Synthesis and Structural Study of Dichloro Di-2-benzothiazolylphenylmethanol Zinc(II)

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Abstract

The structure of the chelate dichloro di-2-benzothiazolylphenylmethanol zinc(II) is described by X-ray diffraction analysis. It was prepared from di-2-benzothiazolylphenylmethanol, which is readily available from di-2-benzothiazolylmethane.

Introduction

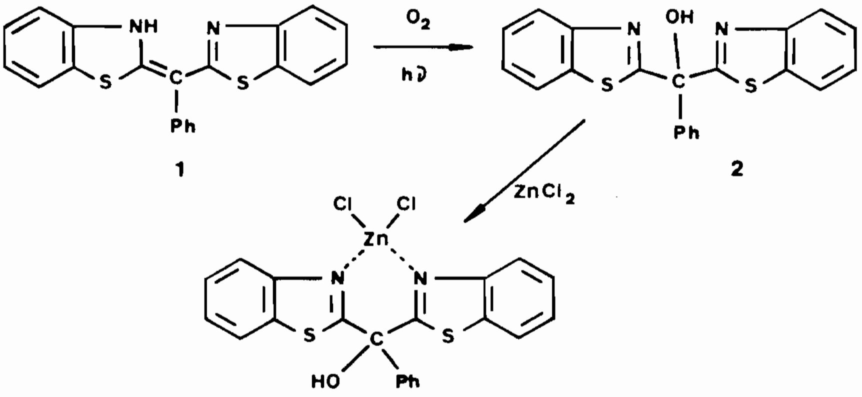
Several reports about di- and triheteroarylmethanes, -methanols and related compounds as ligands of different metals have been published [1–7]. Thus, di-2-benzothiazolylmethane has been proposed as a fluorimetric reagent for Li^+ and Zn^{2+} determination because it forms fluorescent chelates with these metals [8].

In previous papers [9–11], we have reported the synthesis and tautomerism of C-substituted di-2-benzothiazolylmethanes, and the study of the photooxidation reaction of these compounds to the corresponding methanols [12].

Although both types of compounds could be proposed as bidentate or tridentate ligands, we have tested the ability of di-2-benzothiazolylphenylmethanol (2) to chelate Zn^{2+}. The X-ray diffraction analysis of crystals thus obtained has shown that 2 is a bidentate ligand through both nitrogen atoms (Scheme 1).

Experimental

For X-ray experimental data, refinement procedures [13–19], coordinates and thermal parameters, see 'Supplementary Material'. The IR spectra were recorded in the solid state (KBr) on a Perkin-Elmer 577 spectrophotometer. The ^1H NMR spectra were re-



Scheme 1.

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TABLE 1. Bond distances and angles

Bond distances (Å)

Zn–Cl1	2.227(1)	Zn–Cl2	2.197(1)
Zn–N1	2.030(3)	Zn–N2	2.037(3)
S1–C1	1.721(4)	S1–C11	1.734(4)
S2–C2	1.721(4)	S2–C21	1.730(4)
O–C3	1.417(4)	N1–C1	1.304(4)
N1–C16	1.396(5)	N2–C2	1.297(5)
N2–C26	1.409(5)	C1–C3	1.529(5)
C2–C3	1.523(5)	C3–C31	1.538(4)
C11–C12	1.399(6)	C11–C16	1.390(5)
C12–C13	1.368(6)	C13–C14	1.398(6)
C14–C15	1.381(6)	C15–C16	1.389(5)
C21–C22	1.394(6)	C21–C26	1.396(5)
C22–C23	1.371(7)	C23–C24	1.386(7)
C24–C25	1.389(7)	C25–C26	1.387(6)
C31–C32	1.399(5)	C31–C36	1.378(5)
C32–C33	1.387(5)	C33–C34	1.376(6)
C34–C35	1.372(6)	C35–C36	1.397(5)

Bond angles (°)

