Synthesis and Crystal Structure of two Stereochemical Isomers of the *trans*-Dichloro(1,4,8,11-Tetraazacyclotetradecane)chromium(III) Cation†

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Two stereoisomers of the cationic *trans*-[Cr(cyclam)Cl$_2$]$^+$ complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) were prepared and isolated as the nitrate and tetrachlorozincate salts and their structures determined by X-ray diffraction studies of the monoclinic crystals of the nitrate salt, a = 6.480(2), b = 18.862(12), c = 13.628(6) Å, β = 100.28(3)°, and tetragonal crystals for the tetrachlorozincate salt, a = 16.377(4), c = 6.821(2) Å. The two complexes show an octahedral geometry about the metal atoms with the *RSSR* configuration but with differences in the conformations of the six-membered rings.

The relationship between molecular shape and chemical reactivity in macrocyclic compounds is a well known feature and several studies[1-3] have been carried out on the kinetics of base-catalysed hydrolysis of *cis* and *trans* isomers of [M(cyclam)-Cl$_2$]$^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) complexes, to determine the effects of isomerization on the mechanism and velocity of this reaction. However, the scope for isomerism is much larger than that arising from different combinations of configurations of the nitrogen atoms.[4]

In the first reaction of chromium(III) chloride and the ligand cyclam Ferguson and Tobe[5] readily prepared the derivative *cis*-[Cr(cyclam)Cl$_2$]$^+$ and occasionally found the *trans* isomer as a side product, which was described as grey-pink. Later Poon and Pun[6] reported the isomerization of the *cis* to the *trans* derivative, and described it as red-pink. This same product was later prepared by Sosa and Tobe.[1] We observed that when the last technique was carried out with some changes a green product is obtained.

As part of a study on the structure and reactivity of several polyamine, cyclic and non-cyclic metal complexes, we now describe the synthesis and structural characterization of the green species as well as the structural characterization of the pink product. The two compounds proved to be stereoisomers of the cation [Cr(cyclam)Cl$_2$]$^+$ in the form of their tetrachlorozincate (green) and nitrate (pink) salts.

Experimental

Preparations.—The ligand 1,4,8,11-tetraazacyclotetradecane was prepared as described in the literature.[7] *trans*-Dichloro-(1,4,8,11-tetraazacyclotetradecane)chromium(III) nitrate, **1** was prepared as reported in ref. 1 (Found: C, 32.95; H, 6.70; N, 18.2. Calc. for $C_{10}H_{24}Cl_2CrN_5O_3$: C, 31.15; H, 6.25; N, 18.20%). Crystals were obtained from an aqueous nitric acid solution.

trans-*Dichloro*(1,4,8,11-*tetraazacyclotetradecane*)-*chromium*(III) *tetrachlorozincate*, **2**. The ligand cyclam (0.37 g) was dissolved in dry methanol (75 cm^3) and anhydrous CrCl$_3$ (0.25 g) was added followed by zinc amalgam (3 g, prepared as for use in a Clemmensen reduction).[8] The mixture was refluxed for 3 h, during which a pink precipitate was observed while the solution became violet. When the reaction was over and air was allowed to enter the flask the precipitate redissolved and the solution changed to a red-wine colour. The solution was filtered and the filtrate concentrated to 25 cm^3. Acetone (25 cm^3) was added and the final solution was concentrated to half its volume. The brown-purple precipitate formed was recrystallized from 1 mol dm^{-3} HCl as green needles (0.16 g) (Found: C, 28.20; H, 5.70; N, 13.00. Calc. for $C_{20}H_{48}Cl_8Cr_2N_8Zn$: C, 28.10; H, 5.65; N, 13.10%).

Crystal and Molecular Structure Determinations.—The crystals of both compounds were air stable and were mounted on glass fibres.

Crystal data. Compound **1**. $C_{10}H_{24}Cl_2CrN_5O_3$, M = 385.0, monoclinic, space group $P2_1/c$, a = 6.480(2), b = 18.862(12), c = 13.628(6) Å, β = 100.28(3)°, U = 1638.97 Å (by least-squares refinement from 25 automatically centred reflections in the range $3 \leqslant 2\theta \leqslant 20°$), Z = 4, D_c = 1.56 g cm^{-3}, D_m not measured, $F(000)$ = 804, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 10.3 cm^{-1}.

