Influence of Introduced Substituents on the Anion-selectivity of [14]Tetraazaannulene Complexes

Takayo MORIUCHI-KAWAKAMI,[†] Minako OBITA, Toshiki TSUJINAKA, and Yasuhiko SHIBUTANI

Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, 5-16-1 Omiya, Asahi, Osaka 535-8585, Japan

Nickel(II) complexes of [14]tetraazaannulene derivatives incorporating aromatic rings into their azaannulene framework were synthesized, and the anion-selectivity of the [14]tetraazaannulene nickel complexes **1**–**4** was evaluated by potentiometric measurements with solvent polymeric membrane electrodes. All of the [14]Tetraazaannulene nickel complexes, except **3**, were found to exhibit high selectivity for the I[−] ion over the SCN[−] ion, although considerable interference of the ClO₄[−] ion was observed in all **1**–**4** complexes. Concerning the anion-selectivities of **1** and **4**, the incorporation of naphthalene rings into the azaannulene framework decreased not only the interference of the ClO₄[−] ion but also the I[−] ion-selectivity over the SCN[−] ion. Comparison studies between the dibenzotetraaza[14]annulene nickel complexes **1**–**3** indicated that differences in the attached substituents of the [14]tetraazaannulene nickel complexes greatly influenced the ion-selectivity as ionophores. According to our computational results, the ionophoric properties of [14]tetraazaannulene nickel complexes **1**–**4** were influenced by their electrostatic properties rather than their topological properties.

Keywords [14]Tetraazaannulene, nickel complex, anion-selectivity, substituent effect, ion-selective electrode, DFT calculation, topological property, electrostatic property

(Received April 28, 2015; Accepted June 23, 2015; Published September 10, 2015)

Introduction

Aza-crown ethers exhibit binding selectivity for specific cations, and this characteristic has led to their widespread use. The ionophoric properties of aza-crown ether derivatives are largely governed by the nature of the incorporated heteroatoms and the number of ring members. In analytical chemistry, aza-crown ether derivatives have been used in solvent extractions, sorptions in chromatography, ion-selective electrodes (ISEs), and separations.¹ The ISE responds to the activity (concentration) of the sensed ion in the tested solution.^{2,3} The potentiometric liquid membrane for the ISE includes an ionophore that captures a specific ion more tightly than other ions. Aza-crown ethers as ionophores of ISEs have attracted much attention due to their facile design as analytical reagents for the target ions.^{1,4–6}

Cyclam (1,4,8,11-tetraazacyclotetradecane) is a 14-membered azacrown ether containing four nitrogen atoms. Various cyclam derivatives have been designed as ion recognition compounds.⁷ Although the unsubstituted cyclam works as a highly selective and efficient carrier for the transport of the Pb²⁺ ion,^{8,9} the introduction of various substituents on the nitrogen atoms of the cyclam can significantly vary the ion-selectivity. For example, the introduction of the tosyl (*p*-toluenesulfonyl)¹⁰ and 2-pyridylmethyl^{11,12} groups as substituents into the cyclam led to the formation of complexes with high Ni²⁺ and Cu²⁺ ion-selectivities, respectively. Furthermore, fluoroionophores for

the Hg²⁺ and Zn²⁺ ions were synthesized by the introduction of 1-pyrenyl acetamide,¹³ 1*H*-isochromen-1-one¹⁴ and methylbenzimidazole¹⁵ as substituents into the cyclam. Interestingly, the number of benzyl groups as introduced substituents on the nitrogen atoms of the cyclam determined the Cu²⁺, Ag⁺ or non ion-selectivity.¹⁶ On the other hand, the ethylene cross-bridged of cyclam derivatives improved the Cu²⁺ ion-selectivity.¹⁷ Moreover, the introduction of C=O groups and benzene rings into the carbons of the cyclam backbone induced anion-selectivity.¹⁸ Likewise, ISEs based on cyclam derivatives have been developed as cation sensors.^{11,19–22} Although ISEs based on a cyclam derivative with four 2-pyridylmethyl groups as substituents showed good ion-selectivity for the Cu²⁺ ion,^{11,22} this result seems to depend greatly on the nature of the 2-pyridylmethyl groups. The ISE based on a cyclam derivative with two benzene rings into the carbons of the cyclam backbone also exhibited good ion-selectivity for the Cu²⁺ ion.²¹ Moreover, there are also a few ion-selective electrodes based on cyclam derivatives and complexes for anion sensing.^{23–26} The ISEs based on a cyclam derivative with four *n*-octyl groups as substituents showed anion-selectivity for the ClO₄[−] and CH₃(CH₂)₅OSO₃[−] ions.^{25,26} The ClO₄[−] and I[−] ion-selectivities were observed by ISEs based on the Cu(II), Co(II) and Ni(II) complexes of cyclams with four and three *n*-octyl groups as substituents.^{23,24} In general, anion-selective ISEs exhibit roughly the same selectivity sequence with preference of lipophilic anions and rejection of hydrophilic anions (Hofmeister lyotropic anion selectivity sequence).²⁷ Therefore, ISEs based on Co(II) and Ni(II) complexes of a cyclam with three *n*-octyl groups are attractive due to their I[−]-selectivity (non-Hofmeister selectivity

