tional contributions to ΔE were considered.

1. Enlargement of the Carbon sp Basis. By fully contracting (except for the outer four s and three p basis functions) the 1s and 2s atomic orbitals, van Duijneveldt's much larger (13s 8p) basis[17] was adapted to the present study. However, the CI energy lowerings for the $^3B_1$ and $^1A_1$ states were only 0.17 and 0.08 kcal, respectively, and thus have little effect on ΔE ($^3B_1 - {}^1A_1$).

2. Addition of Diffuse p Functions to the Basis Set. This was done relative to a smaller (than our standard) set of 32 basis functions. Using the Raffenetti–Ruedenberg even-tempered scheme,[18] a set of p functions with $\alpha = 0.034$ was added, and this had the effect of decreasing the predicted ΔE value by 0.12 kcal.

3. Consideration of Core and Core–Valence Correlation Effects. Since this substantially increases the number of Slater determinants, the smaller 32 function basis was used. Without the $1a_1$ orbital constrained to be doubly occupied, the numbers of determinants increase from 2505 to 4891 ($^3B_1$) and 2981 to 5469 determinants ($^1A_1$). We find that these effects increase the predicted ΔE value by 0.37 kcal.

4. Additional Triplet Spin Eigenfunctions. The procedure used in our standard (and previous[9]) calculations includes only those configurations having nonzero Hamiltonian matrix elements with the respective Hartree–Fock reference configurations. However, for the $^3B_1$ state there are numerous spin eigenfunctions which do not interact[19,20] directly with the SCF configuration, but have no counterpart in the close-shell $^1A_1$ state. For example, consider the excitation

$$2a_1\ 1b_2 \rightarrow ia_1\ jb_2 \tag{3}$$

corresponding to electron configuration

$$1a_1{}^2\ 2a_1\ 1b_2\ ia_1\ jb_2\ 3a_1\ 1b_1 \tag{4}$$

Only six of the Slater determinants arising from eq 4 are included in the standard CI. However a total of fifteen determinants are possible and, using the 32 function basis set, all fifteen (and the comparable determinants for all other configurations) determinants have been included. For the 32 function case, this increases the number of $^3B_1$ Slater determinants from 2505 to 4204 and also allows our wavefunction to be a pure triplet spin eigenfunction. However, the $^3B_1$ total energy changes from -39.05160 hartrees to -39.05186 hartrees, a difference of only 0.17 kcal. It is quite clear that this correlation effect does not significantly change the predicted standard ΔE value.

5. Effects of Higher Spin Orbital Excitations. These are extremely difficult to completely account for in an ab initio way, leading to approximate schemes such as the coupled electron-pair approximation (CEPA).[21] Perhaps the simplest such scheme is Davidson's approximation[22] for the correlation energy contribution due to quadruple excitations

$$\Delta E_Q = (1 - C_0{}^2)\Delta E_D \tag{5}$$

where C_0 is the coefficient of the SCF configuration in the CI expansion and ΔE_D is the correlation energy due to double excitations. If in addition we assume that ΔE_D is about the same as the correlation energy due to single and double excitations, the $^3B_1$ and $^1A_1$ unlinked cluster contributions[23] are estimated to be 0.0066 and 0.0101 hartrees. This difference (2.2 kcal) lowers the predicted ΔE value from 13.5 to 11.3 kcal, our final result. These results indicate that higher excitations lower the singlet–triplet separation, as implied by the importance[12] of the second configuration $3a_1{}^2 \rightarrow 1b_1{}^2$ for the $^1A_1$ state.

In conclusion the present state-of-the-art electron correlation studies predict ΔE ($^3B_1 - {}^1A_1$) = 11.3 kcal. Theoretical considerations suggest that if any corrections need to be made to this result, they will be small. Thus, it is clear that the present, far more exhaustive study, as well as that of Roos,[10] supports the earlier theoretical work of Bender and co-workers.[9]

Finally, it cannot be overemphasized that our predicted ΔE value is what spectroscopists would call T_e, the energy difference between the *minima* of the $^3B_1$ and $^1A_1$ potential energy surfaces. However, Roos[10] has shown that the zero-point vibrational energies of the $^3B_1$ and $^1A_1$ states are nearly identical, implying that T_e is essentially the same as the observed separation T_0.

