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Versatile Chelating Behavior of Benzil Bis(thiosemicarbazone) in Zinc, Cadmium, and Nickel Complexes

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Reactions of benzil bis(thiosemicarbazone), LH_6, with $M(NO_3)_2 \cdot nH_2O$ (M = Zn, Cd, and Ni), in the presence of $LiOH \cdot H_2O$, show the versatile behavior of this molecule. The structure of the ligand, with the thiosemicarbazone moieties on opposite sides of the carbon backbone, changes to form complexes by acting as a chelating molecule. Complexes of these metal ions with empirical formula [MLH_4] were obtained, although they show different molecular structures depending on their coordinating preferences. The zinc complex is the first example of a crystalline coordination polymer in which a bis(thiosemicarbazone) acts as bridging ligand, through a nitrogen atom, giving a 1D polymeric structure. The coordination sphere is formed by the imine nitrogen and sulfur atoms, and the remaining position, in a square-based pyramid, is occupied by an amine group of another ligand. The cadmium derivative shows the same geometry around the metal ion but consists of a dinuclear structure with sulfur atoms acting as a bridge between the metal ions. However, in the nickel complex LH_6 acts as a N_2S_2 ligand yielding a planar structure for the nickel atom. The ligand and its complexes have been characterized by X-ray crystallography, microanalysis, mass spectrometry, IR, ^{1}H, and ^{13}C NMR spectroscopies and for the cadmium complex by ^{113}Cd NMR in solution and in the solid state.

Introduction

The synthesis of coordination polymers is currently of great interest as a method for the construction of new supramolecular architectures, due to their properties such as luminescence and conductivity and their applications in catalysis.[1] Factors influencing the formation of coordination polymers are not well understood; for a simple bifunctional ligand, the metal ratio is important in the construction of novel architectures[2] and various other factors such as the nature of the metal ions and the counteranions may also influence the formation of one structure over the other. Moreover, experimental conditions can add complexity to the problem and variation of these may lead to polymorphism.[3] The fascinating structural and catalytic properties of metal−enzymes have stimulated the design of synthetic polydentate ligands that mimic the coordination environment of metal ions in proteins. Zn(II) usually favors tetrahedral coordination; in this respect a recent review[4] cited over 600 Zn(II) complexes which are predominantly tetrahedral. Recently, a zinc coordination polymer with this geometry around the metal ion has been described.[5] Among the less common five-coordinate complexes, trigonal bipyramidal (tbp) geometry occurs more frequently than square-based pyramidal (sbp). The latter case is usually sustained by a basal plane of the donor atoms in a tetradentate macrocycle, with the apical position occupied by a terminal ligand such as pyridine or chloride.

Polynuclear complexes from thiosemicarbazones are not very common; however, some derivatives of [1 + 1] condensation products have been published. A bridging sulfur atom is observed in the polymeric structures of copper and lead complexes of 1-methylisatin 3-thiosemicarbazone and 2-acetylpyridine-4-*N*-methylthiosemicarbazone, respectively.[6,7]

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A polymeric structure of a zinc complex is formed by sulfur and oxygen atoms from 2-acetylpyridine *N*-oxide 4-*N*-methylthiosemicarbazone bridging between ZnI_2 units giving a tetrahedral coordination for the metal ion,[8] and two bridging oxygen atoms provided by the thiosemicarbazone and an acetate group are observed in a polymeric zinc(II) complex, in which the pentacoordinated geometry of the metal atom is completed by the terminal amine nitrogen.[9] This group, besides the sulfur atom, is also involved in the coordination in the salicylaldehyde thiosemicarbazonato heterooctametallic complex containing a cyclic Ru_4Ni_4 core.[10]

Structural data for the $[MN_2S_2]$ complex unit resulting from the coordination of bis(thiosemicarbazones) with copper(II) and nickel(II) are well-known. Both ions preferably form mononuclear planar complexes.[11−14] Since Zn(II) usually favors tetrahedral coordination, the question arises how the conformation of these kind of ligands affects the structure of the corresponding zinc complexes. Therefore, these complexes should be stabilized either by additional coordination of monodentate Lewis bases giving a five-coordinated zinc atom[15−19] or through dimerization if a bidentate group is present.[20,21] An example of a bis(thiosemicarbazone) acting as a bridge between two zinc atoms is the complex derived from 1-phenylglyoxal bis(3-piperidylthiosemicarbazone), in which the anionic thiosemicarbazone moieties lead to a $[ZnN_3S_2]$ unit for each atom in a binuclear compound.[22] Polymeric compounds can be obtained if an additional Lewis base acts as a bridge ligand.[23−26]

Most of the cadmium(II) thiosemicarbazone complexes studied by X-ray diffractometry are adducts of cadmium dihalide; only a few of them contain thiosemicarbazonate anions. The first complex with the last situation is that with pyridinethiosemicarbazone in which the two N,N,S-coordinate ligands give the metal ion a highly distorted octahedral coordination polyhedron. A polynuclear complex $[Cd_3(HMeOSTSC)_4](OAc)_2\cdot 0.5DMSO\cdot 2H_2O$ is characterized, in which cadmium ions are bridged by the oxygen atoms of the deprotonated phenolic hydroxy groups belonging to the four TSC ligands. Each terminal Cd(II) is additionally coordinated to N and S atoms of the two TSC ligands in a *Z*-configuration giving a $[CdN_2O_2S_2]$ kernel with distorted octahedral geometry, while the central metal ion attains a coordination number of 8 through additional bonding to the four methoxy group, giving a triangular dodecahedral coordination geometry.[15] Recently, the complex with pyrazineformamide N(4)-methylthiosemicarbazone has been reported,[27] where the cadmium ion is hexacoordinated by two ligands acting as a tridentate through the imine and the pyridine nitrogen atoms, as well as the thiolate sulfur.

