

works in Cu_2O . (Cu_2O also has the $Pn3$ space group with 4 Cu in b and 2 O in a.) The linearly coordinated Cu becomes Bi(1) which is also linearly coordinated to oxygen in the first approximation. The tetrahedrally coordinated O in Cu_2O becomes the $\text{Bi}(2)_4\text{O}(1)_4$ tetrahedron in $\text{Bi}_3\text{GaSb}_2\text{O}_{11}$. The pyrochlore structure has also been described as interpenetrating networks⁸ where one of the networks is analogous to that found in Cu_2O .

The bonding of Bi(2) is typical of a lone-pair cation such as Bi^{3+} . In $\text{Bi}_4\text{Si}_3\text{O}_{12}$, for example,⁹ Bi is also on a threefold axis with three oxygens at 2.15 Å, three at 2.62 Å, and three at 3.55 Å. The bonding of Bi(1) is less common for a lone-pair cation, but an essentially identical coordination of Bi is found in pyrochlores such as $\text{Bi}_2\text{Ru}_2\text{O}_7$ and $\text{Bi}_2\text{Ir}_2\text{O}_7$. In $\text{Bi}_2\text{Ru}_2\text{O}_7$, for example,¹⁰ Bi is again on a threefold axis with two oxygens at 2.23 Å and six oxygens at 2.53 Å.

The coordination of the Ga-Sb "atom" is very close to octahedral. The average metal-oxygen distance of this octahedron is 2.01 Å; this compares favorably to 1.99 Å which is the sum of the radii.¹¹ The metal-metal distance across the shared edge is 2.96 Å. For two perfect octahedrons sharing an edge, this distance would be 2.84 Å for metal-oxygen distances of 2.01 Å. Thus, the metals are displaced away from each other as would be expected from electrostatic repulsion. This is in contrast to the situation found

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in $\text{La}_4\text{Re}_6\text{O}_{19}$ where the Re-Re distance is only 2.42 Å and metal-metal bonding is assumed.⁶

All the oxygens in the $\text{Bi}_3\text{GaSb}_2\text{O}_{11}$ structure are in approximate tetrahedral coordination if *intranetwork* and *internetwork* bonds are taken into account. Thus, there are no metal-oxygen-metal angles close to 180°. Such angles tend to be avoided in post transition metal oxides as was first pointed out by Blasse.^{12,13} The π interaction between the filled cation d orbitals and the filled oxygen p orbitals is, of course, strongly antibonding for 180° M-O-M linkages. However, this unfavorable interaction can be largely avoided by oxygen sp^3 hybridization which results in M-O-M angles closer to 109° and tends to eliminate the π interaction.

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Registry No. $\text{Bi}_3\text{GaSb}_2\text{O}_{11}$, 39322-88-8.

Supplementary Material Available. A listing of observed and calculated relative intensities for $\text{Bi}_3\text{GaSb}_2\text{O}_{11}$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2314.

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Helical Coordination. Structure and Bonding of the Five-Coordinate Complex Bis(2-thiobenzaldimino)-2,6-diacetylpyridinezinc(II)

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The crystal and molecular structure of a helical five-coordinate zinc complex of bis(2-thiobenzaldimino)-2,6-diacetylpyridine has been determined from three-dimensional single-crystal X-ray diffraction data. The complex crystallized with the monoclinic space group $P2_1$ (C_2^2 ; No. 4) with cell dimensions $a = 9.267$ (8) Å, $b = 13.174$ (13) Å, $c = 8.172$ (7) Å, and $\beta = 105.00$ (4)°. There are two molecules of the complex per unit cell ($\rho_{\text{exptl}} = 1.50$ (2) g/cm^3 , $\rho_{\text{calcd}} = 1.519$ (3) g/cm^3 for $Z = 2$). The intensities were obtained on a Picker automatic diffractometer (Mo $K\alpha$ radiation, $\lambda 0.71069$ Å); least-squares refinement of positional and thermal parameters for all the nonhydrogen atoms converged to a discrepancy index of $R = 5.68\%$ ($R_w = 5.05\%$) for 1769 independent reflections. The ligand has a helical conformation arising from intramolecular steric interactions. The zinc(II) ion is coordinated to three nitrogen atoms and two sulfur atoms forming a five-coordinate complex with an approximate C_2 axis passing through the zinc atom and the nitrogen atom of the pyridine moiety. The average Zn-S distance is 2.335 (3) Å and the average of Zn-N distances is 2.17 (1) Å. There is little evidence for electron delocalization in the potentially highly conjugated ligand system.

