Of the three types of Cu–Cu bridge, two are monatomic oxygen bridges linking the apical coordination site of one copper atom with a basal site of an adjacent metal ion. Though recent work has clearly demonstrated that detectable copper–copper magnetic interactions can occur *via* this type of linkage, such interactions have invariably been substantially smaller than that observed in the present case.[37–40] Thus a recent tabulation of magnetic parameters for oxo-bridged dimers of this structure type[41] lists values of $2J$ ranging from -18 to $+40\ \mathrm{cm^{-1}}$. We thus consider it unlikely that the bridging oxygen atoms O(5) or O(7) could provide the major pathway for the observed magnetic coupling. In further support of this conclusion, we note the fact that the bridges formed by O(5) and O(7) are nonequivalent, with apical Cu–O distances of 2.318 (13) and 2.465 (14) Å, respectively. The conformity of the magnetic data to the dimer model would require that the two structurally different configurations be associated with interactions which are approximately equal, or which combine fortuitously to give the magnetic behavior of a dimer. Such an interpretation, though conceivable, is certainly unappealing. Finally, it should be noted that apical-to-basal Cu–O–Cu linkages, much like those observed in the present case, are found in anhydrous cupric propionate[35] and appear to have no significant influence on the magnetic properties of the anhydrous salt. That the observed pairwise interaction in the anhydrous cupric alkanoates occurs between the carboxylate-bridged copper atoms rather than between the oxo-bridged pairs is concluded from the very similar magnetic susceptibility behavior of the discrete dimer $[\mathrm{Cu(O_2CCH_3)_2\cdot H_2O}]_2$ and the anhydrous salts.[5,42] We conclude that the magnetic susceptibility behavior of bis(propionato)-*p*-toluidinecopper(II) can best be accounted for by a pairwise interaction between Cu(1) and Cu(2) for which the principal pathway is an indirect one involving the triatomic carboxylate bridges. Again it must be emphasized that other coupling terms may well be present, but are likely to be much smaller than the principal mode of interaction.

Finally, it is important to note that copper(II) propionate·*p*-toluidine conforms to all of the criteria which have commonly been taken to infer for a cupric carboxylate adduct a structure of the dimeric copper(II) acetate hydrate type. These criteria include the $\mathrm{Cu(O_2CR)_2\cdot L}$ stoichiometry, conformity of the temperature dependence of the magnetic susceptibility to eq 1, and the presence of an absorption band at *ca.* 3800 Å, both in the solid state and in solution. Clearly these criteria are insufficient in themselves to specify the dimeric copper(II) acetate structure and must be amended.

Acknowledgments. Support of this work by the National Science Foundation is gratefully acknowledged. We also thank Mr. Patrick Grant for his help with the neutron activation analysis.

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Synthesis and Structure of a Tetranuclear Zinc(II) Complex of *N*,*N*′-Dimethyl-*N*,*N*′-bis(β-mercaptoethyl)ethylenediamine

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Abstract: The preparation of a zinc derivative of the new ligand *N*,*N*′-dimethyl-*N*,*N*′-bis(β-mercaptoethyl)ethylenediamine is described. The molecular structure of a hydrate of the tetranuclear complex, $[\mathrm{Zn_2(C_8H_{18}N_2S_2)_2Cl_2}]_2\cdot 2\mathrm{H_2O}$, has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with a = 11.874 (3) Å, b = 10.260 (2) Å, c = 14.260 (3) Å, and β = 113.92 (1)°. The density of 1.782 g/cm³ calculated on the basis of two formulas per unit cell is in agreement with the measured density 1.778 (3) g/cm³. The structure was solved using 1156 independent, statistically significant reflections collected on a full-circle automated diffractometer. Refinement of all atoms including the water and methylene hydrogens led to a final value for the discrepancy index, R_1, of 0.054. The structure is a centrosymmetric array of four coplanar zinc atoms with four bridging mercaptide ligands. There are two types of zinc atoms, one with a strongly distorted tetrahedral $\mathrm{N_2S_2}$ donor atom set, and the other with a regular tetrahedral $\mathrm{Cl_2S_2}$ donor atom set. The lattice water is hydrogen bonded to chlorine atoms. The geometrical consequences of the sterically constraining ligand L are described.

