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(dmpe)$_2$Cl].[23] cis-Bis(trimethylsiloxy)ethylene was also found to react with excess water in THF-d_8 on a much slower time scale (20 min to 24 h) to form first trimethylsilanol (by ^{1}H NMR and GC/MS analysis) and eventually hexamethyldisiloxane. Similar problems with hydrolysis occurred in isolating the free olefin from hydrogenation of [Ta(Me$_3$SiOC≡COSiMe$_3$)(dmpe)$_2$Cl], which were partly solved by use of the more sterically encumbered ^{t}BuMe$_2$Si derivative.[23]

Interestingly, subjecting the electronically saturated [V-(Me$_3$SiOC≡COSiMe$_3$)(dmpe)$_2$Br] (3) complex to the same hydrogenation conditions as described above for compound 2 also gave cis-bis(trimethylsiloxy)ethylene, in 41% yield. No metal-dmpe-containing species was observed by NMR spectroscopy, and the other organic product was hexamethyldisiloxane. Dissociation of the bromide ligand from 3 would afford the same 16-electron species as in 2, which could then react with dihydrogen in the absence of an external catalyst. No diminution in the yield of olefin was observed when the reaction of 3 with H$_2$ was run in the less polar solvent C$_6$D$_6$, rather than THF-d_8, in contrast to what one might expect for rate-limiting loss of bromide ion. In a separate experiment, no free olefin was detected when [Ta-(Me$_3$SiOC≡COSiMe$_3$)(dmpe)$_2$Cl] was subjected to the same hydrogenation conditions; only starting material was observed in the ^{1}H NMR spectrum. As was found with 2, addition of 1 equiv of H$_2$O to 3 in THF-d_8 yielded predominantly hexamethyldisiloxane and a small amount (4%) of free olefin.

Summary and Prospectus. The present study has significantly extended the generality of the CO reductive coupling reaction to a first-row transition metal, vanadium. Reductive coupling of the CO ligands in Na[V(CO)$_2$(dmpe)$_2$] has afforded both the un-

precedented 16-electron, six-coordinate and the more commonly encountered 18-electron, seven-coordinate bis(trialkylsiloxy)-acetylene complexes. These acetylene complexes react directly with hydrogen at ambient temperature and modest pressures to yield cis-disiloxyethylene. Furthermore, we have structurally characterized the first unambiguous example of a vanadium carbyne complex. Such species are believed to be key intermediates in the formation of CO-derived acetylene complexes by reductive coupling. Current work is directed toward the incorporation of other ligands into the coordination sphere of the 16-electron acetylene complex to promote further insertion and functionalization of the original CO ligands. In this regard we have recently found that complex 2 reacts with 1 equiv of CO to yield cis-[V(Me$_3$SiOC≡COSiMe$_3$)(CO)(dmpe)$_2$]OTf.[56] We are also exploring the reactivity of Na[V(CO)$_2$(dmpe)$_2$] with carbon-centered electrophiles in attempts to generate the analogous dialkoxyacetylene complexes.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank E. M. Carnahan for assistance with the crystallographic analyses.

Supplementary Material Available: PLUTO diagrams containing the complete atom-labeling schemes and tables of positional and isotropic thermal parameters and anisotropic temperature factors for 2–4c (15 pages); tables of observed and calculated structure factors for 2–4c (72 pages). Ordering information is given on any current masthead page.

