# Magnesium Versus Zinc Coordination to Multidentate Schiff Base Ligands

**Andrea Erxleben*[a] and Dinah Schumacher[a]**

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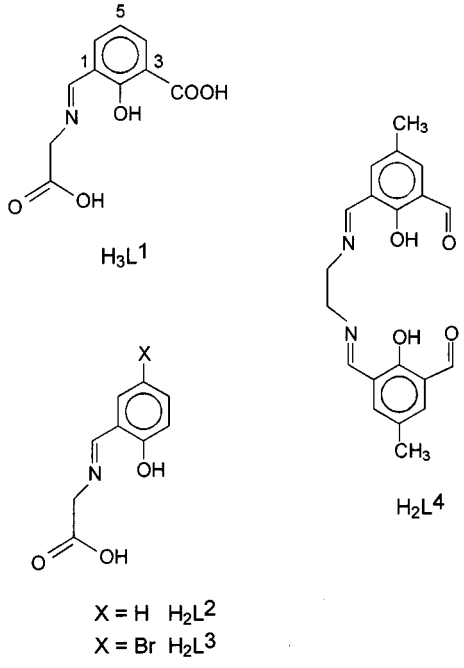
The reactions of two mononuclear zinc complexes, $[Zn(HL^1)(H_2O)_2]$, **1**, and $[ZnL^4(H_2O)]$, **7**, ($H_3L^1$ = Schiff base derived from 3-formylsalicylic acid and glycine, $H_2L^4$ = Schiff base derived from 2,6-diformyl-4-methylphenol and 1,2-diaminoethane), with $Mg^{2+}$ has been studied. These complexes contain binucleating Schiff base ligands and have vacant coordination sites. For both compounds, substitution of zinc by magnesium has been observed in DMSO. Likewise, the Zn complex of $H_2L^2$ (Schiff base derived from salicylaldehyde and glycine) can be converted into the corresponding Mg compound. The following complexes were characterized by single-crystal X-ray analysis: $[MgL^3(H_2O)_3]$, **4**, $[MgL^2(H_2O)_2]_n$, **5**, $[Mg(sal)_2(H_2O)_2]$, **6**, and $[MgL^4(H_2O)(CH_3OH)]$, **8** ($H_2L^3$ = Schiff base derived from 5-bromosalicylaldehyde and glycine, Hsal = salicylaldehyde). The tri- and tetradentate *N,O* ligands $H_2L^3$ and $H_2L^4$ form discrete complex molecules in the solid state, while a carboxylate-bridged polymeric structure is formed by $H_2L^2$. In **4** and **8** the aqua ligands hydrogen bond with the deprotonated phenolate and carboxylate oxygen atoms, resulting in the formation of dimers. In **6** two aqua ligands, two phenolate oxygens and two aldehyde oxygens give rise to an $O_6$ coordination sphere.

## Introduction

Magnesium and zinc are indispensable elements in biology. They are involved in several biochemical processes and are essential cofactors required for the activation of a variety of enzymes. To date, a large number of coordination compounds of Zn have been prepared, many of which represent low-molecular-weight model compounds for Zn enzymes.[1−11] By contrast, Mg complexes have received much less attention.[12−19] Relative to other biologically relevant cations, Mg is unique in that it possesses the smallest ionic radius and the highest charge density. Furthermore, $Mg^{2+}$ shows a strong tendency to bind six water molecules in the inner coordination sphere as manifested by the wide range of crystal structures containing the octahedral $[Mg(H_2O)_6]^{2+}$ dication.[12] Consequently, the presence of hexahydrated $Mg^{2+}$ as the counterion in the crystal structure of $[Mg(H_2O)_6][\{Zn_2L(CH_3CO_2)\}_2(\mu_3\text{-}OH)_2]\cdot 6H_2O$ ($H_3L$ = Schiff base derived from 2,6-diformyl-4-methylphenol and glycine) previously reported by us was not unusual.[20] However, in nonaqueous solution (DMSO) substitution of zinc by magnesium was observed and the heteronuclear complex $[MgZnL]^+$ was identified in solution.

As part of our ongoing study on dinucleating Schiff base ligands[21] we have now investigated Zn and Mg coordination to $H_3L^1$, as well as to the salen derivative $H_2L^4$. The ability of the deprotonated phenolic oxygen atoms of *N,N*-ethylenebis(salicylideneimine), $H_2$salen, to bridge two metal ions has been known for a long time. Several examples of neutral salen complexes acting as bidentate oxygen-donor ligands, and forming adducts of the type $[(ML)M']^{n+}$ or $[(ML)_2M']^{n+}$ (M = transition metal ion, M′ = transition metal, alkali or alkaline earth metal ion) are documented in the literature.[22] Fukuhara et al. and Carbonaro et al. showed that Mg reacted with Cu(salpd), Ni(salpd)[23] and Ni(salen)[24] to give di- and trinuclear complexes [$H_2$salpd = *N,N*-propylenebis(salicylideneimine)]. Besides the formation of heteronuclear compounds, metal substitution has been observed for transition metal complexes of salen and related ligands: Co was replaced by Cu in [Co(salen)],[25] while Ni substituted Cu in [Cu(amben)] [$H_2$amben = *N,N′*-ethylenebis(2-aminobenzaldimine)].[26]




Here we report on the reaction of $[Zn(HL^1)(H_2O)_2]$, $[ZnL^2(H_2O)]$ and $[ZnL^4(H_2O)]$ with $Mg^{2+}$, leading to the conversion of the Zn complexes into the corresponding Mg compounds. The crystal structures of $[MgL^3(H_2O)_3]$,

[a] Fachbereich Chemie der Universität Dortmund,
Otto-Hahn-Straße 6, 44221 Dortmund, Germany
Fax: (internat.) + 49-(0)231/755−3797
E-mail: aerx@platon.chemie.uni-dortmund.de

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$[MgL^2(H_2O)_2]_n$, $[Mg(sal)_2(H_2O)_2]$ (Hsal = salicylaldehyde) and $[MgL^4(H_2O)(CH_3OH)]$ are presented.

