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Journal of Organometallic Chemistry 630 (2001) 67–77

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Diazadioxadecalin and salen podands and macrocycles within dynamic combinatorial virtual libraries: structure, prototropy, complexation and enantioselective catalysis

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Received 8 January 2001; received in revised form 20 March 2001; accepted 22 March 2001

Dedicated to Professor Myron Rosenblum on the occasion of his 75th birthday

Abstract

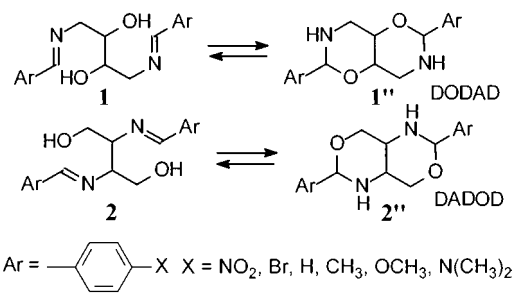
The reactions of L-1,4-diaminobutanediol (**3**) and D-2,3-diaminobutanediol (**4**) with salicyl aldehyde provide the tautomeric manifolds of L-1,4-bis(salicylideneamino)-2,3-butanediol (**5**) and D-2,3-bis(salicylideneamino)-1,4-butanediol (**6**), respectively. O-alkylation of the salicyl moiety stabilizes the closed dioxadiazadecalin (DODAD) and diazadioxadecalin (DADOD) isomers (**7**″, **8**″) and accordingly, the dialdehyde 1,2-bis(*o*-formylphenoxy)-ethane (**9**) led to the respective macrocyclic manifolds (**10**–**10**″ and **11**–**11**″). These tautomeric manifolds are typical target-driven *dynamic combinatorial virtual libraries*, which can be biased by complex formation with metal ions of different ionic radius. A rare instance of simultaneous occurrence of keto–enamine and phenol–imine tautomers in the solid state of **6** was unravelled (X-ray at two temperatures) and the strength of the intramolecular hydrogen bonding (and hence, the extent of ring closure) in **6** is temperature dependent. Compounds **6**, **11** and **12**–**14** constitute a new class of salens, which form heavy and transition metal complexes. Some such Mn(III) complexes are good chirality inducing catalysts, as found in asymmetric indene epoxidation reactions.

Keywords: Salens; Dioxadiazadecalins; Tautomerism; Combinatorial virtual libraries; Complexes; Enantioselective catalysis

1. Introduction

We have recently put forward the novel *cis*- and *trans*-1,5-dioxa-3,7-diazadecalin (DODAD) and -1,5-diaza-3,7-dioxadecalin (DADOD) systems (Scheme 1) [1], with various *para*-aryl substituents and their interesting tautomeric equilibrium with the respective Schiff bases (**1** ⇌ **1**″ and **2** ⇌ **2**″) [1c].

cis-DODAD (*cis*-**1**″) systems prevailed only with electron-withdrawing substituents, but *cis*-DADOD (*cis*-**2**″) systems were more stable than their parent Schiff bases in all cases. The ring–chain tautomeric process has been analyzed [1c] using the Hammett equation ($\log K = \rho\sigma^+ + \log K_0$, $K = [\text{ring}]/[\text{chain}]$ and σ^+ is the Hammett–Brown constant of the 2(6)-aryl substituents) and the slope ρ was 0.69, close to that found earlier in ring–chain tautomeric studies [2] of 1,3-oxazanes [2a].



Scheme 1. The 1,4-bis(arylideneamino)-2,3-butanediol (**1**)/dioxadiazadecalin (DODAD, **1**″) and 2,3-bis(arylideneamino)-1,4-butanediol (**2**)/diazadioxadecalin (DADOD, **2**″) equilibria.

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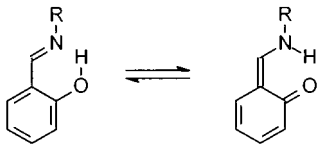


Scheme 2. Phenol–imine/keto–enamine tautomerism.

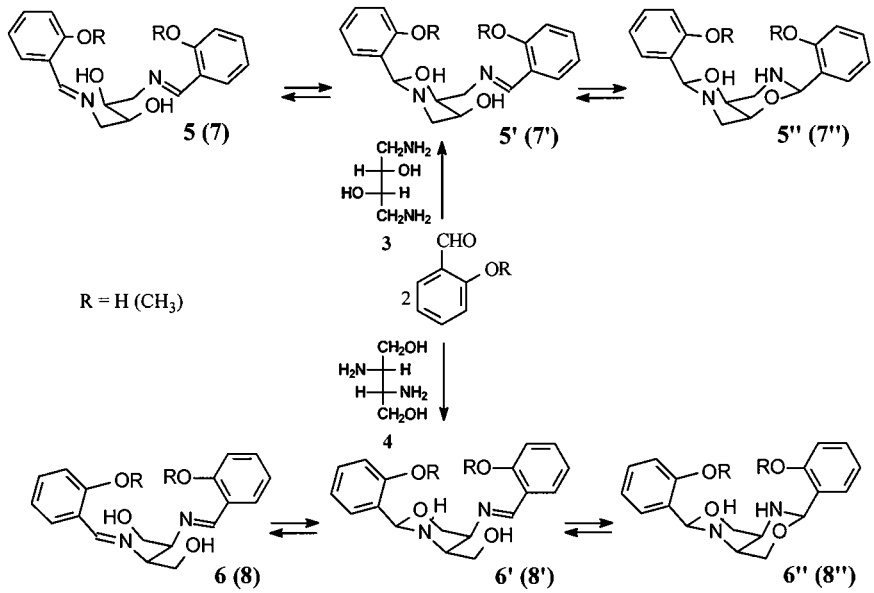
The hydroxy and alkoxy groups have similar inductive effect ($\sigma_m = 0.12$), but contribute by resonance rather differently ($\sigma^+ = -0.92$ vs. -0.78) [3]. The OH group is more electron-donating than OCH_3, due to the contribution of the keto-resonance form. All linear free energy relationship studies have dealt only with *meta* and *para* substituents, because *ortho* substituted 2-aryl systems are outstanding [2c], often exhibiting hydrogen bonding and steric hindrance in addition to electronic effects. We were, however, very much interested in salicyl derivatives, as precursors for macrocylic systems and complexation agents [4].

N-Salicylideneaniline derivatives have been shown to exist as tautomeric forms due to intramolecular proton shifts between the (phenol) oxygen and the (imine) nitrogen, via intramolecular hydrogen bonding (O–H···N ⇌ O···H–N) (Scheme 2, R = aryl) [5–9]. These prototropic shifts, which occur also in the well-known salen systems, are inevitably accompanied by π-electron configurational changes, either in the ground state or in the excited state, in solution and in the crystal. Some crystals of such internally hydrogen bonded Schiff bases exhibit thermochromism by a thermally induced intramolecular proton shift to the quinoid tautomer, or photochromism, by an irradiation induced proton migration [5a,5d].

Double Schiff bases in open or cyclic array and, in particular the salen systems are, as long known, good ligands [10,11]. Chiral salen manganese complexes based on optically active 1,2-diamines (mainly 1,2-diaminocyclohexane) have been used as synthetically useful catalysts for the asymmetric epoxidation of a variety of olefins [11]. Complexes with other metals have been also prepared and their structures studied in the solid state [10,11]. It is on this background, that we report now our findings in this area.

