Organometallic Chemistry

Synthesis and stereochemical nonrigidity of isomeric Zn(II) *bis*-[*N*-isopropyloxy(mercapto)naphthaldiminates]

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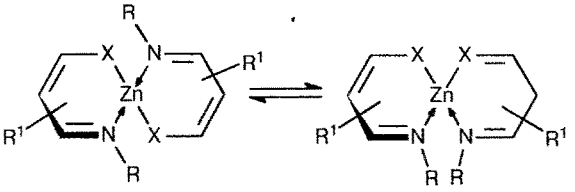
Kinetics and reaction mechanisms governing inversion of the tetrahedral configuration at the metal center in the series of *bis*-chelate Zn(II) complexes of 3,2-, 1,2-, and 2,1-oxy(mercapto)naphthaldimines, respectively **4—6**, have been studied with the use of dynamic ^{1}H NMR spectroscopy. A polytopal rearrangement of the diagonal twist type has been found to be an energetically preferable pathway of the inversion reaction for complexes **4** and **5** with a ZnN_2O_2 coordination site, whereas the inversion reaction for complexes with a ZnN_2S_2 coordination site occurs by an intramolecular dissociation-recombination pathway that involves cleavage of a Zn—N coordination bond. In the case of complexes **6**, the inversion reaction is governed mainly by intramolecular degenerate ligand exchange reactions.

Key words: stereochemical nonrigidity, inversion of the tetrahedral configuration, dynamic NMR spectroscopy, *bis*-chelate metal complexes, Zn(II) *bis*-(*N*-isopropyloxynaphthaldiminates), Zn(II) *bis*-(*N*-isopropylmercaptonaphthaldiminates).

Tetrahedral complexes of transition metals undergo fast and reversible inversion of configuration at the metal centers; their structures are considered to be stereochemically nonrigid. These processes (1) were thoroughly studied for *bis*-chelate Zn(II) complexes with *N*-alkyl(aryl)aminopropenone(thione, selenone) ligands of general formula **1** and their derivatives.[1,2]

An intramolecular mechanism of diagonal twist without metal-ligand cleavage was shown to be preferable for *bis*-salicylaldiminates **2** (X = O), while an intramolecular dissociation-recombination mechanism becomes energetically favorable for *bis*-aminopropenethionates **3** and *bis*-thiosalicylaldiminates **2** (X = S), governed by breaking-formation processes of Zn—N bonds.[3—6]



(1)

1(*R*) **1**(*S*)

X = O, S, Se; R = Pr^i, CH_2Ph, Aryl;
R^1 = Pr^i, Ph, Arene, Heterene

The annelation of benzene ring to aminopropenethione fragment of metal chelates **3** decreases significantly the energy barrier for the inversion of tetrahedral

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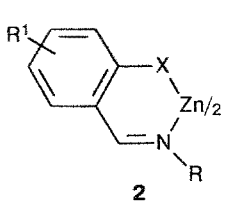
configuration at the metal atom in complexes **2**.[2]



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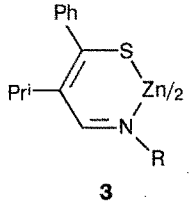
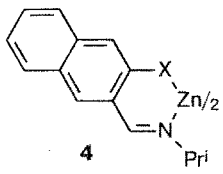


3

To develop the studies made previously, we accomplished the synthesis of *N*-isopropyloxy- and mercaptonaphthaldiminates **4—6** (X = O, S) and studied, in the given series, the kinetics of inversion for tetrahedral configuration at central Zn atom by dynamic ^{1}H NMR (^{1}H DNMR).



