Amine Adducts of Thiocarbamate Complexes. Crystal and Molecular Structure of Bis(cyclopentamethylenethiocarbamato)bis(piperidine)zinc(II)

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The crystal and molecular structure of the four-coordinate complex $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$ has been determined from three-dimensional X-ray data collected by the $\theta-2\theta$ scan technique. The structure was solved by standard heavy-atom methods and has been refined by least-squares procedures to a conventional R factor of 0.073 for 2520 nonzero reflections. The complex crystallizes in space group $P\bar{1}$ of the triclinic system in a cell of dimensions $a = 10.279$ (5) Å, $b = 12.690$ (5) Å, $c = 12.161$ (5) Å, $\alpha = 107.44$ (5)°, $\beta = 92.67$ (5)°, $\gamma = 117.27$ (5)°, and $V = 1313$ Å^3. There are two molecules per unit cell ($\rho_{exptl} = 1.31$ (2) g/cm^3; $\rho_{calcd} = 1.32$ g/cm^3). The coordination geometry about the Zn(II) ion is approximately tetrahedral with the sulfur atoms of the two thiocarbamate ligands occupying two coordination sites and nitrogen atoms of the piperidine ligands in the remaining two sites. The molecule has approximate twofold symmetry. Uncoordinated oxygen atoms of the thiocarbamate ligands are hydrogen bonded to the amine protons of the coordinated piperidine ligands. The compound represents the first monomeric thiocarbamate complex reported.

Introduction

Recent studies on complexes of the thiocarbamate ligands have indicated significant and unusual differences in the properties of these complexes relative to the related dithiocarbamates.[1] While dithiocarbamate ligands form simple monomeric bis and tris complexes with a variety of metals, simple thiocarbamate complexes have all been found to be polymeric. Structural studies on $[Ni(SOCN(C_3H_7)_2)_2]_6{}^2$ and $[M-(SOCN(C_3H_7)_2)]_6$ (M = Cu, Ag)[3,4] have indicated a cyclic polymeric geometry of six- and three-coordinate units, respectively. In each case the thiocarbamate ligand was found to bridge adjacent metal ions through the sulfur donor. Bond distances within the ligands have indicated that delocalization is mainly confined to the $C\!\dot{-}\!O$ and $>\!C\!\dot{-}\!NR_2$ bonds with C–S bond lengths indicating nearly single-bond character. These observations are consistent with infrared data on thiocarbamate complexes where strong coupling is observed between the $\nu(C\!\dot{-}\!O)$ and $\nu(C\!\dot{-}\!N)$ bands in the region between 1450 and 1550 cm^{-1}.[1] Of the resonance structures envisioned for this ligand system it would appear that structure II is of minor importance in contrast to the dithiocarbamates, where the C–S bond has been observed to have significant multiple character.
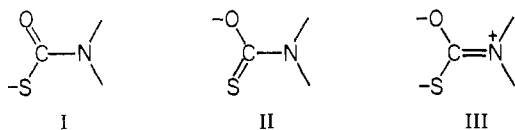
A distinctive chemical property of certain of the thiocarbamate complexes is their ability to form nitrogen base adducts. On addition of nitrogen base ligands to solutions of the simple bis Ni(II) or Zn(II) complexes, the polymeric units are broken up with formation of stable monomeric amine addition products.[5,6] In the case of the bis(cyclopentamethylenethiocarbamato)nickel(II) complex five- and six-coordinate adducts are readily formed with a variety of amine ligands. This contrasts with the relative inertness of the analogous bis(dithiocarbamato) complexes of Ni(II) toward base addition.[7] The Zn(II) complexes of the dithiocarbamates are known to add nitrogen base ligands forming stable trigonal-bipyramidal or unstable six-coordinate bis(amine) adducts. Bis(cyclopentamethylenethiocarbamato)zinc(II), however, has been found to form exclusively bis addition products with piperidine, with no evidence for stable products containing a single amine ligand. Adduct formation of the Zn(II) complex is accompanied by significant changes in the infrared spectrum of the complex in the region assignable to the $\nu(C\!\dot{-}\!O)$ and $\nu(C\!\dot{-}\!N)$ modes. To aid in understanding the unusual coordination behavior of thiocarbamate ligands a single-crystal X-ray diffraction study has been undertaken on the bis(piperidine) adduct $Zn(SOCN(C_5H_{10}))_2\text{-}(NC_5H_{11})_2$. The results of this study have appeared previously in a preliminary communication.[8]

Collection and Reduction of the X-Ray Data

The complex $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$ was prepared by procedures described previously.[5] Crystals of the colorless adduct suitable for space group determination and X-ray data collection were grown from a hexane–benzene solution. On the basis of Weissenberg and precession photographs of the $hk0$, $hk1$, $h0l$, $h1l$, $0kl$, and $1kl$ zones, it was established that the complex crystallizes in the triclinic system. The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 18 strong reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 10.279$ (5) Å, $b = 12.690$ (5) Å, $c = 12.161$ (5) Å, $\alpha = 107.44$ (5)°, $\beta = 92.67$ (5)°, $\gamma = 117.27$ (5)°, and $V = 1313$ Å^3. This refinement was performed using the PICKLST program of Dr. R. Eisenberg.[9] An experimental density of 1.31 (1) g/cm^3 obtained by the flotation method agrees with a calculated value of 1.32 g/cm^3 for two $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$ molecules per unit cell. Space group $P\bar{1}$ ($C^1{}_i$, No. 2) was chosen for the refinement and was verified by the successful completion of the structure.[10]

