Anion-Dependent Substitution of Zinc by Magnesium in Mononuclear Schiff Base Complexes

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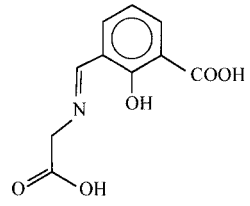
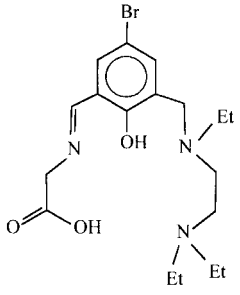
The zinc and magnesium Schiff-base complexes $[ZnL(H_2O)(NO_3)]NO_3$ (**1**) and $[MgL(H_2O)_3](NO_3)_2{\cdot}H_2O$ (**2**) (L = Schiff base derived from 4-bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol and glycine) have been prepared and structurally characterized. The reaction of **1** with Mg^{2+} has been studied in water, methanol and DMSO. Substitution of Zn by Mg^{2+} was observed in DMSO and methanol and the amount of Mg complex formed was found to be strongly dependent on the nature and concentration of the anions in solution: Cl^- and $CH_3CO_2^-$ mediate conversion of **1** into **2**, while ClO_4^-, NO_3^-, F^-, Br^-, I^- and SO_4^{2-} are ineffective.

Introduction

In previous papers we outlined our interest in Mg coordination chemistry.[1,2] Mg is an essential cofactor in biology, yet, compared with other biologically relevant metal ions, its coordination chemistry has received little attention.[3−10] Recently, we have studied the reaction of mononuclear Zn complexes derived from binucleating Schiff-base ligands like L′ with $MgCl_2$ and observed substitution of Zn by Mg in DMSO, which appeared to contradict the order of stability predicted by the Irving−Williams series.[11] However, the low solubility of the compounds prevented more detailed studies, for example, the use of different solvents. Furthermore, only $MgCl_2$ was used as the Mg salt, and salts with other anions were not considered. We have now studied the Schiff-base ligand derived from 4-bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol and glycine (L) that forms the mononuclear Zn complex $[ZnL(H_2O)(NO_3)]NO_3$ (**1**) with Zn binding to the glycine side arm, while the protonated ammonium nitrogens render the complex soluble. Besides the effect of the solvent we have also investigated the reaction of **1** with different Mg salts and found that the metal ion exchange is strongly dependent on the anions present in solution.



L'



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Results and Discussion

Synthesis and Characterisation of $[ZnL(H_2O)(NO_3)]NO_3$ (1) and $[MgL(H_2O)_3](NO_3)_2{\cdot}H_2O$ (2)

The zinc complex $[ZnL(H_2O)(NO_3)]NO_3$ (**1**) was prepared in situ by Schiff base condensation of 4-bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol with glycine in the presence of $Zn(NO_3)_2{\cdot}6H_2O$. X-ray suitable crystals were obtained from methanol/water at pH 5.4. As shown in Figure 1, the ligand coordinates to zinc in a tridentate manner through the deprotonated phenolic oxygen,

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the carboxylate group and the imine nitrogen. The amine nitrogens are both protonated and remain uncoordinated. The coordination sphere of Zn is completed by a water molecule and a nitrate ion that binds in an asymmetric chelating mode [Zn(1)−O(4) 2.470(9) Å, Zn(1)−O(5) 2.076(6) Å]. In the crystal packing hydrogen bonding interactions occur that involve the aqua ligand, the carboxylate and nitrate oxygens as well as the ammonium nitrogens (Table 1).

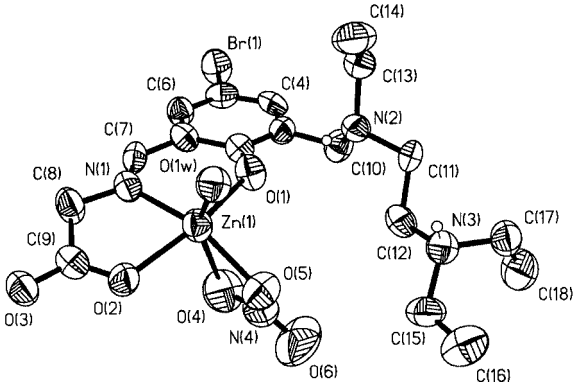

Figure 1. View of the cation of $[ZnL(H_2O)(NO_3)]NO_3$ (**1**) with atom numbering scheme; except for the ammonium protons, hydrogen atoms are omitted for clarity

