

Crystal structure and DFT calculations of Zn(II)-NN'O Schiff base complex

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Abstract

The structure of the Zn^{II} complex with NN'O-donor ligand N-(2-Pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine (**1H**) [Zn^{II}(C₂₁H₂₇N₂O)₂]. 3CH₃OH is described. Pentadentate coordination around the Zn^{II} metallic centre is observed, with one ligand acting as tridentate and another ligand as bidentate [Zn(**1**- κ^3 N,N',O)(**1**- κ^2 N,N',O)], and three methanol solvate molecules. A similar structure was also obtained from DFT calculations.

Keywords

Crystal structure, DFT calculations, Zinc complex, NN'O-donor ligand

1. Introduction

Synthesis of Zn^{II} complex with NN'O-donor ligand (**1H**) (Figure 1) has been reported in the literature by reaction of Zn(OAc)₂·2H₂O with **1H** in methanol in the presence of NEt₃ [1].¹ The structure of the resulting complex was described as a distorted octahedron in which the two ligands **1** acted as tridentate and were coordinated in a *meridional* fashion [Zn(**1**- κ^3 N,N',O)₂]. It has also been previously reported that the reaction of [Zn(N(SiMe₃)₂)₂] with **1H** in THF (1:2 molar ratio) led to the formation of a brown solid also proposed as [Zn(**1**- κ^3 N,N',O)₂].² Though, the solid structure of those complexes has not been reported in any

¹ M. Orio, C. Philouze, O. Jarjays, F. Neese and F. Thomas, *Inorg. Chem.* **2010**, 49, 646–658

² J. B. L. Gallaway, J. R. K. McRae, A. Decken, M. P. Shaver, *Can. J. Chem.* **2012**, 90, 419-426

case. We recently reported the synthesis of the complex $[\text{Zn}(\mathbf{1})_2]$, as a yellow solid, by reaction of ZnI_2 with **1H** in methanol in the presence of NaOH .³ X-ray structure of the crystals of $[\text{Zn}(\mathbf{1})_2]$, obtained from a MeOH solution, showed a five-coordinate environment around the Zn^{II} centre with one ligand acting as tridentate and another one as bidentate, $[\text{Zn}(\mathbf{1}-\kappa^3\text{N},\text{N}',\text{O})(\mathbf{1}-\kappa^2\text{N}',\text{O})]$. Here we describe a similar X-ray structure of the complex $[\text{Zn}(\mathbf{1})_2]$ with three methanol solvate molecules forming hydrogen-bonds interactions. DFT calculations showed a quite similar distribution of those molecules around the complex structure.

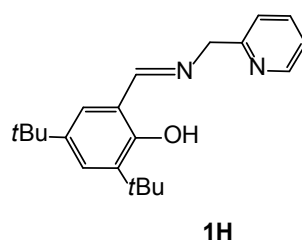


Figure 1. NNO- Schiff base ligand **1H**

2. Experimental

2.1. Synthesis and crystallisation

Ligand **1H** was synthesized following the procedure described by Finney and Mitchell by condensation of 3,5-di-*tert*-butyl salicylaldehyde and 2-methylaminopyridine.⁴ For the preparation of complex $[\text{Zn}(\mathbf{1})_2] \cdot 3\text{MeOH}$. The procedure was as follows:

To a solution of ligand **1H** (400 mg, 1.23 mmol) in MeOH (38 mL), NaOH (49.3 mg, 1.23 mmol) was added. After 10 min stirring, a solution of ZnI_2 (196.3 mg, 0.615 mmol) in MeOH (5mL) was added. The yellow mixture was stirred for 4.5 h at r.t. The resulting solution was dried under vacuum. Cold diethyl ether was added to the residue and a white solid appeared. The solid was separated by filtration and the filtrate was dried under vacuum to obtain a yellow solid, 357.4 mg (Yield 74 %).

