A Novel Methylene Dithioether as a Ligand: Synthesis and Molecular Structure of a Zinc(II) Complex with $N_4S_2$ Coordination Environment

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The octadentate ligand $[N(CH_2CH_2NH_2)(CH_2CH_2CH_2OH)(CH_2CH_2S)]_2CH_2$, (NNOS-232)$_2$CH$_2$, was synthesized accidentally by the reaction of the unsymmetrically substituted tripod $[N(CH_2CH_2NH_2)(CH_2CH_2CH_2OH)(CH_2CH_2SH)]$, NNOS-232, with dichloromethane in the presence of aluminum hydroxide. Ligand (NNOS-232)$_2$CH$_2$ was reacted with zinc bis(perchlorate) hexahydrate to yield the complex $[Zn((NNOS-232)2CH2)](ClO4)_2$ exhibiting a distorted octahedrally coordinated zinc atom in an $N_4S_2$ coordination environment, as shown by an X-ray diffraction study.

Key words: Zinc, Dithioacetal, Tripodal Ligands

Introduction

The field of unsymmetrically substituted, aliphatic tripodal ligands is still a sparsely explored area of coordination chemistry. We have prepared unsymmetrically substituted tripodal ligands which are derived from tren (tren = tris(2-aminoethyl)amine) that provide an $N_4$ coordination environment with different spaces between the central nitrogen atom and the primary amine donors [1]. Later we focussed on tripodal ligands with different donor groups providing $N_2O_2$ and $N_2O$ donor sets [2]. Most recently we prepared the totally unsymmetrical tripod NNOS-232 (Scheme 1) with an $N_2OS$ donor set and studied its coordination chemistry with nickel(II) [3]. In our efforts to develop synthetic models for the active site in horse liver alcohol dehydrogenase [4], we became interested in the coordination chemistry of NNOS-232 with zinc(II). In this contribution we describe the Al(OH)$_3$ catalyzed reaction of ligand NNOS-232 with dichloromethane during an improved work-up procedure yielding the octadentate ligand (NNOS-232)$_2$CH$_2$.

Experimental Section

Manipulations concerning the synthesis of the ligand were performed in an atmosphere of dry argon by standard Schlenk techniques. Solvents other than dichloromethane were dried by standard methods and freshly distilled prior to use for ligand syntheses. $N$-(cyanomethyl)-$N$-(2-thiaoctetethyl)aminopropionic ethyl ester was prepared according to a published procedure [3].

(NNOS – 232)$_2$CH$_2$: 4.06 g (0.102 mol) of lithium aluminum hydride was suspended in 60 ml of dry THF and 120 ml of diethyl ether. The mixture was stirred for 2 h before 1.72 g (0.017 mol) of concentrated sulfuric acid was added cautiously dropwise while cooling the reaction mixture with an ice bath. After stirring for another 2 h at room temperature the mixture was cooled to $-5 \degree C$ again and a solution of 4.0 g (0.0155 mol) of concentrated sulfuric acid was added cautiously dropwise while cooling the reaction mixture with an ice bath. After stirring for another 2 h at room temperature the mixture was cooled to $-5 \degree C$ again and a solution of 4.0 g (0.0155 mol) of concentrated sulfuric acid was added cautiously dropwise while cooling the reaction mixture with an ice bath. After stirring for another 2 h at room temperature the mixture was cooled to $-5 \degree C$ again and a solution of 4.0 g (0.0155 mol) of concentrated sulfuric acid was added cautiously dropwise while cooling the reaction mixture with an ice bath. Then the mixture was hydrolyzed with 7.4 ml of deionized water (CAUTION: exothermic reaction and hydrogen evolution). The crude solid product NNOS-232 was separated by filtration. The solid residue, which contained aluminum hydroxide and the ligand, was extracted continuously with dichloromethane for 24 h. This extraction in the presence of dichloromethane caused the formation of the triacetal from two equivalents of NNOS-232. The extract was dried over sodium sulfate.
and the solvent was removed under reduced pressure. Ligand (NNOS-232)CH2 was obtained as a yellow oil. Yield: 1.85 g (5.1 mmol, 60%). ¹H NMR (300.1 MHz, CDCl₃): δ = 3.87 (t, 4 H, CH₂OH), 3.87 (s, 2 H, SCH₂S), 3.54 (s, 6 H, NH₂ + OH), 3.00–2.86 (m, 12 H, CH₂), 2.79 (t, J = 6.6 Hz, 4 H, NCH₂CH₂CH₂OH), 2.72 (t, 4 H, CH₂), 1.83 (q, J = 6.0 Hz, 4 H, NCH₂CH₂CH₂OH). ¹³C NMR (75.5 MHz, CDCl₃): δ = 61.4 (CH₂OH), 55.9 (NCH₂CH₂CH₂OH), 52.1 (NCH₂CH₂NH₂), 39.2 (NCH₂CH₂NH₂), 36.6 (SCH₂S), 35.9 (NCH₂CH₂CH₂OH), 29.2 (NCH₂CH₂CH₂OH), 28.6 (NCH₂CH₂S).