In a study of the effect of steric strain on the electronic and redox properties of metal–sulfur complexes,[1] the ligand *N*,*N*′-dimethyl-*N*,*N*′-bis(β-mercaptoethyl)ethylenediamine (I) was designed.[2] The synthesis was achieved by mercaptoethylation of the parent diamine using ethylene monothiocarbonate.[3] In order to assess

[1] (a) D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, **94**, 1563 (1972); (b) W. J. Hu, K. D. Karlin, and S. J. Lippard, work currently in progress.

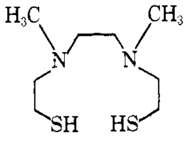
[2] Chemical control of this steric strain is synthetically possible by varying the number of methylene groups between the donor atoms in I.

[3] D. D. Reynolds, M. K. Massad, D. L. Fields and D. J. Johnson, *J. Org. Chem.*, **26**, 5109 (1961).

Table I. Final Positional and Thermal Parameters of the Nonhydrogen Atoms[a,b]

	x	y	z	β_{11}[c,d]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn(I)	−0.3404 (1)	0.1496 (2)	0.1226 (1)	6.0 (2)	7.3 (2)	4.9 (1)	−0.1 (2)	1.8 (1)	−0.4 (1)
Zn(II)	−0.3366 (1)	−0.1366 (2)	−0.0181 (1)	7.0 (2)	9.8 (2)	5.4 (1)	−0.2 (2)	2.4 (1)	−1.1 (1)
Cl(1)	−0.4112 (4)	−0.1869 (5)	0.1011 (3)	11.8 (5)	21.9 (8)	6.5 (3)	1.8 (5)	5.2 (3)	2.0 (4)
Cl(2)	−0.1827 (3)	−0.2700 (4)	−0.0079 (3)	9.0 (4)	12.2 (6)	8.0 (3)	3.2 (4)	2.9 (3)	−0.2 (3)
S(1)	−0.2676 (3)	0.0811 (4)	0.0050 (3)	7.5 (4)	9.7 (5)	5.7 (3)	−0.7 (4)	2.7 (3)	−1.1 (3)
S(2)	−0.4959 (3)	0.1469 (4)	0.1780 (3)	7.1 (4)	9.6 (5)	5.1 (3)	−1.0 (3)	2.5 (3)	−0.2 (3)
N(1)	−0.317 (1)	0.350 (1)	0.1459 (8)	7.4 (12)	7.0 (13)	5.7 (9)	2.2 (11)	3.5 (9)	2.1 (9)
N(2)	−0.166 (1)	0.128 (1)	0.2435 (9)	8.2 (12)	5.1 (14)	6.4 (10)	−0.4 (11)	1.2 (9)	−0.8 (9)
C(1)	−0.107 (1)	0.071 (2)	0.099 (2)	6.7 (16)	15.9 (27)	9.3 (17)	2.1 (18)	3.3 (13)	−3.5 (18)
C(2)	−0.090 (2)	0.041 (2)	0.208 (1)	8.4 (17)	9.5 (21)	7.7 (15)	1.9 (16)	3.7 (13)	1.3 (15)
C(3)	−0.116 (2)	0.261 (2)	0.258 (1)	6.4 (18)	12.0 (25)	6.6 (15)	0.6 (18)	0.2 (12)	−0.9 (16)
C(4)	−0.215 (1)	0.359 (2)	0.250 (1)	8.2 (18)	9.4 (19)	6.8 (13)	−2.2 (16)	2.6 (12)	−1.9 (13)
C(5)	−0.435 (1)	0.404 (2)	0.145 (1)	8.9 (19)	9.9 (20)	5.6 (12)	−0.1 (15)	2.9 (12)	−0.9 (13)
C(6)	−0.486 (1)	0.324 (2)	0.206 (1)	7.8 (16)	11.5 (21)	5.7 (11)	−0.6 (15)	4.0 (12)	−2.2 (14)
C(7)	−0.284 (1)	0.423 (2)	0.071 (1)	13.0 (19)	9.3 (18)	8.6 (14)	1.2 (16)	7.6 (14)	−0.5 (14)
C(8)	−0.170 (2)	0.074 (2)	0.341 (1)	14.6 (21)	16.3 (25)	5.0 (12)	3.0 (20)	2.1 (13)	2.9 (14)
OXY	−0.162 (1)	−0.295 (1)	0.277 (1)	15.8 (16)	20.6 (20)	10.6 (11)	4.3 (15)	4.9 (11)	2.3 (12)