A crystal of dimensions 0.18 × 0.20 × 0.22 mm was mounted along the a axis and prepared for data collection. The mosaic spread of the crystal was determined using the narrow-source open-counter ω-scan technique.[11] The average width at half-height was found to be 0.06°. An independent set of intensity data was collected by the

(1) B. J. McCormick and B. P. Stormer, *Inorg. Chem.*, **11**, 729 (1972), and references therein.

(2) P. Method, Ph.D. Thesis, West Virginia University, Morgantown, W. Va., 1973.

(3) R. Hesse and A. Aava, *Acta Chem. Scand.*, **24**, 1355 (1970).

(4) P. Jennische and R. Hesse, *Acta Chem. Scand.*, **25**, 423 (1971).

(5) B. J. McCormick and D. L. Greene, *Inorg. Nucl. Chem. Lett.*, **8**, 599 (1972).

(6) B. J. McCormick and D. L. Greene presented at the 4th Central Regional Meeting of the American Chemical Society, Pittsburgh, Pa., May 1972; see Abstracts, No. 139.

(7) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1969).

(8) C. G. Pierpont, D. L. Greene, and B. J. McCormick, *J. Chem. Soc. D*, 960 (1972).

(9) In addition to the PICKLST setting program, other programs used were versions of the Busing–Levy ORFLS least-squares program, the Busing–Martin–Levy ORFFE function and error program, and the Johnson ORTEP plotting program. All computing was performed on the West Virginia University IBM 360/75 computer.

(10) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1960, p 75.