2. Results and discussion

The reaction of salicyl aldehyde with L-1,4-diaminobutanediol (**3**) provided L-1,4-bis(salicylideneamino)-2,3-butanediol (**5**), while D-2,3-diaminobutanediol (**4**) gave D-2,3-bis(salicylideneamino)-1,4-butanediol (**6**) (Scheme 3). These Schiff bases had been prepared earlier [12] and we report now their full physical characterization. Moreover, no attention had been paid earlier to any possible tautomeric forms and, in fact, we observed (by NMR monitoring) formation of the isomeric dioxadiazadecalin systems, albeit with prevalence and final crystallization of the open forms. The stability of the latter is undoubtedly due to strong intramolecular O–H···O and O–H···N hydrogen bonding. **5** is all but insoluble in chloroform and its NMR spectrum in DMSO-d_6 shows no closed tautomeric forms. Similarly, in a variable solvent and temperature (NMR) probe of **6**, no common solvent was able to overcome the intramolecular hydrogen bonding in the open tautomer (**6**) and to stabilize the closed forms (**6′** and **6″**) (Table 1). However, on lower-



Scheme 3. The formation of the **5**–**5″** (**7**–**7″**) and **6**–**6″** (**8**–**8″**) tautomeric manifolds in the reactions of salicylaldehyde (*o*-anisylaldehyde) with L-1,4-diamino-2,3-butanediol (**3**) or D-2,3-diamino-1,4-butanediol (**4**), respectively.

Table 1
Selected NMR data and composition vs. temperature and solvent (from NMR) for **6**–**6**″, **7**–**7**″, **10** and **12**

X	T (K)	X (%)	X′ (%)	X″ (%)	δ_{Ph-OH}	$\delta_{N=CH}$
6 [a]	223	70	25	5	13.52	8.46
	298	100			13.06	8.40
6 [b]	298	100			13.54	8.54
	323	100			13.11	8.52
7 [a]	298	16	30	54		
	323	39	27	42		
10 [a]	298			100		
	323			100		
10 [b]	298	3.5	1.5	95		
	323	9.5	5	85.5		
	368	28	32	40		
	410	45	47	8		
12 [a]	298	100			13.30	8.39

[a] Solvent: $CDCl_3$.
[b] Solvent: DMSO-d_6 (also MeOH-d_4 and Py-d_5).

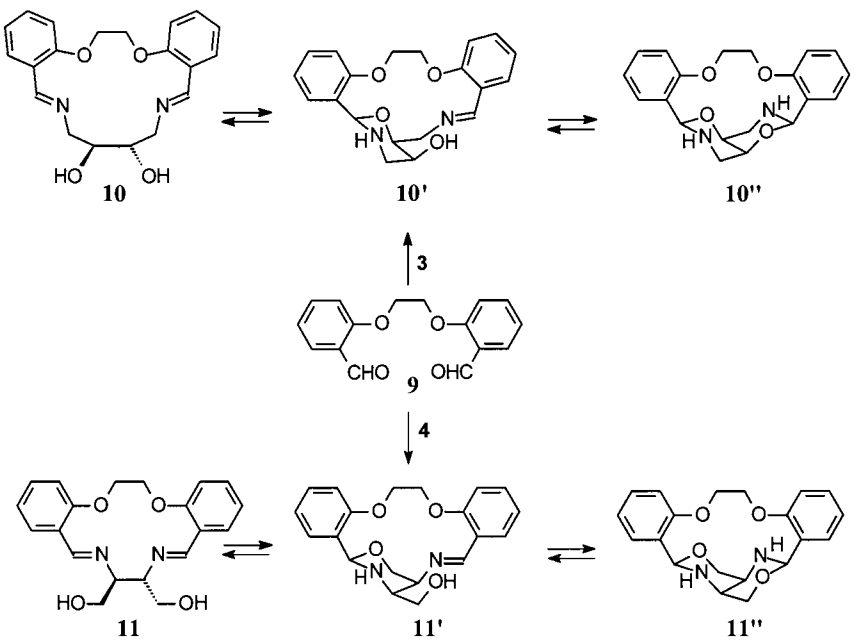
ing the temperature (to -50 °C in $CDCl_3$), both closed oxazane forms (prevalently **6**′) were observed.

As in simpler 2-hydroxy systems [3], these internal hydrogen bonds could be averted by oxygen alkylation. Indeed, reaction of **3** or **4** with *o*-anisaldehyde (Scheme 3) produced the **7** and **8** O-methylated molecular manifolds with higher dioxadiazadecalin stability. In case of DODAD (**7**), the ratio is: **7**/**7**′/**7**″ = 16/30/54% (Table 1) and the contribution of ring closed species (**7**′,**7**″) diminished at higher temperature. However, in the case of **8**, there is complete ring closure to the DADOD form (**8**″). It should be reiterated that the formation and all shown reactions of **5** (**7**) and **6** (**8**) are completely stereospecific.

Some of the stability of the bicyclic forms may be attributed to N–H···OR hydrogen bonding, but this is somewhat weakened by the steric interference of two OMe groups. This interference should abate by connecting the two phenolic termini, leading to the much desired macrocyclic DODAD and DADOD systems. The length of the best fitting spacer was probed by MM calculations (CFF91) of different glycol spacers in a DODAD model, the criterion being the phenolic O···O distance, which is 2.70–3.07 Å in an unsubstituted strainless molecule (e.g. **5**″). The explored bridges were: –OCH_2O– (2.34 Å), –OCH_2CH_2O– (2.88 Å), –$OCH_2CH_2CH_2O$– (3.52 Å) and –$OCH_2CH_2OCH_2CH_2O$– (5.00 Å). For –OCH_2CH_2O– this distance roughly coincided with that of the unsubstituted molecule.

Our first attempts of *O*-alkylation on the Schiff bases was largely ineffectual, but using the known dialdehyde 1,2-bis(*o*-formylphenoxy)-ethane (**9**) [10a] in the reaction with each of the diaminobutanediols (Scheme 4) at high dilution, readily provided the desired macrocycles, (2*R*,6*R*;9*S*;9,10-*P*)-2,6-(1′,2′;7′,8′-dibenzo-3′,6′-dioxa-1′,8′-octanylidene)-*cis*-dioxadiazadecalin (**10**″) and (2*R*,6*R*;9*S*;9,10-*M*)-2,6-(1′,2′;7′,8′-dibenzo-3′,6′-dioxa-1′,8′-octanylidene)-*cis*-diazadioxadecalin (**11**″) in all but quantitative yields and, notably, with no help of any metal template. The structure of **10**″ has been unequivocally proven by X-ray diffraction analysis [4].

Strong intramolecular hydrogen bonding of NH···OR type in **10**″ and **11**″ is manifest in each by a clear double doublet for NH with large *anti* vicinal coupling constants, and by strong deshielding (2 ppm) of these protons, compared to the earlier *p*-nitrophenyl substituted molecules [1c,1d]. The X-ray structure of **10**″



Scheme 4. The formation of the **10**–**10**″ and **11**–**11**″ tautomeric macrocyclic manifolds.

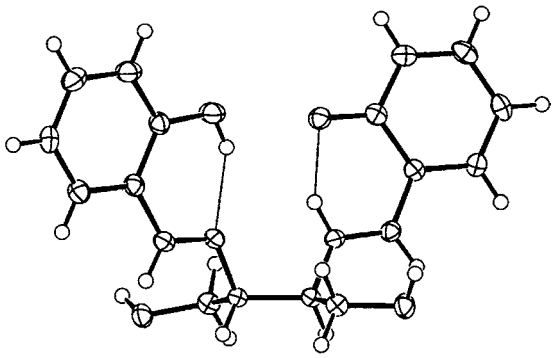


Fig. 1. ORTEP drawing of 2,3-bis(salicyldeneamino)-1,4-butanediol (**6**).

confirms these strong intramolecular hydrogen bonds [4], which are bound to contribute considerably to the smooth macrocyclization reaction.

