

Seven-coordinate Mn²⁺ ions in [Mn(15-crown-5)(H₂O)₂]²⁺ as luminescent probes for dynamic supramolecular events†

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Spectra and temperature dependent decay rates of emission from [Mn(15-crown-5)(H₂O)₂]²⁺ ions anchored by a network of O–H...Br...H–O bonds in two- and one-dimensional supramolecular arrays of {[Mn(15-crown-5)(H₂O)₂][TlBr₅]}_n **1 and {[Mn(15-crown-5)(H₂O)₂][Br₂]}_n **2** demonstrate the potential efficacy of manganese(II) ions as luminescent probes for supramolecular dynamics.**

The good response of the manganese(II) ⁴T₁(⁴G) state to changing ligand field strength and symmetry as well as the high sensitivity of luminescence techniques, such as time resolved luminescence spectroscopy, make the Mn²⁺[⁴T₁(⁴G)→⁶A₁] emission attractive as a potential diagnostic tool for coordination characteristics of divalent metal ions.^{1,2} Besides classical four- and six-coordinate oxide and halide species,³ Mn²⁺[⁴T₁(⁴G)→⁶A₁] emission was recently shown to occur in well defined seven- and eight-coordinate environments⁴ thereby expanding the range of Mn²⁺ coordination environments accessible by luminescence techniques. Herein we demonstrate the diagnostic efficacy of the Mn²⁺[⁴T₁(⁴G)→⁶A₁] emission by probing the behaviour of coordinated H₂O in response to thermal tuning of the structural rigidity of [Mn(15-crown-5)(OH₂)₂]²⁺ cations anchored in two- and one-dimensional supramolecular arrays of {[Mn(15-crown-5)(H₂O)₂][TlBr₅]}_n **1**⁴ and {[Mn(15-crown-5)(H₂O)₂][Br₂]}_n **2**.⁵

Compounds **1**⁴ and **2**⁵ were prepared as described previously, whilst compound **3** was obtained by a procedure similar to that used for **2** but with D₂O and CH₃OD replacing H₂O and CH₃OH respectively. X-Ray analysis‡ shows compound **1** to be composed of two-dimensional corrugated sheets of [TlBr₅]²⁻ anions and [Mn(15-crown-5)(OH₂)₂]²⁺ cations cross-linked via O–H...Br hydrogen bonds (Fig. 1). The symmetry at the seven-coordinate manganese centre is crystallographically imposed C_{2h} with the two symmetry related aqua ligands lying on the mirror plane. The 15-crown-5 component is disordered, having four resolved symmetry-imposed partially overlapping orientations. The [TlBr₅]²⁻ dianion has crystallographic C_{2v} symmetry, adopting a slightly distorted trigonal bipyramidal geometry; the equatorial Tl–Br bonds subtend angles of 116.43(5), 116.43(5) and 127.15(10)° and the axial bonds an angle of 175.36(9)°, and there is a very marked asymmetry between the axial [2.883(2) Å] and the equatorial [2.540(2) and 2.552(3) Å] bond lengths. The anion geometry observed here {the first reported structural characterisation of [TlBr₅]²⁻} differs markedly from that observed in the only two reported examples of the closely related anion [TlCl₅]²⁻, both of which are slightly distorted square pyramidal with only small asymmetries in the bond lengths.⁶ A [Br...TlBr₄]²⁻ species was reported recently.⁷

In contrast, the structure of **2** comprises one-dimensional chains of [Mn(15-crown-5)(OH₂)₂]²⁺ cations linked by pairs of O–H...Br hydrogen bonds to the Br⁻ anions.⁵

In the light of these structural results, it was interesting to determine if this difference in structural rigidity would translate into contrasts in the ability of H₂O to quench Mn²⁺[⁴T₁(⁴G)→⁶A₁] emission from the [Mn(15-crown-5)(H₂O)₂]²⁺ cations of **1** and **2**. The excitation and luminescence spectra of dihydrates **1** and **2** were too weak to measure reliably on the LS5B spectrometer.§ We thus sought to prepare deuterates of **1** and **2**, namely [Mn(15-crown-5)(D₂O)₂][TlBr₅] and [Mn(15-crown-5)(D₂O)₂][Br₂], since D₂O vibrations are much less effective quenchers. However, impracticably large amounts of the CH₃OD–CH₂Cl₂ mixed solvent system were required for the deuteration of **1** and thus its synthesis was abandoned. Crystals of [Mn(15-crown-5)(D₂O)₂][Br₂] **3** are readily prepared and upon microscopic examination were found to have a morphology similar to that of **2**. The emission and excitation spectra of seven-coordinate manganese(II) in [Mn(15-crown-5)(D₂O)₂]²⁺ are shown in Fig. 2(b). These are the first pure spectra for seven-coordinate Mn²⁺; the excitation spectrum reported in ref. 4 is contaminated by transitions of the sensitizing MnBr₄²⁻ anion.

