Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dichloro{2-[2-(dimethylammonio)-ethyliminomethyl]-4-nitrophenolato}-zinc(II) in unsolvated and hemihydrate forms

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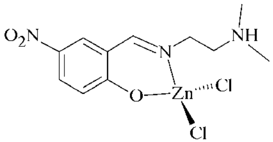
Received 27 June 2005
Accepted 29 June 2005
Online 23 July 2005

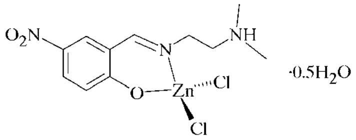
The two title complexes, $[ZnCl_2(C_{11}H_{15}N_3O_3)]$, (I), and $[ZnCl_2(C_{11}H_{15}N_3O_3)]\cdot 0.5H_2O$, (II), are mononuclear zinc(II) compounds. In both structures, the Zn^{II} atom is four-coordinated in a tetrahedral configuration by one imine N atom and one phenolate O atom of a Schiff base, and by two Cl atoms. The structure of each of the two zinc(II) complex molecules of (II) is similar to that of (I). In (I), the molecules are linked through intermolecular hydrogen bonds, forming a three-dimensional framework. In (II), the solvent water molecules are linked to the zinc(II) moieties through intermolecular O—H$\cdots$O and O—H$\cdots$Cl hydrogen bonds. The molecules in (II) are further linked via other intermolecular hydrogen bonds, forming a three-dimensional framework.

Comment

Transition metal complexes containing Schiff base ligands have been of great interest for many years (Yamada, 1999). These complexes play an important role in coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures (Lacroix, 1996; Goswami & Eichhorn, 1999; Rybak-Akimova *et al.*, 1998). The study of the variety of products in self-assembly processes between labile metal ions and flexible multidentate ligands is an interesting topic in supramolecular chemistry. The balance between the formation of different structures is often subtle. Factors that affect the coordination topology include not only the highly influential factors of metal and ligand coordination preferences, but also solvent-based influences, which have been extensively studied for silver(I) complexes (Smith *et al.*, 1996; Kristiansson, 2001; Nomiya *et al.*, 2000; Wei *et al.*, 1998). However, for zinc(II) complexes, solvent-based influences on the structures have seldom been reported. Thus, more work needs to be carried out in order to understand better the controlling effect of solvents on Schiff base zinc(II) complexes, which is now becoming an interesting topic in supramolecular chemistry.



(I)



(II)

We have focused our attention on the assembly of transition metal ions with flexible ligands, since they can adopt diverse coordination modes according to the geometric needs of the metal ion (You, 2005*a*,*b*). In order to investigate the relationship between the solvents used in the syntheses of the complexes and the resulting structures, we report here two novel mononuclear zinc(II) complexes, which have been synthesized in different solvents with the same starting materials.

The two title complexes, (I) and (II), are mononuclear zinc(II) compounds (Figs. 1 and 2). The major difference between the complexes is in the components of the molecules: complex (I), synthesized and crystallized in methanol solution, has no methanol molecules in the crystal, while complex (II), synthesized and crystallized in MeOH–H_2O (2:1 *v*/*v*) mixed solution, has solvent water molecules in the crystal structure.

In both structures, the Zn^{II} atom is four-coordinated in a tetrahedral configuration by one imine N atom and one

