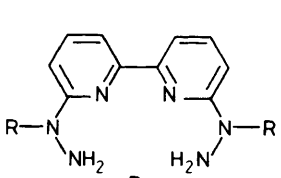
The Transient Template Effect: Chromium(III)-directed Syntheses of Metal-Free Macrocyclic Ligands and Crystal Structure of 1,11-Bis(2'-hydroxyethyl)-4,8;12,16;17,21-trinitrilo-1,2,10,11-tetra-azacyclohenicosa-2,4,6,9,12,14,18,20-octaene Hydrochloride Tetrahydrate†

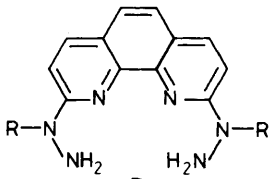
Lap-Yan Chung, Edwin C. Constable,* Adrian R. Dale, Muhammed S. Khan, Michael C. Liptrot, Jack Lewis,* and Paul R. Raithby
University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW

A range of metal-free quinquedentate macrocyclic ligands incorporating 2,2'-bipyridine or 1,10-phenanthroline donor groups has been prepared by the use of a chromium(III) transient template. The transient template effect is shown to be due to pH effects resulting from the presence of chromium(III) complexes in aqueous solution, rather than a process in which the open-chain ligands become co-ordinated to the metal centre. The crystal and molecular structure of a free macrocyclic ligand is reported, as is the preparation of some chromium(III) complexes of open-chain and macrocyclic complexes.

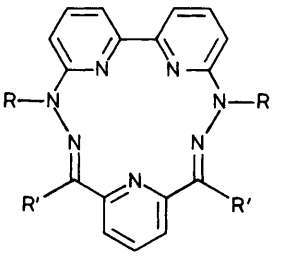
It has been known for many years that metal ions may direct the course of 'organic' reactions.[1] Synthetic methodology based upon this modification of reactivity has been particularly important in the preparation of macrocyclic compounds in condensation reactions.[2] The metal ion may be pictured as playing a steric role in forcing a co-ordinated ligand to adopt the correct conformation for the formation of cyclic products, and this led to the phenomenon being described as the 'template effect.' A common feature of template reactions is the isolation of the macrocyclic ligand as a complex of the metal template ion, and such reactions are frequently the synthetic method of choice for the preparation of macrocyclic complexes. Unfortunately, not all metal ions act as templates for a particular reaction, and determining the correct conditions may be time-consuming. In some cases it is possible to perform a template condensation using one metal ion, and then perform a transmetallation reaction to prepare the desired complex, but this is not a general phenomenon. The demetallation of macrocyclic complexes frequently requires forcing conditions, and it is common to observe undesired reactions at the ligand. We have recently been interested in the consequences of mismatches between the donor properties of ligands and the acceptor properties of metal ions, and have demonstrated that these may control the stoicheiometry and topology of metal–ligand interactions.[3,4] We have also demonstrated that when template condensations are performed about metal ions which do not match with the desired cyclic products the macrocyclic complexes are labile and the free macrocyclic ligands are obtained.[5] We termed the above phenomenon the 'transient template effect,' and demonstrated the intermediacy of macrocyclic complexes of the template ion. These reactions were very metal-ion specific, and in this paper we describe some more general types of template reaction in which metal-free macrocyclic ligands are obtained using kinetically inert chromium(III). A preliminary communication of some of these results has appeared.[6]



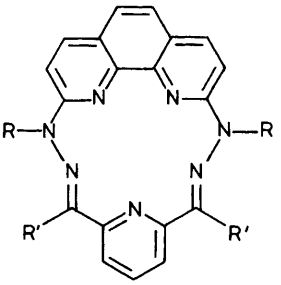
	R
L^1	H
L^2	Me
L^3	CH_2CH_2OH



	R
L^4	H
L^5	Me
L^6	CH_2CH_2OH



	R	R'
L^7	H	H
L^8	Me	H
L^9	CH_2CH_2OH	H
L^{10}	H	Me
L^{11}	Me	Me
L^{12}	CH_2CH_2OH	Me



	R	R'
L^{13}	H	H
L^{14}	Me	H
L^{15}	CH_2CH_2OH	H
L^{16}	H	Me
L^{17}	Me	Me
L^{18}	CH_2CH_2OH	Me

Experimental

Proton and ^{13}C n.m.r. spectra were recorded on Brüker WM250 or AM400 spectrometers in CD_2Cl_2, CD_3CN, or CD_3SOCD_3 solution, i.r. on a Perkin-Elmer 983 spectrophotometer for compressed KBr discs and mass spectra using a Kratos MS-50 spectrometer. Magnetic moments were recorded at room temperature using a Johnson Matthey susceptibility balance. The bis(hydrazino) ligands L^1—L^6 and their hydrochlorides were prepared as described previously.[3,5–7]

Preparation.—$[HL^9]Cl{\cdot}4H_2O$. The complex $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ (0.789 g, 3 mmol) and $[HL^3]Cl$ (1.020 g, 3 mmol)

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

were dissolved in water (500 cm^3) and heated to reflux for 30 min, after which period 2,6-pyridinedialdehyde (0.405 g, 3 mmol) was added. The yellow-green solution turned deep red and was heated to reflux for a further 3 h, after which period it was concentrated *in vacuo* to 50 cm^3 and cooled, when $[HL^9]Cl{\cdot}4H_2O$ was obtained as a red crystalline solid (1.3 g, 87%) (Found: C, 49.2; H, 5.8; Cl, 6.9; N, 19.1. Calc. for $C_{21}H_{30}ClN_7O_6$: C, 49.2; H, 5.8; Cl, 6.9; N, 19.1%); *m/z* 403 (L^{9+}). I.r. (Nujol): 3600br, 1 615w, 1 585s, 1 566m, 1 495s, 1 300m, 1 086s, 1 028s, 856s, 819m, 796m, and 744m cm^{-1}.

$[HL^9]BF_4{\cdot}4H_2O$. The salt $[HL^9]Cl{\cdot}4H_2O$ (0.511 g, 1 mmol) was dissolved in warm water (50 cm^3) and $Na[BF_4]$ (0.11 g, 1 mol) was added. Upon cooling $[HL^9]BF_4{\cdot}4H_2O$ was obtained as an orange-red crystalline solid (90—95%) (Found: C, 44.5; H, 5.3; N, 17.4. Calc. for $C_{21}H_{30}BF_4N_7O_6$: C, 44.8; H, 5.3; N, 17.4%); *m/z* 403 (L^{9+}). I.r. (Nujol): 3 600br, 1 616w, 1 590s, 1 590s, 1 566m, 1 495s, 1 300m, 1 150s, 1 086s, 1 028s, 856s, 820m, 796m, and 744m cm^{-1}. The same compound was obtained when $[HL^3][BF_4]$ was substituted for the chloride in the preparation of $[HL^9]Cl{\cdot}4H_2O$. The $[PF_6]^-$ and $[BPh_4]^-$ salts were similarly obtained as the tetrahydrates (Found: C, 40.5; H, 4.8; N, 15.5; P, 4.9. Calc. for $C_{21}H_{30}F_6N_7O_6P$: C, 40.6; H, 4.9; N, 15.8; P, 5.0. Found: C, 67.5; H, 6.2; N, 12.0. Calc. for $C_{45}H_{50}BN_7O_6$: C, 68.0; H, 6.3; N, 12.3%).

