

involved in coordination. The nonbonded azide ion forms hydrogen bonds $N(8) \cdots H-O(1)$ 2.603(9) Å, $N(10) \cdots H-O(1)$ 2.705(9) Å, and $N(10) \cdots H-O(3)$ 2.718(11) Å (symmetry code $i: 0.5-x, -0.5+y, 1.5-z$). The N-Zn-N angles of six-membered chelate rings of **1** are larger than those of the five-membered chelate rings. The complex **1** also adopts a thermodynamically most stable *trans*-III conformation in the solid state. The IR spectrum of **1** shows two strong peaks of $\nu_{N=N}$ at 2055 and 2005 cm^{-1} , which are assigned to the nonbonded shorter N=N distance of 1.056(7) Å and the axial N=N distance of 1.125(6) Å, respectively. This is also expected by comparison with FAB mass spectra of $[Zn(L^1)(N_3)]^+$ (m/z 443.9).

Conclusion

The complex $[Zn(L^1)(N_3)][N_3] \cdot 3H_2O$ (**1**) has been prepared and characterized by X-ray crystallography. The coordination of the zinc atom is a distorted square-pyramid with four nitrogens of the macrocycle occupying the basal sites [$Zn-N_{bc}$ = 2.126(4) Å] and a terminal azide ligand at the apical position with a Zn-N distance of 1.996(5) Å.

Acknowledgements. The present studies were supported by the Basic Science Research Institute Program, Ministry of Korea, 1997, Project No. BSRI-97-3435 and the Research Fund of Mokwon University, 1997.

Supporting Information Available. Tables of crystallographic details, atomic coordinates, interatomic distances and angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for **1** (26 page) are available. Supplementary materials are available from K.-Y. Choi.

References

1. Chlebowski, J. F.; Coleman, J. E. In *Metal Ions in Bio-*

- logical Systems*; Sigel, H., Ed.; Dekker: New York, 1976; Vol. 6, pp 1-40.
2. Silverman, D. N.; Lindskog, S. *Acc. Chem. Res.* **1988**, *21*, 30.
3. Kimura, E. *Prog. Inorg. Chem.* **1994**, *41*, 443.
4. Greener, B.; Moore, M. H.; Walton, P. H. *J. Chem. Soc., Chem. Commun.* **1996**, 27.
5. Pocker, Y.; Deits, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3949.
6. Pocker, Y.; Deits, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 2424.
7. Yachandra, V.; Powers, L.; Spiro, T. G. *J. Am. Chem. Soc.* **1983**, *105*, 6596.
8. Eriksson, A. E.; Kysten, P. M.; Jones, T. A.; Liljas, A. *Proteins* **1988**, 283.
9. Kimura, E.; Shiota, T.; Koike, T.; Shiro, M.; Kodama, M. *J. Am. Chem. Soc.* **1990**, *116*, 5805.
10. Kimura, E.; Koike, T.; Shionoya, M.; Shiro, M. *Chem. Lett.* **1992**, 787.
11. Choi, K. Y.; Suh, I.-H. *Polyhedron* **1997**, *16*, 2393.
12. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd Ed.; Pergamon Press: New York, 1985.
13. Choi, K. Y.; Suh, I.-H.; Kim, J. C. *Polyhedron* **1997**, *16*, 1783.
14. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
15. Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Refinement*; Göttingen University: Göttingen, Germany, 1993.
16. Choi, K. Y. *Polyhedron* **1997**, *16*, 2073.
17. D'Aniello, M. J.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.

