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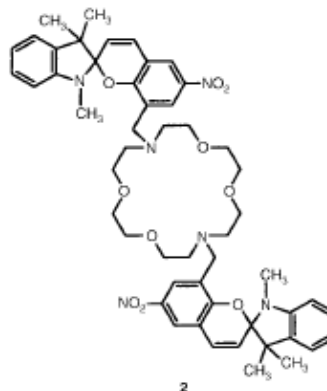
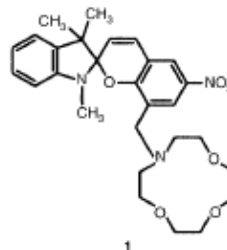
Metal-ion complexation of crown ether derivatives incorporating one and two spirobenzopyran units was investigated by electrospray ionization mass spectrometry. The crowned spirobenzopyran derivatives exhibited very different metal ion-complexing behavior from their corresponding parent crown ether rings, preferring multivalent to monovalent metal ions owing to the additional ionic interaction with the nitrophenolate anion of the merocyanine moiety. The on-line photochemical reaction for mass spectrometry indicated that the metal ion-complexing ability and ion selectivities of the crowned spirobenzopyrans can be switched photochemically, taking advantage of the difference between the spiroopyran and merocyanine isomers.

Introduction

Macrocyclic polyethers, crown ethers, form complexes with metal ions such as alkali and alkaline-earth metal ions and the complex formation can be studied by various analytical methods. Mass spectrometry is a useful analytical approach for studying crown ether-metal complexes owing to their ionic properties.¹⁻⁴ High-energy ionization, such as electron ionization (EI), often causes the fragmentation of crown ether complexes, which makes it difficult to detect the complex metal ions as pseudomolecular ions. Softer ionization techniques, such as fast atom bombardment (FAB) and electrospray (ES) ionization, alleviate the fragmentation. Specifically, electrospray ionization mass spectrometry (ESI-MS) can afford pseudomolecular ions of crown ether-metal complexes with little or no fragmentation.⁵⁻⁷

We have been engaged in the design of photochromic crown ethers, aiming at photochemical control in the metal-ion complexation of crown ethers. For instance, crown ether derivatives carrying one and two spirobenzopyran units (crowned spirobenzopyrans) undergo photoinduced complexation switching of monovalent and divalent metal ions, respectively, which has been studied by absorption spectroscopy and ionic conductivity measurements.⁸⁻¹² Recently, we also started to apply ESI-MS to study competitive metal-ion complexation of crowned spirobenzopyrans under dark conditions and also to obtain direct evidence for the photoinduced changes of metal ion-complexing ability.¹³

This paper deals with ESI-MS studies of metal-ion complexation of crowned spirobenzopyrans **1** and **2** under dark and photoirradiated conditions. The metal ion-complexing behavior of **2** was compared with that for its parent crown ether **3**. Photoinduced complexation switching between monovalent and multivalent metal ions was also demonstrated by using ESI-MS with an interface for on-line photoirradiation.



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This paper deals with ESI-MS studies of metal-ion complexation of crowned spirobenzopyrans 1 and 2 under dark and photoirradiated conditions. The metal ion-complexing behavior of 2 was compared with that for its parent crown ether 3. Photoinduced complexation switching between monovalent and multivalent metal ions was also demonstrated by using ESI-MS with an interface for on-line photoirradiation.

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merocyanine form of 1, its phenolate anion interacts strongly with the metal ion in its crown ether moiety (Scheme 1).

The additional binding of the merocyanine phenolate anion modifies the metal ion-complexing behavior of the parent crown ether moiety of 1, monoaza-12-crown-4, dramatically. Competitive metal ion-complexing abilities of crowned spirobenzopyran 1 under dark conditions were first followed by ESI-MS. For alkali metal ions, crowned spirobenzopyran 1 can bind

Experimental

Li⁺ most strongly, the cation-complexing ability decreasing in the order Li⁺ > Na⁺ > K⁺ [Fig. 2(a)]. The high Li⁺ affinity

Materials

reflects the ionic interaction with the phenolate anion and also the size fit to the 12-crown-4 moiety. Crowned spirobenzopyran derivatives 1 and 2 were prepared according to a procedure reported elsewhere.^{9,11,14} Diaza-18-crown-6 (3) was purchased from Aldrich (Milwaukee, WI, USA). Metal nitrates were of analytical-reagent grade. Acetonitrile was purified by distillation over P

