Journal of Chemical Crystallography, Vol. 36, No. 11, November 2006 (© 2006)
DOI: 10.1007/s10870-006-9131-3

Synthesis, characterization and crystal structure of a mononuclear zinc(II) complex derived from 2-methoxy-6-[(3-cyclohexylaminopropylimino)methyl]phenol

Xiao Han,[1] Zhong-Lu You,[1]* Yong-Ting Xu,[2] and Xiao-Min Wang[2]

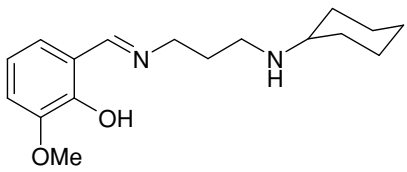
Received May 1, 2006; accepted July 3, 2006
Published Online August 2, 2006

Colourless block-shaped crystals of Dichloro{2-methoxy-6-[(3-cyclohexylaminopropylimino)methyl]phenolato}zinc(II) methanol, $[Zn(C_{17}H_{26}N_2O_2)Cl_2].CH_3OH$, have been obtained and characterized by elemental analysis, IR and X-ray single crystal determination. The complex crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 12.980(3)$ Å, $b = 13.139(3)$ Å, $c = 13.277(3)$ Å, $\beta = 107.00(3)^\circ$, $V = 2165.4(8)$ Å^3, $Z = 4$, $R_1 = 0.0631$ and $wR2 = 0.1110$. X-ray structure determination revealed that the complex consists of a $[Zn(C_{17}H_{26}N_2O)Cl_2]$ moiety and a lattice MeOH molecule. In the crystal structure, molecules are linked through intermolecular N–H···O, C–H···Cl and O–H···Cl hydrogen bonds, forming chains. It is the first complex derived from the Schiff base ligand 2-methoxy-6-[(3-cyclohexylaminopropylimino)methyl]phenol.

KEY WORDS: schiff base; zinc(II) complex; crystal structure; hydrogen bonds; coordination chemistry.

Introduction

Schiff base complexes play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures.[1–6] Zinc is an important metal in biology and acts as the active site of hydrolytic enzymes, where it is in a coordination environment of the hard donors nitrogen and oxygen.[7,8] Zinc has been recognized as an important co-factor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt the coordination numbers 4, 5, or 6.[9] Recently, we have reported a few complexes derived from the Schiff base ligand 2-[(3-cyclohexylaminopropylimino)methyl]phenol[10–12] and its derivatives.[13,14] However, to the best of our knowledge, no studies have been reported based on the Schiff base ligand 2-methoxy-6-[(3-cyclohexylaminopropylimino)methyl]phenol (HMCP; see Scheme 1) with metals. In this paper, we report the synthesis and structure of a mononuclear Schiff base zinc(II) complex derived from the ligand HMCP.



Scheme 1. The Schiff base ligand HMCP.

[1] Department of Chemistry and Chemical Engineering, Liaoning Normal University, Huanghe Road 850#, Dalian 116029, People's Republic of China.
[2] Analysis test center, Liaoning Normal University, Dalian 116029, People's Republic of China.
* To whom correspondence should be addressed; e-mail: youzhonglu@yahoo.com.cn.

Experimental

Materials and measurements

All chemicals (reagent grade) were commercially available and used without further purification. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were measured with a FT-IR 170-SX (Nicolet) spectrophotometer. The ^{1}HNMR spectra were recorded on Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal reference.