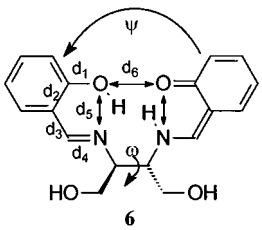
Each of these macrocyclic dioxadiazadecalins (**10**″, **11**″) is actually a member of a manifold of three possible tautomeric structures (Scheme 4) (without mentioning the respective five-membered higher energy isomeric forms) [4]. Indeed, while **10**″ is exclusive in $CDCl_3$ even when heated, the contribution of the mono- and di-imine forms (**10** and **10**′) becomes significant in DMSO-d_6, in particular at higher temperatures (Table 1).

We regard these manifolds (Schemes 3 and 4) as (albeit small) Dynamic Combinatorial Virtual Library [4]. These are sets of isomeric systems, any member of which may but need not exist in significant amounts, if not in the presence of a recognizable target or demanded by extraneous conditions (medium, temperature, etc.) [13]. Our above ring–chain tautomeric molecular sets, as well as analogous ones previously described [1c,1d,4], qualify particularly well for this definition.

We turn to the interesting behavior of the salen type compound (**6**) (Scheme 3) and its corresponding DADOD (**6**″) derivative and their complexes.

The crystal structure of D-2,3-bis(salicylideneamino)-1,4-butanediol (**6**) was determined by X-ray diffraction at both 295 and 116 K (Fig. 1 and Table 2(a)). There is evidently strong intramolecular Ar–OH···N hydrogen bonding in one wing, but in the second one the hydrogen is located mainly at the nitrogen with strong hydrogen bonding to the oxygen site. Cooling enhanced this effect, which is a clear case of phenol–imine/keto–

Table 2
Relevant structural parameters from X-ray analysis (a) of **6** at two temperatures and (b) of selected literature examples of salens and salophenes (Fig. 2), retrieved from the Cambridge Structural Database (CSD) [14]



6

Interatomic distances (Å)							Dihedral angles (°)	
Compound	d_1	d_2	d_3	d_4	d_5	d_6	ω [a]	ψ [b]
(a)								
$\mathbf{6}_{295\ K}$	1.348	1.396	1.453	1.269	2.624	2.927	53.9	15.7
	1.320	1.407	1.431	1.295	2.535			
$\mathbf{6}_{116\ K}$	1.344	1.416	1.454	1.281	2.666	2.866	52.6	16.1
	1.293	1.440	1.429	1.297	2.556			
(b)								
I [7a]	1.345	1.412	1.457	1.270	2.597			
II [7b]	1.346	1.425	1.442	1.292	2.627	3.523	8.2	60.0
	1.345	1.415	1.456	1.284	2.570			
III [8a]	1.358	1.397	1.452	1.283	2.620	3.517	5.3	45.0
	1.358	1.401	1.446	1.285	2.612			
IV [8b]	1.348	1.406	1.452	1.270	2.604	6.082	58.6	56.5
	1.347	1.416	1.447	1.276	2.610			
V [8c]	1.346	1.407	1.471	1.284	2.521	5.544	63.1	83.1
	1.340	1.412	1.467	1.288	2.508			
VI [8d]	1.365	1.414	1.462	1.271	2.604	5.868	64.9	76.3
	1.361	1.403	1.451	1.272	2.602			
VII [8e]	1.277	1.429	1.406	1.303	2.578			

[a] N–C–C–N torsion angle.
[b] Dihedral angle between the two aromatic rings

enamine (N···H–O–CΔN–H···O=C) tautomerism. From comparing the structural parameters of the hydrogen bonded chelate ring at both temperatures, the stronger OH···N hydrogen bond was observed at room temperature, as indicated by the shorter N···O distance.

The Cambridge Structural Database (CSD) [14] contains numerous salen type complexes but only 12 structures of free ligands. The relevant geometrical parameters of the hydrogen-bonded chelate rings of some of these salen and salophen type compounds (**I**–**VI**) (Fig. 2) are assembled in Table 2(b), for comparison with our own results.

The pseudoaromatic six-membered ring formed by intramolecular hydrogen bonding in general *N*-salicylideneanilines and naphtylamines is planar and ranges between non-chromatic to photochromic. The hydrogen bond type appears to depend neither on the stereochemistry of the molecule nor on the R–N=C substituent, but on the kind of aldehyde used [9] and, in solid state, the keto–enamine tautomer (cf. Scheme 2) appears to dominate in naphthaldimine (e.g. **VII**), while the phenol–imine prevails in salicylaldimine Schiff bases. Thus, the existence of the enol tautomer has been established in all crystal structures of N-alkyl substituted salicylaldimines listed so far in the Cambridge Structural Database and an intramolecular N–H···O hydrogen bond is present in naphthaldimines in the solid state regardless of the kind of N-substituent, aryl or alkyl. Indeed, the salen (**I**, with is N–C–C–N *anti* conformation) [7a] and the salophen (**II**, **III**) [7b] derivatives (Table 2(b)) exhibit bond lengths and angles consistent with double N=C and single O–C bonds, in full conformity with the enoliminic structure.

While some of the existing structures show slight lack of symmetry between the two aromatic wings (Table 2(b)), it can be seen from the geometrical parameters of the hydrogen-bonded chelate rings that only in our case (**6**) there is complete asymmetry, due to the two different, phenol–imine and keto–enamine, tautomeric flanks (cf. **VII** for typical data of keto–enamine species). To the best of our knowledge, **6** is the first example of coexistence of two tautomers in the same salicylaldimine molecule. The very short O···O distance and near coplanarity (16°) of the aromatic rings (Table 2(a)) (and implicitly of the two pseudoaromatic chelate rings) are outstanding features in this context.

In solution, UV–vis spectroscopic studies showed that the keto–enamine form exhibits an absorption band at >400 nm, always observed in 2-hydroxynaphthaldehyde/aniline Schiff bases, but not in salicylaldehyde/aniline ones (except in acidic media). The extinction coefficients of the keto–enamine bands at >400 nm depend on solvent polarity, decreasing from EtOH, via DMSO and $CHCl_3$, to cyclohexane [9]. NMR spectra also reflect the intramolecular N–H···O hydrogen bonds in Schiff bases of the *N*-salicylideneaniline and *N*-naphthylideneaniline type in solution [9]. The ^{1}H-NMR signals for the phenol–imine form in $CDCl_3$ are singlets at δ 13.75 ppm for ArOH and at δ 8.73 ppm for CH=N, whereas the keto–enamine form in the same solvent peaks at δ 15.57 ppm and at δ 9.20 ppm ($^3J = 7.6$ Hz).

