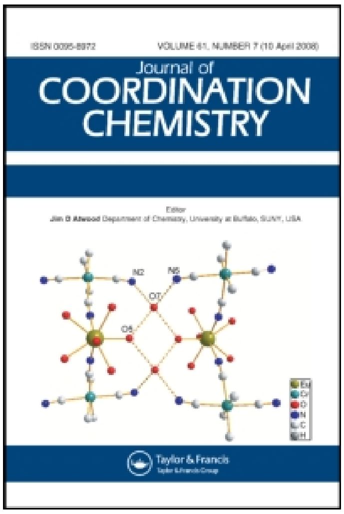

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Coordination behavior of symmetrical hexadentate $O_2N_2S_2$-donor Schiff bases toward zinc (II): synthesis, characterization, and crystal structure

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Coordination behavior of symmetrical hexadentate $O_2N_2S_2$-donor Schiff bases toward zinc (II): synthesis, characterization, and crystal structure

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Two series of zinc(II) complexes of two Schiff bases (H_2L^1 and H_2L^2) formulated as $[Zn(HL^1/HL^2)]ClO_4$ (**1a** and **1b**) and $[Zn(L^1/L^2)]$ (**2a** and **2b**), where $H_2L^1 = $ 1,8-bis(salicylideneamino)-3,6-dithiaoctane and $H_2L^2 = $ 1,9-bis(salicylideneamino)-3,7-dithianonane, have been prepared and isolated in pure form by changing the chemical environment. Elemental, spectral, and other physicochemical results characterize the complexes. A single crystal X-ray diffraction study confirms the structure of $[Zn(HL^1)]ClO_4$ (**1a**). In **1a**, zinc(II) has a distorted octahedral environment with a $ZnO_2N_2S_2$ chromophore.

Keywords: Zinc(II) complexes; Hexadentate Schiff bases; Crystal structure

1. Introduction

Research in our group [1–3] has been directed toward the design and synthesis of transition metal complexes with nitrogen–sulfur donors because the coordination chemistry of transition metal complexes involving nitrogen and sulfur donors has application in modeling biomolecules, in chemical and biological reactivity, and in nuclear medicine [4–8]. Transition metal complexes coordinated to the Schiff-base ligands have been studied extensively, mainly because of their ease of preparation, flexibility, and versatility in terms of chemical properties, geometry, coordination sites, and ease of substitution [9–13]. Zinc complexes with N,S-donor sets are potential mimics of various zinc-containing metalloproteins [14–17]. Although zinc is redox inactive, in most cases it provides structural integrity to polymetallic enzymes so that a redox-active metal ion can exhibit maximum efficiency. The active site is connected to a network of hydrogen bonds formed by adjacent residues and water molecules. Zinc as active center is often surrounded by an NxSy donor set and in enzymes and zinc fingers it is almost always attached to at least one of the sulfurs of cysteine. Zinc is also well-suited [18, 19] for the preparation of functional materials as its d^{10} configuration

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permits a wide range of symmetries and coordination numbers and has a significant role in bioinorganic chemistry.

