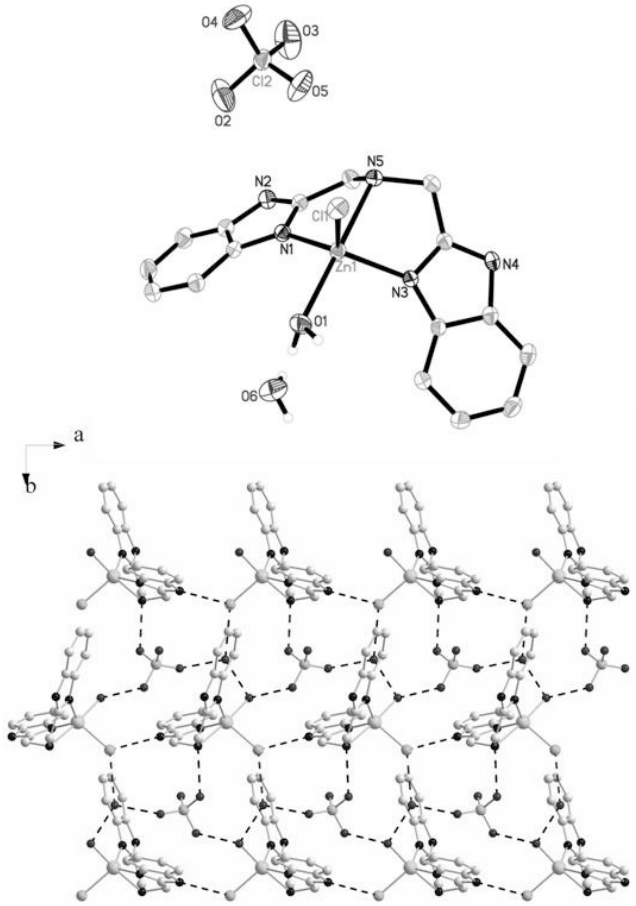
Crystal structure of chloro-aqua(*bis*(benzimidazol-2-yl-methyl)-amine)-zinc(II)perchlorate monohydrate, $[ZnCl(H_2O)(C_{16}H_{15}N_5)]ClO_4{\cdot}H_2O$, $C_{16}H_{19}Cl_2N_5O_6Zn$

Guan-Nan Li and Feng-Mei Nie*

Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China

Received January 23, 2012, accepted June 12, 2012, available online August 02, 2012, CCDC no. 1267/3800



Abstract

$C_{16}H_{19}Cl_2N_5O_6Zn$, monoclinic, $P2_1/c$ (no. 14), a = 7.9152(4) Å, b = 15.4534(7) Å, c = 16.7508(8) Å, β = 94.131(1)°, V = 2043.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0286, $wR_{ref}(F^2)$ = 0.0804, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.18×0.40×0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.08 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	55.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12067, 4811
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4245
$N(param)_{refined}$:	271
Programs:	SHELXTL [6]

* Correspondence author (e-mail: niefm@mail.cnu.edu.cn)

Source of material

Bis-(benzimidazol-2-yl-methyl)amine (bbma) was synthesized according to the published procedure [1]. The title complex was synthesized by refluxing stoichiometric quantities (1:1:1 molar ratio) of bbma (0.139 g, 0.5 mmol), zinc perchlorate hexahydrate (0.186 g, 0.5 mmol) and sodium chloride (0.029 g, 0.5 mmol) for 4 h. The solution was cooled to room temperature, filtered and evaporated to obtain the colourless crystals (yield 47%).

Discussion

The imidazole groups of histidine play an important role at the active sites of numerous metalloproteins [2]. Therefore, complexes containing imidazole or benzimidazole as ligands are often used to model the active sites of the relevant metalloenzymes [1,3,4]. *Bis*(benzimidazol-2-yl-methyl)amine (bbma) is a ligand containing two benzimidazole groups. It is selected due to its similarity to histidine imidazole. Till now, only one zinc complex containing bbma and chloride has been reported [3]. In this study, we report the synthesis and the crystal structure of a new complex, $[ZnCl(H_2O)(C1_6H_{15}N_5)]ClO_4{\cdot}H_2O$.