[†] To whom correspondence should be addressed.
E-mail: takayo.moriuchi@oit.ac.jp

patterns).

[14]Tetraazaannulene (1,8-dihydro-[1,4,8,11]tetraazacyclotetradeca-2,4,6,9,11,13-hexaene) is a 14-membered azaannulene containing four nitrogen atoms, which is an analog of the cyclam. [14]Tetraazaannulene derivatives have more rigid molecular structures than cyclam analogs due to the C=N and C=C bonds in the azaannulene framework. Hence, [14]tetraazaannulene complexes are expected to be good candidates for ionophores of anion-selective ISEs. In fact, ISEs based on Ni(II) and Zn(II) complexes of [14]tetraazaannulenes have been reported as I⁻, SCN⁻, and ClO₄⁻-selective electrodes.²⁸⁻³⁰ These facts encouraged us to investigate the anion-selectivities of other [14]tetraazaannulene nickel complexes as ISE ionophores. In this study, we have focused on the design of [14]tetraazaannulene nickel complexes with two aromatic rings incorporated into the azaannulene framework for anion sensing. To investigate the topological and electrostatic influences of the introduced substituents on anion-selectivity, four [14]tetraazaannulene Ni(II) complexes were synthesized. Three compounds were nickel(II) complexes of [14]tetraazaannulenes incorporating benzene rings into the azaannulene framework (**1**–**3**), resulting in dibenzo[*b,i*][14]tetraazaannulene derivatives; one was nickel(II) complexes of [14]tetraazaannulene incorporating naphthalene rings (**4**), resulting in the dinaphtho[*b,i*][14]tetraazaannulene derivative. The anion selectivities of these [14]tetraazaannulene nickel complexes were evaluated by potentiometry with the ISEs. The topological and electrostatic properties of these [14]tetraazaannulene nickel complexes were investigated by DFT calculations at the B3LYP/6-31+G* level.

Experimental

Reagents and chemicals

All reagents were commercially available in the highest grade and used for the syntheses of [14]tetraazaannulene nickel complexes as such unless otherwise specified. Methyl alcohol and ethyl alcohol were dried over molecular sieve 4 Å. All reactions were carried out under dry nitrogen. Tetrahydrofuran (THF) was dried over sodium and distilled for the preparation of potentiometric polymeric membranes. High-molecular-weight PVC was twice purified in MeOH. Aqueous solutions were prepared with double quartz-distilled water and salts of the highest purity available.

Apparatus

The ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz, respectively. Samples for NMR spectra were examined in CDCl₃ and CD₂Cl₂ solutions at 25.0°C on a Varian 300 MHz NMR spectrometer (XL-300). Chemical shifts are given in δ (ppm) relative to deuterated solvents (¹³C NMR) or to TMS (¹H NMR) as an internal standard. IR spectra were run in KBr disks on a Shimadzu FTIR-8600 spectrometer. High-resolution mass (HRMS) spectra (positive mode of FAB mass) were recorded on a JEOL JMS-DX-303.

Syntheses

[14]Tetraazaannulene nickel(II) complexes were prepared by the standard method³¹⁻³³: the reaction of an aromatic 1,2-diamine and a β-diketone was performed in the presence of Ni(II).

