case $Cu^{2+}S^{2-}$ and $\eta = 0°$ to $Cu^{+}S^{-}$. After ionization from S 2p the valence electrons flow toward S which means that the valence hole is now more localized on copper than before ionization. Thus if

$$\varphi' = \sin\zeta\, u_{\mathrm{Cu}} + \cos\zeta\, u_{\mathrm{S}} \qquad (2)$$

is the new valence hole we should have $\zeta > \eta$. The orthogonal complement to φ' is φ'':

$$\varphi'' = -\cos\zeta\, u_{\mathrm{Cu}} + \sin\zeta\, u_{\mathrm{S}} \qquad (3)$$

Using eq 2 and 3 we may write eq 1 as

$$\varphi = \cos(\zeta - \eta)\,\varphi' + \sin(\zeta - \eta)\,\varphi'' \qquad (4)$$

According to the sudden approximation[5] a satellite appears corresponding to φ'' with an intensity proportional to $\sin^2(\zeta - \eta)$.

Let us compare to the case when the ligands are O^{2-} or F^{-}. η should here be close to 90° since the bonding is fairly ionic. ζ should be even closer to 90° and therefore $\zeta - \eta$ will be very small. Thus, if the ionization is done in O 1s or F 1s, it is not likely that any satellite will appear. If the ionization is done in Cu 2p on the other hand, the valence electrons will be attracted to the Cu 3d orbital and the hole to S 3p. Thus $\zeta \ll \eta < 90°$, and a satellite appears.[6] It is likely that the satellite will be smaller the smaller η and that is the more covalent the bond between Cu and the ligand. This is in agreement with experiments.[4,7,8] In particular, complexes with sulfur ligands have very weak Cu 2p satellites[8] which thus may be explained by the large covalency of the Cu–S bond, known in a number of Cu–S complexes.[9]

In a covalent case with η much smaller than 90° it may be possible to have a satellite also to the anion inner-shell lines, since it is possible to have $\zeta - \eta$ significantly different from zero. An S 2p satellite is thus possible. Such a satellite has been found for the diethyl dithiocarbamate complex with Cu(II) although of weak intensity.[8] In many other cases with Cu–S bonds it is apparently very hard to decide whether Cu(II) has been reduced to Cu(I). In the latter case the hole orbital φ is filled and no strong satellites will appear either at Cu 2p or S 2p.

In any case, satellites are theoretically possible for inner-shell ionization from S^{2-} contrary to the case for F^{-} or O^{2-}. One may certainly not exclude the possibility that the HBE line in Cu and Co plastocyanin is a satellite and therefore indicative of Cu–S bonding. It is hard to decide from the XPS spectrum whether methionine or cysteine sulfur is involved.

The model with a delocalized hole ($\sin\eta \ll 90°$) has earlier been suggested by Blumberg and Peisach[10] and by Sugiura et al.[9] to explain ESR data. It is also in substantial agreement with calculations on MeS_4^{6-} clusters with Me = Cu, Ni, Co, and Fe.[11] The latter calculations also suggest that an allowed charge-transfer transition ($1t_1 \rightarrow 5t_2$) should appear in the visible region when S is a ligand to Cu. The transition energy for the corresponding Co–S complex should be larger by a factor of 2–3. This gives some support to the current interpretation of the strong absorption line in the blue copper proteins.[12]

The absence of a satellite to Cu 2p in a compound which has proven to correspond to Cu^{2+} by EPR may be regarded as an anomaly. According to the model presented above a satellite should be weak only when the hole φ is considerably delocalized to the ligand already before Cu 2p ionization. This can happen only if at least one of the ligands has a large donating power. Absence of a Cu 2p satellite may thus be regarded as strong support for a Cu–S bond.

