have potential applications as a pigment dispersant,[10, 22, 23] or in the separation and purification of proteins.[7, 24]

Received: November 26, 2001 [Z 18276]

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[16] At intermediate pH values either side of the IEP, the electrostatic interaction of the oppositely charged blocks can lead to the formation of aggregates (soluble polyelectrolyte complexes), which are stabilized by uncompensated cationic charge on the DEA block (below the IEP) or anionic charge on the VBA block (above the IEP). In contrast, at pH 2 (or pH 10) the VBA block (or DEA block) is uncharged; thus hydrophobic interactions of this neutral block should produce compact, well-defined micelles.

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A Selective Chromogenic Reagent for Nitrate**

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The selective sensing of anions by natural and synthetic receptors is an important area of supramolecular chemistry.[1] Anions play significant roles in biological and environmental processes, therefore the development of new chemosensors for anions is an important topic. Anion-sensing receptors incorporate into their structures groups that are capable of interaction with anions, and sensing subunits in which spectroscopic[2] or electrochemical[3] features change upon anion binding. Chemosensors with changes in their spectroscopic behavior have either fluorogenic[4] or chromogenic[5] signalling subunits. Chromogenic reagents are especially attractive because the anion determination can be carried out by the naked eye, without the use of expensive equipment. Chromogenic reagents for the selective detection of inorganic and organic anions have been reported.[6] However, it is still a challenge to find chromogenic receptors for the selective sensing of poorly coordinating anions such as nitrate. As far as we know, the only example of nitrate sensing by color change, by use of receptors coupled to dyes, was reported recently, and it involved a competitive assay between nitrate and methyl red or resorufin in binding a polyamide cage, in dichloromethane:methanol 50:50 v/v. The system, however, is not specific and addition of bromide or perchlorate also produced color changes, although to a lesser extent.[7] We now report a new and specific chromogenic reagent for nitrate using a *p*-nitrophenylazobenzene group as a dye and a mercuric complex as an anion-binding site. The system shows a selective change of color in acetonitrile but can also be applied to the selective determination of nitrate in water.

The aza-oxa-thia macrocycle (see Scheme 1) was obtained by the cyclization of 3,6-dioxa-1,8-octanedithiol and dimesilated *N*,*N*-diethanolphenylamine in acetonitrile/K_2CO_3 at reflux,[8] under high dilution conditions. The macrocycle was obtained in a 40% yield. The macrocycle was coupled with the azonium salt of *p*-nitroaniline in HCl to obtain $\mathbf{L^1}$ as a red-orange powder (80% yield). ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis are consistent with the proposed formulation.

The visible spectrum of the ligand $\mathbf{L^1}$ in acetonitrile is characterized by an intense band centered at 490 nm ($\varepsilon = 26000\,\text{M}^{-1}\,\text{cm}^{-1}$), which is responsible for the orange color of the solutions and is caused by a charge transfer from the

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[**] This research was supported by the Ministerio de Ciencia y Tecnología (proyecto PB98-1430-C02-02, 1FD97-0508-C03-01, and AMB99-0504-C02-01). F.S. also thanks the Ministerio de Ciencia y Tecnología for a Doctoral Fellowship.

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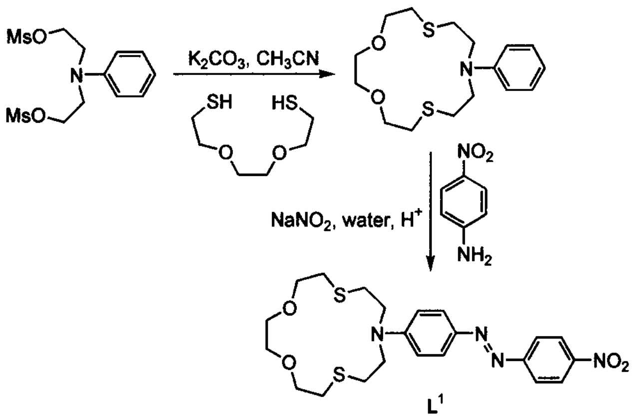

Scheme 1. Synthesis of $\mathbf{L}^1$.