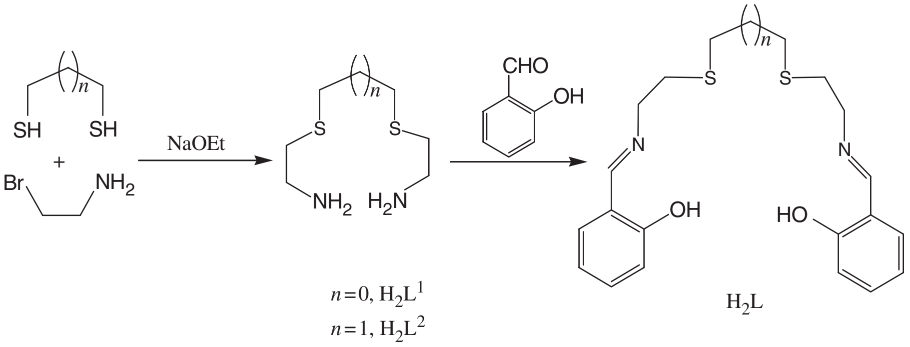
In an effort to isolate and study new zinc(II) complexes, we have explored the coordination behavior of two different hexadentate Schiff-base ligands containing thioether entities (H_2L) toward zinc(II). These ligands have been used to synthesize cobalt(II) and nickel(II) complexes [20, 21], but their reactivity toward zinc(II) have remained unattended so far. In this article, we report the synthetic details, spectral characterization, and different physicochemical properties of zinc(II) complexes of two homologous and very similar hexadentate Schiff bases (H_2L) formulated as $[Zn(HL)]ClO_4$ (**1**) and $[Zn(L)]$ (**2**), where H_2L^1 = 1,8-bis(salicylideneamino)-3,6-dithiaoctane and H_2L^2 = 1,9-bis(salicylidene-amino)-3,7-dithianonane along with the X-ray crystal structure of $[Zn(HL^1)]ClO_4$ (**1a**).

2. Experimental

2.1. *Materials and methods*

Highly pure salicylaldehyde (Spectrochem, India), 2-bromoethylamine hydrochloride (Aldrich, USA), ethylenedisulfide (Aldrich, USA), sodium azide (Aldrich, USA), and triethylamine (Spectrochem, India) were purchased and used as received. Zinc(II) perchlorate hexahydrate was prepared by the treatment of zinc carbonate (E. Merck, India) with perchloric acid (E. Merck, India), followed by slow evaporation on a steam bath and filtration through a fine glass-frit; it was preserved in a desiccator containing concentrated sulfuric acid for subsequent use. All other chemicals and solvents were of AR grade and used as received. The Schiff bases (H_2L^1 and H_2L^2) were prepared following a procedure consisting of two steps (scheme 1) with a slight modification of the reported procedures [20, 21]. The dried products (H_2L) were verified by elemental analyses and spectroscopic studies and used for the study of the reaction toward zinc salts.

Caution: Perchlorate compounds of metal ions are potentially explosive especially in the presence of organic ligands. Only a small amount should be prepared and handled with care.



Scheme 1. Preparation of the hexadentate ligands (H_2L).

2.2. *Physical measurements*

Elemental analyses (carbon, hydrogen, and nitrogen) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded using a JASCO FT-IR model 460 *plus* using KBr discs. Molar conductances (Λ_M) were measured using a Systronics conductivity meter 306 model where the cell constant was calibrated with 0.01 M KCl solution and dry MeOH was used as solvent. UV-Vis spectra were obtained with a JASCO UV-Vis/NIR model V-570. ^{1}H-NMR spectra were obtained on a Bruker AC300 spectrometer with chemical shifts reported relative to the residual solvent resonance of $CDCl_3$.

2.3. *Preparation of [Zn(HL^1)]ClO$_4$ (1a) and [Zn(HL^2)]ClO$_4$ (1b)*

Complexes **1a** and **1b** were prepared from the perchlorate salt of zinc(II) using 1 : 1 mole ratio of the metal and H_2L^1/H_2L^2 in methanolic/ethanolic medium at reflux.

To zinc(II) perchlorate hexahydrate (0.74 g, 2 mmol) in methanol/ethanol solution (10 cm^3), a faint yellow solution of 2 mmol of L^1 (0.78 g) or L^2 (0.81 g) in the same solvent was added dropwise. The light yellow solution was refluxed for 3 h and then filtered. The hot supernatant liquid was cooled and kept in air for slow evaporation. After a few days, the fine crystals of **1** that separated were washed with dichloromethane and dried *in vacuo* over silica gel indicator. Single crystals of **1a** suitable for X-ray measurements were obtained from this reaction.