Introduction

Pentacoordination has been found to be rather common among transition metal complexes in recent years.¹ Most five-coordinate complexes have been synthesized by using branched polydentate chelate ligands, especially the tripod

type with large bulky substituents which force a five-coordinate donor arrangement for steric reasons.² However, a considerable number of five-coordinate complexes containing only unidentate ligands have been prepared in which electronic rather than steric factors predominate in influ-

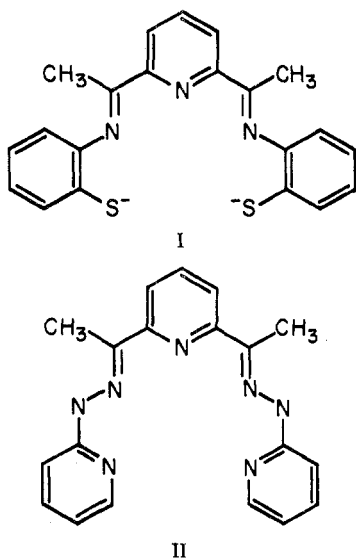
(1) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966); M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *ibid.*, **2**, 99 (1967); P. L. Orioli, *ibid.*, **6**, 285 (1971); L. Sacconi, *ibid.*, **8**, 351 (1972).

(2) (a) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966); (b) N. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *ibid.*, **2**, 99 (1967).

encing their coordination number.³ It has been pointed out by Muetterties that the most important steric arrangements for pentacoordinate molecules are the trigonal bipyramid and the square pyramid.⁴ However, the results of crystal structure analyses reveal that most five-coordinate transition metal complexes have geometries that lie somewhere between these two idealized geometries.

A third possibility, a planar-pentagonal arrangement of donor atoms, has been considered by Lions⁵ in his discussion of the problems in the design and synthesis of pentadentate ligands. For transition metals containing a non-spherical distribution of d electrons, planar-pentagonal coordination is unlikely due to unfavorable crystal field effects, but the possibility of forming complexes of this type should be greater for metal ions of d⁰, high-spin d⁵, or d¹⁰ configurations. Planar-pentagonal arrangements of donor atoms have been observed in complexes with coordination numbers of 6 or 7 in first-row transition metals. A good example of pentagonal coordination is that of a seven-coordinate complex of high-spin iron(III) where the metal ion is girded by a pentadentate macrocyclic ligand.⁶

The possibility of planar-pentagonal coordination may be enhanced by incorporating steric or electronic features into linear pentadentate ligands to prevent them from twisting out of planarity. Two such possible ligands, I and II, are



those derived from the Schiff base condensation of diacetylpyridine with a bidentate ligand such as 2-pyridylhydrazine or *o*-thiobenzaldehyde.^{7,8} Both I and II are potentially pentadentate ligands and it was thought planarity might be preserved in I because of the stabilization resulting from the conjugation of the aromatic rings through the aldimine linkages.

Complexation of ligand I with zinc(II) or cadmium(II)

(3) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **8**, 2331 (1969); F. K. Ross and G. D. Stucky, *ibid.*, **8**, 2734 (1969); L. M. Vallarino, V. L. Goedken, and J. V. Quagliano, *ibid.*, **12**, 102 (1973); V. L. Goedken, L. M. Vallarino, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **92**, 303 (1970); J. S. Coleman, H. Petersen, and R. A. Penneman, *Inorg. Chem.*, **4**, 135 (1965); K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 1362 (1968).

(4) E. L. Muetterties, and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1967).
 (5) F. Lions, *Rev. Pure Appl. Chem.*, **19**, 177 (1969).

(6) J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 592 (1964); E. Fleischer and S. Hawkinson, *ibid.*, **89**, 720 (1967).

(7) J. D. Curry, M. A. Robinson, and D. H. Busch, *Inorg. Chem.*, **6**, 1570 (1967).

(8) L. F. Lindoy, V. Goedken, and D. H. Busch, *J. Chem. Soc., Chem. Commun.*, 683 (1972).