N1–Zn–N2	93.4(1)	Cl2–Zn–N2	112.6(1)
Cl2–Zn–N1	112.6(1)	Cl1–Zn–N2	113.4(1)
Cl1–Zn–N1	107.7(1)	Cl1–Zn–Cl2	115.0(1)
C1–S1–C11	89.1(2)	C2–S2–C21	89.3(2)
Zn–N1–C16	124.0(2)	Zn–N1–C1	124.6(2)
C1–N1–C16	111.2(3)	Zn–N2–C26	125.2(2)
Zn–N2–C2	124.0(2)	C2–N2–C26	110.9(3)
S1–C1–N1	115.8(3)	N1–C1–C3	126.3(3)
S1–C1–C3	117.5(2)	S2–C2–N2	116.2(3)
N2–C2–C3	127.6(3)	S2–C2–C3	115.7(2)
C1–C3–C2	115.2(3)	O–C3–C2	109.0(3)
O–C3–C1	108.4(3)	C2–C3–C31	109.4(3)
C1–C3–C31	107.5(3)	O–C3–C31	107.1(3)
S1–C11–C16	110.2(3)	S1–C11–C12	128.6(3)
C12–C11–C16	121.2(3)	C11–C12–C13	117.6(4)
C12–C13–C14	121.5(4)	C13–C14–C15	120.9(4)
C14–C15–C16	118.1(4)	C11–C16–C15	120.6(3)
N1–C16–C15	125.8(3)	N1–C16–C11	113.5(3)
S2–C21–C26	110.1(3)	S2–C21–C22	129.2(3)
C22–C21–C26	120.7(4)	C21–C22–C23	118.0(4)
C22–C23–C24	121.6(4)	C23–C24–C25	121.1(4)
C24–C25–C26	117.6(4)	C21–C26–C25	121.0(3)
N2–C26–C25	125.5(3)	N2–C26–C21	113.4(3)
C3–C31–C36	121.9(3)	C3–C31–C32	118.9(3)
C32–C31–C36	119.2(3)	C31–C32–C33	120.0(4)
C32–C33–C34	120.6(4)	C33–C34–C35	119.5(4)
C34–C35–C36	120.7(4)	C31–C36–C35	120.0(4)

Some torsion angles (°)

N1–Zn–N2–C2	11.5(3)	Cl2–Zn–N2–C2	−104.7(3)
Cl1–Zn–N2–C2	122.5(3)	N1–Zn–N2–C26	−169.9(3)
Cl2–Zn–N2–C26	73.9(3)	Cl1–Zn–N2–C26	−58.9(3)
Cl2–Zn–N1–C1	106.6(3)	Cl1–Zn–N1–C1	−125.5(3)
Cl2–Zn–N1–C16	−79.5(3)	Cl1–Zn–N1–C16	48.4(3)
N2–Zn–N1–C16	164.2(3)	N2–Zn–N1–C1	−9.6(3)
C11–S1–C1–C3	−173.3(3)	C21–S2–C2–C3	171.3(3)
Zn–N1–C1–S1	174.6(2)	Zn–N1–C1–C3	−11.6(5)

(continued)

TABLE 1. *(continued)*

Some torsion angles (°)

C16–N1–C1–C3	173.8(3)	Zn–N2–C2–S2	179.6(2)
Zn–N2–C2–C3	7.8(5)	C26–N2–C2–C3	−171.0(3)
N1–C1–C3–O	156.1(3)	N1–C1–C3–C31	−88.5(4)
N1–C1–C3–C2	33.7(5)	N2–C2–C3–C1	−31.7(5)
N2–C2–C3–O	−153.8(3)	N2–C2–C3–C31	89.4(4)
C1–C3–C31–C32	−82.3(4)	O–C3–C31–C32	34.0(4)
C2–C3–C31–C36	−30.6(5)		

corded at 60 MHz using a Perkin-Elmer spectrometer. The ^{13}C NMR spectra were obtained at 75.43 MHz on a Varian XL-300 pulse Fourier transformation (PFT) spectrometer.

Compounds

Di-2-benzothiazolylphenylmethane (1) [11]

A mixture of diethyl phenylmalonate (20 mmol) and *o*-aminothiophenol (50 mmol) in polyphosphoric acid (200 ml) was mechanically stirred under a nitrogen stream for 2 h at 80–90 ℃, 3 h at 120 ℃ and 1 h at 140 ℃. The mixture was allowed to cool to 80 ℃ and poured into stirred 'ice-cold' water. The solid precipitate was filtered, washed with an aqueous solution of potassium carbonate and water, and then dried under vacuum over phosphorus pentoxide, yielding crude **1**. Yields up to 90%.