A New Cesium-Selective Ionophore Bearing Two Convergent Kemp's Triacid Functions

Nam Yee Kim, Sung Woo Park¹, and Suk-Kyu Chang*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

¹National Institute of Scientific Investigation, Seoul 158-097, Korea

Received October 9, 1997

The developments of cesium-specific ionophores are very important in view of the application for the nuclear waste treatment.¹ Although many intriguing ionophores for the recognition of alkali metal cations have been developed, relatively little attention has been paid for the cesium-selective ionophores.² Recently, Ungaro *et al.* have reported that the 1,3-dialkoxycalix[4]-crown-6 in the 1,3-alternate conformation exhibited a binding preference for cesium ion.^{3,4} Asfari *et al.* performed cesium removal experiments from nuclear waste water by using supported liquid membranes

containing various structures of calix-bis-crown compounds.¹

Cleft-shaped compounds have been widely studied in the field of supramolecular chemistry because of their unique structural and ion-binding properties as molecular recognition devices.⁵ Kemp's triacid moiety is one of the most interesting structural motifs for this purpose, owing to its convergent *syn* lone pairs of carboxylate as well as U-shaped relationship between carboxylate functions, and has been extensively used by Rebek *et al.* for the construction of many unique host systems.⁶ One of them is a simple mole-

cule derived from *m*-xylylene spacer and two Kemp's triacid moieties, that has unique ionophoric properties toward Ca^{2+} ion.⁷ We have reported the synthesis of related compounds having more lipophilic substituents and the more efficient extraction and transport properties toward Ca^{2+} ion compared with the Rebek's original ionophore.⁸ In this paper, we wish to report a new cesium-selective carrier which has two convergent carboxylate groups by utilizing the structural characteristics of Kemp's triacid and simple framework of methylene dianiline moieties.

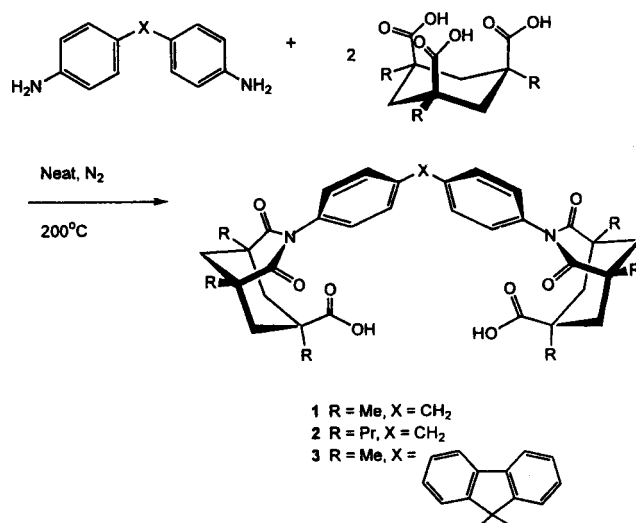
Experimental

The ^1H NMR spectra were recorded with a Varian Gemini 2000 (300 MHz) spectrometer. The IR and UV spectra were recorded with a Nicolet 510P FT-IR spectrometer and a Shimadzu UV 2100 spectrophotometer, respectively. Melting points were determined on a Mettler FP 61 melting point apparatus. The ion chromatography (IC) and inductively coupled plasma (ICP) spectrometric analyses were performed with a Dionex 2000i Ion Chromatography using a conductivity detector and a Jobin Yvon JY 24 ICP spectrometer, respectively. Chemicals (Kemp's triacid, 4,4'-(9-fluorenylidene)dianiline, and 4,4'-methylene dianiline) were purchased from Aldrich Chemical Co., and used without further purification. Propyl analogue of Kemp's triacid was prepared as described in the literature.⁹ Analytical TLC was done on aluminum plate precoated with Silica gel 60 F₂₅₄ and column chromatography was performed on silica gel 60 (230-340 mesh, ASTM).

