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INORGANIC CHEMISTRY | RESEARCH ARTICLE

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

Abir Goswami¹, Nithi Phukan¹ and Jubaraj Bikash Baruah^{1*}

Abstract: A tetranuclear zinc-oxy (benzothiazole)-2-thiolate aggregate whose structure has a C_3 -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 Zn_4O 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-assembly 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 Zn_4O 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,

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Abir Goswami was a Masters student.

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Jubaraj Bikash Baruah was born in 1964 in Assam, India, and holds a senior professor position in Indian Institute of Technology, Guwahati. He obtained his PhD from Indian Institute of Science, Bangalore. His major research interest is to correlate different material properties associated with supramolecular systems with structures. He contributed as a founder member and the head in-charge of Department of Chemistry which started in 1995 and also as the head of Department of Chemistry and dean of Research and Development of Indian Institute of Technology, Guwahati.

PUBLIC INTEREST STATEMENT

Zn_4O unit in inorganic aggregates is considered as a molecular model for ZnO and shows photoluminescence. Thus, it is of interest to study such units in the surrounding of sulfur or nitrogen atoms, as shown in this article. Degradation of aromatic heterocyclic compounds by metal salts is important for environment; we have shown that degradation of 2,2'-dithiobis-(benzothiazole) by copper(I) iodide generates copper(I) phenylthiolate aggregate, which not only shows a method to degrade it, but also to prepare a potential optical material.



Jubaraj Bikash Baruah

Agura, & Iwasaki, 2011; Ohshima, Iwasaki, Maegawa, Yoshiyama, & Mashima, 2008). Polynuclear oxy-bridged aggregates of zinc are of special interest as they are isolable building blocks (Iwasaki et al., 2006) for bottom-up synthesis. Tetranuclear copper(I) aggregates have interesting structural features and show unusual optical properties (Crumbless, Gestaut, Rickard, & McPhail, 1974; Lawton, Rohrbaugh, & Kokotailo, 1972; Schuerman, Fronczek, & Selbin, 1988; Wei et al., 2009; Yue et al., 2009). Thus, preparations of new aggregates with new methods are of great importance. We report here an oxy-zinc (benzothiazole)-2-thiolate and a copper(I) phenylthiolate aggregate.

2. Experimental

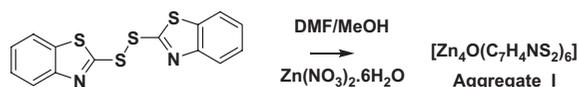
2.1. Synthesis and characterization

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 ($\epsilon = 4.8 \times 10^5 \text{ mol L}^{-1} \text{ cm}^{-1}$), 323 nm ($\epsilon = 1.7 \times 10^5 \text{ mol L}^{-1} \text{ cm}^{-1}$). Fluorescence emission ($\lambda_{\text{ex}} = 325 \text{ nm}$, DMSO) 378 and 435 nm. Crystallographic parameters: CCDC No. 989913. Molecular weight = 1,275.02, Formula = C₄₂H₂₄N₆OS₁₂Zn₄. Space group = R-3, Temperature = 296(2) K, Wavelength = 0.71073 Å, $a = 18.2994 \text{ Å}$, $b = 18.2994 \text{ Å}$, $c = 24.926 \text{ Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 7,228.6(12) \text{ Å}^3$, $Z = 6$, Density = 1.757 gcm⁻³, Abs. Coeff. = 2.529 mm⁻¹, Abs. correction = multi-scan, $F(0\ 0\ 0) = 3,828$, Total No. of reflections = 2,878, Reflections, $I > 2\sigma(I) = 2,503$, Max. 2θ (°) = 50.5°, Ranges (h, k, l), $21 > h > -21$, $21 > k > -21$, $29 > l > -29$, Completeness to 2θ (%) = 99.2%, Goof (F^2) = 0.991, R indices [$I > 2\sigma(I)$] = 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): δ 8.05 (s, 2H), 7.22 (m, 3H). IR (KBr, cm⁻¹): 2,911 (w), 1,467 (s), 1,406 (s), 1,231 (s), 987 (s), 752 (s). ESI-mass (m/e) = 689.5202; calculated exact mass for 687.7632. UV-vis 298 nm ($\epsilon = 6.7 \times 10^4 \text{ mol L}^{-1} \text{ cm}^{-1}$), Fluorescence emission ($\lambda_{\text{ex}} = 300 \text{ nm}$) 355 and 410 nm. Crystallographic parameters: Molecular weight = 690.84, Formula = C₂₄H₂₀Cu₄S₄, Space group = $P2_12_12_1$, Temperature = 296(2) K, Wavelength = 0.71073 Å, $a = 11.7449(5) \text{ Å}$, $b = 15.5213(7) \text{ Å}$, $c = 16.0281(7) \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 2,921.9(2) \text{ Å}^3$, $Z = 4$, Density = 1.571 gcm⁻³, Abs. Coeff. = 3.167 mm⁻¹, Abs. correction = multi scan, $F(0\ 0\ 0) = 1,376$, Total No. of reflections = 33,218, Reflections, $I > 2\sigma(I) = 6,939$, Max. 2θ (°) = 49.198°, Ranges (h, k, l) = $-15 > h > 15$; $-19 > k > 17$; $-21 > l > 21$, Completeness to 2θ (%) = 98.6%, Goof (F^2) = 1.006, R indices [$I > 2\sigma(I)$] = 0.1177, and R indices (all data) = 0.1008.

