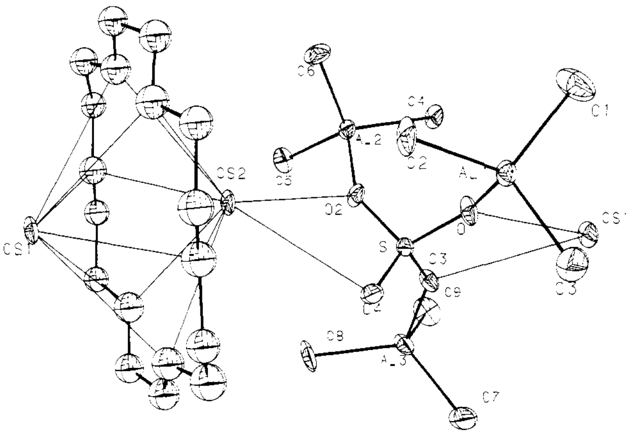

Figure 1. View of the arrangement of the $[Cs_2 \cdot 18\text{-crown-}6]^{2+}$ and $[Al_3Me_9SO_4]^{2-}$ ions in the crystal lattice.

Table I. Metal···Metal Approaches in Bonded and Nonbonded Situations

metals	obsd M···M, Å	2 × ionic radius,^{a} Å	Δ
Na···Na	3.38^{b}	2.02	1.36
K···K	3.8^{c}	2.76	1.04
Cs···Cs	3.92	3.56	0.36
Hg···Hg	2.5–2.7^{d}	1.94	0.56

^{a}Reference 8. ^{b}Reference 9. ^{c}Reference 10. ^{d}Reference 11.

in suboxides and partially oxidized clusters such as Cs_2O_6 and $Rb_7Cs_{11}O_3$[7] range from 3.72 to 4.31 Å. The sum of two Cs^+ ionic radii is 3.56 Å,[8] and to fully appreciate the meaning of this, attention is drawn to Table I. The separations for $Na^+ \cdots Na^+$ and for $K^+ \cdots K^+$ are taken from environments in which each pair is in the same crown ether.[9,10] Certainly, the Cs···Cs contact[12] with a distance only 0.4 Å larger than the sum of ionic radii implies a much more substantial interaction than the Na^+ (Δ = 1.4 Å) and K^+ (Δ = 1.0 Å) cases.[13] Even with the well-known Hg_2^{2+} ion, which exhibits a covalent Hg–Hg bond, the observed bond length is nearly 0.6 Å greater than the sum of ionic radii. The reason for the short Cs···Cs length is the presence of the crown ether, and this result shows that the favorable Cs···crown association is able to overcome the substantial electrostatic repulsion of the two Cs^+ ions. The common and often-justifiable practice of associating bond length with covalency must be carefully considered in complex structural situations.

Within the anion the bond distances and angles appear normal.[14] However, substantial distortions are found in the crown ether portion of the cation. First, the cesium atoms are found asymmetrically disposed with respect to the crown, 1.79 and 2.37 Å from the plane of the oxygens. Both these distances are long compared to values seen in 1:1 complexes (i.e., 1.44 Å in CsNCS·18-crown-6[15]). Second, the atoms of the 18-crown-6 molecule exhibit high thermal motion or disorder and the C–C and C–O bond lengths average 1.40 and 1.32 Å, respectively. These may be compared to 1.49 and 1.41 Å for the C–C and C–O lengths in the free ligand.[16] Nonetheless, the crown ether presents an average configuration which is nearly planar: the largest oxygen atom deviation is 0.11 Å from the least-squares best plane of the oxygens, and the largest carbon atom deviation is 0.24 Å.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(12) The closest Cs···Cs contact in the literature for a related complex is 4.76 Å (calculated from the published coordinates). The compound, $[Cs_9(18\text{-crown-}6)_{14}][Rh_{22}(CO)_{35}H_x][Rh_{22}(CO)_{35}H_{x-1}]$, exhibits cesium–crown associations of 1:1, 1:2, and 2:3 ratios. The 4.76-Å value is found in the 2:3 "club sandwich", which shows two cesium atoms separated by a crown ether: Vidal, J. L.; Schoening, R. C.; Troup, J. M. *Inorg. Chem.* **1981**, *20*, 227.

(13) Since the polarizability increases down a group, it is reasonable to expect that Cs^+ ions can be packed closer relative to ionic radii than can Na^+ or K^+ ions.

(14) The Al–O lengths are 1.81 (1), 1.85 (1), and 1.89 (1) Å; the S–O lengths for oxygens bonded to Al are 1.47 (1), 1.49 (1), and 1.49 (1) Å; the S–O distance for the noncoordinated O is 1.41 (1) Å; the Al–C lengths range from 1.97 (1) to 2.02 (1) Å and average 2.00 Å; the bond angles at S range from 106.8 (7)° to 113.8 (7)°; the Al–O–S angles are 134.3 (6)°, 137.5 (6)°, and 142.2 (6)°.

