



## A Fluorescent Chemosensor Able to Distinguish between Ionic and Covalent Mercury Compounds

ANA M. COSTERO<sup>1\*</sup>, ROSARIO ANDREU<sup>1</sup>, RAMÓN MARTÍNEZ-MÁÑEZ<sup>2\*</sup>, FÉLIX SANCENÓN<sup>2</sup> and JUAN SOTO<sup>2</sup>

<sup>1</sup>Departamento de Química Orgánica, Universidad de Valencia, Doctor Moliner, 50. 46100-Burjassot, Valencia, Spain;

<sup>2</sup>Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, 46071-Valencia, Spain

(Received: 5 April 2002; in final form: 11 July 2003)

**Key words:** fluorescence, macrolactones, mercury salts, selectivity

### Abstract

Macrolactone **1** has shown different fluorescent response depending on the ionic or covalent character of mercury compounds. This ligand also presents a very selective response to  $\text{Hg}(\text{ClO}_4)_2$  versus  $\text{Cd}(\text{ClO}_4)_2$ .

### Introduction

During the last years our research group has been interested in studying crown ethers and related compounds containing 4,4'-bis(dimethylamino)biphenyl units in their structures. One of the reasons that justify this interest is the fluorescent behaviour of the 4,4'-bis(dimethylamino)biphenyl units when they have carbonyl groups in the 2,2' positions that makes them potential fluorescent sensors [1]. The design and synthesis of this type of ligand has become very frequent due to the advantages that fluorescence presents which include simplicity of instrumentation, high sensitivity which allows substrate sensing at trace level and, sometimes, direct visual perception even in very dilute solutions [2].

On the other hand, mercury, cadmium and lead compounds are among the most dangerous salt in sewages. For this reason, the synthesis of efficient sensors to detect them is very interesting. In this sense, some ligands have been recently described to be use with this goal [3]

In our research we have prepared several ligands containing crown ethers attached to the 2,2'-bis(dimethylamino)biphenyl unit and we have studied their fluorescent behaviour in the presence and absence of transition metal cations. Among all the studied compounds lactone **1** [4] showed an interesting behaviour in the complexation of different mercury and cadmium compounds (Chart 1).

### Experimental

Fluorescence measurements were made with an Edinburgh Analytical Instrument. Fluorescence spectra were obtained using a  $1.0 \times 10^{-5}$  M solution of **1** in spectroscopic grade acetonitrile. No efforts were made to exclude water or air.

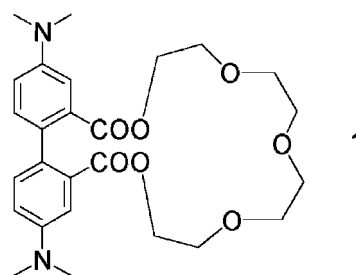


Chart 1.

Metal solutions were prepared by dissolution of the appropriate perchlorate salt (or the mercury covalent compound) in spectroscopic grade acetonitrile. All commercially available reagents were used without further purification. The preparation of compound **1** was previously reported [4]. Fluorescence quantum yields were determined by comparative procedure using tetramethylbenzidine ( $\Phi = 0.13$  in acetonitrile  $\lambda_{\text{exc}} = 310$  nm) as standard. The comparative experiments were carried out using a 1 : 1 metal-to-ligand ratio. Titration experiments were carried out to determine complexation constants.

### Results and discussion

The fluorescent behaviour of compound **1** was studied towards different transition metal cations ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ ) and some alkali and alkaline-earth cations ( $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ). In these experiments it was observed that presence in solution of cations  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (all of them as perchlorate salts) did not substantially modify ligand fluorescence. On the other hand,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  produced a partial quenching of the fluorescence being the effect with  $\text{Cu}(\text{ClO}_4)_2$  stronger because almost a total quenching of the fluorescence was observed

\* Authors for correspondence.

