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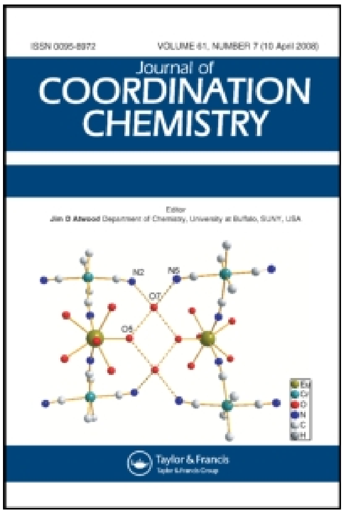

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Synthesis and structural characterization of a new polymeric zinc(II) complex with thiophene-2-carboxylic acid

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Synthesis and structural characterization of a new polymeric zinc(II) complex with thiophene-2-carboxylic acid

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A new polymeric zinc(II) complex with thiophene-2-carboxylic acid (α-tpc) of composition $[Zn_2(C_{20}H_{12}O_8S_4)]_n$ was obtained and structurally characterized by X-ray diffraction, thermal analysis, nuclear magnetic resonance (NMR), and infrared spectroscopies. Upfield shift in the ^{1}H-NMR spectrum is explained by the crystalline structure, which shows the thiophene rings overlapping each other in parallel pairs. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 9.7074(4)$ Å, $b = 13.5227(3)$ Å, $c = 18.9735(7)$ Å, $\beta = 95.797(10)^\circ$, and $Z = 4$. Three α-tpc groups bridge between two Zn(II) ions through oxygens and the fourth one bridges between one of these ions and the third one, symmetry related by a twofold screw axis. This arrangement gives rise to infinite chains along the crystallographic *a* direction. The metal atoms display an approximate tetrahedral configuration. The complex is insoluble in water, ethanol, and acetone, but soluble in dimethyl sulfoxide.

Keywords: Polymeric zinc complex; Thiophene-2-carboxylic acid; Crystal structure; ^{1}H- and ^{13}C-NMR

1. Introduction

Five-membered sulfur-containing heterocycles and in particular, thiophene derivatives are of major importance in chemistry. Thiophene obeys the $4n + 2\pi$ electron rule (Huckel's rule) and is generally considered to be aromatic [1]. The sulfur in the five-membered ring is an electron-donor heteroatom, contributing two electrons to the aromatic sextet, and thiophene is thus considered to be an electron-rich heterocycle. The chemistry of thiophene is dominated by this effect [2]. Thiophene and derivatives have attracted attention due to their applications in technology [3–5], medicine [6–8], and construction of supramolecular frameworks [9–11]. Moreover, thiophene is a structural fragment of conjugated polymers [12], which have gained importance for their potential applications in nonlinear optical materials [13, 14], organic light-emitting diodes [15, 16], and thin film transistors [17], and might be useful for polarized light

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emission as a backlight panel for liquid crystal display devices [18]. In the quest for commercially viable conducting polymers, polythiophene (PT) is a likely candidate because of high stability, doped and undoped states, ease of structural modification, and controllable electrochemical behavior [19].

Zinc(II) complexes with sulfur ligands have been widely studied due to their biological importance [20, 21] and their use as accelerators in rubber vulcanization [22]. Liquid crystal properties were investigated using zinc(II) complexes with dithiocarboxylates [23]. Zinc complex with a thiophene derivative was described in the literature as showing antibacterial activity against two pathogenic bacteria (*Staphylococcus aureus* and *alpha-hemolytic streptococci*) and electrochemical behavior [24, 25]. Recently, luminescent properties of some zinc complexes were published [26–29] and several zinc(II) complex structures using different ligands were described [30–34], among them some interesting carboxylate ligand complexes [35–37].

In this article, a new polymeric complex of zinc(II) with thiophene-2-carboxylic acid, α-tpc, is described. The complex was synthesized and characterized by thermal analysis (TA), nuclear magnetic resonance (NMR; ^{13}C, ^{1}H), infrared spectroscopies, and X-ray crystallography.