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.



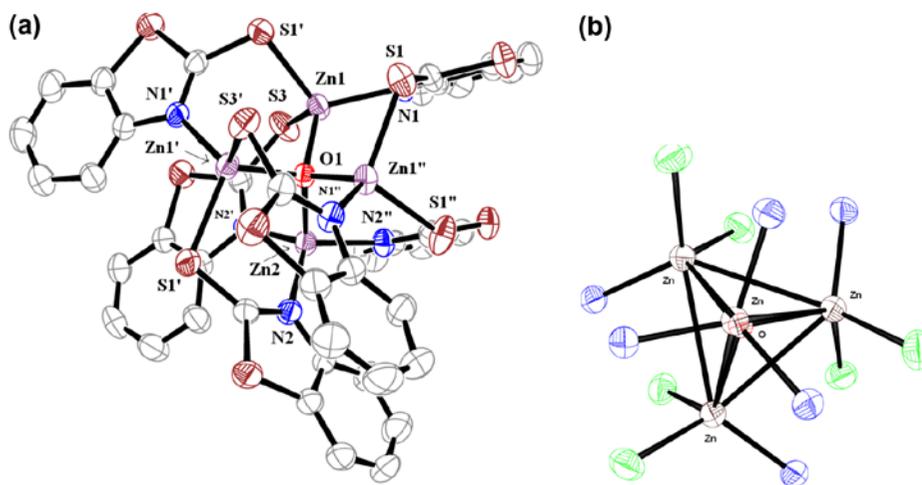
Equation 1: Synthesis of the tetranucle araggregate

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

ring. 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'-dithiobis-(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} .

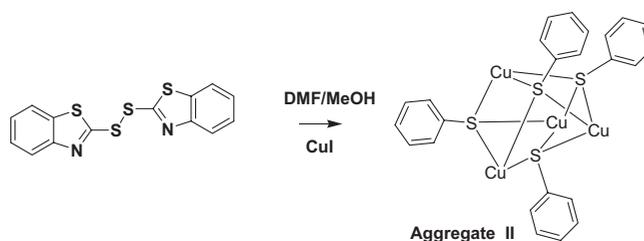
The crystal structure of the zinc aggregate **I** is shown in Figure 1(a). Zinc aggregate is composed of six (benzothiazole)-2-thiolate, an oxide ligand, and four zinc ions. A centrally located oxide ligand coordinates with four different zinc ions to make a Zn_4O core. Three zinc ions are in identical environment which are in S_2NO ligand environment, whereas the fourth zinc ion is in N_3O environment. Coordination environment around each zinc ion is a distorted tetrahedral. There is a C_3 -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 C_3 -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 Zn_6O 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 arylzinc 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 Zn_6O unit. Extreme care could not avoid incorporation of $\mu^4\text{-O}^{2-}$ unit as an anchoring ligand that was picked up from air or moisture. On the other hand, many Zn_6O 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 C_3 -axis passing through the zinc and oxygen.



