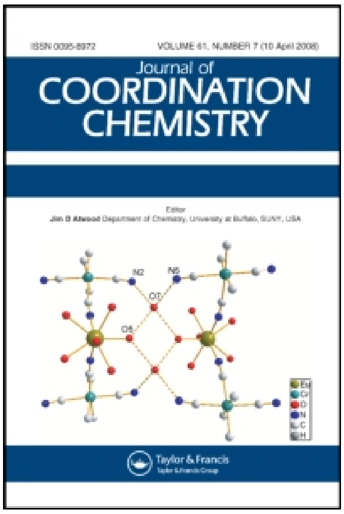

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Structure of Bis(Isothiocyanato)-Bis(4-Methylpyridine)Zinc(II)

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NOTE

STRUCTURE OF BIS(ISOTHIOCYANATO)-BIS(4-METHYLPYRIDINE)ZINC(II)

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$Zn(C_6H_7N)_2(NCS)_2$, $C_{14}H_{14}N_4S_2Zn$, is orthorhombic, space group *Fdd*, $a = 35.144(16)$, $b = 18.119(4)$, $c = 5.078(3)$ Å, $Z = 8$, $D_{calc} = 1.430\ \mathrm{g\,cm^{-3}}$, $I = 17.036\ \mathrm{cm^{-1}}$, $F(000) = 1504$. The structure consists of monomeric units in which the Zn(II) cation is tetrahedrally coordinated by two N_{CS} and two N_{MePy} atoms, the molecule showing twofold axial symmetry.

Keywords: Zinc(II), thiocyanate, 4-methylpyridine, structure, X-ray

INTRODUCTION

Coordination complexes of the formula $M(II)X_2A_2$ are of interest as starting materials for the clathration of many different organic "guest" compounds.[1] It seems that octahedrally coordinated complexes show a greater ability to form clathrate–inclusion compounds.[2] Complexes of formula MX_2A_2 have a tendency to form polymer chain structures which, in turn, may accommodate guest molecules.[3] It thus seemed of interest to study the structure of the title compound in order to test its coordination type and the density of molecular packing in the crystal.

EXPERIMENTAL

Preparation

Some 45 g of $Zn(CH_3COO)_2.2H_2O$ (0.2 mol) and 87 g of KSCN (0.9 mol) were dissolved in 2 dm^3 of water and 100 cm^3 (1 mol) of 4-methylpyridine was added with vigorous stirring. White solid precipitates were then filtered off, washed with distilled water, dried in air and recrystallized from methanol by slow evaporation at room temperature. Colourless, prismatic crystals thus obtained show no observable deterioration when kept in open air at room temperature.

Structure analysis

A crystal of approximate dimensions 0.3 × 0.3 × 0.35 mm was chosen for X-ray studies. Intensity data for 3718 reflections were measured on an Enraf-Nonius CAD4 single-crystal diffractometer with the use of graphite-monochromatized MoKα radiation and the ω–2θ scan technique. The data were corrected for Lorentz and polarization effects; absorption was ignored.

The structure was solved by the Patterson method (SHELX-86[4] was used) in the triclinic cell: $a = 5.078$, $b = 9.414$, $c = 18.752$ Å, $\alpha = 87.84$, $\beta = 82.06$, $\gamma = 74.23°$ and refined to $R = 0.17$ (with isotropic thermal factors). Analysis of atomic coordinates at this stage of structure solution led to suggestion of higher symmetry. Transformation [-1 0 2/-1 2 0/-1 0 0] gave an orthogonal unit cell of the F type. The transformed atomic coordinates were in fair agreement with twofold symmetry. Averaging of equivalent intensity data (after transformation as above) with the consistency index equal $R_{int} = 0.066$ (for "observed" reflections) also seemed to be in favour for the above suggestion. Thus, the final refinement was performed in the orthorhombic unit cell, numeric details being listed in Table I. The final R value obtained was $R = 0.049$ (unit weights used). Hydrogen atoms were included in final cycles at calculated positions ($d_{C-H} = 1.08$ Å) as "riding" on corresponding carbon atoms and with temperature factors fixed to free variables: one for aromatic ring hydrogens and another for hydrogen atoms of the methyl group.