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2. Experimental

2.1. *Chemicals*

Thiophene-2-carboxylic acid, $C_5H_4O_2S$, and zinc(II) acetate dihydrate, $Zn(H_3C_2O_2)_2 \cdot 2H_2O$, were purchased from Fluka and Synth products, respectively, with analytical-grade purities.

2.2. *Synthesis*

Thiophene-2-carboxylic acid (2.0 mmol) was dissolved in distilled water (5.0 mL) under stirring and heating (50°C). The pH was adjusted to 5.0 by slowly adding aqueous ammonia ($0.1\,\mathrm{mol\,L^{-1}}$). The Zn(II) aqueous solution containing 0.5 mmol (3.0 mL) of zinc acetate dihydrate was added. This reaction was carried out with stirring at room temperature for 1 day. The mixture was concentrated into 2.0 mL. After a few days, colorless crystals of $[Zn_2(C_5H_3O_2S)_4]$ were obtained.

2.3. *Physical measurements*

Infrared (IR) spectra were recorded on an Fourier transform infrared (FT-IR) Spectrum Perkin Elmer 2000 with samples prepared as KBr pellets. TA was performed on a thermoanalyzer thermogravimetric analysis/differential thermal analysis (TGA/DTA) simultaneous SDT 2960, TA instruments, under the following conditions: atmospheric air, $100\,\mathrm{mL\,min^{-1}}$, and heating at $10^{\circ}\mathrm{C\,min^{-1}}$, from 25°C to 900°C. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian 500 MHz spectrometer. Samples were analyzed in dimethylsulfoxide (DMSO) solutions. The crystal was mounted on an Enraf–Nonius Kappa-CCD diffractometer with graphite monochromated Mo-Kα

($\lambda = 0.71073$ Å) radiation. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program [38]; integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [39]. Absorption corrections were carried out using the Gaussian method [40]. The structure was solved by direct methods with SHELXS-97 and the model was refined by full-matrix least squares on F^2 by means of SHELXL-97 [41].

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3. Results and discussion

3.1. *IR spectra*

A comparison of the IR absorption spectra data obtained for thiophene-2-caboxylic acid and zinc complex suggests that the coordination is through bidentate carboxylate. The difference between vibrational frequencies (Δ) ν_{asym} (COO^-) and ν_{sym} (COO^-) generally increases when the M–O bond strength increases, depending on the carboxylate coordination [42, 43]. The monodentate coordination gives higher Δ values than bidentate coordination. The vibration frequencies related to ν_{asym} (COO^-) and ν_{sym} (COO^-) in thiophene-2-carboxylic acid occur at 1690 and 1432 cm^{-1}, while for our zinc complex they occur at 1594 and 1424 cm^{-1}, respectively. The Δ values are 258 cm^{-1} for thiophene-2-carboxylic acid and 170 cm^{-1} for the zinc complex, indicating both oxygens of COO^- are involved through bridging, resulting in a polymeric metal complex with thiophene-2-carboxylic acid. The spectroscopic studies indicate that each (COO^-) is bidentate bridging, forming a polymeric structure as confirmed by the X-ray structure.

3.2. *Thermogravimetric analysis*

The thermogravimetric data suggests the chemical formula of the complex to be $[Zn_2(C_5H_3O_2S)_4]$ (Supplementary material). The observed melting point is 192°C. The TA results are summarized in table 1. The most significant weight loss is observed as ligand decomposition, which leaves a final residue of ZnO.

3.3. *X-ray structure*

X-ray single-crystal analysis shows that the carbonyl oxygens of three thiophenes bridge two independent Zn^{2+} ions. Both zincs display approximate tetrahedral symmetry.

Table 1. Stages of complex decomposition.

