Luminescence from cerium(III) acetate complexes in aqueous solution: considerations on the nature of carboxylate binding to trivalent lanthanides

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The luminescence of cerium(III) has been studied in aqueous solutions in the presence of acetate ion. In contrast to previous reports that cerium(III) carboxylate complexes do not luminesce, a weak emission is observed, which has a similar spectrum to the aquo cerium(III) species but a much shorter lifetime. Results from a variety of studies on complexation of various trivalent lanthanide ions with carboxylates, including NMR spectral and relaxation measurements, molecular mechanics calculations, deuterium isotope effects on Tb(III) luminescence lifetimes, together with literature data strongly suggest that the dominant mode of complexation between carboxylates and trivalent lanthanides involves a weak, predominantly bidentate, binding to the metal cation. We suggest that the observed emission arises from a 1 : 1 cerium acetate species involving such bidentate coordination.

Introduction

Complexes of trivalent lanthanide ions with carboxylates are finding increasing importance in areas as diverse as catalyst precursors,[1] pharmaceutical formulations,[2] analytical chemistry,[3] metallomesogens for advanced material applications,[4–6] precursors for formation of metal oxides for ceramic phosphor,[7] or other optoelectronic applications,[8] and components of photosensitive polymer films.[9] Cerium(III) has also recently been shown to have potential in electroluminescent devices,[10] and complexation with carboxylate ligands would provide an excellent route towards incorporation of such systems in organic or polymeric matrices. In addition, the valuable spectroscopic and magnetic properties of lanthanide ions, coupled with the fact that they can isomorphously substitute biologically relevant cations, such as aluminium(III) or the spectroscopically silent Ca(II) and Zn(II),[11] make them good probes for metal ion interactions with polyelectrolytes in aqueous solutions.[12–14] We have been particularly interested in the use of the luminescence of cerium(III) for studying interaction of polyacrylates and polymethacrylates with trivalent metal ions in water.[13,14] In contrast to the other trivalent lanthanides, where luminescence comes from the spin and Laporte forbidden f→f transitions,[11] the main electronic transition in cerium(III) corresponds to an allowed 4f→5d transition, meaning that it has a reasonable molar

extinction coefficient, and can thus be studied in relatively dilute solutions.[15–17] In addition, the luminescence is highly sensitive to the environment,[18] and the excited Ce(III) ion can transfer energy to the other lanthanide ions,[19] providing the possibility of obtaining more detailed information on these systems. However, although emission has been observed from tris(pyrazine-2-carboxylato)cerium(III)[20,21] which has been assigned to a metal-to-ligand charge transfer (MLCT) transition, in general cerium(III) luminescence is normally quenched upon complexation with carboxylates.[4,22] This suppression has been ascribed to an electron transfer process in which the excited 5d electron decays to a closely lying π* orbital of the ligand (*i.e.* a nonemissive metal-to-ligand charge transfer state). With other anions, complete electron transfer is possible from excited Ce(III) leading to photooxidation.[23] In the complex tris(pyrazine-2-carboxylato)cerium(III),[20,21] as indicated by the authors, the MLCT transition is predominantly from the metal to the strongly electron accepting pyrazine moiety in the ligand. We were, therefore, surprised to see in studies of the interaction of cerium(III) with polymethacrylates[14] that, although there was some quenching of the emission, time-resolved studies of excited Ce(III) decay showed a previously unreported fast component in addition to the known component with lifetime around 40 ns (attributed to the hydrated cerium(III) cation).[17] To obtain more information on what is happening between cerium(III) and carboxylates, we have carried out a luminescence spectral and lifetime study on the interaction between cerium(III) and acetate ion in aqueous solutions under conditions where, from literature formation constant data,[24] the dominant species are the aquo cerium(III) ion and a monoacetate complex. These are complemented by studies on the mode of binding of trivalent lanthanide ions to

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acetate using ^{1}H NMR spectral and relaxation measurements, molecular mechanics calculations and isotopic effects on luminescence lifetimes.

