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Synthesis, characterization, crystal structures and biological activities of eight-coordinate zirconium(IV) Schiff base complexes

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Abstract Two eight-coordinate Zr(IV) complexes of tetradentate Schiff base ligands, bis(3-ethoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine (H_2L) and bis(3-ethoxysalicylidene)-2,2-dimethyl-1,3-propanediamine (H_2L'), were prepared from $Zr(acac)_4$ in refluxing methanol. The complexes were characterized by physico-chemical and spectroscopic methods. Also, their solid-state structures were determined by single-crystal X-ray diffraction. The crystal structure data showed a tetradentate mode of coordination for both Schiff bases, through N_2O_2 donor sets. The geometries of the complexes were dodecahedral and square antiprismatic for $Zr(L)_2$ and $Zr(L')_2$, respectively. The complexes were screened in vitro against various microbes, revealing their antimicrobial activity.

Introduction

Schiff bases are one of the most prevalent ligands in coordination chemistry. Their metal complexes have a variety of biological, medicinal and analytical applications, in addition to their important roles in catalysis and organic syntheses [1–9]. Schiff bases with oxygen and nitrogen donor atoms operate as good chelating agents for both transition and non-transition metals [10–13]. Complexes with tetradentate N_2O_2 donor set Schiff base ligands have been used as models for metalloproteins, for example oxygen transport proteins [14]. There are a few reports of the synthesis and structural characterization of potentially tetradentate salicylaldimine Schiff base ligands with Zr(IV) [15–19]. Solari et al. used salophen (salicylaldiminatophenylenediamine) for the synthesis of eight-coordinate Zr(IV) complexes, giving both dodecahedral and square antiprismatic coordination geometries. A comparative study of antibacterial activities by Al-Resayes et al. [20] showed that the free Schiff base was inactive, while its complexes showed considerable antibacterial activity. Other studies have also revealed the antibacterial properties of Schiff base complexes [21]. However, to date, there are only limited reports on the biological activity of zirconium Schiff base complexes. In the current project, we synthesized two zirconium(IV) Schiff base complexes based on Schiff base ligands derived from 4,5-dimethyl-1,2-phenylenediamine and 2,2-dimethyl-1,3-propanediamine, as shown in Scheme 1. The complexes were characterized using FTIR, ^{1}H NMR and $^{13}C\{^1H\}$ NMR, elemental analyses and single-crystal X-ray diffraction. The in vitro biological activities of the complexes were evaluated against *Staphylococcus aureus* and *Escherichia coli*.

Experimental

Materials and methods

All chemicals were of reagent grade and used without further purification. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature with a BRUKER

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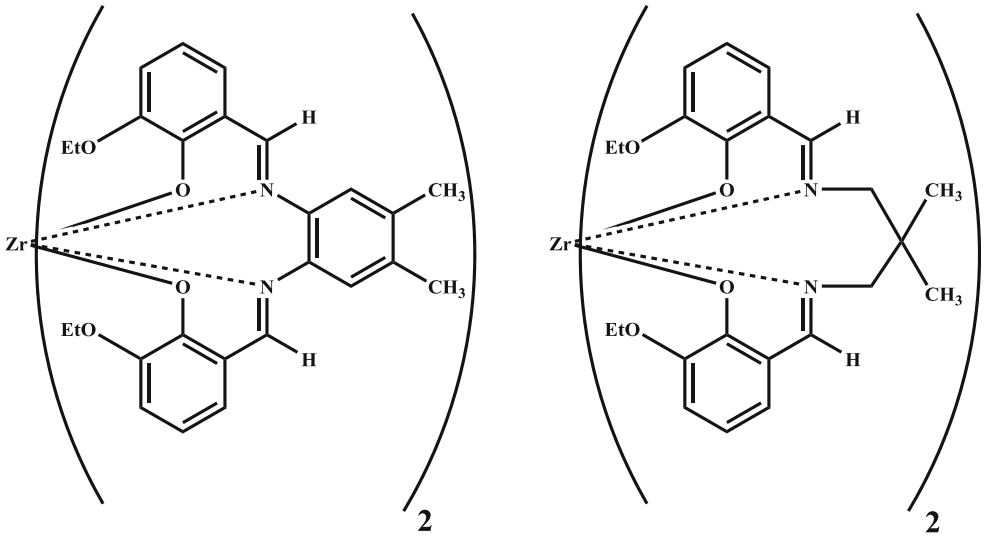
Scheme 1 Structural formulae of the complexes