donor nitrogen atom of the macrocycle to the acceptor nitro moiety.[9] No changes were observed in the UV/Vis spectrum in acetonitrile, upon addition of one equivalent of Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}, and Mg^{2+} (perchlorate salts) or upon addition of up to 100 equivalents of the anions F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, and NO_3^- (tetra-*N*-butylammonium salts). Whereas the addition of the metal ions Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+}, and Ag^+ did not have any significant effect, the presence of Cu^{2+}, Hg^{2+}, and Fe^{3+} cations induced a red shift of the $\mathbf{L}^1$ visible band to 520–540 nm, which resulted in a color change of the solution from orange to red. The 520 nm band intensity (concentration of $\mathbf{L}^1$ 1.0×10^{-4} M in acetonitrile) was monitored upon addition of the metal ions Cu^{2+}, Hg^{2+}, and Fe^{3+}, which allowed us to determine complex stability constants. Titration of $\mathbf{L}^1$ with Cu^{2+} indicated the formation of 1:1 ligand-to-metal complexes. The log K value for the complex-formation equilibrium, calculated through nonlinear least-squares treatment of the titration profiles,[10] was 5.9 ± 0.2. For Hg^{2+} and Fe^{3+} ions, the titration data suggested the formation of sandwichlike complexes with 2:1 ligand:metal stoichiometries. Calculated log K values were 11.2 ± 0.3 and 10.9 ± 0.2 for the formation of the $[Hg(\mathbf{L}^1)_2]^{2+}$ and $[Fe(\mathbf{L}^1)_2]^{3+}$ complexes, respectively. Additional ^1H and ^{13}C NMR spectroscopic studies were carried out on the Hg^{2+}–$\mathbf{L}^1$ system. NMR spectroscopy confirmed the formation of the 1:2 metal:ligand complex $[Hg(\mathbf{L}^1)_2]^{2+}$ with significant shifts of the signals arising from the protons and carbons of the $\mathbf{L}^1$ aza-oxa-thia ring, in the presence of the mercuric cation.

These $[Cu(\mathbf{L}^1)]^{2+}$, $[Hg(\mathbf{L}^1)_2]^{2+}$, and $[Fe(\mathbf{L}^1)_2]^{3+}$ complexes have proved to be suitable chromogenic receptors for anion sensing. Thus, changes in the visible spectrum were recorded in acetonitrile solutions of these receptors upon addition of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, and NO_3^- ions. Each complex showed quite different behavior in the presence of the anions studied, the most remarkable effect being observed with the $[Hg(\mathbf{L}^1)_2]^{2+}$ complex. Hence, while addition of every anion to the $[Cu(\mathbf{L}^1)]^{2+}$ complex solution resulted in a shift of the visible band of the complex and color change (the color variation is more remarkable for F^-, Cl^-, I^-, $H_2PO_4^-$, and NO_3^- ions than Br^- and HSO_4^- ions, see Supporting Information), the $[Fe(\mathbf{L}^1)_2]^{3+}$ and $[Hg(\mathbf{L}^1)_2]^{2+}$ complexes showed a more selective response. For $[Fe(\mathbf{L}^1)_2]^{3+}$, only addition of I^- and NO_3^- ions resulted in a shift of the 540 nm band to 490 nm with a concomitant change in color from red to yellow, whereas the $[Hg(\mathbf{L}^1)_2]^{2+}$ complex gave a specific response to NO_3^- ions, as this was the only anion which produced a color change of the receptor solution (Figure 1). Competitive experiments have been carried out using the $[Hg(\mathbf{L}^1)_2]^{2+}$ complex. The same spectral variation was found upon nitrate addition in solutions containing a five-fold excess of chloride, bromide, iodide, or sulfate. In contrast, some interference was detected in the presence of an excess of fluoride or phosphate.

