

Optical recognition elements. Macrocyclic imidazole chromoionophores entrapped in silica xerogel

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Materials containing new chromoionophores consisting of crown residue and azole moiety as parts of macrocycles were encapsulated by the sol-gel procedure in silica xerogel matrices and proposed as chemical recognition elements especially for such metal ions as Li⁺, Cs⁺ and Cu²⁺. Action of these recognition elements is in principle based on changes of reflectance. The recognition elements containing 21-membered chromogenic derivatives of unsubstituted imidazole and 4-methylimidazole are able to distinguish in aqueous solution whether the Li⁺ concentration ratio is lower or higher than 1. In the case of Cu²⁺ complexes with 18-membered macrocyclic chromoionophore in which phenol residue was replaced by imidazole and 21-membered chromogenic derivative of 4-methylimidazole, values of the EPR parameters *g* and *A* suggest participation of two oxygen and two nitrogen atoms of the ligand in the equatorial plane of the tetragonally distorted octahedral environment of the central ion.

Key words: *azole azocrown ether; chromoionophore; fluoroionophore; silica xerogel matrix; optical recognition element*

1. Introduction

Polyfunctional molecules combining dyes and polyethers form crown ether analogues belonging to chromoionophores. These compounds show colour changes on complexation with metal ions and may be useful as metallochromic reagents or may serve as sensing compounds for optical chemical sensors. Earlier, majority of such reagents were combinations of chemically bonded azobenzene, phenol residues and polyoxaethylene bridges [1]. Recently, we have described synthesis and properties of

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18-membered macrocyclic chromoionophores in which phenol residue was replaced by pyrrole or imidazole [2] (compounds **1** and **2**, Fig. 1). It was found that in acetonitrile solution 18-membered imidazole derivative **2** preferentially complexes sodium among alkali and alkaline earths metal cations. It is known that ligands containing imidazole moiety are of great importance in chemistry and biology; they form very stable complexes with 3d transition metal ions [3]. They are used to mimic binding sites of various metalloenzymes, and they have been used as enzyme inhibitors [4]. A comprehensive review regarding azocrown ethers has been published [1].

In the present work, we describe properties of new chromogenic crown reagents containing imidazole moiety as a part of macrocycle. We have studied the complexation properties of larger, 21-membered chromogenic derivatives of unsubstituted imidazole **3** and 4-methylimidazole **4** in xerogel matrix.

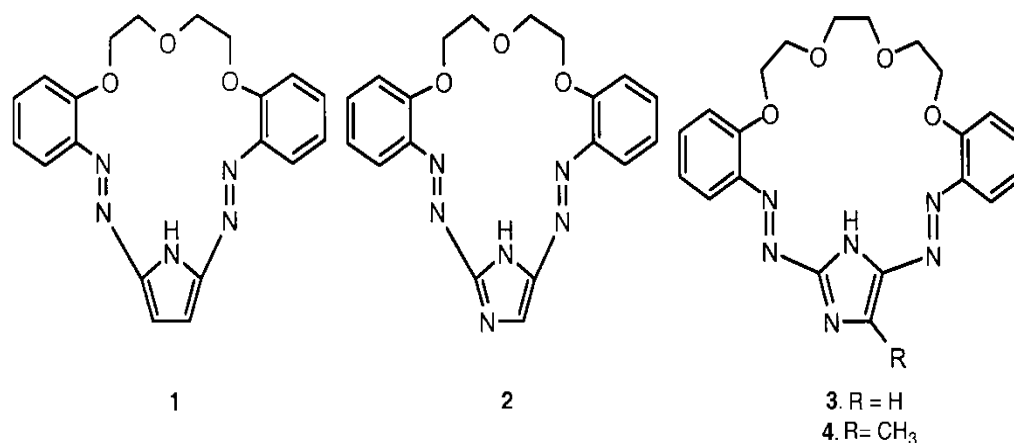


Fig. 1. 18-Membered macrocyclic derivative of pyrrole **1** and imidazole **2** (see Ref. 2) and newly synthesized 21-membered chromogenic derivatives of imidazole **3** and 4-methylimidazole **4**

We have been interested in developing materials which are able to recognize metal ions in aqueous solutions. These materials consist of the above-mentioned chromoionophores entrapped in a porous matrix. Owing to utilizing a low-temperature preparation of oxide materials, such as the sol-gel process [5], it is possible to incorporate organic molecules into an inorganic oxide xerogel. By this technique, a three dimensional network of metal-oxide bonds is formed at room temperature *via* the hydrolysis and condensation reactions of metal alkoxide, followed by low temperature dehydration.

