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New Crown Ethers Containing Kemp's Triacid and Their Binding Properties with Alkali Metal Cations

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The development of neutral hosts for binding metal ions has been extensively pursued for the last two decades due to the potential applications in the various areas; analytical, environmental and biological chemistry.[1] Most works were based on the modification of crown ether by replacing the ethylene glycol units with other building molecules that may introduce different size, shape, and conformational properties of the binding sites.[2] For the development of efficient ion-selective electrodes and synthetic ion transporters, highly lipophilic molecules should be incorporated into crown ethers. Recently, Moriarty *et al.*[3] reported that the rigid and compact hydrocarbons such as cubane are more relevant for this purpose than long-chain hydrocarbons that may increase lipophilicity but decrease mobility of the carrier.

Kemp's triacid, a highly rigid and compact molecule, has proven to be a versatile building block for the construction of synthetic molecular clefts[4] and self-replicating molecules.[5] Using its unique structural feature, U-shaped relationship between any two carboxyl functional groups, we recently introduced the alkali metal cation hosts such as bis(crown ether)s, functionalized podands, and cage-type molecules.[6] We here report the synthesis and binding properties of new crown ethers in which one of the ethylene glycol units is

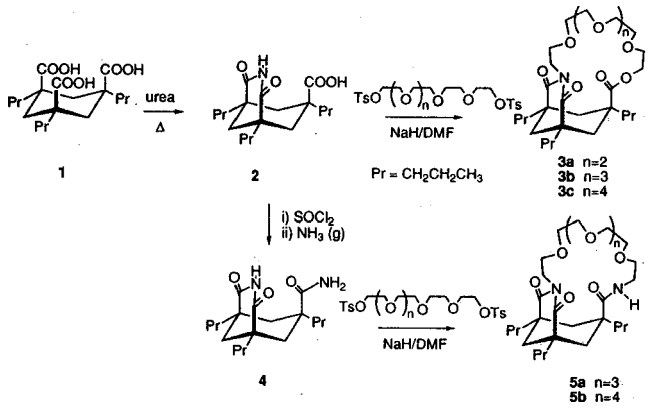


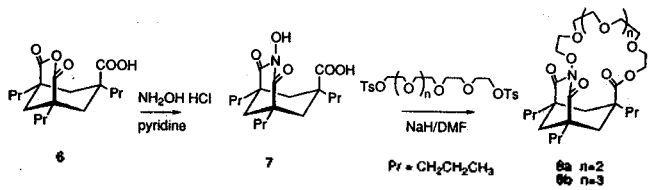
Table 1. The Extraction Percentages (± 1.5%) and Association Constants (values in parentheses, $K_a \times 10^{-4}$, M^{-1}) of Hosts with Alkali Metal Picrates at 25± 0.5 ℃

host	Li^+	Na^+	K^+	Rb^+	Cs^+
3a (n=2)	<2	<2	<2	<2	<2
3b (n=3)	<2	12 (31)	15 (28)	9.2 (8.0)	7.1 (4.9)
3c (n=4)	<2	2.2 (4.3)	20 (42)	20 (23)	17 (15)
5a (n=3)	<2	21 (68)	22 (49)	18 (21)	6.2 (4.2)
5b (n=4)	<2	8.8 (20)	33 (105)	33 (57)	27 (33)
8a (n=2)	<2	28 (110)	37 (140)	20 (23)	8.0 (6.0)
8b (n=3)	<2	7.2 (16)	28 (76)	32 (55)	26 (30)

replaced with the Kemp's triacid derivatives. A more lipophilic analogue **1** of Kemp's triacid was synthesized by a known procedure[7] from a commercially available trimethyl *cis,cis*-1,3,5-cyclohexanetricarboxylate. Simple heating (180 ℃, 1.5 h) of the triacid **1** and urea in triglyme gave imide acid **2** which was coupled with appropriate oligoethylene glycol ditosylates to afford the corresponding imide ester hosts **3** (Scheme 1). To examine an effect of the carbonyl group on the binding with alkali metal ions, we also prepared in a similar manner imide amide hosts **5** in which the ester groups in the imide ester hosts **3** were replaced with the more basic amide groups. The cyclization reactions proceed cleanly with small unidentified impurities (<10%), but the isolated yields (20-32%), not optimized, are relatively low due to the intrinsic difficulty of the purification of crown ether-type molecules.

