Thermodynamic and Electrochemical Studies of Lanthanide and Alkaline-earth-metal Cryptates in Dimethyl Sulfoxide

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The thermodynamic functions ($\Delta G°$, $\Delta H°$ and $\Delta S°$) for the complexation of Eu^{2+} and alkaline-earth-metal ions (Ca^{2+}, Sr^{2+} and Ba^{2+}) by the cryptands 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane have been determined in dimethyl sulfoxide (dmso) using calorimetry and potentiometry at 25 °C in a 0.1 mol dm^{-3} ionic medium. These investigations, supported by other electrochemical measurements, showed that, in contrast to the literature, the lanthanide(III) ions do not exhibit any tendency towards complexation by these cryptands in dmso. The stability constants of the divalent europium cryptates (determined using Na^+ as a competing ion and a selective glass electrode) and their enthalpies of formation are compatible with those of Sr^{2+}, the alkaline-earth-metal ion having similar ionic radius. The effect of the ion charge and solvent donicity on the complexation reactions is discussed and, in particular, the relative importance of the ion– and ligand–solvent interactions in the stabilisation of cryptates is shown to rationalise the apparent anomalous stability sequence of alkali- and alkaline-earth-metal cryptates in water and in dmso.

Cryptands are macrobicyclic amines with polyether linkages connecting the bridgehead nitrogen atoms. Since their discovery by Lehn and co-workers, a considerable amount of work has been published on the interactions of these molecules with metal cations in aqueous and non-aqueous media.[1–3] These investigations have pointed out that various factors may contribute to the stability of the inclusion compounds (cryptates) formed by the cryptands; among these, of particular importance are the relative sizes of the cation and the ligand cavity, the number of co-ordination sites of the ligand, the charge density of the cation, the solvent properties, and the nature of the metal–ligand interactions.

Up to now, most of the experimental work has been done to study the cryptates of 'hard' metal ions, such as alkali-, alkaline-earth-metal and lanthanide cations. The chemical behaviour of these ions, similar in many aspects (most of their reactions can be interpreted by a simple electrostatic interaction model), differs significantly for some others. For example, experimental investigations on the complex-formation reactions of alkali- and alkaline-earth-metal ions with cryptands in aqueous solution can easily be carried out, while the same measurements with lanthanide(III) ions have proved to be rather difficult for two reasons: the very slow kinetics of formation and the metal-ion hydrolysis, which can compete with the cryptate formation.[4–6]

In order to overcome these difficulties and to study the solvent effect, a number of investigations have been carried out in mixed[7] (water–solvent) or anhydrous[8–18] solvents. Not all the results of this research are consistent with what should be expected on the grounds of an electrostatic interaction model. There are, for example, at least two remarkable incongruences in the literature data.

(i) The stability constants of the alkaline-earth-metal cryptates are sensitive to solvent variation and increase in the order dmso < dmf ⩽ water < MeOH < pc[19] [dmso = dimethyl sulfoxide, dmf = dimethylformamide, pc = propylene carbonate (4-methyl-1,3-dioxalan-2-one)], in agreement with the decrease in the solvating properties of the solvents as estimated by Gutmann's donor number.[20] The stability constants of the lanthanide(III) cryptates show an inversion in the stability sequence between dmso[9] and dmf,[16] the cryptates being more stable in the solvent having more pronounced solvating properties.

(ii) The stability constants of some divalent lanthanide cryptates, particularly of Eu^{2+}, determined in various solvents (water,[4,5] pc,[15] dmf,[16] MeCN[18]), surprisingly are solvent independent[18] and generally higher, sometimes noticeably, than the corresponding solvent-dependent values for the formation of the cryptates of the alkaline-earth-metal cations of similar size. For example, the logarithms of the stability constants of the 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane (L^1) cryptates of Ca^{2+} and Sr^{2+} in dmf are 3.79 and 7.3 respectively,[19] while for Eu^{2+} a value of 14.8 has been reported.[16]

Both cases (*i*) and (*ii*) raise some questions about the real factors involved in the formation of tri- and di-valent lanthanide cryptates and, therefore, they suggest the utility of further investigations on these co-ordination systems. Thus we decided to investigate the interactions of some lanthanide(III), *i.e.*, La, Nd, Eu and Yb, with the cryptands L^1 and 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (L^2) in the aprotic solvent dimethyl sulfoxide. Each system was examined by means of potentiometric and calorimetric measurements in order to determine the stability constants and the enthalpies of the co-ordinated species formed. With the same experimental methods we also studied the complex formation, still in dmso, of these cryptands with the Eu^{2+} ion and, for the sake of comparison, with the alkaline-earth-metal ions Ca^{2+}, Sr^{2+} and Ba^{2+}, for which only the values of the stability constants in dmso are available.[19] Conclusive, very significant, information on the interaction of the cations Eu^{3+}, Eu^{2+} and Yb^{3+}, Yb^{2+} with the same cryptands in dmso was obtained by means of cyclic voltammetry.

Experimental

In order to obtain and keep throughout experimentation the water and oxygen contents in the systems as low as possible, all the measurements and manipulations were performed in a glove-box under a controlled atmosphere containing less than 10 ppm of water and 1 ppm of oxygen. The measurements were conducted at 25 °C in a medium of ionic strength adjusted to 0.1 mol dm^{-3} with NEt_4ClO_4.

Reagents.—Adducts of the lanthanide(III) perchlorates, $Ln(ClO_4)_3{\cdot}n$dmso (n = 8 for La and Nd; 7.8 for Eu or 7 for Yb), were prepared and characterised as previously described.[21] Calcium, strontium and barium perchlorates were prepared by reaction of perchloric acid (Carlo Erba) with a slight excess of the respective carbonates (Aldrich). After filtration and evaporation of the solvent, the anhydrous products were obtained by drying under high vacuum at temperatures increasing stepwise from 60 to 120 °C. The dehydration apparatus was maintained at the highest temperature for at least 1 week. Anhydrous $AgClO_4$ and $NaClO_4$ were obtained by heating under vacuum the salts $AgClO_4{\cdot}H_2O$ (Fluka) and $NaClO_4$ (Merck) at 50 and 100 °C, respectively, for several days. Dimethyl sulfoxide and tetraethylammonium perchlorate were purified and dehydrated according to ref. 21. Cryptands L^1 and L^2 were commercial samples (Merck) used without further purification after their purity had been checked by pH-metric measurements. The water content in the solutions (typically 10–30 ppm) was determined at the end of each experiment using a Metrohm 684 KF coulometer.

