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Crystal structure of dichlorido-bis((*E*)-2-((pyridin-4-ylmethylene)amino)phenol)zinc(II), $C_{24}H_{20}Cl_2N_4O_2Zn$

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Abstract

$C_{24}H_{20}Cl_2N_4O_2Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 9.9265(6)$ Å, $b = 15.368(1)$ Å, $c = 16.636(1)$ Å, $\alpha = 102.760(1)^\circ$, $\beta = 90.385(2)^\circ$, $\gamma = 94.112(3)^\circ$, $V = 2311.4(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0260$, $wR_{ref}(F^2) = 0.0653$, $T = 100(2)$ K.

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One of two crystallographically independent complexes present in the asymmetric unit of the title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.32 \times 0.24 \times 0.13$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.32 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	42934, 11554, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 9948
$N(\text{param})_{\text{refined}}$:	599
Programs:	Bruker [1], SHELX [2, 4], Mercury [3]

Source of material

The synthesis of the ligand (*E*)-2-((pyridin-4-ylmethylene)amino)phenol (pap) has been reported by us earlier [5–7]. This educt (2 mmol, 0.397 g) was dissolved in anhydrous ethanol (ca. 10 mL) and was added slowly to the solution of $ZnCl_2$ (1 mmol, 0.136 g) in anhydrous ethanol (ca. 10 mL) and kept under stirring at ambient temperature for 6 h. A yellow precipitate was formed which was isolated *in vacuo*. The yellow precipitate was crystallized using DCM/toluene [8]. **Yield** = 0.456 g, 85.55%, **m.p.** = 226–227 °C, **1H NMR** (400 MHz, DMSO- d_6 , 25 °C, δ in ppm): δ = 9.19 (2H, s, H_j -OH), 8.78 (2H, s, H_c -C=N–), 8.74 (4H, d, J = 5.91 Hz, H_b -C₅H₄N–), 8.00 (4H, d, J = 5.44 Hz, H_a -C₅H₄N), 7.28