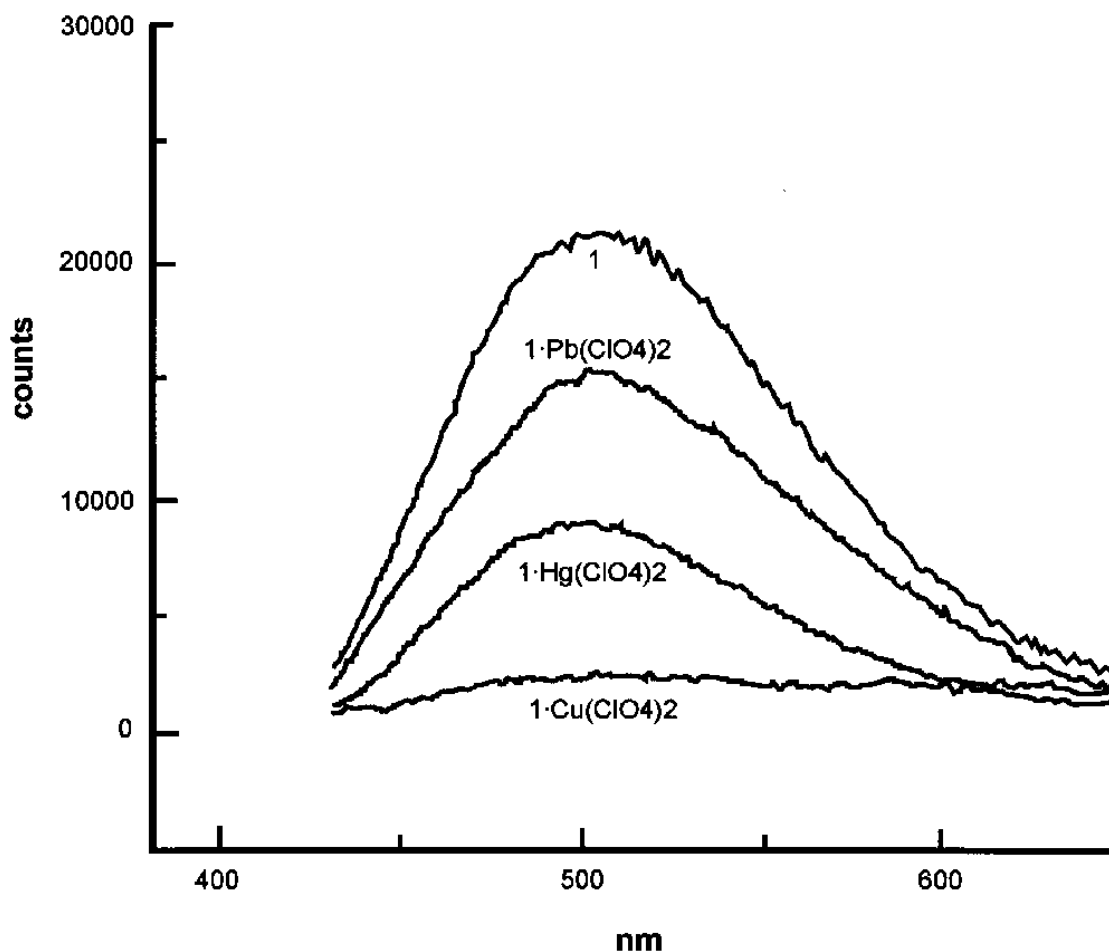


Figure 1. Emission spectrum of **1** in acetonitrile and in the presence of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ .

(some of these results are showed in Figure 1). These results were hoped for because these cations are known as fluorescence quenchers via enhanced spin-orbit coupling ( $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ) or energy or electron transfer ( $\text{Cu}^{2+}$ ) [5] Finally,  $\text{Cd}^{2+}$  gave rise to an increment of the intensity [6] in addition to a splitting of the emission into two bands ( $\lambda_1 = 465 \text{ nm}$  and  $\lambda_2 = 575 \text{ nm}$ ), being the intensity of the second band higher than this of the first one (see Figure 2).