$[H_2L^8]Cl_2{\cdot}H_2O$. This was prepared in the same manner as $[HL^9]Cl{\cdot}4H_2O$, substituting L^2 for $[HL^3]Cl$, as blood-red needles (90%) (Found: C, 52.6; H, 4.8; Cl, 16.3; N, 22.2. Calc. for $C_{19}H_{21}Cl_2N_7O$: C, 52.5; H, 4.8; Cl, 16.4; N, 22.5%); *m/z* 343 (L^{8+}). I.r. (Nujol): 1 615 (sh), 1 589s, 1 566m, 1 492s, 1 300m, 1 035br, 860m, 820m, 792m, and 743m cm^{-1}.

$[H_2L^{14}]Cl_2{\cdot}H_2O$. This was prepared in the same manner as $[HL^9]Cl{\cdot}4H_2O$, substituting L^5 for $[HL^3]Cl$. The salt was obtained as red needles (80%) (Found: C, 55.1; H, 4.5; Cl, 15.5; N, 21.3. Calc. for $C_{21}H_{21}Cl_2N_7O$: C, 55.0; H, 4.6; Cl, 15.5; N, 21.4%); *m/z* 367 (L^{14+}). I.r. (Nujol): 1 615w, 1 588s, 1 566m, 1 495s, 1 300m, 1 030s, 856s, 818m, 792m, and 743m cm^{-1}.

$[HL^{15}][PF_6]{\cdot}H_2O$. This was prepared in the same manner as $[HL^9]Cl{\cdot}4H_2O$, substituting L^6 for $[HL^3]Cl$. The red solution obtained was treated with $[NH_4][PF_6]$ to give $[HL^{15}][PF_6]{\cdot}H_2O$ as an orange solid (55%) (Found: C, 46.7; H, 4.1; N, 16.7. Calc. for $C_{23}H_{24}F_6N_7O_3P$: C, 46.7; H, 4.1; N, 16.6%); *m/z* 427 (L^{15+}).

$[H_2L^7][PF_6]_2{\cdot}H_2O$. This was prepared in the same manner as $[HL^9]Cl{\cdot}4H_2O$, substituting L^1 for $[HL^3]Cl$. The red solution obtained was treated with $[NH_4][PF_6]$ to give $[H_2L^7][PF_6]_2{\cdot}H_2O$ as an orange solid (70%) (Found: C, 32.5; H, 2.7; N, 15.4. Calc. for $C_{17}H_{17}F_{12}N_7OP_2$: C, 32.6; H, 2.7; N, 15.6%); *m/z* 315 (L^{7+}).

$[H_2L^{10}]Cl_2{\cdot}3H_2O$. This was prepared in the same manner as $[HL^9]Cl{\cdot}4H_2O$, substituting L^1 for $[HL^3]Cl$ and 2,6-diacetylpyridine for 2,6-pyridinedialdehyde. It was obtained as an orange solid (75%) (Found: C, 48.9; H, 5.3; Cl, 15.1; N, 21.1. Calc. for $C_{19}H_{25}Cl_2N_7O_3$: C, 48.5; H, 5.3; Cl, 15.1; N, 20.8%); *m/z* 343 (L^{10+}).

$[H_2L^{16}]Cl_2{\cdot}3H_2O$. This was prepared in the same manner as $[HL^9]Cl{\cdot}4H_2O$, substituting L^4 for $[HL^3]Cl$ and 2,6-diacetylpyridine for 2,6-pyridinedialdehyde. It was obtained as an orange solid (65%) (Found: C, 51.1; H, 5.0; Cl, 14.3; N, 19.9. Calc. for $C_{21}H_{25}Cl_2N_7O_3$: C, 51.0; H, 5.0; Cl, 14.4; N, 19.8%); *m/z* 367 (L^{16+}).

$[H_2L^{13}][BPh_4]_2{\cdot}H_2O$. This was prepared in the same manner as $[HL^9]Cl{\cdot}4H_2O$, substituting L^4 for $[HL^3]Cl$. The red solution obtained was treated with $Na[BPh_4]$ to give $[H_2L^{13}][BPh_4]_2{\cdot}H_2O$ as a yellow solid (70%) (Found: C, 80.6; H, 5.7; N, 9.6. Calc. for $C_{67}H_{57}B_2N_7O$: C, 86.7; H, 5.7; N, 9.8%); *m/z* 339 (L^{13+}).

$[CrL^3Cl_2]Cl{\cdot}H_2O$. The complex $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ (0.266 g, 1 mmol) and L^3 (0.268 g, 1 mmol) were dissolved in ethanol (100 cm^3) and the mixture heated to reflux for 4 h. The brown solution so obtained was concentrated *in vacuo* and cooled to yield $[CrL^3Cl_2]Cl{\cdot}H_2O$ as a green crystalline solid (>80%) (Found: C, 38.35; H, 4.8; Cr, 10.6; N, 17.8. Calc. for $C_{14}H_{22}Cl_3CrN_6O_3$: C, 35.0; H, 4.6; Cr, 10.8; N, 17.5%); $\mu_{eff.}$ 3.88, Λ_m (H_2O) 323.7 ohm^{-1} cm^2 mol^{-1}.

$[CrL^5Cl_2]Cl{\cdot}H_2O$. The complex $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ (0.266 g, 1 mmol) and L^5 (0.304 g, 1 mmol) were dissolved in ethanol (100 cm^3) and the mixture heated to reflux for 4 h. The brown solution so obtained was concentrated *in vacuo* and cooled, to yield $[CrL^5Cl_2]Cl{\cdot}H_2O$ as a brown crystalline solid (>80%) (Found: C, 38.4; H, 4.2; N, 17.8. Calc. for $C_{14}H_{18}Cl_3CrN_6O$: C, 38.0; H, 4.0; N, 17.9%); $\mu_{eff.}$ 3.88, $\Lambda_m(H_2O)$ 332.4 ohm^{-1} cm^2 mol^{-1}.

$[CrL^{14}(H_2O)_2]Cl_3{\cdot}3H_2O$. Hydrochloric acid (2 cm^3, 35%) and 2,6-pyridinedialdehyde (0.22 g, 1.63 mmol) were added to a solution of $[CrL^5Cl_2]Cl{\cdot}H_2O$ (0.7 g, 1.63 mmol) in water (1 000 cm^3) and the mixture heated to reflux for 4 h. After this period, the brown solution was concentrated *in vacuo* to 50 cm^3 and the brown crystalline product collected by filtration to yield $[CrL^{14}(H_2O)_2]Cl_3{\cdot}3H_2O$ (0.7 g, 70%) (Found: C, 40.8; H, 4.4; Cr, 8.3; N, 15.7. Calc. for $C_{21}H_{21}Cl_3CrN_7O_2$: C, 40.9; H, 4.4; Cr, 8.4; N, 15.9%); $\mu_{eff.}$ 3.97, $\Lambda_m(H_2O)$ 464.5 ohm^{-1} cm^2 mol^{-1}.

$[CrL^9(H_2O)_2]Cl_3$. Hydrochloric acid (0.5 cm^3, 35%) and 2,6-pyridinedialdehyde (0.054 g, 0.40 mmol) were added to a solution of $[CrL^3Cl_2]Cl{\cdot}H_2O$ (0.193 g, 0.40 mmol) in water (300 cm^3) and the mixture heated to reflux for 5 h. After this period, the brown solution was concentrated *in vacuo* to 10 cm^3 and cooled in ice to give a red crystalline product which was collected by filtration to yield $[CrL^9(H_2O)_2]Cl_3$ (0.18 g, 75%). Recrystallisation by the diffusion of acetone vapour into an aqueous solution furnished *X*-ray quality crystals (Found: C, 42.5; H, 4.1; N, 16.4. Calc. for $C_{21}H_{25}Cl_3CrN_7O_4$: C, 42.2; H, 4.2; N, 16.4%); $\mu_{eff.}$ 3.98, $\Lambda_m(H_2O)$ 427.3 ohm^{-1} cm^2 mol^{-1}.

