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Molecular Complexes of Cobalt(II) and Zinc(II) Chlorides and Bromides with 1-Piperidinyl Dimethylcarbamodithioate (L): Crystal Structures of L and [$ZnLBr_2$]

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Abstract—Complexes of MX_2(M = Co, Zn; X = Cl, Br) with 1-piperidinyl dimethylcarbamodithioate (L) of composition [MLX_2] have been synthesized. The compounds have been studied by elemental analysis; X-ray diffraction; thermogravimetry; conductometry; magnetochemistry; and IR, ^1H NMR, and electronic absorption spectroscopy. The ligand molecule is coordinated to the metal atoms in a bidentate chelating mode through the thione sulfur atom and the sulfenamide nitrogen atom to form a five-membered chelate ring. The structures of L and [$ZnLBr_2$] have been determined by X-ray crystallography.

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Dithiocarbamic acid derivatives, as chelating polydentate ligands, attract ever increasing attention of coordination chemists. These derivatives have been used for synthesis of a large amount of different complexes, which are widely used in modern technologies [1]. Unfortunately, this is not the case for thiocarbamoylsulfenamides, presumably because of their low stability on storage [2, 3]. We are interested in studying the possibility of increasing their stability by means of complexation with transition metal ions. The presence of active donor sites (S and N) and the labile S–N bond in thiocarbamoylsulfenamides suggests the possibility to synthesize complexes of different composition, electronic structure, and geometry, which will exhibit high thermal stability, curing activity, catalytic activity, and other valuable properties.

In this work, we determined the structure of 1-piperidinyl dimethylcarbamodithioate (L) by X-ray crystallography, synthesized its molecular complexes with cobalt(II) and zinc(II) chlorides and bromides, and studied their composition, properties, and structure.

EXPERIMENTAL

The reagents were $CoCl_2$ and $CoBr_2$ obtained by dehydration of $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$, $ZnCl_2 \cdot 1.5H_2O$, HBr, and KI (all of the pure for analysis grade), as well as zinc powder, Br_2, I_2, sodium *N,N*-dimethyldithiocarbamate, and piperidine (all of the pure grade). Zinc bromide was synthesized by the reaction of zinc powder with HBr and Br_2 [4]. Organic solvents were purified by common methods [5]. Ligand L (**1**) was synthesized by oxidative condensation of sodium *N,N*-dimethyldithiocarbamate and piperidine in the presence of iodine [6, 7].

Complexes were synthesized by the reaction of saturated solutions of L in diethyl ether and equimolar amounts of $CoCl_2$ and $CoBr_2$ in acetone or $ZnCl_2$ and $ZnBr_2$ in diethyl ether. The precipitates formed immediately after mixing the solutions were filtered off, washed with diethyl ether, and fried in air. Yield, 61–82%.

Cobalt and zinc in the complexes were determined complexometrically [8]; chlorine, bromine, and sulfur were determined by the Schoeniger method; and nitrogen was determined by the Dumas method [9].

For $C_8H_{16}N_2S_2Cl_2Co$ (**2**) anal. calcd. (%): N, 8.38; S, 19.19; Cl, 21.22; Co, 17.63.

Found (%): N, 8.49; S, 19.23; Cl, 21.16; Co, 17.68.

For $C_8H_{16}N_2S_2Br_2Co$ (**3**) anal. calcd. (%): N, 6.62; S, 15.16; Br, 37.77; Co, 13.93.

Found (%): N, 6.81; S, 15.23; Br, 37.85; Co, 13.87.

For $C_8H_{16}N_2S_2Cl_2Zn$ (**4**) anal. calcd. (%): N, 8.82; S, 18.83; Cl, 20.82; Zn, 19.19.

Found (%): N, 8.34; S, 18.97; Cl, 20.74; Zn, 19.23.

For $C_8H_{16}N_2S_2Br_2Zn$ (**5**) anal. calcd. (%): N, 6.52; S, 14.93; Br, 37.20; Zn, 15.22.

Found (%): N, 6.64; S, 15.02; Br, 37.31; Zn, 15.18.