To 50 mL of dry methanol was added Ni(CH₃COO)₂ tetrahydrate (4.9 g), acetylacetone (4.0 g) and *o*-phenylenediamine (4.3 g). The reaction mixture was refluxed under nitrogen for 2 h. After cooling in an ice bath, the filtrate was removed and the formed greenish-black solid was washed thoroughly with

cold methanol. Further purification was performed by silica gel column chromatography with CH₂Cl₂, resulting in 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) **1** (1.5 g) in 19% yield; greenish-black powder; mp, 245–256°C. ¹H NMR (CDCl₃): δ 2.09 (s, 12H), 4.86 (s, 2H), 6.53–6.73 (m, 8H). ¹³C NMR (CDCl₃): δ 22.0, 113.1, 120.9, 121.8, 147.3, 155.4.

To 15 mL of dry methanol was added Ni(CH₃COO)₂ tetrahydrate (1.59 g), 1-phenyl-2,4-butanedione (1.64 g) and *o*-phenylenediamine (1.08 g). The reaction mixture was refluxed under nitrogen for 48 h. After cooling in an ice bath, the filtrate was removed and the formed greenish-black solid was washed thoroughly with cold methanol. Further purification was performed by silica gel column chromatography with hexane:ethyl acetate = 8:1, resulting in 5,12-dimethyl-7,14-diphenyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) **2** (0.64 g) in 26% yield; greenish-black powder. ¹H NMR (CDCl₃): δ 2.21 (s, 6H), 5.02 (s, 2H), 5.57–5.60 (m, 2H), 5.92–5.96 (m, 2H), 6.63–6.66 (m, 2H), 6.83–6.85 (m, 2H), 7.32–7.34 (m, 2H). ¹³C NMR (CDCl₃): δ 22.7, 112.5, 120.7, 121.2, 121.7, 122.3, 128.3, 128.3, 128.5, 138.7, 147.0, 147.2, 156.4, 156.5. IR (KBr): 1518, 1464, 1398, 741, 700 cm⁻¹. HRMS(FAB+): *m/z* calcd. for C₃₂H₂₆N₄Ni, 524.1511; found 524.1509.

To 15 mL of dry methanol was added Ni(CH₃COO)₂ tetrahydrate (1.86 g), 3-phenyl-2,4-butanedione (1.77 g) and *o*-phenylenediamine (1.08 g). The reaction mixture was refluxed under nitrogen for 4 days. After cooling in an ice bath, the filtrate was removed and the obtained green solid was washed thoroughly with cold methanol. Further purification was performed by washing with acetonitrile, resulting in 6,13-diphenyl-5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) **3** (0.03 g) in 1% yield; green powder. ¹H NMR (CD₂Cl₂): δ 1.74 (s, 12H), 6.53–6.56 (m, 4H), 6.63–6.66 (m, 4H), 7.22–7.32 (m, 6H), 7.38–7.42 (m, 4H). ¹³C NMR (CD₂Cl₂): δ 22.6, 121.9, 122.0, 122.2, 126.7, 129.0, 132.5, 143.4, 148.4, 155.3. IR (KBr): 1533, 1447, 1360, 748, 706 cm⁻¹. HRMS(FAB+): *m/z* calcd. for C₃₄H₃₀N₄Ni, 552.1824; found 552.1828.

To 15 mL of dry methanol was added Ni(CH₃COO)₂ tetrahydrate (1.59 g), acetyl acetone (0.58 g) and 2,3-diaminonaphthalene (1.01 g). The reaction mixture was refluxed under nitrogen for 48 h. After cooling in an ice bath, the filtrate was removed. The obtained greenish-black solid was washed thoroughly with cold methanol, and vacuum dried to give 5,7,12,14-tetramethyl-dinaphtho[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) **4** (0.15 g) in 9% yield; greenish-black powder. ¹H NMR (CDCl₃): δ 2.28 (s, 12H), 5.04 (s, 2H), 7.04 (s, 4H), 7.23 (dd, 4H, *J* = 6.00 and 3.30), 7.47–7.50 (m, 4H). ¹³C NMR (CDCl₃): δ 22.3, 110.5, 117.2, 124.6, 126.8, 129.8, 145.7, 155.9. IR (KBr): 1545, 1445, 1389, 743 cm⁻¹. HRMS(FAB+): *m/z* calcd. for C₃₀H₂₆N₄Ni, 500.1511; found 500.1515.