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [d] Values reported are $\times 10^3$.



I

the stereochemical constraints imposed by the ligand when coordinated to a typically tetrahedral metal ion, a zinc derivative was prepared. The structure of a hydrated form, $Zn_2LCl_2 \cdot H_2O$ (L is the dianion of I), revealed by single-crystal X-ray diffraction methods, is described in this report.

Experimental Procedure and Results

Synthesis. The ligand (I) was synthesized by mercaptoethylation of *N,N'*-dimethylethylenediamine. To a refluxing mixture of 1.5 mol (132 g) of the diamine in 500 ml of anhydrous toluene, 1 mol (104 g) of ethylene monothiocarbonate was added dropwise over a 15-min period. Refluxing was continued for 15 hr under an efficient condenser. The cooled solution was washed with two 100-ml portions of water and dried over anhydrous magnesium sulfate. The toluene was removed by distillation under reduced pressure, leaving ~50% of the crude product. This was used without further purification. (*Caution: The ligand has been found to cause severe allergic reactions, and all contact of the compound or its vapor with the skin should be avoided.*)

The reaction of a saturated zinc chloride–methanol solution with I in ratio of 2:1, followed by recrystallization from water, yielded colorless prismatic crystals. After thorough drying, analysis showed the empirical formula to be Zn_2Cl_2L, where L is the dianion of I.

Anal. Calcd for $Zn_2C_8H_{18}N_2S_2Cl_2$: C, 23.55; H, 4.45; N, 6.86; S, 15.72; Cl, 17.38. Found: C, 23.71; H, 4.57; N, 6.57; S, 15.69; Cl, 17.38.

The crystals suitable for X-ray work were prepared after two or three times of recrystallization. The microcrystals were dissolved in a minumum amount of hot water and the saturated solution was allowed to evaporate at room temperature for a few days. Large prismatic crystals formed, which retain their crystalline character only in the presence of water vapor (*e.g.*, the atmosphere).

Collection and Reduction of X-Ray Data. The structural determination was carried out by single-crystal X-ray diffraction on the hydrated form of the compound, shown to be $[Zn_2Cl_2L]_2 \cdot 2H_2O$. The space group and approximate unit cell dimensions were determined by film methods on a precession camera. The observed Laue symmetry, $2/m$, and extinctions $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, established the space group to be $P2_1/c$.

The unit cell parameters were then refined by a least-squares technique to give the best fit between calculated and observed settings χ, Φ, and 2θ for 27 independent reflections, centered on a Picker full-circle automated X-ray diffractometer using Cu Kα (λ 1.5418 Å) radiation.[4] The results are a = 11.874 (3) Å, b = 10.260 (2) Å, c = 14.260 (3) Å, and β = 113.92 (1)°. The density of 1.778 (3) g/cm^3 measured by flotation in bromoform–carbon tetrachloride mixtures agrees with the calculated density, 1.782 g/cm^3, based on four formula units of $Zn_2C_8H_{18}N_2S_2Cl_2 \cdot H_2O$ per unit cell.

A crystal of approximate dimensions 0.16 mm along a^*, 0.22 mm along b^*, and 0.25 mm along c^*, and mounted along b^*, was sealed in a glass capillary and used for data collection. Data were measured out to a 2θ value of 41° using Zr-filtered Mo Kα radiation (λ 0.7107 Å) and the θ–2θ scan technique. A symmetric scan range of 1.5° in 2θ was used, plus the angular separation of Kα_1 and Kα_2, with individual 10-sec background counts recorded at both ends of the scan. The (223), (312), (33$\bar{1}$), and (23$\bar{5}$) reflections were used to monitor the crystal and instrument stabilities. In no case did the intensity of a standard vary by more than ±7.6% of its mean, and no systematic trend was observed. A total of 1686 reflections were measured including the $0kl$ and $0k\bar{l}$ equivalent forms which were averaged with an agreement factor based on F^2 of 0.025.

