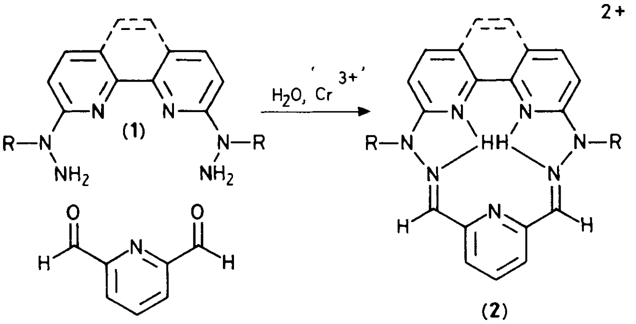
Structural Characterisation of a Pentagonal Bipyramidal Macrocyclic Chromium(III) Complex; an Explanation of a Chromium-mediated 'Transient-template' Effect

L-Y. Chung, Edwin C. Constable, Mohammed S. Khan, Jack Lewis,* Paul R. Raithby, and Maria D. Vargas
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

The template condensation of 6,6′-bis(hydrazino)-2,2′-bipyridines or 2,9-bis(hydrazino)-1,10-phenanthrolines with 2,6-pyridine dicarbonyls in the presence of chromium(III) chloride leads to the formation of free macrocycles rather than the expected metal complexes; the origin of this 'transient-template' effect is discussed and the crystal structural analysis of a chromium(III) macrocyclic complex is described.

We have recently shown that the course of macrocyclic template condensations may be profoundly affected if there is a mis-match between the donor properties of the macrocycle and the acceptor properties of the metal template.[1,2] Specifically, we have demonstrated the use of dimethyltin(IV) as a template in the formation of metal-free pentadentate macrocycles based on 2,2′:6′,2″-terpyridine, and have ascribed the formation of the metal-free species to a labilisation of the metal ion in the macrocyclic complex. In the course of this work,[1,2] and in other studies of 2,2′-bipyridine-based macrocycles, we observed the formation of free macrocycles when chromium(III) was used as a template. In this communication, we describe the use of chromium(III) in the preparation of pentadentate N_5 macrocycles, and report the crystal structure of a pentagonal bipyramidal chromium(III) complex of such a macrocycle.



(2)

a; R = CH_2CH_2OH

a; R = CH_2CH_2OH

The condensation of the bis(hydrazines) (**1**) (2,2′-bipyridine or 1,10-phenanthroline; R = H, Me, or CH_2CH_2OH) with 2,6-pyridinedialdehyde in the presence of aqueous chromium(III) chloride (green commercial form) led to the formation of respectable yields (60—80%) of the metal-free macrocycles (**2**). In no case could a chromium(III) containing complex of either (**1**) or (**2**) be isolated from the reaction mixture. A number of other examples are known in which iron(III),[3] chromium(III),[4] or tin(IV)[1,2] act as transient templates in the formation of metal-free macrocyclic ligands, and these effects are commonly ascribed to hole-size mis-match phenomena. It seems unlikely that this is a simple ionic radius mis-match,[5,6] since complexes of these ligands with iron(II) and cobalt(III) are known to be stable to demetallation, and we considered a proton mediated process, driven by the acidity of the water molecules co-ordinated to the hard chromium(III) ion.[7]

Support for this mechanism comes from the observations that identical yields of free macrocycles were obtained when the reaction was conducted in the presence of chromium(III) chloride, chromium(III) chloride and hydrochloric acid (pH = 1), or hydrochloric acid alone (pH = 1). Only low yields (*ca.* 20%) of macrocycle were obtained in the absence of acid (pH = 6) or in an acetate buffer (pH = 4.5).[8] This indicates that the 'true' template in these chromium-mediated reactions is the proton, and to establish this we investigated the interaction of chromium(III) chloride with 6,6′-bis(α-2-hydroxyethylhydrazino)-2,2′-bipyridine (**1a**, R = CH_2CH_2OH) and 2,6-pyridinedialdehyde.

