Synthesis and Structural Characterization of Thiolato-Bridged Zinc(II) Complexes with NNS-Tridentate Thiolic Ligands

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Zinc(II) complexes with 2-[(2-aminoethyl)amino]ethanethiol (HL^1), 2-[(3-aminopropyl)amino]ethanethiol (HL^2), 2-[(2-pyridylmethyl)amino]ethanethiol (HL^3), and 2-{[2-(2-pyridyl)ethyl]amino}ethanethiol (HL^4), $[Zn(L^1)](ClO_4)$ (**1**), $[Zn\{Zn(L^1)_2\}_2](ClO_4)_2$ (**2**), $[Zn(L^2)](ClO_4)$ (**3**), $[Zn\{Zn(L^3)_2\}_2](ClO_4)_2$ (**4**), and $[Zn_3(L^4)_3](ClO_4)_3$ (**5**), have been synthesized and characterized by measurements of the infrared and electronic spectra. The molecular structures of these complexes were determined by the single-crystal X-ray structure analysis. Complex **1** has a thiolato-bridged polymeric chain structure, in which each metal atom is essentially four-coordinated in a distorted tetrahedron. Complexes **2** and **4** have a thiolato-bridged trinuclear complex with a linear arrangement of three metal atoms. Complex **5** is a thiolato-bridged trinuclear complex displaying a six-membered ring of Zn_3S_3.

There has been considerable interest in coordination chemistry of thiolato-bridged metal complexes over the past decades because of their rich chemistry.[1—4] Of these metal thiolates, the chemistry of the closed-shell d^{10} elements of group 12 such as zinc(II) is unique, showing a characteristic manner by their tendency to form polynuclear aggregates of tetrahedral building blocks.[1] The interst in this class of compounds has been stimulated not only by their chemistry but also by the potential utilities as model compounds of metalloproteins which show the significant involvement of the metal–cysteine bondings in various biological systems. For example, metallothionein is a zinc- and cadmium-containing protein which has been implicated in a variety of biological functions.[5] However, only a few zinc thiolate complexes have been previously synthesized and structurally characterized.[6—17] Most of these contain aromatic thiolates instead of aliphatic thiols. As part of our continuing interest in the fundamental chemistry of metal thiolates,[18—27] we reported on the synthesis and characterization of thiolato-bridged manganese(II), iron(II), nickel(II), palladium(II), and some heterometal complexes with thiolic ligands having S and N donor atoms. These complexes include dinuclear,[18—23,25] trinuclear,[24,25,27] tetranuclear,[26] and polynuclear[24] species. In this study, we have extended our efforts to zinc chemistry in order to obtain new zinc(II) complexes with such aliphatic thiolic ligands. The thiolic ligands utilized in this study are 2-[(2-aminoethyl)amino]ethanethiol (HL^1), 2-[(3-aminopropyl)amino]ethanethiol (HL^2), 2-[2-pyridylmethyl)amino]ethanethiol (HL^3), and 2-{[2-(2-pyridyl)ethyl]amino}ethanethiol (HL^4) (Chart 1). Herein we report our findings on X-ray crystal structures of zinc(II) complexes with these ligands.

Experimental

Synthesis of the Complexes. The thiolic ligands —HL^1, HL^2, HL^3, and HL^4— were synthesized using a procedure described in the literature.[19] All reactions were performed under an atmosphere of argon using standard Schlenk techniques.

$[Zn(L^1)](ClO_4)$ (1). To a solution of HL^1 (51 mg, 0.42 mmol) in acetonitrile (2.5 cm^3)–methanol (0.5 cm^3)–diethylether (1 cm^3) was added one drop of triethylamine (12 mg, 0.12 mmol). A solution of zinc(II) perchlorate hexahydrate (157 mg, 0.42 mmol) in the same amount of the mixed solvents was added dropwise. The resulting clear solution was left to stand at 7 °C for several days. Colorless cubes were deposited. They were collected by filtration and dried in vacuo over P_2O_5 to remove the solvent: Yield, 79 mg. Found: C, 16.94; H, 3.87; N, 9.70%. Calcd for $C_4H_{11}ClN_2O_4SZn$: C, 16.91; H, 3.90; N, 9.86%. IR (KBr) ν(NH) 3320(m), 3290(m), 3272(m); $\nu_{as}(CH_2)$ 2936(m); $\nu_s(CH_2)$ 2875(m); δ (NH_2) 1587(m); $\nu(ClO_4)$ 1110(sh), 1083(s, br), 625(m) cm^{-1}. Diffuse reflectance spectrum: λ_{max} 205, 318sh nm.

$[Zn\{Zn(L^1)_2\}_2](ClO_4)_2$ (2). To a solution of HL^1 (40 mg, 0.33 mmol) in acetonitrile (2.5 cm^3)–methanol (0.5 cm^3)–diethylether (1 cm^3) was added one drop of triethylamine (12 mg, 0.12

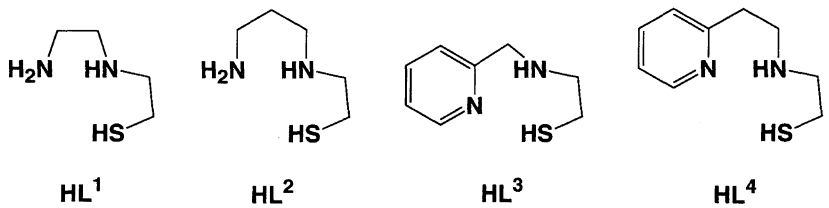

Chart 1.

mmol). A solution of zinc(II) perchlorate hexahydrate (62 mg, 0.17 mmol) in the same amount of the mixed solvents was added dropwise. The resulting clear solution was left to stand at 7 °C for several days. Colorless plates were deposited. They were collected by filtration and dried in vacuo over P_2O_5 to remove the solvent: Yield, 7 mg. Found: C, 21.81; H, 5.12; N, 12.85%. Calcd for $C_{16}H_{44}Cl_2N_8O_8S_4Zn_3$: C, 22.04; H, 5.09; N, 12.85%. IR (KBr) ν(NH) 3328(m), 3256(s); $\nu_{as}(CH_2)$ 2918(m); $\nu_s(CH_2)$ 2866(m); $\delta(NH_2)$ 1587(m); $\nu(ClO_4)$ 1110(sh), 1090(s, br), 625(m) cm^{-1}. Diffuse reflectance spectrum: λ_{max} 226 nm.

