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Mononuclear and mixed-metal dimethyltin Pacman complexes of a Schiff-base pyrrole macrocycle**

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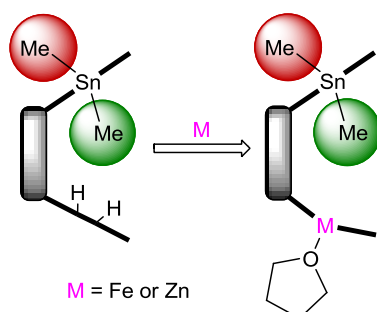
Supporting information:

Full experimental details, X-ray crystal structure of [SnMe₂Fe(THF)(L)]. This material is available free of charge via the Internet at <http://pubs.acs.org>

Synopsis:

A six coordinate, mononuclear dialkyl tin complex of the octadentate macrocycle H₄L has been prepared and adopts a Pacman structure in solution that desymmetrizes the two alkyl groups. Incorporation of Fe or Zn cations into the vacant N₄-donor pocket is straightforward and results in heterobimetallic complexes in which the solid state structures display significant distortion when compared to homobimetallic analogues.

Graphical abstract:



Abstract

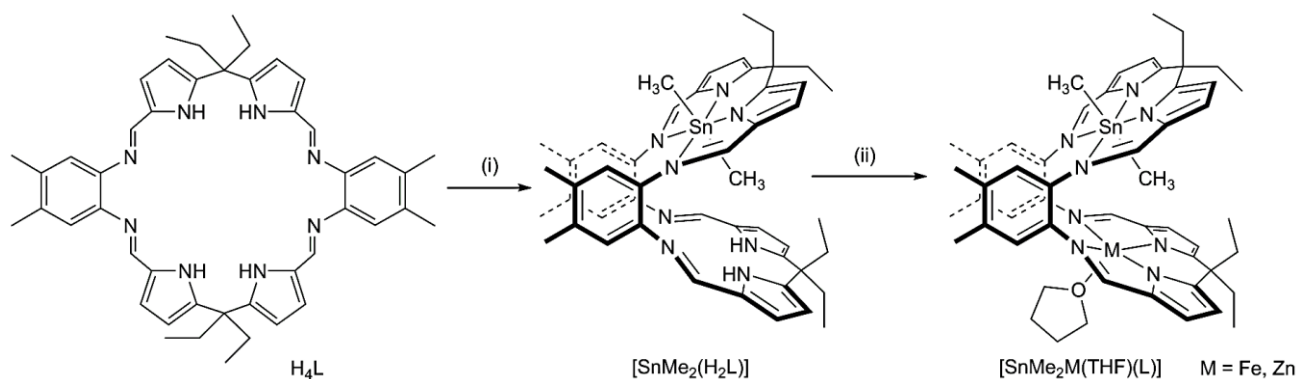
The synthesis of a dialkyltin complex $[\text{SnMe}_2(\text{H}_2\text{L})]$ of an octadentate Schiff-base pyrrole macrocycle is described in which the gross Pacman geometry enforces structural discrimination between the two methyl groups. The presence of the metal-free compartment engenders the formation of mixed-metal Sn-Fe and Sn-Zn complexes in which the macrocyclic cleft has distorted considerably upon the introduction of the transition metal cation.

Main text

The well-defined metal cation microenvironments found within cavities, metal-based capsules, and deep-cavity complexes encourage chemical reactivity very different to the bulk medium. For example, the encapsulation of organometallic complexes within tetrahedral coordination cages has been shown to affect the rates and selectivities of C-H activation and hydroformylation reactions,¹ while copper complexes of podand-calixarenes with deep cavities display unusual reactivity towards O_2 .² Similarly, the use of very bulky terphenyl substituents enables the catalytic formation of NH_3 from N_2 in Mo 'tren' chemistry, reactivity that was not seen when using less bulky substituents.³

We have shown recently that remarkable reactivity of the oxo-groups of the uranyl dication $[\text{UO}_2]^{2+}$ is promoted within the unique molecular microenvironment provided by a Schiff-base pyrrole macrocyclic Pacman framework.^{4,5} Complexation of $[\text{UO}_2]^{2+}$ by the macrocycle H_4L (Scheme 1) desymmetrizes the linear $\text{O}=\text{U}=\text{O}$ motif and allows selective manipulation of the oxo-group within the macrocyclic cleft to promote the selective reductive silylation of uranyl.⁶ This similarity between actinyl and transition metal oxo chemistry has prompted us to evaluate synthetic approaches to new monometallic Pacman complexes of H_4L ; furthermore, organometallic chemistry based on this ligand architecture is relatively unexplored.⁷ In this contribution we describe the synthesis of the mononuclear Sn^{IV} complex $[\text{SnMe}_2(\text{H}_2\text{L})]$, a rare example of a stable, six coordinate, dialkyl Sn cation supported by an N_4 -donor set, and its reactions with Fe and Zn cations to form the mixed metal complexes $[\text{SnMe}_2\text{M}(\text{THF})(\text{L})]$ ($\text{M} = \text{Fe}, \text{Zn}$).

