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Electrochemical characterisation of bis(1,10-phenanthroline) gadolinium (III) trichloride formed *in situ*

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Abstract

The *in situ* formation and electrochemical behaviour of a complex between Gadolinium (III) and 1,10-phenanthroline (phen) are discussed. The electron withdrawing ability of phen decreases the redox potential of Gd(III). A cathodic peak at ~ -1.7 V vs. Ag/Ag⁺ 10mM, corresponds to an irreversible electron transfer reaction involving the exchange of two electrons, where the first charge transfer reaction is the rate-determining step. The diffusion coefficient and the total number of electrons were derived using the Shoup-Zsabo equation. Kinetic parameters such as k^0 , α and i^0 are calculated. Voltammetric simulations are carried out to evaluate the accuracy of the results. A fast chemical reaction consumes the reduced species formed at ~ -1.7 V, which is then oxidised at ~ -0.1 V. The stoichiometry of the complex is determined by the Yoe and Jones' method. An average value for the stability constant of the complex of $(2.3 \pm 0.8) 10^5 \text{ M}^{-2}$ is obtained.

Keywords: Gadolinium; dimethylsulfoxide (DMSO); stability constant; irreversible reaction; cyclic voltammetry; 1,10-phenanthroline.

1. Introduction

The electronic configuration of Gadolinium is [Xe] 4f⁷ 5d¹ 6s². Given the large energy difference between the 5d or 6s electronic levels and the 4f level, gadolinium,

like other lanthanides, is a highly reactive metal; it slowly dissolves in water to produce hydrogen and Gd^{3+} . Because of its very negative standard reduction potential, -2.28 V vs. Normal Hydrogen Electrode [1], the electrochemical deposition of the metal has only been achieved in molten salts [2,3]. This process has been proposed to remove Gd^{3+} from nuclear waste. The efficiency of the separation is enhanced if reactive materials such as Al, Cu or Ni are employed as cathodes. Under these experimental conditions, the electrodeposition of gadolinium takes place at lower cathodic potentials, enhancing its deposition rate by the formation of an alloy with the material of the cathode [3].

Metallic gadolinium is one of four elements that are ferromagnetic at room temperature. Its Curie temperature is 17°C . There is a large family of technologically important intermetallic compounds of a lanthanide with iron or cobalt; some examples are SmCo_5 or $\text{Nd}_2\text{Fe}_{14}\text{B}$ for permanent magnets [4], $(\text{Dy,Tb})\text{Fe}_2$ for magnetostriction [5] and $\text{La}(\text{Fe}_{11}\text{Si})$ for magnetocaloric applications [6]. The manufacture of these compounds by electrodeposition would be very convenient given their possible technological applications as thin or thick films. Gadolinium, at the middle of the series is a good proxy for the lanthanides and if it were successfully electrodeposited it could be easily detected, even in small amounts, because of its ferromagnetism in the metallic form.

The Gd^{3+} ion has seven unpaired 4f electrons which makes it strongly paramagnetic with a spin moment of 7 Bohr magneton. For this reason, gadolinium organic complexes are important in Magnetic Resonance Imaging (MRI), since they alter the proton relaxation time of the nearby tissues, enhancing the contrast among different features. Electrochemical investigations of the radiation sensitizer Gadolinium (III) Texaphyrin (PCI-0120) complex show two quasi-reversible one-electron reductions

at ~ -0.27 V and ~ -0.74 V vs. Ag/AgCl in deoxygenated DMF [7]. Provided the reduction potential for the $\text{Gd}^{3+}/\text{Gd}^{2+}$ couple is much more negative than -0.27 V or -0.74 V, and the replacement of Gadolinium by other lanthanide ions leads to quite similar electrochemical behaviour, it is established that the reduction processes take place on the texaphyrin ligand, rather than at the metal centre. Similar results were obtained with sandwich-like bis(phthalocyaninato) complexes of lanthanide(III) ions such as Europium, Gadolinium, Lutetium and Ytterbium [8]. Motexafin gadolinium (III), another electroactive organocomplex, is currently under development for the treatment of cancer and other diseases [9]. This complex has a strong affinity for electrons and under certain circumstances it forms superoxide and other reactive oxygen species which are cytotoxic to tumor cells. The presence of the aromatic π system is responsible for the easy reduction of the complex, since gadolinium requires a much larger potential to accept electrons [10]. In many redox reactions involving organic gadolinium complexes, it is the ligand that is electroactive, rather than the metallic centre.

The goal of the present work is to research the redox properties of a complex formed by Gd^{3+} and a π acceptor ligand, such as 1,10-phenanthroline [14]. This type of ligand withdraws the electronic density from the metallic centre, stabilising lower oxidation states. In electrochemical terms, this is detected by shifts in the redox potential of the central ions. Here, we determine the stoichiometry, the stability constant and the diffusion coefficient of the complex, along with kinetic parameters for the reduction of the Gd-phen complex.

