Formation, Crystal Structure, and Reactions of *catena*-(μ-SPh)[(μ-SPh)$_6$Zn$_4$(CH$_3$OH)(SPh)], a Model for Zinc Thiolate Metalloenzymes

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Abstract: The solvent-dependent reactions of benzenethiol with basic zinc precursors form soluble solvated {Zn(SPh)$_2$} species (I), and from them crystalline one-dimensional polymers *catena*-(μ-SPh)[(μ-SPh)$_6$Zn$_4$(ROH)(SPh)], R = CH$_3$, C$_2$H$_5$, 1-C$_3$H$_7$, 1-C$_4$H$_9$ (II). These polymers dissolve in acetonitrile to form uncharacterized soluble species (III), which then polymerize again to form a different crystalline polymer tentatively formulated [Zn$_4$(SPh)$_8$(NCCH$_3$)]$_\infty$ (IV). The repeating unit in crystalline II (R = CH$_3$, isostructural with the homologues) is a cluster of four zinc atoms, arrayed approximately as a tetrahedron, bridged by six benzenethiolate ligands along the edges of the tetrahedron. Tetrahedral coordination of each zinc atom is completed by either terminal benzenethiolate, methanol, or (twice) intercluster bridging benzenethiolate: Zn–S$_{terminal}$ = 2.265 (4), ⟨Zn–S$_{bridging}$⟩ = 2.347 ± 0.006, Zn–O = 2.045 (8) Å. Linear chains of Zn$_4$ clusters result from the intercluster bridging by benzenethiolate ligands, and these chains are linked by hydrogen bonding of the methanol proton to the sulfur atom of the terminal benzenethiolate ligand. Crystal data for *catena*-(μ-SPh)[(μ-SPh)$_6$Zn$_4$(CH$_3$OH)(SPh)]: *a* = 16.529 (2) Å, *b* = 22.129 (3) Å, *c* = 14.241 (2) Å, $P2_12_12_1$, Z = 4, d_{obsd} = 1.52 g cm^{-3}, d_{calcd} = 1.49 g cm^{-3}, 2344 reflections ($I > \sigma(I)$), R = 0.056. These compounds provide pertinent structural models for substrate bound alcohol dehydrogenase enzymes. The prevalence of clusters and of polymerization/depolymerization reactions in the zinc thiolate system is discussed with relevance to the formation and unknown structures of the metallothionein proteins.

Introduction

The binary zinc thiolates, Zn(SR)$_2$, and derivatives have not been investigated in detail, particularly with regard to synthesis and structure.[1] Reactions which lead to the formation of {Zn(SPh)$_2$} species are, as described in this paper, more complicated than implied by the limited synthesis information published,[2,3] and involve solvent-dependent polymerization and depolymerization.

The chemistry of zinc thiolate coordination is pertinent to two groups of zinc metalloproteins,[4] the alcohol dehydrogenases and the metallothioneins. Liver alcohol dehydrogenase (LADH) contains zinc atoms coordinated by two and by four cysteinate residues.[5] The metallothioneins, which regulate levels of zinc, cadmium, mercury, and copper in animals, are characterized by unusually high cysteinate content (ca. 33% of all amino acid residues, with no disulfide linkages) and a cysteinate/metal ratio of ca. 3.[6-8] There is evidence that all cysteinate residues are metal coordinated[8,9] and that each metal atom is coordinated by four cysteinate residues,[10] which requires at least some cysteinate bridging of metal atoms, and suggests the existence of metal–cysteinate clustering. Definitive structural information on any metallothionein is not yet available.

Crystal structure determinations have been reported for only three zinc complexes containing nonchelating thiolate ligands: tetrahedral [Zn(SPh)$_4$]$^{2-}$,[11] [CH$_3$ZnSCH(CH$_3$)$_2$]$_8$,[12] and [CH$_3$ZnSC(CH$_3$)$_3$]$_5$.[13] The latter two methylzinc compounds are very reactive and are not chemically comparable with zinc thiolate clusters which may form in protic media. As part of a research program on metal complexes with monothiolate ligands the zinc–benzenethiol system has been investigated. This paper describes (a) the reactions of benzenethiol with basic zinc precursors, forming (i) soluble species [Zn(SPh)$_2$(solvent)$_x$], (ii) the series of complexes [Zn$_4$(SPh)$_8$(ROH)]$_\infty$, and (iii) [Zn$_4$(SPh)$_8$(NCCH$_3$)]$_n$; (b) the solvent-dependent polymerization and depolymerization reactions which interconvert these compounds; (c) the crystal structure of [Zn$_4$(SPh)$_8$(CH$_3$OH)], in which {(μ-SPh)$_3$-Zn(CH$_3$OH)} zinc–alcohol coordination occurs. Possible implications of these results for metallothionein structure are discussed.

Experimental Section

Laboratory reagent solvents and benzenethiol were used as received. The basic zinc carbonate was British Drug Houses product of unspecified formulation: its composition was probably close to that of the mineral hydrozincite, Zn$_5$(OH)$_6$(CO$_3$)$_2$, as the maximum amount that would dissolve in 5.0 g of the acid benzenethiol was 2.45 g (calculated for Zn$_5$(OH)$_6$(CO$_3$)$_2$, 2.48 g; for ZnCO$_3$, 2.84 g; for Zn(OH)$_2$, 2.25 g). All operations were performed in an atmosphere of dinitrogen.

General Information on Zn(SPh)$_2$ Synthesis. Reactions in which a zinc salt in solution is added to a solution of benzenethiol plus equimolar noncoordinating base (trialkylamine) readily yield anionic complexes [Zn(SPh)$_4$]$^{2-}$, [Zn$_4$(SPh)$_{10}$]$^{2-}$, [Zn$_4$(SPh)$_8$Cl$_2$]$^{2-}$,[14] and other complexes still uncharacterized. The different approach investigated here is dissolution of a basic zinc precursor such as zinc hydroxide or basic zinc carbonate in benzenethiol solution, such that the ratio of *deprotonated* PhS$^-$ to Zn^{2+} in the resulting solutions is exactly 2. The absence of counterions or added potential ligands in these solutions permits observation of the effects of solvent coordination.

The reactions of benzenethiol with basic zinc carbonate are dependent, in both rate and product composition, on the solvent identity and on temperature. The products contain solvent. In alcohols the rate of dissolution decreases through the sequence methanol, ethanol, 1-propanol, but in these solvents it is not possible to increase the rate of dissolution by temperature increase much above room temperature, because the soluble solvated species formed in the initial dissolution are subject to thermal polymerization yielding compounds [Zn$_4$(SPh)$_8$(ROH)]$_\infty$ insoluble in alcohols. In order to avoid heterogeneous reaction mixtures of insoluble precursors and insoluble products it is necessary to choose solvent and temperature conditions which allow separation of the dissolution and polymerization reaction stages and their products. Polymerization reactions occur in alcohols and in acetonitrile, but not in refluxing acetone, even at high concentrations of Zn(SPh)$_2$.