Crystal Structure Determination of $[HL^9]Cl{\cdot}4H_2O$.—Suitable single crystals of $[HL^9]Cl{\cdot}4H_2O$ were obtained as orange-red blocks by the slow crystallisation of an aqueous solution.

Crystal data. $C_{21}H_{30}ClN_7O_6$, M = 511.96, monoclinic, a = 13.598(6), b = 7.827(4), c = 22.836(16) Å, β = 90.05(5)°, U = 2 430.46 $Å^3$, $F(000)$ = 1 080, space group $P2_1/n$, Z = 4, D_m = not measured, D_c = 1.399 g cm^{-3}, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 1.65 cm^{-1}.

Data collection and processing. A suitable orange-red crystal of size 0.49 × 0.26 × 0.23 mm was mounted on a glass fibre with epoxy resin. The space group and unit-cell dimensions were determined from preliminary Weissenberg (Cu-K_α) photography. The crystal was mounted on a Syntex $P2_1$ diffractometer and accurate unit-cell dimensions were determined from angular measurements of 15 strong reflections in the range $15 < 2\theta < 30°$. A total of 5 356 intensity data were recorded using graphite-monochromated Mo-K_α radiation in the range $3.0 < 2\theta < 50.0°$ using a 96-step ω—2θ scan technique; scan speeds varied from 2.5 to 29.3° min^{-1}. Reflections for which the intensity was less than 8 counts s^{-1} in a preliminary 1-s prescan were not recorded. Two standard reflections showed no significant variations in intensity during data collection.

A semiempirical absorption correction based on a pseudo-ellipsoid model and 508 azimuthal scan data from 48 independent reflections was applied. Transmission factors ranged from 1.000 to 0.999 for the full data set. Equivalent reflections averaged to give 2 150 unique observed intensities with [$F > 5\sigma(F)$]. The data were solved in the monoclinic space group $P2_1/n$.

Structure analysis and refinement. The structure was solved using direct methods with subsequent Fourier difference

Table 1. Atomic co-ordinates ($\times 10^4$) for $[HL^9]Cl{\cdot}4H_2O$

Atom	x	y	z	Atom	x	y	z
Cl	2 239(2)	1 219(3)	4 974(1)	C(12)	10 864(5)	2 568(9)	−768(4)
O(3)	4 958(3)	737(7)	2 250(2)	C(13)	10 097(5)	2 196(9)	−381(3)
O(4)	4 776(4)	3 824(8)	1 733(2)	C(14)	10 119(4)	2 715(8)	242(3)
N(1)	6 736(4)	−364(7)	207(2)	C(15)	10 873(5)	3 573(10)	516(4)
C(1)	6 391(5)	−424(8)	764(3)	C(16)	10 757(6)	3 998(10)	1 106(4)
C(2)	5 559(5)	−1 397(10)	868(3)	C(17)	9 923(6)	3 516(9)	1 414(3)
C(3)	5 132(6)	−2 287(10)	412(4)	C(18)	9 182(5)	2 666(8)	1 119(3)
C(4)	5 529(5)	−2 239(10)	−145(4)	N(4)	9 274(4)	1 346(7)	−532(2)
C(5)	6 354(5)	−1 245(9)	−248(3)	N(5)	9 307(3)	2 296(6)	549(2)
C(6)	6 849(5)	−1 052(9)	−803(3)	N(6)	8 331(4)	2 119(7)	1 376(2)
N(2)	7 676(4)	−272(7)	−768(2)	N(7)	7 758(4)	1 134(7)	1 027(2)
N(3)	8 270(4)	23(7)	−1 229(2)	C(19)	8 018(5)	2 723(9)	1 961(3)
C(7)	8 052(6)	−573(10)	−1 817(3)	C(20)	8 297(6)	1 488(10)	2 436(3)
C(8)	7 611(7)	821(13)	−2 214(3)	O(2)	7 817(5)	2 123(9)	2 950(3)
O(1)	6 724(5)	1 447(8)	−1 984(3)	C(21)	6 932(5)	564(9)	1 195(3)
C(9)	9 155(5)	897(9)	−1 092(3)	O(6)	13 043(4)	5 694(9)	1 314(3)
C(10)	9 833(6)	1 275(10)	−1 519(3)	O(5)	8 314(6)	107(9)	3 911(4)
C(11)	10 684(7)	2 108(11)	−1 351(4)				

Table 2. Bond lengths (Å) and bond angles (°) in $[HL^9]Cl{\cdot}4H_2O$

C(1)–N(1)	1.357(8)	C(5)–N(1)	1.349(8)
C(21)–C(1)	1.452(9)	C(4)–C(3)	1.381(12)
C(6)–C(5)	1.444(9)	N(2)–C(6)	1.282(9)
C(7)–N(3)	1.452(9)	C(9)–N(3)	1.418(9)
C(8)–C(7)	1.540(12)	O(1)–C(8)	1.404(12)
C(10)–C(9)	1.376(10)	N(4)–C(9)	1.335(8)
C(11)–C(10)	1.382(12)	C(12)–C(11)	1.394(12)
C(13)–C(12)	1.380(10)	C(14)–C(13)	1.480(9)
N(4)–C(13)	1.346(8)	C(15)–C(14)	1.375(10)
N(5)–C(14)	1.349(8)	C(16)–C(15)	1.398(12)
C(17)–C(16)	1.388(11)	C(18)–C(17)	1.382(10)
N(5)–C(18)	1.346(8)	N(6)–C(18)	1.367(8)
N(7)–N(6)	1.355(7)	C(19)–N(6)	1.480(8)
C(21)–N(7)	1.269(8)	C(20)–C(19)	1.501(10)
O(2)–C(20)	1.433(9)	N(3)–N(2)	1.348(8)
C(1)–C(2)	1.384(10)	C(2)–C(3)	1.381(11)
C(4)–C(5)	1.385(10)		
C(5)–N(1)–C(1)	124.7(5)	C(2)–C(1)–N(1)	117.7(6)
C(21)–C(1)–N(1)	116.2(6)	C(21)–C(1)–C(2)	126.1(6)
C(3)–C(2)–C(1)	119.3(7)	C(4)–C(3)–C(2)	121.2(7)
C(5)–C(4)–C(3)	119.2(7)	C(4)–C(5)–N(1)	117.9(6)
C(6)–C(5)–N(1)	116.2(6)	C(6)–C(5)–C(4)	125.9(7)
N(2)–C(6)–C(5)	113.9(6)	N(3)–N(2)–C(6)	124.0(6)
C(7)–N(3)–N(2)	123.0(6)	C(9)–N(3)–N(2)	114.8(5)
C(9)–N(3)–C(7)	122.2(6)	C(8)–C(7)–N(3)	113.3(6)
O(1)–C(8)–C(7)	111.2(6)	C(10)–C(9)–N(3)	121.1(6)
N(4)–C(9)–N(3)	116.2(6)	N(4)–C(9)–C(10)	122.7(6)
C(11)–C(10)–C(9)	117.8(7)	C(12)–C(11)–C(10)	121.2(8)
C(13)–C(12)–C(11)	116.1(7)	C(14)–C(13)–C(12)	122.9(6)
N(4)–C(13)–C(12)	123.6(6)	N(4)–C(13)–C(14)	113.4(6)
C(15)–C(14)–C(13)	125.9(6)	N(5)–C(14)–C(13)	114.6(5)
N(5)–C(14)–C(15)	119.5(6)	C(16)–C(15)–C(14)	118.1(7)
C(17)–C(16)–C(15)	121.1(7)	C(18)–C(17)–C(16)	118.7(7)
N(5)–C(18)–C(17)	118.9(6)	N(6)–C(18)–C(17)	124.0(6)
N(6)–C(18)–N(5)	117.1(5)	C(13)–N(4)–C(9)	118.4(6)
C(18)–N(5)–C(14)	123.7(5)	N(7)–N(6)–C(18)	114.4(5)
C(19)–N(6)–C(18)	122.1(5)	C(19)–N(6)–N(7)	123.2(5)
C(21)–N(7)–N(6)	122.1(5)	C(20)–C(19)–N(6)	111.9(6)
O(2)–C(20)–C(19)	104.7(6)	N(7)–C(21)–C(1)	115.5(6)