The observed intensities were corrected for background, use of attenuators, Lorentz, polarization, and absorption effects (μ 36.7 cm^{-1}) using the program ACAC-3.[4] The minimum and maximum calculated transmission factors are 0.55 and 0.65, respectively. A Wilson plot subsequently yielded an approximate absolute scale factor. Scattering factors for the zerovalent zinc, chlorine, sulfur, nitrogen, carbon, oxygen, and hydrogen atoms were obtained from the International Tables.[5] The calculated structure factors were corrected for the effects of anomalous dispersion of the zinc, chlorine, and sulfur atoms.[6] The integrated intensity corrected for background and attenuators is given by I, the standard deviation of which, $\sigma(I)$, was obtained from the expression $\sigma(I) = [E + (T_E/2T_B)^2(B_1 + B_2) + (\epsilon I)^2]^{1/2}$ where E is the total count in the peak plus background observed for time T_E, B_1 and B_2 are the background counts observed for time T_B at each end of the scan, and ϵ is an "ignorance factor"[7] assumed in this case to be 0.04. Weights used in the refinement, w, were assigned according to $4F^2/\sigma^2(F^2)$, where $\sigma(F^2)$ is the standard deviation of F^2 obtained from $\sigma(I)$ after absorption, Lorentz, and polarization corrections were applied.

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(4) Programs for the IBM 360-91 computer used in this work include local versions of MODE-1, the Brookhaven diffractometer setting and cell constant and orientation refinement program; GSET, the Prewitt diffractometer setting program; ACAC-3, a revised version of the Prewitt absorption correction and data reduction program; XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; CULS, a local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS); ORFFE, the Busing–Martin–Levy molecular geometry and error function program; and ORTEP, the Johnson thermal ellipsoid plotting program.

(5) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202, 204.

(6) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(7) (a) G. M. Brown and H. A. Levy, *J. Phys.* (*Paris*), **25**, 497 (1964); (b) R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, **19**, 260 (1965); (c) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

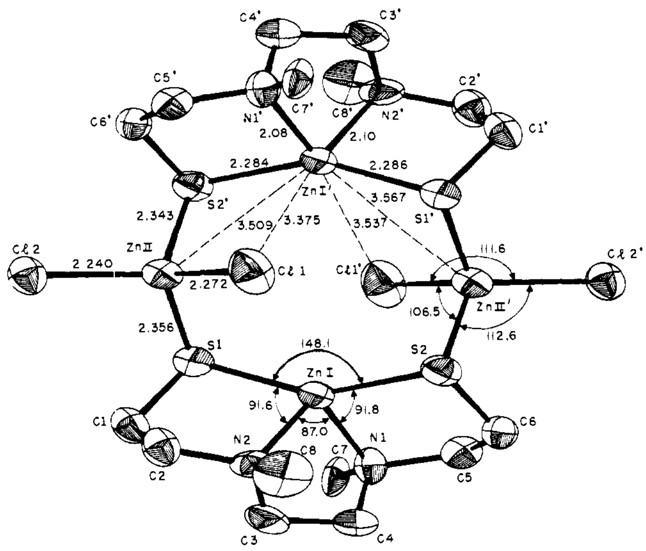

Figure 1. The tetranuclear cluster in $[Zn_2Cl_2L]_2 \cdot 2H_2O$ showing selected geometrical features. Standard deviations in bond distances are ±0.01 Å and in interbond angles ±0.4° or less (Tables II–IV). Primed and unprimed atoms are related by a crystallographically required inversion center. Angles not shown include S(1)-Zn(I)-N(1), 110.8°; S(2)-Zn(I)-N(2), 112.4°; S(1′)-Zn(II′)-S(2), 106.8°; Cl(1′)-Zn(II′)-S(1′), 109.2°; and Cl(2′)-Zn(II′)-S(1′), 110.0°

Only reflections which satisfied the condition $I > 3\sigma(I)$ were included in the refinement, a total of 1156 data points.