Table 1. Selected bond lengths (Å), angles (°) and hydrogen bonding interactions (Å) for **1**

Zn(1)−N(1)	2.091(7)	Zn(1)−O(1)	2.017(6)
Zn(1)−O(2)	2.108(6)	Zn(1)−O(4)	2.470(9)
Zn(1)−O(5)	2.076(6)	Zn(1)−O(1w)	2.035(6)
N(1)−Zn(1)−O(1)	89.2(3)	N(1)−Zn(1)−O(2)	77.5(3)
N(1)−Zn(1)−O(1w)	110.3(3)	N(1)−Zn(1)−O(5)	152.7(3)
O(1)−Zn(1)−O(2)	165.5(2)	O(1)−Zn(1)−O(1w)	94.0(2)
O(1w)−Zn(1)−O(4)	151.5(3)	O(5)−Zn(1)−O(4)	55.4(3)
O(1w)···O(3)[a]	2.675(8)	O(1w)···O(7)[a]	2.71(1)
N(2)···O(3)[b]	3.17(1)	N(3)···O(2)[b]	2.779(9)

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

As described below the reaction of **1** with Mg^{2+} leading to the conversion of the Zn complex into the Mg complex of L was studied in solution by NMR spectroscopy; for an unambiguous assignment of the NMR resonances the Mg complex was prepared on a preparative scale. Reaction of 4-bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol with sodium glycinate in the presence of $Mg(NO_3)_2{\cdot}6H_2O$ and NaOH yielded the Schiff-base complex of composition $[MgL(H_2O)_3](NO_3)_2{\cdot}H_2O$ (**2**), the X-ray structure of which is depicted in Figure 2. Mg binds to the phenolate oxygen, one carboxylate oxygen and the imine nitrogen and to three water ligands. Again, both amine nitrogens are protonated and noncoordinating. Due to the narrow bite angle of the chelating ligand, Mg adopts a distorted octahedral coordination geometry with the angles around Mg ranging from 76.7 to 100.0° (Table 2).

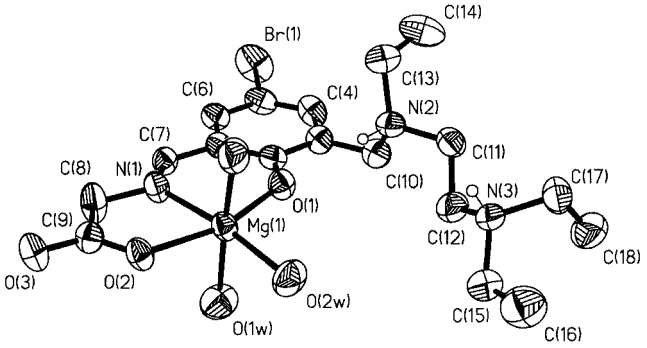

Figure 2. View of the cation of $[MgL(H_2O)_3](NO_3)_2{\cdot}H_2O$ (**2**) with atom numbering scheme; except for the ammonium protons, hydrogen atoms are omitted for clarity

Table 2. Selected bond lengths (Å) and angles (°) for **2**

Mg(1)−N(1)	2.144(5)	Mg(1)−O(1)	2.007(5)
Mg(1)−O(2)	2.120(4)	Mg(1)−O(1w)	2.119(5)
Mg(1)−O(2w)	2.068(4)	Mg(1)−O(3w)	2.046(5)
N(1)−Mg(1)−O(1)	86.3(2)	N(1)−Mg(1)−O(2)	76.7(2)
N(1)−Mg(1)−O(1w)	87.8(2)	N(1)−Mg(1)−O(2w)	172.4(2)
N(1)−Mg(1)−O(3w)	98.9(2)	O(1)−Mg(1)−O(2)	162.3(2)
O(1)−Mg(1)−O(1w)	93.6(2)	O(2)−Mg(1)−O(3w)	87.2(2)
O(1w)−Mg(1)−O(3w)	172.2(2)		

Solution Studies

Mg^{2+} shows a strong tendency to bind six water molecules in its inner coordination sphere so that in aqueous solution no reaction of **1** with Mg salts was observed. Consequently it was not unexpected that addition of one equivalent of $Zn(NO_3)_2$ to a solution of **2** in D_2O (pD 9.7) resulted in complete conversion into **1**. Even in the presence of 10 equivalents of $MgCl_2$ (for the choice of Cl^- ions see below) the percentage of **2** is less than 5%. We note that there is no indication for metal binding to the second coordination site of the ligand even under basic conditions.

