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Preliminary communication

DIBENZO-18-CROWN-6-TRICARBONYLCHROMIUM COMPOUNDS. SYNTHESIS AND SUBSTITUENT DERIVED REVERSAL OF ION EXTRACTION SELECTIVITY

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Summary

Mono- and bis-(tricarbonylchromium) compounds of dibenzo-18-crown-6 have been synthesized. The compounds exhibit a decreased ability to extract alkali metal salts into organic solvents, indicating an overall electron withdrawal from the oxygen crown by the $Cr(CO)_3$ substituents. For the disubstituted compound, the normal selectivity for K^+ over Na^+ is reversed.

The major factors influencing the formation of cation cyclic polyether complexes are the relative sizes of the oxygen crown and cation, and the degree of cation solvation [1-4]. We wish to report the formation and cation complexing ability of novel metal carbonyl-substituted crown ethers; namely mono- and bis-(tricarbonylchromium) derivatives of dibenzo-18-crown-6 (I), i.e., $(CO)_3CrDBC$ (II) and $[(CO)_3Cr]_2DBC$ (III), which exhibit an important substituent effect.

The optimum preparation of the chromium compounds involves the ultraviolet irradiation of a refluxing mixture of I and $Cr(CO)_6$ in a 50/50 mixture of THF and 2,2,4-trimethylpentane. The resulting solutions are concentrated to 70% volume, filtered and cooled at —10 °C to produce yellow crystalline products identified as pure II and III when the ratios of $I/Cr(CO)_6$ are 0.9 and 2.5 respectively, yield ~70%. The PMR spectra of II and III, Table 1, exhibit upfield shifts for the aromatic protons of the $Cr(CO)_3$ coordinated ring, and coupled with the infrared spectra ($\nu(C{\equiv}O)$) for both compounds, confirm coordination of the chromium to the aromatic system rather than to the oxygen crown.

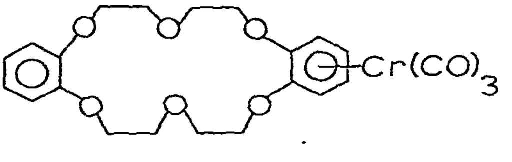
While it is generally accepted that the $Cr(CO)_3$ group frequently has an electron-withdrawing electronic effect, there are special situations where

TABLE 1

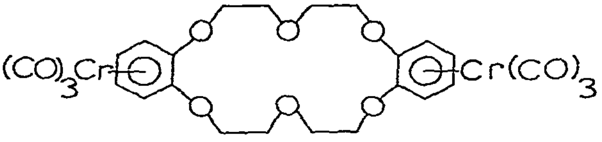
SPECTRAL PROPERTIES OF CROWN ETHERS I, II, AND III[a]

Crown ether	$\nu(C\equiv O)$[b]	$\tau(C_6H_4)$[c]	$\tau(Cr(C_6H_4))$	$\tau(CH_2)$
I	—	6.92 s	—	4.11 m
II	1961, 1875	6.89 a	5.14 m(br)	3.98 m
III	1961, 1875	—	5.10 m(br)	3.90 m

[a] Chemical analyses of the chromium compounds were performed by Chemalytics, Tucson, Arizona. II, m.p. 142-143 °C. Found: C, 55.8; H, 4.87. $C_{25}H_{24}CrO_9$ calcd.: C, 55.6; H, 4.87 %. III, m.p. 155-158 °C (dec.). Found: C, 49.7; H, 3.83. $C_{26}H_{24}Cr_2O_{12}$ calcd.: C, 49.4; H, 3.82%. [b] CH_2Cl_2 solution. [c] $CDCl_3$ solution.



(II)



(III)*

TABLE 2

Log K_{ext} FOR CROWN ETHERS I, II AND III

Crown ether	Log K_{ext} (K^+)	Log K_{ext} (Na^+)
I	3.99	3.39
II	3.57	3.36
III	2.90	3.20

that group can act as a source of electrons if this will stabilize an electron deficient transition state or intermediate [5]. We have studied the electronic effect of the $Cr(CO)_3$ group in the crown ether environment by determining the relative cation complexing abilities of I, II, and III using the Pederson techniques of salt extraction [2]. Table 2 expresses the efficiency of extraction of Na and K (*p*-(dimethylamino)phenylazobenzenesulphonate as log K_{ext} following the analysis of Iwachido et al. [6]. Our results demonstrate that the $Cr(CO)_3$ group reduces the complexing ability of the ether indicating an overall electron-withdrawal from the oxygen crown**. Thus, although the electron deficient Na^+ ion would be further stabilized in the oxygen crown by a release of electrons via either σ—π conjugation or by direct Cr bridging, there is no evidence that in this system such effects are operating.

The data also demonstrate the greater effect of the $Cr(CO)_3$ substituent upon the extraction of K^+ as compared to Na^+. It is well established that I and other 18-crown-6 ethers exhibit a large selectivity for the extraction of K^+ over Na^+ into low-dielectric organic solvents [2]. This is caused by the

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[*] Compound III can exist as either a *cis* or *trans* isomer depending upon whether the $Cr(CO)_3$ groups are on the same or opposite sides of the plane containing the oxygen crown. Our isolated samples are not mixtures as determined by gel permeation chromatography. An X-ray analysis of II and III has been commenced.

[**] Molecular models constructed using known structural parameters of I and $C_6H_6Cr(CO)_3$ indicate steric inhibition of cation approach to the oxygen crown is minimal.

combination of greater compatibility of the ether cavity, 2.6-3.2 Å, with K^+, diameter 2.66 Å, than with Na^+, diameter 1.99 Å, and increased hydration of the Na^+.

A close examination of the structural data published for the various 18-crown-6-ether cation complexes indicates that for the Na^+ complexes the cation is not symmetrically situated with respect to all of the oxygen atoms of the crown [7]. Although the same feature is observed for the larger cations, K^+ and Rb^+, it is to a markedly less degree. It is possible, therefore, that in solution Na^+ has a certain mobility within the oxygen crown unavailable for larger K^+. Thus with one substituent the Na^+ can compensate for the electron withdrawal by strengthening its interaction with the other oxygen atoms less subject to the inductive effect of the $Cr(CO)_3$ substituent, thereby minimizing the substituent effect. This internal compensation is less available for the larger K^+. Upon disubstitution, the ion mobility will be considerably less important since both ends of the crown are equally subject to a $Cr(CO)_3$ substituent. Consequently, the reduction in extraction of the Na^+ salt is now greater than for monosubstitution, and there is a further substantial reduction for the extraction of the K^+ salt. However, as a result of this apparent ability of Na^+ to overcome the initial adverse effects of monosubstitution, coupled with an expected attenuation of substituent effect on the initially weaker Na^+ oxygen crown interaction, the disubstituted crown ether now exhibits a selectivity toward Na^+ over K^+, the first such substituent-derived reversal reported. We are extending this aspect of the work to other systems containing more conventional substituents and indeed have observed a similar ion extraction reversal using *trans*-dinitrobenzo-18-crown-6 [8].

It is of interest that despite the well-documented variations of $\nu(C\equiv O)$ as a function of substituent X in the series $p\text{-}XC_6H_4Cr(CO)_3$ [9], we have observed no variation of $\nu(C\equiv O)$ for the complexes II and III upon cation complexation. We are currently studying smaller ring systems, e.g., dibenzo-12-crown-4, where the effect of the cation may be better transmitted to the $Cr(CO)_3$ group, and any frequency shifts may be delicate monitors of the extent and strength of the cation complexation.

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