Table I. Crystal Data

Space group $P2_1$	$\cos \beta = -0.2588 (7)$
Mol wt ($C_{21}H_{17}N_3S_2Zn$) 440.85	$\rho_{\text{exptl}} = 1.50 (2) \text{ g/cm}^3$
$Z = 2$	$\rho_{\text{calcd}} = 1.519 (4) \text{ g/cm}^3$
$a = 9.268 (8) \text{ \AA}$	$V = 936.6 \text{ \AA}^3$
$b = 13.174 (13) \text{ \AA}$	$\lambda(\text{Mo K}\alpha) 0.71069 \text{ \AA}$
$c = 8.172 (7) \text{ \AA}$	$\mu(\text{Mo K}\alpha) 15.26 \text{ cm}^{-1}$

yields compounds assumed to be five-coordinate, although the possibility of higher coordination numbers achieved through bridging of sulfur donors in the solid state could not be eliminated. The failure to obtain similar compounds with transition metals such as cobalt(II) or nickel(II) attests to the importance of crystal field effects in product formation and at the same time lends some credence to the possibility of planar-pentagonal coordination of the ligand.

Because of absence of diagnostic information obtainable from these complexes of d¹⁰ electronic configurations, the crystal and molecular structure of the zinc complex was determined to establish the mode of coordination of the ligand. The results of this structure analysis reveal a unique helical ligand conformation resulting from steric interactions of the ligand. The five-coordinate zinc(II) complex is mononuclear with a coordination geometry approximately midway between idealized trigonal-bipyramidal and square-pyramidal geometries. A preliminary account of this structure has appeared elsewhere.⁸

Experimental Section

A generous sample of the title compound was obtained from Dr. L. F. Lindoy. The sample was recrystallized by dissolving in a well-insulated dewar flask. The small, ruby red parallelepiped crystals were stable to air and to X-radiation. A series of precession photographs showed monoclinic symmetry with the only systematic absences being $k = 2n + 1$ for the $0k0$ reflections, indicating $P2_1$ or $P2_1/m$ as the possible space group. A well-formed crystal of dimensions $0.25 \times 0.35 \times 0.40 \text{ mm}$ was selected and mounted with the needle axis (a^*) collinear with the goniometer ϕ axis. The cell constants, obtained by least-squares refinement of the 2θ , ϕ , and χ angles of 12 accurately centered general reflections were found to be $a = 9.267 (8) \text{ \AA}$, $b = 13.174 (13) \text{ \AA}$, $c = 8.172 (7) \text{ \AA}$, and $\beta = 105.00 (4)^\circ$. (All numbers in parentheses here and elsewhere in this report are estimated standard deviations of the least significant digits.) The calculated density assuming two molecules per unit cell is 1.519 g/cm^3 , in good agreement with the observed value of $1.50 (2) \text{ g/cm}^3$ measured by flotation in carbon tetrachloride-chloroform. (A summary of crystal data is given in Table I.)

A Picker FACS-1 automated diffractometer using graphite-monochromatized Mo K α radiation with a takeoff angle of 1.5° was used for the data collection. The intensities of 1999 reflections were measured up to $2\theta = 50^\circ$ using θ - 2θ scans with a scan rate of $1.0^\circ/\text{min}$. The scan width, 2.0 at $2\theta = 0.0^\circ$, was increased as a function of θ to compensate for α_1 - α_2 splitting. Stationary crystal-stationary counter background counts of 10 sec each were collected at the high- and low-angle limits of the scan window for each reflection. The 313, 0, 10, 0, and 514 reflections were remeasured every 100 reflections to check on crystal alignment and condition. The fluctuations in the check-reflection intensities were random and varied no more than 2%. The data were reduced in the conventional manner with corrections for Lorentz and polarization effects included prior to the averaging of the multiply measured or equivalent reflections. The formula used for the Lp correction under the condition of monochromatized radiation was that given by Azaroff.⁹ Estimated standard deviations in the reflection intensities and the derived F^2 based primarily on counting statistics were calculated using the equation

$$\sigma(I) = \left[S + \frac{T_S^2(B_1B_2)}{T_B^2(B_1 + B_2)} + (pS)^2 \right]^{1/2} \quad (1)$$

S , B_1 , and B_2 are the accumulated counts for the scan and the two backgrounds, T_S and T_B are the scan and individual background

(9) L. V. Azaroff, *Acta Crystallogr.*, **8**, 701 (1955).