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Synthesis of a Capto-Dative Diradical and Its Reversible Oligomerization to Macrocycles of Coronand Structure[1]

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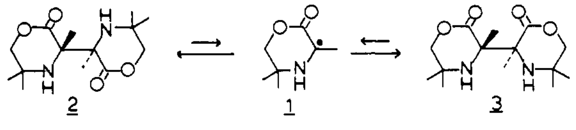
3,5,5-Trimethyl-2-oxomorpholin-3-yl (**1**) is a capto-dative[3] or merostabilized[4] free radical which exists in equilibrium with meso and *dl* dimers **2** and **3**.[5] The activation energy for bond homolysis of **2** and **3** is solvent dependent and varies from 23 kcal/mol in methanol[6] to 27 kcal/mol in chloroform.[7] Steric[8] and electronic effects[6] contribute to the facile bond homolysis.

The reluctance of **1** to disproportionate and its propensity to dimerize prompted the synthesis of diradicals based upon the 3,5,5-trimethyl-2-oxomorpholin-3-yl radical unit. These diradicals were conceived as compounds that might oligomerize reversibly. The synthesis of *dl*-bi(3,5,5-trimethyl-2-oxomorpholin-6-yl)-3,3′-diyl (**4**) and characterization of the oligomers of **4** as equilibrating macrocycles of different molecular size in solution are described. CPK models and preliminary metal-binding studies suggest that at least some of these macrocycles likely exist in a coronand structure.



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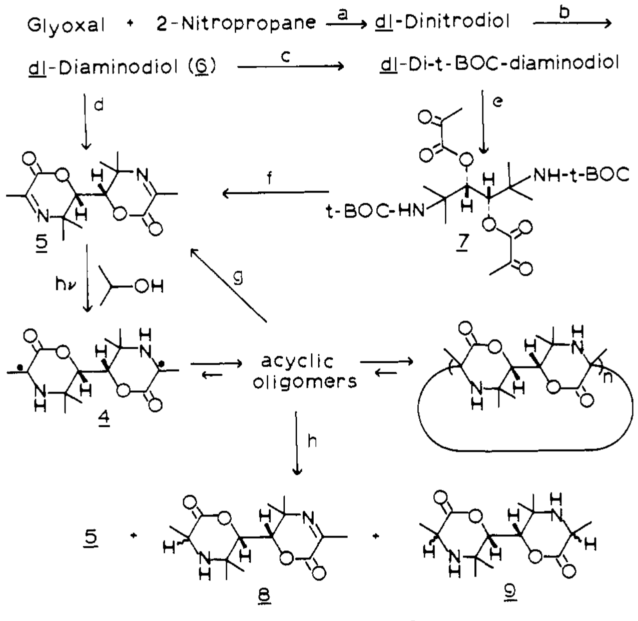
Scheme I[a]



[a] Reagents and conditions: (a) K_2CO_3, 5 °C, 24 h; (b) H_2, Pd/C, $EtOH/CH_3CO_2H$ 10:1 v/v; (c) di-*tert*-butyl dicarbonate; (d) ethyl pyruvate, mesitylene, Δ; (e) pyruvoyl chloride, CH_2Cl_2, Na_2HPO_4; (f) anhydrous CF_3CO_2H; (g) O_2; (h) Δ.

Oligomers of **4** were prepared in 60% isolated yield by photoreduction of *dl*-bi(5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-on-6-yl) (**5**) in 2-propanol solvent (Scheme I). The photolysis was performed with a nitrogen atmosphere using a 450-W mercury lamp in a Pyrex immersion well in a refrigerated bath thermostated at −40 °C. Reduction of 900 mg was complete in 20 h as indicated by disappearance of the 318-nm n–π* absorption band of **5**. The product that precipitated during the irradiation was collected cold by centrifugation.

The bis(oxazinone) **5** was synthesized in two ways from *dl*-2,5-diamino-2,5-dimethyl-3,4-hexanediol (**6**). Direct condensation of **6** as its bis(acetic acid) salt with 2.5 equiv of ethyl pyruvate in refluxing mesitylene for 15 h gave an 18% yield of **5** after silica gel flash chromatography eluting with ethyl acetate.[9] Alternatively, reaction of **6** with 2 equiv of di-*tert*-butyl dicarbonate followed by 3 equiv of pyruvoyl chloride[10] in the presence of an excess of disodium monohydrogen phosphate gave a 40% overall yield of the bis *t*-BOC derivative of *dl*-2,5-diamino-2,5-dimethyl-3,4-bis(pyruvoyloxy)hexane (**7**). Deprotection–cyclization was accomplished in 19% yield with trifluoroacetic acid at 0 °C for 20 min.

