Inorg. Chem. **2008**, *47*, 410–412

Inorganic Chemistry
Communication

Creation of a Nonsymmetric Dimethanolpyridine Ligand: A Rare Zn(salphen) Template Effect

Eduardo C. Escudero-Adán, Jordi Benet-Buchholz, and Arjan W. Kleij*

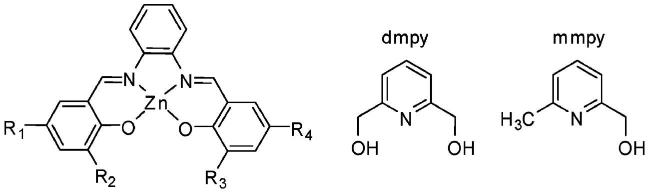
*Institute of Chemical Research of Catalonia (ICIQ), Avenida Països Catalans 16,
43007 Tarragona, Spain, and Institució Catalana de Recerca i Estudis Avançats (ICREA),
Pg. Lluís Companys 23, 08010 Barcelona, Spain*

Received November 12, 2007

An interesting reversible, templated synthesis of unsymmetrical pyridine-ligated Zn complexes has been observed in solution and solid-state phases when Zn(salphen) complexes are reacted with methanol-substituted pyridine substrates. The X-ray molecular structure of an unusual Zn_3 supramolecular assembly is reported, in which the central Zn atom is embedded in a distorted octahedral geometry and each of the single anionic O atoms of the pyridine groups coordinates to a Zn(salphen) unit.

Salen structures have a long-standing tradition within the field of homogeneous (asymmetric) catalysis[1] and can be considered as one of the key ligands in the quest for environmentally benign process chemistry. The reactivity and catalytic properties of Zn^{II}-centered salen species remain surprisingly unexplored,[2] despite the fact that these species possess a high potential for use as Lewis acidic catalysts and supramolecular motifs in various nanosize structures such as self-assembled catalysts, box-shaped structures, and templated ligands.[3] Strong association with various N- and O-donor systems has been reported for the Zn(salphen) family of salen complexes [salphen = *N*,*N′*-phenylenebis(salicylideneimine)].[4] We recently successfully explored the transmetalation of these derivatives and again revealed that these complexes have an intriguing reactivity.[5] Here we report the unusual reactivity of a small series of Zn(salphen) complexes toward 2,6-dimethanolpyridine (dmpy) and 2-methanol-6-methylpyridine (mmpy), which leads to a bis(dmpy/mmpy)-ligated Zn complex through the unique, selective activation of a single OH group in each of the two dmpy/mmpy units. This observed reactivity may be of use in order to devise new (catalytic) conversions that are based on Zn(salphen) complexes and alcoholic substrates.

Scheme 1. Overview of Used Zn(salphen) Structures and Pyridine-Based Ligands dmpy and mmpy



1. $R_1 = R_2 = R_3 = R_4 = t\text{-Bu}$
2. $R_1 = R_4 = H$; $R_2 = R_3 = t\text{-Bu}$
3. $R_1 = R_2 = t\text{-Bu}$; $R_3 = R_4 = NO_2$

4

5

When Zn(salphen) complex **1** (Scheme 1) and dmpy (**4**) in CH_3CN were heated to reflux for a short period of time, an orange solution was obtained. Cooling to ambient temperature slowly afforded a crystalline material. A representative portion of these crystals were isolated for NMR investigation (acetone-d_6) and revealed the presence of a complex mixture of components that could not be directly assigned (see the Supporting Information). However, the presence of a singlet resonance at 13.78 ppm in the ^1H NMR spectrum yet indicated that the formation of (partially)

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* To whom correspondence should be addressed. E-mail: akleij@iciq.es.