Determination and Refinement of the Structure. The atomic coordinates of the two crystallographically independent zinc atoms were determined from a Patterson synthesis.[4] The remaining nonhydrogen atoms were located in three subsequent electron density difference Fourier maps, phased on the heavy atoms. The discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ were 0.064 and 0.086, respectively, after the refinement on the positional parameters and anisotropic temperature factors of the 17 nonhydrogen atoms.

An electron density difference map revealed the location of the hydrogen atoms. The water and methylene hydrogen positional parameters were varied on further refinement cycles with their isotropic thermal parameters set at 4.7 Å^2. The water hydrogen atoms were first refined together with all the nonhydrogen atoms for six cycles, and their final parameter shifts were on the order of 0.01 of their standard deviations. The methylene hydrogen atoms were then refined with all the nonhydrogen atoms for two cycles after which their final parameter shifts were on the order of 0.1 of their standard deviations. The refinement was stopped here because the methylene hydrogen atoms began to oscillate on subsequent cycles with increasing amplitude. The final unweighted and weighted R factors are 0.054 and 0.069, respectively.[8]

The atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the last least-squares refinement cycle, are given in Tables I and II. The atomic labeling scheme and the orientation of the thermal ellipsoids are shown in Figure 1. Intramolecular bond distances and angles appear in Tables III and IV.

Discussion

The structure consists of a cyclic tetranuclear array of zinc atoms, all lying rigorously in a plane (Figure 1). Type I zinc atoms are each coordinated to one ligand L with a strongly distorted tetrahedral N_2S_2 donor atom set. The mercaptide groups form bridges to the other,

Table II. Atomic Positional Parameters for the Hydrogen Atoms[a,b]

	x	y	z
H(1O)	−0.18 (2)	−0.30 (2)	0.34 (1)
H(2O)	−0.20 (2)	−0.25 (2)	0.22 (1)
H(11)	−0.09 (2)	0.02 (2)	0.07 (1)
H(12)	−0.08 (1)	0.18 (2)	0.11 (1)
H(21)	−0.10 (2)	−0.05 (2)	0.21 (1)
H(22)	−0.02 (1)	0.03 (2)	0.29 (1)
H(31)	−0.09 (2)	0.28 (2)	0.20 (1)
H(32)	−0.07 (2)	0.26 (2)	0.30 (1)
H(41)	−0.26 (2)	0.34 (2)	0.29 (1)
H(42)	−0.15 (1)	0.45 (2)	0.27 (1)
H(51)	−0.49 (2)	0.38 (2)	0.08 (1)
H(52)	−0.40 (1)	0.49 (2)	0.21 (1)
H(61)	−0.59 (1)	0.38 (1)	0.19 (1)
H(62)	−0.44 (1)	0.33 (2)	0.28 (1)
H(71)[c]	−0.33	0.37	0.01
H(72)	−0.21	0.38	0.07
H(73)	−0.28	0.51	0.09
H(81)	−0.24	0.13	0.36
H(82)	−0.23	0.02	0.31
H(83)	−0.12	0.04	0.40

[a] Hydrogen atoms are labeled to correspond to the carbon (or oxygen) atom to which they are attached. [b] See footnote b, Table I. [c] Methyl hydrogen atoms were not refined.