Synthesis of the ligand HMCP

To a MeOH solution (20 mL) of 3-methoxysalicylaldehyde (6.0 mmol, 913.2 mg) was added a MeOH solution (10 mL) of *N*-cyclohexyl-1,3-diaminopropane (6.0 mmol, 942.3 mg) with stirring. The mixture was stirred for 10 min at room temperature to give a great deal of yellow precipitation. The product was filtered, washed three times with MeOH, and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Analysis calculated for $C_{17}H_{26}N_2O_2$: C, 70.31; H, 9.02; N, 9.65%; found: C, 70.17; H, 9.13; N, 9.72%. Selected IR data (KBr, cm^{-1}): 3554 (w), 3432 (w), 3067 (w), 2933 (m), 2859 (w), 1639 (vs), 1280 (s), 754 (s). ^{1}HNMR data ($CDCl_3$, ppm): $\delta = 1.05$ (q, 2H), 1.17 (m, 1H), 1.26 (m, 2H), 1.62 (m, 2H), 1.72 (m, 2H), 1.87 (m, 4H), 2.40 (q, 1H), 2.74 (m, 2H), 3.67 (t, 2H), 3.90 (s, 3H), 6.79 (t, 1H), 6.86 (d, 1H), 6.91 (d, 1H), 8.32 (s, 1H), 14.0 (e, 1H).

Synthesis of the complex $[Zn(C_{17}H_{26}N_2O_2)Cl_2].CH_3OH$

To a MeOH solution (5 mL) of $ZnCl_2$ (0.1 mmol, 13.6 mg) was added a MeOH solution (10 mL) of HMCP (0.1 mmol, 15.2 mg), with stirring. The mixture was stirred for 10 min at room temperature and filtered. Upon keeping the filtrate in air for 5 days, colourless block-shaped crystals of the complex, suitable for X-ray single crystal structural determination, formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with cold MeOH and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Analysis calculated for $C_{18}H_{30}Cl_2N_2O_3Zn$: C, 47.13; H, 6.59; N, 6.11%; found: C, 46.96; H, 6.67; N, 6.23%. Selected IR data (KBr, cm^{-1}): 3563 (m), 3447 (m), 3067 (w), 2933 (m), 2859 (w), 1631 (vs), 1468 (s), 1447 (s), 1299 (m), 1243 (s), 1219 (s), 1086 (w), 746 (m).

Crystal structure determination

X-ray diffraction intensities were collected using a Bruker SMART Apex CCD area detector equipped with graphite-monochromated Mo-*Ka* radiation ($\lambda = 0.71073$ Å) at 298(2) K. Absorption correction was applied by SADABS program.[15] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL version 5.1.[16] All of the non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and constrained to ride on their parent atoms. The details of the crystallographic data are summarized in Table 1. Selected bond lengths and angles are summarized in Table 2. Hydrogen bonds are listed in Table 3.

Results and discussion

To design novel structures of metal complexes, the ligands used in the synthesis are important. In this paper, we designed and synthesized a new Schiff base ligand, HMCP. The reason we use HMCP as the ligand is that it could adopts versatile coordination modes through the phenolate O atom, imine N atom and/or amine N atom. HMCP was prepared in an excellent yield (82.3%) in a MeOH solution. The compound is yellow crystallite, stable in air at room tempera-

Table 1. Crystal Data and Refinement Parameters for the Complex

CCDC deposit no.	606067
Molecular formula	$C_{18}H_{30}Cl_2N_2O_3Zn$
Molecular weight	458.71
Temperature (K)	298(2)
Radiation λ	Mo Kα (0.71073 Å)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.980(3)
b/Å	13.139(3)
c/Å	13.277(3)
β/°	107.00(3)
V/Å^3	2165.4(8)
Z	4
D_{calc} (g cm^{-3})	1.407
Crystal size (mm)	0.10 × 0.08 × 0.05
Crystal colour	Colourless
Absorption coefficient (mm^{-1})	1.400
Absorption correction T_{min} and T_{max}	0.873 and 0.933
F(0 0 0)	960
Reflections collected/unique	18460/5108 [$R_{int} = 0.1212$]
Range/indices (h, k, l)	−16, 16; −17, 17; −17, 17
θ limit (°)	1.93–28.26
No. of observed data, $I > 2\sigma(I)$	2278
No. of variables	238
No. of restraints	0
Goodness of fit on F^2	0.933
Largest diff. Peak and hole (e Å^{-3})	0.379 and −0.298
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0631, 0.1110
R_1, wR_2 (all data)[a]	0.1748, 0.1412

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$, $w = [\sigma^2(Fo)^2 + (0.0434(Fo^2 + 2Fc^2)/3)^2]^{-1}$.

ture. It is soluble in common polar organic solvents, such as DMSO, DMF, MeOH, EtOH, and MeCN, *etc*., but poorly soluble in water and Et_2O. The elemental analysis is in good agreement with the chemical formula proposed for the compound. Zinc(II) is a good candidate of tetrahedral coordination. The complex is also stable in air at room temperature, soluble in DMF, DMSO, MeOH, EtOH and MeCN, and poorly soluble in water and Et_2O.