The porous xerogel matrix obtained by this way can trap chromoionophore molecules [6]. Very often silica xerogel plays a role of host matrix for organic molecules with sensor function [7–9]. Several recent observations revealed the feasibility of making one of the most important parts of the chemical sensor, the so-called optical recognition element, which consists, as in our case, of chromoionophore molecules immobilized in a xerogel matrix [10]. In this paper, studies on optical absorption of

chemical recognition elements for potential optical absorption sensors based on chromoionophores (sensing molecules) entrapped in silica xerogel are described. Thus, the aim of our study is to determine the complexation and sensing properties of the optical recognition elements for metal ions in aqueous solutions [11].

2. Experimental

All materials and solvents were of analytical reagent grade. Preparation of compounds **1** and **2** has been described elsewhere [2]. For the synthesis of azacrown ethers with imidazole units **3** and **4** (Fig. 1), their crystallography, cation complexation and behaviour in ion-selective membrane electrodes see [12]. Tetramethoxysilane (TMOS), $\text{Si}(\text{OCH}_3)_4$, from Aldrich Chemicals Co. and methanol (POCH, Poland) were used without further purification. Metal perchlorates were purchased from Aldrich Chemicals Co.

The sols were prepared by a typical sol-gel procedure [5] from the starting mixture of TMOS (10 g or 0.066 mole), deionized water ($[\text{TMOS}]/[\text{H}_2\text{O}] = 1/4$), and methanol as diluent ($[\text{TMOS}]/[\text{CH}_3\text{OH}] = 1/10$). The mixture was stirred to obtain a homogeneous solution and then diluted with NH_3 aqueous solution ($\text{NH}_3:\text{H}_2\text{O} = 1:2$, v/v) as a catalyst and one of the sensing compounds (in methanol solution, 1×10^{-4} M) as a dopant was added. The ammonia solution was added dropwise to reach pH 8 of the mixture. The sol was then vigorously stirred at room temperature for 2-3 min.

The obtained alcogels were allowed to age and dried for 3 days in air. The xerogel was prepared by heating for 3 h at 120°C under vacuum to remove ammonia and methanol as well as some water from the pores. The concentration of the sensing dopant in the xerogel was equal to $1.0 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$, estimated on pure and dried SiO_2 xerogel obtained from the alkoxide. Xerogel materials with the immobilized chromo/fluoroionophores, their specific surface area ranging between 312 and 358 (± 11) $\text{m}^2 \cdot \text{g}^{-1}$, were crushed and the grain fraction of 0.25–0.50 mm was used for measurements.

Chemisorption (complexation) of the metal ions by the entrapped sensing dopants in the silica matrix was performed by immersion and agitation in aqueous solutions of a selected metal salt (concentration 1.0×10^{-2} M). After 1 min the recognition material was filtered off, rinsed with deionized water, and then dried at 343 K. By this chemisorption method complexes of the metal ions with the ligands **1–4** were formed. Amounts of the recognition material and the aqueous solutions used in the complexation experiment secured 1:1 ligand to metal molar ratio.

Nitrogen sorption at 77 K was used to determine the specific surface area of the prepared silica based recognition materials. Adsorption measurements were made on an AREA meter II (Stroenlein Instruments, Germany) for samples using the Brunauer–Emmett–Teller (BET) theory.

Reflectance spectra of the materials in the UV-Vis region were recorded with a Perkin-Elmer Lambda 35 spectrophotometer equipped with a Labsphere reflection spectra accessory.



EPR spectra were obtained on a Bruker ESP 300E spectrometer operating at X-band (9.1-9.9 GHz) and equipped with the Bruker NMR gaussmeter ER033m as well as the Hewlett-Packard microwave frequency counter. Sealed quartz capillaries (1 mm in diameter) were the sample holders. The magnetic field was modulated at 100 kHz. Standard deviations of the EPR spectral parameters were estimated as follows: $g_{\parallel} \pm 0.003$, $g_{\perp} = \pm 0.005$, $A_{\parallel} = \pm 4 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = \pm 1 \times 10^{-4} \text{ cm}^{-1}$.

