DOI: 10.1002/anie.200702468

Salen Frameworks

Material Applications for Salen Frameworks

*Sander J. Wezenberg and Arjan W. Kleij**

homogeneous catalysis · N,O ligands · nanotechnology · self-assembly · supramolecular chemistry

Dedicated to Professor Gerard van Koten on the occasion of his 65th birthday

Salens are among the most widely studied ligands in chemistry. They are primarily applied in homogeneous catalysis, a use that helps to increase our knowledge of environmentally benign and cost-attractive chemical and/or pharmaceutical processes. Lately, the interest in salen chemistry has shifted to the use of these scaffolds in various other applications in which the immense versatility of the salen framework as a molecular building block can be exploited. Herein, we highlight the most recent research involving the incorporation of salen motifs in new materials and sophisticated catalysts.

1. Introduction

N,*N*′-bis(salicylidene)ethylenediamine (salen) ligands and their complexes are well-studied substances within the field of homogeneous catalysis.[1] They have been used as catalytic species in numerous organic conversions including the epoxidation of olefins, lactide polymerization, asymmetric ring opening of epoxides, and Michael reactions. In analogy to porphyrins,[2] the salen scaffold has an excellent potential as a molecular building block in the development of new materials. In addition, salen species (Figure 1) can be prepared simply and in one step from the reaction of an aldehyde with a diamine (followed by filtration),[3] fulfilling criteria such as, accessibility, cost-effective synthesis, and ease of derivatization.

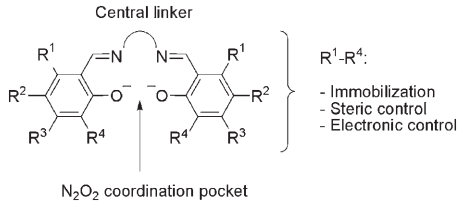


Figure 1. General structure of a symmetrical salen. The substitution at the phenyl rings may be used for immobilization and/or easy control over the ligand properties.

[*] S. J. Wezenberg, Dr. A. W. Kleij
Institut Català d'Investigació Química (ICIQ)
Av. Països Catalans, 16, 43007 Tarragona (Spain)
Fax: (+34) 977-920-224
E-mail: akleij@iciq.es
Dr. A. W. Kleij
Institució Catalana de Recerca i Estudis Avançats (ICREA)
Pg. LLuís Companys 23, 08010 Barcelona (Spain)

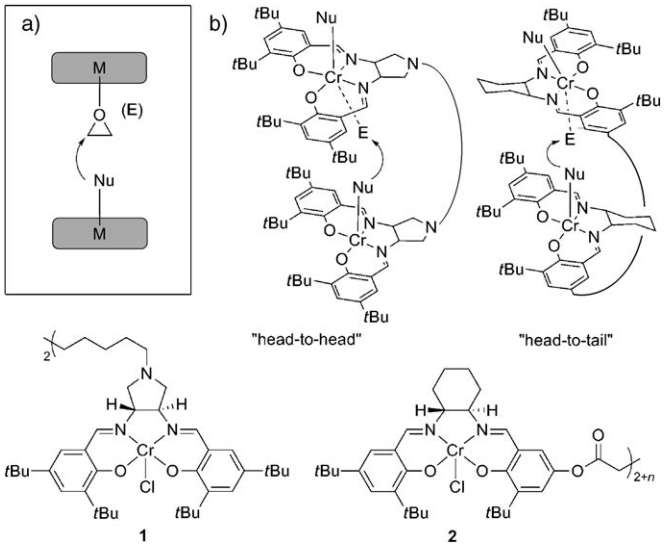
However, salens have received little attention as sources of planar, supramolecular building blocks. Herein, we present the most recent developments of the utilization of salen structures as (supramolecular) synthons in new nanosize materials and as sophisticated homogeneous catalysts. Although the catalytic performance can also be influenced by immobilization of metallosalens in zeolite matrices,[4] on monolayers,[5] or on polymer supports,[6] a discussion of these themes falls outside the scope of this Minireview.

2. Creation of Improved Catalyst Structures

Cooperative catalysis involving two metal ions is a common feature in enzymatic systems.[7] The resulting cooperative activation of both reaction partners leads to enhanced reactivity and more specific control and thus makes enzymes very powerful catalysts. Supramolecular catalysis is a rapidly growing field focusing on attempts to imitate such enzyme processes by using noncovalent, biomimetic structures. To date, few examples of chemical transformations that proceed through cooperative bimetallic catalysis[8] based on salen scaffolds have been reported. Nevertheless, these systems are promising candidates for further development of such highly efficient catalysts.

2.1. Cooperative Salen Catalysis

Jacobsen and co-workers discovered that some transformations, such as the asymmetric ring opening (ARO) and hydrolytic kinetic resolution (HKR) of epoxides, catalyzed by monomeric {Co^{III}(salen)} or {Cr^{III}(salen)} scaffolds, proceed by catalytic activation of both the nucleophile (Nu) and electrophile (E) in a bimetallic, cooperative intermediate (Scheme 1).[9] This observation led to the design of a catalyst



Scheme 1. a) Proposed cooperative bimetallic mechanism for the asymmetric ring opening (ARO) reaction of epoxides catalyzed by metallosalen complexes; Nu = nucleophile, E = electrophile. b) Covalently linked {Cr(salen)} units **1** and **2** that can adopt "head-to-head" and "head-to-tail" orientation respectively. $n = 2$, 4, 5, 6, 7, 8, or 10.

that enforces this cooperative mechanism.[10] In this case, two {Cr^{III}(salen)} units were covalently linked in both a "head-to-head" and "head-to-tail" orientation to obtain the dimeric complexes **1** and **2**. Depending on the length of the linker, this system is able to induce cooperative intramolecular catalysis in the ARO of *meso*-epoxides. However, it must be noted that in the "head-to-head" orientation the enantioselectivity was dramatically decreased. Likewise, dimerized[11] or dendrimer-bound[12] {Co^{III}(salen)} complexes also exhibit a significantly enhanced catalytic activity in the HKR of terminal epoxides. For example, a dendrimer functionalized with eight cobalt(III) centers shows activity at a much lower cobalt loading level than found for the monomeric {Co^{III}(salen)} analogue.

Inspired by this work, Weberskirch and co-workers[13] prepared an amphiphilic block copolymer, in the hydrophobic block were pendant carboxylic acid groups which were covalently attached to {Co^{III}(salen)} moieties. In water, these polymers formed micellar aggregates which, in a concentration range of $c_p = 1$–4 mg mL^{-1}, have a particle diameter of about 10–12 nm (dynamic light scattering (DLS)) to 14.3 nm (TEM). These "nanoreactors" allowed the use of very low amounts of catalyst and shorter reaction times compared to the homogeneous catalyst, while the level of enantioselectivity was retained. More importantly, the reaction can be performed in water without it penetrating into the hydrophobic core. This feature prevents the undesired early hydrolysis of the epoxides.

2.2. Other Catalytic and Self-Assembled Metallosalens

In addition to the constructs mentioned above, weak coordination interactions between salen ligands and transition-metal components can be successfully used to prepare bimetallic assemblies. To date, two general approaches can be distinguished. Both are based on reversible metal–ligand interactions involving either a metal–phosphine/thioether bond or a metal–pyridine bond. The first type of metal–ligand interaction was used by Nguyen and Mirkin, who connected either a {Cr^{III}(salen)} or a {Zn^{II}(salen)} unit to a rhodium(I) center by means of a metal–phosphine or a metal–thioether bond. The metal–thioether bond can be broken as a result of an allosteric arising from the reversible binding of carbon monooxide and a chloride anion (Scheme 2). In this fashion, they prepared a bimetallic macrocycle[14] and a bimetallic tweezer complex with better solubility.[15]

