

Contribution from The Procter & Gamble Company,
Miami Valley Laboratories, Cincinnati, Ohio 45247**Structural Characterization of Bis(*N*-oxopyridine-2-thionato)zinc(II)**

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The crystal and molecular structures of two crystalline products (I and II) of bis(*N*-oxopyridine-2-thionato)zinc(II) have been solved by single-crystal x-ray diffraction techniques. The crystals of I are monoclinic, space group $P2_1/c$ (No. 14) with unit cell dimensions $a = 8.405$ (1) Å, $b = 10.183$ (1) Å, $c = 13.731$ (1) Å, $\beta = 97.24$ (1)°, $Z = 4$, and $\rho = 1.808$ g/cm³. Crystals of II are triclinic, space group $P\bar{1}$ (No. 2) with unit cell dimensions of $a = 11.664$ (3) Å, $b = 12.120$ (3) Å, $c = 7.892$ (1) Å, $\alpha = 67.05$ (2)°, $\beta = 74.82$ (2)°, $\gamma = 113.18$ (2)°, $Z = 2$, and $\rho = 1.764$ g/cm³. Both I and II contain dimers of bis(*N*-oxopyridine-2-thionato)zinc(II). Two *N*-oxopyridine-2-thionate groups are chelated to each zinc atom through oxygen and sulfur atoms; two monomeric units are linked together by two zinc-oxygen bonds. Thus, in both cases the zinc atom is pentacoordinated in a distorted trigonal bipyramidal environment. Product II is distinguished structurally from I primarily by the presence of solvent molecules (chloroform) which are interspersed between dimeric units. X-ray diffraction pattern measurements demonstrate the presence of product I crystals in a commercial, antidandruff shampoo product. Molecular weight and NMR measurements indicate that the title compound is monomeric in solutions of organic solvents.

Introduction

Bis(*N*-oxopyridine-2-thionato)zinc(II), commonly known as zinc pyrithione,¹ Zn(PT)₂, is an effective antifungal agent and is used as the active component of some antidandruff shampoo products.

Robinson² has reported the synthesis of Zn(PT)₂ and, on the basis of elemental analysis, molecular weight determination, and conductivity measurements, proposed the structure of Zn(PT)₂ to be a monomer comprised of one zinc atom chelated by two pyrithione units by way of sulfur and oxygen atoms.

The title compound exists predominantly (~99% on a weight basis) as a dispersed solid in a lotion shampoo product.³ Consequently, it was of interest to rigorously characterize the solid-state structure of Zn(PT)₂ as a part of an overall program that is aimed at understanding the physical and chemical aspects of this type of antifungal agent. This paper reports the structure determination of two crystalline products of zinc pyrithione by single-crystal x-ray diffraction methods, as well as new data which support the proposed monomeric structure in organic solvents.

Experimental Section

Preparation. Zinc pyrithione was obtained from Olin Corp. Pale yellow prisms (product I) were obtained by recrystallization of Zn(PT)₂ from either dimethyl sulfoxide (Me₂SO) or chloroform. Colorless, elongated parallelepiped crystals (product II) were isolated after prolonged standing of I in chloroform.

Retail samples of shampoo (Head & Shoulders lotion and cream) were used for x-ray powder measurements. Data were collected using CuK α radiation (λ 1.542 Å) and with the aid of a 143.2 mm diameter camera which was mounted on a Picker x-ray generator. Debye-Scherrer photographic methods⁴ were employed; relative intensities were estimated visually.

Crystal Data. Preliminary x-ray investigations revealed the diffraction symmetries to be monoclinic for product I and triclinic for product II. The systematic absences for product I are consistent with the uniquely defined space group $P2_1/c$ (No. 14). Space group $P\bar{1}$ (No. 2) for product II was confirmed by the solution and refinement of the structure. Cell dimensions (Table I) were obtained from least-squares refinement of three instrument angles for 15 general, high-order ($2\theta > 60^\circ$) reflections which represented four quadrants of reciprocal space. The instrument angles were measured with Cu K α (1.5418 Å) radiation using a Syntex $P2_1$ four-circle diffractometer that was equipped with a graphite monochromator ($2\theta_m = 26.57^\circ$) at $t \sim 22^\circ\text{C}$. Crystal quality of each compound was determined by ω scans, and the mosaic spreads of product I and product II were 0.2 and 0.4°, respectively. No constraints were placed on the least-squares refinement of the lattice parameter. The values of α and γ in the monoclinic space group were within one estimated standard deviation at 90.00°.