3. Results

3.1. Compounds immobilized in silica

Reflectance. Each of the sensing molecules (Fig. 1) entrapped in silica xerogel exhibits distinctive spectral changes in UV range due to coordination with at least one of the metal ions from the following groups of metals: alkali (Li^+ , Na^+ , K^+ and Cs^+), alkaline earth (Mg^{2+} , Ca^{2+} and Ba^{2+}), heavy (Cd^{2+} , Sn^{2+} and Pb^{2+}) and transition (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) ions. The most distinctive reflectance spectral changes for some metal ions are shown in Figs. 2A-D. Hence, Cs^+ ion complexed with the ligand **1** shows quite dissimilar reflectance spectrum than the other cations of the alkali group and the free chromoionophore (Fig. 2A). Similarly, spectrum of ligand **1** undergoes specific change after coordination with Mg^{2+} (Fig. 2B). On the other hand, chromoionophore **3** distinguishes Sn^{2+} from Cd^{2+} and Pb^{2+} by spectral change, as illustrated in Fig. 2C. Chromoionophore **4** embedded in silica differentiates spectrally Cu^{2+} ions comparing changes caused by Co^{2+} , Ni^{2+} and Zn^{2+} in aqueous solution (Fig. 2D).

In order to decide which of the reflectance spectra shown in Figs. 2A, C and D are specific for Cs(I), Sn(II) and Cu(II) complexed with ligands **1**, **3** and **4**, the spectra are compared with significant reflectance spectra of the pure silica matrix and the matrix coordinated (adsorbed) to the mentioned metal ions (see Fig. 3A-C). It is evident that the specific spectral changes are attributed only to complexes Cs(I) and Cu(II) with ligands **1** and **4**, respectively, while, the spectrum of the Sn(II) complex with **3** is similar to the spectra of Sn(II) adsorbed on SiO_2 and pure SiO_2 . In this case specific spectra show Pb(II) or Cd(II) complexed to chromoionophore **3** because their distinct bands at low wavelength are placed at various positions.

Surprisingly, the spectral changes of 21-membered macrocycle **3** and **4** in xerogel matrix upon coordination of Li^+ ions depend on molar ratio $x = [\text{Li}^+]/[\text{chromoionophore}]$. The spectra dramatically differ for the ratio lower or higher than 1. The respective spectra for **3** and **4** are collected in Figs. 4A and B, respectively. Three of the bands at ca. 270, 320 and 360 nm are characteristic of free ligands and the ligands complexed with Li^+ if $x < 1$. However, if the molar ratio x exceeds 1, a typical band appears additionally at 237 nm.