Di-2-benzothiazolylphenylmethanol (2)

Attempts to crystallize crude **1** in ethanol–water afforded nearly quantitatively **2**, melting point (m.p.) 146–48 ℃. *Anal.* Found: C, 67.07; H, 4.00; N, 7.60. Calc. for $C_{21}H_{14}N_2OS_2$: C, 67.35; H, 3.77; N, 7.48%. IR (KBr) ν: 3360, 1485, 1450, 1440, 1330, 1315 cm^{-1}. ^{13}C NMR (DMSO-d$_6$): 175.9, 152.7, 142.4, 134.9, 128.2, 128.0, 126.9, 126.3, 125.5, 123.0, 122.3, 79.6 ppm .

Dichloro di-2-benzothiazolylphenylmethanol zinc(II) (3)

Compound **3** was prepared by addition of a hot methanolic solution of **2** over a methanolic solution of zinc chloride, and precipitated on cooling. Yield 75%; m.p. 273–276 °C. *Anal.* Found: C, 49.05; H, 2.50; N, 5.09. Calc. for $C_{21}H_{14}N_2OS_2ZnCl_2$: C, 49.38; H, 2.76; N, 5.48%. IR (KBr) ν: 3390s, 1595w, 1570w, 1490s, 1460s, 1450s, 1440s cm^{-1}.

Results and Discussion

Description of the Structure

Figure 1 displays a view of the molecule with the crystallographic numbering, while bond lengths and bond angles are given in Table 1.

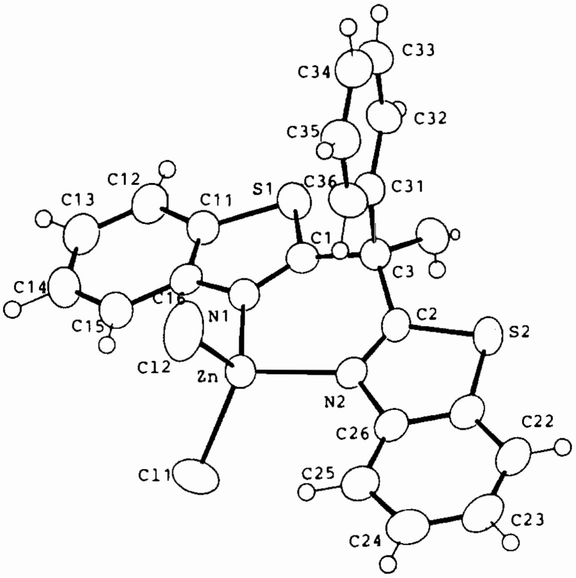

Fig. 1. Perspective view of molecule **2** with crystallographic numbering.

The molecule presents a pseudo-mirror plane defined by Zn, C3, O and C31 atoms, Cl1, Cl2 and C34 being clearly deviated from it. Details of this plane are given in Table 2.

The chlorine and nitrogen atoms coordinated to zinc appear at the apexes of a distorted tetrahedron; the N1–Zn–N2 angle is decreased to 93.4(1)° by the restricted position of the N atoms and, consequently, the Cl1–Zn–Cl2 angle increases to 115.0(1)°; this geometry is in good agreement with other Zn compounds which present the same coordination pattern [20, 21]. The five condensed rings are not in a plane, the angle between the two benzothiazole rings being 16.5(1)°. The central cyclohexane ring presents a boat conformation with Zn and C3 atoms being 0.214(1) and 0.357(3) Å, respectively, from the plane defined by the others. Ring puckering coordinates [22] are $q_2 = 0.342(3)$, $q_3 = -0.048(3)$, $\phi_2 = -3.3(5)°$, $\theta_2 = 98.0(4)°$. The C3 atom presents a tetrahedral environment. The O atom of the hydroxyl group is at 2.876(3) and 2.870(3) Å from the S1 and S2 atoms, respectively, therefore showing no preferred interaction with either of them.

