

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

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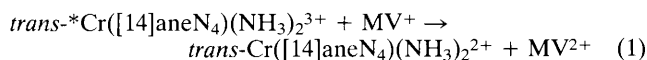
Methyl viologen radical cation reduces the ²E excited state of *trans*-Cr([14]aneN₄)(NH₃)₂³⁺ in acidic solutions to yield a novel chromium(II) macrocycle, *trans*-Cr([14]aneN₄)(H₂O)₂²⁺, as a final product.

The ²E excited state of *trans*-Cr([14]aneN₄)(NH₃)₂³⁺† has a long lifetime in solution (at 20 °C, τ₀ is 55 μs in H₂O 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 deuteration of the macrocyclic -NH groups and the amines, but deuteration of the solvent is without effect.¹

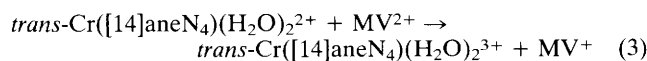
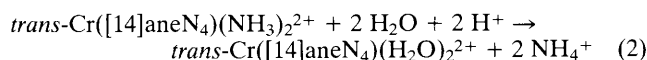
In contrast to other long-lived ²E excited states of chromium(III) complexes,¹⁻⁴ *trans*-*Cr([14]aneN₄)(NH₃)₂³⁺ appeared to have no chemical reactivity. It is not quenched by O₂, and does not photoaquate even with prolonged photolysis.¹ This species decays mainly by radiationless relaxation.

In contrast to these reports, we have now found that *trans*-*Cr([14]aneN₄)(NH₃)₂³⁺ and its [²H₁₀] 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 D₂O.‡ The luminescence quenching at 680 nm occurs at the same rate as does the decrease of MV⁺ absorbance at 600 nm (ε = 1.37 × 10⁴ dm³ mol⁻¹ cm⁻¹),⁶ in full accord with equation 1. The value of *k*₁, (5.28 ± 0.08) × 10⁸ dm³ mol⁻¹ s⁻¹ in 5 mmol dm⁻³ HClO₄, increases with ionic strength, as expected for a reaction between two cations. At μ = 0.050 mol dm⁻³

(HClO₄ + LiClO₄), *k*₁ = (1.09 ± 0.03) × 10⁹ dm³ mol⁻¹ s⁻¹, independent of [H⁺] in the range 1–50 mmol dm⁻³.



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 NH₄⁺ at the end of the reaction⁷ showed that overall two moles of NH₄⁺ were liberated per mole of *trans*-*Cr([14]aneN₄)(NH₃)₂³⁺ quenched by MV⁺. All these observations can be accounted for by reactions 1–3.



Added Cl⁻ strongly accelerates the secondary electron transfer of equation 3, rate = *k*[Cr([14]aneN₄)(H₂O)₂²⁺][MV²⁺][Cl⁻], where *k* = (4.5 ± 0.3) × 10⁵ dm⁶ 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 amines rapidly dissociate from *trans*-Cr([14]aneN₄)(NH₃)₂³⁺,¶ as expected, but also that the macrocyclic ligand does not. The

† [14]aneN₄ = 1,4,8,11-tetraazacyclotetradecane.

‡ The use of the deuterated 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 HClO₄ and LiClO₄ in H₂O.

¶ The rapid loss of the two common ligands from Cr(II) in eqn 2 effectively presents the back-electron transfer between MV²⁺ and *trans*-Cr([14]aneN₄)(NH₃)₂²⁺.

novel chromium(II) macrocycle formed in reaction 2, *trans*-Cr([14]aneN₄)(H₂O)₂²⁺, is a strong reductant. It reduces MV²⁺ (eqn. 3), PhCH₂Br ($k = 9.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)[§] and t-butyl hydroperoxide ($k = 1.5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).[§]

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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 $k_{\text{obs}} = k[\text{PhCH}_2\text{Br}]$. Based on the known redox chemistry of PhCH₂Br and the known reactivity of MV⁺ towards radicals, we assign the rate-determining step to the reaction $\text{Cr}([\text{14}]\text{aneN}_4)(\text{H}_2\text{O})_2^{2+} + \text{PhCH}_2\text{Br} \rightarrow \text{BrCr}([\text{14}]\text{aneN}_4)(\text{H}_2\text{O})_2^{2+} + \text{PhCH}_2\cdot$. Subsequent rapid reaction of PhCH₂· with MV⁺ provides the colour change observed. Similar mechanism can be assigned to the reaction of Cr([14]aneN₄)(H₂O)₂²⁺ with Bu^tOOH, in which case CH₃· is the intermediate reacting with MV⁺.

References

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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]aneN₄)(NH₃)₂³⁺ rapidly hydrolyses to give the monoamine complex and free NH₃.¹ This, however, presented no problem, because at this stage NH₄⁺ has no effect on the final absorbance, as shown in independent experiments.