[Zn(L^2)](ClO$_4$) (3). To a solution of HL^2 (35 mg, 0.26 mmol) in methanol (2.5 cm^3) was added a methanol solution (2.5 cm^3) of zinc(II) perchlorate hexahydrate (97 mg, 0.26 mmol). The resulting clear solution was allowed to stand for one day at 7 °C to give colorless plates which were collected by filtration and dried in vacuo over P_2O_5 to remove the solvent: Yield, 42 mg. Found: C, 20.35; H, 4.44; N, 9.59%. Calcd for $C_5H_{12}ClN_2O_4SZn$: C, 20.15; H, 4.40; N, 9.40%. IR (KBr) ν(NH) 3285(m), 3262(s); $\nu_{as}(CH_2)$ 2928(m); $\nu_s(CH_2)$ 2875(m); $\delta(NH_2)$ 1588(m); $\nu(ClO_4)$ 1110(sh), 1087(s, br), 626(m) cm^{-1}. Diffuse reflectance spectrum: λ_{max} 205 nm.

[Zn{Zn(L^3)$_2$}$_2$](ClO$_4$)$_2$ (4). HL^3 (23 mg, 0.14 mmol) was dissolved in a mixture of *N*,*N*-dimethylacetamide (0.5 cm^3), methanol (2.5 cm^3), and diethylether (2.5 cm^3). A solution of zinc(II) perchlorate hexahydrate (51 mg, 0.14 mmol) in the same amount of the mixed solvents was added dropwise with stirring. The resulting clear solution was left to stand at 7 °C for several days. Colorless plates were deposited. They were collected by filtration and dried in vacuo over P_2O_5 to remove the solvent: Yield, 8 mg. Found: C, 36.02; H, 4.30; N, 10.56%. Calcd for $C_{32}H_{44}Cl_2N_8O_8S_4Zn_3$: C, 36.12; H, 4.17; N, 10.53%. IR (KBr) ν(NH) 3250(m); $\nu_{as}(CH_2)$ 2914(m); $\nu_s(CH_2)$ 2854(w); ν(pyridyl) 1598(s), 1569(m), 1479(m), 1436(s); $\nu(ClO_4)$ 1117(s, br), 1089(s, br), 625(m) cm^{-1}. Diffuse reflectance spectrum: λ_{max} 258 nm.

[Zn$_3$(L^4)$_3$](ClO$_4$)$_3$ (5). To a solution of HL^4 (41 mg, 0.22 mmol) in acetonitrile (0.3 cm^3)–methanol (2.5 cm^3) was added one drop of triethylamine (12 mg, 0.12 mmol). A solution of zinc(II) perchlorate hexahydrate (82 mg, 0.22 mmol) in the same amount of the mixed solvents was added dropwise. The resulting clear solution was left to stand at 7 °C for three days. Pale yellow needles were deposited. They were collected by filtration and dried in vacuo over P_2O_5 to remove the solvent: Yield, 15 mg. Found: C, 30.95; H, 3.78; N, 7.88%. Calcd for $C_{27}H_{39}Cl_3N_6O_{12}S_3Zn_3$: C, 31.23; H, 3.79; N, 8.09%. IR (KBr) ν(NH) 3240(m); $\nu_{as}(CH_2)$ 2914(m); $\nu_s(CH_2)$ 2855(m); ν(pyridyl) 1608(s), 1565(m), 1485(m), 1441(s), $\nu(ClO_4)$ 1115(s, br), 1087(s, br), 623(m) cm^{-1}. Diffuse reflectance spectrum: λ_{max} 218, 267 nm.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrophotometer model IR 700 in the 4000—400 cm^{-1} region. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100.

X-Ray Crystal Structure Analysis. X-Ray quality crystals were collected from each solution and were not dried. Each crystal was sealed in a glass capillary together with the mother liquor and mounted on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1°C. Unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \leq 2\theta \leq 30°$. Crystal data and details of the data collection are given in Table 1. Intensity data were corrected for Lorentz-polarization effects, but not for absorption. The struc-

Table 1. Crystal Data and Data Collection Details

Complex	[Zn(L^1)]ClO$_4$ (**1**)	[Zn{Zn(L^1)$_2$}$_2$](ClO$_4$)$_2$ ·2.5CH$_3$CN (**2**·2.5CH$_3$CN)	[Zn{Zn(L^3)$_2$}$_2$](ClO$_4$)$_2$ ·2CH$_3$OH (**4**·2CH$_3$OH)	[Zn$_3$(L^4)$_3$](ClO$_4$)$_3$·CH$_3$OH (**5**·CH$_3$OH)
Formula	$C_4H_{11}ClN_2O_4SZn$	$C_{21}H_{51.5}Cl_2N_{10.5}O_8S_4Zn_3$	$C_{34}H_{52}Cl_2N_8O_{10}S_4Zn_3$	$C_{28}H_{43}Cl_3N_6O_{13}S_3Zn_3$
F.W.	284.0	974.5	1128.1	1070.4
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$Pna2_1$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	10.517(11)	15.534(15)	10.402(4)	12.428(4)
b/Å	14.264(12)	17.453(6)	14.085(6)	13.583(3)
c/Å	6.394(6)	16.177(13)	17.108(6)	13.938(4)
α/°			88.85(3)	97.58(2)
β/°		97.22(4)	72.36(3)	96.54(2)
γ/°			78.64(3)	104.43(2)
V/Å^3	959.3(15)	4351.0(57)	2339.8(17)	2232.1(11)
Z	4	4	2	2
D_c/g cm^{-3}	1.97	1.49	1.60	1.59
D_m/g cm^{-3}	1.93	1.57	1.60	1.65
μ(Mo $K\alpha$)/cm^{-1}	30.97	20.39	19.09	20.15
Crystal size/nm	0.41 × 0.35 × 0.30	0.41 × 0.21 × 0.19	0.43 × 0.42 × 0.22	0.51 × 0.38 × 0.35
2θ range/°	1.0—50.0	1.0—50.0	1.0—50.0	1.0—50.0
Total no. of reflections measured	1029	7882	7768	7836
No. of unique reflections with $I \geq 3\sigma(I)$	750	2295	3786	3616
R	0.032	0.070	0.044	0.073
R_w	0.037	0.079	0.050	0.082

