Macrocyclic derivatives of imidazole as chromoionophores for bismuth (III)/lead(II) pair

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ABSTRACT

18-membered diazomacrocycles with imidazole or 4-methylimidazole residue as a part of macrocycle were used as chromoionophores in bismuth(III) and lead(II) dual selective optodes for the first time. Cellulose triacetate membranes doped with macrocyclic chromoionophores are bismuth(III) and lead(II) selective with color change from orange/red to different shades of blue and violet, respectively. Results obtained for model and real samples of bismuth(III) and lead(II) showed that easily accessible and regenerable sensor materials can be used for spectrophotometric and colorimetric detection and determination of bismuth(III) and lead(II). The obtained LOD values for bismuth(III) are 1.63×10^{-7} M and 3.03×10^{-7} M with spectrophotometric and colorimetric detection, respectively, when using optode with imidazole residue. For sensing material with 4-methylimidazole in macroring the lowest detection limits were obtained for lead(II): 2.14×10^{-7} M and 3.99×10^{-7} M with spectrophotometric and digital color analysis detection mode, respectively.

1. Introduction

Bismuth(III) is a heavy metal with a relatively low toxicity and has been used by man in various areas of his activity since ancient times, although being confused with other metals, e.g. lead or tin [1,2]. Currently it is used in medicine, electronics or nuclear industry [3–11]. Bismuth(III) is used as a leading non-toxic substitute for lead(II) in brass hydraulic devices, fishing weights, free machining steel and solder, and as a metallurgical additive in casting. Bismuth applications also cover ceramic glazes, pearl pigments, lubricants and crystal products. The lack of toxicity associated with some bismuth salts has led to a growing number of reports exploring their potential applications in synthetic chemistry [12–15]. Interesting and important seems to be the potential of a photocatalytic process based on bismuth(III) catalyst for the ammonia production [16]. It can be an environmentally friendly alternative for energy consuming Haber-Bosch process. Bismuth(III) complexes also show antibacterial activity. However, it has been shown that under certain conditions it can be toxic to the human body [17].

The above is causing a growing interest in finding reliable, but also convenient for the analyst, methods of determining bismuth(III) which can be alternatives to the currently used methods. Most current methods

for the determination of bismuth(III) are instrumental techniques [18–23] including atomic absorption spectroscopy (AAS), X-ray fluorescence spectroscopy (XRF) and others. These methods require significant economic outlays, taking into account the costs of both equipment and the properly qualified personnel. Optical sensors, that can also be used in field analysis, can be an alternative or complementary to many analytical methods that are used in research laboratories [24–36].

The expanding interest in the coordination chemistry of lead(II) and bismuth(III) is connected, among the others, with the potential applications of the radioisotopes of these metal cations as radiopharmaceuticals. Bismuth-212 and bismuth-213 have relatively short half-lives (61 and 46 min respectively). Therefore the usage of longer-lived radionuclides such as ^{212}Pb (half-life 10.6 h) can be proposed as an in situ generator of ^{212}Bi. Thanks to this, the half-life of radioactive bismuth-212 can be extended to about 11 h [37,38]. Therefore the eventual chelators should have high affinity towards both lead(II) and bismuth (III). Acyclic azo derivative was found to form hypervalent bismuth(III) compound in which a nitrogen of azo group and oxygen atoms were engaged in coordination [15]. Authors reported that the binding constant must be very low in the case of this acyclic derivative of azobenzene thus was not given. Macrocyclic compounds, providing the

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selectivity of the molecular recognition, are well known host molecules for the metal cations. Suitably designed compounds, in terms of the type and number of donor sites, can also be used for quantitative determination of metal ions through colorimetric detection. Among macrocyclic ligands forming complexes with bismuth(III) and lead(II) a series of ligands was investigated, such as cyclens and others [39–41] acting as N, O donor ligands. An excellent selectivity towards bismuth(III) was also found for tetra-substituted benzimidazole zinc(II) phthalocyanine [42]. Several ideas of the application of optical sensors (Table 1 and Table 2) for bismuth(III) [43–47] and/or lead(II) [48–59] determination were also proposed. Various approaches can be used to achieve selective materials. The most popular and longest-used optode design uses an ionophore/chromophore system, as for example in the case of lead(II) optical sensors with an acyclic [48,49] or a macrocyclic ionophore such as crown ether [50,51] or calix[4]arene [55]. Reducing the number of components in the detection layers is achieved by using a selective chromogenic complexing reagents of the metallochromic indicator type. Such solutions can be found for both lead(II) [56–58] and bismuth(III) [46,47] optodes. Some attempts include the use of chromogenic macrocycles as a more selective complexing reagents [59], but these are few examples. Another option in metal cation optical sensor design is to change the material used to immobilize the components of the sensing layer. It is relatively common to use PVC [43,48–51,53,55], CTA [44–46,52,54,56,59] or others such as agarose [57] or, for example, chitosan-silica matrix [58]. Porous glass in combination with macrocyclic chromoionophore was proposed as aluminum sensitive optical sensor [60].

In this article we describe azo macrocyclic compounds acting as O,N effective colorimetric receptors for borderline Lewis acids: lead(II) and bismuth(III). The possible application of macrocycles for determination of bismuth(III) and lead(II) in water samples is also proposed.

2. Materials and methods

2.1. Chemicals

Diazomacrocycles **1** and **2** (Fig. 1) were prepared according to the previously reported by us method [61,62]. The identity of chromoionophores was confirmed by the comparison of NMR and FT-IR spectra and TLC data with data for genuine samples of these compounds deposited in our lab.

All chemicals of the highest available purity were purchased from commercial sources and used without further purification. The complexation of metal cations was studied using appropriate nitrates: $NaNO_3$ ($\geq$99.8 %), KNO_3 ($\geq$99.8 %), $Mg(NO_3)_2 \times 6\ H_2O$ ($\geq$99.0 %), $Ca(NO_3)_2 \times 4\ H_2O$ ($\geq$99.0 %), $Ni(NO_3)_2 \times 6\ H_2O$ ($\geq$98.0 %), $Zn(NO_3)_2 \times 6\ H_2O$ ($\geq$98.0 %), $Al(NO_3)_3 \times 9\ H_2O$ ($\geq$98.0 %), $Cr(NO_3)_3 \times 9\ H_2O$ ($\geq$99.0 %), $Fe(NO_3)_3 \times 9\ H_2O$ ($\geq$98.0 %) from POCh, $Cu(NO_3)_2 \times 3\ H_2O$ ($\geq$99.5 %) from Merck, $Pb(NO_3)_2$ ($\geq$99.0 %) from Alfa Aesar

Table 1
Spectrophotometric linear response with equations, LOD and LOQ for optode **1** and **2** for bismuth(III) or lead(II).

Optode	Ion	Equation	R^2	Dynamic range [M]	LOD [M]	LOQ [M]
1	Bi (III)	y = 32,530.50 ×x + 0.0030	0.9995	7.13×10^{-7} – 1.50×10^{-5}	1.63×10^{-7}	5.38×10^{-7}
	Pb (II)	y = 22,902.52 ×x − 0.0017	0.9990	8.91×10^{-7} – 1.70×10^{-5}	2.31×10^{-7}	7.62×10^{-7}
2	Bi (III)	y = 27,465.62 ×x + 0.0053	0.9992	7.13×10^{-7} – 1.76×10^{-5}	1.71×10^{-7}	5.64×10^{-7}
	Pb (II)	y = 21,954.11 ×x + 0.0138	0.9987	8.91×10^{-7} – 2.02×10^{-5}	2.14×10^{-7}	7.06×10^{-7}

Table 2
Colorimetric linear response with equations, LOD and LOQ values for optode **1** and **2** for bismuth(III) or lead(II).