$C_{20}H_{23}ClN_2O_6S_2Zn$ (1a). Yield: 70%. Anal. Found (%): C, 43.55; H, 4.17; N, 5.15; Calcd (%): C, 43.45; H, 4.20; N, 5.07. IR (KBr, cm^{-1}): 1612 ($\nu_{C=N}$), 769(ν_{C-S}), 1088 ($\nu_{s(ClO_4)}$), 623 ($\nu_{as(ClO_4)}$). ^{1}H NMR (δ, in $CDCl_3$) ppm: 2.84–2.91(m, 8H), 3.94(m, 4H), 6.78(m, 2H), 6.83(m, 2H), 7.21(m, 2H), 7.51(m, 2H), and 8.42(s, 2H). Conductivity (Λ_o, Ohm^{-1} cm^2 mol^{-1}) in MeOH: 98.

$C_{21}H_{25}ClN_2O_6S_2Zn$ (1b). Yield: 72%. Anal. Found (%): C, 44.62; H, 4.39; N, 5.02. Calcd (%): C, 44.52; H, 4.45; N, 4.95 %. IR (KBr, cm^{-1}): 1615 ($\nu_{C=N}$), 768 (ν_{C-S}), 1088 ($\nu_{s(ClO_4)}$), 623 ($\nu_{as(ClO_4)}$), 1090 ($\nu_{s(ClO_4)}$), 625 ($\nu_{as(ClO_4)}$). ^{1}H NMR (δ, in $CDCl_3$) ppm: 2.11(m, 2H), 2.68(m, 4H), 2.99(m, 4H), 3.98(m, 4H), 6.76(m, 2H), 6.85(m, 2H), 7.17(m, 2H), 7.39(m, 2H), and 8.39(s, 2H). Conductivity (Λ_o, Ohm^{-1} cm^2 mol^{-1}) in MeOH: 102.

2.4. *Synthesis of [Zn(L^1)] (2a) and [Zn(L^2)] (2b)*

A methanol/ethanol solution (5 cm^3) of triethylamine (Et_3N) (0.2 g, 2 mmol) was added to the solution of 1 mmol of L^1 (0.39 g) or L^2 (0.40 g) in the same solvent (15 cm^3) and then the solution was stirred for 0.5 h at ambient temperature. To this resulting solution, a methanol/ethanol solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.74 g, 2 mmol) (10 cm^3) was added dropwise with constant stirring. The yellow solution was allowed to reflux for 4 h and then filtered after cooling. The supernatant was left for slow evaporation in air. Light yellow **2** were separated after a few days and dried *in vacuo* over silica gel indicator.

$C_{20}H_{22}N_2O_2S_2Zn$ (2a). Yield: 80%. Anal. Found (%): C, 53.24; H, 4.99; N, 6.10. Calcd: C, 53.15; H, 4.91; N, 6.20; IR (KBr, cm^{-1}): 1595 ($\nu_{C=N}$), 762 (ν_{C-S}). ^{1}H NMR

(δ, in $CDCl_3$) ppm: 2.82–286(m, 8H), 3.98(m, 4H), 6.99(d, 2H), 7.02(m, 2H), 7.18(m, 2H), 7.46(d, 2H), and 8.35(s, 2H). Conductivity (Λ_o, $Ohm^{-1} cm^2 mol^{-1}$) in MeOH: 35.

$C_{21}H_{24}N_2O_2S_2Zn$ (2b). Yield: 80%. Anal. Calcd (%): C, 54.13; H, 5.20; N, 6.01. Found (%): C, 54.26; H, 5.12; N, 5.91; IR (KBr, cm^{-1}): 1605 ($\nu_{C=N}$), 763 (ν_{C-S}). ^{1}H NMR (δ, in $CDCl_3$) ppm: 2.13(m, 2H), 2.65(m, 4H), 2.88(m, 4H), 3.92(m, 4H), 6.91(d, 2H), 6.99(m, 2H), 7.15(m, 2H), 7.49(m, 2H) and 8.37(s, 2H). Conductivity (Λ_o, $Ohm^{-1} cm^2 mol^{-1}$) in MeOH: 28.