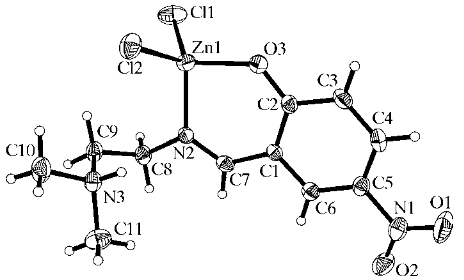


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

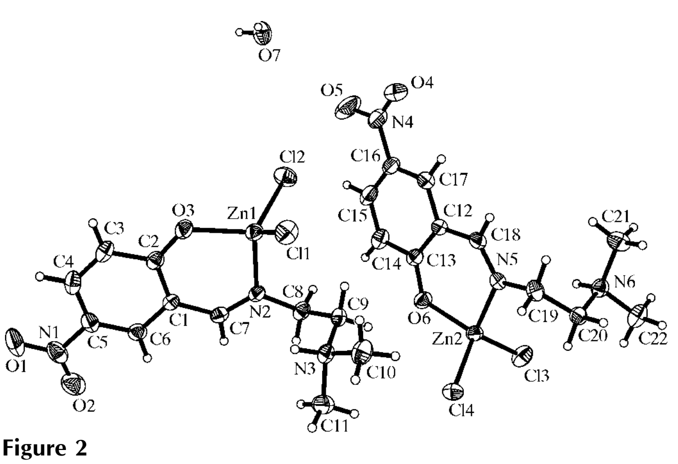


Figure 2
The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

phenolate O atom of a Schiff base, and by two Cl atoms. The structure of each zinc moiety of (II) is similar to that of (I). For the two complexes, each $ZnONCl_2$ coordination forms a slightly distorted tetrahedral geometry, as usually observed in the structures of Zn^{II} complexes (McCleverty *et al.*, 1980; You *et al.*, 2003), with angles subtended at the Zn^{II} atom in the range 108.16 (9)–115.52 (9)° for Zn1 in (I), 95.35 (10)–117.09 (8)° for Zn1 in (II) and 95.37 (10)–115.79 (8)° for Zn2 in (II) (Table 1). The average Zn—O bond lengths [1.940 (3) Å in (I) and 1.936 (2) Å in (II)] are comparable with the corresponding values observed in other Schiff base Zn^{II} complexes (Usman *et al.*, 2003; Erxleben 2001; Chisholm *et al.*, 2001). The mean Zn—N bond lengths [2.031 (3) Å in (I) and 2.016 (3) Å in (II)] are also comparable with the values observed in the above-mentioned complexes.

The dihedral angle between the O1—N1—O2 plane and the benzene ring in (I) is 8.8 (3)°, which is much larger than the corresponding values of 6.4 (3) [for the Zn1 moiety of (II)] and 5.0 (3)° [for the Zn2 moiety of (II)]. This is probably caused by intermolecular hydrogen bonds, which pull the two O atoms of each nitro group in opposite directions with different intensity.

In (I), the molecules are linked via intermolecular N—H···Cl, C—H···O and C—H···Cl hydrogen bonds (Table 2), forming a three-dimensional framework. In (II), the solvent water molecules are linked to the zinc(II) moieties through intermolecular O—H···O and O—H···Cl hydrogen bonds. The molecules in (II) are further linked via intermolecular N—H···Cl, N—H···O, C—H···Cl and C—H···O hydrogen bonds, forming a three-dimensional framework.

In conclusion, the solvents used in the preparation and crystallization of complexes can influence their crystal structures.

Experimental

For the preparation of complex (I), 5-nitrosalicylaldehyde (0.1 mmol, 20.1 mg) and *N*,*N*′-dimethylethane-1,2-diamine (0.1 mmol, 8.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a yellow solution, to which was added an MeOH solution (5 ml) of $ZnCl_2\cdot 6H_2O$ (0.1 mmol, 24.4 mg) with stirring. The mixture was stirred for another 10 min at room temperature. After keeping the filtrate in air for 8 d, colourless needle-shaped crystals of (I) were formed. Complex (II) was prepared by a procedure similar to that described for (I), with $ZnCl_2\cdot 6H_2O$ dissolved in distilled water (5 ml) rather than in MeOH. Colourless block-shaped crystals of (II) were obtained after evaporating the solvents from the filtrate in air for 11 d.

Compound (I)

Crystal data

$[ZnCl_2(C_{11}H_{15}N_3O_3)]$
$M_r = 373.53$
Orthorhombic, $P2_12_12_1$
$a = 7.668$ (2) Å
$b = 13.691$ (3) Å
$c = 14.698$ (3) Å
$V = 1543.0$ (6) Å^3
$Z = 4$
$D_x = 1.608$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2733 reflections
$\theta = 2.8$–23.7°
$\mu = 1.95$ mm^{-1}
$T = 298$ (2) K
Needle, colourless
0.20 × 0.08 × 0.05 mm

Table 1
Selected geometric parameters (Å, °) for (I).