The *dl*-diamino diol **6** was obtained as its bis(acetic acid) salt in 19% yield from potassium carbonate induced condensation of glyoxal with an excess of 2-nitropropane followed by palladium on charcoal catalyzed hydrogenation of the nitro functional groups in 10:1 (v/v) ethanol/acetic acid. The major byproduct from the condensation was 2,5-dimethyl-4-hydroxy-5-nitrohexan-3-one (38%). The stereochemistry assigned to **6** was established by single-crystal X-ray analysis.[11]

The material that precipitated from the irradiation of **5** in 2-propanol solvent was characterized as a mixture of macrocyclic oligomers of **4** from the following evidence. The analysis for all elements including oxygen was correct. Calcd for $(C_{14}H_{22}N_2O_4)_n$: C, 59.55; H, 7.85; N, 9.92; O, 22.67. Found: C, 59.38; H, 7.89; N, 9.65; O, 22.84. UV and IR absorptions at 318 nm and 6.1 μm, respectively, characteristic of the conjugated carbon–nitrogen double bond of **5** were absent. An N–H stretching band was observed at 3.03 μm in the infrared spectrum characteristic of the morpholinone structural unit. The ^1H and ^{13}C NMR spectra were complex but consistent with the proposed structure. A freeze–pump–thaw degassed chloroform solution of the photoproduct mixture showed no EPR signal at ambient temperature but a weak 24-line signal characteristic of the trimethyloxomorpholinyl radical[6] at temperatures above 60 °C: $g = 2.0036$; $a_{CH_3} = 11.46$ G, $a_N = 6.25$ G, and $a_{NH} = 3.50$ G. No triplet EPR signal appeared at any temperature. The osmometric molecular weight in chloroform solvent at 37 °C varied from 900 to 1500 amu depending upon batch. Material equilibrated in degassed chloroform or acetonitrile solvents gave a reproducible average molecular weight in the respective solvents of 900 amu, suggesting predominance of a trimer structure. Bubbling oxygen through an ethanol solution of the oligomers resulted in 70% conversion to **5** after about 20 h. Heating of a freeze–thaw degassed chloroform solution of the oligomers at 60 °C for 31 h gave three major products **5**, 6-(3,5,5-trimethyl-2-oxomorpholin-6-yl)-5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**8**), and bi(3,5,5-trimethyl-2-oxomorpholin-6-yl) (**9**).[9] Products **8** and **9** were identical with products obtained from incomplete and complete palladium on charcoal catalyzed hydrogenation of **5** in ethyl acetate, respectively. At ambient temperature in chloroform solvent, disproportionation takes almost 1 yr to complete. A similar mixture of disproportionation products was observed upon pyrolysis of oligomers at 140 °C in a vacuum sublimer and at 200 °C in the injection port of a gas chromatograph.

The lack of any EPR signal at ambient temperatures even at a 0.1 M concentration (3% w/v) together with the results of the molecular weight measurements precludes the presence of any substantial amount of open-chain oligomers. This leads to the proposal of macrocyclic oligomer structures that can equlibrate for the photoproduct mixture. The oligomers must be capable of equilibraing through bond homolysis because when prepared under kinetic control at −40 °C in 2-propanol, average oligomer size varied from three to five monomeric units. Material heated in acetonitrile or chloroform gave reproducible average oligomer size of three monomeric units independent of batch.

Inspection of a CPK model of an oligomeric trimer suggests that steric interactions are minimized when the methyl substituents are located on the outside of the macrocycle and the lactone functional groups on the inside. Such a structure places these oligomers in the family of coronands. Preliminary metal-binding studies with picrate salts indicate that methylene chloride solutions of the oligomers dissolve approximately 1 Li^+/oligomer and 0.4 M_g^{2+}/oligomer in methylene chloride solvent at 24 °C. The oligomers increase the solubility of other alkali and alkaline-earth metal picrates but to a lesser extent.

Other relevant capto-dative diradical systems which have been described include the transition state in the thermal isomerization of 1,2-bis(4-methoxyphenyl)-1,2-bis(4-cyanophenyl)ethylene,[12] the product of two-electron reduction of linked paraquat units,[13] and 1,1′-trimethylenebis(4-(carbomethoxy)pyridinyl).[14] The latter two systems appear to cyclize intramolecularly rather than oligomerize. Oligomerization of diradicals based upon the triarylmethyl radical unit has also been proposed.[15]

Supplementary Material Available: Details of the crystal structure analysis, tables of atomic parameters, a figure showing the atomic numbering scheme, tables of derived results for diamino diol **6**, tables of observed and calculated structure factor amplitudes, physical, spectroscopic, and analytical data for synthetic intermediates, and diradical disproportionation products (13 pages). Ordering information is given on any current masthead page.

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