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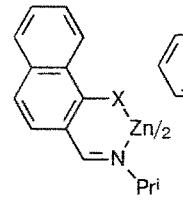

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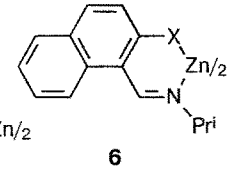


6

4—6 : X = O, S

Experimental

NMR spectra were recorded on a Varian XL-100/15 or a Varian UNITY-300 spectrometer, using the Fourier transformation regime. The chemical shifts are given relative to internal HMDS. $CDCl_3$, $C_6D_5CD_3$, $C_6D_5NO_2$, and C_6D_5Br were used as solvents. The simulation of temperature dependent ^{1}H NMR spectra for determination of kinetic parameters of exchange processes was performed by full profile analysis, using a known technique.[7] The extreme separation values of the signals from diastereotopic groups ($\Delta\nu$) and their half-width ($\Delta\nu_{1/2}$) were chosen as starting parameters. The calculated and observed spectra were compared visually. The rate constants of exchange processes were determined as $k = 1/\tau$, where τ is the lifetime of the isomer. The activation parameters of exchange processes were calculated by applying the Eyring $\ln k$—$1/T$ relationship. The values of activation parameters presented below (Table 1) are given within the standard error deviations.

The synthesis of 1,2- and 2,3-hydroxynaphthaldehydes were performed by known procedures.[8,9] The previously unknown 1,2- and 2,3-mercaptonaphthaldehydes, as well as 2,1-mercaptonaphthaldehyde,[10] were synthesized from corresponding *N*,*N*-dimethylthiocarbamates of naphthaldehydes (prepared in quantitative yields by reactions of thiocarbamoyl chloride with hydroxynaphthaldehydes) using thermal Newman—Quart rearrangement in diphenyl oxide at 240 °C, followed by basic hydrolysis in methanol solution.[11] Free mercaptonaphthaldehydes are unstable; their ether solutions, whose concentrations were measured by ^{1}H NMR spectroscopy, were further manipulated. The yields were 15—20 %.

Zn(II) *bis*-(*N*-isopropyloxynaphthaldiminates) (4—6, X = O). Isopropylamine (3 mmol) and anhydrous zinc acetate (1.5 mmol), each dissolved in a minimum amount of methanol, were added successively to 10 mL methanolic solution of the corresponding hydroxynaphthaldehyde (3 mmol). The reaction mixture was boiled for 15 min and cooled to 30 °C, and 10 % solution of sodium methoxide (3 mmol) was slowly added with stirring. The mixture was stirred for another 15 min and cooled to about 20 °C. The crystals precipitated were removed by filtration, washed with methanol, and recrystallized from toluene.

Table 1. Kinetics and activation parameters of inversion for tetrahedral configuration at the central zinc atom in *bis*-chelate complexes **2—6** (solvent is bromobenzene-d_5)

Complex	X	$\Delta H^{\#}$ kJ/mol	$\Delta S^{\#}$ J/mol·K	$\Delta G_{25}^{\#}$ kJ/mol	k_{25} s^{-1}
2	O[a]	38.9±4.7	−82.0±5.1	63.2±0.3	$5.1 \cdot 10$
	S[a]	74.1±1.9	11.5±3.8	70.7±0.2	1.67
3[b]		80.3±1.7	24.0±5.0	73.2±0.3	0.93
4	O	54.2±2.3	−40.5±4.2	66.9±0.4	$1.49 \cdot 10$
	S	92.0±1.2	75.2±5.2	69.6±0.2	3.85
5	O	63.9±4.1	−21.8±4.1	70.4±0.2	2.8
	S	99.5±3.8	91.2±4.9	72.8±0.3	1.3
6	O[c]	37.5±1.4	−52.1±5.0	53.0±0.2	$3.1 \cdot 10^3$
	S[d]	54.7±1.9	−29.9±4.7	63.0±0.3	$4.39 \cdot 10$

[a] Data are taken from Ref. 1. [b] Data are taken from Ref. 6. [c] $C = 0.03$ mol·L^{-1}. [d] $C = 0.02$ mol·L^{-1}.

Zn(II) *bis*-(*N*-isopropyl-3-oxy-2-naphthaldiminate) (4, X = O). Yield 72 %; m.p. 298—300 °C. Found (%): C, 68.57; H, 5.79; N, 5.68. $C_{28}H_{28}N_2O_2Zn$. Calculated (%): C, 68.65; H, 5.76; N, 5.72. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 1.21 (d, 3 H, Me, J = 6.4); 3.74 (sept, 1 H, C<u>H</u>Me$_2$, J = 6.4); 7.00—7.76 (m, 6 H, —CH=); 8.5 (s, 1 H, CH=N).