Elemental analysis $\text{C}_{42}\text{H}_{54}\text{N}_4\text{O}_2\text{Zn}$ (712.28): calcd. C 70.82, H 7.64, N 7.87; found C 69.84, H 7.51, N 7.89. MALDI-TOF (MeOH) calc for $\text{C}_{42}\text{H}_{54}\text{N}_4\text{O}_2\text{Zn}$ m/z : 710.3538

³ L. Cuesta-Aluja, A. Campos-Carrasco, J. Castilla, M. Reguero, A. M. Masdeu-Bultó, A. Aghmiz, *Journal of CO2 Utilization*. **2016**, 14, 10–22

⁴ J. M. Mitchell, N. S. Finney, *J. Am. Chem. Soc.* **2001**, 123, 862-869

Yellow crystals suitable for X-ray diffraction analyses were obtained by slow diffusion of hexane into a methanolic solution of the complex.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Data collection: APPEX2 (BRUKER AXS, 2005); cell refinement: APPEX2 (BRUKER AXS, 2005); data reduction: APPEX2 (BRUKER AXS, 2005); program(s) used to solve structure: *SIR97* (Giacovazzo *et al.*, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

Table 1

Experimental details

Crystal data

$C_{42}H_{54}N_4O_2Zn \cdot 3(CH_4O)$	$Z = 2$
$M_r = 808.39$	$F(000) = 868$
Triclinic, $P1$	$D_x = 1.228 \text{ Mg m}^{-3}$
Hall symbol: $-P 1$	Mo $K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$
$a = 10.7040 (13) \text{ \AA}$	Cell parameters from 1840 reflections
$b = 14.2886 (18) \text{ \AA}$	$\theta = 2.3\text{--}19.8^\circ$
$c = 14.5957 (18) \text{ \AA}$	$\mu = 0.61 \text{ mm}^{-1}$
$\alpha = 100.010 (8)^\circ$	$T = 100 \text{ K}$
$\beta = 93.870 (9)^\circ$	Needle, Yellow
$\gamma = 93.633 (8)^\circ$	$0.17 \times 0.07 \times 0.06 \text{ mm}$
$V = 2186.9 (5) \text{ \AA}^3$	

Data collection

BRUKER APPEX-II CCD diffractometer	7960 independent reflection
Radiation source: fine-focus sealed tube graphite	4702 reflections with $I > 2\sigma(I)$
ω and ϕ scans	$R_{\text{int}} = 0.119$
Absorption correction: Multi-scan	$\theta_{\text{max}} = 25.4^\circ$, $\theta_{\text{min}} = 1.8^\circ$
BRUKER <i>SADABS</i>	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.767$, $T_{\text{max}} = 0.906$	$k = -17 \rightarrow 16$
34848 measured reflections	$l = 0 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: Structure-invariant direct methods
Least-squares matrix: Full	Secondary atom site location: Difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.071$	Hydrogen site location: Inferred from neighbouring sites
$wR(F^2) = 0.195$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0985P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
7960 reflections	$(\Delta/\sigma)_{\max} < 0.001$
531 parameters	$\Delta\rho_{\max} = 1.00 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\min} = -0.92 \text{ e } \text{\AA}^{-3}$

2.3. Computational details

DFT calculations were run with the Gaussian 09 package⁵ using the M06 functional to include dispersion effects and to account for the possible π -stacking interactions of the pyridine rings. A 6-31G (d,p) basis set with LANL2TZ (Los Alamos National Laboratory 2 double z) pseudo potential for the zinc atom was used. The optimized geometry was verified as true minima by frequency calculations.

3. Results and discussion

X-Ray diffraction structure of complex [Zn(1)₂] \cdot 3MeOH

The structure of [Zn(1)₂] \cdot 3MeOH contains one Zn^{II} atom in a pseudo square-pyramidal environment chelated to two deprotonated ligands (**1**) (Figure 2). One of the ligands acts as a tridentate κ^3N,N',O -donor, coordinating through the O(2) (phenol), N(3) (imine) and N(4) (pyridine) and occupying the square plane. The other ligand coordinates as a bidentate $\kappa^2N'O$ -donor by the O(1) (phenol) and the N(1) (imine) while the pyridine nitrogen remains non

⁵ Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

coordinated (distance Zn(1)···N(2) 4.794 Å). The N(1) occupies the axial position of the square-pyramid. The phenolato O(1) is *trans* to the coordinated imino group N(3).