Table 2. Selected Bond Distances (Å) and Angles (°) for the Compound

Bond distances			
Zn1–O1	1.950(3)	Zn1–N1	2.015(4)
Zn1–Cl2	2.235(2)	Zn1–Cl1	2.236(2)
Bond angles			
O1–Zn1–N1	94.9(1)	O1–Zn1–Cl2	115.2(1)
N1–Zn1–Cl2	113.2(1)	O1–Zn1–Cl1	110.0(1)
N1–Zn1–Cl1	111.8(1)	Cl2–Zn1–Cl1	110.8(1)

Table 3. Geometrical Parameters for Hydrogen Bonds

Hydrogen bonds	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N2–H2A···O3	0.90	1.99	2.855(6)	162
N2–H2B···O1[a]	0.90	1.95	2.800(5)	157
N2–H2B···O2[a]	0.90	2.29	2.900(5)	125
O3–H3···Cl1[b]	0.82	2.28	3.102(5)	174
C10–H10B···Cl1[c]	0.97	2.72	3.622(5)	155

[a] 3/2 − x, 1/2 + y, 1/2 − z [b] 1/2 + x, 1/2 − y, 1/2 + z [c] 1 − x, − y, − z.

Crystal structure description of the complex

Figure 1 gives a perspective view of the complex with the atomic labeling system. The complex is a mononuclear zinc(II) compound, which consists of a $[Zn(C_{17}H_{26}N_2O_2)Cl_2]$ moiety and a lattice MeOH molecule. In the zinc(II) moiety, the Zn atom is four-coordinated by the phenolate O and imine N atom of the ligand MCP, and by two terminal Cl atoms, forming a tetrahedral coordination. The bond lengths related to the Zn atom are comparable to the values observed in other similar Schiff base zinc(II) complexes we reported recently.[17−19] The bond angles subtended at the Zn atom are ranged from 94.87(14) to 115.25(11)°, indicating a distorted tetrahedral geometry. As expected, the N1–C8–C9–C10–N2–C11 moiety in the complex adopts zigzag form and the cyclohexyl group adopts chair conformation to minimize steric effects. The torsion angles N1–C8–C9–C10 and C9–C10–N2–C11 are −73.4(5)° and 4.7(5)°, respectively.

In the crystal structure, the MeOH molecules are linked to the zinc complex moieties through intramolecular N–H···O hydrogen bonds and intermolecular O–H···Cl hydrogen bonds. The molecules are further linked through

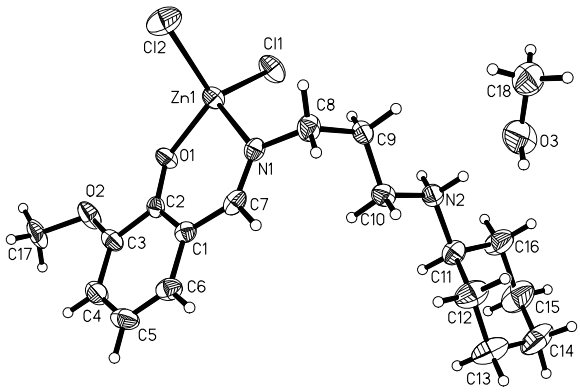


Fig. 1. Molecular structure of the complex. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radii; numbering according to Table 2.

intermolecular N–H···O and C–H···Clhydrogen bonds, forming chains as shown in Fig 2.

Conclusions

The present study shows that the ligand HMCP coordinates to the Zn atom through the phenolate O and imine N atoms. The amine N atom of the ligand HMCP is protonated, and not coordinates to the Zn atom. The structure of the complex is stabilized by the intermolecular H-bonding interactions.