Preparation of ion-selective electrode membranes

The composition of the potentiometric liquid membranes used was 2.5 mg (2.0 wt%) of [14]tetraazaannulene, 37.3 mg of poly(vinyl chloride), and 87.4 mg of *o*-nitrophenyl octyl ether (*o*-NPOE) as a plasticizer. No additional salt was employed for the potentiometric anion-sensing membranes to investigate the original anion selectivity of [14]tetraazaannulene nickel complexes **1**–**4**. The components were put into a 5 mL sample glass tube and dissolved in *ca.* 3 mL of THF entirely. A potentiometric polymeric membrane was obtained by evaporating of THF.

Fig. 1 Synthesized [14]tetraazaannulene nickel complexes.

EMF measurements and evaluations

Potentiometric liquid membranes were formed on the tip of the ISE body assembly with an electrode kit (DKK Co., Ltd., Tokyo, Japan) by a casting method. The obtained polymer membrane-based ISE was then conditioned in an aqueous 0.01 M KCl solution overnight. EMF measurements were performed on cells of type Ag–AgCl | 3.3 M KCl || 0.1 M CH₃COOLi | sample solution || membrane || 0.01 M KCl | AgCl–Ag using a pH/mV meter equipped with a double junction type Ag–AgCl reference electrode. The activity coefficients were calculated according to the Davies equation.³⁴ All test solutions were made from potassium salts without any pH-adjusting buffer reagent. The selectivity coefficients, K_{ij}^{pot} , where i is the primary ion (I^-) and j is the interfering ion, were determined by the fixed interference method (FIM).²

Computational studies

All of the computational calculations were performed using the program Spartan'14 for Windows (Version 1.1.2).³⁵ As preliminary experiments, optimized geometries of metal-free [14]tetraazaannulenes were investigated by PM3 semi-empirical calculations^{36,37} from the start conformation optimized with MMFF program. DFT calculations of [14]tetraazaannulene nickel complexes were carried out with B3LYP functional in combination with 6-31G* basis sets.³⁸

Results and Discussion

The aim of this study is to investigate the substituent effect of [14]tetraazaannulene nickel complexes **1–4** on the anion-selectivities. To evaluate their anion selectivities of [14]tetraazaannulene nickel complexes **1–4** as ionophores of ISEs, a series of [14]tetraazaannulene nickel complexes bearing methyl and phenyl groups as well as benzene and naphthalene rings was prepared, as illustrated in Fig. 1.

Electrode performance

The synthesized [14]tetraazaannulene nickel complexes **1–4** were applied as ionophores for polymer membrane-based ISEs. The contents employed as ionophores was 2.0 wt% each, and 2-nitrophenol (*o*-NPOE) was used as the membrane solvent. Preliminary experiments by the single solution method (SSM)² showed that ISEs incorporating [14]tetraazaannulene nickel complexes **1**, **2** and **4** but not **3** responded more strongly to the I^- ion than to other anions, although ISEs by applying the 0.1 M H₃PO₄ buffered solution have showed the selectivity for the ClO₄⁻ ion.²⁸ The I^- ion was, therefore, chosen as the primary ion for calculations of the selectivity coefficients. ISEs incorporating

Fig. 2 EMF responses of solvent polymeric membrane electrodes based on [14]tetraazaannulene nickel complexes for the I^- ion: ●, using **1**; ○, using **2**; ▲, using **3**; ■, using **4**.

[14]tetraazaannulene nickel complexes **1–4** were conditioned in KCl solutions and EMF measurements were carried out in increasing KI concentrations. As shown in Fig. 2, ISEs incorporating [14]tetraazaannulene nickel complexes **1–4** exhibited apparently super-Nernstian responses³⁹ to I^- -activity changes. For example, the ISE incorporating [14]tetraazaannulene nickel complex **4** displayed a linear response of the I^- ion over an activity range of $10^{-2.5}$ – $10^{-1.1}$ M and a calibration slope of -83.1 mV decade⁻¹. The potential responses of ISEs based on [14]tetraazaannulene derivatives **1–4** would be similar to that of ISEs based on metalloporphyrins.^{39,40} No interference effects of the HPO₄²⁻, H₂PO₄⁻ or SO₄²⁻ ion were observed on all ISEs incorporating [14]tetraazaannulene nickel complexes **1–4**.