Bond distances Zn-O (1.965 (3) and 1.991 (3) Å), Zn-N (pyridine) (2.207 (4) Å) and Zn-N (imine) (2.025 (4) and 2.074 (4) Å) in complex [Zn(1)₂] lay in the range observed for analogous N,N',O-donor ligands (Table 2).^{1, 6} As expected the Zn-N(pyridine) distance is longer than the Zn-N (imine) one.⁷ The N(imine)-C bond lengths of the imine group C=N (1.304 (6) and 1.291 (6) Å) are in the range of the ones reported for Zn-N(imine) complexes.^{1, 6a, 6c} This distance is slightly longer in the tridentate ligand (1.304 (6) Å) than in the bidentate one (1.291 (6) Å).

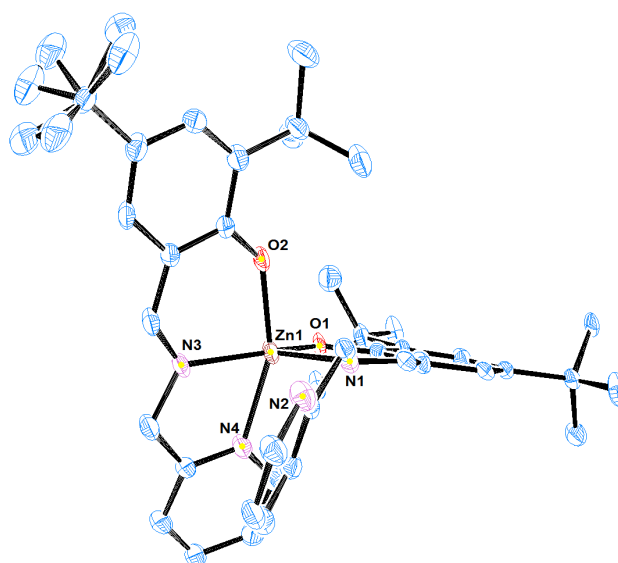


Figure 2. X-ray diffraction molecular structure of [Zn(1)₂]. Solvate methanol molecules and H atoms are omitted for clarity. Thermal ellipsoids are depicted at 50 % probability. One of the *tert*-butyl groups shows disorder.

Table 2

Selected bond lengths (Å) and angles (°) of [Zn(1)₂]₂·3MeOH

Bond lengths			
Zn1-O1	1.965(3)	Zn1-O2	1.991(3)

⁶ a) N. Sheng, *Acta Cryst.* **2009**, E65, m1295. b) A. Trösch, H. Vahrenkamp, *Z. Anorg. Allg. Chem.* **2004**, 630, 2031–2034. c) H.-W. Huang, *Acta Cryst.* **2011**, E67, m313. d) P. U. Maheswari, S. Barends, S. Özalp-Yaman, P. de Hoog, H. Casellas, S. J. Teat, C. Massera, M. Lutz, A. L. Spek, G. P. van Wezel, P. Gamez, J. Reedijk, *Chem. Eur. J.* **2007**, 13, 5213–5222. e) C. Zhang, Z.-X. Wang, *J. Organomet. Chem.* **2008**, 693, 3151–3158

⁷ .-L. You, *Acta Cryst.* **2005**, C61, m456–m458

Zn1-N1	2.025(4)	Zn1-3	2.074(4)
Zn1-N4	2.207(4)	N1-C7	1.291 (6)
N3-C28	1.304(6)	Zn1·····N2	4.794
Angles			
O1-Zn1-O2	97.91(13)	O1-Zn1-N3	148.79(16)
O1-Zn1-N1	93.80(15)	O2-Zn1-N4	157.26(15)
O2-Zn1-N1	93.49(15)	O1-Zn1-N4	88.54 (14)
O2-Zn1-N3	87.71 (14)	N1-Zn1-N4	107.89 (16)
N1-Zn1-N3	116.58 (16)	N3-Zn1-N4	76.00 (15)

The distortion of the 5-coordinated environment can be described by the τ -factor⁸ (Figure 3). The low value of $\tau = 0.14$ is indicative of a square-pyramidal distortion rather than a distorted trigonal bipyramid geometry ($\tau = 0$ for a perfect square-pyramidal geometry while $\tau = 1$ for a trigonal bipyramidal).

