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Synthesis, Characterization, and Crystal Structure of Di{bis[2-[(2-dimethylaminoethylimino)methyl]-6-methoxyphenolato]thiocyanatozinc(II)} Tetrakis(thiocyanato)zinc(II)

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A new Schiff base zinc(II) complex with the formula $2[Zn(C_{12}H_{18}N_2O_2)_2(NCS)]\cdot[Zn(NCS)_4]$ was prepared and structurally characterized by elemental analysis, IR spectrum, and single crystal X-ray diffraction. The compound consists of two mononuclear $[Zn(C_{12}H_{18}N_2O_2)_2(NCS)]$ complex cations, in which the Zn atom is in a trigonal-bipyramidal geometry, and one $[Zn(NCS)_4]$ complex anion, in which the Zn atom is in a tetrahedral geometry.

Keywords crystal structure, Schiff base, synthesis, thiocyanate, zinc complex

INTRODUCTION

In recent years, Schiff base compounds have been widely used as versatile ligands involved in various metal chelation reactions to form transition metal complexes with interesting properties in material sciences and biological systems.[1–6] These complexes can be easily synthesized from simple starting materials, where the metal ions, ligands, and coordination modes are the important factors for the self-assembly processes. Thiocyanate is a versatile ligand, which acts as monodentate or bridging group with end-on or end-to-end coordination mode to form complexes with interesting structures.[7–9] In order to investigate the aggregate of the Schiff base ligand, thiocyanate and zinc ion, we report in this article the synthesis and crystal structure of the complex $2[Zn(C_{12}H_{18}N_2O_2)_2(NCS)]\cdot[Zn(NCS)_4]$.

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EXPERIMENTAL

Materials and Measurements

All chemicals were of reagent grade and used without further purification. 3-Methoxysalicylaldehyde and *N*,*N*-dimethyl-1,2-diaminoethane were purchased from Lancaster corporation. Elemental analyses were performed with a Finnigan EA 1112 elemental analyzer. The infrared spectra of KBr pellets were recorded on an FTS-40 spectrophotometer. The crystal determination was carried out on a Bruker Smart 1000 CCD area diffractometer.

Synthesis of $2[Zn(C_{12}H_{18}N_2O_2)_2(NCS)]\cdot[Zn(NCS)_4]$

3-Methoxysalicylaldehyde (0.1 mmol, 15.2 mg) and *N*,*N*-dimethyl-1,2-diaminoethane (0.1 mmol, 8.8 mg) were mixed in a methanol solution (10 mL). The mixture was stirred for 30 min at room temperature to give a clear yellow solution. To the solution was slowly added with stirring an aqueous solution (5 ml) of KSCN (0.2 mmol, 19.5 mg) and a methanol solution (10 ml) of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.1 mmol, 22.0 mg). The final mixture was stirred for another 30 min to give a clear colorless solution. The solution was allowed to stand at room temperature for a week to deposit colorless block-shaped crystals of the complex in 45.0% yield. Anal. calcd. (%) for $C_{54}H_{72}N_{14}O_8S_6Zn_3$: C, 45.23; H, 5.01; N, 13.68. Found (%): C, 45.01; H, 5.12; N, 13.80. Selected IR data (cm^{-1}): 3203 (w), 3061 (m), 2936 (m), 2861 (m), 2080 (vs), 1617 (s), 1426 (s), 1220 (s), 754 (m), 655 (w), 470 (w).

DATA COLLECTION, STRUCTURAL DETERMINATION, AND REFINEMENT

Crystal Structure Determination

A colorless crystal with dimensions of 0.22 mm × 0.20 mm × 0.17 mm for the complex was selected and mounted on a glass fiber in air. The diffraction data were collected on a Bruker Smart 1000 CCD area diffractometer equipped with a graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) in the range

TABLE 1
Crystallographic and experimental data for the complex

Formula	$C_{54}H_{72}N_{14}O_8S_6Zn_3$
FW	1433.73
Crystal shape/colour	Block/colorless
Crystal size /mm	0.22 × 0.20 × 0.17
Crystal system	Triclinic
Space group	*P*-1
a/Å	13.907(3)
b/Å	14.251(3)
c/Å	19.473(4)
α/°	109.50(3)
β/°	104.44(3)
γ/°	93.45(3)
V /Å^3	3479.3(13)
Z	2
λ (Mo*K*α) /Å	0.71073
T /K	298(2)
μ /mm^{-1} (Mo-K$_\alpha$)	1.263
T_{min}	0.7686
T_{max}	0.8139
Reflections/parameters	14092/790
Independent reflections	6027
F(000)	1488
Goodness of fit on F^2	0.949
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0836, 0.1504
R_1, wR_2 (all data)^a	0.1969, 0.1957

