Electron-transfer Reactivity of the ^2E Excited State of *trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III)

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Methyl viologen radical cation reduces the ^2E excited state of *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$ in acidic solutions to yield a novel chromium(II) macrocycle, *trans*-$Cr([14]aneN_4)(H_2O)_2^{2+}$, as a final product.

The ^2E excited state of *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$† has a long lifetime in solution (at 20 °C, τ_0 is 55 μs in H_2O and 136 μs in dimethylsulphoxide)[1] and it exhibits a strong phosphorescence centred at 680 nm. The lifetime and luminescence intensity both increase dramatically upon deuteriation of the macrocyclic –NH groups and the ammines, but deuteriation of the solvent is without effect.[1]

In contrast to other long-lived ^2E excited states of chromium(III) complexes,[1–4] *trans*-$^*Cr([14]aneN_4)(NH_3)_2^{3+}$ appeared to have no chemical reactivity. It is not quenched by O_2, and does not photoaquate even with prolonged photolysis.[1] This species decays mainly by radiationless relaxation.

In contrast to these reports, we have now found that *trans*-$^*Cr([14]aneN_4)(NH_3)_2^{3+}$ and its $[^2H_{10}]$ derivative react with methyl viologen radical cation, MV^+, at an almost diffusion-controlled rate. The kinetics, studied by laser flash photolysis,[5] were mostly done with the perdeuterio complex in D_2O.‡ The luminescence quenching at 680 nm occurs at the same rate as does the decrease of MV^+ absorbance at 600 nm ($\varepsilon = 1.37 \times 10^4$ dm^3 mol^{-1} cm^{-1}),[6] in full accord with equation 1. The value of k_1, $(5.28 \pm 0.08) \times 10^8$ dm^3 mol^{-1} s^{-1} in 5 mmol dm^{-3} $HClO_4$, increases with ionic strength, as expected for a reaction between two cations. At $\mu = 0.050$ mol dm^{-3} ($HClO_4 + LiClO_4$), $k_1 = (1.09 \pm 0.03) \times 10^9$ dm^3 mol^{-1} s^{-1}, independent of $[H^+]$ in the range 1–50 mmol dm^{-3}.

$$\textit{trans}\text{-}^*Cr([14]aneN_4)(NH_3)_2^{3+} + MV^+ \rightarrow \textit{trans}\text{-}Cr([14]aneN_4)(NH_3)_2^{2+} + MV^{2+} \quad (1)$$

After completion of reaction 1, a slow step develops that regenerates MV^+. The magnitude of the absorbance increase at 600 nm is comparable to that for the absorbance decrease in reaction 1. The analysis of NH_4^+ at the end of the reaction[7] showed that overall two moles of NH_4^+ were liberated per mole of *trans*-$^*Cr([14]aneN_4)(NH_3)_2^{3+}$ quenched by MV^+. All these observations can be accounted for by reactions 1–3.

$$\textit{trans}\text{-}Cr([14]aneN_4)(NH_3)_2^{2+} + 2\,H_2O + 2\,H^+ \rightarrow \textit{trans}\text{-}Cr([14]aneN_4)(H_2O)_2^{2+} + 2\,NH_4^+ \quad (2)$$

$$\textit{trans}\text{-}Cr([14]aneN_4)(H_2O)_2^{2+} + MV^{2+} \rightarrow \textit{trans}\text{-}Cr([14]aneN_4)(H_2O)_2^{3+} + MV^+ \quad (3)$$

Added Cl^- strongly accelerates the secondary electron transfer of equation 3, rate $= k[Cr([14]aneN_4)(H_2O)_2^{2+}][MV^{2+}][Cl^-]$, where $k = (4.5 \pm 0.3) \times 10^5$ dm^6 mol^{-2} s^{-1} at 25 °C and 0.05 mol dm^{-3} ionic strength.

The implication of equation 2 is not only that both ammines rapidly dissociate from *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$,¶ as expected, but also that the macrocyclic ligand does not. The

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† [14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane.

‡ The use of the deuteriated solvent prevents any H–D exchange, which would cause a decrease in the lifetime of the excited state as solutions age. The deuterium content in kinetic solutions was typically *ca.* 98%. Small amounts of H (*ca.* 2%) were introduced with solutions of $HClO_4$ and $LiClO_4$ in H_2O.

¶ The rapid loss of the two common ligands from Cr(II) in eqn 2 effectively presents the back-electron transfer between MV^{2+} and *trans*-$Cr([14]ane\,N_4)(NH_3)_2^{2+}$.

novel chromium(II) macrocycle formed in reaction 2, *trans*-$Cr([14]aneN_4)(H_2O)_2^{2+}$, is a strong reductant. It reduces MV^{2+} (eqn. 3), $PhCH_2Br$ ($k = 9.2 \times 10^3$ dm^3 mol^{-1} s^{-1})§ and t-butyl hydroperoxide ($k = 1.5 \times 10^5$ dm^3 mol^{-1} s^{-1}).§

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§ The measurements were done by use of MV^+ as a coloured probe. The initial loss of MV^+ in reaction 1 is followed by a second, slower decrease of absorbance at 600 nm with $k_{obs} = k[PhCH_2Br]$. Based on the known redox chemistry of $PhCH_2Br$ and the known reactivity of MV^+ towards radicals, we assign the rate-determining step to the reaction $Cr([14]aneN_4)(H_2O)_2^{2+} + PhCH_2Br \rightarrow BrCr([14]aneN_4)(H_2O)^{2+} + PhCH_2^{\bullet}$. Subsequent rapid reaction of $PhCH_2^{\bullet}$ with MV^+ provides the colour change observed. Similar mechanism can be assigned to the reaction of $Cr([14]aneN_4)(H_2O)_2^{2+}$ with Bu^tOOH, in which case $CH_3^{\bullet}$ is the intermediate reacting with MV^+.

References

1 N. A. P. Kane-Maguire, K. C. Wallace and D. B. Miller, *Inorg. Chem.*, 1985, **24**, 597.
2 A. D. Kirk, *Coord. Chem. Rev.*, 1981, **39**, 225.
3 V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri, *Top. Curr. Chem.*, 1978, **75**, 1.
4 R. B. Lessard, J. F. Endicott, M. W. Perkovic and L. A. Ochrymowycz, *Inorg. Chem.*, 1989, **28**, 2574.
5 J. D. Melton, J. H. Espenson and A. Bakac, *Inorg. Chem.*, 1986, **25**, 4104; M. A. Hoselton, C.-T. Lin, H. A. Schwartz and N. Sutin, *J. Am. Chem. Soc.*, 1978, **100**, 2383. The energy of the laser pulse is 250 mJ and the pulse width 600 ns.
6 T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617.
7 W. T. Bolleter, C. J. Bushman and P. W. Tidwell, *Anal. Chem.*, 1961, **33**, 592. During the latter stages of this analytical procedure the solution is made alkaline and the excess *trans*-$Cr([14]aneN_4)(NH_3)_2^{3+}$ rapidly hydrolyses to give the monoammine complex and free NH_3.[1] This, however, presented no problem, because at this stage NH_4^+ has no effect on the final absorbance, as shown in independent experiments.