(11) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

Table I. Final Positional and Anisotropic Thermal Parameters for $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	−0.1642 (1)	0.2083 (1)	0.0552 (1)	0.0087 (2)	0.0037 (2)	0.0058 (1)	0.0027 (1)	0.0007 (1)	0.0019 (1)
S(1)	−0.2936 (3)	0.3102 (3)	0.1368 (2)	0.0109 (5)	0.0078 (6)	0.0090 (4)	0.0055 (1)	0.0009 (2)	0.0007 (2)
S(2)	−0.2308 (3)	0.1412 (3)	−0.1464 (2)	0.0169 (5)	0.0059 (5)	0.0061 (2)	0.0067 (2)	0.0013 (2)	0.0022 (1)
O(1)	−0.0725 (8)	0.3940 (6)	0.3137 (5)	0.0256 (15)	0.0082 (10)	0.0061 (9)	0.0107 (6)	−0.0003 (7)	0.0015 (5)
O(2)	−0.1545 (7)	−0.0262 (7)	−0.1293 (5)	0.0181 (15)	0.0114 (14)	0.0068 (9)	0.0107 (5)	0.0007 (6)	0.0021 (5)
N(1)	−0.1979 (6)	0.0603 (6)	0.1124 (5)	0.0060 (11)	0.0014 (13)	0.0054 (8)	0.0000 (1)	0.0010 (5)	0.0016 (4)
N(2)	0.0615 (7)	0.3406 (7)	0.1171 (5)	0.0045 (14)	0.0065 (14)	0.0109 (9)	0.0013 (6)	−0.0009 (5)	−0.0014 (5)
N(3)	−0.1763 (8)	0.5177 (7)	0.3355 (6)	0.0141 (16)	0.0042 (15)	0.0071 (11)	0.0029 (7)	0.0004 (7)	0.0012 (6)
N(4)	−0.2882 (8)	−0.0815 (8)	−0.3075 (6)	0.0158 (18)	0.0043 (15)	0.0066 (9)	0.0047 (6)	−0.0012 (7)	0.0013 (6)
C(1)	−0.3628 (9)	−0.0350 (10)	0.0894 (9)	0.0082 (12)	0.0046 (15)	0.0127 (11)	−0.0002 (10)	−0.0027 (9)	0.0031 (10)
C(2)	−0.3942 (9)	−0.1446 (10)	0.1268 (9)	0.0119 (14)	0.0040 (15)	0.0127 (11)	0.0015 (11)	−0.0002 (9)	0.0064 (10)
C(3)	−0.3224 (10)	−0.0971 (9)	0.2578 (8)	0.0132 (20)	0.0067 (19)	0.0095 (15)	0.0031 (8)	0.0044 (8)	0.0031 (7)
C(4)	−0.1529 (10)	−0.0071 (10)	0.2765 (8)	0.0127 (17)	0.0026 (20)	0.0106 (15)	0.0027 (9)	−0.0010 (10)	0.0006 (8)
C(5)	−0.1239 (10)	0.1092 (9)	0.2381 (7)	0.0200 (13)	0.0020 (13)	0.0066 (8)	0.0045 (11)	−0.0021 (9)	0.0030 (8)
C(6)	0.1678 (9)	0.2922 (8)	0.0784 (7)	0.0081 (17)	0.0032 (18)	0.0083 (10)	0.0028 (7)	0.0003 (8)	0.0005 (7)
C(7)	0.3293 (9)	0.3912 (9)	0.1347 (8)	0.0071 (15)	0.0015 (18)	0.0138 (15)	0.0015 (7)	−0.0007 (9)	0.0035 (7)
C(8)	0.3712 (9)	0.5126 (10)	0.1163 (9)	0.0075 (15)	0.0078 (18)	0.0133 (15)	0.0024 (9)	0.0021 (9)	0.0035 (9)
C(9)	0.2599 (10)	0.5632 (9)	0.1540 (9)	0.0106 (14)	0.0035 (15)	0.0143 (9)	0.0006 (9)	−0.0001 (10)	0.0035 (8)
C(10)	0.1010 (9)	0.4582 (9)	0.0939 (7)	0.0085 (15)	0.0028 (16)	0.0082 (10)	0.0031 (7)	0.0003 (7)	0.0020 (7)
C(11)	−0.1677 (10)	0.4144 (10)	0.2734 (7)	0.0130 (15)	0.0108 (20)	0.0033 (8)	0.0035 (10)	0.0008 (8)	0.0014 (7)
C(12)	−0.0629 (12)	0.6125 (9)	0.4434 (8)	0.0242 (20)	0.0029 (16)	0.0070 (9)	0.0062 (9)	−0.0019 (10)	0.0002 (8)
C(13)	0.0466 (9)	0.7297 (10)	0.4170 (8)	0.0063 (16)	0.0100 (18)	0.0107 (15)	0.0032 (8)	−0.0033 (9)	0.0000 (9)
C(14)	−0.0402 (10)	0.7810 (9)	0.3633 (8)	0.0145 (20)	0.0042 (18)	0.0102 (13)	0.0021 (9)	0.0019 (9)	0.0025 (8)
C(15)	−0.1592 (9)	0.6819 (9)	0.2595 (7)	0.0140 (20)	0.0027 (18)	0.0073 (13)	0.0038 (8)	−0.0006 (8)	0.0019 (7)
C(16)	−0.2627 (9)	0.5637 (10)	0.2861 (8)	0.0058 (15)	0.0074 (19)	0.0125 (15)	0.0035 (9)	−0.0009 (8)	0.0020 (9)
C(17)	−0.2202 (9)	0.0019 (9)	−0.1933 (7)	0.0099 (17)	0.0097 (19)	0.0049 (10)	0.0038 (8)	0.0018 (7)	0.0021 (7)
C(18)	−0.2912 (11)	−0.2030 (10)	−0.3512 (9)	0.0173 (15)	0.0030 (14)	0.0119 (11)	0.0077 (12)	0.0020 (10)	0.0006 (9)
C(19)	−0.4497 (11)	−0.3085 (9)	−0.3938 (9)	0.0154 (15)	0.0017 (12)	0.0117 (9)	0.0030 (8)	0.0008 (10)	0.0025 (8)
C(20)	−0.5387 (11)	−0.2917 (12)	−0.4861 (9)	0.0138 (15)	0.0129 (13)	0.0115 (9)	0.0029 (12)	−0.0008 (11)	0.0033 (10)
C(21)	−0.5326 (11)	−0.1644 (11)	−0.4372 (9)	0.0162 (14)	0.0074 (15)	0.0125 (9)	0.0044 (10)	−0.0055 (11)	0.0017 (10)
C(22)	−0.3714 (12)	−0.0563 (9)	−0.3923 (8)	0.0271 (13)	0.0025 (11)	0.0064 (8)	0.0060 (10)	−0.0024 (10)	0.0016 (7)

a Standard deviations of the least significant figures are given in parentheses here and in subsequent tables. b Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

θ-2θ scan technique using Zr-filtered Mo Kα radiation at a takeoff angle of 1.5°. A receiving aperture of dimensions 4.5 × 4.5 mm was positioned 24 cm from the crystal. An unsymmetrical scan range in 2θ was used from −0.6° to +0.7° of the Mo Kα peak with allowances made for the Kα_1-Kα_2 separation at higher 2θ values. The data set was collected within the angular range 5° ≤ 2θ ≤ 50°. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded about 10,000 counts/sec during the scan. The attenuators used were brass foil of thickness chosen to give an approximate attenuation factor of 2.5. During data collection the intensities of six standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 3% during the time required to collect data. The data were processed in the usual way with the values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. The intensities of a total of 3383 reflections were measured, of which 2520 were observed to be greater than 2σ. Since the crystal was approximately equidimensional and the linear absorption coefficient small ($\mu = 11.0$ cm^{-1}), no correction was made for absorption effects.

Solution and Refinement of the Structure

The position of the zinc atom was determined from a three-dimensional Patterson function. After a cycle of least-squares refinement of the positional and isotropic thermal parameters of this atom and a single scale factor, the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ were 0.437 and 0.520, respectively. From a difference Fourier map based on phases obtained from the Zn contribution, the positions of the coordinated sulfur and nitrogen atoms were determined. Two cycles of least-squares refinement of the scale factor and the positional and isotropic thermal parameters of these five atoms reduced the discrepancy factors to $R_1 = 0.344$ and $R_2 = 0.446$. A difference Fourier map based on this refinement revealed the positions of all other nonhydrogen atoms in the structure.