		Weight (%)		
Complex	Temperature (°C)	Stage	Calculate	Experimental
$[Zn_2(C_5H_3O_2S)_4]$	73–94	$1.0 \times H_2O$ adsorbed	2.89	3.00
	180–800	Δm ligand	71.9	71.6
Residual mass	900	$2 \times ZnO$	25.2	24.9

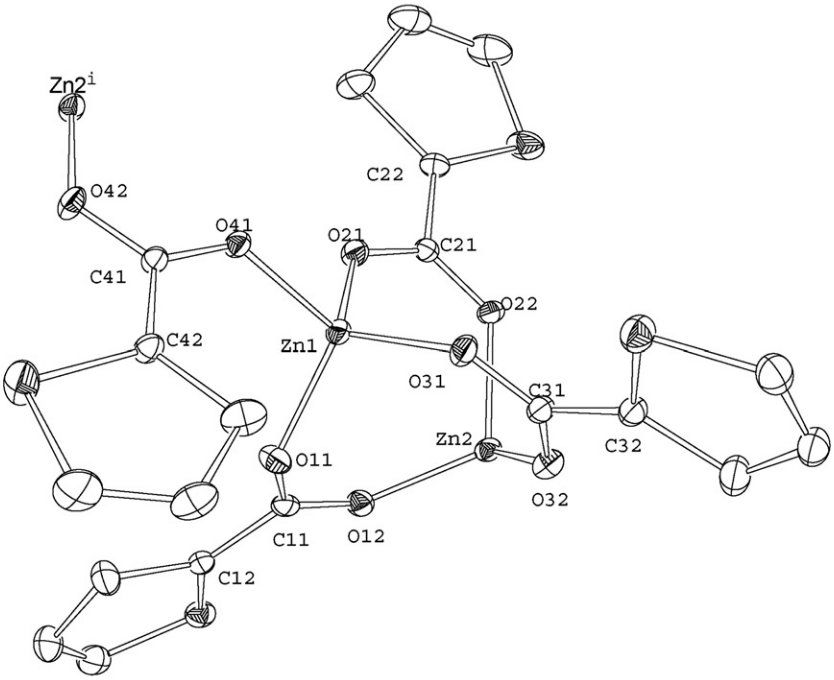

Figure 1. ORTEP-3 projection of the complex. Displacement ellipsoids are shown at 30% probability level. Superscript *i* indicates the symmetry operation $2-x$, $½+y$, and $½-z$.

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The rings display some degree of disorder as shown by anomalous behavior of the displacement parameter of the sulfur and carbon attached to C12, C22, C32, and C42, and also because of anomalous interatomic distances subtended by these atoms. These facts were interpreted as due to the rings occupying two positions related to one another by a 180° rotation. This disorder was dealt with by refining a sulfur and carbon (those bonded to C12, C22, C32, and C42) in the same positions, constraining their respective occupancies to add up to one. The *R*1 agreement index was significantly improved but, of course, the interatomic distances in the rings are not very significant since the disorder produces an average between the C–C and C–S bond distances. Hydrogens were not included in the model. Figure 1 was prepared using ORTEP-3 for Windows® [44]. Data collection and experimental details are summarized in table 2. There are two Zn^{2+} ions and four thiophene-2-carboxylic acid moieties in the asymmetric unit. Three of these moieties bridge metal ions through their carbonyl oxygens and the other bridges Zn(1) and Zn(2), obtained by the one in the asymmetric unit from the symmetry operation $2-x$, $½+y$, and $½-z$. This arrangement gives infinite chains along the unique *b*-axis. Table 3 shows the lengths and angles of the complex bonds. Figure 2 shows the position of parallel heterorings which are separated by 3.327(6) Å, indicative of π–π interactions, justifying the upfield shift in NMR spectra.

3.4. *NMR spectroscopy*

The structure of α-tpc with hydrogen and carbon numbering is shown in figure 3. The ^{13}C-NMR spectrum of α-tpc in DMSO shows chemical shifts from all carbons.

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Table 2. Crystal data and structure refinement.