2. Experimental

Electrochemical measurements were carried out using a CHI 660 potentiostat with iR drop compensation, in a M. Braun 130 glovebox with O₂ level < 1 ppm and H₂O 3-4 ppm. A three-electrode arrangement was used. A 5mm diameter gold disk was employed as the working electrode and platinum mesh as the counter electrode. The reference electrode was a silver wire immersed in a 10 mM AgNO₃, 0.1 M tetrabutylammonium perchlorate solution, in dimethylsulfoxide, DMSO. The working electrode was polished prior to every experiment with solutions of alumina powder of 1 μ m, 0.3 μ m and 0.01 μ m followed by chemical cleaning in a 0.2 M H₂SO₄ solution purged with Argon: potential pulses of 2 seconds at 2.0 V and -2.0 V vs. Ag/AgCl/0.1 M Cl⁻ were applied during 1 minute. The electrode was rinsed with deionised water, carefully dried with N₂ and placed in the glovebox.

Dimethylsulfoxide was dried with activated molecular sieves, 4 Å (Sigma). The molecular sieves were activated in a furnace at 350°C during 1 day and added to the DMSO. The solvent was allowed to dry for one week and stored in the glovebox. Tetrabutylammonium perchlorate was purchased from Sigma and dried at 70°C under vacuum. Dried gadolinium chloride and 1,10-phenanthroline were obtained from Sigma, opened, weighed and kept in a dry atmosphere. Solutions were prepared inside the glovebox and stirred at 50°C for 45 minutes before use.

3. Results and Discussion

3.1 Cyclic voltammetry at different scan rates

Cyclic voltammograms were recorded between 0.2 and -2.0 V vs. Ag/Ag⁺ 10 mM. Fig. 1 is the voltammogram recorded at 0.05 V s⁻¹ with a solution containing phen and GdCl₃ in a 3:1 ratio (black line) together with the responses obtained for solutions containing GdCl₃ or phen, alone. GdCl₃ or phen were not electroactive in this potential window, but when the two species are present in the same solution, a reductive peak at ~ -1.7 V vs. Ag/Ag⁺ 10 mM was recorded. This is an indication that Gd³⁺ and phen together form an electroactive species. Higher negative potentials were avoided because Gd³⁺ reacts with components of the organic bath to form insulating films at the electrode surface, inhibiting further electrochemical reactions (results not shown). It has been reported that similar behaviour is found when salts containing Li⁺ are used instead of tetraalkylammonium cations [11]. It is important to remark that the voltammetric response was reproducible even after several days, indicating that the system was in equilibrium at all times. The interaction between a Gd³⁺ and an electron withdrawing ligand such as phen [12] produces a new complex with redox activity. It is well known that aromatic ligands have empty antibonding π molecular orbitals with the same symmetry as some d orbitals of metal ion. When ligand and metal interact in octahedral geometry, these molecular orbitals overlap and some of the electron density is transferred from the metal to the ligand, leading to electron deficiency on the ion, which ultimately modifies its redox potential. This is the case of Fe(phen)₃³⁺ whose standard redox potential is 1.06 V while the normal value for Fe³⁺ is 0.77 V [13]. It is evident that the ligand stabilises the ion in its 2+ state. The appearance of electroactivity when

phen is added to a solution that contains Gd^{3+} shows that the $\pi^* - d$ interaction present in octahedral complexes is somewhat similar to the one established in this complex between π^* and f orbitals.

A set of voltammograms recorded when varying the negative limit of the potential window is displayed in the inset of Fig. 1. It can be seen that the reduction process taking place at -1.7 V vs. Ag/Ag^+ 10 mM it is related to the occurrence of the anodic process registered at -0.1 V.

To characterise the electrochemical behaviour of the Gd-phen complex, the scan rate was varied in the range 0.05 to 1 $V s^{-1}$. In Fig. 2 (a) the variation of the peak current, I_p , with the square root of the scan rate, $v^{1/2}$ is depicted; in Fig. 2 (b) and 2 (c) the current function, $I_p/v^{1/2}$, vs. the log v ; and in the peak potential, E_p , are plotted vs. log v , respectively. For both processes, I_p is directly proportional to $v^{1/2}$ and E_p shifts to higher values of log v , in a linear fashion. This indicates that both electrochemical processes are irreversible kinetically controlled electron transfer reactions [14]. Equations (1) and (2) are the expressions for I_p and E_p , for a totally irreversible process [14],

$$I_p^c = 2.99 \times 10^5 \times n \times (\alpha n_a)^{1/2} \times D^{1/2} \times A \times C^\infty \times v^{1/2} \quad (1)$$

where n is the total number of electrons transferred, α is the cathodic transfer coefficient, n_a the number of electrons involved in the rate-determining step, D the diffusion coefficient, A the surface area of the electrode and C^∞ the concentration of the electroactive species in the bulk.

$$E_p = E^0 - \frac{RT}{\alpha n_a F} \left[0.78 - \ln \left(\frac{k^0}{D} \right)^{1/2} + \ln \left(\frac{\alpha n_a F}{RT} \right)^{1/2} + \frac{1}{2} \ln 10 \log v \right] \quad (2)$$

In this expression k^0 is the standard kinetic constant.