$^a R_1 = \sum ||Fo| - -|Fc|| / \sum |Fo|$, $wR_2 = [\sum w(Fo^2\text{-}Fc^2)^2 / \sum w(Fo^2)^2]^{1/2}$.

of $4.4 < 2\theta < 49.0°$ by using an ω scan mode at 298(2) K. The unit cell dimensions were obtained with the least-squares refinements and the structure was solved by direct methods with SHELXTL-97 package.[10] The final refinement was performed by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms on F^2. H(2), H(4A), H(7A) and H(9) were located on a different Fourier map, with N–H distances restrained to 0.90(1) Å. Other H atoms were introduced geometrically. Multi-scan absorption correction was applied by using the SADABS software.[11] The crystallographic data are summarized in Table 1. Crystallographic data for the complex has been deposited with the Cambridge Crystallographic Data Centre (CCDC 662890).

RESULTS AND DISCUSSION

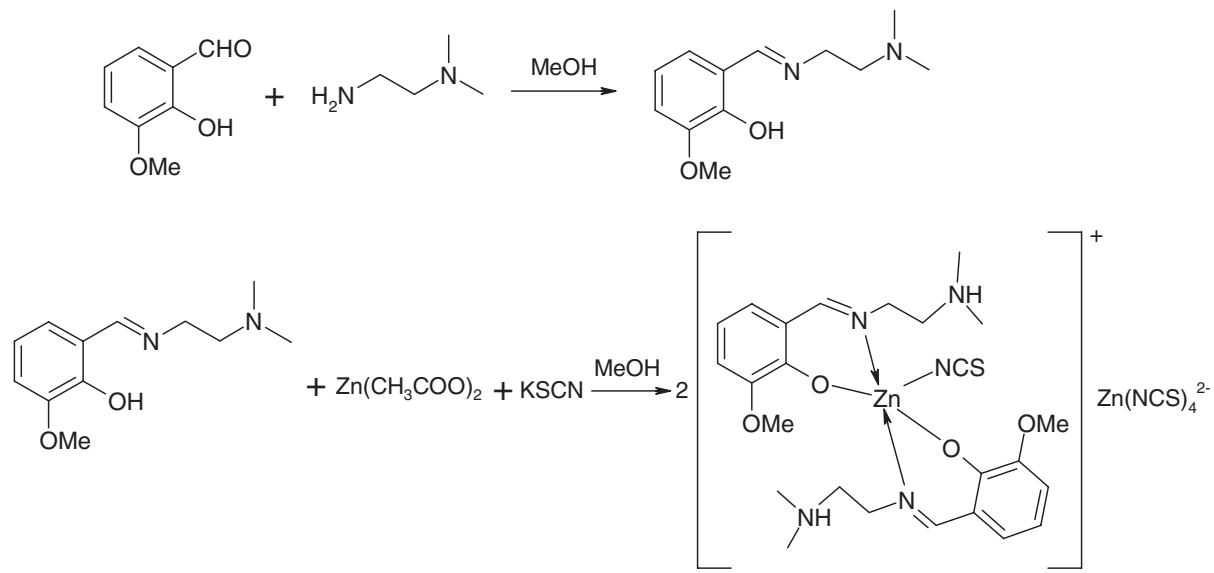
The complex is colorless crystals, stable in air at room temperature, soluble in MeOH, EtOH, MeCN and their mixture solution, insoluble in water and Et_2O.

Synthesis

The synthetic procedure is described as Scheme 1. The Schiff base ligand was synthesized very easily through the condensation reaction of 3-methoxysalicylaldehyde with *N,N*-dimethyl-1,2-diaminoethane in a methanol solution at room temperature. The complex was also simply synthesized through the reaction of the Schiff base ligand and potassium thiocyanate with zinc acetate in a methanol solution at room temperature.

Structure Description of the Complex

The structure of the complex is shown in Figure 1. The molecular packing is shown in Figure 2. The selected bond lengths and bond angles are listed in Table 2. The distances



SCH. 1.