Results and discussion

Absorption and luminescence spectra were run of aqueous solutions of cerium(III) perchlorate (0.5 mM) alone and in the presence of various concentrations of sodium acetate. The
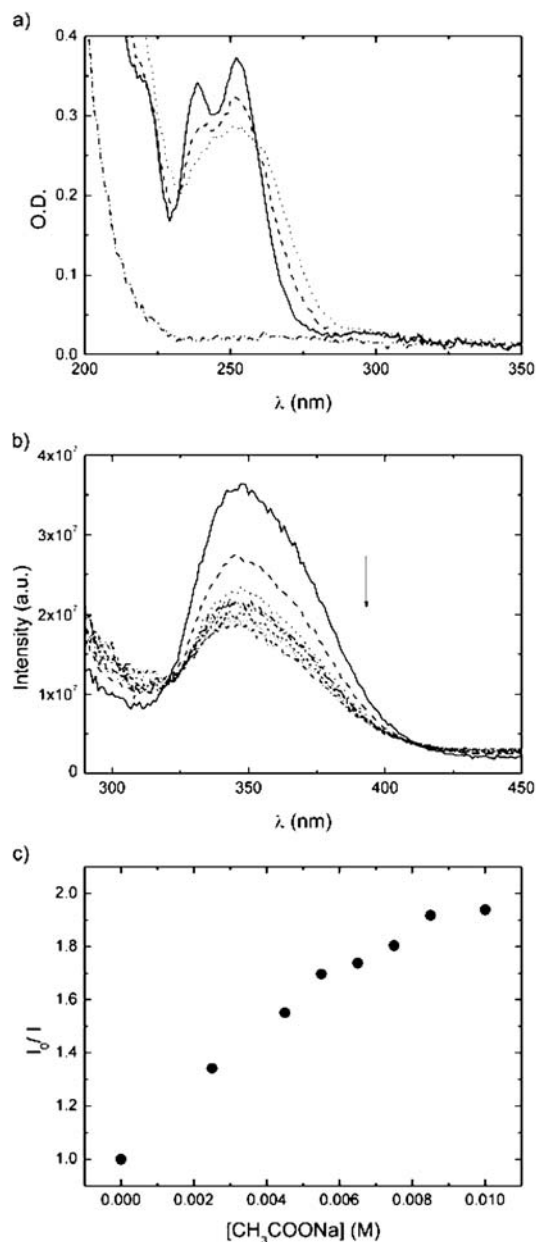

absorption and emission spectra in the absence of acetate ion (Fig. 1(a) and (b)) are identical to previous reports,[17] and are attributed to the species $[Ce(H_2O)_8]^{3+}$ and $[Ce(H_2O)_9]^{3+}$. Upon addition of acetate, changes were seen in the structured absorption spectrum, which can be attributed to complexation by the hydrated cerium(III) cation.

The luminescence was markedly quenched upon addition of sodium acetate, although there was no significant change in the shape of the spectrum. However, a nonlinear Stern–Volmer plot (Fig. 1(c)) was observed, suggesting that the dominant quenching is likely to be static due to cerium(III) acetate complex formation. The decay of cerium(III) luminescence was measured for solutions of cerium(III) (2 mM) in the presence of increasing concentrations of sodium acetate. A typical trace is shown in Fig. 2, and clearly shows that the decays cannot be analysed with a single exponential rate law. In addition to the slow component of 43–48 ns, an initial fast component with lifetime 1.4–1.75 ns was also seen. The long lifetime component is identical to that previously reported for the decay of aquo-cerium(III) in water (48 ns).[17] However, the fast decay is considerably longer than that reported (430 ps) for a short-lived excited species observed with hydrated Ce^{3+} in ethylene glycol solution or poly(vinyl alcohol) films, which was attributed to emission from $[Ce(H_2O)_9]^{3+}$.[17] Further, this fast component is not observed with aqueous solutions of cerium(III), and the fact that it is only seen when acetate ion is present indicates that it must be associated with a cerium(III) acetate complex. In addition, while the lifetimes of both fast and slow components did not change significantly upon varying the concentration of acetate, marked differences in their amplitudes were observed, with that of the fast component increasing (up to 8 mM acetate) and then decreasing (see Fig. 3). From literature data on complexation,[24] we attribute this fast component to a 1 : 1 cerium(III) acetate complex.

