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J. Bernard Heyns, L. Malia Sears,
Robert C. Corcoran and Keith T. Carron

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J. Bernard Heyns
Department of Chemistry
University of Stellenbosch
South Africa

L. Malia Sears
Robert C. Corcoran
and
Keith T. Carron
Department of Chemistry
University of Wyoming
Laramie, Wyoming

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SERS Study of the Interaction of Alkali Metal Ions with a Thiol-Derivatized Dibenzo-18-Crown-6

J. Bernard Heyns,[†] **L. Malia Sears, Robert C. Corcoran, and Keith T. Carron***
Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

This report demonstrates that crown ethers can be modified with thiol functionalities and anchored to silver surfaces without loss of activity. Once attached the responsivity of the crown can be examined with surface-enahnced Raman spectroscopy. The crown examined was a diaminodibenzo-18-crown-6 coupled to mercaptonicotinic acid with DCC to form an amide. We found that the derivitized diaminodibenzo-18-crown-6 responded to alkali chlorides. The $K_{\mathrm{formation}}$ and selectivity were determined and followed a trend similar to that observed in aqueous solutions. An ionic strength test indicated that the phenomenon was due to the cation and not the anion. However, a larger $K_{\mathrm{formation}}$ was observed with SCN^-.

Crown ethers are known to form stable stoichiometric complexes with metal cations.[1,2] They are of particular interest for their ability to complex with alkali metal cations, which do not accept most of the ligands common to transition metals. The crown ethers have found analytical applications in solvent extraction of alkali metals and as ion carriers in the membranes of ion-selective electrodes.[3,4] Recently, we have shown that Raman spectroscopy can be used to examine the interaction between coatings anchored to surface-enhanced Raman spectroscopy (SERS) substrates and ionic species in solution.[5,6] In this study we report the results of a study with a thiol-modified crown ether and aqueous solutions of alkali chlorides.

We have modified dibenzo-18-crown-6 witha thiol through an amide linkage using DCC as a coupling reagent.[7,8] The synthetic scheme is shown in Scheme 1. The 4,5′-diaminodibenzo-18-crown-6 was purchased from Parish Chemical Co., Orem, UT. All other reagents were purchased from Aldrich. The stoichiometry was adjusted to favor a 1:1 crown/mercaptonicotinic acid (MNA) complex **1**. The DCC coupling reaction was carried out overnight at room temperature under nitrogen. The product **1** was filtered and washed with $NaHCO_3$ to remove any unreacted MNA. The filtrate was extracted into CH_2Cl_2/THF and as this mixture was used to coat the SERS substrates. MNA was chosen due to its ability to bind to noble metals through both the thiol sulfur and the pyridine nitrogen.[9]

The Raman spectra of the starting materials and the product are shown in Figure 1. It can be seen that the product (Figure 1c) is the sum of the two starting materials (Figure 1a,b) with an additional peak at 1380 cm^{-1} that corresponds to the C–N stretch of an amide.[10] The Raman bands of interest for this study are the 1055-cm^{-1} in-plane C–H deformation of MNA[11] and the broad envelop of CH_2 deformations of the diaminodibenzo-18-crown-6 at 1355 cm^{-1}. The assignment of the crown Raman bands is taken from a normal coordinate analysis of dibenzo-18-crown-6 performed by Miyazawa et al.[12] They found that the 1355-cm^{-1} peak changed intensity in a regular fashion in the presence of alkali metals. The 1055-cm^{-1} peak remains constant and can be used as an internal standard for quantification of alkali metal ion/crown complex concentration.

We found that the crown responded differently to dissimilar alkali metal ions. The response of a surface coated only with MNA was tested, and no activity toward alkali metal ions was found. The trend was similar to that found with dibenzo-18-crown-6 in water.[13] We found a isothermal $K_{\mathrm{formation}}$ for Li^+, Na^+, K^+, Rb^+, and Cs^+ to be 0, 740, 7700, 7200, and 7400 $(M)^{-1}$. In our case, $K_{\mathrm{formation}}$ was found by taking a fractional coverage, θ, on the linear $\theta = Kc$ region of the isotherm and dividing by the solution concentration. Three points, including the origin, were used in the determination of $K_{\mathrm{formation}}$. Illustrative spectral changes for K^+ with **1** are shown in Figure 2a. The resulting isotherms are shown in Figure 2b. In order to normalize the isotherms to different species the highest point was taken as $\theta = 1$, where θ is the fractional coverage. All the alkali metal ions appear to reach surface saturation above a solution concentration of 100 mM.

[†] Permanent address: Department of Chemistry, The University of Stellenbosch, Stellenbosch 7600, South Africa.