$Zr(L)_2$ $Zr(L')_2$

AVANCE 400 MHz spectrometer using $CDCl_3$ as solvent. The chemical shift values (δ) are given in ppm. Infrared spectra were recorded using KBr disks on an FTIR Prestige21 spectrophotometer. C, H and N microanalyses were obtained with a LECO CHNS-932 elemental analyzer. X-ray data for the complexes were collected at 293(2) K on a Bruker Smart APEX CCD diffractometer (Mo $K_\alpha = 0.71073$ Å). Full spheres of reciprocal lattice were scanned by 0.3° steps in omega with a crystal–to–detector distance of 5 cm. Cell refinement and data reduction were performed with the help of the SAINT program [22]. Corrections for absorption were made with the multi-scan method and SADABS program [22]. The structures were solved with direct methods using SHELXL-2014, and structure refinement on F^2 was carried out with the SHELXL-2014 program [23]. All non-hydrogen atoms were refined using anisotropic displacement parameters. All calculations were done with PLATON [24]. Four ethyl groups in the $Zr(L)_2$ complex were disordered over two positions with a refined site occupancy ratio of 0.729(6)/0.271(6) and 0.623(6)/0.377(6).

Syntheses of H_2L and H_2L'

To a stirred MeOH (20 mL) solution of 3-ethoxy-salicylaldehyde (0.66 g, 4 mmol) was added a MeOH (20 mL) solution of 4,5-dimethyl-1,2-phenylenediamine (0.27 g, 2 mmol) or 2,2-dimethyl-1,3-propanediamine (0.21 g, 2 mmol). The reaction mixture was heated at reflux for 1 h, and upon cooling to room temperature, the resulting precipitate was collected by suction filtration and washed with cold MeOH (3 × 10 mL) to afford the desired Schiff base. The Schiff bases were spectroscopically pure and used as obtained for the synthesis of the corresponding zirconium complexes. The crystal structures of the free Schiff bases were reported previously [25, 26].

(3-ethoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine (H_2L) Bright orange solid. Yield: 0.81 g (93%); m.p.: 89° C. Anal. calcd. for $C_{26}H_{28}N_2O_4$ (%): C, 72.20; H, 6.53; N, 6.48. Found: C, 72.14; H, 6.61; N, 6.37. IR (KBr, cm^{-1}): 1614 (C=N), 1575, 1463 (C=C), 1249 (C–O). ^1H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 13.40$ (s, 2 H, O–H), 8.63 (s, 2 H, HC=N), 7.03 (d, $^3J = 7.8$ Hz, 2 H_c), 7.01 (s, 2 H_d), 6.98 (d, $^3J = 7.8$ Hz, 2 H_a), 6.86 (d, $^3J = 7.8$ Hz, 2 H_b), 4.16 (q, $^3J = 7.0$ Hz, 4 H, $–CH_2–CH_3$), 2.35 (s, 6 H, CH_3), 1.53(t, $^3J = 7.0$ Hz, 6 H, $CH_3–CH_2–$).

(3-ethoxysalicylidene)-2,2-dimethyl-1,3-propanediamine (H_2L') Bright yellow solid. Yield: 0.69 g (87%); m.p.: 97° C. Anal. calcd. for $C_{23}H_{30}N_2O_4$ (%): C, 69.32; H, 7.59; N, 7.03. Found: C, 69.57; H, 7.66; N, 6.92. IR (KBr, cm^{-1}): 1637 (C=N), 1570, 1458 (C=C), 1246 (C–O). ^1H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 14.05$ (s, 2 H, O–H), 8.35 (s, 2 H, HC=N), 6.96 (dd, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 2 H, H_c), 6.91 (dd, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 2 H, H_a), 6.82 (t, $^3J = 7.8$ Hz, 2 H, H_b), 4.16 (q, $^3J = 7.0$ Hz, 4 H, $–CH_2–CH_3$), 3.53 (s, 4 H, $–CH_2–N$), 1.53 (t,, $^3J = 7.0$ Hz, 6 H, $CH_3–CH_2–$), 1.13 (s, 6 H, CH_3).