CAUTION: Perchlorate salts of lanthanides are potentially explosive. Only small amounts of material should be prepared and handled with great care; particular caution must be exercised when they are heated under vacuum.

Potentiometric Measurements.—Data for the calculation of the stability constants were obtained by potentiometric measurements using the appropriate electrochemical cell for each system examined. In all cases the reference electrode was a Metrohm Ag–Ag$^+$ electrode (cat. no. 6.0718.000) in contact with a 0.1 mol dm^{-3} solution of $AgClO_4$ in dmso separated from the working half-cell by a salt bridge containing 0.1 mol dm^{-3} tetraethylammonium perchlorate in dmso.

Data concerning the interaction of the cryptands with lanthanide(III) (La^{3+}, Nd^{3+}, Eu^{3+} and Yb^{3+}) and with alkaline-earth-metal ions (Ca^{2+}, Sr^{2+} and Ba^{2+}) were obtained by the method of competitive reactions.[22] Silver(I) was used as auxiliary metal ion and a Metrohm (cat. no. 6.0328.000) massive silver electrode was employed to monitor the free silver(I) concentration. The titrations were conducted in jacketed vessels maintained at 25.0 ± 0.1 °C. Aliquots of cryptand solutions of known concentration were added to the titration half-cell containing solutions of silver(I) and lanthanide(III) or alkaline-earth-metal perchlorates, of exactly known concentrations. The electromotive force (emf) of the cell, measured after each addition, quickly reached stationary equilibrium values. For each system, three different initial concentrations of metal ion in the range 10–30 mmol dm^{-3} were used. Some of the titrations, repeated twice, showed that the emf values were usually reproducible within 0.3 mV. The working electrode was periodically checked in the concentration range 10^{-5}–10^{-2} mol dm^{-3} Ag$^+$ in the presence of lanthanide(III) or alkaline-earth-metal ions. No significant deviations from Nernst's law were observed.

The values of the stability constants for the silver(I) cryptates, necessary for the calculation of the lanthanide cryptate stabilities, were determined by direct potentiometry in separate experiments.

Since silver(I) oxidises the unstable Eu^{2+}, the stability constants of europium(II) cryptates were obtained using Na^+ as the auxiliary cation instead of Ag^+. In this case a Philips G15 sodium-selective glass electrode was used as working electrode. Its response, checked by adding increasing amounts of $NaClO_4$ solution to a solution of 10 mmol dm^{-3} $Ln(ClO_4)_3$, followed the Nernst law in the concentration range 10^{-5}–5×10^{-3} mol dm^{-3}. The values of the stability constants for the sodium complexes with the cryptands, obtained by direct potentiometry, were in very good agreement (within one standard deviation) with those calculated by a competitive potentiometric method, using Ag^+ as the auxiliary cation and the Ag–Ag$^+$ electrode as working electrode. This was a further proof of the correct behaviour of the sodium selective glass electrode in dmso solution. The solutions containing known concentrations of europium(II) perchlorate were prepared immediately before each experiment by exhaustive electrolysis of europium(III) solutions.

Stability constants were computed using the program SUPERQUAD.[23]

Calorimetric Measurements.—A Tronac model 87-588 precision calorimeter (titration vessel 25 cm^3) was used to study the metal–ligand systems in dmso. The calorimetric titrations were performed by adding a cryptand solution at a constant rate to a solution of the metal-ion perchlorates. For each system investigated generally three titrations were performed with a metal-ion concentration in the range 10–30 mmol dm^{-3}. Corrections for the heats of dilution of the ligand and the metal perchlorates were determined in separate runs. In all cases they were so small as to be neglected. The enthalpy changes for the systems investigated were calculated using the least-squares program LETAGROP KALLE.[24]

Electrochemical Measurements.—All experiments were performed in anhydrous, carefully deoxygenated, dmso solutions with 0.1 mol dm^{-3} NEt_4ClO_4 as the supporting electrolyte, using a conventional three-electrode liquid-jacketed cell. Cyclic voltammetry measurements were performed with an Amel 551 potentiostat modulated by an Amel 566 function generator, and the recording device was either an Amel model 863 X-Y recorder or a Hewlett-Packard 7090 A measurement plotting system, depending on the scan rate employed. The working electrode was a planar platinum microelectrode (*ca.* 0.3 mm^2) surrounded by a platinum-spiral counter electrode.

Controlled-potential electrolyses were performed with an Amel 552 potentiostat linked to an Amel 731 digital integrator. The working electrode was a mercury pool, and the counter electrode was external, the connection being made through an appropriate salt bridge.

In all cases an aqueous saturated calomel electrode (SCE), separated from the test solution by 0.1 mol dm^{-3} NEt_4ClO_4 in dmso solution sandwiched between two fritted discs, was used as the reference electrode. All potentials are referred to the SCE. Compensation for *iR* drop was achieved by positive feedback. Under the experimental conditions employed, the ferrocene–ferrocenium couple possessed an $E_{\frac{1}{2}}$ value of 0.440 V *vs.* SCE.

Results

Stability Constants.—The stability constants of the cryptates of the metal ions we have studied are reported in Table 1 together with the values obtained by other authors for the same systems under analogous experimental conditions.[1,19] Our results are in good, or in fairly good, agreement with the literature values. Presumably due to the very low affinity of calcium ion for cryptand L^1, the potentiometric titrations carried out to study this system using both Ag^+ and Na^+ as competing ions did not indicate any appreciable metal–ligand interaction for this system.

The analysis of the experimental data obtained for the two systems Eu^{2+}–L^1 and –L^2 clearly indicates that in both cases a 1 : 1 complex is formed. In Fig. 1 are reported, for example, the values of $\bar{n}$ *vs.* $-\log[L]$ for the Eu^{2+}–L^1 system. The values of $\bar{n}$ [the average number of ligands bound to each europium(II) ion] were calculated with the relationship $\bar{n} = (c_L - \bar{n}'c_{Na} - [L])/c_M$,

Table 1 Stability constants (log *K*) for cryptate complexes in dimethyl sulfoxide at 25 °C and ionic strength 0.1 mol dm^{-3}. The errors given correspond to three times the standard deviation calculated by the minimisation program

		Cryptand	
Cation	Ionic radius[a]/Å	L^1	L^2
Ag$^+$	1.15	7.15 ± 0.06	9.56 ± 0.05
		(7.16)[b]	(9.18)[b]
Na$^+$	1.02	5.15 ± 0.04	6.91 ± 0.07
		(5.22)[b]	(7.04)[b]
Ca^{2+}	1.00	—	3.47 ± 0.05
		(≤2.1)[c]	(3.90)[c]
Sr^{2+}	1.18	4.98 ± 0.04	5.97 ± 0.05
		(5.26)[c]	(6.10)[c]
Ba^{2+}	1.35	6.21 ± 0.03	5.04 ± 0.03
		(6.50)[c]	(5.30)[c]
Eu^{2+}	1.17	5.33 ± 0.27	5.80 ± 0.30

[a] From ref. 25 for co-ordination number six. [b] Calculated from the average value of log *K*, ref. 1. [c] Ref. 19.