Compound **2**. $C_{20}H_{48}Cl_8Cr_2N_8Zn$, M = 845.4, tetragonal, space group $P4_2/n$, a = 16.377(4), c = 6.821(2) Å, U = 1830(2) Å^3 (by least-squares refinement from 25 automatically centred reflections in the range $3.5 \leqslant 2\theta \leqslant 23.6°$), Z = 2, D_c = 1.55 g cm^{-3}, D_m not measured, $F(000)$ = 876, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 18.52 cm^{-1}.

Data collection and processing. Both sets of data were collected on a Nicolet R 3m four-circle diffractometer using a 2θ scan width 2.0°, and a variable scan rate of 4–30° min^{-1} using graphite-monochromated Mo-Kα radiation. In the case of **1**, 2911 reflections were measured ($3.0 < 2\theta < 50.0°$) of which 2367 were unique [$I > 3\sigma(I)$]. In the case of **2**, 1906 reflections were measured and 1201 unique. After corrections for absorption, **2** showed transmission factors of 0.8641 and 1.1481.[9] No absorption corrections were made in the case of **1**.

Structure analyses and refinement. The structures were solved by direct methods and Fourier difference syntheses. Blocked-cascade least-squares refinement with all non-hydrogen atoms assigned anisotropic thermal parameters. Hydrogen atoms

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Cr	4710(1)	6227(1)	2770(1)
Cl(1)	7034(1)	6591(1)	1744(1)
Cl(2)	2383(1)	5851(1)	3786(1)
N(1)	5234(5)	7171(2)	3533(3)
C(2)	3328(7)	7607(2)	3230(4)
C(3)	2590(7)	7525(2)	2133(4)
N(4)	2255(4)	6761(2)	1901(2)
C(5)	1831(7)	6582(3)	819(3)
C(6)	1512(7)	5798(3)	640(3)
C(7)	3444(8)	5334(3)	909(4)
N(8)	4203(5)	5278(2)	1995(3)
C(9)	6163(7)	4864(2)	2279(4)
C(10)	6911(7)	4938(2)	3380(4)
N(11)	7180(5)	5707(2)	3639(3)
C(12)	7557(7)	5860(3)	4716(3)
C(13)	7862(7)	6655(3)	4916(3)
C(14)	5937(7)	7121(3)	4628(3)
N	1646(6)	3666(2)	2064(3)
O(1)	1211(8)	3185(3)	1453(4)
O(2)	574(7)	4188(2)	2000(4)
O(3)	3223(8)	3595(3)	2711(4)

Table 2 Atomic coordinates for compound **2**

Atom	*x*	*y*	*z*
Zn	1/4	1/4	1/4
Cl(1)	0.176 79(6)	0.158 94(5)	0.428 3(1)
Cr	1/2	1/2	0
Cl(2)	0.550 57(5)	0.420 00(5)	0.258 4(1)
N(1)	0.515 8(2)	0.405 4(2)	−0.198 4(4)
C(2)	0.449 0(2)	0.346 1(2)	−0.154 3(5)
C(3)	0.371 3(2)	0.392 8(2)	−0.112 8(5)
N(4)	0.386 4(2)	0.450 6(2)	0.051 0(4)
C(5)	0.317 9(2)	0.508 3(2)	0.085 1(6)
C(6)	0.336 1(2)	0.567 1(2)	0.251 5(6)
C(7)	0.402 3(2)	0.631 0(2)	0.211 7(6)
H(1)	0.509(3)	0.422(2)	−0.282(6)
H(4)	0.389(2)	0.424(2)	0.150(6)

Table 3 Infrared spectra of the different isomers of the cation $[Cr(cyclam)Cl_2]^+$ with various counter ions (in parentheses)[a]

cis (Cl)	*trans* (Cl)	*trans* ($ZnCl_4$)	*trans* (NO_3)	*trans* (ClO_4)
Deep red	Purple	Green	Purple	Dark pink
1460vs	1460vs	1465vs	1465w	1470(br, s)
1440w	1450m(d)	1450vw		
	1425m	1425s	1430vw	1435m
1390vw	1385w(d)		*b*	1380vw
1370vw	1345vw	1320m	1335vw	1345vw
1310m	1335vw	1300m	1320vw	1335vw
1285m	1320m		1300m	1320w
	1300m			1300m

Estimated relative intensities: s = strong; m = medium; w = weak; br = broad; and d = doublet.