Collection and Treatment of X-Ray Intensity Data. Three-dimensional single-crystal intensity data were collected by the θ - 2θ

Table I. Crystal Data

	Product I	Product II
Formula	C ₁₀ H ₈ N ₂ O ₂ S ₂ Zn	C ₁₀ H ₈ N ₂ O ₂ S ₂ Zn·CHCl ₃
Cell, <i>a</i> , Å	8.405 (1)	11.664 (3)
<i>b</i> , Å	10.183 (1)	12.120 (3)
<i>c</i> , Å	13.731 (1)	7.892 (1)
Angles, deg	$\beta = 97.24$ (1)	$\alpha = 67.05$ (2), $\beta = 74.82$ (2), $\gamma = 113.18$ (2)
<i>V</i> , Å ³	1165.82	822.99
Crystal dimensions, mm	0.20 × 0.18 × 0.10	0.30 × 0.05 × 0.05
Formula wt	317.685	317.685 + 119.378
ρ (calcd), g/cm ³	1.808	1.764
<i>Z</i>	4	2
Space group	$P2_1/c$	$P\bar{1}$
Total independent reflections	1460	1886
$I > 2\sigma(I)$	1370	1577
$I < 2\sigma(I)$	90	209
R_1, R_2	0.056, 0.079	0.057, 0.045
R_1, R_2 (including $I < 2\sigma(I)$)	0.059, 0.079	0.080, 0.045

Table II. Final Atomic Parameters for Product I^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Zn	0.18054 (15)	0.06343 (12)	0.03256 (8)	
S1	0.3292 (3)	-0.1274 (3)	0.0361 (2)	
S2	0.1684 (4)	0.2760 (2)	-0.0260 (2)	
O1	0.0394 (7)	-0.0352 (5)	-0.0904 (4)	
O2	0.3035 (8)	0.1420 (6)	0.1574 (4)	
N1	0.1068 (9)	-0.1471 (7)	-0.1232 (5)	
N2	0.3067 (9)	0.2736 (7)	0.1622 (6)	
C7	0.3740 (13)	0.4585 (11)	0.2608 (8)	
C8	0.3176 (14)	0.5401 (11)	0.1828 (9)	
C5	0.2424 (11)	-0.1990 (9)	-0.0709 (6)	
C10	0.2476 (12)	0.3476 (9)	0.0826 (6)	
C1	0.0353 (12)	-0.2003 (10)	-0.2080 (6)	
C6	0.3671 (12)	0.3274 (10)	0.2494 (7)	
C4	0.3043 (12)	-0.3153 (9)	-0.1081 (7)	
C2	0.0903 (13)	-0.3149 (10)	-0.2425 (7)	
C9	0.2531 (13)	0.4856 (10)	0.0963 (8)	
C3	0.2283 (14)	-0.3710 (10)	-0.1925 (8)	
H1	-0.0616	-0.1541	-0.2466	5.50
H2	0.0316	-0.3607	-0.3023	5.50
H3	0.2739	-0.4536	-0.2199	5.50
H4	0.4040	-0.3581	-0.0723	5.50
H6	0.4057	0.2681	0.3068	5.50
H7	0.4213	0.4975	0.3259	5.50
H8	0.3252	0.6388	0.1913	5.50
H9	0.2079	0.5446	0.0403	5.50

^a Standard deviations are in parentheses.

technique. Variable scan rates (2–12°/min) were chosen, so that the less-intense reflections could be scanned at a slower rate to improve their counting statistics. Individual background measurements were

Table III. Final Thermal Parameters for Product I^{a,b}

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	3.45 (6)	2.35 (6)	2.49 (6)	-0.05 (5)	0.16 (4)	-0.30 (4)
S1	2.86 (12)	2.41 (11)	2.20 (11)	0.68 (10)	-0.65 (9)	-0.60 (9)
S2	5.29 (16)	2.07 (11)	1.54 (10)	-0.37 (11)	-0.28 (11)	0.33 (9)
O1	2.28 (28)	1.30 (28)	1.95 (27)	0.15 (23)	0.26 (23)	0.08 (22)
O2	3.84 (36)	1.11 (28)	2.14 (28)	0.47 (26)	-0.73 (26)	-0.22 (22)
N1	2.30 (37)	1.83 (36)	1.45 (32)	-0.06 (30)	0.43 (29)	-0.21 (27)
N2	2.27 (38)	2.12 (39)	2.15 (36)	-0.19 (31)	0.08 (30)	-0.22 (30)
C7	3.08 (51)	3.44 (58)	3.22 (51)	-0.39 (45)	0.16 (42)	-0.99 (45)
C8	3.74 (57)	2.60 (52)	5.04 (62)	-0.61 (47)	1.06 (49)	-1.45 (48)
C5	2.56 (46)	1.83 (42)	1.80 (38)	-0.43 (37)	0.44 (36)	0.10 (34)
C10	3.22 (50)	1.82 (43)	1.85 (41)	-0.50 (38)	0.15 (38)	0.07 (35)
C1	2.64 (47)	3.20 (49)	1.61 (38)	-0.39 (41)	0.44 (36)	-0.49 (37)
C6	2.62 (47)	2.81 (51)	2.27 (43)	-0.20 (41)	-0.07 (38)	-0.57 (38)
C4	3.01 (49)	1.91 (43)	2.91 (47)	0.38 (40)	0.94 (40)	-0.53 (38)
C2	2.96 (52)	3.27 (52)	2.81 (47)	-0.40 (45)	0.94 (42)	-1.68 (43)
C9	4.04 (56)	1.63 (45)	3.65 (54)	-0.07 (42)	0.68 (46)	0.49 (39)
C3	4.31 (60)	2.23 (46)	3.51 (52)	-0.17 (45)	2.29 (48)	-0.88 (40)