Syntheses of the complexes

$Zr(L)_2$: [bis(3-ethoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine] zirconium(IV): A solution of $Zr(acac)_4$ (0.49 g, 1 mmol) in methanol (10 ml) was added to a solution of bis(3-ethoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine (0.86 g, 2 mmol) in methanol (20 ml). The mixture was refluxed for 5 h, then filtered. The solvent was evaporated, and the orange precipitate was recrystallized from

methanol to obtain the pure complex. Suitable crystals of the complex for crystal structure determination were obtained upon slow evaporation at room temperature from methanol solution within a week. The complex was characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, elemental analyses and single-crystal X-ray diffraction.

Anal. calcd. for $C_{52}H_{52}N_4O_8Zr$ (%): C, 65.59; H, 5.50; N, 5.88. Found: C, 65.55; H, 5.55; N, 5.90. IR (KBr, cm^{-1}): 1616, 1593 (C=N), 1548, 1452 (C=C), 1305 (C–O), 550 (Zr–O), 416 (Zr–N). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 8.81$ (s, 2 H, $H_{i'}$–C=N), 8.19 (s, 2 H, H_i–C=N), 7.61 (s, 2 H, $H_{d'}$), 6.96 (dd, $^{3}J = 8.6$, $^{4}J = 2.9$ Hz, 2 H, $H_{c'}$), 6.82 (dd, $^{3}J = 8.6$, $^{4}J = 3.2$ Hz, 2 H, H_c), 6.57 (t, $^{3}J = 7.7$ Hz, 2 H, $H_{b'}$), 6.49 (d, $^{3}J = 6.6$ Hz, 2 H, $H_{a'}$), 6.47 (t, $^{3}J = 7.7$ Hz, 2 H, H_b), 6.42 (s, 2 H, H_d), 6.36 (d, $^{3}J = 7.0$ Hz, 2 H, H_a), 3.86 (dq, $^{2}J = 13.9$, $^{3}J = 6.9$ Hz, 2 H, $H_{f'}$), 3.72 (dq, $^{2}J = 13.9$, $^{3}J = 6.9$ Hz, 2 H, H_f), 3.62 (dq, $^{2}J = 13.9$, $^{3}J = 6.9$ Hz, 2 H, $H_{e'}$), 3.49 (dq, $^{2}J = 13.9$, $^{3}J = 6.9$ Hz, 2 H, H_e), 2.42 (s, 6 H, –$CH_{3(m')}$), 2.17 (s, 6 H, –$CH_{3(m)}$), 1.42 (t, $^{3}J = 6.9$ Hz, 6 H, –$CH_{3(o')}$), 1.35 (t, $^{3}J = 6.9$ Hz, 6 H, –$CH_{3(o)}$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): $\delta = 160.54$, 159.09, 157.77, 155.25, 150.74, 149.34, 143.60, 143.16, 135.33, 134.59, 124.59, 123.62, 122.72, 121.87, 118.38, 117.97, 115.58, 114.95, 114.27, 112.92, 62.92, 62.86, 20.19, 19.67, 15.01, 14.47.

$Zr(L')_2$: [bis(3-ethoxysalicylidene)-2,2-dimethyl-1,3-propanediamine] zirconium(IV): A solution of $Zr(acac)_4$ (0.49 g, 1 mmol) in methanol (10 ml) was added to a solution of bis(3-ethoxysalicylidene)-2,2-dimethyl-1,3-propanediamine (0.80 g, 2 mmol) in methanol (20 ml). The mixture was refluxed for 5 h, then filtered. The solvent was evaporated, and the yellow precipitate was recrystallized from methanol to obtain the pure complex. Suitable crystals of the complex for crystal structure determination were obtained upon slow evaporation at room temperature from methanol solution within a week. The complex was characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, elemental analyses and single-crystal X-ray diffraction.

