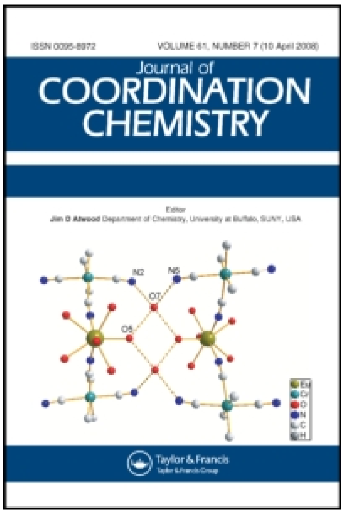

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Synthesis and Characteristics of a Europium(III) Complex of N, N, N',' N'''-Tetrakis(2-Quinolinemethyl-1-Oxide)-1,4,8,H-Tetraazacyclotetradecane

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SYNTHESIS AND CHARACTERISTICS OF A EUROPIUM(III) COMPLEX OF *N*, *N*′, *N*′,′*N*″-TETRAKIS(2-QUINOLINEMETHYL-1-OXIDE)-1,4,8,11-TETRAAZACYCLOTETRADECANE[‡]

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Reaction of 1,4,8,11-tetraazacyclotetradecane (cyclam) with 2-chloromethylquinoline-1-oxide leads to the formation of the tetrasubstituted title compound which forms a stable 1:1 complex with europium perchlorate. Cyclic voltammetric studies of the complex in MeCN solution revealed reversibility of the Eu(III)/Eu(II) couple. The formal potential, E_f, of Eu(III)/Eu(II) in the complex was found to be -0.510 V. The difference between log K_{EuIII} and log K_{EuII} is 4.83, showing much higher stability for EuIII complex, at 25°C. Photochemcial studies of the uncomplexed ligand revealed an absence of fluorescence of the ligand itself upon excitation at 333 nm, and a phosphorent 0–0 transition was observed at 77 K at 433 nm, indicating that the energy level of the triplet state T_1 lies above the resonance level ^5D of the Eu(III) cation. The complex appeared to be non-luminescent when irradiated at 328 and 360 nm.

Keywords: Europium(III), cyclam, electrochemistry, photochemistry

INTRODUCTION

Much attention has been devoted in the past few years to metal ion chelates as potential probes in biology, medicine and biochemistry. In particular, lanthanide complexes have many interesting applications as contrast agents in NMR imaging,[1] fluorimetric immunoassays,[2] and photochemical processes.[3]

Recent achievements in biotechnology allow for development of particularly sensitive fluorimetric immunoassays based on lanthanide-labelled monoclonal antibodies, and this subject has been reviewed recently.[4] Fluorescent lanthanide labels must possess a few essential features to be useful in the fluoroimmunoassays, such as high thermodynamic and kinetic stability in aqueous solutions, efficient energy

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transfer from the aromatic excited triplet state to the resonance level of the lanthanide ion, minimal fluorescence of the free ligand and a long emission lifetime of the lanthanide ion.

Usually, non-cyclic lanthanide chelates are not stable enough in aqueous solution. Furthermore, water was found to be a good quencher for lanthanide ion emission in these systems.

In an effort to avoid problems with water and enhance stability of lanthanide complexes, numerous heteroaromatic cryptands[6] have been elaborated, in which the lanthanide cation is held strongly in the molecular cavity, surrounded by a hydrophobic macrobicyclic framework and protected in this way from interaction with water molecules. Indeed, good stability and emission of Eu(III) and Tb(III) ions was observed when appropriate cryptates incorporating three 2,2'-bipyridine units were irradiated in water solution.[7]