The luminescence decays reveal that the longer lived component is likely to be the dominant species present, with more than 85% of the total emission originating from this species (see Fig. 2). The second species, present for all Ce : acetate ratios,
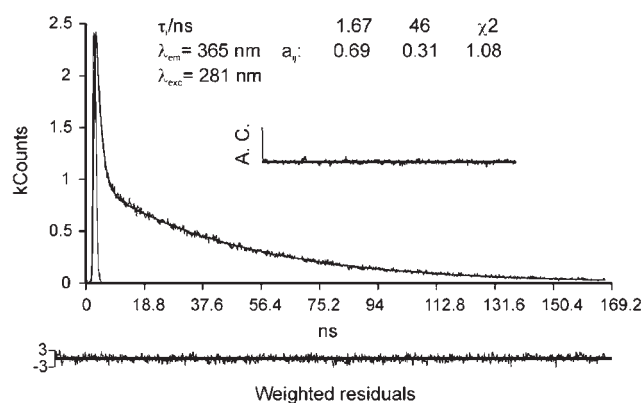

Fig. 1 (a) Absorption spectrum for a 0.5 mM aqueous solution of Ce(III) (solid line) alone and in the presence of 2.5 and 10 mM sodium acetate (dashed and dotted lines, respectively). The absorption spectrum of a 2.5 mM sodium acetate solution is also shown (dash-dotted line). (b) Fluorescence spectra (λ_{ex} = 252 nm) for a 0.5 mM Ce(III) solution in the absence (solid line) and in the presence of increasing concentrations of sodium acetate (2.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 10 mM). (c) Stern–Volmer plot for the fluorescence quenching.

Fig. 2 Fluorescence decay analysed with a biexponential rate law for aqueous solutions of cerium(III) perchlorate (2 mM) in the presence of sodium acetate (4 mM). For a better judgment of the quality of the fits, autocorrelation functions (A.C.), weighted residuals (W.R.), and chi-squared values (χ^2) are presented as insets.
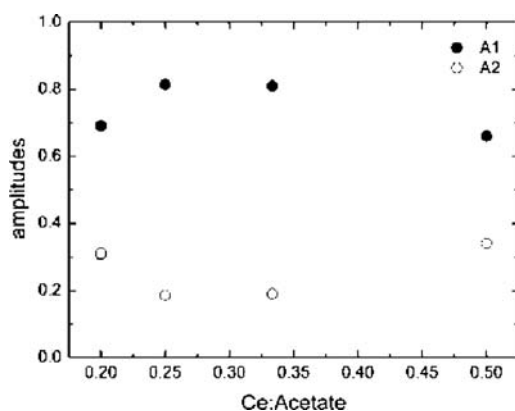
Fig. 3 Pre-exponential factors variation for the different cerium : acetate mixtures. The amplitude $A1$ is associated with the shorter lived component (1.4–1.75 ns) whereas $A2$ is associated with the longer lived component (43–48 ns).

seems to be immediately formed upon addition of small quantities of acetate. Moreover, since the lifetimes of the two species do not change appreciably with the cerium : acetate molar ratio, this indicates that after their formation, there is no change in the structure of the complex species within their fluorescence lifetimes, which provides an upper limit on the rate constant for loss of acetate from the 1 : 1 complex of $\leq 6 \times 10^8$ s^{-1}. It is also worth noting that from the time-resolved luminescence data, the relative contribution from the emission of the longer lived species slightly increases upon addition of acetate (from ~ 86 to 93% of the total emission), although it is difficult to quantify the contributions from the two species as this requires independent knowledge of both the formation constant and their luminescence quantum yields. Nevertheless, since there is a decrease of the total emission, as can be seen from Fig. 1(b), this suggests that the shorter lived species is more emissive and that although the addition of acetate does not affect the type of complex formed it preferentially quenches the longer lived species.