The hosts and their complexes with metal ions studied here are highly soluble in organic solvents such as $CHCl_3$ and CH_2Cl_2, but not soluble at all in water. The binding affinities are therefore determined by Cram's liquid-liquid extraction method.[8] The extraction experiments was performed at 25± 0.5 ℃ by employing 0.5 mL (30 mM) of hosts in $CHCl_3$ and 0.5 mL (30 mM) of metal picrates in deionized water. The amount of extractions has been determined by measuring changes in absorbances of metal picrates in aqueous layer at 373 nm. The extraction percentages (± 1.5 %) and stability constants, calculated by assuming 1 : 1 complex formation, are summarized in Table 1.

As shown in Table 1, the imide ester host **3b** ($n=3$) shows a moderate selectivity toward Na^+ and K^+ ions, and the host **3c** ($n=4$) toward K^+, Rb^+ and Cs^+ ions, indicating that the selectivity correlates directly with the cavity size of hosts.



The binding affinities of the hosts **3b** and **3c** are however much lower than those of benzo-15-crown-5 or benzo-18-crown-6 derivative to alkali metal ions.[6a] To enhance the stability of complexes, we first prepared the imide amide hosts **5a** and **5b** which contain more basic carbonyl oxygen and thus are expected to show higher binding affinities than the corresponding imide ester hosts **3b** and **3c**. As expected, hosts **5a** and **5b** exhibit 2-3 times higher stability constants in all cases than **3b** and **3c**, and both host systems exhibit the same trend of selectivity, indicating that the carbonyl oxygen is directly involved in the binding events.

As another approach to increase the binding affinity, we synthesized the hydroxyimide ester hosts **8a** and **8b**. These hosts possess one more oxygen for binding of metal ions than the imide ester hosts **3a** and **3b**, but the number of ethylene units remains same. This approach may result in the minimal entropic loss upon complexation, compared with the way of simply increasing the number of ethylene glycol units in order to provide an additional oxygen atom for coordinating to metal ions. The synthesis of the hydroxyimide ester hosts **8a** and **8b** is outlined in Scheme 2. A mixture of anhydride acid **6** and hydroxylamine hydrochloride in pyridine was heated at reflux to afford N-hydroxyimide acid **7** (91%), which was reacted with penta- and hexaethylene glycol ditosylates to give the corresponding hydroxyimide ester hosts **8** (35-40%).

As summarized in Table 1, the extractions of metal ions by the imide ester host **3a** is negligible (<2%), while the corresponding hydroxyimide ester host **8a** considerably extracts metal ions in the same conditions. Addition of one oxygen atom to host **3a** increased the stability constants by one to two orders of magnitude. This clearly demonstrates that a subtle variation in the binding cavity causes a significant change in the binding property of the hosts. The stability constants between host **8a** and alkali metal ions are now comparable to those between benzo-15-crown-5 derivative and alkali metal ions.[6a]

In conclusion, we have prepared the crown-type hosts that contain highly lipophilic and compact hydrocarbon unit. The binding affinity between the hosts and alkali metal ions has been studied and increased by the systematic variations, that is, the modification in basicity of the carbonyl oxygen and in number of the coordinating oxygens of the hosts.

Experimental

General. All chemicals were reagent grade. Dimethylformamide was pre-dried over anhydrous $MgSO_4$, distilled under reduced pressure, and then stored over 4 Å molecular sieves. Chloroform and acetonitrile were distilled from CaH_2, and pyridine from KOH prior to use. Water was deionized and distilled. Sodium hydride was used as a 55% dispersion in mineral oil. Column chromatography was performed on

silica gel 60 (E. Merck, particle size 0.040-0.063 mm, 230-400 ASTM). The picrate salts were prepared as reported previously,[9] and dried under high vacuum for 24 h before use. Ultraviolet Measurements were made with a Shimadzu UV 160A. Melting points were measured on a Laboratory Devices, USA Mel-Temp II and are uncorrected. Infrared spectra were taken on a Nicolet Impact 400 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker DPX 250 MHz (^{1}H) or a Varian Gemini 300 MHz (^{1}H) spectrometer using Me_4Si or $CDCl_3$ as an internal standard.