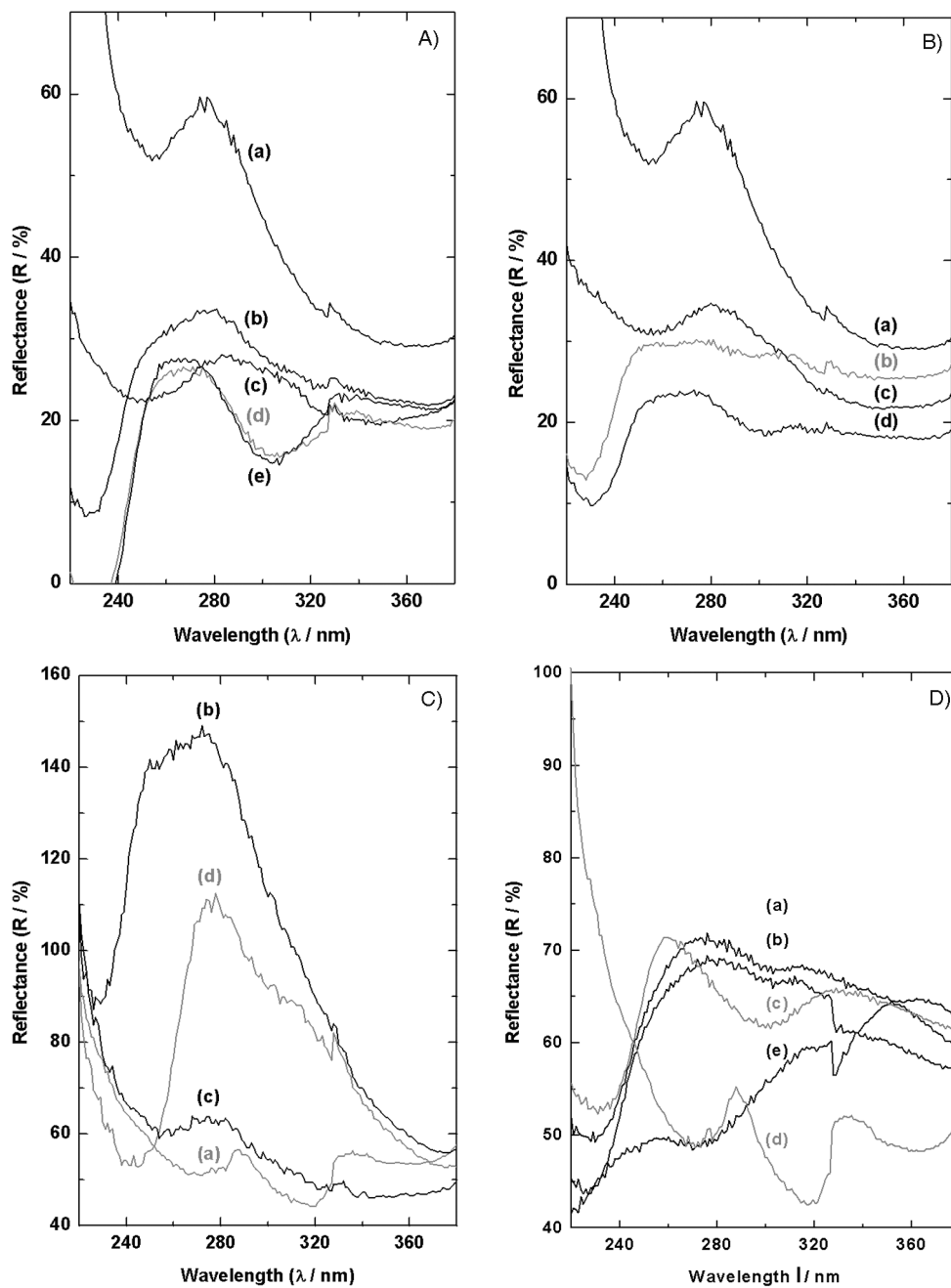


Fig. 2. Reflectance spectra of chromoionophores immobilized in silica xerogel and complexed with metal ions: A) alkali cations with ligand 1: free ligand (a), K^+ (b), Cs^+ (c), Li^+ (d), Na^+ (e); B) alkaline earth cations with ligand 1: free ligand (a), Ba^{2+} (b), Mg^{2+} (c), Ca^{2+} (d); C) heavy cations with ligand 3: free ligand (a), Cd^{2+} (b), Sn^{2+} (c), Pb^{2+} (d); D) transition cations with ligand 4: Ni^{2+} (a), Co^{2+} (b), Zn^{2+} (c), free ligand (d), Cu^{2+} (e)