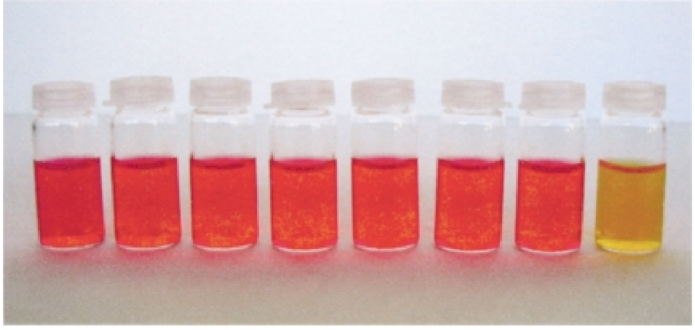

Figure 1. Color changes induced in $[Hg(\mathbf{L}^1)_2]^{2+}$ (9.6×10^{-5} mol dm^{-3}) in acetonitrile. From left to right: no anion, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, and NO_3^-.

Titration of acetonitrile solutions of the complexes $[Cu(\mathbf{L}^1)]^{2+}$, $[Hg(\mathbf{L}^1)_2]^{2+}$, and $[Fe(\mathbf{L}^1)_2]^{3+}$ by addition of aliquots of the corresponding anion solution gave isosbestic points in all cases, which indicate the formation of 1:1 anion:receptor complexes. From the titration data, stability constants for the formation of anion–receptor complexes were determined (Table 1).[10]. The receptor $[Cu(\mathbf{L}^1)]^{2+}$ forms strong complexes with all the anions studied. Stability constants are in the order $F^- > H_2PO_4^- > NO_3^- > Cl^- = I^- > HSO_4^- = Br^-$. The $[Hg(\mathbf{L}^1)_2]^{2+}$ and $[Fe(\mathbf{L}^1)_2]^{3+}$ receptors, though they show a more selective response, also form strong complexes with values of the stability constants of the same order of those of the copper receptor.

Table 1. Stability constants from titration experiments in acetonitrile for the formation of 1:1 anion:receptor complexes.[a]

	NO_3^-	F^-	Cl^-	Br^-	I^-	HSO_4^-	$H_2PO_4^-$
$[Cu(\mathbf{L}^1)]^{2+}$	6.2(2)	7.5(5)	4.7(1)	3.4(1)	4.6(2)	3.7(1)	7.1(2)
$[Fe(\mathbf{L}^1)_2]^{3+}$	5.7(1)	–	–	–	4.8(1)	–	–
$[Hg(\mathbf{L}^1)_2]^{2+}$	6.2(2)	–	–	–	–	–	–

[a] Values in parentheses are the standard deviations in the last significant digit.

These results show that dye-containing metal complexes can act as efficient and selective chromogenic reagents for anion sensing.[11] Additionally, there is a remarkable control of the selectivity by simple selection of the metal cation. Thus, metal ions such as Fe^{3+}, Cu^{2+}, and Hg^{2+} are able to change the color of the dye $\mathbf{L}^1$ probably by a suitable coordination with the aza-oxa-thia ring. In fact, Fe^{3+}, Cu^{2+}, and Hg^{2+} ions, among the metals studied, give the strongest complexes with amines and therefore an effective coordination between the metals and the nitrogen atom of the aza-oxa-thia ring of the dye would be expected.[12] This interaction causes the disappearance of the **L**^{1} charge-transfer band and the appearance of a new red-shifted band that probably arises from a new charge-transfer transition, in which orbitals of the metal centers are involved. This metal–dye interaction is very sensitive to local electronic disturbances produced by the presence of the anions and hence, coordination or formation of ion-pairs between certain anions and $[Cu(\mathbf{L}^1)]^{2+}$, $[Hg(\mathbf{L}^1)_2]^{2+}$, and $[Fe(\mathbf{L}^1)_2]^{3+}$ receptors could induce the observed color changes. NMR spectroscopic studies of the $[Hg(\mathbf{L}^1)_2]^{2+}$-nitrate system showed a slight shift of the signals assigned to the protons *ortho* to the azo group, in the presence of nitrate ions. This shift could be related to the presence of π-stacking interactions between the nitrate ion and the *p*-nitrophenylazobenzene group. Therefore, as both the nitrate anion and the **L**^{1} molecule are planar, and nitrate forms equally strong complexes with all three receptors $[Cu(\mathbf{L}^1)]^{2+}$, $[Hg(\mathbf{L}^1)_2]^{2+}$, and $[Fe(\mathbf{L}^1)_2]^{3+}$, we suggest that the interaction between the NO_3^- ions and the receptors must proceed through the **L**^{1} molecule and not through the cationic metal center. Hence, though the interaction between nitrate and the receptors must be favored by electrostatic forces, π-stacking interactions between the planar nitrate and the also planar *p*-nitrophenylazobenzene could be responsible for the color changes observed in the presence of nitrate.

