

## Electronic supplementary information (ESI)

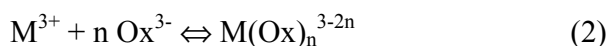
### Data analysis

#### $M^{3+}$ -Ox system

The partitioning of  $M^{3+}$  = Am, Cm and Eu into the aqueous (6.60 m (NaClO<sub>4</sub>)) and the organic phase (HDEHP, represented as H<sub>2</sub>A<sub>2</sub>, in the dimeric form) can be expressed as:



where (a) and (o) represent respectively, the aqueous and organic phases. In the presence of Ox in the aqueous phase the complexation of the metal ions can be written as:



where n= 1 and 2. The concentration range of Ox was so chosen to form only 1:1 and 1:2 complexes. A non-linear curve of 1/D (D = distribution ratio =  $[M^{3+}]_{total(o)}/[M^{3+}]_{total(a)}$ ) vs.  $[Ox^{2-}]$  for the metal ion at four temperatures (Figure S1)

indicating the formation of more than one complex species. The stability constants ( $\beta_{101}$  and  $\beta_{102}$ ) of the complexes formed were evaluated using the polynomial

$$D_0/D-1 = \beta_{101}[L] + \beta_{102}[L]^2 \quad (3)$$

where D<sub>0</sub> is the distribution ratio in the absence of ligand, L= Ox<sup>2-</sup>. [The first stability constant,  $\beta_{101}$ , was calculated as a slope of linear regression between (D<sub>0</sub>/D-1) and the [L]. The second stability constants,  $\beta_{102}$ , were calculated as the slope of the linear regression between (D<sub>0</sub>/D-1)/[L] and [L]. Equal weight was given to each data point. Values with a deviation  $\geq 3\sigma$  from the regression curve were excluded in the final calculation of the stability constants. All experiments were performed at least twice and six to eight data points were obtained in each measurement.

#### $M^{3+}$ -EDTA-Ox system

In the presence of both the ligands EDTA and Ox the ternary complexes are formed, which can be represented by the equations:



A non-linear plot of 1/D vs.  $[Ox^{2-}]$  at fixed  $[EDTA^{4-}]$  for all these metal ions at four temperatures indicated the formation of more than one ternary complex. The

stability constants ( $\beta_{111}$  and  $\beta_{112}$ ) of the ternary complex were evaluated using the polynomial:

$$D_1/D-1 = \beta_{111}[\text{EDTA}^{4-}][\text{Ox}^{2-}]/(1 + \beta_{101}[\text{EDTA}^{4-}]) + \beta_{112}[\text{EDTA}^{4-}][\text{Ox}^{2-}]/(1 + \beta_{101}[\text{EDTA}^{4-}]) \quad (5)$$

where

$$D_1 = \frac{[\text{M}^{3+}]_{(O)}}{[\text{M}^{3+}]_{(a)}} (1 + \beta_{101}[\text{EDTA}^{4-}]) \quad (6)$$

From the knowledge of the stability constants ( $\beta_{101}$ ,  $\beta_{102}$  and  $\beta_{111}$ ,  $\beta_{112}$ ) at temperatures 0, 25, 45 and  $60 \pm 0.1$  °C, the enthalpies of formation of the binary and the ternary complexes were determined using the Van't Hoff equation, and the entropy values with the Gibbs-Helmoltz equation.

The stability constants in molarity ( $\log \beta_M$ ) at different temperature were converted to molality ( $\log \beta_m$ ) by the relation [1-3]

$$\log \beta_m = \log \beta_M + \sum \nu_r \log \theta \quad (7)$$

where  $\theta$  is the ratio of the values of molality to molarity for the specific ionic medium and  $\sum \nu_r$  is the stoichiometric coefficient of the reaction  $\text{M}^{3+} + n \text{Ox}^{2-} \rightleftharpoons \text{M}(\text{Ox})_n^{3-2n}$ , ( $\nu_r$  is positive for the products and negative for the reactants). For the above reaction  $\sum \nu_r$  is equal to -1 and -2 respectively, for  $n=1$  and 2. The density data of 6.60 m ( $\text{NaClO}_4$ ) solution at temperatures 0, 25, 45, and 60 °C were taken from ref. [3]. The thermodynamic parameters were computed using stability constants in the molality.

