Inorg. Chem. **2008**, *47*, 2925−2927

Versatile Approach toward the Self-Assembly of Heteromultimetallic Salen Structures

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Received January 9, 2008

A general route is presented toward the template-directed preparation of self-assembled heteromultimetallic salen structures using noncovalent coordinative metal–ligand interactions. Various higher order assemblies have been studied in detail using a combination of NMR spectroscopy and X-ray crystallography.

Most enzymes contain two or more metal ions in the active site separated by a fixed mutual distance.[1] These ions can cooperatively catalyze chemical reactions, leading to improved kinetics and higher selectivity. Ideally, these processes are mimicked in supramolecular catalysis utilizing self-assembled, macromolecular architectures. Recently, Jacobsen et al. found that certain transformations catalyzed by chromium(III) or cobalt(III) salen complexes occur in a bimetallic, cooperative step.[2] This discovery boosted the development of new bimetallic salen structures comprising either a covalent linkage between two separate salen scaffolds[3] or noncovalent coordinative interactions between pyridyl-modified salen ligands and transition-metal salts.[4] Our approach toward functional multimetallic salen structures is based on the use of readily available zinc(II) salphen templates [salphen = *N*,*N*′-phenylenebis(salicylideneimine)]. The strong interaction of these zinc(II) derivatives with pyridine and amine donors[5] has been recently exploited for the assembly formation of various supramolecular systems including encapsulated catalysts,[6] functional porous materials,[7] and self-assembled, tetrameric structures.[8] Here, we demonstrate that these zinc(II) salphen templates are well-suited for the effective positioning of salpyr-based and pyridyl-derived salphen complexes [where salpyr stands for *N*,*N*′-3-pyridylenebis(salicylideneimine)]. Evidence will be provided that the metal centers of these complexes can be positioned at close range from each other using an appropriate template (Scheme 1).[9] The large diversity of assemblies that can be accessed with this new approach creates a large potential for their use in supramolecular catalysis.

In general, the salpyr complexes could not be prepared via classical preparation routes. Therefore, we decided to prepare these complexes via an alternative approach using zinc(II) complex **1** (Scheme 1). Complex **1** was prepared by in situ treatment of 3,5-di-*tert*-butylsalicylaldehyde with 3,4-diaminopyridine in the presence of zinc acetate in methanol following a previously reported procedure.[8a] Subsequently,

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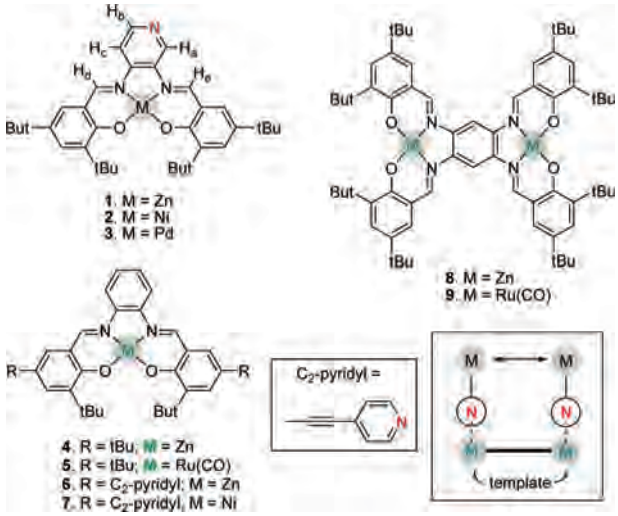
10.1021/ic800033v CCC: $40.75
Published on Web 03/14/2008

Scheme 1. Metallosalpyr Complexes **1**–**3**, Salphen Derivatives **4**–**7**, and Metallosalphen Templates **8** and **9**[a]



[a] The M (in green/highlighted in green) stands for the template derivative.

Table 1. ^{1}H NMR Shifts of Protons H_a−H_e of the Metallosalpyr Unit **1**–**3** upon Template Addition Using Complexes **4**, **5**, and **8**[a]

assembly	H_a	H_b	H_c	H_d	H_e
4·2	−0.22	−0.27	+0.04	−0.09	−0.55
4·3	−0.19	−0.21	+0.02	−0.07	−0.50
8·(2)$_2$	−0.11	−0.13	+0.03	−0.05	−0.33
8·(3)$_2$	−0.09	−0.11	+0.03	−0.04	−0.30
5·1	−0.35	−0.23	−0.10	+0.55	+0.16
5·2	−0.27	−0.76	−0.18	−0.23	−0.81
5·3	−0.32	−0.72	−0.17	−0.20	−0.86

[a] All NMR shifts are given in ppm with ± designations for upfield and downfield displacements, respectively. The solvent in each experiment was acetone-d_6. For the different proton assignments a−e, please follow the structure presented in Scheme 1.

the corresponding nickel(II) and palladium(II) derivatives **2** and **3** could be easily obtained through a recently described transmetalation method[10] that involves treatment with nickel(II) or palladium(II) acetate in THF. The nickel(II) complex **7** was prepared analogously using known Zn(salphen) **6** (see the Supporting Information).[4c]

