

Synthesis and Metal-Binding Properties of Novel "Fullerenocrowns"

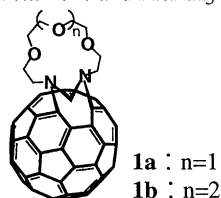
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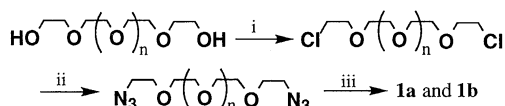
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"Fullerenocrowns" in which C₆₀ carbons are directly included as a ring member in the crown ring were synthesized for the first time; the UV-Vis absorption spectra were sensitively changed by the addition of metal and ammonium cations.

The large availability of C₆₀ has offered the increasing attention toward exploration of outstanding new physical and chemical properties of this fullerene. Among them, one of the most attractive research objects is the superconductivity observed for certain endohedral C₆₀-metal complexes.¹ It occurred to us that the similar phenomenon may emerge not only from such endohedral metal complexes but also from exohedral metal complexes: that is, the metal cation immobilized onto the C₆₀ surface should facilitate the electron injection into the C₆₀ moiety and stabilize the C₆₀⁻M⁺ complexes. As the primary step to test this hypothesis, one has to synthesize ionophoric C₆₀ derivatives in which a metal-binding site is situated very closely to the C₆₀ surface. Such C₆₀ derivatives with ionophoric functional groups have been reported by several groups²⁻⁷ but spectroscopic evidence for the direct C₆₀-metal interaction was obtained only in a few systems.^{4,7} We considered that the most favorable structure to facilitate the C₆₀-metal interaction would be "fullerenocrown" in which several carbons in C₆₀ are included as a ring member in the crown ring. To the best of our knowledge, however, such an ionophoric C₆₀ derivative has never been synthesized. We here report the first example for "fullerenocrown" **1** which satisfies such steric requirements. We have found that the absorption spectra sensitively change in the presence of several metal ions and MeNH₃⁺ ion.



Compounds **1a** and **1b** were synthesized according to Scheme 1. The yields for the last step to give **1a** and **1b** were 0.8% and 28%, respectively.⁸ The products were identified by ¹H NMR (the details are discussed below) and Mass [positive SIMS, *m/z* 908 (M⁺) for **1a** and 952 (M⁺) for **1b**] spectral evidence and elemental analyses.



Scheme 1. Reagents and conditions: i, SOCl₂, pyridine; ii, NaN₃, DMF; iii C₆₀, chlorobenzene.

It is known that there are two theoretically possible bond-formation manners, 5,6-open and 6,6-closed isomers, when C₆₀

reacts with one azide reagent.⁹ The ¹³C NMR spectra of **1a** and **1b** (100 MHz, CDCl₃, 25 °C) both gave 32 peaks assignable to fullerene carbons. This number results from 28 pairs of two equivalent carbons and four inequivalent carbons created by the adduct formation and supports the 5,6-open bisaza-substituted fulleroid structure.⁹ In the ¹H NMR spectra of **1a** and **1b** (400 MHz, CDCl₃, 25 °C) two protons of each methylene unit in -NCH₂CH₂O- all appeared separately, indicating that two sides of the crown ring are non-symmetrically affected by the π -electron ring current on the C₆₀ surface. Using ¹H-¹H COSY and ¹H-¹H NOESY the proton signals could be assigned as shown in Figure 1.

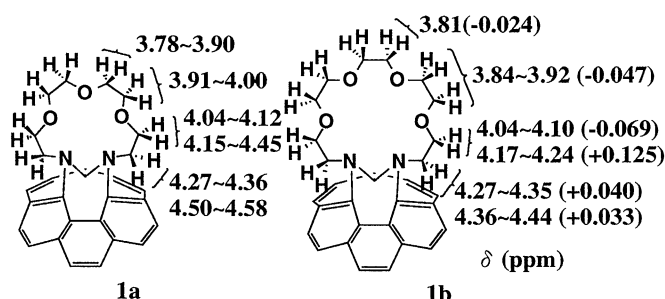


Figure 1. Partial structures of **1a** and **1b** with a 5,6-open linkage and ¹H NMR chemical shifts in the absence and the presence of NaClO₄ (only for **1b**): 400 MHz, CDCl₃, 25 °C, [**1a** or **1b**] = 2.0 × 10⁻³ mol dm⁻³, [NaClO₄] = 200 × 10⁻³ mol dm⁻³. The values in parentheses are the shift induced by added NaClO₄ (+ down-field shift, - up-field shift).

It is seen from Figure 1 that after Na⁺ complexation, the δ_H for the NCH₂ protons shifts to lower magnetic field whereas that for other OCH₂CH₂O protons shifts to higher magnetic field. Generally saying, the δ_H in crown ring protons tends to move to lower magnetic field upon metal cation complexation unless the metal cation induces a large conformational change. The discrepancy can be rationalized by the Na⁺-induced conformational change: that is, in the absence of Na⁺ the crown ring inclines toward the C₆₀ surface and the OCH₂CH₂O protons are affected by the strong deshielding effect of the C₆₀ π -system. In the presence of Na⁺ the crown ring stands up to include Na⁺, leaving the C₆₀ deshielding area. The NCH₂ protons, the position of which is scarcely affected by the conformational change, show the usual down-field shift induced by the Na⁺-binding.