Fig. 3 Selectivity coefficients of electrodes based on [14]tetraazaannulene nickel complexes **1–4** (determined by the fixed interference method (FIM)).

Ion-selectivity

The selectivity coefficients of the ISEs based on [14]tetraazaannulene nickel complexes **1–4** against a series of anions were evaluated using the fixed interference method (FIM).² The selectivity coefficients against ClO_4^- , SCN^- , NO_3^- , Br^- , Cl^- and AcO^- ions were examined using aqueous potassium salt solutions. No selectivity coefficients against HPO_4^{2-} , H_2PO_4^- and SO_4^{2-} ions were measured, since no interference of these ions was observed in experiments with the single solution method (SSM). Figure 3 compares the selectivity coefficients of ISEs based on [14]tetraazaannulene nickel complexes **1–4** with different substituents. The ISE based on [14]tetraazaannulene nickel complexes **1**, **2** and **4** recognized the I^- ion as the primary ion reasonably well, except for the ClO_4^- ion, even when some other anion was present. The selectivity coefficient ($\log k_{\text{I,X}}^{\text{Pot}}$) values of the [14]tetraazaannulene nickel complexes **1**, **2** and **4** lie in the range of -0.13 to -5.34 for the anions except the ClO_4^- ion. Moreover, this indicates that, against the ClO_4^- and SCN^- ions, the selectivity was highest for the I^- ion of the ISEs based on **2**. The ISE based on **1** also showed good I^- ion-selectivity against the examined anions, except for the ClO_4^- ion. However, the selectivity for the I^- ion of the ISEs based on **3** was inferior to that for the SCN^- ion.

[14]Tetraazaannulene nickel complexes **1**, **2** and **3** incorporate two benzene rings into their azaannulene framework at the same positions. In contrast to complex **1**, [14]tetraazaannulene nickel complexes **2** and **3** have two attached phenyl groups, which are attached at different positions of the azaannulene framework. The difference in the attached positions of the introduced substituents significantly influenced the ion selectivity of the [14]tetraazaannulene nickel complexes. On the other hand, complex **4** incorporates two naphthalene rings into its azaannulene framework, although **1** and **4** have four methyl groups attached at the same positions of their azaannulene framework. The selectivity for the I^- ion against the SCN^- ion of the ISEs based on **4** was inferior to that of the ISEs based on **1**. The difference in the incorporated aromatic rings also influenced the ion-selectivity of the complexes. From potentiometric investigations, it was confirmed that both the incorporated and attached substituents influenced the ionophoric properties of [14]tetraazaannulene nickel complexes **1–4**.

Computational studies

In order to understand the topological and electrostatic properties, DFT calculations of the [14]tetraazaannulene nickel complexes were carried out with the B3LYP functional in

Fig. 4 DFT-optimized structures and dipole moments of [14]tetraazaannulene nickel complexes.

Fig. 5 Isosurfaces of LUMO wave functions (isosurfaces at 0.032 au) for [14]tetraazaannulene nickel complexes.

combination with 6-31G* basis sets.³⁸ As preliminary experiments, optimized conformations of metal-free [14]tetraazaannulenes were investigated by PM3 semi-empirical calculations^{36,37} first optimized with the MMFF program. The calculations yielded saddle-shaped structures of metal-free [14]tetraazaannulenes with the PM3 semi-empirical method. Likewise, DFT calculations demonstrated that all [14]tetraazaannulene nickel complexes **1–4** have saddle-shaped structures. The obtained DFT-optimized structures of [14]tetraazaannulene nickel complexes **1–4** are illustrated together with their dipole moments in Fig. 4, and correspond well with their reported X-ray structures.^{41–43} Regardless of the kind of incorporated or attached substituent, the optimized structures of [14]tetraazaannulene nickel complexes **1–4** strongly resembled each other. It is known that dibenzotetraaza[14]annulene nickel complexes without any substituents on the azaannulene framework have planar structures.⁴⁴ On the other hand, dibenzotetraaza[14]annulene nickel complexes with substituents on the C atom adjacent to the N atom of the azaannulene framework have saddle-shaped structures due to their steric interactions with the *ortho* aromatic hydrogens of the two benzene rings.^{31,45,46} Hence, the obtained computational results seem to be reasonable. As can be seen from the obtained structures, the steric difference caused by the introduced substituents was little observed between the [14]tetraazaannulene nickel complexes **1–4**. One of the reasons will be that aromatic rings and phenyl groups are flat and do not create a valid steric hindrance.