In practice, basic zinc carbonate can be reacted cleanly with benzenethiol to generate solutions of solvated Zn(SPh)$_2$ in acetone, methanol, and ethanol; acetone can be used at reflux, but 30 °C is the upper limit for the two alcohols, with methanol the preferred solvent.

The rate of dissolution depends on the basic zinc compound. Freshly precipitated zinc hydroxide and commercial basic zinc carbonate react rapidly, but zinc oxide dissolves very slowly. The use of zinc acetate produces a different sequence of compounds which will be described separately. The generally applicable synthetic procedure involves

dissolution of basic zinc carbonate in benzenethiol using either methanol (30 °C) or acetone (reflux) as solvent, followed by solvent replacement using low-temperature distillation, followed by thermal polymerization.

***catena*-μ-Benzenethiolato-(methanolbenzenethiolatohexa-μ-benzenethiolato-*tetrahedro*-tetrazinc(II)), Zn₄(SPh)₈(CH₃OH).** Basic zinc carbonate was added in portions less than 0.5 g to a solution of benzenethiol (5.0 g) in methanol (80 mL) at a temperature not greater than 30 °C. Within 1 h 2.5 g of basic zinc carbonate had dissolved, but further dissolution was extremely slow and not attempted. After filtration the solution was reduced in volume at 30 °C to 60 mL, and then maintained at 55 °C for 5 days while the product crystallized. At higher temperatures the product separates more rapidly as a microcrystalline precipitate. The colorless crystals were filtered, washed with methanol, and air dried: yield 3.5 g (53% based on PhSH). Anal. Calcd for $Zn_4S_8C_{49}H_{44}O$: C, 50.44; H, 3.80; S, 21.98. Found: C, 50.14; H, 3.66; S, 22.23.

Crystal Growth. A solution of $Zn(SPh)_2$ in methanol, prepared as above, was maintained at a temperature close to 20 °C (the temperature depending on the concentration of the solution) in a closed flask such that very slow crystal growth occurred over a period of 4–6 weeks. Crystals of 1-mm dimensions can be obtained.

***catena*-μ-Benzenethiolato-(ethanolbenzenethiolatohexa-μ-benzenethiolato-*tetrahedro*-tetrazinc(II)), Zn₄(SPh)₈(C₂H₅OH). A.** Basic zinc carbonate was added in portions of 0.5 g to a solution of benzenethiol (5.0 g) in absolute ethanol (100 mL) at less than 30 °C; approximately 2.0 g dissolved during 3 h. After filtration the solution was held at 55 °C in a sealed flask while the product crystallized. At reflux temperature the product separates as a microcrystalline precipitate during 2 h. The isolated product was washed with ethanol and air dried.

B. Basic zinc carbonate (2.5 g) was added to a solution of benzenethiol (5.0 g) in acetone (70 mL), and the mixture refluxed for ca. 1 h, after which almost complete dissolution had occurred. After filtration, ethanol (100 mL) was added and the acetone removed by distillation. The white, crystalline product separated, slowly at ambient temperature and rapidly at reflux; it was filtered, washed with ethanol, and vacuum dried, yield 3.75 g. Anal. Calcd for $Zn_4S_8C_{50}H_{46}O$: C, 50.85; H, 3.93; S, 21.72. Found: C, 50.93; H, 3.84; S, 20.36.

***catena*-μ-Benzenethiolato-(propan-1-olbenzenethiolatohexa-μ-benzenethiolato-*tetrahedro*-tetrazinc(II)), Zn₄(SPh)₈(1-C₃H₇OH). A.** According to the procedure for $Zn_4(SPh)_8(CH_3OH)$, a solution of $Zn(SPh)_2$ in methanol (110 mL) was prepared, by dissolution of basic zinc carbonate (2.5 g) in benzenethiol (5.0 g) at less than 30 °C followed by filtration. An equal volume of 1-propanol was added, and the methanol removed by distillation at less than 10 °C. The resulting solution in 1-propanol was warmed to cause crystallization of the product over a period of several hours, and finally refluxed to complete precipitation. The microcrystalline, white precipitate was washed with 1-propanol and vacuum dried.

B. An alternative procedure used refluxing acetone as the solvent for reaction of basic zinc carbonate and benzenethiol. Addition of 1-propanol and removal of acetone by distillation at atmospheric pressure yielded a microcrystalline product, which was washed with 1-propanol and vacuum dried, yield 4.0 g. Anal. Calcd for $Zn_4S_8C_{51}H_{48}O$: C, 51.26; H, 4.05; S, 21.47. Found: C, 50.71, 51.31; H, 3.92; S, 21.01, 20.73.

***catena*-μ-Benzenethiolato-(butan-1-olbenzenethiolatohexa-μ-benzenethiolato-*tetrahedro*-tetrazinc(II)), Zn₄(SPh)₈(1-C₄H₉OH).** Both of the procedures described for $Zn_4(SPh)_8(1-C_3H_7OH)$ were used, with 1-butanol instead of 1-propanol. The product is a fine, microcrystalline, white precipitate which was vacuum dried, yield 4.5 g. Anal. Calcd for $Zn_4S_8C_{52}H_{50}O$: C, 51.66; H, 4.17; S, 21.22. Found: C, 51.76; H, 4.01; S, 20.31.

The compounds $Zn_4(SPh)_8(ROH)$, R = CH_3, C_2H_5, 1-C_3H_7, 1-C_4H_9, are, in the crystalline state, stable with respect to alcohol loss (dynamic vacuum, room temperature, 10 h) and to oxidation by dioxygen (room temperature, 20 h). Large, well-formed crystals of $Zn_4(SPh)_8(CH_3OH)$ have shown no evidence of decomposition after a period of many months in laboratory atmosphere. Compounds $Zn_4(SPh)_8(ROH)$ are slightly soluble in hot alcohols R'OH, the solubility increasing as the size of R increases and the size of R' decreases; there is no solubility in cold water, and decomposition in hot water. None of the compounds shows appreciable solubility in hot acetone or hot nitromethane, but in hot THF there is some solubility which increases with the length of R. With acetonitrile the behavior

of the compounds $Zn_4(SPh)_8(ROH)$ is unique: they are slowly soluble at room temperature, but as the concentration increases or the temperature is raised another polymerization reaction occurs, yielding an insoluble microcrystalline product not containing alcohol.

