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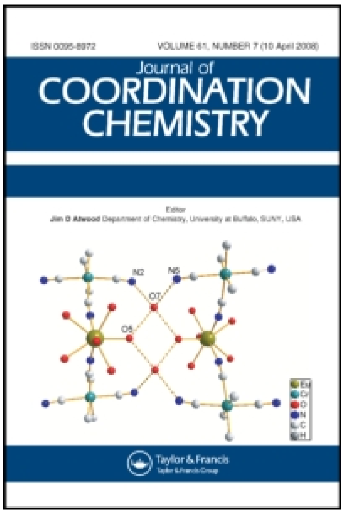

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Zinc(II)-pyridylthioazophenol system: synthesis, characterization and crystal structure

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Reactivities of pyridylthioazophenols (**1**) with zinc(II) salts have been studied and the complexes isolated in pure form and characterized. Pyridylthioazophenols react with zinc(II) acetate in MeOH/EtOH at room temperature to give a series of pyridylsulfinylazophenols (**2**) but no zinc(II) complex. The sulfoxides (**2**) have been characterized by IR and NMR. One of the pyridylsulfinylazophenols (**2a**) has been subjected to single-crystal X-ray analysis in order to confirm details of its structure. A series of dimeric zinc(II) complexes of tetradentate NSNO pyridylthioazophenolates has been isolated through reaction of zinc nitrate in MeOH followed by *in situ* reaction with azide ion, which acts as a μ-(1, 1) bridge. All complexes have been characterized spectroscopically. The detailed structure of one of the dinuclear zinc(II) complexes has been established by a single-crystal X-ray structure determination. In complex **3a** two octahedrally coordinated zinc(II) ions are bridged by two end-on azide ions. No reactions of pyridylthioazophenols with zinc chloride in refluxing EtOH have been observed.

Keywords: Zinc(II); Pyridylthioazophenols; Pyridylsulfinylazophenols; Crystal structure

1. Introduction

Interest in the coordination chemistry of S-ligated transition metal complexes arises in part from the fact that they mimic the ligation of certain biomolecules. The design of molecular architecture in coordination chemistry with donor centres having relevance in biological processes is interesting because their coordination to metals serves as a reference model. Ligands containing thioether and aromatic nitrogen groups are of particular interest. Zinc complexes with N,S donor sets, especially those with heterocyclic N-donors are potential mimics of various zinc-containing metalloproteins [1–4]. Although zinc is redox inactive, in most cases it provides structural integrity to polymetallic-enzymes so that some other redox-active metal ion can exhibit maximum efficiency. The active site is connected to a network of hydrogen bonds formed by

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adjacent residues and water molecules. Zinc as active centre is often surrounded by an N_xS_y donor set and in enzymes and zinc fingers is almost always attached to at least one sulfur atom of cysteine.

As part of a continuing study of new N,S-donor polydentate ligands [5–8], considering the above and the fact that complexes containing N,S donor sets are of biological relevance [9], we report here the chemistry of a series of pyridylthioazophenolates with different zinc(II) salts. The thioethers in pyridylthioazophenols have been converted into sulfoxides on reaction with zinc(II) acetate. Reaction of zinc(II) nitrate with pyridylthioazophenolates (**1**) in refluxing MeOH followed by addition of sodium azide at ambient temperatures gave a series of dimeric zinc(II) complexes of the tetradentate NSNO pyridylthioazophenolates and bridging azide ion [10, 11]. No zinc(II) complex was obtained on reaction with zinc(II) chloride and the pyridylthioazophenols remain unchanged. The new pyridylsulfinylazophenols (**2**) and the dimeric zinc(II) complexes have been characterized by analyses and spectroscopically. Detailed structures of one of the pyridylsulfinylazophenols (**2a**) and one of the zinc(II) complexes have been established by single-crystal X-ray methods. In complex **3a** two octahedral zinc(II) ions are bridged by two end-on azide ions.

2. Experimental

2.1. *Materials and measurements*

The organic compounds **1** were synthesized by a reported procedure [5]. All reagents were obtained from commercial sources and used without further purification. IR spectra were recorded on a Jasco 420 FTIR (KBr discs) and NMR spectra were obtained using a Bruker AC300 spectrometer with chemical shifts reported in δ values relative to the solvent resonance of $CDCl_3$. Microanalyses were performed with a Perkin Elmer 2400 CHN system. Molar conductances (Λ_M) were measured with a Systronics 304 conductivity meter using $\sim 10^{-3}$ M solutions in MeOH.