## Results and Discussion

### Reaction of $[Zn(HL^1)(H_2O)_2]$ and $[ZnL^2(H_2O)]$ with $Mg^{2+}$

Metal complexes of Schiff bases are generally easily accessible in high yields in a one-step synthesis, by condensation of an aldehyde with an amine in the presence of the metal ion. Despite the well-known susceptibility of imine bonds to hydrolysis, metal complexes of Schiff bases are usually resistant towards hydrolytic cleavage, and as a result the syntheses can be carried out in aqueous solutions.[27] Reaction of 3-formylsalicylic acid with glycine and $Zn(CH_3CO_2)_2$ in ethanol/water gave a pale yellow precipitate of $[Zn(HL^1)(H_2O)_2]$ (**1**). Formation of the Schiff base complex is seen by the $^1H$ NMR spectrum displaying a singlet for the azomethine proton at $\delta = 8.49$. In the infrared spectrum characteristic bands at 1653 and 1617 $cm^{-1}$ which are assigned to CO and C=N vibrations are observed. In analogy to compound **4** (see below), the polydentate ligand is assumed to coordinate to Zn via the deprotonated phenolic oxygen, the imine nitrogen and the aliphatic carboxylate group. The aromatic carboxyl group is protonated and not coordinated, as deduced from the $^1H$ NMR spectrum featuring a sharp resonance at $\delta = 16.11$. The assignment of the aromatic carboxyl proton was confirmed by an HMBC experiment that indicated coupling between the proton and the ring carbon C2 at $\delta = 170.0$. Since **1** is only sparingly soluble in most common solvents, attempts to crystallize this compound were unsuccessful.

Complex **1** is potentially suitable to bind a second metal ion through the aromatic carboxyl group and the (bridging) phenolate oxygen. It was reacted with $MgCl_2 \cdot 6H_2O$ in DMSO and the reaction was monitored by $^1H$ NMR spectroscopy (Figure 1). On addition of increasing amounts of $MgCl_2$ new singlets appear at $\delta = 16.97$ and $\delta = 8.25$. By comparison with a genuine sample prepared by the reaction of 3-formylsalicylic acid with glycine and $Mg(CH_3CO_2)_2$, the new resonances can be assigned to the azomethine and carboxyl protons of the mononuclear magnesium complex of $H_3L^1$ (**2**).[28] Conversion of **1** into **2** is complete after addition of two equivalents $Mg^{2+}$. As in the case of **1**, crystallization of **2** is hampered by its low solubility, however, coordination through the chelating ligand side-arm and protonation of the aromatic carboxyl group is consistent with the NMR spectroscopic data and the X-ray structures of the related Mg compounds **4** and **5** (see below).

Metal ion exchange is also observed for the Zn complex of $H_2L^2$, **3**. Addition of one equivalent $Mg^{2+}$ leads to ca. 30% conversion of **3** into the corresponding Mg compound.

The reaction of **1** and **3** with $MgCl_2 \cdot 6H_2O$ deserves some further comments. Obviously, in DMSO $Mg^{2+}$ competes efficiently with $Zn^{2+}$ for the binding sites of the chelate ligand. Mg coordination is probably supported by the use of a nonaqueous reaction medium. The dielectric properties of the solvent are known to have a crucial influence on the coordination behavior of metal ions. Recently, the dependence of water-(monodentate)ligand exchange reactions of Mg complexes on the dielectric constant has been studied theoretically by Lim and co-workers.[29] They demonstrated that water-carboxylate exchange can take place in media with a low ε, while it is thermodynamically unfavorable in aqueous solutions. In general, the basicity of negatively charged oxygen donors increases significantly with decreasing solvent polarity.[30] Consequently, $M^{2+}/O^-$ binding is stabilized in a medium with a low dielectric constant. Unfortunately, the low solubilities of **1** and **3** prevent studies in other solvents (for the effect of small amounts of water added to the DMSO solution, see below).

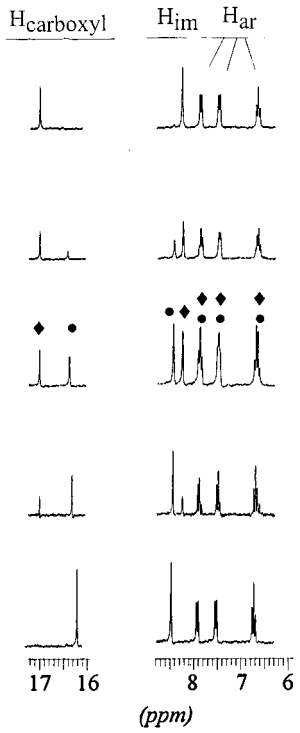


Figure 1. Reaction of **1** with $Mg^{2+}$ in [D$_6$]DMSO. Proton NMR spectra ($\delta = 6-9$ and $\delta = 16-17$) of **1** (bottom) and after addition of 0.7, 1.0, 1.3 and 2.0 equiv. of $MgCl_2$ (top). **1** (•), **2** (◆).

### Solid-State Structures of $[MgL^3(H_2O)_3]$, $[MgL^2(H_2O)_2]_n$ and $[Mg(sal)_2(H_2O)_2]$

Tridentate coordination of the Schiff base ligand via the deprotonated phenolic oxygen, the aliphatic carboxylate group and the imine nitrogen has been verified by X-ray crystallography for the magnesium complexes $[MgL^3(H_2O)_3]$ (**4**) and $[MgL^2(H_2O)_2]_n$ (**5**). A perspective view of the complex molecule of **4** is displayed in Figure 2, selected bond lengths and angles are listed in Table 1. Due to the narrow bite of the chelating Schiff base ligand, Mg assumes a distorted octahedral coordination geometry with the angles around Mg ranging from 76.7 to 98.9°. The bond lengths are normal, Mg−O(water) distances compare well with those found in other Mg aqua complexes. The ligand deviates significantly from the planar conformation that might be expected, the aromatic ring is inclined at 20.61(5)°