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Zn1A	0.53123(2)	0.50168(2)	0.74864(2)	0.01497(4)
Cl1A	0.45239(4)	0.39154(2)	0.64279(2)	0.02351(8)
Cl2A	0.73240(4)	0.48070(2)	0.81512(2)	0.01996(8)
O1A	0.49354(14)	0.81901(8)	0.35948(7)	0.0302(3)
H1A	0.499361	0.779826	0.387227	0.045*
O2A	−0.32494(12)	0.67340(8)	0.94117(7)	0.0234(2)
H2AA	−0.256651	0.648163	0.915162	0.035*
N1A	0.61731(14)	0.82862(8)	0.51152(8)	0.0188(3)
N2A	0.56483(13)	0.61225(8)	0.69916(7)	0.0164(2)
N3A	−0.07106(13)	0.63077(8)	0.99315(8)	0.0171(2)
N4A	0.37381(13)	0.53458(8)	0.83253(7)	0.0160(2)
C1A	0.57005(17)	0.89563(11)	0.39851(9)	0.0223(3)
C2A	0.58197(18)	0.96709(12)	0.35904(10)	0.0261(4)
H2A	0.535949	0.961743	0.306835	0.031*
C3A	0.66073(18)	1.04549(12)	0.39602(10)	0.0268(4)
H3A	0.669072	1.093760	0.368774	0.032*
C4A	0.72802(18)	1.05465(11)	0.47268(11)	0.0267(3)
H4A	0.783210	1.108511	0.497289	0.032*
C5A	0.71398(17)	0.98465(11)	0.51289(10)	0.0228(3)
H5A	0.758939	0.991034	0.565532	0.027*
C6A	0.63426(16)	0.90468(10)	0.47677(9)	0.0190(3)
C7A	0.62881(16)	0.83752(10)	0.58946(9)	0.0178(3)
H7A	0.648031	0.895443	0.623854	0.021*
C8A	0.61255(15)	0.75883(10)	0.62664(9)	0.0169(3)
C9A	0.61682(18)	0.76942(10)	0.71207(9)	0.0224(3)
H9A	0.636919	0.827043	0.746871	0.027*
C10A	0.59151(18)	0.69517(10)	0.74567(9)	0.0223(3)
H10A	0.593078	0.703219	0.803962	0.027*
C11A	0.56507(17)	0.60208(10)	0.61674(9)	0.0210(3)
H11A	0.548607	0.543463	0.583267	0.025*
C12A	0.58806(17)	0.67262(10)	0.57861(9)	0.0208(3)
H12A	0.587200	0.662495	0.520167	0.025*
C13A	−0.30638(16)	0.67668(10)	1.02341(9)	0.0178(3)
C14A	−0.42056(17)	0.69890(10)	1.07575(10)	0.0207(3)
H14A	−0.510347	0.710676	1.054344	0.025*
C15A	−0.40219(17)	0.70370(10)	1.15948(10)	0.0231(3)
H15A	−0.479961	0.718605	1.195464	0.028*
C16A	−0.27063(17)	0.68684(11)	1.19116(10)	0.0228(3)
H16A	−0.258339	0.691538	1.248739	0.027*
C17A	−0.15757(17)	0.66321(10)	1.13890(9)	0.0210(3)
H17A	−0.068263	0.651272	1.160771	0.025*
C18A	−0.17425(15)	0.65683(9)	1.05397(9)	0.0166(3)
C19A	0.04993(16)	0.60463(10)	1.01075(9)	0.0184(3)
H19A	0.070786	0.601673	1.066025	0.022*
C20A	0.15804(16)	0.57893(10)	0.94734(9)	0.0168(3)
C21A	0.29266(16)	0.55769(10)	0.97106(9)	0.0182(3)
H21A	0.312813	0.557966	1.027182	0.022*
C22A	0.39695(16)	0.53617(10)	0.91255(9)	0.0177(3)
H22A	0.488413	0.521988	0.929680	0.021*
C23A	0.24256(17)	0.55403(11)	0.80920(9)	0.0207(3)
H23A	0.225028	0.552593	0.752576	0.025*
C24A	0.13278(16)	0.57588(10)	0.86374(9)	0.0203(3)
H24A	0.041638	0.588621	0.844836	0.024*
Zn1B	−0.09512(2)	0.02925(2)	0.74854(2)	0.01920(5)
Cl1B	−0.03373(4)	−0.09137(2)	0.65881(2)	0.02339(8)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cl2B	−0.30760(4)	0.02279(3)	0.80974(2)	0.02481(8)
O1B	−0.09580(14)	0.59846(8)	0.69823(8)	0.0308(3)
H1B	−0.114188	0.546258	0.704952	0.046*
O2B	0.78118(13)	0.20379(9)	0.95782(7)	0.0302(3)
H2BA	0.713921	0.173824	0.927777	0.045*
N1B	0.02106(14)	0.44309(9)	0.63420(8)	0.0211(3)
N2B	−0.07254(14)	0.13371(8)	0.69008(8)	0.0201(3)
N3B	0.53289(14)	0.12836(9)	1.00096(8)	0.0210(3)
N4B	0.06352(14)	0.06222(9)	0.83847(8)	0.0212(3)
C1B	0.00852(18)	0.59813(11)	0.64173(10)	0.0239(3)
C2B	0.0507(2)	0.67848(11)	0.61925(11)	0.0313(4)
H2B	0.005424	0.731480	0.642592	0.038*
C3B	0.1583(2)	0.68019(12)	0.56301(11)	0.0329(4)
H3B	0.187847	0.734991	0.548373	0.039*
C4B	0.2243(2)	0.60317(12)	0.52733(12)	0.0318(4)
H4B	0.297735	0.605183	0.488205	0.038*
C5B	0.18237(18)	0.52359(12)	0.54919(11)	0.0273(4)
H5B	0.227771	0.470890	0.525100	0.033*
C6B	0.07372(16)	0.51977(10)	0.60645(10)	0.0204(3)
C7B	0.05899(17)	0.36583(10)	0.60088(10)	0.0216(3)
H7B	0.123060	0.359494	0.556057	0.026*
C8B	0.00609(16)	0.28590(10)	0.63003(9)	0.0202(3)
C9B	−0.10257(17)	0.28683(11)	0.68759(10)	0.0230(3)
H9B	−0.151193	0.339458	0.707176	0.028*
C10B	−0.13855(17)	0.20986(11)	0.71577(10)	0.0234(3)
H10B	−0.212850	0.210858	0.754816	0.028*
C11B	0.02741(18)	0.13200(11)	0.63172(10)	0.0243(3)
H11B	0.071768	0.077900	0.611394	0.029*
C12B	0.06801(18)	0.20572(11)	0.60023(10)	0.0251(3)
H12B	0.137899	0.201689	0.558425	0.030*
C13B	0.77353(18)	0.18657(10)	1.03498(10)	0.0222(3)
C14B	0.89429(19)	0.20876(11)	1.08737(10)	0.0257(3)
H14B	0.980258	0.235198	1.069468	0.031*
C15B	0.8883(2)	0.19205(12)	1.16568(11)	0.0287(4)
H15B	0.969914	0.207913	1.201992	0.034*
C16B	0.7633(2)	0.15214(14)	1.19143(11)	0.0339(4)
H16B	0.760488	0.139886	1.244947	0.041*
C17B	0.64268(19)	0.13010(13)	1.13964(11)	0.0300(4)
H17B	0.557601	0.102869	1.157711	0.036*
C18B	0.64601(17)	0.14791(10)	1.06071(10)	0.0211(3)
C19B	0.40400(18)	0.10979(11)	1.01926(10)	0.0238(3)
H19B	0.382120	0.107049	1.074385	0.029*
C20B	0.28787(17)	0.09244(10)	0.95603(10)	0.0216(3)
C21B	0.14505(19)	0.08259(13)	0.97796(11)	0.0319(4)
H21B	0.121667	0.085829	1.033994	0.038*
C22B	0.03650(19)	0.06801(13)	0.91805(11)	0.0307(4)
H22B	−0.060850	0.061894	0.934230	0.037*
C23B	0.20125(18)	0.07332(12)	0.81689(10)	0.0279(4)
H23B	0.221218	0.070796	0.760526	0.033*
C24B	0.31511(18)	0.08825(12)	0.87301(10)	0.0263(3)
H24B	0.411241	0.095614	0.855250	0.032*