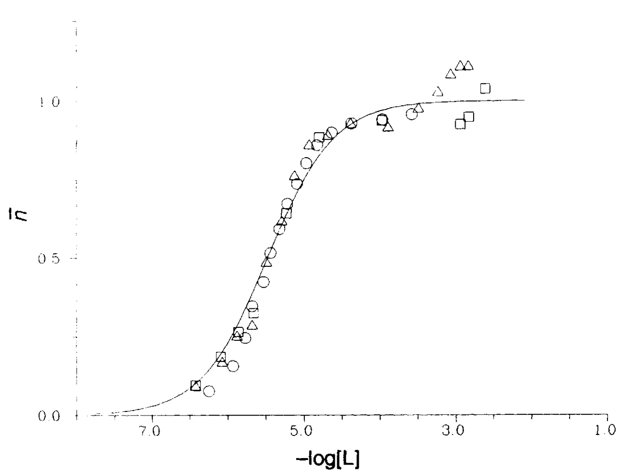

Fig. 1 Complex-formation functions for the europium(II)–L^1 cryptand system (□, $c^0_{Eu^{2+}}$, $c^0_{Na^+}$ = 0.62, 0.9; △, 0.92, 2.36; ○, 2.24, 1.97 mmol dm^{-3}). The full curve was obtained using the value of *K* reported in Table 1

where c_L and [L] are the total and free cryptand concentration, respectively, c_M is the total europium(II) concentration, and $\bar{n}'$ and c_{Na} refer to the competitive Na$^+$ ion. The values calculated for the stability constants of the two cryptates are reported in Table 1.

All the potentiometric measurements performed to study the interactions between the lanthanide ions La^{3+}, Nd^{3+}, Eu^{3+} and Yb^{3+}, and the cryptands revealed that the emf values measured were independent of lanthanide(III) concentration in the working half-cell, in the range of concentration examined and within the sensibility of the apparatus used. This means that of the two supposed equilibria in competition, *i.e.* that, (1),

$$Ag^+ + L \rightleftharpoons [AgL]^+ \qquad (1)$$

involving the auxiliary cation, and the one, (2), involving the

$$Ln^{3+} + L \rightleftharpoons [LnL]^{3+} \qquad (2)$$

lanthanide(III) ions (Ln^{3+}), only (1) is effective in the systems examined.

Thermodynamic Parameters.—Calorimetric titrations performed by adding solutions of the cryptands to a solution containing one of the alkaline-earth-metal cations considered or Eu^{2+} gave well measurable heat changes from which the enthalpies of reaction were calculated. They are reported in Table 2 together with the values of the free energy and entropy.

Very recently, a set of thermodynamic data for the reaction of alkaline-earth-metal ions with cryptand in dmso have been reported.[27] They were determined from the temperature dependence of the formation constants investigated by means of a competitive spectrophotometric technique. The values reported for $\Delta H°$ and $\Delta S°$ are greatly different from our values. Strangely, the previous authors ignored in their discussion the earlier published stability data.[19]

All the calorimetric measurements carried out on the systems formed by each lanthanide(III) examined (La^{3+}, Nd^{3+}, Eu^{3+}, Yb^{3+}) and the cryptands in dmso gave negligible heats of reactions, that is the heat changes throughout each calorimetric titration did not exceed to a significant extent the values attributable to the dilution effect of the reagents.

Electrochemical Behaviour.—A representative cyclic voltammogram of a Eu^{3+} solution, recorded at 25 °C in 0.1 mol dm^{-3} NEt$_4$ClO$_4$ in dmso is depicted in Fig. 2 (full line). Under these conditions the metal cation appears to be reduced in an uncomplicated ($i_p^a/i_p^c = 1$), virtually reversible, one-electron step ($\Delta E_p = 75$ mV, $E_p{}^c - E_{p/2} = 62$ mV) centred at $E_{\frac{1}{2}} = -0.850$ V, as a mean value of the potentials for the cathodic and anodic peak currents. Addition of an equimolecular quantity of cryptand L^1 to the metal-ion solution produces the complete disappearance of the reversibly coupled anodic signal, while the cathodic peak appears to be slightly sharper ($E_p^c - E_{p/2} = 55$ mV) and shifted to less-negative potentials (Fig. 2, dashed line). This pattern is that anticipated for a simple one-electron reversible charge transfer followed by an irreversible rapid chemical reaction.[28] Hence, as soon as Eu^{2+} is formed at the surface of the electrode the cation is quenched by the cryptand to give the electroinactive [EuL^1]$^{2+}$ cryptate. Compelling evidence in favour of an electrochemical–chemical mechanism is provided by the course of controlled-potential coulometry experiments. Exhaustive electrolysis carried out at potentials past the cathodic peak and in the absence of the cryptand requires 1 mol of electrons per mol of Eu^{3+} and leads to a quite stable, but exceedingly air-sensitive, solution with a voltammetric oxidation profile corresponding to the reduction pattern of the precursor. Addition to the catholyte of increasing amounts of cryptand L^1 leads to a concomitant decrease in the peak currents, so that the signal completely disappears when the stoichiometric amount of the cryptand is present. Under these conditions, cyclic voltammetry inspection in the potential region round 0.0 V reveals the presence of a new redox couple centred at $E_{\frac{1}{2}} = -0.090$ V (Fig. 3). Analysis of the voltammetric profile indicates an essentially reversible one-electron oxidation ($\Delta E_p = 80$ mV) followed by a chemical reaction recordable in the time window of the experiment (see below for the kinetic measurements). Exhaustive electrochemical oxidation confirms the removal of 1 mol of electrons per mol of starting metal cation and restores completely the original voltammetric picture (Fig. 2, dashed line).