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Kinetic Evidence for the Template Effect of Added Cations on the Rate of Formation of Benzo-18-crown-6 in Water Solution

Sir:

The possibility that certain cations facilitate the formation of many-membered rings has been ascribed to a template effect,[1] which presumably operates by complexing the open-chain precursor(s) prior to ring formation and organizing the latter in a conformation close enough to the ring being formed. Convincing evidence of the operation of the template effect in crown ether syntheses has been presented,[2] as based on sets of comparative yields. However, any kinetic information on these reactions is missing, as is any quantitative estimate of the energetic factors involved in this most interesting type of catalysis, implying a crucial interaction of the host-guest type.[3]

Being currently engaged in a systematic study of the energetics of ring-closure reactions,[4] we have undertaken a kinetic investigation on the effect of added cations on the rate of formation of benzo-18-crown-6 (**4**). To isolate the cation effect in the cyclization step, and to avoid any kinetic interference from the intermolecular nucleophilic substitution leading to the crown's precursor (**1**), we have not followed the "shotgun" approach in the construction of **4**, i.e., the reaction of catechol with the proper α,ω-dihalopolyoxa compound in the presence of base. Rather, *o*-hydroxyphenyl-3,6,9,12-tetraoxa-14-bromotetradecyl ether (**1**) was synthesized first,[5] and then subjected to base-promoted cyclization to **4** in the presence of a variety of added alkali and alkali-earth metal cations in water solution at 50 °C. In view of its far too large size for a good fit into the cavity of **4** (or of its ring-shaped precursor), Et_4N^+ cation was used as a reference. In the runs with the monovalent cations 0.022 M $Et_4N^+OH^-$ was present, and the cation was added as the bromide. The divalent cations were added as the hydroxides up to concentrations close to saturation. The concentration of the substrate was in the order of 2×10^{-4} M, i.e., sufficiently low as to let any contribution of the second-order dimerization be negligible.[6] In all experiments the conversion of **1** to **2** was complete, so that corrections for incomplete dissociation were unnecessary. The kinetics were followed spec-

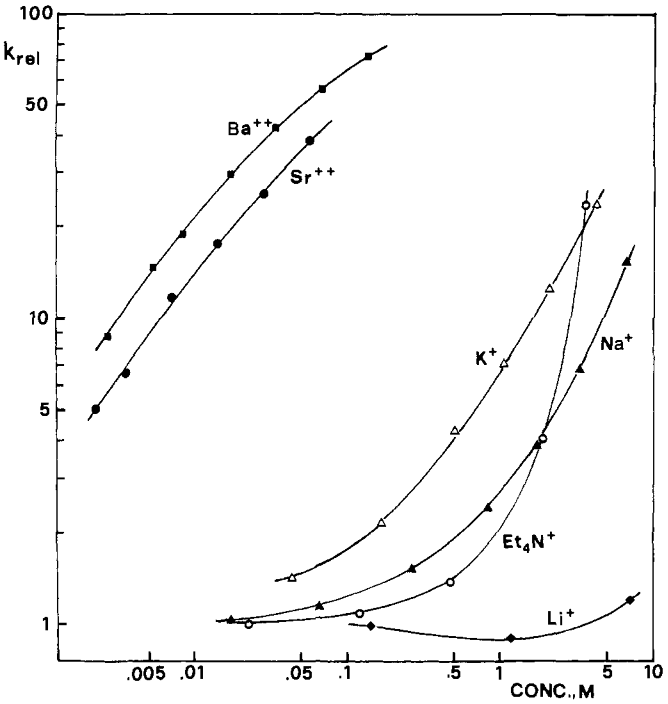
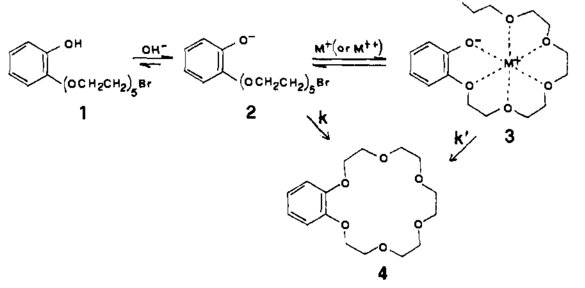


Figure 1. Cation concentration-rate profiles for the base-promoted cyclization of **1**-**4** in the presence of added cations. The cyclization rate constant in the presence of 0.022 M $Et_4N^+OH^-$ was taken as the reference in the calculation of k_{rel} values.