An alternative to this approach would be to use a macrocyclic polyamine bearing photoactive and ligating groups on the nitrogen atoms. It has already been demonstrated that macrocyclic polyamines possessing pendant ligating groups form very stable and kinetically inert complexes with lanthanide ions.[8] There are also numerous reports on strongly fluorescent and stable lanthanide complexes with heterocyclic *N*-oxides,[9] and therefore it is conceivable to link heterocyclic *N*-oxide functionalities with macrocyclic polyamines to obtain simple ligands capable of forming very stable and fluorescent complexes with Eu(III). This would represent an alternative to more elaborated cryptands comprising *bis*-heteroaromatic systems.[6]

We have used a cyclam as a model macrocyclic tetraamine and quinolinemethyl-1-oxides as ligating groups attached to nitrogen atoms, since it has been shown that quinoline-1-oxide ligands form fluorescent complexes with europium(III).[9b] The ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) was condensed with 2-chloromethylquinoline-1-oxide to form the title compound, as shown in Figure 1.

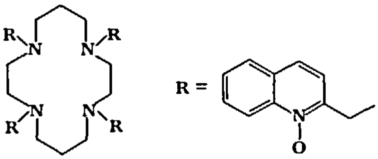

FIGURE 1 Schematic representation of the title ligand.

EXPERIMENTAL

General

All reagents were of analytical grade. Solvents for photochemical studies were of spectroscopic grade (Merck). MeCN and DMF were distilled over CaH_2 prior to use. 2-Chloromethylquinoline (Fluka) was oxidized with *m*-chloroperbenzoic acid in $CHCl_3$ to its *N*-oxide and crystallized from hexane. ^1H NMR spectra were recorded on a Bruker SY-200 instrument with TMS as standard. Fluorescence and phosphorescence measurements were performed on a spectrofluorimeter constructed by Jasny.[10]

Synthesis

N, N', N'',N'''-tetrakis(2-quinolylmethyl-1-oxide)-1,4,8,11-tetraazacyclotetradecane

To the suspension of cyclam (200 mg, 1 mmol) in DMF (20 cm^3), powdered and dried K_2CO_3 (2.0 g) was added and 2-chloromethylquinoline-1-oxide (851.4 mg, 4.4 mmol) was introduced gradually with stirring at 60°C during 1 h. After 12 h the mixture was concentrated *in vacuo* to volume of *ca.* 10 cm^3, filtered, and the filter cake was washed with ethanol. The white precipitate was suspended in water to dissolve K_2CO_3, the product filtered off, washed with water and dried in vacuum over P_2O_5. Yield 654 mg (79%). Anal.; Calcd. for $C_{50}H_{52}N_8O_4$: C, 72.44; N, 13.51; H, 6.32%. Found: C, 72.5; N, 13.46; H, 6.28%. FAB(+) MS: 829 (M + 1). ^1H NMR ($CDCl_3$) δ: 1.75 (m, 4H, 2 × $C{-}CH_2{-}C$), 2.84 (s, 8H, 2 × NCH_2CH_2N), 2.92 (t, 8H, 2 × $NCH_2CH_2CH_2N$), 4.06 (s, 8H, 4 × CH_2quin.), 7.48 (m, 20H, Ar), 8.63 (d, 4H, Ar). UV ($CHCl_3$) λ(ε): 340 (25000), 328 (28200). M. p.: 172°C, decomp.

Preparation of the Eu III complex with the ligand

Equimolar amounts of europium perchlorate hexahydrate (139.6 mg, 0.25 mmol) and the ligand (207 mg, 0.25 mmol) were mixed in MeCN (15 cm^3) with ethyl orthoformate (1 cm^3) and heated at reflux for 3 hrs. The clear solution was concentrated to 5 cm^3 and left for crystallization. Pale yellow crystals deposited on standing overnight. These were collected by filtration, washed with MeCN and dried. Yield 230 mg (72%). Anal.; Calcd. for $C_{50}H_{52}Cl_3N_8O_{16}Eu$: C, 46.94; N, 8.76; H, 4.09%. Found: C, 46.72; N, 8.68; H, 3.95. FAB(+) MS: 1179 (M-ClO_4). UV (MeCN): λ(ε): 318 (25200), 334 (21800). M.p.: 250°C, decomp.

