coord. Chem., 22*, 407 (1982).

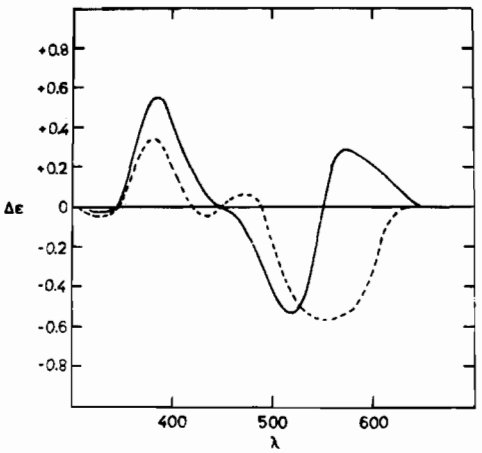

Fig. 7. CD spectra of Λ-*cis*-α-$CrCl_2$(entnen)$^+$ in DMF (—— × 3) and 12 *M* NCl (----- × 3).

plex isolated from the reaction between *cis*-[$CrCl_2$(entnen)]Cl and NaNCS in neutral aqueous solution had the *trans*-(RS)- configuration.

We have repeated the Macke *et al.* synthesis using purified *cis*-α-dichloro but cannot confirm their observation. Even in slightly basic medium (hexamine buffer) only *cis*-[Cr(NCS)$_2$(entnen)]NCS could be isolated. The IR spectra of the *cis*-α- and *trans*-(RS)-[Cr(NCS)$_2$(entnen)]NCS are quite distinct, as are the visible absorption spectra (Table III).

When *cis*-α-[$CrCl_2$(entnen)]ClO_4 is refluxed in 2 *M* trifluoroacetic acid for 1–2 hours, the colour changes to orange-yellow. Addition of $NaClO_4 \cdot H_2O$ allows the isolation of *cis*-α-[Cr(TFA)$_2$(entnen)]$\cdot ClO_4 \cdot H_2O$ as bright orange crystals. Again this reaction appears to proceed with retention of geometric and optical configuration as Λ-*cis*-α-[Cr(TFA)$_2$(entnen)]$HgCl_3$ (?) can be isolated by concentrating a solution of Λ-*cis*-α-[$CrCl_2$(entnen)]ClO_4 in 1 *M* TFA containing 7×10^{-2} *M* $Hg(NO_3)_2$. Reanation of the bis(trifluoroacetato) complex with 12 *M* HCl plus $HClO_4$ forms *cis*-α-[$CrCl_2$(entnen)]ClO_4.

Conclusion

The key to the assignment of the stereochemistry in these *cis*-CrX_2(entnen)$^{n+}$ complexes is to establish the polyamine configuration in the *cis*-dichloro. A previous preliminary communication [22] was in error as we failed to appreciate the considerable solvent dependence (Fig. 7) on the CD spectrum of this complex and an incorrect assignment of the absolute configuration was made. There now seems little doubt that the Cr(ox)(entnen)$^+$ → $CrCl_2$(entnen)$^+$ reaction in 12 *M* HCl (Fig. 2) results in an inversion with a *cis*-β → *cis*-α configurational change being the most likely cause. The alternative *cis*-α-oxalato → *cis*-β-dichloro inversion cannot be completely excluded, but by analogy with the trien [18] and tnentn [1] systems we prefer the former at this stage. Thus the CD spectral changes illustrated in Figs. 2, 3 and 4 reflect the reaction sequences

Λ-(+)-*cis*-β-(RR)-Cr(ox)(entnen)$^+$ (Fig. 2)
↓
Δ-(+)-*cis*-α-(RR)-$CrCl_2$(entnen)$^+$ then

Λ-(−)-*cis*-α-(SS)-$CrCl_2$(entnen)$^+$ (Fig. 3)
↓
Λ-(−)-*cis*-α-(SS)-CrCl(entnen)$(OH_2)^{2+}$ (Fig. 4)
↓
Λ-(−)-*cis*-α-(SS)-Cr(entnen)$(OH_2)_2^{3+}$

The path of stereochemical change in this and analogous tetraamine ligands is apparently dependent

on the nature of the polyamine. While all the Cr(ox)-$(N_4)^+$ (N_4 = trien, entnen, tnentn) have been assigned to the *cis*-β-(RR,SS)- configuration, there are two possible isomerism paths that can be adopted on removal of the oxalate in acid solution: (a) to give *cis*-β-(RR,SS)- and thence *cis*-α-(RR,SS)- or (b) to give *cis*-β-(RR,SS)- and thence *trans*-(RR,SS)- Fig. 1). The former is adopted by trien [17, 18] and entnen, while the latter is adopted by tnentn [1].

