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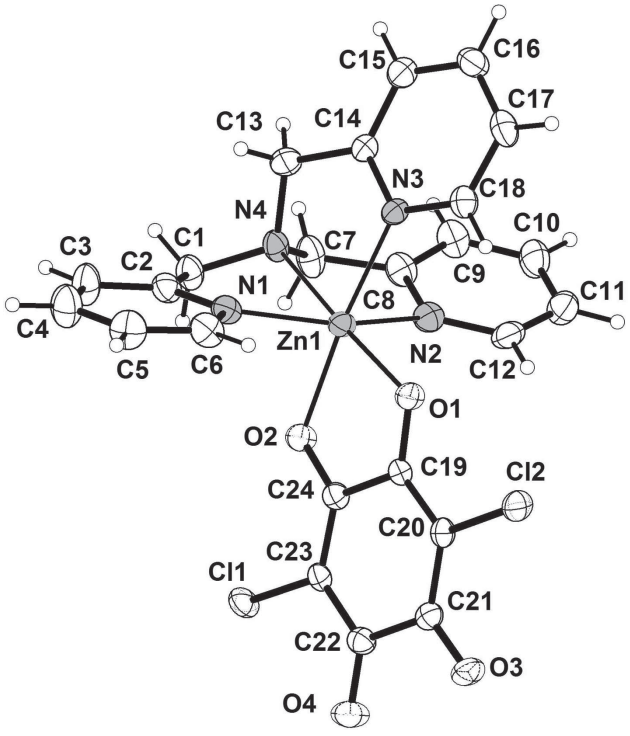
Crystal structure of (tris(2-pyridylmethyl)amine-κ^4*N*,*N*′,*N*″,*N*‴)-chloranilato-κ*O*,*O*′-zinc(II) – methanol (1/1), $C_{25}H_{22}Cl_2N_4O_5Zn$



DOI 10.1515/ncrs-2016-0237
Received August 1, 2016; accepted January 21, 2017; available online February 25, 2017

Abstract

$C_{25}H_{22}Cl_2N_4O_5Zn$, monoclinic, $P2_1/c$ (no. 14), $a = 16.302(3)$ Å, $b = 11.324(2)$ Å, $c = 14.636(3)$ Å, $\beta = 111.43(3)°$, $V = 2515.1(9)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0511$, $wR_{ref}(F^2) = 0.1109$, $T = 123(2)$ K.

CCDC no.: 1528751

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.12 × 0.08 × 0.06 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	12.3 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	52°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	21913, 4932, 0.053
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4419
$N(param)_{refined}$:	337
Programs:	SHELX [1], PLATON [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.26637(2)	0.81232(3)	0.25800(3)	0.02211(14)
Cl2	0.02192(5)	0.96845(7)	0.35808(6)	0.0267(2)
Cl3	0.41477(5)	1.15424(7)	0.47332(6)	0.0273(2)
N4	0.20777(17)	0.6530(2)	0.1779(2)	0.0236(6)
N2	0.30709(18)	0.6797(2)	0.3777(2)	0.0256(6)
N1	0.19251(17)	0.8790(2)	0.1134(2)	0.0244(6)
N3	0.37739(17)	0.7465(2)	0.23119(18)	0.0204(6)
O1	0.32649(14)	0.95507(19)	0.33964(16)	0.0234(5)
O2	0.16452(14)	0.87168(19)	0.29929(17)	0.0253(5)
O3	0.27648(15)	1.2438(2)	0.54296(17)	0.0300(5)
O4	0.10899(16)	1.1706(2)	0.49166(19)	0.0351(6)
C1	0.1204(2)	0.6898(3)	0.1073(3)	0.0281(7)
H1A	0.0793	0.6973	0.1411	0.034*
H1B	0.0979	0.6301	0.0567	0.034*
C5	0.1371(3)	1.0267(3)	−0.0106(3)	0.0359(9)
H5	0.1412	1.1026	−0.0327	0.043*
C2	0.1275(2)	0.8063(3)	0.0608(2)	0.0255(7)
C6	0.1966(2)	0.9871(3)	0.0776(3)	0.0305(8)
H6	0.2417	1.0375	0.1140	0.037*
C4	0.0708(3)	0.9509(3)	−0.0656(3)	0.0401(9)
H4	0.0298	0.9747	−0.1258	0.048*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C3	0.0666(2)	0.8395(3)	−0.0297(3)	0.0360(9)
H3	0.0231	0.7869	−0.0659	0.043*
C11	0.4102(2)	0.5961(3)	0.5243(3)	0.0346(8)
H11	0.4546	0.6073	0.5854	0.041*
C7	0.2013(2)	0.5642(3)	0.2492(3)	0.0333(8)
H7A	0.1983	0.4859	0.2213	0.040*
H7B	0.1473	0.5772	0.2613	0.040*
C9	0.3156(2)	0.4706(3)	0.4002(3)	0.0315(8)
H9	0.2962	0.3956	0.3759	0.038*
C12	0.3720(2)	0.6914(3)	0.4654(3)	0.0298(8)
H12	0.3922	0.7668	0.4875	0.036*
C10	0.3812(2)	0.4836(3)	0.4909(3)	0.0341(8)
H10	0.4056	0.4179	0.5293	0.041*
C8	0.2787(2)	0.5700(3)	0.3453(3)	0.0278(7)
C17	0.5319(2)	0.7189(3)	0.2712(3)	0.0302(8)
H17	0.5892	0.7458	0.3031	0.036*
C14	0.3613(2)	0.6459(3)	0.1793(2)	0.0237(7)
C13	0.2657(2)	0.6132(3)	0.1265(3)	0.0319(8)
H13A	0.2452	0.6477	0.0614	0.038*
H13B	0.2611	0.5281	0.1190	0.038*
C18	0.4610(2)	0.7809(3)	0.2770(2)	0.0250(7)
H18	0.4719	0.8496	0.3144	0.030*
C15	0.4291(2)	0.5789(3)	0.1705(3)	0.0308(8)
H15	0.4167	0.5097	0.1338	0.037*
C16	0.5158(2)	0.6158(3)	0.2170(3)	0.0310(8)
H16	0.5620	0.5719	0.2117	0.037*
C20	0.3073(2)	1.1027(3)	0.4428(2)	0.0199(6)
C24	0.1852(2)	0.9620(3)	0.3544(2)	0.0201(7)
C21	0.2526(2)	1.1607(3)	0.4842(2)	0.0210(7)
C23	0.1296(2)	1.0192(3)	0.3915(2)	0.0196(6)
C22	0.1558(2)	1.1174(3)	0.4557(2)	0.0222(7)
C19	0.27968(19)	1.0087(3)	0.3797(2)	0.0179(6)
O5	0.23853(17)	0.2391(3)	0.7139(2)	0.0408(6)
H5A	0.2352	0.2423	0.6566	0.061*
C25	0.1551(2)	0.2592(3)	0.7179(3)	0.0357(9)
H25A	0.1558	0.2377	0.7816	0.054*
H25B	0.1121	0.2125	0.6687	0.054*
H25C	0.1404	0.3414	0.7061	0.054*