Anal. calcd. for $C_{46}H_{58}N_4O_8Zr$ (%): C, 62.34; H, 6.60; N, 6.32. Found: C, 62.16; H, 6.72; N, 6.18. IR (KBr, cm^{-1}): 1624, 1597 (C=N), 1556, 1467 (C=C), 1313 (C–O), 551 (Zr–O), 426 (Zr–N). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 8.09$ (s, 4 H, H_i–C=N), 6.64 (dd, $^{3}J = 7.6$, $^{4}J = 1.6$, 4 H, H_c), 6.38 (dd, $^{3}J = 7.6$, $^{4}J = 1.6$, 4 H, H_a), 6.33 (t, $^{3}J = 7.6$, 4 H, H_b), 5.81 (d, $^{2}J = 10.8$, 4 H, $H_{d'}$), 3.89 (q, $J = 7.2$, 8 H, –$CH_{2(f)}$–), 2.92 (d, $^{2}J = 10.8$, 4 H, H_d), 1.32 (s, 12 H, –$CH_{3(e)}$), 1.27 (t, $J = 7.2$, 12 H, –$CH_{3(g)}$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): $\delta = 165.49$, 154.86, 148.76, 123.41, 122.26, 114.50, 113.71, 68.59, 63.14, 37.44, 25.82, 15.18.

Antibacterial activities

Antibacterial activities of the free Schiff bases and their zirconium(IV) complexes were assayed in vitro against the bacterial species *E. coli* ATCC 25922 (gram negative) and *S. aureus* ATCC 25923 (gram positive) by the disk diffusion method. The antibacterial tests used 64 μg/mL concentrations of the test compounds dissolved in DMSO. Bacteria culture Petri dishes treated with the test compounds were incubated for 24 h at 37 °C. The antibacterial activity was determined by evaluating the inhibition zone (mm), MIC (minimum inhibitory concentration) and MBC (minimum bactericidal concentration). MIC is the lowest concentration of an antimicrobial compound that inhibits the noticeable growth of microorganisms at 37 °C after overnight incubation. The MIC values of the test compounds were assayed against bacterial strains through a broth dilution method, using test compound concentrations from 0.128 to 0.00025 mg/ml in DMSO.

Results and discussion

Syntheses and spectroscopic characterization

The Schiff bases were synthesized from 4,5-dimethyl-1,2-phenylenediamine and 2,2-dimethyl-1,3-propanediamine, respectively, in a Schiff base condensation reaction with 3-ethoxy-salicylaldehyde, in methanol. Reaction of $Zr(acac)_4$ and H_2L or H_2L', in refluxing methanol, afforded the neutral zirconium(IV) complexes. Both Schiff bases and the related complexes were obtained in high yields and are stable in the solid state and in solution. The complexes are insoluble in ethanol, methanol, *n*-hexane, acetone and acetonitrile but soluble in chloroform, dichloromethane, warm DMSO and DMF.

The stretching frequencies of the C=N and C–O bonds of the free Schiff bases and their corresponding Zr(IV) complexes are reported in Table 1. The strong bands around 1614 and 1637 cm^{-1} due to the azomethine group in the free Schiff bases are shifted to lower wavenumbers,

Table 1 IR spectral data of the Schiff bases and their corresponding Zr(IV) complexes

Compound	υ(C=C)	υ(C–O)	υ(C=N)	υ(Zr–O)	υ(Zr–N)
H_2L	1575, 1463	1249	1614	–	–
$Zr(L)_2$	1548, 1452	1305	1616, 1593	550	416
H_2L'	1570, 1458	1246	1637	–	–
$Zr(L')_2$	1556, 1467	1313	1624, 1597	551	426

Table 2 Crystal data and refinement parameters for $Zr(L)_2$ and $Zr(L')_2$

Complex	$Zr(L)_2$	$Zr(L')_2$
Empirical formula	$C_{52}H_{52}N_4O_8Zr.H_2O$	$C_{46}H_{56}N_4O_8Zr$
Formula mass	970.21	884.7
Crystal size (mm)	0.04 × 0.08 × 0.15	0.23 × 0.25 × 0.30
Color	Orange	Yellow
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
θ_{max} (°)	27.2	27.2
a (Å)	11.4198(8)	13.9359(7)
b (Å)	13.8911(10)	18.0826(9)
c (Å)	17.0897(12)	18.6098(9)
α (°)	86.135(4)	74.397(2)
β (°)	71.914(4)	74.265(2)
γ (°)	67.125(3)	82.262(3)
V (Å^3)	2370.0(3)	4337.9(4)
Z	2	2
D_{calc} (Mg/m^3)	1.360	1.354
μ (mm^{-1})	0.293	0.311
F (000)	1012	1856
Index ranges	$-14 \le h \le 14$	$-17 \le h \le 17$
	$-17 \le k \le 17$	$-23 \le k \le 23$
	$-21 \le l \le 21$	$-23 \le l \le 23$
No. of measured reflns.	36,794	68,577
No. of independent reflns./R_{int}	10,483/0.041	19,227/0.042
No. of observed reflns. $I > 2\sigma(I)$	7790	19,227
No. of parameters	620	1077
Goodness-of-fit (GOF)	1.04	1.02
R_1 (observed data)	0.0445	0.0417
wR_2 (all data)	0.1062	0.1035