(2H, d, *J* = 7.26 Hz, H_d–C₆H₄), 7.14 (2H, t, *J* = 8.11, 7.26 Hz, H_f–C₆H₄), 6.92 (2H, d, *J* = 8.11 Hz, H_g–C₆H₄), 6.86 (2H, t, *J* = 7.69 Hz, H_e–C₆H₄). ¹³C-NMR (400 MHz, DMSO-*d*₆, 25 °C, δ in ppm): δ = 157.39 (–C=N–), 151.55 (–OH), 150.23 (C₅H₄N,

2C's), 149.95 (C_5H_4N), 136.85 (C_6H_4), 128.49 (C_6H_4), 122.36 (C_5H_4N , 2C's), 122.12 (C_6H_4), 119.47 (C_6H_4), 116.35 (C_6H_4). **FT-IR** (cm^{-1}): (Ar-CH) 3055, ($-C=N-$) 1622, (pyridyl) 1483, (C-OH) 1139, 1056. **MS** (ESILC-MS): m/z Calcd. for $[C_{24}H_{20}Cl_2N_4O_2Zn]$: 532.73; found $[ZnL_2 - Cl_2 + 1L + EtOH + Na]^+$: 726 (21%), $[Zn(L_2) - Cl_2 + 1L + EtOH + Na]^+$: 727 (10%). **Anal. Calcd.** (%) for $[Zn(L)2Cl_2]$. C, 54.11; H, 3.78; N, 10.52; found (%): C, 54.11; H, 3.64; N, 10.71.

Experimental details

The structure was solved by the direct method using the *SHELXS* [2] program and refined. The visual crystal structure information was performed using *Mercury* [3] system software. The C-H and O-H distances were restrained to 0.950 Å and 0.84 Å, respectively with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 1.5U_{eq}(O)$.

Comment

Schiff base metal complexes are known to be widely studied mainly because of their numerous applications. Most importantly, most Schiff bases are biologically active and the activity can be further enhanced when complexed with transition metals [9]. Reports have shown that Zn is one of the twenty four essential elements in life [10] and it has found usage in medicine for the treatment of ailments such as athletes foot [11], eczema [11], rheumatoid arthritis [12], diabetes [13], ring-worms [9], fungi [9, 14] and cancer [15]. Zn^{2+} is a redox-stable ion with the ability to interact with amino acid residues side chain in proteins [16] by involving in direct chemical catalysis or by maintaining protein structure and stability [16]. This is only possible when in complexed form according to de Fátima *et al.* [16]. Zn^{2+} ion showed insignificant activity as anti-urease agents but when complexed with a ligand especially those containing *N*-donor atom [89], its activity was improved. As such, its coordination to Schiff base ligands will further improve its role as part of a metalloenzymes [17] by contributing to metalloproteins structure and activity.

The asymmetric unit of the title compound contains two symmetrically independent complexes. Each complex contains two pap ligands and two chlorido ligands coordinating to a Zn^{2+} ion. The two pyridinyl moieties in each molecule coordinate to Zn^{2+} through the nitrogen atom. Furthermore, the conformation of the coordinated ligands is best described by the dihedral angles between pyridinyl and anilinyl rings in each pap ligand which were found to range between $1.15(5)^\circ$ and $27.43(6)^\circ$. The metal centres adopt a distorted tetrahedral geometry with $N_{py}-Zn-N_{py}$, $Cl-Zn-Cl$ and $N_{py}-Zn-Cl$ bond angles of $102.69(5)-104.14(5)^\circ$, $116.61(1)-118.42(2)^\circ$ and $104.87(4)-111.66(4)^\circ$, respectively. These are in agreement with closely related Zn(II) complexes reported [10, 15, 18, 19].

Intermolecular $\pi \cdots \pi$ and $O-H \cdots Cl$ interactions exist in the crystal.

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