The selective nitrate sensing using the $[Hg(\mathbf{L}^1)_2]^{2+}$ complex is a remarkable effect, thus some preliminary studies were carried out to use this color change as a method for direct nitrate determination in water. We realized that the addition of small quantities of water (up to 0.5 %) to acetonitrile solutions of $[Hg(\mathbf{L}^1)_2]^{2+}$ did not have any effect in the selective color change from red to yellow observed in the presence of nitrate. Therefore, using a calibration curve for nitrate in an acetonitrile:water solution (Figure 2), nitrate concentration in aqueous solutions can be approximately determined by the addition of small aliquots of aqueous nitrate ions (few μL) to solutions of the $[Hg(\mathbf{L}^1)_2]^{2+}$ complex in acetonitrile. By this method, the concentration of nitrate in the 20–200 ppm range was determined in the presence of other anions (carbonate, sulfate, chloride, calcium, magnesium, and sodium in typical concentration ranges 1×10^{-3}–5×10^{-4}). Table 2 shows the nitrate concentration in water determined by addition of 50 μL of the aqueous sample to 10 mL of acetonitrile solutions of $[Hg(\mathbf{L}^1)_2]^{2+}$ and further measurement of the absorption band. The method is easy to carry out and allows colorimetric determination of nitrate in the presence of the other anions and cations typically present in water. We also found that lower concentrations of nitrate can also be determined by the simple preconcentration of diluted aqueous samples.

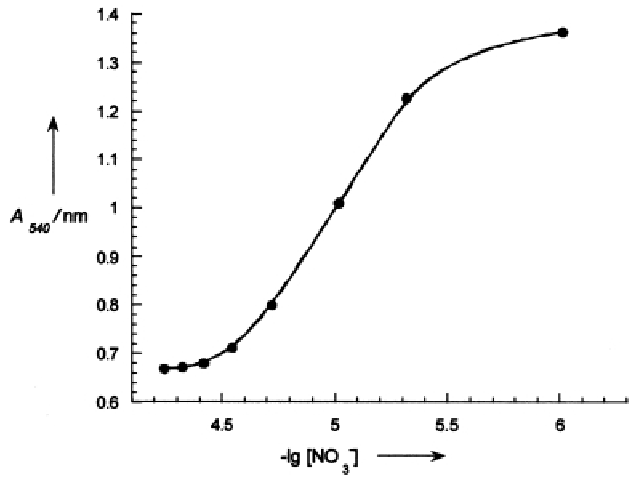

Figure 2. Calibration curve used to determine nitrate concentration in water. Absorption (A) versus logarithm of the nitrate concentration in acetonitrile:water 99.5:0.5 v/v. Concentration of $[Hg(\mathbf{L}^1)_2]^{2+}$: 9.6×10^{-5} mol dm^{-3}.

Table 2. Concentration of nitrate ($-\log[NO_3^-]$) in different samples of water.

Real concentration	Determined [a] with $[Hg(\mathbf{L}^1)_2]^{2+}$
2.36	2.40
2.66	2.70
3.02	3.10
3.43	3.50

[a] Concentration of nitrate was determined using the calibration curve (Figure 2).

In conclusion, Cu^{2+}, Fe^{3+}, and Hg^{2+} complexes with the receptor **L**^{1} are very sensitive to the electronic perturbations produced by anions and have proved to be suitable chromogenic reagents for anion sensing. The selective detection of the poorly coordinating anion nitrate, and the possibility of its direct quantification in water using a simple color change are especially significant. These findings might open up new opportunities in the chromogenic sensing of traditionally poorly coordinating anions by synthetic receptors.