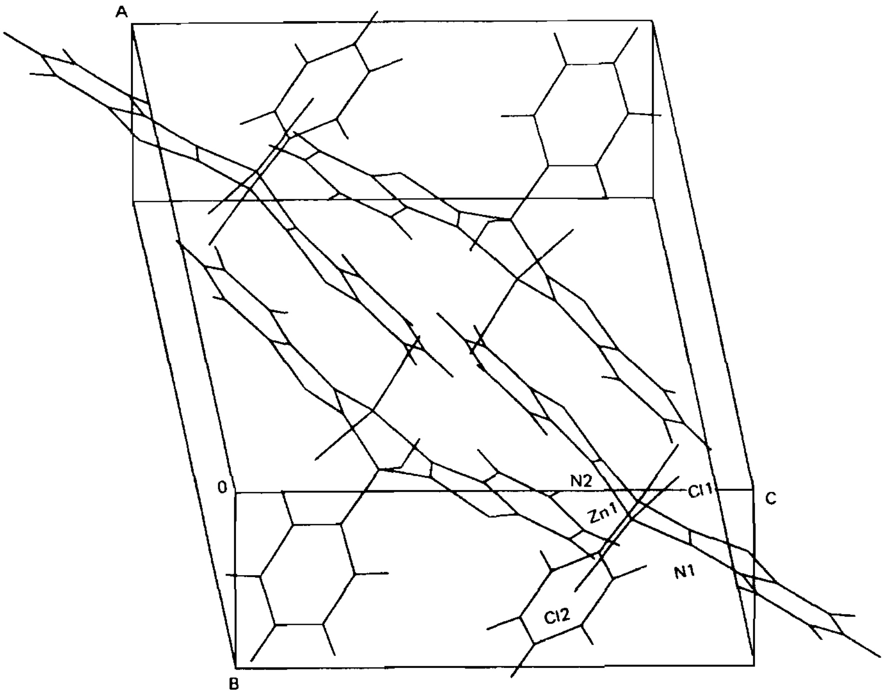

Fig. 2. Packing in the unit cell of compound 2.

TABLE 2. Deviations (Å) of the atoms from the mean plane defined by Zn, C3, O, C31

Zn (*)	0.000(1)	C1	-1.291(3)
C3 (*)	0.007(3)	C2	1.286(3)
O (*)	-0.003(3)	N1	-1.481(3)
C31 (*)	-0.002(4)	N2	1.479(3)
		S1	-2.688(1)
Cl1	-0.187(1)	S2	2.681(1)
Cl2	0.049(1)	C11	-3.634(4)
C34	-0.165(4)	C21	3.648(4)
		C12	-5.013(4)
C32	-0.701(4)	C22	5.030(4)
C36	0.614(4)	C13	-5.529(4)
C33	-0.784(4)	C23	5.566(5)
C35	0.531(4)	C14	-4.712(4)
		C24	4.768(5)
		C15	-3.353(4)
		C25	3.390(4)
		C16	-2.821(3)
		C26	2.842(4)

Packing in the crystal is viewed in Fig. 2; molecules are linked only by van der Waals forces.

Infrared Spectra

The IR spectrum of **3** in the solid state shows strong bands at 3395, 1495 and 1440 cm^{-1}. By comparison with the IR spectrum of **2** (KBr), the main significant differences are the shifts at higher frequencies of the νOH and 'benzothiazole III' bands which appear in the ligand at 3360 and 1485 cm^{-1}, respectively.

NMR Spectra

Due to the low solubility of **3** in $CDCl_3$, ^1H NMR spectra were recorded in DMSO-d$_6$, but the spectrum thus obtained was identical to that of ligand **2** in the same solvent: δ (ppm) 8.54 (1H, s, OH), 8.10–7.30 (13H, m, aromatic protons). From here it follows that the DMSO dissociates the chelate. This was also confirmed by comparing the ^{13}C NMR spectra of compounds **2** and **3** in DMSO-d$_6$ which were also identical.

Supplementary Material

Details of X-ray experimental data, refinement procedures, coordinates and thermal parameters are available from the authors on request.

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