#### References:

1. L. Rao, Z. Zhang, P.L. Zanonato, P.D. Bernardo, A. Bismondo, S.B. Clark, *Dalton Trans.* 2004, 2867
2. R. Guillamont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, H.M. Rand, *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, Eds. F.J. Mompean, M. Illemassene, C. Domenech-Orti, K. BenSaid, Elsevier B.V., Amsterdam, 2003, Ch. 2, pp. 28-29
3. K. Cernochova, J.N. Mathur and G.R. Choppin, *Radiochim Acta* (in press)

**Table S1** Stability constants of Am<sup>3+</sup>, Cm<sup>3+</sup> and Eu<sup>3+</sup> with EDTA (log  $\beta_{101}$ ) at pcH = 3.60, I= 6.60m (NaClO<sub>4</sub>), T= 0-60°C.

Temp (°C)	Am <sup>3+</sup>	Cm <sup>3+</sup>	Eu <sup>3+</sup>
0	14.85±0.09	15.18±0.10	15.20±0.09
10	15.03±0.08	15.56±0.11	15.52±0.09
25	15.88±0.09	16.06±0.09	15.76±0.08
35	16.12±0.11	16.85±0.12	16.85±0.11

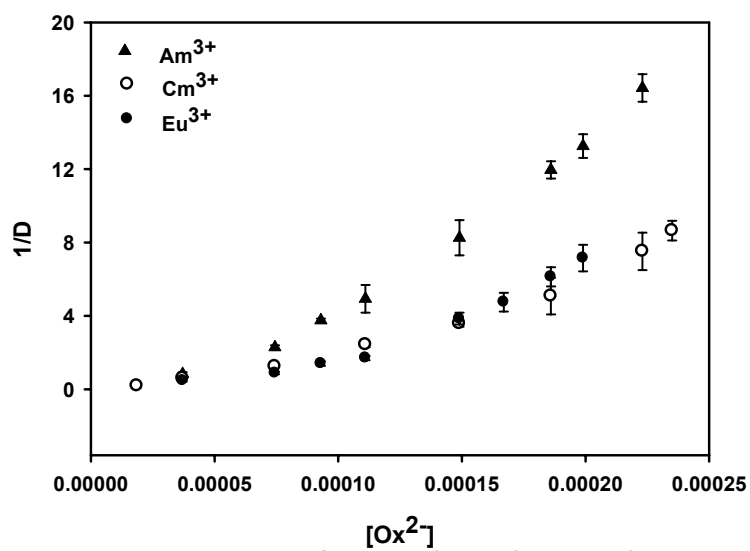
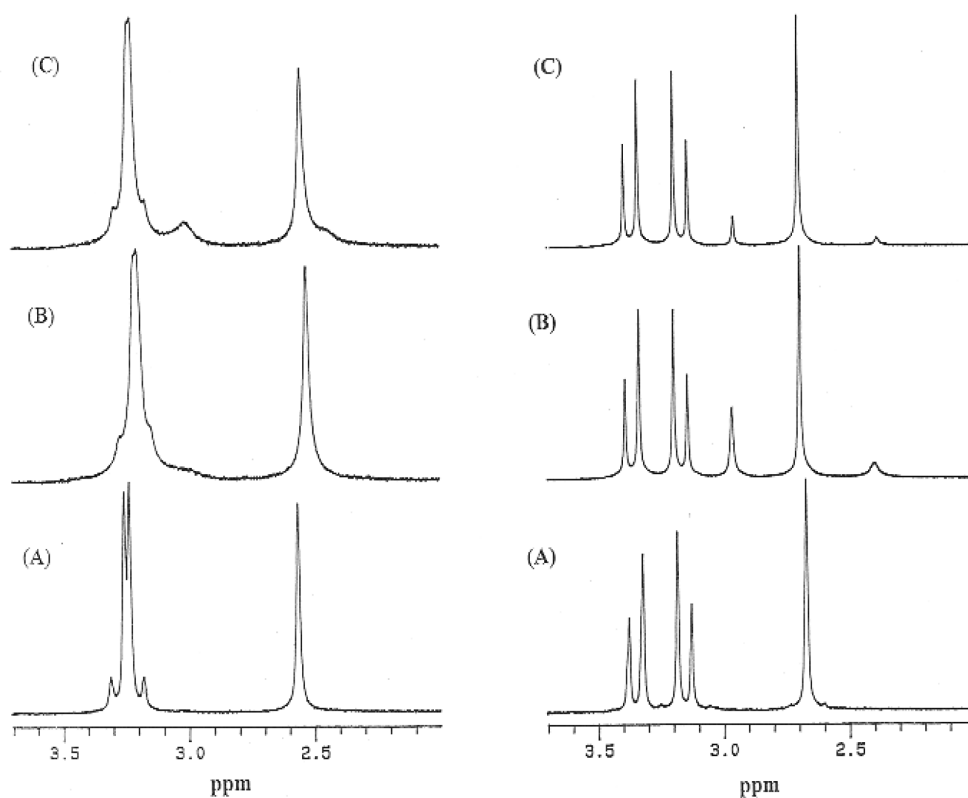