Optode	Ion	Equation	R^2	Dynamic range [M]	LOD [M]	LOQ [M]
1	Bi (III)	y = 8,402,510 ×x + 2.9592	0.9957	7.13×10^{-7} – 1.50×10^{-5}	3.03×10^{-7}	1.00×10^{-6}
	Pb (II)	y = 5,777,870 ×x + 2.3911	0.9972	8.91×10^{-7} – 1.70×10^{-5}	4.41×10^{-7}	1.46×10^{-6}
2	Bi (III)	y = 7,304,100 ×x + 0.0053	0.9982	7.13×10^{-7} – 1.76×10^{-5}	3.22×10^{-7}	1.06×10^{-6}
	Pb (II)	y = 5,895,590 ×x − 1.0959	0.9975	8.91×10^{-7} – 2.02×10^{-5}	3.99×10^{-7}	1.32×10^{-6}
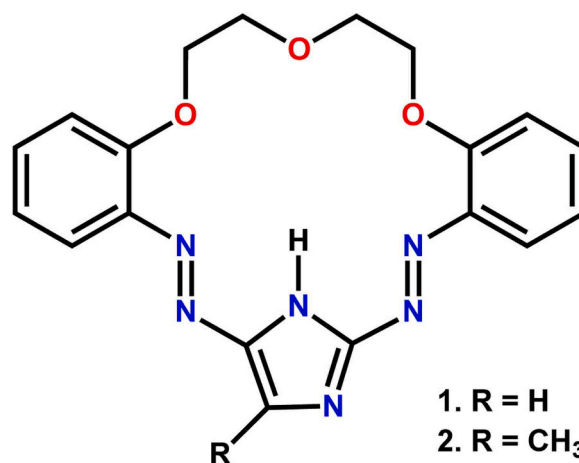
Fig. 1. Chromoionophores **1** and **2** [61,62].

and $Bi(NO_3)_3 \times 5\ H_2O$ ($\geq$98.0 %) from Sigma Aldrich. Dimethyl sulfoxide (DMSO), dichloromethane, acetone, 2-propanol, nitric acid, sodium hydroxide and disodium ethylenediaminetetraacetate dihydrate (EDTA) were purchased from POCh. All aqueous solutions were prepared using ultra-pure water obtained by the reverse osmosis (RO) from Hydrolab Poland station (conductivity <1 μS/cm^{-1}). For recovery studies Standard Reference Solution of bismuth(III) 1000 ppm and lead (II) 1000 ppm from Merck was used.

For the preparation of the receptor layers of optical sensors cellulose triacetate (CTA), triethylene glycol $\geq$ 99.0 % (TEG) and potassium tetrakis(4-chlorophenyl)borate $\geq$ 98.0 % (KTClPB) from Sigma Aldrich were used.

2.2. Instrumentation

All UV-Vis absorption spectra were registered in 1 cm quartz cuvettes (Starna® Brand) using a Unicam UV-300 spectrometer. pH was monitored using pH-meter CPC-511 with glass electrode EPS-1 (ELMETRON), standardized with buffer solutions. Portable LED light box ($23 \times 23 \times 23$ cm) was used to guarantee the reproducibility of the photos (PULUZ, Photography Light Box, Shenzhen Puluz Technology Limited). Pictures were taken by a Smartphone Vivo Y11s.

2.3. Complexation studies

Considering the possible application of macrocycles for the determination of metal ions in aqueous media, we have chosen a mixture of polar and protic solvent - water - with polar DMSO mixing freely with water as solvent. The 1:1 (v/v) ratio of these solvents ensures the

solubility of macrocyclic compounds, which are insoluble in water. The use of a mixture of organic solvent and water also ensures the solubility of bismuth salts. That's why metal cation complexation studies were carried out using UV-Vis titration in DMSO:water (v/v, 1:1) mixture. A series of solutions of pH values ranging from 1 to 10 was fixed by addition of small amounts of sodium hydroxide solution (0.1 M) or nitric acid (0.1 M). The stock solutions of chromoionophores ($\sim 10^{-4}$ M) and metal nitrates ($\sim 10^{-4}$ M) were prepared by weighting the respective quantities of them and dissolving in the solvent system in volumetric flasks. The values of binding constant (logK) were calculated with the use of OPIUM [63] program on the basis of titration experiment data. The stoichiometry of complexes was confirmed by Job's method [64].

2.4. Membrane preparation

CTA optodes were prepared according to previously described procedures [59,65]. Membranes contained 250.0 mg of CTA, 1.0 mg of chromoionophore **1** or **2**, 168.6 mg (150.0 µL) of TEG and 1.5 mg of KTClPB. All components of optodes were dissolved in dichloromethane (6 mL) with continuous stirring using a magnetic stirrer for 2 h and were sonicated for ca. 15 min – until a clear solution is formed. In the next step, solutions were poured on, prepared in advance (washed with nitric acid, deionized water, acetone and 2-propanol) Petri dish (9 cm diameter), covered loosely with a lid and left for solvent evaporation. After 24 h obtained optode films were peeled off from the Petri dish and cut into 0.9 × 4.5 cm strips. Blank membranes were prepared in an analogous way using all components besides chromoionophores and a lipophilic salt.

2.5. Absorbance measurements

Before measurements, membranes were washed three times with deionized water to remove water-soluble additives from the surface. Then membranes were placed in a quartz cuvette containing water (2.4 mL) in the sample path of the spectrophotometer. Measurements were carried out against blank membranes in the reference path of the spectrophotometer. Then the content of the measurement cell was titrated with a solution of bismuth(III) or lead(II) nitrate.

Limits of detection (LOD) for bismuth(III) and lead(II) were calculated using relationship: LOD $= 3\sigma/k$, where σ is the standard deviation of the blank and k is the slope of the linear function A = f(molar concentration of analyte). Limits of quantitation (LOQ) were approximated by multiplying the LOD by 3.3. The spectral response towards bismuth (III) and lead(II) was expressed as $\Delta A = A_{Bi/Pb} - A_0$, where A_0 stands for absorbance of optode with compound **1** or **2** and $A_{Bi/Pb}$ absorbance value of optode in the presence of bismuth(III) or lead(II) salt. The influence of interfering ions on spectrophotometric response towards bismuth(III) or lead(II) was expressed as the absolute value of relative response RR% = | $[(A - A_{Bi/Pb})/A_{Bi/Pb}] \times$ 100 %, where $A_{Bi/Pb}$ stands for absorbance of optode with diazocrowns in the presence of bismuth(III) or lead(II) nitrate and A is absorbance value of optode measured just after addition of interfering metal nitrate in the 10-fold molar excess in relation to bismuth(III) or lead(II) nitrate [59,65,66].

2.6. Digital color analysis

Pictures were analyzed using free software ImageJ [67–69]. The change of optode color given as ΔE_{RGB} [59,65,70–72] was calculated using the equation: $\Delta E_{RGB} = [(R_0 - R)^2 + (G_0 - G)^2 + (B_0 - B)^2]^{1/2}$ where R_0, G_0 and B_0 values correspond to color of optode in the absence of bismuth(III) or lead(II) salt, and R, G and B values correspond to color of optode in the presence of bismuth(III) or lead(II) ions.

3. Results and discussion

3.1. Investigation of the complexing properties in solution

In order to determine the ion complexing ability and the effect of the presence of metal ions on the spectroscopic characteristics of compounds **1** and **2**, a series of spectrophotometric titrations were carried out in a DMSO:water (v/v, 1:1) mixture. Changes in the absorption spectra of solutions of compounds **1** and **2** during titration with a solution of bismuth(III) and lead(II) nitrate in a mixture of DMSO:water (1:1, v/v) are shown in Fig. 2. The absorption maxima for **1** and **2** are located at 502 nm and 516 nm, respectively. In both cases, the presence of bismuth(III) or lead(II) salts results in a appearance of new, redshifted of 80 or 46 nm for **1** and 96 or 58 nm for **2**, band respectively for the complex with bismuth(III) or lead(II). The presence of a well-defined isosbestic point indicates the existence of one equilibrium under the conditions of spectrophotometric titration.

^{1}H NMR spectra of **2** (Fig. 3 and full range spectra Fig. S1-S3) registered in DMSO-d_6 indicate that the formation of the complex with bismuth(III), as expected, involves the coordination of metal ion by oxygen atoms of the oligoether chain which is manifested by downfield shift of signals labeled as a,a′ and b,b′. When spectrum is registered for 1:1 molar ratio of complex components, a double set of oligoether proton signals is observed pointing out that under measurement conditions complex of higher stoichiometry can be formed. The position of most signals of aromatic protons is unchanged, however an additional signal of low intensity at ~8 ppm is present. Single set of signals (with residual double set) is observed when the 10-fold excess of bismuth(III) nitrate was used in experiment. The signal of methyl group protons shifts + 0.26 ppm in complex, which points to the engagement of the nitrogen of the imidazole ring in complex formation (see Fig. S1-S3).

This can correlate with the results obtained from the analysis of the molar ratio curves obtained during the spectrophotometric titration (Fig. S4) and Job's plots (Fig. S5) on the basis of which a triple-decker complex (double sandwich complex 3:2 crown:bismuth(III)) can be proposed. The formation of the complex is accompanied by a change in the equivalence of the protons of the oligoether chain, which indicates the symmetry of the forming system. The spectrum recorded in the presence of a 10-fold excess of salt indicates that the formation of the complex may be accompanied by deprotonation of the imidazole ring. However, it cannot be ruled out that the signal of the N-H proton observed in the spectrum of compound **2** at 11.99 ppm (in the presence of an equimolar salt, a weakly visible signal in this region of the spectrum) is not visible in the spectrum of the complex due to the significant share of water in the analyzed sample derived from the hydrated salt.