Preparation of Ionophores 1-3.¹⁰ A mixture of Kemp's triacid or propyl analogue of Kemp's triacid (3.0 mmol) and the diamine (1.5 mmol) was dispersed in CH_2Cl_2 to ensure the complete mixing. The solution was evaporated completely and heated at 200 °C for 4 h under the nitrogen atmosphere. After cooling, the crude product was dissolved in 500 mL of CH_2Cl_2 and filtered, and the filtrate was evaporated under reduced pressure. Purification by column chromatography on silica gel (15% MeOH/ethyl acetate) and subsequent crystallization from CH_2Cl_2 /hexane yielded 1-3 as white or slightly brown powder. **1**: yield 60%; mp >300 °C; ^1H NMR (CDCl_3) δ 7.10 (d, $J=8.4$ Hz, 4H), 6.97 (d, $J=8.4$ Hz, 4H), 3.86 (s, 2H), 2.70 (d, $J=13.5$ Hz, 4H), 2.31 (d, $J=13.5$ Hz, 2H), 1.97 (t, $J=13.5$ Hz, 4H), 1.46-1.39 (m, 10H), 1.27-1.24 (m, 16H), 0.94-0.85 (m, 18H); IR (KBr) 3443, 1734, 1686, 1458, 1332 cm^{-1} ; MS (FAB) m/z for $\text{C}_{46}\text{H}_{67}\text{O}_8\text{N}_2$ ($\text{M}+\text{H}$)⁺ calcd 811.4, found 811. **2**: yield 65%; mp >300 °C; ^1H NMR ($\text{DMSO}-d_6$) δ 7.96 (d, $J=7.5$ Hz, 4H), 7.51-7.34 (m, 6H), 7.10 (d, $J=8.4$ Hz, 4H), 7.03 (br, 4H), 2.44 (d, $J=13.2$ Hz, 4H), 2.11 (d, $J=13.2$ Hz, 2H), 1.48 (d, $J=13.2$ Hz, 2H), 1.29 (d, $J=13.2$ Hz, 4H), 1.13 (s, 18H); IR (KBr) 3443, 1734, 1686, 1458, 1332 cm^{-1} ; MS (FAB) m/z for $\text{C}_{46}\text{H}_{49}\text{O}_8\text{N}_2$ ($\text{M}+\text{H}$)⁺ calcd 793.4, found 793.

The competitive extraction and transport experiments were performed as described earlier and the concentration of the ions was determined by IC or ICP techniques.⁸

FAB Mass Measurements. Complexation of **1** (2.0 mM) with mixtures of alkali or alkaline earth metal cations (each in 20 mM) in *m*-nitrobenzyl alcohol was studied by measuring the relative ratio of the heights of $[\text{1}+\text{M}]^+$ and $[\text{1}+$



Scheme 1.

$\text{H}]^+$. FAB-MS spectra were recorded with a JEOL JMS AX 505WA spectrometer using Xe beam.

Results and Discussion

Ionophores **1** and **2** were prepared by the condensation reaction of 4,4'-methylenedianiline with Kemp's triacid under nitrogen atmosphere following the standard procedure (Scheme 1).¹⁰ The fluorenyl analogue **3** was also prepared following the similar procedure.

The lipophilicity of the ionophores is a very important factor for their applications as analytical tools or carriers. To increase the lipophilicity of the parent ligand **1** without altering the binding site significantly, either replacement of methyl groups of Kemp's triacid with propyl groups or employment of methylenedianiline moiety having quite lipophilic fluorenyl group was performed. In this case, the expected increase in lipophilicity expressed by logP is estimated to be 6.4 and 2.1 for **2** and **3**,¹¹ respectively, and the logP of **2** seems to be large enough to endow sufficient lipophilicity into ligand. As expectedly, the ionophore **2** exhibited sufficiently high lipophilicity even at weakly basic pH region (pH 8-9). The limited solubility of **3** in CHCl_3 , however, precludes the detailed investigations of its ionophoric properties.