The whole of the electrochemical observations point convincingly to the reaction sequence shown in equations (3)–(6) where the terms fast and slow refer to the cyclic voltammetry

$$Eu^{3+} + e \rightleftharpoons Eu^{2+}; \quad E_{\frac{1}{2}} = -0.850\text{ V} \qquad (3)$$

$$Eu^{2+} + L^1 \xrightarrow{\text{fast}} [EuL^1]^{2+} \qquad (4)$$

$$[EuL^1]^{2+} - e \rightleftharpoons [EuL^1]^{3+}; \quad E_{\frac{1}{2}} = -0.090\text{ V} \qquad (5)$$

$$[EuL^1]^{3+} \xrightarrow{\text{slow}} Eu^{3+} + L^1 \qquad (6)$$

Table 2 Thermodynamic parameters for the complexation of Ca^{2+}, Sr^{2+}, Ba^{2+} and Eu^{2+} with cryptands in dmso solution at 25 °C and corresponding literature values for aqueous solution [ref. 26 for alkaline earths and ref. 4 for europium(II)]. The errors given refer to three times the standard deviations calculated by the minimisation programs for log *K* and Δ*H*

Cryptand	Cation	Solvent	$-\Delta G^\circ$/ kJ mol^{-1}	$-\Delta H^\circ$/ kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}	$T\Delta S^\circ$/ kJ mol^{-1}
L^2	Ca^{2+}	dmso	19.81 ± 0.28	25.6 ± 0.4	−19.4 ± 2.4	−5.8
		water	39.75	12.1	93	27.6
	Sr^{2+}	dmso	34.08 ± 0.28	46.0 ± 0.3	−40.0 ± 2.0	−11.90
		water	41.87	25.5	54.9	16.3
	Ba^{2+}	dmso	28.77 ± 0.17	39.6 ± 0.4	−36.3 ± 2.0	−10.8
		water	35.98	26.4	32.1	9.6
	Eu^{2+}	dmso	33.1 ± 1.7	50.2 ± 0.4	−57 ± 7	−17.1
		water	53.1	36.8	54.7	16.3
L^1	Sr^{2+}	dmso	28.43 ± 0.23	31.7 ± 0.4	−11.0 ± 1.8	−3.3
		water	45.60	43.1	8.4	2.5
	Ba^{2+}	dmso	35.44 ± 0.17	48.1 ± 0.3	−42.5 ± 1.6	−12.70
		water	54.00	59.0	−16.8	−5.0
	Eu^{2+}	dmso	30.4 ± 1.5	36.0 ± 0.3	−19 ± 6	−5.6
		water	59.83	57.3	8.5	2.5

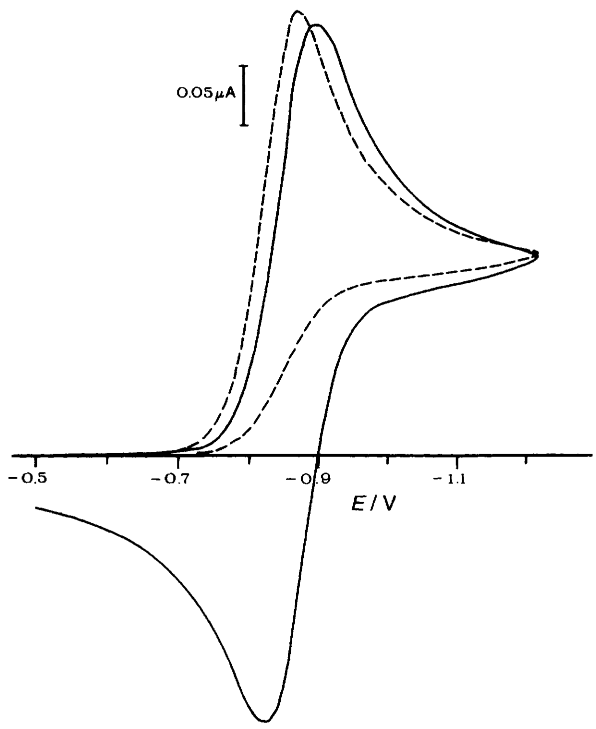

Fig. 2 Cyclic voltammogram for reduction of 3.0 mmol dm^{-3} Eu^{3+} in 0.1 mol dm^{-3} NEt_4ClO_4 in dmso at 25 °C in the absence (full line) and in the presence (dashed line) of 3.0 mmol dm^{-3} L^1. Scan rate 20 mV s^{-1}

time-scale and 25 °C. Thus these data indicate that the electrogenerated cryptate $[EuL^1]^{3+}$ undergoes complete dissociation in dmso [equation (6)].

Additional evidence to support the proposed mechanism stems from kinetic investigations of the chemical steps following the charge-transfer reactions. The rate constant of the chemical step (4) was measured following the procedure suggested in ref. 28 by cyclic voltammetry under pseudo-first-order conditions ($[L^1]/[Eu^{3+}] \geqslant 10$) at three, ten-fold-spaced, cryptand concentrations. For each cryptand concentration, the anodic shift of the reduction peak potential of Eu^{3+}, ΔE^c_p, was measured and plotted *vs.* log V (V = scan rate, mV s^{-1}). Fig. 4 shows one of these plots as an example. Extrapolation to zero ΔE^c_p of the linear portion of the plots, slope ≈ 30 mV per decade as required by theory, gave V^0, *i.e.* the scan rate at which the extent of chemical reaction [equation (4)] is negligible.

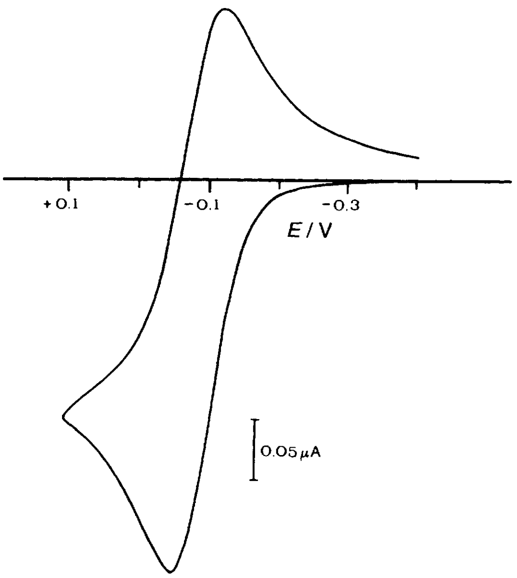

Fig. 3 Cyclic voltammogram for oxidation of 3.0 mmol dm^{-3} of $[EuL^1]^{2+}$ in 0.1 mol dm^{-3} NEt_4ClO_4 in dmso at 25 °C. Scan rate 20 mV s^{-1}

From the equation $\log k^* = \log V^0 - 1.70$ we obtained the pseudo-first-order rate constant, k^*, from which the second-order rate constant of reaction (4), k_4, for each ligand concentration was calculated at 25 °C. The effective constancy of these values, $k_4 = 700 \pm 50$ dm^3 mol^{-1} s^{-1}, corroborates the proposed mechanism.