Table II

Positional Parameters			
Atom	x	y	z
Zn	0.0537 (1)	0.0	0.2688 (1)
S(1)	0.8438 (2)	0.4345 (2)	0.9388 (3)
S(2)	0.7585 (2)	0.5364 (2)	0.4843 (3)
N(1)	0.0597 (7)	0.3509 (5)	0.7692 (8)
N(2)	0.1765 (7)	0.5256 (5)	0.7568 (7)
N(3)	0.9753 (7)	0.6629 (5)	0.7173 (8)
C(1)	0.8497 (8)	0.3047 (6)	0.8692 (8)
C(2)	0.7444 (9)	0.2324 (7)	0.8877 (10)
C(3)	0.7560 (10)	0.1320 (7)	0.8379 (10)
C(4)	0.8659 (10)	0.1041 (7)	0.7695 (11)
C(5)	0.9728 (10)	0.1720 (7)	0.7472 (10)
C(6)	0.9630 (9)	0.2721 (7)	0.7998 (10)
C(7)	0.2008 (8)	0.3484 (6)	0.8140 (9)
C(8)	0.2981 (10)	0.2630 (7)	0.9003 (11)
C(9)	0.2716 (9)	0.4452 (6)	0.7932 (9)
C(10)	0.4247 (11)	0.4626 (8)	0.8077 (12)
C(11)	0.4714 (12)	0.5593 (9)	0.7894 (13)
C(12)	0.3748 (10)	0.6407 (7)	0.7584 (11)
C(13)	0.2226 (9)	0.6198 (6)	0.7437 (9)
C(14)	0.1002 (9)	0.6968 (6)	0.1001 (9)
C(15)	0.1348 (10)	0.8007 (6)	0.6472 (10)
C(16)	0.8352 (9)	0.7159 (6)	0.6551 (9)
C(17)	0.8083 (9)	0.8121 (7)	0.8082 (9)
C(18)	0.6676 (10)	0.8531 (7)	0.6676 (10)
C(19)	0.5595 (9)	0.8013 (7)	0.5314 (11)
C(20)	0.5843 (9)	0.7034 (7)	0.4827 (10)
C(21)	0.7237 (9)	0.6577 (7)	0.5445 (10)

Anisotropic Thermal Parameters ($\times 10^4$)^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	85 (1)	30 (1)	164 (2)	1 (1)	34 (1)	-48 (1)
S(1)	119 (3)	36 (1)	170 (4)	-4 (2)	54 (3)	-7 (2)
S(2)	122 (3)	36 (1)	159 (4)	3 (1)	1 (3)	9 (2)
C(8)	147 (14)	64 (6)	161 (15)	42 (8)	32 (12)	6 (8)
C(15)	167 (15)	34 (5)	185 (15)	-20 (7)	54 (12)	11 (7)

Isotropic Temperature Factors

Atom	B, Å ²	Atom	B, Å ²	Atom	B, Å ²
N(1)	3.2 (1)	C(6)	3.4 (1)	C(14)	3.3 (2)
N(2)	3.1 (1)	C(7)	3.2 (1)	C(16)	3.2 (1)
N(3)	3.0 (1)	C(9)	3.4 (1)	C(17)	3.9 (2)
C(1)	3.0 (1)	C(10)	5.1 (2)	C(18)	4.8 (2)
C(2)	3.7 (2)	C(11)	5.7 (2)	C(19)	4.3 (2)
C(3)	4.3 (2)	C(12)	4.5 (2)	C(20)	3.7 (2)
C(4)	5.0 (2)	C(13)	3.2 (1)	C(21)	3.5 (1)

^a The form of anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^4]$.

counting times, and p is a factor,¹⁰ here taken to be 0.02, to account for machine fluctuations and other factors which would be expected to cause variations proportional to the reflected intensity. The F^2 's and F 's were calculated in the usual way from the intensities and the $\sigma(F)$'s were calculated using the approximation

$$\sigma(F) = \sigma(I)/2FLp \quad (2)$$

The multiply measured reflections were averaged using weights defined by $w = \sigma(F^2)^{-2}$ and based upon the F^2 values

$$F(hkl)^2 = \frac{\sum_i w_i F_i^2}{\sum_i w_i} \quad (3)$$

where the summations are taken over the n measurements. The standard deviation in the mean was calculated from

$$\sigma^2(F^2) = \left[\frac{\sum_i 1}{\sum_i (\sigma(F_i^2))^2} \right]^{-1} \quad (4)$$

The total number of reflections having F 's > 0 after averaging was 1768.