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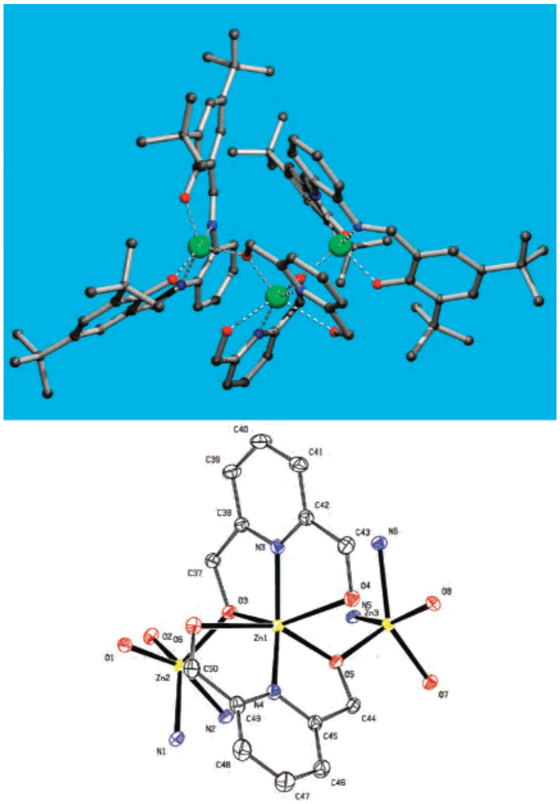

Figure 1. X-ray molecular structure for assembly $(\mathbf{1})_2$·[(dmpy)$_2$Zn]. H atoms, cocrystallized solvent molecules, and the numbering scheme are omitted for clarity (Zn, green; O, red; N, blue). Directly below, the central nonsymmetrical (dmpy)$_2$Zn unit (with Zn atoms shown in yellow) is presented together with the coordination geometry around the other two Zn centers.

demetalated **1** had occurred. A closer inspection of the crystalline material revealed the presence of two separate species, of which one was characterized by a yellow color (assigned to the demetalated salphen complex **1**) while the other was orange-colored. The latter crystals were then subjected to X-ray diffraction analysis. Much to our surprise, the X-ray molecular structure (Figure 1) that was determined proved to be an unusual three-component, supramolecular assembly consisting of a central (dmpy)$_2$Zn unit accompanied by two Zn(salphen) motifs that are axially ligated by one of the O-donor atoms of each dmpy ligand.

Remarkably, the Zn−O bond lengths within the central unit are significantly different. The shorter Zn−O distances (1.97−1.98 Å) fall well in the range of those reported for Zn(salphen) complexes,[2c,4a] and the O atoms can thus be considered as truly ionic. The presence of anionic O atoms infers the monodeprotonation of the dmpy ligand. The Zn ion that is present in the central unit originates from the Zn(salphen) complex **1** and, therefore, requires demetalation. This is in good agreement with the ^{1}H NMR data for the crystalline material, which indeed shows the presence of demetalated **1**. The longer Zn−O distances (2.4−2.5 Å) correspond to weak coordinative Zn···OH interactions, while the OH protons are pointing to the nearest O atom of the adjacent Zn(salphen) unit, indicating a hydrogen-bonding pattern. The presence of considerably different Zn−O distances in the (dmpy)$_2$Zn part results in the severe distortion of an octahedral geometry around the metal center,[6] with the Zn atom acquiring a nonsymmetrical position with respect to both dmpy planes.

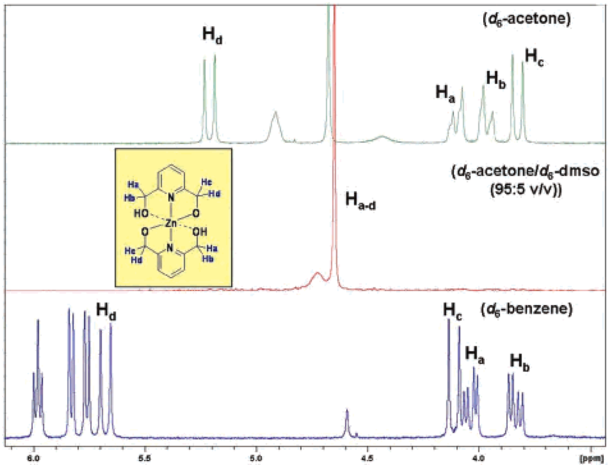

Figure 2. Selected ^{1}H NMR methylene region for the product containing the assembly $(\mathbf{1})_2$·[(dmpy)$_2$Zn] in different solvents. From the upper spectrum to the lower spectrum: acetone-d_6 (100%), acetone-d_6/DMSO-d_6 (95:5, v/v), and benzene-d_6 (100%).