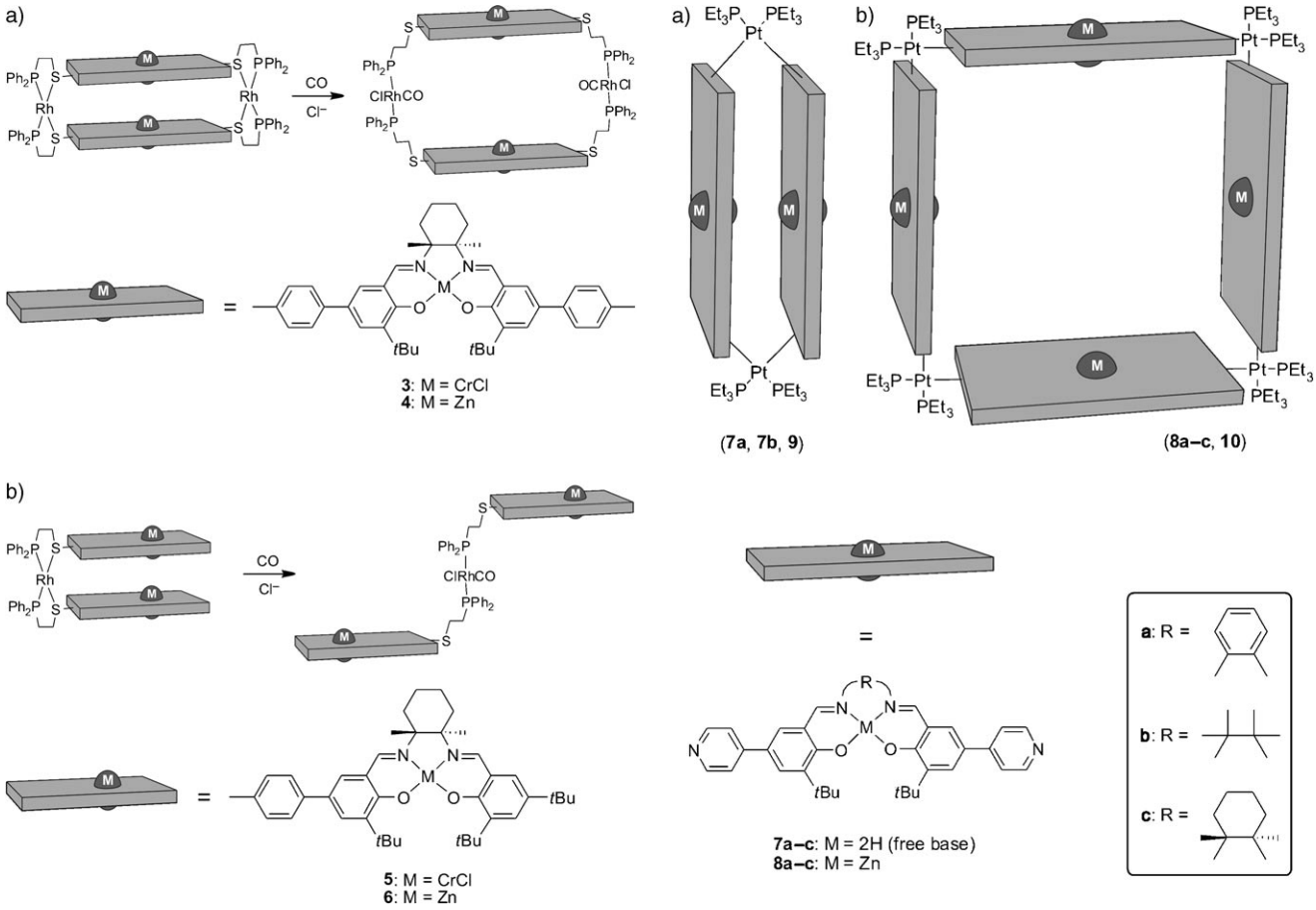
Similar to the results of Jacobsen et al.[10] the {Cr^{III}(salen)}-based macrocycle **3** showed a 20-fold increase in reaction rate and improved enantioselectivity in the ARO of cyclohexene oxide, compared to its monomeric {Cr^{III}(salen)} analogue. After alteration of the assembly induced by the addition of both CO and Cl anion, this rate was even doubled. Likewise, the {Cr^{III}(salen)}-based tweezer **5** also shows enhanced catalytic behavior although in contrast to the macrocyclic species, activity and enantioselectivity decreased after the CO/Cl^--induced opening of the structure.

In line with the preceding finding, a {Zn^{II}(salen)}-based macrocycle was found to increase the reaction rate of the acyl transfer from acetic anhydride to pyridyl carbinol.[16] In this case, the substrate could not undergo intramolecular bimetallic activation in the closed conformation of the macrocycle. However, upon opening, the cavity is large enough to accommodate the substrate and catalysis is "switched on".

In the second type of reversible metal–ligand interaction, the salen is modified with pyridyl groups that can be used to coordinate to transition metals. For example, a pyridyl-functionalized {Zn^{II}(salen)} was inserted into rectangular

Sander J. Wezenberg obtained a BSc and an MSc in supramolecular chemistry from Nijmegen University (Netherlands), where he worked in the groups of Prof. Roeland J. M. Nolte and Prof. Alan E. Rowan. Recently he began his PhD at the ICIQ (Tarragona, Spain), where he is studying anchored salen systems and Hybrid networks.

Arjan W. Kleij studied at the Utrecht university (Netherlands) and completed his PhD there under the supervision of Prof. Gerard van Koten. Subsequently he joined the group of Prof. Javier de Mendoza (Madrid, Spain) on a NWO-Talent-Fellowship before working as a Post Doc with Prof. Joost Reek and Prof. Piet van Leeuwen. In addition he spent three years in various principle research scientist positions at Avantium Technologies and Hexion Specialty Chemicals. He is currently a group leader and ICREA-Fellow at the ICIQ (Tarragona, Spain).



Scheme 2. Induced allosteric "opening" effect caused by the addition of CO and Cl^- ion to a) a macrocycle and b) a tweezer complex.

boxes based on four rhodium centers.[17] Moreover, Nguyen and Hupp[18] found that with platinum complexes the free-base pyridine-modified salens **7** and **9** gave access to loop-type structures (Scheme 3). A subsequent ligand rigidification, either by post-metalation or direct use of the respective {Zn^{II}-(salen)} precursors **8** and **10**, favors the formation of box-like structures. The use of a related Zn^{II}- or Cr^{III}-rigidified 3-pyridyl analogue of **8** again gave formation of bimetallic loop species. Following a similar approach, the same authors reported box assemblies with {Zn^{II}(salen)} substructures **8a**,**b**, in which the pendant pyridyl groups coordinate to rhenium centers;[19] the photophysical properties of the assemblies were studies in detail.

In a related study, two zinc porphyrin units (ZnTPP) were added to a dipyridyl-substituted {Mn^{III}(salen)} complex that allowed formation of a 2:1 supramolecular assembly through coordination bonds.[20] Interestingly, the supramolecular complex showed a threefold increase in catalyst activity in the ARO of styrene and dimethylchromene, and also a significant increase in catalyst lifetime resulting from the steric protection of the Mn^{III} metal center. Likewise, this {Mn^{III}(salen)} unit was incorporated into metal–organic frameworks (MOFs)[21] and this resulted in an increase in turnover number of nearly four times, with only slightly lower observed enantioselectivities. It may be possible to expanded this work by the use of carboxylic acid functionalized {Mn^{III}(salen)} ligands.[22] In this case, the pyridyl–metal motif will then be replaced by a metal–acid interaction.

Scheme 3. Platinum-mediated assembly of pyridyl-modified salens. When the ligands are not sufficiently rigid, the loop-structure (a) is obtained. In other cases, the box-structure (b) is preferred. The numbers in parentheses indicate which of the building blocks have been used in the various assemblies

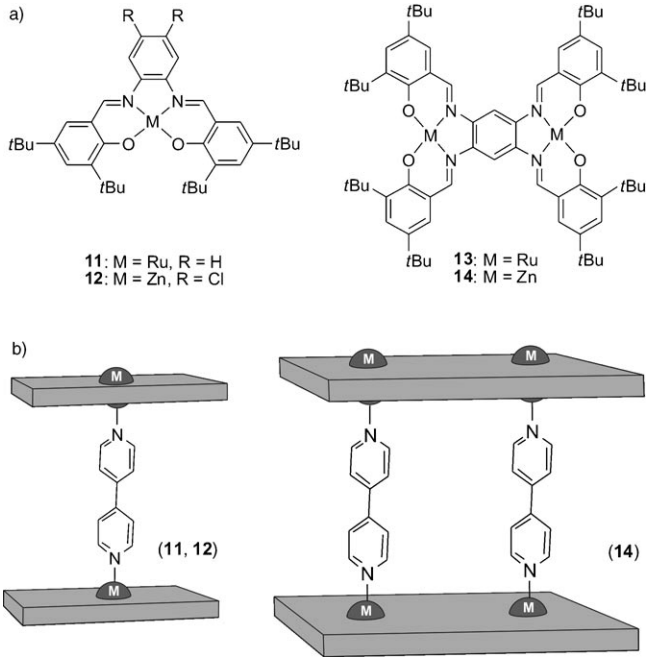
3. Design of Functional Materials

The catalytic behavior of metallosalens has been widely explored. On the other hand, there are only a few reports of its use as a modular building block in the design of new materials. This function can be realized through the use of weak coordination interactions or through covalent linkages to other macromolecules. Both approaches will be discussed below.

3.1. Salen–Pyridine-Based Assemblies

Like porphyrins, certain metallosalens may have vacant axial coordination sites that allow the binding of suitable donor ligands, such as THF or pyridine.[23] Although this interaction has been well exploited in the construction of porphyrin-based architectures,[24] relatively few reports have appeared describing analogous supramolecular assemblies utilizing metallosalens.

The earliest study reported describes the use of a ditopic 4,4′-bipyridine ligand that is able to coordinate to two {Co^{III}Me(salen)} complexes to afford ligand-bridged binuclear chelates.[25] More recently, Branda and co-workers achieved similar results using the {Ru^{II}(salphen)} (salphen = N,N′-bis(salicylidene)-1,2-phenylendiamine) building block **11** (Scheme 4a).[26] In addition, the preparation of diruthenium complex **13** was reported, in which a double axial pyridine coordination was found to take place at each metal center, in both a *cis*- and *trans*-fashion.



Scheme 4. a) Mono- (left) and bis(salphen) (right) building blocks, b) assemblies formed upon addition of 4,4′-bipyridine.

Recently, Kleij and Reek explored the axial coordination of pyridine to {Zn^{II}(salphens)} as a binding motif. For example, a non-symmetric {Zn^{II}(salphen)} complex was found to assemble cooperatively with 1,4-diazabicyclo[2.2.2]octane (dabco) into a 2:1 adduct.[27] This cooperativity may be induced by π interactions,[28] which are also present in the dimeric species which is formed in the absence of suitable donor molecules. Moreover, various bipyridine-bridged assemblies were prepared using the zinc complexes **12** and **14** (Scheme 4a). These assemblies were studied in solution as well as in the solid state.[29] Addition of 4,4′-bipyridine to **12** gave smooth access to a 2:1 assembly with strong pyridine binding at the zinc center (K_{ass} typically 10^5–10^6). Addition to **14** resulted in the formation of a stable 2:2 assembly (Scheme 4b); the aggregate can be regarded as an open box-like structure. The use of extended bipyridine ligands allowed the formation of box structures with even larger dimensions. Most interestingly, the X-ray studies revealed that the individual boxes line up in the solid state leading to a porous material with open channels that may be useful in applications such as storage and molecular separation.