***catena*-(Octabenzenethiolatotetrazinc(II) acetonitrile), [Zn₄-(SPh)₈(NCCH₃)]ₙ.** To acetonitrile (400 mL) stirred at room temperature, $Zn_4(SPh)_8(1-C_4H_9OH)$ was added in small portions only after the previous portion had dissolved. At the first indication of clouding and imminent precipitation the solution was rapidly filtered and allowed to stand for 20 h while the crystallization continued. The mixture was boiled to complete the polymerization and filtered hot, and the product washed with acetonitrile and vacuum dried, yield >70% by mass. The composition of this compound is not yet certain. Although there is no doubt about the presence of coordinated acetonitrile in all samples (IR, N analysis), the analytical data are variable. Found: C, 51.55, 50.21, 50.37; H, 3.89, 3.63, 3.53; N, 2.23, 1.04, 1.91; S, 19.86, 20.63, 21.00, respectively, for three samples. Calcd for $Zn_4(SPh)_8(NCCH_3)$: C, 51.07; H, 3.69; N, 1.19; S, 21.81. Calcd for $Zn_4(SPh)_8(NCCH_3)_2$: C, 51.32; H, 3.81; N, 2.30; S, 21.07. Crystal growth and characterization by crystal structure determination are currently being attempted. Powder diffraction pattern (Å): 12.50 vvs, 10.42 m, 9.52 m, 7.88 m, 7.32 w, 7.12 m, 4.80 m, 4.71 vw, 4.65 w, 4.56 w, 4.49 vw, 4.44 w, 4.20 vw, 4.08 w, 4.03 m, 3.95 w, 3.86 vw, 3.81 vw, 3.67 s, 3.56 vw, 3.52 s, 3.41 w, 3.26 w, 3.15 w, 3.10 w, 2.917 w, 2.885 ms, 2.807 m, 2.767 w, 2.520 w. This product dissolves slowly in methanol and THF.

Vibrational Spectra. Infrared (IR) and laser (488 nm) Raman (R) spectra of crystalline samples $Zn_4(SPh)_8(ROH)$ and $[Zn_4-(SPh)_8(CH_3CN)_x]_\infty$ contain the following collection of essentially invariant bands (cm⁻¹) characteristic of coordinated benzenethiolate: 480 (IR, m), 615 (R, w), 690 (IR, s; R, w), 730–735 (IR, s), 820–830 (IR, wm), 885–900 (IR, m), 930 (IR, vw), 955 (IR, vw), 1000 (IR, m; R, vs), 1025 (IR, vs; R, s), 1070 (IR, m), 1085 (IR, s; R, s), 1120 (IR, w; R, w), 1155 (IR, w; R, w), 1180 (IR, vw; R, w), 1270 (IR, vw), 1300 (IR, w), 1440–1450 (IR, m; R, w); 1480 (IR, s; R, vw), 1580 (IR, s; R, vs), 2990 (IR, w), 3010 (R, w), 3050–3060 (IR, m; R, s), 3140 (R, w). The compounds $Zn_4(SPh)_8(ROH)$, as concentrated mulls, each show in addition one R-dependent absorption band: R = CH_3, 990 (IR, m); R = C_2H_5, 857 (IR, m); R = 1-C_3H_7, 976 (IR, m); R = 1-C_4H_9, 957 (IR, m). These absorptions, which are not reduced in intensity when the samples are exposed to dynamic vacuum at room temperature, confirm the presence of coordinated alcohol in these compounds. In each compound the frequency of the coordinated alcohol absorption is close to that of the most intense IR absorption of the corresponding pure liquid alcohol in this region, in which C–O stretching vibrations contribute (CH_3OH, 1030; C_2H_5OH, 880; 1-C_3H_7OH, 966; 1-C_4H_9OH, 952 cm⁻¹). Higher frequency absorptions representing O–H vibrations are not apparent in $Zn_4(SPh)_8(ROH)$, which is consistent with the O–H - - - S hydrogen bonding found in the crystal structure.

All samples of $[Zn_4(SPh)_8(NCCH_3)]_n$ show weak, sharp absorptions at (IR, R) 2244, 2280, and 2307 cm⁻¹, not diminished on pumping at room temperature.

Crystallography. Polycrystalline diffraction patterns of $Zn_4(SPH)_8(ROH)$, R = CH_3, C_2H_5, 1-C_3H_7, 1-C_4H_9, reveal that they all have the same crystal structure, with small variations in lattice dimension. The powder pattern of $[Zn_4(SPh)_8(NCCH_3)]_n$, dominated by an intense spacing of 12.50 Å, is different.

Single crystals of $Zn_4(SPh)_8(CH_3OH)$ were obtained by the slow polymerization reaction described above. The space group was determined to be $P2_12_12_1$ by Weissenberg photography, and unit-cell dimensions were obtained using reflections accurately centered with a Siemens diffractometer, using Cu Kα radiation: a = 16.529 (2) Å, b = 22.129 (3) Å, c = 14.241 (2) Å, Z = 4 ($x Zn_4S_8OC_{49}H_{44}$, mol wt 1166.88), d_{obsd} = 1.52 g cm⁻³, d_{calcd} = 1.49 g cm⁻³. Crystals of this compound suffer X-radiation damage which results in changed cell dimensions and eventually crystal cleavage parallel to (010). This crystal decomposition is accelerated by the chemical oxidant dioxygen, but is dependent on irradiation and has not been observed with dioxygen alone. The crystal used for diffraction intensity measurements was coated with shellac, which reduced the rate of decay of diffraction quality. Reflections were measured in shells of increasing 2θ to a maximum of 100°, beyond which there were very few observed reflections: scan width = 1.2–1.6°; counting time variable, about 29 s, but the same for both peak (N_p counts) and background (N_b counts); $I = N_p - N_b$; $\sigma(I) = [N_p + N_b + (0.04N_p)^2]^{1/2}$.
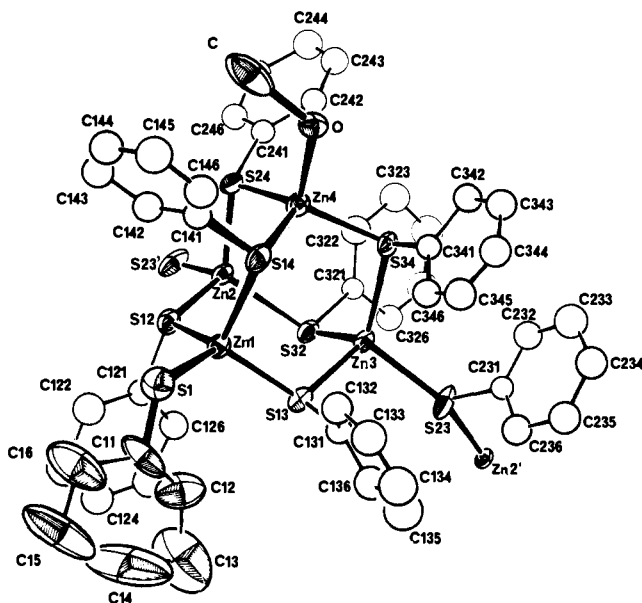
Figure 1. The [(μ-SPh)₆Zn₄(CH₃OH)(SPh)] cluster, together with the intercluster bridging benzenethiolate ligand 23. The ellipsoids are drawn at 20% probability, and hydrogen atoms are omitted.

Figure 2. The linkage of Zn₄ clusters by bridging benzenethiolate parallel to c, and by CH₃OH- - -SPh hydrogen bonds, in crystalline *catena*-(μ-SPh)[(μ-SPh)₆Zn₄(CH₃OH)(SPh)]. Phenyl ring atoms are omitted.

At the end of data collection the standard reflection intensity had decreased by about 30%; an appropriate decay correction was applied to the data. Absorption corrections were made, using $\mu = 53.3$ cm^{-1} (Cu Kα). Of the 3015 independent reflections measured, 2344 had $I > \sigma(I)$ and were included in the structure analysis.