Zn(II) *bis*-(*N*-isopropyl-1-oxy-2-naphthaldiminate) (5, X = O). Yield 76 %; m.p. 229—230 °C. Found (%): C, 68.71; H, 5.70; N, 5.67. $C_{28}H_{28}N_2O_2Zn$. Calculated (%): C, 68.65; H, 5.76; N, 5.72. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 1.17 (d, 3 H, Me, J = 6.4); 1.32 (d, 3 H, Me, J = 6.4); 3.64 (sept, 1 H, C<u>H</u>Me$_2$, J = 6.4); 7.05—7.72 (m, 5 H, —CH=); 8.31 (s, 1 H, CH=N); 9.25 (d (br), 1 H, H-8).

Zn(II) *bis*-(*N*-isopropyl-2-oxy-1-naphthaldiminate) (6, X = O). Yield 84 %; m.p. 258—260 °C. Found (%): C, 68.59; H, 5.83; N, 5.68. $C_{28}H_{28}N_2O_2Zn$. Calculated (%): C, 68.65; H, 5.76; N, 5.72. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 1.25 (d (br), 3 H, Me, J = 6.0); 1.33 (d (br), 3 H, Me, J = 6.0); 3.73 (sept, 1 H, C<u>H</u>Me$_2$, J = 6.0); 7.00—8.00 (m, 6 H, —CH=); 9.20 (s, 1 H, CH=N).

Zn(II) *bis*-(*N*-isopropylmercaptonaphthaldiminates) 4—6 (X = S). The addition of an equimolar amount of isopropylamine to an ether solution containing 1—2 mmol of mercaptonaphthaldehyde was immediately followed by the addition of a stoichiometric amount of zinc acetate in methanol solution. The ether was then distilled off on a rotary evaporator, and 10 % solution of sodium methoxide was added with stirring until the solution thus obtained turned muddy. The crystals formed were filtered off and recrystallized from toluene.

Zn(II) *bis*-(*N*-isopropyl-3-mercapto-2-naphthaldiminate) (4, X = S). Yield 63 %; m.p. 288—289 °C. Found (%): C, 64.49; H, 5.34; N, 5.31. $C_{28}H_{28}N_2S_2Zn$. Calculated (%): C, 64.42; H, 5.41; N, 5.37. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 1.21 (d, 3 H, Me, J = 6.7); 1.40 (d, 3 H, Me, J = 6.7); 3.91 (sept,

1 H, C<u>H</u>Me$_2$, J = 6.7); 7.30—7.78 (m, 5 H, —CH=); 7.80 (s, 1 H, H-4); 8.17 (s, 1 H, H-1); 8.54 (s, 1 H, CH=N).

Zn(II) *bis*-(*N*-isopropyl-1-mercapto-2-naphthaldiminate) (5, X = S). Yield 52 %; m.p. 201—202 °C. Found (%): C, 64.38; H, 5.48; N, 5.30. $C_{28}H_{28}N_2S_2Zn$. Calculated (%): C, 64.42; H, 5.41; N, 5.37. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.17 (d, 3 H, Me, J = 6.7); 1.37 (d, 3 H, Me, J = 6.7); 3.82 (sept, 1 H, C<u>H</u>Me$_2$, J = 6.7); 7.25—8.00 (m, 5 H, —CH=); 8.49 (s, 1 H, CH=N); 9.25 (d (br), 1 H, H-8).

Zn(II) *bis*-(*N*-isopropyl-2-mercapto-1-naphthaldiminate) (6, X = S). Yield 54 %; m.p. 254—256 °C. Found (%): C, 64.36; H, 5.34; N, 5.40. $C_{28}H_{28}N_2S_2Zn$. Calculated (%): C, 64.42; H, 5.41; N, 5.37. ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.20 (br.d, 3 H, Me, J = 6.1); 1.35 (br.d, 3 H, Me, J = 6.1); 3.92 (sept, 1 H, C<u>H</u>Me$_2$, J = 6.1); 7.35—7.90 (m, 6 H, —CH=); 9.21 (s, 1 H, CH=N).