[a] In KBr disks. [b] It is not possible to distinguish any other absorbance peak in this region, due to the presence of a broad nitrate peak.

bonded to nitrogen atoms were located directly in an electron-density map while methylene hydrogen atoms were placed in geometrically idealized positions. The weighting scheme $w = [\sigma^2(F_o) + \sigma F^2]^{-1}$ gave satisfactory agreement analyses. Final R and R' values were 0.053 and 0.056 for **1**, and 0.031 and 0.045 for **2**. The structures were solved and refined using the SHELXTL set of programs[10] on a Nova 4S computer for **1**, and with the TEXSAN-TEXRAY structure-analysis package[11] in a Vax Station II for **2**. Complex neutral-atom scattering factors were employed.[12] The atomic coordinates for compounds **1** and **2** are listed in Tables 1 and 2 respectively.

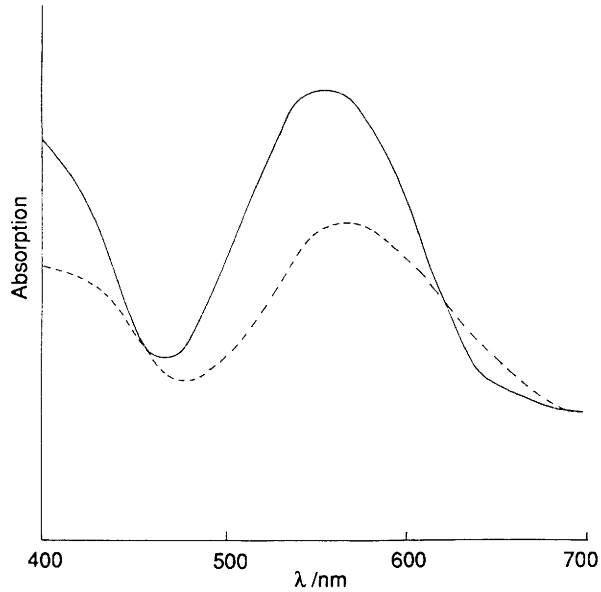


Fig. 1 Electronic spectra of *trans*-$[Cr(cyclam)Cl_2]NO_3$ (——) and *trans*-$[Cr(cyclam)Cl_2]_2[ZnCl_4]$ (– – –) in the solid state

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Analyses.—Elemental analyses were carried out on a Perkin-Elmer 240B instrument at the Chemistry Faculty (Universidad de México) and at University College London.

Infrared spectra of KBr pellets of the complexes, in the range of 4000–200 cm^{-1}, were recorded on a Perkin-Elmer 599B spectrometer, electronic absorption spectra in aqueous solution on a Schimatzu UV-240 spectrophotometer. The solid-state electronic spectra were measured on a Cary 17D spectrophotometer.

Results and Discussion

The two isomeric complexes **1** and **2** can be isolated by changing the reaction conditions from those used to prepare **1**, namely the solvent, methanol instead of ethanol, and the zinc amalgam which this time was used as a solid in direct contact with the reactants in solution, instead of the use of Soxhlet apparatus. Complex **2** is apparently stabilized by the presence of the $[ZnCl_4]^{2-}$ anion, when the reaction is carried out in methanol. In order to see whether other large counter ions could stabilize **2**, the chloride salt was dissolved in methanol with a small amount of water and a perchlorate salt was added; a pink precipitate was obtained. When a hexafluorophosphate salt is added to the same solution no precipitation is observed. When tetrabutylammonium or tetraethylammonium tetrafluoroborate is added a grey-pink precipitate is obtained in each case.

Both compounds **1** and **2** show in their infrared spectra the characteristic pattern for the *trans* isomer described by Poon,[13] at 800–1000 cm^{-1}, although there are slight differences around 1300–1400 cm^{-1} (see Table 3).

There have been other examples of a similar behaviour reported by Gibson and McKenzie[14] in *cis*-dichlorobis(1,10-phenanthroline)chromium(III) compounds. For instance, *cis*-$[Cr(phen)_2Cl_2]Cl{\cdot}xH_2O$ (x = 2–4) has been obtained as different polymorphs. Their colours in sunlight range from red-brown to various shades of green, but all have a reddish colour in tungsten light and all give the same species in solution. The authors proposed a *cis* configuration for all the complexes.