By contrast, Zn is replaced by Mg when **1** is treated with $MgCl_2$ in DMSO, as observed before for related Schiff-base ligands.[1,2] Addition of three equivalents of $MgCl_2$ leads to approximately 44% conversion of **1** into **2**. The NMR spectra of the reaction solution reveal no change with time. In MeOD 11 equivalents of $MgCl_2$ are required to give an approximately 1:1 mixture of **1** and **2**. Consequently, the concentration of the Mg complex in DMSO is significantly reduced upon addition of MeOD, as shown in Figure 3. In the presence of 10 and 20% MeOD the percentage of **2** decreases to 33 and 22%, respectively. The effect of D_2O is even more pronounced: Upon addition of 20% D_2O the equilibrium is completely shifted towards the Zn complex. Exchange of Zn with Mg in DMSO can be attributed to the low dielectric constant of DMSO that stabilizes Mg binding to the N,O-ligand.

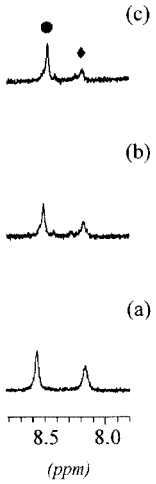

Figure 3. Reaction of **1** with 3 equiv. $MgCl_2$ in [D_6]DMSO solutions containing increasing amounts of MeOD; ^1H NMR spectra (δ = 7.8−8.8 ppm, resonance of the azomethine proton) for (a) 0, (b) 10 and (c) 20% MeOD; (•) $[ZnL]^{2+}$ (◆) $[MgL]^{2+}$

Apart from the effect of the solvent the equilibrium between the Zn and Mg complex is dependent on the anions present in solution. When **1** is treated with $Mg(NO_3)_2$, $Mg(ClO_4)_2$ or $MgSO_4$ instead of $MgCl_2$, no metal-ion substitution is observed in DMSO, while two equivalents of $Mg(CH_3CO_2)_2$ yield 38% of **2**. Addition of NaCl to a 1:1 mixture of **1** and $Mg(ClO_4)_2$ mediates formation of **2**. As shown in Figure 4 the concentration of **2** increases with increasing concentrations of NaCl until ca. 40% of the Mg complex is formed in the presence of 20 equivalents of NaCl.

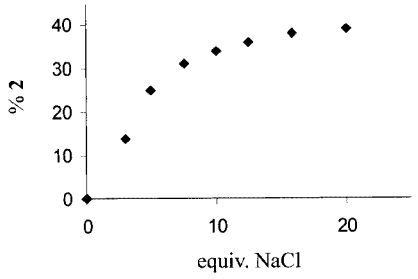

Figure 4. Percentage of **2** upon addition of increasing amounts of NaCl to a 1:1 mixture of **1** and $Mg(ClO_4)_2$ in DMSO

Analogously, addition of $NaCH_3CO_2$ triggers the substitution of Zn by Mg in a 1:1 mixture of $Mg(ClO_4)_2$ and **1**. Acetate is even more effective than Cl^- in promoting replacement of Zn by Mg: Addition of 7.5 equivalents to an equimolar solution of **1** and $Mg(ClO_4)_2$ gives 43% conversion of **1** into **2** in comparison with 31% in the case of Cl^-. Unfortunately, the limited solubility of sodium acetate in DMSO prevents a further increase of the amount of Mg complex formed. No Zn/Mg exchange is observed in the presence of F^-, Br^- and I^- ions. In line with the effect of the anions described so far, Mg is completely substituted by Zn when **2** is treated with one equivalent of $Zn(NO_3)_2$ in the absence of Cl^- or $CH_3CO_2^-$, while treatment of **2** with one equivalent of $Zn(CH_3CO_2)_2$ gives a mixture of 68% **1** and 32% **2**. Elias et al. have studied the replacement of Cu by Ni in [Cu(amben)] [H_2amben = *N,N′*-ethylenebis(2-aminobenzaldimine)].[12] They found a catalytic effect of the anion with the rate of the substitution reaction increasing as follows: $ClO_4^- < Br^- < SCN^- << Cl^-$. In our case, the reaction of **1** with $MgCl_2$ and $Mg(CH_3CO_2)_2$ is fast, the NMR spectra of the reaction mixtures (including those with counterions where no exchange is observed) do not change with time. In other words, the equilibrium is reached immediately and the lack of observation of a reaction in the absence of Cl^- and acetate is clearly not the result of a much slower reaction rate.