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Crown Ether Alcohols as Bifunctional Ligands for Simultaneous Cation Complexation and Anion Solvation

Uriel Olsher,*,† Felix Frolow,† N. Kent Dalley,‡ Jiang Weiming,‡ Zong-Yuan Yu,§ John M. Knobeloch,§ and Richard A. Bartsch*,§

Contribution from the Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, Department of Chemistry, Brigham Young University, Provo, Utah 84602, and Department of Chemical Services. The Weizmann Institute of Science, Rehovot 76100, Israel. Received February 28, 1991

Abstract: Structural modification of crown ethers by attachment of one or more pendant hydroxyl groups offers the potential for anion solvation as well as cation complexation by the ligand. Molecular structures have been determined for LiNCS complexes of two dibenzo-14-crown-4 alcohols and a dibenzo-14-crown-4 diol as well as a LiNO$_3$ complex for one of the alcohols. Crystal structures for these four complexes show intracomplex "scorpion-like" and intercomplex "head-to-tail" hydrogen bonding of the crown ether hydroxyl groups with the anions. These complexes provide the first demonstration of the exploitation of structurally modified crown ethers as bifunctional ligands for simultaneous anion solvation and cation complexation.

Introduction

Cyclic polyethers (crown ethers) are selective complexing agents for alkali-metal cations.[1–4] They are utilized to extract alkali-metal cations from aqueous solutions into hydrophobic, nonpolar organic solvents[5–16] and to carry these cations selectively through solvent-polymeric[17,18] and liquid membranes.[19,20] For such extractions and membrane processes, the identity of the anion that must be concomitantly transported into the organic medium is very important. Extraction efficiency and membrane transport rates are favorable for large and highly polarizable organic anions,

such as picrate,[5–10,19,20] tetraphenylborate,[11] and dipicrylaminate.[12] Large inorganic anions, such as permanganate,[5] perchlorate,[12]

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* To whom correspondence should be addressed.
† The Weizmann Institute of Science.
‡ Brigham Young University.
§ Texas Tech University.

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Table I. Crystal Data and Experimental Conditions for X-ray Studies

	2·LiNCS	3·LiNCS	4·LiNCS	4·LiNO$_3$
formula	[Li(C$_{18}$H$_{20}$O$_5$)NCS]	[Li(C$_{18}$H$_{20}$O$_6$)NCS]	[Li(C$_{19}$H$_{22}$O$_5$)NCS]	[Li(C$_{19}$H$_{22}$O$_5$)NO$_3$]
M_r	381.2	397.4	395.4	399.14
$F(000)$	1600	832	416	420
cryst size, mm	0.4 × 0.3 × 0.2	0.30 × 0.25 × 0.10	0.5 × 0.3 × 0.1	0.35 × 0.30 × 0.15
μ, cm^{-1}	1.93	1.89	1.83	1.01
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
no. of data used to detm lattice param (scan range, deg)	25 (15 < 2θ < 29.2)	20 (10.2 < 2θ < 26.2)	18 (5.3 < 2θ < 19.7)	25 (11.2 < 2θ < 25.0)
a, Å	22.277 (7)	13.118 (6)	8.656 (2)	8.684 (1)
b, Å	10.025 (3)	9.977 (2)	9.428 (3)	9.050 (2)
c, Å	16.833 (5)	15.122 (3)	13.073 (3)	13.290 (3)
α, deg	90	90	74.48 (2)	98.89 (2)
β, deg	96.75 (2)	91.94 (2)	72.45 (2)	106.57 (1)
γ, deg	90	90	73.72 (2)	102.65 (2)
V, Å^3	37 733 (2)	1978.1 (9)	997.3 (4)	950.01 (3)
Z	8	4	2	2
ρ_x, g/cm^3	1.36	1.34	1.32	1.40
scan rate range, deg min^{-1}	5–60	3–60	4–60	4–60
$(\sin\theta)/\lambda$, Å^{-1}	0.54	0.54	0.59	0.59
no. of tot. data	5446	2919	2891	3629
no. of unique data	3639	1543	1704	2043
no. of unobsd data ($F > 3\sigma(F)$)	1249	1058	997	1323
constraints used in refinement	none	none	positions of disordered atoms in less populated sites not refined	NO$_3^-$ refined as trigonal planar group
R, R_w	0.062, 0.078	0.071, 0.041	0.062, 0.054	0.098, 0.118
data/param ratio	7.8	6.0	7.2	7.5
goodness of fit	1.88	1.54	1.57	1.90
G value in weight	0.000 68	0.000 00	0.000 26	0.001 68
largest peaks in Δ map	0.57, −0.45	0.33, −0.33	0.24, −0.21	0.86, −0.46