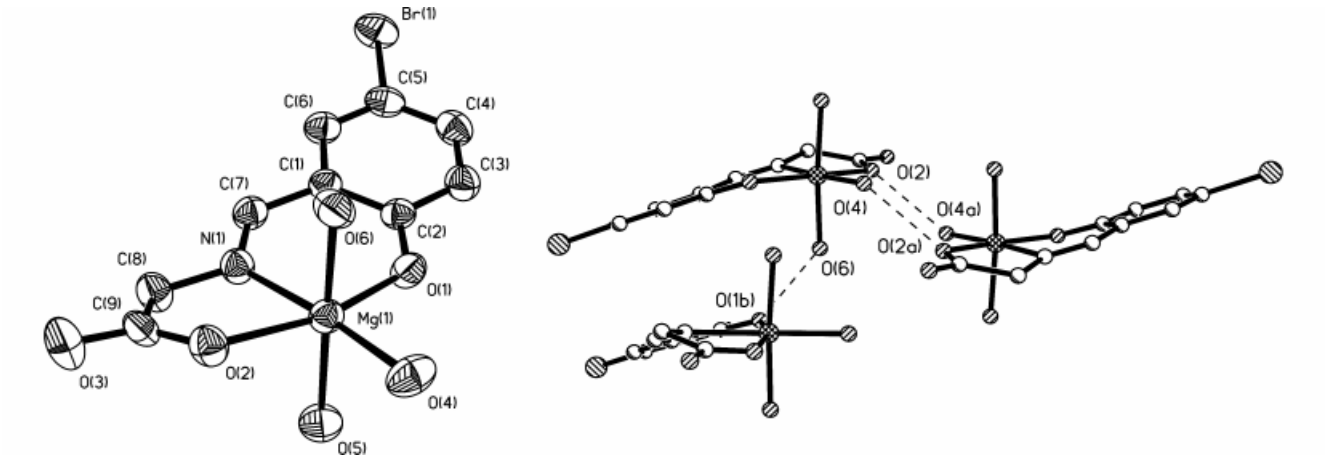


Figure 2. Molecular structure of **4** and details of intermolecular H-bonding interactions. Hydrogen atoms are omitted for clarity.

Table 1. Bond lengths [Å], angles [°] and hydrogen-bonding interactions [Å] in **4**

| | | | |
|---|---|---|---|
| Mg(1)−N(1) | 2.127(2) | Mg(1)−O(1) | 2.018(2) |
| Mg(1)−O(2) | 2.103(2) | Mg(1)−O(4) | 2.032(2) |
| Mg(1)−O(5) | 2.108(2) | Mg(1)−O(6) | 2.080(2) |
| N(1)−Mg(1)−O(1) | 86.79(9) | N(1)−Mg(1)−O(2) | 76.71(8) |
| O(1)−Mg(1)−O(2) | 163.22(9) | O(1)−Mg(1)−O(4) | 98.92(9) |
| O(1)−Mg(1)−O(5) | 93.43(9) | O(2)−Mg(1)−O(4) | 97.64(9) |
| O(2)−Mg(1)−O(6) | 87.83(8) | O(5)−Mg(1)−O(6) | 174.87(9) |
| O(1)···O(5)[a] | 2.937(3) | O(1)···O(6)[b] | 2.721(3) |
| O(2)···O(4)[c] | 2.777(3) | O(3)···O(4)[d] | 2.971(3) |
| O(3)···O(5)[e] | 2.954(3) | O(3)···O(6)[f] | 2.786(3) |

[a] $x, -y + 1/2, z + 1/2$. − [b] $x, -y + 1/2, z - 1/2$. − [c] $-x - 1, -y + 1, -z$. − [d] $-x - 1, y + 1/2, -z - 1/2$. − [e] $x, -y + 1/2 + 1, z + 1/2$. − [f] $x, -y + 1/2 + 1, z - 1/2$.

to the plane defined by the three donor atoms. In the crystal lattice two molecules dimerize via two hydrogen bonds involving the coordinating carboxylate oxygens O(2) and the aqua ligands O(4).

Adjacent dimers form stacks along the crystallographic z-axis that are stabilized by hydrogen-bonding interactions between the phenolate oxygen and the aqua ligands O(5) and O(6). The metal ions are indirectly bridged through the phenolate oxygen as H-bonding takes place between O(1) and the Mg-bound water molecules. Further H bonding occurs between the carboxylate oxygen O(3) and the water ligands O(4), (O5) and O(6).

In contrast to **4**, the Mg complex derived from the related ligand $H_2L^2$ is polymeric in the solid state. Figure 3 gives a view of the X-ray structure of $[MgL^2(H_2O)_2]_n$ (**5**), selected bond lengths, angles and hydrogen-bonding interactions are summarized in Table 2. The asymmetric unit comprises the Schiff base ligand that is bonded to Mg via the three donor sites and the two aqua ligands. Adjacent $MgL^2(H_2O)_2$ entities are linked through carboxylate bridges in a *syn-anti* fashion forming infinite chains extending in the z-direction. The C(9)−O(2) [1.264(3) Å] and C(9)−O(3) [1.256(3) Å] distances indicate full delocalization of the carboxylate negative charge. The Mg(1)−O(2) and Mg(1)−O(3) bond lengths differ only slightly [2.120(2) and 2.085(2) Å]. Again, the phenolic oxygen is involved in hydrogen-bonding interactions. Neighboring chains are connected through hydrogen bonds involving the aqua ligand O(5) and the phenolate oxygen O(1), as well as the carboxylate oxygens O(2) and O(3).

