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Synthesis, Crystal Structure, and Some Spectrochemical Properties of S-Bridged Hexanuclear Zinc(II) Complex with 2-Aminoethanethiolate: Formation of Zn_3S_3- and Zn_4S_4-Cyclic Cores

Yasunori Yamada,* Yoshitaro Miyashita,
Kiyoshi Fujisawa, and Ken-ichi Okamoto*

Department of Chemistry, University of Tsukuba,
Tsukuba, Ibaraki 305-8571

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The reaction of $[Zn(aet)_2]$ (aet = 2-aminoethanethiolate) with $Zn(ClO_4)_2·6H_2O$ in aqueous acetonitrile gave an S-bridged hexanuclear complex, $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2]^{4+}$, accompanied by the ligand-transfer of aet from $[Zn(aet)_2]$ units to Zn^{2+} ions. In the hexanuclear complex, all of the Zn and S atoms are included in the Zn_3S_3- and/or Zn_4S_4-cyclic structures.

The mononuclear complexes ligated by 2-aminoethanethiolate (aet) are available as metalloligands for constructions of the S-bridged polynuclear structures.[1–10] The structures of these polynuclear complexes significantly depend on coordination modes of the metal ions which participate in the reactions.[3–10] For instance, a reaction of the octahedral $[Co(aet)_3]$ with Co^{3+} ion gave a linear-type trinuclear complex, $[Co\{Co(aet)_3\}_2]^{3+}$.[4] Similarly, the square-planar $[Ni(aet)_2]$ reacted with Ni^{2+} ion to form a linear-type trinuclear complex, $[Ni\{Ni(aet)_2\}_2]^{2+}$.[1–3] On the other hand, a reaction between the square-planar $[Pd(aet)_2]$ and Pd^{2+} ion produced a pin-wheel type hexanuclear complex, $[Pd_2\{Pd(aet)_2\}_4]^{4+}$.[5] Although the reactions of the octahedral $[M(aet)_3]$- ($M = Co^{III}, Rh^{III}, Ir^{III}, Cr^{III}$) or square-planar $[M'(aet)_2]$-type ($M' = Ni^{II}, Pd^{II}$) mononuclear complexes with various metal ions were investigated in detail,[1–10] little has been known about the reactions of the tetrahedral $[M''(aet)_2]$-type ($M'' = Zn^{II}, Cd^{II}$) mononuclear complexes with tetrahedral metal ions and/or polynuclear complexes including tetrahedral $[M''(aet)_2]$ units. In the present paper, we will describe the structure and some spectrochemical properties of hexanuclear zinc(II) complex derived from the reaction of $[Zn(aet)_2]$ with $Zn(ClO_4)_2·6H_2O$.

An X-ray structural analysis revealed the presence of a discrete tetravalent complex cation, four perchlorate anions, and two acetonitrile molecule. In the complex cation, two Zn^{2+} ions are coordinated by two aet ligands to form tetrahedral $[Zn(aet)_2]$ units (Fig. 1). Each of the remaining four Zn^{2+} ions is chelated by one aet ligand and bridged by two S atoms, forming tetrahedral $[Zn(aet)(\mu\text{-}S)_2]$ units. The formation of $[Zn(aet)(\mu\text{-}S)_2]$ units are caused by the ligand-transfer of aet from $[Zn(aet)_2]$ units to Zn^{2+} ions in the reaction of $[Zn(aet)_2]$ with Zn^{2+} ion. The structural feature of the hexanuclear zinc(II) complex $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2](ClO_4)_4·2CH_3CN$ has been contrasted with that of the hexanuclear palladium(II) complex $[Pd_2\{Pd(aet)_2\}_4]^{4+}$ with the same total number of metal ions and aet ligands.[5] Although all of the Zn^{2+} ions in the $[Zn(aet)_2]$ and $[Zn(aet)(\mu\text{-}S)_2]$ units take tetrahedral geometries, the S–Zn–N bite angles (av 90.4(2)°) and Zn–S–Zn bridging angles (av 109.43(8)°) are almost identical with the corresponding angles in the S-bridged polynuclear complexes with square-planar $[M(aet)_2]$ or octahedral $[M'(aet)_3]$ units.[5–10] It is noteworthy that a six-membered ring is formed by the Zn1, Zn2, Zn3, S1, S2, and S4 atoms, and an eight-membered one is formed by the Zn2, Zn2*, Zn3, Zn3*, S3, S3*, S4, and S4* atoms. In addition, the former six-membered ring takes a boat-like conformation, while the latter eight-membered ring takes a chair-like conformation. The eight aet ligands seem to occupy reasonable spaces to minimize the steric repulsion, depending on these rings. Therefore, the formation of such Zn_3S_3- and Zn_4S_4-cyclic cores may contribute to stabilization of the present hexanuclear complex.