^a Standard deviations are in parentheses. ^b The temperature factor is of the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

made at the end points of the scan range, each at a time of one-half the scan time. In both data sets four reflections were monitored periodically and in both cases there were only random fluctuations (5% in product I and 6% in product II) of the intensities for these reflections. Lorentz and polarization corrections were applied, but no absorption correction was made. Values of the linear absorption coefficient for products I and II are 61.5 and 89.3 cm⁻¹, respectively.

Standard deviations of the observed structure factor amplitudes were based solely on counting statistics. Only those reflections with intensities greater than 2σ were used in the solution and refinement of the structures; σ is defined as the product of the scan rate and the sum of the total scan count and the total background count raised to the one-half power.

Differential Scanning Calorimetry (DSC) Measurements. DSC thermograms of crystalline products I and II were obtained with a Perkin-Elmer DSC-2 calibrated with indium and lead reference standards. Samples were hermetically sealed in aluminum pans and scanned from 320 to 600 K at scan rates of 10 K/min.

Molecular Weight and NMR Measurements. Molecular weight determinations were made by vapor pressure osmometry (Galbraith Laboratories, Inc., Knoxville, Tenn.). Freshly prepared solutions of product I crystals in chloroform were used.

NMR spectra were recorded on solutions of product I crystals dissolved in deuterated Me₂SO or deuterated chloroform. Tetramethylsilane (Me₄Si) was employed as an internal reference standard. Proton NMR spectra were recorded on a Bruker HX-270 spectrometer. Proton homonuclear decoupling experiments were performed on a Varian HA-100 spectrometer. Carbon-13 NMR spectra were obtained on a Varian CFT-20 spectrometer. Proton heteronuclear decoupling experiments were performed on a Bruker HX-90 operating at 22.6 MHz.

Solution and Refinement of the Structures. Product I. Solution of the structure was accomplished by obtaining the zinc and two sulfur positions from a sharpened Patterson map. A Fourier map, which was calculated with phases that were based on the two sulfur positions and the zinc position, revealed the nonhydrogen atoms of the structure. Least-squares refinement of positions and isotropic temperature factors gave an *R* value of 0.10 after four cycles. After converting to anisotropic temperature factors, the refinement converged to *R* = 0.085 in three cycles. Ideal hydrogen atom positions were calculated and held fixed with constant isotropic temperature factors (*B* = 5.5 Å²) for the remainder of the refinement. An additional five cycles of least-squares calculations, where all nonhydrogen positional parameters, all anisotropic temperature factors, and an overall scale factor were varied, served to complete the refinement at *R* = 0.057. Shifts in the final cycle were less than 0.1σ for all parameters. A final difference density map contained only a randomly fluctuating background below 0.4 e/Å³. Weights equal to 1/σ²(*F*_o) were utilized in the least-squares calculations.

Final atomic parameters are given in Tables II and III. The estimated standard deviations were calculated from the inverse matrix of the final least-squares cycle. The final *R* value for these parameters was (0.57, 0.079 for weighted *R*) for the observed reflections only.

