tribute to the enhanced activity. Then, why would the native pancreatic PLA2 have Lys instead of Met at position 56? The problem could be related to substrate specificity. K56M is a better enzyme than WT for PC and under in vitro conditions, but not for negatively charged substrates PG or NOB. Since the physiological substrates of pancreatic PLA2 are negatively charged mixed micelles, the native pancreatic PLA2 should be as efficient as K56M physiologically. However, even for negatively charged substrates, it is unclear why pancreatic PLA2 would not have evolved to higher catalytic efficiency, as some snake venom PLA2 did under different physiological conditions.

Electron-Transfer Reaction of a Selenium Coronand–Copper(II) Complex. Formation of the Stable 1,5,9,13-Tetraselenacyclohexadecane Dication

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We recently reported the synthesis and conformational analysis of selenium coronands.[1] These novel ligands could act as hosts for soft metal guests, and we proposed to test the importance of conformation on chelation. In addition, the rich redox chemistry exhibited by metal complexes of sulfur coronands[2] promised an exciting period of discovery with complexes of the heavier congeners. In particular, the preferential stabilization of lower oxidation states of metals was expected to be amplified with the third-row analogues. We report herein the first complex of a selenium coronand, namely, (1,5,9,13-tetraselenacyclohexadecane)copper(II) trifluoromethanesulfonate, $[Cu(16Se4)][SO_3CF_3]_2$ (**1**), and its spontaneous electron-transfer reaction in organic solvents to give Cu(I) as well as the intermediate radical cation $[16Se4]^{\bullet+}$ and the stable dication $[16Se4]^{2+}$. The salts $[(Cu(16Se4))_\infty]^{\infty+}([SO_3CF_3]^-)_\infty$ (**2**) and $[16Se4]^{2+}([SO_3CF_3]^-)_2$ (**3**) have been isolated from these solutions by selective crystallization. The complexes of Cu(II) with macrocyclic tetrathia ethers are stable, and the ligands are not oxidized.[3]

Complex **1**[4] (shown in Figure 1) is structurally[5] similar to the thia ether complex $[Cu(16S4)][ClO_4]_2$.[6] Both display square-planar coordination of Cu by the chalcogen atoms and have a

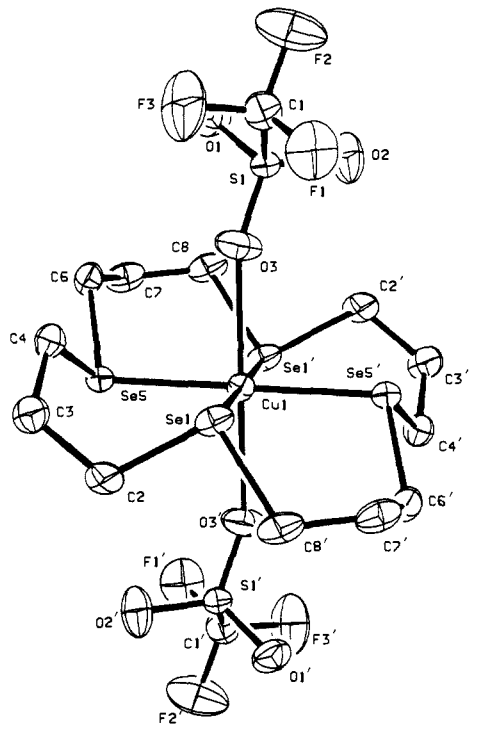

Figure 1. Molecular structure of $[Cu(16Se4)][CF_3SO_3]_2$ (**1**).

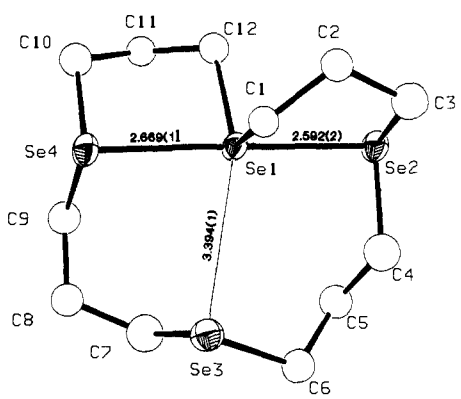

Figure 2. Molecular structure of the dication from $[16Se4]^{2+}([SO_3CF_3]^-)_2$ (**3**).