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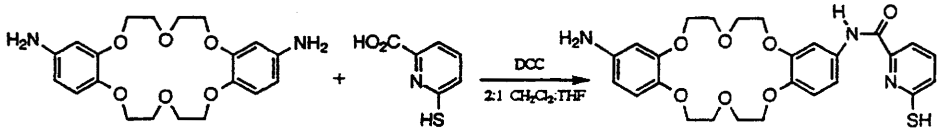
Scheme 1



1

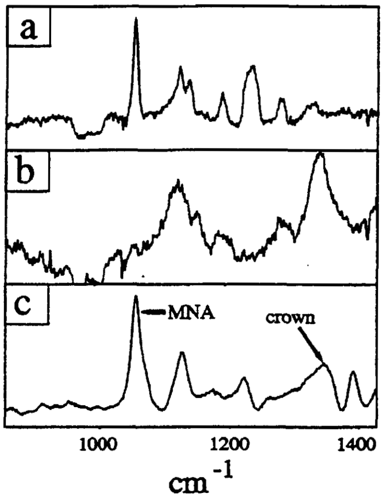


Figure 1. Raman spectra of materials used in this study. The spectra were taken with a CCD (Photometrics) and an HR-320 spectrograph using 647-nm excitation. The integration times were 150 s, and the slit width was 20 μm: (a) SERS spectrum of MNA on silver; (b) normal Raman spectrum of diaminodibenzo-18-crown-6; (c) SERS spectrum of **1** on silver.

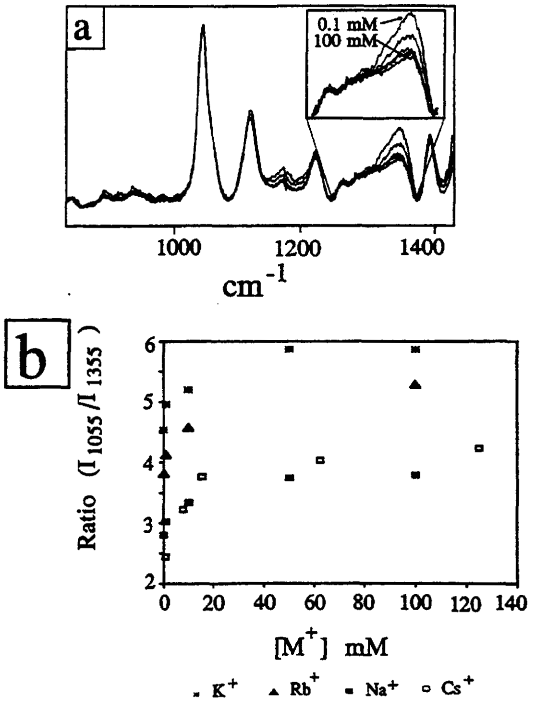


Figure 2. (a) Spectral changes observed in **1** as a function of K$^+$ concentration; (b) isotherms of **1** binding with the alkali metals. The experimental conditions are the same as in Figure 1.

These values compare qualitatively with the findings of Lamb et al.[13] They reported $K_{\text{formation}}$ values of 0, 6.3, 100, 36.3, and 9.8 for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, respectively. However, we have found that the drop-off is not as significant at larger ionic radii. This may be attributed to the conformation of the crown on the surface. In particular, we would anticipate that tight packing may prohibit folding of the crown around the ion and increase the acceptable range of ion radii. A second possibility is that the close proximity of the crowns on the surface may favor sandwich formation. The formation of 1:2 and 2:3 metal ion/ether complexes has been observed for the larger metals.[14] The high concentration of the crown on the surface relative to the solution species should favor sandwich formation.

The effect of the ions on the SERS spectrum of the crown is to decrease the intensity of the CH deformations. A viable explanation for this phenomenon is an overall decrease in the polarizability of the crown species upon complexation. This would be due to the metal ions acting as Lewis acid and withdrawing electron density from the oxygen atoms of the crown. A second possibility would be reorientation of the crown with respect to the surface. The SERS surface selection rules state that a normal coordinate perpendicular to the surface will be enhanced relative to a parallel normal coordinate.[15,16] However, since the C–H and the C–C, C–O stretching coordinates in the 1000–1200-cm^{-1} region all decrease in intensity, it is unlikely that orientational effects are the cause of the decrease in intensity. It would be expected that some of these vibrations would be orthogonal to the C–H deformations and would be relatively enhanced.

It is known that anions that adsorb strongly to surfaces can enhance SERS spectra. The enhancement arises from the static electric field dependence of the polarizability.[17,18] The observed absence of changes in the crown spectrum in the presence of LiCl rules out an anion effect. However, in order to exclude the phenomenon as the source of our observed intensity changes with other alkali chlorides, we performed an experiment at constant ionic strength. Since LiCl was not observed to produce a change in the SERS specrum of **1**, LiCl was used as the inert species. No ionic strength effect was observed.

The counteranion can play a significant role in the formation of stabile crown/metal ion complexes.[1,2] We tested SCN$^-$ with Na$^+$ and K$^+$ cations. We found that the $K_{\text{formation}}$ for NaSCN and KSCN are 3.1×10^6 and 3.5×10^6, respectively. The stronger binding constant for soft anionic species capable of ion pairing was observed previously.[19]

To summarize, we have shown that it is feasible to tether chemically selective ionophores to SERS substrates and follow

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the binding of metal ions with SERS. Future work will be directed at a more thorough examination of the binding process. We are currently designing systems that will contain heteroatoms and various macrocycle ring sizes to greater improve the selectivity.

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