The stability constants of the complexes were calculated using the OPIUM [63] software and titration data. For the assumed 3:2 crown: metal cation complexation model, stability constant values (logK) for bismuth(III) complexes of **1** and **2** are 17.51 ± 0.08 and 16.67 ± 0.06, respectively.

Molar ratio curves with lead(II) nitrate and Job's plot (Fig. S6 and Fig. S7) also allow to assume the formation of a triple-decker complex. This similar complexation model that was found for pyrrole bearing macrocyles [66]. The stability constants values (logK) of the complexes of compounds **1** and **2** with lead(II) are 17.10 ± 0.04 and 17.46 ± 0.03, respectively. Comparison of the stability constant values of the above complexes (Fig. 4) shows that both macrocycles form complexes with bismuth(III) and lead(II) of comparable stability. However for macrocycle **1** the binding constant for bismuth(III) is slightly higher than for **2**. On the other hand **2** binds lead(II) stronger than macrocycle **1**.

Complexation of bismuth(III) by chromogenic macrocyclic azo compounds is to our knowledge reported for the first time.

3.2. UV-Vis spectral characterization of optodes

The spectral properties of the prepared sensing materials (optodes)
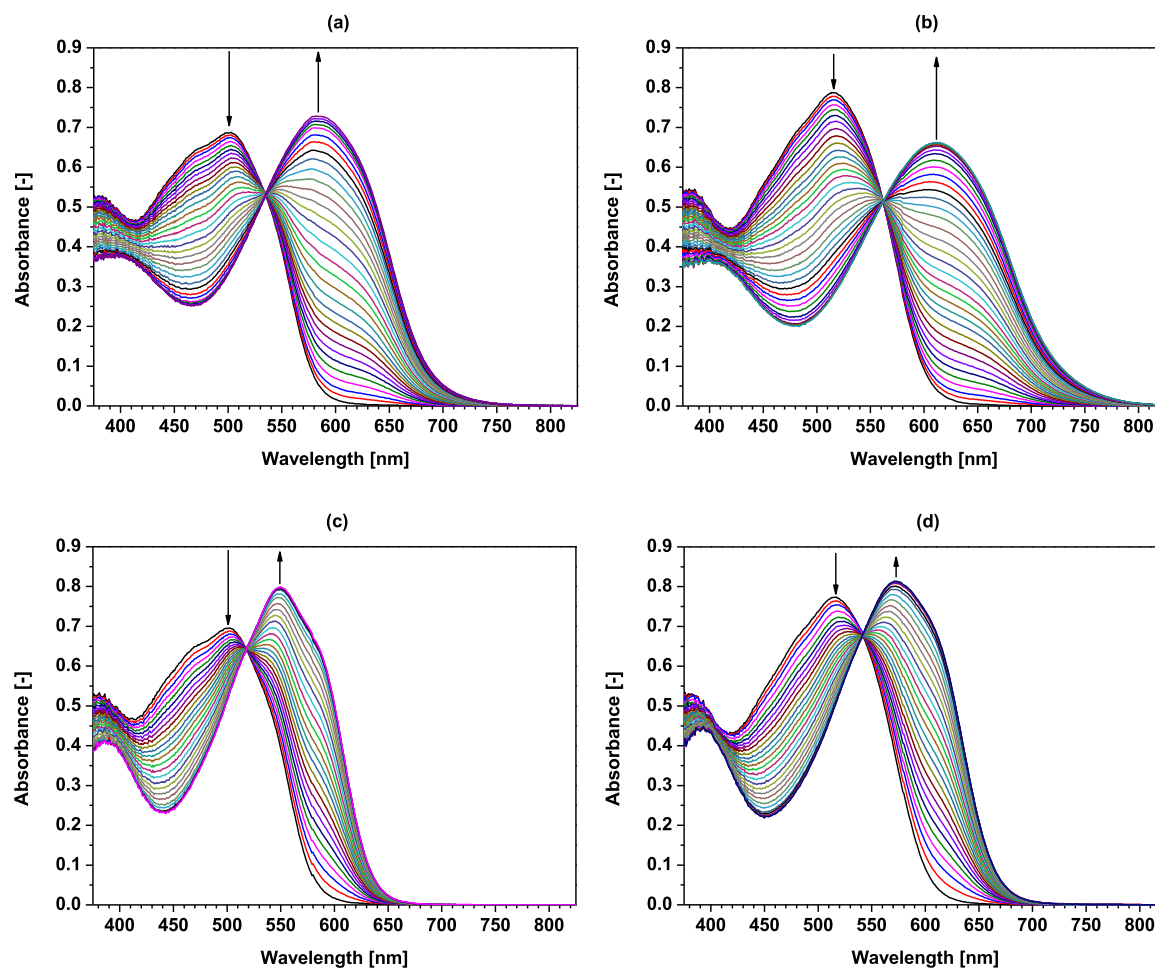
Fig. 2. Changes in the absorption spectra of chromoionophores during spectrophotometric titration with a solution of bismuth(III) nitrate: a) **1** ($c_1 = 4.10 \times 10^{-5}$ M) ($c_{Bi(III)} = 0 - 6.29 \times 10^{-5}$ M), b) **2** ($c_2 = 4.11 \times 10^{-5}$ M) ($c_{Bi(III)} = 0 - 7.91 \times 10^{-5}$ M); and with solution of lead(II) nitrate c) **1** ($c_1 = 4.10 \times 10^{-5}$ M) ($c_{Pb(II)} = 0 - 7.35 \times 10^{-5}$ M) and d) **2** ($c_2 = 4.11 \times 10^{-5}$ M) ($c_{Pb(II)} = 0 - 7.83 \times 10^{-5}$ M) in DMSO:water (1:1, v/v).
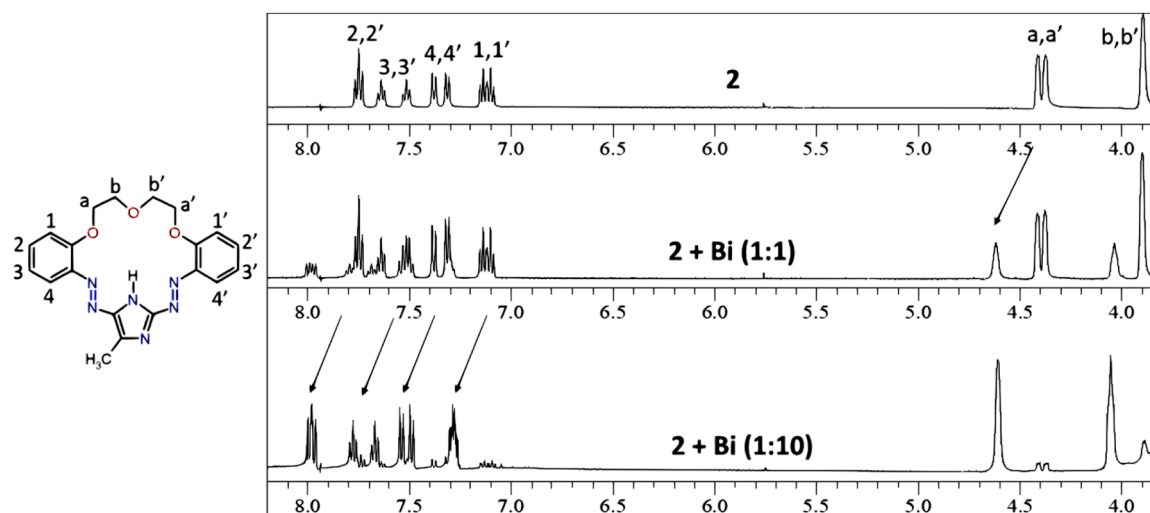
Fig. 3. ^{1}H NMR spectrum of **2** ($c_2 = 3.64 \times 10^{-3}$ M) and its spectra recorded in the equimolar amount and ten-fold excess of bismuth(III) nitrate in DMSO-d$_6$.

based on the macrocycles **1** or **2** and cellulose triacetate as polymer matrix have been studied. For preliminary studies the membranes were obtained without the addition of the lipophilic salt. In Fig. 5 changes in the absorption spectra of optodes in the presence of bismuth(III) and lead(II) nitrates in water are shown. The maximum of absorption for

optode with macrocycle **1** is located at 472 nm and for **2** at 502 nm. It shifts towards 587 (for **1**, Δ +115 nm) and 604 nm (for **2**, Δ +102 nm), when titrated with aqueous solution of bismuth(III) nitrate. Upon titration with aqueous solution of lead(II) nitrate the absorption bands are located at 550 (for **1**, Δ +78 nm) and 572 nm (for **2**, Δ +70 nm). The