The X-ray structure of the bis(salicylaldehydato) complex $[Mg(sal)_2(H_2O)_2]$, **6**, is depicted in Figure 4. This complex was obtained as a by-product during the synthesis of **5**. As pointed out above, Schiff base formation is generally quantitative and the coordination of metal ions renders imine bonds resistant towards hydrolytic cleavage. Thus, in the case of the Zn complexes dissociation to the aldehyde and amine due to the presence of water was not observed. However, as for Mg, slow decomposition of the complex during crystallization results in hydrolysis of the ligand and the formation of the aldehyde complex. In the centrosymmetric molecule of **6**, the deprotonated salicylaldehydes act as chelating, bidentate ligands, and two water molecules complete the octahedral coordination sphere around the Mg atom. Salicylaldehyde and the metal ion are located on a mirror plane and the Mg−O(water) bond coincides with a crystallographic twofold axis of symmetry. Thus, except for O(1)−Mg(1)−O(2) and O(1)−Mg(1)−O(2a), ideal 90° values are observed for the valence angles around Mg. Due to the chelating coordination mode of the ligand, the O(1)−C(7)−C(1) bond angle involving the aldehyde carbon increases to 128.1(7)°. In the crystal lattice the neutral complex molecules form layers parallel to the crystallographic ac plane. Adjacent layers are linked through hydrogen bonds involving the water ligands, as well as the carbonyl and phenolate oxygens (Table 3). Thus, again the deprotonated phenolic oxygen acts as an H bond acceptor. The structure of **6** is in contrast with that of $[Mg(salicylate)_2(H_2O)_4]$ and [Mg(*p*-aminosalicylate)$(H_2O)_4$] reported in the literature.[18,19] In the latter complexes the salicylate ligands act as monodentate O-donors and bind to the Mg atom through one carboxylate oxygen, while the phenolic groups are protonated and do not take part in the coordination.

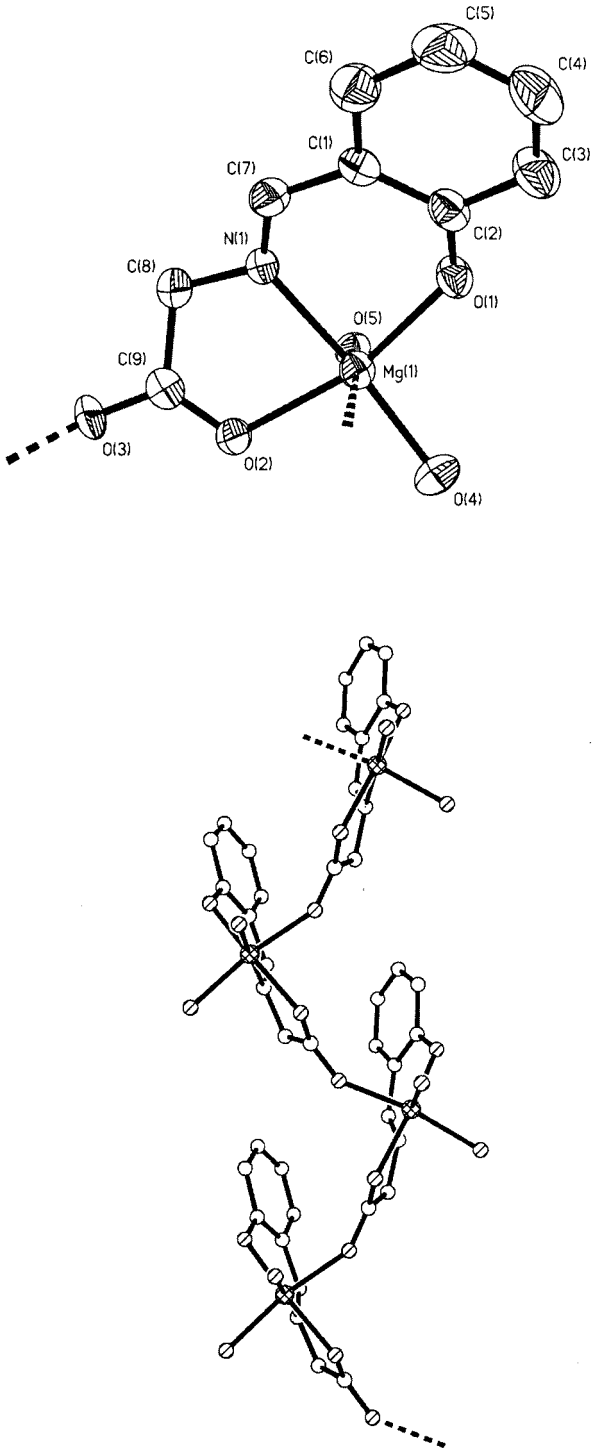


Figure 3. Asymmetric unit of the crystal structure of **5** with the atom numbering scheme and a section of the polymer. Hydrogen atoms are omitted for clarity.

Table 2. Bond lengths [Å], angles [°] and hydrogen-bonding interactions [Å] in **5**

| | | | |
|---|---|---|---|
| Mg(1)−N(1) | 2.105(2) | Mg(1)−O(1) | 2.017(2) |
| Mg(1)−O(2) | 2.120(2) | Mg(1)−O(4) | 2.024(2) |
| Mg(1)−O(5) | 2.159(2) | Mg(1)−O(3) [a] | 2.085(2) |
| N(1)−Mg(1)−O(1) | 86.18(8) | N(1)−Mg(1)−O(2) | 77.30(8) |
| O(1)−Mg(1)−O(2) | 162.84(8) | O(1)−Mg(1)−O(4) | 98.85(8) |
| O(1)−Mg(1)−O(5) | 100.23(8) | O(2)−Mg(1)−O(4) | 97.69(8) |
| O(2)−Mg(1)−O(3)[a] | 83.60(7) | O(3)−Mg(1)−O(5)[a] | 166.40(8) |
| O(1)···O(5)[b] | 2.716(2) | O(2)···O(4)[c] | 3.089(3) |
| O(2)···O(5)[d] | 2.789(3) | O(3)···O(4)[d] | 2.798(3) |
| O(3)···O(4)[e] | 2.846(3) | O(4)···O(5)[c] | 2.815(3) |

[a] $x, -y - 1/2, z - 1/2$. − [b] $x, -y + 1/2, z - 1/2$. − [c] $-x, y - 1/2, -z + 1/2$. − [d] $-x, -y, -z + 1$. − [e] $x, -y - 1/2, z + 1/2$.