The rate constant of the reaction (6), successive to the electrochemical oxidation of the $[EuL^1]^{2+}$ cryptate [reaction (5)], was evaluated from the variation of the ratio of the cathodic to anodic peak currents, i^c_p/i^a_p, as a function of the scan rate and $[EuL^1]^{2+}$ concentration. Stoichiometric as well as excess amounts of cryptand L^1 were used in exhaustively reduced solutions of Eu^{3+}. The data were found to be fit satisfactorily by the theory developed for a first-order chemical reaction following charge transfer[28] and gave a rate constant of 0.020 ± 0.001 s^{-1} at 25 °C. The activation parameters, estimated with a least-squares fitting of the rate constants at four temperatures in the range 25–50 °C, are $\Delta H^\ddagger = 45.7 \pm 0.7$ kJ mol^{-1} and $\Delta S^\ddagger = -124 \pm 4$ J K^{-1} mol^{-1}.

A similar behaviour is observed in the case of the $Eu^{3+/2+}$–L^2 systems, the one significant difference being a slightly lower rate of complexation of Eu^{2+} [equation (4)] and a much lower rate of dissociation of the cryptate $[EuL^2]^{3+}$ [equation (6)].

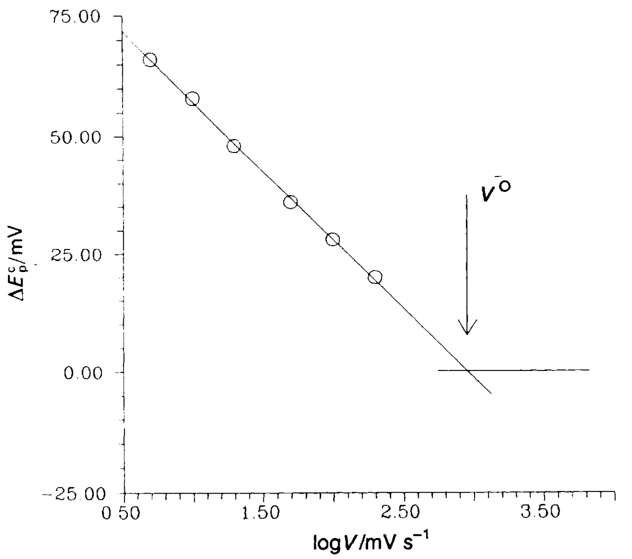

Fig. 4 Typical determination of the pseudo-first-order rate constant for the formation of the $[EuL^1]^{2+}$ complex. The anodic shift of the reduction peak potential, ΔE^c_p, is shown as a function of the scan rate (mV s^{-1}). Conditions: 0.1 mol dm^{-3} NEt_4ClO_4 in dmso at 25 °C; $[Eu^{3+}]$ = 2.6 mmol dm^{-3}; $[L^1]$ = 27 mmol dm^{-3}

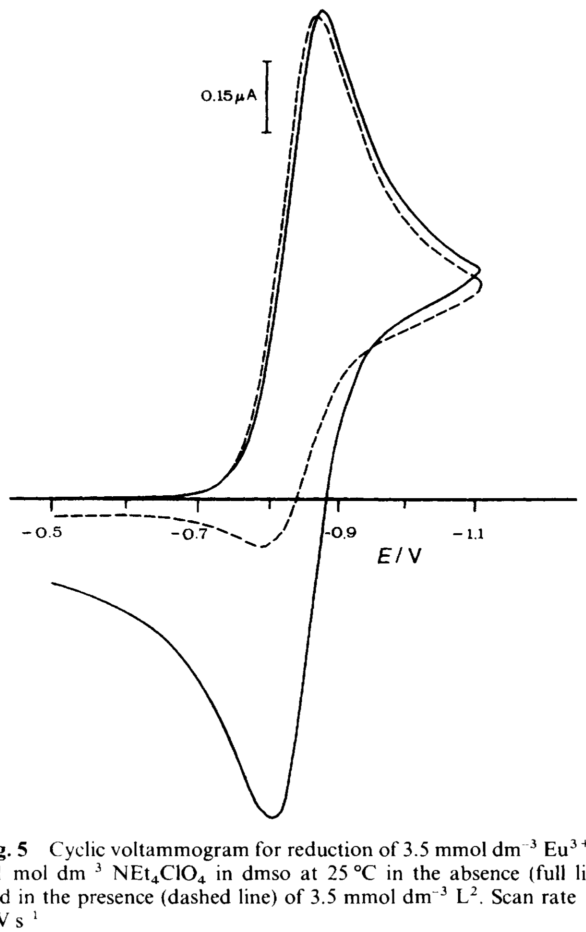

Fig. 5 Cyclic voltammogram for reduction of 3.5 mmol dm^{-3} Eu^{3+} in 0.1 mol dm^{-3} NEt_4ClO_4 in dmso at 25 °C in the absence (full line) and in the presence (dashed line) of 3.5 mmol dm^{-3} L^2. Scan rate 100 mV s^{-1}

Indeed, cyclic voltammograms of Eu^{3+} recorded in the presence of a stoichiometric amount of the cryptand allow the reversibly coupled anodic peak to be detected at relatively low scan rates (Fig. 5, dashed line). By the same approach used for the cryptand L^1 (see above), the second-order rate constant, k_4 = 350 ± 30 dm^3 mol^{-1} s^{-1}, was obtained. Similarly, cyclic voltammograms recorded on solutions of the electrogenerated $[EuL^2]^{2+}$ cryptate show a redox couple centred at $E_{\frac{1}{2}} = -0.300$ V, fully developed ($i^c_p/i^a_p = 1$) even at the lowest scan rate (5 mV s^{-1}) explored. Kinetic investigations carried out by amperometric monitoring of the reduction wave of both the disappearing $[EuL^2]^{3+}$ cryptate, electrogenerated by oxidation of $[EuL^2]^{2+}$, and the appearing Eu^{3+}, confirmed that the dissociation reaction obeys a first-order law with a rate constant of (4.7 ± 0.2) × 10^{-5} s^{-1} at 25 °C.