Table IV. Final Atomic Parameters for Product II^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Zn	0.01637 (13)	0.11312 (14)	0.56886 (20)	
Cl1	0.3835 (3)	0.6854 (3)	-0.3879 (5)	
Cl2	0.1385 (4)	0.4605 (4)	0.0232 (5)	
Cl3	0.1352 (4)	0.4672 (4)	-0.3442 (6)	
S1	0.2626 (3)	0.2344 (3)	0.4230 (4)	
S2	-0.1620 (3)	0.1526 (3)	0.5693 (4)	
O1	0.0632 (6)	0.1064 (6)	0.2876 (8)	
O2	-0.0320 (7)	0.1080 (7)	0.8421 (10)	
N1	0.2045 (7)	0.1950 (8)	0.1343 (11)	
N2	-0.1426 (8)	0.1163 (8)	0.9159 (12)	
C	0.1930 (12)	0.5677 (4)	-0.2420 (19)	
C1	0.2371 (12)	0.2206 (12)	-0.0549 (17)	
C2	0.3722 (12)	0.3019 (12)	-0.2156 (17)	
C3	0.4819 (13)	0.3646 (13)	-0.1746 (18)	
C4	0.4511 (11)	0.3437 (12)	0.0180 (17)	
C5	0.3062 (10)	0.2582 (10)	0.1827 (14)	
C6	-0.1857 (12)	0.0980 (12)	1.1078 (18)	
C7	-0.2970 (13)	0.1047 (13)	1.1971 (19)	
C8	-0.3694 (14)	0.1272 (15)	1.0893 (21)	
C9	-0.3273 (12)	0.1486 (13)	0.8946 (19)	
C10	-0.2130 (10)	0.1368 (10)	0.8050 (15)	
H1	0.183 (7)	0.178 (7)	-0.070 (10)	-1.07 (20)
H2	0.398 (7)	0.326 (7)	-0.344 (10)	0.82 (17)
H3	0.576 (10)	0.437 (10)	-0.270 (10)	10.35 (43)
H4	0.517 (10)	0.383 (10)	0.053 (10)	5.06 (30)
H6	-0.141 (10)	0.072 (9)	1.156 (10)	3.84 (28)
H7	-0.320 (10)	0.100 (10)	1.337 (10)	8.96 (36)
H8	-0.410 (10)	0.162 (10)	1.116 (10)	4.53 (31)
H9	-0.370 (10)	0.178 (10)	0.791 (10)	6.60 (29)
H	0.171 (10)	0.632 (10)	-0.281 (10)	6.09 (33)

^a Standard deviations are in parentheses.

Product II. Attempts to solve this structure by conventional Patterson methods and by the Syntex version of MULTAN failed. In testing the centrosymmetric direct methods routine of SHELX, a set of crystallographic programs written by Sheldrick,⁵ the most probable solution did reveal all nonhydrogen atoms in the asymmetric unit. Improvements in the origin selection and correct-solution criterion are probably responsible for the success of this program over MULTAN.

Least-squares refinement for all positional parameters and isotropic temperature factors gave an *R* value of 0.12 after five cycles. After the conversion to anisotropic temperature factors the refinement was continued for six cycles which gave an *R* value of 0.091. The calculated hydrogen atom positions were fixed with constant-temperature factors (*B* = 5.5 Å²) for four additional cycles of least-squares refinement to an *R* value of 0.067. An additional five cycles of least-squares calculations, where all positional parameters, hydrogen isotropic temperature factors, nonhydrogen anisotropic temperature factors, and an overall scale factor were varied, served to complete the refinement at an *R* of 0.057. Shifts in the final cycle were less than 0.2σ for all parameters.

Table V. Final Thermal Parameters of Product I^{a,b}

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	3.65 (7)	4.06 (7)	3.68 (7)	2.06 (6)	-1.64 (6)	-2.31 (6)
Cl1	3.28 (14)	7.43 (20)	5.32 (17)	2.52 (14)	-1.32 (13)	-3.81 (16)
Cl2	8.07 (23)	8.86 (24)	4.15 (18)	6.18 (21)	-0.48 (17)	-0.48 (18)
Cl3	5.72 (20)	6.64 (22)	10.00 (27)	1.73 (17)	-2.77 (19)	-5.18 (21)
S1	2.40 (13)	5.48 (17)	3.11 (14)	0.95 (13)	-1.29 (11)	-2.61 (14)
S2	5.13 (16)	6.02 (17)	2.98 (13)	4.26 (15)	-2.67 (13)	-2.88 (13)
Q1	1.80 (28)	3.18 (32)	2.27 (30)	1.14 (25)	-0.80 (25)	-1.86 (27)
Q2	3.83 (35)	5.62 (41)	3.86 (36)	3.41 (33)	-2.46 (31)	-3.49 (34)
N1	2.36 (37)	2.92 (40)	1.99 (37)	1.67 (33)	-1.01 (33)	-1.33 (33)
N2	3.26 (42)	2.94 (42)	2.78 (41)	1.68 (36)	-1.49 (36)	-1.81 (36)
C	2.82 (55)	5.56 (74)	4.62 (67)	2.59 (57)	-0.34 (49)	-1.28 (61)
C1	3.19 (63)	3.58 (62)	3.26 (60)	1.37 (53)	-1.91 (54)	-2.41 (52)
C2	3.41 (60)	5.55 (71)	2.22 (57)	1.96 (55)	-0.96 (52)	-2.38 (57)
C3	3.13 (61)	4.99 (70)	3.66 (64)	1.93 (56)	-0.84 (55)	-2.42 (59)
C4	2.26 (51)	4.51 (63)	3.49 (57)	1.16 (48)	-1.08 (47)	-1.29 (51)
C5	2.97 (49)	3.32 (51)	3.03 (50)	1.69 (44)	-1.96 (44)	-2.09 (44)
C6	4.15 (65)	4.22 (63)	3.68 (61)	2.47 (55)	-2.54 (55)	-2.61 (53)
C7	4.53 (65)	7.03 (76)	4.01 (64)	3.55 (60)	-2.24 (56)	-3.86 (62)
C8	5.08 (72)	7.70 (89)	4.94 (75)	4.57 (70)	-1.55 (62)	-3.88 (70)
C9	4.68 (64)	7.03 (76)	4.45 (66)	4.34 (60)	-2.59 (56)	-3.82 (62)
C10	3.34 (51)	3.33 (53)	3.40 (53)	1.70 (45)	-1.68 (45)	-2.17 (47)