Fig. S1 Plots of 1/D vs. [Ox<sup>2-</sup>] for Am<sup>3+</sup>, Cm<sup>3+</sup> and Eu<sup>3+</sup> at I=6.60 m (NaClO<sub>4</sub>), T= 25°C and pCH=3.60



**Fig. S2**  $^1\text{H}$  NMR spectra of (left) (A) La:EDTA, 1:1, p $\text{cH}$  = 9.3, (B) La-EDTA-Ox, 1:1:1, p $\text{cH}$  = 9.1 and (C) La-EDTA-Ox, 1:1:2, p $\text{cH}$  = 9.2; (right) (A) Y-EDTA, 1:1, p $\text{cH}$  = 9.2, (B) Y-EDTA-Ox, 1:1:1, p $\text{cH}$  = 9.3 and (C) Y-EDTA-Ox, 1:1:2, p $\text{cH}$  = 9.3.

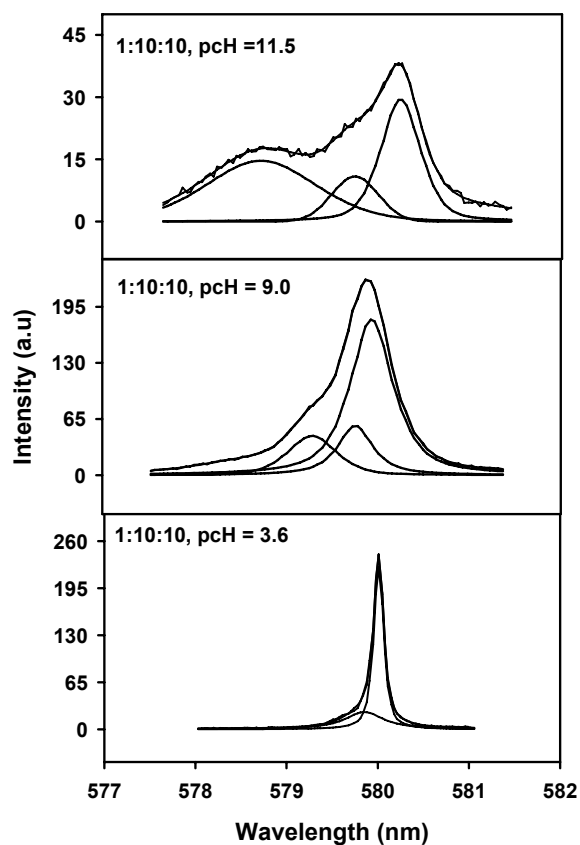


Fig. S3 The  ${}^5F_0 \rightarrow {}^7D_0$  excitation spectra of Eu(III) complexes with EDTA+Ox,  $[Eu^{3+}] = 1 \times 10^{-4}$  M,  $I = 6.60$  m (NaClO<sub>4</sub>)