Further information on the complexation can be obtained using NMR spectroscopy coupled with molecular mechanics (MM) calculations. ^{1}H NMR spectra were run of solutions of sodium acetate in D$_2$O alone, and in the presence of Ce(III) (Table 1). The ^{1}H NMR spectrum of sodium acetate shows only one signal, which is shifted and slightly broadened in the presence of Ce(III), and which shows further shifts and broadening upon

increasing metal concentration. This is consistent with the acetate being complexed by Ce(III), with the free and bound ligands being in fast exchange, giving rise to the single, broadened signal. With the related Tb(III) ion, two ^{1}H signals are observed. One of these (δ 2.22 ppm) is assigned to the free acetate. The second signal is broad, shifted to high frequencies, and shows increasing chemical shifts as the metal concentration, and consequently the Tb(III) : acetate ratio, increases. Although the presence of two signals in this case may imply that the ligand exchange with Tb(III) is slower than that with Ce(III), consistent with observations from solvent exchange studies[25] that ligand substitution rates with trivalent lanthanide ions decrease with decreasing ionic radius (Ce(III): 107 pm, Tb(III): 93 pm),[26] other factors may be involved and detailed studies on ligand exchange in these systems are beyond the scope of this study. However, the chemical shifts alone do not allow us to distinguish between monodentate and bidentate binding of acetate to the trivalent lanthanide ions.

Shifts as a result of lanthanide binding may come either from through-space dipolar interactions (pseudo-contact), or from direct delocalization of unpaired electron spin-density from the metal (contact shift).[27–29] Information on the nature of binding can be obtained from ^{1}H NMR relaxation data. However, Ce(III) and Tb(III) ions have both contact and pseudocontact contributions. In contrast, the strongly paramagnetic Gd(III) ion is a good relaxation agent and produces only a contact shift. We have therefore studied NMR relaxation behaviour of carboxylates in the presence of Gd(III).

In this case we have used sodium propionate rather than acetate, as this allows us to determine the position of both methyl and methylene groups relative to the metal, and so provides information on the mode of carboxylate binding. By studying the contribution to the relaxation processes when Gd(III) is bound to propionate it is possible to obtain relative distances between the metal ion and the appropriate nuclei. Longitudinal proton relaxation times (T_1) were measured for pure propionate ion and for propionate in the presence of Gd(III), as indicated in Table 2. By use of the Solomon–Bloembergen equations[30,31] proton–metal distances can be calculated. For the present case, where the scalar part can be neglected, the equation has the form

$$(1/T_{1M})_i/(1/T_{1M})_0 = r_i^{-6}/r_0^{-6}$$

Table 1 ^{1}H NMR chemical shifts^a for sodium acetate, sodium acetate–Ce(III) and sodium acetate–Tb(III) at pH 6 and 298 K

System	Chemical shift^a/ppm	
Sodium acetate	1.92	
Sodium acetate/Ce(III)		
10/1 mmol dm^{-3}	2.10	
10/3 mmol dm^{-3}	2.36	
5/2 mmol dm^{-3}	2.31	
Sodium acetate/Tb(III)		
10/1 mmol dm^{-3}	2.22	4.16
10/2 mmol dm^{-3}	2.22	6.07
10/3 mmol dm^{-3}	2.22	7.86
5/2 mmol dm^{-3}	2.22	6.72

^{a} δ Values, in ppm, relative to tetramethylsilane using *tert*-butyl alcohol (1.30 ppm) as external reference.