The electronic spectra of compounds **1** and **2** in the solid state (Fig. 1) have maxima at λ = 550 and 570 nm respectively.

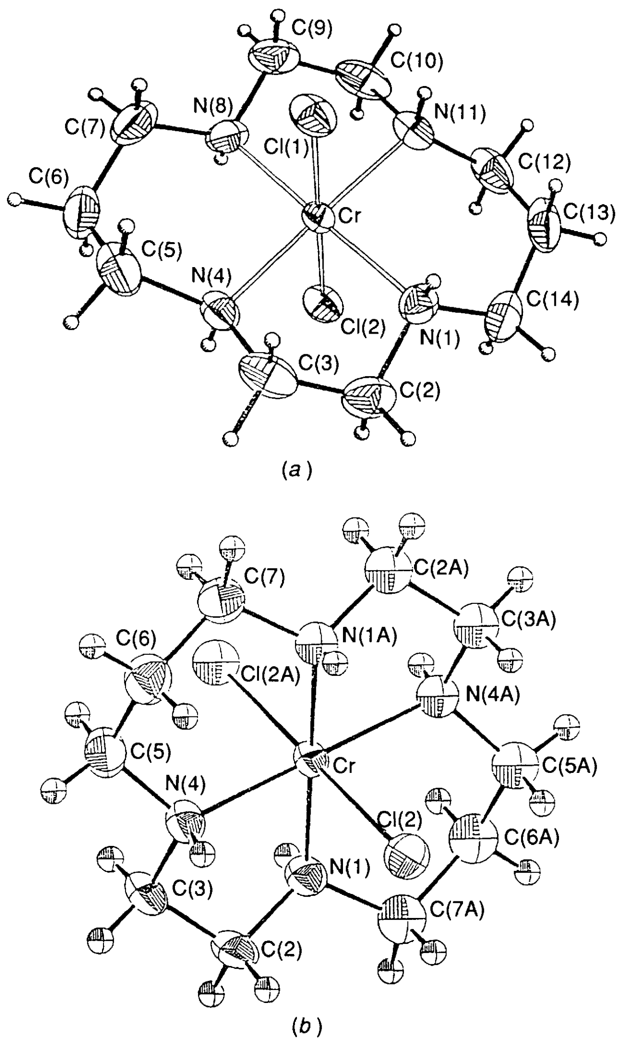


Fig. 2 Molecular structures of *trans*-$[Cr(cyclam)Cl_2]NO_3$ (*a*) and *trans*-$[Cr(cyclam)Cl_2]_2[ZnCl_4]$ (*b*)

Table 4 Bond lengths (Å) and angles (°) for compound **1**

Cr–Cl(1)	2.334(1)	Cr–Cl(2)	2.333(1)
Cr–N(1)	2.060(3)	Cr–N(4)	2.067(3)
Cr–N(8)	2.073(3)	Cr–N(11)	2.062(3)
N(1)–C(2)	1.480(5)	N(1)–C(14)	1.483(5)
C(2)–C(3)	1.494(6)	C(3)–N(4)	1.483(5)
N(4)–C(5)	1.490(5)	C(5)–C(6)	1.505(8)
C(6)–C(7)	1.518(7)	C(7)–N(8)	1.478(6)
N(8)–C(9)	1.483(6)	C(9)–C(10)	1.499(7)
C(10)–N(11)	1.495(6)	N(11)–C(12)	1.472(5)
C(12)–C(13)	1.530(7)	C(13)–C(14)	1.520(7)
N–O(1)	1.229(6)	N–O(2)	1.208(6)
N–O(3)	1.232(6)		
Cl(1)–Cr–Cl(2)	179.4(1)	Cl(1)–Cr–N(1)	89.0(1)
Cl(2)–Cr–N(1)	91.6(1)	Cl(1)–Cr–N(4)	91.5(1)
Cl(2)–Cr–N(4)	88.6(1)	N(1)–Cr–N(4)	84.8(1)
Cl(1)–Cr–N(8)	90.5(1)	Cl(2)–Cr–N(8)	88.8(1)
N(1)–Cr–N(8)	179.5(1)	N(4)–Cr–N(8)	95.3(1)
Cl(1)–Cr–N(11)	88.1(1)	Cl(2)–Cr–N(11)	91.8(1)
N(1)–Cr–N(11)	94.6(1)	N(4)–Cr–N(11)	179.2(1)
N(8)–Cr–N(11)	85.3(1)	Cr–N(1)–C(2)	106.6(2)
Cr–N(1)–C(14)	116.5(3)	C(2)–N(1)–C(14)	114.0(4)
N(1)–C(2)–C(3)	108.9(4)	C(2)–C(3)–N(4)	108.8(3)
Cr–N(4)–C(3)	106.4(2)	Cr–N(4)–C(5)	116.3(3)
C(3)–N(4)–C(5)	115.2(3)	N(4)–C(5)–C(6)	112.3(4)
C(5)–C(6)–C(7)	116.3(4)	C(6)–C(7)–N(8)	113.3(4)
Cr–N(8)–C(7)	116.3(3)	Cr–N(8)–C(9)	105.8(2)
C(7)–N(8)–C(9)	114.5(4)	N(8)–C(9)–C(10)	108.7(4)
C(9)–C(10)–N(11)	109.3(4)	Cr–N(11)–C(10)	106.2(2)
Cr–N(11)–C(12)	116.9(3)	C(10)–N(11)–C(12)	114.7(4)
N(11)–C(12)–C(13)	111.3(4)	C(12)–C(13)–C(14)	116.6(4)
N(1)–C(14)–C(13)	112.8(4)	O(1)–N–O(2)	123.4(4)
O(1)–N–O(3)	117.8(5)	O(2)–N–O(3)	118.7(5)