The dehydrohalogenation reaction between the neutral macrocycle H_4L and SnMe_2Cl_2 in the presence of DABCO results in the rapid and clean formation of the mononuclear tin dialkyl complex $[\text{SnMe}_2(\text{H}_2\text{L})]$ as a yellow powder in good yield (Scheme 1). As with the uranyl chemistry of H_4L , it appears that the presence of a trans-ligand arrangement limits the formation of dinuclear complexes, presumably due to a steric clash of axial ligands within the macrocyclic cleft.⁴ This reaction appears limited to the use of SnMe precursors, as reactions using other tin alkyls such as SnR_2Cl_2 ($\text{R} = \text{Ph}, \text{Bu}^n$) leads to mixtures of complexes that have yet to be identified. While we have been unable to grow crystals of $[\text{SnMe}_2(\text{H}_2\text{L})]$ suitable for X-ray structural analysis, the structure in solution can be identified using ^1H and ^{13}C NMR spectroscopy.



Scheme 1. Formation of SnMe_2 complexes of the Schiff-base calixpyrrole H_4L . Reagents and conditions: (i) SnMe_2Cl_2 , DABCO, PhMe, 73%; (ii) $[\text{M}(\text{THF})_n\{\text{N}(\text{SiMe}_3)_2\}_2]$, THF, M = Zn, $n = 0$, 80 %; M = Fe, $n = 1$, 48%

The ^1H NMR spectrum of $[\text{SnMe}_2(\text{H}_2\text{L})]$ (Figure 1) is characteristic of a folded, Pacman geometry in solution. In particular, resonances due to one metallated and one vacant N_4 -donor compartment are seen, with two resonances at 8.00 and 7.87 ppm for the imine protons, a pyrrole N-H resonance at 9.29 ppm, and furthermore, four resonances for each of the CH_2 and CH_3 protons of the endo- and exo-*meso*-ethyl substituents. The $\text{Sn}-\text{CH}_3$ groups are clearly in very different chemical environments, resonating at 1.28 and 0.55 ppm, and the averaged magnitude of the $^2J_{\text{SnH}}$ coupling constants (100.5 Hz) suggests a *trans*-configuration with a C-Sn-C angle of 163.4° , calculated using Lockhart and Manders' empirical correlation;⁸ in NOE experiments, the resonance at 0.55 ppm shows no enhancement to other ligand resonances and is therefore identified as the CH_3 group that resides within the macrocyclic cleft.

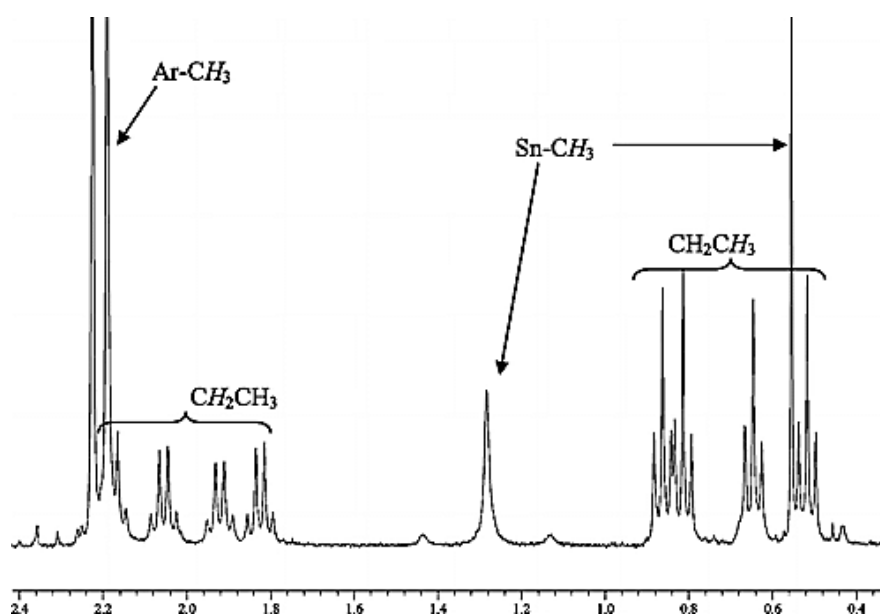


Figure 1. ^1H NMR spectrum of $[\text{SnMe}_2(\text{H}_2\text{L})]$ in C_6D_6 displaying the aliphatic region.