The complete trial structure was refined by a least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weights w were assigned as $4F^2/\sigma^2(F^2)$ where the standard deviations $\sigma(F^2)$ were estimated from counting statistics according to the formula given by Corfield, *et al.*,[12] with a value of 0.03 for the un-

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

Atom	Min	Intermed	Max
Zn	0.134 (3)	0.182 (3)	0.207 (3)
S(1)	0.183 (7)	0.207 (6)	0.275 (8)
S(2)	0.151 (7)	0.199 (7)	0.266 (8)
O(1)	0.16 (1)	0.20 (1)	0.33 (2)
O(2)	0.18 (1)	0.21 (1)	0.30 (2)
N(1)	0.07 (2)	0.19 (2)	0.19 (2)
N(2)	0.13 (2)	0.20 (2)	0.32 (2)
N(3)	0.15 (2)	0.22 (2)	0.26 (3)
N(4)	0.14 (2)	0.19 (2)	0.28 (2)
C(1)	0.14 (3)	0.21 (2)	0.32 (2)
C(2)	0.07 (2)	0.22 (2)	0.32 (2)
C(3)	0.18 (2)	0.22 (2)	0.28 (3)
C(4)	0.12 (3)	0.22 (3)	0.29 (3)
C(5)	0.09 (3)	0.19 (2)	0.32 (2)
C(6)	0.13 (2)	0.18 (2)	0.25 (2)
C(7)	0.04 (3)	0.17 (2)	0.31 (3)
C(8)	0.17 (2)	0.23 (2)	0.29 (3)
C(9)	0.12 (2)	0.23 (2)	0.32 (2)
C(10)	0.10 (3)	0.18 (2)	0.24 (2)
C(11)	0.15 (2)	0.23 (2)	0.29 (2)
C(12)	0.10 (3)	0.21 (2)	0.34 (2)
C(13)	0.13 (2)	0.24 (2)	0.32 (2)
C(14)	0.15 (2)	0.26 (2)	0.27 (2)
C(15)	0.10 (3)	0.20 (2)	0.27 (2)
C(16)	0.14 (2)	0.21 (2)	0.31 (2)
C(17)	0.18 (2)	0.20 (2)	0.25 (2)
C(18)	0.11 (3)	0.27 (2)	0.30 (2)
C(19)	0.07 (3)	0.25 (2)	0.29 (2)
C(20)	0.22 (2)	0.29 (2)	0.32 (2)
C(21)	0.19 (2)	0.21 (2)	0.36 (2)
C(22)	0.06 (3)	0.19 (2)	0.36 (2)

certainty parameter p. In all refinements only the 2520 reflections for which $F_o^2 \geq 2\sigma(F_o^2)$ were used. The atomic scattering factors of the nonhydrogen atoms were taken from Cromer and Waber's report[13] while those of hydrogen were taken from the report by Stewart, *et al.*[14] The effects of anomalous dispersion were included in the cal-

(12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

Table III. Fixed Positional Parameters of Hydrogen Atoms

Atom[a]	x	y	z
HN(1)	−0.120	0.080	0.041
HN(2)	0.101	0.362	0.201
H(1)C(1)	0.013	0.009	0.008
H(2)C(1)	−0.340	0.040	0.120
H(1)C(2)	−0.541	−0.140	0.142
H(2)C(2)	−0.520	−0.200	0.043
H(1)C(3)	−0.361	−0.039	0.338
H(2)C(3)	−0.420	−0.179	0.259
H(1)C(4)	−0.121	−0.060	0.203
H(2)C(4)	−0.043	−0.041	0.380
H(1)C(5)	−0.141	0.059	0.302
H(2)C(5)	0.022	0.179	0.260
H(1)C(6)	0.140	0.262	0.002
H(2)C(6)	0.021	0.159	0.080
H(1)C(7)	0.360	0.422	0.239
H(2)C(7)	0.442	0.403	0.100
H(1)C(8)	0.389	0.499	0.020
H(2)C(8)	0.441	0.559	0.061
H(1)C(9)	0.300	0.619	0.141
H(2)C(9)	0.302	0.601	0.262
H(1)C(10)	0.103	0.460	0.001
H(2)C(10)	0.021	0.483	0.141
H(1)C(12)	−0.119	0.679	0.521
H(2)C(12)	0.002	0.489	0.572
H(1)C(13)	0.142	0.761	0.480
H(2)C(13)	0.120	0.679	0.360
H(1)C(14)	0.021	0.861	0.366
H(2)C(14)	−0.063	0.802	0.421
H(1)C(15)	−0.160	0.739	0.200
H(2)C(15)	−0.142	0.619	0.179
H(1)C(16)	−0.341	0.502	0.220
H(2)C(16)	−0.342	0.600	0.302
H(1)C(18)	−0.179	−0.190	−0.343
H(2)C(18)	−0.220	−0.179	−0.440
H(1)C(19)	−0.402	−0.381	−0.453
H(2)C(19)	−0.502	−0.401	−0.341
H(1)C(20)	−0.660	−0.380	−0.481
H(2)C(20)	−0.481	−0.322	−0.542
H(1)C(21)	−0.603	−0.239	−0.360
H(2)C(21)	−0.641	−0.179	−0.500
H(1)C(22)	0.361	−0.081	0.342
H(2)C(22)	0.341	0.062	0.481