Table 5 Bond lengths (Å) and angles (°) for compound **2**

Zn–Cl(1)	2.268(1)	Cr–Cl(2)	2.3472(9)
Cr–N(4)	2.058(3)	Cr–N(1)	2.074(3)
N(1)–C(7)	1.470(5)	N(1)–C(2)	1.494(5)
C(2)–C(3)	1.512(5)	C(3)–N(4)	1.486(4)
N(4)–C(5)	1.484(5)	C(5)–C(6)	1.518(5)
C(6)–C(7)	1.532(5)		
Cl(1)–Zn–Cl(1)	115.11(5)	Cl(1)–Zn–Cl(1A)	106.73(2)
N(4)–Cr–N(4A)	180(3)	N(4)–Cr–N(1)	86.0(1)
N(4)–Cr–N(1A)	94.0(1)	N(4)–Cr–Cl(2)	88.44(8)
N(4)–Cr–Cl(2A)	91.56(8)	N(1)–Cr–Cl(2)	91.66(9)
N(1)–Cr–Cl(2A)	88.34(9)	Cl(2)–Cr–Cl(2A)	180 (4)
C(7)–N(1)–C(2)	114.7(3)	C(7)–N(1)–Cr	117.2(2)
C(2)–N(1)–Cr	105.2(2)	N(1)–C(2)–C(3)	109.0(3)
N(4)–C(3)–C(2)	108.8(3)	C(5)–N(4)–C(3)	113.4(3)
C(5)–N(4)–Cr	117.4(2)	C(3)–N(4)–Cr	105.9(2)
N(4)–C(5)–C(6)	111.9(3)	C(5)–C(6)–C(7)	116.1(3)
N(1)–C(7)–C(6)	112.3(3)		

However, in aqueous solution the green species converts instantaneously into the pink complex, showing almost twice the absorbance value. In order to determine whether these compounds were truly isomeric, X-ray crystal structure determinations of both complexes were undertaken.

The molecular structures of both $[Cr(cyclam)Cl_2]^+$ cations are illustrated in Fig. 2 along with the numbering scheme adopted. Associated bond lengths and angles are given in Tables 4 and 5. In both cases the structures consist of *trans*-$[Cr(cyclam)Cl_2]^+$ cations linked *via* hydrogen bonds with the corresponding anions which in turn interact with other molecules of the cations. This can be observed in the packing diagrams, Fig. 3. The macrocyclic ligands adopt, both in **1** and **2**, a planar configuration with the four nitrogen atoms coordinated to the metal atom. Two chloride anions in the axial positions complete the overall octahedral geometry about the metal atoms.