iodide,[12] and thiocyanate,[13] are also satisfactory anions in these processes. In contrast, distribution ratios for extractions of alkali-metal halides (other than iodides) from aqueous solution into nonpolar organic solvents are low.[14,15,19,20] The halide ions have insufficient hydrophobicity to be extracted into organic media[15,16] and are not effectively solvated in them.

The addition of an alcohol to a nonhydroxylic organic solvent increases the ability of a crown ether to extract alkali metals from a contacting aqueous solution into the organic medium. Crown ethers extract alkali-metal thiocyanates from aqueous solutions into a solvent consisting of 0.30 volume fraction of 1-butanol in toluene quite efficiently.[13] Such a solution is a biological membrane model. The ability of dicyclohexano-18-crown-6 to solubilize sodium or potassium halides in benzene is markedly enhanced when 0.25 M methanol is added to the benzene.[13] The effect of added alcohol is related to solvation of the anion and not solvation of the cation.[21-28] Thus, methanol is not required for solubilization

of alkali-metal salts in chloroform or dichloromethane when larger anions, such as iodide, are used.[14]

Structural modification of crown ethers by attachment of one or more pendant hydroxyl groups offers the potential for anion solvation as well as cation complexation. By providing an intramolecular hydroxyl group to solvate the anion, such crown ether alcohols may provide a highly favorable entropy of interaction with both the cation and the anion. Crown ether alcohols could be considered to be cyclic derivatives of polyethylene glycols,[30,31] which provide both ethereal oxygens to coordinate the cation and hydroxyl groups as potential anion-solvating sites. Evidence for simultaneous cation complexation and anion solvation by acyclic ligands is also provided in the crystal structure of a KI–phenacyl kojate complex.[29]

To probe the possibility that crown ether alcohols may act as bifunctional ligands, three-dimensional crystal structures of lithium soft and hard anion salt[15,32] complexes with a series of crown ether alcohols are now examined. This approach involves the basic assumption that the structures of such crown ether–lithium salt complexes in the solid state will resemble their structures in solution.[33] In this case, crystallographic data will provide important information for the design of improved ligands that may interact with both the cation and the anion.

In the reported structure for the complex of dibenzo-14-crown-4 (1) and LiNCS, the lithium ion is pentacoordinated to the four ethereal oxygens and to the nitrogen of the thiocyanate anion in

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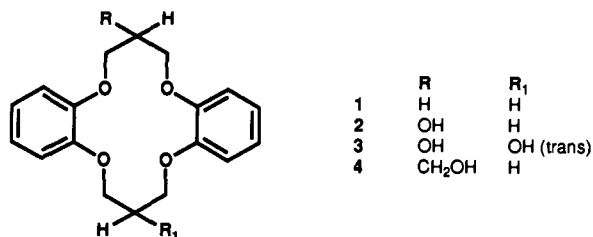(29) Hughes, D. L.; Phillips, S. E. V.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1974**, 907.

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a nearly square-pyramidal geometry.[34] In the present investi-

gation, LiNCS complexes have been prepared from dibenzo-14-crown-4 alcohols **2** and **4** and diol **3**[35] and their molecular structures have been determined. In addition, the structure of the LiNO₃ complex of **4** has been determined to examine the effect of changing from a soft anion to a hard one. We now report the crystal structures for these four complexes, in which interesting patterns are observed for hydrogen bonding of the hydroxyl groups with the thiocyanate and nitrate anions.

Experimental Section

Materials. The synthesis of compounds **2–4** has been reported.[35] Other chemicals were reagent grade and were used as received from commercial suppliers.