The thermal stability of the compounds was studied in platinum crucibles in the temperature range 20–1000°C on a Paulik-Paulik-Erdey Q derivatograph in air. Samples were heated at a rate of 10 K/min. The DTA and DTG sensitivity was 1/5 of the maximum one. Al_2O_3 was used as a reference. The molar electric conductivity of the complexes was calculated from the resistances of their 0.001 M solutions in CH_3CN measured at 25°C on a L.C.R. E7-8 digital instrument in a glass cell with platinum electrodes coated with platinum black. The electronic absorption spectra of solutions of the compounds in CH_3CN were recorded on a

Table 1. Crystallographic data and refinement parameters for the L and [ZnLBr$_2$] structures

Compound	**1**	**5**
Molecular formula	$C_8H_{16}N_2S_2$	$C_8H_{16}Br_2N_2S_2Zn$
FW	204.36	429.54
Symmetry system	Monoclinic	Orthorhombic
Space group	$P2_1/m$	$P2_12_12_1$
T, K	100(2)	100(2)
a, Å	7.6401(13)	12.8057(10)
b, Å	6.9050(13)	12.8209(10)
c, Å	10.2956(16)	17.2678(14)
β, deg	104.435(4)	90.00
V, Å^3	526.0(2)	2835.0(4)
Z	2	8
F(000)	216	1680
ρ_{calcd}, g/cm^3	1.277	2.013
μ, mm^{-1}	0.46	7.64
Crystal shape, color	Colorless prism	Colorless prism
Crystal size, mm	0.28 × 0.18 × 0.16	0.46 × 0.26 × 0.18
Correction for absorption	–	Semiempirical on the basis of equivalents
T_{min}	–	0.107
T_{max}	–	0.256
Number of measured reflection	5264	33669
Number of unique reflections	1650 (R_{int} = 0.030)	8222 (R_{int} = 0.085)
Number of observed reflections ($I > 2\sigma(I)$)	1429	6735
Number of parameters	67	275
R_1 (on F for reflections with $I > 2\sigma(I)$)	0.034	0.036
wR_2 (on F^2 for all reflections)	0.093	0.074
GOOF	1.00	1.00
Weight scheme	$w^{-1} = \sigma^2\left(F_o^2\right) + \left(aP\right)^2 + bP$, where $P = 1/3\left(F_o^2 + 2F_c^2\right)$	
A	0.050	0.022
B	0.23	0.00
Residual electron density (max/min), e/Å^3	0.43/–0.39	1.48/–0.73
Flack parameter		0.038 (8)

Specord UV VIS spectrophotometer in quarts cells with a pathlength of 1 cm. The diffuse reflectance spectra of the cobalt(II) complexes in the range 4000–25000 cm^{-1} were recorded on a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer. Magnetic susceptibility was measured by the Gouy method. Calibration was against Co[Hg(CNS)$_4$]. Diamagnetic corrections were introduced on the basis of increments taken from [10]. The IR absorption spectra were recorded as KBr pellets on a Specord 75 IR spectrophotometer in the range 400–4000 cm^{-1}. THe ^{1}H NMR spectra of solutions of cobalt(II) and zinc(II) compounds in acetone were recorded on a Bruker MSL 400 spectrometer. TMS was used as the internal reference.

X-ray crystallography. Colorless single crystals of L and [ZnLBr$_2$] were obtained by recrystallization from acetone in diethyl ether vapor. An experimental reflection set was collected at 100 K on a Bruker Apex II CCD area detector diffractometer with a graphite monochromator (λMoK_α, ω scan, $2\theta_{max}$ = 60°). The structures were solved by direct methods. All non-hydrogen atoms were located from difference electron density maps and refined on F_{hkl}^2 in the anisotropic approximation. The hydrogen atoms were introduced into geometrically calculated positions and refined as

