

5 and the rest of the  $\pi$  system decreases dramatically upon one-electron reduction, from  $82^\circ$  in the neutral molecule to  $25^\circ$  in the radical anion. Those systems that resist electrochemical cyclization are precisely those in which electronic localization of the odd electron inhibits extended  $\pi$  interaction or in which steric interactions drive the  $1^- \rightleftharpoons 2^-$  equilibrium toward  $1^-$ .

A catalytically driven electrocyclization, i.e., that  $2^-$  might reduce **1**, producing **2** and  $1^-$  (eq 2) which could reenter eq 2 in a repetitive chain sequence, was not achieved, for coulometry indicates that a stoichiometric one-electron reduction is required for the cyclization.<sup>9</sup>

The identity of the electrocyclization product and that observed by photolysis of **1b**, the only molecule studied that contains a stereochemical probe, establishes that the radical anionic cyclization, like the photoinduced one, proceeds in conrotatory fashion.<sup>9</sup> The like stereochemical course in the photochemical and radical anionic cyclizations is predicted by simple FMO theory, since the nodal properties of the highest lying singly occupied molecular orbital are identical in both the ground-state radical anion and in the neutral photoexcited state. The same conclusion is also reached from semiempirical (MNDO) calculations, in which the conrotatory reaction path of the radical anion **7** is significantly favored over the alternate disrotatory route. Moreover, Bauld and Cessac predicted in 1977 that for the parent  $C_6^-$  (hexatriene  $\rightleftharpoons$  cyclohexadiene) conrotation would be the preferred reaction mode, even through orbital symmetry/topology favors disrotation.<sup>1a</sup>

The facilitation of cyclization observed here upon radical ion generation is reminiscent of the dramatic acceleration of pericyclic reactivity induced by hole catalysis, e.g., in Bauld's cation radical Diels-Alder reactions.<sup>10</sup> Our case represents a parallel approach to reducing activation enthalpies by reversible electroreduction. Several other cases are known in which electroreduction of  $\pi$  systems induces pericyclic reactivity.<sup>11</sup> In these instances, however, the rearranged products were either solely studied spectroscopically or, if isolated, were obtained at a reduced oxidation level. Furthermore, mechanistic detail is often lacking. The reactions in eq 1 are unique as triene cyclizations induced by reversible electroreduction.

It is interesting to note that the radical cations of **1** failed to cyclize in parallel fashion,<sup>12</sup> an observation that can be explained reasonably by the opposing demands of the helical canting of **1** (a geometry favoring a conrotatory approach) and orbital topo-

logical requirements (favoring disrotation). A current thrust of our research effort is involved with establishing predictive norms for understanding the proclivity for rearrangement of radical ions.

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## How Short Is a Bond of Order Zero? A Close Cs...Cs Contact in the $[Cs_2(18\text{-crown-6})]^{2+}$ Cation

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The reaction of aluminum alkyls with alkali metal salts has produced several interesting chemical results. Two comparatively recent developments have concerned (1) the use of crown ethers to solubilize the salts<sup>1</sup> and (2) the observation of the surprisingly high thermal stability of high-oxygen content anions.<sup>2</sup> We have previously reported the synthesis and structure of  $K_2[Al_4Me_{12}SO_4]$ ,<sup>2</sup> and in a subsequent effort to find stoichiometries other than 4:1 for the sulfate ion, we have carried out the reaction of  $AlMe_3$  with  $Cs_2SO_4$  in the presence of 18-crown-6.<sup>3</sup> The major product (and the only one isolated) is a colorless crystalline compound of formulation  $[Cs_2 \cdot 18\text{-crown-6}][Al_3Me_9SO_4]$ . To our great surprise the X-ray structural analysis<sup>4</sup> has shown that the cation exhibits a Cs...Cs contact only slightly longer than the sum of ionic radii.

The compound crystallizes in infinite (sulfate/aluminum)cesium(18-crown-6)cesium(sulfate/aluminum) chains as shown in Figure 1. Each cesium can be considered to be nine-coordinate, each interacting with the six crown oxygens, two sulfate oxygens, and the other cesium. Cs(2) is coordinated to an "aluminum oxygen" at Cs-O = 3.08 Å and the unique sulfate oxygen at Cs-O = 3.24 Å, while Cs(1) is found at 3.16 and 3.20 Å from the remaining sulfate oxygens in an adjacent asymmetric unit. The crown ether oxygen atoms interact in a weaker fashion, especially with Cs(1), the distances ranging from 3.33 to 3.59 Å (av = 3.48 Å) and 3.13 to 3.48 Å (av = 3.29 Å) for Cs(2).

The Cs...Cs distance is to our knowledge the closest contact (corrected for ionic radii) found to date between alkali metal ions. Indeed, the metal ion separation in the zero bond order  $Cs_2^{2+}$  ion is close to what one would predict for a full bond between cesium ions. The distance in cesium metal is 5.38 Å,<sup>5</sup> and the lengths

(9) While coulometry results make a cyclization mechanism involving a radical anion likely, they do not strictly exclude the possible intervention of a reversibly formed dianionic intermediate. A conrotatory mechanism is required by our data only if geometrical isomerization of the starting material (either as a neutral or a reduced species) is much slower than the electrocyclic reaction.