The effects of absorption, $\mu_\lambda 15$, were judged to be minimal and were not compensated for. Transmission coefficients for the mini-

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Table III. Interatomic Bond Distances (Å)

Zn-S(1)	2.331 (3)	C(7)-C(9)	1.46 (1)
Zn-S(2)	2.339 (2)	C(9)-N(2)	1.36 (1)
Zn-N(1)	2.212 (7)	C(9)-C(10)	1.41 (1)
Zn-N(2)	2.117 (6)	C(10)-C(11)	1.37 (1)
Zn-N(3)	2.170 (7)	C(11)-C(12)	1.38 (1)
S(1)-C(1)	1.767 (8)	C(12)-C(13)	1.41 (1)
S(2)-C(21)	1.766 (9)	C(13)-N(2)	1.33 (1)
C(1)-C(2)	1.40 (1)	C(13)-C(14)	1.49 (1)
C(2)-C(3)	1.40 (1)	C(14)-C(15)	1.51 (1)
C(3)-C(4)	1.34 (1)	C(14)-N(3)	1.27 (1)
C(4)-C(5)	1.38 (1)	N(3)-C(16)	1.45 (1)
C(5)-C(6)	1.40 (1)	C(16)-C(17)	1.37 (1)
C(6)-C(1)	1.39 (1)	C(17)-C(18)	1.38 (1)
C(6)-N(1)	1.44 (1)	C(18)-C(19)	1.35 (1)
N(1)-C(7)	1.26 (1)	C(19)-C(20)	1.39 (1)
C(7)-C(8)	1.50 (1)	C(20)-C(21)	1.40 (1)
		C(21)-C(16)	1.41 (1)

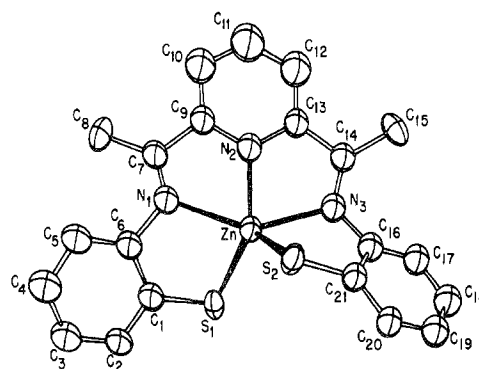


Figure 1. Labeling scheme for the bis(2-thiobenzaldimino)-2,6-diacetylpyridinezinc(II) molecule. Hydrogen atoms have been omitted for clarity.

mum and maximum dimensions of the crystal were 0.47 and 0.68, respectively. However, as mounted about the needle axis, the effective transmission coefficients varied between 0.50 and 0.60.

Structure Determination and Refinement

The structure was solved by standard heavy-atom methods and refined by full-matrix least squares. Scattering factors of neutral atoms were taken from standard sources.¹¹ The statistical distribution of E 's calculated from the Wilson plot was in good agreement with that predicted for an accentric model, and the refinement was successfully completed assuming $P2_1$ as the correct space group. The coordinates of the zinc and two sulfur atoms were located from an $E^2 - 1$ Patterson map. The zinc y parameter was arbitrarily fixed at 0.0 throughout the refinement. The positional and isotropic thermal parameters of the heavy atoms were refined using unit weights and the rest of the nonhydrogen atoms located by application of successive least-squares and difference Fourier calculations.¹² Least-squares refinement of the positional and thermal parameters (light atoms isotropic) of the nonhydrogen atoms with a limited data set (1169 most significant observations) yielded an R factor¹³ of 5.1%. The positions of the 11 aromatic hydrogen atoms were then calculated assuming C-H distances of 0.98 Å and normal aromatic C-H geometry. The hydrogen atom parameters were included but not varied, and the two methyl carbon atoms were refined with anisotropic thermal parameters, in the subsequent refinement. Anomalous dispersion corrections¹⁴ were applied for the zinc and sulfur atoms. Refinement to convergence gave an R factor of 4.2%.

(11) (a) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); (b) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(12) Patterson and electron density calculations were done on an IBM 7094 computer with the Sly-Shoemaker-van den Hende ERFR-2 program. The least-squares refinement was performed using the program SORFLS (substantially modified version of ORFLS by W. Busing, K. O. Martin, and H. Levy, "A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-395, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962).

(13) $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. The quantity minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$.