Photochemistry

The uncomplexed ligand and its complex were found to be non-fluorescent in *i*-PrOH or MeCN solution when excited at 328 or 360 nm. The phosphorescence of the free ligand was observed in *n*-PrOH at 77 K (0–0 line at 433 nm) after excitation at 333 nm.

Electrochemistry

Electroreduction of the Eu(III) complex was studied at 25°C by voltametry at mercury and glassy carbon electrodes in a 1 M solution of tetraethylammonium perchlorate in MeCN. The cyclic voltametry curves were recorded using a three electrode arrangement with a saturated calomel reference electrode and platinum foil counter electrode, both separated from the cell solution by a glass frit. Cyclic voltametry was performed on either a Laboratorni Pristroje polarographic analyser with a 4105 X–Y Recorder, or with a BAS-100 electrochemical analyser (Bioanalytical Systems Inc.) with a KX-P1091 printer (Panasonic) and a HIPLOT DMP-40 Plotter (Houston Instruments). Tetraethylammonium perchlorate (TEAP) was crystallized twice from methanol and dried for 48 hrs at 60°C *in vacuo*. Stock solutions of Eu(III) were prepared from Eu_2O_3 and HNO_3.

RESULTS AND DISCUSSION

The title ligand is very easily accessible by a simple route and is insoluble in water, DMF, MeCN, alcohols and hydrocarbons. Good solubility was noted in halogenated hydrocarbons. The ligand forms a 1:1 complex with the Eu(III) cation, which is insoluble in halogenated hydrocarbons and aromatics. DMF, MeCN or alcohols were found to be good solvents.

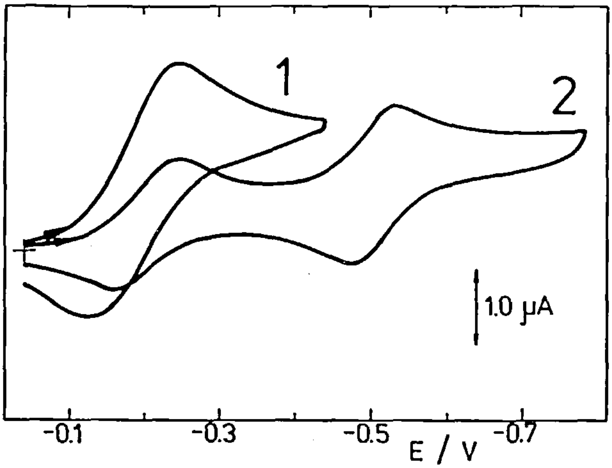

FIGURE 2 Effect of ligand addition on cyclic voltamogram of 3×10^{-4} mol dm^{-3} Eu(III) in 1 mol dm^{-3} TEAP in MeCN. C_{ligand}: (1) 0; (2) 1.5×10^{-4} mol dm^{-3}; S_{GCE}: 0.07 cm^2; scan rate: 20 mVs^{-1}.

The cyclic voltamogram for Eu(III) in 1 M TEAP/acetonitrile solution recorded on a glassy carbon electrode is shown in Figure 2 (curve 1) and appears at −0.255 V. The peak may be attributed to $Eu(MeCN)_x^{3+}$ reduction to $Eu(MeCN)_x^{2+}$. Upon addition of ligand, the peak potential remains unchanged but its height decreases and a second peak appears at −0.541 V, together with an anodic counterpart at −0.483 V. These peaks can be assigned to the reduction of the Eu(III) to the Eu(II) complex and reoxidation of product. On the basis of changes in the heights of $Eu(MeCN)_x^{3+}$ and Eu(III) complex reduction peaks on addition of ligand, the stoichiometry of complex is 1:1. The cyclic voltamograms in solution prepared from crystallized $Eu(ClO_4)_3$ complex are shown in Figure 3. The peak potentials remain constant over a voltage scan range of 20–500 mVs^{-1}, thus confirming reversibility. The anodic and cathodic peak separation, E_{pA}–E_{pC}, is close to 58 mV and the difference, E_{pC}–$E_{pC/2}$, is close to that predicted for a reversible 1e reduction process.

