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Zn(II) Complexes with Aliphatic Thiolates. $(Et_4N)[Zn(SAd)_3]$ and $(Et_4N)_2[\{Zn(ScHex)_2\}_2(\mu\text{-}ScHex)_2]$

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New homoleptic aliphatic thiolato complexes with Zn(II), $(Et_4N)[Zn(SAd)_3]$ (**1**) (HSAd = 1-adamantanethiol), and $(Et_4N)_2[\{Zn(ScHex)_2\}_2(\mu\text{-}ScHex)_2]$ (**2**) (HScHex = 1-cyclohexanethiol), have a novel three-coordinate geometry for monomeric **1** and a tetrahedral geometry for dimeric **2**, respectively. The complexes have been fully characterized by far-IR, Raman, and UV–vis absorption spectroscopy.

Zinc is an essential metal, which performs vitally important roles in biological systems.[1,2] In these enzymes, the Zn–S bonds are prevalent, and thus the structures and properties of thiolato complexes with Zn(II) have been investigated as model compounds.[1,2] In recent years, we have been preparing thiolato complexes with Zn(II), Cd(II), and Hg(II) from the viewpoint of not only the model complexes, but also systematic research.[3] We report herein on the full characterization of two Zn(II) complexes with homoleptic aliphatic thiolate ions, $(Et_4N)[Zn(SAd)_3]$ (**1**) and $(Et_4N)_2[\{Zn(ScHex)_2\}_2(\mu\text{-}ScHex)_2]$ (**2**), to provide fundamental information about their physicochemical properties and their coordination geometries.

Both complexes were synthesized by the reaction of $ZnCl_2$ (1 equiv) with the corresponding thiolate ligands (3 equiv) and Et_4NCl (1 equiv). After removing undissolved $[\{Zn(\mu\text{-}SAd)_2\}_n]$,[4] **1** was extracted with hot acetonitrile. Complex **2** was also extracted with hot acetonitrile after the same procedure. Both complexes were stable in the air.

The crystal structure of **1**, isolated as an acetonitrile solvate, established the monomeric, three-coordinate geometry of the anion in $(Et_4N)[Zn(SAd)_3]$, as shown in Fig. 1a. The sum of the three S–Zn–S angles equals 360.0°, and is indicative of a trigonal planar ZnS_3 coordination geometry. No significant distortions from the ideal D_{3h} symmetry are evident, and the Zn(II) ion lies only 0.032(1) Å above the S1–S3 least-squares plane. To our knowledge, this is the first authenticated (by crystallography) three-coordinate Zn(II) complex containing aliphatic thiolate ligands. Three such examples have been reported with ortho-disubstituted aromatic thiolates, i.e. in the mononuclear complex $[(n\text{-}Pr)_4N][Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H_3)]$[5a] and in the dinuclear complexes $[Zn(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2]_2$[5b] and $[Zn(S\text{-}2,6\text{-}(Me_3Si)_2C_6H_3)_2]_2$.[5c] The three-coordinate geometries defined by homoleptic thiolate ligands are extremely rare for Zn(II),[6,7] but are more commonly observed for other d^{10} metals: Cd(II),[8] Hg(II),[8,9] Cu(I),[10] and Ag(I).[10a,11] The trigonal planar structure in **1** is stabilized by sterically demanding ligands that preclude supramolecular association.[12]