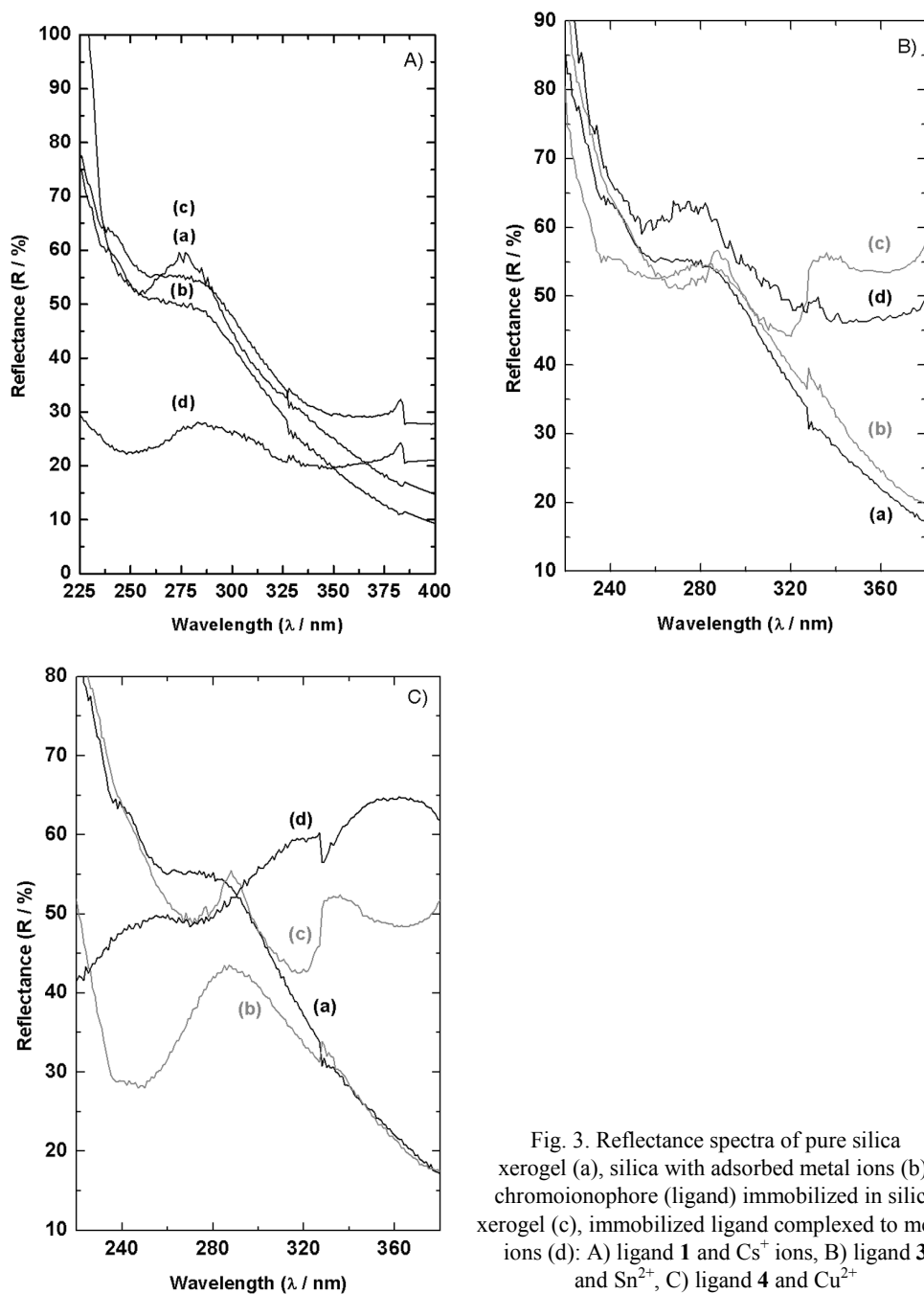


Fig. 3. Reflectance spectra of pure silica xerogel (a), silica with adsorbed metal ions (b), chromoionophore (ligand) immobilized in silica xerogel (c), immobilized ligand complexed to metal ions (d): A) ligand **1** and Cs^+ ions, B) ligand **3** and Sn^{2+} , C) ligand **4** and Cu^{2+}

In contrast, no drastic spectral changes are observed in the case of 18-membered chromoionophores **1** and **2**, when they coordinate Li^+ ions at the molar ratio x lower and higher than 1. This is shown, for instance, for **2** in Fig. 4C. For the crown ether of