Competition experiments, carried out using both salts  $\text{Hg}(\text{ClO}_4)_2$  and  $\text{Cd}(\text{ClO}_4)_2$  simultaneously, demonstrated that the spectrum was similar to this registered when only  $\text{Hg}(\text{ClO}_4)_2$  was present. Under these conditions only one broad band was observed instead the two peaks corresponding to the complexation with the cadmium salt. Thus, ligand **1** could be considered a selective fluorescent sensor for  $\text{Hg}^{2+}$  in the presence of  $\text{Cd}^{2+}$ . This behaviour seems to indicate that interaction between ligand **1** and  $\text{Hg}(\text{ClO}_4)_2$  is stronger than with the cadmium salt. One reason for this complexation can be found in the different ionic radio shown by these two cations that makes mercury fit better than cadmium into the crown cavity.

On the other hand, previous studies carried out with compound **1** showed that this ligand was unable to complex  $\text{Hg}(\text{CN})_2$  into the cavity probably due to steric effects [7]. However, it has been observed that the fluorescence of compound **1** is clearly modified in the presence of this covalent

mercury compound (Figure 3). Thus, the fluorescence spectrum of ligand **1** in the presence of  $\text{Hg}(\text{CN})_2$  showed a band at  $\lambda_{\text{max}} = 500 \text{ nm}$  (a similar value to that observed in the ligand) which is 2 times the intensity observed in the ligand. The increase in the emission involves an interaction between the ligand and the mercury compound that necessarily must be different to the classical co-ordination in the cavity of the crown compound. This behaviour is interesting because only few examples showing a fluorescence enhancement with heavy transition metal ions have been reported [8]. In addition, when both mercury compounds ( $\text{Hg}(\text{ClO}_4)_2$  and  $\text{Hg}(\text{CN})_2$ ) were simultaneously present, the presence of the ionic salt seems to annul the effect of  $\text{Hg}(\text{CN})_2$  because the result was practically the same as that obtained in the experiment carried out only with  $\text{Hg}(\text{ClO}_4)_2$ . This effect seems to be related to the different character of the mercury in both compounds that gives rise to different interaction with ligand **1**. Thus,  $\text{Hg}^{2+}$  is complexed within the crown cavity whereas  $\text{Hg}(\text{CN})_2$  is unable to pass one of the CN group through the cavity due to steric hindrance and the metal is complexed involving one of the dimethyl amino groups. This different behaviour allows detecting ionic mercury salts in the presence of covalent mercury compounds. These experiments were carried out with other covalent mercury compounds ( $\text{Hg}(\text{SCN})_2$  and  $\text{HgI}_2$ ) and the results agree with the former explanation.