The decrease in the current function at high scan rates (see Fig. 2 (b)) is related to the occurrence of a fast, irreversible chemical step taking place after the electron transfer reaction has occurred (see section 3.4) [15]. In Fig 2 (a) and at low scan rates, the I_p values follow the trend described by equation (1). Nevertheless, at higher scan rates, there is a slight deviation which can be explained considering that in EC mechanisms, where the electron transfer reaction is slow and the chemical step irreversible, there is a decrease in the rate of the electron transfer reaction [15] which leads to a decrease in I_p .

3.2 Stoichiometry of the complex

In order to determine the stoichiometry of the complex, Yoe and Jones' method is employed [16]. Here, the molar ratio of ligand/metal is varied and the analytical signal is plotted for a wide range of molar ratio values. Initially, the signal increases linearly with the molar ratio: here the metal is in excess and the ligand added augments the complex concentration and thus the analytical signal. At large ratios, a maximum is reached and maintained: the entire metal ion is chelated and an excess of ligand does not change the analytical signal. When it is very stable, the intersection of the two straight lines gives the stoichiometry of the complex and the experimental points approach these two asymptotes. For complexes with intermediate stability, the stoichiometry is derived from the point where this plot changes its slope and the saturation plateau is reached at molar ratio values much higher than the one corresponding to the stoichiometric ratio. For weak complexes there are no straight segments in the graph and this method cannot be applied.

To employ Yoe-Jones' method, several solutions were prepared, keeping the concentration of GdCl_3 constant and varying the phen concentration. For each solution, a set of voltammograms was recorded varying the scan rate in the range between 0.05 and 0.35 V.s^{-1} and the slope of I_p^c vs. $v^{1/2}$ was calculated. The slope value derived for each solution was the analytical signal used. Fig. 3 shows the slope for molar ratios in the range of 0 to 10. The black lines are obtained by extrapolating the experimental points at low and high molar ratios. The fact that the experimental data do not follow these lines reflects that the stability constant is not very large: it takes a large excess of phen to obtain the saturated signal. The intersection of the two asymptotes (dotted lines), takes place at a ratio phen/Gd equal to 2.2, which means that there are two phen molecules directly bonded to Gd^{3+} in the complex. A recent publication reports the photoinduced DNA and protein cleavage activity of La^{3+} and Gd^{3+} complexes with two phen molecules and three nitrate ligands, in distorted bicapped dodecahedron geometry [17]. Lanthanide ions present high coordination numbers because they have more valence orbitals than transition metals. Therefore, it is believed that the Chloride ions from the gadolinium salt employed are also acting as ligands.

3.3 Determination of electrochemical parameters

In this section α , n_a , n , k^0 and I^0 for the reduction of $\text{Gd(phen)}_2\text{Cl}_3$ and D are determined. According to equation (2), a graph of E_p vs. $\log v$ is linear with a slope equal to $2.303 RT/2\alpha n_a F$. These graphs were obtained for all the solutions tested and the average value of the slope was $(0.065 \pm 0.008) \text{ V. dec}^{-1}$. The product αn_a is 0.45 ± 0.06 , which means that the number of electrons involved in the kinetic step is 1, with $\alpha = 0.45 \pm 0.06$.

Microdisk chronoamperometry is a useful technique to simultaneously determine the total number of electrons involved in an electrochemical process, n , and the diffusion coefficient, D , of the electroactive species. At very short times, the transient current depends on the square root of D , and at the steady state, it varies linearly with D . If the time scale of the experiment is long enough, these two different trends can be monitored. It is worth mentioning that since the current is always proportional to the total number of electrons involved in the electrochemical step, n will appear as a constant in both cases. Shoup and Szabo [18] derived an analytical expression for the current dependence with time:

$$I = -4nFDC^\infty r f(\tau) \quad (3)$$

with $f(\tau) = 0.7854 + 0.8862 \tau^{-1/2} + 0.2146 \exp(-0.7823 \tau^{-1/2})$ and $\tau = \frac{4Dt}{r^2}$, where