tures were solved by the direct methods and refined by the full-matrix least-squares methods. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed at their positions. The final discrepancy factors, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are listed in Table 1. The weighting scheme; $w = 1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$ was employed. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[28] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 2. Selected bond distances and angles are listed in Table 3. The anisotropic thermal parameters of the non-hydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, and the $F_o - F_c$ tables were deposited as Document No. 71046 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Reaction of 2-[(2-aminoethyl)amino]ethanethiol (HL^1) with zinc(II) perchlorate hexahydrate in an organic solvent gave colorless crystals of $[Zn(L^1)](ClO_4)$ (**1**) or $[Zn\{Zn(L^1)_2\}_2](ClO_4)_2$ (**2**), depending on the stoichiometric ratio of the reactants. The X-ray crystallography of **1** reveals polymerism which derived from the linkages of the zinc(II) ions by the thiolato-sulfur atoms of the ligands L^1. The zinc(II) ions are related by a screw-axis, they form a zig-zag infinite chain (Fig. 1). The helical chain extends along the crystallographic *c*-axis. The Zn–Zn′ separation is 3.776(1) Å and Zn′–Zn–Zn″ angle is 115.7(1)° [primes and double primes refer to the equivalent positions $(1-x, -y, z+1/2)$ and $(1-x, -y, z-1/2)$, respectively]. The L^1 ligand coordinates to the zinc atom with the thiolato sulfur atom, S, and the two amino nitrogen atoms, N1 and N2, in a facial fashion [Zn–S 2.301(2), Zn–N1 2.109(7), Zn–N2 2.045(7) Å]. The zinc atom is further coordinated by the thiolato-sulfur atom of the neighboring mononuclear fragment, S′, at a distance of 2.283(2) Å, forming a distorted tetrahedral geometry. The Zn–S and Zn–N distances lie within the range of those of ZnS_2N_2 units in tetrahedral zinc(II) thiolates [Zn–S 2.244(3)—2.324(1) Å, Zn–N 2.037(6)—2.158(21) Å].[6,12,13,15,17] The deviations of the ZnS_2N_2 unit from T_d symmetry are evident in the small S–Zn–N1 and N1–Zn–N2 angles (89.1(2) and 85.8(3)°) and the opening up of the remaining bond angles (116.7(2)—119.8(2)°). In addition, an oxygen atom (O1) of a perchlorate ion approaches the zinc atom with a relatively long distance of 2.960(7) Å. Considering this weak coordination, the geometry about the zinc atom may be described as a distorted trigonal bipyramid with S, N2, and S′ atoms being in the equatorial plane while the N1 and O1 atoms occupy the apical positions. The infrared spectrum of **1** shows essentially no splitting of the ν(Cl–O) band at 1080—1110 cm^{-1}, indicative of vey weak coordination of the perchlorate ion.[29]

The crystal structure of **2**·2.5CH_3CN consists of a trinuclear cation, $[Zn\{Zn(L^1)_2\}_2]^{2+}$, two perchlorate ions, and three acetonitrile molecules in an asymmetric unit. A perspective view of $[Zn\{Zn(L^1)_2\}_2]^{2+}$ is illustrated in Fig. 2. The three zinc atoms are nearly linear (Zn2–Zn1–Zn3 = 178.2(1)°). The Zn1–Zn2, Zn1–Zn3, and Zn2–Zn3 separations are 3.405(3), 3.392(4), and 6.796(3) Å, respectively. The central zinc atom, Zn1, has a distorted tetrahedral geometry, while the terminal zinc atoms, Zn2 and Zn3, have distorted octahedral coordination spheres. The central Zn–S bond distances and S–Zn–S angles are 2.340(6)—2.366(6) Å and 100.5(2)—117.0(2)°, respectively. It is to be noted that the Zn–S bond distances are a little longer than those found in **1**. These values fall within the range reported in a few tetrahedral zinc(II) thiolates with ZnS_4 [2.329(3)—2.363(3) Å].[8] The thiolic ligand, L^1, forms a meridional bis-chelate with one thiolato-sulfur atom and two amino-nitrogen atoms coordinated to the terminal zinc atom, forming two adjacent five-membered chelate rings. The terminal Zn–S distances

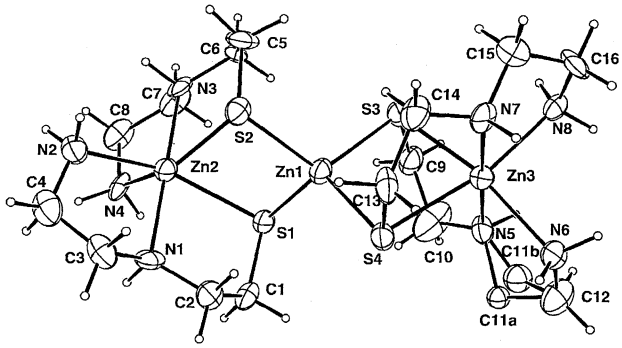

Fig. 2. ORTEP view of the structure of the complex cation of $[Zn\{Zn(L^1)_2\}_2](ClO_4)_2$·2.5$CH_3CN$ (**2**·2.5CH_3CN), showing the atom-labeling scheme. Thermal ellipsoids are shown at the 35% probability level. The carbon atom C11 was subjected to disorder and divided into two positions C11a and C11b with occupancy factors of 0.6 and 0.4, respectively.

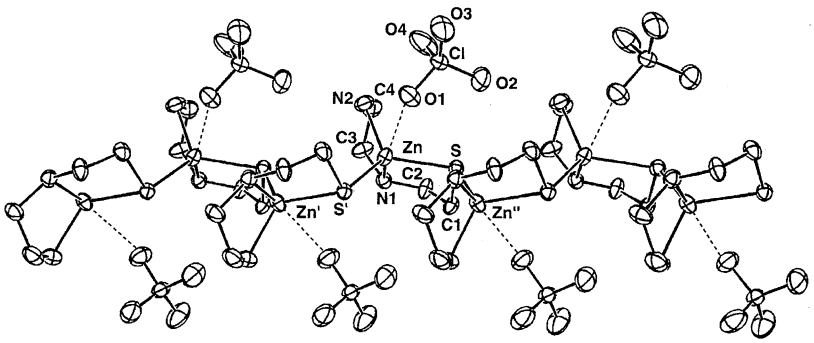

Fig. 1. Chain structure of $[Zn(L^1)](ClO_4)$ (**1**). Hydrogen atoms are omitted for clarity.