Using a similar axial-pyridine coordination motif, the same authors also prepared a new class of encapsulated catalysts.[30] Assemblies of different pyridyl phosphane templates and {Zn^{II}(salphen)} complexes enforced phosphine encapsulation. These assemblies were applied as ligands in the rhodium-catalyzed hydroformylation of 1-octene. This "Reek"-approach[31] furnished catalyst systems with unprecedented behavior, with selectivities and reactivities exceeding those reported for the non-encapsulated analogues.

3.2. Heterometallic Inorganic Assemblies

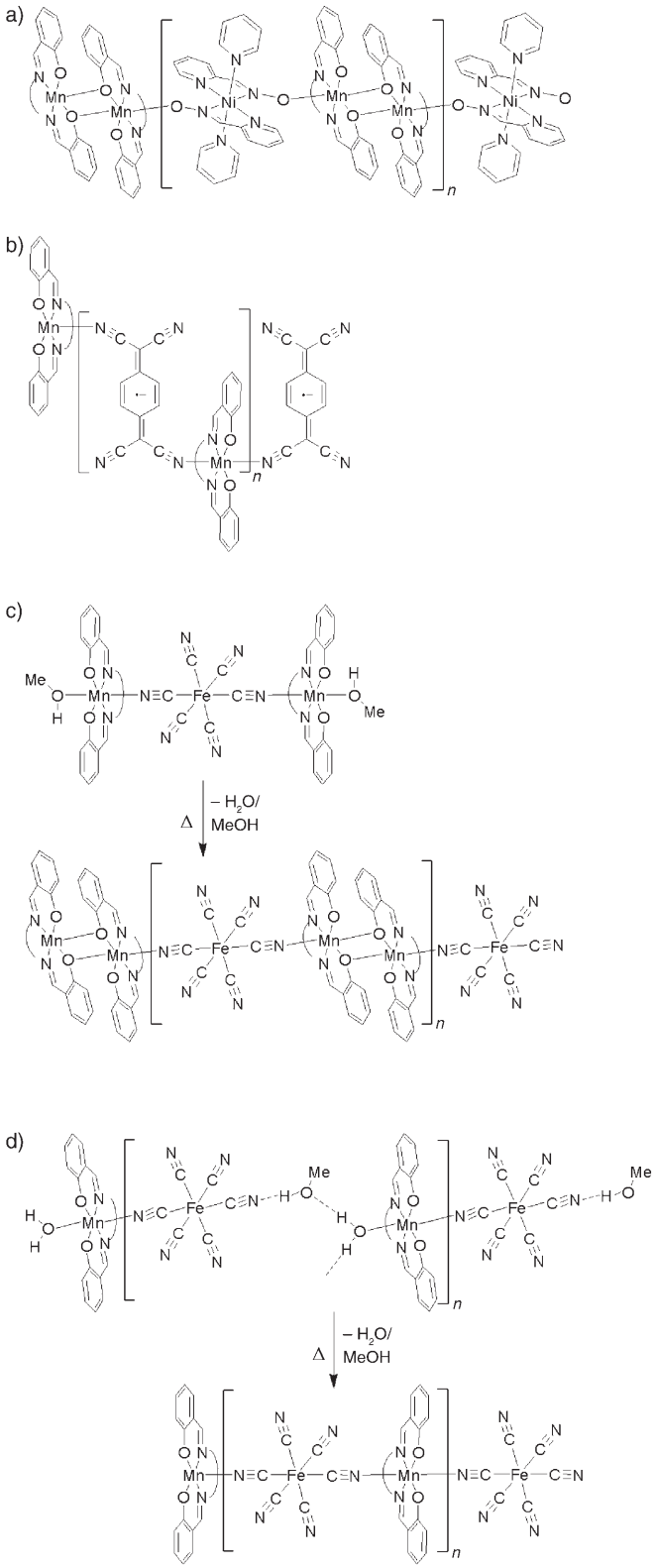
The vacant axial coordination site of metallosalens can be used to link with inorganic fragments as well. This situation gives an opportunity to prepare multimetallic complexes, which are very attractive for the development of new magnetic materials.[32] Overall, most inorganic salen-based systems are assembled by a metal–oxygen interaction, or more commonly by a metal–cyanide interaction. In this Section we will discuss the most essential[33] linear and higher order assemblies that are based on both these interactions.

Using the metal–oxygen interaction approach, Yamashita and Coulon obtained a heterometallic system of {Mn^{III}(salen)} and Ni^{II} ions,[34] in which {Mn^{III}(salen)} dimers[35] are linked by a nickel complex to form an alternating one-dimensional chain (Scheme 5a).

Similar work was carried out with various nickel complexes containing pendant ligands and all these heteromultimetallic complexes were found to exhibit unique magnetic properties.[36]

Matsumoto and Floriani also reported networks based on {Mn^{III}(salen)} units linked to [$Fe(CN)_6$] by cyano-bridges.[37] Depending on the nature of the salen ligand and the solvent, combination of both these building blocks gave rise to either one-, two-, or three-dimensional structures. In simple linear di-, tri-, or pentanuclear species, network formation is normally prevented by apical solvent molecules, such as water or methanol, which can be regarded as "stoppers". Higher order structures that include additional hydrogen-bonding motifs can also be observed, however the removal of the solvent molecules at elevated temperatures proved to be a better method towards preparation of the desired heterometallic assemblies. (Scheme 5c–d).[37d–e,38] This procedure furnishes systems in which magnetic communication proceeds through the metal ions. In a related approach, a tetradentate cyanide ligand 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) was employed to prepare a new one-dimensional magnetic material (Scheme 5b).[39]

Kim et al. reported the preparation of cyano rhenium clusters, which were linked to a {Mn^{III}(salen)} unit. When a



Scheme 5. Heterometallic alternating chains of a) a $\{Mn^{III}(salen)\}$ with Ni^{II}-ions and b) a $\{Mn^{III}(salen)\}$ with TCNQ. Solvent removal of the solvent-capped trinuclear species (c) and hydrogen-bridged network (d) leads to the alternating chains of $\{Mn^{III}(salen)\}$ and $\{Fe(CN)_6\}$ shown at the bottom.

$\{Re_6Te_8\}$ core unit is used,[40] a two-dimensional structure can be obtained, in which four of the cyano groups are bridged by a $\{Mn^{III}(salen)\}$ and the two remaining cyano groups are linked to terminal $\{Mn^{III}(salen)\}$ units. The use of a $\{Re_6Se_8\}$ core unit led to formation of a three-dimensional arrangement in which all the cyano groups are bridged by $[\{Mn^{III}(salen)\}]$.[41] When both $\{Re_6Te_8\}$ and $\{Re_6Se_8\}$ core structures were mixed, both two and three-dimensional networks were obtained.

The combination of octahedral niobium cyano chloride clusters $[(Nb_6Cl_{12})(CN)_6]^{4-}$ and $\{Mn^{III}(salen)\}^+$ building blocks was investigated by Lachgar and co-workers.[42] Depending on the tetraalkyl ammonium counter ions used in this preparation, they observed two kinds of networks: Me_4N^+ led to formation of a layered material with four $\{Mn^{III}(salen)\}^+$ units linked to each niobium cluster; Et_4N^+ led to the formation of a one-dimensional arrangement, with each niobium cluster connected by two cyanide ligands.

More recently, a trimetallic species, that also incorporates $\{Fe(CN)_6\}^{4-}$ units, was described.[43] In this architecture, $\{Mn^{III}(salen)\}^+$ units link with the iron and niobium clusters in Fe–C≡N–Mn–N≡C–Nb arrangements to form a three-dimensional framework (Figure 2). Sato et al.[44] prepared a cyanide species $[Fe^{III}(bpmb)(CN)_2]^-$ (H_2bpmb = 1,2-bis(pyridine-2-carboxamido)-4-methylbenzene) that organizes with $Mn^{III}(salen)^+$ into a unique nanosize, dodecanuclear molecular wheel. Interestingly, the use of the related $[Fe^{III}(bpb)(CN)_2]^-$ (H_2bpb = 1,2-bis(pyridine-2-carboxamido)benzene) building block led to an alternating chain structure.

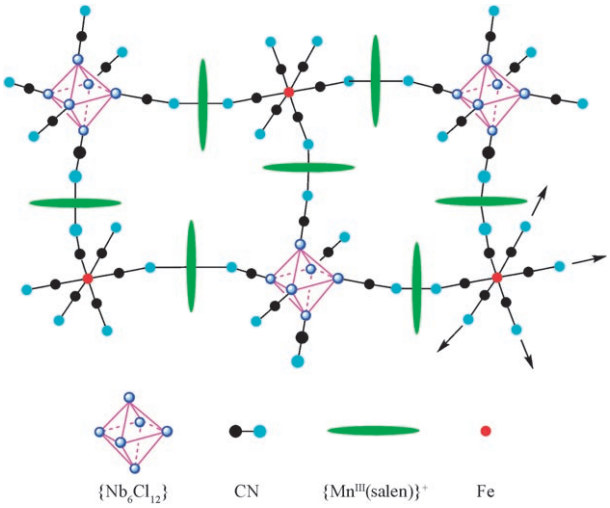


Figure 2. Partial cross-section of the 3D trimetallic structure based on Fe–C≡N–Mn–N≡C–Nb arrangements, showing the linking of $\{Fe(CN)_6\}^{4-}$ and $\{(Nb_6Cl_{12})(CN)_6\}^{4-}$ units through $\{Mn^{III}(salen)\}^+$ units.