(14) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table IV. Bond Angles (deg)

S(1)-Zn-S(2)	110.4 (1)	C(5)-C(6)-N(1)	122.4 (7)	C(12)-C(13)-C(14)	125.0 (8)
S(1)-Zn-N(1)	79.7 (2)	C(1)-C(6)-N(1)	114.9 (7)	N(2)-C(13)-C(14)	114.2 (7)
S(1)-Zn-N(2)	125.5 (2)	C(6)-N(1)-C(7)	125.3 (7)	C(13)-C(14)-C(15)	117.9 (7)
S(1)-Zn-N(3)	120.1 (2)	C(6)-N(1)-Zn	111.8 (5)	C(13)-C(14)-N(3)	113.8 (7)
S(2)-Zn-N(3)	81.1 (2)	C(7)-N(1)-Zn	118.8 (6)	C(15)-C(14)-N(3)	128.1 (8)
S(2)-Zn-N(2)	124.1 (2)	N(1)-C(7)-C(8)	127.4 (8)	C(14)-N(3)-Zn	118.8 (6)
S(2)-Zn-N(1)	120.5 (2)	N(1)-C(7)-C(9)	113.9 (7)	C(14)-N(3)-C(16)	123.9 (7)
N(1)-Zn-N(2)	72.4 (2)	C(8)-C(7)-C(9)	118.4 (7)	C(16)-N(3)-Zn	112.6 (5)
N(1)-Zn-N(3)	145.6 (3)	C(7)-C(9)-C(10)	127.1 (8)	N(3)-C(16)-C(17)	123.9 (7)
N(2)-Zn-N(3)	73.2 (2)	C(7)-C(9)-N(2)	114.8 (6)	N(3)-C(16)-C(21)	113.9 (7)
S(1)-C(1)-C(2)	121.8 (6)	N(2)-C(9)-C(10)	118.1 (8)	C(17)-C(16)-C(21)	122.1 (8)
S(1)-C(1)-C(6)	120.9 (6)	C(9)-C(10)-C(11)	118.9 (9)	C(16)-C(17)-C(18)	118.6 (8)
C(1)-C(2)-C(3)	120.3 (8)	C(10)-C(11)-C(12)	122.4 (9)	C(17)-C(18)-C(19)	121.2 (9)
C(2)-C(3)-C(4)	120.6 (9)	C(11)-C(12)-C(13)	116.8 (9)	C(18)-C(19)-C(20)	120.8 (8)
C(3)-C(4)-C(5)	121.7 (9)	N(2)-C(13)-C(14)	114.2 (7)	C(19)-C(20)-C(21)	120.4 (8)
C(4)-C(5)-C(6)	117.7 (8)	Zn-N(2)-C(9)	118.4 (5)	C(20)-C(21)-C(16)	116.9 (8)
C(5)-C(6)-C(1)	122.4 (8)	Zn-N(2)-C(13)	118.6 (5)	C(20)-C(21)-S(2)	121.3 (6)
		C(9)-N(2)-C(13)	122.9 (7)	S(2)-C(21)-C(16)	121.8 (6)

Final refinement was carried out using weights based on the σ 's from eq 2. All data with $F^2 > 0$, 1769, were included in the final refinement for which $R = 5.6\%$, $R_w = 5.1\%$ ¹⁵ at convergence. At this point, all the y coordinates were inverted to test for the absolute configuration and refinement to convergence yielded $R = 5.5\%$, $R_w = 6.1\%$. Application of Hamilton's significance test¹⁶ to R_w leads to the conclusion that the absolute configuration is best described by the first coordinate assignment at the 99.5% probability level.

The residual electron density of the final difference Fourier map based on the original coordinate assignment had a general background of $0.3 \text{ e}/\text{Å}^3$ with the highest peak, $0.6 \text{ e}/\text{Å}^3$, in the region expected for the hydrogens of the methyl groups. Final atomic coordinates and thermal parameters are listed in Table II. Selected interatomic distances, angles, and errors¹⁷ are listed in Tables III and IV. A table of observed and calculated structure factor amplitudes is available.¹⁸

Description and Discussion of the Structure

Bis(2-thiobenzaldimino)-2,6-diacetylpyridinezinc(II) is a five-coordinate complex with the ligand donor atoms describing an approximate trigonal bipyramid. The overall conformation of the ligand, however, is decidedly helical with the Λ conformation for the particular crystal studied. The molecule and atomic labeling are illustrated in Figure 1.¹⁹