Single crystal *X*-ray diffraction analysis reveals that the title complex consists of one $[ZnCl(H_2O)(C_{16}H_{15}N_5)]^+$ cation, one perchlorate anion and a lattice water molecule.The zinc(II) has a trigonal bipyramidal geometry, coordinated by the tridentate bbma, one chloride and a water. The equatorial positions are occupied by the Cl1, and the benzimidazole N1, N3 atoms of bbma. The axial positions have the N5 of bbma and the O1 of H_2O.

The bond distances of Zn–N (benzimidazole) are 2.018(2) Å for Zn–N1 and 2.043(1) Å for Zn–N3, which is shorter than the bond distance between zinc and the axial N5 atom, 2.285(2) Å. The Zn1–Cl1 distance is 2.2819(5) Å. This is similar to the already reported complex $[Zn(C_{16}H_{15}N_5)Cl_2]{\cdot}MeOH$, in which the bond distances Zn–Cl are 2.304(7) and 2.316(1) Å [3]. The distance of Zn to the O1 of H_2O is 2.092(1) Å.

The angles of the basal plane are in the range of 114.99(4)° to 121.08(5)°, and the N5–Zn1–O1 bond angle is 174.40(6)°. The zinc(II) ion lies approximately 0.26 Å towards the O1. It could be found that the τ value is 0.89, which is consistent with the trigonal bipyramidal geometry of the complex [τ = 0 (square pyramid) and τ = 1 (trigonal bipyramid)] [5]. The dihedral angle of the two benzimidazole groups is 116°. This is very different from the reported complexes $[Zn(C_{16}H_{15}N_5)Cl_2]{\cdot}MeOH$ [3] and $[MnCl_2(C_{16}H_{15}N_5)(C_2H_6O)]$ [4], in which the dihedral angle of the two benzimidazole groups is almost up to 180°.

In the crystal structure, intermolecular O–H···O, N–H···Cl and N–H···O interactions are found in the 2-D layer. The Cl1 atom of each cation is linked with the N2 atom of the adjacent cation to form a 1-D chain [N2–H2N···Cl1, 3.2594(17) Å]. The 2-D layer

network is formed along the *c*-axis through the hydrogen bonding interactions between the cationic units and the three oxygen atoms of the perchloate anion, the oxygen atom of the crystal water molecule, respectively, which could be be found that N5–H5N···O5, 3.003(3) Å, O1-H1A···O4, 2.965(3) Å, O6–H6A···Cl1, 3.188(2) Å, O1–H1B···O6, 2.696(3) Å, O6–H6B···O3, 2.890(3) Å. All of the hydrogen bonding interactions contribute to the stabilization of the crystal.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	–0.1719	0.1470	0.4768	0.056
H(2)	4*e*	0.0127	0.0973	0.5804	0.059
H(3)	4*e*	0.2923	0.0716	0.5618	0.057
H(4)	4*e*	0.4012	0.0921	0.4382	0.049
H(8A)	4*e*	–0.0335	0.1477	0.1556	0.045
H(8B)	4*e*	–0.0441	0.2467	0.1761	0.045
H(9A)	4*e*	0.2690	0.2187	0.0379	0.047
H(9B)	4*e*	0.0791	0.1886	0.0382	0.047
H(13)	4*e*	0.4665	–0.1013	0.1927	0.049
H(14)	4*e*	0.5002	–0.2266	0.1202	0.057
H(15)	4*e*	0.4098	–0.2346	–0.0135	0.054
H(16)	4*e*	0.2865	–0.1167	–0.0802	0.050
H(5N)	4*e*	0.2130	0.2670	0.1525	0.050
H(4N)	4*e*	0.1886	0.0564	–0.0472	0.050
H(1A)	4*e*	0.6204	0.0293	0.2745	0.050
H(2N)	4*e*	–0.1692	0.1944	0.3110	0.050
H(1B)	4*e*	0.4903	–0.0035	0.3169	0.050
H(6A)	4*e*	0.3863	–0.1377	0.3495	0.050
H(6B)	4*e*	0.2603	–0.0890	0.3493	0.050