The spectral studies were carried out about **1b** which gave the higher yield and showed the better metal-binding properties. For the Li⁺ and Ba²⁺ complexes with **1b** the chemical shift changes in ¹H NMR spectroscopy were so large that the stoichiometry could be estimated by a continuous variation method. The plots of δ_H for the N-C-CH₂ protons vs. [Li⁺ or

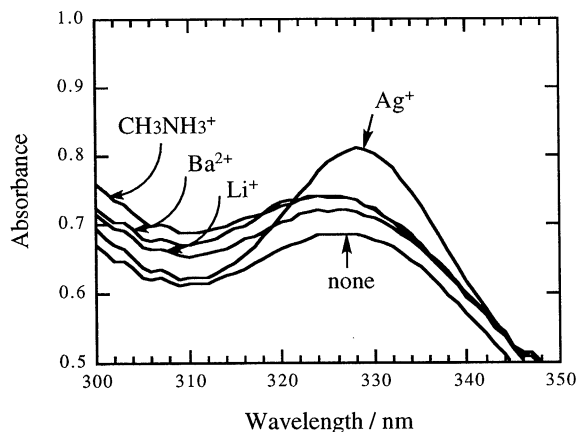


Figure 2. Absorption spectral change: $[1b] = 2.00 \times 10^{-5}$ mol dm $^{-3}$, $[additive] = 4.00 \times 10^{-3}$ mol dm $^{-3}$, MeOH:CHCl $_3$ = 1 : 5 v / v, 25 °C.

Ba $^{2+}$ / ([Li $^{+}$ or Ba $^{2+}$] + $[1b]$) (= 5.0×10^{-3} mol dm $^{-3}$: constant) in methanol- d_4 : CDCl $_3$ = 1:9 v / v at 25 °C gave the largest δ_H shift at 0.5 and established that these complexes possess the 1:1 stoichiometry.¹⁰ Although it was difficult to estimate the stoichiometry for other metal complexes by 1H NMR spectroscopy, the appearance of the mass spectral signals for (**1b** + metal) $^{+}$ (e.g., m/z 974 (**1b** + Na) $^{+}$ and 1060 (**1b** + Ag) $^{+}$) suggests that other complexes also feature the 1:1 stoichiometry.

The UV-Vis absorption spectroscopic studies were carried out in MeOH-CHCl $_3$ = 1:5 v / v at 25 °C. The significant spectral change was induced by the addition of LiClO $_4$, NaClO $_4$, KPF $_6$, Ca(ClO $_4$) $_2$, Ba(ClO $_4$) $_2$, Zn(ClO $_4$) $_2$, AgCF $_3$ SO $_3$, and MeNH $_3$ BPh $_4$. The typical examples are shown in Figure 2. Among them Ag $^{+}$ ion showed the largest change, which was visually detectable as a solution color change from brownish orange to reddish orange.¹¹ From plots of A_{325} (where the significant absorbance change was obtained reproducibly) vs. additive concentration (Figure 3) the association constants (K_{ass}) were determined according to the Benesi-Hildebrand equation assuming the formation of a 1:1 complex: $\log K_{ass} = 4.81$ for LiClO $_4$, 3.04 for NaClO $_4$, 3.78 for AgCF $_3$ SO $_3$,¹¹ 4.15 for Ba(ClO $_4$) $_2 \cdot 6H_2O$, 3.41 for Zn(ClO $_4$) $_2 \cdot 6H_2O$, and 4.51 for MeNH $_3$ BPh $_4$. These values are nearly comparable with those of regular crown ethers.¹²

In conclusion, the present paper has shown a novel synthesis of "fullerenocrown" and its unique metal-binding properties. Although it is not yet clear if metal cations directly interact with the C $_{60}$ surface, they can sensitively change the electronic state of C $_{60}$. We believe that this change would lead to

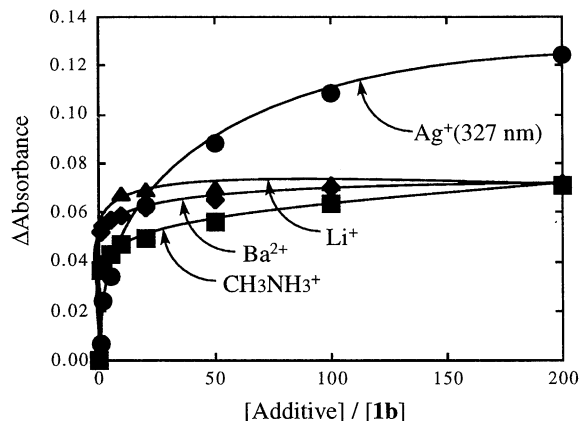


Figure 3. Plots of A_{325} vs. $[additive]$. The plot for Ag $^{+}$ is made with A_{327} (λ_{max}).

novel redox and conductivity properties controllable by the metal-binding.

References and Notes

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- The low yield for **1a** (0.8%) is due to the shortness of the N $_3$ CH $_2$ CH $_2$ (OCH $_2$ CH $_2$) $_3$ N $_3$ chain for ring closure. In fact, we obtained a large amount of the precipitated intermolecular reaction products.
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- 400 MHz, 25 °C, methanol- d_4 :CDCl = 1:9 v/v. The δ_H of N-C-CH $_2$ in the absence of metal cations is 4.330 ppm whereas the maximum δ_H at $[Li^{+} \text{ or } Ba^{2+}] / ([Li^{+} \text{ or } Ba^{2+}] + [1b]) = 0.5$ is 4.340 ppm for Li $^{+}$ and 4.311 ppm for Ba $^{2+}$.
- Ag $^{+}$ induced the largest spectral change, but its K_{ass} is not the largest among metal cations. This discrepancy can be explained as such that Ag $^{+}$ mainly interacts with N whereas Li $^{+}$ and Ba $^{2+}$ mainly interacts with O.
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