The program MULTAN revealed the locations of the four zinc atoms, the eight sulfur atoms, and the atom subsequently identified as methanol oxygen. The methanol carbon atom and most of the ring carbon atoms were located by difference Fourier methods, but it was also apparent that some ring atoms were poorly defined. After some least-squares refinement, omitting reflections with sin $\theta/\lambda < 0.1$, all 62 nonhydrogen atoms were located. Least-squares refinement of all positional parameters, anisotropic temperature factors for the zinc and sulfur atoms (for which real and imaginary corrections for anomalous dispersion were included[15]), and individual isotropic temperature factors for the oxygen and carbon atoms converged with discrepancy residuals $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.063$, $R_w = \{\Sigma w|\Delta F|^2/\Sigma w|F_o|^2\}^{1/2} = 0.053$. At this stage the dimensions of the phenyl ring on S1 (the only nonbridging benzenethiolate ligand) were abnormal and the thermal parameters were large. A difference map was examined, the ring was idealized, and all phenyl ring hydrogen atoms were included at calculated positions, with the isotropic temperature factor of each set equal to that of the bonded carbon atom. Further refinement of an individual atom model, including refinement and analysis of anisotropic temperature factors for benzenethiolate ring 1 and methanol atoms, indicated that these two groups could be described only with low accuracy.

During the latter stages of the least-squares refinement the population of the methanol carbon atom was varied (with $B = 10$ Å^2, comparable with the thermal motion of surrounding atoms). A multiplicity of 0.80 (3) was obtained, with slightly poorer structure factor agreement and structure dimensions. This confirmed the conclusion from the analytical and IR data that the terminal ligand on Zn4 was methanol.

It was concluded that the terminal ligands methanol and benzenethiolate 1 (which are joined by an intercluster hydrogen bond) occupy regions of the crystal where the radiation-induced decomposition and resultant loss of crystallinity are most pronounced. It was apparent that further structure modeling with anisotropically vibrating groups for the phenyl rings would not advance the extraction of chemically desirable information from the poor data available. The refined structure presented here is the enantiomorph of lower refined R (Friedel pairs were not measured, and no significance should be attached to the chirality presented), with Zn, S, ring 1, and methanol atoms vibrating anisotropically and other ring atoms isotropic: $R = 0.056$, $R_w = 0.044$, $\{\Sigma w|\Delta F|^2/(m - n)\}^{1/2} = 1.36$, $m = 2312$ data (sin $\theta/\lambda \geq 0.1$), $n = 349$ parameters.

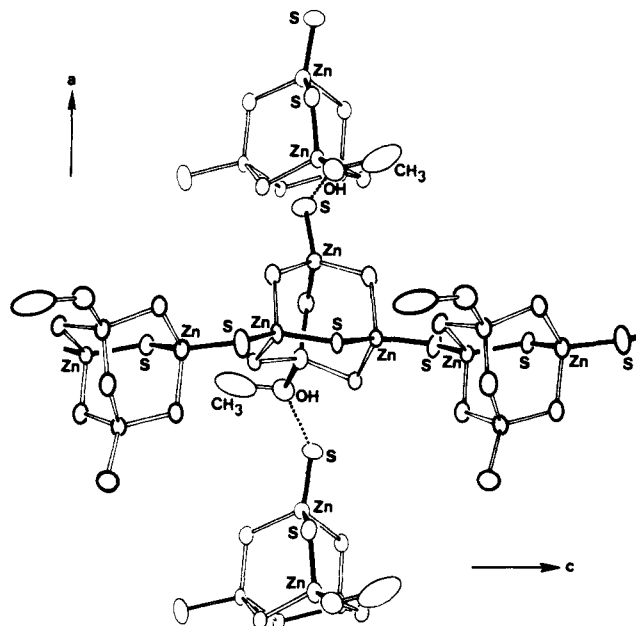Figure 1 shows the contents and labeling of the asymmetric unit

(and related atoms S23′ and Zn2′), with thermal ellipsoids presented as refined without constraints. Figure 2 shows how the Zn₄ clusters are linked by bridging benzenethiolate (approximately along the c direction) and by one type of hydrogen bond. The zinc atoms are labeled Znp, $p = 1$–4; the terminal sulfur atom on Zn1 is S1; the sulfur atom bridging Znp and Znq is labeled Spq; S32 bridges Zn3 and Zn2 within one cluster, and S23 bridges Zn2 and Zn3 atoms on different clusters; phenyl ring carbon atoms on Spq are labeled Cpqr, $r = 1$–6, with Cpq1 bonded to Spq; the hydrogen atom bonded to Cpqr is HCpqr; the methanol atoms are labeled O and C.

Atom fractional coordinates and their estimated standard deviations are given in Table I. A summary of atomic vibrational amplitudes is included with the supplementary material;[16] all individual atom vibrations are normal except those of the methanol carbon atom and the phenyl ring 1 carbon atoms.

Results

Synthesis. The reaction of benzenethiol with basic zinc carbonate or zinc hydroxide in appropriate solvents (acetone, lower alcohols at low temperature) generates solutions containing very soluble {Zn(SPh)₂} species. It is possible to isolate soluble complexes [Zn(SPh)₂(solvent)$_x$] from these solutions, and these compounds, which are presumed to be structurally molecular, will be described in a separate publication.

When dissolved in alcohols these soluble complexes undergo polymerization reactions, at rates which increase strongly with concentration and with temperature above ambient, to yield isostructural crystalline compounds [Zn₄(SPh)₈(ROH)], R = CH₃, C₂H₅, 1-C₃H₇, 1-C₄H₉. These compounds, which have only slight solubility in alcohols, are one-dimensional polymers in the crystalline state. The crystal structure, determined for the methanol derivative, is presented in Figures 1 and 2. The repeating unit is a cluster of four zinc atoms, arrayed approximately as a tetrahedron and bridged by six benzenethiolate ligands along the edges of the tetrahedron. Approximately tetrahedral coordination around each zinc atom is completed by a fourth ligand, which is terminal benzenethiolate at Zn1, methanol at Zn4, and the intercluster bridging benzenethiolate ligand (23) at Zn2 and Zn3. The formulation of these compounds is therefore *catena*-(μ-SPh)[(μ-SPh)₆Zn₄(ROH)(SPh)]. The linear polymer chains are linked by intercluster hydrogen bonding of the methanol proton to the sulfur atom of the terminal benzenethiolate ligand.