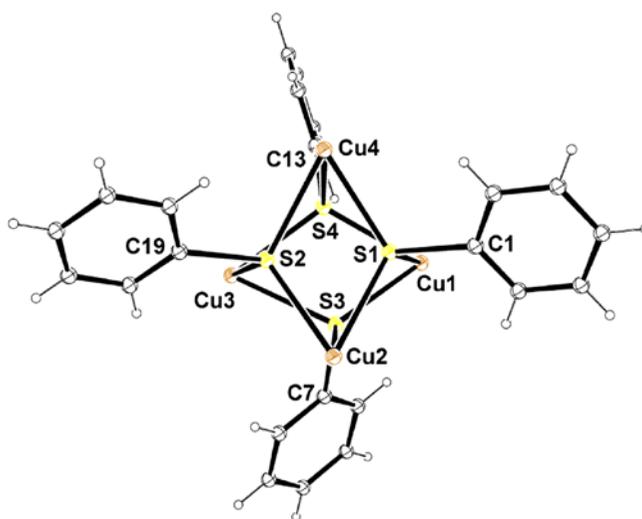
A solution of 2,2'-dithiobis-(benzothiazole) in dimethylsulphoxide absorbs at 265 nm, while the tetranuclear zinc aggregate absorbs at 270 and 323 nm. In solid state, 2,2'-dithiobis(benzothiazole) absorbs at 275 nm, whereas the zinc aggregate **I** shows three closely spaced emission peaks at 306, 332, 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 Zn_4O 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 $Cu_6(btt)_6$ or $Cu_4(btt)_4$ (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 $C_6H_5S_2Cu_2$. 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)

Figure 2. Structure of the copper(I) phenylthiolate aggregate (ORTEP drawn with 20% thermal ellipsoids) (selected bond distances are Cu1-S1 = 2.66 Å, Cu1-S3 = 2.67 Å, Cu1-S4 = 2.73 Å, Cu2-S1 = 2.80 Å, Cu2-S2 = 2.63 Å, Cu2-S3 = 2.69 Å, Cu3-S2 = 2.80 Å, Cu3-S3 = 2.70 Å, Cu3-S4 = 2.70 Å, Cu4-S1 = 2.71 Å, Cu4-S2 = 2.68 Å, and Cu4-S4 = 2.68 Å).



Copper(I) arylthiolates have special interests as *p*-type charge carriers. Generally, such compounds form infinite chains, but some of such complexes possess μ^3 -bridging arylthiolate ligands (Che, Li, Chui, Roy, & Low, 2008). In fact, the structure of aggregate **II** has μ^3 -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 $\{\text{Cu}^{\text{I}}_4(\text{SR})_6\}^{2-}$; however, we observe that aggregate **II** is non-ionic and it is easily soluble in chloroform. It has a molar conductance of $12.4 \text{ cm}^2 \text{ mol}^{-1}$ in methanol, which suggests it to be neutral. The copper-sulfur bond lengths are relatively larger than the distances generally observed in copper(I) clusters ($\sim 2.2\text{--}2.3 \text{ \AA}$). Relatively large Cu-S bond distances in aggregate **II** show it to be more like a self-assembly of copper(I) phenylthiolates. This is further proved from the fact that the mass of the radical cation of the dimeric assembly is seen in the ESI mass spectra of the aggregate **II**.

A methanol solution of copper(I) aggregate shows an absorption at 298 nm due to $\pi\text{--}\pi^*$ 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'-dithiobis(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'-dithiobis-(benzothiazole) by copper(I) chloride has led to a tetranuclear copper(I) phenylthiolate aggregate, in which each sulfur atom is involved in μ^3 -bridging mode. Besides their interesting structural features, these aggregates show photoluminescence properties.