Acknowledgment. This research was supported by the National Foundation, Grant CHE-7622621.

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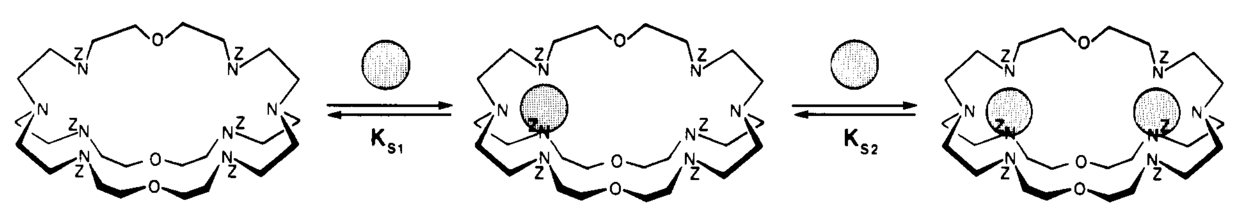
Binuclear Cryptates. Synthesis and Binuclear Cation Inclusion Complexes of Bis-tren Macrobicyclic Ligands

Sir:

Macropolycyclic ligands incorporating receptor sites for two or more metal cations may form binuclear or polynuclear inclusion complexes, *polynuclear cryptates*, in which the distance and arrangement of the cations, held inside the intramolecular cavity, may be regulated via ligand design. They provide a novel entry into the study of cation interactions at short distances; at larger intercationic distances inclusion of

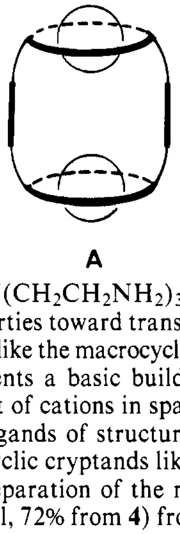


1 **1-M** **1-M$_2$**

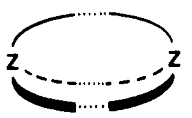
Figure 1. Schematic representation of the formation of mononuclear and binuclear cryptate complexes of the bis-tren-type ligands **1**.

a substrate molecule between the two cations may become possible allowing developments into bioinorganic modeling and catalysis.[1]

We have previously described cylindrical macrotricyclic ligands built on two "face to face" macrocyclic subunits linked by two bridges; they form binuclear cation inclusion complexes, *binuclear cryptates*, where the cations are located on each macrocycle (structure A).[2,3] We now report a new type of macrobicyclic ligand B, built on the *coaxial arrangement of two tripod subunits*, which may be expected to form binuclear cryptates, each subunit taking up one cation.



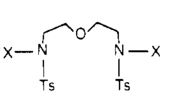
A



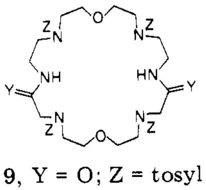
B

Tren, $N(CH_2CH_2NH_2)_3$, displays remarkable complexation properties toward transition metal cations.[4,5] This structural unit, like the macrocycles in the cylindrical macrotricycles A, represents a basic building block for the controlled arrangement of cations in space. Linking two tren units yields bis-tren ligands of structure **1** which belong to the class of macrobicyclic cryptands like **2**.[6,7]

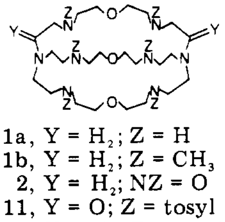
The preparation of the required diamine-ditosylamide **5** (viscous oil, 72% from **4**) from **3** via **4** (mp 73-75 °C, 77%) is straightforward. The diacid dichloride component **8** (mp 115 °C) is obtained from **3** via **6** and **7** (mp 132 °C).