Crystal Data. Single crystals of the LiNCS complexes with **2–4** and of the LiNO₃ complex with **4** were grown from 1:1 (volume) solutions of CH₂Cl₂ and acetonitrile. All crystal and intensity data were obtained by utilizing a Nicolet R3 automated diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The lattice parameters and orientation matrix for each compound were obtained by using a least-squares procedure involving several carefully centered data. Single-crystal intensity data were obtained by using a variable scan rate θ–2θ scanning technique. The crystal data and experimental conditions for these studies are summarized in Table I.

The four structures were solved by direct methods. The data in Table I indicate that there are two molecules of **2·**LiNCS in the asymmetric unit. Both molecules were located in the solution of that structure and will be referred to as molecules A and B. Refinement for each compound proceeded normally, but it became evident that there was some disorder in all the compounds with the exception of **3·**LiNCS. In **2·**LiNCS molecule B, there is orientational disorder with a partial OH (occupancy factor 0.15) on C2. Also, there is a static disorder as O5B occupies two different sites, O5B and O5B'. The disorders in **4·**LiNCS and **4·**LiNO₃ are similar, involving the atoms of the CH₂OH chain. The disorder of both the C and the O was resolved in **4·**LiNCS, but only the disorder of the O was resolved in **4·**LiNO₃. The disordered atoms that were resolved and their site occupancy values in parentheses are as follows: in **2·**LiNCS molecule B, O5B (0.70), O5B' (0.15), O6B' (0.15), and HO5B (0.70); in **4·**LiNCS, C19 (0.85), HC19 (0.85), O5 (0.85), C19' (0.15), and O5' (0.15); and in **4·**LiNO₃, O5 (0.55), HO5 (0.55), and O5' (0.45). Atom labels for disordered atoms with the smaller occupancy value contain the prime. O6B' is the orientationally disordered atom in **2·**LiNCS molecule B. In addition, the large thermal motion of the O atoms of the nitrate ion of **4·**LiNO₃ and the rather large peaks located near these oxygens in the difference map of the complex indicate disorder of that group. This disorder was not resolved and likely accounts for the rather large R value for that structure.

Positions for all hydrogens bonded to carbon atoms were calculated on the basis of stereochemical considerations with the exceptions of those bonded to disordered carbons and to their neighboring carbons. Hydrogen positions for the more populated site of C19 in **4·**LiNCS and to the carbons next to disordered atoms in all structures were located in difference maps. Also, hydrogen atoms bonded to oxygens in molecule A of **2·**LiNCS, the more populated oxygen O5B in molecule B of **2·**LiNCS, both alcoholic oxygens of **3·**LiNCS, and the more populated alcohol oxygen O5 in **4·**LiNO₃ were located in the difference maps. The hydrogens of O5B' and O6B' in **2·**LiNCS, C19', O5, and O5' of **4·**LiNCS, and O5' and one H of C19 in **4·**LiNO₃ could not be located in difference maps, nor were positions for these atoms calculated. All non-hydrogen atoms with the exception of O5B' and O6B' in **2·**LiNCS and C19' and O5' in **4·**LiNCS were refined anisotropically. Weights used in the refinement of the compounds are of the form $1/[\sigma(F)^2 + GF^2]$. Data for **2·**LiNCS and **3·**LiNCS were corrected for secondary extinction.
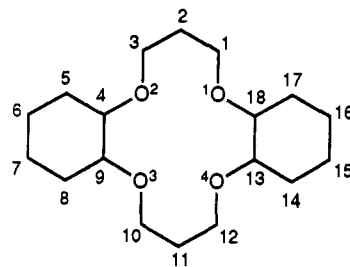
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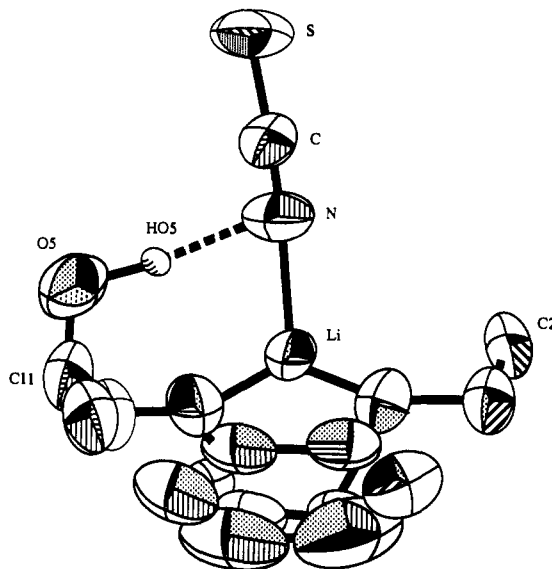**Figure 1.** Molecular numbering scheme for dibenzo-14-crown-4.