The corresponding data of **6** (Table 1) indicate that cooling in $CDCl_3$ increase the keto–enamine contribution, whereas heating in DMSO enhance the phenol–imine form and the variable solvent NMR data show

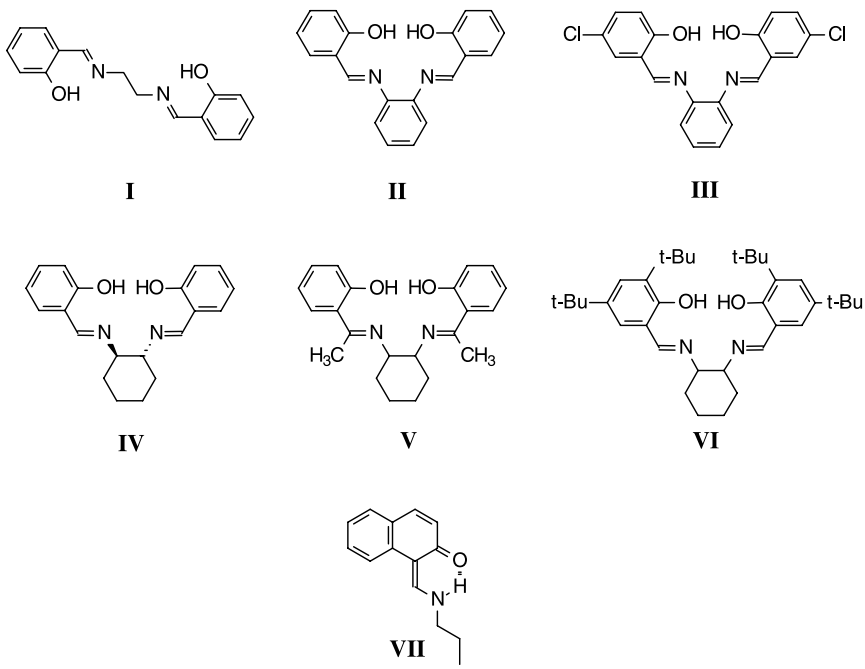


Fig. 2. Literature examples of salens and salophenes, retrieved from the Cambridge Structural Database (CSD) [14].

that the keto–enamine form is enhanced as function of solvent polarity. This was, in fact, corroborated by UV–vis spectral data of both **6** and **12** (see Section 4), which showed an enhanced contribution of the keto–amine forms (at >400 nm) in MeOH, as compared to MeCN.

A compelling sequel was to probe the complexation ability of these systems. The described Dynamic Combinatorial Virtual Libraries (DCVL) (Schemes 3 and 4) are far from being ideally unbiased and, in principle, one could scan them for their constituents, by varying temperature and/or solvent (Table 1). However, any biased or unbiased DCVL, when target-driven, the preferred interaction of a virtual or insignificant constituent with the target may overturn the equilibrium in the set. An obvious choice of target is metal ion complexation.

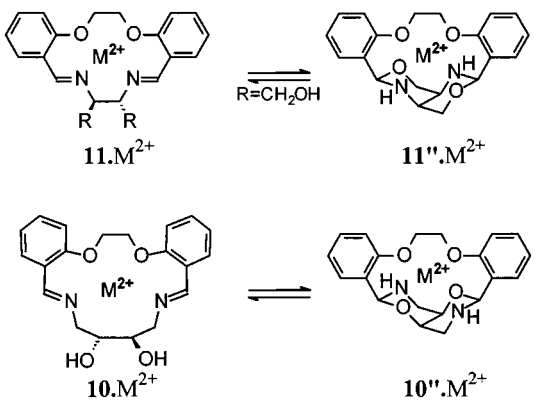
In the reaction of **11″** with nickel chloride in methanol at room temperature, we observed (NMR) the slow formation of a transient imine form (at 8.5 ppm), but the final product was clearly a DADOD complex and (Scheme 5), if a diimine macrocyclic complex **11**·Ni^{2+} had initially formed [10a], it underwent efficient tautomeric ring closure to the more stable complex **11″**·Ni^{2+}. The latter's FABMS analysis reveals a peak at 447 (20%) that fits exactly the $[NiLCl]^+$ species. Similarly, complexation of **11″** with $Ni(ClO_4)_2$ in acetonitrile afforded **11″**·Ni^{2+}, as observed by UV–vis spectrometry, by which a 1:1 complexation stoichiometry could also be deduced [4].

In contrast, attempts to isolate or observe a lead ion complex **11″**·Pb^{2+} in methanol failed, apparently because the Ni^{2+} ion of small ionic radius (0.69 Å) can readily inhabit its DADOD cavity, which the larger metal ion Pb^{2+} (1.18 Å) cannot (Scheme 5). The tautomeric ring opening within the macrocylic ligand to the diimine (**11**) doesn't really help, since its cavity is similarly sized.

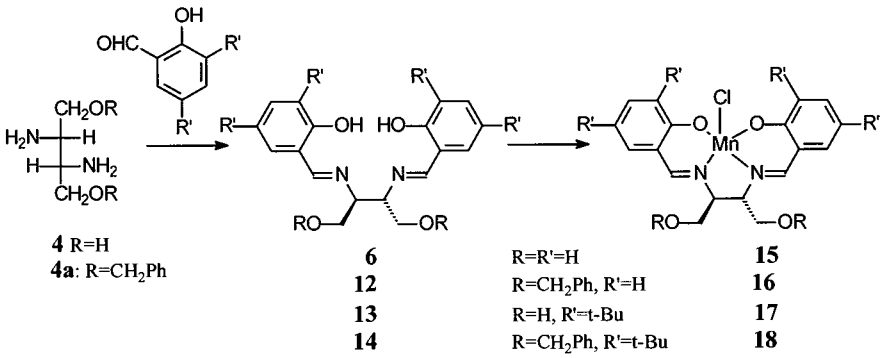
In the dioxadiazadecalin (DODAD) macrocyclic series (Scheme 2, top), after treatment of **10″** with nickel chloride in methanol, the end product is exclusively (NMR) the dioxadiazadecalin complex (**10″**·Ni^{2+}) (Scheme 5). In the FABMS experiment, however, the occurrence of peaks at 447 (30%) of $[NiLCl]^+$ and at 411 (65%) of $[NiL-H]^+$, indicate also the presence of the tautomeric diimine complex (**10**·Ni^{2+}). This is a general and diagnostic feature in all FABMS analyses of complexes in the macrocyclic series **10** and **11**: the complexes of both the bicyclic DODAD (**10″**) and DADOD (**11″**) exhibit $[MLX]^+$ ions, but only in the ring–chain tautomeric **10** series can one find an $[ML-H]^+$ ion characteristic for the dimine (**10**).

When either cadmium perchlorate or lead perchlorate were added to **10″** in methanol, the respective complexes precipitated, but could, however, be dissolved in DMSO-d_6 for NMR purposes. It turned out that during complexation with Cd^{2+}, **10″** underwent tautomeric ring opening and all forms (**10**, **10′**, **10″**) became present in the complexes. This was corroborated by FABMS (peaks at 567 (25%) $[CdL(ClO4)]^+$ and 467 (7%) $[CdL-H]^+$ and 465 (15%) $[CdL-3H]^+$). In the case of lead, however, the NMR spectrum in DMSO-d_6 shows only the diimine complex (**10**·Pb^{2+}) (Scheme 5), with FABMS peaks characteristic to the open chain form (561 (70%) $[PbL-H]^+$ and 559 (140%) $[PbL-3H]^+$). The larger Cd^{2+} (0.97 Å) and the largest Pb^{2+} (1.18 Å) ions appear to be readily complexed by **10″** (in contrast to **11″**) due to its ability (Scheme 2) to modify its cavity size by a successive ring-opening process, ending up with a ring increase by two atoms to **10**·Pb^{2+}. Eventually, the latter may undergo gradual reverse macrocycle folding, providing a mechanism of fine-tuning until an optimum cavity size for ion bonding is reached. That is how Ni(II), Cd(II) and Pb(II) were complexed by **10**–**10″** in different, cation size depending tautomeric modes.

