INORGANIC CHEMISTRY | RESEARCH ARTICLE

Tetranuclear zinc(II)-oxy (benzothiazole)-2-thiolate aggregate and copper(I) phenylthiolate aggregate

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Abstract: A tetranuclear zinc-oxy (benzothiazole)-2-thiolate aggregate whose structure has a C₃-axis passing through ZnO unit relating three other zinc ions and a tetranuclear copper(I) phenylthiolate aggregate having each thiphenolate ligand bridging three copper ions are reported. These aggregates were prepared by hydrothermal reactions of 2,2'‐dithiobis‐(benzothiazole) with zinc nitrate or copper(I) iodide, respectively. The reaction of zinc nitrate passed through in situ abstraction of a oxy ligand from moisture to form a Zn₄O core holding six 2-benzothiazolethiolate ligands, and during the formation of the aggregate, cleavage of S–S bond of 2,2'-dithiobis-(benzothiazole) took place. Whereas, an aggregate formed by self-assemblying of copper(I) phenylthiolate was formed after extensive degradation of 2,2'-dithiobis-(benzothiazole) during solvothermal reaction.

Subjects: Chemistry; Inorganic Chemistry; Physical Sciences

Keywords: solvothermal reactions; zinc(II)-oxy (benzothiazole)-2-thiolate aggregate; copper(I) phenylthiolate

1. Introduction
Tetranuclear zinc carboxylate aggregates having Zn₄O environment are considered as molecular models for ZnO, as such aggregates show high photoluminescence (Bertoncello et al., 1992). Thus, it would be interesting to synthesize such units within an environment of fluorescent ligands. For this reason, benzothiazole derivatives are of interest and several zinc complexes having a thiazole ligand show interesting optical properties (Dey, Efimov, Giri, Rissanen, & Lemmetyinen, 2011; Li et al., 2013; Wang, Deng, Fu, Cheng, & Li, 2012). Zinc aggregates are often used as catalysts for organic transformations (Iwasaki, Maegawa, Hayashi, Ohshima, & Mashima, 2008; Maegawa, Ohshima, Hayashi,
2. Experimental

2.1. Synthesis and characterization

Zinc(II)-oxy (benzothiazole)-2-thiolate aggregate (I): It was prepared by reacting zinc nitrate hexahydrate (74 mg, 0.25 mmol) and 2,2’-dithiobis-(benzothiazole) (166 mg, 0.5 mmol) in methanol/DMF solution (1:3 v/v, 6 mL) in a sealed Teflon-lined stainless steel reactor, heated at 120°C for 2 days and then cooled to room temperature for 10 h. Colorless crystals of the zinc aggregate were collected and washed with methanol (3 mL) and dried. Isolated yield = 72 mg (21%) on the basis of zinc. 1H-NMR (DMSO-d6, 400 MHz): 8.02 (s, 1H), 7.49 (s, 1H), 7.21 (s, 1H), 7.12 (s, 1H). IR (KBr, cm⁻¹): 3,052 (vw), 1,452 (s), 1,367 (s), 1,243 (s), 1,087 (s), 1,029 (s), 505 (s). UV–vis (DMSO), 270 nm (ε = 11.7449(5) Å, β = 15.5213(7) Å, γ = 16.0281(7) Å, α = β = γ = 90°, V = 2,921.2 Å³, Z = 4, Density = 1.571 g cm⁻³, Abs. Coeff. = 3.167 mm⁻¹, Abs. correction = multi-scan, F(0 0 0) = 3,828, Total No. of reflections = 212121, Temperature = 296(2) K, Wavelength = 0.71073 Å, λ = 1.7 × 10⁵ mol L⁻¹ cm⁻¹), Fluorescence emission (λₑₓ = 325 nm, DMSO) 378 and 435 nm. Crystallographic parameters: CCDC No. 989913. Molecular weight = 690.84, Formula = C₄₂H₂₂N₆O₄S₁₂Zn₄, Space group = R-3, Temperature = 296(2) K, Wavelength = 0.71073 Å, a = 18.2994 Å, b = 18.2994 Å, c = 24.926 Å, α = 90°, β = 90°, γ = 120°, V = 7,228.6(12) Å³, Z = 6, Density = 1.757 g cm⁻³, Abs. Coeff. = 2.529 mm⁻¹, Abs. correction = multi-scan, F(0 0 0) = 3,828, Total No. of reflections = 2,878, Reflections, I > 2σ(I) = 2,503, Max. 2θ (°) = 50.5°, Ranges (h, k, l), 21 > h > −21, 21 > k > −21, 29 > l > −29, Completeness to 2θ (%) = 99.2%, Goof (F²) = 0.991, R indices [I > 2σ(I)] = 0.0262, and R indices (all data) = 0.0336.