Table 2 Relaxation data for the Gd(III)–propionate complex in D$_2$O at pH 6 and 293 ± 1 K, and molecular mechanics calculations for Gd(III)–propionate and Ce(III)–propionate complexes

	CH_2	CH_3
T_1/s (propionic acid)	4.08	4.92
T_1/s (propionic acid–2 mmol dm^{-3} Gd(III))	9.37×10^{-4}	1.38×10^{-3}
T_1^{-1} ratio^a	1.00	0.67
Metal$\cdots$proton distance ratio^b	—	1.07
Mean calculated Gd$\cdots$H distances (Å) from MM+ calculations		
Bidentate binding	4.797 ± 0.001	5.399 ± 0.640 (1.125)^b
Monodentate binding	5.119 ± 0.384	5.549 ± 0.703 (1.084)^b

^{a} Relative to CH$_2$ protons. ^{b} Metal–proton distance ratio Gd$\cdots$CH$_3$/Gd$\cdots$CH$_2$.

where the subscripts i and 0 refer to the respective spin–lattice relaxation times (T_{1M}) and metal–proton distance (r) in the presence and absence of Gd(III). Proton–metal distance ratios are also presented in Table 2. For the complex, the results indicate a ligand conformation in which the CH_2 group is only slightly closer to the metal than CH_3.

Molecular mechanics can provide a valuable tool for interpreting atom or ion dynamics of solute–solvent interactions in molecular systems involving large numbers of molecules or ions.[32] MM+ calculations were made on complexes of propionate with gadolinium(III) for both monodentate and bidentate carboxylate coordination, including water molecules. Snapshots of the relevant species are given in Fig. 4, and appropriate bond distances are also included in Table 2. Calculations (not shown) were also carried out on the binding of propionate to Ce(III), and suggest a similar structure. Unfortunately, probably as a consequence of conformational flexibility within the complexes, large uncertainties were observed in the Gd···H (or Ce···H) distances with the methyl protons, which preclude conclusive assignment of the mode of binding. The calculations, however, strongly suggest that the two configurations are relatively close energetically, which support the idea of a relatively weak binding of acetate ion in aqueous solution.

The strongest evidence for the mode of carboxylate binding comes from an FT-IR study of various metal acetates in aqueous solution.[33] Differences between the frequencies of the asymmetric and symmetric carboxylate stretching vibrations support a model involving bidentate carboxylate binding between cerium(III) and acetate ion. Studies of long-chain cerium carboxylates in the solid state also indicate bidentate complexation of the carboxylate group by the metal ion.[4] We, therefore, feel that the dominant species, which is responsible for the short lived emission in fluorescence, corresponds to the complex $[Ce(H_2O)_x(O_2CCH_3)]^{2+}$ (where $x = 6$ or 7), with a structure close to that in Fig. 4(b).

Support for water loss on complexation comes from luminescence studies on the Tb(III) acetate complex. With terbium(III), information on the effect of interaction of ligand and lanthanide ions on the primary hydration sphere can be obtained by studying the decay of its luminescence in H_2O and

Fig. 4 Snapshots after MM+ calculations of the minimized geometry of complexes of Gd(III) with propionate: (a) monodentate complex plus eight first-sphere coordination water molecules; (b) bidentate complex plus seven first-sphere coordination water molecules.

Table 3 Lifetime, τ, and the number of coordinated water molecules, n, of Tb(III) in water and D_2O given for different Tb(III) : sodium acetate ratios

Ratio Tb(III) : acetate	$\tau(D_2O)$/ms	$\tau(H_2O)$/ms	n (± 0.5)
1 : 1	3.25	0.48	7.5
1 : 3	3.37	0.49	7.3
1 : 5	3.45	0.49	7.3

D_2O solutions.[10,34,35] We will assume that the complexation behaviour of Ce(III) and Tb(III) with acetate are similar. The decay of terbium(III) luminescence was studied in H_2O and D_2O solutions alone and in the presence of various concentrations of sodium acetate (Table 3).