As in the case of the uranyl complex $[\text{UO}_2(\text{THF})(\text{H}_2\text{L})]$,⁴ the presence of the vacant N_4 -donor compartment in $[\text{SnMe}_2(\text{H}_2\text{L})]$ facilitates the incorporation of a second metal cation to form heterobimetallic complexes. As such, the transamination reactions between $[\text{SnMe}_2(\text{H}_2\text{L})]$ and the low co-ordinate metal silylamides $[\text{M}(\text{THF})_n\{\text{N}(\text{SiMe}_3)_2\}_2]$ ($\text{M} = \text{Fe}$, $n = 1$; $\text{M} = \text{Zn}$, $n = 0$) result in the ready isolation of the mixed metal complexes $[\text{SnMe}_2\text{M}(\text{THF})(\text{L})]$ in good yield (Scheme 1). While the ^1H NMR spectrum of the iron complex $[\text{SnMe}_2\text{Fe}(\text{THF})(\text{L})]$ shows paramagnetically-shifted and broadened resonances between 102 and -12 ppm, it is clear from the number of resonances and their integral values that a Pacman structure is retained on addition of the second metal. This conclusion is reinforced by the ^1H NMR spectrum of the zinc analogue $[\text{SnMe}_2\text{Zn}(\text{THF})(\text{L})]$, which clearly displays resonances for two distinct N_4 -donor compartments and four pairs of resonances for endo- and exo-*meso*-ethyl groups that are expected for a Pacman geometry. As with $[\text{SnMe}_2(\text{H}_2\text{L})]$, the Sn- CH_3 groups are in separate environments, in this case at 1.13 and 0.06 ppm, with the latter resonance associated with the endo- CH_3 group protons by NOE experiments and, as such, becoming shielded by the transition metal cation. Furthermore, analysis of the $^2J_{\text{SnH}}$ coupling constants suggests that a compression of the C-Sn-C angle has occurred from 163.4 in $[\text{SnMe}_2(\text{H}_2\text{L})]$ to 150.5° in $[\text{SnMe}_2\text{Zn}(\text{THF})(\text{L})]$.

Crystals of both $[\text{SnMe}_2\text{Fe}(\text{THF})(\text{L})]$ and $[\text{SnMe}_2\text{Zn}(\text{THF})(\text{L})]$ were grown that were suitable for X-ray diffraction and their solid state structures determined. Due to the similarity of these two structures and the ability to correlate these data to the solution structure, only that of the SnZn complex is described here (Figure 2, see SI Fig. S1 for the SnFe complex). In this complex, the trans- SnMe_2 fragment is six co-ordinate and bound in one N_4 -donor pocket in a distorted octahedral geometry, while the Zn cation is located in the opposing compartment and adopts a five co-ordinate square pyramidal geometry due to axial co-ordination of a molecule of THF, exogenous to the molecular cleft. X-ray structural data for six co-ordinate dialkyltin complexes of nitrogen based ligands are rare,^{9, 10} with only a few structures of dialkyltin porphyrins known, none of which contain simple alkyl ligands such as ethyl or methyl.¹⁰ There are also only a handful of structures based on related salen-type ligands, although six co-ordinate SnMe_2 complexes have been described.¹¹ While the Sn1-N1 bond distance at 2.153(2) Å is similar to Sn-N(pyrrole) bond distances seen in Sn^{IV} porphyrins (*ca.* 2.1 Å), the Sn1-N2 bond (2.534(2) Å) is appreciably longer than the Sn-N(imine) bond distances seen in Sn^{IV} salen complexes (2.25 – 2.29 Å), and is likely due to a combination of the more acute C100-Sn1-C200 angle (150.06(16)°) and the ability of the aryl hinge groups to splay away from each other; this feature is similar to that seen by us in the uranyl complexes $[\text{UO}_2(\text{THF})(\text{H}_2\text{L})]$ in which the THF adopts an equatorial position in-between the aryl hinge groups.⁴ Significantly, the C100-Sn1-C200 angle is commensurate with that calculated from the averaged $^2J_{\text{SnH}}$ coupling constants for $[\text{SnMe}_2\text{Zn}(\text{THF})(\text{L})]$ in solution (150.5°).