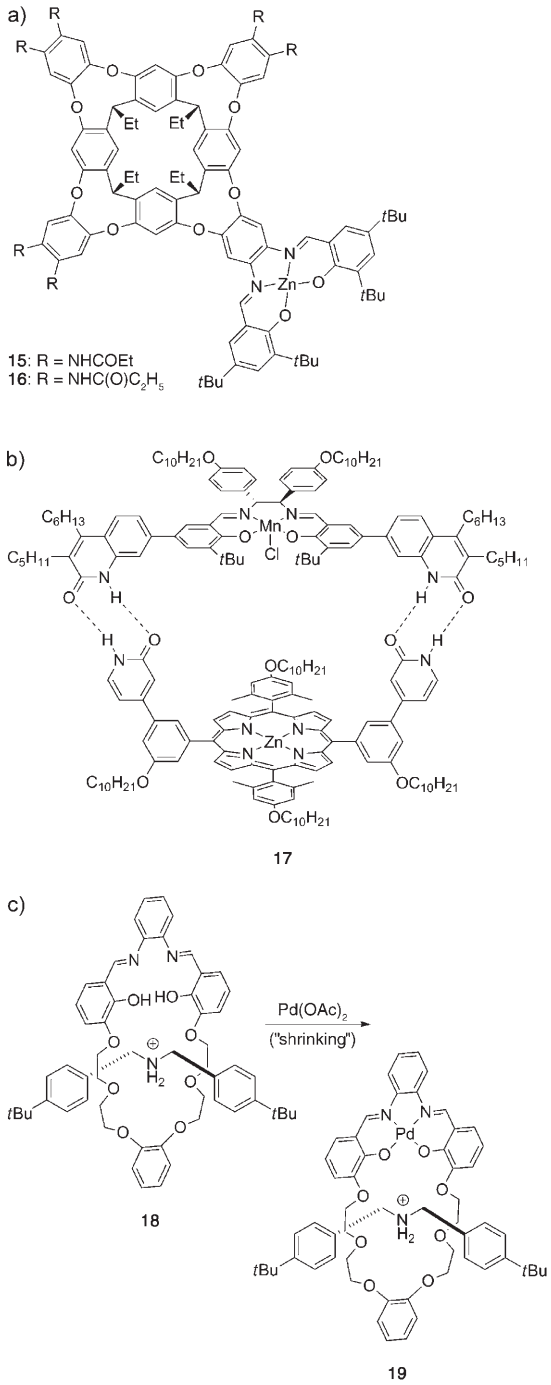
3.3. Host–Guest Complexes

In enzymatic systems, protein units have a high affinity for specific substrates, a process that is referred to as "molecular recognition". Through the years, supramolecular chemists have tried to imitate this process with a variety of cavitand-

like systems based on calix[*n*]arenes,[45] rotaxanes,[46] and others.[47] Rebek et al. described a {Zn^{II}(salen)}-functionalized resorcin-[4]-arene cavitand (Scheme 6a).[48] The zinc(II)-center located in the cavity interior of **15** was shown to accelerate the hydrolysis of choline derivatives and similar results were obtained with **16** in the esterification of choline using anhydrides. Furthermore, it was shown that the cavitand can mimic protein recognition sites in that it can act as a receptor for phosphocholine esters.[49]

A cyclic epoxidation catalyst, that self-assembled through hydrogen bonding between a {Mn^{III}(salen)} catalyst and a {Zn^{II}(porphyrin)} receptor (Scheme 6b), was presented by Wärnmark and co-workers.[50] Its catalytic binding pocket was shown to have different selectivities for several *cis*-β-substituted styrene derivatives that were attached to phenyl or pyridyl groups. Though the higher selectivity found for pyridine-tagged substrates was of a modest nature, it was sufficient to demonstrate the concept. Presumably, the main factor that governs the selectivity for these hydrogen-bonded, macrocyclic catalysts is the strength of the pyridine–zinc interaction.[24,29]

Yoon et al. reported the synthesis of a macrocycle prepared from a {Pd^{II}(salen)}, that was covalently connected to a crown ether.[51] This macrocycle can form dimers when the crown ether moiety complexes sodium. Though, more importantly, it can be used to construct [2]rotaxanes (Scheme 6c). This process involves the threading of a secondary dialkyl ammonium salt and subsequent shrinking of the free space within the macrocycle upon coordination of its salphen moiety to a palladium center (threading-followed-by-shrinking method).[52] If even bulkier triphenylphosphonium stopper groups are desired to prevent unthreading, these can only be introduced before the full salen moiety is formed.[53] Recently, Dalla Cort et al. described a related pseudorotaxane based on a {Zn^{II}(salphen)}/crown ether macrocycle,[54] in which, by changing in pH value, the dialkylammonium thread can bind to either the crown ether or the zinc metal center.

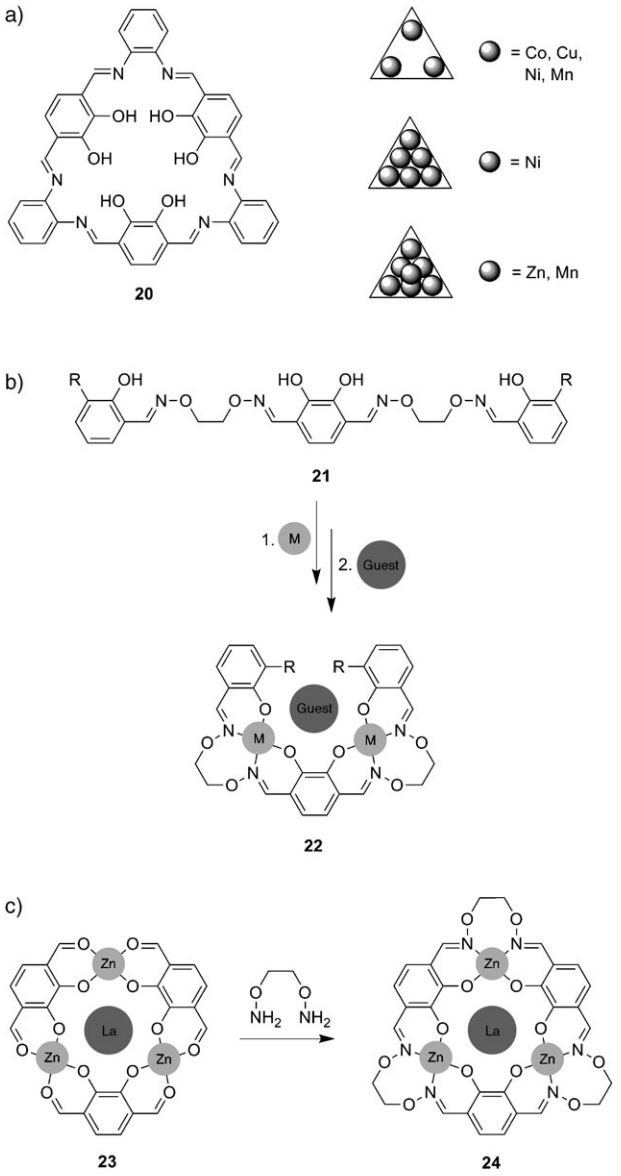


Scheme 6. a) {Zn^{II}(salen)}-modified monofunctionalized resorcin-[4]-arene cavitand. b) Macrocyclic epoxidation catalyst self-assembled through hydrogen bonding. c) A rotaxane based on a salen–crown ether hybrid, threaded by a dialkyl ammonium salt. The cavity is able to "shrink" upon addition of a palladium salt.

3.4. Multimetallic and Multinuclear Macrocycles

Macrocycles bearing a salen analogue offer a unique and cooperative binding site for guests, such as metal ions. When several different metal centers are incorporated, these multimetallic complexes can exhibit various functions and properties, such as catalytic activity, magnetism, and axial coordination sites that are useful for assembly formation.

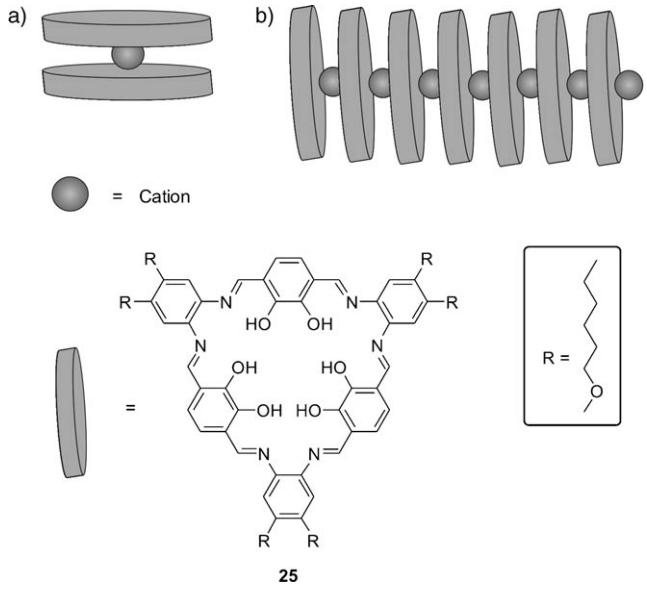
While previous syntheses of cyclic bis- and trissalen ligands was always template dependent,[55] Nabeshima and co-workers reported the first preparation of macrocyclic trissalphens without the use of a template.[56] These tris(H_2salphen) macrocycles have a central cavity that provides three metal binding sites (Scheme 7a). Addition of copper or cobalt cations to **20** exclusively led to trinuclear compounds, whereas manganese, nickel or zinc cation addition led to various multinuclear species.[57] Nabeshima et al. recently introduced *O*-alkyloxime salen analogues.[58] A bis-salen ligand based on these oximes, was shown to form C-shaped semi-macrocycles upon addition of metal ions (Scheme 7b).[59] The resulting cavity is able to function as a host for the recognition of large cations. Subsequently, the same metal-ion interactions were used to act as a template in the synthesis of a novel hexaoxime [3+3] macrocycle (Scheme 7c, **24**).[60] In this case, first a central tetranuclear {Zn_3La} core unit is introduced which can be completely and



Scheme 7. a) Macrocycle containing three salen moieties with the binding sites inside the cavity. b) formation of C-shaped semi-macrocycle through the addition of metal ions; M = Zn. c) $\{Zn_3La\}$-template-directed hexa-oxime synthesis.

quantitatively converted into the desired macrocyclic structure upon diamine addition.