The reaction of [$Zn(L'^{2-})(H_2O)_2$] (**3**) with $MgCl_2$ has been described recently by us,[2] and in continuation of this work we have now investigated the anion dependence of the reaction for comparison with the system **1**/Mg^{2+}. Similarly to the reaction behavior of **1**/Mg^{2+}, $MgCl_2$ substitutes Zn in **3**, while $Mg(NO_3)_2$, $Mg(ClO_4)_2$ and $MgSO_4$ are ineffective. Furthermore, no substitution takes place in the presence of iodide, bromide or fluoride ions. Again, the effect of chloride ions can be confirmed by treating mixtures of **3** and $Mg(ClO_4)_2$ with NaCl. Addition of four equivalents of NaCl to a 1:2 mixture of **3** and $Mg(ClO_4)_2$ induces formation of the Mg complex of L′ (**4**) in 67% yield. Complete conversion is achieved with four equivalents of $Mg(ClO_4)_2$ and eight equivalents of NaCl. Thus, as observed for the direct reaction with $MgCl_2$, exchange of Zn with Mg occurs more easily in **3** than in **1**, where the substitution reaction does not go to completion. Investigation of the reaction of **3** with $Mg(CH_3CO_2)_2$ was hampered by the deprotonation of the aromatic carboxylate group by acetate.[13] An NMR spectrum displaying several imine signals indicates the formation of dinuclear complexes that will be isolated and characterized in future work.

Replacement of Zn by Mg in the coordination sphere of the Schiff-base ligand apparently contradicts the order of stability predicted by the Irving−Williams series and, interestingly, the substitution strongly depends on the nature of the anions present in solution. One plausible explanation for the effect of the anions is their interaction with Zn^{2+} in solution. Non- or weakly coordinating ions like ClO_4^-, NO_3^- and SO_4^{2-} do not interact with metal ions in solution — coordination of NO_3^- to Zn in the X-ray structure of **1** is a feature of the solid-state structure and is unlikely to be maintained in solution.[14] By contrast, Cl^- and $CH_3CO_2^-$ do interact with Zn^{2+} in DMSO, and Zn^{2+} is released when a solution of **3** is treated with NaCl as evident from the appearance of a signal set for the free ligand as well as that of **3** in the NMR spectrum. After addition of 2.3 equivalents of NaCl, the intensities of the resonances of **3** and L correspond to a 4:3 ratio of Zn complex and free ligand. The existence of distinct sets of resonances for the free ligand and for the Zn complex shows that the Zn complex is nonlabile on the NMR time-scale in DMSO. This behavior is in contrast to the kinetic properties of the majority of Zn complexes, although it has been observed previously for related Zn Schiff base complexes.[1,15] Coor-

dination of acetate to Zn^{2+} and Mg^{2+} in DMSO solutions can easily be followed by the change in the chemical shift of the acetate resonance in the NMR spectra of solutions of $NaCH_3CO_2$ containing increasing amounts of Mg^{2+} or Zn^{2+} ions. Addition of $Mg(ClO_4)_2$ or $Zn(NO_3)_2$ shifts the methyl signal of the acetate ion to lower fields ($\Delta\delta$ = 0.20 ppm with 1 equiv. Mg^{2+} and 0.24 ppm with 1 equiv. Zn^{2+}). Addition of NaCl to mixtures of $NaCH_3CO_2$ and $Mg(ClO_4)_2$ or $Zn(NO_3)_2$ gives slight upfield shifts of the acetate resonance indicating that Cl^- competes weakly with acetate for metal-ion coordination in DMSO.