syntheses. The aromatic, methine, and methylene hydrogen atoms were constrained to lie in geometrically idealised positions, 1.08 Å from the relevant C atoms, and each type was assigned a common isotropic thermal parameter. The proton within the macrocyclic cavity, the hydroxyl, and lattice water protons were not located. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. In the final stages of refinement, 25 reflections with 2θ values below 18° were zero weighted in order to reduce the effects of partial disorder within the structure.

The structure was refined by blocked-cascade least-squares methods. In the final stages of refinement a weighting scheme of the form $w = [\sigma^2(F) + 0.0008(F)^2]^{-1}$ was introduced, since this reduced the dependence of $w\Delta^2$ on $|F|$ and sinθ. The final residuals converged to $R = 0.0956$, $R' = 0.0976$ for 2 150 observed reflections. A final difference synthesis showed no regions of electron density greater than 0.7 e Å^{-3}.

Computations were made using the SHELX program [8] on the University of Cambridge IBM 370/165 computer. Neutral atom scattering factors were taken from ref. 9. Atomic co-ordinates are presented in Table 1 and bond lengths and bond angles in Table 2.

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

Results and Discussion

The template condensation of 6,6′-bis(hydrazino)-2,2′-bipyridines or 2,9-bis(hydrazino)-1,10-phenanthrolines with 2,6-pyridinedialdehyde or 2,6-diacetylpyridine has been utilised in the synthesis of transition-metal complexes of a variety of planar quinquedentate N_5-donor macrocycles.[3–7] A range of metal-ion environments has been observed in these complexes, depending upon the number and nature of axial interactions experienced. However, the template reactions have proved to be very metal-ion specific, and we have had little success in performing transmetallation reactions. Attempts to remove transition-metal ions from these complexes by the use of cyanide results in the initial formation of *trans* diaxial dicyano complexes, followed by nucleophilic attack upon the ligand leading to the reformation of the precursor bis(hydrazines). Treatment with base leads to the formation of intractable oxo complexes which we have not fully characterised. In the course of various attempts to prepare novel complexes we have investigated the use of chromium(III) as a template.

The reaction of L^3 with 2,6-pyridinedialdehyde in water results in the predominant formation of insoluble red polymeric materials. However, in the presence of a stoicheiometric amount of commercial green chromium(III) chloride hexahydrate, *trans*-$[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$, a deep red solution is obtained. Evaporation of this solution leads to the separation of a bright

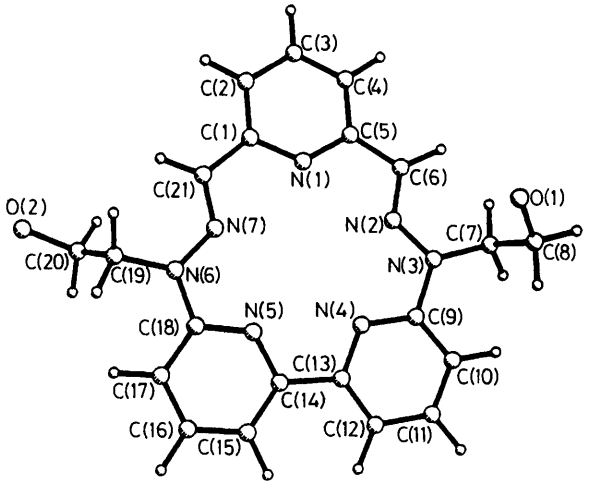


Figure 1. The crystal and molecular structure of the macrocyclic cation $[HL^9]^+$ in $[HL^9]Cl{\cdot}4H_2O$ showing the numbering scheme adopted

Table 3. Intermolecular non-bonded constants (Å) for $[HL^9]Cl{\cdot}4H_2O$

		Second atom related to first by symmetry operator
O(1)···O(3)	2.92	$1-x, -y, -z$
O(4)···O(3)	2.70	x, y, z
O(5)···O(2)	2.78	x, y, z
O(5)···Cl(1)	2.86	$1-x, -y, 1-z$
O(6)···O(1)	2.73	$2-x, 1-y, -z$
O(6)···O(4)	2.94	$1+x, y, z$
O(6)···Cl(1)	2.99	$\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

red crystalline solid. We initially thought that this might be the chromium(III) complex of the macrocyclic ligand L^9, but microanalysis (C, H, N) indicated the metal-free formulation $[HL^9]Cl{\cdot}4H_2O$ to be appropriate. On the basis of this formulation a yield of 87% of the free macrocycle is obtained. Clearly a polymeric or oligomeric analogue of the macrocycle would also give similar analytical results, although the observed solubility of the product might preclude formulation as a high polymer. The electron impact (e.i.) mass spectrum of the product reveals the highest mass peak at m/z 403, consistent with the presence of the [1 + 1] condensation product L^9. The ^1H n.m.r. spectrum of the product was fully consistent with the metal-free [1 + 1] formulation. Significantly, there was no paramagnetic broadening, and sharp well resolved peaks were observed. Aqueous solutions of $[HL^9]Cl$ underwent metathesis reactions, and the orange-red salts $[HL^9][BF_4]{\cdot}4H_2O$, $[HL^9][PF_6]{\cdot}4H_2O$, and $[HL^9][BPh_4]{\cdot}4H_2O$ were obtained as analytically pure crystalline materials.