^a Standard deviations are in parentheses. ^b The temperature factor is of the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table VI. Interatomic Distances (Å) in Zn(PT)₂ Complexes^a

	Product I	Product II
Zn-S1	2.308 (3)	2.316 (4)
Zn-S2	2.307 (3)	2.310 (4)
Zn-O1	2.181 (6)	2.185 (6)
Zn-O1'	2.122 (6)	2.092 (7)
Zn-O2	2.049 (6)	2.050 (7)
S1-C5	1.718 (9)	1.70 (1)
S2-Cl0'	1.716 (9)	1.70 (1)
O1-N1	1.37 (1)	1.37 (1)
O2-N2	1.34 (1)	1.33 (1)
N1-C1	1.35 (1)	1.31 (1)
N1-C5	1.37 (1)	1.38 (2)
N2-C6	1.36 (1)	1.36 (2)
N2-Cl0'	1.37 (1)	1.37 (2)
C1-C2	1.36 (2)	1.35 (2)
C2-C3	1.39 (2)	1.40 (2)
C3-C4	1.37 (1)	1.36 (2)
C4-C5	1.42 (1)	1.43 (2)
C6-C7	1.34 (2)	1.36 (2)
C7-C8	1.39 (2)	1.37 (2)
C8-C9	1.36 (2)	1.36 (2)
C9-C10'	1.42 (1)	1.42 (2)
C-Cl1		1.784 (15)
C-Cl2		1.734 (13)
C-Cl3		1.730 (17)

^a Standard deviations are in parentheses.

A final difference density Fourier contained no features other than a randomly fluctuating background. Weights equal to $1/\sigma^2(|F_o|)$ were utilized in the least-squares calculations.

Final atomic parameters are given in Tables IV and V. The estimated standard deviations were calculated from the inverse matrix of the final least-squares cycle. The final *R* value for these parameters is 0.057 (weighted *R* = 0.045) for those reflections included in the refinement and is 0.080 (weighted *R* = 0.045) when all data are included.

With the exception of the solution of the product II structure, all calculations were performed on a Data General Nova 1200 computer with standard crystallographic programs that were modified for the Nova 1200 by Syntex Analytical Instruments. Least-squares calculations were performed by full-matrix methods. The solution of product II was accomplished on an IBM 370/168 with the programs of SHELX written by Sheldrick. Atomic scattering factors were those of Stewart, Davidson, and Simpson⁶ for hydrogen and Cromer⁷ for the remaining atoms.

Results and Discussion

Crystallographic Studies. The molecular structures of the two crystalline products of zinc pyrithione are remarkably