Fig. 4. Comparison of the values of stability constants (logK) of bismuth(III) and lead(II) complexes (3:2) of macrocycles **1** and **2** in DMSO:water (1:1, v/v) solvent system.

nature of spectral changes for macrocycles entrapped in a polymeric matrix is similar to those which are observed for the corresponding systems in solution (Fig. 2), however it is worth to noting that the spectral bathochromic shifts observed upon metal cation complexation
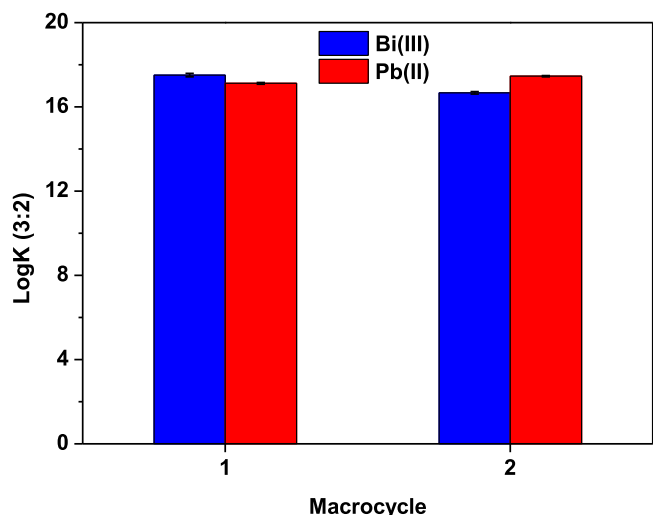
are higher for system entrapped in cellulose triacetate polymeric matrix than in DMSO:water solvent mixture. It can be connected with the competing interactions with the chemical environment, namely the polarity and hydrogen bonding affinity of the components. It can be assumed that the spectral changes observed for the optodes are the result of the formation by bismuth(III)/lead(II) complexes with chromoionophores **1** or **2** immobilized in the membranes.

3.2.1. The effect of lipophilic salt

The effect of the lipophilic salt - KTClPB - and its amount (0.5 – 3.0 mg) on parameters like: the value of the generated signal ΔA, time of response and the percentage of leaching of chromoinononophores from membranes (after ten times usage) was investigated. As a model system, optodes with macrocycle **1** were taken. Fig. S8a shows that the highest increase of optical signal, defined as ΔA, is obtained for membranes containing 2.0 mg of the KTClPB. The lipophilic salt content also affects the response time of optodes (Fig. S8b). In general, the response time is lower for bismuth(III) than for lead(II). The response time increases depending on the amount of lipophilic salt from 3 to 6 min for bismuth (III) and from 10 to 16 min for lead(II). The presence of lipophilic salt has also an effect on the stability of membranes regarding as leaching out of chromoionophore from the membrane. If the content of lipophilic salt is 1.5 or 2.0 mg the leaching percentage of chromoionophore from membranes is less than 2 % (Fig. S8c) after 10 regeneration cycles. Having in mind the previously proposed model of the lead(II) binding by pyrrole macrocycles entrapped CTA membranes [59] we assume the possible functioning mechanism of optodes for bismuth(III) (Eq.1) and
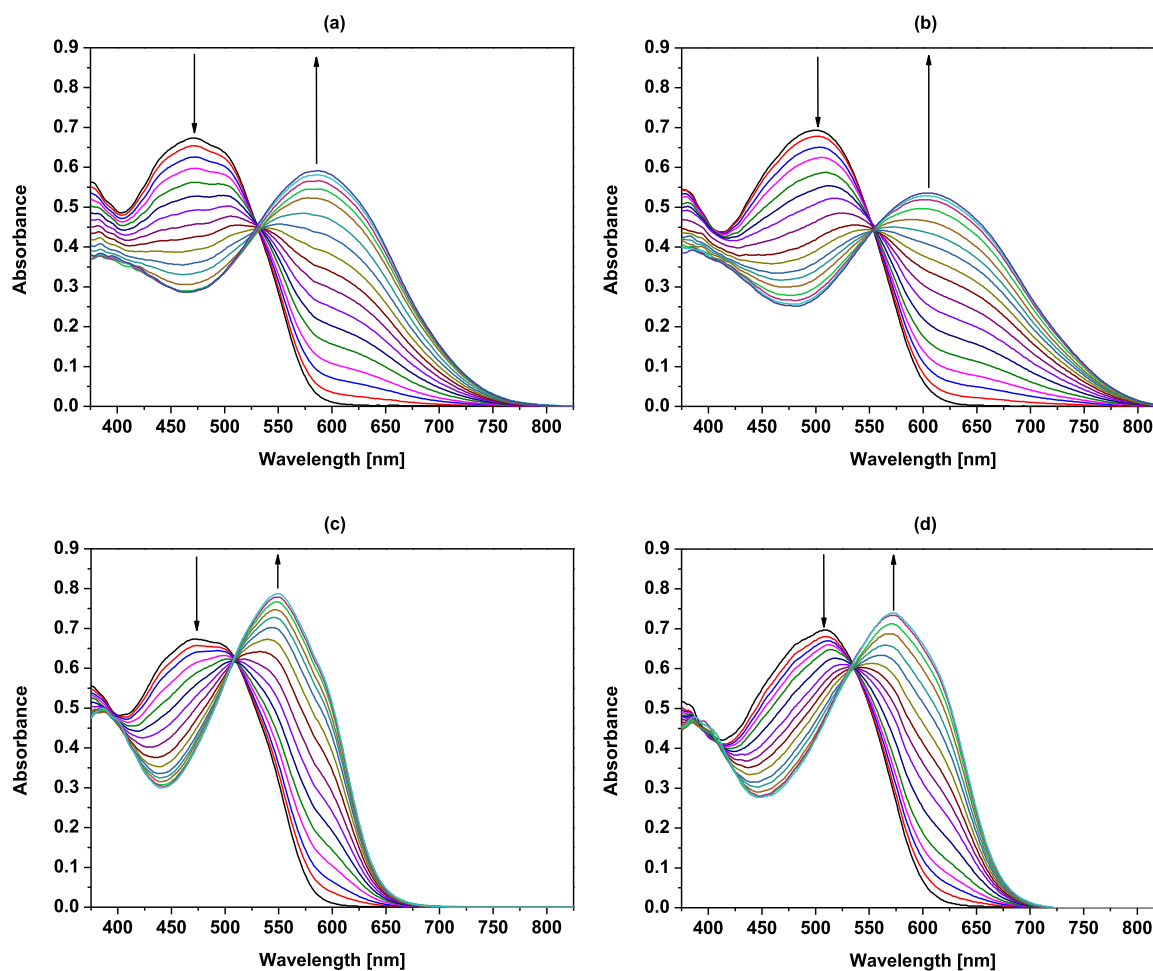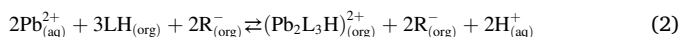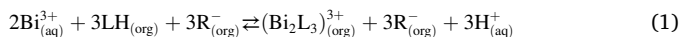

Fig. 5. Change of absorption spectra for optodes with macrocyclic derivatives **1** or **2** as chromoionophores upon titration with bismuth(III): a) **1** ($c_{Bi(III)} = 0 - 2.02 \times 10^{-5}$ M) and b) **2** ($c_{Bi(III)} = 0 - 2.14 \times 10^{-5}$ M); lead(II): c) **1** ($c_{Pb(II)} = 0 - 2.33 \times 10^{-5}$ M) and d) **2** ($c_{Pb(II)} = 0 - 2.33 \times 10^{-5}$ M).

lead(II) (Eq.2):

$$2Bi^{3+}_{(aq)} + 3LH_{(org)} + 3R^-_{(org)} \rightleftarrows (Bi_2L_3)^{3+}_{(org)} + 3R^-_{(org)} + 3H^+_{(aq)} \tag{1}$$

$$2Pb^{2+}_{(aq)} + 3LH_{(org)} + 2R^-_{(org)} \rightleftarrows (Pb_2L_3H)^{2+}_{(org)} + 2R^-_{(org)} + 2H^+_{(aq)} \tag{2}$$

It suggests chromoionophore (L)/lipophilic salt (R) ratio 1.0 and 1.5 with bismuth(III) and lead(II), respectively. Taking all above into account, 1.5 mg of lipophilic salt was selected for further testing of optodes. Membranes of such composition were investigated as described in the next sections.