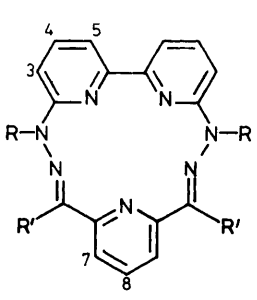
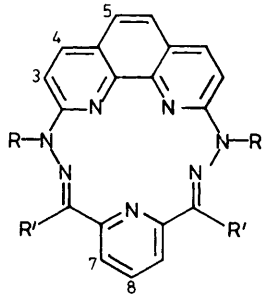
In order to verify the formation of the metal-free macrocyclic ligand a single-crystal *X*-ray structural determination was performed. The structure determination confirmed the presence of the [1 + 1] condensation product, and the crystal and molecular structure of the $[HL^9]^+$ cation is shown in Figure 1 with the numbering scheme adopted. The macrocycle is approximately planar, with the maximum deviation of any nitrogen atom from the least-squares plane through the donor set being 0.04 Å, but the 2,2′-bipyridyl and pyridine subunits are tilted by 10° with respect to each other. The 2,2′-bipyridine and pyridine subunits subtend angles of 1.5 and 8.5° respectively, with respect to the N_5 least-squares plane. The individual pyridine rings are all approximately planar, but a dihedral angle of 4.2° is observed between the two pyridine rings of the 2,2′-bipyridine fragment. The N(2)–N(3) and N(6)–N(7) distances are 1.348(8) and 1.355(7) Å respectively and the sums of the bond angles about N(3) and N(6) are 359.9 and 359.6° respectively, indicating that both are effectively sp^2 hybridised. This is indicative of a considerable degree of delocalisation within the macrocycle. A second feature of interest is the displacement of the two hydroxyethyl groups to the same side of the macrocyclic ligand. This involves no additional intramolecular van der Waals contacts, and the same configuration is observed in the complexes $[Cr(L^9)(H_2O)_2]Cl_3$[6] and $[Fe(L^{12})Cl_2]Cl$.[10] The two hydroxyethyl oxygen atoms are, however, involved in hydrogen bonding to waters of crystallisation (Table 3), and there is a hydrogen-bonding network linking the water molecules to the chloride anion. The anion also has contacts under 3.8 Å with all the nitrogen atoms except N(3), the two shortest distances being N(1)···Cl(1) (3.36 Å) and N(7)···Cl(1) (3.25 Å). A stacking interaction is observed between the 2,2′-bipyridine group of one macrocycle and the adjacent molecule running along the *b* direction; the interplanar distance is approximately 3.9 Å, which is reminiscent of the non-bonded stacking interactions we have observed in other ligands and complexes containing pyridine rings.[4] The best-fit circle through the five nitrogen donor atoms has a radius of 2.05 Å, essentially the same as is observed in complexes of this and related ligands.[3–7,10,11]

Analogous reactions occurred between L^2 or L^1 and 2,6-pyridinedialdehyde in the presence of $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ to yield the red crystalline free macrocycle salts $[H_2L^8]Cl_2{\cdot}H_2O$ (m/z 343) and $[H_2L^7][PF_6]_2{\cdot}H_2O$ (m/z 315) respectively. The 1,10-phenanthroline analogues of L^{13}—L^{15} are obtained from the reaction of 2,6-pyridinedialdehyde with L^4—L^6 respectively in the presence of chromium(III) chloride. Similar reactions occur with 2,6-diacetylpyridine, and in the presence of $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$, L^1 or L^4 yields the salts $[H_2L^{10}]Cl_2{\cdot}3H_2O$ or $[H_2L^{16}]Cl_2{\cdot}3H_2O$ respectively. It proved to be impossible to prepare the macrocycles L^{11}, L^{12}, L^{17}, or L^{18} by these methods, and we ascribe this observation to the steric interactions between the various substituents on the macrocycle. It has been previously noted that condensations with 2,6-diacetylpyridine may not lead to the expected macrocyclic products if there is a steric interaction between the methyl groups and any other substituents in the molecule.[12]

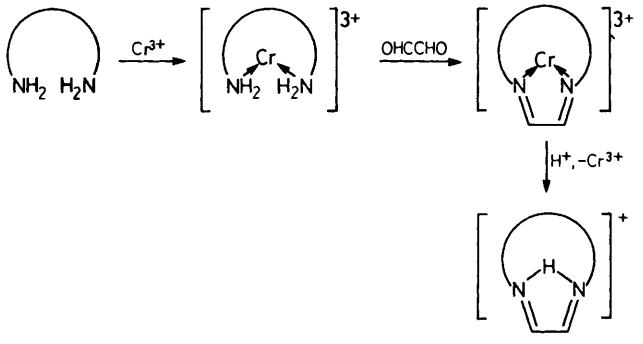
Well resolved ^1H n.m.r. spectra were obtained for all of the salts of the ligands L^7—L^{10} and L^{13}—L^{16} in D_2O or CF_3CO_2D solution, in accord with the discrete [1 + 1] formulations (Table 4). It was noted that in CD_3SOCD_3 solution the spectra were considerably broadened. Variable-temperature experiments established that the spectra sharpened upon warming and were consistent with the [1 + 1] macrocycles. We believe that the solutions contain equilibrium mixtures of the species $[HL^n]^+$ and $[H_2L^n]^{2+}$. In D_2O proton exchange is fast on the n.m.r. time-scale, and sharp averaged signals are obtained, whereas in the strong acid CF_3CO_2D only diprotonated (deuteriated) species are present. However, in the viscous solvent CD_3SOCD_3 the rate of proton exchange is reduced and an intermediate-exchange region is reached. Attempts further to investigate these phenomena have not proved successful. Support for this explanation would come from detailed n.m.r. studies of pK_a determinations. Unfortunately, solutions of the macrocycles in hot CD_3SOCD_3 are short-lived due to hydrolysis and other degradative reactions, and pK_a determination have proved to be unreliable owing to the very high affinities of these ligands for both proton and alkali-metal ions.[13]

Although transient template reactions have been reported using a number of labile metal ions as templates,[14] the use of the kinetically inert d^3 chromium(III) ion in this role has a single precedent.[15] We considered a number of possible mechanisms for the formation of these free macrocyclic ligands from the

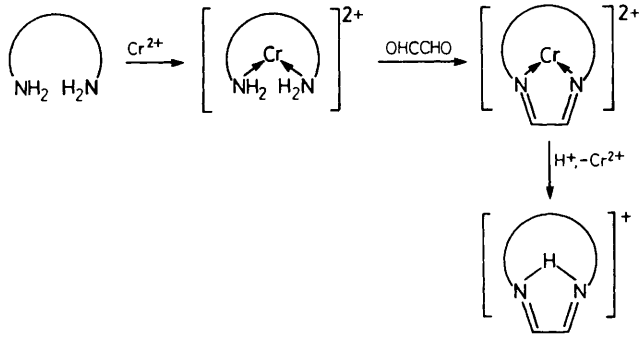
Table 4. 250-MHz ^{1}H n.m.r. data (CD_3SOCD_3) for the aromatic resonances of the macrocyclic ligands

	H^3	H^4	H^5	H^7	H^8	
L^1	7.63 (d)	7.98 (dd)	7.10 (d)			$J(H^3H^4)$ 7.0, $J(H^4H^5)$ 8.0
$[HL^2]^+$	7.67 (d)	8.08 (dd)	7.21 (d)			$J(H^3H^4)$ 7.0, $J(H^4H^5)$ 8.0
$[HL^3]^+$	7.74 (d)	8.22 (dd)	7.24 (d)			$J(H^3H^4)$ 7.0, $J(H^4H^5)$ 8.1
L^4	6.92 (d)	7.93 (d)	7.36 (s)			$J(H^3H^4)$ 9.0
$[HL^5]^+$	7.63 (d)	8.29 (d)	7.60 (s)			$J(H^3H^4)$ 9.1
$[HL^6]^+$	7.81 (d)	8.22 (d)	7.73 (s)			$J(H^3H^4)$ 9.1
$[H_2L^7]^{2+}$	8.18 (d)	7.58 (dd)	8.20 (d)	8.00 (d)	8.41 (t)	$J(H^3H^4)$ 7.5, $J(H^4H^5)$ 7.8, $J(H^7H^8)$ 8.0
$[H_2L^8]^{2+}$	8.17 (d)	7.64 (dd)	8.21 (d)	8.12 (d)	8.51 (t)	$J(H^3H^4)$ 7.4, $J(H^4H^5)$ 7.7, $J(H^7H^8)$ 8.1
$[HL^9]^+$	8.24 (d)	7.82 (dd)	8.22 (d)	8.40 (d)	8.57 (t)	$J(H^3H^4)$ 7.5, $J(H^4H^5)$ 7.7, $J(H^7H^8)$ 8.0
$[H_2L^{10}]^{2+}$	8.14 (d)	7.57 (dd)	8.12 (d)	7.95 (d)	8.65 (t)	$J(H^3H^4)$ 7.4, $J(H^4H^5)$ 7.6, $J(H^7H^8)$ 8.1
$[H_2L^{14}]^{2+}$	8.20 (d)	8.94 (d)	8.21 (s)	8.23 (d)	8.58 (t)	$J(H^3H^4)$ 9.1, $J(H^7H^8)$ 7.9
$[HL^{15}]^+$	8.44 (d)	8.79 (d)	8.31 (s)	8.35 (d)	8.71 (t)	$J(H^3H^4)$ 9.0, $J(H^7H^8)$ 7.4
$[H_2L^{16}]^{2+}$	7.44 (d)	8.36 (d)	7.71 (s)	8.28 (d)	8.44 (t)	$J(H^3H^4)$ 9.1, $J(H^7H^8)$ 7.8