[Zn((NNOS-232)CH₂)]([ClO₄]₂) C. A solution of 362 mg (1.00 mmol) of (NNOS-232)CH₂ in 10 ml of methanol was added to a solution of 430 mg (1.15 mmol) of zinc bis(perchlorate) hexahydrate in 10 ml of acetonitrile. Methanol was added to a solution of 430 mg (1.15 mmol) of (NNOS-232)CH₂ in 10 ml of methanol. Yield: 230 mg (0.36 mmol, 36%). – ¹H NMR (300.1 MHz, [D₆]DMSO): δ = 6.49 (s br, 2 H, OH), 4.34 (s br, 4 H, NH₂), 4.08 (s, 2 H, SCH₂S), 3.62 (t, 4 H, CH₂OH), 3.37 (s br, 4 H, CH₂), 3.04 (s br, 8 H, CH₂), 2.89 (s br, 8 H, CH₂), 1.80 (q, 4 H, NCH₂CH₂CH₂OH), 1.72 (s br, 8 H, CH₂), 1.35 (s br, 8 H, CH₂), 1.25 (s br, 8 H, CH₂), 1.20 (s br, 8 H, CH₂), 0.945 (s, 3 H, CH₃). ¹³C NMR (75.5 MHz, [D₆]DMSO): δ = 29.2 (CH₂), 32.4 (NCH₂CH₂NH₂), 39.9 (NCH₂CH₂NH₂), 35.8 (NCH₂CH₂S), 32.4 (NCH₂CH₂CH₂OH), 22.6 (NCH₂CH₂S), 18.3 (SCH₂S). – C₁₅H₃₆N₄Cl₂O₁₀S₂Zn (632.88): calcd. C 28.47, H 5.73, N 8.85, S 9.29. Found C 28.25, H 5.54, N 8.57, S 9.54.

X-ray structure determination: Formula C₁₅H₃₆N₄Cl₂O₁₀S₂Zn, M = 632.88, colorless crystal, 0.10 × 0.07 × 0.02 mm, a = 8.3522(11), b = 9.4040(12), c = 17.528(2) Å, α = 77.324(3), β = 83.649(3), γ = 78.053(3)°, V = 12452.3 (3) Å³, ρcalcd = 1.688 g cm⁻³, µ = 14.26 cm⁻¹, empirical multi-scan absorption correction (0.8705 ≤ T ≤ 0.9720), Z = 2, triclinic, space group P1̅, λ = 0.71073 Å, T = 173(2) K, Ω, ϕ and θ scans, 9708 reflections collected (±h, ±k, ±l), [[sinθ/λ] = 0.704 Å⁻¹, 6691 independent (Rint = 0.035) and 4808 observed reflections (I ≥ 2σI), 320 refined parameters, R = 0.070, wR² = 0.176 (refinement on F²), max residual electron density 1.916 (−0.945) e Å⁻³, hydrogen atom positions calculated and refined as riding atoms. Diffraction data were collected on a Bruker AXS 2000 CCD diffractometer with a rotating anode generator M12XCE. Programs used: structure solution SHELXS-97 [5], structure refinement SHELXL-97 [6], graphics ORTEP3 [7]. Oxygen atom O1, carbon atom C14 and two oxygen atoms of one ClO₄⁻ anion are disordered. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-215467. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [fax: int. code +44(1223)36-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

The novel Ligand (NNOS-232)CH₂ was obtained during an attempt to improve the work-up conditions after synthesis in the ligand NNOS-232 (Scheme 1). In the published procedure [3] the ligand was carefully separated from Al(OH)₃ after hydrolysis [8] by washing of the solid residue with THF/water. In an attempt to isolate the ligand NNOS-232 by Soxhlet extraction with dichloromethane, this procedure led to the linkage of two equivalents of NNOS-232 via a methylene bridge, giving the thioalcal (NNOS-232)CH₂ in 60% yield. The synthesis of such methylene dithioacetals from thiols and formaldehyde [9] or alkyl halides [10] is a well known procedure. A similar reaction path is assumed for the formation of (NNOS-232)CH₂ on the Al(OH)₃ surface. Even the in situ reduction of disulfides followed by reaction with dihaloalkanes to produce bis(organylthio)alkanes has been reported recently [11]. The ligand (NNOS-232)CH₂ is easily identified by elemental analysis and by the presence of eight (instead of seven for NNOS-232) resonances in the ¹³C NMR spectrum.

Ligand (NNOS-232)CH₂ was reacted with a 1.15 fold excess of zinc bis(perchlorate) hexahy-
distances. Although one of the Zn-SCH$_2$ distances \(2.37\) to \(2.45\) Å while this distance can expand in hexacoordinated compounds to \(2.70\) Å [16]. Owing to the constraints caused by the chelate rings in \(1\), this complex constitutes only the second example of a methylene dithioether ligand chelating one metal center.

As seen with the nickel(II) complex of ligand NNOS-232 \(3\) the hydroxyl groups in \(1\) are not coordinated to the zinc center. Upon coordination, they would be part of six-membered chelate rings which are less stable than the found five-membered rings in \(1\) [17]. Ligands of type (NNOS-232)$_2$CH$_2$ belong to the rare class of potentially octadentate species with an N$_4$O$_2$S$_2$ donor set. Since the methylene bridge between the sulfur atoms can be substituted by an ethyl bridge, this type of ligands should be capable to coordinate in an unstrained fashion to metal centers which prefer high coordination numbers, e.g. the lanthanide(III) ions.

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