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors of Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2
[Zn(L^1)](ClO$_4$) (**1**)				
Zn	0.42104(8)	0.03964(7)	0	2.97(1)
Cl	0.0087(2)	0.2378(1)	0.6831(4)	3.52(4)
S	0.3933(2)	0.0093(1)	−0.3505(4)	2.72(4)
O1	0.0697(7)	0.3049(5)	0.815(1)	5.6(2)
O2	−0.0169(8)	0.2806(5)	0.490(2)	7.2(2)
O3	0.0860(8)	0.1599(5)	0.643(1)	7.0(2)
O4	−0.0998(8)	0.2082(6)	0.788(1)	7.9(2)
N1	0.2583(6)	−0.0404(5)	0.064(1)	3.0(1)
N2	0.3230(8)	0.1493(5)	0.128(1)	4.0(2)
C1	0.2958(8)	−0.0946(6)	−0.294(1)	3.3(2)
C2	0.2002(8)	−0.0697(6)	−0.135(1)	3.6(2)
C3	0.1774(8)	0.0212(6)	0.198(2)	4.0(2)
C4	0.1908(9)	0.1212(7)	0.132(2)	4.4(2)
[Zn{Zn(L^1)$_2$}$_2$](ClO$_4$)$_2$·2.5CH$_3$CN (**2**·2.5CH$_3$CN)				
Zn1	0.7523(2)	0.1302(2)	0.5076(1)	3.35(5)
Zn2	0.6067(2)	0.1225(1)	0.6482(1)	3.11(5)
Zn3	0.8981(2)	0.1439(1)	0.3689(1)	3.34(5)
Cl1	0.4364(5)	0.1348(4)	0.2156(6)	9.7(2)
Cl2	0.8583(6)	0.0465(6)	0.0703(4)	9.4(3)
S1	0.7325(4)	0.2121(3)	0.6188(3)	3.2(1)
S2	0.6445(4)	0.0382(3)	0.5210(3)	3.4(1)
S3	0.8968(3)	0.0846(3)	0.5185(3)	3.5(1)
S4	0.7370(3)	0.1840(3)	0.3741(3)	3.6(1)
O1	0.352(2)	0.127(2)	0.206(2)	19(1)
O2	0.468(2)	0.202(1)	0.238(2)	18(1)
O3	0.463(2)	0.081(1)	0.274(2)	22(1)
O4	0.477(3)	0.127(2)	0.151(3)	30(2)
O5	0.817(2)	0.058(2)	−0.008(1)	12.4(9)
O6	0.841(3)	0.098(2)	0.122(1)	21(1)
O7	0.830(3)	−0.019(2)	0.101(2)	30(2)
O8	0.942(2)	0.037(3)	0.068(2)	25(2)
N1	0.530(1)	0.2100(8)	0.5825(9)	3.4(4)
N2	0.479(1)	0.072(1)	0.644(1)	3.9(4)
N3	0.683(1)	0.0377(9)	0.7154(9)	3.4(4)
N4	0.605(1)	0.1662(9)	0.7761(9)	3.4(4)
N5	0.959(1)	0.237(1)	0.4375(9)	4.3(4)
N6	0.913(1)	0.225(1)	0.2670(9)	4.4(4)
N7	0.839(1)	0.051(1)	0.2987(8)	3.8(4)
N8	1.015(1)	0.076(1)	0.3541(9)	3.9(4)
N9	0.104(2)	0.172(2)	0.215(1)	10.6(8)
N10	0.430(2)	0.090(2)	0.840(2)	11.9(9)
N11	0.177(3)	0.215(2)	0.441(2)	6(1)[a,b]
C1	0.660(1)	0.285(1)	0.568(1)	3.7(5)
C2	0.576(1)	0.253(1)	0.523(1)	4.5(5)
C3	0.448(1)	0.174(1)	0.548(1)	4.2(5)
C4	0.416(1)	0.127(1)	0.614(1)	5.1(6)
C5	0.705(1)	−0.032(1)	0.586(1)	4.3(5)
C6	0.749(1)	−0.000(1)	0.669(1)	4.0(5)
C7	0.721(1)	0.072(1)	0.795(1)	4.8(6)
C8	0.646(2)	0.110(1)	0.833(1)	4.8(6)
C9	0.955(1)	0.165(1)	0.568(1)	4.7(6)
C10	0.946(2)	0.239(2)	0.522(1)	8.4(9)
C11a	0.932(2)	0.311(2)	0.385(2)	2.7(6)[a,c]
C11b	0.976(4)	0.297(3)	0.394(3)	4(1)[a,d]
C12	0.952(2)	0.295(1)	0.302(1)	5.9(7)
C13	0.696(1)	0.104(1)	0.310(1)	4.3(5)
C14	0.754(1)	0.034(1)	0.318(1)	4.5(5)
C15	0.902(2)	−0.014(1)	0.309(1)	5.1(6)
C16	0.990(2)	0.014(1)	0.296(1)	5.2(6)
C17	0.126(2)	0.150(2)	0.155(1)	7.9(8)
C18	0.154(3)	0.119(3)	0.084(2)	19(1)
C19	0.412(2)	0.056(2)	0.895(2)	10(1)
C20	0.387(3)	0.011(3)	0.964(3)	16(2)
C21	0.221(3)	0.243(3)	0.401(3)	5(1)a,b)
C22	0.262(4)	0.274(4)	0.346(4)	9(2)[a,b]
[Zn{Zn(L^3)$_2$}$_2$](ClO$_4$)$_2$·2CH$_3$OH (**4**·2CH$_3$OH)				
Zn1	0.2558(1)	0.96615(8)	0.74187(6)	2.79(2)
Zn2	0.45405(9)	0.75151(7)	0.74212(6)	2.67(2)
Zn3	0.0448(1)	1.17956(7)	0.75039(6)	2.54(2)
Cl1	0.3379(2)	0.4410(2)	0.5806(2)	3.87(6)
Cl2	0.2274(3)	0.2402(2)	0.0498(2)	4.15(6)
S1	0.2545(2)	0.8596(2)	0.8499(1)	3.11(5)
S2	0.4363(2)	0.8778(2)	0.6350(1)	2.91(5)
S3	0.0416(2)	1.0017(2)	0.7153(1)	3.04(5)
S4	0.2777(2)	1.1225(2)	0.7728(1)	3.19(5)
O1	0.4127(8)	0.3693(6)	0.5193(5)	6.6(2)
O2	0.2954(8)	0.5302(5)	0.5489(5)	5.8(2)
O3	0.4249(9)	0.4592(7)	0.6277(5)	8.7(3)
O4	0.222(1)	0.4135(6)	0.6328(7)	11.0(4)
O5	0.1877(8)	0.2837(6)	−0.0166(5)	6.8(2)
O6	0.123(1)	0.2661(6)	0.1248(6)	8.2(3)
O7	0.3459(7)	0.2764(6)	0.0529(4)	6.2(2)
O8	0.2619(9)	0.1386(5)	0.0379(6)	7.1(3)
O9	0.197(1)	−0.011(1)	0.4137(8)	15.2(5)
O10	0.446(1)	0.838(1)	0.122(1)	16.8(6)
N1	0.5763(6)	0.8137(5)	0.7985(4)	2.8(2)
N2	0.6662(7)	0.6750(5)	0.6772(4)	3.0(2)
N3	0.3339(7)	0.6829(5)	0.6877(4)	2.6(2)
N4	0.4348(7)	0.6149(5)	0.8112(4)	3.4(2)
N5	−0.0833(7)	1.1462(5)	0.8693(4)	2.9(2)
N6	−0.0183(7)	1.3193(5)	0.8230(4)	3.1(2)
N7	0.1688(7)	1.2091(5)	0.6299(4)	2.7(2)
N8	−0.1075(7)	1.2439(5)	0.6870(4)	3.1(2)
C1	0.336(1)	0.9074(7)	0.8966(5)	3.8(2)