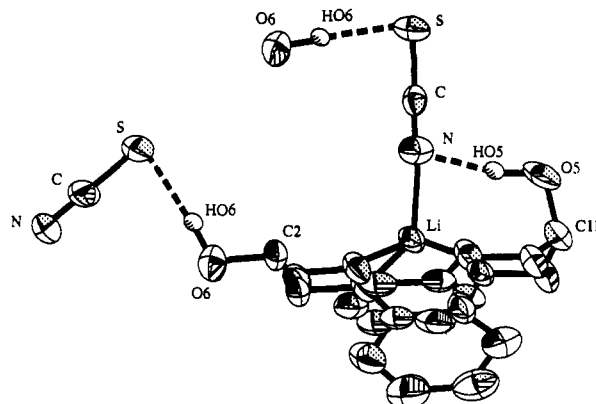**Figure 2.** Crystal structure for the **2·**LiNCS complex.

Figure 3. Crystal structure for the **3·**LiNCS complex.

Scattering factors were obtained from ref 36. All programs used in the solution and display of the structures are contained in the SHELXTL package.[37]

Results

The molecular numbering scheme for the basic 14-crown-4 unit is given in Figure 1. The numbering of the additional atoms attached to the basic unit is given in Figures 2–5. For coronands **2–4**, the molecular conformations of the LiNCS complexes are shown in Figures 2–4, respectively. The molecular conformation of the LiNO₃ complex of **4** is presented in Figure 5.

Tables of positional parameters of the atoms, bond distances and angles, and anisotropic thermal parameters are given in the supplementary material. In all four complexes, Li⁺ has square-

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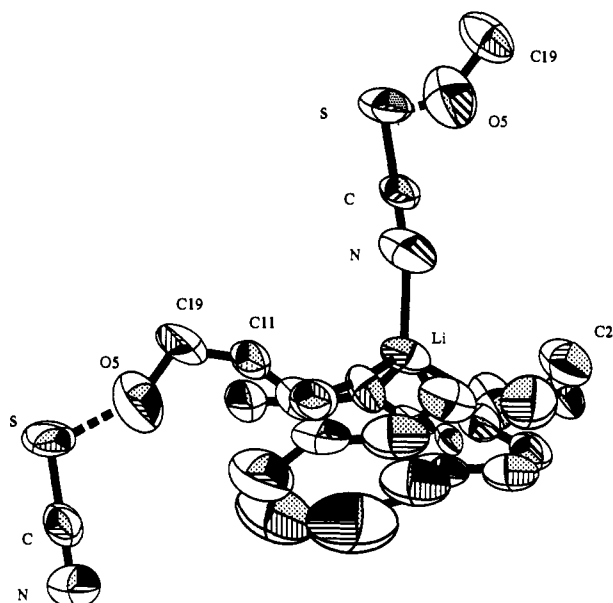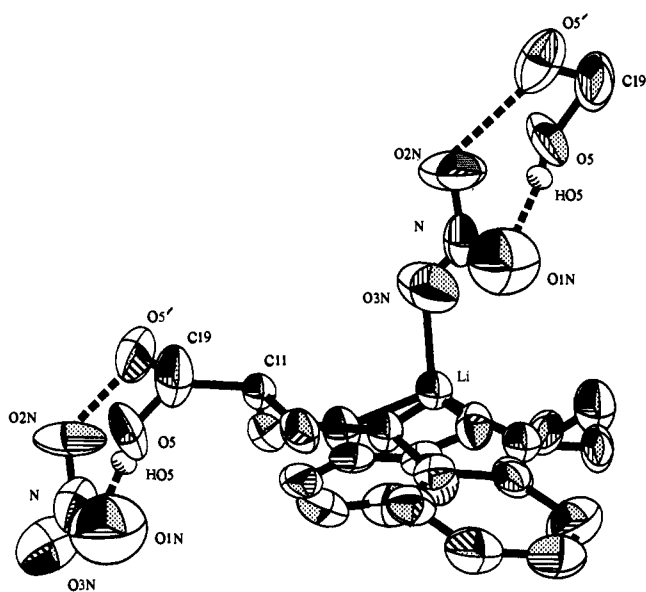
Crown Ether Alcohols as Bifunctional Ligands