Table VII. Interatomic Angles (deg) in Zn(PT)₂ Complexes^a

Atoms	Product I	Product II
S1-Zn-S2	142.9 (1)	141.7 (1)
S1-Zn-O1	82.4 (2)	81.9 (2)
S1-Zn-O2	95.6 (2)	99.0 (2)
S1-Zn-O1'	111.9 (2)	106.3 (2)
S2-Zn-O2	85.4 (2)	84.8 (2)
S2-Zn-O1	99.6 (2)	96.4 (2)
S2-Zn-O1'	104.8 (2)	111.2 (2)
O1-Zn-O2	174.0 (2)	177.0 (3)
O1-Zn-O1'	79.2 (2)	81.1 (3)
O2-Zn-O1'	96.4 (2)	95.8 (3)
Zn-S1-C5	99.7 (3)	99.5 (4)
Zn-S2-Cl0'	95.8 (3)	96.4 (4)
Zn-O1-N1	115.5 (4)	113.2 (6)
Zn-O1-Zn'	100.8 (2)	98.9 (3)
N1-O1-Zn'	115.1 (4)	115.7 (5)
Zn-O2-N2	115.9 (5)	116.7 (6)
O1-N1-C1	117.2 (7)	118.9 (10)
O1-N1-C5	119.8 (7)	118.7 (8)
C1-N1-C5	123.0 (8)	122.4 (10)
O2-N2-C6	116.8 (7)	117.6 (10)
O2-N2-C10	120.4 (7)	120.6 (9)
C6-N2-C10	122.8 (8)	121.7 (11)
N1-C1-C2	120.6 (9)	124.0 (10)
C1-C2-C3	118.5 (10)	116.5 (13)
C2-C3-C4	121.1 (10)	120.7 (14)
C3-C4-C5	119.8 (9)	120.8 (13)
S1-C5-N1	121.2 (7)	122.3 (9)
S1-C5-C4	121.9 (7)	122.4 (9)
N1-C5-C4	116.9 (8)	115.3 (10)
N2-C6-C7	120.6 (9)	122.3 (13)
C6-C7-C8	119.9 (10)	117.7 (14)
C7-C8-C9	119.2 (10)	121.4 (15)
C8-C9-C10	121.6 (10)	120.3 (14)
S2-Cl0-N2	121.4 (7)	121.2 (9)
S2-Cl0-C9	122.7 (8)	122.5 (10)
N2-Cl0-C9	115.9 (8)	116.2 (11)
Cl1-C-Cl2		109.4 (8)
Cl1-C-Cl3		109.5 (8)
Cl2-C-Cl3		112.5 (9)

^a Standard deviations are in parentheses.

similar with the principal difference being the presence of discrete molecules of chloroform in product II. The coordination geometry (Figure 1) about each zinc atom is best described as trigonal bipyramidal where the oxygen atoms of two pyrithione moieties occupy the axial positions and the sulfur atoms form two vertices of the basal plane. In the remaining vertex, a centrosymmetrically related oxygen atom

Table VIII. X-Ray Powder Pattern Data^a

Lotion formulation ^b		Cream formulation		NaAGS ^c	
<i>d</i> , Å	Intens	<i>d</i> , Å	Intens	<i>d</i> , Å	Intens
		18.4	s	18.4	s
		12.0	ms	12.0	ms
8.13	vs	8.13	ms		
6.79	wm	6.80	vvw		
				6.05	vvw
6.40	vw				
6.02	vw				
5.62	s	5.60	w		
				5.35	vvw
		4.70	vw	4.64	vw
4.44	vw	4.40	w	4.46	m
		4.27	vs	4.29	vs
4.16	ms	4.08	m	4.08	m
		3.83	m	3.85	wm
3.52	ms	3.53	m		

^a Only principal lines are tabulated. Abbreviations: s, strong; m, medium; w, weak; v, very. ^b Values listed are equivalent to those of product I crystals. ^c Sodium alkylglycerol sulfate where alkyl is a mixture containing C₈-C₁₈ alkyl groups.

Table IX. Molecular Weight Data

Concn (mg/mL)	2.0	2.5	3.0	3.5	4.0
Mol wt	296	291	286	281	276

(O1') completes the coordination sphere so that one axial oxygen atom (O1) is also in the basal plane for the centrosymmetrically related zinc atom. Consequently, both crystalline products are composed of discrete dimeric units of Zn(PT)₂. Molecules of chloroform (one CHCl₃ per Zn(PT)₂ unit), which are present in product II, separate the dimeric units but have no contacts less than the sum of the van der Waals radii. Accordingly, there appears to be no unique role which can be assigned to the chloroform molecules in II.

An examination of the geometric parameters, which are given in Tables VI and VII, reveal some interesting features of the complexes. The sum of the Pauling covalent radii for zinc and sulfur is 2.35 Å, which is longer than the observed Zn-S bond lengths (2.314 (7) Å av) in the present structures. Similar observations have been made in other zinc sulfur chelate complexes.⁸ No such clear distinction can be made for the Zn-O bonds, which seem to be divided into three classes. First of all the Zn-O2 bond lengths (2.050 (8) Å av), which involve the oxygen atoms that are coordinated to only one zinc atom, are very near the sum of the covalent radii for zinc and oxygen (2.05 Å). The second type, which is the other

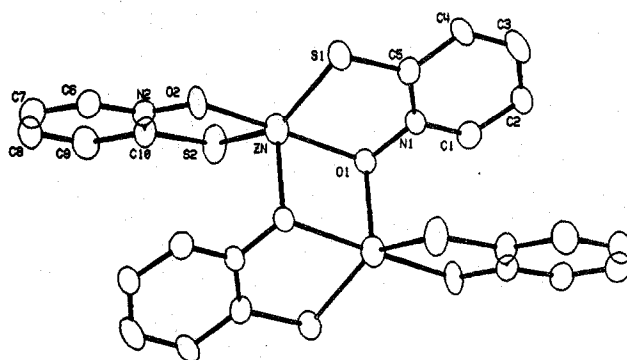


Figure 1. Perspective view of the dimeric Zn(PT)₂ complex of product I (identical with product II). The numbering scheme for both structures is given on the top half of the molecule.

