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Journal of Molecular Structure 788 (2006) 89-92

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

Reactions of bis[bis(trimethylsilyl)amido] zinc with amides of sulfonimidic acids. Crystal structure and NMR studies of bischelate zinc complex

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Received 23 May 2005; received in revised form 17 November 2005; accepted 18 November 2005 Available online 18 January 2006

Abstract

Reactions of bis[bis(trimethylsilyl)amido] zinc with amides of sulfonimidic acids are leading to the corresponding bischelate complexes 1–3. Compounds 1–3 were characterized by means of NMR spectroscopy and elemental analysis. The X-ray analysis of $[p-MeC_6H_4S(O)(Nt-Bu)_2]_2Zn$ (3) demonstrates a tetrahedral environment of the Zn atom in the solid state and dynamic ¹H NMR studies showed interconvention between two conformers in solution at high temperatures.

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Keywords: Complexes; Sulfur; Zinc; N ligands; Solid-state structures

1. Introduction

The chemistry of main group and transition metal complexes containing sulfur-nitrogen multiple bonded systems as ligands has been widely investigated since the preparation of the first adducts with tetrasulfur tetranitride [1-3]. Such complexes are attracting attention due to their structural peculiarities, such as the coordination fashion of a metal to the ligand, as well as a possible stabilization route for non-isolable under normal conditions intermediates. Among them, compounds containing the NSN fragment as a ligand are of particular interest. Diimides are known to function as mono or bidentante ligands in main group and transition metal complexes [1–5]. Reactions of sulfur diimides with main group metal alkyls, alkoxides or Grignard reagents are leading to a nucleophilic addition to N=S bond, and formation of complexes with the $[RNS(R')NR]^-$ ligand [6–9], which subsequently are bonded to transition metals via metathesis reactions [7,10,11]. However, to the best of our knowledge,

complexes containing one metal cation and the $[RNS(O)(R')NR]^-$ monoanions as bischelating ligands are unknown.

One of the synthetic routes for the preparation of main group and transition metal complexes are the reactions, involving the metal alkyls or amides, and compounds containing donor atoms and protic moieties [12]. Among the available reagents main group and transition metals bis(trimethylsilyl) amides are of particular interest due to their high reactivity combined with stability, solubility and easy availability from simple starting materials [13,14]. For instance, it was shown that the reaction of bis[bis(trimethylsilyl)] amides of Zn^{2+} and Cd^{2+} with (E–NH)₂ (E=As, P) four-membered ring systems resulted in the deprotonation of the NH moiety, ring opening, and formation of bischelate complexes with low coordination numbers of As and P (2) respectively [15–17]. Thus, this method was shown to be generally suitable for the synthesis of metal chelate complexes.

Due to our broad interest in the chemistry of compounds containing sulfur–nitrogen multiple bonds [18–20], we decided to study the possibility for the preparation of bischelate metal complexes, containing RNS(O)(Ar)NR fragment as a bidentate ligand. As a synthetic route to such type of compounds, we reacted amides of sulfonimidic acids with bis[bis(trimethyl-silyl)] amido zinc. The results of our investigation are presented in the current paper.

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2. Experimental

2.1. General methods and materials

All reactions were performed in deoxygenated argon or dinitrogen atmosphere using high vacuum techniques. Aromatic, hydrocarbon, and etherated solvents were distilled over P_4O_{10} and stored over sodium wire. Acetonitrile, trichloromethane, and dichloromethane were dried over P_4O_{10} . NMR spectra were recorded on a Bruker AM-200, Bruker WP-200, and Variant VXR-300 instruments. Chemical shifts are reported in δ scale with reference to SiMe₄. Melting points were measured on Nagema melting-point apparatus and are uncorrected. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine.

The starting materials were prepared according to literature methods [21–25] and were purified prior to use. Compound p-MeC₆H₄S(O)[N(*t*-Bu)]NH(*t*-Bu) have not been reported in literature. A few data are given here.

 $p-MeC_6H_4S(O)[N(t-Bu)]NH(t-Bu)$. Yield: 2.88 g (36%). Mp: 162 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): 1.25 [s, 18H, C(CH₃)₃], 2.37 (s, 3H, CH₃), 3.95 (s, 1H, NH), 7.19 (d, 2H, aromat H), 7.77 (d, 2H, aromat H). Anal. calcd for C₁₅H₂₆N₂OS: C 63.78, H 9.30, N 9.92, S 11.35. Found: C 63.88, H 9.98, N 9.87, S 11.57.