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	0.37910(2)	0.12663(1)	0.22369(1)	0.0285(1)	0.0338(1)	0.0279(1)	0.00190(7)	–0.00108(8)	–0.00348(7)
Cl(1)	4*e*	0.59411(6)	0.22257(3)	0.20966(3)	0.0310(2)	0.0411(2)	0.0454(3)	–0.0041(2)	0.0003(2)	–0.0055(2)
O(1)	4*e*	0.5336(2)	0.0441(1)	0.29592(9)	0.0440(8)	0.0515(9)	0.0453(8)	0.0161(7)	–0.0015(6)	0.0048(6)
N(1)	4*e*	0.2028(2)	0.1482(1)	0.30260(9)	0.0296(7)	0.0344(8)	0.0306(7)	0.0016(6)	–0.0010(6)	–0.0014(6)
C(1)	4*e*	–0.0586(3)	0.1362(1)	0.4692(1)	0.046(1)	0.052(1)	0.043(1)	–0.0028(9)	0.0137(9)	–0.0053(9)
Cl(2)	4*e*	0.09310(7)	0.42830(3)	0.27910(3)	0.0481(3)	0.0452(3)	0.0377(3)	–0.0063(2)	–0.0016(2)	–0.0070(2)
O(2)	4*e*	0.0735(4)	0.3812(2)	0.3503(1)	0.137(2)	0.116(2)	0.054(1)	–0.062(2)	–0.011(1)	0.019(1)
N(2)	4*e*	–0.0647(2)	0.1768(1)	0.3224(1)	0.0282(7)	0.0481(9)	0.0378(8)	0.0034(6)	0.0026(6)	–0.0002(7)
C(2)	4*e*	0.0522(3)	0.1068(2)	0.5302(1)	0.067(1)	0.050(1)	0.032(1)	–0.005(1)	0.0102(9)	–0.0011(9)
O(3)	4*e*	–0.0645(3)	0.4426(2)	0.2365(2)	0.054(1)	0.188(3)	0.082(2)	0.016(2)	–0.019(1)	–0.007(2)
N(3)	4*e*	0.3205(2)	0.04996(9)	0.12622(8)	0.0372(8)	0.0293(7)	0.0252(7)	0.0012(6)	–0.0012(6)	0.0004(5)
C(3)	4*e*	0.2213(3)	0.0909(1)	0.5188(1)	0.065(1)	0.044(1)	0.032(1)	0.002(1)	–0.0052(9)	–0.0003(8)
O(4)	4*e*	0.1752(3)	0.5081(1)	0.3009(1)	0.099(2)	0.047(1)	0.099(2)	–0.013(1)	0.015(1)	–0.023(1)
N(4)	4*e*	0.2313(2)	0.0402(1)	–0.00180(9)	0.0456(9)	0.0437(9)	0.0234(7)	0.0019(7)	–0.0047(6)	–0.0003(6)
C(4)	4*e*	0.2877(3)	0.1029(1)	0.4454(1)	0.044(1)	0.041(1)	0.035(1)	0.0050(8)	–0.0028(8)	–0.0027(8)
O(5)	4*e*	0.2022(3)	0.3830(2)	0.2301(1)	0.083(2)	0.090(2)	0.084(2)	0.011(1)	0.003(1)	–0.046(1)
N(5)	4*e*	0.1882(2)	0.2097(1)	0.14897(9)	0.0321(7)	0.0302(7)	0.0333(8)	0.0004(6)	0.0028(6)	0.0012(6)
C(5)	4*e*	0.1767(2)	0.1318(1)	0.3827(1)	0.0367(9)	0.0315(9)	0.0300(9)	0.0002(7)	0.0017(7)	–0.0041(7)
O(6)	4*e*	0.3723(3)	–0.0881(1)	0.3630(1)	0.071(1)	0.050(1)	0.093(1)	0.0027(9)	0.005(1)	–0.009(1)
C(6)	4*e*	0.0080(2)	0.1490(1)	0.3955(1)	0.0371(9)	0.0366(9)	0.037(1)	–0.0006(7)	0.0032(7)	–0.0036(7)
C(7)	4*e*	0.0552(2)	0.1749(1)	0.2699(1)	0.0290(8)	0.0328(9)	0.0343(9)	–0.0011(7)	0.0006(7)	–0.0021(7)
C(8)	4*e*	0.0257(2)	0.1953(1)	0.1830(1)	0.0277(8)	0.048(1)	0.0364(9)	0.0002(7)	–0.0022(7)	0.0046(8)
C(9)	4*e*	0.1911(3)	0.1826(1)	0.0652(1)	0.047(1)	0.038(1)	0.0317(9)	0.0075(8)	0.0021(8)	0.0067(7)
C(10)	4*e*	0.2464(2)	0.0904(1)	0.0636(1)	0.0346(9)	0.0350(9)	0.0265(8)	–0.0002(7)	–0.0002(6)	0.0018(7)
C(11)	4*e*	0.3005(2)	–0.0395(1)	0.0184(1)	0.0358(9)	0.0377(9)	0.0283(8)	–0.0038(7)	0.0010(7)	–0.0018(7)
C(12)	4*e*	0.3559(2)	–0.0336(1)	0.0994(1)	0.0360(9)	0.0307(8)	0.0262(8)	–0.0032(7)	0.0028(6)	–0.0015(6)
C(13)	4*e*	0.4306(3)	–0.1041(1)	0.1386(1)	0.056(1)	0.037(1)	0.0293(9)	0.0039(9)	0.0017(8)	0.0016(7)
C(14)	4*e*	0.4499(3)	–0.1785(1)	0.0951(1)	0.066(1)	0.033(1)	0.044(1)	0.0060(9)	0.010(1)	0.0036(8)
C(15)	4*e*	0.3954(3)	–0.1832(1)	0.0141(1)	0.056(1)	0.037(1)	0.045(1)	–0.0052(9)	0.0129(9)	–0.0117(8)
C(16)	4*e*	0.3211(3)	–0.1139(1)	–0.0260(1)	0.046(1)	0.047(1)	0.0314(9)	–0.0069(9)	0.0020(8)	–0.0109(8)