Received: December 7, 2001 [Z18347]

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Selective Recognition of Fluoride Anion Using a Li^+–Metallacrown Complex

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With the final goal of constructing specific chemosensors for fluoride anions, considerable efforts have been put into the synthesis of compounds that are able to bind fluoride ions with high affinity and selectivity. The receptors described include organic macrocycles with convergent H-bond donor groups and compounds containing Lewis acidic boron, silicon, or tin atoms.[1, 2] Here we report a conceptually new fluoride receptor, the basic principle of which is shown in Figure 1. A lithium ion, which serves as a binding site, is coordinated inside a three-dimensional host compound. The accessibility of the Li^+ center is controlled by the steric requirements of the host: the small fluoride anion is able to enter the cavity whereas larger anions are efficiently blocked. Since the radius of the fluoride ion is significantly shorter than that of most other anions,[1b] a highly specific receptor is obtained.

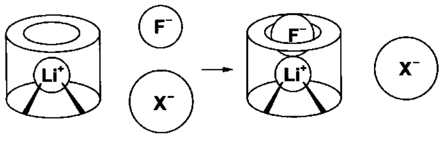

Figure 1. Schematic representation of a selective fluoride receptor with a Li^+ ion binding site.

The utilization of the hard acid Li^+ ion for the binding of the hard base F^- appears to be very attractive, but so far Li^+-based fluoride receptors have not been described. In fact, there is not even structural data available on complexes containing molecular LiF,[3, 4] although numerous examples of other alkali metal halide complexes are known. The difficulty of stabilizing molecular LiF arises from its very high lattice energy which makes crystalline LiF a thermodynamic trap.[4b]

Recently, we have described the synthesis of trimeric organometallic complexes of the general formula $[L_nM(C_5H_3NO_2)]_3$ (L_nM = arene-Ru or Cp*Rh; Cp* = C_5Me_5).[5] These analogues of [12]crown-3[6] were shown to bind alkali metal halides with remarkable affinity and selectivity. In an extension of this work we have investigated the reaction of $[\{Cp^*IrCl_2\}_2]$ with 3-hydroxy-2-pyridone in the presence of base. As in the cases with the analogous ruthenium and rhodium complexes, a trimeric complex $[Cp^*Ir(C_5H_3NO_2)]_3$ (**1**) was obtained. The metallamacrocycle was characterized by NMR spectroscopy (^1H, ^{13}C), elemental analysis, and single-crystal X-ray analysis (Figure 2).[7] A pseudo-C_3-symmetric geometry is observed in the solid state, with dianionic pyridonate ligands bridging the Cp^*Ir^{III} frag-

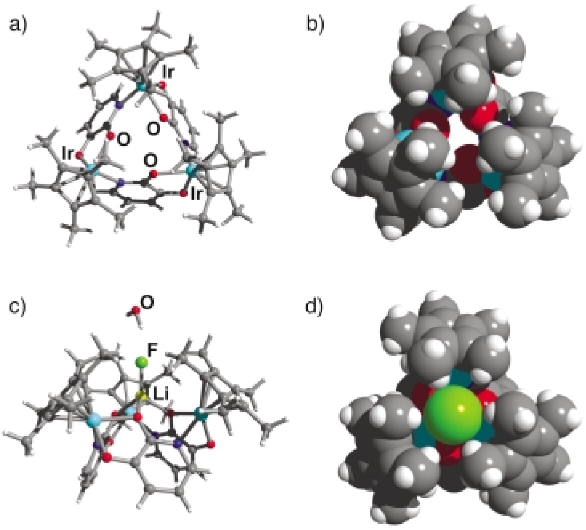

Figure 2. a) The molecular structure of **1** in the crystal; b) view along the pseudo-C_3 axis of **1** highlighting the sterically shielded binding site (space filling representation); c) the molecular structure of **1**·LiF in the crystal; d) view along the pseudo-C_3 axis of **1**·LiF. Four very short CH···F contacts are observed (the water molecule is omitted in the space filling representation).

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[+] X-ray structural analyses.

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