[a] Each H atom was assigned a fixed isotropic thermal parameter of 5.0 Å².

culated structure factors with the values of $\Delta f'$ and $\Delta f''$ for Zn and S taken from Cromer's tabulation.[15] Two cycles of refinement including all nonhydrogen atoms with individual isotropic temperature factors reduced the discrepancy factors R_1 and R_2 to values of 0.104 and 0.113, respectively.

Least-squares refinement was continued with anisotropic thermal models assumed for all of the atoms. Three cycles of least squares converged to $R_1 = 0.079$ and $R_2 = 0.092$. A difference Fourier map based on this cycle of refinement was then used to locate the positions of 39 of the 42 hydrogen atoms of the structure. Approximate positions for the three hydrogen atoms not located were determined and all 42 atoms were included in the refinement as fixed contributions. Two additional cycles of refinement converged with $R_1 = 0.073$ and $R_2 = 0.086$. No parameter changed by more than 30% of its standard deviation on the final cycle of refinement. The estimated standard deviation of an observation of unit weight is 1.78. A final difference Fourier map showed residual electron density equivalent to about 20% the height of a carbon atom in the vicinity of O(2). The final positional and anisotropic thermal parameters of the atoms in this structure are given in Table I. A table of the final F_o and $|F_c|$ values (in electrons × 10) for the 2520 reflections used in the refinement is available.[16] In Table II, the root-mean-square amplitudes of

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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

(16) A listing of observed and calculated structure factors 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. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2148.

Table IV. Intramolecular Distances and Angles

Intramolecular Distances, Å

Zn-S(1)	2.314 (3)	C(19)-C(20)	1.54 (1)
Zn-S(2)	2.294 (3)	C(20)-C(21)	1.52 (1)
Zn-N(1)	2.084 (7)	C(21)-C(22)	1.52 (1)
Zn-N(2)	2.069 (6)	N(1)-C(1)	1.51 (1)
S(1)-C(11)	1.76 (1)	N(1)-C(5)	1.48 (1)
S(2)-C(17)	1.74 (1)	C(1)-C(2)	1.49 (1)
O(1)-C(11)	1.24 (1)	C(2)-C(3)	1.53 (1)
O(2)-C(17)	1.24 (1)	C(3)-C(4)	1.54 (1)
N(3)-C(11)	1.35 (1)	C(4)-C(5)	1.58 (1)
N(4)-C(17)	1.37 (1)	N(2)-C(6)	1.51 (1)
N(3)-C(12)	1.47 (1)	N(2)-C(10)	1.48 (1)
N(3)-C(16)	1.46 (1)	C(6)-C(7)	1.51 (1)
C(12)-C(13)	1.54 (1)	C(7)-C(8)	1.49 (1)
C(13)-C(14)	1.54 (1)	C(8)-C(9)	1.57 (1)
C(14)-C(15)	1.47 (1)	C(9)-C(10)	1.51 (1)
C(15)-C(16)	1.53 (1)	S(1)-O(1)	2.624 (7)
N(4)-C(18)	1.46 (1)	S(2)-O(2)	2.636 (7)
N(4)-C(22)	1.50 (1)	O(1)-N(2)	2.874 (9)
C(18)-C(19)	1.49 (1)	O(2)-N(1)	2.946 (8)

Intramolecular Angles, Deg

S(1)-Zn-S(2)	108.2 (1)	C(17)-N(4)-C(22)	122.0 (9)
S(1)-Zn-N(1)	112.8 (2)	C(18)-N(4)-C(22)	116.2 (7)
S(1)-Zn-N(2)	106.6 (2)	N(4)-C(18)-C(19)	109.5 (8)
S(2)-Zn-N(1)	112.3 (2)	C(18)-C(19)-C(20)	112.0 (9)
S(2)-Zn-N(2)	111.2 (2)	C(19)-C(20)-C(21)	110.7 (9)
N(1)-Zn-N(2)	105.6 (3)	C(20)-C(21)-C(22)	110.9 (9)
Zn-S(1)-C(11)	99.7 (4)	C(21)-C(22)-N(4)	109.8 (8)
Zn-S(2)-C(17)	102.5 (3)	Zn-N(1)-C(1)	111.6 (6)
S(1)-C(11)-O(1)	121.2 (8)	Zn-N(1)-C(5)	111.3 (5)
S(2)-C(17)-O(2)	123.5 (7)	C(1)-N(1)-C(5)	111.7 (7)
S(1)-C(11)-N(3)	119.3 (8)	N(1)-C(1)-C(2)	114.2 (8)
S(2)-C(17)-N(4)	118.6 (8)	C(1)-C(2)-C(3)	110.4 (8)
O(1)-C(11)-N(3)	119.5 (8)	C(2)-C(3)-C(4)	108.4 (7)
O(2)-C(17)-N(4)	118.0 (8)	C(3)-C(4)-C(5)	110.6 (8)
C(11)-N(3)-C(12)	120.1 (8)	C(4)-C(5)-N(1)	109.0 (7)
C(11)-N(3)-C(16)	123.3 (8)	Zn-N(2)-C(6)	115.6 (5)
C(12)-N(3)-C(16)	114.0 (8)	Zn-N(2)-C(10)	112.3 (5)
N(3)-C(12)-C(13)	109.2 (8)	C(6)-N(2)-C(10)	110.8 (7)
C(12)-C(13)-C(14)	110.2 (7)	N(2)-C(6)-C(7)	112.3 (7)
C(13)-C(14)-C(15)	112.2 (8)	C(6)-C(7)-C(8)	112.2 (8)
C(14)-C(15)-C(16)	111.8 (8)	C(7)-C(8)-C(9)	112.2 (8)
C(15)-C(16)-N(3)	110.8 (7)	C(8)-C(9)-C(10)	109.1 (8)
C(17)-N(4)-C(18)	121.7 (8)	C(9)-C(10)-N(2)	113.0 (7)