Scheme I



trophotometrically by monitoring the disappearance of the phenoxide ion absorption at 291 nm. Clean first-order behavior was observed in all cases. The kinetic results[7] are shown graphically in Figure 1. The most striking finding is a marked Ba^{2+}- and Sr^{2+}-induced increase in the cyclization rate, which strongly suggests that a template effect is involved in the process according to Scheme I, where the rate constant k' for the conversion of the complexed form (**3**) of the open-chain precursor (**2**) is much greater than the rate constant k for the uncatalyzed path. The observed effect occurs at reasonably low cation concentration (0.1 M or less), so that the operation of significant medium effects on the reaction rates is unlikely. In contrast, with the monovalent alkali metal and the quaternary ammonium ions, rate effects are observed at significantly higher concentrations. Since in the case of Et_4N^+ the formation of a complexed form having structure **3** is most unlikely, the observed reactivity pattern may be attributed to a medium effect, the bulky organic cation being probably responsible for the marked deviation from dilute solution behavior. Although the interpretation of the results obtained with the alkali metal cations is made difficult by the high concentrations required for the rate-enhancing effect to be significant, the following points are worth noting. The behavior of both K^+ and Na^+ is markedly different from that of Li^+, where a negligible effect is observed, as well as from that of Et_4N^+, whose curve intersects those of both K^+ and Na^+. Notably, in the concentration range ~0.1-1 M, the rate-enhancing effect of the latter cations is appreciably larger than that of Et_4N^+, and, therefore, seems far too large to be attributed to a general medium effect. Moreover, the curves of the different metal cations are displaced to higher concentrations by roughly the same extent as the logarithms of the related association constants with dibenzo-18-crown-6 in water at 25 °C,[8] which are reported in parentheses: Ba^{2+} (3.6) > Sr^{2+} (3.2) ≫ K^+ (2.2) > Na^+ (1.7) ≫ Li^+ (0.6). The fact that the complexing ability of different cations with polyoxa compounds appears to follow the same order with either ring compounds or their open-chain analogues[9] strongly indicates that the above close correspondence between catalytic effect as observed in the present study and stability constants with dibenzo-18-crown-6 is hardly fortuitous. Consequently, the operation of a template effect is also suggested in the case of K^+ and Na^+, for which relatively high concentrations are required because of their unfavorable binding constants as compared with those of the divalent metal ions. A medium effect is possibly superimposed into the template effect in the case of K^+ and Na^+, particularly at the highest concentrations used. The present data do not allow to estimate the relative importance of these effects.

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(5) Pentaethylene glycol, bp 160-170 °C (0.4 mm), obtained by fractional distillation of polyethylene glycol 300 (Merck), was treated with PBr_3 and pyridine. The resulting dibromide (0.065 mol), catechol (0.26 mol), and KOH (0.065 mol) were refluxed in ethanol solution until neutral. Aqueous workup followed by CCl_4 extraction gave an oil, which was eluted on silica gel first with 49:1 $CHCl_3$–MeOH and then with 1:1 benzene–ethyl acetate to afford pure 1 (0.008 mol, 12% yield). Bromine content was within 0.2% of theory. ^1H NMR was as expected.

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2,2'-Dimethyl-9,9'-bitriptycyl. A Case of an Enormous Rotational Barrier between sp^3-Hybridized Carbon Atoms[1]

Sir:

Highly hindered compounds capable of exhibiting appreciable rotation barriers between sp^3-hybridized carbon atoms have been the subject of considerable interest and numerous reports in recent years.[2] The largest rotational barrier of this kind that has been reported is 37.7 kcal mol^{-1} for 9,10-bis(1-