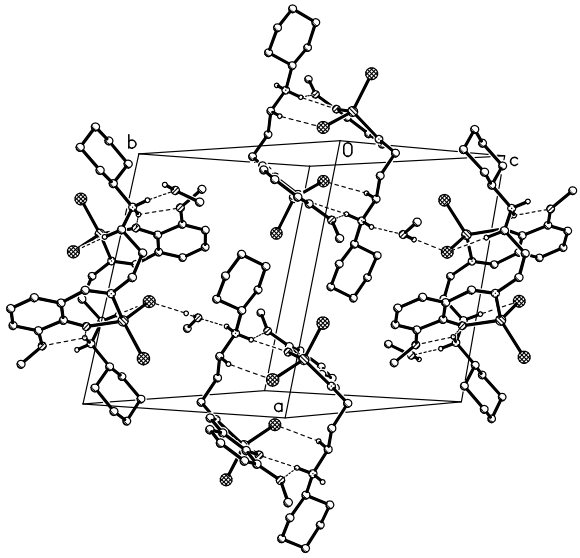


Fig. 2. Molecular packing of the complex, viewed along the *c* axis. Intermolecular hydrogen bonds are shown as dashed lines.

Supplementary material CCDC-606067 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdccam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This project is financially supported by the Natural Science Foundation of China (No. 20571037).

References

1. Yamada, S. *Coord. Chem. Rev.* **1999**, *190–192,* 537–555.
2. Ruck, R.T.; Jacobsen, E.N. *J. Am. Chem. Soc.* **2002**, *124,* 2882–2883.
3. Kim, H.-J.; Kim, W.; Lough, A.J.; Kim, B.M.; Chin, J. *J. Am. Chem. Soc.* **2005**, *127,* 16776–16777.
4. Paschke, R.; Liebsch, S.; Tschierske, C.; Oakley, M.A.; Sinn, E. *Inorg. Chem.* **2003**, *42,* 8230–8240.
5. Zhu, H.-L.; Li, S.-Y.; Wang, Z.-D.; Yang, F. *J. Chem. Crystallogr.* **2004**, *34,* 203–206.
6. Wan, X.-B.; Jin, C.-M.; Shi, Z.-W.; Lu, G.-Y. *J. Chem. Crystallogr.* **2004**, *34,* 57–60.
7. Bertini, I.; Gray, H.B.; Lippard, S.J.; Valentine, J.S. *Bioinorganic Chemistry*. University Science Books: Mills Valley, CA. **1994**.
8. Lipscomb, W.N.; Sträter, N. *Chem. Rev.* **1996**, *96,* 2375–2434.
9. Vallee, B.L.; Auld, D.S. Acc. *Chem. Res.* **1993**, *26,* 543–551.
10. You, Z.-L.; Xiong, Z.-D.; Liu, W.-S.; Tan, M.-Y.; Zhu, H.-L. *Acta Crystallogr.* **2004**, *E60,* m79–m81.
11. You, Z.-L.; Qu, Y.; Liu, W.-S.; Tan, M.-Y.; Zhu, H.-L. *Acta Crystallogr.* **2003**, *E 59,* m1038–m1040.
12. You, Z.-L.; Lin, Y.-S.; Zhu, H.-L.; Liu, W.-S. *Acta Crystallogr.* **2004**, *E 60,* m887–m889.
13. You, Z.-L. *Acta Crystallogr.* **2005**, *E 61,* m1807–m1809.
14. You, Z.-L. *Acta Crystallogr.* **2006**, *E 62,* m10–m11.
15. Sheldrick, G.M. SADABS. Program for Empirical Absorption-Correction of Area Detector, University of Göttingen, Germany, 1996.
16. Sheldrick, G.M. SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA.
17. You, Z.-L.; Zhu, H.-L. *Z. Anorg. Allg. Chem.* **2006**, *632,* 140–146.
18. You, Z.-L. *Acta Crystallogr.* **2006**, *E 62,* m10–m11.
19. You, Z.-L. *Acta Crystallogr.* **2005**, *C61,* m383–m385.