2.2. Preparation of $[p-MeC_6H_4S(O)N(n-Bu)NPh]_2Zn$ (1)

Zn[N(SiMe₃)₂] (1.00 g, 2.60 mmol) was added dropwise via syringe at room temperature to the suspension of p-MeC₆H₄ S(O)[N(n-Bu)]NHPh (1.57 g, 5.19 mmol) in dry benzene (30 mL). The reaction mixture was stirred for an additional 15 h. All volatiles were removed in vacuum, and the residue treated with dry hexane (10 mL). The precipitate was filtered off, and dried in vacuum, resulting in compound **1**. Yield: 1.72 g (99%). Mp: 160 °C. ¹H NMR (200 MHz, CDCl₃, 25 °C): 0.73 [m, 6H, n-C₄H₉, C(4)–H], 1.13 [br, 4H, n-C₄H₉, C(3)–H], 1.35 [br, 4H, n-C₄H₉, C(2)–H], 2.35 (s, 6H, CH₃), 2.92 [br, 4H, n-C₄H₉, C(1)–H], 6.84–7.69 (br, mult, 9H, aromat H). Anal. calcd for C₃₄H₄₂N₄O₂S₂Zn: C 61.12, H 6.34, N 8.38, S 9.59. Found: C 61.08, H 6.35, N 8.39, S 9.42.

2.3. Preparation of $[PhS(O)N(SO_2Ph)NPh]_2Zn$ (2)

Zn[N(SiMe₃)₂] (0.52 g, 1.34 mmol) was added via syringe at room temperature to the suspension of PhS(O)(NSO₂ Ph)NHPh (1.00 g, 2.68 mmol) in dry benzene (30 mL). The reaction mixture was stirred for an additional 15 h. All volatiles were removed in vacuum, and the residue treated with dry hexane (10 mL). The precipitate was filtered off, dried in vacuum, and finally recrystallized from dry benzene (10 mL), resulting in compound **2**. Yield: 0.36 g (33%). Mp: 225 °C. ¹H NMR (200 MHz, hexametapole- d^{18} , 25 °C): 6.75–7.75 (br, mult, 30H, aromat H). Anal. calcd for C₃₆H₃₀N₄O₆S₄Zn: C 53.49, H 3.74, N 6.93, S 15.87. Found: C 53.55, H 3.76, N 6.68, S 15.85.

2.4. Preparation of $[p-MeC_6H_4S(O)N(t-Bu)N(t-Bu)]_2Zn$ (3)

Zn[N(SiMe₃)₂] (0.77 g, 2.00 mmol) was added via syringe at room temperature to the solution of p-MeC₆H₄S(O) [N(*t*-Bu)]NH(*t*-Bu) (1.13 g, 4.00 mmol) in dry benzene (10 mL). The reaction mixture was stirred for an additional 15 h, and refluxed for 1 h. All volatiles were removed in vacuum, and the residue recrystallized from dry acetonitrile (20 mL), resulting in compound **3**. Yield: 1.01 g (80%). Mp: 237 °C. ¹H NMR (200 MHz, CDCl₃, 25 °C): 1.18 [s, 18H, C(CH₃)₃], 1.19 [s, 18H, C(CH₃)₃], 2.40 (s, 6H, CH₃), 7.21 [d, 4H, J^2 (HH)=8.10 Hz, aromat H], 7.84 [d, 4H, J^2 (HH)=8.10 Hz, aromat H]. Anal. calcd for C₃₆H₅₀N₄O₂S₂Zn: C 57.35, H 8.02, N 8.92, S 10.21. Found: C 57.30, H 8.10, N 8.94, S 10.65.

2.5. Crystal structure determination

Single crystals of **3** were grown by slow evaporation of its acetonitrile–benzene solution at room temperature. Crystal data for **3**: $C_{30}H_{50}N_4O_2S_2Zn$, M=628.20, monoclinic, a=11.274(8) Å, b=19.205(5) Å, c=16.047(6) Å, $\beta=91.33(5)^\circ$, V=3473.5 Å³, Z=4, d=1.20 Mg/m³, space group $P2_1/c$, F(000)=1344, crystal size $0.34 \times 0.44 \times 0.53$ mm.