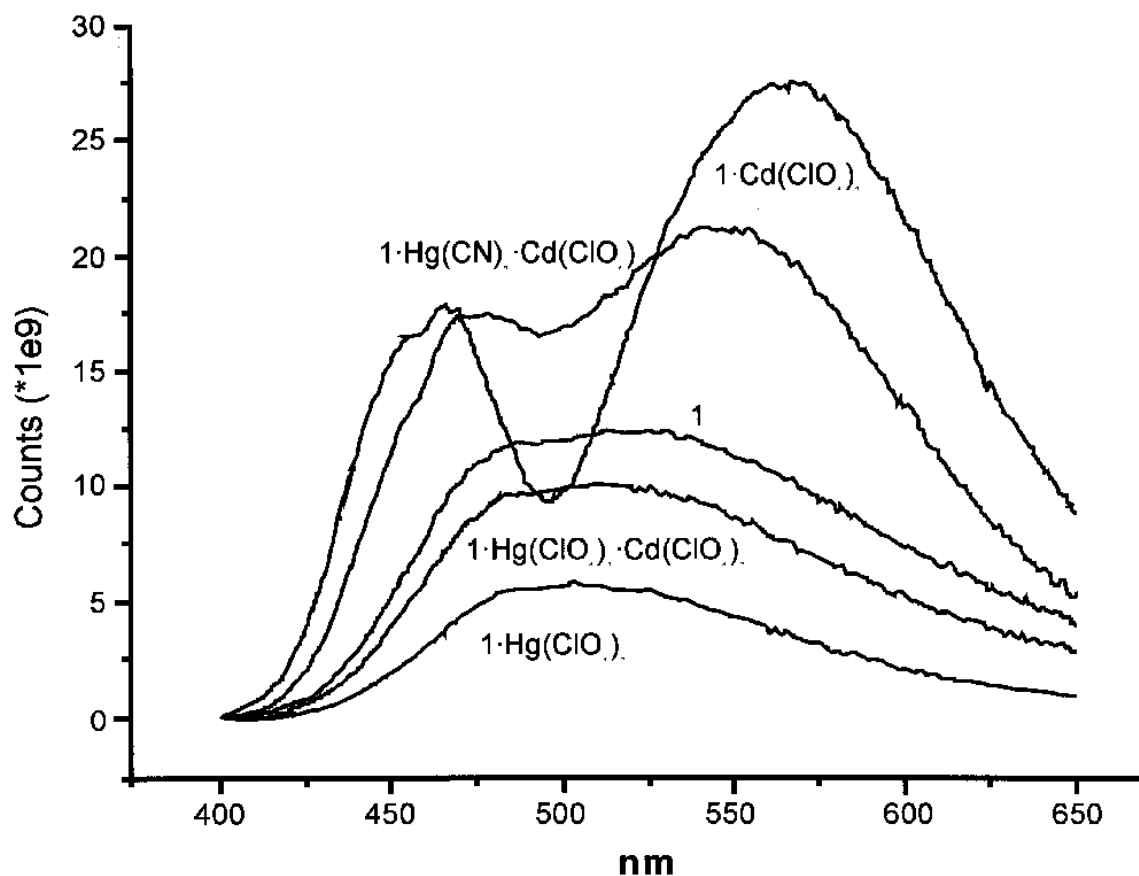


Figure 2. Emission spectrum of 1 in acetonitrile and in the presence of Cd(ClO<sub>4</sub>)<sub>2</sub>, Hg(ClO<sub>4</sub>)<sub>2</sub> and mixtures of Cd(ClO<sub>4</sub>)<sub>2</sub> with Hg(ClO<sub>4</sub>)<sub>2</sub> and Hg(CN)<sub>2</sub>.