Results and Discussion

The presence in molecules of chelate complexes **4—6** of a chiral tetrahedral center, a tetracoordinated zinc atom, and a prochiral isopropyl group make it possible, recording the temperature dependence of the NMR for diastereotopic methyl groups, to establish and characterize quantitatively the enantiomerization process (*R*)⇌(*S*) of type (1) without a single enantiomer being isolated or the racemic mixture being enriched by one of them.

At low temperature the methyl protons of the prochiral isopropyl group of complexes **4—6** are anisochronous in the ^{1}H NMR spectrum and show themselves as double doublets. The rising of the temperature results consecutively in broadening, coalescence, and formation of averaged doublet signal for diastereotopic methyl groups. The usual DNMR spectrum of metal chelate complex **4** (X = S) is shown in Figure 1.

The presented DNMR spectra are typical of stereochemically nonrigid chelate complexes that show in solution fast inversion, on the ^{1}H NMR time scale, at such stereogenic center as tetrahedral metal atom.[1—5] The kinetics and activation parameters for enantiomerization (1) in complexes **4—6** are presented in Table 1. Their values were found to be independent of concentration, within the studied interval of concentration ($3 \cdot 10^{-2}$—$3 \cdot 10^{-3}$ mol · L^{-1}), that supports the intramolecular mechanism for the reaction of inversion of stereochemical configuration.

For each type of zinc oxy(mercaptonaphthaldiminates) **4—6** (X = O, S) as well as the previously known complexes **2** (X = O, S),[4] data of analysis (Table 1) shows the values of activation barriers for enantiomerization (1) to be higher for sulfur as compared with oxygen derivatives. For complexes **4, 5** (X = O) and **2** (X = O) as well, the observed in solution inversion processes accompany by the negative values of activation entropy, which are characteristic of polytopal rearrangement of digonal twist type.[2] By contrast, the values of activation entropy for exchange processes in solution are

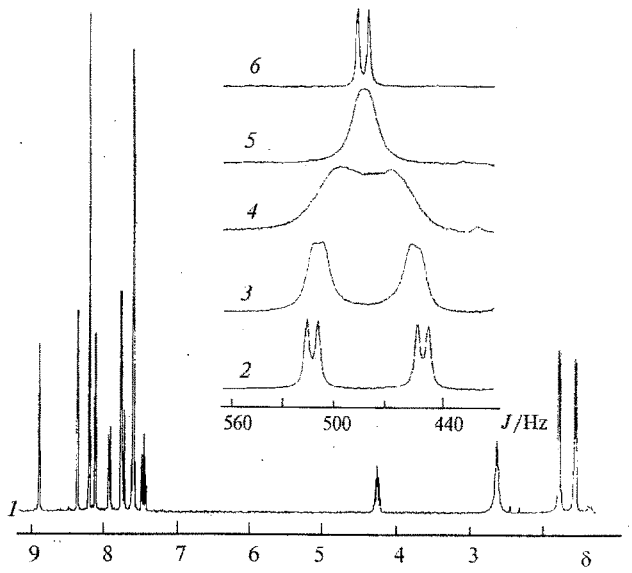
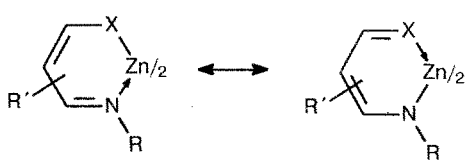