Only a few structures based on the dmpy ligand are known.[7] Yilmaz and co-workers reported on the crystal structure of (dmpy)$_2$Zn·2sac (sac = saccharinate), with the dmpy ligand acting as a neutral tridentate donor system flanked by two anionic saccharinates.[8] In this complex, the observed Zn−O bond lengths are in the range 2.14−2.18 Å and are thus significantly different from those observed within the assembly $(\mathbf{1})_2$·[(dmpy)$_2$Zn]. With the structure $(\mathbf{1})_2$·[(dmpy)$_2$Zn] elucidated, the ^{1}H NMR spectrum recorded for the crystalline product could be readily assigned and each component characterized (Figure 2; see also the Supporting Information).

Because of the asymmetry within the central (dmpy)$_2$Zn unit, all pyridyl protons are magnetically nonequivalent, resulting in the presence of six different resonances. Furthermore, the coordination of the anionic O atom of each dmpy ligand to a Zn(salphen) complex seems to be preserved in solution because two separate signals are observed for the imine H atom and four distinct *t*-Bu resonances (Supporting Information) are evident. As for the methylene region (Figure 2), two discrete AX patterns can be distinguished, of which only one shows a hyperfine coupling with an OH proton. The coupling constants (^2J = 18.1 and 16.3 Hz, respectively) are typical for geminal coupling between diastereotopic protons.

Interestingly, the solution stability of the supramolecular assembly $(\mathbf{1})_2$·[(dmpy)$_2$Zn] seems to depend highly on the solvent medium (Figure 2; see also the Supporting Information). Whereas in acetone-d_6 a mixture of components is

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(6) While the O−Zn−O angles in $(\mathbf{1})_2$·[(dmpy)$_2$Zn] are comparable to those found in the (dmpy)$_2$Zn(sac)$_2$ complex (see ref 8), the N−Zn−N angle of 143.03° is significantly different from the same angle found in the latter complex (173.74°).

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observed (Figure 2), the addition of a small amount (5%, v/v) of dimethyl-d_6 sulfoxide (DMSO-d_6) to the same solution affords a highly simplified spectrum. The components in the latter case were identified as the free ligand **4** and the Zn(salphen) complex **1**. To our surprise, NMR analysis carried out in benzene-d_6 (a noncoordinating solvent) completely reversed the situation and, under these conditions, the *only* components present were the demetalated Zn(salphen) complex **1** and the assembly $(\mathbf{1})_2\cdot[(\text{dmpy})_2\text{Zn}]$.

We then examined the reactivity of two other Zn(salphen) complexes (**2** and **3**) toward **4**. While complex **2** combined with **4** also leads to a similar three-component assembly (see the Supporting Information), complex **3** is recovered unchanged after crystallization.[9] The difference in reactivity can be explained by assuming that the first step in the formation of these peculiar assemblies is the coordination of one of the OH groups to the Zn metal center (Figure 3). Activation of this coordinated OH group leads to an intermediate species with one protonated, phenolic position. From a second molecule of **4**, which attacks this intermediate from the other side, a second proton transfer to the salphen moiety is accommodated. In the last step, elimination of metal-free salphen-H_2 takes place and $(\text{dmpy})_2\text{Zn}$ is formed.[10]

An initial screening of other substrates such as mmpy (**5**) revealed a similar reactivity toward **1** compared to **4**. The ^{1}H NMR (benzene-d_6) spectrum recorded for a crystalline sample of deuterated benzene afforded virtually pure $(\mathbf{1})_2\cdot[(\text{mmpy})_2\text{Zn}]$ with a diagnostic AX pattern ($^2J = 18.4$ Hz) for the methylenic protons (see the Supporting Information). The latter finding suggests a wider scope for Zn(salphen) derivatives in alcohol activation.