TABLE I
Data collection and structure analysis parameters.

Molecular formula	$ZnS_2N_4C_{14}H_{14}$
Molecular weight	367.8
Unit cell (Å)	$a = 37.144(16)$ $b = 18.119(4)$ $c = 5.078(3)$ $V = 3418(10)$ Å^3 $Z = 8$
Density (calc.) [g cm^{-3}]	1.430
Space group	*Fdd*
Radiation	graphite monochromatized MoKα
Absorption coefficient [cm^{-1}]	17.036
Crystal size [mm]	0.3 × 0.3 × 0.35
Number of reflections	
measured	3718*
unique	1042
used in the structure analysis [$I > 2\sigma(I)$]	986
Final R value	0.049
S	3.35
Residual extrema in final difference map	+0.27/ −0.36e Å^{-3}

* The data were collected for a triclinic cell (see text).

TABLE II
Fractional atomic coordinates [× 10^4] and *Beq* with e.s.d.s (in parentheses).

Atom	*x/a*	*y/b*	*z/c*	*Beq*
Zn	1250	1250	−3463	4.78(3)
S(1)	1827(1)	3147(2)	1208(9)	8.45(11)
N(1)	1493(2)	2031(5)	−1624(16)	6.02(22)
C(1)	1627(3)	2506(5)	−454(28)	5.43(31)
N(11)	870(1)	1738(3)	−5728(15)	4.20(15)
C(12)	901(2)	2425(5)	−6565(26)	5.41(31)
C(13)	661(2)	2741(5)	−8273(25)	6.19(27)
C(14)	375(2)	2339(6)	−9237(17)	5.06(22)
C(15)	335(2)	1632(5)	−8288(21)	5.57(24)
C(16)	593(2)	1337(5)	−6575(17)	5.20(24)
C(17)	109(3)	2655(6)	−11200(27)	7.23(29)

Fractional atomic coordinates, bond lengths and angles are listed in Tables II to IV. Lists of coordinates of hydrogen atoms, thermal parameters and F_o/F_c tables have been deposited with the Editor and are available upon request.

TABLE III

Bond distances (Å) with e.s.d.s (in parentheses).

Zn-N(1)	1.924(8)
Zn-N(11)	2.022(5)
S(1)-C(1)	1.617(11)
N(1)-C(1)	1.158(14)
N(11)-C(12)	1.320(11)
N(11)-C(16)	1.333(9)
C(12)-C(13)	1.371(14)
C(13)-C(14)	1.377(12)
C(14)-C(15)	1.378(14)
C(14)-C(17)	1.515(15)
C(15)-C(16)	1.400(12)

TABLE IV

Bond angles (degrees) with e.s.d.s in parentheses.

N(1)-Zn-N(11)	106.39(30)
Zn-N(1)-C(1)	177.13(85)
S(1)-C(1)-N(1)	177.72(98)
Zn-N(11)-C(16)	119.03(52)
Zn-N(11)-C(12)	122.33(44)
C(12)-N(11)-C(16)	118.45(66)
N(11)-C(12)-C(13)	122.70(75)
C(12)-C(13)-C(14)	120.54(90)
C(13)-C(14)-C(17)	122.57(89)
C(13)-C(14)-C(15)	116.73(79)
C(15)-C(14)-C(17)	120.68(86)
C(14)-C(15)-C(16)	119.85(77)
N(11)-C(16)-C(15)	121.61(78)