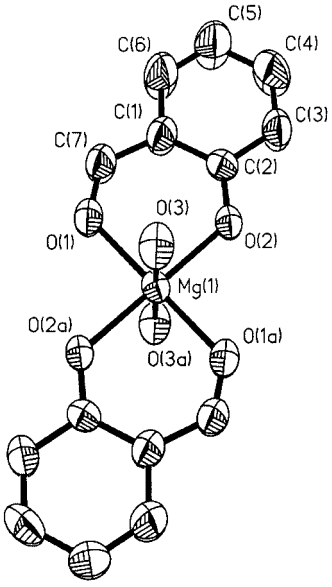


Figure 4. Molecular structure of **6**. Hydrogen atoms are omitted for clarity.

Table 3. Bond lengths [Å], angles [°] and hydrogen-bonding interactions [Å] in **6**

| | | | |
|---|---|---|---|
| Mg(1)−O(1) | 2.044(5) | Mg(1)−O(2) | 2.049(4) |
| Mg(1)−O(3) | 2.056(5) | | |
| O(1)−Mg(1)−O(2) | 89.0(2) | O(1)−Mg(1)−O(2)[a] | 91.0(2) |
| O(1)···O(3)[a] | 2.899(5) | O(2)···O(3)[a] | 2.903(4) |
| O(2)···O(3)[b] | 2.830(4) | | |

[a] $-x - 1, -y, -z$. − [b] $-x - 1/2 - 1, -y + 1/2, -z$.

### Substitution of $Zn^{2+}$ by $Mg^{2+}$ in a Salen-Type Complex

As outlined in the introduction, metal ion exchange and the formation of adducts are observed when first row transition metal complexes of salen are treated with hetero metals. The Zn[31] and Mg[32] complexes of salen have been known for a long time, however, no studies on the formation of adducts, or metal ion substitution have been carried out. We have used the mononuclear Zn complex of the salen derivative $H_2L^4$, $[ZnL^4(H_2O)]$,[33] **7**, and investigated its reaction with $Mg^{2+}$. In principle, **7** provides an $O_4$ coordination site to bind Mg to form a heteronuclear complex. As evident from the solid-state structure of **6**, chelation through the phenolate and aldehyde oxygens is a possible binding mode. However, in the $^1H$ NMR spectrum (Fig-

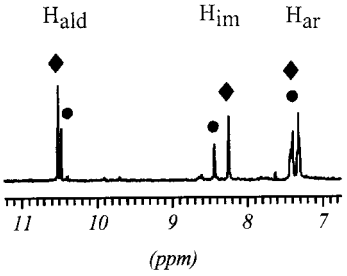


Figure 5. $^1$H NMR spectrum ($\delta$ = 7−11) of **7** in [$D_6$]DMSO after addition of 2 equiv. of $MgCl_2$. **7** (•), **8** (◆). Peaks of very low intensity at $\delta$ = 10.39, 9.90, 9.70, 8.61 and $\delta$ = 7.63 result from hydrolysis of the imine ligand due to traces of water.

ure 5), the new set of signals that emerges after the addition of $MgCl_2 \cdot 6H_2O$ to a solution of **7** in DMSO is unambiguously assigned to the Mg complex [$MgL^4$] (**8**), resulting from metal ion exchange as found for complexes **1** and **3**. Complex **8** was identified by preparation of a genuine sample from $H_2L^4$ and $MgCl_2$. When two equivalents of $MgCl_2$ are added, approximately 62% of **7** is converted into **8**. Small amounts of water shift the equilibrium between **7** and **8** towards the formation of the Zn complex: on addition of 2.5% $D_2O$ to the DMSO solution, the percentage of **8** is halved. The conversion of **8** back into **7** in the presence of water reflects the high affinity of Mg for aqua ligands.

It might be speculated that the substitution reaction proceeds via the heteronuclear Zn,Mg complex as an intermediate, although no evidence for its existence (or lack thereof) is seen from the NMR spectra. It is worth noting that **7** and **8** are nonlabile on the NMR time-scale, since mixtures of the respective complex and the "free" ligand give two distinct sets of resonances. Dissociation to the ligand and solvated metal ions was not observed in the spectra of pure **7** or **8** in DMSO.

The structure of **8** has been determined by single-crystal X-ray analysis. In the solid state the molecules of [$MgL^4(H_2O)(CH_3OH)$] form centrosymmetric dimers via hydrogen-bonding between the water ligand and the phenolic oxygen (Figure 6).

The hydrogen bonds are reinforced by stacking interactions of the aromatic rings (stacking distance ≈ 3.5 Å). As expected, the Schiff base ligand assumes an essentially planar configuration. The dihedral angles between the phenolic rings and the four donor atoms are 8.5(1) and 12.0(1) °. The rigid nature of the chelating ligand causes a significant distortion of the octahedral coordination geometry (range of valence angles around Mg: 78.5−107.9 °). Coordination of $Mg^{2+}$ causes a shift of the $\tilde{\nu}$(C=O) and $\tilde{\nu}$(C=N) IR bands from 1688 and 1645 $cm^{-1}$ [34] to 1655 and 1609 $cm^{-1}$, respectively.

## Conclusions

In conclusion we have demonstrated that in complexes with *N,O* ligands, Zn is susceptible to substitution by $Mg^{2+}$ when DMSO is used as the nonaqueous solvent. The presence of small amounts of water decreases the yield of the Mg complex significantly due to the high affinity of Mg for aqua ligands. The quantity of the Mg complex formed in DMSO is comparable for all ligand systems described here (ca. 30% Mg complex formed on addition of equimolar amounts of $MgCl_2$ to the respective Zn Schiff base complex).