2.5. *X-ray crystal structure analysis*

Crystal data for **1a** are summarized in table 1. Diffraction data were collected at 150(2) K on an Oxford Diffraction X-Calibur CCD System with Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell refinement, indexing, and scaling of all the data sets were performed using the Crysalis program [22]. The structure was solved by direct methods using SHELXS-97 [23] and subsequent Fourier analyses. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. A difference Fourier map showed significant (and equivalent) electron density in positions compatible with the hydrogen atoms bonded to O(11) and O(41) and these were refined with 50% occupancy. An absorption correction was carried out using the ABSPACK program [24]. The structure was refined by full-matrix least-squares based on F^2 with all the observed reflections using the SHELXL-97 program [23].

Table 1. Crystallographic data for **1a**.

Crystal parameters	**1a**
Formula	$C_{20}H_{23}ClN_2O_6S_2Zn$
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	20.4490(17)
b	10.1405(10)
c	21.764(3)
β°	97.496(10)
Volume (Å^3), *Z*	4474.5(9), 8
Wavelength (Å)	0.71073
Temperature (K)	150(2)
Absorption coefficient (mm^{-1})	1.445
F(000)	2272
Crystal size (mm^3)	0.30 × 0.05 × 0.05
θ range for data collection (°)	2.25–30.00
Reflections collected	14,002
Independent reflections	6422
Max. and min. transmission	0.812 and 1.000
Goodness-of-fit on F^2	1.117
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0560$, $wR_2 = 0.1468$
R indices (all data)	$R_1 = 0.0940$, $wR_2 = 0.1634$
Largest peak and hole (e Å^{-3})	0.942 and −0.451

3. Result and discussions

3.1. *Synthesis and formulation*

Reaction of H_2L with zinc(II) perchlorate in alcoholic medium in the absence of triethylamine (Et_3N) led to the formation of complexes of the type $[Zn(HL)]ClO_4$ (**1**), whereas the same reaction in the presence of Et_3N gave $[Zn(L)]$ (**2**). Formation of **2** has also been possible if **1** was refluxed in methanol/ethanol having triethylamine (vide scheme 2).

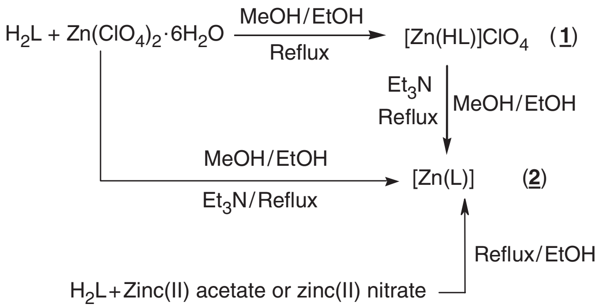
Reactions of H_2L with zinc acetate or zinc nitrate in ethanol having no Et_3N at reflux yielded **2** (scheme 2). Elemental analysis, conductance, and spectroscopic studies suggested the formation of **2** through this method. The observed data are consistent with the data of the complexes obtained in the reaction of H_2L and zinc perchlorate in alcohol containing Et_3N.

The complexes were characterized using microanalytical, spectroscopic, and physicochemical results. The air-stable, moisture-insensitive complexes are soluble in methanol, ethanol, acetonitrile, dimethylformamide, and dimethylsulfoxide. Methanol solution of **1** shows the conductivity of $\sim 100\ \Lambda_o\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$ at 300 K, attributable to 1 : 1 electrolytes; **2** behaves as a nonelectrolyte in solution.