Extractions. Experimental procedure was similar to that described previously.[8] A solution (10 mM) of an alkali metal picrate in deionized water and a solution (30 mM) of a host in $CHCl_3$ were prepared and allowed to stand for at least 2 h at 25± 0.5 ℃. Equal volume of each solution was placed in a stoppered glass tube and vigorously agitated for 2 min on a Vortex mixer (GW-92VM). The two-layer solution was centrifuged for 10 min at high speed and allowed to stand for 1 h at 25± 0.5 ℃ to complete phase separation. An aliquot (10 μL) of the upper aqueous solution was carefully withdrawn with a Hamilton gastight syringe (50 μL size) and diluted to 2.00 mL with CH_3CN. The absorbance of each solution was then measured at 373 nm and all experiments were duplicated. The extraction percentages and stability constants were calculated as described by Cram *et al.*[8]

Preparations of the Imide Ester Hosts 3a-c. Tripropyl imide acid **2** was prepared by following literature procedure[7] from trimethyl *cis,cis*-1,3,5-cyclohexanetricarboxylate purchased from either Aldrich or Fluka co. To a solution of **2** (0.60 g, 1.86 mM) in dry DMF (50 mL) was added a 55% dispersion NaH in mineral oil (0.20 g, 2.5 equiv) at ambient temperature under argon atmosphere. After stirring for 10 min, an appropriate oligoethylene glycol ditosylate (1 equiv) was added in a portion. The resulting solution was heated at 75-80 ℃ overnight (10-15 h). The solution was concentrated under reduced pressure and the residue was taken up in EtOAc (30-50 mL). The organic layer was washed with water, saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was purified by flash column chromatography (hexanes/EtOAc 1 : 2 or CH_2Cl_2/MeOH 10 : 1) to afford the corresponding imide ester hosts **3a-c**. **3a**: oily liquid (25% yield); IR (NaCl, neat) 2967, 2868, 1729, 1683, 1466, 1348, 1183, 946 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 4.12 (t, J=6.1 Hz, 2H), 3.52 (t, J=7.4 Hz, 2H), 3.69-3.62 (m, 14H), 3.46 (t, J=7.4 Hz, 2H), 2.58 (d, J=13.4 Hz, 2H), 2.07 (d, J=13.0 Hz, 1H), 1.94-1.88 (m, 2H), 1.40-1.11 (m, 13H), 0.92 (t, J=7.0 Hz, 6H), 0.81 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.7, 15.0, 17.4, 17.5, 37.0, 39.6, 41.6, 43.1, 43.5, 45.7, 47.9, 64.3, 67.7, 68.8, 70.8, 71.1, 71.2, 71.3, 71.4, 174.7, 175.9. **3b**: oily liquid (32% yield); IR (NaCl, neat) 2967, 2868, 1729, 1677, 1460, 1335, 1282, 1117 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 4.07 (t, J=5.8 Hz, 2H), 3.81 (t, J=7.0 Hz, 2H), 3.73-3.56 (m, 18H), 3.29 (t, J=6.9 Hz, 2H), 2.58 (d, J=13.4 Hz, 2H), 2.08 (d, J=13.0 Hz, 1H), 1.99-1.89 (m, 2H), 1.42-1.11 (m, 13H), 0.92 (t, J=7.0 Hz, 6H), 0.81 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.6, 14.9, 17.3 (2 carbons), 36.7, 38.9, 41.5, 43.1, 43.4, 45.6, 47.5, 64.2, 67.9, 68.5, 70.1, 70.7, 70.8, 70.9, 71.1 (2 carbons), 174.5, 175.7. **3c**: oily liquid (20% yield); IR (NaCl, neat) 2967, 2877, 1736, 1683, 1466, 1335, 1124, 953 cm^{-1}; ^{1}H NMR ($CDCl_3$) **d**: 4.06 (t, J=5.6 Hz, 2H), 3.82 (t, J=6.7 Hz, 2H), 3.70-3.61 (m, 22H), 3.46 (t, J=6.7 Hz, 2H), 2.57 (d, J=13.3 Hz, 2H), 2.09 (d, J=13.0 Hz, 1H), 1.98-1.90 (m, 2H), 1.44-1.08 (m, 13H), 0.91 (t, J=6.9 Hz, 6H), 0.81 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.7, 15.0, 17.3 (2 carbons), 36.7, 38.7, 41.5, 43.2, 43.4, 45.7, 47.5, 64.2, 68.2, 68.7, 70.3, 70.8, 71.0, 71.1, 71.2 (2 carbons), 174.6, 175.7.