both dependences are included in separate terms. In this equation, r is the radius of the disk employed as the working electrode. To determine n and D , the potential was held for 10 seconds at -1.2 V vs Ag/Ag⁺ 10mM and stepped to -1.8 V during 8 seconds. A solution 5.47 mM GdCl₃ was prepared and phen added in a 10:1 ratio. Here it is assumed that all the Gd³⁺ is bonded to phen. Such approximation is considered accurate provided that the analytical signal does not change at molar ratios higher than 8 (See Fig. 3). The chronoamperometric signal was fitted following the work by Paddon *et. al.* [19]. Fig. 4 shows the experimental values and the fitting obtained. The total number of electrons was found to be 2.0 ± 0.17 and the diffusion coefficient $(3.3 \pm 0.2) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The diffusion coefficient values reported in the literature for similar organometallic complexes, like Ru(phen)₃²⁺ or Fe(phen)₃²⁺, in DMSO or acetonitrile are all around $2 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [20,21], close to the one determined here for Gd(phen)₂Cl₃. Its slightly larger value could be understood considering that Gd(phen)₂Cl₃ is smaller than

Ru(phen)_3^{2+} or Fe(phen)_3^{2+} . For ferrocene, a smaller molecule than $\text{Gd(phen)}_2\text{Cl}_3$, the reported diffusion coefficient in DMSO is $4.4 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [22].

Amatore *et al.* developed an alternative method to determine the absolute number of electrons involved in an electrochemical process [23]. It is based on a comparison with an internal standard, such as ferrocene. Two electrochemical techniques are employed: the first one is cyclic voltammetry run at low scan rates with an ultramicro disk electrode, $r \sim 2 \text{ }\mu\text{m}$; the second one, involves a different diffusion mode such as single potential step chronoamperometry at a micro disk electrode, $\sim 0.2 - 0.5 \text{ cm}$. From a comparison of the two corresponding expressions for the current and knowing that the oxidation of ferrocene is a one-electron process, the absolute number of electrons can be derived. This method can be applied to reversible electrochemical reactions, most often used in those cases where the redox reactions take place in multimetallic complexes where several cations may be connected through resonance [24,25].

To calculate the standard kinetic constant equations (1) and (2) are combined to obtain:

$$I_p = 0.227nFAC^\infty k^0 \exp[(-\alpha n_a F / RT)(E_p - E^0)] \quad (4)$$

The slope of $\ln I_p$ vs. $(E_p - E^0)$ is $\alpha n_a F / RT$ and the intercept is $\ln(0.227nFAC^\infty k^0)$.

However, since E^0 is not known, the potential where the reaction starts, E_i , was used instead, as recommended by Nicholson and Shain [26]. This analysis was carried out for all the solutions employed in the determination of the stoichiometry of the complex, (section 3.2). In each case, C^∞ was calculated using equation (1), taking $n = 2$, $n_a = 1$, $\alpha = 0.45$, $D = 3.3 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and $A = 0.196 \text{ cm}^2$. Typical graphs like the one shown in

Fig. 5 were obtained. The average value for k^0 is $(2 \pm 1) 10^{-5} \text{ cm s}^{-1}$. From the slopes of these graphs the average value of α is 0.37 ± 0.04 . The reported standard rate constant for the oxidation of Ru(phen)_3^{2+} , which depends on the nature of the solvent used, ranges from 1.7 cm s^{-1} for acetonitrile to 0.16 cm s^{-1} for nitrobenzene [20]. In comparison to Ru(phen)_3^{2+} , the k^0 value obtained for the reduction of $\text{Gd(phen)}_2\text{Cl}_3$ is rather small.

For irreversible reactions and at low over-potentials, the current depends exponentially on the potential. For a system where there is only reduction, the equation is:

$$I = i^0 \exp[-\alpha n_a F / RT (E - E^0)] \quad (5)$$

where the exchange current $i^0 = j^0 A$ is related to the standard rate constant [14]. To obtain Tafel plots, $\ln I$ is plotted against $(E - E^0)$. In the potential range where the current has an exponential dependence, a straight line is obtained, with slope equal to $\alpha n_a F / RT$ and intercept equal to $\ln i^0$. Fig. 6 presents a cyclic voltammogram scanned at 5 mV s^{-1} plotted against $(E - E_i)$. Here again, E^0 was assumed to be equal to E_i [26]. In Fig. 6, the presence of two peaks can be noted. Previously, it was concluded that the reduction of Gd(phen)_2 is a two-electron transfer reaction, where the first electron transfer is the rate determining step. For an irreversible electrochemical reaction, the E_p shifts with ν and it is expected that at low ν the peak appears at lower potential values. These scans, at very low ν , seem to show that these two electrochemical steps do not take place at the same E^0 . In the inset of Fig. 6 is a linearised Tafel plot. The linear regression was taken in the range from -0.105 to -0.140 V, giving a value of 0.426 ± 0.003 for α and $(4.40 \pm 0.06) 10^{-7} \text{ A}$ for i^0 (or $(2.24 \pm 0.03) 10^{-6} \text{ A cm}^{-2}$, for j_0).