3.2.2. Effect of pH

The influence of pH on the response of the optodes was tested by immersing the membranes in previously prepared solutions of lead(II) or bismuth(III) nitrates (1.05×10^{-5} M) of fixed pH, which were obtained by diluting with small amounts of solution of nitric acid (1.0 M) or sodium hydroxide (0.1 M). The constant response of the optodes in the pH 5 – 9 range and pH 6 – 9, respectively for bismuth(III) and lead(II) (Fig. 6)was found, thus pH 6 was chosen for further research. However, it is worth mentioning that it is possible to detect and determine bismuth(III) in the presence of lead(II) in an acidic environment (below pH 1) in which no spectral response for lead(II) is observed.

3.2.3. Response time of optodes

The response time t_{95} of the optodes was determined as the change of the generated signal (ΔA) over time (Fig. S9). The response time t_{95} for the optodes with compounds **1** and **2** at the bismuth(III) nitrate concentration of 1.05×10^{-5} M is 5 min. Longer response time 15 min was determined for optodes **1** and **2** after contact with solution of lead(II) nitrate. Response time of 5 min was taken for further testing of bismuth(III) ions and 15 min for lead(II).

3.2.4. Reversibility

The possibility of regeneration of optodes after use - to make them reusable - was checked using EDTA and HNO₃ (0.1 M) as regeneration solutions after contact with bismuth(III) or lead(II) salts (1.05×10^{-5} M) at pH 6, respectively. Regeneration time for optodes with compounds **1** and **2** was 2 min, when using EDTA and 1 min when for regeneration

HNO₃ was used. After regeneration, optodes were washed three times with deionized water. In Fig. S10 regeneration of optodes is shown. After ten cycles of immersion in bismuth(III) nitrate a drift of optical signal was less than 1.5 % and 1.2 %, for optodes with macrocycles **1** and **2**, respectively, and less than 1.9 % and 1.4 % after ten cycles with lead(II) salt for membranes with compound **1** and **2**, respectively. It means that optodes can be used without a loss of their properties at least ten times.

3.2.5. Repeatability and lifetime

The reproducibility of optodes was evaluated by comparing the ΔA values of the bismuth(III) and lead(II) loaded membrane samples obtained in the different series for concentration 1.05×10^{-5} M (Fig. S11). The relative standard deviations for the measured ΔA (n = 10) values, were 1.0 % and 1.4 % for optodes with crown **1**, 1.2 % and 1.5 % for optodes with crown **2**, after contact with bismuth(III) and lead(II) nitrates respectively.

The lifetime of all membranes was determined by immersing membranes in water solution and measuring the value of ΔA over time, i.e. after: 1, 2, 3, 7, 14, 21 and 28 days. No significant loss of signal was found. Membranes were found to be insensitive to sunlight after 28 days. Just prepared optodes and not used for measurements can be stored safely for a period of at least 3 months in a dry and dark place (room conditions) without losing their properties (Fig. S12).

3.2.6. Effect of interfering ions

The response of prepared optodes was investigated in the presence of several interfering metal ions: Na(I), K(I), Ca(II), Mg(II), Ni(II), Cu(II), Zn(II), Pb(II), Al(III), Cr(III), Fe(III), Bi(III). The influence of other ions on the generation of optical signal was expressed as RR% value and was realized as addition of 10-fold molar excess of interfering salt to a solution of bismuth(III) or lead(II) nitrates (1.05×10^{-5} M) in which the sensing material was immersed (Fig. 7). The effect of solution composition was measured as a generated signal given as ΔA. For bismuth(III) only in the presence of lead(II) RR% value exceeds 5 % for both optodes (RR% = 10.8 – 13.3 %). For lead(II) the most interfering ion was iron(III) (RR% = 53.2 – 72.6 %) and bismuth(III) (RR% = 96.8 – 208.3 %), but the first one can be masked by sodium fluoride.
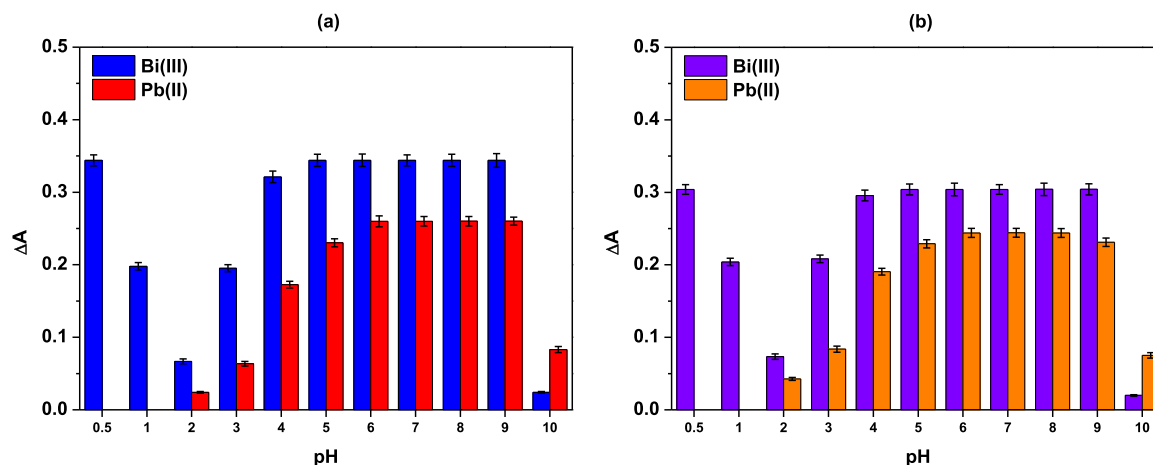

Fig. 6. Influence of pH on the response of the optodes with chromoionophores: a) **1** and b) **2**; towards bismuth(III) nitrate (1.05×10^{-5} M) and lead(II) nitrate (1.05×10^{-5} M) presence.
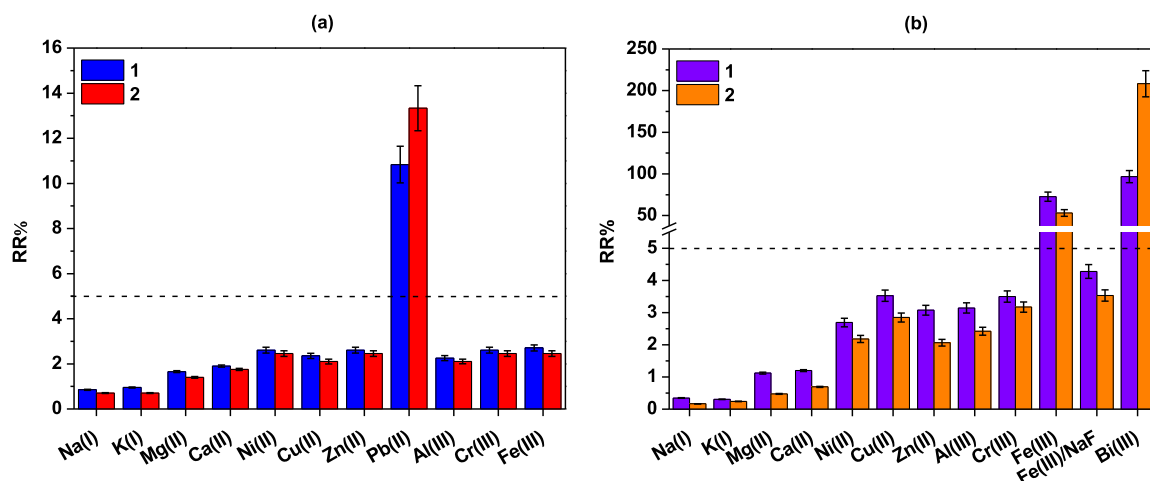
Fig. 7. Interferences from several metal cations (used in 10-fold molar excess), expressed as RR%, to spectral response (ΔA) of optodes with chromoionophores **1** and **2** towards: a) bismuth(III) and b) lead(II) nitrates.

3.3. Linear response range of membranes

The relationship: the value of the generated signal ΔA vs. the concentration of bismuth(III) or lead(II) for the membrane with compound **1** is presented in Fig. S13a and Fig. S13c. Fig. S13b and Fig. S13d show the change of the generated signal with the change of the concentration of bismuth(III) or lead(II) nitrates for membranes with macrocycle **2**. In Table 1 spectrophotometric linear response with equations, LOD and LOQ of optode **1** and **2** for bismuth(III) or lead(II) are collected.

3.4. Digital image colorimetry

Simultaneously with the studies of the spectral linear response of the optodes, the colorimetric analysis of the digital image was carried out. In Fig. 8 photos (taken using Smartphone) showing the color changes of the optodes after contact with aqueous bismuth(III) and lead(II) solutions (pH 6) are presented. In both cases, for both optodes, changes in the color of the membranes are well visible to the naked eye.