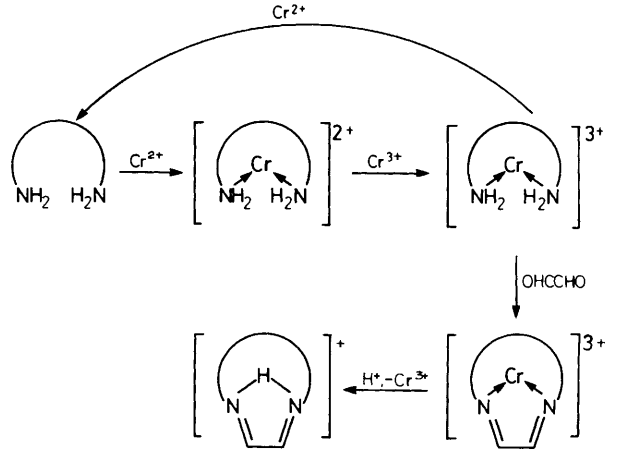


Scheme 1.



Scheme 2.

chromium(III)-directed reactions. The simplest mechanism (Scheme 1) involves the formation of a chromium(III) complex of the bis(hydrazino) precursor followed by a 'normal' template condensation to give a chromium(III) macrocyclic complex. This five- or seven-co-ordinate complex is expected on thermodynamic (and *possibly* kinetic)[16] grounds to be unstable with respect to the formation of a six-co-ordinate hexa-aqua species. The objections to this mechanism centre upon the kinetic inertness of the d^3 chromium(III) starting material;



Scheme 3.

substitution of the ligands in this complex by the bis(hydrazine) is not expected to occur on the time-scale of the reaction. A second mechanism (Scheme 2) which avoids some of the problems associated with Scheme 1 involves a redox-activated catalytic cycle initiated by the reducing properties of hydrazines. The inertness of the chromium(III) starting complexes may be overcome if the bis(hydrazines) are good enough reducing agents to form some (labile) d^2 chromium(II). This is expected to undergo a ready substitution reaction with the bis(hydrazine). The bis(hydrazine) complex could then react with the dicarbonyl to form a chromium(II) macrocyclic complex, which is thermodynamically unstable with respect to an octahedral chromium(II) complex and free macrocycle. The new chromium(II) complex is labile and re-enters the reaction cycle to form chromium(II) bis(hydrazine) complex. In a variant of this scheme, (3), the chromium(II) complex of the bis(hydrazine) undergoes a redox reaction with the chromium(III) starting complex to generate a chromium(III) bis(hydrazine) complex and more labile chromium(II). The chromium(III) bis(hydrazine) complex can then condense with the dicarbonyl to form the

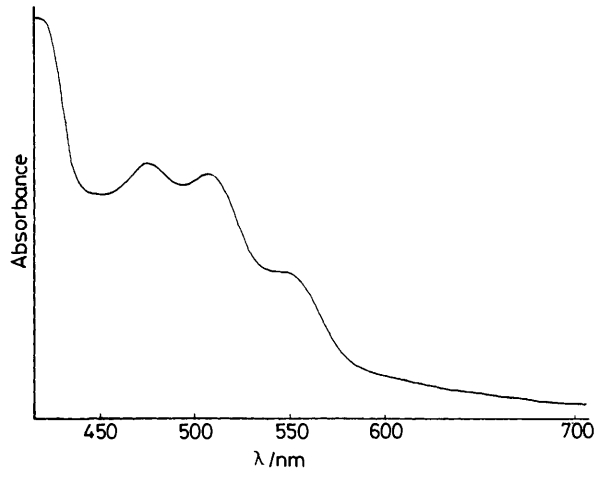


Figure 2. The electronic spectrum of a 0.0132 mol dm^{-3} aqueous solution of $[CrL^3Cl_2]Cl{\cdot}H_2O$

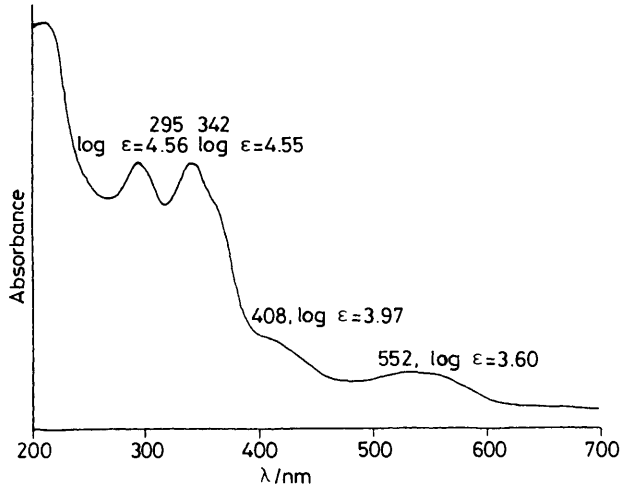


Figure 3. The electronic spectrum of a 0.015 mol dm^{-3} aqueous solution of $[CrL^9(H_2O)_2]Cl_3{\cdot}H_2O$

chromium(III) macrocyclic complex which is thermodynamically unstable with respect to ligand loss and the formation of an octahedral chromium(III) complex. A final mechanism (Scheme 4) may be envisaged in which the chromium plays a 'passive' role in the reaction; the metal ion does not co-ordinate directly to the bis(hydrazine) ligand, but merely acts as a source of protons for a 'normal' acid-catalysed condensation. In order to distinguish between these possibilities we have investigated the reactions in further detail. Mechanisms 1—3 all require that the bis(hydrazine) ligand reacts with the chromium(III) starting material to form an intermediate complex; 1 and 2 further require that chromium(III) complexes of the quinquedentate macrocyclic ligands are unstable with respect to the free ligands under the conditions of the condensation reaction. Finally, mechanism 4 requires that other buffers and acid catalysts should catalyse the formation of the free macrocyclic ligand (*and not polymer*).

$$[CrL^5(H_2O)]^{3+} \rightleftharpoons [CrL_5(OH)]^{2+} + H^+$$

Scheme 4.