RESULTS AND DISCUSSION

The molecular structure of $Zn(NCS)_2(4\text{-methylpyridine})_2$ is depicted in Figure 1. The crystallographic twofold symmetry axis runs diagonally between the two isothiocyanate ligands and the two 4-methylpyridine groups. The Zn(II) cation has a slightly distorted tetrahedral coordination because of the non-equivalence of the $Zn–N_{CS}$ and $Zn–N_{MePy}$ coordination bonds. The distortion seems more pronounced in the structure studied when compared to the similar complex bis(4-*tert*-butyl-1,2,4-triazole-N')bis(isothiocyanato)zinc(II),[6] where the $Zn–N_{CS}$ bond is longer (1.941(3)) and $Zn–N_{triazole}$ bond shorter (2.000(2) Å) than is found in the present structure (1.924(8) and 2.022(5) Å, respectively). As may clearly be seen from Figure 2, the structure consists of monomeric $Zn(NCS)_2(4\text{-methylpyridine})_2$ units. The pyridine ring is planar within 0.02 Å with the methyl carbon atom and the central cation of the

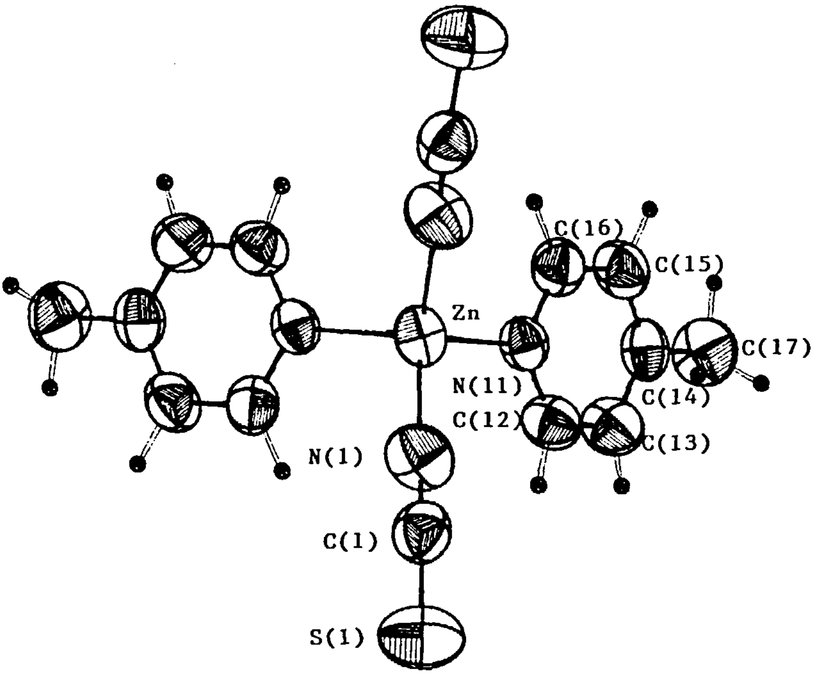

FIGURE 1 ORTEP[5] plot of the $Zn(NCS)_2(4\text{-methylpyridine})_4$ molecule and the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are depicted using arbitrary radii.

complex deviating from the plane by +0.06 and +0.17 Å, respectively. This molecular plane forms an angle equal to 23.8(4)° with that defined by the Zn, N(1) and N(11) atoms. The thiocyanate ligand is linear within the limits of experimental error and forms an angle equal to 177.1(9)° with the Zn–N(1) bond, thus being colinear with the latter.

The intermolecular contacts are consistent with a van der Waals type of packing and the structure displays no sizeable intermolecular voids, as illustrated in Figure 3. This result may suggest little, if any, capability of the structure to accommodate foreign ("guest") molecules. The monomeric structure of the complex makes this substance an appropriate substrate for coordination of further 4-methylpyridine, as proven chemically by Dyadin *et al.*[1]