Table III. Coordination Geometry[a]

Bond distances, Å		Bond angles, deg	
Zn(II)-Cl(1)	2.272 (4)	S(1)-Zn(I)-S(2)	148.1 (2)
Zn(II)-Cl(2)	2.240 (4)	S(1)-Zn(I)-N(1)	110.8 (3)
Zn(II)-S(1)	2.356 (4)	S(1)-Zn(I)-N(2)	91.6 (3)
Zn(II)-S(2′)	2.343 (4)	S(2)-Zn(I)-N(1)	91.8 (3)
Zn(I)-S(1)	2.286 (4)	S(2)-Zn(I)-N(2)	112.4 (4)
Zn(I)-S(2)	2.284 (4)	N(1)-Zn(I)-N(2)	87.0 (4)
Zn(I)-N(1)	2.079 (11)		
Zn(I)-N(2)	2.103 (11)	Cl(1)-Zn(II)-Cl(2)	111.6 (2)
		Cl(1)-Zn(II)-S(1)	109.2 (2)
		Cl(1)-Zn(II)-S(2′)	106.5 (2)
		Cl(2)-Zn(II)-S(1)	110.0 (2)
		Cl(2)-Zn(II)-S(2′)	112.6 (2)
		S(1)-Zn(II)-S(2′)	106.8 (2)

[a] See footnotes a and b, Table I.

Table IV. Ligand Geometry[a]

Bond lengths, Å			Bond angles, deg	
S(1)-C(1)	1.835 (17)	av 1.85	Zn(I)-S(1)-Zn(II)	100.4 (2)
S(2)-C(6)	1.856 (16)		Zn(I)-S(1)-C(1)	94.2 (6)
			Zn(II)-S(1)-C(1)	104.3 (7)
N(1)-C(4)	1.492 (18)	av 1.49	Zn(I)-S(2)-Zn(II′)	98.6 (2)
N(1)-C(5)	1.500 (18)		Zn(I)-S(2)-C(6)	94.3 (5)
N(1)-C(7)	1.481 (17)		Zn(II′)-S(2)-C(6)	102.1 (5)
N(2)-C(2)	1.498 (19)		Zn(I)-N(1)-C(4)	102.9 (9)
N(2)-C(3)	1.462 (22)		Zn(I)-N(1)-C(5)	107.6 (9)
N(2)-C(8)	1.518 (18)		Zn(I)-N(1)-C(7)	116.5 (9)
			C(4)-N(1)-C(5)	111.3 (12)
C(1)-C(2)	1.514 (25)	av 1.51	C(4)-N(1)-C(7)	109.8 (11)
C(3)-C(4)	1.516 (24)		C(5)-N(1)-C(7)	108.7 (11)
C(5)-C(6)	1.494 (21)		Zn(I)-N(2)-C(2)	108.2 (9)
			Zn(I)-N(2)-C(3)	103.2 (9)
			Zn(I)-N(2)-C(8)	113.8 (9)
			C(2)-N(2)-C(3)	110.1 (13)
			C(2)-N(2)-C(8)	109.7 (12)
			C(3)-N(2)-C(8)	111.7 (13)
			S(1)-C(1)-C(2)	115.3 (11)
			N(2)-C(2)-C(1)	112.1 (13)
			N(2)-C(3)-C(4)	110.5 (14)
			N(1)-C(4)-C(3)	109.1 (12)
			N(1)-C(5)-C(6)	113.0 (13)
			S(2)-C(6)-C(5)	114.5 (11)

[a] See footnotes a and b, Table I.

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(8) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1170. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

type II zinc atoms, which are tetrahedrally coordinated to two chlorine and two sulfur atoms. The lattice water is not coordinated, but the two water protons are hydrogen bonded to Cl(1) and one symmetry related Cl(2) atom (Table V, Figure 2).

Table V. Geometry of the Lattice Water and Hydrogen Bonding[a]

Bond length, Å		Bond angle, deg	
O–H(1O)	0.98 (16)	H(1O)–O–H(2O)	130 (15)
O–H(2O)	0.93 (16)		
H(1O)–Cl(2′′)[b]	2.31 (16)		
H(2O)–Cl(1)	2.44 (16)		

[a] See footnotes *a* and *b*, Table I. [b] Cl(2′′) chlorine atom related to Cl(2) by symmetry (x, $-\frac{1}{2} - y$, $\frac{1}{2} + z$).