Table I. Atomic Coordinates for catena-(μ-SPh)[(μ-SPh)6Zn4(CH3OH)(SPh)][a]

atom	x	y	z	atom	x	y	z
Zn(1)	0.4736(1)	0.3831(1)	0.0226(1)	C(141)	0.4315(9)	0.2639(7)	−0.1168(11)
Zn(2)	0.2822(1)	0.4764(1)	−0.0694(1)	C(142)	0.4379(10)	0.3002(7)	−0.1920(13)
Zn(3)	0.2863(1)	0.4167(1)	0.1845(1)	C(143)	0.4621(11)	0.2774(9)	−0.2844(13)
Zn(4)	0.2683(1)	0.3128(1)	−0.0177(1)	C(144)	0.4775(12)	0.2181(10)	−0.2880(15)
S(1)	0.6056(3)	0.3630(2)	−0.0065(4)	C(145)	0.4768(13)	0.1820(10)	−0.2178(18)
S(12)	0.4214(2)	0.4571(2)	−0.0807(3)	C(146)	0.4552(11)	0.2035(9)	−0.1241(14)
S(13)	0.4286(2)	0.4185(2)	0.1683(2)	C(231)	0.2461(9)	0.3769(6)	0.4097(10)
S(14)	0.4036(2)	0.2907(2)	−0.0035(3)	C(232)	0.1808(10)	0.3446(8)	0.3937(12)
S(23)	0.2623(3)	0.4424(2)	0.3411(2)	C(233)	0.1696(12)	0.2907(10)	0.4437(15)
S(24)	0.2403(2)	0.3826(2)	−0.1361(2)	C(234)	0.2206(12)	0.2735(9)	0.5157(15)
S(32)	0.2506(2)	0.4990(2)	0.0877(2)	C(235)	0.2873(12)	0.3080(9)	0.5315(13)
S(34)	0.2097(2)	0.3347(2)	0.1272(3)	C(236)	0.3011(10)	0.3612(7)	0.4757(13)
O	0.2197(7)	0.2335(4)	−0.0653(8)	C(241)	0.1335(8)	0.3853(6)	−0.1550(9)
C	0.2369(15)	0.2128(14)	−0.1902(28)	C(242)	0.0806(10)	0.3428(7)	−0.1162(10)
C(11)	0.6633(10)	0.4207(9)	0.0426(23)	C(243)	0.0015(11)	0.3459(8)	−0.1341(12)
C(12)	0.6360(18)	0.4531(11)	0.1136(20)	C(244)	−0.0339(10)	0.3889(8)	−0.1937(12)
C(13)	0.6845(21)	0.4938(19)	0.1755(46)	C(245)	0.0199(11)	0.4285(7)	−0.2338(12)
C(14)	0.7460(32)	0.5032(22)	0.1232(57)	C(246)	0.1008(10)	0.4261(7)	−0.2166(11)
C(15)	0.7782(15)	0.4947(19)	0.0037(39)	C(321)	0.1441(8)	0.5037(6)	0.0976(10)
C(16)	0.7329(17)	0.4293(12)	−0.0274(28)	C(322)	0.0923(12)	0.4694(8)	0.0468(12)
C(121)	0.4825(9)	0.5224(7)	−0.0538(11)	C(323)	0.0088(12)	0.4705(8)	0.0591(13)
C(122)	0.5543(13)	0.5284(9)	−0.1014(14)	C(324)	−0.0185(11)	0.5125(9)	0.1264(15)
C(123)	0.6025(13)	0.5812(12)	−0.0790(17)	C(325)	0.0266(13)	0.5484(8)	0.1746(13)
C(124)	0.5767(13)	0.6214(9)	−0.0151(14)	C(326)	0.1093(11)	0.5413(7)	0.1627(11)
C(125)	0.5084(13)	0.6155(9)	0.0283(14)	C(341)	0.2346(10)	0.2677(6)	0.1952(10)
C(126)	0.4546(10)	0.5642(8)	0.0115(12)	C(342)	0.1726(10)	0.2230(8)	0.1992(12)
C(131)	0.4718(9)	0.3745(7)	0.2588(12)	C(343)	0.1942(12)	0.1723(8)	0.2582(14)
C(132)	0.5009(11)	0.3172(9)	0.2443(14)	C(344)	0.2664(13)	0.1707(8)	0.3027(13)
C(133)	0.5383(13)	0.2856(10)	0.3215(17)	C(345)	0.3214(11)	0.2130(9)	0.2972(13)
C(134)	0.5433(14)	0.3159(12)	0.4018(18)	C(346)	0.3040(10)	0.2635(8)	0.2432(12)
C(135)	0.5178(15)	0.3703(13)	0.4203(19)				
C(136)	0.4824(11)	0.4050(9)	0.3439(15)				

[a] Estimated standard deviations, in parentheses, refer to the least significant digit(s) quoted.

Crystals of these alcohol-containing polymers are chemically stable with respect to oxidation by dioxygen, alcohol loss at low pressure, and hydrolysis at room temperature. A single IR absorption, R dependent in the range 850–990 cm^{-1}, is assigned as largely C–O stretch for the coordinated alcohol. The methanol derivative, at least, when subjected to X-radiation undergoes crystal damage which appears to be localized in the vicinity of the hydrogen-bonded methanol and benzenethiolate ligands.
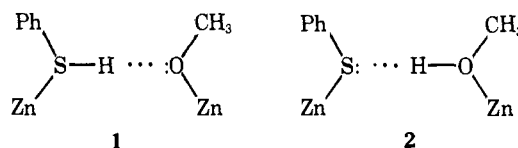
The polymers catena-(μ-SPh)[(μ-SPh)6Zn4(ROH)(SPh)], and also the molecular complexes [Zn(SPh)2(solvent)$_x$], dissolve in acetonitrile, but the resulting dissolved species, even at low concentration and room temperature, undergo another polymerization reaction to form a crystalline compound insoluble in acetonitrile. The IR spectrum of this compound indicates the presence of coordinated acetonitrile, and the analytical data suggest the composition [Zn4(SPh)8(NCCH3)]$_n$, albeit with some uncertainty. Definitive characterization by means of crystal structure determination has been frustrated by difficulty in obtaining adequate crystals, but is being pursued.

Structure of catena-(μ-SPh)[(μ-SPh)6Zn4(CH3OH)(SPh)]. In the crystal the Zn4 clusters are linked (see Figure 2) by bridging benzenethiolate ligands in the c direction and by hydrogen bonds in the a and b directions (a consequence of the twofold screw axes parallel to a and b). Selected interatomic distances and angles are set out in Tables II and III. The ranges of values for chemically comparable dimensions are much larger than the calculated estimated standard deviations of individual dimensions, which in part indicates that the latter are unrealistically low. The following is a statistical summary of chemically comparable dimensions, expressed as dimension, sample size, mean value, esd of sample, esd of mean value: Zn–S$_{bridging}$, 14, 2.347, 0.023, 0.006 Å; zinc coordination an-

gles, 24, 109.4, 6.6, 1.3°; Zn–S$_{br}$–Zn (intracluster), 6, 109.1, 5.1, 2.1°; S–C, 8, 1.78, 0.02, 0.01 Å; Zn–S–C, 15, 107.4 3.0, 0.8°; C–C$_{ring}$ (excluding ring 1), 42, 1.376, 0.050, 0.008 Å; intra-ring angles (excluding ring 1), 42, 120.0, 3.7, 0.6°; Zn- -Zn (intracluster), 6, 3.83, 0.12, 0.05 Å; S$_{br}$- -S$_{br}$ (intracluster), 12, 3.82, 0.18, 0.05 Å.