Copper(I) phenylthiolate aggregate (II): It was prepared by reacting copper(I) iodide (48 mg, 0.25 mmol) and 2,2’-dithiobis(benzothiazole) (166 mg, 0.5 mmol) in a methanol/DMSO solution (1:3 v/v, 6 mL) along with 3–4 drops of concentrated hydrochloric acid placed in a Teflon-lined stainless steel reactor at 120°C for 2 days. The reactor was then cooled to room temperature for 10 h. A yellowish-white solid precipitate was formed, which was washed with methanol (3 mL) and dried. Isolated yield = 31 mg (18%) on the basis of copper. 1H-NMR (CDCl₃, 400 MHz): 8.02 (s, 1H), 7.49 (s, 1H), 7.21 (s, 1H), 7.12 (s, 1H). IR (KBr, cm⁻¹): 3,052 (vw), 1,452 (s), 1,367 (s), 1,243 (s), 1,087 (s), 1,029 (s), 505 (s). UV–vis (DMSO), 270 nm (ε = 11.7449(5) Å, β = 15.5213(7) Å, γ = 16.0281(7) Å, α = β = γ = 90°, V = 2,921.2 Å³, Z = 4, Density = 1.757 g cm⁻³, Abs. Coeff. = 2.529 mm⁻¹, Abs. correction = multi-scan, F(0 0 0) = 3,828, Total No. of reflections = 212121, Temperature = 296(2) K, Wavelength = 0.71073 Å, λ = 1.7 × 10⁵ mol L⁻¹ cm⁻¹), Fluorescence emission (λₑₓ = 325 nm, DMSO) 378 and 435 nm. Crystallographic parameters: CCDC No. 989913. Molecular weight = 690.84, Formula = C₄₂H₂₂N₆O₄S₁₂Zn₄, Space group = R-3, Temperature = 296(2) K, Wavelength = 0.71073 Å, a = 18.2994 Å, b = 18.2994 Å, c = 24.926 Å, α = 90°, β = 90°, γ = 120°, V = 7,228.6(12) Å³, Z = 6, Density = 1.757 g cm⁻³, Abs. Coeff. = 2.529 mm⁻¹, Abs. correction = multi-scan, F(0 0 0) = 3,828, Total No. of reflections = 2,878, Reflections, I > 2σ(I) = 2,503, Max. 2θ (°) = 50.5°, Ranges (h, k, l), 21 > h > −21, 21 > k > −21, 29 > l > −29, Completeness to 2θ (%) = 99.2%, Goof (F²) = 0.991, R indices [I > 2σ(I)] = 0.0262, and R indices (all data) = 0.0336.

3. Results and discussion

Solvothermal reaction of zinc(II) nitrate with 2,2’-dithiobis-(benzothiazole) resulted in the formation of tetranuclear aggregate I as illustrated in Equation 1. The reaction involves a homolytic cleavage of S–S bond of the 2,2’-dithiobis-(benzothiazole) to form a zinc aggregate. This aggregate I was characterized by FT-IR and ¹H-NMR spectroscopic techniques to determine the crystal structure.