In conclusion, in the case of ClO_4^-, NO_3^- and SO_4^{2-} the equilibrium in DMSO

$$[ZnL(DMSO)_x]^{2+} + [Mg(DMSO)_6]^{2+} + nY^- \leftrightarrows [MgL(DMSO)_3]^{2+} + [Zn(DMSO)_m]^{2+} + nY^-$$

lies to the left-hand side due to the coordination properties of Zn and Mg. When coordinating anions are present, the equilibrium

$$[ZnL(DMSO)_x]^{2+} + [Mg(DMSO)_{6-n}X_n]^{(2-n)+} \leftrightarrows [MgL(DMSO)_3]^{2+} + [Zn(DMSO)_mX_y]^{(2-y)+}$$

is to be considered and the position of the equilibrium is determined by the affinities of the metal ions for the Schiff-base ligand *and* for the counterions (solvent effects are also present, see above). For both Zn complexes **1** and **3**, the equilibrium lies further to the right-hand side in the presence of acetate than in the presence of Cl^-. For reaction mixtures containing two equivalents of the respective counterion equilibrium constants of $K = 0.01 \pm 0.03$ (Cl^-) and $K = 0.07 \pm 0.04$ (acetate) can be estimated from the relative intensities of the NMR resonances. In the case of F^-, Br^- and I^-, coordination of Zn to the Schiff-base ligands is favored (100% **1** and **3**).

Although the primary coordination sphere of the metal ion is identical for L and L′ (O_2N), Zn is considerably more susceptible to exchange by Mg in **3** than in **1** as evident from an equilibrium constant of $K \approx 0.18 \pm 0.06$ for the reaction of **3** with Mg^{2+} in the presence of two equivalents of Cl^-. This can be attributed to the presence of the ammonium groups in **1**. Compared with aqueous solutions, the acidity of the ammonium groups is increased in organic solvents, while the acidity of phenols and carboxylic acids decreases significantly.[16] Thus, the metal ions have to compete with the protons of the two tertiary ammonium nitrogens for the binding sites of the ligand. Due to the coordination properties of Zn and Mg, the Mg complex is probably destabilized, while Zn competes efficiently with the protons. This interpretation is in accordance with the observation that upon treating 1:1 mixtures of **1** and **2** with NH_4NO_3 the equilibrium is shifted further towards the Zn complex. On addition of six equivalents of NH_4NO_3 the percentage of **2** is decreased by 25%. Since acetate acts as a relatively strong base in DMSO,[16] deprotonation of the ammonium groups may contribute to the effect of acetate in favoring the formation of the Mg complex.

Conclusions

In conclusion we have isolated and structurally characterized a Zn and Mg complex with the Schiff-base ligand derived from 4-bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol and glycine. These can be interconverted and the position of the equilibrium is determined by the solvent and the nature of the anions added to the reaction mixture.

Experimental Section

Materials and Methods: 4-Bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol was prepared according to the literature procedure.[17] The Zn complex of L′ (**3**) was synthesized as previously described.[1] All chemicals and solvents were reagent grade and used without further purification. ^1H NMR spectra (200.13 MHz) were recorded on a Varian Mercury spectrometer. Spectra were run in [D_6]DMSO, MeOD or D_2O solutions using sodium 3-(trimethylsilyl)propanesulfonate as internal reference. The pD values of D_2O solutions were obtained by use of a glass electrode and addition of 0.4 to the pH meter reading. The CHN analyses were carried out on an Element Analyzer CHNS 932 (LECO). Infrared spectra of KBr pellets were taken on a Bruker IFS 28 FT-spectrometer.

CAUTION: *Perchlorate salts are potentially explosive and should be handled carefully in small quantities only.*