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References

- Bertoncello, R., Bettinelli, M., Casarin, M., Gulino, A., Tondello, E., & Vittadini, A. (1992). Hexakis(acetato)oxotetrazinc, a well-tailored molecular model of zinc oxide. An experimental and theoretical investigation of the electronic structure of $\text{Zn}_4\text{O}(\text{acetate})_6$ and ZnO by means of UV and x-ray photoelectron spectroscopies and first principle local density molecular cluster calculations. *Inorganic Chemistry*, 31, 1558–1565.
<http://dx.doi.org/10.1021/ic00035a008>
- Che, C.-M., Li, C.-H., Chui, S. S.-Y., Roy, V. A. L., & Low, K.-H. (2008). Homoleptic copper(I) arylthiolates as a new class of *p*-type charge carriers: Structures and charge mobility studies. *Chemistry - A European Journal*, 14, 2965–2975.
[http://dx.doi.org/10.1002/\(ISSN\)1521-3765](http://dx.doi.org/10.1002/(ISSN)1521-3765)
- Chen, H.-H., Yang, J., Liu, Y.-Y., & Ma, J.-F. (2013). A series of tetranuclear-cluster-containing complexes based on pendent-arm macrocyclic ligand and different carboxylates: Syntheses, structures, photoluminescence, and magnetic properties. *CrystEngComm*, 15, 5168–5178.
<http://dx.doi.org/10.1039/c3ce40239h>
- Chun, H., & Jung, H. (2009). Targeted Synthesis of a Prototype MOF Based on $\text{Zn}_4(\text{O})(\text{O}_2\text{C})_6$ units and a nonlinear dicarboxylate ligand. *Inorganic Chemistry*, 48, 417–419.
<http://dx.doi.org/10.1021/ic801906e>
- Crumbless, A. L., Gestaut, L. J., Rickard, R. C., & McPhail, A. T. (1974). Preparation and X-ray crystal structure of a novel tetranuclear copper(I) ethylenethiourea cluster complex, μ_4 -ethylenethiourea-cyclo-tetrakis- μ -(ethylenethiourea) tetrakis[ethylenethiourea-copper(I)] nitrate hexahydrate. *Journal of the Chemical Society, Chemical Communications*, 14, 545–546.
<http://dx.doi.org/10.1039/c39740000545>
- Dance, I. G., Bowmaker, G. A., Clark, G. R., & Seadon, J. K. (1983). The formation and crystal and molecular structures of hexa(μ -organothiolato)tetracuprate(I) cage dianions: Bis-(tetramethylammonium)hexa-(μ -methanethiolato)tetracuprate(I) and two polymorphs of bis(tetramethylammonium)hexa-(μ -benzenethiolato)-tetracuprate(I). *Polyhedron*, 2, 1031–1043.
[http://dx.doi.org/10.1016/S0277-5387\(00\)81450-3](http://dx.doi.org/10.1016/S0277-5387(00)81450-3)
- Dey, S., Efimov, A., Giri, C., Rissanen, K., & Lemmetyinen, H. (2011). Electronic structure manipulation of (benzothiazole) zinc complexes: Synthesis, optical and electrochemical studies of 5-substituted derivatives. *European Journal of Organic Chemistry*, 2011, 6226–6232.
<http://dx.doi.org/10.1002/ejoc.201100186>
- Iwasaki, T., Agura, K., Maegawa, Y., Hayashi, Y., Ohshima, T., Iwasaki, T., & Mashima, K. (2006). Direct conversion of esters, lactones, and carboxylic acids to oxazolines catalyzed by a tetranuclear zinc cluster. *Chemical Communications*, 37, 2711–2713.
- Iwasaki, T., Maegawa, Y., Hayashi, Y., Ohshima, T., & Mashima, K. (2008). Transesterification of various methyl esters under mild conditions catalyzed by tetranuclear zinc cluster. *The Journal of Organic Chemistry*, 73, 5147–5150.
<http://dx.doi.org/10.1021/jo800625v>