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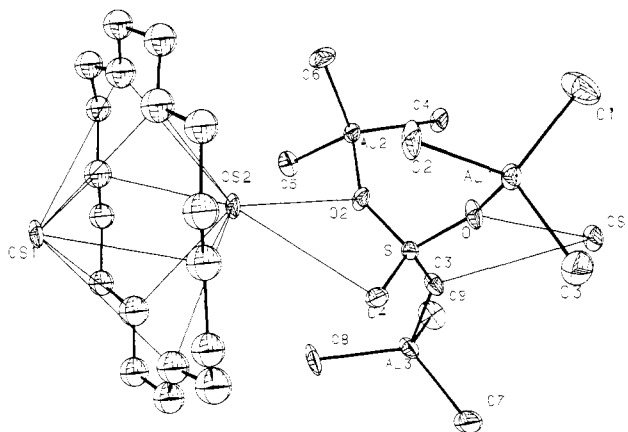
(12) The failure of some attempted radical anion pericyclic reactions has also been noted: Allendoerfer, R. D.; Miller, L. L.; Larscheid, M. E.; Chang, R. *J. Org. Chem.* **1975**, *40*, 97. Blankespoor, R. L.; Snively, C. M. *J. Org. Chem.* **1976**, *41*, 2071.

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(3) The stoichiometry was 0.020 mol of  $AlMe_3$ , 0.010 mol of  $Cs_2SO_4$ , and 0.005 mol of 18-crown-6. The reaction mixture was heated to  $100^\circ C$  for 25 h in toluene. Slow cooling to room temperature afforded the crystalline product.

(4) Single crystals of the title compound were obtained by the slow cooling of a toluene solution. Space group  $P2_1/n$ ; cell constants  $a = 13.552$  (2) Å,  $b = 16.731$  (4) Å,  $c = 17.029$  (4) Å,  $\beta = 94.79$  (2) $^\circ$  with four formula units per unit cell, and  $D_c = 1.46$  g cm $^{-3}$ . Least-squares refinement based on 2311 observed reflections led to a final  $R = \sum(|F_o| - |F_c|) / \sum |F_o| = 0.064$ . The details of data collection and refinement are as given by Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. An empirical absorption correction was done according to Churchill and Hollander: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957. Anisotropic thermal parameters were used for all atoms except those of the crown ether. Hydrogen atoms were not located.



**Figure 1.** View of the arrangement of the  $[\text{Cs}_2 \cdot 18\text{-crown-6}]^{2+}$  and  $[\text{Al}_3\text{Me}_9\text{SO}_4]^{2-}$  ions in the crystal lattice.

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

metals	obsd M...M, Å	2 × ionic radius, <sup>a</sup> Å	Δ
Na...Na	3.38 <sup>b</sup>	2.02	1.36
K...K	3.8 <sup>c</sup>	2.76	1.04
Cs...Cs	3.92	3.56	0.36
Hg...Hg	2.5-2.7 <sup>d</sup>	1.94	0.56

<sup>a</sup>Reference 8. <sup>b</sup>Reference 9. <sup>c</sup>Reference 10. <sup>d</sup>Reference 11.

in suboxides and partially oxidized clusters such as  $\text{Cs}_2\text{O}_6$  and  $\text{Rb}_7\text{Cs}_{11}\text{O}_3$ <sup>7</sup> range from 3.72 to 4.31 Å. The sum of two  $\text{Cs}^+$  ionic radii is 3.56 Å,<sup>8</sup> and to fully appreciate the meaning of this, attention is drawn to Table I. The separations for  $\text{Na}^+ \cdots \text{Na}^+$  and for  $\text{K}^+ \cdots \text{K}^+$  are taken from environments in which each pair is in the same crown ether.<sup>9,10</sup> Certainly, the  $\text{Cs} \cdots \text{Cs}$  contact<sup>12</sup> with a distance only 0.4 Å larger than the sum of ionic radii implies a much more substantial interaction than the  $\text{Na}^+$  ( $\Delta = 1.4$  Å) and  $\text{K}^+$  ( $\Delta = 1.0$  Å) cases.<sup>13</sup> Even with the well-known  $\text{Hg}_2^{2+}$  ion, which exhibits a covalent  $\text{Hg}-\text{Hg}$  bond, the observed bond length is nearly 0.6 Å greater than the sum of ionic radii. The reason for the short  $\text{Cs} \cdots \text{Cs}$  length is the presence of the crown ether, and this result shows that the favorable  $\text{Cs} \cdots \text{crown}$  association is able to overcome the substantial electrostatic repulsion of the two  $\text{Cs}^+$  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.<sup>14</sup> However, substantial distortions are found in the crown ether

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(12) The closest  $\text{Cs} \cdots \text{Cs}$  contact in the literature for a related complex is 4.76 Å (calculated from the published coordinates). The compound,  $[\text{Cs}_9(18\text{-crown-6})_{14}][\text{Rh}_{22}(\text{CO})_{35}\text{H}_x][\text{Rh}_{22}(\text{CO})_{35}\text{H}_{x-1}]$ , 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  $\text{Cs}^+$  ions can be packed closer relative to ionic radii than can  $\text{Na}^+$  or  $\text{K}^+$  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)°.

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  $\text{CsNCS} \cdot 18\text{-crown-6}^{15}$ ). 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.<sup>16</sup> 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.

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**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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### Synthesis of a Cpto-Dative Diradical and Its Reversible Oligomerization to Macrocycles of Coronand Structure<sup>1</sup>

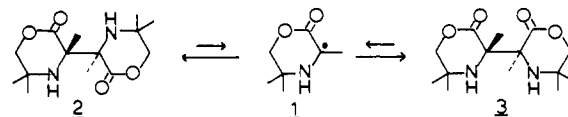
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3,5,5-Trimethyl-2-oxomorpholin-3-yl (**1**) is a cpto-dative<sup>3</sup> or merostabilized<sup>4</sup> free radical which exists in equilibrium with meso and *dl* dimers **2** and **3**.<sup>5</sup> The activation energy for bond homolysis of **2**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