2.2. *Preparation of compounds 2*

Syntheses of compounds **2** were carried out following a common procedure. The procedure for the synthesis of 4-methyl-2-[2-(pyridylmethylsufinyl)phenylazo]phenol (**2a**) is as follows. A methanolic solution of zinc(II) acetate dihydrate (0.44 g, 2.0 mmol) was added to a solution of **1a** (0.67 g, 2.0 mmmol) in methanolic dichloromethane (50 cm^3). The mixture was stirred at ambient temperatures for 3 h. The volume of the solution was reduced by 75% on a rotary evaporator, and solid **2a** filtered off, washed with water and methanol, and dried *in vacuo*. The compound was recrystallized from methanol solutions by slow evaporation. Yield 0.56 g (80%). The yield of the other sulfoxides varied from 75–82% following a similar method. Anal. **2a**, Calcd (%): C, 64.96; H, 4.84; N, 11.97. Found: C, 64.88; H, 4.75; N, 11.87; **2b**: Calcd C, 67.17; H, 5.85; N, 10.69. Found: C, 67.10; H, 5.88; N, 10.62; **2c**: Calcd C, 58.14; H, 3.77; N, 11.31. Found: C, 58.23; H, 3.68; N, 11.38; **2d**: Calcd C, 56.54; H, 3.66; N, 14.66. Found: C, 56.62; H, 3.54; N, 14.60; **2e**: Calcd C, 68.21; H, 4.39; N, 10.85. Found: C, 68.28; H, 4.42; N, 10.73.

2.3. *Preparation of Zn(II) complexes 3*

Syntheses of compounds **3** were performed using a common procedure. A methanolic solution of zinc(II) nitrate hexahydrate (0.3 g, 1.0 mmol) and compound **1a** (0.34 g, 1.0 mmol) was refluxed for 6 h. The mixture was then cooled to room temperature. To the reddish solution, sodium azide (0.08 g, 1.2 mmol) in aqueous methanol was added slowly and the solution filtered after stirring for 15 min. The filtrate set aside to slowly evaporate for two days. Solid complex **3a** was filtered off, washed with water and methanol, and dried *in vacuo*. The yield was 0.48 g. For others, yields were 40–45%. The complexes were recrystallized from dichloromethane–toluene.

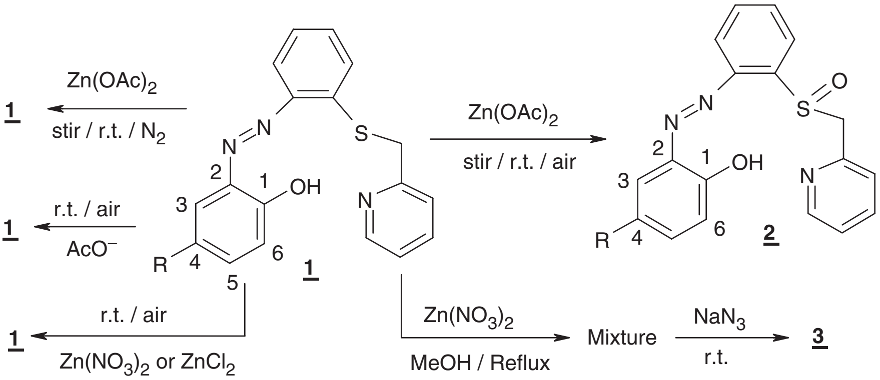
2.4. *X-ray crystallography*

Single crystals of **2a** suitable for X-ray analysis were grown by slow evaporation of a methanol solution at ambient temperatures while crystals of **3a** were grown from dichloromethane–toluene solution (5 : 3) at 298 K. Intensity data were measured with Mo-Kα radiation using the MA Research Image Plate System. The crystals were positioned at 70 mm from the image plate. Some 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [12] to provide independent reflections. The structures were solved using direct methods with the SHELX86 program [13]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon were included in calculated positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was applied using DIFABS [14]. The structure was refined on F^2 using SHELXL [15] for reflections with $I > 2\sigma(I)$.