The complexing abilities of ionophores **1** and **2** were examined by competitive extraction experiment¹² using a mixture of alkali or alkaline earth metal salts and the results are summarized in Tables 1 and 2. The ionophores **1** and **2** showed a large affinity towards alkaline earth metal cations, particularly for Ca^{2+} ion, and the selectivity is quite good. More lipophilic propyl analogue **2** exhibited much pronounced extraction efficiency compared to the methyl analogue **1**. As the pH of the solution increases, **1** and **2** exhibited much more efficient extraction behavior but with somewhat reduced selectivity toward Ca^{2+} over Sr^{2+} and Mg^{2+} ions. Interesting thing is that the ionophore **2** has a remarkably high affinity toward Cs^+ ion among the alkali metal cations. The percent extraction value increases as the pH of the buffered aqueous solution: namely, 13.0%, 40.6%, and 48.7% at pH 8, 9, and 10, respectively. The selectivity

Table 1. Competitive extraction of alkali metal ions from water into chloroform at 25 °C^a

pH	Ionophore	Extractability (%)					Selectivity ^b	
		Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Cs ⁺ /K ⁺	Cs ⁺ /Rb ⁺
8	1	<0.5	6.3	2.0	<0.5	1.8	0.9	-
	2	1.1	4.2	2.6	3.4	13.0	5.0	3.8
9	1	<0.5	6.9	2.1	<0.5	2.5	1.2	-
	2	1.9	7.7	2.1	6.8	40.6	19.3	6.0
10	1	<0.5	5.0	1.1	<0.5	2.2	2.0	-
	2	9.6	9.0	6.1	12.4	48.7	8.0	3.9

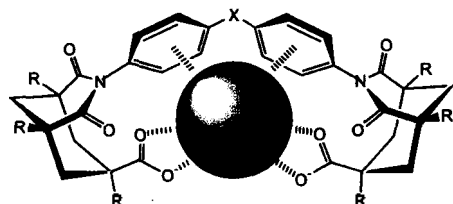
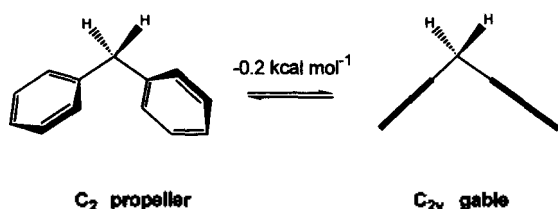
^aExtraction condition: [ionophore]=5.0 mM (in 2.0 mL of CHCl₃), [metal chloride]=1.0 mM each (in 2.0 mL of buffered solution). ^b"-": can not be estimated.

Table 2. Competitive extraction of alkaline earth metal ions from water into chloroform at 25 °C^a

pH	Ionophore	Extractability (%)				Selectivity	
		Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Ca ²⁺ /Mg ²⁺	Cs ²⁺ /Sr ²⁺
8	1	0.5	9.8	2.0	2.4	20.9	5.0
	2	6.9	40.0	17.8	12.1	5.8	2.2
9	1	1.3	19.4	5.4	4.0	15.0	3.6
	2	23.9	59.8	28.5	22.3	2.5	2.1
10	1	1.7	22.6	8.1	7.3	13.6	2.8
	2	33.2	62.9	29.8	24.3	1.9	2.1

^aConditions are the same as in Table 1.

in extraction of Cs⁺ ion over K⁺ and Rb⁺ ions is found to be a maximum at pH 9 and is 19.3 and 6.0, respectively. The high affinity of **2** toward Cs⁺ ion could be partly explained by the increased lipophilicity of the ligand as well as the complementary interaction with the two convergent carboxylate functions. The structure of **2**-Cs⁺ complex as examined by the Corey-Pauling-Koltun space-filling model and the HyperChem molecular model¹³ suggests that the ionophore **2** has a highly favorable geometry of the two carboxylic acids for the recognition of large Cs⁺ guest ion (Figure 1). In this case, the diphenylmethane group, which acts as a spacing unit, might provide extra stabilization through the interaction with the deeply nested Cs⁺ guest ion by the π -charge interaction. Similar type of cation/ π -electron interactions in the 1:1 complex of 1,3-dimethoxy-calix[4]-

**Figure 1.** Proposed binding mode of ionophore 1 with metal ionic guest.**Figure 2.** The conformational behavior of diphenylmethane unit.

crown-6 with cesium picrate have been clarified by the X-ray crystal structure.³ In contrast to the ionophore **2**, the ionophore **1** showed rather poor extraction ability toward alkali metal ions even under basic aqueous conditions of pH 10, that could be explained by the lower lipophilicity of the ligand.