C2	0.507(1)	0.9103(7)	0.8390(6)	3.8(2)
C3	0.7086(9)	0.8148(7)	0.7354(6)	3.9(2)
C4	0.7616(8)	0.7189(6)	0.6907(5)	2.8(2)
C5	0.9000(9)	0.6774(8)	0.6634(7)	4.6(3)
C6	0.941(1)	0.5899(9)	0.6200(7)	5.3(3)
C7	0.845(1)	0.5465(8)	0.6064(7)	4.9(3)
C8	0.709(1)	0.5887(7)	0.6350(6)	4.2(3)
C9	0.3420(9)	0.8106(7)	0.5872(5)	3.4(2)
C10	0.2532(8)	0.7514(6)	0.6461(5)	3.2(2)
C11	0.2471(9)	0.6327(6)	0.7540(6)	3.4(2)
C12	0.3351(9)	0.5745(6)	0.8011(5)	3.0(2)
C13	0.311(1)	0.4866(7)	0.8338(6)	4.3(3)
C14	0.394(1)	0.4399(7)	0.8767(6)	5.0(3)
C15	0.498(1)	0.4809(8)	0.8883(6)	5.2(3)
C16	0.514(1)	0.5687(7)	0.8538(6)	4.4(3)
C17	−0.0744(9)	0.9822(7)	0.8156(6)	4.0(2)
C18	−0.0640(9)	1.0420(6)	0.8843(6)	3.5(2)
C19	−0.053(1)	1.2047(7)	0.9300(5)	3.7(2)
C20	−0.0621(8)	1.3068(7)	0.9035(5)	3.2(2)
C21	−0.110(1)	1.3865(8)	0.9583(6)	4.9(3)
C22	−0.115(1)	1.4770(8)	0.9302(7)	6.3(3)
C23	−0.073(1)	1.4891(7)	0.8481(7)	5.2(3)
C24	−0.026(1)	1.4089(7)	0.7959(6)	4.0(2)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
C25	0.3756(9)	1.1579(7)	0.6720(7)	4.3(3)	O16	0.086(4)	0.844(3)	0.580(2)	16(1)[b]
C26	0.3090(9)	1.1508(7)	0.6053(6)	3.6(2)	O17	0.215(2)	0.091(3)	0.589(2)	31(2)
C27	0.095(1)	1.1975(8)	0.5712(5)	4.1(2)	N1	0.7756(9)	0.1414(9)	0.1215(8)	5.8(3)
C28	−0.0540(9)	1.2411(7)	0.6052(5)	3.3(2)	N2	0.6083(8)	0.2749(8)	0.0916(7)	5.0(3)
C29	−0.138(1)	1.2730(7)	0.5568(5)	4.0(2)	N3	0.8351(9)	−0.0223(9)	−0.2349(8)	5.4(3)
C30	−0.275(1)	1.3108(8)	0.5918(6)	4.6(3)	N4	0.5814(9)	−0.0641(8)	−0.3231(7)	5.1(3)
C31	−0.3261(9)	1.3155(7)	0.6744(6)	4.1(2)	N5	0.8119(9)	0.4464(9)	−0.2022(9)	6.1(3)
C32	−0.2426(9)	1.2825(7)	0.7212(6)	4.0(2)	N6	1.0252(8)	0.3705(8)	−0.2112(8)	4.6(3)
C33	0.100(1)	0.0721(7)	0.4099(6)	4.3(2)	C1	0.673(1)	−0.017(1)	0.006(1)	7.0(5)
C34	0.3991(7)	0.7810(6)	0.0864(5)	2.7(2)	C2	0.711(2)	0.036(1)	0.076(1)	8.6(5)
					C3	0.720(1)	0.151(1)	0.208(1)	7.3(5)
$[Zn_3(L^4)_3](ClO_4)_3\cdot CH_3OH$ (**5**·CH_3OH)					C4	0.717(1)	0.260(1)	0.242(1)	7.5(5)
Zn1	0.7171(1)	0.2138(1)	0.0169(1)	4.88(4)	C5	0.628(1)	0.295(1)	0.190(1)	5.0(3)
Zn2	0.7025(1)	0.0385(1)	−0.2218(1)	4.94(4)	C6	0.563(1)	0.350(1)	0.239(1)	7.3(4)
Zn3	0.8661(1)	0.3206(1)	−0.1801(1)	4.83(4)	C7	0.483(1)	0.381(1)	0.190(1)	8.8(5)
Cl1	0.0799(4)	0.1910(3)	0.0560(3)	7.0(1)	C8	0.459(1)	0.357(1)	0.088(1)	8.2(5)
Cl2	0.4908(4)	0.2611(4)	0.7587(4)	9.7(1)	C9	0.524(1)	0.301(1)	0.043(1)	6.6(4)
Cl3	0.3230(7)	0.4779(6)	0.4615(6)	6.5(2)[b]	C10	0.899(1)	0.120(1)	−0.323(1)	6.2(4)
Cl4	0.0417(7)	0.7541(6)	0.5745(6)	6.4(2)[b]	C11	0.931(1)	0.057(1)	−0.252(1)	6.2(4)
S1	0.6261(3)	0.0573(3)	−0.0807(3)	5.18(9)	C12	0.805(1)	−0.116(1)	−0.317(1)	7.2(4)
S2	0.7838(3)	0.1759(3)	−0.2951(3)	5.24(9)	C13	0.693(2)	−0.188(1)	−0.314(1)	8.1(5)
S3	0.8522(3)	0.3502(3)	−0.0157(3)	5.6(1)	C14	0.595(1)	−0.155(1)	−0.359(1)	6.5(4)
O1	−0.009(1)	0.186(1)	−0.014(1)	11.0(4)	C15	0.521(2)	−0.220(1)	−0.437(1)	8.3(5)
O2	0.099(2)	0.102(1)	0.059(1)	18.5(6)	C16	0.430(2)	−0.192(1)	−0.477(1)	8.4(5)
O3	0.045(2)	0.218(2)	0.143(1)	16.7(7)	C17	0.414(2)	−0.096(1)	−0.439(1)	8.2(5)
O4	0.168(2)	0.263(2)	0.046(2)	25(1)	C18	0.493(1)	−0.035(1)	−0.362(1)	6.5(4)
O5	0.480(1)	0.351(1)	0.808(1)	13.9(6)	C19	0.784(2)	0.451(1)	−0.033(1)	10.2(5)
O6	0.5882(9)	0.239(1)	0.799(1)	11.9(5)	C20	0.777(2)	0.488(2)	−0.113(1)	15.9(6)
O7	0.403(2)	0.189(2)	0.795(2)	21(1)	C21	0.896(1)	0.524(1)	−0.243(1)	7.8(5)
O8	0.453(2)	0.238(2)	0.677(1)	22(1)	C22	0.949(1)	0.471(1)	−0.320(1)	7.0(4)
O9	0.355(2)	0.502(2)	0.378(1)	9.8(8)[b]	C23	1.041(1)	0.430(1)	−0.284(1)	5.3(4)
O10	0.396(2)	0.483(2)	0.533(2)	11(1)[b]	C24	1.144(1)	0.448(1)	−0.318(1)	7.9(5)
O11	0.290(3)	0.551(2)	0.487(3)	15(1)[b]	C25	1.226(1)	0.409(1)	−0.281(1)	8.6(5)
O12	0.247(3)	0.404(2)	0.447(2)	14(1)[b]	C26	1.210(1)	0.349(1)	−0.208(1)	7.5(5)
O13	0.033(2)	0.741(2)	0.660(2)	9.5(7)[b]	C27	1.107(1)	0.332(1)	−0.176(1)	5.2(4)
O14	0.097(3)	0.706(3)	0.543(2)	16(1)[b]	C28	0.124(2)	0.060(3)	0.565(2)	22(1)
O15	−0.042(3)	0.741(3)	0.521(2)	14(1)[b]					