Equation 1: Synthesis of the tetranuclear aggregate

¹H-NMR spectra of 2,2’-dithiobis-(benzothiazole) has two doublets and two triplets in the aromatic region with equal integration, whereas zinc aggregate has four singlets from protons on the aromatic...
This is due to the asymmetry caused to (benzothiazole)-2-thiolate ligand upon coordination through sulfur and nitrogen atoms of ligands to zinc ions in the aggregate I. IR spectra of 2,2′-dithiobiobis-benzothiazole has two strong C=S stretchings at 1,463 cm⁻¹ and 1,436 cm⁻¹, while the aggregate has a sharp C=S stretching at 1,452 cm⁻¹.

The crystal structure of the zinc aggregate I is shown in Figure 1(a). Zinc aggregate is composed of six (benzothiazole)-2-thiolate, an oxide ligand, and four zinc ions. A centrally located oxide ligand coordinates with four different zinc ions to make a Zn₄O core. Three zinc ions are in identical environment which are in S₂NO ligand environment, whereas the fourth zinc ion is in N₂O environment. Coordination environment around each zinc ion is a distorted tetrahedral. There is a C₃-axis passing through the Zn₂–O₁; thus other three zinc ions are related to this axis, and hence are in symmetry in equivalent positions. Figure 1(b) shows the zinc environment and it is drawn so that one of the zinc atom is at the top of oxygen atom to show the C₃-axis. Sulfur atom of the thiolate group and the nitrogen atom of thiazole ring act as a bridge to anchor two zinc ions. The constituent sulfur atom of benzothiazole ring remains free. Aggregates of Zn₄O benzoate units were earlier prepared from alkylzinc (Redshaw, Jana, Shang, Elsegood, & Lu, 2010). Metallorganic frameworks based on such aggregates have attracted attention as they have the ability for high hydrogen uptake (Chen, Yang, Liu, & Ma, 2013; Chun & Jung, 2009; Yaghi et al., 2003). On the other hand, use of alylzinc as a precursor (Redshaw et al., 2010) resulted in tetranuclear aggregates in which peripheral zinc ions form tetrahedral arrangements. However, use of aminobenzoic acid yielded an aggregate which had a Zn₄O unit. Extreme care could not avoid incorporation of μ₄–O²⁻ unit as an anchoring ligand that was picked up from air or moisture. On the other hand, many Zn₄O carboxylate aggregates were prepared from zinc oxide (Ötvös, Berkesi, Körtvélyesi, & Pálinkó, 2010). In aggregate I, the oxide incorporation from moisture took place during solvothermal reaction.

![Figure 1. (a) Structure of the tetranuclear zinc aggregate (I) (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) are Zn₁–O₁, 1.955(12); Zn₂–O₁, 1.939(3); Zn₁–N₁, 2.037(2), Zn₂–N₂, 2.031(2); Zn₁–S₁, 2.347(9); Zn₁–S₃, 2.339(8); and bond angles (°) Zn₁–O₁–Zn₁, 107.81(9); Zn₂–O₁–Zn₁, 111.09(9); O₁–Zn₂–N₂, 104.30(7); O₁–Zn₂–N₂, 104.30(7); N₂–Zn₂–N₂, 114.11(6); O₁–Zn₂–N₂, 104.30(7); N₂–Zn₂–N₂, 114.11(6); O₁–Zn₁–N₁, 109.77(7); O₁–Zn₁–S₃, 107.17(8); N₁–Zn₁–S₃, 113.11(7); O₁–Zn₁–S₁, 106.02(7); N₁–Zn₁–S₁, 113.16(7); and S₃–Zn₁–S₁, 107.20(3). (Symmetry codes * = −y, x − y, z; and ** = −x + y, −y, z.) (b) Coordination environment around zinc ions. One zinc ion is drawn over the oxide ligand to visualize frontal view of C₃-axis passing through the zinc and oxygen.](image-url)
A solution of 2,2′-dithiobis-(benzothiazole) in dimethylsulphoxide absorbs at 265 nm, while the tetranuclear zinc aggregate absorbs at 270 and 323 nm. In solid state, 2,2′-dithiobis(benzothiazole) absorbs at 275 nm, whereas the zinc aggregate I shows three closely spaced emission peaks at 306, 332, and 355 nm. In solution, 2,2′-dithiobis(benzothiazole) shows fluorescence emission at 398 nm on excitation at 270 nm. Whereas, a solution of aggregate I, when excited at 325 nm, shows a weak emission at 378 nm and a strong emission at 435 nm. Considering the importance of ZnO as an optical material, an aggregate having different ligand atoms around ZnO core showing fluorescence properties is of a definite interest. Tetranuclear zinc aggregate is thermally stable up to 300°C, but decomposes beyond this temperature.