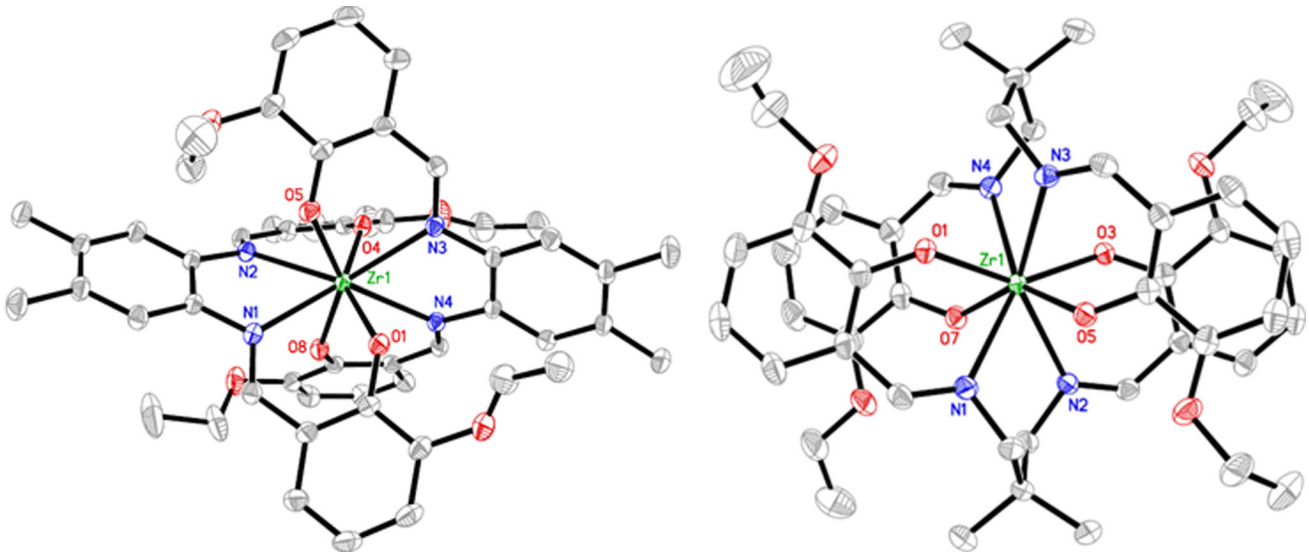


Fig. 1 ORTEP plots of $Zr(L)_2$ (*left*) and $Zr(L')_2$ (*right*, only one complex with major component) with atom numbering and ellipsoids probability at 30%