axial oxygen distance, has an average Zn-O1 bond length of 2.183 (6) Å and is significantly larger than the sum of the covalent radii. The third type is the Zn-O1 bond length (2.107 (8) Å), which involves the basal oxygen. This bond length has a value which is intermediate between the other two types. Similar trends in Zn-O bond lengths have been observed in bis(*N*-methylsalicylaldiminato)zinc(II), which is also dimeric in the solid state.⁹

In the organic portion of the molecule the geometric parameters reflect little or no distortion upon complexation. The planarity as well as the aromatic character appear undisturbed. Also, the C-S bond length (1.708 Å) agrees with the sum of the covalent radii of an sp² carbon and sulfur (1.71 Å).

X-Ray Powder Patterns. Powder measurements taken on a lotion sample of finished shampoo product are listed in Table VIII. These measurements are equivalent to the *d* spacings for product I crystals. Similar measurements that were obtained on a sample of cream product (see Table VIII) reveal lines coincident with product I crystals. The cream sample exhibits an additional pattern which is ascribed to the presence of crystalline sodium alkylglycerol sulfate, NaAGS, in the cream formulation. The interfering lines from NaAGS can be readily removed if the cream sample is treated with distilled water prior to the measurement.

Thermal Data. The DSC thermogram obtained with product I crystals is characterized by a single endotherm located at 534 K. The asymmetrical shape of the peak and its behavior upon rescanning indicate that the crystals melt with decomposition.

Table X. ¹H and ¹³C NMR Spectral Data for Zn(PT)₂ and NaPT

Compd/solvent	Nucleus	Chemical shift and assignment ^a				
Zn(PT) ₂ /Me ₂ SO- <i>d</i> ₆	¹ H	7.64 (3, 3')	7.28 (4, 4')	7.03 (5, 5')	8.45 (6, 6')	
Zn(PT) ₂ /DCCl ₃	¹ H	7.75 (3, 3')	7.25 (4, 4')	6.94 (5, 5')	8.32 (6, 6')	
NaPT/Me ₂ SO- <i>d</i> ₆	¹ H	7.44 (3)	6.87 (4)	6.67 (5)	8.10 (6)	
Zn(PT) ₂ /Me ₂ SO- <i>d</i> ₆	¹³ C	159.4 (2, 2')	117.8 (3, 3')	129.3 (4, 4')	128.4 (5, 5')	137.2 (6, 6')
NaPT/Me ₂ SO- <i>d</i> ₆	¹³ C	166.9 (2)	113.7 (3)	131.4 (4)	123.2 (5)	138.2 (6)
Compd/solvent		Proton spin-spin coupling constants ^a				
Zn(PT) ₂ /Me ₂ SO- <i>d</i> ₆	8.4 (<i>J</i> _{3,4} , <i>J</i> _{3',4'})	1.6 (<i>J</i> _{3,5} , <i>J</i> _{3',5'})	< 0.5 (<i>J</i> _{3,6} , <i>J</i> _{3',6'})	7.0 (<i>J</i> _{4,5} , <i>J</i> _{4',5'})	1.2 (<i>J</i> _{4,6} , <i>J</i> _{4',6'})	6.8 (<i>J</i> _{5,6} , <i>J</i> _{5',6'})
Zn(PT) ₂ /DCCl ₃	8.6 (<i>J</i> _{3,4} , <i>J</i> _{3',4'})	1.8 (<i>J</i> _{3,5} , <i>J</i> _{3',5'})	0.6 (<i>J</i> _{3,6} , <i>J</i> _{3',6'})	7.0 (<i>J</i> _{4,5} , <i>J</i> _{4',5'})	1.4 (<i>J</i> _{4,6} , <i>J</i> _{4',6'})	6.8 (<i>J</i> _{5,6} , <i>J</i> _{5',6'})
NaPT/Me ₂ SO- <i>d</i> ₆	8.2 (<i>J</i> _{3,4})	2.1 (<i>J</i> _{3,5})	< 0.5 (<i>J</i> _{3,6})	7.0 (<i>J</i> _{4,5})	1.1 (<i>J</i> _{4,6})	7.0 (<i>J</i> _{5,6})

^a Chemical shift in ppm relative to Me₄Si. Assignments are in parentheses and are relative to the positions of ring carbon atoms. See text for numbering sequence. ^b In Hz, ±0.2.

Crystals of II give rise to two endotherms. The first occurs with a peak maximum located at 343 K and the second at 534 K. The former is not reversible and most likely reflects the volatilization of chloroform from the crystal matrix. The latter behaves in a manner which is identical with the single endotherm observed for product I crystals.