3, X = H
4, X = CH_2CH_2Br
5, X = $CH_2CH_2NH_2$
6, X = CH_2COOCH_3
7, X = CH_2COOH
8, X = CH_2COCl



9, Y = O; Z = tosyl
10, Y = H_2; Z = tosyl



1a, Y = H_2; Z = H
1b, Y = H_2; Z = CH_3
2, Y = H_2; NZ = O
11, Y = O; Z = tosyl
12, Y = H_2; Z = tosyl

High dilution cyclization of the diamine **5** with **8** following the previously described procedure[6] gives the macrocyclic bicarboxamide tetratosylamide **9** (mp 123 °C, 30%) which is then converted into the selectively protected hexaamine **10** (waxy solid, 98%) by reduction with diborane followed by hydrolysis with 6% HCl in methanol at reflux and treatment with aqueous lithium hydroxide. Such a 24-membered macrocyclic hexaamine (**10**, Z = H) is interesting in itself, since it should be able to form binuclear macrocyclic complexes[8] via its diethylenetriamine chelate subunits and provide a framework for further structural elaboration, for instance by attachment of $-CH_2CH_2X$ side chains on several of the ring nitrogens.

High dilution condensation[6] of **10** with **8** affords the macrobicyclic bicarboxamide hexatosylamide **11** (white solid, mp 165 °C, 60%) which on reduction with diborane, followed by acid hydrolysis and LiOH treatment as above, affords **12** (glassy solid, 97%). The tosyl groups of **12** are removed with lithium in a liquid ammonia-tetrahydrofuran-ethanol mixture (see also ref 9). The macrobicyclic octaamine **1a** was obtained as a viscous oil in 65% yield after filtration of the crude reaction product through alumina. The hexahydrochloride of **1a** is obtained from ethanol-water as a highly crystalline nonhygroscopic solid (mp >260 °C). Methylation of **1a** by the Eschweiler-Clarke method gives **1b** as a viscous oil (90%). The spectral and microanalytical data of the compounds reported are in agreement with the proposed structures.

The in-in forms[5,10] of the bis-tren octaamines **1** is represented in Figure 1; it should be suited for complexation of two cations at each end of the ellipsoidal cavity.

We were first interested in the complexation properties of bis-tren toward those cations with which tren itself or its methylated derivatives have been shown to form 1:1 pentacoordinate complexes with trigonal bipyramide geometry, for instance, Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II).[4,11,12] With such cations bis-tren **1** should form mononuclear and binuclear cryptate complexes (Figure 1).

Addition of 2 equiv of a metal perchlorate $M(ClO_4)_2 \cdot 6H_2O$ (M = Zn, Cu, Co) to ligand **1a** in refluxing methanol results in immediate precipitation of the binuclear complex. Elemental analysis indicated that the complexes contain only the ligand and $M(ClO_4)_2$ in 1:2 stoichiometry. On the basis of the crystal structures of tren complexes,[11,12] the structure of these complexes may be schematically represented by **1**-M_2 (Figure 1) with an intercation distance of ~4.5 ± 0.5 Å. Complexation of the nitrogen sites in the bridges is expected to block the nitrogen inversion process and to lead to several isomers differing by the configuration at these nitrogen sites. The fifth ligand of each cation may be one of the ether oxygens, resulting in distortion of the ligand, or the two cations may symmetrically share the three ether oxygens. The stability constants of the complexes have not yet been determined; they should lie in the range or above those of tren itself.[4,5]

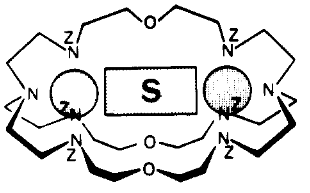
A 250-MHz ^1H NMR study (at 25 °C) of the addition of increasing amounts of ZnI_2 to a solution of **1a** in D_2O shows the successive formation of the mononuclear and binuclear Zn^{2+} complexes. After addition of 1 equiv of ZnI_2, only the mononuclear species appears to be present (>80%); the spectrum observed is unsymmetrical indicating that the left and right sides of the molecule are different; this agrees with structure **1**-M (Figure 1) for this species and shows that the side to side exchange of the cation inside the molecular cavity is slow. The data also indicate that the cation exchange between the free ligand **1** and **1**-M is slow, but no firm indication about the rate of cation exchange between **1**-M and **1**-M_2 has been obtained. The processes involved are represented in Figure 1. The ^1H and ^{13}C spectra of the zinc complexes display broad signals which may be due to the coexistence of several isomers as noted above.