Table 3 Selected bond lengths (Å) and angles (°) of $Zr(L)_2$ and $Zr(L')_2$

Bond lengths (Å)	$Zr(L)_2$	Bond lengths (Å)	$Zr(L')_2$
Zr(1)–O(1)	2.0895(17)	Zr(1)–O(1)	2.0843(15)
Zr(1)–O(3)	2.0681(19)	Zr(1)–O(3)	2.0829(15)
Zr(1)–O(5)	2.0828(17)	Zr(1)–O(5)	2.0814(16)
Zr(1)–O(8)	2.0686(18)	Zr(1)–O(7)	2.0948(16)
Zr(1)–N(1)	2.407(2)	Zr(1)–N(1)	2.4573(19)
Zr(1)–N(2)	2.456(2)	Zr(1)–N(2)	2.4495(19)
Zr(1)–N(3)	2.411(2)	Zr(1)–N(3)	2.4534(19)
Zr(1)–N(4)	2.453(2)	Zr(1)–N(4)	2.4408(19)
Bond angles (°)	$Zr(L)_2$	Bond angles (°)	$Zr(L')_2$
O(1)–Zr(1)–O(4)	146.38(7)	O(1)–Zr(1)–O(3)	145.30(6)
O(1)–Zr(1)–O(5)	97.88(7)	O(1)–Zr(1)–O(5)	106.34(7)
O(1)–Zr(1)–O(8)	95.04(7)	O(1)–Zr(1)–O(7)	84.48(6)
O(1)–Zr(1)–N(1)	73.64(7)	O(1)–Zr(1)–N(1)	73.44(6)
O(1)–Zr(1)–N(2)	139.94(8)	O(1)–Zr(1)–N(2)	140.44(6)
O(1)–Zr(1)–N(3)	78.34(7)	O(1)–Zr(1)–N(3)	73.77(6)
O(1)–Zr(1)–N(4)	75.07(7)	O(1)–Zr(1)–N(4)	78.62(6)
O(4)–Zr(1)–O(5)	95.70(7)	O(3)–Zr(1)–O(5)	84.02(6)
O(4)–Zr(1)–O(8)	90.75(7)	O(3)–Zr(1)–O(7)	106.30(6)

appearing at 1593–1624 cm^{-1} in the spectra of the complexes. This indicates the involvement of azomethine nitrogen in coordination [27]. The C–O stretching bands of the free Schiff bases shift from 1246–1249 to 1305–1313 cm^{-1} upon coordination to Zr [28]. Medium sharp bands at 550, 551 cm^{-1} and 416, 426 cm^{-1} in the spectra of the complexes can be related to Zr–O and Zr–N bonds, respectively [29].

The ^1H and $^{13}C\{1H\}$ NMR spectra of the complexes are shown in the supporting information (Figs. S1–S4). The ^1H NMR spectra show the absence of a phenolic proton signal and downfield shift of the azomethine H, confirming coordination of the phenolic oxygen and azomethine nitrogen to the metal. The presence of two ^1H NMR peaks for the azomethine protons in the $Zr(L)_2$ complex is indicative of the magnetic non-equivalence of these protons. Similarly, on coordination of H_2L to Zr, the CH_2 protons become non-equivalent and a geminal coupling ($^2J = 13.9$ Hz) is observed. The $^{13}C\{^1H\}$ NMR spectra of the of zirconium(IV) complexes are in agreement with the ^1H NMR data. Thus, $Zr(L)_2$ and $Zr(L')_2$ (Figs. S2 and S4) show two and one resonances for the iminic carbon, respectively. According to the $^{13}C\{^1H\}$ NMR spectra, the $Zr(L)_2$ and $Zr(L')_2$ complexes have 26 and 12 signals,

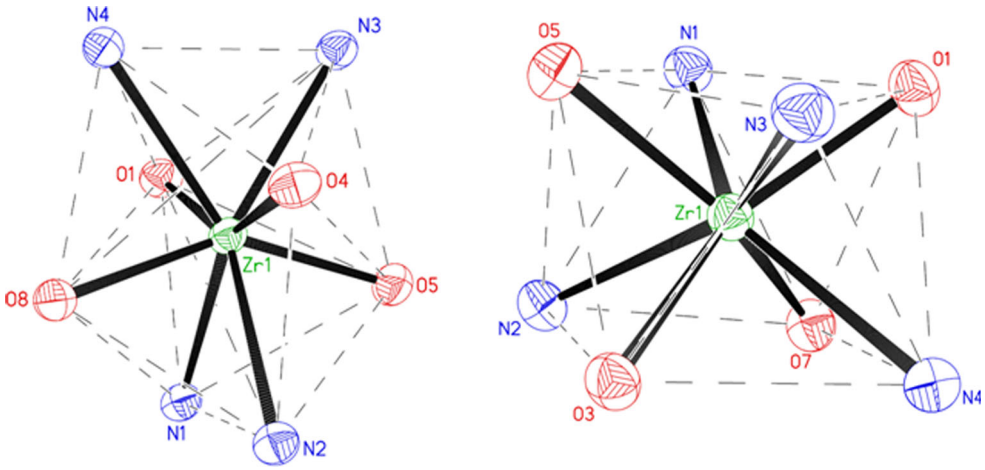


Fig. 2 The dodecahedral (*left*) and square antiprism (*right*) geometries of the ligands around Zr1 in $Zr(L)_2$ and $Zr(L')_2$

