Available online at www.sciencedirect.com
ScienceDirect
Polyhedron 25 (2006) 3562–3568
POLYHEDRON
www.elsevier.com/locate/poly

The synthesis, structural features and thermal behaviour of thiophene-containing dithiocarboxylate complexes of zinc(II)

Mary S. Thomas [a], David C. Liles [b], Marilé Landman [c], Elizabeth M. van der Merwe [c], Simon Lotz [b,*]

[a] Department of Chemistry, University of Limpopo, Post Bag 1106, Sovenga 0727, South Africa
[b] Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa
[c] Department of Chemistry, University of South Africa, P.O. Box 392, Pretoria 0003, South Africa

Received 15 May 2006; received in revised form 4 July 2006; accepted 5 July 2006
Available online 14 July 2006

Abstract

The complexes $[Zn_2(S_2CTR)_4]$ (T = 2,5-disubstituted thiophene, R = C_4H_9 (**1**), C_6H_{13} (**2**), C_8H_{17} (**3**), $C_{12}H_{25}$ (**4**) and $C_{16}H_{33}$ (**5**)) have been synthesized and their structural features investigated. Compared to the analogous dithiobenzoate complexes, the crystal structure determination of **2** revealed that the thiophene induces a "step-rod" chain pattern instead of the linear, rodlike structure found for the corresponding dithiobenzoates. Complexes **1**–**5** did not display mesophases under thermal conditions, but an irregular melting pattern was observed for **3** and **4**.

Keywords: Zinc dithiocarboxylate complexes; Crystal structure; Chain structure; Thiophene; Liquid crystals

1. Introduction

Complexes of zinc with sulfur ligands have been studied widely because of their biological importance [1] and their use as accelerators in the vulcanization of rubber [2]. Zinc(II) complexes with dithiocarboxylate ligands have been studied to see whether they displayed liquid crystalline properties [3]. The addition of *p*-alkyl or *p*-alkyloxy chains to the phenyl rings of $[Zn(S_2CPh)_2]$ would give rod-like molecules that may exhibit mesophases [4]. The crystal structure of $[Zn(S_2CPh)_2]$ revealed a monomeric molecule with a tetrahedral ligand arrangement consisting of two strained four-membered chelate rings [3]. It has been noted that mesomorphism in metallomesogens seemed to be incompatible with a tetrahedral geometry about the central metal [5]. Hoshino ascribed the fact that the zinc analogues of the mesomorphic copper salicylaldimine complexes did not display liquid crystalline properties to their tetrahedral structures [6]. An important group of zinc metallomesogens is one with nitrogen donor atoms found in flat, macrocyclic rings. The macrostructures act as tetradentate ligands and two important classes of such compounds are substituted porphyrins [7] and phthalocyanines [8].

In 1998, Adams et al. synthesized the alkyloxy dithiobenzoate complexes of zinc, nickel and palladium and reported on their mesomorphic properties [9]. The octyloxy dithiobenzoate complex of zinc showed a nematic phase, while the nickel and the palladium analogues showed both nematic and smectic phases. Interestingly, $[Zn(S_2CC_6H_4O\text{-}C_8H_{17})_2]$ formed dimeric five-coordinated complexes of distorted trigonal bipyramidal geometry in the solid state. This structural feature has also been reported for a number of diethyldithiocarbamate complexes of zinc(II) [10] and 4-butyloxydithiobenzoate [9]. Recently mesomorphism for zinc complexes have been reported regardless of the geometry (including tetrahedral) around the metal ion, with bis[3,5-bis(*p*-decyloxyphenyl)pyrazolyl]ethane

* Corresponding author. Fax: +27 12 362 5297.
E-mail address: simon.lotz@up.ac.za (S. Lotz).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.07.003

[11] and hexacatenar 4,4′-disubstituted 2,2′-bipyridines [12] as ligands.

In this paper we report on the structural features of bis-dithiocarboxylate complexes of zinc. The focus of this study is on the role of 2,5-disubstituted thiophene as a chain-director being part of a dithiocarboxylate ligand and whether this can have an effect on the liquid-crystalline properties of zinc complexes. Unlike *p*-substituted dithiobenzoate ligands that afford linear rods, the presence of thiophene results in the formation of small kinks in the chains. An interesting field of recent research deals with bent-shaped molecules that can exhibit either columnar or lamellar mesophases [13]. The 2,5-disubstituted thiophene derivatives reported by Swager [14] displayed an antiparallel bent-rod structure resulting from the disubstituted thiophene and alkyl chains. However, a hexagonal columnar phase was observed because of the symmetrically substituted benzene molecules at the end of the chains. There is some controversy over claims that 2,5-disubstituted 5-membered heterocycles display bent-core and not conventional calamitic liquid crystal behaviour.