Solutions of the metallosalpyr complexes **2** and **3** in acetone-d_6 were added to a stoichiometric amount of Zn(salphen) complex **4**, the assemblies were studied by ^{1}H NMR, and all assignments were fully supported by COSY and NOESY. Typical shifts for the metallosalpyr complexes upon assembly formation are shown in Table 1. The ^{1}H NMR spectrum of a mixture of the Ni(salpyr) complex **2** and the Zn(salphen) template **4** is shown in Figure S1 of the Supporting Information. Significant proton shifts are observed that corroborate with the assembly formation. The magnitude of these shifts is mainly dependent on the sum of two factors: the presence of a coordinative donor–acceptor pattern (i.e., the Zn−N_{pyr} bond), which should result in a particular downfield shift for the pyridyl protons, and a shorter through-space distance to the π-electron density of the salphen structure, which will result in a significant upfield shift. As can be expected, H_a and H_b showed a higher upfield shift than H_c (Table 1) because they will be relatively close to the template upon coordination. It can be assumed that the electron-withdrawing effect is dominant in the case of H_c (downfield shift). For imine H_e, a very large upfield shift was found, which suggests that this proton is positioned relatively near the Zn(salphen) plane as compared to imine H_d. From these NMR solution studies, it is evident that pyridine coordination takes place and that the expected heterometallic 1:1 assembly is formed.

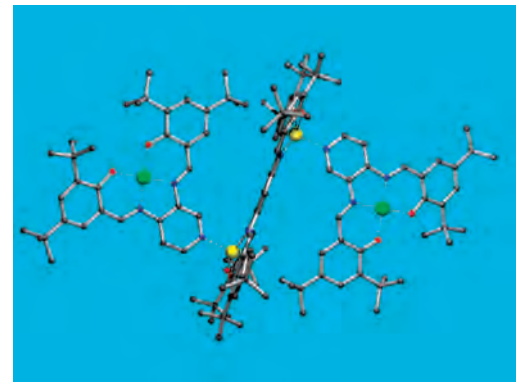


Figure 1. X-ray molecular structure of the 2:1 assembly **8·(3)**$_2$. Color code: green = Pd, yellow = Zn, red = O, blue = N.

Almost identical results were found for the 1:1 combination of Pd(salpyr) complex **3** with Zn(salphen) template **4** and for both 2:1 assemblies derived from Pd- and Ni(salpyr) complexes **2** and **3** and bis-Zn(salphen) template **8** (see Table 1), although in the latter cases lower upfield shifts were observed and a weaker Zn−N_{pyr} interaction is envisioned. This is likely related to a lower Lewis acidity of the Zn centers in **8** as compared to **4** because of an electronic coupling between the individual chromophores.[7] For the 2:1 assembly **8·(3)**$_2$, suitable crystals for X-ray analysis were obtained after crystallization from acetone (Figure 1). In the solid state, the centrosymmetric molecule contains two antipositioned metallosalpyr units with respect to the template **8**. It is obvious from the packing diagram of this particular structure (Supporting Information) that favorable π interactions exist between the salpyr units of adjacent molecules leading to this anti configuration, while in solution, the syn and anti isomers should rapidly interconvert as a result of the dynamic character of the coordinative bond. The Zn−N_{pyr} bond length amounts to 2.09 Å, which is comparable to previously reported Zn−N_{pyr} distances.[5] The potential formation of both isomers was supported by separate molecular modeling studies (Supporting Information) and, furthermore, the observation of comparable syn and anti isomers was reported for a bis-Ru(CO)(pyridine)salen analogue (cf. **9**).[7a]

The versatility of this assembly concept toward heteromultimetallic salen systems could be additionally demonstrated by the use of the ruthenium(II)-centered complex **5**,[7a] which is known to have strong interactions with pyridine donors. Solutions in acetone-d_6 were prepared in a manner similar to that described above, and characteristic shifts are reported in Table 1. The shift patterns are equal to the ones found for the assemblies with zinc complex **4**; however, the observed shift dimensions are much larger. The much higher association constant of the Ru−N_{pyr} bond (>10^6 M^{-1}) as

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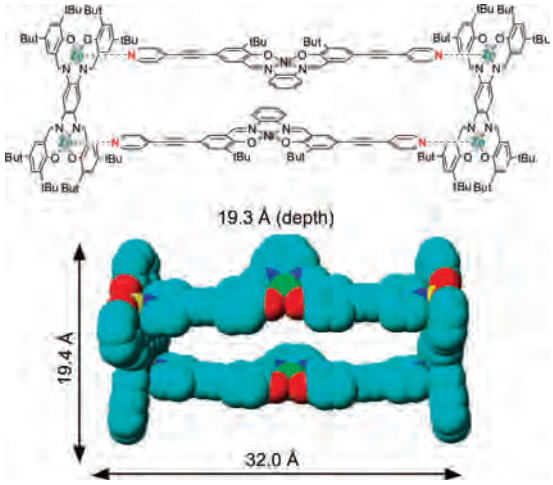
Scheme 2. Schematic Structure of the 2:2 Assembly $(\mathbf{8})_2 \cdot (\mathbf{7})_2$ and the Energy-Minimized Modeled Structure[a]