3.2. *Spectral studies*

IR spectra for **1** exhibits a very strong and sharp absorption at *ca* $1088\,\mathrm{cm}^{-1}$ along with a weak band at *ca* $623\,\mathrm{cm}^{-1}$ due to the symmetric ($\nu_{s(ClO_4)}$) and asymmetric ($\nu_{as(ClO_4)}$) stretching vibration of perchlorate [1] along with a weak band around $3340\,\mathrm{cm}^{-1}$ attributable to ν_{OH} [25]. The bands due to perchlorate and the band due to ν_{OH} are absent in the complex of type **2**. A band around $1595–1615\,\mathrm{cm}^{-1}$ due to the $\nu_{C=N}$ stretching frequency of the Schiff base and the band at *ca* $762\,\mathrm{cm}^{-1}$ corresponding to $\nu_{C–S}$ frequency were observed in the IR spectra of all complexes, **1** and **2**. Weak bands in the range $2980–2900\,\mathrm{cm}^{-1}$ are assigned to aliphatic C–H stretch.

^1H NMR spectra of the complexes showed proton signals at lower field than those in the corresponding free ligand. No signal for the proton attached to phenol was observed in ^1H NMR spectra of **1**. The spectra reveal that the deprotonated species of type **2** have effective two-fold symmetry having two equivalent halves of each molecule,



Scheme 2. Reactions of zinc(II) ion with H_2L.

Table 2. Selected bond distances (Å) and angles (°) for **1a**.

Bond distance (Å)		Bond angles (°)			
Zn(1)–S(21)	2.767(1)	O(41)–Zn(1)–N(45)	92.1(1)	N(15)–Zn(1)–S(18)	82.8(1)
Zn(1)–N(45)	2.040(3)	O(41)–Zn(1)–N(15)	101.9(1)	O(11)–Zn(1)–S(18)	163.9(1)
Zn(1)–O(11)	2.178(3)	N(45)–Zn(1)–N(15)	164.8(1)	O(41)–Zn(1)–S(21)	168.8(1)
Zn(1)–O(41)	2.013(3)	O(41)–Zn(1)–O(11)	92.3(1)	N(45)–Zn(1)–S(21)	79.0(1)
Zn(1)–S(18)	2.556(1)	N(45)–Zn(1)–O(11)	92.4(1)	N(15)–Zn(1)–S(21)	87.7(1)
Zn(1)–N(15)	2.049(3)	N(15)–Zn(1)–O(11)	81.3(1)	O(41)–Zn(1)–S(18)	93.5(1)
		N(45)–Zn(1)–S(18)	102.4(1)	O(11)–Zn(1)–S(21)	94.7(1)
				S(18)–Zn(1)–S(21)	82.0(1)

whereas the protonated species **1** have a little deviation from this symmetry. However, this little effect has not been realized in appearance of the distinct singlet of azomethine proton (δ of *ca* 8.40 ppm) except the appearance of signals of the *ortho* hydrogens with respect to the phenolic oxygen in terms of their chemical shift and spin–spin coupling. For **1**, the multiplet signal appeared at relatively high field (δ of 6.78 ppm for **1a** and 6.76 ppm for **1b**) in comparison to the doublet signal of the corresponding protons in **2** (δ of 6.99 ppm for **2a** and 6.91 ppm for **2b**). Otherwise, the observed resonances in the spectra are readily assignable to individual proton types on the basis of spin–spin structure and chemical shift trends.

3.3. *Structure of the Zn(II) complex 1a*

In order to define the coordination sphere, a single-crystal X-ray diffraction study of **1a** was carried out. The bond distances and angles in the Zn coordination sphere are given in table 2. The solid-state structure of the dimeric cation of **1a** has been depicted in figure 1. L^1 is a hexadentate ligand and the coordination polyhedron around zinc(II) is a distorted octahedron containing a $ZnN_2S_2O_2$ chromophore. The metal ion is bonded to two thioether sulfurs, S(18) and S(21), two imine nitrogens, N(15) and N(45), and two phenolate oxygens, O(11) and O(41). An equatorial plane can be defined by the two oxygens and two sulfurs with the two nitrogens in axial positions (figure 1). The Zn(1)–S(18) bond distance [2.556(1) Å] is shorter than that of Zn(1)–S(21) [2.767(1) Å] by 0.211 Å; while the Zn1–O11 bond which is *trans* to S(18) is longer at 2.178(3) Å than the Zn(1)–O(41) bond at 2.013(3) Å by 0.165 Å. Here both Zn–O distances are longer than the Zn–O(phenolate) [1.965(5) Å] observed in octahedral zinc(II) complex [26]. Despite this difference which might indicate that O(11) is more likely to be protonated than O(41), the two C–O distances are not dissimilar with C–O(11) 1.350(4) Å compared with C–O(41) 1.335(4) Å. The two axial bonds are similar with Zn(1)–N(15) 2.049(3) Å and Zn(1)–N(45) 2.040(3) Å.