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Figure 4. Crystal structure for the 4·LiNCS complex.

Figure 5. Crystal structure for the 4·LiNO₃ complex.

pyramidal coordination with the ethereal oxygens forming the base of the pyramid and an atom of the anion at the apex of the pyramid.[33] There are two types of hydrogen bonds, one involving intracomplex interactions (Figure 2) and the other involving intercomplex interactions (Figures 4 and 5). In the structure of the complex of crown ether diol **3** with LiNCS, both types of hydrogen-bonding interactions are evident (Figure 3). The hydrogen-bond data are listed in Table II. Unfortunately, it was not possible to locate the hydrogen atoms of both disordered oxygen, O5 and O5′, in 4·LiNCS and of O5′ in 4·LiNO₃, so another interaction criterion for the hydrogen bonds involving those oxygens is listed. If the angle D–H···A is approximately linear, the C–D···A angle should be close to 105°.[38] In each case listed in Table II, that angle is sufficiently close to 105° to provide evidence for the presence of a hydrogen bond.

Discussion

In each of the four complexes, the ligand molecule interacts with an anion via hydrogen bonds. To our knowledge this is the first demonstration of exploiting structurally modified crown ethers

Table II. Hydrogen Bonds and Possible Hydrogen-Bond Data

bond	dist, Å		angle, deg	sym translation of acceptor atom
	2·LiNCS			
D–H···A	H···A	D···A	D–H···A	
O5–HO5···N	1.85 (2)ᵃ	2.942 (5)	172 (1)ᵃ	*x, y, z*
O5′–HO5′···N	1.83 (2)ᵃ	3.042 (6)	174 (1)ᵃ	*x, y, z*
	3·LiNCS			
D–H···A	H···A	D···A	D–H···A	
O5–HO5···N	1.77 (2)ᵃ	2.915 (7)	169 (1)ᵃ	*x, y, z*
O6–HO6···S	2.18 (2)ᵃ	3.245 (5)	170 (1)ᵃ	−0.5 − *x*, −0.5 + *y*, 0.5 − *z*
	4·LiNCS			
X–D···A		D···A	X–D···A	
C19–O5···S		3.374 (5)	107.6 (5)	−1 − *x*, −*y*, 2 − *z*
C19′–O5′···S		3.19 (2)ᵇ	114 (2)ᵇ	
	4·LiNO₃			
D–H···A	H···A	D···A	D–H···A	
O5–HO5···O1N	2.01 (2)ᵃ	2.754 (12)	167 (1)ᵃ	1 + *x, y, z*
X–D···A	X···A		X–D···A	
C19′–O5′···O2N	2.821 (12)		123.9 (7)	1 + *x, y, z*

ᵃ Esd value estimated as H is allowed to ride on the neighboring oxygen atom in the refinement. ᵇ Esd value estimated as CC9′ and OC9′ were held fixed in the refinement.

as bifunctional ligands for simultaneous cation complexation and anion solvation.