Lowest unoccupied molecular orbital (LUMO) analysis shows which regions of a molecule are most electron deficient. Hence, the shape of the LUMOs in the [14]tetraazaannulene nickel complexes can anticipate interactions with the negative I[−] ion.⁴⁷ We have plotted the isosurfaces of LUMO wave functions (isosurfaces at 0.032 au) and the molecular electrostatic potential (ESP) (isosurfaces at 0.002 au) for [14]tetraazaannulene nickel

Table 1 Calculated total energies (in a.u.), HOMO and LUMO energies (in eV) and molecular dipole moments (in debye) of [14]tetraazaannulene nickel complexes at the B3LYP/6-31+G* level

Complex	Total energies/a.u.	HOMO/eV	LUMO/eV	Dipole moments/D
1	−2578.85788	−4.49	−1.57	0.84
2	−2962.33151	−4.53	−1.75	1.08
3	−3040.94732	−4.48	−1.60	0.91
4	−2886.14996	−4.69	−1.59	1.38

complexes **1–4** in Figs. 5 and S1 (Supporting Information). The isosurfaces of the LUMOs and ESPs for complexes **1–4** were found to strongly resemble each other, although different patterns between their isosurfaces were caused by the substituent effect. The calculated total energies (in a.u.), HOMO and LUMO energies (in eV) and molecular dipole moments (in debye) of the [14]tetraazaannulene nickel complexes at the B3LYP/6-31+G* level are summarized in Table 1. The evident difference in the HOMO–LUMO gap energies and molecular dipole moments between complexes **1–4** was confirmed from the data of Table 1. According to these computational results, the difference in the anion selectivities between the ISEs based on [14]tetraazaannulene nickel complexes **1–4** may be produced from electrostatic properties rather than topological properties, caused by the introduced substituents.

Moreover, DFT calculations for the formation of the complex between [14]tetraazaannulene nickel complex **1** and the I[−] ion were carried out with the B3LYP functional in combination with 6-31G* basis sets. DFT calculations suggested that the complex of derivative **1** with the downside I[−] ion (−2590.33052 au) will be more stable than that with the upside I[−] ion (−2590.32460 au) (Fig. 6). Further, the ($E_{\text{HOMO}} - E_{\text{LUMO}}$) gap⁴⁸ of the downside complex between derivative **1** and the I[−] ion (−1.43 eV) was

Fig. 6 DFT calculation for the complexes of derivative **1** with the upside and downside I^- ions.

more negative than that of the upside complex between derivative **1** and the I^- ion (-1.37 eV). Therefore, the preferable orientation of the I^- ion for the interaction is assumed to be the downside of the saddle-shaped structure of the [14]tetraazaannulene nickel complexes **1**–**4**. Compared with this result, the [14]tetraazaannulene iron and cobalt complexes have formed the upside complexes with the Cl^- ions.⁴⁹

Conclusions

This is the first report concerning investigations on the influence of introduced substituents on the anion-selectivity of [14]tetraazaannulene nickel complexes by potentiometry and DFT calculations. Nickel(II) complexes **1**–**4** of [14]tetraazaannulene derivatives incorporating benzene and naphthalene rings into their azaannulene framework and attached methyl and phenyl groups on the framework were prepared. The anion-selectivity of these [14]tetraazaannulene nickel complexes **1**–**4** was evaluated by potentiometric measurements with solvent polymeric membrane electrodes. The ISEs based on complexes **1**–**4** displayed non-Hofmeister selectivity patterns: [14]tetraazaannulene nickel complexes **1**, **2** and **4** but not **3** were found to exhibit high selectivity for the I^- ion over the SCN^- ion, although considerable interference of the ClO_4^- ion was observed in all [14]tetraazaannulene nickel complexes **1**–**4**. The potentiometric experimental results indicated that the difference in the introduced substituents of the nickel complexes greatly influenced the ion-selectivity as ionophores. DFT calculations demonstrated that all [14]tetraazaannulene nickel complexes **1**–**4** have saddle-shaped structures and strongly resemble each other. Moreover, DFT calculations exhibited the difference in the HOMO-LUMO gap energies and molecular dipole moments between complexes **1**–**4**, although the I^- ion showed preference for the underside of saddle-shaped structures for all interactions. According to these experimental results, the difference in the anion-selectivities between the ISEs based on [14]tetraazaannulene nickel complexes **1**–**4** may be due to their electrostatic properties rather than their topological properties, caused by the introduced substituents.