Complex 1: Glycine (141 mg, 1.89 mmol) was dissolved in water (20 mL) and added to a solution of 4-bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol (675 mg, 1.89 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (1178 mg, 3.96 mmol) in MeOH (9 mL). The solution was stirred at room temperature for 24 h. Slow evaporation of the solution yielded yellow needles of $[ZnL(H_2O)(NO_3)]NO_3{\cdot}nH_2O$ (elemental analysis $n = 1$, X-ray analysis $n = 0$) in 81% yield. Selected IR data (KBr): $\tilde{\nu}$ = 3002, 1640 (C=N), 1604, 1551, 1452, 1384 (NO_3^-), 1309, 1288, 1201, 1074, 1020, 879, 824 (NO_3^-), 769 cm^{-1}. ^1H NMR [D_2O, pD = 6.8]: δ = 1.14 (t, ^3J = 7.58 Hz, 6 H, CH_3), 1.27 (t, ^3J = 7.58 Hz, 3 H, CH_3), 2.96−3.26 (m, 10 H, CH_2-N), 3.96 (br. s, 2 H, CH_2-COO), 4.21 (s, 2 H Ar-CH_2), 7.49 (s, 1 H, H_{ar}), 7.55 (s, 1 H, H_{ar}), 8.35 (s, 1 H, HC=N). $C_{18}H_{32}BrN_5O_{11}Zn$ (639.78): calcd. C 33.8, H 5.0, N 11.0; found C 33.7, H 4.8, N 11.3.

Complex 2: 4-Bromo-2-[(2-diethylaminoethyl)ethylaminomethyl]-6-formylphenol (258 mg, 0.72 mmol), $Mg(NO_3)_2{\cdot}6H_2O$, (923 mg, 3.60 mmol), sodium glycinate hydrate (105 mg, 0.913 mmol) and NaOH (85 mg, 2.13 mmol) were reacted in methanol/water (5:1, 12 mL) at room temperature. After stirring overnight some insoluble precipitate was filtered off. From the filtrate small needles of composition $[MgL(H_2O)_3](NO_3)_2{\cdot}H_2O{\cdot}CH_3OH$ (**2·CH$_3$OH**) were obtained. Yield: 27%. Selected IR data (KBr): $\tilde{\nu}$ = 3391, 1655 (C=N), 1604, 1545, 1384 (NO_3), 1237, 1199, 1147, 1094, 1037, 829 (NO_3^-), 771 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ = 1.03 (br. s, 6 H, CH_3), 1.22 (br. s, 3 H, CH_3), 2.6−3.1 (br. m, 10 H, CH_2-N), 3.92 (br. s, 2 H, CH_2-COO), 4.04 (br. s, 2 H, Ar-CH_2), 7.38 (s, 2 H, H_{ar}), 8.16 (br. s, 1 H, HC=N). $C_{19}H_{40}BrMgN_5O_{14}$ (666.78): calcd. C 34.2, H 6.1, N 10.5; found C 33.9, H 5.7, N 10.1. Recrystallization yielded X-ray suitable crystals of $[MgL(H_2O)_3](NO_3)_2{\cdot}H_2O$ (**2**).

Table 3. Crystallographic data and experimental details of the X-ray studies of **1** and **2**

	1	**2**
Empirical formula	$C_{18}H_{30}BrN_5O_{10}Zn$	$C_{18}H_{36}BrMgN_5O_{13}$
Molecular mass	621.75	634.74
Crystal system	monoclinic	monoclinic
Space group	*Cc*	*Cc*
a [Å]	9.814(1)	9.915(1)
b [Å]	20.444(1)	23.395(1)
c [Å]	12.811(1)	12.411(1)
β [°]	100.49(1)	102.85
V [Å^3]	2527.4(3)	2806.8(4)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.634	1.502
No. measured reflections	2240	2666
No. observed reflections [$I > 2\sigma(I)$]	1266	1782
R_1 [$I > 2\sigma(I)$][a]	0.048	0.050
wR_2 [$I > 2\sigma(I)$][b]	0.078	0.117

[a] $R_1 = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$. [b] $wR_2 = [\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2$; $P = (F_o^2 + 2F_c^2)/3$ with $a = 0.0473$ for **1** and 0.0843 for **2**.

X-ray Crystallography: Crystal data for compounds **1** and **2** (Table 3) were recorded at room temperature on an Enraf−Nonius-KappaCCD diffractometer[18] using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). For data reduction and cell refinement the programs DENZO and SCALEPACK were applied.[19] The structures were solved by conventional Patterson (**1**) and direct methods (**2**) and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 using the SHELXTL PLUS and SHELXL-93 programs.[20] The scattering factors were those given in the SHELXL programs. Transmission factors were calculated with SHELXL-97.[20] All non-hydrogen atoms except for the oxygen of water of crystallization in **2** were refined anisotropically. Hydrogen atoms were generated geometrically and given fixed isotropic U values.

CCDC-177901 (**1**) and -177902 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving. html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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