There are two types of hydrogen bonds. The first consists of an intracomplex hydrogen bond (Figure 2) that possesses a "scorpion" shape.[39] The second type of hydrogen-bonding interaction is an intercomplex "head-to-tail" arrangement (Figures 4 and 5) that involves interaction of the hydroxyl group of one complex and the anion of a second. Thus one end of the anion is coordinated to the complexed Li⁺ and the other is hydrogen-bonded to the hydroxyl group of an adjacent complex.

The type of hydrogen bond is dictated by the ligand conformation. Intracomplex hydrogen bonds are formed when the hydroxyl group is directed toward the crown ether cavity (Figure 2 and for one of the hydroxyl groups in Figure 3). Intercomplex hydrogen bonds are produced when the hydroxyl groups are not available for formation of intracomplex hydrogen bonds due to conformational restrictions (Figures 4 and 5 and for one of the hydroxyl groups in Figure 3).

Complexes of 4·LiNCS and 4·LiNO₃ differ in the replacement of the soft thiocyanate anion in the former with a hard nitrate anion[15,32] in the latter. The structures for the two complexes (Figures 4 and 5, respectively) reveal intercomplex hydrogen bonding for the anions in both complexes. Thus the change from a soft to hard anion did not alter the type of hydrogen-bonding interaction with the anion.

In the crystal structures of anhydrous uncomplexed crown ether alcohol **4** and diol **3**, orientations of the alcohol groups with respect to the crown ether cavities are very similar to those found in the LiNCS and LiNO₃ complexes.[40] Thus conformational preorganization of the ligand itself plays an important role in determining whether intracomplex or intercomplex hydrogen bonding of the hydroxyl group with the anion of the complexed lithium salt will take place. When a contact ion pair is formed by complexation of a metal salt with a crown ether, which is the case in nonpolar organic solvents,[15] intracomplex hydrogen bonds would be favored due to entropy and enthalpy considerations. Thus preorganized ligands that provide simultaneous cation complexation and intracomplex anion solvation are preferred.

In the solid-state structure of the KI complex of the acyclic ligand phenacyl kojate,[29] hydroxyl groups are simultaneously involved in cation complexation and anion solvation. In contrast for the LiNCS and LiNO₃ complexes of the cyclic polyether

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(39) These structures are designated as "scorpion-like" because the interaction of the host molecule (crown ether alcohol) with the guest species (lithium salt) resembles the way that a scorpion holds its victim while striking it.

(40) Olsher, U.; Dalley, N. K.; Bartsch, R. A. Unpublished results.

ligands **2–4** that are examined in this study, the hydroxyl groups participate only in anion solvation. Involvement of the anion-binding sites in cation complexation could be a disadvantage if it changes the total number of potential coordination sites for cation binding that might produce conformational changes. Both factors would be expected to influence the selectivity with which different cations are complexed. On the other hand, the separate involvement of the crown ether ring oxygen and hydroxyl group in cation complexation and anion solvation, respectively, observed for the metal salt complexes with crown ether alcohols **2–4** should maintain cation selectivity while enhancing with which the metal salt is transported into an organic medium in solvent extraction or liquid membrane transport processes.

Synthetic attempts are now underway to provide additional crown ether alcohols with structures suitable for simultaneous cation complexation and intracomplex anion solvation.

