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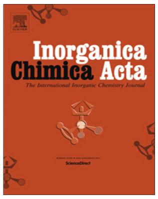

Anion selectivity of Zn–salophen receptors: Influence of ligand substituents

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ABSTRACT

Four Zn–salophen complexes that differ for the electrodonating/electrowithdrawing character of the substituents located in the positions para to the phenolic oxygens have been used for the molecular recognition of several anions. Spectrophotometric and spectrofluorimetric titrations carried out in ethanol show for three of them strong binding affinity and also marked selectivity in the recognition of ATP^{4-}, when methoxy electrodonating substituents are present. The finding that a Zn–salophen derivative with overall electrodonating ($-I < +R$) substituents is a more selective receptor for this anion than those decorated with electron withdrawing groups, support the occurrence in this case of supramolecular π–π stacking interactions between the adenosine residue and the aromatic ligand surface that counterbalance the decrease in electrophilicity of the metal center.

1. Introduction

It is well known that anions play an important role in a wide range of chemical and biological processes [1,2]. They are ubiquitous in both the organic and mineral worlds, play different key roles in biology [3–6], and cause dramatic effects as environmental pollutants [7]. For these reasons, the supramolecular recognition of anions is a topic of constant interest that is witnessed by the rich literature focused on the design and preparation of new receptors addressing this target [8–13].

One of the most handy and simplest means of detection is the use of optical chemosensors that show changes in absorption or emission bands in the presence of target analytes. Chemosensors are indeed more convenient and inexpensive and they display high sensitivity and low detection limit [14].

Sal(oph)en-type derivatives represent a fundamental class of compounds in coordination chemistry that have been also extensively used in the molecular recognition of anions and in several interesting applications [15–17]. Such ligands, easily obtained through the condensation of *o*-phenylendiamine with two equivalents of salicylaldehyde, can indeed coordinate transition and main group metals to form stable complexes. The possibility of functionalizing the starting building blocks, i.e. the amine and the salicylaldehydes, provides easy access to a variety of derivatives in which the role of the metal center and of its coordination geometry is fundamental to determine the properties of the complex. In the case of Zinc, the metal displays a square-planar arrangement formed by the N_2O_2-donor atoms, while the axial positions are available for coordinating solvent molecules or other guests endowed with donating groups [10]. Thus, the insertion of the metal ion in the organic frame of the salophen ligand provides an electron deficient Lewis acid coordinating site that can reversibly bind anions that donate a lone pair to the metal.

In this work, we report the use of four differently substituted Zn–salophen complexes, see Chart 1, in the molecular recognition of several anions in ethanol. The effect of the electrodonating and electrowithdrawing character of the substituents has been examined together with the observed selectivity.

2. Results and discussion

2.1. Synthesis and characterization

The new compounds **1** and **2** were prepared according to the standard template procedure for salen and salophen metal complexes [18] using 5-cyanosalicylaldehyde and 1,2-diaminobenzene as starting materials, and by adding also the stoichiometric amount of zinc acetate salt to obtain compound **2**. The reactants were stirred at r.t. in methanol for 24 h. The products precipitated as yellow solids in pure form. Characterization by different spectroscopic and

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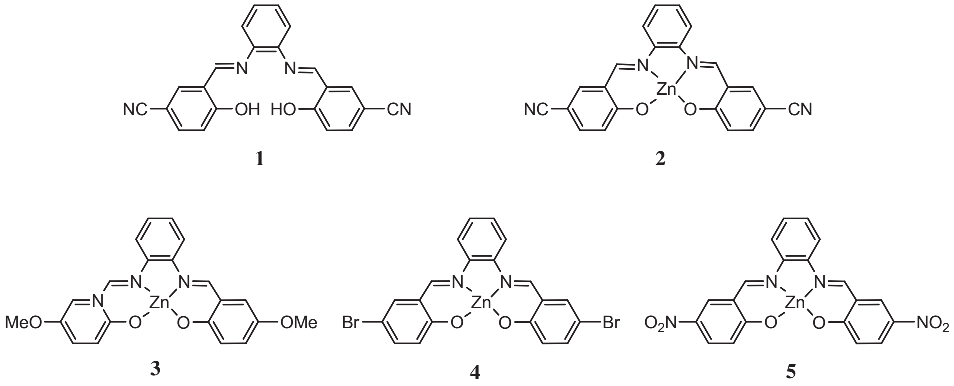

Chart 1. Salophen derivatives studied in this work.

spectrometric techniques confirmed their structure. ^{1}H NMR spectra show the expected signals of the salophen derivatives. Protons are clearly affected by metal coordination, e.g. while the signal of phenolic protons obviously disappear upon coordination, imine protons are ca. 0.2 ppm downfield shifted. HRMS-ESI spectra let us identify unequivocally the products since they display the corresponding protonated molecular peak in all cases.