Acknowledgements

This study was supported in part by a Grant-in-Aid for Scientific Research (C) (Grant No. 25410155 to T. M.-K.)

Supporting Information

Supplementary data includes the ESP maps and HOMO-LUMO

structures. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. Y. A. Zolotov, “*Macrocyclic Compounds in Analytical Chemistry* (Chemical Analysis 143)”, **1997**, John Wiley and Sons, New York, Chichester, Weinheim, Brisbane, Singapore, Toronto.
2. E. Bakker, P. Bühlmann, and E. Pretsch, *Chem. Rev.*, **1997**, 97, 3083.
3. E. Bakker and M. T. Diaz, *Anal. Chem.*, **2002**, 74, 2781.
4. T. Araki and H. Tsukube, “*Liquid Membranes: Chemical Applications*”, **1990**, CRC Press, Boca Raton, Florida.
5. P. Bühlmann, E. Pretsch, and E. Bakker, *Chem. Rev.*, **1998**, 98, 1593.
6. Y. Umezawa, “*CRC Handbook of Ion-Selective Electrodes: Selectivity Coefficients*”, **1990**, CRC Press, Boston.
7. E. Kimura, *Tetrahedron*, **1992**, 48, 6175.
8. S. Y. Kazemi and A. S. Hamidi, *J. Chem. Eng. Data*, **2011**, 56, 222.
9. G. Khayatian and F. Esmaeily, *Indian J. Chem. Technol.*, **2012**, 19, 409.
10. M. Calligaris, O. Carugo, G. Crippa, G. D. Santis, M. D. Casa, L. Fabbri, A. Poggi, and B. Seghi, *Inorg. Chem.*, **1990**, 29, 2964.
11. B. B. Petković, M. Milčić, D. Stanković, I. Stambolić, D. Manojlović, V. M. Jovanović, and S. P. Sovilj, *Electrochim. Acta*, **2013**, 89, 680.
12. L. M. P. Lima, D. E. Gómez, R. Delgado, C. P. Iglesias, and R. Tripiet, *Inorg. Chem.*, **2012**, 51, 6916.
13. S. H. Kim, J. S. Kim, S. M. Park, and S. K. Chang, *Org. Lett.*, **2006**, 8, 371.
14. S. Voutsadaki, G. K. Tsikalas, E. Klontzas, G. E. Froudakis, S. A. Pergantis, K. D. Demadis, and H. E. Katerinopoulos, *RSC Adv.*, **2012**, 2, 12679.
15. A. E. Majzoub, D. Dadiou, I. D. Olivier, B. Tinant, and F. Chuburu, *Inorg. Chem.*, **2011**, 50, 4029.
16. Y. Dong, S. Farquhar, K. Floe, L. F. Lindoy, B. R. Rumbel, P. Turner, and K. Wichmann, *Dalton Trans.*, **2003**, 1558.
17. L. M. P. Lima, Z. Halime, R. Marion, N. Camus, R. Delgado, C. P. Iglesias, and R. Tripiet, *Inorg. Chem.*, **2014**, 53, 5269.
18. X. F. Shang, X. F. Xu, H. Lin, J. Shao, and H. K. Lin, *J. Mol. Recognit.*, **2007**, 20, 139.
19. Z. Brózka, *Analyst*, **1988**, 113, 891.
20. K. Suzuki, K. Watanabe, Y. Matsumoto, M. Kobayashi, S. Sato, D. Siswanta, and H. Hisamoto, *Anal. Chem.*, **1995**, 67, 324.
21. V. K. Gupta, R. Prasad, and A. Kumar, *J. Appl. Electrochem.*, **2003**, 33, 381.
22. B. B. Petković, S. P. Sovilj, M. V. Vudimir, R. M. Simonović, and V. M. Jovanović, *Electroanalysis*, **2010**, 22, 1894.
23. M. J. Seguí, J. L. Sabater, R. M. Mániez, F. Sancenón, and J. Soto, *Analyst*, **2002**, 127, 387.
24. J. L. Sabater, R. M. Mániez, F. Sancenón, M. J. Seguí, and J. Soto, *Anal. Chim. Acta*, **2002**, 459, 229.
25. J. L. Sabater, M. J. Seguí, J. M. Lloris, R. M. Mániez, T. Pardo, F. Sancenón, and J. Soto, *Sens. Actuators, B*, **2004**, 101, 20.
26. J. L. Sabater, R. M. Mániez, F. Sancenón, M. J. Seguí, and J. Soto, *Talanta*, **2008**, 75, 317.
27. D. Wegmann, H. Weiss, D. Ammann, W. E. Morf, E. Pretsch, K. Sugahara, and W. Simon, *Mikrochim. Acta*,