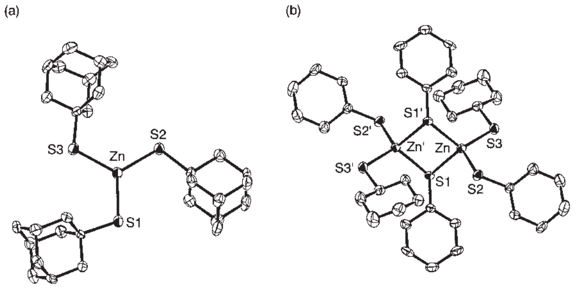

Fig. 1. Molecular structure of the anions of **1** (a) and **2** (b) (ORTEP, 50% probability ellipsoids) with atomic numbering. Selected bond distances (Å) and angles (deg) are as follows: Zn–S1, 2.264(3); Zn–S2, 2.259(2); Zn–S3, 2.263(4); S1–Zn–S2, 120.9(1); S1–Zn–S3, 118.4(1); S2–Zn–S3, 120.7(1). (b) Zn–S1, 2.429(1); Zn–S2, 2.320(1); Zn–S3, 2.306(1); Zn–S1′, 2.458(1); Zn···Zn′, 3.3120(8); S1···S1′, 3.594(2); S1–Zn–S2, 104.84(5); S1–Zn–S3, 119.33(5); S2–Zn–S3, 114.31(5); S1–Zn–S1′, 94.68(5); S2–Zn–S1′, 107.32(5); S3–Zn–S1′, 114.13(5); Zn–S1–Zn′, 85.32(4). The primed atoms are related by the symmetry operation $1-x, -y, -z$.

With a less sterically hindered thiolate, $^{-}$ScHex, a dimeric complex, $(Et_4N)_2[\{Zn(ScHex)_2\}_2(\mu\text{-}ScHex)_2]$ (**2**), containing two ZnS_2 units connected by two bridging thiolate ligands, was obtained, as shown in Fig. 1b. The Zn(II) sites have a distorted tetrahedral geometry in which the averaged S–Zn–S angle is 109.1°. The dimeric anion has an exactly planar Zn_2S_2 ring, dictated by crystallographic C_i symmetry; the substituents are therefore in an anti configuration. Compared with the reported structural parameters of $[\{Zn(SR)_2\}_2(\mu\text{-}SR)_2]^{2-}$ (R = Et and Ph),[13] the $M\text{–}S_{bridging}$, $M\text{–}S_{terminal}$, and $M\cdots M'$ distances of **2** are normal. A dimeric structural motif has often been obtained for other d^{10} metal complexes, when smaller thiolate ligands, e.g. ethanethiolate and benzenethiolate, are present (Cd(II),[13b,13c,14] Hg(II),[9d,15] and Cu(I)[16]). Very recently, O'Halloran and co-workers reported new type of metalloregulatory proteins of Zn(II) (ZntA and ZntR).[17] In these enzymes, Zn(II) ions have a monomeric structure as $[Zn(Cys)_2(Asp)(X)]$ (X: unknown amino acid) for ZntA[17b,17c] and a dimeric structure as $[(Cys)_2Zn(\mu\text{-}Cys)(\mu\text{-}PO_4)Zn(Cys)_2(His)]$ for ZntR,[17a] i.e. containing aliphatic thiolate ligands. Therefore, our complexes will provide a good structural model for this class of enzymes.

The UV–vis absorption spectra in the 500–210 nm region showed only one absorption band at 217 nm (**1**) and at 215 nm (**2**). These bands were assigned to the sulfur to the Zn(II) CT band, because neither the Zn(II) ion nor the thiolate ligand has absorption bands in this region. The UV–vis absorption spectra of $[\{M(SPh)_2\}_2(\mu\text{-}SPh)_2]^{2-}$ (M = Zn and Cd),[13b] having the same dinuclear structure as found for **2**, revealed that their CT bands were masked by strong $\pi\text{–}\pi^*$ transitions of the aromatic groups. Thus, the *exact* CT band of the Zn–S

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bonds involving aliphatic thiolate ligands can be assigned unambiguously. The UV–vis absorption spectra of the Cd(II) analogue, as $(Et_4N)_2[\{Cd(ScHex)_2\}_2(\mu\text{-}ScHex)_2]$,[14a] showed only one CT band at 247 nm, which is red-shifted from that of **2**, as expected from Spiro's[18] and our[3,4] results. Spiro et al. reported that an absorption band at 247 nm was assigned to the same CT band in Cd(II)-bound CP1.[18]