All crystallographic measurements were performed at 293 K on a CAD-4-Enraf-Nonius diffractometer operating in the $\omega/2\theta$ scan mode (the ratio of the scanning rates $\omega/2\theta = 1.2$). The intensity data were collected within the range $3 < \theta < 63^{\circ}$ (0 < h < 11, 0 < k < 22, -18 < l < 18) using graphite monochromated Cu-K_{α} radiation ($\lambda = 1.54184$ Å). Unit cell parameters were calculated from the setting angles of 24 strong, carefully centered reflections.

Intensities of 6022 reflections (5496 unique reflections, $R_{int} = 0.026$) were measured. The structure was solved by direct methods [26] and refined against F^2 by full-matrix leastsquares technique in the anisotropic approximation [27]. In the refinement 5496 independent reflections [4480 reflections with $I > 2\sigma(I)$] were used. Convergence was obtained at R(F) = $0.040, wR2 = 0.120 \text{ GOF} = 1.022 [I > 2\sigma(I)]; R = 0.052, wR2 =$ 0.1286 for all data (461 refined parameters; obs/variabl., 8.1; the largest and minimal peaks in the final difference map, 0.39 and -0.32 e/Å^3). The weighting scheme $w^{-1} = \sigma^2(F_0^2) +$ $(0.0752P)^2 + 2.4171P$, with $P = (F_0^2 + 2F_c^2)/3$ was used. Corrections for Lorentz and polarization effects but not for absorption were applied. Positions of hydrogen atoms were calculated according to an ideal geometry and refined riding their supporting carbon atoms.

3. Results and discussion

3.1. Reactions of bis[bis(trimethylsilyl)]amido zinc with amides of sulfonimidic acids

We found that the reactions of bis[bis(trimethylsilyl)]amido zinc with amides of sulfonimidic acids are taking place at room temperature with elimination of 2 equiv. of hexamethyldisilasane and formation of the corresponding bischelate complexes 1-3 in analytically pure state (Scheme 1).



Scheme 1.

No reaction with zinc bis[bis(trimethylsilyl)]amide was observed when p-MeC₆H₄S(O)NHt-Bu and p-MeC₆H₄ S(O)NHPh were used as reagents. In both cases the starting materials were recovered unchanged even after refluxing the reaction mixture for several hours. This observation indicates that although acidity of the hydrogen atom is high enough to eliminate HN(SiMe₃)₂, the main driving force for the formation of chelating complexes seems to be coordination of the Zn atom by the lone pair of the nitrogen atom of S=N bond, which appears to be an energetically unfavourable process due to the lower donor ability of the lone pair of the oxygen atom in the case of the S=O bond. Although dimeric complexes {Me₂Al[MeS(O)(NR)]}₂ containing the RNS(R')O fragment as a ligand are known [8], their preparation involves the addition reaction of trimethylalane to sulfinylanilines.

The spectral and analytical data for the obtained complexes are summarized in Section 2. Compounds **1–3** are colorless or pale yellow air-sensitive solids good soluble in trichloromethane or aromatic solvents.

3.2. Spectroscopic studies

¹H NMR spectra of compounds **1** and **2** at room temperature showed broad resonances for the protons of groups attached to the nitrogen atoms as well as for the substituents on sulfur atoms. This fact can be explained taking into account that the main group and transition metal bischelate complexes are stereochemically non-rigid and exhibiting fast isomerisation in solution via different possible mechanisms [28,29]. Application of dynamic NMR

technique allowed to study the kinetics of inversion processes and was pioneered by Ernst et al. on bischelate aminopropenethionate complexes of Zn (II) and Cd (II) [30,31].

One of the stabilization routes for the conformation of nonrigid molecules is the introduction of bulky substituents [32]. With this aim we performed the synthesis of compound 3, containing *tert*-butyl groups attached to the nitrogen atoms. ¹H NMR spectrum of compound 3 at room temperature in CDCl₃ showed sharp resonances: two singlets for the protons of tertbutyl groups (1.18 and 1.19 ppm), a singlet (2.40 ppm, methyl protons), and a characteristic AB system at low field (7.21-7.84 ppm, aromatic protons of p-MeC₆H₄ groups), with the correct integration 36:6:8. The presence of two resonances for the protons of t-Bu groups is in a good agreement with the solid-state structure of compound 3 (vide infra), which shows different environment for *tert*-butyl groups in the solid state. Thus, compound 3 exists in solution as a mixture of two conformers. The frequency separation $\Delta \nu$ for the protons of the t-Bu groups at room temperature was found to be solvent dependent, and varies from 2.00 Hz (CDCl₃), and 3.17 Hz (toluene- d^8), to 3.40 Hz (DMSO- d^6).