The crystal lattice of **1a** consists of discrete $[Zn(HL^1)]^+$ cations and perchlorate anions. Thus one phenolate oxygen must be protonated. However, as stated in Section 2, the proton is disordered between the two positions, being 50% bonded to O(11) and 50% bonded to O(41). Dimensions of the hydrogen bonds $O(11)–H(11)\cdots O(41)(-x, y, 1/2-z)$ and $O(41)–H(41)\cdots O(11)(-x, y, 1/2-z)$ are $O\cdots O$ 2.496 Å and $H\cdots O$ 1.68, 1.78 Å, and $O–H\cdots O$ 161, 141°, respectively. The $H(11)\cdots H(41)$

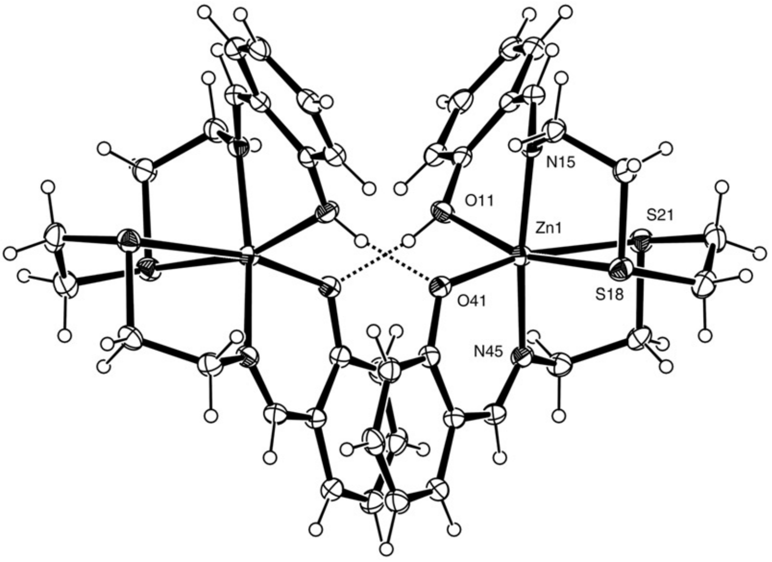


Figure 1. The structure of **1a** with ellipsoids at 30% probability showing formation of a hydrogen bonded dimer across a two-fold axis. Phenolate hydrogen atoms are disordered over two sites, being bonded either to O(11) as shown or to O(41).

$(-x, y, 1/2–z)$ distance is 0.96 Å, so those two hydrogens cannot coexist so dimers must contain either both O(11) atoms protonated or both O(41) atoms protonated.

4. Conclusion

This work reports the synthesis and structure of two types of Zn(II) complexes having octahedral geometry. The hexadentate Schiff bases having $N_2S_2O_2$ donor centers are hexadentate monoanionic and hexadentate dianoinic ligands. On the reaction of H_2L with zinc(II) perchlorate in alcohol, complexes of the type $[Zn(HL)]ClO_4$ (**1**) were formed and [Zn(L)] complexes (**2**) were formed in the presence of Et_3N. Complex **2** was obtained following the similar type of reactions of H_2L with acetate or nitrate salts of zinc(II) even in the absence of a base and we could not isolate complex **1** having the hydrogen bonded counter anion what we observed for zinc(II)perchlorate. This type of the coordination behavior of the Schiff bases toward this 3d member of Group 12 is rarely observed [9–13].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre No. 744549 for **1a**. Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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