Acknowledgments. This study was supported by Beijing Natural Science Foundation (grant no. 2092010) of China and Science and Technology Program, Beijing Municipal Education Commission (grant no. KM200810028009) and the Scientific Research Foundation for Returned Overseas Chinese Scholars, Beijing Municipal Government.

References

1. Calderazzo, F.; Englert, U.; Hu, C. H.; Marchetti, F.; Pampaloni, G.; Passarelli, V.; Romano, A.; Santi, R.: Synthesis and structural characterization of iron(II) derivatives of heterocyclic tridentate amines. Inorg. Chem. Acta. **344** (2003) 197-206.
2. Kaim, W.; Rall, J.: Copper-a "modern" bioelement. Angew. Chem. Int. Ed. Engl. **35** (1996) 43-60.
3. Hay, W. R.; Clifford T.; Lightfoot, P.: Copper(II) and zinc(II) complexes of *N,N-bis*-(benzimidazole-2-ylmethy)-amine. Synthesis, formation constants and the crystal structure of $[ZnLCl_2]\cdot MeOH$. Catalytic activity of the complexes in the hydrolysis of the phosphotriester 2,4-dinitrophenyl diethyl phosphate. Polyhedron. **17** (1998) 3575-3581.
4. Yu, B. B.; Meng, X. G.; Liao, Z. R.: [*Bis*-(1*H*-benzimidazol-2-yl-methyl) amine]-dichloro(ethanol)manganese(II). Acta Crystallogr. **E62** (2006) m1519-Cm1521.
5. Addison, A.W.; Rao,T.N.; Reedjik,J.; Van Rijn, J.; Verschoor, G.C.: J. Chem. Soc., Dalton Trans. (1984) 1349.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.