The equal mean values of the nonbonding Zn- -Zn and S$_{br}$- -S$_{br}$ distances within the cluster, and the tetrahedral mean value for the intracluster angle Zn–S$_{br}$–Zn, indicate the absence of symmetric distortion of the cluster from idealized geometry. There is a slight but significant distortion of the cluster at Zn4, in that the O–Zn–S$_{br}$ angles are all less than 109.5°, the S$_{br}$–Zn- -S$_{br}$ angles are greater than 109.5°, and the Zn- -Zn distances involving Zn4 are distinctly shorter than the others. The implication of this is that the Zn4–methanol coordination is slightly weaker than the coordination of Zn by bridging benzenethiolate. No significance is attached to other nonsystematic derivations from the mean dimensions listed above.[17] This cluster, like others,[14] is angularly floppy.

The distance between the S1 and O atoms of contiguous clusters, 3.03 Å, is clearly indicative of the presence of the hydrogen bond linking these two atoms. The hydrogen atom could not be located in this X-ray investigation. Although there is little reason, on the basis of known acidities, to expect protonation of coordinated benzenethiolate, 1, rather than coor-

1　　　　　　　　　**2**

dinated methoxide, 2, the question arises concerning structural differentiation of these alternatives. No differentiation is

Table II. Selected Interatomic Distances (Å) in *catena*-(μ-SPh)-[(μ-SPh)$_6$Zn$_4$(CH$_3$OH)SPh)]

Zinc Coordination		Nonbonded Cluster Dimensions	
Zn1-S1	2.265(4)		
Zn1-S12	2.364(3)	Zn1--Zn2	3.998(3)
Zn1-S13	2.339(3)	Zn1--Zn3	3.932(3)
Zn1-S14	2.380(4)	Zn1--Zn4	3.777(3)
Zn2-S12	2.346(4)	Zn2--Zn3	3.850(2)
Zn2-S23^a	2.322(4)	Zn2--Zn4	3.701(2)
Zn2-S24	2.385(3)	Zn3--Zn4	3.696(2)
Zn2-S32	2.350(3)		
Zn3-S13	2.365(4)	S12--S13	3.649(5)
Zn3-S23	2.336(3)	S12--S14	3.854(5)
Zn3-S32	2.360(3)	S12--S24	3.508(5)
Zn3-S34	2.356(4)	S12--S32	3.819(5)
Zn4-S14	2.297(4)	S34--S13	4.108(6)
Zn4-S24	2.333(3)	S34--S14	3.832(5)
Zn4-S34	2.331(4)	S34--S24	3.929(5)
Zn4-O	2.045(8)	S34--S32	3.740(5)
		S13--S14	3.761(5)
Ligands		S14--S24	3.872(5)
O-C	1.87(4)	S24--S32	4.101(5)
S1-C11	1.74(2)	S32--S13	3.627(5)
S12-C121	1.80(1)		
S13-C131	1.77(1)		
S14-C141	1.78(1)	**Hydrogen Bond**	
S23-C231	1.77(1)		
S24-C241	1.79(1)	O--S1^b	3.03(1)
S32-C321	1.77(1)		
S34-C341	1.82(1)		

^{a} ($\frac{1}{2} - x$, $1 - y$, $-\frac{1}{2} + z$). ^{b} ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $- z$).

Table III. Selected Interatomic Angles (deg) in *catena*-(μ-SPh)-[(μ-SPh)$_6$Zn$_4$(CH$_3$OH)(SPh)]

Zinc Coordination		Ligands	
S1-Zn1-S12	112.0(2)	Zn1-S12-Zn2	116.2(1)
S1-Zn1-S13	122.3(2)	Zn1-S13-Zn3	113.4(1)
S1-Zn1-S14	105.7(1)	Zn1-S14-Zn4	107.7(1)
S12-Zn1-S13	101.8(1)	Zn3-S23-Zn2^b	140.1(2)
S13-Zn1-S14	105.7(1)	Zn2-S24-Zn4	103.3(1)
S14-Zn1-S12	108.7(1)	Zn2-S32-Zn3	109.7(1)
S12-Zn2-S24	95.7(1)	Zn3-S34-Zn4	104.1(1)
S12-Zn2-S23^a	114.4(2)	Zn1-S1-C11	108.2(6)
S12-Zn2-S32	108.8(1)	Zn1-S12-C121	102.6(4)
S32-Zn2-S23^a	106.7(1)	Zn2-S12-C121	112.9(5)
S32-Zn2-S24	120.0(1)	Zn1-S13-C131	109.6(5)
S24-Zn2-S23^a.	111.3(1)	Zn3-S13-C131	108.7(4)
S23-Zn3-S13	105.0(1)	Zn1-S14-C141	107.5(4)
S23-Zn3-S34	115.3(1)	Zn4-S14-C141	104.0(4)
S23-Zn3-S32	109.1(1)	Zn3-S23-C231	110.7(4)
S13-Zn3-S32	100.3(1)	Zn2^b-S23-C231	106.5(5)
S13-Zn3-S34	120.9(1)	Zn2-S24-C241	108.5(4)
S32-Zn3-S34	104.9(1)	Zn4-S24-C241	109.1(4)
O-Zn4-S14	103.2(3)	Zn2-S32-C321	108.0(4)
O-Zn4-S24	104.5(3)	Zn3-S32-C321	104.4(4)
O-Zn4-S34	108.0(3)	Zn3-S34-C341	108.8(5)
S14-Zn4-S24	113.5(1)	Zn4-S34-C341	101.9(4)
S24-Zn4-S34	114.8(1)		
S34-Zn4-S14	111.8(1)		
Hydrogen Bonding			
Zn1-S1--O^c	132.7(3)	Zn4-O--S1^d	137.5(4)
C11-S1--O^c	92.3(6)	C-O--S1^d	104.1(8)

^{a} ($\frac{1}{2} - x$, $1 - y$, $-\frac{1}{2} + z$). ^{b} ($\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$). ^{c} ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$). ^{d} ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$).