Aqueous solutions containing (**1a**) and chromium(III) chloride initially exhibited electronic spectra identical to a superimposition of the components. However, upon heating to 80 °C, a slow reaction occurred, with maxima developing at 475, 510, and 550 nm, over a period of 6—7 h. This behaviour is in marked contrast to the instantaneous change to the red colour of the corresponding bipyridine macrocycle (**2a**, R = CH_2CH_2OH) upon adding 2,6-pyridinedialdehyde. Although no chromium containing species could be isolated under aqueous conditions, chromium(III) chloride reacted with (**1a**) in ethanol to give the brown compound $[Cr(\mathbf{1a})Cl_2]Cl$ (1 : 1 electrolyte in water), which also exhibited absorption maxima at 475 (log ε 2.74), 510 (2.72), and 550 nm (2.49). This establishes that the chromium(III) complex of (**1a**) is only formed slowly in water.

The involvement of the complex $[Cr(\mathbf{1a})Cl_2]Cl$ in the transient template reaction was precluded by a study of its reaction with 2,6-pyridinedialdehyde. When $[Cr(\mathbf{1a})Cl_2]Cl$ was treated with the dialdehyde under conditions identical to those utilised in the transient template reaction (water, pH = 1), a slow reaction occurred (*ca.* 4 h), to give the chromium(III) complex $[Cr(\mathbf{2a})(H_2O)_2]Cl_3 \cdot 2H_2O$. This compound did not demetallate under the reaction conditions, which establishes that any mis-match between chromium(III) and the macrocyclic ligand does not result in a labilisation of the metal ion.

The macrocyclic complex was obtained as a red crystalline solid, and the structure was confirmed by a single crystal *X*-ray analysis (Figure 1).†‡ The chromium atom is in a regular

---

† New compounds have all given satisfactory elemental analyses, and where appropriate, magnetic measurements, n.m.r. or e.s.r. spectra.

‡ *Crystal data* for $[Cr(\mathbf{2a})(H_2O)_2]Cl_3 \cdot 2H_2O$: $C_{21}H_{29}N_7O_6CrCl_3$, M = 633.5, triclinic, space group $P\bar{1}$, a = 7.385(1), b = 11.504(7), c = 16.120(2) Å, α = 96.19(2), β = 93.28(1), γ = 101.54(3)°, U = 1329.6 Å^3, Z = 2, D_c = 1.58 g cm^{-3}, $F(000)$ = 654, (Mo-K_α) = 7.22 cm^{-1}. Intensity data ($2\theta_{max}$ = 42.5°) were recorded on a Stoe-Siemens four-circle diffractometer using graphite-monochromated Mo-K_α radiation and an ω–θ scan technique. The data were corrected for absorption and averaged to give 2490 unique observed reflections [$F > 4\sigma(F)$]. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least squares (all non-hydrogen atoms anisotropic) to R = 0.062. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