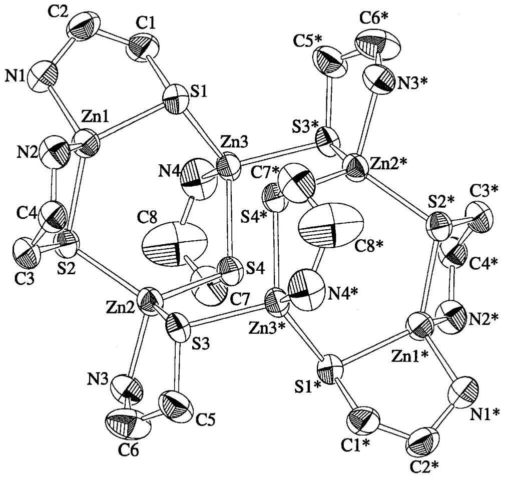

Fig. 1. Perspective view of $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2]^{4+}$ with the atomic labeling scheme (ellipsoids at 50% probability).

The diffuse reflection spectrum of $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2]^{4+}$ exhibits two characteristic bands at 30.9 and 44.9 × 10^3 cm^{-1}. Taking into account the facts that the aet ligand has no corresponding bands around these band regions, and that the Zn^{2+} ion takes a d^{10} electron configuration, the 30.9 and 44.9 × 10^3 cm^{-1} bands in the crystalline state are considered to be due to the metal-to-ligand CT transitions. These bands are located at a higher-energy side than the corresponding bands of $[Zn(aet)_2]$,[11] indicating that the electronic state of Zn(II) in the hexanuclear complex is considerably different from that in the mononuclear $[Zn(aet)_2]$.

In a 1:1 mixed solvent of CH_3CN and H_2O, the two characteristic bands of $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2]^{4+}$ in the solid state are considerably shifted toward the higher-energy side and appear at 37.2 and 45.4×10^3 cm^{-1}. This suggests the possibility for a difference between the structure in crystalline state and that in solution. Assuming that the complex retains its structure in solution, two kinds of Zn(II) units, $[Zn(aet)_2]$ and $[Zn(aet)(\mu\text{-}S)_2]$, are present in the complex, and at least four signals for sixteen carbon atoms are expected to be observed in the ^{13}C NMR spectrum of the complex. However, the spectrum in a 1:1 mixed solvent of CD_3CN and D_2O exhibits only two signals at δ 29.31 ($-CH_2S$) and 44.10 ($-CH_2N$). It is known that the ^{13}C NMR spectra of the other S-bridged polynuclear complexes ligated by 2-aminoethanethiolate show signals due to $-CH_2S$ groups around δ 30 and those due to $-CH_2N$ groups around δ 50.[5,6,8,10] On the other hand, 2-aminoethanethiol hydrochloride (Haet•HCl) has two signals at δ 24.14 ($-CH_2S$) and 44.63 ($-CH_2N$) in D_2O. Taking these facts into consideration, we conclude that the Zn–S bonds are present in solution. This is supported by the observation of the MLCT bands in the absorption spectrum in solution. However, the Zn–N bonds may be cleaved to form free $-NH_2$ groups in solution, as suggested from the signal due to $-CH_2N$ groups. It can be concluded, therefore, that the different species from $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2]^{4+}$ complex cation are formed in solution.