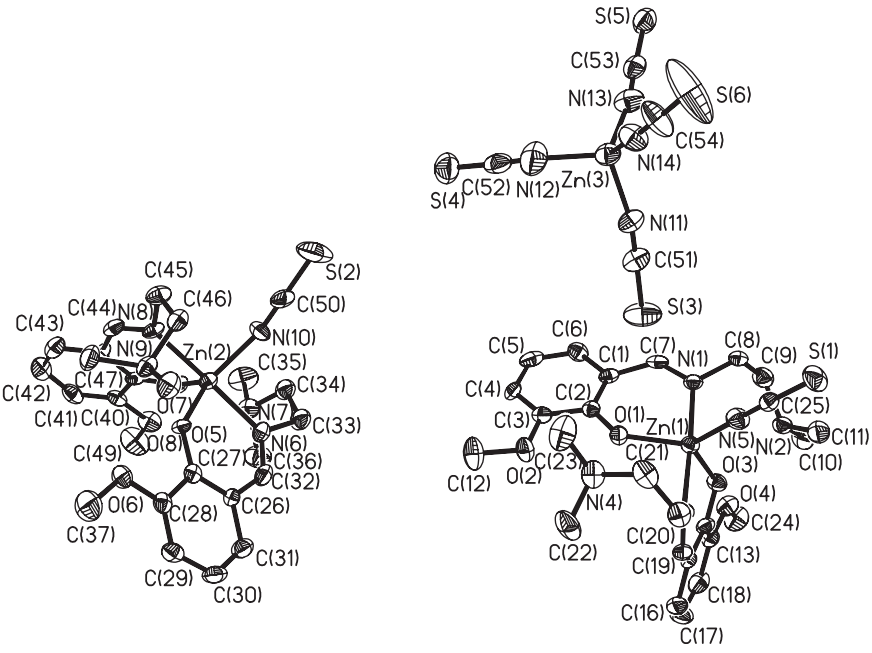


FIG. 1. The structure of the complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

and angles related to the hydrogen bonding are listed in Table 3.

X-ray single crystal analysis revealed that the compound consists of two mononuclear $[Zn(C_{12}H_{18}N_2O_2)_2(NCS)]$ complex cations and one $[Zn(NCS)_4]$ complex anion. In each of the cations, the Zn atom is in a trigonal-bipyramidal coordination environment, coordinated by two phenolic O atoms from two Schiff bases and one terminal N atom of the thiocyanate group

TABLE 2
Selected bond lengths (Å) and bond angles (°) for the complex

Zn(1)-O(1)	1.996(5)	Zn(1)-O(3)	2.005(5)
Zn(1)-N(1)	2.108(6)	Zn(1)-N(3)	2.136(6)
Zn(1)-N(5)	2.018(7)	Zn(2)-O(5)	2.000(4)
Zn(2)-O(7)	1.976(5)	Zn(2)-N(6)	2.127(6)
Zn(2)-N(8)	2.130(6)	Zn(2)-N(10)	2.017(7)
Zn(3)-N(11)	1.965(8)	Zn(3)-N(12)	1.952(10)
Zn(3)-N(13)	1.937(8)	Zn(3)-N(14)	1.952(8)
O(1)-Zn(1)-O(3)	120.7(2)	O(1)-Zn(1)-N(5)	121.1(2)
O(3)-Zn(1)-N(5)	118.1(2)	O(1)-Zn(1)-N(1)	89.1(2)
O(3)-Zn(1)-N(1)	91.2(2)	N(5)-Zn(1)-N(1)	92.8(3)
O(1)-Zn(1)-N(3)	88.7(2)	O(3)-Zn(1)-N(3)	87.9(2)
N5)-Zn(1)-N(3)	90.4(3)	N(1)-Zn(1)-N(3)	176.8(2)
O(7)-Zn(2)-O(5)	116.8(2)	O(7)-Zn(2)-N(10)	120.1(2)
O(5)-Zn(2)-N(10)	123.0(2)	O(7)-Zn(2)-N(6)	92.7(2)
O(5)-Zn(2)-N(6)	89.9(2)	N(10)-Zn(2)-N(6)	90.7(3)
O(7)-Zn(2)-N(8)	88.6(2)	O(5)-Zn(2)-N(8)	88.0(2)
N(10)-Zn(2)-N(8)	90.2(3)	N(6)-Zn(2)-N(8)	177.8(2)
N(13)-Zn(3)-N(14)	107.8(3)	N(13)-Zn(3)-N(12)	108.3(4)
N(14)-Zn(3)-N(12)	111.5(4)	N(13)-Zn(3)-N(11)	113.2(3)
N(14)-Zn(3)-N(11)	111.0(3)	N(12)-Zn(3)-N(11)	105.1(4)