Compound **3** was studied in the solution by means of dynamic ¹H NMR spectroscopy. The ¹H NMR spectrum of **3** was studied in DMSO-d⁶ at different temperatures. Resonances for the protons of the *tert*-butyl groups appeared as two separated singlets at 295 K. They are broadened with increasing temperature and coalesce at ca. 360 K as a result of the inversion of the tetrahedral core. This observation indicates stereochemical non-rigidity of **3** in solution and also explains the broad resonances in the ¹H NMR spectra observed for compounds **1** and **2** at room temperature. As it was expected for **3**, introduction of bulky substituents on nitrogen atoms increases the energetical barrier of inversion and allowed to observe separated resonances for the organic groups at room temperature.

3.3. X-ray single crystal structure of 3

General view of the molecule is shown in Fig. 1; selected bond lengths and angles are listed in Table 1.



Fig. 1. Molecular structure of [p-MeC₆H₄S(O)N(t-Bu)N(t-Bu)]₂Zn (3) in the solid state.

Table 1							
Selected	bond l	engths	(Å)	and	angles	(°) for	r 3

Zn-N(1)	2.023(3)	S(1)–N(2)	1.571(2)	
Zn-N(2)	2.014(3)	S(1)–O(1)	1.444(2)	
Zn-N(3)	2.002(3)	S(1)-C(1)	1.778(3)	
Zn-N(4)	2.033(3)	S(2)–N(3)	1.573(3)	
$Zn \cdots S(1)$	2.665(2)	S(2)–N(4)	1.566(3)	
$Zn \cdots S(2)$	2.669(2)	S(2)–O(2)	1.445(3)	
S(1)–N(1)	1.571(3)	S(2)-C(16)	1.782(3)	
N(1)ZnN(2)	71.0(1)	ZnN(1)S(1)	94.9(1)	
N(3)ZnN(4)	71.2(1)	ZnN(2)S(1)	95.2(1)	
N(1)S(1)N(2)	96.5(1)	ZnN(3)S(2)	95.8(1)	
N(3)S(2)N(4)	96.9(2)	ZnN(4)S(2)	94.8(1)	

Compound **3** crystallizes in the monoclinic space group $(P2_1/c)$. In the X-ray structure the two ZnN₂S four-membered rings are interconnected by a common zinc atom and are mutually orthogonal (interplane angle ZnN(1)N(2)S(1)/ZnN (3)N(4)S(2) 89.6°). The central Zn atom as well as the S(1) and S(2) atoms adopt significantly distorted tetrahedral coordination geometry. The bond configuration for all N atoms is trigonal planar (sum of the bond angles 356–358°). Both four-membered heterocycles are slightly non-planar (max. deviation from the least-square plane is 0.107 and 0.075 Å, respectively) and folded by 16.1 and 11.2 Å about N–N axis. Due to the steric repulsions the C(1–6) and C(16–21) benzene rings attached to the four-membered heterocycles showing substantial twisting around the S(1)–C(1) and S(2)–C(16) bonds (corresponding dihedral angles are 87.7 and 86.0°).

The Zn–N distances (2.002–2.033(3) Å, av. 2.018 Å) are in the normal range [33,34]. The important feature of the structure is the considerable electron density delocalisation in the N(1)– S(1)–N(2) and N(3)–S(2)–N(4) linkages: the S–N bond lengths [1.566–1.573(3) Å, av. 1.570 Å] are significantly shortened in comparison with that for a S–N single bond (1.65 Å [35,36]), reflecting the multiple bond character. The S=O and S–C bond lengths in **3** [1.444(3) and 1.770(12) Å] are comparable with those in MeS(O)Ph [37].

4. Conclusions

We found that the reactions of bis[bis(trimethylsilyl)amido] zinc with amides of sulfonimidic acids are taking place at mild conditions and are leading to the formation of corresponding bischelate complexes 1-3. NMR spectroscopic studies of compounds 1-3 showed non-rigidity of the bischelate complexes in the solution. Single crystal X-ray analysis of compound 3 showed the tetrahedral environment of the Zn atom in the solid state.

5. Supplementary material

CCDC-220873 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033).

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft for partial support of this research.

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