The dynamic range of the optodes, tested above spectrophotometrically, was determined as the dependence of the color change (ΔE_{RGB}) vs. concentration of bismuth(III) and lead(II) nitrates. The obtained

relationships are shown in Fig. S14 and summarized in Table 2. It is worth noting that with the comparable range of linear response and similar LOD values, the optode with compound **1** characterizes with more significant color change than the optode with compound **2**, which translates into greater sensitivity of the membrane for bismuth(III) (Table 2). The opposite situation takes place in the presence of lead(II) ions, because in this case the optode with compound **2** generates a higher color change value, which indicates a higher selectivity.

3.5. Dual detection

Additional tests were carried out to check the possibility of the simultaneous detection and determination of bismuth(III) and lead(II). For this purpose, spectrophotometric titration was carried out with a solution containing both bismuth(III) and lead(II) in a molar ratio of 1:1 (total concentration 1.13×10^{-5} M). Changes in the absorption spectra of solutions of macrocycles **1** and **2** upon the titration with the mixture Bi(III)/Pb(II) in the DMSO:water (1:1) mixture are shown in Fig. 9.

The spectral trace is in correlation with the changes of spectra obtained for sensing materials with chromoionophores **1** and **2** (Fig. 10). The obtained values of stability constants of complexes with bismuth

Fig. 8. Color change of the optodes with the compound: a) **1** and b) **2**; after contact with bismuth(III) and lead(II) nitrates of different concentrations in water.
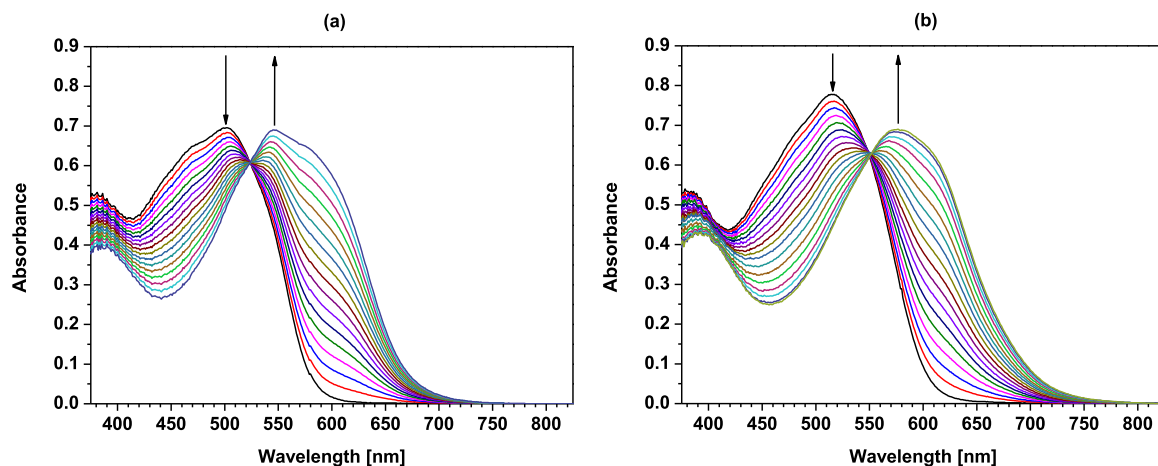
Fig. 9. Changes in the absorption spectra during spectrophotometric titration of **1** and **2** with bismuth(III) and lead(II) mixture: a) **1** ($c_1 = 4.10 \times 10^{-5}$ M) ($c_{Bi(III)/Pb(II)}$ = 0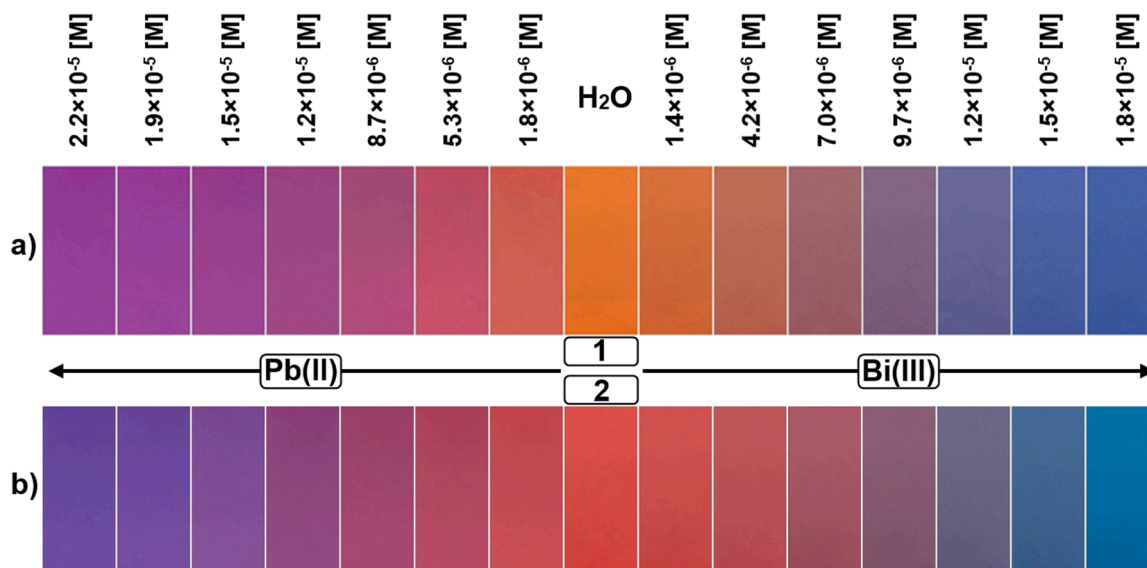 – 1.71×10^{-5} M) and b) **2** ($c_2 = 4.11 \times 10^{-5}$ M) ($c_{Bi(III)/Pb(II)}$ = 0 – 1.97×10^{-5} M) in DMSO:water (1:1) mixture.
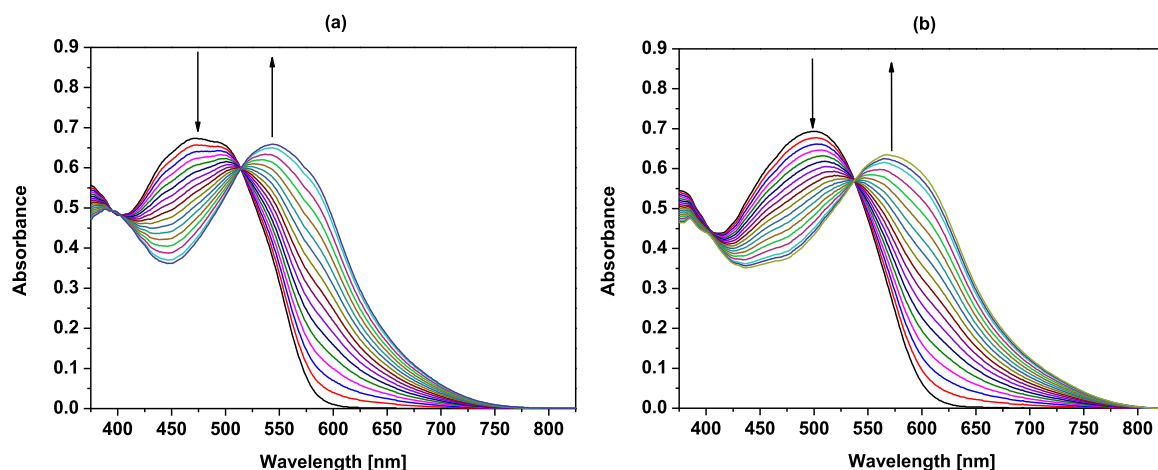
Fig. 10. Change of absorption spectra for optodes: a) **1** and b) **2**, in the presence of bismuth(III) and lead(II) ($c_{Bi(III)/Pb(II)}$ = 0 –1.09×10^{-5} M).

(III) and lead(II) are comparable, which means that both ions can effectively compete for binding sites of chromoionophores. During the titration, a new bathochromically shifted band is formed, the maximum of which is located at the wavelength corresponding to the maximum of lead(II) complex. However, the absorption band covers a broader spectral range - above 690 nm - which can correspond to the formation of a complex with bismuth(III) in the presence of lead(II). Therefore it can be assumed that the proposed system can be potentially regarded for

Table 3
Spectrophotometric linear response with equations, LOD and LOQ for optode **1** and **2** for dual detection of bismuth(III) and lead(II).

Optode	Ion	Equation	R^2	Dynamic range [M]	LOD [M]	LOQ [M]
1	Bi(III)	y = 10,574.87 ×x − 5.8280	0.9993	7.13×10^{-7} – 1.50×10^{-5}	5.00×10^{-7}	1.65×10^{-6}
	Pb(II)	y = 15,248.56 ×x + 8.1053	0.9982	8.91×10^{-7} – 1.70×10^{-5}	3.47×10^{-7}	1.15×10^{-6}
2	Bi(III)	y = 9604.91 ×x − 1.1736	0.9991	7.13×10^{-7} – 1.76×10^{-5}	4.88×10^{-7}	1.61×10^{-6}
	Pb(II)	y = 15,998.31 ×x − 5.1136	0.9981	8.91×10^{-7} – 2.02×10^{-5}	2.93×10^{-7}	9.67×10^{-7}

Table 4
Comparison of obtained optodes selective to bismuth(III) with already existing ones.