Table 2. Results of thermal analysis of the complex compounds

Compound	Temperature range according to TG, °C	T_{max} according to DTA, °C	Total weight loss according to TG, %
1	50–100	77(↓)	0
	120–410	200(↑), 210(↓)	87
2	50–210	155(↑)	0
	260–290	280(↓)	29
	320–380	340(↓)	51
	390–890	490(↓), 570(↓), 850(↑)	79
3	50–180	155(↑)	0
	220–280	265(↓)	21
	340–400	390(↓)	38
	430–820	460(↓), 570(↓), 750(↑)	88
4	50–270	190(↑)	17
	290–450	300(↓), 400(↑)	48
	500–820	620(↑), 750(↑)	85
5	50–280	150(↑)	17
	300–450	310(↓), 420(↑)	63
	480–780	590(↑), 710(↑)	93

riding on their bonded carbon atoms with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups and $1.2U_{eq}(C)$ for the other H atoms, where $U(C)$ is the equivalent temperature factor of the carbon atom bound to the corresponding H atom. All calculations were performed with the SHELXTL PLUS 5 program package [11]. The crystallographic data and refinement parameters for the L and $[ZnLBr_2]$ structures are summarized in Table 1. The atomic coordinates and temperature parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC 732405 and 732406) and can be received free of charge through www.ccdc.cam.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 335 033; or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

According to elemental analysis data, the products have the equimolar composition ($MX_2 : L = 1 : 1$, M = Co, Zn; X = Cl, Br). They are readily soluble in acetone, acetonitrile, ethanol, DMF, and DMSO; moderately soluble in chloroform and benzene; and nearly insoluble in water.

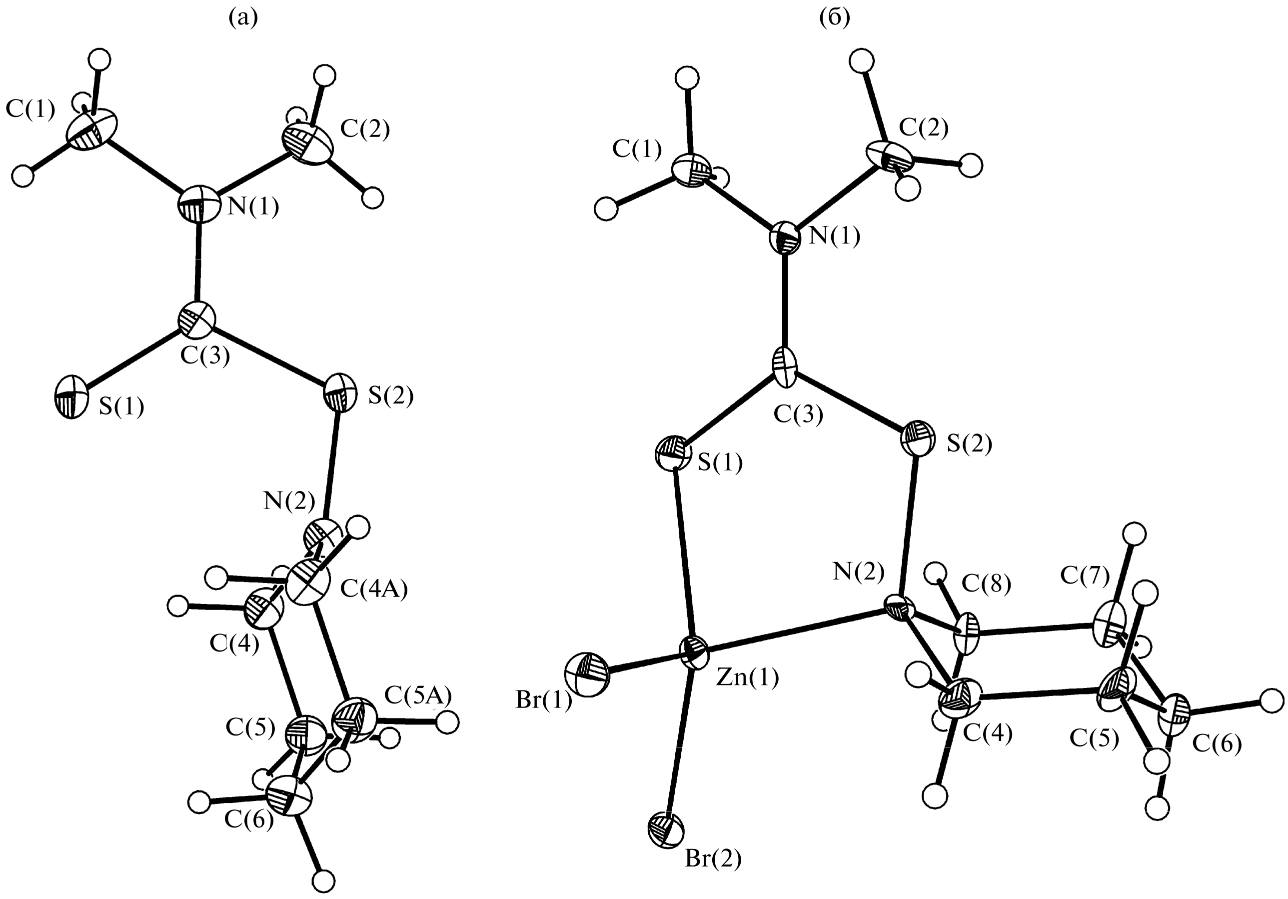
Thermogravimetric analysis revealed significant differences in the thermal behavior of L and the complexes. In particular, the DTA curve of 1-piperidinyl dimethylcarbamodithioate at 77°C shows an endotherm without weight loss (Table 2), corresponding to melting. The subsequent thermal events are accompanied by strong weight loss and point to the almost complete decomposition of L.