Very slight changes in the electronic spectrum were detected when aqueous solutions containing L^3 and $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ were heated to reflux for 3 h; the most significant changes are the development of maxima at 510 and 555 nm. The bulk of the free ligand (95%) was recovered unchanged from the reaction mixture. The addition of 1 equiv. of 2,6-pyridinedialdehyde to such a reaction mixture resulted in the previously described colour changes and the formation of a red solution containing the free ligand L^9. No changes in the electronic spectrum occurred when an aqueous solution containing equimolar amounts of $[HL^9]^+$ and $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ was heated to reflux for 2 h. The macrocyclic ligand was recovered unchanged from the reaction mixture. These results indicate that mechanisms involving the direct formation of chromium-(III) or -(II) complexes of the bis(hydrazines) are unlikely; specifically, the formation of such complexes is dramatically slower than the observed rate of formation of free macrocycle. Whilst this observation does not preclude the mechanism, it seems unlikely that such complexes are involved.

In contrast to the lack of reaction observed in water, in boiling ethanolic solution L^3 reacts with $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ to give a brown solution, from which a brown microcrystalline solid could be obtained upon concentration. The brown solid is paramagnetic ($\mu_{eff.}$ 3.88) and microanalysis indicates a formulation $CrL^3Cl_3(H_2O)$. The i.r. spectrum of the solid exhibits NH and CH stretching modes at 3 300 and 2 950 cm^{-1} respectively. The brown solid is readily soluble in water, and the electronic spectrum of an aqueous solution (Figure 2) exhibits maxima at 475 (log ε 2.74), 510 (log ε 2.72), and 550 nm (log ε 2.49). It is evident that the spectral changes associated with the prolonged reaction of L^3 with $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ in water are due to the formation of small amounts of a chromium(III) complex of L^3. A comparison of the band intensities indicates the formation of 5—7% of the complex after 4 h at 80 °C under aqueous conditions; in contrast, reaction is complete in ethanol under these conditions. Identical changes in the electronic spectrum occurred when *aqueous* solutions of L^3 were boiled with $[Cr(H_2O)_6][NO_3]_3$. An exactly similar reaction occurred between $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ and L^5 in ethanolic solution to form the green paramagnetic ($\mu_{eff.}$ 3.88) solid $CrL^5Cl_3(H_2O)$. In the absence of full structural data, we consider that these chromium(III) complexes are most likely to be 'normal' octahedral species with the N_4 donor ligands occupying the equatorial plane and two axial chloride ligands giving a formulation $[CrLCl_2]Cl{\cdot}H_2O$. Conductivity of aqueous solutions of the two complexes indicate that they behave as 1:1 electrolytes, in accord with this formulation.

The green solid $[CrL^5Cl_2]Cl{\cdot}H_2O$ dissolves in water to give a green solution, which darkens slightly upon the addition of hydrochloric acid, but exhibits no significant changes in its electronic spectrum. The addition of 2,6-pyridinedialdehyde to this slightly acidified solution results in an immediate colour change to deep red-brown. Concentration of the reaction mixture allowed the isolation of a brown crystalline solid, which was soluble in water and other polar solvents, but insoluble in non-polar solvents. The i.r. spectrum exhibited absorptions at 3 400 and 2 900 cm^{-1} which are assigned to lattice and co-ordinated water respectively, but no bands which could be assigned to NH or CO stretching or bending modes. The compound is paramagnetic ($\mu_{eff.}$ 3.97) and conductivity measurements of aqueous solutions were consistent with a 1:3 electrolyte. These results, combined with microanalytical data, suggested the formation of a chromium(III) macrocyclic complex $[CrL^{14}(H_2O)_2]Cl_3{\cdot}H_2O$. An exactly analogous reaction occurred with $[CrL^3Cl_2]Cl$ to yield a paramagnetic ($\mu_{eff.}$ 3.98) brown crystalline solid formulated as $[CrL^9(H_2O)_2]Cl_3{\cdot}H_2O$. These putative macrocyclic complexes did not give observable n.m.r. spectra and only gave broad featureless e.s.r. spectra in glassy or liquid aqueous solution. The electronic spectrum of the macrocyclic complex $[CrL^9(H_2O)_2]Cl_3{\cdot}H_2O$ (Figure 3) differs significantly from that of the non-cyclic precursor.

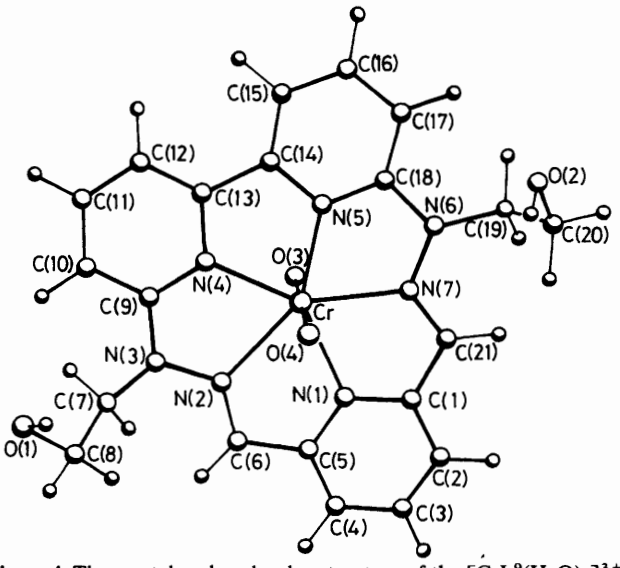


Figure 4. The crystal and molecular structure of the $[CrL^9(H_2O)_2]^{3+}$ cation in $[CrL^9(H_2O)_2]Cl_3 \cdot H_2O$[6]

We have previously reported the crystal and molecular structure of the complex $[CrL^9(H_2O)_2]Cl_3 \cdot H_2O$[6] which is shown in Figure 4. The structural determination confirmed the formation of the macrocyclic ligand and a pentagonal-bipyramidal chromium(III) complex. The planar quinquedentate macrocyclic ligand occupies the equatorial plane and the two co-ordinated water molecules are in the axial sites. The Cr–N bond lengths in the plane are in the range 2.017(5)—2.259(5) Å, with those to the 2,2′-bipyridine nitrogen atoms significantly shorter than those to the imine and unique pyridine nitrogen atoms. In the context of the studies reported in this paper, the significant observation is that the chromium(III) macrocyclic complex is indefinitely stable under aqueous acidic conditions. Further details of the structure of this compound have been discussed elsewhere.[10] We have not observed any loss of ligand from the macrocyclic complex under the reaction conditions in which the transient template reaction proceeds; indeed, we have been unable to demetallate the complex with concentrated hydrochloric acid or concentrated aqueous sodium cyanide solution. These observations conclusively prove that the chromium(III) macrocyclic complexes play no role in the transient template reactions. Furthermore, the chromium(III) complexes of the open-chain precursors are only very slowly formed in water, but when they are formed they are indefinitely stable in aqueous solution. All of these observations suggest that mechanisms 1—3 are untenable.

