A29-G30 (Figure 1) there is no obvious reason for the lack of drug binding. The explanation that this site is inaccessible seems unlikely since an osmium complex has been observed to bind covalently to the N7 atom of G30.[22] Other workers have observed regions of DNA where drug binding was expected but not observed.[37] In that case incubating the DNA with ethidium bromide prior to reaction with the drug resulted in the expected binding at a 5′-$(dG)_6$-dC-$(dG)_2$-3′ site. At A14-G15 in $tRNA^{Phe}$ the N7 atom of A14 is involved in a reverse Hoogsteen base pair with N3 of U8 which is probably the reason for the lack of drug binding at this site. At A21-G22-A23-G24 the N7 of G22 is hydrogen bonded to N1 of m^7G46 and the N7 of A23 is hydrogen bonded to N6 of A9[38,39] which presumably prevents drug binding in this region. *cis*-DDP intrastrand cross-linking at G18-G19-G20 would not be expected since the bases are not stacked on one another and the N7 atoms of adjacent bases are a considerable distance apart [N7(G18)···N7(G19) = 8.1 Å; N7(G19)···N7(G20) = 10.0 Å]. Also residue G57 intercalates between G18 and G19 which will certainly prevent drug cross-linking between these latter two bases. At A9-m^2G10 the donor atom–donor atom distance is rather long to allow intrastrand cross-linking [N7(A9)···N7-(m^2G10) = 6.4 Å]. Drug binding is not observed at A35-A36 or at A66-A67 even though the geometry at these two sites appears to be favorable for binding which suggests that one G residue is required for intrastrand cross-linking, at least at the concentrations used in the present work. Binding is also not observed at A36-Y37 even though Y37 is, in effect, a modified G residue. Certainly the geometry at this site should not preclude drug binding.

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Communications to the Editor

Ester Side-Arm Participation in a Crystalline Lariat Ether–Sodium Bromide Complex

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An interesting aspect of ionophore chemistry is that naturally occurring cation carriers utilize ester carbonyl donor groups to complex cations.[1] In this respect, valinomycin[2] is typical. It has six amide carbonyls which are involved in hydrogen bonding around the periphery of the three-dimensional structure and six ester carbonyl groups which bind the cation.[3] Crown ethers have been extensively used as ionophore models even though they generally lack ester linkages.[4] In numerous cases, ester residues have been incorporated,[5] but in 15- or 18-membered rings, the carbonyls must be turned outward, geometrically prohibiting interaction with an intraannular cation. If the ester donor is part of a flexible, lariat ether side arm, this restriction should be lifted. The first X-ray crsytal structure of a lariat ether ionophore in which an ester carbonyl group interacts directly with the ring-bound cation is reported here.

This structure should be viewed in the context of other macrocyclic polyether compounds with side-chain interactions with a metal cation.[6] These laboratories[6a] and others[6b] have reported crystal structures of complexes with side arms containing ether and alcohol oxygens. Other laboratories have reported crystal structures of complexes with carboxamide[6c] and carboxylate[6d] side arms.

The structure of the complex that forms between sodium bromide and ethyl (1-aza-4,7,10,13-tetraoxacyclopentadecyl)-ethanoate[7] (**1**) is shown in Figure 1 along with a skeletal drawing of the donor atoms and the metal. Of the six lariat donor atoms, the ester carbonyl oxygen, O18, is closest to the metal ion. As the skeletal drawing reveals, the five donor atoms of the macroring approximate a half-chair conformation, C_2 symmetry with O7 on the axis. Bromide ion also serves as a donor making Na^+ heptacoordinate in this complex.

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(7) Compound **1** was prepared by alkylation of 1-aza-4,7,10,13-tetraoxacyclopentadecane[8] with ethyl bromoacetate (CH_3CN/Na_2CO_3) in 53% yield. The nearly colorless oil was treated with an equivalent amount of NaBr and crystallized from cold acetone and gave a white solid: mp 114-115 °C; ^1H NMR ($CDCl_3$) δ 1.3 (t), 2.8 (t), 3.5 (s), 3.6 (s), 3.7 (s), 4.2 (q); IR (KBr) 1740-1735 (C=O), 1205, 1115-1105, 1085-1045 (COC) cm^{-1}. Anal. Calcd for $C_{14}H_{27}NO_6BrNa$: C, 41.19; H, 6.84; N, 3.22; Br, 20.10. Found: C, 41.02; H, 6.84; N, 3.22; Br, 20.10.