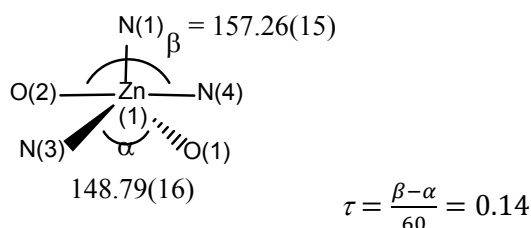


Figure 3. Angles α and β for complex $[\text{Zn}(\mathbf{1})_2] \cdot 3\text{MeOH}$

The X-ray structure of the complex $[\text{Zn}(\mathbf{1})_2] \cdot 3\text{MeOH}$ described in this work (Figure 2) is quite similar to this reported previously by our group.³ Selected bond lengths and angles of both structures are compared in Table 3.

⁸ A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349-1356

Table 2Selected bond lengths (Å) and angles (°) of [Zn(**1**)₂] structures

Bond lengths	Structure of [Zn(1) ₂]·3MeOH (this work)	Structure of [Zn(1) ₂] (ref 3)
Zn-O(tridentate ligand)	1.991(3)	1.976(2)
Zn-N(imine tridentate ligand)	2.047(4)	2.086(2)
Zn-N(pyridine tridentate ligand)	2.207(4)	2.152(3)
C=N(imine tridentate ligand)	1.304(6)	1.284(4)
Zn-O(bidentate ligand)	1.965(3)	1.9785(19)
Zn-N(imine bidentate ligand)	2.025(4)	2.033(2)
Zn·····N(pyridine bidentate ligand)	4.794	4.418
C=N(imine bidentate ligand)	1.291(6)	1.279(4)
Angles	Structure of [Zn(1) ₂]·3MeOH (this work)	Structure of [Zn(1) ₂] (ref 3)
O _{bidentate ligand} -Zn-O _{tridentate ligand}	97.91(13)	95.66(8)
O _{bidentate ligand} -Zn-N _{imine bidentate ligand}	93.80(15)	92.08(8)
O _{bidentate ligand} -Zn-N _{imine tridentate ligand}	148.79(16)	153.42(9)
O _{bidentate ligand} -Zn-N _{pyridine tridentate ligand}	88.54(14)	90.61(9)
O _{tridentate ligand} -Zn-N _{imine bidentate ligand}	93.49(15)	103.39(9)
O _{tridentate ligand} -Zn-N _{imine tridentate ligand}	87.71(14)	86.76(9)
O _{tridentate ligand} -Zn-N _{pyridine tridentate ligand}	157.26(15)	155.09(9)
N _{imine bidentate ligand} -Zn-N _{imine tridentate ligand}	116.58(16)	113.17(9)
N _{imine bidentate ligand} -Zn-N _{pyridine tridentate ligand}	107.89(16)	100.44(9)
N _{imine tridentate ligand} -Zn-N _{pyridine tridentate ligand}	76.00(15)	77.23(10)

The main difference of the present structure in comparison with the one obtained previously is the presence of three molecules of solvent in the crystal structure, forming hydrogen-bond

interactions with each other and with the N atom of the pyridine in the bidentate ligand (N₂) (Table 3).

