Abstract

The structural, spectroscopic and photophysical properties of supramolecular cubic *F*23 crown ether complexes, $[(A18C6)_4MnBr_4][TlBr_4]_2$, were studied in order to determine the influence of the nature of the crown ether and its chelated ion, A^+, on the formation and stabilization of the complexes. Members of the bromide series of these cubic *F*23 complexes, $[(A18C6)_4MnBr_4][TlBr_4]_2$, A = Tl (**1**) and Rb (**2**) were successfully prepared and were shown to be isomorphous with the chloride series already reported (*Chem. Abstr.* 118: 180538t; 121: 98310r). Temperature dependent luminescence decay dynamical studies on **2** revealed solid state 18-crown-6 reorientational motion, occurring at *ca.* 210 K. The energy barrier associated with the hindered motion was determined to be *ca.* 26 kJ mol^{-1}. The rotation-reorientation is thought to facilitate energy migration on the Mn^{2+} sublattice by generating a dynamic crystal electric field which enhances the transition dipole moment on the Mn^{2+} centers. In $[(RbHM18C6)_4MnBr_4][TlBr_4]_2$ (HM18C6 = 2-hydroxymethyl-18-crown-6) (**3**), which features a dipolar arm attached to the 18-crown-6 backbone, the onset of $MnBr_4^{2-}$ luminescence quenching occurs at a much lower temperature

(≤ 77 K compared to *ca.* 210 K for **2**). This may be due either to coupling of the vibration of the lariat -OH moiety to the T_d $MnBr_4^{2-}$ ($^4T_1(^4G)$) excited state or to enhanced energy migration on the Mn^{2+} sublattice, facilitated by the increased transition dipole moment afforded by coupling of Mn^{2+} to the polar -CH_2OH lariat arm.

Crown ether reorientation was further qualitatively determined in $[(K18C6)_4MnBr_4][TlBr_4]_2$ (**4**), by a solid state CP MAS ^{13}C NMR study, which revealed a single CH_2 resonance, whereas a doublet, representing the two carbon environments of **4**, was expected. Luminescence studies confirmed the presence of lattice defects strongly electronically coupled to the T_d $MnBr_4^{2-}$ excited state. The mixed metal complexes, $[(K_xRb_{1-x}18C6)_4MnBr_4][TlBr_4]_2$ (**5**) show that interaction of the lattice defects with T_d $MnBr_4^{2-}$ is dependent on the concentration of the K ion. Melting, recrystallization and annealing of **4** and **5** resulted in the modification of the luminescence spectral properties, revealing distinct T_d $MnBr_4^{2-}$ and defect emission. Subsequent decay dynamical studies showed equilibration between the two luminescent centers, with T_d $MnBr_4^{2-}$ - defect energy transfer and defect - T_d $MnBr_4^{2-}$ back energy transfer of equal rates.

The successful preparation of $[(Na18C6)_4MnBr_4][TlBr_4]_2$ (**6**), is indicative of the considerable overall stability of the cubic *F*23 system, since 18-crown-6 in the $(Na18C6)^+$ units of the complex adopts an unfavourable D_{3d} conformation instead of the C_i conformation usually found in simple Na^+ - 18C6 complexes. The doubly charged Ba^{2+} ion binds to either an $-OH^-$ or Br^- ion to form the cubic *F*23 complex, $[(Ba18C6\gamma)_4MnBr_4][TlBr_4]_2$ (γ = OH/Br) (**7**). Its weak emission spectrum is similar to that of thermally treated **5** (x = 0.9), suggesting the presence of luminescent lattice defects which trap $MnBr_4^{2-}$ excitation. The emission of $[(BaHM18C6)_4MnBr_4][TlBr_4]_2$ (**8**) (in which the lariat is deprotonated) is marginally more intense than that of **7**, and suggests that defects are also present.

Temperature dependent luminescence decay dynamical studies of $[(NH_418C6)_4MnBr_4][TlBr_4]_2$ (**9**) and its chloride analogue, $[(NH_418C6)_4MnCl_4][TlCl_4]_2$ (**10**), reveal solid state rotational motion of the 18-crown-6-bound ammonium ion, with an associated thermal barrier of *ca.* 1.4 kJ mol^{-1}. Complex **10** displays strong T_d $MnCl_4^{2-}$ at 298 K, but dominant defect emission at 77 K. Temperature dependent luminescence decay dynamical studies of both emissions reveal solid state crown ether reorientation. Thermal barriers of *ca.* 35 and 29 kJ mol^{-1} were obtained for the 510 and 590 nm emissions, respectively.

Substitution of 7,16-diaza-18-crown-6 (DA18C6) for 18-crown-6 results in the formation of the cubic *F*23 complex, $[(\mathrm{KDA18C6})_4\mathrm{MnBr}_4][\mathrm{TlBr}_4]_2$ (**11**) for potassium, but not for rubidium. Instead, the complex, $(\mathrm{RbDA18C6})_2\mathrm{MnBr}_4$ (**12**) is formed. Substitution of dibenzo-18-crown-6 (DB18C6) for 18-crown-6 in the preparation of complexes of the cubic *F*23 system results in the formation of the sandwich complex, $[\mathrm{Rb(DB18C6)}_2]_2[\mathrm{TlBr}_4]_2$ (**13**) for rubidium and $[\mathrm{KDB18C6}]_2[\mathrm{TlBr}_4]_2$ (**14**) for potassium.

Substitution for 18-crown-6 of 15-crown-5, which has a smaller cavity and lower symmetry, in the preparation of the analogues of **2** and **4**, yields the sandwich complexes, $[\mathrm{Rb(15C5)}_2][\mathrm{TlBr}_4]$ (**15**) and $[\mathrm{K(15C5)}_2][\mathrm{TlBr}_4]$ (**16**). Interestingly, with the smaller metal ion, sodium, a novel complex, $[(\mathrm{Na15C5})_4\mathrm{Br}][\mathrm{TlBr}_4]_3$ (**17**) is formed, which features the concentration of four $(\mathrm{Na15C5})^+$ ions in a tetrahedral arrangement around the Br^- ion.

The bis-(crown) complexes, (Acrown)$_2$MnX$_4$ (**18** **24**) were prepared from stoichiometric amounts of respective reagents. The existence of an equilibrium between these bis-(crown) complexes and those of the cubic *F*23 system is indicated by the formation of **12** under conditions expected to produce a cubic *F*23 complex and of **1** under conditions intended to prepare a bis-(crown) complex. A relationship between the complexes is also demonstrated in the fast atom bombardment mass spectra of the cubic *F*23 complexes, which show clusters of peaks which may be attributed to molecular ions of the corresponding bis-(crown) complexes.