a) Atom was refined isotropically. b) Atom was refined with occupancy factor of 0.5. c) Atom was refined with occupancy factor of 0.6. d) Atom was refined with occupancy factor of 0.4. e) Anisotropically refined atoms are given in the form of the isotropic equivalent displacement displacement parameter defined as: $\frac{4}{3}[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$.

[2.593(6)—2.656(6) Å] are significantly longer than the central Zn–S distances. The Zn–N bond distances [2.11(1)—2.21(1) Å] are also longer than those of ZnS_2N_2 moieties in **1**. These elongations reflect the increasing coordination number of the metal. The bond lengths are comparable with the values reported for very few octahedral zinc(II)–thiolates (Zn–S 2.546(3)—2.627(2) Å, Zn–N 2.085(6)—2.202(7) Å).[11] The Zn–S–Zn angles are 85.2(2)—87.0(2)°. The perchlorate ions are located in the vicinity of the amino nitrogen atoms of the L^1 ligands, as indicated by the distances [O3(ClO_4)···N2 $(1-x, -y, 1-z)$ 3.06(3) Å, O3(ClO_4)···N3, $(1-x, -y, 1-z)$ 3.09(3) Å, O6(ClO_4)···N7 2.99(3) Å], which suggest the occurrence of hydrogen bondings.

A similar reaction of a related thiolic ligands, 2-[(3-aminopropyl)amino]ethanethiol (HL^2), with zinc(II) perchlorate hexahydrate in methanol afforded an analogous complex, [Zn(L^2)](ClO_4) (**3**). In the infrared spectrum of **3**, essentially no splitting of the ν(Cl–O) band of the perchlorate ion was observed. This shows weak or no coordination of the perchlorate ion to the metal in **3**.[29] Although the X-ray crystallographic work was unsuccessful for **3**, it is reasonable to assume the complex has a chain structure similar to that of **1**.

In attempting to prepare the analogous species with 2-[(2-pyridylmethyl)amino]ethanethiol (HL^3), only a trinuclear complex of $[Zn\{(L^3)_2\}_2](ClO_4)_2$ (**4**) could be isolated. The X-ray crystal structure of **4**·2CH_3OH consists of trinuclear cation, $[Zn\{Zn(L^3)_2\}_2]^{2+}$, two perchlorate ions, and two methanol molecules. A perspective view of the trinuclear cation is shown in Fig. 3. The trinuclear structure is

Table 3. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°) with Their Estimated Standard Deviation in Parentheses