In both complexes **1** and **2** the angles about the octahedron are within 5° of the regular angle of 90°; N–Cr–N which are part of five-membered rings form angles smaller than 90°, while in six-membered rings the N–Cr–N angles are larger than 90°. This behaviour had been previously observed in *trans*-$[Ru(cyclam)Cl_2]^+$.[15]

The Cr–Cl bond lengths are very similar in **1** and **2** and also practically equal to the corresponding value of *cis*-$[Cr(cyclam)Cl_2]^+$.[16] However, the Cr–N distances are significantly longer in both derivatives of *cis*-$[Cr(cyclam)Cl_2]^+$ than in the *trans* complexes.[4,16] Significant differences in Cr–N bond lengths were observed between the chloride and perchlorate salts of *cis*-$[Cr(cyclam)Cl_2]^+$ and were explained in terms of the hydrogen-bond system present in the first complex. Complexes **1** and **2**, as mentioned above, also show hydrogen bonds between amine protons and oxygen or chlorine atoms in the corresponding counter ions: H(1)···O(1) 2.43, H(8)···O(2) 2.616 and H(4)···Cl(1) 2.57 Å. Therefore this does not seem to be the determining factor that causes the differences between the two complexes.

Another, very likely reason is the greater distortion of the macrocycle in the *cis* isomer which then produces longer Cr–N distances. To our knowledge, Ru^{III} is the only other metal ion for which both *cis*[17] and *trans*[15] cyclam derivatives have been structurally characterized and it can be seen than the Ru–N distances are longer in the *cis* than in the *trans* isomer.

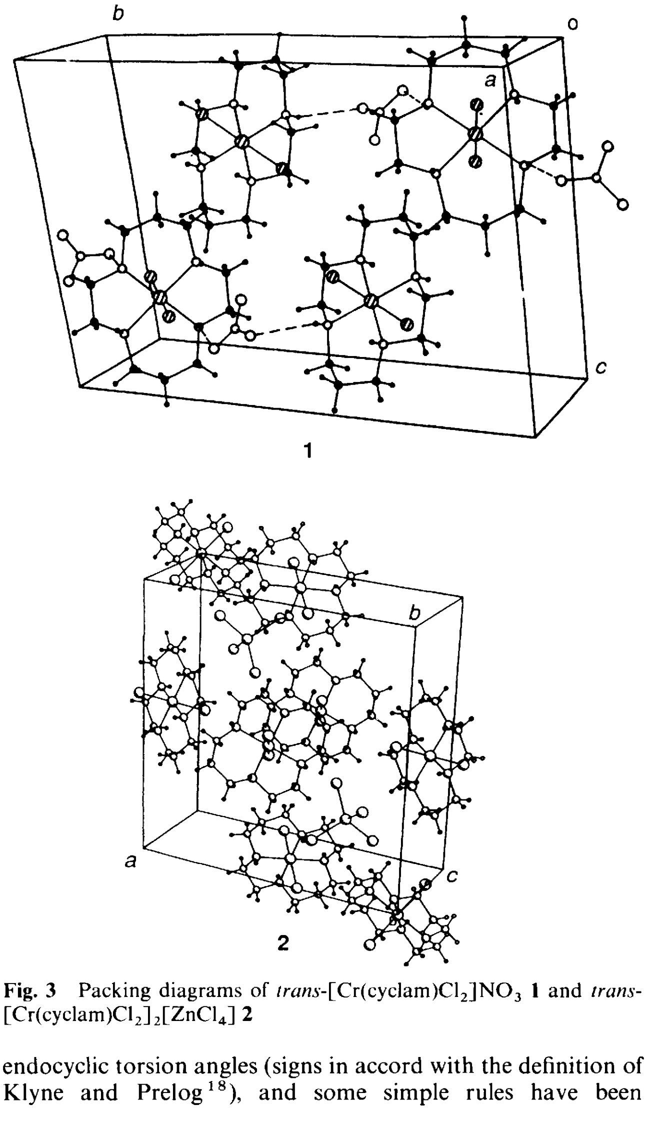
The ring conformation in molecules is described by the