Source of material

A methanol solution (10.0 mL) of the ligand tri(2-pyridylmethyl)amine (TPA) (0.2 mmol) was added into a MeOH solution (10 mL) of $Zn(ClO_4)_2$ (0.2 mmol). Then, chloranilic acid (H_2CA) (0.2 mmol) and triethylamine (0.4 mmol) were added into the mixture. The mixture was refluxed for 1 h, filtered and the resulting solution was kept at room temperature for about two days, producing block red crystals of the title complex with a yield of 65.0%. Elemental analysis–calculated for $C_{25}H_{22}Cl_2N_4O_5Zn$: C, 50.48%; H, 3.73%; N, 9.42%; found: C, 50.36%, H, 3.71%; N, 9.38%.

Experimental details

All H atoms bond to C atoms were introduced using the HFIX command in the SHELX program [1], with the value of 0.93 Å or 0.96 Å for C—H bonds distances. All H atoms were allowed to ride with $U_{iso}(H) = 1.5U_{eq}$(methyl) and $U_{iso}(H) = 1.2U_{eq}(C)$ for all other hydrogen atoms. The structure was checked using PLATON [2].

Discussion

In the past decades, molecule-based functional materials have been paid extensively attentions because of their excellent properties and their structures [3–6]. During the process of preparing metal complexes with special topologies and interesting properties such as magnetic, optical, catalytic and electric properties, the selection of suitable coordination ligands and the central metal ions usually plays important roles. Among the enormous number of ligands, multi-nitrogen organic compounds are common ligands which have been widely investigated. The tris(2-pyridylmethyl)amine ligand (TPA) and its derivatives containing four nitrogen atoms have been usually exploited as capping tetradentate ligands for assemblying low-dimensional complexes [7–9]. In addition, chloranilic acid and its derivatives can be employed as bridging ligands or terminal bidentate ligands [10, 11].

The title compound consists of the [Zn(TPA)(CA)] unit and one methanol molecule. The central metal Zn(II) ion of the title complex is six-coordinated by four nitrogen atoms from the capping ligand TPA and two oxygen of CA^{2-} ligand at its two *cis* positions, forming a slightly distorted octahedral coordination geometry. The Zn—$N_{pyridine}$ bond lengths are very similar and located within the narrow scope from 2.122(3) to 2.217(3) Å, which are similar to that of the Zn—N_{amine} bond length of 2.153(2) Å. The Zn—O bond lengths are 2.036(2) and 2.075(2) Å, respectively. The Zn—O bond lengths are significantly shorter than those of the above Zn—N bond lengths, indicating that the oxygen atoms are strong electron donors. The two C—O bond lengths are similar (1.269(4) and 1.274(4) Å), and the two other C—O bond lengths are 1.231(4) and 1.238(4)Å. The three important bond angles around Zn(II) ion are 174.06(10)° for O2—Zn1—N3, 176.43(10)° for O1—Zn1—N4 and 155.87(10)° for N1—Zn1—N2. The bond angle of O1—Zn1—O2 is 80.60(8)°. In addition, there exists one O—H···O hydrogen bond between the methanol molecule and one oxygen atom of the CA^{2-} ligand.

Acknowledgements: This work was supported by the Fundamental Research Funds for the Central Universities (2015QNA24).

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