The C=N bonds of the azomethine linkages are both short, 1.26 (1) and 1.27 (1) Å, and the neighboring N-C bonds are long, indicative of highly localized double bonds. Both the overall conformation of the molecule and the strongly localized double-bond structure result from steric interactions between the methyl groups C(8) and C(15) with the protons of C(10), C(12), C(5), and C(17) of the aromatic rings. The resultant unusual helical ligand conformation, as shown in Figure 1, results from the minimization of these nonbonding repulsions. Table V gives a number of torsion angles and dihedral angles for the ligand. The largest torsion angles, about 56° , are those about the N-C(aryl) bonds N(1)-C(6) and N(3)-C(16) which are responsible for the sulfur atoms about 1.33 and 1.68 Å above and below the least-squares plane defined by Zn, N(2), C(9), and C(13). As can be seen in Figure 2, the ligand presents a somewhat puckered

Table V. Selected Torsion Angles and Dihedral Angles

Defining planes		Angle, deg
A	B	
N(1)-N(2)-N(3)	S(1)-Zn-S(2)	+64.7 (1)
C(5)-C(6)-N(1)	C(6)-N(1)-C(7)	-56 (1)
C(14)-N(3)-C(16)	N(3)-C(16)-C(17)	-57 (1)
N(1)-C(7)-C(9)	C(7)-C(9)-N(2)	+11 (1)
N(2)-C(13)-C(14)	C(13)-C(14)-N(3)	+10 (1)
C(6)-N(1)-C(7)	N(1)-C(7)-C(8)	-3 (1)
C(15)-C(14)-N(3)	C(14)-N(3)-C(16)	-8 (1)
C(8)-C(7)-C(9)	C(7)-C(9)-C(10)	+16 (1)
C(12)-C(13)-C(14)	C(13)-C(14)-C(15)	+12 (1)

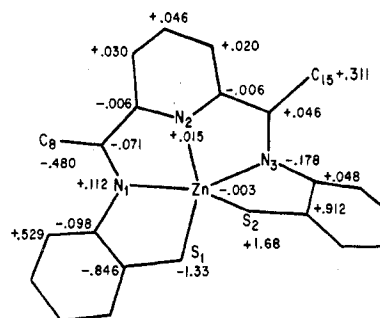


Figure 2. Diagram illustrating the displacement of atoms from the least-squares plane defined by atoms Zn, N(2), C(9), and C(13).

appearance going around the helix from S(1) to S(2); S(1) and C(8) both point down and C(15) and S(2) both point up.

Although the sulfur atoms possess formal negative charges and thus may exert some repulsive Coulomb force on each other, the methyl steric interactions are undoubtedly the dominant conformation determining factors. The S-S distance of 3.834 (4) Å is greater than the S-S van der Waals distance of 3.70 Å²⁰ and also greater than the distances between nonbonded sulfur atoms in several metal dithiolate complexes.²¹ It should be pointed out that the normal van der Waals distance between two sulfur atoms in the cis positions of the coordination sphere is too great to be spanned by a dimethylene bridge; attempts to cyclize this pentadentate ligand with 1,2-dihaloethanes have been unsuccessful. However, metal template macrocyclization of similar chelates has been successful by employing the longer

(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Table 7.20.

(21) (a) R. Eisenberg, Z. Dori, H. B. Gray, and J. A. Ibers, *Inorg. Chem.*, **7**, 741 (1968); (b) M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4253 (1968); (c) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500 (1964).

(15) $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$.

(16) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(17) Distances, angles, dihedral angles, rms displacements, and deviations from least-squares planes were computed with the program SORFFE (a modification of ORFFE by W. Busing and K. O. Levy, "A Fortran Crystallographic Function and Error Program," Report ORNL-TM306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964).

(18) See paragraph at end of paper regarding supplementary material.

(19) This plot was drawn using the program of C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

bridge afforded by α,α' -dibromo-*o*-xylene.²² Macrocyclic ligand complexes of thioethers which contain dimethylene bridges are well known²³ but it was necessary to prepare the ligands by conventional organic synthetic methods. The structures of these latter complexes are probably distorted in a manner to accommodate the large sulfur atoms.