$[Zn(L^1)](ClO_4)$ (**1**)			
Zn–S	2.301(2)	Zn–S′	2.283(2)
Zn–N1	2.098(7)	Zn–N2	2.045(7)
Zn–O1	2.960(7)		
S–Zn–S′	117.3(8)	Zn–S–Zn′	110.90(9)
S–Zn–N1	89.1(2)	Zn–S–C1	91.7(3)
S–Zn–N2	118.1(2)	Zn″–S–C1	108.3(3)
S′–Zn–N1	116.7(2)	Zn–N1–C2	108.9(5)
S′–Zn–N2	119.8(2)	Zn–N1–C3	104.9(5)
N1–Zn–N2	85.8(3)	Zn–N2–C4	106.2(6)
$[Zn\{Zn(L^1)_2\}_2](ClO_4)_2\cdot 2.5CH_3CN$ (**2**·2.5CH_3CN)			
Zn1–S1	2.348(6)	Zn1–S2	2.349(6)
Zn1–S3	2.366(6)	Zn1–S4	2.340(6)
Zn2–S1	2.593(6)	Zn2–S2	2.656(6)
Zn2–N1	2.14(2)	Zn2–N2	2.17(2)
Zn2–N3	2.11(1)	Zn2–N4	2.21(1)
Zn3–S3	2.635(6)	Zn3–S4	2.611(6)
Zn3–N5	2.12(2)	Zn3–N6	2.20(2)
Zn3–N7	2.12(2)	Zn3–N8	2.20(2)
S1–Zn1–S2	100.5(2)	S3–Zn3–N5	82.8(5)
S1–Zn1–S3	111.2(2)	S3–Zn3–N6	162.2(5)
S1–Zn1–S4	117.0(2)	S3–Zn3–N7	98.0(4)
S2–Zn1–S3	116.3(2)	S3–Zn3–N8	89.5(4)
S2–Zn1–S4	111.6(2)	S4–Zn3–N5	98.1(5)
S3–Zn1–S4	100.9(2)	S4–Zn3–N6	92.6(5)
S1–Zn2–S2	86.9(2)	S4–Zn3–N7	82.6(5)
S1–Zn2–N1	82.2(5)	S4–Zn3–N8	162.5(5)
S1–Zn2–N2	161.6(5)	N5–Zn3–N6	79.6(6)
S1–Zn2–N3	97.4(5)	N5–Zn3–N7	179.0(7)
S1–Zn2–N4	93.5(4)	N5–Zn3–N8	98.6(6)
S2–Zn2–N1	100.1(4)	N6–Zn3–N7	99.7(6)
S2–Zn2–N2	92.6(5)	N6–Zn3–N8	95.5(6)
S2–Zn2–N3	81.1(4)	N7–Zn3–N8	80.8(6)
S2–Zn2–N4	161.3(4)	N1–Zn2–N2	79.7(6)
N1–Zn2–N3	178.8(6)	N1–Zn2–N4	98.5(6)
N2–Zn2–N3	100.7(6)	N2–Zn2–N4	92.7(6)
N3–Zn2–N4	80.3(6)	S3–Zn3–S4	87.5(2)
Zn2–N4–C8	108(1)	Zn3–N5–C10	115(2)
Zn3–N5–C11a	106(1)	Zn1–S1–Zn2	87.0(2)
Zn3–N5–C11b	116(2)	Zn1–S1–C1	102.2(6)
Zn2–S1–C1	94.0(7)	Zn1–S2–Zn2	85.5(2)
Zn1–S2–C5	101.0(7)	Zn3–N6–C12	109(1)
Zn2–S2–C5	94.1(7)	Zn3–N7–C14	113(1)
Zn1–S3–Zn3	85.2(2)	Zn3–N7–C15	107(1)
Zn1–S3–C9	100.9(8)	Zn3–S3–C9	92.4(7)
Zn3–N8–C16	109(1)	Zn1–S4–Zn3	86.3(2)
Zn1–S4–C13	101.9(7)	Zn3–S4–C13	92.2(7)
Zn2–N1–C2	114(1)	Zn2–N1–C3	107(1)
Zn2–N2–C4	109(1)	Zn2–N3–C6	115(1)
Zn2–N3–C7	108(1)		
$[Zn\{Zn(L^3)_2](ClO_4)_2\cdot 2CH_3OH$ (**4**·2CH_3OH)			
Zn1–S1	2.356(3)	Zn1–S2	2.347(2)
Zn1–S3	2.363(3)	Zn1–S4	2.346(3)
Zn2–S1	2.564(2)	Zn2–S2	2.551(3)
Zn2–N1	2.129(8)	Zn2–N2	2.212(6)
Zn2–N3	2.141(8)	Zn2–N4	2.249(7)
Zn3–S3	2.596(3)	Zn3–S4	2.538(3)
Zn3–N5	2.168(6)	Zn3–N6	2.223(7)
Zn3–N7	2.157(6)	Zn3–N8	2.223(8)
S1–Zn1–S2	100.65(8)	S3–Zn3–N5	82.0(2)
S1–Zn1–S3	112.36(9)	S3–Zn3–N6	157.2(2)
S1–Zn1–S4	113.6(1)	S3–Zn3–N7	96.2(2)
S2–Zn1–S3	114.2(1)	S3–Zn3–N8	94.4(2)
S2–Zn1–S4	116.32(9)	S4–Zn3–N5	98.2(2)
S3–Zn1–S4	100.30(9)	S4–Zn3–N6	98.4(2)
S1–Zn2–S2	90.11(7)	S4–Zn3–N7	83.0(2)
S1–Zn2–N1	83.0(2)	S4–Zn3–N8	158.6(2)
S1–Zn2–N2	159.4(2)	N5–Zn3–N6	75.8(3)
S1–Zn2–N3	97.9(2)	N5–Zn3–N7	177.8(3)
S1–Zn2–N4	94.9(2)	N5–Zn3–N8	103.2(3)
S2–Zn2–N1	98.4(2)	N6–Zn3–N7	105.9(3)
S2–Zn2–N2	96.5(2)	N6–Zn3–N8	86.0(3)
S2–Zn2–N3	84.1(2)	N7–Zn3–N8	75.6(2)
S2–Zn2–N4	160.2(2)	N1–Zn2–N2	76.7(3)
N1–Zn2–N3	177.4(3)	N1–Zn2–N4	101.3(3)
N2–Zn2–N3	102.2(3)	N2–Zn2–N4	85.4(2)
N3–Zn2–N4	76.3(3)	S3–Zn3–S4	89.51(8)
Zn2–N3–C10	112.5(5)	Zn2–N3–C11	106.8(6)
Zn2–N4–C12	112.5(6)	Zn1–S1–Zn2	84.37(7)
Zn2–N4–C16	128.6(7)	Zn1–S1–C1	100.1(3)
Zn2–S1–C1	94.3(3)	Zn3–N5–C18	113.4(4)
Zn1–S2–Zn2	84.87(7)	Zn3–N5–C19	105.6(5)
Zn1–S2–C9	101.4(2)	Zn2–S2–C9	93.4(3)
Zn3–N6–C20	112.1(6)	Zn1–S3–Zn3	84.25(9)
Zn3–N6–C24	128.5(6)	Zn1–S3–C17	100.7(4)
Zn3–S3–C17	95.0(3)	Zn3–N7–C26	113.7(5)
Zn1–S4–Zn3	85.91(9)	Zn3–N7–C27	108.4(5)
Zn1–S4–C25	101.5(3)	Zn3–S4–C25	94.5(3)
Zn3–N8–C28	113.3(5)	Zn2–N1–C2	113.4(6)
Zn3–N8–C32	127.9(6)	Zn2–N1–C3	107.3(6)
Zn2–N2–C4	112.3(5)	Zn2–N2–C8	128.9(6)
$[Zn_3(L^4)_3](ClO_4)_3\cdot CH_3OH$ (**5**·CH_3OH)			
Zn1–S1	2.310(4)	Zn1–S3	2.303(4)
Zn1–N1	2.03(1)	Zn1–N2	2.06(1)
Zn2–S1	2.291(4)	Zn2–S2	2.312(4)
Zn2–N3	2.03(1)	Zn2–N4	2.037(9)
Zn3–S2	2.296(4)	Zn3–S3	2.307(4)
Zn3–N5	2.03(1)	Zn3–N6	2.04(1)
S1–Zn1–S3	129.7(1)	S1–Zn1–N1	90.9(3)
S1–Zn1–N2	111.8(3)	S3–Zn1–N1	113.2(3)
S3–Zn1–N2	107.2(3)	N1–Zn1–N2	99.0(5)
S1–Zn2–S2	123.2(2)	S1–Zn2–N3	124.0(3)
S1–Zn2–N4	106.7(3)	S2–Zn2–N3	91.3(3)
S2–Zn2–N4	108.3(3)	N3–Zn2–N4	100.6(4)
S2–Zn3–S3	129.3(2)	S2–Zn3–N5	114.6(3)
S2–Zn3–N6	104.6(3)	S3–Zn3–N5	91.2(4)
S3–Zn3–N6	114.3(3)	N5–Zn3–N6	98.4(5)
Zn1–S1–Zn2	110.7(2)	Zn1–S1–C1	93.8(5)
Zn2–S1–C1	111.3(6)	Zn3–N6–C23	118.1(9)
Zn2–S2–Zn3	111.0(2)	Zn3–N6–C27	120.6(9)
Zn2–S2–C10	92.2(5)	Zn3–S2–C10	105.3(4)
Zn1–S3–Zn3	108.2(1)	Zn1–S3–C19	106.4(6)
Zn3–S3–C19	91.6(6)	Zn1–N1–C2	108(1)
Zn1–N1–C3	111(1)	Zn1–N2–C5	120(1)
Zn1–N2–C9	120.3(9)	Zn2–N3–C11	109(1)
Zn2–N3–C12	111.6(9)	Zn2–N4–C14	121(1)
Zn2–N4–C18	119.6(9)	Zn3–N5–C20	109(1)
Zn3–N5–C21	112(1)		

Prime and double prime refer to the equivalent positions $(1-x, -y, z+1/2)$ and $(1-x, -y, z-1/2)$, respectively.