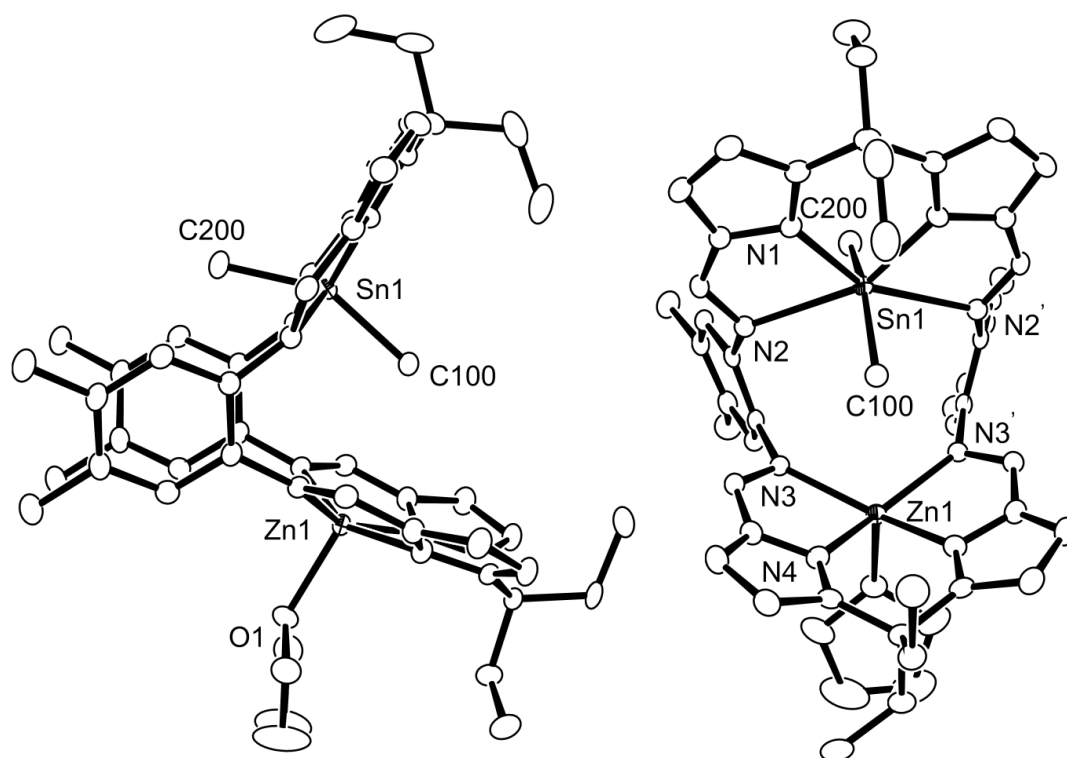


Figure 2. The solid state structure of $[\text{SnMe}_2\text{Zn}(\text{THF})(\text{L})]$. For clarity, all hydrogen atoms are omitted (50% probability displacement ellipsoids, symmetry related atoms generated using the operators $x, -y+1/2, z$ and $x, -y+1, -z+3/2$)

In order to accommodate the two metals and the endogenous methyl group, the gross macrocyclic structure has distorted significantly from that seen in the homobimetallic complexes $[\text{M}_2(\text{L})]$ ($\text{M} = \text{transition metal}$),¹² with the ‘bite’ angle (72.3°) considerably more obtuse (usual range $45\text{--}62^\circ$) and the $\text{M}\cdots\text{M}$ separation (4.56 \AA) elongated (range $3.15\text{--}4.12 \text{ \AA}$). Furthermore, the SnN_4 donor plane has folded away from the cleft at the $\text{N2}/\text{N2}'$ hinge nitrogen atoms by 19.8° . The resulting steric clash between the *exo*- Sn-Me group and the aryl hinge groups between the two donor compartments, coupled with compression of the C-Sn-C angle has caused the aryl hinge groups to move away from co-planarity and adopt a V-shaped conformation with a dihedral angle of 43.4° . The zinc cation sits exogenous to the N_4 -donors by 0.43 \AA which causes the imine-pyrrole chelates to fold about the *meso*-carbon by 38.2° (*cf.* 15.4° for the Sn compartment).

We have shown that a stable mononuclear dialkyl Sn^{IV} complex of L can be prepared and that the Pacman molecular cleft arrangement causes the desymmetrization of the two Sn-methyl environments. Moreover, this complex can be functionalized further by incorporation of transition metals into the lower vacant coordination pocket. The influence of the introduction of the second metal on the reactivity of the SnMe_2 moiety is being studied.

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