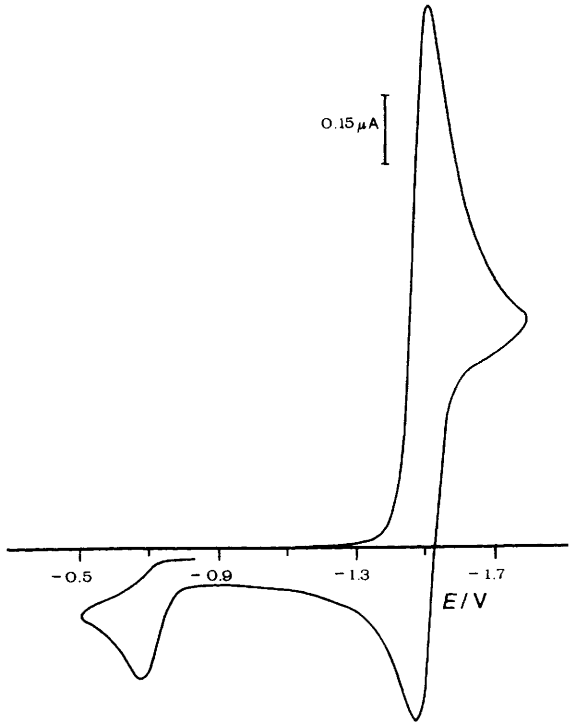

Fig. 6 Cyclic voltammogram for reduction of 3.9 mmol dm^{-3} Yb^{3+} in 0.1 mol dm^{-3} NEt_4ClO_4 in dmso at 25 °C in the presence of an equivalent quantity of L^1. Scan rate 100 mV s^{-1}

A cyclic voltammogram of the Yb^{3+}–L^1 system is shown in Fig. 6. The electrochemical path ($Yb^{3+} + e \rightleftharpoons Yb^{2+}$; $E_{\frac{1}{2}} = -1.500$ V) reveals once more the lack of any interaction between the lanthanide(III) ion and the cryptand in dmso. Moreover, a comparison of these data with those of the $Eu^{3+/2+}$–L^1 system suggests that the formation of the divalent metal cryptate is much slower for Yb^{II} than for Eu^{II}, while the dissociation of the electrogenerated $[YbL^1]^{3+}$ is much faster (within seconds) than that of its europium analogue.

Discussion

The electrochemical measurements clearly show that in dmso the cryptates of trivalent europium and ytterbium completely dissociate once they are formed by anodic oxidation of the corresponding divalent-ion cryptates. In particular the measurements with Eu^{3+} demonstrated that the dissociation follows a relatively slow first-order reaction with $t_{\frac{1}{2}}$ = 14.7 × 10^3 and 35 s for the L^2 and L^1 cryptates, respectively. The results of the potentiometric and calorimetric measurements with La^{3+}, Nd^{3+}, Eu^{3+} and Yb^{3+} are in accord with this conclusion.

It may be of interest that our electrochemical data are in good agreement with those obtained by other authors for the same systems.[12,14] For example, the values of the difference in formal potential of the redox couples of the complexed and uncomplexed europium ions obtained by us for the $Eu^{3+/2+}$–L^2 and –L^1 systems ($\Delta E_{\frac{1}{2}}$ = 550 and 760 mV, respectively) are in good agreement with the corresponding literature values of 541 and 747 mV.[12]

Table 3 Thermodynamic parameters for cryptate formation and for solvent transfer of some alkali- and alkaline-earth-metal cations; $\Delta G°$, $\Delta H°$ and $T\Delta S°$ are in kJ mol^{-1}, T = 298 K

		Cation (ionic radius[a]/Å)			
Cryptand	Parameter	Na^+ (1.02)	Ca^{2+} (1.00)	K^+ (1.38)	Ba^{2+} (1.35)
	Water[b]				
L^2	$-\Delta G°$	30.1	39.7	22.6	36.0
	$-\Delta H°$	22.4	12.1	28.5	26.4
	$T\Delta S°$	7.7	27.6	−5.9	9.6
L^1	$-\Delta G°$	22.2	25.1	30.1	54.0
	$-\Delta H°$	31.0	0.8	47.7	59.0
	$T\Delta S°$	−8.8	24.3	−17.6	−5.0
	Dimethyl sulfoxide				
L^2	$-\Delta G°$	39.8[c]	19.81	34.1[c]	28.77
	$-\Delta H°$		25.6		39.6
	$T\Delta S°$		−5.8		−10.8
L^1	$-\Delta G°$	30.5[d]	—	39.9[d]	35.44
	$-\Delta H°$	44.6[d]	—	61.2[d]	48.1
	$T\Delta S°$	−14.1[d]	—	−21.3[d]	−12.7
Transfer from water to dmso[e]	$-\Delta G°_{tr}$	13.8		12.1	25.1
	$-\Delta H°_{tr}$	27.6		34.7	78.5
	$T\Delta S°_{tr}$	−13.8		22.6	−53.4

Transfer of L^1 from water to dmso[d]: $\Delta G° = 6.4$, $\Delta H°_{tr} = 60.3$, $T\Delta S°_{tr} = 53.9$

[a] From ref. 25 for co-ordination number six. [b] Ref. 26. [c] Computed from the stability constants in ref. 32. [d] Ref. 36. [e] Ref. 37.

A number of authors have applied to the lanthanide cryptate systems the Nernst–Peters relationship[29] in the approximate form $\Delta E_{\frac{1}{2}} = (2.303RT/F)\log(K_{II}/K_{III})$, where K_{II} and K_{III} are the stability constants of the complexes formed by a given cryptand with a given lanthanide in the 2+ and 3+ oxidation state, respectively. In this way, from the stability constants for divalent europium cryptates obtained by voltammetric and potentiometric measurements in aqueous solution, the stability constants for trivalent europium cryptates were calculated,[4] and from the stability constant determined for some lanthanide(III) cryptates the stability constant of the corresponding lanthanide(II) cryptate was calculated in methanol,[8] in propylene carbonate,[15] in dimethylformamide[16] and in acetonitrile.[18] Applying this equation in the unapproximated form[30,31] to the systems considered here a negative value for the stability constants of both the trivalent europium cryptates can be calculated from the directly determined stability constants of the divalent europium complexes. This is consistent with the conclusion stated above and drawn from experimental evidence, *i.e.* there is no appreciable cryptate formation with lanthanide(III) ions in dmso.