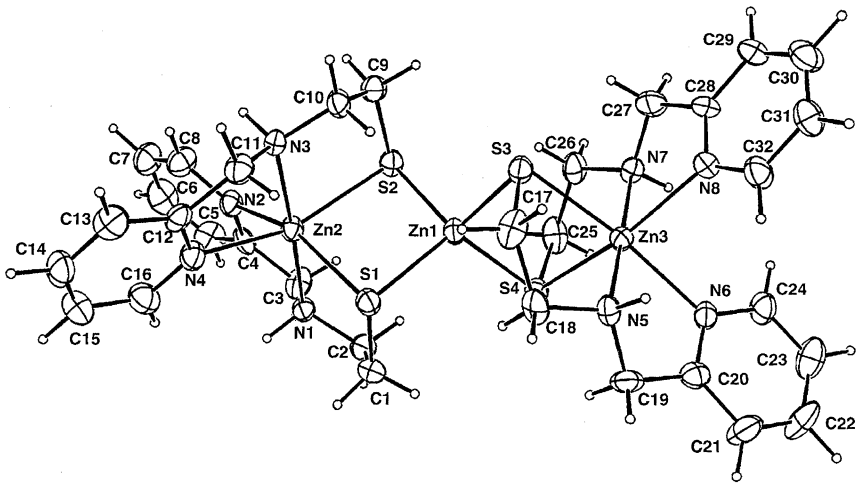

Fig. 3. ORTEP view of the structure of the complex cation of $[Zn\{Zn(L^3)_2\}_2](ClO_4)_2 \cdot 2CH_3OH$ (**4**·$2CH_3OH$), showing the atom-labeling scheme. Thermal ellipsoids are shown at the 35% probability level.

similar to that of **2**. The Zn1–Zn2, Zn1–Zn3, and Zn2–Zn3 distances are 3.308(1), 3.331(1), and 6.637(1) Å, respectively. The Zn2–Zn1–Zn3 angle is 177.1(1)°. The L^3 ligand forms two adjacent five-membered chelate rings with the terminal zinc atom in the same manner as **2**. The central zinc atom, Zn1, has a distorted tetrahedral geometry with Zn–S bond distances of 2.346(3)—2.363(3) Å. On the other hand, the terminal zinc atoms, Zn2 and Zn3, have distorted octahedral geometries with the Zn–S distances of 2.538(3)—2.596(3) Å and the Zn–N distances of 2.129(8)—2.249(7) Å, respectively. These bond distances are comparable to those of **2**. The perchlorate ions are in the vicinity of the amino nitrogen atoms of the L^3 ligands by possible hydrogen bondings [O3···N3 3.20(1) Å, O4···N7 ($x, y-1, z$) 3.04(1) Å, O7···N1 ($1-x, 1-y, 1-z$) 3.07(1) Å]. During our study on this system, Vahrenkamp et al. reported on some zinc(II) complexes with the L^3 ligand and obtained a similar trinuclear zinc(II) species which has a crystallographic S_4 symmetry for the tinuclear cation in $[Zn_3(L^3)_4](BF_4)_2 \cdot 2H_2O$, resulting in an exact colinear array of the three zinc atoms.[17] They used aqueous condition instead of our nonaqueous solvents for the preparation of the zinc(II) complexes and they also elucidated a polymeric chain structure of $[Zn(L^3)Cl]$ like our manganese compound $[Mn(L^3)Cl]$.[24b]

When 2-{[2-(2-pyridyl)ethyl]amino}ethanethiol (HL^4) was allowed to react with $Zn(ClO_4)_2 \cdot 6H_2O$ in an organic solvent, a zinc(II) complex, $[Zn_3(L^4)_3](ClO_4)_2$ (**5**), was isolated. In the X-ray crystal structure of **5**·CH_3OH (Fig. 4), the complex cation has a novel trinuclear structure which forms a nearly equilateral triangle core, the Zn1–Zn2, Zn1–Zn3, and Zn2–Zn3 separations being 3.786(2), 3.734(1), and 3.798(2) Å, respectively, and the Zn1–Zn2–Zn3, Zn1–Zn3–Zn2, and Zn2–Zn1–Zn3 angles 59.01(4), 60.35(4), and 60.65(4)°, respectively. The cation contains a Zn_3S_3 ring with trigonal pyramidal Zn_2SC and tetrahedral ZnS_2N_2 units. The central Zn_3S_3 ring becomes slightly ruffled in the direction of a boat conformation. The Zn1, Zn3, S1, and S2 atoms are nearly in a plane with the deviations within ±0.02 Å, while the Zn2 and S3 atoms deviate from the mean plane by −0.53 and −0.16 Å, respectively. The coordination sphere of each zinc atom in **5** is a distorted tetrahedron with the Zn–S distances of 2.291(4)—2.312(4) Å and the Zn–N distances of 2.03(1)—2.06(1) Å, respectively. The observed zinc–sulfur and zinc–nitrogen bond lengths are comparable to those found in **1** which has essentially a distorted tetrahedral N_2S_2 arrangement around the metal atom. There seem to be hydrogen bondings between the perchlorate ions and the amino nitrogen atoms of the L^4 ligands [O2···N3 ($1-x, -y, -z$) 2.92(2) Å, O3···N1 ($x-1, y, z$) 3.21(2) Å]. This example of the Zn_3S_3 ring structure is very rare and interesting, because such a structure is found in metallothioneins.[5] Based on NMR and X-ray analyses,[5b,5c] it has been shown that zinc- and cadmium-containing metallothioneins bind metals in two domains: an α domain with an M_4S_{11} cluster and a β domain with an M_3S_9 cluster having an M_3S_3 ring. In both domains, zinc and cadmium atoms are exclusively tetrahedrally coordinated to cysteinyl sulfur atoms.

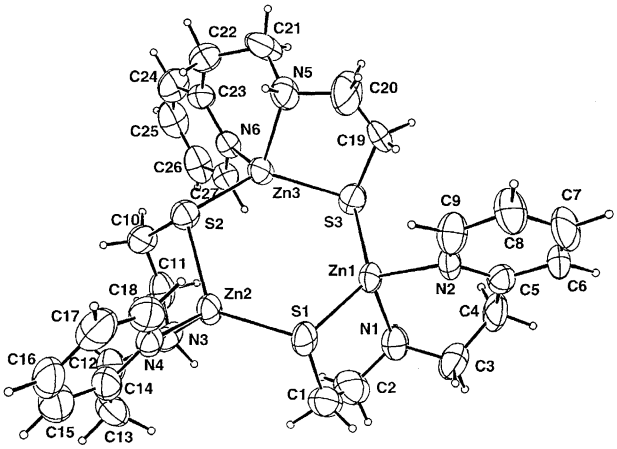

Fig. 4. ORTEP view of the structure of the complex cation of $[Zn_3(L^4)_3](ClO_4)_3 \cdot CH_3OH$ (**5**·CH_3OH), showing the atom-labeling scheme. Thermal ellipsoids are shown at the 35% probability level.

Conclusion

The four tridentate NNS-chelating ligands, 2-[(2-aminoethyl)amino]ethanethiol (HL^1), 2-[(3-aminopropyl)amino]-ethanethiol (HL^2), 2-[(2-pyridylmethyl)amino]ethanethiol (HL^3), and 2-{[2-(2-pyridyl)ethyl]amino}ethanethiol (HL^4), have proved to be aliphatic thiols that enable us to attain polymeric chain, linear trinuclear, and triangle trinuclear complexes for Zn(II). The latter trinuclear species is the first example of M_3S_3 ring core for metal thiolates with these ligands. The unique M_3S_3 core formation may be ascribed to the favorable tetrahedral coordination of zinc atoms.

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