3.4 Simulations and mechanism analysis

To corroborate the accuracy of the parameters obtained in previous sections and the assumption that $E^0 = E_i$, a set of simulations were carried out, employing the Windows-based software supplied with the 660 CHI potentiostat. Fig. 7 shows in open symbols the experimental voltammogram to be simulated.

Two electrochemical steps were used for the simulations:

For the first electrochemical step, the kinetic parameters derived in section 3.3 were used: α_f was averaged to 0.41, k_1^0 was taken as $2 \cdot 10^{-5} \text{ cm s}^{-1}$ and E^0 equal to -1.425 V for both reactions ($E_1^0 = E_2^0$). Voltammograms like the one in the solid black line were obtained in these simulations for different α_2 values chosen. The experimental and the simulated curve have the same E_p but different I_p values. Besides, at low overpotentials, the current of the simulated curve is larger than the experimental one. Given that at very low scan rates two different cathodic peaks are recorded (see Fig. 6), a more negative standard reduction potential value was chosen for the second electron transfer reaction. E_2^0 was calculated considering that the second process is reversible or at least faster than the first one. Therefore, E_2^0 should be anodically shifted by $\sim 30 \text{ mV}$ from E_p^2 , i.e. around -1.78 V. The simulation obtained taking $E_1^0 \neq E_2^0$ is included in the figure (dashed line). This curve fits the cathodic peak perfectly. Nevertheless, unlike the simulations, the experimental voltammograms do not have anodic peaks in the range -1.7 to -1.0 V. This difference is a strong indication that after the reduction process takes

place, a fast chemical reaction occurs, which product oxidises at ~ -0.1 V (see inset Fig. 1). The red curve is the simulation obtained including this chemical step with a forward kinetic constant, $k_f = 2000 \text{ s}^{-1}$ and a backwards constant, $k_b = 0$.

According to equation (4), an anodic shift in E_1^0 of 100 mV would cause a ten fold decrease in the k^0 value derived from the linear regression of $\ln I_p$ vs. $(E_p - E^0)$ (see Section 3.3, Fig. 5). With the aim of evaluating the assumption made in the estimation of E^0 , a series of simulations were carried out, varying E^0 and k^0 in this fashion. The rest of the parameters were kept constant, i.e. $\alpha_i = 0.41$, $E_2^0 = -1.78$ V, $k_f = 2000 \text{ s}^{-1}$ and $k_b = 0$. It is evident that the potential where the reaction starts is the same for the three simulations shown in Fig. 7 (b). The differences among these simulations to note are:

- a shift in E_p towards more negative values,
- a decrease in I_p and
- a less steep increase in the current at low over-potentials.

It can be concluded that it is correct to take $E^0 = E_i$ to determine k^0 because it depends on the shift of E_p relative to E^0 (or E_i) and I_p . Nevertheless, a more careful study would have to be done in order to find E^0 .

3.5 Stability constant

Providing the stoichiometry found for the Gd-phen complex is 2:1 (section 3.2), the reaction for the formation of $\text{Gd(phen)}_2\text{Cl}_3$ can be written as:

Reaction (6) is the result of two consecutive steps:

where each phen molecule is added consecutively.

The expression for the stability constant of the complex is:

$$K = \frac{[Gd(phen)_2Cl_3]}{[GdCl_3][phen]^2} \quad (7)$$

where $[Gd(phen)_2Cl_3]$, $[GdCl_3]$ and $[phen]$ are the concentrations of the species at the equilibrium. Even though the complex formation is a stepwise process, the electrochemical measurements were carried out under equilibrium conditions, where the analytical signal is proportional to $[Gd(phen)_2Cl_3]$. Provided that n , α , n_a , D and A are known, the concentration of the complex at the equilibrium can be calculated. $[GdCl_3]$ and $[phen]$ are derived taking into account that

$$[GdCl_3] = [GdCl_3]_i - [Gd(phen)_2Cl_3] \quad (8)$$

$$[phen] = [phen]_i - 2[Gd(phen)_2Cl_3] \quad (9)$$

where $[GdCl_3]_i$ and $[phen]_i$ are the concentrations of $GdCl_3$ and phen initially present in the solution. The experimental points that deviate from the theoretical lines in Fig. 3 are considered. $[GdCl_3]$ and $[phen]$ could not be measured independently because at more cathodic potentials, where phen is electroactive, Gd^{3+} forms insulating precipitates that block the electrode surface. Table 1 lists the slope values obtained at each molar ratio phen/Gd together with $[Gd(phen)_2Cl_3]$, $[GdCl_3]$ and $[phen]$ and the calculated stability constants, whose average is $K = (2.3 \pm 0.8) 10^5 M^{-2}$.