[4444] coronand conformation in which the chalcogen atoms occupy the central positions on the sides of the quadrilateral. Each anion coordinates much more weakly via one oxygen atom located on the pseudotetragonal axis of the complex (cf. sums of accepted covalent radii: Cu + Se, 2.54 Å; Cu + O, 2.11 Å). The Cu atom is located on a crystallographic center of inversion. The complex thus displays a tetragonally distorted octahedral arrangement typical of Cu(II).

Compound **1** is unstable in organic solvents such as CH_3CN, CH_3NO_2, $(CH_3)_2CO$, or THF. Indeed, prolonged reaction of 16Se4 and $Cu(CF_3SO_3)_2$ followed by precipitation with ether yielded colorless crystals of **2**.[4,7] A more detailed investigation of the electron-transfer process by UV-visible spectroscopy reveals the following salient features. The absorbance due to **1** at λ_{max} 466 nm in CH_2Cl_2 decays with a concomitant increase in the absorbance at λ_{max} 318 nm. This peak decays in turn and leads to the growth of an absorbance band at λ_{max} 223 nm. Analysis of the kinetic data from experiments performed at different concentrations of **1** and at different added-ligand concentrations indicates an initial rate that is first order in both complex **1** and ligand, and a mechanism for the reaction that is consistent with the following stoichiometry: $2[Cu^{II}(16Se4)]^{2+} + (16Se4) \rightleftarrows$

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(4) Synthetic details, UV spectroscopic and microanalytical data for **1**–**3**, ^{77}Se CP-MAS solid state NMR data for **2** and **3**, and EPR data for **1** are given in the supplementary material.

(5) $[Cu(Se(CH_2)_3)_4][SO_3CF_3]_2$; monoclinic; $P2_1/n$; T = 190 K; a = 8.220 (2) Å; b = 10.965 (4) Å; c = 14.657 (5) Å; β = 105.44 (2)°; Z = 2; λ = 0.71069 Å; μ(Mo Kα) = 67.49 cm^{-1}; crystal dimensions 0.15 × 0.31 × 0.43 mm; transmission 0.139–0.476, corrected analytically; $4° \le 2\theta \le 50°$; 1707 data ($I \ge 2.5\sigma(I)$); refined parameters, 152; $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.037$; maximum |shift/error| ≤ 0.01. Bond distances: Cu(1)–Se(1), 2.4593 (6) Å; Cu(1)–Se(5), 2.4554 (6) Å; Cu(1)–O(3), 2.464 (5) Å; ⟨Se–C⟩, 1.96 Å. Bond angles: Se(1)–Cu(1)–Se(5), 88.40 (2)°; Se(1)–Cu(1)–O(3), 82.7 (1)°; Se(5)–Cu(1)–O(3), 90.1 (1)°.

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$2[Cu^{I}(16Se4)]^{+} + [16Se4]^{2+}$. The reaction likely proceeds via the radical cation $[16Se4]^{\bullet+}$ (λ_{max} 318 nm). In support of this contention, oxidation of the free ligand with $NOBF_4$[8] leads to the appearance of an absorbance band at 318 nm.