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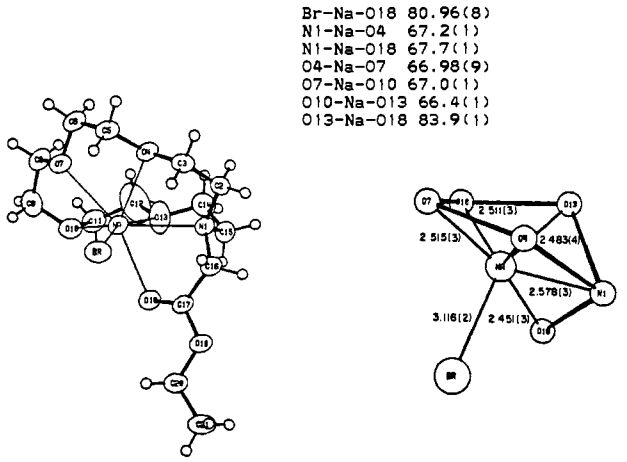
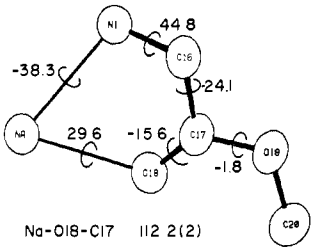


Figure 1. Perspective (left) and skeletal (right) drawings of 1·NaBr.

Distances and angles are given in a table as supplementary material. Values associated with C12 and O13 are not reliable because of thermal motion or disorder associated with these atoms. Values for the other atoms in the macrocycle are typical for macrocyclic polyethers. Values for the amino ester moiety are also typical for this fragment[9] except for C16–C17, which is slightly longer.

The structure fragment shown below depicts the interaction



of the amino ester moiety with the sodium ion. The angle Na–O18–C17 is close to that expected to give maximum overlap of the carbonyl oxygen lone-pair electrons with the metal. The metal ion resides slightly (0.647 (2) Å) out of the plane defined by the four atoms (C16, C17, O18, O19) of the ester group. The N1–C16–C17–O18 torsion angle is in the range (-28.4° to 15.0°) observed for uncomplexed aminoethanoate esters.[9] In fact, the more frequent value is closer to 0°. This suggests that the position of O18 with respect to the macroring is similar in the uncomplexed and complexed states.

Structural studies of the crystalline state complement the solution binding studies.[11] In fact, the structure reported here suggests why **1** is better than a corresponding ether lariat, *N*-(2-methoxyethyl)-1-aza-4,7,10,13-tetraoxacyclopentadecane (**2**) at binding sodium ion.[12] The reason is that ester carbonyl oxygen is a better donor than ether oxygen. A recent report[13] of donor ability of various solvents toward sodium ion states that solvents with oxygen are better donors than those with nitrogen, i.e., O=PN > O=CN > O=CO > —O— > —N—. This order parallels solvent polarity and the expected electron density on oxygen for these functional groups. The strong ligation between the ester carbonyl oxygen and the sodium ion in this structure and the larger binding constant for **1** compared to **2** support the general hypothesis that ester carbonyl oxygen is a better donor than ether oxygen toward sodium ion.

The structural studies and the solvent donicities study help to illuminate nitrogen's role in lariat ethers. The improved binding observed[8b,c] for N-pivot lariat ethers compared to their C-pivot analogues should be attributed to the greater flexibility of ligands attached to nitrogen and not to the complexing ability of nitrogen. The ease of synthesis and the multitude of possibilities for modification of the side arm offer considerable advantages for N-pivot lariat ethers as specific metal ion complexing agents.

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Registry No. 1, 92669-55-1; [NaBr·1], 92669-56-2.

Supplementary Material Available: Crystal data, table of distances and angles, positional parameters, and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Uranium–Carbon Multiple-Bond Chemistry. 4.[1] Addition of Coordinated Carbon Monoxide across a Uranium–Carbon Multiple Bond

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An extensive chemistry is developing around the uranium–carbon multiple bond in $Cp_3U{=}CHPMePhR$ **1a**, R = Me, **1b**, R = Ph, where Cp = η-$C_5H_5^-$, Me = CH_3, and Ph = C_6H_5.[1-5] This includes the insertion of polar, unsaturated molecules[1,4] and a reaction with $[CpFe(CO)_2]_2$ in which the attachment of a CHPMePhR ligand from **1** to a terminal carbonyl in $[CpFe(CO)_2]_2$ is accompanied by coupling of this terminal carbonyl with a bridging carbonyl to form an $\eta^1{:}\eta^3$-allyl group bonded to two iron atoms.[5] We proposed[5] that the first step in the formation of this allyl involves the insertion of the terminal carbonyl into the uranium–carbon multiple bond. In order to gain further insight into this and related reactions we have investigated the interactions of **1** with several complexes that contain only terminally bonded carbonyls and report here that a terminal carbonyl in $CpMn(CO)_3$ does, in fact, insert into the uranium–carbon bond in **1a**.

After 3 days at ambient temperature, an equimolar mixture of **1a** and $CpMn(CO)_3$ in THF under dinitrogen produces a red-brown solution from which crystals of **2** can be obtained in 60% yield after addition of an equal volume of a 1:1 toluene/pentane solution. The ^1H NMR spectrum of **2** contains[6] peaks

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