Interesting phenomena concerning the structural requirements for diphenylmethane units to act as an efficient spacer have been reported and the diphenylmethane unit in the host is known to prefer the gable conformation C_{2v} over the C₂ or propeller geometry (Figure 2).¹⁴ With this gable conformation, which is better preorganized for the complex-

Table 3. Competitive transport of alkali metal cations through chloroform liquid membrane at pH 9^a

Carrier	Transport rate ($\times 10^{-8}$ mol/h)					Selectivity	
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Cs ⁺ /K ⁺	Cs ⁺ /Rb ⁺
1	<0.1	<0.1	<0.1	<0.1	<0.1	-	-
2	5.5	1.5	8.1	11.2	76.6	9.5	6.8

^aSource phase: 0.1 M each of alkali metal chloride (5.0 mL of Tris-HCl buffer, pH=9). Membrane phase: 5.0 mM of carrier in CHCl₃ (15 mL). Receiving phase: 1.0 M HCl (5.0 mL). At 25 °C.

Table 4. Competitive transport of alkaline earth metal cations through chloroform liquid membrane at pH 9^a

Carrier	Transport rate ($\times 10^{-8}$ mol/h)				Selectivity	
	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Ca ²⁺ /Mg	Ca ²⁺ /Sr ²⁺
1	<0.1	0.2	<0.1	<0.1	-	-
2	1.1	4.7	1.9	1.3	4.3	9.5

^aSource phase: 0.1 M each of alkaline earth metal chloride (5.0 mL of Tris-HCl buffer, pH=9). Other conditions are the same as in Table 3.

ation of guest in its pseudo-cavity, the accommodation and interaction with the Cs^+ guest as modeled in Figure 1 should be more favorable.

To investigate the properties of ionophore **1** and **2** as a carrier,^{15,16} the competitive transport experiments through the chloroform liquid membrane were performed at pH 9 using a U-tube (inner diameter=1.8 cm) for the time period of 2 days. The results are summarized in Tables 3 and 4. Interesting thing is that the transport rate of ionophore **2** for Cs^+ ion was considerably high and the transport selectivity of **2** for Cs^+ over K^+ and Rb^+ was 9.5 and 6.8, respectively. Ionophore **2** showed much reduced transport rate toward alkaline earth metal cations with low selectivity towards Ca^{2+} ion. However, the carrier **1** does not show any transport efficiency that might be due to the low extraction efficiency of this compound.

To have a further insight into the molecular recognition properties of the present system, we performed competitive FAB mass spectral studies of **1** in the presence of a mixture of alkali or alkaline earth metal chloride salts (each in 10 molar excess with respect to the ionophore). With alkali metal chlorides, ionophore **1** exhibited an intense peak at $[\text{I}+\text{Cs}]^+$ and the ratio of the heights¹⁷ of $[\text{I}+\text{Cs}]^+$ to $[\text{I}+\text{H}]^+$ peaks is 24.8, which manifests that the molecule **1** forms a strong complex with Cs^+ ion. The ratio of the heights for the other metal ions is 8.5 (Li^+), 0.6 (Na^+), 1.0 (K^+), and 2.1 (Rb^+). Interesting fact is that the $[\text{I}+2\text{Cs}-\text{H}]^+$ peak at m/z 907 is quite prominent having the ratio of 15.5. This observation suggests that the ionophore **1** could bind two Cs^+ ions simultaneously, probably by using the individual phenyl ring and Kemp's triacid moiety as an independent binding site for the Cs^+ ion, by the simple rotation around the methylene spacer. The alkaline earth metal cations were found to exhibit relatively weak peaks under the employed condition and the $[\text{I}+\text{M}-\text{H}]^+ / [\text{I}+\text{H}]^+$ ratio is 2.48 (Mg^{2+}), 0.22 (Ca^{2+}), and 0.13 (Ba^{2+}).