Empirical formula	$C_{20}H_{12}O_8S_4Zn_2$
Formula weight	639.28
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	9.7074(4)
b	13.5227(3)
c	18.9735(7)
β	95.7970(10)
Volume (Å^3), Z	2477.92(15), 4
Calculated density (g cm^{-3})	1.714
Absorption coefficient (mm^{-1})	2.316
$F(000)$	1280
Crystal size (mm^3)	$0.253 \times 0.289 \times 0.488$
θ range for data collection (°)	2.59–26.00
Limiting indices	$-10 \le h \le 11$; $-14 \le k \le 16$; $-18 \le l \le 23$
Reflections collected	17,003
Independent reflection	4846 [$R(\text{int}) = 0.0438$]
Completeness to $\theta = 26.00$ (%)	99.7
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4846/0/312
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0408$, $wR_2 = 0.1116$
R indices (all data)	$R_1 = 0.0591$, $wR_2 = 0.1254$
Extinction coefficient	0.0020(7)
Largest difference peak and hole (e Å^{-3})	0.363 and −0.514

Table 3. Bond lengths (Å) and angles (°).

O(11)–C(11)	1.257(5)	O(31)–Zn(1)	1.932(3)
O(11)–Zn(1)	1.919(3)	O(32)–C(31)	1.254(5)
O(12)–C(11)	1.262(4)	O(32)–Zn(2)	1.933(3)
O(12)–Zn(2)	1.937(3)	O(41)–C(41)	1.256(4)
O(21)–C(21)	1.254(4)	O(41)–Zn(1)	1.932(2)
O(21)–Zn(1)	1.937(3)	O(42)–C(41)	1.254(4)
O(22)–C(21)	1.251(4)	O(42)–Zn(2)#1	1.932(2)
O(22)–Zn(2)	1.963(2)	Zn(2)–O(42)#2	1.932(2)
O(31)–C(31)	1.253(4)		
C(11)–O(11)–Zn(1)	128.1(2)	O(11)–Zn(1)–O(41)	108.79(11)
C(11)–O(12)–Zn(2)	128.8(3)	O(11)–Zn(1)–O(31)	112.07(13)
O(11)–C(11)–O(12)	125.0(4)	O(41)–Zn(1)–O(31)	109.70(11)
C(21)–O(21)–Zn(1)	128.1(2)	O(11)–Zn(1)–O(21)	110.51(12)
C(21)–O(22)–Zn(2)	128.3(2)	O(41)–Zn(1)–O(21)	98.87(10)
O(22)–C(21)–O(21)	125.4(3)	O(31)–Zn(1)–O(21)	115.96(11)
C(31)–O(31)–Zn(1)	129.1(3)	O(42)#2–Zn(2)–O(32)	110.63(12)
C(31)–O(32)–Zn(2)	131.2(2)	O(42)#2–Zn(2)–O(12)	111.88(12)
O(31)–C(31)–O(32)	125.5(4)	O(32)–Zn(2)–O(12)	117.17(12)
C(41)–O(41)–Zn(1)	134.8(2)	O(42)#2–Zn(2)–O(22)	96.58(11)
C(41)–O(42)–Zn(2)#1	118.7(2)	O(32)–Zn(2)–O(22)	107.49(12)
O(42)–C(41)–O(41)	121.6(3)	O(12)–Zn(2)–O(22)	111.08(11)

Symmetry transformations used to generate equivalent atoms: #1: $-x+2$, $y+½$, $-z+½$; #2: $-x+2$, $y-½$, $-z+½$.