Chemistry of Catalytic Dehydrogenative Oligomerization of Tetrahydroquinoline and Structural Characterization of Nonsubstituted Quinoline Oligomers

L. Y. Chiang,* J. W. Swirczewski, R. Kastrup, C. S. Hsu, and R. B. Upasani

Contribution from Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801. Received July 24, 1990

Abstract: A new catalytic dehydrogenative polycondensation (CDHP) of 1,2,3,4-tetrahydroquinoline (THQ) using transition metal sulfides or tris- or bis(*o*-aminobenzenethiolate) complexes of groups VIB, VIIB, and VIII transition metals as catalyst precursors is described. The method provides a direct route to the synthesis of nonsubstituted quinoline oligomers, which have not been prepared by known methods. The effective heterogeneous CDHP catalysts were generated in situ in reaction media from precursors by a preheating treatment at 180–210 °C. These active catalysts were found to consist of metal and sulfur stoichiometric composition approaching MoS$_2$, ReS$_2$, RuS, RhS$_2$, PtS, and PdS. We observed a periodic trend on the CDHP activities of transition metal sulfides, showing a maximum oligomer yield (97%) with a ruthenium sulfide catalyst. The structure of quinoline oligomers was elucidated on the basis of X-ray crystallographic studies and various spectroscopic data including the 2D COSY ^{1}H NMR spectra. The full structural characterization of two quinoline dimers and a trimer, which were successfully isolated from the bulk product, resolved the puzzle of carbon positions at the ring conjunction between quinoline moieties in oligomers. The first dimer of 2,3′-biquinoline crystallized in a space group of $P2_1/a$ (No. 14) with the monoclinic cell dimensions $a = 12.492$ (2) Å, $b = 5.3821$ (9) Å, $c = 19.253$ (3) Å, and $\beta = 100.20$ (1)°, showing a quinoline ring conjunction at carbons C$_2$ and C$_3'$. The second dimer of 2,6′-biquinoline crystallized in a space group of Pa (No. 7) with the monoclinic cell dimensions $a = 8.1687$ (6) Å, $b = 5.9748$ (5) Å, $c = 13.126$ (1) Å, and $\beta = 95.032$ (7)°, showing a quinoline ring conjunction at carbons C$_2$ and C$_6'$. The structure of one quinoline trimer was found to contain two quinoline ring conjunctions at carbons C$_2$–C$_6'$ and C$_2'$–C$_3''$. On the basis of results from the structural and kinetic studies, a hypothetical CDHP reaction mechanism was proposed. That leads to two major oligomeric quinoline products **1a** and **1b** differing in only the orientation of the head unit in structure. In the CDHP chemistry, we conclude that a delicate balance between dehydrogenation and polymerization activities of catalyst is required to optimize the yield and the molecular weight of resulting products. We also observed a coexistence of hydrogenation and dehydrogenation activity, probably at different surface sites of transition metal sulfide.

Transition metal sulfides (TMS) have been shown to display the catalytic behavior in both the heterogeneous hydrogenation (in the presence of a low hydrogen pressure) and dehydrogenation (in the absence of hydrogen) of organic compounds in a reversible manner.[1] They have been used extensively in the industrial process as hydrotreating catalysts and the synthetic chemistry to add or remove hydrogen from organic molecules. Under high hydrogen pressure (>1000 psi) transition metal sulfides exhibit hydro-

Scheme I

2 : x = 1;   4 : x = 2
3 : x = 1
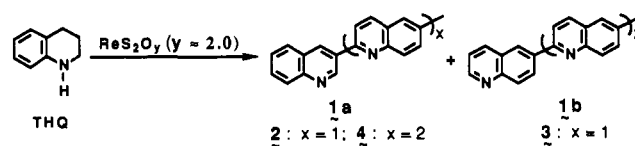
desulfurization (HDS) and hydrodenitrogenation (HDN) activities in addition to hydrogenation. Thus, they are valuable heterogeneous catalysts used for the removal of sulfur and nitrogen from heavy petroleum feedstocks.[2] In both the hydrogenation and

(1) Weiser, O.; Landa, S. *Sulfide Catalysts: Their Properties and Applications*; Pergamon: Oxford, 1973; p 370.