3. Results and discussion

3.1. *Synthesis*

Compounds **1** were converted into a new series of sulfinyl organic compounds **2** as red solids in the presence of zinc(II) acetate and air at room temperature, and metal complex was isolated. This oxidation of thioether-S in (**1**) to sulfoxides (RR′S=O) (**2**) is by molecular oxygen in the presence of zinc(II) acetate as mediator. If the reaction is carried out under dinitrogen or in presence of acetate ion under aerobic condition, compounds **1** remained unchanged. Compounds **2** could not be obtained using zinc(II) nitrate or zinc(II) chloride in place of zinc(II) acetate (scheme 1). On reaction of **1** with zinc(II) nitrate/zinc(II) chloride in methanol/ethanol under similar conditions to the above, no zinc(II) complex was obtained and **1** remained unchanged. On the contrary, reaction with zinc(II) nitrate and in refluxing methanol followed by *in situ* addition of sodium azide at ambient temperatures gave a series of dimeric zinc(II) complexes of the tetradentate NSNO pyridylthioazophenolate and azide ion as an end-on bridging ligand. All reactions are summarized in scheme 1. Dimeric zinc(II) complexes **3** have been characterized by elemental analyses and other physicochemical techniques (table 1).



R = Me	^{t}Bu	Cl	NO$_2$	3,4-Benzo
HL = 1a	1b	1c	1d	1e

Scheme 1. Reaction scheme.

Table 1. Microanalytical data and conductances of Zn(II) complexes **3**.

Compound	C	H Obs. (Calcd) %	N	Conductance (Λo) mho mol^{-1} cm^{-1}
[Zn(L1)(N$_3$)]$_2$ (**3a**)	51.72 (51.65)	3.67 (3.62)	19.12 (19.03)	12
[Zn(L2)(N$_3$)]$_2$ (**3b**)	54.56 (54.61)	4.62 (4.55)	17.31 (17.38)	15
[Zn(L3)(N$_3$)]$_2$ (**3c**)	46.82 (46.76)	2.77 (2.81)	18.12 (18.19)	10
[Zn(L4)(N$_3$)]$_2$ (**3d**)	45.87 (45.72)	2.69 (2.75)	20.82 (20.75)	16
[Zn(L5)(N$_3$)]$_2$ (**3e**)	55.22 (55.30)	3.47 (3.55)	17.51 (17.60)	9

3.2. *Crystal structures of 2a and 3a*

ORTEP views of **2a** and **3a** are illustrated in figures 1 and 2, respectively. Selected bond distances and angles are listed in tables 2 and 3, respectively. The structure of **2a** confirms the structural conversion of **1a**. Crystals contain one molecule of water of crystallization per organic residue. The S1–O1 bond distance (1.498(4) Å) is slightly longer than that in metal-bound sulfenates but slightly shorter than in metal-bound sulfenates [16–18]; this is also reflected in $\nu_{(SO)}$ (*vide infra*). The N=N bond length is 1.276(7) Å, which is slightly longer compared to that (1.261(4) Å) in **1** [19]. The S1–C28(aromatic) bond distance (1.812(6) Å) is slightly shorter than S1–C31(aliphatic) (1.831(6) Å), whereas in **1**, the S–C (benzene ring) bond distance (1.762(4) Å) is much shorter than the S–C(methylene) distance (1.817(4) Å). This is presumably due to the oxidation of the sulfur to a sulfoxide.

A perspective view of the structure of **3a** with one water molecule and one toluene molecule of crystallization is shown in figure 2. Two zinc(II) ions are octahedrally coordinated with two azide-N, one pyridinic-N and one azo-N atoms in the equatorial