In contrast to L, the thermolysis of the complexes (Table 2) is a stepwise process.

A specific feature of thermolysis of cobalt(II) compounds is the presence of well-pronounced exotherms

Table 3. Parameters of electronic absorption spectra, molar electric conductivity in CH_3CN, and effective magnetic moments of the compounds at room temperature

Compound	λ_{max}, nm	log ε	Transition	λ, Ω^{-1} cm^2 mol^{-1}	μ_{eff}, μ_B
1	345	1.87	$n \longrightarrow \pi^*$		–
	279	3.95	$n \longrightarrow \sigma^*$	–	
	235	3.96	$\pi \longrightarrow \pi^*$		
2	690, 637, 595	2.36–2.65	$^4A_2 \longrightarrow {}^4T_1(P)$	108	4.66
	277	3.92	$n \longrightarrow \sigma^*$		
	234	3.99	$\pi \longrightarrow \pi^*$		
3	676, 621, 606	2.81–3.02	$^4A_2 \longrightarrow {}^4T_1(P)$	90	4.54
	278	4.02	$n \longrightarrow \sigma^*$		
	234	4.12	$\pi \longrightarrow \pi^*$		
4	278	3.81	$n \longrightarrow \sigma^*$	96	–
	239	3.81	$\pi \longrightarrow \pi^*$		
5	279	3.81	$n \longrightarrow \sigma^*$	99	–
	239	3.79	$\pi \longrightarrow \pi^*$		



View of (a) L and (b) [$ZnLBr_2$] (one of the two independent molecules is shown). Thermal ellipsoids are drawn at the 50% probability level.

at 155°C in the DTA curves, which are not accompanied by weight loss events on the corresponding TG curves. At the same time, for the zinc(II) complexes, no similar effects were observed.

The synthesized complexes have been characterized by physicochemical methods (Table 3). All the complexes are non-electrolytes [12].

Comparison of the electronic absorption spectra of L and those of the complexes shows that the latter lack a weak band arising from the transition of one of the electrons of the lone pair at the thione sulfur atom to the excited state in the antibonding π orbital. This is evidence that L is coordinated to M through the thione sulfur atom.

The electronic absorption spectra of the complexes show an insignificant hypsochromic effect for the strong absorption bands inherent in dithiocarbamic acid derivatives [1] and related to $n \longrightarrow \sigma^*$ transitions in the N–C=S group and $\pi \longrightarrow \pi^*$ transitions of electrons from the bonding orbital of the ground state to the higher energy orbital in the S–C=S group.