In this study, thiophene-containing ligands is used in four coordinated complexes of zinc and the structural features resulting from the five-membered thiophene rings should display a ''step-rod'' type of structure. In addition, the thiophene unit can electronically affect the coordination properties of dithiocarboxylato ligands by π-delocalization in a similar fashion as observed in thienyl carbene complexes [15].

2. Experimental

2.1. General

All commercially available chemicals were used as received. Solvents were dried and distilled under nitrogen prior to use. Diethyl ether, tetrahydrofuran and hexane were distilled from sodium metal, with benzophenone as indicator in the case of the etheral solvents. Dichloromethane was distilled from phosphorus pentoxide. Thiophene was purified as described by Spies and Angelici [16]. Reactions were performed in an inert atmosphere of either nitrogen or argon using standard Schlenk and vacuum-line techniques. Column chromatography was carried out under a nitrogen atmosphere using silica gel (particle size 0.063–0.200 nm) as stationary phase. All other reagents were purchased from commercial suppliers and used without further purification. All NMR spectra were recorded in degassed deuterated chloroform on a Bruker ARX-300 spectrometer. Chemical shifts were referenced to chloroform. ^{1}H and ^{13}C NMR spectra were measured at 300.133 and 75.469 MHz, respectively. Infrared spectra were recorded on a Perkin–Elmer Spectrum RX1 FT-IR spectrophotometer with a NaCl cell using hexane as solvent. Melting points were recorded on a hot stage Gallenkamp melting point apparatus and are uncorrected. Liquid-crystalline properties were examined on a differential scanning calorimeter (DSC) Q 100 V8.2 Build 268 and Hot-stage Polarising Optical Microscope (POM) Olympus BX60 equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller.

2.2. Synthesis

2.2.1. Synthesis of the 5-alkyl-2-thiophenedithiocarboxylate ligands ($RTCS_2^-$)

(a) Preparation of 2-alkylthiophene (RT). The procedure used was similar to the one described by Brandsma [17]. *n*-Butyl lithium (15.6 ml, 25.0 mmol) was added to a mixture of THF (50.0 ml) and hexane (30.0 ml), which was cooled to −20 °C. Thiophene (1.68 g, 20.0 mmol) was introduced over 10 min with cooling between 0 °C and 10 °C. The cooling bath was removed and the mixture allowed to warm to room temperature. The alkyl bromide (2.74 g for butyl bromide, 20.0 mmol) was added in one portion without external cooling. The temperature of the solution was raised to 50 °C and kept at this temperature for a further 30 min. The rest of the procedure was carried out in air. Ice water (100 ml) was added with vigorous stirring. Two separate layers formed and were separated. Two further extractions of the aqueous phase with 20 ml diethyl ether gave a combined organic solution that was dried over anhydrous $MgSO_4$. The mixture was concentrated in a rotary evaporator to afford the crude product. Yield = 2.38 g; 85% for R = butyl and in the range 78–89% for the other R groups.

(b) Preparation of 5-alkyl-2-thiophenedithiocarboxylic acid ($RTCS_2H$). *n*-Butyl lithium (12.5 ml, 20.0 mmol) was added to a solution of THF (50.0 ml) and hexane (30.0 ml), which was cooled to −20 °C. 2-Alkyl thiophene (R = butyl, 2.38 g, 17.0 mmol) was introduced over 10 min with cooling between 0 °C and 10 °C. The cooling bath was removed and the mixture warmed to room temperature while being stirred for a further 10 min. The solution was cooled to 0 °C and copper(I) bromide (0.1 g) added. Carbon disulfide (1.29 g, 17.0 mmol) was added drop-wise to the stirred mixture. The colour of the reaction mixture changed to deep-red. The cooling bath was removed and the mixture was allowed to reach room temperature while stirring was continued for a further 1 h. Ice water (100.0 ml) was added followed by dilute hydrochloric acid (20.0 ml, 1 mol/dm^3). The organic layer was separated in air and the product extracted into diethyl ether (70.0 ml) and washed with 2 × 50.0 ml of water. The product was dried over $MgSO_4$ and the solvent removed *in vacuo*. Yield = 3.30 g; 89.8% for R = butyl and in the range of 69–90% for the other R groups.

(c) Preparation of sodium 5-alkyl-2-thiophenedithiocarboxylate ($RTCS_2Na$). Sodium metal (0.35 g, 15.28 mmol) was added over 10 min to vigorously stirred methanol (50.0 ml). When all the sodium had dissolved, additional (20.0 ml) methanol was added. 5-Alkyl-2-thiophenedithiocarboxylic acid (for R = butyl, 3.30 g, 15.28 mmol) was added over 5 min to the mixture and left stirring for