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

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Methyl viologen radical cation reduces the ^{2}E 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$_2$O)$_2^{2+}$, as a final product.

The ^{2}E 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$_2$O 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 ^{2}E 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 [^{2}H$_{10}$] 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$_2$O.[‡] 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}.

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

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.

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

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

Added Cl$^-$ strongly accelerates the secondary electron transfer of equation 3, rate = k[Cr([14]aneN$_4$)(H$_2$O)$_2^{2+}$][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$_2$O.

[¶] 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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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.

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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^+.