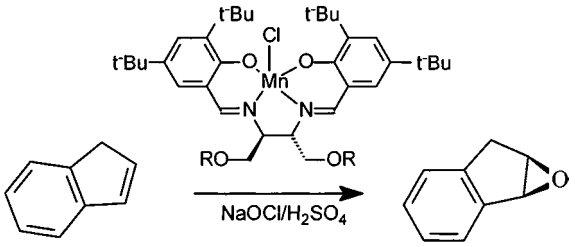
Having shown that cyclic diazadioxadecalin/salen systems complex well with selectively heavy and transition metal ions, it was compelling then to examine the complexation ability of **6** (vide supra) and of judiciously chosen related salen analogues and the catalytic activity [11,15] of the complexes. We picked the Mn(III) complexes, in particular since we could use Jacobsen's well-forged procedures [15,16] for their use as catalysts of epoxidation of olefins and indene as a prototypical substrate [16]. Thus, after preparing **6** (Schemes 3 and 5) and its dibenzyl ether (12) [1d] and their Mn(III) complexes (**15**, **16**) (Scheme 6), and realizing, as actually anticipated [11], that the latter catalyse the epoxidation of indene but without any asymmetric induction, we prepared the tetra-*tert*-butyl derivatives **13** and **14** and their Mn(III) complexes (**17** and **18**). The use of the latter in the epoxidation of indene (Scheme 7) gave 2,3-epoxyindane in yields (ee) of 50% (48%) and 51% (30%), respectively. This is less then the high yield achieved by Jacobsen [11,15,16b] with his rigid salen



Scheme 5. Host–guest size interdependent complex formation in the **10**–**10″** and **11**–**11″** tautomeric macrocyclic series.



Scheme 6. The synthesis of D-2,3-bis(arylideneamino)-1,4-butanediol derivatives (**12**–**14**) and of their Mn(III) complexes (**15**–**18**).



Scheme 7. The epoxidation of indene using the Mn(III) complexes of D-2,3-bis(di-*t*-butyl-salicylideneamino)-1,4-butanediol and -dibenzyl ether (**17**, **18**).

built on the *trans*-cyclohexano core, but sufficient to maintain our incentive for further probing and optimizing these readily available and variegated catalytic systems.

3. Conclusions

We have shown that L-1,4-bis(salicylideneamino)-2,3-butanediol (**5**) and D-2,3-bis(salicylideneamino)-1,4-butanediol (**6**) exist in solvent and temperature dependent tautomeric equilibria, with the ring-closed (DODAD and DADOD) systems. The equilibrium is influenced by phenol O-alkylation, stabilizing the closed dioxadiazadecalin (DODAD) and diazadioxadecalin (DADOD) isomers (**7**″, **8**″). This led the way to using the dialdehyde 1,2-bis(*o*-formylphenoxy)-ethane (**9**) for securing the respective macrocyclic manifolds (**10**–**10**″ and **11**–**11**″). These tautomeric manifolds are typical target-driven *dynamic combinatorial virtual libraries*, which can be biased by complex formation with metal ions of different ionic radius. We unravelled a unique instance of simultaneous occurrence of keto–enamine and phenol–imine tautomers in solution and in the solid state of **6**. The latter and a number of analogues constitute a new class of salens, which form heavy and transition metal complexes. Such Mn(III) complexes (**17**, **18**) are potentially good chirality inducing catalysts, as established in moderately enantioselective indene epoxidation reactions.

4. Experimental

4.1. General

Melting points were recorded on a capillary melting point apparatus and are uncorrected. The ^{1}H- and ^{13}C-NMR spectra were obtained on 200 or 500 MHz spectrometers and referenced to Me_4Si as internal standard. Mass spectra (DEI-MS, DCI-MS and FAB) were recorded on an Autospec 250 mass spectrometer. UV spectra were taken on a Unikon 931 spectrophotometer. Since we dealt with tautomeric mixtures, optical purity was measured using chiral NMR shift reagents, usually $Eu(hfc)_3$, unless otherwise mentioned.

4.2. General procedures

L-1,4-Diaminobutanediol (**3**) and D-2,3-diamino-1,4-butanediol (**4**) were prepared as described [1d]. 3,5-Di-*t*-butylsalicylaldehyde was prepared by a published procedure [16a]. Each diaminobutanediols or derivative was stirred at room temperature with two mole equivalents of the chosen salicylaldehyde in EtOH, until full conversion.

L-1,4-Bis(salicylideneamino)-2,3-butanediol (**5**) was prepared from L-1,4-diamino-2,3-butanediol [12c] (**3**) and salicylaldehyde. **5** precipitated from EtOH solution as yellow crystals; m.p. 224 °C (MeOH). ^{1}H-NMR (DMSO-d_6): $\delta = 13.67$ (brs, ArOH), 8.55 (s, N=CH), 7.45 (dd, $^{3}J = 7.6$, $^{4}J = 1.0$ Hz, H_a), 7.35 (dt, $^{3}J = 7.8$, $^{4}J = 1.3$ Hz, H_c), 6.90 (t, $^{3}J = 7.5$ Hz, H_b), 6.89 (d, $^{3}J = 8.0$ Hz, H_d), 5.02 (brd, $^{3}J = 4.6$ Hz, OH), 3.89 (dd, $^{2}J = 12$, $^{3}J = 3.3$ Hz, H_1), 3.77 (m, H_2), 3.58 (dd, $^{2}J = 12$, $^{3}J = 7.6$ Hz, H_1). ^{13}C-NMR (DMSO-d_6): $\delta = 166.9$ (d, N=CH), 161.1, 118.7 (s, Ar), 132.3, 131.7, 118.4, 116.6 (d, Ar), 71.5 (d, C_2), 61.2 (t, C_1). DCIMS; m/z (relative intensity %): 329.1 ($[MH]^+$, 100). UV: λ_{max}

(nm) (ε $M^{-1}\,cm^{-1}$) (MeOH): 402 (3000), 315 (6800), 255 (22 200), 216 (43 200).

D-2,3-Bis(salicylideneamino)-1,4-butanediol (**6**) was prepared from D-2,3-diamino-1,4-butanediol [12c] (**4**) and salicylaldehyde. **6** precipitated from EtOH solution as yellow crystals, m.p. 163 °C (MeOH). ^{1}H-NMR ($CDCl_3$): $\delta = 13.06$ (brs, OH), 8.40 (s, N=CH), 7.31 (dt, $^3J = 7.8$, $^4J = 1.6$ Hz, H_c), 7.24 (dd, $^3J = 7.7$, $^4J = 1.5$ Hz, H_a), 6.98 (d, $^3J = 8.3$ Hz, H_d), 6.86 (dt, $^3J = 7.5$, $^4J = 0.8$ Hz, H_b), 3.90 (dd, $^2J = 11.2$, $^3J = 4.1$ Hz, H_1), 3.83 (dd, $^2J = 11.0$, $^3J = 6.7$ Hz, H_1), 6.67 (m, H_2), 1.88 (brs, OH). ^{13}C-NMR ($CDCl_3$): $\delta = 168.2$ (d, N=CH), 133.6, 132.5, 119.6, 117.9 (d, Ar), 72.6 (t, C_1), 64.4 (d, C_2). DCIMS; m/z (relative intensity %): 329.1 ($[MH]^+$, 100). UV–vis: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (MeOH): 403 (1000), 315 (7500), 256 (23 000), 214 (40 500); (MeCN): 402 (95), 315 (7844), 256 (22 434), 215 (41 935).