- 1984 III**, 1.
28. M. Ying, R. Yuan, X. M. Zhang, Y. Q. Song, Z. Q. Li, G. L. Shen, and R. Q. Yu, *Analyst*, **1997**, 112, 1143.
29. M. R. Ganjali, M. Uousefi, M. Javanbakht, T. Poursaberi, M. S. Niasari, L. H. Babaei, E. Latifi, and M. Shamsipur, *Anal. Sci.*, **2002**, 18, 887.
30. V. K. Gupta, A. K. Singh, P. Singh, and A. Upadhyay, *Sens. Actuators, B*, **2014**, 199, 201.
31. D. A. Place, F. P. Ferrara, J. J. Harland, and J. C. Dabrowiak, *J. Heterocycl. Chem.*, **1980**, 17, 439.
32. A. R. Cutler, C. S. Alleyne, and D. Dolphin, *Inorg. Chem.*, **1985**, 24, 2276.
33. H. Schumann, *Z. Naturforsch., B*, **1996**, 51, 989.
34. C. W. Davies, *J. Chem. Soc.*, **1938**, 2093.
35. W. J. Hehre, "A Guide to Molecular Mechanics and Quantum Chemical Calculation", **2003**, Wavefunction, Irvine.
36. J. J. P. Stewart, *J. Comput. Chem.*, **1989**, 10, 209.
37. J. J. P. Stewart, *J. Comput. Chem.*, **1989**, 10, 221.
38. A. Dreuw and M. H. Gordon, *Chem. Rev.*, **2005**, 105, 4009.
39. S. Amemiya, P. Bühlmann, and K. Odashima, *Anal. Chem.*, **2003**, 75, 3329.
40. E. D. Steinle, S. Amemiya, P. Bühlmann, and M. E. Meyerhoff, *Anal. Chem.*, **2000**, 72, 5766.
41. P. C. Andrews, J. L. Atwood, L. J. Barbour, P. D. Croucher, P. J. Nichols, N. O. Smith, B. W. Skelton, A. H. White, and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, **1999**, 2927.
42. B. K. Jiang, X. Shen, X. Wang, F. Su, and D. R. Zhu, *Acta Crystallogr.*, **2012**, E68, m871.
43. J. U. Franco, J. C. Hammons, D. Rios, and M. M. Olmstead, *Inorg. Chem.*, **2010**, 49, 5120.
44. M. C. Weiss, G. Gordon, and V. L. Goedken, *Inorg. Chem.*, **1977**, 16, 305.
45. F. A. Cotton and J. Czuchajowska, *Polyhedron*, **1990**, 9, 2553.
46. E. V. Basiuk (G. D.), E. V. R. Akimova, V. A. Basiuk, D. A. Najarro, and J. M. S. Goedken, *Nano Lett.*, **2002**, 2, 1249.
47. V. A. Basiuk, *J. Phys. Chem. B*, **2004**, 108, 19990.
48. M. Karelson, V. S. Lobanov, and A. R. Katritzky, *Chem. Rev.*, **1996**, 96, 1027.
49. F. A. Cotton and J. Czuchajowska, *Polyhedron*, **1990**, 9, 2553.
-