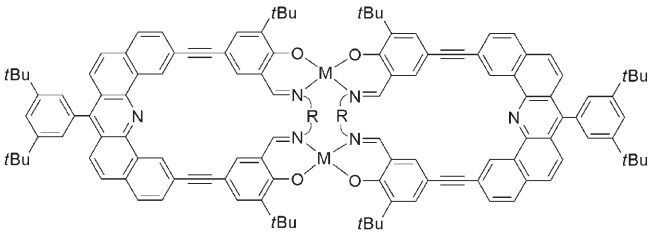
MacLachlan et al.[61] prepared related compounds with better solubility than to **20** and used small cations to assemble these macrocycles into higher order structures (Scheme 8). At low cation/macrocycle ratios dimers were formed, while at higher ratios tubular structures were obtained. These results indicate that these kinds of macrocycles show great similarity to crown-ethers. To increase the size of the central cavity, larger conjugated macrocycles were prepared.[62] These can react with transition-metal salts to form trinuclear macrocycles that show very strong tendency to aggregation in solution. This behavior appears to be facilitated by Zn–O coordinative interactions between the macrocycles. Very recently, MacLachlan and Hui reported the synthesis of



Scheme 8. Dimeric (a) and tubular (b) structures, which are formed by the macrocycles upon addition of cations.

[6+6] salen-based macrocycles,[63] which could be valuable new building blocks for aggregation studies.

A rather different type of macrocyclic salen ligand was prepared by Ko et al.[64] This structure resulted from a metal-directed assembly of two identical conjugated salen building blocks (Figure 3). In addition, various macrocyclic ligands that resemble salen-based ones, but which, upon coordination, typically share their oxygen ligands with different cations, have been reported.[65] All these structures have a high potential for use in the preparation of new supramolecular salen-like frameworks but are not discussed further herein.



26: M = Co, R = cyclohexyl
27: M = Zn, R = cyclohexyl

Figure 3. A salen-based macrocycle that is formed by metal-directed self-assembly of two identical building blocks.

4. DNA–Salen Hybrids

In organic reactions, DNA templates can be used to position molecules and thus to design and control reactions.[66] Metallosalen–DNA conjugates offer a new approach to metal–DNA hybrids. Furthermore, the incorporation of metal ions into DNA is particularly interesting in view of new catalytic and electronic properties, making use of the unique micro-environment provided by this biosystem.

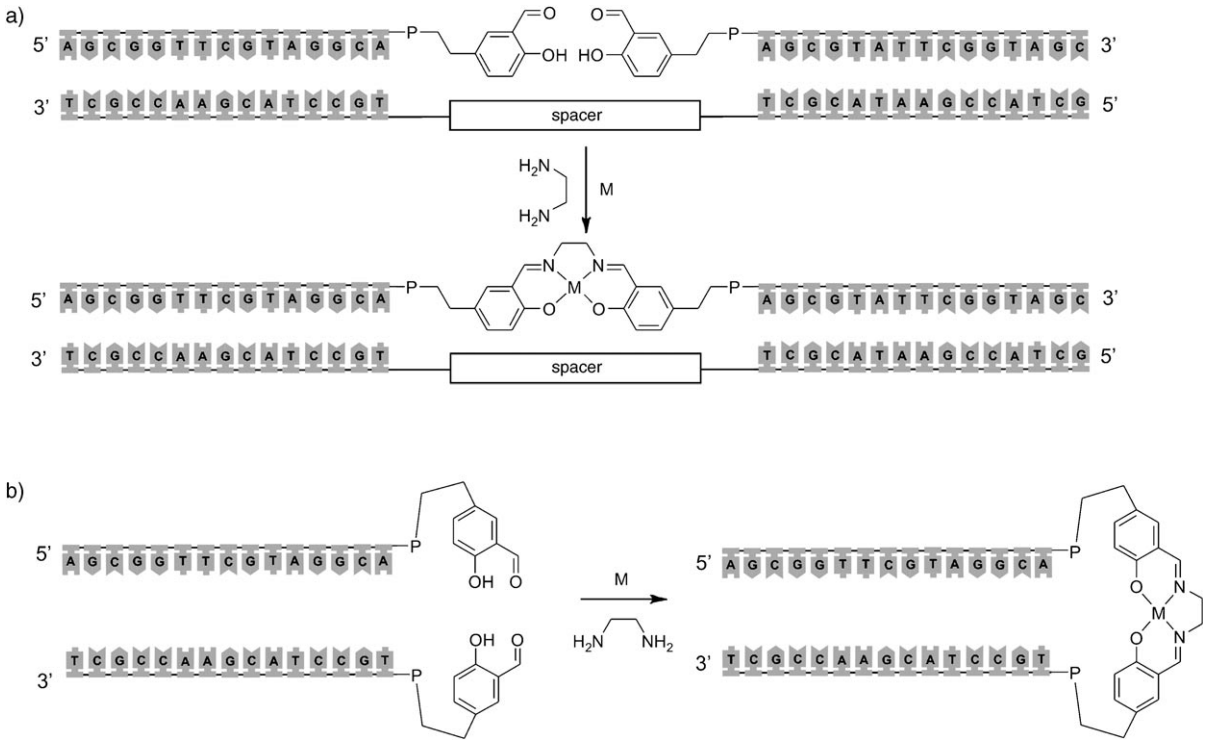
The DNA-templated synthesis of metallosalens was first carried out by Czlapinski and Sheppard (Scheme 9a).[67] In their approach they used two DNA oligonucleotides modified with salicylaldehyde moieties at either the 3′- or 5′-end. These were aligned on a complementary nucleic acid template and after an annealing step and subsequent incubation in the presence of ethylenediamine and either $Mn(OAc)_2$ or $Ni(OAc)_2$, a new DNA duplex was formed. The necessity of the complementary nucleic acid template is not warranted since the use of two complementary DNA oligonucleotides modified with a salicylaldehyde moiety at either the 3′or 5′ end (Scheme 9b) also leads to a salen-bridged biomolecule.[68] In this case, the strands align by complementary base pairing and after a similar incubation procedure, a salen–DNA conjugate is obtained that adopts a hairpin-loop motif. In contrast to the template-directed synthesis, the hairpin formation is also possible in the absence of metal ions and hence suggests that hairpin formation is more efficient.

Salen-type complexes are well-suited for DNA modification.[69] {Ni(salens)} are unique in this respect; after their combination with DNA, cleavage is highly preferred at guanidine residues, this is probably caused by the formation of {Ni(salen)}–guanidine adducts. The cleavage only occurs after treatment with piperidine. The {Ni(salen)}–DNA conjugate of Czlapinski and Sheppard was treated in a similar fashion to cleave a complementary oligonucleotide at specific guanidine sites.[70] By modifying the {Ni(salen)} moiety with, for instance, biotin,[71] its remarkable specific binding to guanidine residues can be used to introduce functional groups into the DNA strands.

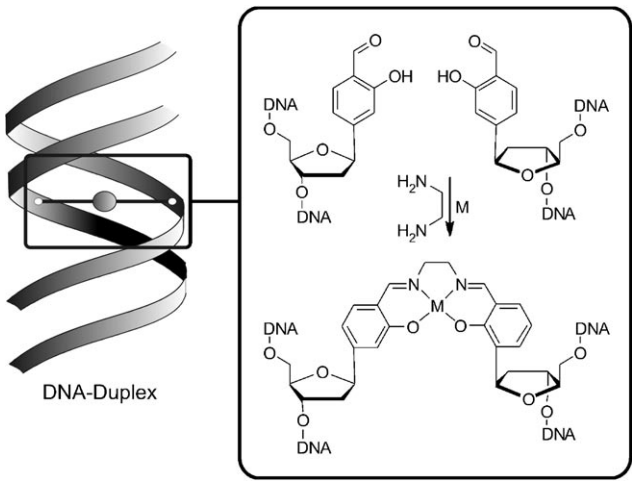
Gothelf and colleagues used an identical hairpin-loop template-directed synthesis to prepare linear and trimeric branched conjugated molecules.[72] In this case, the salicylaldehyde moieties are functionalized with 15 nucleotides that are located at the termini of linear and tripoidal conjugated modules. After annealing and incubation with $Mn(OAc)_2$ and ethylenediamine, the salicylaldehyde groups are brought close enough to form a {Mn(salen)} unit. In this way, different assemblies could be constructed. Subsequently, they reported the use of cleavable disulfide DNA-linkers to remove the oligonucleotides after formation of the salen moiety.[73] However, for this purpose aluminum was used instead of manganese as the metal ion, because the manganese ion is unstable in the presence of reducing agents.