Table 2 summarises the logarithm of some K values for complexes formed with two phen molecules and M^{3+} ions. For those ions where the valence orbitals are d and p type, K is much larger than for those with f atomic orbitals. This could be understood in terms of symmetry: it seems that the interaction between orbitals from the ligand and d orbitals are much more effective than those established with f orbitals in a lanthanide

ion. In addition, the K value derived here is in good agreement with the one reported for $\text{Ce}(\text{phen})_2$, which has been obtained by calorimetric titration in DMF containing 0.2 M $\text{N}(\text{C}_2\text{H}_5)_4\text{ClO}_4$ as an ionic medium at 25 °C [27].

4. Conclusions

The formation of a complex between Gd^{3+} and 1,10-phenanthroline decreases the redox potential of Gd^{3+} . The reduction process recorded at ~ -1.7 V vs. Ag/Ag^+ 10mM corresponds to an irreversible electron transfer reaction consisting of two steps: the first electron transfer reaction is slow and the second one, fast. The species formed after the second electron has been transferred, undergoes a fast irreversible chemical reaction, whose product oxidises at -0.1V vs. Ag/Ag^+ 10 mM in the reverse scan.

Kinetic and electrochemical parameters for the reduction process were obtained. An average cathodic transfer coefficient value of 0.45 ± 0.06 was calculated from the slope values of the graphs of E_p vs. $\log v$. This coefficient was also derived from the linear fitting of $\ln I_p$ vs $E_p - E^0$ giving an average value of 0.37 ± 0.04 ; from the Tafel plots, α was found to be 0.426 ± 0.003 . For the analysis and given that E^0 is not known, it was assumed to be equal to -1.425 V vs. Ag/Ag^+ 10mM, the potential value where the reaction starts [26]. The average value obtained for k^0 was $(2 \pm 1) 10^{-5} \text{ cm s}^{-1}$. The exchange current density derived from tafel plots was $(2.24 \pm 0.03) 10^{-6} \text{ A cm}^{-2}$. All these conclusions were supported by voltammetric simulations.

To calculate D , the analytical expression derived by Shoup and Zsabo [18] was employed, together with the method suggested by Compton *et. al* [19]. The derived value was $(3.3 \pm 0.2) 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The stoichiometry of the complex was determined by Yoe and Jones' method, whereby the analytical signal is plotted against the molar ratio of ligand/metal. There are two phen molecules directly bonded to Gd^{3+} . The stability constant value derived was $(2.3 \pm 0.8) 10^5 \text{ M}^{-2}$. The stoichiometry and the K value calculated in this work are in very good agreement to the ones obtained by other methods for a similar complex, $\text{Ce}(\text{phen})_2$.

In the absence of phen, Gd^{3+} shows electroactivity at very negative potentials. The voltammograms show a first cycle with a broad cathodic peak, followed by scans reflecting the electrode passivation. Similar responses were obtained with different bath composition: varying the supporting electrolyte, the counter ion in the gadolinium salts, using organic solvents or ionic liquids. We believe that given its polarizing character, Gd^{3+} reacts with organic species upon an electron transfer step, to give insulating films containing Gd species. For this reason, it seems unlikely to carry out the electrodeposition of 4f metals in organic baths. Although the interaction with 1,10-phenanthroline decrease the potential required for the reduction of Gd^{3+} , the species formed is not further reduced to metallic Gadolinium.

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References

- [1] R. Mishra, E. J. Podlaha, *Electrochem. Sol. State Lett.*, 9 (2006) C199–C202.
- [2] C. Nourry, L. Massot, P. Chamelot, P. Taxil, *Electrochim. Acta*, 53 (2008) 2650–2655.

- [3] M.R. Bermejo, J. Gómez, J. Medina, A.M. Martínez, Y. Castrillejo, J. Electroanal. Chem., 588 (2006) 253–266.
- [4] J.M.D. Coey, Rare earth iron permanent magnets, Oxford University Press Inc., New York, 1996.
- [5] P. Ruuskanen, J. Magn. Mag. Mater., 265, (2003) 257-268.
- [6] M-K. Han, G.J. Miller, Inorg. Chem., 47 (2008) 515-528.
- [7] J.L. Sessler, N.A. Tvermoes, D.M. Guldi, T.D. Mody, W.E. Allen, J. Phys. Chem. A, 103 (1999) 787-794.
- [8] J. J. Roger, C. W. Liu, T.C.W. Mak, T.W.D. Chan, D.K.P. Ng, Polyhedron, 16 (1997) 515-520.
- [9] D. Khuntia, M. Mehta, Expert Re.v Anticancer Ther., 4 (2004) 981–989.
- [10] D. Magda, R.A. Miller, Sem. Cancer Biol., 16 (2006) 466-476.
- [11] D. Aurbach, Y. Gofer, Non aqueous electrochemistry, Marcel Dekker, Inc., New York, 1999, Chapter 4.
- [12] A.J. Blake, V. Lippolis, T. Pivettac, G. Verani, Acta Cryst., (2007) C63, m364-m367.
- [13] S. Kotrly, L. Sucha, Handbook of Chemical Equilibria in Analytical Chemistry, John Wiley & Sons, New York, 1985.
- [14] C.M.A. Brett, A.M. Oliveira Brett, Electrochemistry. Principles, Methods and Applications, Oxford University Press, 2000.
- [15] Bard, A. J.; Faulkner, L. R. Electrochemical Methods, Wiley, New York, 1980
- [16] J.M. Bosque-Sendra, E. Almansa-Lopez, A.M. Garcia-Campana, L. Cuadros-Rodriguez, Anal. Sci., 19 (2003) 1431-1439.
- [17] A. Hussain, D. Lahiri, M. S. A. Begum, S. Saha, R. Majumdar, R. R. Dighe, A. R. Chakravarty, Inorg. Chem, (2010) *in press*.

