A long-lived ^{2}E state for a Cr(III)N$_6$ amine chromophore at 298 K: [Cr(*fac*-Me$_5$-D_{3h}tricosaneN$_6$)]Cl$_3$†

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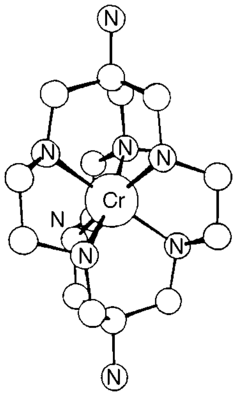
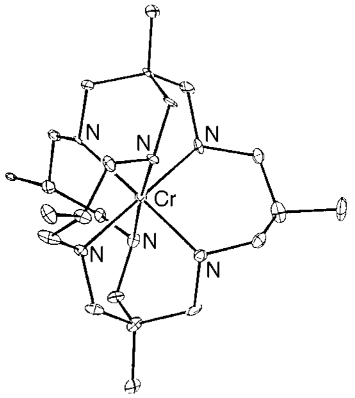
The ^{2}E state lifetime of the C_3 ion [Cr(*fac*-Me$_5$-D_{3h}tricosaneN$_6$)]$^{3+}$ is 235 μs in H$_2$O and 1.5 ms in D$_2$O at 298 K, the longest lifetimes yet reported for a saturated Cr(III)N$_6$ chromophore at room temperature.

The Cr(III) sarN$_6$ cage complexes (example shown in **I**) feature surprisingly short ^{2}E lifetimes at 298 K (<10 ns)[1,2] in comparison with that of the parent [Cr(NH$_3$)$_6$]$^{3+}$ ion (2.2 μs at 293 K).[3] In contrast, the larger [Cr(*fac*-Me$_5$-D_{3h}tricosaneN$_6$)]$^{3+}$ complex (**II**) has a considerably longer ^{2}E lifetime of 235 μs in aqueous solution at the same temperature. This latter complex was obtained recently from the reaction of [Cr(py)$_3$Cl$_3$] and the free Me$_5$-tricosaneN$_6$ ligand in the presence of zinc dust under anaerobic conditions and was characterised by microanalysis, X-ray crystallography, electrochemistry and electronic spectroscopy.[4–6]



I



II

Cooling the [Cr(*fac*-Me$_5$-D_{3h}tricosaneN$_6$)]$^{3+}$ ion to 77 K merely doubles the ^{2}E lifetime (to 440 μs) and deuteration of the secondary amines extends it to 1.5 ms at 298 K. In contrast, the ^{2}E lifetime for the [Cr(sar)]$^{3+}$ ion increases by $\geqslant 10^4$-fold upon cooling to 77 K (Fig. 1), to 60 μs, a value consistent with those for a range of related Cr(III) hexaamine complexes.[1,2] Why these apparently similar cage complexes have markedly different photophysical properties needs to be explored.

The rate of excited state relaxation is determined by radiative and non-radiative processes. In the latter instance, electronic energy is dissipated into vibrational energy of the chromophore or the solvent molecules. Photochemical processes such as bond dissociation and redox processes can also contribute to the decay. The Cr(III) cage complexes **I** and **II** have no discernible photochemical ligand dissociation from either the ^{2}E or ^{4}T$_2$ states, unlike the parent [Cr(NH$_3$)$_6$]$^{3+}$ ion and related di-, tri- and multi-dentate Cr(III)N$_6$ complexes.[1–4,6–9] It should also be noted that a proposed associative pathway[9–11] is unlikely since the steric constraints of the cage complexes hinder the coordination of a seventh donor group.[1,2] There is also no redox quenching in the presence of a reductant,[4] so it is unlikely that such a process contributes significantly to the ^{2}E decay rate. Back intersystem crossing (^{2}E $\longrightarrow$ ^{4}T$_2$) can sometimes provide a deactivation route for Cr(III) complexes; however, the ^{4}T$_2$ state is *ca.* 7000 cm^{-1} higher in energy than the ^{2}E state for both cage complexes. This energy gap is similar to that of other Cr(III) hexaamine complexes where back intersystem crossing has been considered negligible.[8,12–15]

The ^{2}E lifetimes of most saturated amine Cr(III)N$_6$ complexes lie in the range 60–440 μs in the temperature-independent regime[1,2,8,9,13,15–18] and quantum efficiencies for the luminescence are *ca.* 1%.[1,13,15–17,19] The relaxation rate is thus dominated by non-radiative deactivation, a multiphonon process and as such, strongly dependent on the energy of vibrations accessible in ground and excited states (accepting and promoting modes, respectively). High energy acceptors include N–H stretching modes in this instance and the ^{2}E lifetime dependence on the number of N–H modes in the first coordination sphere has been addressed for a range of Cr(III)N$_6$ complexes.[17,20] Although deuteration of the coordinated amines increases the lifetime for both cage complexes roughly tenfold at 77 K, the N–H acceptors alone do not account for their very different temperature dependences.