Finally, dissolution of **1** in CH_2Cl_2/CH_3CN (1/1) for 5 min at room temperature followed by cooling gave yellow crystals[4] that were identified crystallographically as the salt $[16Se4]^{2+}\cdot([CF_3SO_3]^{-})_2$ (**3**).[9] The structure of **3** contains the $[16Se4]^{2+}$ cation shown in Figure 2. The two transannular Se–Se bonds are nearly collinear. This configuration permits greater charge delocalization than would a single Se–Se transannular bond similar to the S–S bond in the recently published structure of the dithiacyclooctane dication.[10] The bonds to the central Se atom (Se(1)) have a ψ-trigonal-bipyramidal arrangement typical of tetracoordinate Se(IV), with the more electron withdrawing substituents ($Se^{\delta+}$) in the axial positions and the nonbonding electron pair in the equatorial plane. Similar nearly linear Se–Se–Se arrangements, displaying comparable Se–Se bond lengths, have been observed previously in the triselenourea dication[11] (Se–Se, 2.664 (2) Å) and 6a-selenaselenophthene and its derivatives (2.548 (3)–2.583 (3) Å).[12] The Se(1)···Se(3) distance, which is significantly less than twice the accepted van der Waals radius of Se (3.8 Å), suggests a weak secondary interaction between these atoms, although this could merely represent a constraint of the ring size. A few Se···O distances, which are slightly shorter than the sum of the van der Waals radii, 3.42 Å (the shortest being 3.152 (7) Å to Se(2)), are consistent with reasonable dipolar electrostatic attraction between cation and anion. These interactions are clearly weaker than the S···O interactions in the dithiacyclooctane dication[10] (S···O, 2.682(6) Å; cf. sum of van der Waals radii, 3.32 Å) where the positive charge is more localized.

While the formation of radical monocations and dications of polythia ethers is documented,[13] and Musker et al.[14] have reported the oxidation of dithiacyclooctane derivatives by Cu(II) complexes, the present study reports the first selenium coronand dication resulting from an electron-transfer reaction of a metal–selenium coronand complex. The structures of other cyclic selena cations have also been reported, e.g., the radical monocation and dication of 1,2,4-triselena-3,5-diazacyclopentane,[15] Se_8^{2+}, and Se_{10}^{2+}.[16,17] We note also that the dication of 1,5-diselenacyclooctane has recently been prepared.[18]

Further studies of the redox chemistry of metal–selenium coronand complexes and of the free ligands[1] themselves are currently in progress, and the results will be reported in due course.

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Supplementary Material Available: Synthetic details and spectroscopic and microanalytical data for **1–3** and details of the structure determination and tables of atomic coordinates, anisotropic thermal parameters, selected bond lengths, bond angles, and torsion angles for **1** and **3** (21 pages); tables of calculated and observed structure factors for **1** and **3** (36 pages). Ordering information is given on any current masthead page.

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Demonstration of a Conformational Equilibrium in Acyl Carrier Protein from Spinach Using Rotating Frame Nuclear Magnetic Resonance Spectroscopy

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Advances in NMR technology and computational methods have made it possible to determine the three-dimensional structures of small proteins in solution on the basis of distance constraints from interproton nuclear Overhauser effects (NOEs).[1-5] Most of the structures determined have been calculated with the assumption that the structure is static. While in most cases good agreement with X-ray structures supports the validity of this assumption,[2,4,6] there are cases where violation of this assumption can lead to structures of poor quality or even misrepresentation of the state of the system. Errors are most likely to occur when conformers interconvert rapidly enough to show a single set of resonances but slowly enough to average NOEs observed in each state (10^3–10^7 s^{-1}).

Recently we have introduced a structure determination procedure that takes account of averaged NOEs in the limit where two discrete conformers are involved, and we have applied this procedure in a structure determination of *Escherichia coli* acyl carrier protein (ACP, 8847 Da (daltons)).[7] However, other than some improvement in the fit of the structural model to experimental data, and a general improvement in the quality of the structure, there is little direct evidence for the existence of two and only two conformers for this protein. In the rapid exchange limit, only a single set of resonances would be observed, regardless of the number of conformational states. Here we present data on a closely related protein, ACP-I from spinach (9173 Da). While the NMR spectrum has not been completely assigned, it is clear that in this protein there are more resonances than can be assigned to protons from a single structural species.[8] We are now able to demonstrate, using rotating frame NMR experiments, that the extra resonances arise from a second conformer in dynamic equilibrium with the first. This clear demonstration underscores the importance of considering dynamic equilibrium

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