Table 4 The inhibition diameter zone values (mm), MIC and MBC for ligands and its Zr complexes

Compound	MIC (mg/ml)		MBC (mg/ml)		Inhibition zone (mm)	
	E. coli	*S. aureus*	*E. coli*	*S. aureus*	*E. coli*	*S. aureus*
H_2L	0.128	0.128	0.128	0.128	8	7
$Zr(L)_2$	0.001	0.004	0.002	0.004	14	12.7
H_2L'	0.128	0.128	0.128	0.128	–	–
$Zr(L')_2$	0.008	0.116	0.016	0.320	10.7	9.8
Cefazolin	0.015	0.007	–	–	18	28

respectively, indicating that the structures in solution are different. Hence, the complex of H_2L is assigned a dodecahedral geometry, while H_2L' gives a square antiprism geometry.

X-Ray crystal structures

The solid-state structures of $Zr(L)_2$ and $Zr(L')_2$ were determined by X-ray diffraction. The crystal data and refinement parameters are summarized in Table 2, and ORTEP plots of $Zr(L)_2$ and $Zr(L')_2$ are shown in Fig. 1. Selected bond lengths and angles are summarized in Table 3. The metal in $Zr(L)_2$ is eight-coordinate, such that the N_2O_2 planes of the two Schiff bases intersect perpendicularly [dihedral angle of 89.56(5)°] giving rise to a dodecahedral arrangement of the nitrogen and oxygen atoms (Fig. 2). The bond lengths and angles and the geometry around the Zr atom in $Zr(L)_2$ are comparable to those of previously reported structures [15, 18, 19]. The asymmetric unit of $Zr(L')_2$ comprises two chemically equivalent but crystallographically independent molecules. The eight-coordination around zirconium in $Zr(L')_2$ is provided by the nitrogen and oxygen atoms of two Schiff base ligands. In each complex, the ligands coordinate in a bis-bidentate mode in which the N_2O_2 donor atoms of the different ligands occupy top and bottom coordination sites of Zr. The bond lengths and angles and the geometry around the Zr atom in $Zr(L')_2$ are comparable to those of a previously reported structure [17]. The resulting coordination polyhedron around zirconium can be described as a distorted square antiprism, with the N_2O_2 cores of the two ligands defining the bases (Fig. 2). The N_2O_2 cores are close to planarity (maximum displacements 0.0376(9), −0.044(1), −0.0484(9) and 0.0604(9) Å for N1/N3/O1/O5, N2/N4/O3/O7, N5/N8/O10/O14 and N6/N7O9/O13, respectively) and nearly parallel to each other (dihedral angle 0.79(4) and 0.36(6)° in the crystallography independent Zr1 and Zr2 complexes, respectively). An interesting feature of the crystal packing of $Zr(L')_2$ is the intermolecular C5–H5···O9B, O9B–H1W2…O3 and O9B–H2W2…O4 interactions which make two parallel infinite chains of the complexes running along the *a*-axis.

Antibacterial activities

The free Schiff bases and their Zr complexes were tested for their in vitro antibacterial activities. The minimum inhibitory concentrations (MIC) values are summarized in Table 4. As is frequently observed, the complexes exhibit higher antibacterial activities than the free ligands. Thus, the free ligands have low inhibitory effects on the growth of the test organisms. $Zr(L)_2$ was the most effective compound against both bacteria, with MIC values of (0.001–0.004 mg/ml). The better performance of $Zr(L)_2$ compared to $Zr(L')_2$ may be due to the lower polarity of the former, allowing for easier crossing of cell membranes. Comparison of the antibacterial properties of the present zirconium complexes with similar examples in the literature indicates that our new complexes are more potent. [30, 31].

Conclusion

In this paper, the preparation and crystal structures of two eight-coordinate zirconium(IV) Schiff base complexes have been reported. In these complexes, the Zr(IV) centers adopt either dodecahedral or square antiprismatic geometries on the basis of steric hindrance and the flexibility of the diamine segment of the Schiff base ligand. The in vitro biological screening experiments showed higher activities for the complexes compared to the free Schiff bases.

Supplementary materials

CCDC **1525264** and **1525265** contain the supplementary crystallographic data for complexes. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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