Imide Amide 4. A solution of **2** (1.60 g, 4.7 mmol) in distilled $SOCl_2$ (10 mL) was heated at reflux for 2 h. and excess $SOCl_2$ was removed. The resulting solid was directly dissolved in ammonia-saturated MeOH (70 mL) and the solution was stirred for 30 min at room temperature and concentrated. The residue was taken up in EtOAc and the organic solution was washed with water and brine. The solution was dried over anhydrous $MgSO_4$, filtered and concentrated to give **4** (1.43 g, 95%). mp 196-197 ℃; IR (NaCl, film) 3210, 2960, 2872, 1692, 1465, 1372, 1203 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 10.09 (s, 1H, NH), 8.07 (s, 1H, NH), 5.68 (s, 1H, NH), 2.44 (d, J=13.8 Hz, 2H), 2.20 (d, J=13.0 Hz, 1H), 1.98-1.91 (m, 2H), 1.39-1.14 (m, 13H), 0.91 (t, J=6.8 Hz, 6H), 0.83 (t, J=7.0 Hz, 3H).

Preparations of the Imide Amide Hosts 5a-b. The preparative method of **5a** and **5b** is the same as that described for hosts **3a-c** except that **4** was used instead of **2**. **5a**. oily liquid (28% yield); IR (NaCl, neat) 3438, 2956, 2871, 1691, 1470, 1345, 1118 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 5.81 (br t, 1H, NH), 3.85 (t, J=6.4 Hz, 2H), 3.73-3.57 (m, 18H), 3.47 (t, J=6.4 Hz, 2H), 3.32 (q, J=5.2 Hz, 2H), 2.44 (d, J=14.3 Hz, 2H), 2.10 (d, J=12.9 Hz, 1H), 1.99-1.91 (m, 2H), 1.36-1.12 (m, 13H), 0.92 (t, J=7.0 Hz, 6H), 0.80 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.8, 15.0, 17.4, 37.0, 39.1, 40.1, 41.7, 43.5, 43.8, 45.7, 48.9, 68.4, 69.6, 70.3, 70.4, 70.8, 71.1, 71.2, 71.4, 173.2, 176.2. **5b**. oily liquid (40% yield); IR (NaCl, neat) 3435, 2955, 2872, 1692, 1473, 1344, 1119 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 5.85 (br t, 1H, NH), 3.81 (t, J=6.5 Hz, 2H), 3.74-3.60 (m, 20H), 3.55 (t, J=5.4 Hz, 2H), 3.46 (t, J=6.5 Hz, 2H), 3.32 (q, J=5.2 Hz, 2H), 2.44 (d, J=13.5 Hz, 2H), 2.09 (d, J=12.9 Hz, 1H), 1.98-1.90 (m, 2H), 1.36-1.12 (m, 13H), 0.91 (t, J=7.1 Hz, 6H), 0.80 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.8, 15.0, 17.4, 36.9, 40.0, 41.7, 43.5, 43.8, 45.7, 48.8, 68.4, 69.6, 70.2, 70.4, 70.8, 71.1 (2 carbons), 71.2, 71.3, 173.2, 176.2.

***N*-Hydoxyimide Acid 7.** After simple heating (180 ℃, 1 h) of solid tripropyl triacid **1** (0.90 g, 2.6 mmol) under argon atmosphere, the resulting anhydride acid **6** (0.85 g, 2.6 mmol) and hydroxylamine hydrochloride (0.40 g, 2 equiv) was heated at reflux in dry pyridine overnight. The pyridine was removed and the residue was dissolved in 1 N aqueous NaOH. The aqueous solution was acidified with concentrated HCl and extracted with CH_2Cl_2 and the organic solution was dried over anhydrous $MgSO_4$. The solvent was removed to give a pure N-hydroxyimide acid **7** as white solid (0.81 g, 91%). mp 186-188 ℃; IR (KBr) 3304, 2966, 2878, 1697, 1434, 1185, 913 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.70 (br s, 1H, OH), 2.63 (d, J=13.5 Hz, 2H), 2.22 (d, J=12.9 Hz, 1H), 2.02-1.94 (m, 2H), 1.51-1.12 (m, 13H), 0.92 (t, J=7.0 Hz, 6H), 0.84 (t, J=7.2 Hz, 3H).