2

O

5

It is worth noting that crowned spirobenzopyran 1 forms comparably stable complexes with multivalent metal ions [Fig. 2(b) and (c)]. Crowned spirobenzopyran 1 forms complexes with alkaline-earth metal ions such as Mg²⁺ and Ca²⁺ and it can also complex trivalent metal ions such as La³⁺ and Eu³⁺. Significant peaks assigned to the 1 complexes of other multivalent metal ions (Pb²⁺, Zn²⁺, Cd²⁺, Cu²⁺, Co²⁺, Ni²⁺ and

Measurements

Fe³⁺) were hardly observed in ESI-MS. In ESI-MS using the corresponding parent crown ether, monoaza-12-crown-4, in-

A sector-type mass spectrometer (JEOL-D300; JEOL, Tokyo, Japan) connected with a laboratory-made ESI interface was used to obtain ESI-MS spectra. A sample solution was sprayed with a flow rate of 0.15 cm³ h⁻¹ at the tip of a needle applied by a voltage 3.5 kV higher than that of a counter-electrode. Heated nitrogen was applied between the needle and the counter-electrode to enhance desolvation of the charged droplets sprayed. The resulting ions were then introduced into the

stead of 1, distinct complex formation could not be detected owing to the relatively poor metal ion-complexing ability.

Crown ethers generally possess an affinity to alkali and alkaline-earth metal ions owing to the ion-dipole interaction.¹⁵ Some affinity of crowned spirobenzopyran 1 to multivalent metal ions can be attributed to the additional ionic interaction between the phenolate anion and the metal ion in the crown ether ring (Scheme 1). However, the metal ion-complexing

vacuum system through the first and second skimmers of the mass analyzer. The pressures of differential pumping stages were about 1 and 1.3 × 10⁻² Torr, respectively. A rotary pump and a mechanical booster pump in their region were floating electrically to depress discharge. The voltage of the first skimmer was the same as that of the counter-electrode and was 50 V higher than that of the second skimmer.

Unless stated otherwise, the solutions for mass spectrometry contained an equimolar amount (1.3 × 10⁻⁴ mol dm⁻³) of a crowned spirobenzopyran and metal salts (1.3 × 10⁻⁴ mol dm⁻³ each in the case of metal salt mixtures) in a solvent without any additive for promoting ionization.

Photoirradiation was applied in situ on a glass capillary containing an acetonitrile solution by using visible light (> 500 nm), which was obtained by passing light from a 500 W Xe lamp equipped with a quartz waveguide through a Toshiba Y-50 color filter. The quartz glass interface for on-line photoirradiation consisted of a 14 mm length capillary part and a 3 mm diameter ball part. A stainless-steel syringe needle of 0.7 mm id was inserted into the glass interface for applying an

Fig. 1 Absorption spectra of acetonitrile solutions containing crowned spirobenzopyran 1 and a metal ion in an equimolar amount under dark conditions. [1] and [metal nitrate] = 1.3 × 10⁻⁵ mol dm⁻³.

electric voltage. Absorption spectra were taken with an acetonitrile solution containing an equimolar amount (1.3 × 10⁻⁵ mol dm⁻³) of a crowned spirobenzopyran and a metal salt.

Results and discussion

Metal-ion complex formation of crowned spirobenzopyran **1** under dark conditions

The spirobenzopyran derivative incorporating a monoaza-12-crown-4 moiety at the 8-position is almost colorless in acetonitrile under dark conditions. On addition of a metal salt to the solution in an equimolar amount, a new absorption peak was found between 500 and 600 nm, the absorbance depending on the kind of metal ion (Fig. 1). The appearance of the absorption peak indicates that the spirobenzopyran moiety of **1** isomerizes to its corresponding merocyanine form by the metal-ion complexation of the crown ether moiety. Multinuclear NMR spectrometry⁹ has proved that, in the metal ion complexes of the

Scheme 1

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Absorbance

00400

1-metal ion complex

500 600

700

CA3 "CH3

2-metal ion complex

o.c.s.r.s.b.u.p//:p.t.t.h.n.o.0.0.0.2.y.a.M.2.2.n.o.d.e.h.s.i.l.b.u.P

Its ability of 1 is not very high, taking account of the appearance of

affinity strong peaks for the protonated species of 1 in the mass

bis(spirobenzo- spectra.