possible on the basis of angles at O and S1 (see Table III), particularly in view of the well-characterized bending of O-H---S bonds.[18] Given appropriate comparison data, the values of the Zn-O and Zn-S distances should distinguish between **1** and **2**. A reliable prediction of 2.28$_3$ Å can be made for the Zn1-S1 distance when the benzenethiolate is deprotonated, using[19] data from the structures of [Zn(SPh)$_4$]$^{2-}$,[11] [Co(SPh)$_4$]$^{2-}$,[11] and [(μ-SPh)$_6$(CoSPh)$_4$]$^{2-}$.[14] Protonation of S1 would be expected to give an Zn1-S1 distance ca. 0.1 Å longer than 2.28$_3$ Å, rather than the slightly shorter 2.26$_5$ Å observed. Comparison distances in similar environments for zinc-methanol coordination and the contrasted terminal zinc methoxide coordination are not plentiful. Values for alcohol and comparable uncharged oxygen ligands (Å) follow: Zn-HOCH$_3$ = 2.081 (3), 2.080 (4) in six-coordinate (Zn-(tta)$_2$(HOCH$_3$)$_2$;[20] Zn-HOC$_2$H$_5$ = 2.068 (7) in five-coordinate Zn(bzac)$_2$(HOC$_2$H$_5$);[21] Co-HOCH$_3$ = 2.13, 2.07 in [CoCl$_2$(HOCH$_3$)$_4$];[22] Zn-OH$_2$ = 2.04, 2.11 in [Cl$_2$ZnOH$_2$]$^-$.[23] For methoxide-zinc coordination structural data is available only for triply bridged methoxide: Zn-O = 2.09 Å in (μ$_3$-OCH$_3$)$_4$(ZnCH$_3$)$_4$.[24] The M-O distance for triply bridging alkoxide is expected to be ca. 0.15 Å longer than nonbridging coordination. In summary, these data give predicted values for the Zn-S and Zn-O distances of 2.38 and 1.95 Å, respectively, for structure **1** and 2.28 and 2.05 Å for structure **2**. The observed distances of 2.265 and 2.05 Å are therefore clearly indicative of the proton location shown in **2**.

The stereochemistry around S23, the intercluster bridging thiolate sulfur atom, is unusual in that Zn3-S23-Zn2' (see Figure 1) is 140°, much larger than the mean value of 109° for Zn-S$_{br}$-Zn angles at the intracluster bridging ligands. Concomitant with this, the angle between the S-C$_\alpha$ vector (S23-C231) and the normal to the Zn3-S23-Zn2' plane is 68.7°, instead of the usual tetrahedral value of 35.8°. Thus the stereochemistry at S23 is midway between tetrahedral and planar. The angle between the plane of the benzene ring of ligand 23 and the Zn3-S23-Zn2' plane is 75.2°.

Polymerization and Depolymerization Reactions. The observations on the formation of and transformations between {Zn(SPh)$_2$} derivatives of differing solubilities are summarized in Scheme I. Two species, I and III, have substantial solubilities in the solvents indicated, while the other two, II and IV, are very much less soluble, and appear to dissolve only by reaction to form the more soluble species. Structural information is available on one type only, II, but it is reasonably presumed that the solubility differences reflect different structure types, and that I and III are structurally molecular (nonpolymeric) while IV, like II, is structurally nonmolecular.

The species and transformations shown in Scheme I appear to occur only when the PhS$^-$/Zn^{2+} molar ratio is very close to 2, which is a consequence of the synthetic method employed

Scheme I. Transformations of Zn(SPh)$_2$ Derivatives^a

^{a} Solvent = ROH (R = CH$_3$, C$_2$H$_5$, 1-C$_3$H$_7$, 1-C$_4$H$_9$), acetone, or THF. The II → I change is indicated by the slight solubility of II in ROH and THF.

here. Solutions with PhS^-/Zn^{2+} ratio greater than 2 do not form compounds II or IV under comparatively vigorous polymerization conditions, but instead yield a different set of anionic complexes. With PhS^-/Zn^{2+} less than 2 the formation of II or IV has not been observed. The presence of excess protonated ligand PhSH appears to retard the I → II polymerization when $PhS^-/Zn^{2+} = 2$.

Although it is very probable that the transformations between I, II, III, and IV involve structural changes in the bridging by benzenethiolate ligands, it is evident that zinc-solvent coordination is an influential structural feature. Details must await further crystal-structure determinations. However, it can be noted that the general behavior in the $Zn(II)/SPh$ system is different from that in the $M(I)/SPh$ (M = Cu, Ag^{25}) and $Cr(III)/SPh^{26}$ systems, where the formation of insoluble polymers $[MSPh]_{\infty}$ and $[Cr(SPh)_3]_{\infty}$ is observed to be solvent dependent. In these cases the polymers are the result of dissociation of $PhS^-(solv)$ from structurally molecular anionic complexes, and the solvent effects arise as differential influences on the activities of the anionic species in equilibrium.

Discussion

The zinc thiolate cluster reported here is a further example of the ubiquitous adamantane structure type.[14] The same cluster coordination occurs, for complexes with thiolate ligands, in $[(\mu-SPh)_6(MSPh)_4]^{2-}$ (M = Co, Zn)[14] and $[(\mu-SPh)_6(MSPh)_2(MCl)_2]^{2-}$ (M = Co, Zn),[14,27] and is expected in $(Me_4N)_2[Zn_4(SPh)_9Cl]^{27}$ and $(Me_4N)_2[Cd_4(SPh)_{10}]$.[27] The same structure occurs with the uncharged thiourea ligand (tu) in $[(\mu-tu)_6(Cutu)_4]^{4+}$.[28] With the dianionic ligand S^{2-}, zinc again occurs with this structure, but in three-dimensionally nonmolecular form, zinc blende. This cluster structure is quite distinct from the centrally ligated tetrahedral Zn_4 cluster type, for instance, $SZn_4(S_2AsMe_2)_6$,[29] which occurs with chelating ligands able to avoid bridging metals with a single donor atom. It appears reasonable to predict more widespread occurrence of the adamantane cluster $\{(\mu-SR)_6(ML)_4\}$ in complexes with monothiolate ligands and metals usually adopting tetrahedral stereochemistry.

The compounds *catena*-$(\mu-SPh)[(\mu-SPh)_6Zn_4(ROH)(SPh)]$ are significant in demonstrating three new types of coordination of zinc by unconstrained monodentate thiolate ligand, namely, $\{(\mu-SR)_4Zn\}$, $\{(\mu-SR)_3ZnSR\}$, and $\{(\mu-SR)_3Zn-O(H)R\}$, to add to the previously known type $\{Zn(SR)_4\}$.[11] The $\{(\mu-SR)_3Zn-O(H)R\}$ coordination of Zn4 is of particular interest as the closest synthetic analogue of the primary catalytic site of horse LADH, where zinc is bound by two cysteine and one histidine residues, with the fourth coordination site almost certainly that of alcohol substrate binding.[5,30] The enzymes studied crystallographically contained water[5] or inhibitor[30] at the fourth zinc coordination site. The present compounds provide the first example with alcohol bound, and as such provide reference structural data for the *substrate-bound* active site of LADH. Alcohols other than methanol and ethanol may be incorporated in this model.

catena-$(\mu-SPh)[(\mu-SPh)_6Zn_4(ROH)(SPh)]$ and the soluble compounds $[Zn(SPh)_2(ROH)_x]$, the latter still incompletely characterized but no doubt with similar coordination, should be valuable as model systems for LADH reactivity studies.