The far-IR and Raman spectra of both complexes were measured in the 600–100 cm^{-1} region. The Zn(II) site is close to an ideal trigonal planar having with D_{3h} symmetry. For this point group symmetry, the four normal modes of vibration of a planar ZnS_3 molecule are $A_1{}'$ (Raman active), E' (IR and Raman active), E' (IR and Raman active), and $A_2{}''$ (IR active).[19] The bands at 381 (far-IR) and 383 cm^{-1} (Raman) were assigned to Zn–S stretching vibrations as E' (IR and Raman active), owing to their strong intensity. These assignments were confirmed by the reported frequencies of the same trigonal plane geometry with Cu(I),[10a,10c] Ag(I),[10a] and Hg(II).[9d,15] The stretching vibration of $A_1{}'$ (Raman active) was expected to be at 372 cm^{-1} (Raman) for the same reason as the assignment of E'. In **2**, two types of Zn–S bonds, terminal and bridging, are present and the anion has C_i symmetry. The bands at 357 (far-IR) and 355 cm^{-1} (Raman) were assigned to $\nu(\text{Zn–S})_{\text{terminal}}$. Moreover, the bands at 235 (far-IR) and 232 cm^{-1} (Raman) were also assigned to $\nu(\text{Zn–S})_{\text{bridging}}$. These frequencies are in the range reported previously for the M–S stretching frequencies of related complexes.[9a,9d,15] The terminal Zn–S bonds are significantly shorter than the bridging bonds in **2**, and therefore the terminal ν(Zn–S) modes are expected at higher wavenumbers than the bridging modes. Moreover, the force constants of the bridging bonds are about half those of the terminal bonds; thus, the stretching vibration bands of the bridging bonds were observed in lower region.[19]

In this paper, we report on two structural types of new homoleptic aliphatic thiolato complexes with Zn(II). Further studies are in progress designed to gain greater insight into the relevance between the coordination geometry and the physicochemical/spectroscopic properties.

Experimental

General. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Acetonitrile and diethyl ether were carefully purified by refluxing/distilling under an argon atmosphere over P_2O_5 and sodium/benzophenone ketyl, respectively.[20] Ethanol and propionitrile were commercially spectroscopic grade and stored in an argon atmosphere after bubbling argon gas prior to use. Other reagents were commercially available and used without further purification. NaSAd was prepared with a modified method described in the literatures.[21] NaScHex was prepared by the corresponding thiol and 0.8 equiv NaH in diethyl ether. IR (4000–400 cm^{-1}) and far-IR (600–100 cm^{-1}) spectra were recorded on KBr pellets and CsI pellets using a JASCO FT/IR-550 spectrometer, respectively. FT-Raman (600–100 cm^{-1}) spectra were recorded using a Perkin Elmer Spectrum GX spectrophotometer. ^{1}H NMR spectra were measured on a JEOL-EX-270 (270 MHz) or a Brucker AM-500 NMR (500 MHz) spectrometer. UV–vis absorption (500–210 nm) spectra at room temperature were recorded on a quartz cell (1 cm path length) using a JASCO V-570 spectrophotometer. Elemental analyses (C, H, N) were performed by the Chemical Analysis Center of the University of Tsukuba.

Preparations. $\mathbf{(Et_4N)[Zn(SAd)_3]}$ **(1):** A solution of $ZnCl_2$ (0.044 g, 0.32 mmol) in acetonitrile (15 cm^3) was slowly added with stirring to a solution of NaSAd (0.183 g, 0.96 mmol) and Et_4NCl (0.053 g, 0.32 mmol) in ethanol (3 cm^3) and acetonitrile (15 cm^3). After stirring overnight, insoluble material was filtered off. The obtained solution was concentrated to dryness. The residue was extracted with hot acetonitrile. Colorless crystals were obtained by keeping the extract solution at −30 °C (0.109 g, 49% yield) after adding a small amount of propionitrile. Found: C, 65.06; H, 9.25; N, 2.10%. Calcd for $C_{38}H_{65}S_3NZn$: C, 65.44; H, 9.39; N, 2.01%. IR ν/cm^{-1} (KBr): 2976w, 2898vs, 2843s, 1480w, 1448m, 1341m, 1294m, 1172w, 1040m, 685w. far-IR ν/cm^{-1} (CsI): 480m, 397s, 381s, 363m, 313vs, 218w, 186m. FT-Raman ν/cm^{-1}: 478m, 449s, 420w, 403w, 383m, 372m, 317w, 285w, 264m, 250vs, 206w, 188w. ^{1}H NMR (270 MHz, CD_3CN): δ 1.42 (t, $J = 7$ Hz, 12H, CH_2CH_3), 1.59 (br, 9H, $C_{10}H_{15}$), 1.66 (br, 9H, $C_{10}H_{15}$), 1.93 (br, 9H, $C_{10}H_{15}$), 2.01 (br, 9H, $C_{10}H_{15}$), 2.04 (br, 9H, $C_{10}H_{15}$), 3.47 (q, 8H, $J = 7$ Hz, CH_2CH_3). UV–vis λ/nm (CH_3CN): 217.