[a] All *t*-Bu groups in the calculated structure are omitted for clarity.

compared to the Zn−N_{pyr} bond (∼10^5 M^{-1}) will most likely result in a shorter bond and consequently a shorter through-space distance to the ruthenium(II) salphen framework, giving a higher upfield shift. Because of the very strong nature of the Ru−N_{pyr} bond, a small excess of the metallosalpyr complex results in the observation of both bonded and free salpyr complexes in the ^{1}H NMR spectrum (Supporting Information), confirming the much less dynamic behavior of the Ru−N_{pyr} bond.

The NMR shifts upon mixing of Zn(salpyr) complex **1** with **5** are significantly different compared to those noted for assemblies **5·2** and **5·3** (Table 1, H_d). However, they cannot be interpreted equally because it was recently shown that complex **1** itself organizes into a stable, tetrameric structure via intermolecular Zn−N_{pyr} interactions.[8] As a result, the calculated shifts are hence the sum of the breakup of this tetrameric structure followed by the formation of the 1:1 assembly **5·1**.

We also examined the templated formation of 2:2 assemblies in which the Ni(salphen) derivative **7** was combined with the bis-Zn(salphen) complex **8** (Scheme 2). We anticipated that the formation of a rectangular-shaped structure would prevail, with both nickel(II) sites residing at the same side of the template because of the presence of four complementary Zn−N_{pyr} interactions.[11] The 2:2 stochiometry was first examined by ^{1}H NMR in dry $CDCl_3$, which showed a complicated spectrum (Supporting Information). Disruption of the solution structure in the presence of a competing ligand (pyridine-d_5) converted the assembly in the original, individual components. Variable-temperature NMR was then performed (dry $C_2D_2Cl_4$, 25–125 °C) for this 2:2 assembly to study the dynamics of the structure. As may be expected, the spectrum sharpens significantly upon heating and at 125 °C, several resonances could be readily assigned to both building blocks. Remarkably, at this temperature, the pyr−H_{ortho} bond of the assembly is located 0.20 ppm upfield as compared to the free complex, while a $\Delta\delta$ of ∼0.34 ppm was noted for the 2:2 combination at room temperature. This implies that part of the assembly is still intact at these elevated temperatures as pyridine coordination is evident. Because of the more dynamic character of the Zn−N_{pyr} bond, probably only nondiscrete ("open") structures are present. Subsequent cooling of this NMR sample to room temperature afforded the original NMR spectrum, and the addition of a small aliquot of pyridine-d_5 converted the spectrum into a combination of nonassembled, individual components.

Interestingly, only a single species was detected by ^{1}H DOSY NMR and the diffusion coefficient was subsequently used to calculate the hydrodynamic radius of the formed assembly. The experimental hydrodynamic radius obtained (r_{exp} = 12.7 Å) corresponds remarkably well with the predicted, averaged radius (r_{calc} = 11.8 Å) that was derived from molecular modeling results for the 2:2 box-shaped assembly (Supporting Information). The combined spectroscopic features can thus be explained by the formation of distinct isomeric 2:2 assemblies, in which the two Ni(salphen) units (i.e., **7**, Scheme 1) have different relative positions. Therefore, we conclude that at ambient temperature the discrete 2:2 structure is in very slow exchange with small, "open" assemblies.

In conclusion, we have presented a novel, versatile strategy aimed at the formation of a series of self-assembled heteromultimetallic salen structures. In these assemblies, metallosalpyr/salphen donor complexes can be reversibly immobilized on metallosalphen acceptors via coordinative interactions to obtain a series of 1:1, 2:1, and 2:2 heteromultimetallic assemblies. The obvious advantage of the presented approach is that any combination of Zn−M (where M stands for the metal ion in the donor complex) can be foreseen and the strength of the M−N_{pyr} interaction may be varied by use of Zn- or Ru(salphen) acceptors. The correct positioning of catalytically active objects is of crucial importance to induce cooperativity effects, and we have shown that this can be achieved by utilization of the bis-Zn(salphen) template **8**. Our current activities focus on the use of other metal-centered salpyr and/or pyridine-tagged salen complexes (e.g., where M = Mn, Co) for the directed assembly formation of catalytically active supramolecules.

Acknowledgment. A.W.K. thanks both ICREA and ICIQ for financial support. S.J.W. thanks ICIQ for a predoctoral fellowship.

Supporting Information Available: Synthesis and characterization of all new compounds, relevant NMR spectra, an ORTEP picture for the X-ray molecular structure, X-ray crystallographic data in CIF format, and results of modeling studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Such box-shaped assemblies are highly stable and have an overall association constant of ∼10^{20} M^{-3}. See ref 7b.