Dihedral Angles between Planes, Deg

(Zn, S(1), S(2))-(Zn, N(1), N(2))	88.0 (2)
(Zn, S(1), N(1))-(Zn, S(2), N(2))	91.7 (2)
(Zn, S(1), N(2))-(Zn, S(2), N(1))	93.6 (2)
(S(1), O(1), C(11))-(N(3), C(12), C(16))	174 (1)
(S(2), O(2), C(17))-(N(4), C(18), C(22))	177 (1)

vibration of the anisotropically refined atoms are presented. The fixed positional parameters of the hydrogen atoms are given in Table III.

Description and Discussion of the Structure

The coordination geometry about the metal atom in the $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$ molecule is essentially tetrahedral. Perspective views of the molecule are shown in Figures 1 and 2. Intramolecular bond distances and angles for the molecule are presented in Table IV. (Least-squares planes and deviations of the atoms from the planes are given in Table V.) The thiocarbamate ligands are bonded to the metal through the sulfur atoms with Zn–S distances of 2.294 (3) and 2.314 (3) Å. These distances are shorter than the sum of the covalent radii of Zn and S (2.35 Å)[17] and are short compared to Zn–S distances found in dithiocarbamate and other related structures (Table VI). While the angles formed by the donor atoms about the Zn vary significantly, this variation does not seem to be chemically significant and the angular values are consistent with a tetrahedral complex. The

(17) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 246.
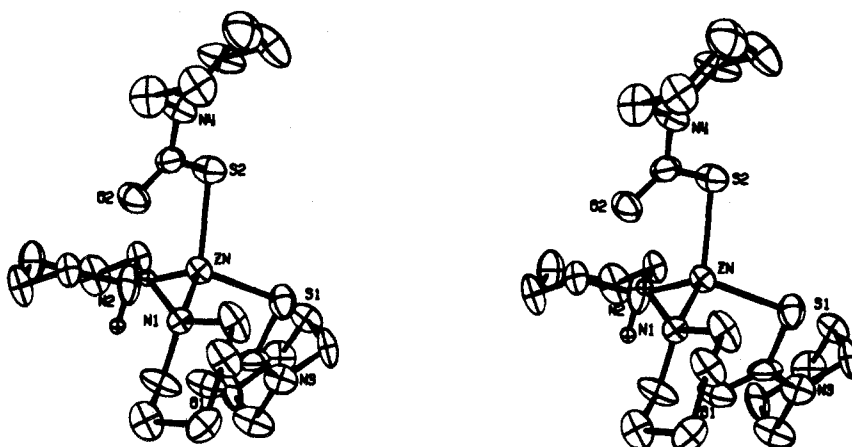
Figure 1. A view of the $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$ molecule showing the coordination geometry about the zinc(II) ion. These drawings constitute a stereopair and should be viewed with a hand viewer.
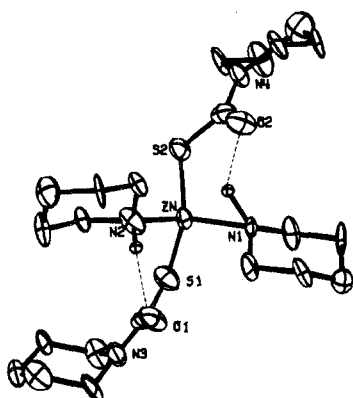

Figure 2. A perspective view of the $Zn(SOCN(C_5H_{10}))_2(NC_5H_{11})_2$ molecule showing its approximate twofold symmetry and hydrogen bonding.