The zinc-sulfur bond lengths in this complex are remarkably similar to those found in the extensively studied metal-thiolato complexes.²⁴ The zinc-sulfur distances, 2.331 (3) and 2.339 (2) Å, are in good agreement with the sum of the zinc(II) and sulfur covalent radii, 2.35 Å.²³ The range of Zn-S distances in dithiolate complexes for nonbridging sulfur atoms is 2.312 (6)²⁵ to 2.42 Å.²⁶ The C-S bond distances found here, 1.767 (8) and 1.766 (9) Å, are very similar to those found in 1,2-dithiolene complexes which have the sulfur atoms bonded to benzenoid or other aromatic rings. For example, the C-S distance in $[\text{Co}(\text{S}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)]^-$ is 1.77 (2) Å and in $[\text{Co}(\text{S}_2\text{C}_6\text{Cl}_4)_2]^{2-}$ is 1.76 (2) Å.²⁵ The C=N, C(aryl)-N, C(aryl)-C, and aryl C-C bond distances are all reasonable in comparison with analogous bonds in macrocyclic complexes. The C=N distance is slightly shorter than found in several salicylaldehyde complexes, 1.30 (2) Å,²⁷ and in the tetradentate macrocyclic complex 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienickel(II), 1.30 (1) Å,²⁸ indicating slightly less delocalization in this complex, consistent with sterically induced nonplanarity of the ligand. The average of the three Zn-N distances is 2.17 (3) Å.

Least-squares planes through each of the three aromatic rings revealed no significant deviations from planarity in any of them. The azomethine carbons C(7) and C(14) are below and above the pyridine plane by 0.07 and 0.05 Å, respectively, primarily as a result of the steric interactions of the methyl groups with the hydrogen atoms of C(10) and C(12) of the pyridine rings.

Thermal motions in the molecule are within expected limits. The methyl groups possess the largest rms excursions, but they are only slightly greater than those of the zinc and sulfur atoms, as expected by the steric restrictions imposed by the adjoining parts of the molecule. Table VI gives the rms displacements for all the nonhydrogen atoms.

The closest nonbonded intra- and intermolecular contacts are given in Table VII. The intramolecular C-C contacts involving the methyl groups are uniformly about 3.05 Å, which is about 0.5 Å less than the sum of the appropriate

Table VI. Root-Mean-Square Amplitudes of Vibration (Å)

Anisotropically Refined Atoms ^a			
Atom	Min	Intermed	Max
Zn	0.161 (1)	0.184 (1)	0.229 (1)
S(1)	0.177 (3)	0.205 (3)	0.239 (3)
S(2)	0.173 (3)	0.204 (3)	0.259 (3)
C(8)	0.181 (13)	0.227 (11)	0.291 (13)
C(15)	0.155 (13)	0.244 (10)	0.267 (11)
Isotropically Refined Atoms			
Atom	Atom		
N(1)	0.201 (4)	C(11)	0.268 (5)
N(2)	0.199 (4)	C(12)	0.238 (5)
N(3)	0.195 (4)	C(13)	0.201 (5)
C(1)	0.195 (4)	C(14)	0.205 (5)
C(2)	0.217 (5)	C(16)	0.200 (5)
C(3)	0.234 (4)	C(17)	0.222 (5)
C(4)	0.251 (5)	C(18)	0.247 (5)
C(5)	0.226 (5)	C(19)	0.233 (5)
C(6)	0.210 (4)	C(20)	0.218 (5)
C(7)	0.202 (5)	C(21)	0.210 (5)
C(9)	0.209 (5)		
C(10)	0.254 (5)		

^a Calculated along principal axes of thermal motion.

Table VII. Selected Nonbonded Contacts, Å

Intramolecular			
Atoms	Distance	Atoms	Distance
S(1)-S(2)	3.83	C(12)-C(15)	3.03
C(5)-C(8)	3.18	C(15)-C(16)	3.01
C(6)-C(8)	3.00	C(15)-C(17)	3.18
C(8)-C(10)	3.05		
Intermolecular			
Atoms	Distance	Transformation	
C(15)-S(1)	3.79	$2-x, \frac{1}{2}+y, 2-z$	
S(2)-C(5)	3.94	$2-x, \frac{1}{2}+y, 1-z$	
C(15)-S(2)	3.47	$2-x, \frac{1}{2}+y, 1-z$	
C(2)-C(19)	3.94	$1-x, \frac{1}{2}-y, 1-z$	
C(2)-C(20)	3.71	$1-x, \frac{1}{2}-y, 1-z$	
C(3)-C(20)	3.66	$1-z, \frac{1}{2}-y, 1-z$	
C(4)-C(17)	3.90	$x, y-1, z$	
C(4)-C(18)	3.79	$x, y-1, z$	
C(11)-C(20)	3.51	$x+1, y, z$	
C(11)-C(21)	3.68	$x+1, y, z$	
C(12)-C(20)	3.43	$x+1, y, z$	
C(12)-C(21)	3.53	$x+1, y, z$	

van der Waals radii, again pointing up the substantial steric interactions of these methyl groups.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2316.

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