The diffuse reflectance spectra of [$CoLCl_2$] and [$CoLBr_2$] show the ${}^4A_2 \longrightarrow {}^4T_1(P)$ transitions in the range 13800–16800 and 13800–17200 cm^{-1} and the ${}^4A_2 \longrightarrow {}^4T_1(F)$ transitions in the range 6100–7100 and 5900–7100 cm^{-1}, respectively, which is evidence of their tetrahedral structure [13]. The complexes are paramagnetic and high-spin ones (Table 3). The higher μ_{eff} values than the spin-only value (3.87 μ_B) are caused by the orbital contribution, which is a function of the ligand field and complex symmetry. The tem-

Table 4. Selected vibrational frequencies (cm^{-1}) in the IR spectra of the compounds

Compound	Thioamide bands				
	I	II	III	IV	V
1	1510	1245	1140, 1160	985	560
2	1525	1245	1140, 1160	970	560
3	1540	1245	1145, 1160	970	560
4	1535	1245	1140, 1160	970	560
5	1530	1245	1145, 1160	970	560

Table 5. ^{1}H NMR spectra

Compound	δ, ppm
1	1.6 (m, 6H, CH_2-Pip), 3.15 (s, 3H, CH_3), 3.23 (br s, 3H, CH_3), 3.9 (br s), 4.1 (br s, 4H, CH_2-Pip)
3	1.2 (br s, 6H, CH_2-Pip), 32.7 (s, 3H, CH_3), 37.7 (br s, 3H, CH_3), –19.2 (s), –21.0 (s, 4H, CH_2-Pip
4	1.74 (br s, 6H, CH_2-Pip), 3.2 (br s, 3H, CH_3), 3.34 (s, 3H, CH_3), 3.7 (br s), 3.9 (br s, 4H, CH_2-Pip)
5	1.8 (br s, 6H, CH_2-Pip), 3.32 (br s, 3H, CH_3), 3.5 (s, 3H, CH_3), 3.75 (br s), 3.82 (br s, 4H, CH_2-Pip)

perature dependence of molar magnetic susceptibility in the range 100–300 K for [$CoLBr_2$] obeys the Curie–Weiss law $\chi_M = \frac{2.807}{T + 23.2}$, which is evidence of the mononuclear character of this complex.

The L molecule contains the dithiocarbamate fragment. Its structure can be represented by three canonical structures with different C–N bond length and multiplicity:

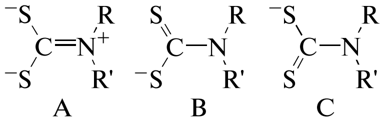


Table 6. Selected bond lengths and bond angles in the L and [$ZnLBr_2$] structures

Bond, Å	d, Å	
	1	**5**
Zn(1)–Br		2.327(1)–2.362(1)
Zn(1)–S(1)		2.334(1)–2.327(1)
Zn(1)–N(2)		2.124(4)–2.139(4)
C3–S(1)	1.667(2)	1.698(5)–1.700(5)
C3–S(2)	1.799(2)	1.767(5)
C3–N(1)	1.334(2)	1.307(5)–1.315(5)
N(1)–C(sp^3)*	1.463(3)–1.467(3)	1.450(6)–1.481(6)
S(2)–N(2)	1.655(2)	1.741(4)–1.743(4)
N(2)–C(sp^3)	1.472(2)	1.502(6)–1.520(6)
	ω, deg	
Angle	**1**	**5**
Br(1)Zn(1)Br(2)		113.99(3)–114.42(3)
N(2)Zn(1)Br(2)		110.9(1)–112.3(1)
S(1)Zn(1)Br(1)		116.70(4)–115.60(4)
S(1)ZnN(2)		88.6(1)–90.5(1)
C(sp^3)N(1)C(sp^3)	114.7(2)	116.8(4)–117.5(4)
S(1)C(3)N(1)	124.6(1)	121.6(4)–122.4(3)
S(1)C(3)S(2)	121.2(1)	124.2(3)–124.7(3)
S(2)C(3)N(1)	114.2(1)	112.9(3)–114.2(4)
C(3)S(2)N(2)	108.3(1)	102.6(2)–103.9(2)

* The symbol C(sp^3) denotes the methyl carbon atoms bound to the N(1) atom and the carbon atoms of the piperidine ring bound to the N(2) atom.

This representation and the concept of thioamide bands [14–16] were used for comparative analysis of the IR spectra of L and the complexes (Table 4).

In the spectra, the thioamide I band id significantly shifted toward higher frequencies and band IV is slightly shifted toward lower frequencies, whereas the positions of bands II, III, and V remain unaltered. This is indicative of the increase in the C–N bond multiplicity, the dominance of polar structure A, and the involvement of the thione sulfur atom in coordination. It was difficult to conclude on the basis of IR data whether the sulfenamide nitrogen atom was bound to M in the complexes; therefore, ^{1}H NMR was used (Table 5).