This reflects a previous observation [15] that the *trans*-configuration for $CrCl_2(tn)_2^+$ is favoured relative to the *cis*-, and connecting the two 6-membered rings with a central 5-membered bridge in tnentn does little to change the situation.

In basic solution, where proton inversion can occur, there is some *cis*-α-(RR,SS) → *trans*-(RS)-isomerism for entnen, but this process is not observed for trien [14], where the *trans*-configuration is highly strained, and Cr–N bond rupture is competitive.

A now standard route [23, 24] in the synthesis of $CrCl_2(N_4)^+$ complexes [(N_4) = linear or macrocyclic tetraamine] is via the reaction of $CrCl_3 \cdot 6H_2O$, dehydrated in DMF or DMSO, with the polyamine. Table VIII lists the isomeric composition of the products obtained in such a reaction. The interesting feature of such a compilation is that the stereochemistry of the isomers formed is such that they are not interconvertible. Thus, in most cases, the product ratio is not determined by equilibrium conditions, but by some other, unknown factors. It is possible that the nature of the $CrCl_x(sol)_{6-x}^{3+}$ species, in some way determines the steric course and we are currently investigating this aspect of the reaction.

Acknowledgements

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References

1 D. Yang and D. A. House, *Inorg. Chem., 21,* 2999 (1982), Note in this reference, Fig. 1 refers specifically to the linear tetraamine ligands trien and tnentn. For entnen, the R, S assignments must be reversed in each case [2].
2 G. R. Brubaker and D. P. Schaefer, *Inorg. Chem., 10, 968 (1972).*
3 B. Bosnich, R. D. Gillard, E. D. McKenzie and G. A. Webb, *J. Chem. Soc. A.,* 1331 (1966).
4 C. Kutal and A. W. Adamson, *Inorg. Chem., 12,* 1990 (1973).
5 J. Glerup, J. Josephsen, K. Michelsen, E. Pedersen and C. E. Schaffer, *Acta Chem. Scand., 24A,* 247 (1970).
6 E. Bang and E. Pedersen, *Acta Chem. Scand., 32A,* 833 (1978).
7 H. R. Macke, B. F. Mentzen, J. P. Puaux and A. W. Adamson, *Inorg. Chem., 21,* 3080 (1982).
8 G. R. Brubaker and D. P. Schaefer, *Inorg. Chem., 10,* 811 (1971).
9 H. G. Hamilton and M. D. Alexander, *Inorg. Chem., 5,* 2060 (1966).
10 J. van Alphen, *Rec. Trav. Chim., 55,* 935 (1936).
11 D. A. House, *Inorg. Chim. Acta, 60,* 143 (1980).
12 D. A. House and O. Nor, *Inorg. Chim. Acta, 70,* 13 (1983).
13 D. A. House and O. Nor, *Inorg. Chim. Acta, 72,* 195 (1983).
14 D. A. House and C. S. Garner, *J. Am. Chem. Soc., 88,* 2156 (1966).
15 E. Pedersen, *Acta Chem. Scand., 24,* 3362 (1970).
16 C. S. Garner and D. A. House, *Trans. Met. Chem., 6,* 59 (1970).
17 W. A. Fordyce, P. S. Sheridan, P. S. Zinato, P. Riccieri and A. W. Adamson, *Inorg. Chem., 16,* 1154 (1977).
18 D. A. House, *Aust. J. Chem., 35,* 659 (1982).
19 R. Niththyananthan and M. L. Tobe, *Inorg. Chem., 8,* 1589 (1969).
20 I. J. Kindred and D. A. House, *J. Inorg. Nucl. Chem., 37,* 1359 (1975).
21 E. Campi, J. Ferguson and M. L. Tobe, *Inorg. Chem., 9,* 1781 (1970).
22 D. A. House, *Proc. Int. Conf. Coord. Chem., 22,* 143 (1982).
23 C. S. Garner and D. A. House, *Transition Metal Chem., 6,* 64 (1970).
24 J. C. Chang, *J. Indian Chem. Soc., 54,* 98 (1977).
25 C. K. Poon and K. C. Pun, *Inorg. Chem., 19,* 568 (1980).
26 D. Yang and D. A. House, *Inorg. Chim. Acta, 64,* L167 (1982).
27 D. A. House and R. W. Hay, *Inorg. Chim. Acta, 54,* L145 (1981).