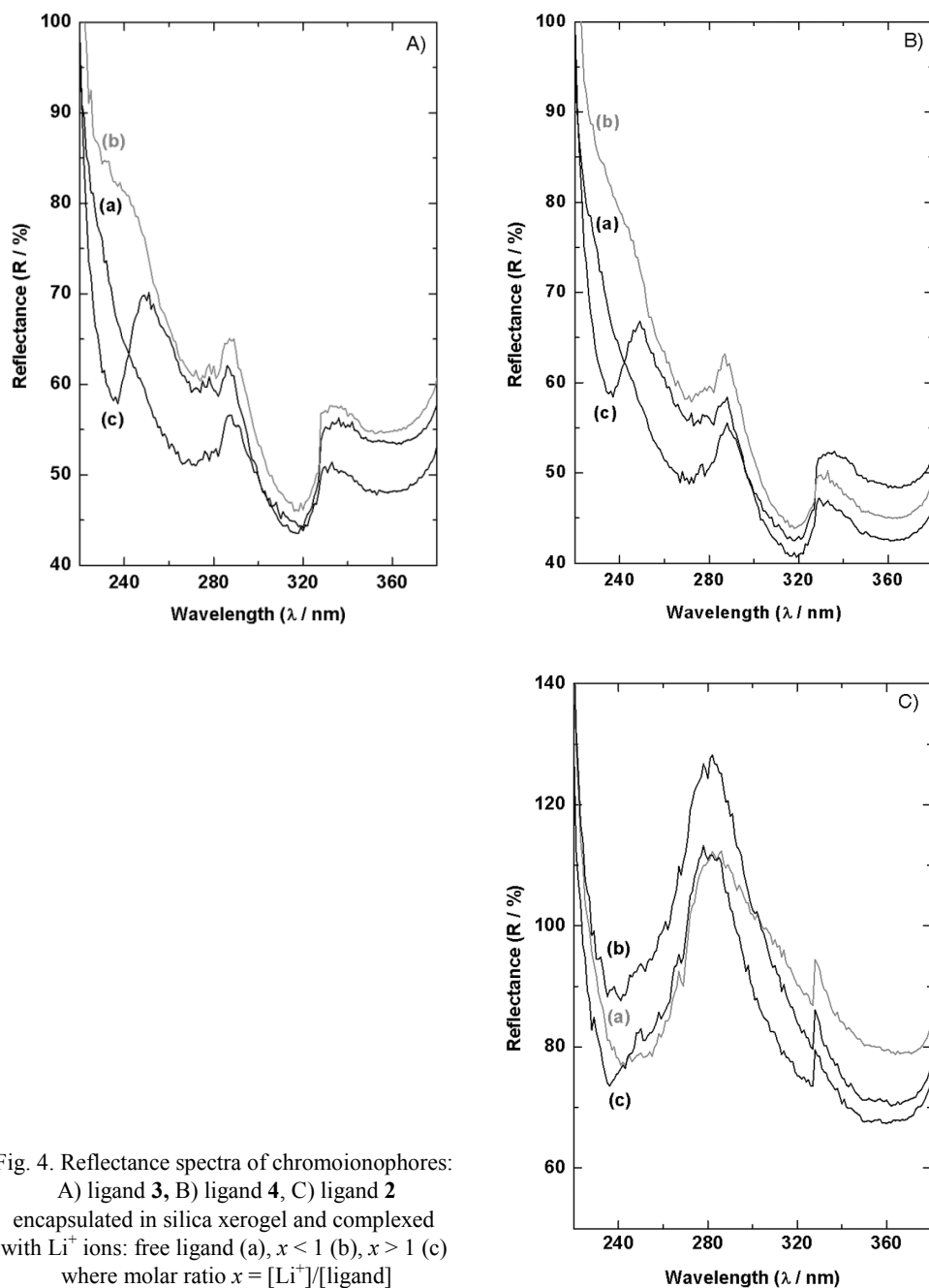


Fig. 4. Reflectance spectra of chromoionophores: A) ligand **3**, B) ligand **4**, C) ligand **2** encapsulated in silica xerogel and complexed with Li^+ ions: free ligand (a), $x < 1$ (b), $x > 1$ (c) where molar ratio $x = [\text{Li}^+]/[\text{ligand}]$

a smaller size each spectrum consists of two bands but for the solution with $x > 1$ the band at low wavelength is blue shifted in comparison with the free ligand (**1** or **2**) and for the ligand complexed with Li^+ , when $x < 1$.