Preparations of the Hydroxyimide Ester Hosts 8a-b. The preparative method of **8a** and **8b** is the same as that described for hosts **3a-c** except that **7** was used instead of **2**. **8a**. White solid (35% yield); mp 84-85 ℃; IR (NaCl,

film) 2969, 2880, 1735, 1459, 1183, 1135 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.15 (t, J=5.9 Hz, 1H), 4.05 (t, J=4.3 Hz, 2H), 3.80-3.68 (m, 16H), 2.64 (d, J=13.8 Hz, 2H), 2.11 (d, J=13.1 Hz, 1H), 1.98-1.90 (m, 2H), 1.44-1.13 (m, 13H), 0.92 (t, J=6.9 Hz, 6H), 0.81 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.7, 14.9, 17.3, 17.5, 36.8, 41.2, 43.1, 44.2, 45.6, 47.2, 65.1, 68.7, 69.0, 70.6, 71.0 (2 carbons), 71.1, 71.2, 71.6, 171.8, 174.5. **8b**. White solid (40% yield); mp 78-80 ℃; IR (NaCl, film) 2966, 2878, 1734, 1470, 1177, 1118 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.14 (t, J=5.6 Hz, 1H), 4.04 (t, J=4.3 Hz, 2H), 3.82-3.63 (m, 20H), 2.65 (d, J=13.5 Hz, 2H), 2.11 (d, J=12.9 Hz, 1H), 1.98-1.90 (m, 2H), 1.44-1.13 (m, 13H), 0.93 (t, J=6.9 Hz, 6H), 0.83 (t, J=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.6, 14.9, 17.3, 17.4, 36.8, 41.2, 43.1, 44.2, 45.5, 47.1, 64.8, 68.8, 68.9, 70.5, 70.9, 71.0, 71.1, 71.2, 71.3, 71.6 (2 carbons), 171.7, 174.5.

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Synthesis of Cobalt(III) Complexes of N,N'-Bis (β-mercaptoethyl)-trans-2.5-dimethylpiperazine

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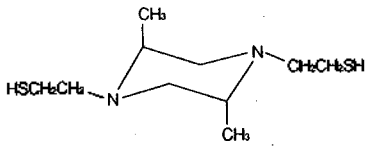
Various types of the metal complexes, monomeric, binuclear or tetranuclear metal complexes, with the tetradentate ligands containing the SNNS donor system have been known in the literature.[1,2]

In this work, a new SNNS-type ligand, N,N'-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine (H_2medpa) and the cobalt(III) complexes of medpa have been prepared. The medpa ligand can have both chair and boat conformations. A binuclear complex will be obtained if the lignad coordinates to a metal ion in the chair conformation, while a monomeric complex will be formed upon coordination of the ligand in the boat conformation (Figure 1). It is of interest to observe what type of metal complexes, monomeric or binuclear, would be obtained in this work.

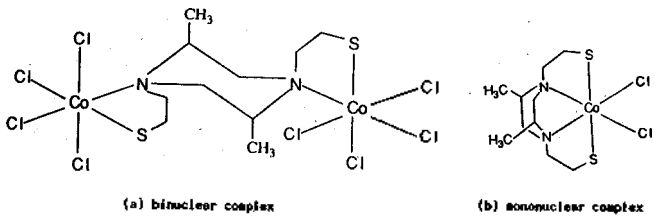


N,N'-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine (medpa)

Experimental

Preparation of N,N'-Bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine (H_2medpa). Ethylene sulfide (0.6 g, 0.1 mmol) in 10 mL of benzene was added slowly to a solution of trans-2,5-dimethylpiperazine (5.7 g, 0.05 mol) at 40 ℃ under nitrogen. After digesting for 2 hrs, the temperature of the reaction system was raised to 60 ℃, at which it was maintained for 24 hrs with stirring under nitrogen. The solution was cooled to room temperature, washed with water several times, and then throughly dried over $MgSO_4$. The solution was filtered and the solvent was removed by rotary evaporation. The pale yellow oil product was vacuum dried and kept under nitrogen. Yield: 1.9 g (16%).

Prepration of Sodium Octachloro[N,N'-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine]dicobaltate (III), $Na_4[Co_2(medpa)Cl_8]$. A solution of H_2medpa (1.2



(a) binuclear complex (b) mononuclear complex

Figure 1. Possible geometry of (a) $[Co_2(medpa)Cl_8]^{4-}$ and (b) $[Co(medpa)Cl_2]^-$ complexes.