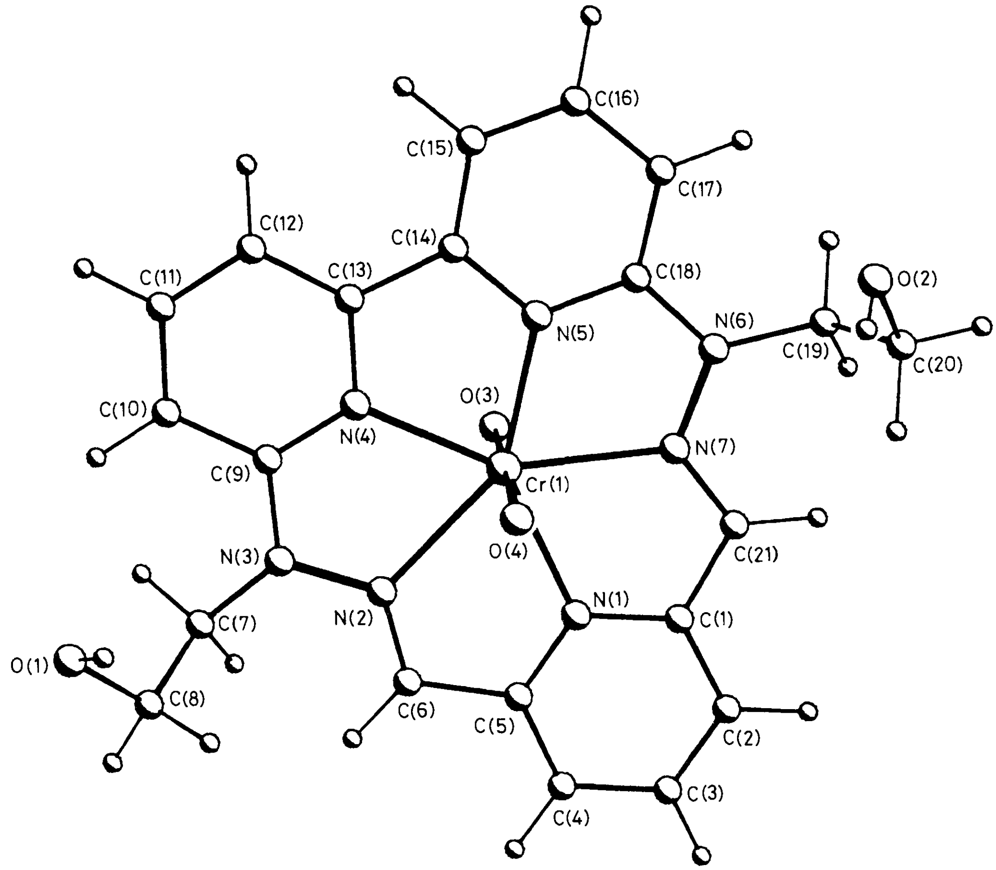


Figure 1. Molecular structure of the $[\mathrm{Cr}(\mathbf{2a})(\mathrm{H_2O})_2]^{3+}$ cation. Some hydrogen atoms have been omitted for clarity. Selected bond lengths: Cr(1)–N(1), 2.206(5); Cr(1)–N(2), 2.259(5); Cr(1)–N(4), 2.059(4); Cr(1)–N(5), 2.017(5); Cr(1)–N(7), 2.196(4); Cr(1)–O(3), 2.036(4); Cr(1)–O(4), 2.009(4); N(2)–N(3), 1.376(6); N(6)–N(7), 1.372(7); N(2)–C(6), 1.303(8); N(7)–C(21), 1.298(8) Å.

pentagonal bipyramidal environment, with the axial positions occupied by water molecules. The macrocyclic ligand is strictly planar, although the axial water molecules are bent back towards the pyridine derived from the dialdehyde (∠O–Cr–O, 177.4°). There is no evidence for any interaction of the metal with the chloride counter ions or the hydroxyethyl substituents.

This is the first example of a seven-co-ordinate macrocyclic complex of chromium, and is only the second pentagonal bipyramidal chromium(III) complex to be described.[9]

In conclusion, the sole function of the chromium(III) in these transient template reactions is to provide a source of protons, which act as the true template. Chromium(III) complexes of the macrocyclic ligands and their open-chain precursors are stable with respect to demetallation under the reaction conditions.

We thank the Commissioners for the Royal Exhibition of 1851 for the award of a Science Research Fellowship (M. S. K.), and the S.E.R.C for the award of a Research Studentship (L-Y. C.).

Received, 2nd August 1984; Com. 1132

References

1 E. C. Constable, J. Lewis, M. C. Liptrot, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1984, 2177.
2 E. C. Constable, F. K. Khan, J. Lewis, M. C. Liptrot, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, in the press.
3 N. Sadasivan and J. F. Endicott, *J. Am. Chem. Soc.*, 1966, **88**, 5468.
4 G. Muhmel and E. Breitmaier, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 772.
5 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
6 M. C. Liptrot, Ph.D. Thesis, Cambridge, 1984.
7 J. Burgess, 'Metal Ions in Solution', Ellis Horwood, 1978.
8 E. C. Constable, S. Corr, and J. Lewis, unpublished results.
9 G. J. Palenik, D. W. Wester, U. Rychlewska, and R. C. Palenik, *Inorg. Chem.*, 1976, **15**, 1814.