Table 3

Hydrogen-bonds geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3D \cdots N2	0.72 (6)	2.17 (6)	2.820 (6)	150 (7)
O4—H4D \cdots O3	0.86 (2)	1.85 (3)	2.695 (7)	167 (10)
O5—H5D \cdots O4	0.84	1.94	2.774 (8)	169

DFT calculations

Complex [Zn(1)₂] \cdot 3MeOH was the subject of a computational study. The starting point structure used was the most stable pentacoordinated isomer found in a previous study³ that did not include explicitly solvent molecules. Three methanol molecules were added to the system and a geometry optimization has then been performed. Given the difficulties to reproduce a crystal environment, a gas phase calculation was run instead. In the obtained structure (Figure 4a), the three methanol molecules adopt a distribution quite similar to the one shown by X-ray (Figure 4b).

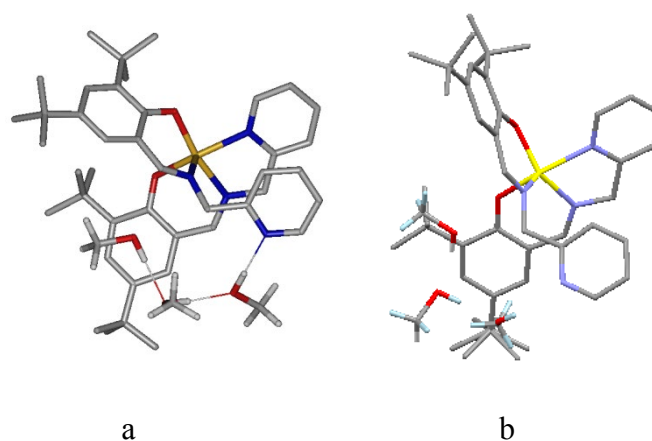


Figure 4. a) Geometry of the minimum energy structure obtained at DFT level, b) X-ray structure for complex [Zn(1)₂] \cdot 3MeOH with three methanol molecules. H atoms have been omitted (except those of methanol molecules) for clarity.

Comparison of some characteristic distances and angles is shown in Table 4. The mean error in distances is only 2.3%, while if angles are also included in the comparison the mean error increases to a 8.2% due to some discrepancies of 10°-15°. The distances from the complex to the methanol molecules also differ noticeably. Nevertheless, taken into account the absence of the crystal environment in the modelization, the results can be considered quite satisfactory.

Table 4

Characteristic distances (Å) and angles (°) for the X-ray structure and the one obtained computationally of $[\text{Zn}(\mathbf{1})_2] \cdot 3\text{MeOH}$.

Distances	X-ray structure	DFT structure
Zn1-O1	1.965	1.987
Zn1-N1=	2.025	2.113
Zn1-O2	1.991	2.004
Zn1-N3=	2.074	2.104
Zn1-N4	2.207	2.204
N3=C28	1.304	1.299
N1=C7	1.291	1.295
N3-C29	1.45	1.436
N1-C8	1.457	1.442
Zn1·····N2	4.794	4.541
O3—H3D···N2	2.172	1.827
O5···N1	4.033	3.13
Angles	X-ray structure	DFT structure
O1-Zn1-O2	97.91	99.9
O1-Zn1-N1	93.8	88.71
O2-Zn1-N1	93.49	104.97
O2-Zn1-N3	87.71	86.47

N1-Zn1-N3	116.58	99.98
O1-Zn1-N3	148.79	167.6
O2-Zn1-N4	157.26	142.67
O1-Zn1-N4	88.54	93.02
N1-Zn1-N4	107.89	110.23
N3-Zn1-N4	76	75.74

4. Conclusion

In summary, a new X-ray structure of a Zn^{II} complex with 2 NN'O-donor ligands N-(2-Pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzalimine and three methanol solvate molecules is described. Pentadentate coordination around the Zn^{II} metallic centre is observed, with one ligand acting as tridentate and another ligand as bidentate [$\text{Zn}(\mathbf{1}-\kappa^3\text{N},\text{N}',\text{O})(\mathbf{1}-\kappa^2\text{N},\text{N}',\text{O})$]. The identical structure was also obtained from DFT calculations, in which the distribution adopted by the three methanol molecules is quite similar to the shown by X-ray.

Acknowledgements

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