Table V. Equations of Weighted Least-Squares Planes[a] and Deviations of the Atoms from the Planes

Atom	Distance, Å	Atom	Distance, Å
Plane through S(1), O(1), C(11), N(3)			
$4.89x + 5.66y - 8.80z = 0.89$			
S(1)	0.000 (3)	Zn	0.77[b]
O(1)	−0.001 (7)	C(12)	0.14[b]
C(11)	0.003 (9)	C(16)	0.17[b]
N(3)	−0.001 (7)		
Plane through S(2), O(2), C(17), N(4)			
$7.48x + 2.75y - 6.47z = 0.39$			
S(2)	0.000 (3)	Zn	−0.62[b]
O(2)	0.000 (6)	C(18)	−0.07[b]
C(17)	0.000 (8)	C(22)	−0.00[b]
N(4)	0.000 (7)		

[a] Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961). Equations are given in triclinic coordinates. [b] Not included in the calculation of the plane.

coordination geometry is stabilized by weak hydrogen bonds between the amine protons of the coordinated piperidine groups and the uncoordinated oxygen atoms of the thiocarbamate ligands. The distances between the oxygen atoms and the unrefined positions of the amine protons are 2.41 and 2.20 Å.

Bond distances and angles within the thiocarbamate ligands reflect significant differences in electronic structure compared with related dithiocarbamate ligands and therefore different bonding properties to metals. The C–S bond lengths of 1.74 (1) and 1.76 (1) Å for $Zn(SOCN(C_5H_{10}))_2$-$(NC_5H_{11})_2$ are longer than values found in dithiocarbamate structures. Similar distances found for $[Cu(SOCN(C_3H_7)_2)]_6$

average to 1.77 (3) Å,[3] with an average C–S value of 1.77 (2) Å found in $[Ni(SOCN(C_3H_7)_2)_2]_6$[2] (Table VII). Eisenberg's compilation of structural information on dithiolate complexes[18] indicates a range of average values of 1.70–1.72 Å for 1,1-dithiolate C–S distances, although unusually large values of 1.75 (2) Å have been found for individual C–S distances in $[Zn(S_2CN(CH_3)_2)_2]_2$[19] and $Fe(S_2CN(C_5H_{10}))_2$-$(CO)_2$.[20] The C⋯O and >C⋯NR_2 distances within the thiocarbamate ligands average to values of 1.24 (1) and 1.36 (1) Å, respectively. These values compare well with values found in organic amides where each bond has significant multiple character.[21] However, the average >C⋯NR_2 bond lengths of 1.36 (1) Å in the present structure, 1.37 (4) Å in $[Cu(SOCN(C_3H_7)_2)]_6$,[3] and 1.37 (3) Å in $[Ni(SOCN-(C_3H_7)_2)_2]_6$[2] seem to indicate a decrease in the multiple character of this bond in the thiocarbamato complexes relative to the dithiocarbamates where values of 1.33 Å are commonly encountered.

The C–S, C⋯O and >C⋯NR_2 bond lengths are consistent with the proposal that resonance structure I, discussed in the Introduction, is extremely important in an electronic description of the thiocarbamate ligand system and that structure II is of secondary importance. This is further reflected in the mercaptide-like bonding properties of the sulfur: bridging metal ions in the Ni, Cu, and Ag hexamers and acting as an effective donor to the Zn in the present complex.

As with the dithiocarbamates, resonance structure III is important in distinguishing the properties of thiocarbamate complexes from other related oxygen–sulfur donor ligands. A structural study on the thiobenzoate complex Ni_2-$(SOCC_6H_5)_4(C_2H_5OH)$ reports average C–S and C–O distances of 1.71 (1) and 1.25 (1) Å, respectively.[22] The intermediacy of these values between single- and double-bond order suggests delocalization over the thiocarboxylate group and significant contributions to the electronic structure of the ligand from resonance forms analogous to I and II. Thus, the amide nitrogen of the thiocarbamate group enables delocalization of the double bond at the virtual exclusion of the C–S bond. This electronic description for the coordinated thiocarbamate in the present structure is similar to that proposed for the thiourea ligands where the double bond is

(18) R. Eisenberg, *Progr. Inorg. Chem.*, 12, 925 (1970).
(19) H. P. Klug, *Acta Crystallogr.*, 21, 536 (1966).
(20) J. S. Ricci, C. A. Eggers, and I. Bernal, *Inorg. Chim. Acta*, 6, 97 (1972).
(21) Reference 17, p 281.
(22) G. A. Melson, P. T. Greene, and R. F. Bryan, *Inorg. Chem.*, 9, 1116 (1970).

Table VI. Distances (Å) and Angles (deg) in Related Zn(II) Complexes with Sulfur Donor Ligands

	Zn–S	C–S	C⋯NR$_2$	S–C–S	M–S–C	Ref
Zn(SOCN(C$_5$H$_{10}$))$_2$(NC$_5$H$_{11}$)$_2$	2.304 (3)	1.75 (1)	1.36 (1)	122.4 (8)^f	101.1 (3)	
[Zn(S$_2$CN(CH$_3$)$_2$)$_2$]$_2$	2.362 (6)	1.72 (1)	1.35 (2)	118 (1)	87.5 (7)	g
[Zn(S$_2$CN(C$_2$H$_5$)$_2$)$_2$]$_2$	2.376 (3)^c	1.73 (1)	1.33 (1)	117.7 (8)	84.7 (6)	h
Zn(S$_2$CN(CH$_3$)$_2$)$_2$(NC$_5$H$_5$)	2.605 (4)^d	1.72 (1)	1.33 (1)	118^b	80^{d,b}	i
	2.327 (4)^e				88^e	
Zn(tu)$_2$Cl$_2$ ^{a}	2.35 (1)	1.78 (2)	1.28 (3)		108.6 (7)	j
Zn(tu)$_3$SO$_4$ ^{a}	2.321 (4)	1.73 (2)	1.32 (2)		105.5 (5)	k