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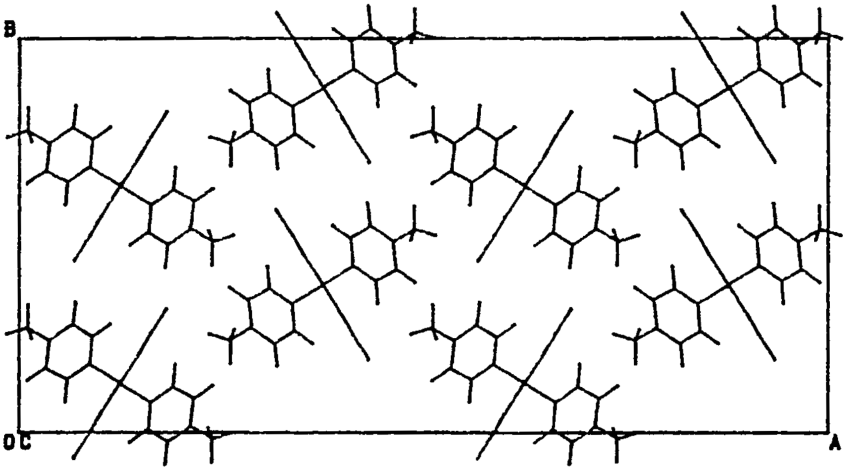

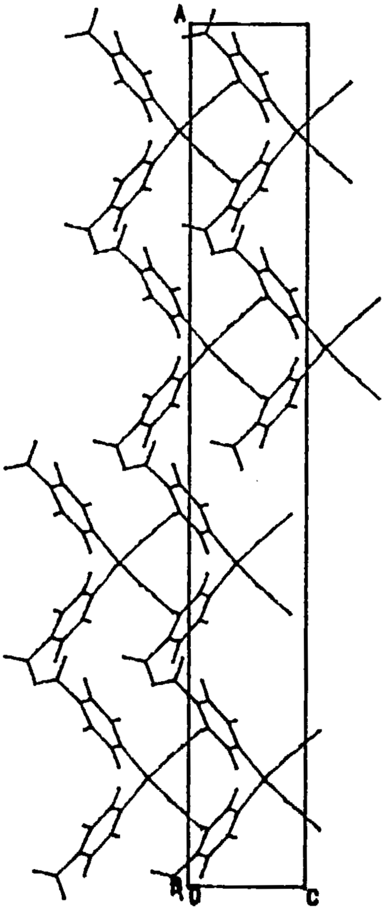

FIGURE 2 Molecular packing viewed: (a) along the *c* crystallographic axis and (b) along *b* (in this picture only half of the unit cell is given for the sake of clarity).

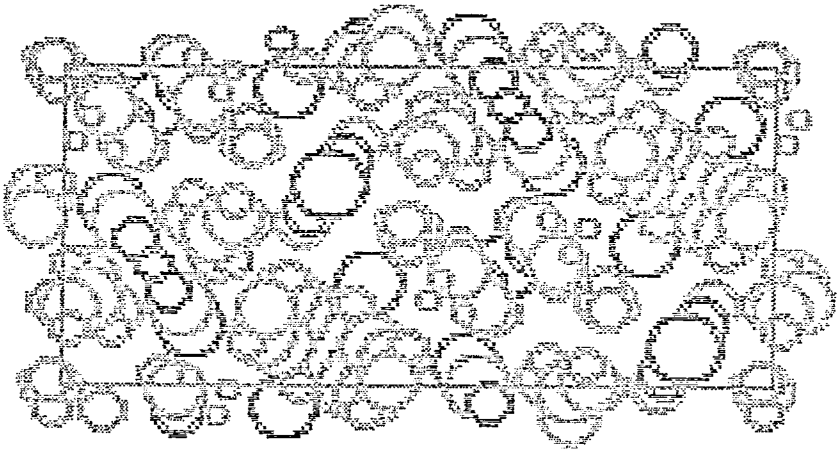

FIGURE 3 A section drawing[7] of the molecular packing. Orientation is as in Figure 2a, and the section plane is at $c = 0.5$.

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