We are not able to suggest any explanation for the quite different results reported by other authors.[9] In any case, since our conclusion is based on different, quite independent, experimental evidence, we think that the formation of stable lanthanide(III) complexes with cryptands L^1 and L^2 previously claimed[9] has to be ruled out.

An inspection of the stability constant values for the alkaline-earth-metal cryptates reported in Table 1 confirms the general observations put forward by Cox *et al.*[19,32]: (*i*) in dmso, as well as in other solvents, the stabilities of these cryptates depend strongly upon the relative size of the cation and of the ligand cavity, so that cations forming the most stable complexes with L^2 and L^1 are Sr^{2+} and Ba^{2+}, respectively; (*ii*) a comparison between the corresponding values obtained in various solvents indicates that the stabilities are sensitive to solvent variation and increase in the order dmso < dmf ⩽ water < MeOH < pc. This sequence suggests that one of the important factors in these co-ordination systems is the cation–solvent interaction,[19] the intensity of which may be correlated both with the solvent donor number and with the free energy of transfer, ΔG_{tr}, of the cation from one solvent to another.

The values of the thermodynamic parameters for the formation of the alkaline-earth-metal cryptates in dmso can profitably be compared with those obtained in aqueous solution[26] reported in Table 2 as well. Thermodynamic data for the same cryptates in other solvents are not available, except for some data referring to methanol.[33,34]

First, it is of interest that all the cryptates of the alkaline-earth-metal cations in dmso are enthalpy stabilised whereas the entropy contributions oppose the complex formation ($\Delta H < 0$ and dominant, $T\Delta S < 0$). In water the same cryptates are also stabilised by the enthalpy changes, but the entropy contributions are generally favourable (except for $[BaL^1]^{2+}$). For all the cryptates considered here the higher stability in water than in dmso is mainly due to the more favourable entropy contributions. This effect might be attributed, at least in part, to the influence of solvent–ligand interactions, which is also a factor of some importance in these co-ordination systems, though frequently ignored.[35] It is well known that solvation of a cryptand in water, but not in dmso, proceeds largely through hydrogen bonding and this results in a more negative entropy of solvation in water than in dmso (see ΔS_{tr} for L^1 in Table 3). A more positive contribution to the entropy of complexation in water than in dmso may result from a greater degree of solvent disorder created by desolvation of the cryptand when the complex forms in water.

An interesting feature of the cryptate thermodynamics is its dependence upon the cation charge when changing from one solvent to another. In order to discuss this subject it is necessary to compare values of thermodynamic parameters concerning cryptate formation of pairs of cations having similar ionic radii and different charges as, for example, the pairs Na^+–Ca^{2+} and K^+–Ba^{2+} thermodynamic data for which in water and in dmso are given in Table 3. In aqueous solution, the $-\Delta G°$ values for complex formation with both cryptands L^1 and L^2 are markedly greater for the divalent compared with the monovalent cations. The corresponding values obtained in dmso show the opposite trend: on increasing the charge the cryptate stabilities decrease.

The behaviour in water of pairs of cations with cryptands like those in Table 3, has been interpreted as due to the different effect of the charge variation on the ion–dipole interactions between both the ether moieties of the cryptand and the solvent molecules with the metal ion. An increase in the cationic charge will result in increasingly favourable interactions with both these dipole species. However, on account of the smaller dipole moment of dimethyl ether (μ = 1.30 D; D ≈ 3.35 × 10^{-30} C m) *vs.* that of water (μ = 1.85 D), the interactions involving the ether moieties of the cryptands are expected to be relatively less favourable compared with those involving the solvent molecules.[4,26] Generally, these factors bring about a less favourable enthalpy change for the divalent compared with the monovalent metal cryptates. These differences are nevertheless largely compensated by more favourable entropy changes, so that $-\Delta G^\circ$ values are typically greater for the divalent metal cryptates compared with the monovalent ones. The more positive (or less negative) ΔS° values for the divalent metal cryptates result from the more negative hydration entropies of the divalent *vs.* mono-valent cations.[4]

The above rationalisation of the thermodynamic data in water could be extended to the analogous data in dmso in the following way. This solvent has stronger solvating properties towards metal cations than water according to its higher dipole moment and donor number (μ = 1.85 and 3.96 D; donor number = 18.0 and 29.8 for water and dmso, respectively). This different solvating power is well demonstrated by the values in Table 3 of ΔG_{tr}, ΔH_{tr} and ΔS_{tr} for transfer of the cations from water to dmso. On increasing the cation charge from 1+ to 2+ the difference in solvation energy becomes greater in dmso than in water, as can be seen by considering, for instance, the enthalpy changes associated with the transfer of mono- and di-valent cations from water to dmso. The markedly more negative solvation enthalpies in dmso for divalent cations compared with those for monovalent cations of similar size bring about a less favourable cryptate formation enthalpy for the divalent ones so marked as not to be compensated by the more favourable entropy change. Thus, in contrast to what happens in water, the values of $-\Delta G^\circ$ in dmso are smaller for the divalent metal cryptates than for the monovalent ones.

It is reasonable to assume that the above trend can be extrapolated to the trivalent cations in dmso. In the case of lanthanide(III) cations the still more negative solvation enthalpies could even prevent cryptate formation, in accord with our experimental data.

A balance of the various contributions to cryptate formation thermodynamics due to the solvent interactions with the metal cation and with the cryptand may also account for an apparent anomalous behaviour of the alkali-metal cations when the solvent is changed from water to dmso. The stability constants of the alkali-metal cryptates are lower in water than in any of the non-aqueous solvents examined till now[32] and thus the relative positions of water and dmso are reversed with respect to the sequence of increasing stability with decreasing donor number of the solvents. From a comparison of thermodynamic data for the same alkali-metal cryptates in water and in dmso[26,36] (some data in Table 3) it can be seen that the higher stability in dmso is due to the enthalpy term whereas the entropy one is unfavourable. A rationale for this can be found in the fact that the free cryptands are more solvated in water than in non-aqueous solvents,[38,39] these differences being greater in enthalpy terms than the opposite differences between the solvation of alkali-metal cations by the two solvents (see thermodynamic transfer parameters in Table 3). As soon as cations of greater charge are considered, for instance alkaline-earth-metal cations, the effect due to the stronger solvation of the cations in dmso than in water becomes prevalent and the stability sequence changes to dmso < water.