pyran) 2 is derived from the intramolecular ionic interaction of a high charge density metal ion in its crown ether ring with the two phenolate anions of its merocyanine moiety, that is, 'two-

the 2 bis(spirobenzopyran) 2 under dark conditions

complex of a small divalent ion, Mg^{2+} , and only a tiny peak for the complex of a small trivalent lanthanide ion, Eu^{3+} , in the In

pyran units (2), the two spirobenzopyran units can be expected

intra- to isomerize to their corresponding merocyanine form and to

interact with the metal ion in the crown ether moiety

Ca^{2+} simultaneously. Therefore, the metal ion-complexing behavior

of crowned bis(spirobenzopyran) 2 may be more dramatic than

merocyanine that of 1. Crowned bis(spirobenzopyran) 2 showed similar

absorption spectral changes to 1 on addition of an equimolar

case for amount of metal salt to its acetonitrile solution under dark

La^{3+} conditions.¹² Multivalent metal ions such as La^{3+} and Ca^{2+}

with afforded much more intense absorption based on the mero-

for [2 + cyanine form of the spirobenzopyran monovalent ions such as Li^+ .

moieties of 2 than

La^{3+} (NO

3

A competitive ESI-MS study suggested that the metal ion- complexing selectivity for crowned bis(spirobenzopyran) 2 is very different from that for 1 (Fig. 3). The crowned bis(spiro- benzopyran) forms much more stable complexes with Ca^{2+} than with monovalent metal ions such as Na^+ and K^+ , as illustrated in Fig. 3(a). Of the divalent metal ions, Cd^{2+} and Pb^{2+} can be bound to 2 less stably than Ca^{2+} [Fig. 3(b)]. It is of interest to compare the peak intensities among the trivalent and divalent metal ions [Fig. 3(c)]. The 2- La^{3+} complex shows a much more intense peak than those of Ca^{2+} and Eu^{3+} .

For comparison, similar competitive MS was carried out with the parent crown ether of 2, diaza-18-crown-6 (3) (Fig. 4). Peaks

is to be expected, of course, that such an anomalous

to the multivalent metal ions in the crowned

point' ionic interaction. However, there was no peak for

the diaza-18-crown-6 derivative carrying two spirobenzo- mass spectrum. Therefore, stable complex formation by

crowned bis(spirobenzopyran) 2 requires not only an

molecular ionic interaction but also adequate size fit of the

crown ether moiety of 2 to given metal ions. In the 2-

complex, the positive charge of the metal ion is probably

canceled out by the two phenolate anions of its

moieties, as suggested by the observation of a single peak

assigned to [2 + Ca^{2+}] in the mass spectrum. This is the

the 2 complexes of trivalent metal ions. Also, in the 2-

complex, the two phenolate anions interact powerfully

La^{3+} in the crown ether ring.¹³ The single intense peak

assigned to the crown ether complexes of Na⁺, K⁺ and Ca²⁺ were observed, but significant peaks for the complexes of the other metal ions could hardly be detected. The metal-ion selectivity of 3 is as expected from the conventional crown ether chemistry, i.e., the affinity to alkali and alkaline-earth metal ions and the size fit to the crown ether ring cavity.¹⁵

2) indicates clearly that a nitrate anion also participates in the complex formation for electric charge cancellation.

The present MS findings, especially the high affinity of crowned bis(spirobenzopyran) 2 to multivalent metal ions La³⁺ and Ca²⁺, is supported strongly by ¹H NMR studies reported

Fig. 2 Competitive ESI-MS of acetonitrile solutions of crowned spirobenzopyran 1 and a mixture of metal nitrates under dark conditions. [1] and [metal nitrate] = 1.3 × 10⁻⁴ mol dm⁻³. (a) Li⁺-Na⁺-K⁺ system; (b) Li⁺-Na⁺-Mg²⁺-Ca²⁺ system; (c) Li⁺-Na⁺-La³⁺-Eu³⁺ system.

Fig. 3 Competitive ESI-MS of acetonitrile solutions of crowned bis(spirobenzopyran) 2 and a mixture of metal nitrates under dark conditions. [2] and [metal nitrate] = 1.3 × 10⁻⁴ mol dm⁻³. (a) Na⁺-K⁺-Ca²⁺ system; (b) Ca²⁺-Cd²⁺-Pb²⁺ system; (c) Ca²⁺-La³⁺-Eu³⁺ system.

Fig. 4 Competitive ESI-MS of acetonitrile solutions of diaza-18-crown-6 (3) and metal (Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺) nitrates under dark conditions. [3] and [metal nitrate] = 1.3 × 10⁻⁴ mol dm⁻³.