The promoting modes couple the excited state and the ground state and modify the electronic gap by their frequency.[13,21] The population of promoting modes can lead to a strong temperature dependence of the ^{2}E lifetime. In particular, the rapid decrease in the ^{2}E lifetimes from 150 to 200 K for the Cr(III) sar complexes[2] indicates the existence of such an efficient

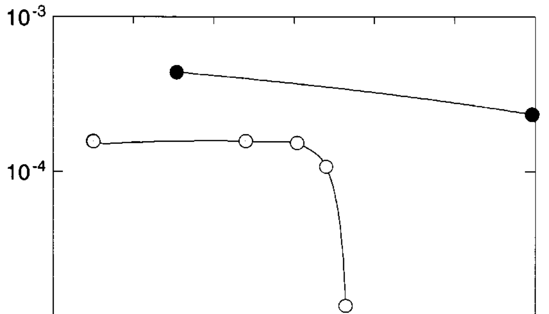


Fig. 1 Temperature dependences of the ^{2}E lifetimes for [Cr(*fac*-Me$_5$-D_{3h}tricosaneN$_6$)]Cl$_3$ (●) and [Cr(sar)]Cl$_3$ (○) in ethylene glycol–water (2 : 1 and 1 : 1, respectively).

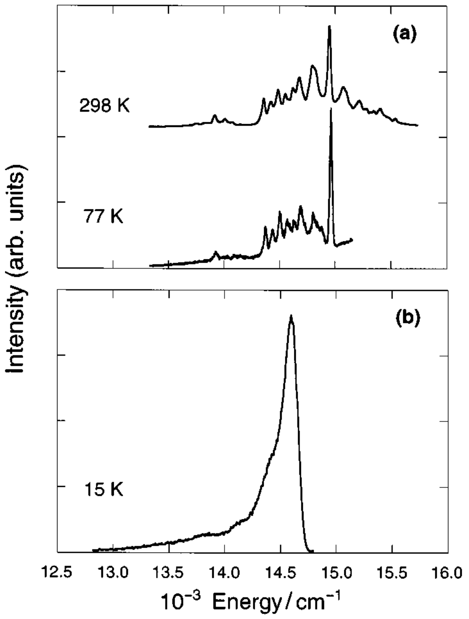


Fig. 2 Emission spectra of (a) $[Cr(\textit{fac}\text{-}Me_5\text{-}D_{3h}tricosaneN_6)]Cl_3$ at 298 and 77 K (2 : 1 ethylene glycol–water) and (b) $[Cr(sar)](CF_3SO_3)_3$ at 15 K (2 : 1 ethylene glycol–water).

promoting mode which becomes thermally activated. In contrast, the lifetime of the $[Cr(\textit{fac}\text{-}Me_5\text{-}D_{3h}tricosaneN_6)]^{3+}$ ion is decreased only slightly at 298 K, inferring that there is no corresponding and effective promoting mode for this complex.

The 0–0 transition is accompanied by relatively intense vibrational sidelines in the $[Cr(\textit{fac}\text{-}Me_5\text{-}D_{3h}tricosaneN_6)]^{3+}$ spectrum, characteristic of magnetic dipole-allowed transitions [Fig. 2(a)]. In contrast, the 0–0 transition dominates the emission spectrum of the $[Cr(sar)]^{3+}$ ions [Fig. 2(b)] and the vibrational fine-structure is poorly resolved due to more pronounced inhomogeneous broadening.[22,23] As the N–H interactions for the two types of complexes with the surrounding matrix are likely to be similar, the magnitude of this broadening can be ascribed to the $[Cr(sar)]^{3+}$ ion existing in different conformations. The sar complexes are able to undergo conformational changes such as twisting the ligand caps to change the symmetry from C_3 to D_3. This movement is coupled to other conformational changes involving the alignment of the C–C bond of the ethylenediamine chelate strap with the C_3 axis. The C–C bond may be oblique (*ob*) or parallel (*lel*) to the C_3 axis, giving rise to ob_3, ob_2lel, $oblel_2$ or lel_3 conformations. The same conformational lability is anticipated in the ^2E state, since its electronic configuration and thus equilibrium geometry are similar to that of the ground state. The number of effective accepting modes is governed by symmetry and interconversion results in variations in microsymmetry about the Cr(III)N_6 chromophore which induces more accepting modes. It follows that the conformational changes may result in a promoting mode which can be thermally activated.

Conformer interconversion is rather more difficult for the $[Cr(\textit{fac}\text{-}Me_5\text{-}D_{3h}tricosaneN_6)]^{3+}$ ion. Topological constraints require that cap twisting converts the six-membered chelate rings forming the straps from the stable chair to the less stable skew-boat conformations. The equatorial methyl groups are thereby driven to more axial and less stable positions. Both factors restrict the conformational changes. It is anticipated that the excited state complex also has the same conformational preference and conformational interconversion therefore would not act as a promoting mode in this case. This rigidity may account for the remarkably long ^2E state lifetime at 298 K, in contrast to those of the Cr(III) sar complexes. The greater inhomogeneous broadening in the emission spectra of the smaller cage complexes independently supports this argument.

Notes and references

† Abbreviated ligand names used in this paper: $\textit{fac}\text{-}Me_5\text{-}D_{3h}tricosaneN_6$: *facial*-1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane; sar = sarcophagine: 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (see *J. Chem. Soc., Chem. Commun.*, 1994, 1513.

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