Clever, Carell, and co-workers developed salen–DNA hybrids with the metallosalen motif located between two nucleic acid strands (Scheme 10).[74] They connected the salicylaldehyde at the C4-atom to the C1′-atom of 2′-deoxyribose. Two of these moieties facing each other in the DNA duplex may react in the presence of a suitable metal ion and ethylenediamine to form a metallosalen. Titration of a solution including divalent metal ions into an ethylenediamine-containing DNA solution showed a large increase in DNA-duplex stability, caused by the induced cross-linking. A variety of metal ions were tested and the highest stabilization was found for copper, for which the addition of one equivalent was sufficient even in the absence of ethylenediamine.

Even more recently, this high metal-induced stability was applied in a template-directed DNA-duplex formation, in which the double helix is stabilized by the metallosalen moiety instead of hydrogen bonding between base pairs. Two complementary single strands, each containing multiple salicylaldehyde moieties, have been shown to hybridize into



Scheme 9. DNA-templated synthesis of metallosalens by use of a spacer (a) and without a spacer which results in the formation of DNA loops (b). P = phosphate, M = Ni, Zn.



Scheme 10. A DNA–metallosalen hybrid: the salen moiety is formed between two complementary DNA strands; M = Cu, Mn, Zn, Ni.

a double helix upon addition of an appropriate metal salt (e.g., Cu^{2+} and Mn^{2+}),[75] the salen structure is formed subsequently on ethylenediamine addition. In this fashion, up to ten metal ions could be stacked inside the DNA duplex, the length of the structure corresponds to a full helical turn. Alternatively, the salicylaldehyde moieties can be accompanied by neighboring thymine base pairs, which are able to complex Hg^{2+} ions. Using this approach, an interesting heterodecanuclear DNA-based complex with five Cu^{2+} and five Hg^{2+} ions was prepared.[76]

5. Conclusion and Outlook

It is evident that salen frameworks are receiving growing interest in material applications.[77] To date, they have been used as building blocks in the creation of sophisticated homogeneous, multimetal catalysts and have been shown to be very valuable motifs in the design of novel (bio-inspired) materials. In general, these materials are constructed by noncovalent assembly or by using covalent linkages to other macromolecules, such as DNA and cavitand-based macrocycles. Because of the accessibility and ease of derivitization, salen frameworks have great potential as synthons for wider use in supramolecular chemistry and nanotechnology. Future research directions will almost certainly focus on a more detailed investigation into the specific structure–reactivity/function relationships of the known and also of new salen materials. One vital parameter that needs to be addressed is the multidisciplinary nature of the chemistry involved once salen motifs are combined with other types of building blocks, such as biomolecules and inorganic materials. Such new combinations may lead to assembled materials with unprecedented properties and/or improved functionality which have an impact beyond their conventional fields of application. We therefore believe that the unique salen framework will play an important role as a relatively cheap and accessible molecular building block in the decades to come.

This work was supported by ICREA and ICIQ. A.W.K. thanks both ICREA and ICIQ for financial support. S.J.W. thanks the ICIQ for a pre-doctoral fellowship.

Received: June 6, 2007
Published online: February 27, 2008

[1] For reviews see: a) E. N. Jacobsen in *Comprehensive Organometallic Chemistry II*, *Vol. 12* (Hrsg.: E. W. Abel, F. G. A. Stone, E. Willinson), Pergamon, New York, **1995**, S. 1097–1135; b) T. Katsuki, *Coord. Chem. Rev.* **1995**, *140*, 189–214; c) L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, *28*, 85–93; d) E. N. Jacobsen, *Acc. Chem. Res.* **2000**, *33*, 421–431; e) D. A. Atwood, M. J. Harvey, *Chem. Rev.* **2001**, *101*, 37–52; f) T. Katsuki, *Synlett* **2003**, 281–297; g) P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410–421; h) T. Katsuki, *Chem. Soc. Rev.* **2004**, *33*, 437–444; i) J. F. Farlow, E. N. Jacobsen, *Top. Organomet. Chem.* **2004**, *7*, 123–152; j) E. M. McGarrigle, D. G. Gilheany, *Chem. Rev.* **2005**, *105*, 1563–1602.

[2] a) J.-C. Chambron, V. Heitz, J.-P. Sauvage in *The Porphyrin Handbook*, *Vol. 6* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, pp. 1–43; b) J.-H. Chou, H. Singh-Nalwa, M. E. Kosal, N. A. Rakow, K. S. Suslick, *The Porphyrin Handbook*, *Vol. 6* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, pp. 43–133; c) H. Ogoshi, T. Mizutani, T. Hayashi, Y. Kuroda, *The Porphyrin Handbook*, *Vol. 6* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, pp. 279–341, and references therein.

[3] For examples, see: a) J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C. M. Zepp, *J. Org. Chem.* **1994**, *59*, 1939–1942; b) T. V. Hansen, L. Skattebøl, *Tetrahedron Lett.* **2005**, *46*, 3829–3830; c) A. W. Kleij, D. M. Tooke, A. L. Spek, J. N. H. Reek, *Eur. J. Inorg. Chem.* **2005**, 4626–4634; d) M. Holbach, X. Zheng, C. Burd, C. W. Jones, M. Weck, *J. Org. Chem.* **2006**, *71*, 2903–2906.

[4] Among others see: a) S. B. Ogunwumi, T. Bein, *Chem. Commun.* **1997**, 901–902; b) M. J. Sabater, A. Corma, A. Domenech, V. Fornés, H. García, *Chem. Commun.* **1997**, 1285–1286; c) J. Wöltinger, J.-E. Bäckvall, A. Zsigmond, *Chem. Eur. J.* **1999**, *5*, 1460–1467; d) C. Jin, W. Fan, Y. Jia, B. Fan, J. Ma, R. Li, *J. Mol. Catal. A* **2006**, *249*, 23–30; e) M. Silva, C. Freire, B. de Castro, J. L. Figueirido, *J. Mol. Catal. A* **2006**, *258*, 327–333; f) P. K. Saha, B. Dutta, S. Jana, R. Bera, S. Saha, K.-I. Okamoto, S. Koner, *Polyhedron* **2007**, *26*, 563–571.

[5] Among others see: a) S. S. Sundari, A. Dhathathreyan, M. Kanthimathi, B. U. Nair, *Langmuir* **1997**, *13*, 4923–4925; b) H. Abe, K. Miyamura, *Inorg. Chim. Acta* **2000**, *298*, 90–93; c) M. Nielsen, N. B. Larsen, K. V. Gothelf, *Langmuir* **2002**, *18*, 2795–2799; d) A. Pasc-Banu, C. Sugisaki, T. Gharsa, J.-D. Marty, I. Gascon, G. Pozzi, S. Quici, I. Rico-Lattes, C. Mingotaud, *Angew. Chem.* **2004**, *116*, 6300–6303; *Angew. Chem. Int. Ed.* **2004**, *43*, 6174–6177; e) A. Pasc-Banu, C. Sugisaki, T. Gharsa, J.-D. Marty, I. Gascon, M. Krämer, G. Pozzi, B. Desbat, S. Quici, I. Rico-Lattes, C. Mingotaud, *Chem. Eur. J.* **2005**, *11*, 6032–6039.

[6] For reviews and recent examples see: a) N. Leadbeater, M. Marco, *Chem. Rev.* **2002**, *102*, 3217–3274; b) A. Heckel, D. Seebach, *Helv. Chim. Acta* **2002**, *85*, 913–926; c) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.-I. Noro, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 2738–2741; *Angew. Chem. Int. Ed.* **2004**, *43*, 2684–2687; d) C. Baleizão, H. Garcia, *Chem. Rev.* **2006**, *106*, 3987–4043; e) X. Zheng, C. W. Jones, M. Weck, *Chem. Eur. J.* **2006**, *12*, 576–583; f) X. Zheng, C. W. Jones, M. Weck, *J. Am. Chem. Soc.* **2007**, *129*, 1105–1112.

[7] a) N. Sträter, W. N. Lipscomb, T. Klabunde, B. Krebs, *Angew. Chem.* **1996**, *108*, 2158–2191; *Angew. Chem. Int. Ed. Engl.* **1996**,

35, 2024 – 2055; b) H. Steinhagen, G. Helmchen, *Angew. Chem.* **1996**, *108*, 2489 – 2492; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2339 – 2342.

[8] For general reviews on cooperative catalysis see: a) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290 – 1311; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1236 – 1256; b) M. Shibasaki, M. Kanai, K. Funabashi, *Chem. Commun.* **2002**, 1989 – 1999; c) M. Shibasaki, N. Yoshikawa, *Chem. Rev.* **2002**, *102*, 2187 – 2209; d) M. Shibasaki, S. Matsunaga, *Chem. Soc. Rev.* **2006**, *35*, 269 – 279.

[9] a) K. B. Hansen, J. L. Leighton, E. N. Jacobsen, *J. Am. Chem. Soc.* **1996**, *118*, 10924 – 10925; b) M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *277*, 936 – 938; c) G. M. Sammis, H. Danjo, E. N. Jacobsen, *J. Am. Chem. Soc.* **2004**, *126*, 9928 – 9929.

[10] R. G. Konsler, J. Karl, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 10780 – 10781.

[11] a) J. M. Ready, E. N. Jacobsen, *J. Am. Chem. Soc.* **2001**, *123*, 2687 – 2688; b) J. M. Ready, E. N. Jacobsen, *Angew. Chem.* **2002**, *114*, 1432 – 1435; *Angew. Chem. Int. Ed.* **2002**, *41*, 1374 – 1377.

[12] R. Breinbauer, E. N. Jacobsen, *Angew. Chem.* **2000**, *112*, 3750 – 3753; *Angew. Chem. Int. Ed.* **2000**, *39*, 3604 – 3607.