Sensing material	Support	Method	Dynamic range [M]	LOD [M]	LOQ [M]	Response time [min]	Reference
(2E,4E)− 5-(2,4-dinitrophenylamino)penta-2,4-dienal	PVC	Absorbance	9.6×10^{-7} – 2.9×10^{-4}	4.5×10^{-7}	1.5×10^{-6}	0.3	[43]
Methyltrioctylammonium chloride	CTA	Absorbance	3.4×10^{-6} – 4.8×10^{-5}	1.0×10^{-6}	3.3×10^{-6}	7	[44]
4-(4-nitrophenyl)− 1-naphthol	CTA	Absorbance	1.9×10^{-6} – 1.7×10^{-5}	6.7×10^{-7}	2.2×10^{-6}	0.5	[45]
Pyrocatechol violet	CTA	Absorbance	5.0×10^{-6} – 4.8×10^{-5}	8.5×10^{-7}	2.8×10^{-6}	10	[46]
Methyl thymol blue	Cellulose	Colorimetric	2.4×10^{-5} – 2.4×10^{-4}	1.4×10^{-5}	4.6×10^{-5}	10	[47]
1	CTA	Absorbance	7.1×10^{-7} – 1.5×10^{-5}	1.6×10^{-7}	5.3×10^{-7}	5	This work
		Colorimetric		3.0×10^{-7}	1.0×10^{-6}		
2	CTA	Absorbance	7.1×10^{-7} – 1.8×10^{-5}	1.7×10^{-7}	5.6×10^{-7}	5	This work
		Colorimetric		3.2×10^{-7}	1.1×10^{-6}		

dual detection bismuth(III) and lead(II) using the concentration dependence at two different analytical wavelengths values. One wavelength corresponds to the isosbestic point of the complex formed with bismuth(III). At this wavelength there is an increase in absorbance only in the presence of lead(II), namely at 532 and 554 nm, while the second one is 692 and 710 nm characteristic for bismuth(III) complex in the range where two bands do not overlap, for optode with compound **1** and **2**, respectively.

In Fig. S15 the range of linear response and comparison with the change of absorbance during spectrophotometric titration with individual ion salts at the wavelengths described above for a mixture of bismuth(III) and lead(II) is shown. These ranges overlap, which allows to determine the ranges of linear response for the concentrations of both analytes at the same time. Unfortunately, using colorimetric analysis, it was not possible to quantify bismuth(III) and lead(II) side by side. The dual sensing ranges of the linear response coincide with the ranges for single analytes, however, due to the smaller slopes of the characteristics, higher values of the detection limit are obtained (Table 3).

3.6. Comparison of optodes with other sensing materials

In Table 4 and Table 5 the properties of bismuth(III) and lead(II) selective optodes described in literature [43–59] are listed for comparison with the characteristics of membranes obtained in our studies. From this comparison it is quite well seen that optodes obtained by us are, in general, more or less comparable with those proposed by other authors.

3.7. Determination of bismuth(III) and lead(II) in model and real samples

Applications of the proposed optodes were tested using different samples: of known bismuth(III) and lead(II) concentrations – commercial bismuth(III) and lead(II) standard solution, and next spiked tap water from different regions of Northern Poland (3 series of 5 samples each). All measurements were done at pH 6. Both attempts were tested: spectrophotometric (ΔA) and colorimetric (ΔE_{RGB}) detection of bismuth (III) and lead(II), and ΔA for dual sensing of bismuth(III) with lead(II).

Comparison of recovery results obtained for optodes with chromoionophore **1** upon immersion of the sensor layer in Standard Reference Solution of bismuth(III) of different concentrations is collected in Table S1 and for optode with compound **2** in Table 6. The recoveries are at least about 98.92 – 101.56% for spectrophotometric detection (ΔA) for bismuth(III) in concentration range from 4.78×10^{-7} M to 9.57×10^{-6} M. Colorimetric determination is possible at the same concentration range with recovery 98.85 – 102.01 %. To evaluate the influence of the sample matrix three different samples of tap water were spiked with known concentration of bismuth(III). In this case recoveries are within 98.61 – 100.75 % for spectrophotometric detection (ΔA) and 98.80 – 101.02 % for colorimetric attempt (ΔE_{RGB}).

In Table S2 recovery results for obtained optodes with compound **1** after immersion in lead(II) solutions are presented and in Table 7 for optodes with chromionophore **2**. The recoveries in Standard Reference Solution of lead(II) are at least about 98.96 – 101.90% for ΔA and 98.18 – 100.85 % for ΔE_{RGB}. For samples of tap water spiked with lead(II) recoveries are 98.37 – 101.64 % for spectrophotometric detection and 99.05 – 101.74% for colorimetric detection.

Dual detection of bismuth(III) and lead(II) was possible only by using the spectrophotometric method. Comparison of recovery results are compiled in Table S3 an Table 8, respectively for optode **1** and **2**.

4. Conclusion

Easily available on non-complicated synthetic protocols, 18-membered chromogenic macrocycles bearing imidazole (**1**) or 4-methyl-imidazole (**2**) residues were investigated as bismuth(III) and lead(II) receptors in solution and after immobilization them in polymeric matrix (CTA). Investigated macrocycles are to our best knowledge the first

Table 5
Comparison of obtained optodes selective to lead(II) with already existing ones.

Sensing material	Support	Method	Dynamic range [M]	LOD [M]	LOQ [M]	Response time [min]	Reference
ETH 5435 + ETH 5418	PVC	Absorbance	$5.0 \times 10^{-9} - 5.0 \times 10^{-5}$	3.2×10^{-12}	1.1×10^{-11}	order of minutes	[48]
ETH 5493 + ETH 2439	PVC	Absorbance	$1.0 \times 10^{-7} - 5.0 \times 10^{-2}$	N/D	N/D	N/D	[49]
PAN + Dibenzodiaza-18-crown-6	PVC	Absorbance	$1.0 \times 10^{-8} - 5.0 \times 10^{-5}$	1.0×10^{-8}	3.3×10^{-8}	20	[50]
3′,3′,5,5′-Tetrabromophenolphthalein ethyl ester potassium salt + Dibenzo-18-crown-6	PVC	Absorbance	$1.0 \times 10^{-5} - 1.0 \times 10^{-4}$	8.0×10^{-6}	2.6×10^{-5}	15	[51]
2-amino-cyclopentene-1-dithiocarboxylic acid	CTA	Absorbance	$1.0 \times 10^{-6} - 5.0 \times 10^{-1}$	6.9×10^{-7}	3.8×10^{-6}	10	[52]
Diphenylcarbazone	PVC	Absorbance	$6.9 \times 10^{-6} - 1.1 \times 10^{-2}$	6.5×10^{-6}	2.1×10^{-5}	3	[53]
4-hydroxy salophen	CTA	Absorbance	$1.0 \times 10^{-7} - 1.0 \times 10^{-3}$	8.6×10^{-8}	2.4×10^{-7}	10	[54]
Lead ionophore IV + ETH 5294	PVC	Absorbance	$6.2 \times 10^{-8} - 5.0 \times 10^{-5}$	2.5×10^{-8}	8.3×10^{-8}	30	[55]
Dithizone	CTA	Absorbance	$2.4 \times 10^{-6} - 2.7 \times 10^{-5}$	7.3×10^{-7}	2.4×10^{-6}	11–15	[56]
Dithizone	Agarose	Absorbance	$1.2 \times 10^{-7} - 2.4 \times 10^{-6}$	4.0×10^{-9}	1.3×10^{-8}	28	[57]
Dithizone	Chitosan-Silica	Absorbance	$9.7 \times 10^{-7} - 5.3 \times 10^{-6}$	5.3×10^{-7}	1.7×10^{-6}	3	[58]
18-membered diazocrown with pyrrole residue	CTA	Absorbance	$8.1 \times 10^{-8} - 2.2 \times 10^{-5}$	1.2×10^{-8}	4.0×10^{-8}	7	[59]
		Colorimetric	$7.8 \times 10^{-7} - 2.1 \times 10^{-4}$	8.6×10^{-7}	2.8×10^{-6}		
1	CTA	Absorbance	$8.9 \times 10^{-7} - 1.7 \times 10^{-5}$	2.3×10^{-7}	7.6×10^{-7}	15	This work
		Colorimetric		4.4×10^{-7}	1.5×10^{-6}		
2	CTA	Absorbance	$8.9 \times 10^{-7} - 2.0 \times 10^{-5}$	2.1×10^{-7}	6.9×10^{-7}	15	This work
		Colorimetric		4.0×10^{-7}	1.3×10^{-6}		

Table 6
Determination of bismuth(III) by optodes with chromoionophore **2** in real samples and for commercial standard reference solution.