- [18] D. Shoup, A. Szabo, J. Electroanal. Chem., 140 (1982) 237-245.
- [19] C.A. Paddon, F.L. Bhatti, T.J. Donohoe, R.G. Compton, J. Electroanal. Chem., 589 (2006) 187-194.
- [20] K. Winkler, N. McKnight, W.R. Fawcett, J. Phys. Chem B, 104 (2000) 3575-3580
- [21] M. Morita, Y. Tanaka, K. Taraka, Y. Matsuda, T. Matsumura-Inove, Bull. Chem. Jpn, 61 (1988) 2711-2714.
- [22] N. G. Tsierkezos, J Solution Chem, 36 (2007) 289–302.
- [23] C. Amatore, M. Azzabi, P. Calas, A. Jutand, C. Lefrou, Y. Rollin, J. Electroanal. Chem., 288 (1990) 45-63.
- [24] D. M. D'Alessandro, F. R. Keene, Chem. Rev., 106 (2006) 2270-2298.
- [25] S. Santi, F. Benetollo, A. Ceccon, L. Crociani, A. Gambaro, P. Ganis, M. Tiso, A. Venzo, Angew. Chem. Int. Ed., 47 (2008) 5331–5334.
- [26] R.S. Nicholson, I. Shain, Anal. Chem. 36 (1964) 706-723.
- [27] M. Komiya, Y. Nishikido, Y. Umebayashi, S. Ishiguro, J. Sol. Chem. 31 (2002) 931-946.

Figure Captions

Fig. 1. Cyclic voltammograms of — 5.47 mM GdCl₃ + 16.41 mM phen solution and --- 5.47 mM GdCl₃ or 16.41 mM phen in 0.1 M TBAClO₄ in DMSO, at 0.05 V s⁻¹. Inset: Cyclic voltammograms recorded varying the negative limit of the potential window: (1) -1.70 V, (2) -1.80 V, (3) -1.90 V and (4) -2.00 V vs. Ag/Ag⁺ 10 mM. Solution composition: 10 mM GdCl₃ + 33 mM phen, 0.1 M TBAClO₄ in DMSO, at 0.1 V s⁻¹. Working electrode: 5mm diameter gold disk.

Fig. 2 (a). Variation of peak current, I_p , with the scan rate, ν ; **(b)** Current function, $I_p/\nu^{1/2}$ as a function of $\log \nu$; **(c)** peak potential, E_p , vs. $\log \nu$. Solution composition: 5.47 mM GdCl_3 + 20.62 mM phen, 0.1 M TBAClO_4 in DMSO.

Fig. 3. Yoe-Jones plot for the stoichiometry determination of the complex Gd-phen. — Theoretical lines; --- is a sinusoidal fitting of the experimental points. Asymptotes obtained by fitting experimental points.

Fig. 4. Chronoamperometric graphs: $\circ$ experimental values and — fitted curve. The potential was held during 10 seconds at -1.2 V vs Ag/Ag^+ 10 mM and stepped to -1.8 V during 8 seconds. Solution composition: 5.47 mM GdCl_3 + 54.70 mM phen, 0.1 M TBAClO_4 in DMSO. n was found to be 2 and D $(3.3 \pm 0.2) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Fig. 5. Plot of $\ln I_p$ vs $E_p - E_i$. I_p and E_p values obtained from voltammograms recorded in the range 0.05 to 0.35 V s^{-1} . In this figure, the experimental points were taken with a solution 5.47 mM GdCl_3 + 10.94 mM phen, 0.1 M TBAClO_4 in DMSO. The slope value from the fitting is $-14.96 \pm 0.24 = \alpha n_a F/RT$ and the intercept $-13.99 \pm 0.48 = \ln(0.227 n F A C^\infty k^0)$, regression coefficient = -0.9933. The potential where the reaction starts, E_i , was used instead of E^0 [26], $E_i = -1.425 \text{ V}$. The average value for k^0 is $(2 \pm 1) \times 10^{-5} \text{ cm s}^{-1}$.