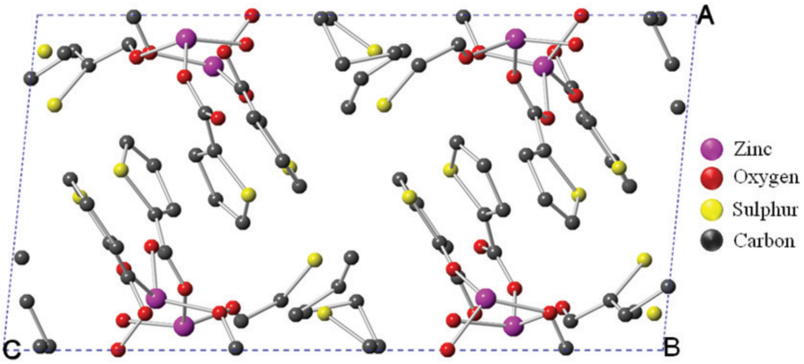

Figure 2. Representation of the asymmetric units and the position of parallel heterorings.

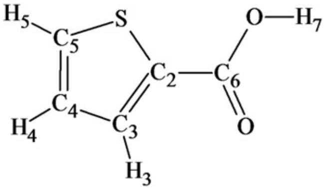

Figure 3. Schematic structure of α-tpc showing hydrogen and carbon numbering.

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^{13}C- and ^{1}H-NMR spectra of the Zn(II)–α-tpc complex were analyzed in comparison to the ^{13}C and ^{1}H spectra of the free ligand.

The ^{13}C-NMR spectra (Supplementary material) give two pieces of evidence for coordination of α-tpc to Zn(II) through oxygen of carboxylate, i.e., chemical shift of C6 and C2 (figures 3 and S2). The chemical shift at 162.84 ppm in the spectrum of the ligand is assigned to the carbon of COOH (C6 in figure 3). In the spectrum of the complex, the signal of C6 is shifted downfield by 3.07 ppm, indicating coordination through oxygen of the carboxylate. Pronounced changes are also observed for the chemical shift of C2 in the spectrum of the Zn(II)–α-tpc complex compared to the spectrum of the free ligand. The chemical shift observed for C2, which varies from 133.15 ppm in the ligand to 141.77 ppm in the complex is confirmation of coordination through COOH.

All ^{1}H-NMR signals were shifted upfield in the complex (Supplementary material). Usually the metal ion decreases the ligand electronic density, making the proton signals shift downfield. In this case, in contrast, the proton signals shift upfield. This could be ascribed to the rather high polarizability of sulfur supplies additional electronic density, more than compensating that withdrawn by zinc. Another possible explanation for this upfield shift could be attributed to the protection effect due to the position of the heterorings. As the crystal structure shows, these rings are packed in parallel pairs, related by a crystallographic center of symmetry, at 3.327(6) Å, as shown in figure 2. This π-stacking shields the protons from the external magnetic field. The ^{13}C and ^{1}H chemical shifts for α-tpc and Zn(II)–α-tpc complex are given in table 4.

Table 4. ^{1}H- and ^{13}C-NMR chemical shifts for α-tpc and for the Zn(II)–α-tpc complex.

	H3	H4	H5	H7	C2	C3	C4	C5	C6
Ligand	7.932		7.681	–	133.15	134.62	128.13	133.11	162.84
	7.930	7.180	7.679						
	7.925	7.172	7.671						
	7.922	7.170	7.679						
Complex	7.585	7.057	7.476	–	141.77	130.07	127.24	129.75	165.91
	7.583	7.050	7.473						
	7.575	7.047	7.469						
	7.573	7.040	7.466						

4. Conclusions

The molar composition of the polymeric zinc(II) complex with thiophene-2-carboxylic acid was 1 : 2 (metal : ligand). TA shows complete decomposition of the complex, leaving ZnO. IR, ^{1}H- and ^{13}C-NMR spectra indicate coordination *via* carboxylate, confirmed by the X-ray crystal structure. In many cases, zinc(II) complexes with carboxylates are monodentate with six coordination [36, 37], but in this study, zinc(II) has coordination number four and the ligands are bonded as bridges. The zinc is an approximate tetrahedron. In ^{1}H-NMR, all signals were shifted upfield because of the position of the heterorings. Together, spectroscopic and crystallographic results furnish a possible mechanism to explain the anomalous upfield shifting of the ^{1}H-NMR spectrum in the Zn complex.

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