Comparison of the spectra of [Mn(15-crown-5)(D₂O)₂]²⁺ [Fig. 2(b)], [Mn(12-crown-4)₂]²⁺ [Fig. 2(c)], classical [MnBr₄]²⁻ [Fig. 2(d)], [MnBr₃]⁻ [Fig. 2(a)] and the previously reported⁸ absorption spectrum of species [MnBr(Me₆tren)]⁺ reveals major variations in emission and excitation/absorption spectral profiles for Mn²⁺ ions in coordination numbers 7, 8, 4, 6 and 5 respectively. Luminescence techniques may thus be informative in probing such common Mn²⁺ coordination sites⁹ in a wide range of materials including phosphors,³ polymers,¹⁰ industrial minerals,¹¹ biomolecules and potential MRI contrast agents for which the behaviour of the Mn–OH₂ linkage is crucial.¹²

To establish whether the decay rates of Mn²⁺[⁴T₁(⁴G)→⁶A₁] emission from the seven-coordinate Mn(II) centre in [Mn(15-

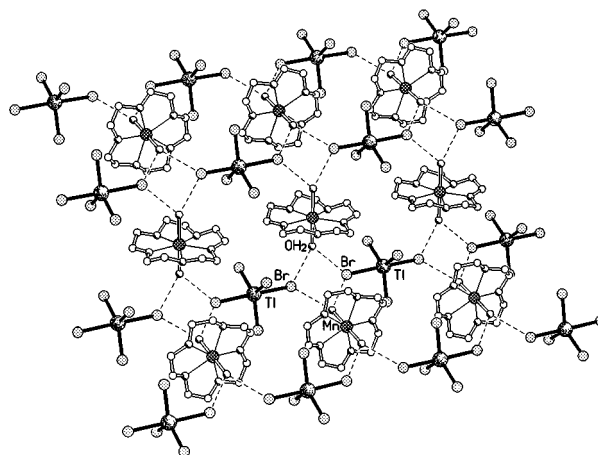


Fig. 1 Part of one of the corrugated hydrogen bonded sheets of [TlBr₅]²⁻ anions and [Mn(15-crown-5)(H₂O)₂]²⁺ cations in the structure of **1**. The O...Br distances are all 3.25 Å.

† Dedicated to Dr Earle V. Roberts in celebration of his service to the Department of Chemistry, University of the West Indies, Mona Campus.

crown-5)(H₂O)₂]²⁺ are sensitive enough to allow the detection of dynamic supramolecular lattice events we compared the luminescence decay dynamics of compounds **1–3**. The absorption energy of the broad Mn²⁺[⁴T₁(⁴G)←⁶A₁] transition (λ_{max} ≈ 520 nm) of [Mn(15-crown-5)(H₂O)₂]²⁺ [Fig. 2(b)] overlaps well with the second harmonic of Nd:YAG lasers (532 nm). Our powerful Nd:YAG laser§ was thus used to directly excite the Mn²⁺[⁴T₁(⁴G)] energy level in complexes **1–3**; a broad emission centered at ca. 590 nm [Fig. 2(b)] was observed in each case. The temperature dependence (10–320 K)§ of this emission revealed remarkable similarities between the behaviour of the more rigid two-dimensional hydrate **1** and that of the one-dimensional deuterate **3**, with both of these differing dramatically from the behaviour of the one-dimensional hydrate **2**. For T < 100 K, compounds **1** and **3** exhibit similar double exponential luminescence decay kinetics with a common minor short-lived temperature independent emission (component A) decaying at ca. 1 × 10³ s⁻¹. The major emission comes from a marginally temperature dependent and much longer-lived component (decay rate is ca. 7 × 10⁻¹ s⁻¹ at 10 K) with phonon type thermal barriers of ca. 2.1 × 10² and 2.7 × 10² cm⁻¹ for **1** and **3** respectively. By sharp contrast, compound **2** exhibits temperature independent perfectly double exponential decay behaviour for T < 160 K. Besides the common minor component A (decay rate ca. 1.1 × 10³ s⁻¹), compound **2** features a major very short-lived emission (decay rate ca. 7.0 × 10³ s⁻¹).