Electron paramagnetic resonance spectra (EPR). EPR spectra for the complexes formed as a result of Cu^{2+} chemisorption (coordination) by the chromoionophores **2** and **4** entrapped in silica xerogel are shown in Fig. 5, together with appropriate simulated curves. The spectra are compared with that measured for silica xerogel loaded by Cu^{2+} ions. The lines of parallel orientation transitions (resolved due to copper hyperfine coupling) and line of perpendicular orientation transitions are partly overlapped. The anisotropic spectra of Cu^{2+} -ligand **2** and Cu^{2+} -ligand **4** systems are very close to each other and typical of Cu^{2+} complexes of axial symmetry. The spectral parameters of Cu^{2+} coordinated by **2**, $g_{\parallel} = 2.285$, $g_{\perp} = 2.055$, $A_{\parallel} = 176 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = 20 \times 10^{-4} \text{ cm}^{-1}$ (sim (a/b)), are analogous, within experimental error, to the parameters derived from the spectrum of Cu^{2+} coordinated by **4**. The EPR parameters of Cu^{2+} ions adsorbed in the silica xerogel are distinctly different, $g_{\parallel} = 2.411$, $g_{\perp} = 2.078$, $A_{\parallel} = 135 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = 15 \times 10^{-4} \text{ cm}^{-1}$ (sim (c)).

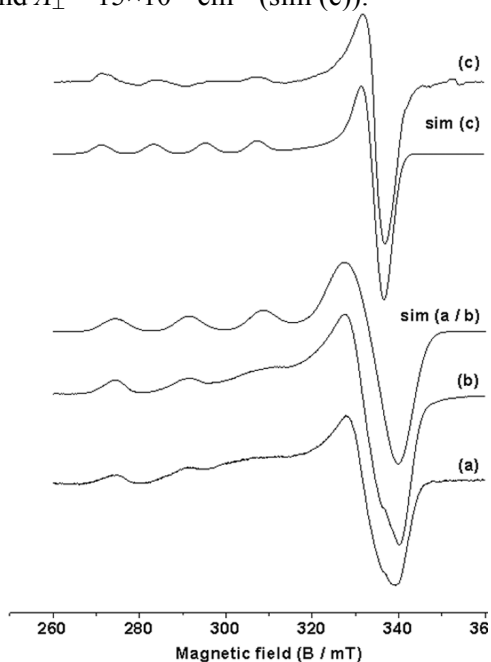


Fig. 5. X-band EPR spectra of the complexes formed by Cu^{2+} with compounds **2** (a) and **4** (b) entrapped in silica xerogel in comparison with the spectrum of silica xerogel loaded by Cu^{2+} (c). The spectra sim (a/b) and sim (c) were simulated using the spin Hamiltonian parameters given in the text. The spectra were recorded at 77 K

4. Discussion

The chromoionophores shown in Fig. 1 are molecules with extended framework consisting of a σ -bonding set and an associated conjugated π -system. The lower energy electronic transitions occur when an electron is promoted from an occupied π -orbital to an unoccupied π^* orbital. It is generally assumed that the low energy π - π^* transitions are principally responsible for UV and visible light absorption [13]. The π - π^* transitions in organic dyes which involve considerable charge transfer in donor-acceptor chromogens, are highly probable, resulting in intense optical absorption in

UV-visible range. The dramatically changed band shape after the metal ions complexation (Fig. 2) reflects a phenomenon attributed to large changes in the arrangement of vibrational energy levels in the ligand molecule that depends on charge density of the complexed metal ion. This effect is distinctly demonstrated for Cs^+ and Cu^{2+} complexes with chromoionophore **1** and **4**, respectively (Figs. 2A and D).

Among the analyzed metal ions, Li^+ possessing the smallest diameter (76 pm) [14] gives a chance to form dinuclear complexes with ligands **3** and **4** of relatively large cavities. Due to the deformation of the macrocycle in such a complex, a dramatic spectral change is expected. The expected effect is confirmed by experimental results shown in Figs. 4A and B. The effect exhibited by larger cavities of **3** and **4** after Li^+ complexation may be attributed to the stepwise formation of 1:1 and 1:2 (ligand to metal) lithium complexes. The large spectral change may be attributed to the distribution of vibrational energy levels in the ligand molecule by two complexed lithium cations creating a double charge density in the dinuclear complex as compared with the mononuclear one. As the material indicates changes of lithium(I) concentration in solution in comparison with the ligand concentration at the level ca. 1×10^{-4} M, this effect was used for Li^+ recognition.