Experimental

Preparation. To a solution containing 0.37 g (1.0 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 50 cm^3 of acetonitrile was added 0.42 g (2.0 mmol) of $[Zn(aet)_2]$, which was prepared by a similar procedure to the synthesis of $[Ni(aet)_2]$.[1,11] After the mixture was stirred at room temperature for 1 h, 50 cm^3 of water was added to the reaction mixture. The obtained colorless solution was allowed to stand at room temperature for several days. The resulting colorless crystals of $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2](ClO_4)_4 \cdot 2CH_3CN$ (0.61 g, 82%) were collected by filtration. A well-formed crystal was used for the X-ray structural analysis. Calcd for $[\{Zn(aet)\}_4\{Zn(aet)_2\}_2](ClO_4)_4 \cdot 2CH_3CN = C_{20}H_{54}N_{10}O_{16}S_8Cl_4Zn_6$: C, 16.22; H, 3.67; N, 9.46%. Found: C, 16.21; H, 3.69; N, 9.42%. UV-vis spectrum in a 1:1 mixed solvent of CH_3CN and H_2O [ν_{max}, 10^3 cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})]: 37.2 (3.33), 45.4 (4.42). Diffuse reflection spectrum in the crystalline state [ν_{max}, 10^3 cm^{-1}]: 30.9, 44.9. ^{13}C NMR (500 MHz, a 1:1 mixed solvent of CD_3CN and D_2O) δ 29.31 ($-CH_2S$), 44.10 ($-CH_2N$).

Measurement. The electronic absorption and diffuse reflection spectra were recorded with JASCO Ubest V-560 and V-570 spectrophotometers, respectively. All of the measurements were carried out at room temperature. The ^{13}C NMR spectrum was recorded with a Bruker AM-500 NMR spectrometer in a 1:1 mixed solvent of CD_3CN and D_2O. The tetramethylsilane (TMS) was used as an internal reference. The elemental analysis (C, H, N) was performed by the Analysis Center of the University of Tsukuba.

Crystallography. Intensity data were collected on the Rigaku RASA-7S four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The structure was solved by the direct method using SIR92 and refined by the full-matrix least-squares method using a teXsan program package.[12] All calculations were performed on an Indigo II computer. Crystal data for $([\{Zn(aet)\}_4\{Zn(aet)_2\}_2](ClO_4)_4 \cdot 2CH_3CN)_{0.5}$: $C_{10}H_{27}N_5O_8S_4Cl_2Zn_3$, fw = 740.64, monoclinic, space group $P2_1/n$ (#14), $a = 16.273(5)$, $b = 11.324(3)$, $c = 14.541(3)$ Å, $\beta = 98.40(2)°$, $V = 2650(1)$ $Å^3$, $Z = 4$, $D_{calc} = 1.856$ g cm^{-3}, $\mu = 3.253$ mm^{-1}, crystal size $0.10 \times 0.30 \times 0.40$ mm, trans. factors 0.42–1.00, 6675 reflections measured ($2\upsilon_{max} = 55.0°$), 3599 observed reflections [$I > 2.00\sigma(I)$] used in the refinement, $R = 0.055$, $R_w = 0.063$ and GOF = 1.41 for 289 parameters. The final atomic positional parameters are deposited in Tables S1–S3.[13] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 150986.

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11 Anal. Calcd for $[Zn(aet)_2] = C_4H_{12}N_2S_2Zn$: C, 22.07; H, 5.56; N, 12.87%. Found: C, 22.08; H, 5.60; N, 12.61%. Diffuse reflection spectrum in the crystalline state [ν_{max}, 10^3 cm^{-1}]: 26.1, 41.1.

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13 Lists of final atomic coordinates and equivalent isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles are deposited as Document No. 74003 at the Office of the Editor of *Bull. Chem. Soc. Jpn.*