The results reported here bear also on the formation and structure of the metallothioneins, inducible low molecular weight mammalian proteins which sequester excess zinc, cadmium, mercury, and copper. Equine renal metallothionein $1B^{6,8}$ is a single-chain protein containing 61 amino acids of which 20 are cysteine, and 7 (zinc + cadmium) atoms; the sequence is known.[8] The metal-binding capacity (both kinetic and thermodynamic) of these proteins is pronounced.[7,31,32] Additional data[9,10,33] (X-ray PES, CD, ^1H NMR, ^{113}Cd NMR) indicate that all cysteine residues bind metals, that

cadmium at least is bound by four cysteine residues, and that the protein in aqueous solution has a random coil structure with rigidity conferred by metal binding. These data suggest strongly that bridging of metal ions by cysteinate sulfur occurs in the metallothioneins, and a recent hypothesis of linear oligomer structure incorporates such bridges.[10] Cysteinate bridging in proteins is not yet established crystallographically.[34] In view of the preponderance of clusters in zinc thiolate systems where the thiolate/metal ratio is less than 4, and also the occurrence of cadmium thiolate clusters,[35,36] it is reasonable to suggest further that adamantane-type clusters may occur in the metallothionein storage proteins. Such clusters would be structurally distinct from the cubane-type clusters of the ferredoxins.[37] Three points can be made. First, the protein stoichiometry $M_7(cys)_{20}$ can be accounted for, for example, by $\{(\mu-cys)_6(Mcys)_4\} + \{(\mu-cys)_2(M(cys)_2)_2\} + \{M(cys)_4\}$. Second, metallothionein formation and degradation could occur via reactions analogous to the cluster formation, polymerization, and depolymerization processes in the Zn/SPh system. Third, and most important, is the stereochemical requirement for a polypeptide chain encompassing a cluster. This is a complicated question which will be detailed elsewhere, but three arguments can be advanced: (1) the number density of cysteine residues required for a $(\mu-cys)_6(Mcys)_4$ cluster is not very different from that of $M(cys)_4$ established in two proteins;[5,38] (2) the geometrical possibility of a decacysteinyl polypeptide folding over the surface of the adamantane-type cluster, in which there are many degress of freedom for orientation of S–C vectors, is supported by model-building investigations;.(3) the spatial demands of cysteine are comparable with those of the phenyl ring, and there are no steric interferences between contiguous phenyl groups in $[(\mu-SPh)_6(MSPh)_4]^{2-}$ [14] or *catena*-$(\mu-SPh)[(\mu-SPh)_6M_4(CH_3OH)(SPh)]$.

Supplementary Material Available: A tabulation of the refined atomic parameters, a summary of atomic thermal motion, and a listing of F_o and F_c (10 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Crystal Structures of [(Ph₃P)₂N]₃⁺{Na[Mo₃(CO)₆(NO)₃(μ₂-OCH₃)₃(μ₃-O)]₂}³⁻, an Unusual Organometallic Triple Ion, and [Me₄N]⁺[Mo₃(CO)₆(NO)₃(μ₂-OCH₃)₃(μ₃-OCH₃)]⁻

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Abstract: The compounds [(Ph₃P)₂N]₃⁺{Na[Mo₃(CO)₆(NO)₃(μ₂-OCH₃)₃(μ₃-O)]₂}³⁻ (**1**) and [Me₄N]⁺[Mo₃(CO)₆(NO)₃(μ₂-OCH₃)₃(μ₃-OCH₃)]⁻ (**2**) are synthesized by refluxing Mo(CO)₆, NaNO₂, and NaOH in methanol and adding the appropriate cation. X-ray diffraction studies reveal that **1** crystallizes in space group $P\bar{1}$ [a = 15.057 (6) Å, b = 15.689 (6) Å. c = 17.079 (7) Å, α = 112.91 (3)°, β = 65.90 (3)°, γ = 112.50 (3)°, V = 3270 (2)·Å³, ρ(obsd) = 1.49 (1) g cm⁻³, ρ(calcd) = 1.499 g cm⁻³ for Z = 1], while **2** crystallizes in space group $P2_1/m$ [a = 9.678 (4) Å, b = 11.763 (7) Å, c = 13.162 (5) Å, β = 119.30 (2)°, V = 1307 (1) Å³, ρ (obsd) = 1.89 (1) g cm⁻³, ρ(calcd) = 1.891 g cm⁻³ for Z = 2]. Data were collected with Mo Kα radiation to a 2θ limit of 50°. Standard Patterson, Fourier, and least-squares techniques resulted in final agreement factors: R = 9.5%, R_w = 10.9% for 4674 reflections greater than 3σ for **1**; R = 4.8%, R_w = 5.9% for 2017 reflections greater than 3σ for **2**. The anionic units of both **1** and **2** consist of equilateral triangles of molybdenum atoms; two carbonyl ligands and one nitrosyl ligand are terminally bonded to each Mo. The nonbonding Mo–Mo distances of 3.297 (2) Å for **1** and 3.428 (1) Å for **2** are bridged by methoxy ligands. **1** differs from **2** in that for **1** the Mo triangle is capped by a triply bridging oxygen atom, while **2** is capped by a triply bridging methoxy ligand. **1** exists as a triple ion in the solid state, with two Mo₃ units "sandwiching" a sodium ion such that the Na⁺ ion is octahedrally coordinated by the six oxygen atoms of the methoxy ligands. **1** also contains an unusual example of a linear P–N–P linkage in the (Ph₃P)₂N⁺ cation. Conductivity studies indicate that the triple ion of **1** persists in solution, and that additional ion pairing to the bulky counterions occurs.

Introduction

Few metal carbonyl cluster compounds of the group 6B metals (Cr, Mo, W) are known,[3] due in part to the electron-deficient nature of transition metals on the left side of the periodic table. As an alternative to large charge buildup on these clusters, we hoped that the replacement of CO by the isoelectronic NO⁺ could produce stable clusters with reduced charge. In order to explore group 6B carbonyl nitrosyl compounds, we have synthesized and characterized (μ₂-H)W₂(CO)₉(NO) and (μ₂-H)W₂(CO)₈(NO)[P(OCH₃)₃].[4]

To further our studies, an attempt was made to produce [Mo(CO)₄(NO)]⁻ by refluxing Mo(CO)₆, NaNO₂, and KOH in methanol, since an identical reaction using Fe(CO)₅ produced [Fe(CO)₃NO]⁻.[5] Instead of the expected product, two unusual molybdenum carbonyl cluster ions were isolated: [(Ph₃P)₂N]₃⁺{Na[Mo₃(CO)₆(NO)₃(μ₂-OCH₃)₃(μ₃-O)]₂}³⁻ (**1**) and [Me₄N]⁺[Mo₃(CO)₆(NO)₃(μ₂-OCH₃)₃(μ₃-OCH₃)]⁻ (**2**). We report the synthesis, characterization, and crystal structures of these compounds here.

Experimental Section

All operations were carried out in a prepurified nitrogen atmosphere using Schlenk techniques. Solvents were dried, deaerated, and stored under nitrogen over activated Linde 3A molecular sieves. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer and calibrated against polystyrene. Solution spectra were recorded using CaF₂ cells with a 0.5-mm spacer and solid spectra were recorded using KBr disks. Room temperature ¹H NMR spectra were recorded on Varian A-60A and T-60 spectrometers using Me₄Si as internal standard. Conductivities were measured at 25 °C on a YSI-31 conductivity bridge. Melting points were determined in sealed capillaries and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by PCR Inc., Gainesville, Fla. Metal carbonyls were purchased from Pressure Chemical Co., and