From these decays, the number of bound water molecules can be determined.[34,35] We have used values of constants from ref. 35. Studies in the absence of acetate are consistent with terbium(III) being bound by nine water molecules. In the concentration region studied, the dominant species will be the aquo-ion and the monoacetate complex. From Table 3, upon increasing acetate concentration the number of bound water molecules is 7.3, indicating the loss of 1–2 water molecules, which is consistent with either monodentate or bidentate binding of the acetate to the trivalent lanthanide ion.

Conclusions

Acetate ion interacts with cerium(III) in water, forming a 1 : 1 complex, which is suggested to involve predominantly bidentate binding as the species $[Ce(H_2O)_x(O_2CCH_3)]^{2+}$ (where $x = 6$ or 7). From studies on the solvent isotope effect on the luminescence lifetime of Tb(III) in the presence of acetate, binding of acetate by trivalent lanthanide ions is accompanied by the loss of coordination water. This is in agreement with Grenthe's observations from thermodynamic data nearly five decades ago,[36] supported by subsequent studies,[37] that binding of carboxylates by trivalent lanthanides is driven by the loss of coordination water of the metal ions. Complexation leads to quenching of the cerium(III) fluorescence, in agreement with previous observations on the effects of interaction of carboxylates with this cation in the solid state.[4,22] However, in contrast with the previous systems studied, a short lived emission is observed which we attribute to the $[Ce(H_2O)_x(O_2CCH_3)]^{2+}$ complex. From the fact that fairly rapid ligand exchange is observed in ^1H NMR studies on cerium(III) acetate and from the results of molecular mechanics calculations on lanthanide(III)–carboxylate binding, the observation of this emission in solution and complete quenching in the solid state may result from weaker metal–carboxylate interactions in solution than in the solid, where crystal packing forces may be dominant.

Experimental

Cerium(III), terbium(III) and gadolinium(III) perchlorates, and sodium acetate (Aldrich) were of the purest grade available and were used as received. Deuterium oxide (Aldrich, 99.9%) was used in NMR and Tb(III) lifetime measurements. All other solutions were prepared in Milli-Q Millipore water.
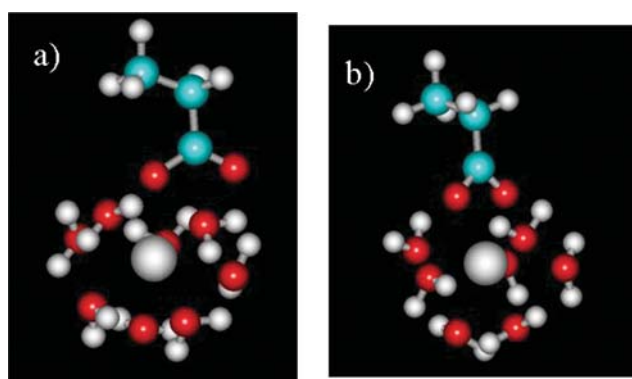
Absorption and luminescence spectra were recorded on Shimadzu UV-2100 and Jobin-Ivon SPEX Fluorolog 3-22 spectrometers, respectively. Fluorescence decays were measured using a home-built TCSPC apparatus with an IBH NanoLED (281 nm) excitation source, Jobin-Ivon excitation and emission monochromators, Philips XP2020Q photomultiplier, and Canberra instruments TAC and MCA which is described in detail elsewhere.[38] Alternate measurements (1000 counts per cycle, cpc) of the pulse profile at the excitation wavelength and the sample emission were performed until 5×10^4 counts at the maximum were reached. The fluorescence decays were analysed using the modulating functions method of Striker,[39] with automatic correction for the photomultiplier "wavelength shift". ^1H NMR spectra were obtained on a Varian UNITY-500 NMR spectrometer. Molecular mechanics calculations were performed using the MM+ geometry optimization with a Polak–Ribiere algorithm and a final RMS gradient of 0.01 kcal $(\text{Å mol})^{-1}$, using HyperChem 6.03 from Hypercube, 2000, USA, in a Compaq dc7600, 3.2 MHz workstation.

Acknowledgements

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