Molecular Weight and NMR Data. Molecular weight determinations were obtained as a function of concentration of product I crystals in chloroform (Table IX). When these data are plotted, a straight line is obtained. Extrapolation of the line to infinite dilution yields a molecular weight value of 316. This result demonstrates that zinc pyrithione is monomeric (theory 318) in chloroform solution and is in good agreement with the value (294) obtained by Robinson in dimethylformamide.² Further, an inspection of the data in Table IX reveals that the experimental molecular weight values decrease with increasing concentration of solute in chloroform. This observation is indicative of an appreciable solute-solvent interaction. Perhaps this interaction involves the formation of hydrogen bonds between the oxygen atom of the coordinated pyrithione group and chloroform and, thus, dimerization via oxygen bridging is prevented in solution. A similar argument has been invoked to accommodate the existence of a monomeric form of bis(*N*-methylsalicylaldiminato)cobalt(II) in chloroform solution.¹⁰

Proton and carbon-13 NMR spectral data obtained on solutions of product I crystals are listed in Table X. The corresponding spectral data for sodium pyrithione¹¹ are included for comparative purposes. Carbon and hydrogen positions in the pyridine ring are indicated by an integer, 2-6, beginning with the nitrogen atom and following in a counterclockwise direction. Assignments on the second ring of the zinc complex are designated with a prime. The proton and carbon-13 assignments were made by comparing the observed chemical shifts with those reported for pyridine *N*-oxide¹² (proton) and γ -picoline *N*-oxide¹³ and substituted pyridines¹⁴ (carbon-13), respectively. Proton assignments were validated by performing a series of homonuclear decoupling experiments. Utilizing the assigned proton spectrum, selected proton heteronuclear decoupling experiments were performed to confirm the carbon assignments.

The presence of a single set of proton resonance signals and their corresponding coupling constants demonstrate that the pyrithione rings of zinc pyrithione are magnetically equivalent in both chloroform and Me₂SO. Magnetic equivalence of the rings is further substantiated by the appearance of only five resonance signals in the carbon-13 spectrum of zinc pyrithione. The chemical shifts of the proton and carbon-13 resonances for zinc pyrithione in Me₂SO solution are significantly different from the corresponding signals for the sodium salt. These differences are ascribed to the coordination of the zinc atom

by pyrithione. The coupling constants for pyrithione as the sodium salt are essentially unchanged when coordination to zinc occurs.

Conclusions

The results of crystal and molecular structural studies demonstrate that zinc pyrithione exists as a rigid dimeric species when isolated from concentrated chloroform or Me₂SO solutions. A structurally similar dimer containing two molecules of solvent for each dimeric unit crystallizes from dilute chloroform solutions of zinc pyrithione. Crystalline zinc pyrithione present in an antidandruff shampoo product is structurally identical with the nonsolvated form. Molecular weight and NMR measurements on solutions of zinc pyrithione in organic solvents are consistent with the presence of only a monomeric species.

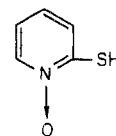
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Registry No. I, 62758-10-5; II, 62758-11-6; ¹³C, 14762-74-4.

Supplementary Material Available: Listings of structure factor amplitudes for products I and II (17 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) The following names have been used in the literature to identify the acid form of the PT ligand, i.e.



- 2-mercaptopyridine *N*-oxide, 1-hydroxypyridine-2-thione, 2-pyridinethiol 1-oxide, 1-hydroxy(1*H*)pyridinethione, pyrithione, and *N*-oxopyridine-2-thiol.
- (2) M. A. Robinson, *J. Inorg. Nucl. Chem.*, **26**, 1277 (1964).
- (3) Measurements obtained on Head and Shoulders lotion. Unpublished results (F. A. Hartman).
- (4) H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials", Wiley, New York, N.Y., 1974, pp 177-222.
- (5) G. M. Sheldrick, unpublished.
- (6) R. F. Stewart, E. R. Davidson, and W. R. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (7) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- (8) V. L. Goodken and G. G. Christoph, *Inorg. Chem.*, **12**, 2316 (1973).
- (9) P. L. Orioli, L. Sacconi, and M. DiVaira, *Chem. Commun.*, 103 (1965).
- (10) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965).
- (11) Sodium pyrithione (NaPT) was obtained from Olin Corp. and recrystallized from ethanol-chloroform, mp 250-252 °C.
- (12) Sadtler NMR Reference Spectra, Sadtler Laboratories, Inc., No. 18710M, 1974.
- (13) K. Tori, Y. Yoshimura, M. Kaivosko, and K. Ajisaka, *Tetrahedron Lett.*, 3127 (1973).
- (14) H. L. Retcofsky and R. A. Friedel, *J. Phys. Chem.*, **71**, 3592 (1967); **72**, 290, 2619 (1968).