The Zn–S and Zn–N distances in the present structure are normal.[9,10] The bond angles N(1)–Zn–S(1) (110.8°) and N(2)–Zn–S(2) (112.4°) are close to the tetrahedral value, while the bond angles N(1)–Zn–N(2) (87.0°), N(1)–Zn(I)–S(2) (91.8°), and N(2)–Zn(I)–S(1) (91.6°) are similar to the N–Zn–N or N–Zn–S angles found in other zinc complexes containing five-membered chelate ring systems.[10] The tetradentate chelation, however, results in an unusual coordination in which one side of the Zn(I) atom is very open, the S(1)–Zn(I)–S(2) angle being 148.1° (Figure 1). The steric strain that causes this severe distortion from tetrahedral geometry also results in a difference of 0.06–0.07 Å (15–18σ) between the Zn(I)–S and Zn(II)–S bond lengths (Table III). In addition, the dihedral angle between the planes defined by N(1)–Zn(I)–N(2) and S(1)–Zn(I)–S(2) is 75.2 (3)°, compared to the idealized tetrahedral value of 90° or to the unconstrained dihedral angle of 88.1 (1)° between the Cl(1)–Zn(II)–Cl(2) and S(1)–Zn(II)–S(2′) planes.

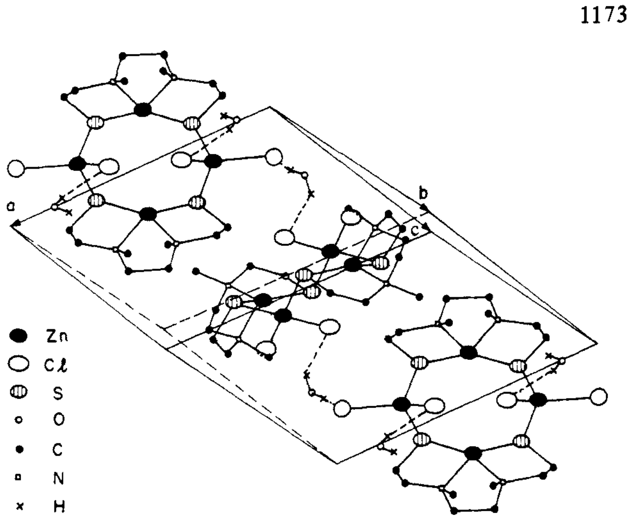

Figure 2. Packing diagram of $[Zn_2Cl_2L]_2 \cdot 2H_2O$ showing hydrogen bonding between the lattice water and chlorine atoms.

The tendency for mercaptide sulfur to form three bonds and bridge metal ions is manifest in the present complex. If the two sulfur atoms of one ZnL unit (S···S bite 4.39 Å) were to bridge to a second zinc atom, an impossibly short nonbonded Zn···Zn contact distance would result. Instead, the two sulfur atoms bridge to different zinc atoms, the result being the observed tetranuclear array.

The present structure clearly shows the constraining stereochemical properties of the tetradentate ligand, providing important information relevant to the current investigation of iron derivatives.[1]

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A Theoretical Study of the Perturbation of Hydrocarbon Chromophores by Cyclopropyl

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Abstract: Transition energies and oscillator strengths have been calculated for the lower excited states of cyclopropane, benzene, and various conformers of vinylcyclopropane and phenylcyclopropane using an SCMO–CI technique based upon intermediate neglect of differential overlap (INDO). Reasonable agreement with experiment was obtained for cyclopropane and benzene. The phenylcyclopropane spectrum is found to be relatively insensitive to the dihedral angle, as has been demonstrated experimentally. In vinylcyclopropane conformational dependence of the spectrum was found, but only within a rather narrow range (60–120°) of the dihedral angle. This result is in keeping with the experimental observation that the uv maximum is only moderately affected by alkyl substitution on the vinyl group. The 1-methyl-1-vinylcyclopropanes, however, exhibit hypsochromic shifts relative to the unmethylated derivatives. This implies that 1-methyl substitution is necessary to significantly populate any but the s-trans conformation.

There is abundant experimental evidence for the conformational dependence of cyclopropyl interaction with neighboring p orbitals, derived primarily from solvolytic studies.[1] The conclusion drawn regarding

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[1] (a) B. R. Bree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970), and the references cited therein; (b) see also ref 4 of L. D.