Zn1—O3	1.940 (3)	Zn1—Cl1	2.217 (2)
Zn1—N2	2.031 (3)	Zn1—Cl2	2.246 (2)
O3—Zn1—N2	94.39 (11)	O3—Zn1—Cl2	108.16 (9)
O3—Zn1—Cl1	115.52 (9)	N2—Zn1—Cl2	112.92 (9)
N2—Zn1—Cl1	109.03 (8)	Cl1—Zn1—Cl2	115.08 (5)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···Cl2^{i}	0.90 (3)	2.55 (3)	3.344 (3)	148 (4)
C4—H4···O1^{ii}	0.93	2.57	3.199 (3)	125
C7—H7···Cl1^{iii}	0.93	2.78	3.695 (3)	170
C8—H8*A*···O2^{iv}	0.97	2.57	3.186 (3)	121
C8—H8*B*···O1^{v}	0.97	2.41	3.306 (3)	154
C10—H10*C*···O3^{i}	0.96	2.39	3.297 (3)	158

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$; (iii) $x+1, y, z$; (iv) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.697$, $T_{\max} = 0.909$
9727 measured reflections
3496 independent reflections
3088 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.036$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 12$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.084$
$S = 1.05$
3496 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: 0.035 (15)

Compound (II)

Crystal data

$[ZnCl_2(C_{11}H_{15}N_3O_3)]\cdot 0.5H_2O$
$M_r = 382.54$
Triclinic, $P\overline{1}$
$a = 12.181$ (2) Å
$b = 12.312$ (2) Å
$c = 12.596$ (2) Å
$\alpha = 66.673$ (1)°
$\beta = 70.632$ (1)°
$\gamma = 69.149$ (1)°
$V = 1580.5$ (4) Å^3
$Z = 4$
$D_x = 1.608$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4057 reflections
$\theta = 2.3$–25.8°
$\mu = 1.90$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.26 × 0.19 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.637$, $T_{\max} = 0.738$
13545 measured reflections
6985 independent reflections
5088 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.026$
$\theta_{\max} = 27.5°$
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—O3	1.942 (2)	Zn2—O6	1.930 (2)
Zn1—N2	2.018 (3)	Zn2—N5	2.013 (3)
Zn1—Cl1	2.219 (2)	Zn2—Cl4	2.228 (2)
Zn1—Cl2	2.224 (2)	Zn2—Cl3	2.231 (2)
O3—Zn1—N2	95.35 (10)	O6—Zn2—N5	95.37 (10)
O3—Zn1—Cl1	110.05 (8)	O6—Zn2—Cl4	111.84 (8)
N2—Zn1—Cl1	117.09 (8)	N5—Zn2—Cl4	105.10 (8)
O3—Zn1—Cl2	113.05 (8)	O6—Zn2—Cl3	114.12 (8)
N2—Zn1—Cl2	107.32 (8)	N5—Zn2—Cl3	115.79 (8)
Cl1—Zn1—Cl2	112.85 (4)	Cl4—Zn2—Cl3	113.09 (4)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*A*···Cl3^{i}	0.90 (4)	2.59 (3)	3.299 (3)	137 (3)
N3—H3*A*···O7^{ii}	0.91 (3)	1.88 (2)	2.746 (4)	160 (4)
O7—H7*A*···O3^{iii}	0.83 (3)	2.03 (3)	2.859 (4)	175 (4)
O7—H7*B*···Cl1^{iii}	0.83 (3)	2.85 (3)	3.384 (3)	124 (3)
C7—H7···Cl4^{iv}	0.93	2.72	3.629 (3)	167
C10—H10*B*···O5^{ii}	0.96	2.57	3.525 (7)	171
C19—H19*B*···Cl2^{v}	0.97	2.74	3.695 (3)	169
C22—H22*B*···O6^{i}	0.96	2.54	3.341 (3)	142
C22—H22*C*···O2^{iv}	0.96	2.56	3.232 (7)	127

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x+1, y, z$; (iii) $-x+1, -y, -z+2$; (iv) $-x+2, -y+1, -z+1$; (v) $-x+1, -y+1, -z+2$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.128$
$S = 0.99$
6985 reflections
386 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Atom H3*A* in (I) and atoms H3*A*, H6*A*, H7*A* and H7*B* in (II) were located in difference Fourier maps and refined isotropically, with the O—H distances restrained to 0.84 (1) Å, the H···H distances restrained to 1.37 (2) Å, and the N—H distances restrained to 0.90 (1) Å. The other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with U_{iso}(H) = 1.2 or $1.5U_{eq}$(C). In (I), an unassigned maximum residual density was observed 0.02 Å from atom Zn1 and the minimum residual density was observed 1.64 Å from atom H6. In (II), an unassigned maximum residual density was observed 0.98 Å from atom O6 and the minimum residual density was observed 1.64 Å from atom Zn1. There are 1463 Friedel pairs in (I).

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); structure solution: *SHELXS97* (Sheldrick, 1997*a*); structure refinement: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); publication software: *SHELXTL*.

The author thanks Liaoning Normal University, People's Republic of China, for funding this study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1856). Services for accessing these data are described at the back of the journal.

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