^{a} tu = thiourea. ^{b} Errors not given. ^{c} Average computed omitting an anomalously long Zn–S distance of 2.815 (3) Å. ^{d} Axial. ^{e} Equatorial. ^{f} O–C–S angle. ^{g} See ref 19. ^{h} M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 898 (1965). ^{i} K. H. Frazer and M. M. Harding, *Acta Crystallogr.*, **22**, 75 (1967). ^{j} N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 3478 (1958). ^{k} G. D. Andreetti, L. Cavalca, and A. Musatti, *Acta Crystallogr., Sect. B*, **24**, 683 (1968).

Table VII. Distances (Å) and Angles (deg) in Complexes of Thiocarbamate Ligands

	C–S	C⋯O	C⋯NR$_2$	S⋯O	S–C–O	M–S–C	Ref
Zn(SOCN(C$_5$H$_{10}$))$_2$(NC$_5$H$_{11}$)$_2$	1.75 (1)	1.24 (1)	1.36 (1)	2.630 (7)	122.4 (8)	101.1 (3)	
[Cu(SOCN(C$_3$H$_7$)$_2$)]$_6$	1.78 (3)	1.21 (3)	1.37 (4)	2.65 (2)	123 (2)	104 (1)	3
[Ni(SOCN(C$_3$H$_7$)$_2$)$_2$]$_6$	1.77 (4)	1.25 (3)	1.37 (3)	2.63 (2)	118 (1)	103.5 (6)	2

partially delocalized over C–N bonds[23]
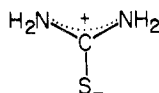
Angles formed by the C–S bonds of the thiocarbamate ligands with the Zn atom of 99.7 (4) and 102.5 (3)° are substantially larger than M–S–C angles of 85–88° commonly found in dithiocarbamate complexes.[20] Additionally, the S–C–O angles of 121.2 (8) and 123.5 (7)° in the thiocarbamate groups much more clearly reflect the effective sp^2 hybridization of C(11) and C(17) than do S–C–S angles of dithiocarbamate complexes where values of 110–112° have been reported.[24] The anomalous angular values found in the dithiocarbamate structures probably result from geometric constraints placed on the ligand by its chelated coordination configuration. In the absence of such constraints angles in the present structure and other thiocarbamate structures more closely approach expected values. The Zn–S–C angles in Zn(SOCN(C$_5$H$_{10}$))$_2$(NC$_5$H$_{11}$)$_2$ are, however, significantly less than values expected for sp^3 hybridized sulfur. The observed values near 100° probably result from the influence of hydrogen bonds formed with the amine protons of the coordinated piperidine ligands. Related M–S–C angles found in thiourea structures commonly have values in the range 107–110°.[25] Similar angular values might be expected for the thiocarbamate ligands in the absence of H bonding or chelating effects. Least-squares planes calculated to include the SOCN atoms of the thiocarbamate groups show the metal to be 0.62 and 0.77 Å above the planes formed by the ligands

containing S(1) and S(2), respectively. The ring carbon atoms bonded to nitrogen atoms associated with each of these planes show slight but insignificant deviations from these planes.

The Zn–N distances for the piperidine ligands are 2.084 (7) and 2.069 (6) Å and agree well with other Zn–N distances found previously for amine complexes. An average Zn–N distance of 2.065 (7) Å was found in Zn(tren)Cl$^+$.[26] The C–N bond lengths in the coordinated piperidine groups average to a value of 1.49 (1) Å agreeing well with an average C–N distance for the thiocarbamate piperidyl fragments of 1.47 (1) Å and a value of 1.47 Å expected for a C–N single bond.[17] The C–N–C angles within the piperidyl groups reflect the difference in hybridization of N(3) and N(4) relative to N(1) and N(2). Thiocarbamate piperidyl C–N–C angles average to 115.1 (7)° while related angles average to 111.3 (7)° for the coordinated piperidine groups. The piperidine and piperidyl groups are all in chair conformations with the conformational configurations of the piperidine ligands fixed by the hydrogen-bonding interactions of the amine protons. The cyclic amine ligands were chosen in an attempt to avoid the severe thermal motion encountered in chain alkyl amines. However, it is clear from the mean-square amplitudes of vibration for the ring atoms and their thermal ellipses that thermal vibrations are still a significant problem.

(23) A. Sirigu, *Inorg. Chem.*, **9**, 2245 (1970).
(24) See Table IV in ref 19.
(25) R. L. Girling and E. L. Amma, *Inorg. Chem.*, **10**, 335 (1971).

(26) R. J. Sime, R. P. Dodge, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **10**, 537 (1971).