	Added Bi (III) [M]	Found Bi (III)					
		ΔA Bi (III) [M]	Recovery %	RSD %	ΔE_{RGB} Bi (III) [M]	Recovery %	RSD %
Standard Reference Solution of bismuth(III)	4.78×10^{-7}	4.85×10^{-7}	101.56	4.40	4.88×10^{-7}	102.01	6.61
	9.57×10^{-7}	9.47×10^{-7}	98.92	3.80	9.58×10^{-7}	100.07	2.86
	4.78×10^{-6}	4.77×10^{-6}	99.78	1.58	4.78×10^{-6}	99.95	2.15
	9.57×10^{-6}	9.58×10^{-6}	100.06	0.76	9.46×10^{-6}	98.85	1.72
Tap water 1	0	< LOD	-	-	< LOD	-	-
	4.78×10^{-7}	4.73×10^{-7}	99.02	7.62	4.78×10^{-7}	100.10	8.59
	9.57×10^{-7}	9.59×10^{-7}	100.19	4.39	9.67×10^{-7}	101.02	3.30
	4.78×10^{-6}	4.79×10^{-6}	100.29	1.76	4.80×10^{-6}	100.33	2.32
	9.57×10^{-6}	9.60×10^{-6}	100.31	0.88	9.48×10^{-6}	99.04	1.66
Tap water 2	0	< LOD	-	-	< LOD	-	-
	4.78×10^{-7}	4.61×10^{-7}	96.48	4.40	4.74×10^{-7}	99.15	5.38
	9.57×10^{-7}	9.35×10^{-7}	97.65	2.20	9.53×10^{-7}	99.59	4.19
	4.78×10^{-6}	4.76×10^{-6}	99.53	1.16	4.77×10^{-6}	99.85	2.01
	9.57×10^{-6}	9.56×10^{-6}	99.93	0.58	9.46×10^{-6}	98.80	1.57
Tap water 3	0	< LOD	-	-	< LOD	-	-
	4.78×10^{-7}	4.73×10^{-7}	99.02	7.62	4.78×10^{-7}	100.10	7.73
	9.57×10^{-7}	9.47×10^{-7}	98.92	6.59	9.58×10^{-7}	100.07	6.29
	4.78×10^{-6}	4.77×10^{-6}	99.78	2.75	4.78×10^{-6}	99.95	3.43
	9.57×10^{-6}	9.58×10^{-6}	100.06	1.32	9.46×10^{-6}	98.85	2.50

Table 7
Determination of lead(II) by optodes with chromoionophore **2** in real samples and for commercial Standard Reference Solution.

	Added Pb (II) [M]	Found Pb (II)					
		ΔA Pb (II) [M]	Recovery %	RSD %	ΔE_{RGB} Pb (II) [M]	Recovery %	RSD %
Standard Reference Solution of lead(II)	4.78×10^{-7}	4.71×10^{-7}	98.47	5.50	4.69×10^{-7}	98.18	5.42
	9.57×10^{-7}	9.41×10^{-7}	98.37	2.75	9.44×10^{-7}	98.66	3.71
	4.78×10^{-6}	4.78×10^{-6}	100.06	1.91	4.78×10^{-6}	100.07	2.42
	9.57×10^{-6}	9.58×10^{-6}	100.11	0.73	9.57×10^{-6}	99.96	1.34
Tap water 1	0	< LOD	-	-	< LOD	-	-
	4.78×10^{-7}	4.78×10^{-7}	100.06	8.25	4.75×10^{-7}	99.36	7.10
	9.57×10^{-7}	9.57×10^{-7}	99.95	4.47	9.50×10^{-7}	99.25	5.32
	4.78×10^{-6}	4.80×10^{-6}	100.37	1.88	4.81×10^{-6}	100.54	2.64
	9.57×10^{-6}	9.60×10^{-6}	100.27	1.10	9.58×10^{-6}	100.08	1.54
Tap water 2	0	< LOD	-	-	< LOD	-	-
	4.78×10^{-7}	4.86×10^{-7}	101.64	4.40	4.86×10^{-7}	101.72	4.10
	9.57×10^{-7}	9.72×10^{-7}	101.54	2.75	9.67×10^{-7}	101.03	3.07
	4.78×10^{-6}	4.75×10^{-6}	99.42	2.20	4.77×10^{-6}	99.83	2.43
	9.57×10^{-6}	9.50×10^{-6}	99.32	1.45	9.52×10^{-6}	99.49	1.41
Tap water 3	0	< LOD	-	-	< LOD	-	-
	4.78×10^{-7}	4.86×10^{-7}	101.64	5.50	4.81×10^{-7}	100.54	5.42
	9.57×10^{-7}	9.57×10^{-7}	99.59	4.76	9.56×10^{-7}	99.84	4.69
	4.78×10^{-6}	4.80×10^{-6}	100.37	1.46	4.78×10^{-6}	99.95	2.25
	9.57×10^{-6}	9.61×10^{-6}	100.43	0.48	9.59×10^{-6}	100.20	1.82

Table 8
Dual determination of bismuth(III) and lead(II) by optodes with chromoionophore **2** in real samples and for commercial Standard Reference Solution (1:1).

	Added Bi (III)/Pb (II) [M]	Found Bi (III)			Found Pb (II)		
		ΔA Bi (III) [M]	Recovery %	RSD %	ΔA Pb (II) [M]	Recovery %	RSD %
Standard Reference Solution of bismuth(III)and lead(II) (1:1)	9.57×10^{-7}	9.14×10^{-7}	95.56	6.28	9.49×10^{-7}	99.13	3.77
	4.78×10^{-6}	4.80×10^{-6}	100.45	4.36	4.78×10^{-6}	100.05	2.62
	9.57×10^{-6}	9.59×10^{-6}	100.22	1.73	9.60×10^{-6}	100.27	1.31
Tap water 1	0	< LOD	-	-	< LOD	-	-
	9.57×10^{-7}	9.84×10^{-7}	102.81	6.28	9.70×10^{-7}	101.31	6.53
	4.78×10^{-6}	4.84×10^{-6}	101.17	4.53	4.80×10^{-6}	100.49	2.72
	9.57×10^{-6}	9.63×10^{-6}	100.58	2.26	9.62×10^{-6}	100.48	1.36
Tap water 2	0	< LOD	-	-	< LOD	-	-
	9.57×10^{-7}	9.14×10^{-7}	95.56	8.62	9.28×10^{-7}	96.96	3.77
	4.78×10^{-6}	4.77×10^{-7}	99.72	4.53	4.76×10^{-6}	99.62	2.72
	9.57×10^{-6}	9.56×10^{-6}	99.85	2.26	9.57×10^{-6}	100.05	1.36
Tap water 3	0	< LOD	-	-	< LOD	-	-
	9.57×10^{-7}	9.49×10^{-7}	99.19	5.44	9.38×10^{-7}	98.04	3.27
	4.78×10^{-6}	4.77×10^{-6}	99.72	3.52	4.76×10^{-6}	99.62	2.51
	9.57×10^{-6}	9.59×10^{-6}	100.22	2.88	9.60×10^{-6}	100.27	2.13

described in literature macrocyclic azo derivatives selectively binding bismuth(III). Satisfactory linear relationship between the value of the generated optical signal and the concentration of bismuth(III) and lead (II) optodes at pH 6 was obtained (the range depends on the chromoionophore used). It was also found that it is possible to detect and determine bismuth(III) and lead(II) ions using color measurement applications for mobile devices. Spectrophotometric measurements characterize with lower values of the limit of detection compared to colorimetric measurements based on the measurement of the color change of photos. Membranes with compound **1** generate a greater change in absorbance, and thus also a greater change in color in the presence of bismuth(III) than in the case of compound **2**, which translates into greater sensitivity in the detection and determination of this analyte. The opposite situation takes place in the presence of lead(II), because in this case the optode with compound **2** generates a greater change in absorbance and in color change.

Although the scope of the work in this manuscript does not include studies of the potential use of the described macrocycles in nuclear medicine, we believe they are worthy of such consideration (once the toxicity of the ligands has been determined) by teams specializing in such issues.

CRediT authorship contribution statement

Błażej Galiński: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing; **Ewa Wagner-Wysiecka**: Conceptualization, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Both authors** discussed the results and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2023.134798.

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