[13] B. M. Rossbach, K. Leopold, R. Weberskirch, *Angew. Chem.* **2006**, *118*, 1331 – 1335; *Angew. Chem. Int. Ed.* **2006**, *45*, 1309 – 1312.

[14] N. C. Gianneschi, P. A. Bertin, S. T. Nguyen, C. A. Mirkin, L. N. Zakharov, A. L. Rheingold, *J. Am. Chem. Soc.* **2003**, *125*, 10508 – 10509.

[15] N. C. Gianneschi, S.-H. Cho, S. T. Nguyen, C. A. Mirkin, *Angew. Chem.* **2004**, *116*, 5619 – 5623; *Angew. Chem. Int. Ed.* **2004**, *43*, 5503 – 5507.

[16] N. C. Gianneschi, S. T. Nguyen, C. A. Mirkin, *J. Am. Chem. Soc.* **2005**, *127*, 1644 – 1645.

[17] A. M. Brown, M. V. Ovchinnikov, C. L. Stern, C. A. Mirkin, *Chem. Commun.* **2006**, 4386 – 4388.

[18] S.-S. Sun, C. L. Stern, S. T. Nguyen, J. T. Hupp, *J. Am. Chem. Soc.* **2004**, *126*, 6314 – 6326.

[19] K. E. Splan, A. M. Massari, G. A. Morris, S.-S. Sun, E. Reina, S. T. Nguyen, J. T. Hupp, *Eur. J. Inorg. Chem.* **2003**, 2348 – 2351.

[20] G. A. Morris, S. T. Nguyen, J. T. Hupp, *J. Mol. Catal. A* **2001**, *174*, 15 – 20.

[21] S. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563 – 2565.

[22] Y. Jeon, J. Heo, C. A. Mirkin, *Tetrahedron Lett.* **2007**, *48*, 2591 – 2595.

[23] a) A. L. Singer, D. A. Atwood, *Inorg. Chim. Acta* **1998**, *277*, 157 – 162; b) G. A. Morris, H. Zhou, C. L. Stern, S. T. Nguyen, *Inorg. Chem.* **2001**, *40*, 3222 – 3227.

[24] For reviews see: a) S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469 – 475; b) T. Imamura, K. Fukushima, *Coord. Chem. Rev.* **2000**, *198*, 133 – 156; c) L. Baldini, C. A. Hunter, *Adv. Inorg. Chem.* **2002**, *53*, 213 – 259.

[25] A. W. Herlinger, K. Ramakrishna, *Polyhedron* **1985**, *4*, 551 – 561.

[26] K. Chichak, U. Jacquemard, N. R. Branda, *Eur. J. Inorg. Chem.* **2002**, 357 – 368.

[27] A. W. Kleij, M. Kuil, M. Lutz, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Inorg. Chim. Acta* **2006**, *359*, 1807 – 1814.

[28] a) K. Miyamura, A. Mihara, T. Fujii, Y. Gohshi, Y. Ishii, *J. Am. Chem. Soc.* **1995**, *117*, 2377 – 2378; b) M. Kondo, K. Nabari, T. Horiba, Y. Irie, Md. K. Kabir, R. P. Sarker, E. Shimizu, Y. Shimizu, Y. Fuwa, *Inorg. Chem. Commun.* **2003**, *6*, 154 – 156; c) V. Madhu, S. K. Das, *Inorg. Chem. Commun.* **2005**, *8*, 1097 – 1100; d) X. Yang, R. A. Jones, *J. Am. Chem. Soc.* **2005**, *127*, 7686 – 7687.

[29] A. W. Kleij, M. Kuil, D. M. Tooke, M. Lutz, A. L. Spek, J. N. H. Reek, *Chem. Eur. J.* **2005**, *11*, 4743 – 4750.

[30] A. W. Kleij, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Commun.* **2005**, 3661 – 3663.

[31] a) V. F. Slagt, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem.* **2001**, *113*, 4401 – 4404; *Angew. Chem. Int. Ed.* **2001**, *40*, 4271 – 4274; b) V. F. Slagt, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2004**, *126*, 1526 – 1536; c) A. W. Kleij, M. Kuil, D. M. Tooke, A. L. Spek, J. N. H. Reek, *Inorg. Chem.* **2005**, *44*, 7696 – 7698; d) A. W. Kleij, J. N. H. Reek, *Chem. Eur. J.* **2006**, *12*, 4218 – 4227.

[32] For reviews on magnetic materials see: a) C. Coulon, H. Miyasaka, R. Clérac, *Struct. Bonding (Berlin)* **2006**, *122*, 163 – 206; b) H. Miyasaka, M. Yamashita, *Dalton Trans.* **2007**, 399 – 406.

[33] For recent related examples that are not discussed herein see: a) W.-F. Yeung, T.-C. Lau, H.-Y. Wei, H.-L. Sun, S. Gao, Z.-D. Chen, W.-T. Wong, *Inorg. Chem.* **2005**, *44*, 6579 – 6590; b) H. H. Ko, J. H. Lim, H. S. Yoo, J. S. Kang, H. C. Kim, E. K. Koh, C. S. Hong, *Dalton Trans.* **2007**, 2070 – 2076.

[34] R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* **2002**, *124*, 12837 – 12844.

[35] a) H. Miyasaka, R. Clérac, T. Ishii, H.-C. Chang, S. Kitagawa, M. Yamashita, *J. Chem. Soc. Dalton Trans.* **2002**, 1528 – 1534; b) H. Miyasaka, R. Clérac, W. Wernsdorfer, L. Lecren, C. Bonhomme, K.-I. Sugiura, M. Yamashita, *Angew. Chem.* **2004**, *116*, 2861 – 2865; *Angew. Chem. Int. Ed.* **2004**, *43*, 2801 – 2805.

[36] a) H. Miyasaka, R. Clérac, M. Mizushima, K. Suguira, M. Yamashita, W. Wernsdorfer, C. Coulon, *Inorg. Chem.* **2003**, *42*, 8203 – 8213; b) H. Miyasaka, K. Mizushima, K. Segiura, M. Yamashita, *Synth. Met.* **2003**, *137*, 1245 – 1246; c) H. Miyasaka, T. Nezu, K. Sugimoto, K. Sugiura, M. Yamashita, R. Clérac, *Chem. Eur. J.* **2005**, *11*, 1592 – 1602; d) A. Saitoh, H. Miyasaka, M. Yamashita, R. Clérac, *J. Mater. Chem.* **2007**, *17*, 2002 – 2012.

[37] a) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, *Angew. Chem.* **1995**, *107*, 1565 – 1568; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1446 – 1448; b) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, *J. Am. Chem. Soc.* **1996**, *118*, 981 – 994; c) N. Re, E. Gallo, C. Floriani, H. Miyasaka, N. Matsumoto, *Inorg. Chem.* **1996**, *35*, 5964 – 5965; d) H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, C. Floriani, *Inorg. Chem.* **1997**, *36*, 670 – 676; e) H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, R. Crescenzi, C. Floriani, *Inorg. Chem.* **1998**, *37*, 255 – 263; f) H. Miyasaka, H. Ieda, N. Matsumoto, K. Sugiura, M. Yamashita, *Inorg. Chem.* **2003**, *42*, 3509 – 3515.

[38] a) H. Miyasaka, H. Okawa, A. Miyazaki, T. Enoki, *J. Chem. Soc. Dalton Trans.* **1998**, 3991 – 3996; b) M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090 – 3099.

[39] H. Miyasaka, T. Madanbashi, K. Sugimoto, Y. Nakazawa, W. Wernsdorfer, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *Chem. Eur. J.* **2006**, *12*, 7028 – 7040.

[40] Y. Kim, S.-M. Park, W. Nam, S.-J. Kim, *Chem. Commun.* **2001**, 1470 – 1471.

[41] Y. Kim, S.-M. Park, S.-J. Kim, *Inorg. Chem. Commun.* **2002**, *5*, 592 – 595.

[42] H. Zhou, C. S. Day, A. Lachgar, *Chem. Mater.* **2004**, *16*, 4870 – 4877.

[43] J. Zhang, A. Lachgar, *J. Am. Chem. Soc.* **2007**, *129*, 250 – 251.

[44] Z.-H. Ni, H.-Z. Kou, L.-F. Zhang, C. Ge, A.-L. Cui, R.-J. Wang, Y. Li, O. Sato, *Angew. Chem.* **2005**, *117*, 7920 – 7923; *Angew. Chem. Int. Ed.* **2005**, *44*, 7742 – 7745.

[45] A. Casnati, D. Sciotto, G. Arena in *Calixarenes 2001* (Ed.: Z. Asfari), Kluwer Academic Publishers, Niederlande, **2001**, pp. 440 – 456.

[46] For rotaxane examples see: a) F. M. Raymo, J. F. Stoddart, *Chem. Rev.* **1999**, *99*, 1643 – 1663; b) P. Thordarson, E. J. A. Bijsterveld, A. E. Rowan, R. J. M. Nolte, *Nature* **2003**, *424*, 915 – 918; c) H. Tian, Q.-C. Wang, *Chem. Soc. Rev.* **2006**, *35*, 361 – 374.