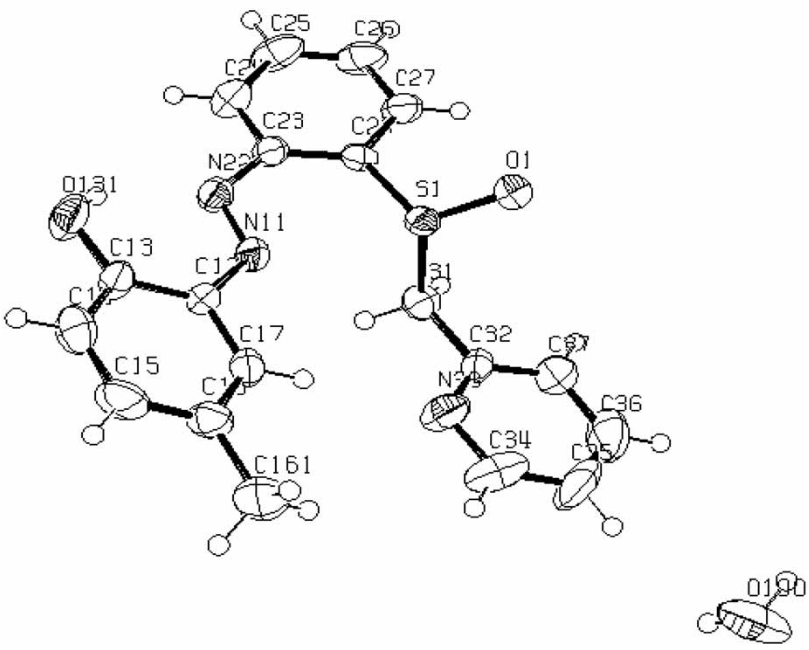


Figure 1. An ORTEP view of **2a** 4-methyl-2-[2-(Pridylmethylsufinyl)phenylazo]phenol monohydrate, with thermal ellipsoids drawn at the 25% probability level and showing the atom numbering scheme.

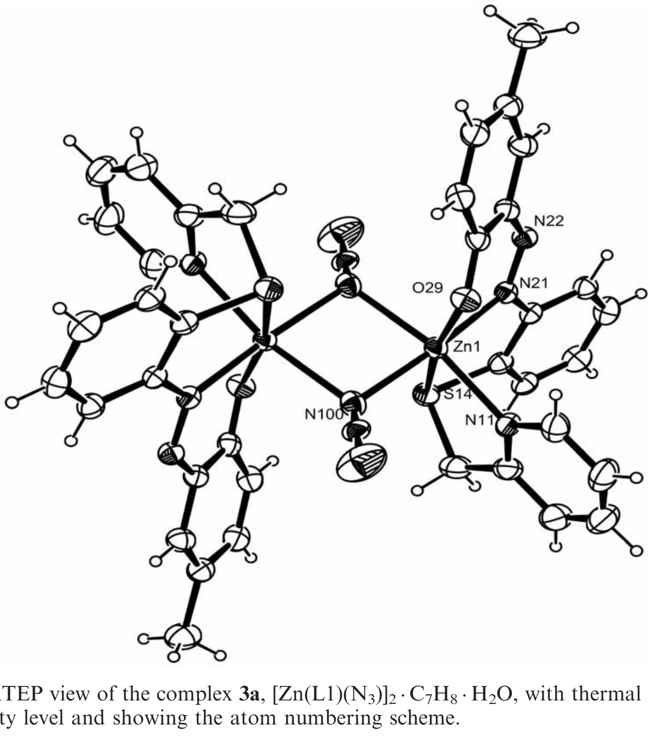


Figure 2. An ORTEP view of the complex **3a**, $[Zn(L1)(N_3)]_2 \cdot C_7H_8 \cdot H_2O$, with thermal ellipsoids drawn at the 25% probability level and showing the atom numbering scheme.

Table 2. Summary of crystallography data for **2a** and **3a**.

	2a	**3a**
Empirical formula	$C_{19}H_{17}N_3O_2S \cdot H_2O$	$C_{38}H_{32}N_{12}O_2S_2Zn_2 \cdot C_7H_8 \cdot H_2O$
Formula weight	369.43	992.76
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	19.804(24)	10.577(12)
b (Å)	4.735(8)	11.702(14)
c (Å)	21.270(25)	12.054(14)
α (°)		119.103(10)
β (°)	112.644(10)	95.282(10)
γ (°)		91.535(10)
V (Å^3)	1840.8(44)	1294(3)
ρ_{Calcd} (g cm^{-3})	1.333	1.373
Z	4	2
Radiation wavelength (Å)	0.71073	0.71073
F(000)	776	546
Temperature (K)	293(2)	293(2)
θ	1.94 to 25.83	1.94 to 25.80
μ(Mo-Kα) (mm^{-1})	0.200	1.062
Total reflections	2705	4615
Reflections with $[I > 2\sigma(I)]$	2009	3380
R	0.1090	0.0866
wR	0.1683	0.1687

Table 3. Selected bond distances (Å) and angles (°) for **2a** and **3a**.