2.2. Photophysical characterization

Absorption and emission spectra of all complexes were recorded in ethanol and the results are summarized in Table 1. In addition, spectroscopic characterization of **3**–**5**, previously reported by us [19], was added for comparison purposes together with absorption spectra of the **3**–**5** uncomplexed ligands (**3a**–**5a** in SI, Fig. S1).

Uncomplexed salophen ligand **1** shows a broad, unstructured absorption band in the 300–500 nm region (Fig. S2). The observed broadening can be assigned to a possible dimerization process [20]. Based on ZINDO/S semi-empirical electronic structure theoretical calculations and, as already reported for similar derivatives [16–19], the observed transitions must be predominantly π–π^* (Fig. S3). Excitation at the lowest energy absorption band gives rise to a broad emission band centered at 430 nm attributed to an intraligand transition (Fig. 1).

Coordination to Zn(II) metal, in complex **2**, gives origin to an absorption pattern similar to those observed by us previously for the other complexes displaying substituents at the para position (see Fig. S1) [19]. Excitation at the lowest energy absorption band produces a broad emission band centered at 505 nm, 75 nm red-shifted with respect to the unmetalated precursor **1** (Fig. 1) and slightly blue shifted with respect to the previously described derivatives **4**–**5** in accordance with the electrowithdrawing character of the substituents [19]. A demetalation process was previously observed for other Zn–salophen complexes in the presence of a guest molecules [21].

Table 1
Absorption and emission data of compounds **1**–**5**.

Compound	Absorption (nm) ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1})	Emission (nm)[a]	QY[c]
1	280 (7.0), 337 (5.2)	470	–
2	383 (2.5), 413 (17.74)	505	0.008
3	300 (10.4), 432 (7.2) [b]	551 [b]	0.13
4	290 (24.9), 400 (19.7) [b]	507 [b]	0.016
5	295 (37.1), 380 (39.6) [b]	476 [b]	0.009

[a] λ_{exc} = 420 nm.
[b] Data retrieved from Ref. [19].
[c] Quantum yields referred to quinine sulfate in H_2SO_4 1 N as reference (ϕ = 0.54).

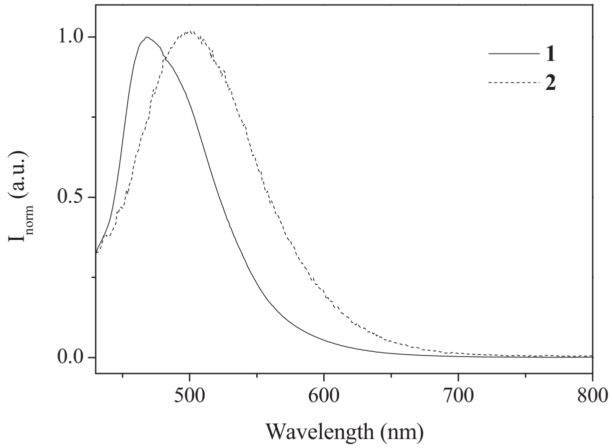

Fig. 1. Normalized emission spectra of **1** (solid line) and **2** (dashed line).

2.3. Molecular recognition of anions

UV–Vis spectroscopic titration experiments were performed by registering the spectra after the addition of increasing amounts of standard solution of the anions, 1×10^{-4} M or 1×10^{-3} M, to the solution of the complex, 5×10^{-7} M in ethanol. Sodium salts were chosen due to the innocent character of this counterion. Unfortunately the addition of all the anions to the solution of **2** leads to demetalation, as proven by ^{1}H NMR and also by the resulting absorption and emission bands corresponding to the free ligand (Fig. S4). Kleij has indeed reported a similar demetalation process for some Zn–salophen derivatives in the presence of potential guest molecules [21]. For this reason we excluded this complex from our investigation and the experiments were limited to complexes **3**–**5** using seven different anions.

As a matter of fact, very few anions produce significant changes on the absorption spectra of the zinc–salophen complexes.

Table 2
Association constant values (log$K$[a]) for complexes between compounds **3** and **4** and different anions[a] retrieved by spectrophotometric titrations. (Estimated error: 4%).

	ATP^{4-}	ADP^{3-}	AMP^{2-}	$P_3O_{10}^{5-}$	PO_4^{3-}	SO_4^{2-}	NO_2^-
3	7.6	–	–	–	–	–	–
4	7.0	7.7	–	8.0	7.3	–	–

[a] Sodium salts.