Fig. 1. ^{1}H NMR spectrum (300 MHz) of Zn(II) *bis*-(*N*-isopropyl-2-mercapto-3-naphthaldiminates) **4** (X = S) (*1*) and its temperature dependence in the range of proton signals for diastereotopic methyl groups (*2—6*), T/°C: 20 (*2*), 40 (*3*), 60 (*4*), 80 (*5*), 120 (*6*); k/s^{-1}: 2.05 (*2*), $2.5 \cdot 10$ (*3*), $1.8 \cdot 10^2$ (*4*), $1.5 \cdot 10^3$ (*5*), $1.9 \cdot 10^4$ (*6*). Solvent — nitrobenzene-d_5.

positive in the case of complexes **2—5** having the coordination ZnN_2S_2 unite that corresponds to heterodissociation of the bonds, which does not require the essential charge separation in transition state.[12] Thus, the comparison of the kinetic data obtained in this work for the complexes **4—6** (X = O, S) with stereodynamic transformation data for complexes **2** (X = O, S) and **3** make it possible to suggest that the polytopal rearrangement mechanism of the digonal twist type determines the kinetics of inversion for tetrahedral zinc atom in bis-chelate complexes with ZnN_2O_2 unite, while mechanism involving the Zn—N cleavage is energetically preferable for the complexes with ZnN_2S_2 unite.

On the basis of X-ray structural data obtained, it was suggested[2] that the tendency for choosing an energetically preferable mechanism of configuration inversion at a metal atom depends upon the character of the Zn←N bond in the chelate ring of complexes **1**. The electron distribution in it can be presented simply as a resonance hybrid



7a **7b**

According to the Zn—N bond length data, the contribution of **7a** form having dative Zn←N bond, *i.e.*,

weakened in comparison with covalent Zn—N bond,[13] is higher for the complexes **2** (X = S) than for the complexes **2** (X = O). This fact accounts for the dissociation-recombination mechanism (1) that is energetically preferable for complexes **2** (X = S) in comparison with polytopal rearrangement mechanism observed in complexes **2** (X = O). The complexes **4** and **5** seem to exhibit the same tendency.

The activation energies for the inversion process of stereochemical configuration established in solution for the metal chelate complexes **4** (X = O, S), based on 2,3-hydroxy(mercapto)naphthaldehydes, are quite similar to those found for the analogous salcyl- and thiosalicylaldiminates **2** (X = O, S), indicating the similarity of electron distribution in the considered chelate rings. As the matter of fact, the character of conjugation in benzene and metal chelate ring should remain nearly indifferent to the transition from **2** to **4.** The activation energies for complexes **5** (X = O, S) involving 3,4-benzannelated aldehyde fragment are higher in comparison with those of corresponding *bis*-chelates **4** (X = O, S). The effect can be explained by the fact that 3,4-annelation should significantly increase the contribution of resonance form **7b** having a covalent Zn—N bond in the series **4—6**. The enhanced equilibrium content of the quinoid tautomer, which has a hydrogen atom in the chelate ring instead of a metal atom, supports this idea.[14]

Unlike complexes **4** and **5**, the complexes **6** (X = O, S), derivatives of 2-hydroxy(mercapto)naphthaldehydes, show distinctly the concentration dependence of profiles for the control signals. The enantiomer lifetime τ for the complexes **6** (X = O) is reciprocal their concentrations that relates to the second order reaction (1), and, therefore, corresponds to the degenerate ligand exchange mechanism.[2] The τ dependence on solution concentration, recorded for complexes **6** (X = S) by a ^{1}H NMR technique, is less distinctive: fivefold dilution (C = 0.02 mol · L^{-1}) causes an approximately twofold increase of τ. In the given range of concentration, it witnesses the inversion of configuration (1) being dealt with two competitive mechanisms: the associative mechanism of intermolecular exchange competes with the intramolecular dissociation-recombination mechanism or the mechanism of the digonal twist type.

The contribution of the low barrier intermolecular mechanism, which has been observed for bis-chelate complexes with ZnN_2X_2 (X = O, S) coordination, is in accordance with the lowest values of the effective free energy of activation for inversion reaction (1) in complexes **2**, **4—6**, see Table 1, as well as with a negative value of the activation entropy for complexes **6** (X = S), which is characteristic of a bimolecular reaction of degenerate ligand exchange.[2]

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