In order further to establish the role of the chromium(III) in the above reactions other experiments were performed. In each case, the reaction investigated was the condensation of L^3 with 2,6-pyridinedialdehyde to yield L^9. In aqueous solution in the absence of either chromium(III) or an acid catalyst the reaction resulted in the precipitation of polymeric orange materials and a clear orange red solution. This solution contained variable amounts of the macrocyclic ligand L^9 (typically 0—20%) which could be precipitated as the hexafluorophosphate salt. The yields in this reaction were very variable, and seemed to be critically dependent upon the concentration and temperature. Frequently, no macrocyclic product was obtained from the reaction. This result is in accord with our earlier studies of this class of macrocyclic ligand where, in general, we have been unable to obtain free macrocycles from metal-free condensations. In the presence of hydrochloric acid (pH 1) clear orange solutions were formed from which the hexafluorophosphate salt of L^9 could be obtained in yields of 70—75%. The presence of the hydrophobic hydroxyethyl substituents on the hydrazine appears to be important in this reaction; our previous studies on the other macrocyclic ligands has suggested that little if any free macrocycle is formed in acid-catalysed, metal-free reactions. Similar, but slightly higher yields of 75—80% of L^9 were obtained in the presence of both hydrochloric acid and chromium(III). Finally, yields of 70—80% of L^9 were obtained from the reaction in the presence of chromium(III) but with no added acid. It is this last observation which is of particular interest. The solution containing chromium(III) but no added acid had a pH of 6, and we consider that the chromium(III) is acting as a general or specific acid catalyst. The condensation of amines and hydrazines with carbonyl compounds is known to be acid catalysed. The macrocycle L^9 was obtained from solutions buffered at pH 4 and 6 but not at 7, and we consider this to be circumstantial evidence for the chromium acting as a source of proton and buffering the solution. The use of the chromium(III) transient template is of most use in the case of the macrocycles which do not possess hydroxyethyl tails which are *not* formed in a simple acid-catalysed condensation. It is significant that we have also found that the addition of lithium salts, which again buffer the solution at pH 5—6, are effective as templates for the formation of these macrocycles, although in this case the primary product *is* the lithium complex of the macrocycle, which undergoes an acid-promoted demetallation upon the addition of an excess of hydrochloric acid.[17]

We have attempted to extend these observations to the preparation of other quinquedentate and quadridentate macrocycles derived from polyamines, but in no case have we had any success. The important conclusion from these studies is that the role of a metal ion in a putative template reaction is not always simple. A related reaction, in which the true template ion in a reaction is H^+, has been reported previously.[18] There is a tendency to ascribe modification of ligand reactivity by metal ions to direct metal–ligand interactions; in the case of the chromium(III)-mediated transient template reactions this is not the case.

Acknowledgements

We thank the Royal Society and the Nuffield Foundation for a Fellowship (to M. S. K.), Dhaka University, Bangladesh for study leave (to M. S. K.), and S.E.R.C. for the studentships (to L-Y. C., A. R. D., and M. C. L.). We should also like to thank the Royal Society for funds towards the purchase of a spectrophotometer.

References

1 P. A. Chaloner, 'Handbook of Coordination Catalysis in Organic Chemistry,' Butterworths, London, 1986; M. M. Jones, 'Ligand Reactivity and Catalysis,' Academic Press, New York, 1968; D. H. Busch (ed.), 'Reactions of Coordinated Ligands and Homogeneous Catalysis,' ACS Symp. Ser. No. 37, 1963.

2 G. A. Melson (ed.), 'Coordination Chemistry of Macrocyclic Compounds,' Plenum, New York and London, 1979; M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, 1964, **86**, 213, 3651; D. H. Busch, *Adv. Chem. Ser.*, 1971, **100**, 44; L. F. Lindoy and D. H. Busch, *Prep. Inorg. Chem.*, 1971, **6**, 1; N. F. Curtis, *Coord. Chem. Rev.*, 1968, **3**, 3; A. M. Sargeson, *Pure Appl. Chem.*, 1984, **56**, 1603; C. O. Dietrick-Buchecker and J-P. Sauvage, *Chem. Rev.*, 1987, **87**, 795.

3 E. C. Constable, J. Lewis, and M. Schröder, *Polyhedron*, 1982, **1**, 311; E. C. Constable, J. Lewis, V. E. Marquez, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1986, 1747; E. C. Constable, M. G. B. Drew, G. Forsyth, and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1988, 1450; E. C. Constable, M. G. B. Drew, G. A. Forsyth, and M. D. Ward, *Polyhedron*, 1989, **8**, 2551; E. C. Constable, M. J. Doyle, S. M. Elder, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1989, 1376.

4 E. C. Constable and J. M. Holmes, *Inorg. Chim. Acta*, 1987, **126**, 187; E. C. Constable, M. G. B. Drew, and M. D. Ward, *J. Chem. Soc.*,

Chem. Commun., 1987, 600; M. Barley, E. C. Constable, S. A. Corr, M. G. B. Drew, R. C. S. McQueen, J. C. Nutkins, and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1988, 2655; E. C. Constable, R. P. Henney, and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1989, 570, 913; E. C. Constable, R. P. G. Henney, T. A. Leese, and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 443.

5 E. C. Constable and J. Lewis, *Polyhedron*, 1982, **1**, 303; E. C. Constable, J. Lewis, M. C. Liptrot, P. R. Raithby, and M. Schröder, *ibid.*, 1983, **2**, 301; E. C. Constable, J. Lewis, M. C. Liptrot, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1984, 2177; E. C. Constable, F. K. Khan, J. Lewis, M. C. Liptrot, and P. R. Raithby, *ibid.*, 1985, 333; E. C. Constable, J. M. Holmes, and R. C. S. McQueen, *ibid.*, 1987, 5; E. C. Constable and J. M. Holmes, *Polyhedron*, 1988, **7**, 2531.

6 L-Y. Chung, E. C. Constable, J. Lewis, P. R. Raithby, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1984, 1425.

7 J. Lewis and T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.*, 1980, 743, 1383; J. Lewis, M. Bishop, T. D. O'Donoghue, P. R. Raithby, and J. Ramsden, *ibid.*, p. 1390; J. Lewis, C. W. G. Ansell, P. R. Raithby, T. D. O'Donoghue, and J. Ramsden, *ibid.*, 1982, 2127; J. Lewis, C. W. G. Ansell, P. R. Raithby, and T. D. O'Donoghue, *ibid.*, 1983, 177; J. Lewis, C. W. G. Ansell, M. Schröder, and J. Ramsden, *Polyhedron*, 1982, **2**, 489; J. Lewis, C. W. G. Ansell, M. C. Liptrot, P. R. Raithby, and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1982, 1593.

8 G. M. Sheldrick, SHELX crystallographic computing package, University of Cambridge, 1980.

9 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

10 M. C. Liptrot, Ph.D. Thesis, Cambridge, 1983.

11 K. Henrick, P. A. Tasker, and L. F. Lindoy, *Prog. Inorg. Chem.*, 1985, **33**, 1.

12 S. M. Nelson, S. G. McFall, M. G. B. Drew, and A. H. B. Otuman, *J. Chem. Soc., Chem. Commun.*, 1977, 370; M. G. B. Drew, A. H. B. Otuman, S. G. McFall, P. D. A. McIllroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 438; M. G. B. Drew, F. S. Esho, A. Lavery, and S. M. Nelson, *ibid.*, 1984, 545; M. G. B. Drew, J. Nelson, F. Esho, V. McKee, and S. M. Nelson, *ibid.*, 1982, 1837.

13 E. C. Constable, S. Corr, and J. Lewis, *Inorg. Chim. Acta*, 1986, **116**, 95.

14 N. Sadasivan and J. F. Endicott, *J. Am. Chem. Soc.*, 1966, **88**, 5468.

15 G. Muhmel and E. Breitmaier, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 772.

16 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1958.

17 E. C. Constable, M. J. Doyle, J. Healy, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1988, 1262; E. C. Constable, L-Y. Chung, J. Lewis, and P. R. Raithby, *ibid.*, 1986, 1719.

18 A. J. Rest, *J. Chem. Soc., Chem. Commun.*, 1981, 149; M. de Sousa Healy and A. J. Rest, *J. Chem. Soc., Perkin Trans. 1*, 1985, 973.

Received 25*th September* 1989; *Paper* 9/04098F