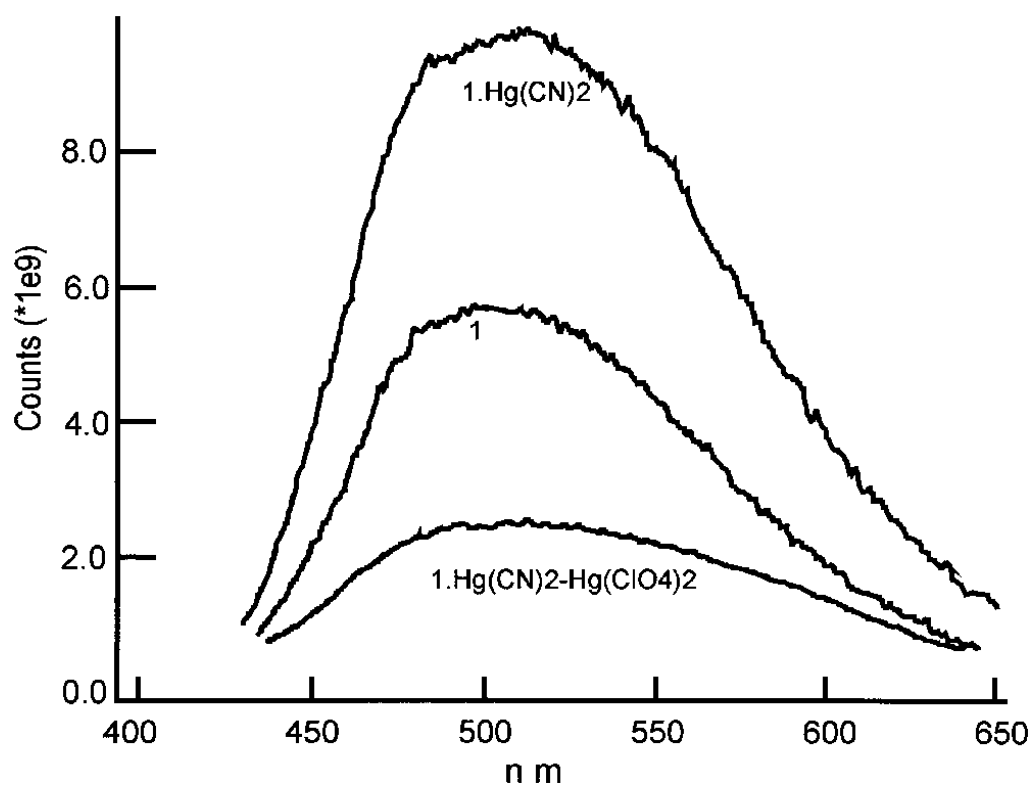


Figure 3. Emission spectrum of 1 in acetonitrile and in the presence of Hg(CN)<sub>2</sub> and a mixture of Hg(CN)<sub>2</sub> and Hg(ClO<sub>4</sub>)<sub>2</sub>.

The behaviour previously described suggests that the complex formed between the ligand and  $\text{Hg}^{2+}$  is stronger than that generated by the interaction between **1** and the covalent mercury compound what is not surprising when it is considered that the guest is not hosted inside the cavity.

Finally an experiment was carried out using  $\text{Cd}(\text{ClO}_4)_2$  and  $\text{Hg}(\text{CN})_2$  simultaneously. Under these conditions two emission bands were observed at values similar to these shown when only  $\text{Cd}(\text{ClO}_4)_2$  was used but in the case of the mixture the intensity of the emission was higher. This behaviour can be understood if the ligand simultaneously interacted with both substrates. The smaller ionic radio of  $\text{Cd}^{2+}$  could allow the ligand to interact simultaneously with this cation in the crown cavity and the covalent mercury compound with the dimethylamino group. This situation could be hindered in the presence of the bulky  $\text{Hg}^{2+}$  cation.

### Conclusions

Firstly, we can conclude that ligand **1** acts as a selective fluorescent sensor for  $\text{Hg}^{2+}$  in the presence of  $\text{Cd}^{2+}$ . In addition compound **1** forms different types of complex depending on the covalent or ion character of the mercury salts. This difference is related to the type of interaction between host and guest. Thus, ionic salts place their cations inside the crown cavity whereas covalent mercury compounds interact probably with the external diamino groups.

### Acknowledgement

We thank the Dirección General de Enseñanza Superior e Investigación Científica (PB98-1430-C02-01, PB98-1430-C02-02 and AMB99-0504.C02-01).

### References

1. A.M. Costero, R. Andreu, E. Monrabal, R. Martínez-Máñez, F. Sancenón, and J. Soto: *J. Chem. Soc. Dalton Trans.* 1796 (2002).
2. (a) L. Fabrizzi and A. Poggi: *Chem. Soc. Rev.* **24**, 197 (1995); (b) A.P. de Silva, H.Q.G. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, and T.E. Rice: *Chem. Rev.* **97**, 1515 (1997).
3. (a) K. Rurack, M. Kollmannberger, U. Resch-Genger, and J. Daub: *J. Am. Chem. Soc.* **122**, 968 (2000); (b) G. Hennrich, W. Walther, U. Resch-Genger, and H. Sonnenschein: *Inorg. Chem.* **40**, 641 (2001).
4. A.M. Costero, C. Andreu, M. Pitarch, and R. Andreu: *Tetrahedron* **52**, 3683 (1996).
5. A.W. Varnes, R.B. Dodson, and E.L. Wehry: *J. Am. Chem. Soc.* **94**, 946 (1972) and references therein.
6. L. Prodi, M. Montalti, N. Zaccheroni, J.S. Bradshaw, R.M. Izatt, and P.B. Savage: *Tetrahedron Lett.* **42**, 2941 (2001).
7. A.M. Costero, E. Monrabal, and R. Andreu: *J. Inclusion Phenom. Mol. Recognit. Chem.* **35**, 147 (1999).
8. P. Ghosh, P.K. Bharadwaj, S. Mandal, and S.J. Ghosh: *J. Am. Chem. Soc.* **118**, 1553 (1996).