Other cations cause characteristic spectral changes which are due to their specific diameter (compared with the ligand cavity size) and/or preferred symmetry of the coordination sphere. Owing to these reasons, they could be able to change the ligand structure by complexation and consequently the spectrum shape (see Figs. 2A–D).

EPR spectroscopy is a powerful tool enabling one to identify changes in the coordination environment of Cu(II) ions complexed by the receptor groups of the fluoroionophore attached to surface of silica matrix. The signals may be well interpreted in terms of the spin Hamiltonian for d^9 ions in axial symmetry:

$$\mathcal{H} = \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + A_{\parallel}I_zS_z + A_{\perp}(I_xS_x + I_yS_y) \quad (1)$$

where z is the symmetry axis, β the Bohr magneton, S and I are the electron and nuclear spin operators, H_x , H_y , H_z are the static magnetic field components, g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the \mathbf{g} tensor, and A_{\parallel} and A_{\perp} are parallel and perpendicular components of the hyperfine tensor \mathbf{A} . The nuclear quadrupole contribution is neglected [15]. In this study, the EPR spectra of amorphous samples of the Cu^{2+} complexes immobilized in silica were interpreted according to Kneubühl's method [16].

Computer line shape simulation was performed based on the spin Hamiltonian (Eq. (1)). Cu(II) sites are randomly oriented with respect to the magnetic field in such a way that a spectral envelope encompassing all possible resonance conditions is observed. The spectra were analyzed by a computer simulation program based on resonance fields calculated according to the method of Sakaguchi et al. [17] as well as using WinEPR SimFonia program, version 1.25.

The g -parameter sequence $g_{\parallel} \gg g_{\perp} > 2.0$ and large $|A_{\parallel}|$ values of the measured EPR spectra (Fig. 5) are typical of d^9 complexes with axial elongated symmetry and a $d_{x^2-y^2}$

ground state. It allows us to identify the Cu^{2+} coordination environment as belonging to tetragonally elongated octahedron (D_{4h}) [18]. The values of EPR parameters derived by simulation of the experimental spectra of the chromoionophores **2** and **4** loaded by Cu^{2+} suggest that coordination sphere in copper(II) plane consists most likely of two nitrogen and two oxygen donors of the ligands [19–21]. The proximity of three nitrogen donors makes also probable their involvement in coordination around Cu(II) plane but increasing width of hyperfine lines (with magnetic field growth) is characteristic for higher participation of oxygen donors. The coordination at axial position is poorly identified by EPR parameters as for $|A_{\parallel}| \gg |A_{\perp}|$ and $g_{\parallel} \gg g_{\perp}$ the most reliable information are provided by the change of $|A_{\parallel}|$ and g_{\parallel} values about the donors at the corners of Cu(II) plane [22]. The spectrum of the reference system Cu–silica xerogel is typical of Cu^{2+} surrounded by water and/or Si-OH group oxygen atoms [23] strongly suggesting that quite different Cu^{2+} complexes with ligand **2** and **4** are formed.

5. Conclusions

Materials composed of chromoionophores **1–4** entrapped in silica xerogel matrix by the sol-gel procedure, at concentration $1.0 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$ silica, treated as optical recognition elements, selectively recognize some metal ions present in aqueous solutions. The chromoionophores **1** and **4** incorporated into silica xerogel matrices are sensitive especially to Cs^+ and Cu^{2+} ions in aqueous solutions in this sense that reflectance spectra specifically change in the presence of these cations, compared with free ligands or the other studied metal complexes. This effect is useful for determination of these cations in environmental and physiological fluids by UV-Vis spectrophotometry.

The studied 21-membered chromoionophores (**3** and **4**) in the recognition elements by their dramatical spectral changes are able to signal when the molar ratio $[\text{Li}^+]/[\text{ligand}]$ exceeds 1 in aqueous solution. Thus, these recognition materials can serve as indicators of Li^+ concentration.

The EPR spectral parameters suggest that in chromoionophores **2** and **4** complexed with Cu(II) ion two nitrogen and two ether oxygen atoms take part in the equatorial plane of the tetragonally distorted octahedral sphere. Probably the same atoms of the chromoionophores take part in the complexes with other transition metal ions.

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