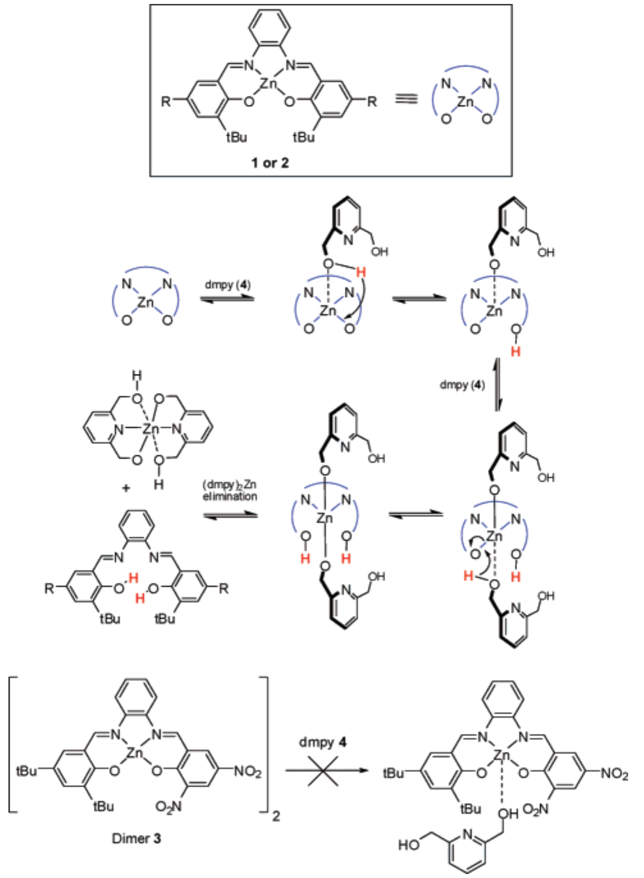

Figure 3. Proposed mechanism of the formation of assembly $(\mathbf{1})_2\cdot[(\text{dmpy})_2\text{Zn}]$.

In summary, this work has shown remarkable reactivity of a metallosalen toward alcoholic ligands. The Zn(salphen) complex **1** acts as a template[11] for the formation of a nonsymmetrical dmpy/mmpy structure via a selective deprotonation−metal transfer sequence. To the best of our knowledge, this procedure represents an unprecedented transformation that may be used to discover new conversions based on similar substrates. An in situ treatment with appropriate electrophiles could provide catalytic behavior of the Zn(salphen) complex under appropriate conditions. Motivated by the importance of salen complexes in (asymmetric) catalysis, we now focus on merging of the observed reactivity behavior of the Zn(salphen) derivatives with the development of new catalytic conversions.

Acknowledgment. This work was financially supported by an ICREA grant (to A.W.K.) and by the ICIQ foundation.

Supporting Information Available: Full experimental details, X-ray crystallographic details in CIF format for the reported three-component assembly, and relevant NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Complexes such as **3** are known to form dimers in the solid state and in solution via μ_2-O bridging (see refs 2c and 4a). Apparently, the dmpy ligand is unable to compete with this dimer formation. This supports the view that the initial coordination of **4** is a vital step in the formation of the Zn_3 assembly.

(10) Salphen ligand free crystals were also obtained and analyzed as the three-component assembly $(\mathbf{1})_2\cdot[(\text{dmpy})_2\text{Zn}]$. NMR analysis (acetone-$d_6$) of these crystals furnished, however, a mixture of demetalated **1**, free dmpy **4**, and assembly $(\mathbf{1})_2\cdot[(\text{dmpy})_2\text{Zn}]$. These results suggest that the templated formation of these assemblies may be reversible. This was further corroborated by the fact that signal integration of the original batch of mixed crystals afforded exactly an equimolar ratio between all salphen and all dmpy components.

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