TABLE 3
Distances (Å) and angles (°) involving hydrogen bonding of the complex

D–H···A	d(D–H)	d(H···A)	d(D···A)	Angle(D–H···A)
N(2)–H(2)···O(3)	0.900(10)	1.828(19)	2.718(8)	170(8)
N(2)–H(2)···O(4)	0.900(10)	2.64(7)	3.187(8)	120(6)
N(9)–H(9)···O(5)	0.903(10)	1.81(3)	2.686(7)	162(7)
N(9)–H(9)···O(6)	0.903(10)	2.40(7)	2.975(8)	122(6)
N(7)–H(7A)···O(7)	0.900(10)	1.84(3)	2.717(8)	163(8)
N(7)–H(7A)···O(8)	0.900(10)	2.41(7)	2.990(9)	122(6)
N(4)–H(4A)···O(1)	0.900(10)	1.92(5)	2.713(8)	145(7)
N(4)–H(4A)···O(2)	0.900(10)	2.32(6)	3.014(8)	134(6)

TABLE 4
Parameters between the planes

Cg	Distance between ring centroids (Å)	Dihedral angle (°)	Perpendicular distance of Cg(I) on Cg(J) (Å)	Perpendicular distance of Cg(J) on Cg(I) (Å)
Cg(2)···Cg(3)^{i}	4.9920	44.39	4.522	3.118
Cg(2)···Cg(4)^{i}	4.7697	43.99	4.585	2.430
Cg(2)···Cg(4)^{ii}	5.3297	43.99	2.811	4.271
Cg(3)···Cg(2)^{iii}	4.9920	44.39	3.118	4.522
Cg(3)···Cg(5)	5.3521	86.21	2.363	3.849
Cg(3)···Cg(5)^{iv}	5.0636	86.21	1.079	4.782
Cg(4)···Cg(2)^{iii}	4.7697	43.99	2.430	4.585
Cg(4)···Cg(2)^{ii}	5.3297	43.99	4.271	2.811
Cg(4)···Cg(5)^{iv}	5.2133	88.54	1.426	4.749
Cg(5)···Cg(1)^{v}	5.7757	77.59	1.329	4.817
Cg(5)···Cg(5)^{iv}	3.6996	0.00	3.442	3.442

Symmetry codes: (i) $-1+x, y, z$; (ii) $1-x, 2-y, 1-z$; (iii) $1+x, y, z$; (iv) $2-x, 2-y, -z$; (v) $1-x, 1-y, -z$. Cg(1), Cg(2), Cg(3), Cg(4), and Cg(5) are the centroids of the rings C(1)-C(2)-C(3)-C(4)-C(5)-C(6), C(13)-C(14)-C(15)-C(16)-C(17)-C(18), Zn(2)-O(5)-C(27)-C(26)-C(32)-N(6), C(26)-C(27)-C(28)-C(29)-C(30)-C(31), and C(38)-C(39)-C(40)-C(41)-C(42)-C(43), respectively.

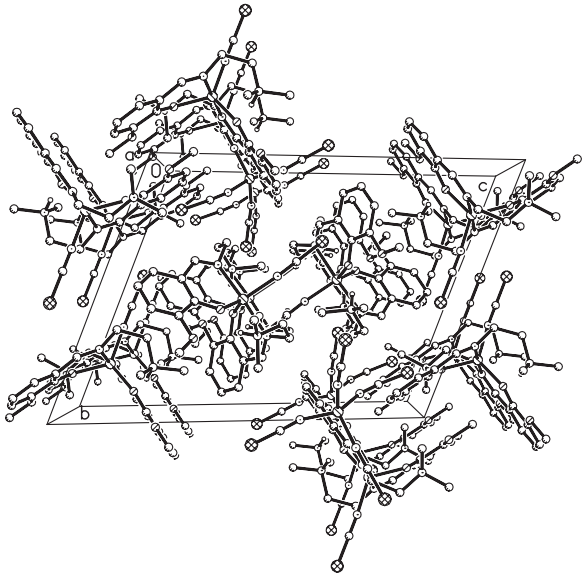


FIG. 2. The molecular packing of the complex, viewed along the *a* axis.

at the basal plane, and by two imine N atoms from two Schiff bases at the apical positions. In the anion, the Zn atom is coordinated by four N atoms from four thiocyanate ligands (Zn–N = 1.937(8) – 1.965(8) Å); the bond angles subtended at the Zn3 atom are range from 105.1(4) to 113.2(3)°, showing a distorted tetrahedral coordination environment. In either the cations or the anion, the thiocyanate groups are nearly linear with the N–C–S bond angles in the range 176.0(11) to 179.6(10)°. All the coordinate bond values are within normal ranges and comparable to those observed in the similar zinc(II) complexes reported previously.[12–15]

In the crystal structure, relatively shorter centroid distances (Table 4) between the adjacent rings are observed, implying the existence of π-π stacking interactions in the complex.[16]

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