The reaction of **3** and *o*-anisaldehyde in ethanol gave a tautomeric mixture of 2,6-bis(*o*-anisyl)-*cis*-DODAD (**7″**) together with small amounts of **7**, **7′**. On evaporation a colorless solid was obtained, m.p. 120–129 °C (*t*-BuOMe). ^{1}H-NMR ($CDCl_3$): (**7**) $\delta = 8.76$ (s, N=CH); (**7′**) 8.68 (s, N=CH), 5.60 (s, H_2); (**7″**) 7.64 (dd, $^3J = 7.5$, $^4J = 1.4$ Hz, H_a), 7.34 (dt, $^3J = 7.8$, $^4J = 1.6$ Hz, H_c), 7.05 (t, $^3J = 7.6$ Hz, H_b), 6.95 (d, $^3J = 8.6$ Hz, H_d), 5.65 (s, H_2), 3.89 (s, CH_3), 3.68 (s, H_9), 3.35 (dd, $^2J = 14.5$ Hz, H_4), 3.27 (d, $^2J = 14.5$ Hz, H_4). ^{13}C-NMR ($CDCl_3$): (**7**) $\delta = 159.6$ (d, N=CH), 72.4 (d, C_2), 65.3 (t, C_1); (**7′**) 156.4 (d, N=CH), 84.9 (d, C_2), 66.1 (d, $C_{5,6}$), 64.6 (t, C_7), 51.0 (t, C_4); (**7″**) 129.6, 126.9, 120.8, 111.0 (d, Ar), 84.6 (d, C_2), 69.9 (d, C_9), 55.6 (OCH_3), 50.1 (t, C_4). UV–vis: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (MeOH): 310 (6000), 252 (17 600), 199 (91 600); (MeCN): 305 (8409), 251 (20 272), 212 (33 182). DCIMS; m/z (relative intensity %): 357.3 ($[MH]^+$, 100), 249.2 (7), 239.2 (9), 221.2 (55), 208.2 (55), 178.1 (79), 149.1 (28), 136.1 (21), 121.1 (35), 104.1 (9), 91.1 (13). HR DCIMS; m/z: 357.1816. Calc. for $C_{20}H_{25}N_2O_4$ $[MH]^+$ 357.1814.

The reaction of **4** with *o*-anisaldehyde in EtOH gave on evaporation 2,6-bis(*o*-anisyl)-*cis*-DADOD (**8″**), as a yellow oil. ^{1}H-NMR ($CDCl_3$): $\delta = 7.50$ (dd, $^3J = 7.6$, $^4J = 1.6$ Hz, H_a), 7.32 (dt, $^3J = 7.8$, $^4J = 1.7$ Hz, H_c), 7.0 (m, H_b), 6.94 (d, $^3J = 8.3$ Hz, H_d), 5.49 (s, H_2), 4.17 (d, $^2J = 11.6$ Hz, H_4), 4.07 (d, $^2J = 11.7$ Hz, H_4), 3.89 (s, OCH_3), 3.02 (s, H_9). ^{13}C-NMR ($CDCl_3$): $\delta = 129.8$, 127.4, 120.8, 111.4 (d, Ar), 86.1 (d, C_2), 71.5 (t, C_4), 55.8 (q, OCH_3), 49.9 (d, C_9). DCIMS; m/z (relative intensity %): 357.3 ($[MH]^+$, 100), 326.3 (8), 249.2 (18), 239.2 (10), 223.2 (26), 206.2 (17), 192.2 (37), 179.2 (71), 162.2 (29), 136.1 (91), 121.1 (56), 91.1 (29). HR DCIMS; m/z: 357.1816. Calc. for $C_{20}H_{25}N_2O_4$ $[MH]^+$ 357.1814.

The macrocyclic compounds **10″** and **11″** were prepared at high dilution: a 0.1 M ethanolic solutions of diaminobutanediol **3** or **4** (1 mmol) was added to a solution of the dialdehyde **9** (1 mmol) in 400 ml of EtOH. The solution was stirred at room temperature (r.t.) until complete conversion (TLC, SiO_2, $CHCl_3$). Subsequent evaporation provided white solid products.

10″: m.p. 172 °C (MeCN). ^{1}H-NMR ($CDCl_3$): $\delta =$ 7.31 (dt, $^3J = 7.9$, $^4J = 1.7$ Hz, H_c), 7.26 (dd, $^3J = 7.8$, $^4J = 1.7$ Hz, H_a), 7.07 (d, $^3J = 7.8$ Hz, H_d), 6.98 (dt, $^3J = 7.4$, $^4J = 0.8$ Hz, H_b), 5.19 (d, $^3J = 12.3$ Hz, H_2), 4.54, 4.31 (ddd, –CH_2CH_2–), 3.94 (t, $^3J = 12.2$ Hz, NH), 3.61 (brs, H_9), 3.28 (dd, $^2J = 14.5$, $^3J = 1.5$ Hz, H_{4eq}), 3.10 (t, $J_{av} = 13$ Hz, H_{4ax}). ^{13}C-NMR ($CDCl_3$): $\delta = 130.3$, 129.8, 121.8, 114.1 (d, Ar), 92.1 (d, C_2), 69.6 (d, C_9), 67.2 (t, C_{bridge}), 50.3 (t, C_4). CIMS; m/z (relative intensity %): 355.2 ($[MH]^+$, 100), 311.1 (14), 253.1 (9). HR DEIMS: Calc. for $C_{20}H_{22}N_2O_4$ $[M]^{+\bullet}$ 354.1580, observed m/z 354.1574. $[\alpha]_D = +32°$ ($c = 5.2$, $CHCl_3$).

The other two tautomers could be seen in the above crude product, in DMSO at higher temperature: **10**: ^{1}H-NMR (DMSO-d_6, 410 K): $\delta = 8.76$ (s, N=CH), 7.81 (dd, $^3J = 7.6$, $^4J = 1.5$ Hz, H), 7.41 (dt, $^3J = 7.2$, $^4J =$ 1.7 Hz, H), 7.15 (d, $^3J = 8.0$ Hz, H), 7.02 (dt, $^3J = 7.5$, $^4J = 2.0$ Hz, H), 4.48 (m, –CH_2CH_2–), 3.85 (m, H_2), 3.79 (m, $2H_1$). **10′**: ^{1}H-NMR (DMSO-d_6, 410 K): $\delta =$ 8.70 (s, N=CH), 7.89 (dd, $^3J = 7.5$, $^4J = 1.6$ Hz, H), 7.42 (overlap, H), 7.34 (t, $^3J = 8.0$ Hz, H), 7.25 (dd, $^3J = 7.4$, $^4J = 1.5$ Hz, H), 7.20 (d, $^3J = 8.0$ Hz, H), 7.15 (overlap, H), 7.02 (overlap, H), 6.98 (t, $^3J = 7.4$ Hz, H) 5.15 (s, H_2), 4.60, 4.48, 4.24 (m, –CH_2CH_2–), 3.63 (m, $2H_7$), 3.58 (m, $H_5 + H_6$), 3.04 (m, H_4).