Fig. 6. Cathodic sweep recorded at 5 mV.s^{-1} , for a 5.47 mM GdCl_3 + 13.67 mM phen, 0.1 M TBAClO_4 in DMSO solution. Inset: $\circ$ Tafel plot. The potential where the reaction starts, E_i , was used instead of E^0 [26], $E_i = -1.425 \text{ V}$. — Linear regression of the experimental points in the range where the current has an exponential dependence

with the potential. The cathodic transfer coefficient obtained is $\alpha = 0.426 \pm 0.003$ and the exchange current $I_0 = (4.40 \pm 0.06) 10^{-7}$ A or the exchange current density $j_0 = (2.24 \pm 0.03) 10^{-6}$ A cm⁻².

Fig. 7 (a). ○ Experimental voltammogram recorded at 50 mV.s⁻¹ with a solution 3.88 mM Gd(phen)₂Cl₃, 0.1 M TBAClO₄ in DMSO. Voltammetric simulations: two successive electrochemical steps — with the same standard redox potential $E_1^0 = E_2^0 = -1.425$ V or different --- $E_1^0 = -1.425$ V ; $E_2^0 = -1.78$ V . Successive electrochemical steps followed by a chemical reaction: — E_1^0 and E_2^0 as in --- with a $k_f = 2000$ s⁻¹, $k_b = 0$. In all cases $\alpha_l = 0.41$, $k_1^0 = 2 \cdot 10^{-5}$ cm² s⁻¹ and $D = 3.3 \cdot 10^{-6}$ cm² s⁻¹ was employed.

(b) ○ and — as in **(a)**. Voltammetric simulations: **(1)** $E_1^0 = -1.325$ V ; $k^0 = 2 \cdot 10^{-6}$ cm² s⁻¹; **(2)** $E_1^0 = -1.225$ V ; $k^0 = 2 \cdot 10^{-7}$ cm² s⁻¹; **(3)** $E_1^0 = -1.125$ V ; $k^0 = 2 \cdot 10^{-8}$ cm² s⁻¹. $\alpha_l = 0.41$, and $D = 3.3 \cdot 10^{-6}$ cm² s⁻¹.

Table 1. Slope values obtained at each molar ratio phen/Gd together with $[Gd(phen)_2Cl_3]$, $[GdCl_3]$ and $[phen]$ and the stability constant values calculated. $n = 2$, $\alpha = 0.45$, $n_a = 1$, $D = 3.3 \cdot 10^{-6}$ cm² .s⁻¹ and $A = 0.196$ cm² were used to derive $[Gd(phen)_2Cl_3]$ from each slope value. An average of $K = (2.3 \pm 0.8) 10^5$ M⁻² was calculated.

Table 2. log K values for complexes formed with two phen molecules and M³⁺ ions.

^a reference [13]. ^b reference [29]. ^c this work.

Fig1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Molar ratio phen/Gd	Slope / $A V^{-1/2} s^{1/2}$	$[Gd(phen)_2Cl_3]$ / [M]	$[GdCl_3]$ / [M]	[phen] / [M]	K / $[M^{-2}]$
1.5	$4.28 \cdot 10^{-4}$	$3.13 \cdot 10^{-3}$	$2.34 \cdot 10^{-3}$	$1.94 \cdot 10^{-3}$	$3.54 \cdot 10^5$
2.0	$5.43 \cdot 10^{-4}$	$3.98 \cdot 10^{-3}$	$1.49 \cdot 10^{-3}$	$2.99 \cdot 10^{-3}$	$2.98 \cdot 10^5$
2.5	$6.24 \cdot 10^{-4}$	$4.57 \cdot 10^{-3}$	$9.03 \cdot 10^{-4}$	$4.54 \cdot 10^{-3}$	$2.45 \cdot 10^5$
3.0	$6.66 \cdot 10^{-4}$	$4.88 \cdot 10^{-3}$	$5.93 \cdot 10^{-4}$	$6.65 \cdot 10^{-3}$	$1.85 \cdot 10^5$
3.5	$6.96 \cdot 10^{-4}$	$5.09 \cdot 10^{-3}$	$3.76 \cdot 10^{-4}$	$8.95 \cdot 10^{-3}$	$1.69 \cdot 10^5$
5.0	$7.30 \cdot 10^{-4}$	$5.34 \cdot 10^{-3}$	$1.24 \cdot 10^{-4}$	$1.66 \cdot 10^{-2}$	$1.55 \cdot 10^5$

Table 1

$M(phen)_2$	$\log K$
Fe^{3+}	11.40 ^a
Ga^{3+}	9.21 ^a
In^{3+}	10.04 ^a
Tl^{3+}	18.30 ^a
Ce^{3+}	4.38 ^b
Gd^{3+}	5.36 ^c

Table 2