The electronic spectrum of the blue $[2Cu^{2+} \subset \mathbf{1a}]\cdot 4ClO_4^-$ cryptate in acetonitrile shows bands at 765 nm (ϵ 350), 640 (sh) (275), 350 (5000), 283 (5600). In the same conditions tren-$Cu(ClO_4)_2$ has bands at 800 nm (ϵ 183) and 275 (4400). The 350-nm band is characteristic of the bis-tren complex and may undergo marked changes (see below).[13] A green bis-$Cu(ClO_4)_2$ complex of **1a** has also been obtained with absorptions at 743, 634 (sh), 351, and 285 nm.

The powder ESR spectrum of the blue $[2Cu^{2+} \subset \mathbf{1a}]$ complex displays a pattern indicating an environment of axial symmetry for the copper ions,[14] in agreement with structure **1**-M_2 ($g_{\parallel}$ = 2.0766 and $g_{\perp}$ = 2.2176). A weak Δm_s ±2 transition is observed at g = 4.7 consistent with the presence of Cu(II) dimers.[15,16] In acetonitrile solution the ESR spectrum is a symmetric band and μ_{eff} is ~2.0 μ_B per copper at 294 K.

We have proposed earlier[1,3] that binuclear cryptates might form *cascade complexes* by insertion of a substrate of compatible size between the metal cations. This involves two successive complexation processes: selection of the metal cations by the ligand and selection of the substrate controlled by the nature and the arrangement of the complexed cations.

Like the cylindrical macrotricyclic cryptands,[1,3] the present bis-tren ligands should be suitable systems. Indeed, in the **1**-M_2 species, the fifth coordination axis of each cation is directed toward the other one so that insertion of a substrate S may be possible leading to a species of type **1**-M_2S, provided that the intercationic distance is compatible. Some preliminary indications about the interaction with substrates will be briefly mentioned here. Addition of water to the $[2Cu^{2+} \subset \mathbf{1a}]\cdot 4ClO_4^-$ complex in acetonitrile leads to a strong decrease in the intensity of the EPR signal which becomes markedly asymmetric; simultaneously the intensity of the 350-nm UV band doubles. Addition of cyanide leads to a change in shape of the EPR signal and to the complete disappearance of the 350-nm UV band. This band also disappears on azide addition while two bands appear at 670 and 380 nm. These results may indicate the formation of species of type **1**-M_2S containing H_2O, CN^-, and N_3^- as substrates. However the estimated distance between the two Cu(II) cations in **1**-M_2 (see above) is probably too short for end to end bridging by a substrate especially for azide (which might involve bridging by a terminal nitrogen).[16,17] Both cyanide[18] and azide[16] bridging has been observed in dimeric tren-Cu(II) complexes; in the latter case an electronic absorption band is present at 670 nm similar to that observed above.



1-M_2S

Cation complexation, intercationic distance, and substrate inclusion in systems of the bis-tren type may be regulated via the length of the bridges linking the tripodal subunits and the nature of the heteroatoms (e.g., NZ = S, PZ in **1**). Cascade complexes like **1**-M_2S, as well as the corresponding species derived from cylindrical macrotricycles A,[2,3] may lead to selective *fixation* and *transport* of a given substrate as well as to the development of new *bi(or poly)nuclear catalysts* for multicenter-multielectronic processes (condensation of two or more included substrates held in proximity, O_2 and N_2 reduction, water splitting,[19] etc.) and of models for polynuclear metalloproteins (hemocyanin, hemerythrin, oxygenases, etc.).[20,21]

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Preparation of $[3,3-(Ph_3P)_2$-3-H-4-(polystyrylmethyl)-3,1,2-$RhC_2B_9H_{10}]$. A Polymer-Bound Metallocarborane Catalyst

Sir:

Considerable interest has recently developed in the attachment of homogeneous transition metal catalysts to insoluble supports in order to aid in product isolation and in catalyst retrieval.[1-5] This concept of supporting active catalytic molecules was initially developed[6,7] by biochemists who utilized bound enzymes as their catalysts. Inorganic approaches to this area have centered on anchoring transition metal catalysts to