Similarly, **11″** m.p. 127 °C (MeCN). ^{1}H-NMR ($CDCl_3$): $\delta = 7.32$ (dt, $^3J = 7.9$, $^4J = 1.7$ Hz, H_c), 7.28 (dd, $^3J = 7.4$, $^4J = 1.7$ Hz, H_a), 7.08 (d, $^3J = 7.8$ Hz, H_d), 7.00 (dt, $^3J = 7.4$, $^4J = 0.8$ Hz, H_b), 5.19 (d, $^3J =$ 13.2 Hz, H_{2ax}), 4.59, 4.38 (ddd, H_{bridge}), 4.49 (t, $^3J_{av} =$ 12.5 Hz, NH), 4.14 (dd, $^2J = 11.6$, $^3J = 1.3$ Hz, H_{4eq}), 4.05 (dd, $^2J = 11.7$, $^3J = 1.8$ Hz, H_{4ax}), 2.95 (d, $^3J = 11.2$ Hz, H_9). ^{13}C-NMR ($CDCl_3$): $\delta = 156.6$, 128.2 (s, Ar), 130.6, 130.0, 122.1, 114.5 (d, Ar), 91.9 (d, C_2), 71.7 (t, C_4), 50.1 (d, C_9), 66.9 (t, C_{bridge}). DCIMS; m/z (relative intensity %): 355.1 ($[MH]^+$, 100), 324.1 (77), 253.1 (60), 121.0 (30). HR MS: Calc. for $C_{20}H_{22}N_2O_4$ $[M]^{+\bullet}$ 354.1580; observed m/z 354.1576. $[\alpha]_D = -85°$ ($c = 2$, $CHCl_3$).

D - 2,3 - Bis(salicylideneamino) - 1,4 - benzyloxybutane (**12**) was prepared from D-2,3-diamino-1,4-benzyloxybutane [12c] (**4a**) and salicyladehyde. Evaporation gave a yellow oil product. ^{1}H-NMR ($CDCl_3$): $\delta = 13.30$ (brs, OH), 8.39 (s, N=CH), 7.26 (m, $H_{a,c}$ + Ph), 7.02 (d, $^3J = 8$ Hz, H_d), 6.88 (t, $^3J = 7.3$ Hz, H_b), 4.50 (d, $^2J = 11.9$ Hz, C*H*HPh), 4.44 (d, $^2J = 11.9$ Hz, CH*H*Ph), 3.85 (m, H_2), 3.70 (dd, $^2J = 9.4$, $^3J = 5.3$ Hz, H_1), 3.52 (dd, $^2J = 9.4$, $^3J = 6.8$ Hz, H_1). ^{13}C-NMR ($CDCl_3$): $\delta = 167.2$ (d, N=CH), 161.4 (s, Ar), 132.6, 131.6, 128.4, 127.7, 118.6, 117.3 (d, Ar), 73.4 (t, C_1), 70.8 (t, *C*H_2Ph), 69.1 (s, C_2). UV–vis: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (MeOH): 406 (1060), 316 (9200), 257 (30 400); (MeCN): 403 (90), 317 (9000), 257 (26 240),

213 (56 164). DCIMS; m/z (relative intensity %): 509.3 ($[MH]^+$, 100), 405.3 (18), 255.2 (8), 122.1 (21), 106.9 (42), 91.0 (70). HR DCIMS; m/z: 509.2439. Calc. for $C_{32}H_{32}N_2O_4$ $[MH]^+$ 509.2440.

D-2,3-Bis(3,5-di-*t*-butylsalicylideneamino)-1,4-butanediol (**13**) was prepared from **4** and 3,5-di-*t*-butylsalicylaldehyde. Evaporation gave **13** as a yellow oil, m.p. 96–103 °C (petroleum ether). ^{1}H-NMR ($CDCl_3$): $\delta =$ 13.3 (brs, OH), 8.42 (s, N=CH), 7.37 (d, $^4J = 2$ Hz, H_c), 7.07 (d, $^4J = 2.6$ Hz, H_e), 3.94 (dd, $^2J = 11.2$, $^3J = 3.8$ Hz, H_1), 3.87 (dd, $^2J = 11.2$, $^3J = 6.6$ Hz, $H_{1'}$), 3.65 (m, H_2), 1.42 (s, $C(CH_3)_3$), 1.27 (s, $C(CH_3)_3$). ^{13}C-NMR ($CDCl_3$): $\delta = 168.6$ (d, N=CH), 158.2 (s, C_b), 140.3, 136.9 (s, $C_{d,f}$), 127.5, 126.4 (d, $C_{c,e}$), 117.6 (s, C_a), 72.2 (t, C_1), 63.8 (d, C_2), 35.1, 34.1 (s, $C(CH_3)_3$), 31.4, 29.4 (q, $C(CH_3)_3$). DCIMS; m/z: (relative intensity %): 553.4 ($[MH]^+$ 100); DEIMS; m/z (relative intensity %): 552.4 ($[M^{+\bullet}]$, 100), 434.3 (12), 276.2 ([M/2], 30). HR DEIMS; m/z: 552.3927. Calc. for $C_{34}H_{52}N_2O_4$ $[M^+]$ 552.3927. UV–vis: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (MeCN): 402 (101), 315 (7844), 256 (22 434), 215 (41 935); (MeOH): 403 (1000), 315 (7500), 256 (23 000), 214 (40 500). $[\alpha]_D = -68°$ ($c = 2$, $CHCl_3$).

D - 2,3 - Bis(3,5 - di - *t* - butylsalicylideneamino) - 1,4-benzyloxybutane (**11**) was prepared from D-2,3-diamino-1,4-benzyloxybutane (**4a**) and 3,5-di-*t*-butylsalicyl aldehyde. Evaporation gave a yellow oil product. ^{1}H-NMR ($CDCl_3$): $\delta = 13.7$ (brs, OH), 8.45 (s, N=CH), 7.45 (d, $^4J = 2.4$ Hz, H_c), 7.34 (m, $5H_{Ph}$), 7.13 (d, $^4J = 2.4$ Hz, H_e), 4.59 (d, $^2J = 12$ Hz, C*H*HPh), 4.54 (d, $^2J = 12$ Hz, CH*H*Ph), 3.90 (m, H_2), 3.81 (dd, $^2J = 9.5$, $^3J = 5.2$ Hz, H_1), 3.63 (dd, $^2J = 9.5$, $^3J = 6.5$ Hz, $H_{1'}$), 1.53 (s, $C(CH_3)_3$), 1.37 (s, $C(CH_3)_3$). ^{13}C-NMR ($CDCl_3$): $\delta = 167.9$ (d, N=CH), 158.5, 140, 138, 136, 117.7 (s, Ar + Ph), 128.4, 127.7, 127.1, 126.2 (d, Ar + Ph), 73.3 (t, C_1), 70.8 (t, CH_2Ph), 69.2 (d, C_2), 35.1, 34.1 (s, $C(CH_3)_3$), 31.5, 29.4 (q, $C(CH_3)_3$). CIMS; m/z (relative intensity %): 732.7 ($[MH]^+$, 100), 366.4 ([M/2], 20), 91.1 ($[C_7H_7]^+$, 55). $[\alpha]_D = +20°$ ($c = 4$, $CHCl_3$).

4.3. Complexation of macrocycles *10″* and *11″* with metal salts

All FABMS assignments were proven by comparison with simulated isotope patterns.

4.4. General procedure for ^{1}H-NMR titration

Metal salt solution (150 μmol in 0.5 ml) was added in portions of 10 μl (3 μmol) to the NMR tube containing a solution of the macrocycle (30 μmol) in the deuterated solvent (0.5 ml) and NMR spectra were taken periodically.