These observations we believe can be rationalised as follows: the sharply contrasting behaviour between the two one-dimensional compounds **2** and **3** is due to the more efficient quenching of the Mn²⁺[⁴T₁(⁴G)→⁶A₁] emission by H₂O in **2** compared to the weak quenching action of D₂O in **3**. The similarity of the behaviour of **1** and **3** however, can be explained by considering the rigidity of the two-dimensional O–H...Br...H–O bonds in **1** which hinders the vibrational motions of the coordinated H₂O molecules of [Mn(15-crown-5)(H₂O)₂]²⁺. At low temperature vibrational restrictions in **1** appear to be so severe that the normal quenching effect of the aqua ligands is stopped and hence the similarity in the decay behaviour of hydrate **1** and deuterate **3**. The thermal barrier of

ca. 210 cm⁻¹ is in this case the energy needed to distort the lattice of **1** and allow some vibrational freedom for the H₂O molecules which triggers quenching of the Mn²⁺[⁴T₁(⁴G)→⁶A₁] emission by those coordinated H₂O molecules. To our knowledge, this is the first example of thermal tuning of the luminescence quenching action of H₂O molecules, in particular, one in which supramolecular manipulations are employed.

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Notes and references

‡ Crystal data: **1**: [C₁₀H₂₄O₇Mn][TlBr₅], M = 915.2, orthorhombic, space group *Pmna* (no. 51), a = 15.879(3), b = 10.122(3), c = 7.109(1) Å, V = 1142.5(5) Å³, Z = 2 (the cation and anion have crystallographic C_{2h} and C_{2v} symmetries respectively), D_c = 2.660 g cm⁻³, μ(Mo–Kα) = 163.6 cm⁻¹, F(000) = 842, T = 293 K; yellow blocks, 0.40 × 0.33 × 0.30 mm, Siemens P4/PC diffractometer, ω-scans, 1102 independent reflections. The structure was solved by direct methods and, because of the severe disorder (see text) only the oxygen atom of the aqua ligand and the manganese, thallium and bromine atoms were refined anisotropically using full matrix least squares based on F² to give R₁ = 0.054, wR₂ = 0.132 for 850 independent observed absorption corrected reflections [|F_o| > 4σ(|F_o|), 2θ ≤ 50°] and 92 parameters. Full structural details of compound **2** will be reported elsewhere.⁵ CCDC 182/1305. See <http://www.rsc.org/suppdata/cc/1999/1565/> for crystallographic files in .cif format.

§ Luminescence and excitation spectra were recorded using a LS5B Perkin Elmer Fluorescence spectrometer that is essentially similar to the one described earlier.¹³ The luminescence decay rates were measured using a Continuum Powerlite 8000 YAG laser and an electronic and computational set up which was described previously.¹³ The Powerlite 8000 YAG laser generates ca. 600 mJ pulses (5–8 ns) of the second harmonic at 532 nm but minimum light intensities required to obtain decay curves of satisfactory signal: noise ratios were used. Variable temperature measurements (8–320 K) were done using an APD Cryogenics Inc. CSW-202 Displex helium refrigerator system with the sample in contact with cryocon conducting grease.

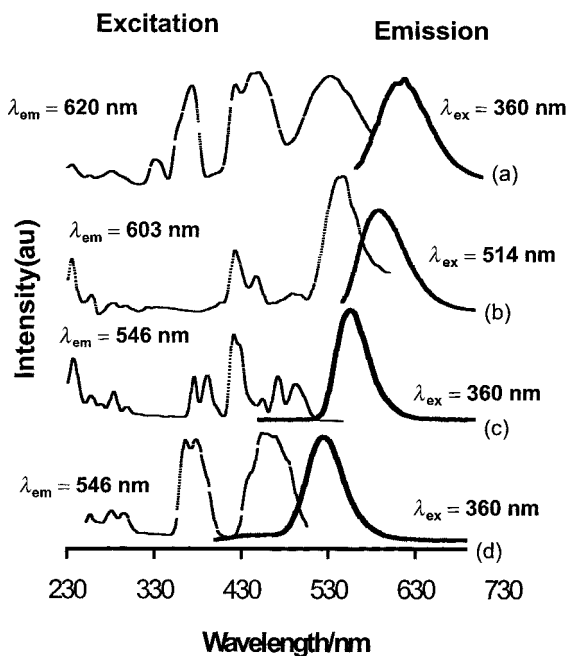


Fig. 2 Excitation and emission spectra of manganese(II) in (T_d = delay time; T_g = gating time): (a) six-coordination, [NMe₄][MnBr₃] (293 K; T_d = 1.00 ms, T_g = 1.00 ms); (b) seven-coordination, [Mn(15-crown-5)(D₂O)₂]Br₂, **3** (77 K; T_d = 0.01 ms, T_g = 5.00 ms); (c) eight-coordination, [Mn(12-crown-4)₂][NMe₄]₂[MnBr₄]_x[ZnBr₄]_{2-x} (77 K; T_d = 12.0 ms, T_g = 0.5 ms); (d) four-coordination, [NMe₄]₂[MnBr₄] (293 K; T_d = 1.00 ms, T_g = 1.00 ms).

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