[47] For other cavitand-based host–guest systems see: a) S. M. Biros, J. Rebek, Jr., *Chem. Soc. Rev.* **2007**, *36*, 93 – 104; b) M. D. Pluth, K. N. Raymond, *Chem. Soc. Rev.* **2007**, *36*, 161 – 171; c) P. Blondeau, M. Segura, R. Pérez-Fernández, J. de Mendoza, *Chem. Soc. Rev.* **2007**, *36*, 198 – 210.
[48] a) S. Richeter, J. Rebek, Jr., *J. Am. Chem. Soc.* **2004**, *126*, 16280 – 16281; b) F. H. Zelder, J. Rebek, Jr., *Chem. Commun.* **2006**, 753 – 754.
[49] F. H. Zelder, R. Salvio, J. Rebek, Jr., *Chem. Commun.* **2006**, 1280 – 1282.
[50] a) S. Jónsson, F. G. J. Odille, P.-O. Norrby, K. Wärnmark, *Chem. Commun.* **2005**, 549 – 551; b) S. Jónsson, F. G. J. Odille, P.-O. Norrby, K. Wärnmark, *Org. Biomol. Chem.* **2006**, *4*, 1927 – 1948.
[51] I. Yoon, M. Goto, T. Shimizu, S. S. Lee, M. Asakawa, *Dalton Trans.* **2004**, 1513 – 1515.
[52] I. Yoon, M. Narita, T. Shimizu, M. Asakawa, *J. Am. Chem. Soc.* **2004**, *126*, 16740 – 16741.
[53] I. Yoon, M. Narita, M. Goto, T. Shimizu, M. Asakawa, *Org. Lett.* **2006**, *8*, 2341 – 2344.
[54] A. Dalla Cort, L. Mandolini, C. Pasquini, L. Schiaffino, *Org. Biomol. Chem.* **2006**, *4*, 4543 – 4546.
[55] For early examples see: a) W. Moneta, P. Baret, J.-L. Pierre, *J. Chem. Soc. Chem. Commun.* **1985**, 899 – 901; b) F. C. J. M. van Veggel, M. Bos, S. Harkema, W. Verboom, D. N. Reinhoudt, *Angew. Chem.* **1989**, *101*, 800 – 802; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 746 – 748; c) F. C. J. M. van Veggel, M. Bos, S. Harkema, H. van de Bovenkamp, W. Verboom, J. Reedijk, D. N. Reinhoudt, *J. Org. Chem.* **1991**, *56*, 225 – 235; d) H. Houjou, S.-K. Lee, Y. Hishikawa, Y. Nagawa, K. Hiratani, *Chem. Commun.* **2000**, 2197 – 2198.
[56] a) S. Akine, T. Taniguchi, T. Nabeshima, *Tetrahedron Lett.* **2001**, *42*, 8861 – 8864; b) S. Akine, D. Hashimoto, T. Saiki, T. Nabeshima, *Tetrahedron Lett.* **2004**, *45*, 4225 – 4227.
[57] T. Nabeshima, H. Miyazaki, A. Iwasaki, S. Akine, T. Saiki, C. Ikeda, *Tetrahedron* **2007**, *63*, 3328 – 3333.
[58] a) S. Akine, T. Taniguchi, T. Nabeshima, *Chem. Lett.* **2001**, 682 – 683; b) S. Akine, T. Taniguchi, T. Nabeshima, *Inorg. Chem.* **2004**, *43*, 6142 – 6144; c) S. Akine, T. Taniguchi, W. Dong, S. Masubuchi, T. Nabeshima, *J. Org. Chem.* **2005**, *70*, 1704 – 1711; d) S. Akine, T. Nabeshima, *Inorg. Chem.* **2005**, *44*, 1205 – 1207; e) S. Akine, W. Dong, T. Nabeshima, *Inorg. Chem.* **2006**, *45*, 4677 – 4684.
[59] a) S. Akine, T. Taniguchi, T. Nabeshima, *Angew. Chem.* **2002**, *114*, 4864 – 4867; *Angew. Chem. Int. Ed.* **2002**, *41*, 4670 – 4673; b) S. Akine, T. Taniguchi, T. Saiki, T. Nabeshima, *J. Am. Chem. Soc.* **2005**, *127*, 540 – 541; c) S. Akine, T. Matsumoto, T. Taniguchi, T. Nabeshima, *Inorg. Chem.* **2005**, *44*, 3270 – 3274; d) S. Akine, T. Taniguchi, T. Nabeshima, *J. Am. Chem. Soc.* **2006**, *128*, 15765 – 15774.
[60] S. Akine, S. Sunaga, T. Taniguchi, H. Miyazaki, T. Nabeshima, *Inorg. Chem.* **2007**, *46*, 2959 – 2961.
[61] a) A. J. Gallant, M. J. MacLachlan, *Angew. Chem.* **2003**, *115*, 5465 – 5468; *Angew. Chem. Int. Ed.* **2003**, *42*, 5307 – 5310; b) A. J. Gallant, J. K. H. Hui, F. E. Zahariev, Y. Alexander-Wang, M. J. MacLachlan, *J. Org. Chem.* **2005**, *70*, 7936 – 7946; c) A. J. Gallant, J. H. Chong, M. J. MacLachlan, *Inorg. Chem.* **2006**, *45*, 5248 – 5250.
[62] a) C. Ma, A. Lo, A. Abdolmaleki, M. J. MacLachlan, *Org. Lett.* **2004**, *6*, 3841 – 3844; b) C. Ma, M. J. MacLachlan, *Angew. Chem.* **2005**, *117*, 4250 – 4254; *Angew. Chem. Int. Ed.* **2005**, *44*, 4178 – 4182.
[63] J. K.-H. Hui, M. J. MacLachlan, *Chem. Commun.* **2006**, 2480 – 2482.
[64] D. Kim, I. Jung, K. H. Song, S. O. Kang, J. Ko, *J. Organomet. Chem.* **2006**, *691*, 5946 – 5954.
[65] Beispiele: a) H. Okawa, H. Furutachi, D. E. Fenton, *Coord. Chem. Rev.* **1998**, *174*, 51 – 75; b) M. Yonemura, H. Okawa, M. Ohba, D. E. Fenton, L. K. Thompson, *Chem. Commun.* **2000**, 817 – 818; c) A. Hori, Y. Mitsuka, M. Ohba, H. Okawa, *Inorg. Chim. Acta* **2002**, *337*, 113 – 121; d) J. Gao, J. H. Reibenspies, R. A. Zingaro, F. R. Woolley, A. E. Martell, A. Clearfield, *Inorg. Chem.* **2005**, *44*, 232 – 241.
[66] For reviews see: a) D. Summerer, A. Marx, *Angew. Chem.* **2002**, *114*, 93 – 95; *Angew. Chem. Int. Ed.* **2002**, *41*, 89 – 90; b) X. Li, D. R. Liu, *Angew. Chem.* **2004**, *116*, 4956 – 4979; *Angew. Chem. Int. Ed.* **2004**, *43*, 4848 – 4870; c) K. V. Gothelf, R. S. Brown, *Chem. Eur. J.* **2005**, *11*, 1062 – 1069.
[67] J. L. Czlapinski, T. L. Sheppard, *J. Am. Chem. Soc.* **2001**, *123*, 8618 – 8619.
[68] J. L. Czlapinski, T. L. Sheppard, *ChemBioChem* **2004**, *5*, 127 – 129.
[69] For a review on salen–DNA cleavage see: J. G. Muller, L. A. Kayser, S. J. Paikoff, V. Duarte, N. Tang, R. J. Perez, S. E. Rokita, C. J. Burrows, *Coord. Chem. Rev.* **1999**, *185–186*, 761 – 774.
[70] J. L. Czlapinski, T. L. Sheppard, *Chem. Commun.* **2004**, 2468 – 2469.
[71] X. Zhou, J. Shearer, S. E. Rokita, *J. Am. Chem. Soc.* **2000**, *122*, 9046 – 9047.
[72] a) K. V. Gothelf, A. Thomsen, M. Nielsen, E. Cló, R. S. Brown, *J. Am. Chem. Soc.* **2004**, *126*, 1044 – 1046; b) M. Nielsen, A. H. Thomsen, E. Cló, F. Kirpekar, K. V. Gothelf, *J. Org. Chem.* **2004**, *69*, 2240 – 2250.
[73] R. S. Brown, M. Nielsen, K. V. Gothelf, *Chem. Commun.* **2004**, 1464 – 1465.
[74] a) G. H. Clever, K. Polborn, T. Carell, *Angew. Chem.* **2005**, *117*, 7370 – 7374; *Angew. Chem. Int. Ed.* **2005**, *44*, 7204 – 7208; b) G. H. Clever, Y. Söltl, H. Burks, W. Spahl, T. Carell, *Chem. Eur. J.* **2006**, *12*, 8708 – 8718.
[75] G. H. Clever, T. Carell, *Angew. Chem.* **2007**, *119*, 254 – 257; *Angew. Chem. Int. Ed.* **2007**, *46*, 250 – 253.
[76] K. Tanaka, G. H. Clever, Y. Takezawa, Y. Yamada, C. Kaul, M. Shionoya, T. Carell, *Nat. Nanotechnol.* **2006**, *1*, 190 – 194.
[77] During and after submission of this Minireview a number of interesting and relevant papers have appeared: a) J.-J. Zhang, H.-J. Zhou, A. Lachgar, *Angew. Chem.* **2007**, *119*, 5083 – 5086; *Angew. Chem. Int. Ed.* **2007**, *46*, 4995 – 4998; b) Y.-M. Jeon, J. Heo, C. A. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 7480 – 7481; c) A. W. Kleij, M. Kuil, D. M. Tooke, A. L. Spek, J. N. H. Reek, *Inorg. Chem.* **2007**, *46*, 5829 – 5831; d) Z.-H. Ni, L.-F. Zhang, V. Tangoulis, W. Wernsdorfer, A. L. Cui, O. Sato, H.-Z. Kou, *Inorg. Chem.* **2007**, *46*, 6029 – 6037.