Table 6 Selected torsion angles (°) for $[Cr(cyclam)Cl_2]NO_3$

N(1)–Cr–N(4)–C(3)	14.8(3)	N(4)–Cr–N(1)–C(2)	14.7(3)
N(1)–C(2)–C(3)–N(4)	55.9(5)	C(2)–C(3)–N(4)–Cr	−40.5(4)
Cr–N(1)–C(2)–C(3)	−41.2(4)	C(2)–C(3)–N(4)–C(5)	−171.1(4)
N(4)–Cr–N(8)–C(7)	34.7(3)	Cr–N(4)–C(5)–C(6)	54.3(4)
N(4)–C(5)–C(6)–C(7)	70.7(5)	C(5)–C(6)–C(7)–N(8)	−70.1(5)
N(8)–Cr–N(4)–C(5)	−35.6(3)	C(6)–C(7)–N(8)–Cr	−52.5(5)
C(3)–N(4)–C(5)–C(6)	179.9(4)	C(6)–C(7)–N(8)–C(9)	−176.5(4)
C(7)–N(8)–C(9)–C(10)	172.0(4)	N(8)–Cr–N(11)–C(10)	−12.2(3)
Cr–N(8)–C(9)–C(10)	42.6(4)	N(8)–C(9)–C(10)–N(11)	−56.2(3)
N(11)–Cr–N(8)–C(9)	−16.5(3)	C(9)–C(10)–N(11)–C(12)	170.0(4)
C(9)–C(10)–N(11)–Cr	39.2(4)	Cr–N(1)–C(14)–C(13)	53.7(4)
N(11)–Cr–N(1)–C(14)	−37.1(3)	C(12)–C(13)–C(14)–N(1)	−68.9(5)
Cr–N(11)–C(12)–C(13)	−55.9(4)	N(11)–C(12)–C(13)–C(14)	69.7(5)
C(10)–N(11)–C(12)–C(13)	178.8(3)	C(14)–N(1)–C(2)–C(3)	−171.2(3)
C(2)–N(1)–C(14)–C(13)	178.5(4)		

Table 7 Selected torsion angles (°) for $[Cr(cyclam)Cl_2]_2[ZnCl_4]$

C(2)–N(1)–Cr–N(4)	165.8(2)	C(2)–C(3)–N(4)–C(5)	171.6(3)
N(4)–C(5)–C(6)–C(7)	69.5(4)	Cr–N(4)–C(3)–C(2)	41.5(3)
Cr–N(1)–C(2)–C(3)	40.8(3)	N(1)–C(2)–C(3)–N(4)	−56.8(4)
N(1)–Cr–N(4)–C(3)	−14.9(2)	C(2)–N(1)–Cr–N(4)	−14.2(2)
C(3)–N(4)–C(5)–C(6)	−179.2(3)	C(3)–C(2)–N(1)–C(7A)	171.0(3)
N(4)–Cr–N(1A)–C(7)	−142.9(3)	Cr–N(4)–C(5)–C(6)	−55.1(4)
N(1A)–C(7)–C(6)–C(5)	−69.5(4)	Cr–N(1A)–C(7)–C(6)	54.3(3)
C(2)–N(1)–C(7A)–C(6A)	−178.4(2)	N(1A)–Cr–N(4)–C(5)	37.4(3)



1

2

Fig. 3 Packing diagrams of *trans*-$[Cr(cyclam)Cl_2]NO_3$ **1** and *trans*-$[Cr(cyclam)Cl_2]_2[ZnCl_4]$ **2**

endocyclic torsion angles (signs in accord with the definition of Klyne and Prelog[18]), and some simple rules have been proposed[19] in order to determine conformational types. These rules have been extended by Boeyens and Dobson[20] and can be applied to define the corners of macrocycles. The torsion angles for complexes **1** and **2** are given in Table 6 and 7 respectively. According to these rules, for planar arrangements of cyclam the conformations 133133 or 3434 are the most frequently found.[15,21] Both **1** and **2** show the 133133 arrangement. This conformation is compatible with the molecular symmetry shown by the torsion angles: a mirror plane in **1** and an inversion centre in **2**. It must be mentioned that the metal atom in complex **2** sits on a crystallographically imposed centre of symmetry.

An analysis of the chelate rings shows that the five-membered rings in both **1** and **2** have half-chair conformations. Both six-membered rings in **1** have sofa conformations, but **2** shows a distorted conformation that does not fit with any of the exact symmetry arrangements. Structural differences between **1** and **2** are observed in the conformations of the rings.

The enantiomeric forms in the unit cell of complexes **1** and **2** have *RSSR* (and *SRRS*) configuration. We have therefore characterized two different conformations in the *trans* configuration for the octahedral complexes.

The nitrate and tetrachlorozincate anions in **1** and **2** respectively show the expected triangular and tetrahedral structures. The Zn atom in **2** is placed in a crystallographically imposed four-rotofold axis.

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