- Lawton, S. L., Rohrbaugh, W. J., & Kokotailo, G. T. (1972). Crystal and molecular structure of the tetranuclear metal cluster complex copper(I) O,O'-diisopropylphosphorodithioate, Cu₄[(iso-PrO)2PS2]4. *Inorganic Chemistry*, 11, 612–618.
<http://dx.doi.org/10.1021/ic50109a039>
- Li, Z., Dellali, A., Malik, J., Motevalli, M., Nix, R. M., Olukoya, T., ... Wyatt, P. B. (2013). Luminescent zinc(II) complexes of fluorinated benzothiazol-2-yl substituted phenoxide and enolate ligands. *Inorganic Chemistry*, 52, 1379–1387.
<http://dx.doi.org/10.1021/ic302063u>
- Maegawa, Y., Ohshima, T., Hayashi, Y., Agura, K., & Iwasaki, T. (2011). Additive effect of N-heteroaromatics on transesterification catalyzed by tetranuclear zinc cluster. *ACS Catalysis*, 1, 1178–1182.
<http://dx.doi.org/10.1021/cs200224b>
- Ohshima, T., Iwasaki, T., Maegawa, Y., Yoshiyama, A., & Mashima, K. (2008). Enzyme-like chemoselective acylation of alcohols in the presence of amines catalyzed by a tetranuclear zinc cluster. *Journal of the American Chemical Society*, 130, 2944–2945.
<http://dx.doi.org/10.1021/ja711349r>
- Ötvös, S. B., Berkesi, O., Körtvélyesi, T., & Pálinkó, I. (2010). Synthesis and spectroscopic and computational characterization of Zn₄O(alcyclic or aromatic carboxylate)₆ complexes as potential MOF precursors. *Inorganic Chemistry*, 49, 4620–4625.
<http://dx.doi.org/10.1021/ic100205n>
- Redshaw, C., Jana, S., Shang, C., Elsegood, M. R. J., & Lu X. (2010). Multinuclear zinc pentafluorobenzene carboxylates: Synthesis, characterization, and hydrogen storage capability. *Organometallics*, 29, 6129–6132.
<http://dx.doi.org/10.1021/om100703c>
- Schuerman, J. A., Fronczek, F. R., & Selbin, J. (1988). Crystal and molecular structures of tetranuclear metal clusters of copper(I) trithioperoxybenzoates. *Inorganica Chimica Acta*, 148, 177–183.
[http://dx.doi.org/10.1016/S0020-1693\(00\)87498-8](http://dx.doi.org/10.1016/S0020-1693(00)87498-8)
- Wang, R., Deng, L., Fu, M., Cheng, J., & Li, J. (2012). Novel ZnII complexes of 2-(2-hydroxyphenyl)benzothiazoles ligands: Electroluminescence and application as host materials for phosphorescent organic light-emitting diodes. *Journal of Materials Chemistry*, 22, 23454–23460.
<http://dx.doi.org/10.1039/c2jm34599d>
- Wei, W., Wu, M., Gao, Q., Zhang, Q., Huang, Y., Jiang, F., & Hong, M. (2009). A novel supramolecular tetrahedron assembled from tetranuclear copper(I) cluster molecules via aryl embrace interactions. *Inorganic Chemistry*, 48, 420–422.
<http://dx.doi.org/10.1021/ic801972e>
- Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M., & Kim, J. (2003). Reticular synthesis and the design of new materials. *Nature*, 423, 705–714.
<http://dx.doi.org/10.1038/nature01650>
- Yue, C., Yan, C., Feng, R., Wu, M., Chen, L., Jiang, F., & Hong, M. (2009). A polynuclear d¹⁰-d¹⁰ metal complex with unusual near-infrared luminescence and high thermal stability. *Inorganic Chemistry*, 48, 2873–2879.
<http://dx.doi.org/10.1021/ic801840g>



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