Furthermore we have isolated and structurally characterized three Mg Schiff base complexes, namely [$MgL^4(H_2O)(CH_3OH)$], [$MgL^3(H_2O)_3$], and polymeric [$MgL^2(H_2O)_2]_n$. Schiff bases have been extensively used in transition metal chemistry, while main-group imine complexes are considerably less abundant. The coordination chemistry of alkaline earth metals has generally received far less attention than the coordination chemistry of transition metals. Thus, it is

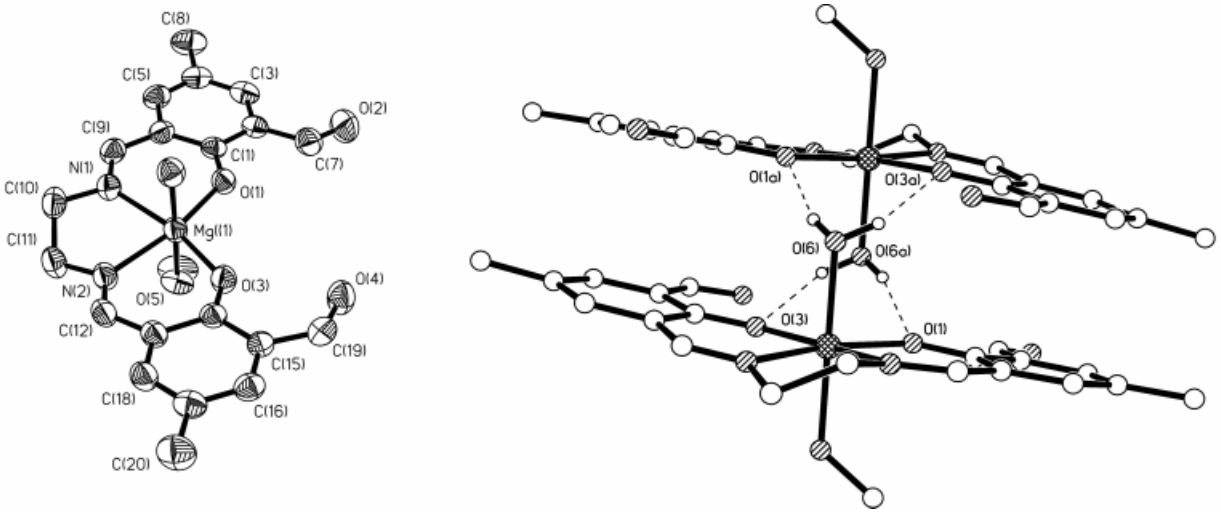


Figure 6. Molecular structure of **8** and arrangement of two molecules with H-bonding interactions indicated. Hydrogen atoms were located in the Fourier-difference map, but for clarity only the hydrogen atoms involved in H-bonding are shown.

our aim to further increase the number of Mg compounds by varying the versatile Schiff base ligands.

## Experimental Section

**Materials and Methods:** 3-Formylsalicylic acid[35] and 2,6-diformyl-4-methylphenol[36] were prepared according to the literature procedures. $H_2L^4$ was prepared by reaction of 2,6-diformyl-4-methylphenol and 1,2-diaminoethane in $CHCl_3$ and subsequent evaporation of the solvent according to a slightly modified literature procedure.[34] All chemicals and solvents were of reagent grade and used without further purification. – $^1$H NMR spectra were recorded on a Varian Mercury spectrometer at 200.13 MHz., the HMBC experiment on a Bruker DRX 400 spectrometer. – Infrared spectra of KBr pellets were measured on a Bruker IFS 28 FT-spectrometer.

**Complex 1:** 3-Formylsalicylic acid (84 mg, 0.51 mmol), glycine (34 mg, 0.45 mmol) and $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (151 mg, 0.69 mmol) were stirred in ethanol/water (1:1, 30 mL) for 3 h. The resulting precipitate was filtered off, washed with ethanol and dried at 40 °C overnight to give $[Zn(HL^1)(H_2O)_2]$, **1** as a yellow powder (98 mg, 0.30 mmol, 68%). – IR (KBr): $\tilde{\nu}$ = 3071, 2925, 1653 (CO), 1617 (C=N), 1566, 1519, 1471, 1399, 1296, 1243, 1097, 1076, 1005, 959 cm$^{-1}$. – $^1$H NMR [$(CD_3)_2SO$]: δ = 3.96 (s, 2 H, $CH_2$), 6.73 (t, $J$ = 7.6 Hz, 1 H, $CH_{arom}$), 7.54 (d, $J$ = 7.8 Hz, 1 H, $CH_{arom}$), 7.93 (d, $J$ = 7.8 Hz, 1 H, $CH_{arom}$), 8.49 (s, 1 H, HC=N), 16.11 (s, 1 H, COOH). – $^{13}$C NMR [$(CD_3)_2SO$]: δ = 59.5 ($CH_2$), 117.6 ($C_{arom}$), 121.6 ($C_{arom}$), 132.4 ($C_{arom}$), 147.3 ($C_{arom}$), 155.0 ($C_{arom}$), 167.7 (C=N), 170.0 ($C_{arom}$), 173.6 (COOH), 177.0 (Ar-COOH). – $C_{10}H_{11}NO_7Zn$ (322.56): calcd. C 37.2, H 3.4, N 4.3; found C 36.8, H 3.5, N 4.3.

Table 4. Bond lengths [Å], angles [°] and hydrogen-bonding interactions [Å] in **8**

| | | | |
|---|---|---|---|
| Mg(1)–N(1) | 2.140(2) | Mg(1)–N(2) | 2.137(2) |
| Mg(1)–O(1) | 1.979(1) | Mg(1)–O(3) | 1.985(1) |
| Mg(1)–O(5) | 2.147(2) | Mg(1)–O(6) | 2.141(2) |
| N(1)–Mg(1)–O(1) | 87.35(6) | N(1)–Mg(1)–N(2) | 78.50(6) |
| O(1)–Mg(1)–O(3) | 107.89(5) | O(1)–Mg(1)–N(2) | 165.22(6) |
| O(1)–Mg(1)–O(5) | 89.90(6) | O(3)–Mg(1)–O(5) | 91.94(6) |
| O(3)–Mg(1)–O(6) | 89.06(6) | O(5)–Mg(1)–O(6) | 178.47(6) |
| O(1)···O(6)[a] | 2.788(2) | O(3)···O(6)[a] | 3.057(2) |
| O(4)···O(5)[b] | 2.721(2) | O(4)···O(6)[a] | 2.939(2) |

[a] $-x, -y + 1, -z$. – [b] $x, -y + 1/2 + 1, z - 1/2$.