In summary, we have developed a new type of carrier that exhibits a unique selectivity toward the large Cs^+ ion among the alkali metal cations with a simple structural motif of diphenylmethane spacer and the convergent Kemp's triacid.

Acknowledgment. This work was supported by the KOSEF (96-0501-04-01-3) and the Basic Science Research Institute Program of Ministry of Education (BSRI-97-3450) and gratefully acknowledged.

References

- Asfari, Z.; Bressot, C.; Vicens, J.; Hill, C.; Dozol, J.-F.; Rouquette, H.; Eymard, S.; Lamare, V.; Tournois, B. In *Chemical Separations with Liquid Membranes*; Bartsch, R. A.; Way, J. D., Eds.; ACS symposium series 642, Chap. 26, ACS: Washington, DC, 1996.
- Davis, J. T.; Tirumala, S. K.; Marlow, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5271 and references therein.
- Ungaro, R.; Casnati, A.; Ugozzoli, F.; Pochini, A.; Dozol, J. F.; Hill, C.; Rouquette, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1506.
- Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767.
- (a) Rebek, J. Jr. *Science* **1987**, *235*, 1478. (b) Rebek, J. Jr. *Pure & Appl. Chem.* **1989**, *61*, 1517. (c) Rebek, J. Jr. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 245.
- Kemp, D. S.; Petrakis, K. S. *J. Org. Chem.* **1981**, *46*, 5140.
- Marshall, L.; Parris, K.; Rebek, J. Jr.; Luis, S. V.; Burguete, M. I. *J. Am. Chem. Soc.* **1988**, *110*, 5192.
- Kim, N. Y.; Park, S. W.; Chang, S.-K. *Bull. Korean Chem. Soc.* **1997**, *18*, 519.
- Jeong, K. S.; Tjivikua, T.; Muehldorf, A.; Deslongchamps, G.; Famulok, M.; Rebek, J. Jr. *J. Am. Chem. Soc.* **1991**, *113*, 201.
- Rebek, J. Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killooran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476.
- ACD/Labs, Advanced Chemistry Developments Inc, 141 Adelaide St. West, Suite 1501, Toronto, Ontario M5H 3L5, Canada.
- Walkowiak, W.; Kang, S. I.; Stewart, L. E.; Ndip, G.; Bartsch, R. A. *Anal. Chem.* **1990**, *62*, 2022.
- HyperChem, Release 4, Hypercube, Inc., 419 Phillip Street, Waterloo, Ontario N2L 3X2, Canada, 1994.
- Barnes, J. C.; Paton, J. D.; Damewood Jr., J. R.; Mislow, K. *J. Org. Chem.* **1981**, *46*, 4975.
- (a) Hirose, T.; Baldwin, B. W.; Wang, Z.-H.; Kasuga, K.; Uchamaru, T.; Yliniemela, A. *Chem. Commun.* **1996**, 391. (b) Hirose, T.; Baldwin, B. W.; Uchamaru, T.; Tsuzuki, S.; Uebaysahi, M.; Taira, K. *Chem. Lett.* **1995**, 231.
- Charewicz, W. A.; Heo, G. S.; Bartsch, R. A. *Anal. Chem.* **1982**, *54*, 2094.
- Ostaszewski, R.; Stevens, T. W.; Verboom, W.; Reinhoudt, D. N.; Kaspersen, F. M. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 294.

1. Asfari, Z.; Bressot, C.; Vicens, J.; Hill, C.; Dozol, J.-F.;