The complexation of **10″** with nickel dichloride was monitored by NMR up to a 1:1 ligand to metal ratio. Final ^{1}H-NMR spectrum (MeOH-d_4): $\delta = 7.18$ (t, $^3J =$ 7.2 Hz, H_c), 7.10 (d, $^3J = 6.7$ Hz, H_a), 7.01 (d, $^3J = 7.8$ Hz, H_d), 6.80 (t, $^3J = 6.8$ Hz, H_b), 5.09 (s, H_2), 4.38, 4.07 (brd, $J = 6.5$, $-CH_2CH_2-$), 3.65 (brs, H_9), 3.06 (m, H_4). FABMS; m/z (relative intensity %): 447.0 ($[NiLCl]^+$, 30), 411 ($[NiL-H]^+$, 65), 355.1 ($[LH]^+$, 100).

The complex of **10″** with Cd(II) perchlorate was obtained as a colorless precipitate from MeOH-d_4 solution. ^{1}H-NMR (DMSO-d_6): $\delta = 8.71$, 8.64, 8.58 (s, CH=N), 7.74, 7.20, 6.93 (m, Ar), 5.11, 5.08 (s, H_2), 4.60, 4.44 (m, $-CH_2CH_2-$), 3.70, 3.51, 3.10, 2.94. FABMS; m/z (relative intensity %): 567.0 ($[CdL(ClO_4)]^+$, 25), 467 ($[CdL-H]^+$, 7), 465 ($[CdL-3H]^+$, 15), 353.2 ($[L-H]^+$, 100).

The complex of **10″** with Pb(II) perchlorate was obtained as a colorless precipitate from MeOH-d_4 solution. m.p. 270 °C (dec.). ^{1}H-NMR (DMSO-d_6): $\delta =$ 9.1–8.6 (m, N=CH), 7.80–7.10 (m, Ar), 4.48 (m, $-CH_2CH_2-$), 4.10 (m, H_1), 3.70–3.40 (m, H_2). FABMS; m/z (%):561 ($[PbL-H]^+$, 50), 559 ($[PbL-3H]^+$, 100), 355.1 ($[LH]^+$, 70).

The complexation of **11″** with nickel dichloride was monitored by NMR up to a 1:1 ligand to metal ratio. Final ^{1}H-NMR spectrum (MeOH-d_4): $\delta = 7.01$ (m, Ar), 6.74 (t, $^3J = 6.1$, Ar), 4.93 (s, H_2), 4.35, 4.07 (brd, J = 6.5, $-CH_2CH_2-$), 3.81 (brd, $^2J = 10$, H_{4eq}), 3.68 (brd, $^2J = 10$, H_{4ax}), 2.72 (brs, H_9). FABMS; m/z (relative intensity %): 447.0 ($[NiLCl]^+$, 20), 355.1 ($[LH]^+$, 100).

(Salen)Mn(III) complexes were prepared according to an existing procedure [16a].

D-2,3-Bis(salicylideneamino)-1,4-butanediol manganese(III) chloride (**15**) was prepared from **6** following the original procedure [16a], but using only EtOH as solvent, which was then evaporated and the product was extracted by trituration with $CHCl_3$. FABMS; m/z (relative intensity %): 381 ($[M-Cl]^+$, 25), 380 ($[(M-H)-Cl]^+$, 95), 379 ($[(M-2H)-Cl]^+$, 100).

D - 2,3 - Bis(salicylideneamino) - 1,4 - benzyloxybutane manganese(III) chloride (**16**) was similarly prepared from **12**. m.p. 275–278 °C. FABMS; m/z (relative intensity %): 561.1 ($[M-Cl]^+$, 100).

D-2,3-Bis(3,5-di-*t*-butylsalicylideneamino)-1,4-butanediol manganese(III) chloride (**17**) was prepared from **13**. m.p. 274 °C. FABMS; m/z (relative intensity %): 605.3 ($[M-Cl]^+$, 100). Anal. Found: C, 64.11; H, 8.16; N, 4.45.Calc. for $C_{34}H_{50}ClMnN_2O_4$ (MW 641.17): C, 63.69; H, 7.86; N, 4.37%.

D-2,3-Bis(3,5-di-*t*-butylsalicylideneamino)-1,4-benzyloxybutane manganese(III) chloride (**18**) was prepared from **14**. m.p. 265 °C. FABMS; m/z (relative intensity %): 785.3 ($[M-Cl]^+$, 100). Anal. Found: C, 70.93; H, 7.93; Cl, 4.22; N, 3.55. Calc. for $C_{48}H_{62}ClMnN_2O_4$ (MW 821.42): C, 70.19; H, 7.61; Cl, 4.32; N, 3.41%.

Epoxidation of indene with (salen)Mn(III) complexes was performed following a published procedure [16b], but with certain changes. To a CH_2Cl_2 (0.6 ml) solution

of indene (0.6 g, 5.2 mmol) and catalyst (0.033 mmol), bleach (0.7 M sodium hypochloride (10 ml) and sulfuric acid (10%, 1 ml)) were added dropwise during 45 min at 0 °C. The reaction is stirred for an additional 3.5 h at 0 °C. Work up [16b] gave epoxyindane as a yellow oil and this was analysed by NMR with the chiral shift reagent Eu(hfc)$_3$.

Yields (ee): Catalyst **17**: 0.34 g, 50% (48%); Catalyst **18**: 0.35 g, 51% (30%).

4.5. X-ray diffraction analysis of *6*

The X-ray diffraction measurements were carried out on single crystals of **6** at the shown temperatures, on a Nonius KappaCCD diffractometer, equipped with a Cryosteam liquid nitrogen cooling device, and using Mo–K$_\alpha$ ($\lambda = 0.7107$ Å) radiation. Diffraction intensity data were collected out to $2\theta = 56.5°$ on 182 Phi-scan (1.0°) frames, and reduced to structure-factors by the DENZO [17] and SCALEPACK [18] procedures. The crystal structures were solved by direct methods (SHELXS-97) [19], and refined by full-matrix least-squares based on F^2 for all reflections (SHELXL-97) [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters.

$C_{18}H_{20}N_2O_4$, FW: 328.37, orthorhombic, space group $P2_12_12_1$.

At 116 K: $a = 7.259(1)$, $b = 11.112(1)$, $c = 20.415(1)$ Å, $V = 1646.7(3)$ Å^3, $Z = 4$, $D_{calc} = 1.325$ g cm^{-3}, μ(Mo–K$_\alpha$) = 0.94 cm^{-1}, $R = 0.052$ for 2790 observations with $F_0 > 4\sigma(F_0)$ and $R = 0.089$ for all 3851 unique data, $S = 1.00$ and $|\Delta\rho| \leq 0.23$ e Å^{-3}.

At 295 K: $a = 7.362(1)$, $b = 11.120(1)$, $c = 20.709(1)$ Å, $V = 1695.4(3)$ Å^3, $Z = 4$, $D_{calc} = 1.286$ g cm^{-3}, μ(Mo–K$_\alpha$) = 0.92 cm^{-1}, $R = 0.058$ for 1839 observations with $F_0 > 4\sigma(F_0)$ and $R = 0.169$ for all 4055 unique data, $S = 0.82$ and $|\Delta\rho| \leq 0.15$ e Å^{-3}. All hydrogen atoms bound to O and N have been located from difference-Fourier maps, but their positions were not refined.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 149020 and 149021 for structures of **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported in part by a research grant from the Israel Science Foundation and by an Intel Scholarship (to A.S.). Mr. Shimon Hauptman provided valuable assistance with mass spectrometry and Mr. Yuri Paskover contributed as an undergraduate research student.

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