**Complex 2:** 3-Formylsalicylic acid (83 mg, 0.50 mmol), glycine (38 mg, 0.51 mmol), $Mg(CH_3CO_2)_2{\cdot}4H_2O$ (107 mg, 0.50 mmol) and KOH (56 mg, 1.00 mmol) were reacted in ethanol/water (5:1, 30 mL). After 3 days a yellow precipitate of $[Mg(HL^1)(H_2O)_2]$, **2**, was filtered off, washed with ethanol and dried at 40 °C overnight (65 mg, 0.23 mmol, 46%). – IR (KBr): $\tilde{\nu}$ = 3395, 1659 (CO), 1613 (C=N), 1546, 1495, 1464, 1436, 1401, 1314, 1220, 1154 cm$^{-1}$. – $C_{10}H_{11}NO_7Mg$ (281.47): calcd. C 42.7, H 3.9, N 5.0; found C 42.3, H 3.8, N 4.9.

**Complex 3:** Salicylaldehyde (117 mg, 0.96 mmol), sodium glycinate hydrate (111 mg, 0.97 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (900 mg, 3.03 mmol) were reacted in methanol (20 mL) for 6 h at room temperature and afforded a pale yellow precipitate of composition $ZnL^2{\cdot}1.5H_2O$, **3** (116 mg, 0.43 mmol, 45%). – IR (KBr): $\tilde{\nu}$ = 3277, 3064, 2909, 1654 (CO), 1611 (C=N), 1581, 1476, 1405, 1282, 1197, 1158, 1076, 1040, 796, 767 cm$^{-1}$. – $^1$H NMR [$(CD_3)_2SO$]: δ = 3.88 (s, 2 H, $CH_2$), 6.41 (t, $J$ = 7.2 Hz, 1 H, $CH_{arom}$), 6.59 (d, $J$ = 8.5 Hz, 1 H, $CH_{arom}$), 7.12 (t, $J$ = 7.2 Hz, 2 H, $CH_{arom}$), 8.34 (s, 1 H, HC=N). – $C_9H_{10}NO_{4.5}Zn$ (269.57): calcd. C 40.1, H 3.7, N 5.2; found C 40.0, H 3.5, N 5.1.

**Complex 4:** 5-Bromosalicylaldehyde (201 mg, 1.00 mmol), sodium glycinate hydrate (115 mg, 1.00 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (769 mg, 3.00 mmol) were stirred in methanol (20 mL) for 3 h. Addition of water (10 mL) yielded a yellow precipitate that was filtered off and washed with $Et_2O$. Recrystallization from methanol/water (4:1, 50 mL) gave pale yellow needles of $[MgL^3(H_2O)_3]$, **4** (140 mg, 0.42 mmol, 42%). – IR (KBr): $\tilde{\nu}$ = 3410, 2911, 1657 (CO), 1607 (C=N), 1532, 1469, 1395, 1381, 1285, 1174 cm$^{-1}$. – $^1$H NMR [$(CD_3)_2SO$]: δ = 3.79 (s, 2 H, $CH_2$), 6.34 (d, $J$ = 8.9 Hz, 1 H, $CH_{arom}$), 7.05 (d, $J$ = 8.9 Hz, 1 H, $CH_{arom}$), 7.17 (s, 1 H, $CH_{arom}$), 8.01 (s, 1 H, HC=N). – $C_9H_{12}BrMgNO_6$ (334.41): calcd. C 32.3, H 3.6, N 4.2; found C 32.3, H 3.7, N 4.1.

Table 5. Crystallographic data for **4**, **5**, **6** and **8**

| | **4** | **5** | **6** | **8** |
|---|---|---|---|---|
| Empirical formula | $C_9H_{12}BrMgNO_6$ | $C_9H_{11}MgNO_5$ | $C_{14}H_{14}MgO_6$ | $C_{21}H_{24}MgN_2O_6$ |
| Molecular mass | 334.42 | 237.50 | 302.56 | 424.73 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $C2/m$ | $P2_1/c$ |
| $a$ [Å] | 16.755(1) | 15.465(1) | 7.379(1) | 12.905(3) |
| $b$ [Å] | 9.844(1) | 7.543(1) | 7.400(1) | 13.574(3) |
| $c$ [Å] | 7.681(1) | 9.148(1) | 13.017(1) | 12.880(3) |
| β [°] | 97.43(1) | 106.24(1) | 90.95(1) | 112.95(3) |
| $V$ [Å$^3$] | 1256.2(2) | 1024.6(2) | 710.7(2) | 2077.6(8) |
| $Z$ | 4 | 4 | 2 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.768 | 1.540 | 1.414 | 1.358 |
| Measured reflections | 5289 | 1858 | 1042 | 5367 |
| Independent reflections | 3070 | 1858 | 636 | 5367 |
| Observed reflections [$I > 2\sigma(I)$] | 2020 | 948 | 464 | 2621 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.038 | 0.039 | 0.082 | 0.043 |
| $wR_2$ [$I > 2\sigma(I)$][b] | 0.108 | 0.071 | 0.227 | 0.089 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. – [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2$; $P = (F_o^2 + 2F_c^2)/3$ with $a$ = 0.0783 for **4**, 0.0393 for **5**, 0.1297 for **6** and 0.0522 for **8**.