The ^{1}H NMR spectrum of L demonstrates the presence of nonequivalent protons of the methyl groups at the thiocarbamoyl nitrogen atom, which is caused by hindered rotation around the C(S)–N bond. Due to its deshielding effect, one of the methyl groups gives rise to a broadened singlet at lower field than the other one. This is evidence of the dominance of polar structure A. It is likely that the differences in the chemical shifts of the proton signals of the methylene groups directly bound to the nitrogen atom of the piperidine ring are caused by their asymmetric position with respect to the magnetic anisotropy cone of the C=S bond.

In the ^{1}H NMR spectra of the complexes, the signals of the protons of the methyl groups at the thiocarbamoyl nitrogen atom are shifted downfield, their nonequivalence persisting as in the case of L. At the same time, the proton signals of the methylene groups at the sulfenamide nitrogen atom are shifted up field, which is likely due to its involvement in coordination.

Combined IR and ^{1}H NMR data allow us to conclude that L acts as a bidentate ligand in the complexes. At the same time, as is known, ligands containing the thioamide group often function as monodentate N- or S-ligands. Therefore, the structure of the complexes was determined by means of X-ray crystallographic study of L and [$ZnLBr_2$] (figure, Table 6).

According to the data obtained, the lengths of single C–N and C–C bonds and bond angles in the *N,N*-dimethyl and piperidine moieties have common values [17]. The heterocyclic ring has a chair conformation in all cases, although, in both independent [$ZnLBr_2$] molecules, this moiety is inverted with respect to the N(2) atom as compared with the initial ligand in such a manner that the chelating (S,N) coordination of L becomes possible (figure). This fact indicates that the S–N bond is single, which is supported by its length (Table 6) and the pyramidal geometry of substituents at the N(2) atom (figure).

The L molecule is coordinated to the zinc atom as a bidentate chelating ligand to form a five-membered chelate ring. In addition to the sulfur and nitrogen atoms of L, the zinc coordination sphere contains two monodentate terminal bromide ions. The coordination polyhedron of zinc is a distorted tetrahedron, which is caused by different natures of the coordinated atoms. The presence of three types of surrounding atoms (Br, S, N) is responsible for both different lengths of coordination bonds and a wide range of bond angles at the zinc atom. The largest bond angles are SZnN and BrZnBr corresponding to maximum repulsion of the lone pairs of bulky bromine and sulfur atoms, and the SZnN bond angles are the smallest ones (≈90°) (Table 6). This value is presumably due to steric hindrances caused by the fact that the S and N atoms belong to the same ligand (in contrast to the bromine atoms, which can move independently of the other ligands), as well as by the repulsion between the nitrogen and bromine atoms. This possibility is indicated by the noticeable decrease in the C(3)S(2)N(2) angle upon coordination of L to zinc (Table 6).

The *N,N*-dimethyldithiocarbamate moiety of L is roughly planar in both the free state (the deviation of the atoms form the C(1)–C(2)–N(1)–C(3)–S(1)–S(2) plane is 0.0(1) Å) and coordinated state (the deviation of the atoms is 0.1(1) Å). The N(1)–C(3) and C(3)–S(1) bond lengths (≈1.3 and ≈1.7 Å, respectively) are evidence of their multiple character. Hence, the geometry of the *N,N*-dimethyldithiocarbamate moiety is consistent with IR spectroscopy evidence about the dominance of polar resonance structure A for the free ligand. Moreover, the coordination of L to zinc leads to a pronounced elongation of the C=S and N–S bonds (by 0.03–0.09 Å) and shortening of the C–N and C–S bonds (by 0.03 Å), which indicates that structure A persists in the coordinated ligand.

Thus, X-ray crystallography, IR spectroscopy, and ^{1}H NMR provide consistent data for L and [$ZnLBr_2$]. Hence, we can conclude that the cobalt(II) and zinc(II) complexes are isostructural, with the same bidentate chelating coordination of 1-piperidinyl dimethylcarbamodithioate through the thione sulfur atom and the sulfenamide nitrogen atom.

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