2a			
S1–O1	1.498(4)	O1–S1–C28	105.8(3)
S1–C28	1.812(6)	O1–S1–C31	102.9(3)
S1–C31	1.831(6)	C28–S1–C31	97.8(3)
C31–C32	1.500(9)	N22–N11–C12	116.5(5)
N11–N22	1.276(7)	C17–C12–N11	114.6(5)
N11–C12	1.410(7)	N11–C12–C13	126.5(6)
N22–C23	1.418(7)	O131–C13–C14	118.8(6)
C12–C17	1.396(8)	O131–C13–C12	122.7(6)
C13–O131	1.359(8)	N11–N22–C23	113.3(5)
C32–N33	1.330(8)	C24–C23–N22	115.8(6)
N33–C34	1.345(10)	C28–C23–N22	124.3(6)
3a			
Zn1–O29	1.965(5)	O29–Zn1–N100	101.5(2)
Zn1–N100	2.132(7)	O29–Zn1–N21	86.51(19)
Zn1–N21	2.139(6)	N100–Zn1–N21	170.1(2)
Zn1–N11	2.169(6)	O29–Zn1–N11	98.1(2)
Zn1–N100	2.223(7)	N100–Zn1–N11	90.5(2)
Zn1–S14	2.554(4)	N21–Zn1–N11	94.2(2)
C20–N21	1.436(7)	O29–Zn1–N100	93.1(2)
N21–N22	1.287(7)	N100–Zn1–N100	81.4(3)
N22–C23	1.384(8)	N21–Zn1–N100	92.4(2)
S14–C13	1.810(8)	N11–Zn1–N100	167.3(2)
C19–S14	1.774(7)	O29–Zn1–S14	165.33(14)
N100–N101	1.040(7)	N100–Zn1–S14	93.05(16)
N101–N102	1.227(10)	N21–Zn1–S14	79.25(14)
C28–O29	1.312(7)	N11–Zn1–S14	79.57(16)
C206–C207	1.16(3)	N100–Zn1–S14	91.05(16)

plane along with thioether-S and phenolic-O atoms in axial positions. The dimer contains a centre of symmetry and the bridging parallelogram is constructed by Zn_2N_2 [N(azido)] motifs. Bridging angles are Zn1–N100–Zn1 98.6(3) and N100–Zn1–N100 81.4(3)°. Azide bridges two zinc centres in a μ-(1, 1) fashion as predicted from the IR. The Zn1–N11 bond length (2.169(6) Å) is longer than Zn1–N21 (2.139(6) Å) but shorter than Zn1–N100 (2.223(7) Å), as expected.

3.3. *Spectroscopic properties*

Compounds **2** display an IR stretch band in the range 991–995 cm^{-1} assigned to $\nu_{(SO)}$, which is absent in IR spectra of **1**. Compounds **3** display a strong stretch at ca 2063 cm^{-1} suggesting the end-on azide bridging mode. A medium intensity band at ca 3300 cm^{-1} (O–H of H bonded phenolic OH) present in **1** and **2** is absent in **3**. This indicates coordination of oxygen to the metal centre [5]. In addition, $\nu_{C\text{–}S}$ at around 790 cm^{-1} for **1** shifts to ca 760 cm^{-1} for complexes **3**. Characteristic peaks of compounds **2** in ^1H NMR are the same, except for the CH_2 peak, which is shifted downfield by 0.03 to 0.05 ppm in comparison to compounds **1**. In ^{13}C NMR spectra recorded in $CDCl_3$, the peak corresponding to the carbon of the methylene group attached to the sulfenate is shifted downfield significantly in comparison to the corresponding carbon in the corresponding thioether. The δ value of 41.1 ppm for this carbon in pyridylthioazophenols **1** is less upfield than the δ value of 60.2 ppm for the same carbon in compounds **2** and other δ values due to the other carbons in **2** are comparable to δ values for corresponding carbons in **1**.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 289333 and 289334. Copies of this information can be had free of charge from CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.ac.uk or www:http://www.ccdc.cam.ac.uk).

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