Copper(I) complexes having composition Cu₆(btt)₆ or Cu₄(btt)₄ (where btt = 2-benzothiazolethiolate) were reported to show near IR luminescence (Yue et al., 2009), hence we reacted 2,2′-dithiobis-(benzothiazole) with cuprous iodide to check if there is a S–S bond cleavage to form a similar aggregate. To our surprise, solvothermal reaction of copper(I) iodide with 2,2′-dithiobis-(benzothiazole) resulted in the formation of tetranuclear copper(I) phenylthiolate aggregate (Equation 2). The aggregate II was formed by extensive degradation of 2,2′-dithiobis-(benzothiazole). The aggregate shows a strong ESI mass peak at 689.5202 (m/z), showing it to be a tetranuclear copper phenylthiolate aggregate. This peak could be due to the radical cation formed on sulfur atom in the mass spectra. In addition to this, it shows a mass peak at 345.4651 due to the dimeric unit C₆H₅S₂Cu₂. ¹H-NMR spectra of the aggregate has two sets of protons at 8.05 ppm for two hydrogen atoms and at 7.22 ppm for three hydrogen atoms. We could not obtain good quality crystals to get a good X-ray single crystal diffraction structure of the aggregate, but the data have helped to establish its skeleton. There are four thiolate ligands, each connects three copper ions to form the tetranuclear aggregate II (Figure 2). It may be suggested to be a self-assembly of four copper(I) phenylthiolate or imagined as a combination of two phenylthiolate-bridged copper dimers which are inter-connected in a manner, such that the phenyl groups remain apart.

Equation 2 : Reaction of copper(I) iodide with 2, 2′-dithiobis-(benzothiazole)
Copper(I) arythiolates have special interests as p-type charge carriers. Generally, such compounds form infinite chains, but some of such complexes possess μ1-bridging arythiolate ligands (Che, Li, Chui, Roy, & Low, 2008). In fact, the structure of aggregate II has μ1-bridging phenylthiolate to make tetrahedral arrangements of copper ions in the aggregate. Each copper ion is flanked by sulfide ions. It was earlier reported by Dance, Bowmaker, Clark, and Seadon (1983) that reactions of copper(II) salt and excess amount of a arylthiol in presence of tertiary amine in alcohol resulted in sulfide ions. It was reported by Dance, Bowmaker, Clark, and Seadon (1983) that reactions of tetranuclear zinc(II)-oxy perchlorate aggregate, in which each sulfur atom is involved in μ3-bridging mode. Besides their interesting structural features, these aggregates show photoluminescence properties.

A methanol solution of copper(I) aggregate shows an absorption at 298 nm due to π-π* transition, whereas it shows fluorescence emission at 355 and 410 nm on excitation at 300 nm. Emission peak at higher wavelength is attributed to exciplex due to metal-to-ligand charge transfer.

In conclusion, under solvothermal conditions, 2,2′-dithio-bis(benzothiazole) undergoes extensive degradation with zinc nitrate or copper(I) chloride. Tetranuclear zinc aggregate has a mixed environment of nitrogen, oxygen, and sulfur atoms around zinc oxide unit. Extensive degradation of 2,2′-dithio-bis(benzothiazole) by copper(I) chloride has led to a tetranuclear copper(I) phenylthiolate aggregate, in which each sulfur atom is involved in μ1-bridging mode. Besides their interesting structural features, these aggregates show photoluminescence properties.

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