**Complex 5: 5** was prepared in an analogous manner to **4** from salicylaldehyde (117 mg, 0.96 mmol), sodium glycinate hydrate (111 mg, 0.97 mmol) and $Mg(NO_3)_2 \cdot 6H_2O$ (735 mg, 2.87 mmol). yield: 53%. X-ray suitable crystals of $[MgL^2(H_2O)_2]_n$ (**5**) were obtained by recrystallization from methanol. − IR (KBr): $\tilde{\nu}$ = 3383, 1658 (CO), 1574, 1539, 1471, 1452, 1406, 1334, 1298, 1193 $cm^{-1}$. − $^1H$ NMR [$(CD_3)_2SO$]: δ = 3.84 (s, 2 H, $CH_2$), 6.28 (t, $J$ = 7.2 Hz, 1 H, $CH_{arom}$), 6.46 (d, $J$ = 8.5 Hz, 1 H, $CH_{arom}$), 7.04 (t, $J$ = 7.1 Hz, 2 H, $CH_{arom}$), 8.08 (s, 1 H, HC=N). − $C_9H_{11}MgNO_5$ (237.50): calcd. C 45.5, H 4.7, N 5.9; found C 45.8, H 4.7, N 5.9.

**Complex 6:** Salicylaldehyde (351 mg, 2.88 mmol), sodium glycinate hydrate (333 mg, 2.89 mmol) and $Mg(NO_3)_2 \cdot 6H_2O$ (2.20 g, 8.58 mmol) were stirred in methanol (36 mL) overnight. The solution was evaporated to dryness and complex **5** was extracted with water. The residue was dissolved in methanol. After a few days microcrystals of $[Mg(sal)_2(H_2O)_2] \cdot 0.5H_2O$, **6**·$0.5H_2O$ formed (82 mg, 0.26 mmol, 18%). − IR (KBr): $\tilde{\nu}$ = 3455, 2887, 2795, 1661 (CO), 1606 (ring), 1531, 1449, 1333, 1201, 1179, 1152, 1124 $cm^{-1}$. − $^1H$ NMR [$(CD_3)_2SO$]: δ = 6.34 (t, br, 1 H, $CH_{arom}$), 7.26 (t, br, 2 H, $CH_{arom}$), 7.45 (d, $J$ = 8.5 Hz, 1 H, $CH_{arom}$), 9.19 (s, 1 H, HC=O). − $C_{14}H_{15}MgO_{6.5}$ (311.58): calcd. C 53.9, H 4.9; found C 53.7, H 4.7.

Recrystallization from methanol yielded pale yellow needles of $[Mg(sal)_2(H_2O)_2]$, **6** suitable for X-ray analysis.

**Complex 7:**[33] $H_2L^4$ (215 mg, 0.61 mmol), $NaOCH_3$ (66 mg, 1.22 mmol) and $ZnCl_2$ (83 mg, 0.61 mmol) were stirred in methanol (20 mL) at room temperature. After 10 min unchanged $H_2L^4$ was filtered off. Addition of water resulted in the precipitation of $[ZnL^4(H_2O)]$, **7** (110 mg, 0.25 mmol, 41%). − IR (KBr): $\tilde{\nu}$ = 3262, 2921, 1664 (CO), 1609 (C=N), 1532, 1449, 1389, 1231, 1029 $cm^{-1}$. − $^1H$ NMR [$(CD_3)_2SO$]: δ = 2.22 (s, 6 H, $CH_3$), 3.81 (s, 4 H, $CH_2$), 7.39 (s, 2 H, $CH_{arom}$), 7.48 (s, 2 H, $CH_{arom}$), 8.53 (s, 2 H, HC=N), 10.55 (s, 2 H, HC=O). − $C_{20}H_{20}N_2O_5Zn$ (433.78): calcd. C 55.4, H 4.7, N 6.5; found C 55.0, H 4.7, N 6.5.

**Complex 8: 8** was prepared in an analogous manner to **7** from $H_2L^4$ (554 mg, 1.55 mmol), $NaOCH_3$ (168 mg, 3.11 mmol) and $MgCl_2 \cdot 6H_2O$ (315 mg, 1.55 mmol) in a 69% yield. Recrystallization from methanol afforded orange-yellow cubes of $[MgL^4(H_2O)(CH_3OH)]$ suitable for X-ray analysis. − IR (KBr): $\tilde{\nu}$ = 3438, 2900, 1655 (CO), 1609 (C=N), 1539, 1522, 1463, 1386, 1231, 1032 $cm^{-1}$. − $^1H$ NMR [$(CD_3)_2SO$]: δ = 2.19 (s, 6 H, $CH_3$), 3.70 (s, 4 H, $CH_2$), 7.32 (s, 2 H, $CH_{arom}$), 7.41 (s, 2 H, $CH_{arom}$), 8.26 (s, 2 H, HC=N), 10.53 (s, 2 H, HC=O). − $C_{21}H_{24}MgN_2O_6$ (424.74): C 59.3, H 5.7, N 6.6; found C 58.9, H 5.8, N 6.5.

**Metal Ion Substitution:** Solutions of **7** (10 mM), **1** and **3** (2 mM due to lower solubility) in $(CD_3)_2SO$ were treated with aliquots of a solution of $MgCl_2 \cdot 6H_2O$. NMR spectra were run 10 to 30 minutes after addition of $MgCl_2$. For a representative sample no change of the spectrum was observed over 24 h.

**X-ray Crystallography:** Crystal data for compounds **4, 5, 6** and **8** were collected at room temperature on an Enraf−Nonius-KappaCCD diffractometer[37] using graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.71069 Å). For data reduction and cell refinement the programs DENZO and SCALEPACK were used.[38] The structures were solved by conventional Patterson (**4**) or direct (**5**, **6** and **8**) methods and subsequent Fourier syntheses, and refined by full-matrix least-squares on $F^2$ using the SHELXTL PLUS and SHELXL-93 programs.[39] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of **4**, **5**, and **8** were located in the final Fourier-difference maps (except for those of the aqua ligands in **4**) and refined isotropically. For **6** carbon-bound hydrogen atoms were placed at calculated positions and given fixed isotropic temperature factors. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161094 (**4**), -161095 (**5**), -161096 (**6**) and 161097 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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