$\mathbf{(Et_4N)_2[\{Zn(ScHex)_2\}_2(\mu\text{-}ScHex)_2]}$ **(2):** A solution of $ZnCl_2$ (0.131 g, 0.96 mmol) in acetonitrile (15 cm^3) was slowly added with stirring to a solution of NaScHex (0.412 g, 2.98 mmol) and Et_4NCl (0.172 g, 1.04 mmol) in ethanol (5 cm^3) and acetonitrile (10 cm^3). After stirring overnight, insoluble material was filtered off. The obtained solution was concentrated to dryness. The residue was extracted with hot acetonitrile. To the extract was added diethyl ether (10 cm^3), then colorless crystals were obtained by keeping the solution at −30 °C (0.430 g, 21% yield). Found: C, 57.38; H, 9.65; N, 2.81%. Calcd for $C_{52}H_{106}S_6N_2Zn_2$: C, 57.70; H, 9.87; N, 2.59%. IR ν/cm^{-1} (KBr): 2977m, 2912vs, 2846s, 1484s, 1443s, 1171m, 997m, 782m. far-IR ν/cm^{-1} (CsI): 515w, 438w, 364s, 357vs, 338m, 321m, 307m, 292m, 235m, 219m, 195m, 176m. FT-Raman ν/cm^{-1}: 511m, 440s, 417vs, 355vs, 336m, 320m, 303w, 288m, 280w, 232s, 197vs. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (t, $J = 7$ Hz, 24H, CH_2CH_3), 1.17 (br, 24H, C_6H_{11}), 1.53 (br, 24H, C_6H_{11}), 1.70 (br, 12H, C_6H_{11}), 2.00 (br, 6H, C_6H_{11}), 3.32 (q, 16H, $J = 7$ Hz, CH_2CH_3). UV–vis λ/nm (CH_3CN): 215.

X-ray Crystallography. Crystallographic data for $\mathbf{1}\cdot(CH_3CN)\cdot0.5(CH_3CH_2CN)$: $C_{41.5}H_{70.5}N_{2.5}S_3Zn$, fw = 766.09, colorless, block, $0.45 \times 0.20 \times 0.20$ mm^3, Trigonal, R-3 (#148), $a = 26.145(7)$ Å, $c = 33.43(1)$ Å, $V = 19793(9)$ Å^3, $Z = 18$, Temp = −65 °C, $D_{\text{calc}} = 1.157$ g/cm^3, $R(\text{int}) = 0.025$, $\mu(\text{Mo K}\alpha) = 7.30$ cm^{-1}, No. of unique reflections = 10119, No. of observed reflections = 6314 ($I > 2\sigma(I)$), $R = 0.078$, $Rw = 0.086$. **2**: $C_{52}H_{106}N_2S_6Zn_2$, fw = 1082.54, colorless, block, $0.20 \times 0.20 \times 0.17$ mm^3, Monoclinic, $P2_1/a$ (#14), $a = 17.29(1)$ Å, $b = 13.905(4)$ Å, $c = 12.315(3)$ Å, $\beta = 101.12(3)°$, $V = 2906(2)$ Å^3, $Z = 2$, Temp = −54 °C, $D_{\text{calc}} = 1.237$ g/cm^3, $R(\text{int}) = 0.027$, $\mu(\text{Mo K}\alpha) = 10.75$ cm^{-1}, No. of unique reflections = 5122, No. of observed reflections = 3132 ($I > 2\sigma(I)$), $R = 0.046$, $Rw = 0.029$. The diffraction data were measured on a Rigaku AFC 7S automated four-circle diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation (50 kV, 30 mA). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the calculated positions and refined isotropically. In **1**, the highly disordered solvent molecules were refined isotropically. All calculations were performed using the CrystalStructure. Deposition numbers CCDC-240111 (**1**) and 240112 (**2**). Copies of the data can be obtained free of charge via http://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; e-mail: deposit @ccdc.cam.ac.uk).

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