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intensity

1200

ion-complexing elsewhere.¹² This means that the competitive ESI-MS technique

behavior, their spirobenzopyran

moieties are is a useful means for screening metal-ion complexation of

not isomerized to the corresponding merocyanine. One

can crown ether derivatives.

therefore expect to switch the metal ion-complexing ability and ion selectivities of crowned spirobenzopyrans 1 and 2 by photoirradiation. Photocontrol of metal-ion complexation with crowned

For instance, a mass spectrum of an acetonitrile

solution spirobenzopyrans

containing equimolar amounts of 1 and LiNO

3

As mentioned above, crowned spirobenzopyran derivatives 1 and 2 undergo complex formation with metal ions, which is accompanied by the isomerization of their spirobenzopyran moieties to the corresponding merocyanine form even under dark conditions. Visible-light irradiation of acetonitrile solutions containing a crowned spirobenzopyran and a metal ion decreased the intensity of the absorption peaks assigned to its merocyanine form. This means that the merocyanine moiety is forced to isomerize back to the corresponding spiropyran form by the photoirradiation even in the presence of a metal ion. The visible light-induced isomerization of the merocyanine moiety to the spiropyran form, in turn, eliminates or alleviates the intramolecular ionic interaction in the metal-ion complexes of crowned spirobenzopyrans. It is considered that the spirobenzopyran moiety of 1 and 2 itself hardly interacts with the metal ions complexed by their crown ether moieties. Crowned spirobenzopyran derivatives 1 and 2 should, therefore, be similar to their corresponding parent crown ethers in their metal

under dark conditions shows a strong peak of an Li⁺ complex, [1 + Li]⁺, and a tiny peak of a protonated species, [1 + H]⁺. On-line visible-light irradiation changed the mass spectrum with a decrease in the peak ratio of [1 + Li]⁺ to [1 + H]⁺. The significant decrease in the peak ratio indicates that the Li⁺-complexing ability of 1 is diminished by the photoinduced isomerization back to its spiropyran form. Such a photoinduced change in the metal ion-complexing ability is greater in the 2–Ca²⁺ system, as demonstrated in Fig. 5. The photoirradiation decreased the peak ratio of [2 + Ca]²⁺ to [2 + H]⁺, which suggests a marked decrease in the Ca⁺-complexing ability of crowned bis(spirobenzopyran) 2.

As shown in the mass spectra, crowned bis(spirobenzopyran) 2 prefers multivalent to monovalent metal ions, whereas its parent crown ether 3 prefers the latter to the former metal ions. Photoinduced switching of ion selectivity is, therefore, feasible with the photochromic crown ethers, taking advantage of the ion-selectivity difference between their spiropyran and mero-

Fig. 5 Photoinduced mass spectral change for acetonitrile solution containing crowned bis(spirobenzopyran) 2 and Ca²⁺, (a) under dark conditions and (b) after visible-light (> 500 nm) irradiation for 20 min. [2] and [Ca(NO

3

Fig. 6 Photoinduced mass spectral change for acetonitrile solution containing crowned bis(spirobenzopyran) 2, K⁺ and La²⁺, (a) under dark conditions and (b) after visible-light (> 500 nm) irradiation for 20 min. [2]

)

2

] = 1 3 1024 mol dm⁻³.

and mol dm⁻³.

[La(NO

3

] = 1 3 1023

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)

3

] = 1.3 × 10²⁵ mol dm⁻³; [KNO

3

Scheme 2

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Intensity

cyanine forms. An example is presented in Fig. 6. In a mass spectrum of an acetonitrile solution containing an equimolar amount of La^{3+} and K^{+} in addition to 2, a single large peak for the 2- La^{3+} complex was seen and a significant peak for the K^{+} complex was hardly detected. In the presence of a 100-fold concentration of K^{+} together with La^{3+} , however, an ion peak for the 2- K^{+} complex could be detected, as shown in Fig. 6(a). Mass spectra were taken immediately after visible-light (> 500 nm) irradiation of an acetonitrile solution of 2 at a glass ESI-MS interface. With on-line visible-light irradiation, the peak ratio of the 2 complexes of La^{3+} and K^{+} was significantly decreased, as shown in Fig. 6(b). The ion selectivity of 2 can definitely be switched from La^{3+} to K^{+} to a great extent by photoirradiation, as shown schematically in Scheme 2. Turning off the light rapidly restored the high La^{3+} selectivity of 2.

In conclusion, the competitive ESI-MS technique suggests that crowned spirobenzopyran derivatives 1 and 2 exhibit a higher affinity to multivalent than to monovalent metal ions owing to the powerful intramolecular ionic interaction of the metal ion in the crown ether moiety with phenolate anion(s) of the merocyanine moiety. Turning on and off visible light led to photochemical switching in the metal ion-complexing ability and ion selectivity of the crowned spirobenzopyran derivatives.

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