The stability constants in Table 1 and the thermodynamic data in Table 2 for the two cryptates of Eu^{2+} show clearly that the data for the formation of europium(II) complexes are very similar to those of strontium(II) which has the same charge and very similar size.

The thermodynamic parameters for the formation of the same cryptates in aqueous solution, Table 2, indicate that in this solvent the lanthanide(II) cryptates are markedly more stable than the strontium ones. It was suggested that this greater stability, due only to the enthalpy contribution, may arise from weak covalent bonding between the oxygen and nitrogen atoms of the cryptand and the unfilled 4f orbitals on europium(II).[4] This effect is not detectable in dmso.

The results of this investigation demonstrates that the co-ordination behaviour of the lanthanide ions with the present cryptands finds its rightful place inside the general scheme accepted for 'hard–hard' interactions. Lanthanide(III) ions form cryptates the stability of which decreases as the solvating properties of the solvents increase. The cryptate formation is particularly sensitive to the solvent effect so that lanthanide(III) cryptates are considerably stable in dmf[16] which has a donor number not very different from that of dmso (26.6 and 29.8, respectively).

As for the divalent lanthanides, our results for the europium(II) cryptate in dmso are quite consistent with the resemblance between the chemical properties of lanthanide(II) and alkaline-earth-metal cations having similar ionic radii.[40] Based on our data, in particular the stability constants directly determined from potentiometric measurements, the statement that 'the stabilities of divalent lanthanide cryptates are solvent independent'[18] is not confirmed. On the contrary, the quite different stability of Eu^{2+}–L^1 and –L^2 cryptates in dmso and dmf (solvents having similar donor numbers) indicates that these species are very sensitive to the solvating properties of the reaction media.

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References

1 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271.

2 J. C. Bunzli and D. Wessner, *Coord. Chem. Rev.*, 1984, **60**, 191.

3 G. Adachi and Y. Hirashima, *Cation Binding by Macrocycles*, eds. Y. Inoue and G. W. Gokel, Marcel Dekker, New York, 1990.

4 E. L. Yee, O. A. Gansow and M. J. Weaver, *J. Am. Chem. Soc.*, 1980, **102**, 2278.

5 J. H. Burns and C. F. Baes, jun., *Inorg. Chem.*, 1981, **20**, 616.

6 R. A. Torres and P. A. Baisden, *Inorg. Chem.*, 1989, **28**, 2807.

7 G. Anderegg, *Helv. Chim. Acta*, 1981, **64**, 1790.

8 M. C. Almasio, F. Arnaud-Neu and M. J. Schwing-Weill, *Helv. Chim. Acta*, 1983, **66**, 1296.

9 R. Pizer and R. Selzer, *Inorg. Chem.*, 1983, **22**, 1359.

10 G. Gillain, P. Barthélemy, J. Massaux and J. F. Desreux, *J. Chem. Soc., Dalton Trans.*, 1984, 2847.

11 O. A. Gansow and A. R. Kausar, *Inorg. Chim. Acta*, 1985, **95**, 1.

12 J. Tabib, J. T. Hupp and M. J. Weaver, *Inorg. Chem.*, 1986, **25**, 1916.

13 F. Arnaud-Neu, E. L. Loufouilou and M. J. Schwing-Weill, *J. Chem. Soc., Dalton Trans.*, 1986, 2629.

14 J. Bessière, M. F. Lejaille and M. Perdicakis, *Bull. Soc. Chim. Fr.*, 1987, **4**, 594.

15 E. L. Loufouilou and J. P. Gisselbrecht, *Can. J. Chem.*, 1988, **66**, 2172.

16 I. Marolleau, J. P. Gisselbrecht, M. Gross, F. Arnaud-Neu and M. J. Schwing-Weill, *J. Chem. Soc., Dalton Trans.*, 1989, 367.

17 A. F. Danil de Namor, M. Claude Ritt, M. J. Schwing-Weill and F. Arnaud-Neu, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 89.

18 I. Morellau, J. P. Gisselbrecht, M. Gross, F. Arnaud-Neu and M. J. Schwing-Weill, *J. Chem. Soc., Dalton Trans.*, 1990, 1285.

19 B. G. Cox, N. van Truong and H. Schneider, *J. Am. Chem. Soc.*, 1984, **106**, 1273.

20 V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978.

21 A. Cassol, P. Di Bernardo, R. Portanova, M. Tolazzi, G. Tomat and P. L. Zanonato, *J. Chem. Soc., Dalton Trans.*, 1992, 469.

22 F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants*, McGraw-Hill, New York, 1961, p. 58.

23 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1995.

24 R. Arnek, *Ark. Kemi*, 1970, **32**, 81.

25 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

26 E. Kauffmann, J. M. Lehn and J. P. Sauvage, *Helv. Chim. Acta*, 1976, **59**, 1099.

27 J. Ghasemi and M. Shamsipur, *J. Coord. Chem.*, 1994, **31**, 265.

28 A. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.

29 L. Sucha and S. Kotrly, *Solution Equilibria in Analytical Chemistry*, Van Nostrand Reinhold, London, 1972, p. 260.

30 L. Meites, *Polarographic Techniques*, Interscience, New York, 1955, p. 116.

31 D. D. De Ford and L. Andersen, *J. Am. Chem. Soc.*, 1950, **72**, 3916.

32 B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, 1981, **103**, 1384.

33 N. Morel-Desrosiers and J. P. Morel, *Nouv. J. Chim.*, 1985, **9**, 629.

34 H. J. Buschmann, *Inorg. Chim. Acta*, 1986, **120**, 125.

35 L. L. Soong, G. E. Leroi and A. I. Popov, *J. Incl. Phenomena*, 1992, **12**, 253.

36 A. F. Danil de Namor and L. Ghousseini, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2349.

37 G. R. Hedwig, D. A. Owensby and A. J. Parker, *J. Am. Chem. Soc.*, 1975, **97**, 3888.

38 B. G. Cox, H. Schneider and J. Stroka, *J. Am. Chem. Soc.*, 1978, **100**, 4746.

39 M. H. Abraham and H. C. Ling, *J. Chem. Soc., Faraday Trans. 1*, 1984, 3445.

40 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edn., Interscience, New York, 1972, pp. 208, 1075.

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