The formal potential, E_f, for the $Eu(Ligand)^{3+}/Eu(Ligand)^{2+}$ couple obtained from the mean cathodic and anodic peak potentials is equal to −0.510 V, which is markedly more negative than that of the $Eu(MeCN)_x^{3+}/Eu(MeCN)_x^{2+}$ couple. On the basis of the equation[11] $\Delta E_f = (2.303\,RT/F)\log(K_{II}/K_{III})$, where K_{II} and K_{III} are stability constants for divalent and trivalent species, the difference between log K_{III} and log K_{II} is 4.83 at 25°C, showing the higher stability of the Eu(III) complex. The peak potentials remain unchanged by substitution of Et_4NBr, $MeNClO_4$, or $NaClO_4$ for Et_4NClO_4 as the supporting electrolyte salt. However, the position of the reduction peak is shifted towards negative potentials upon addition of Et_4NCl, thus revealing interactions of the complex with halogen anions. Absolute values for the stability constants K_{III} and K_{II} could not be evaluated owing to the insolubility of the free ligand in acetonitrile.

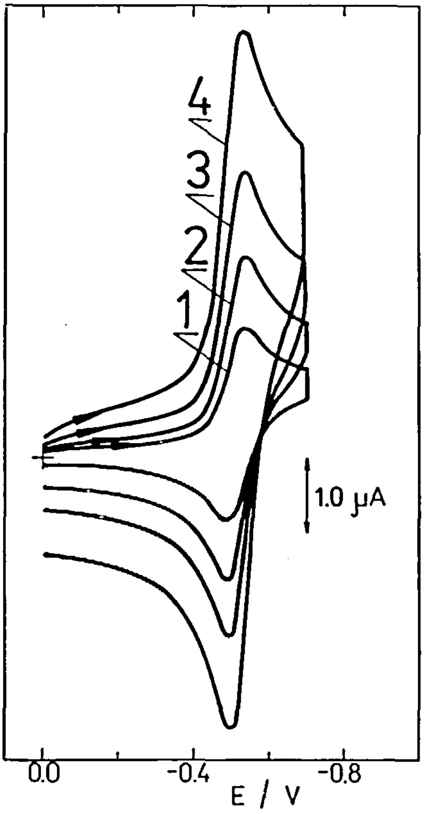

FIGURE 3 Influence of scan rate on cyclic voltamograms of 1.6×10^{-4} mol dm^{-3} Eu(III) complex in 1 mol dm^{-3} TEAP in MeCN; v: (1) 20; (2) 50; (3) 100; (4) 200 mVs^{-1}.

Fluorescence measurements indicated that the ligand and its Eu(III) complex are not fluorescent upon UV irradiation at 328 and 360 nm. Surprisingly, the quinoline-1-oxide unit appeared to be inefficient as a sensitizer for the Eu(III) cation, although there has been a report of a highly fluorescent Eu(III) complex with 2,2′-biquinoline-1,1′-dioxide.[9b]

Complementary phosphorescence measurements in *n*-PrOH at 77 K revealed the 0–0 line at 433 nm upon excitation at 333 nm. Therefore the energy of the triplet state T_1 of the quinoline-1-oxide unit is higher than the resonance level $^5D_0$ of the Eu (III) cation, but there is no energy transfer from T_1 to $^5D_0$. Probably, the ligand losses its energy in a way other than by an absorption-energy transfer-emission process, and a further search for a rational explanation of the observations is required.

Future design and synthesis of photoactive ligands will involve isoquinoline-*N*-oxide functions, since it has been shown that 1,1′-dimethyl-3,3′-biisoquinoline-*N,N*′-dioxide forms a particularly strongly fluorescent complex with Eu(III).[12] Work in this area is being pursued.

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