^{113}Cd has a spin of $^1/_2$ (thus, no quadrupolar contribution to NMR relaxation which broadens signals) and an abundance of 12.26% (compared to 1.11% for ^{13}C). ^{113}Cd has a demonstrated chemical shift range of over 900 ppm, and the value of the chemical shift has been shown to depend on the nature, number, and geometric arrangement of the atoms coordinated to cadmium. This enables one to apply ^{113}Cd NMR spectroscopy as a probe of the metal in binding sites in biological systems and coordination compounds. When cross-polarization magic angle spinning (CP MAS) ^{113}Cd NMR spectroscopy is combined with X-ray crystallography, an excellent opportunity is provided to study and correlate metal ion geometry with the chemical shifts. ^{113}Cd NMR signals in the solid state or in solution are able to describe the ligand and its geometry about the cadmium atom.[28−31]

In a previous work[32] we have established that benzil bis(thiosemicarbazone) (Chart 1), LH_6, requires planar coordination for a cadmium derivative. This complex consists of octahedral units, in which the equatorial positions are occupied by the neutral ligand and the axial ones by monodentate nitrate groups. This is the reason formation of tetrahedral complexes should not occur, but it is easy to get

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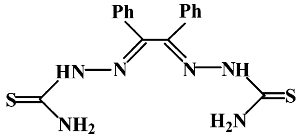
Chart 1. Drawing of LH_6



square-planar geometries. In fact, a zinc complex of LH_6 with a nitrate ion in the apical position of a square-based pyramid has been previously proposed. In this article, we report the direct synthesis and structural characterization of new LH_6 complexes with the same stoichiometry, in which the deprotonate ligand shows a different coordination behavior depending on the preference for a coordinated donor atom and the geometry for the metal ion.

Experimental Section

Physical Measurements. Microanalyses were carried out using a Perkin-Elmer 2400 II CHNS/O elemental analyzer. IR spectra in the 4000−400 cm^{-1} range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer. ^1H, ^{13}C, and ^{113}Cd NMR spectra were recorded on a Bruker AMX-300 spectrophotometer using $CDCl_3$, DMSO-d_6, and DMF/$CDCl_3$ as solvents and TMS or 0.1 M aqueous $Cd(ClO)_4$ as references. The ^{113}Cd CP MAS NMR spectrum was obtained at 298 K in a Bruker Avance-400 spectrometer, using a standard cross-polarization pulse sequence.[33−36] The external magnetic field was 9.4 T, and the sample was spun at 4−4.5 kHz around an axis inclined 54° 44′ with respect to this field. Spectrometer frequencies were set to 88.76 MHz. For the recorded spectrum a contact time of 10 ms was used. The number of scans ranged to 4000. Fast atom bombardment mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzyl alcohol (*m*NBA) as the matrix. MALDI-TOF-MS spectra were recorded using a Bruker Reflex III mass spectrometer equipped with a nitrogen laser emitting at 337 nm, using ditranol as the matrix.

All reagents and other solvents were obtained from standard commercial sources and were used as received.

Synthesis. [$C_{16}H_{14}N_6S_2$], LH_6. Benzil bis(thiosemicarbazone) was prepared by following the procedure previously reported.[37] FAB+ (*m/z*): 357 ($[LH_6 + 1]^+$, 100%), 714 ($[(LH_6)_2 + 1]^+$, 25%). ^1H NMR (DMSO-d_6): δ 9.8 (2H, s), 8.6 (2H, s), 8.3 (2H, s), 7.7 (4H, m), 7.4 (6H, m). ^1H NMR ($CDCl_3$): δ 8.8 (2H, s), 7.6 (6H,m), 7.4 (4H, m), 6.6 (2H, s), 6.0 (2H, s). ^{13}C NMR (DMSO-d_6): δ 179.1 (CS), 140.5 (CN), 133.1, 130.1, 128.9, 126.8 (CPh). IR (KBr) (ν_{max}/cm^{-1}): 3420, 3386, 3342, 3330, 3210, 3151, ν(NH), 1608, $\delta(NH_2)$, 1581, ν(C═N), and 848, ν(CS).

Slow evaporation of an ethanol/water solution (2:1) gave pale yellow crystals suitable for X-ray analysis.

[$ZnC_{16}H_{14}N_6S_2]_\infty$, 1. A 0.249 g (0.84 mmol) amount of $Zn(NO_3)_2 \cdot 6H_2O$ dissolved in 10 mL of ethanol was added over a suspension of 0.300 g (0.84 mmol) of LH_6 and 0.071 g (0.84 mmol) of $LiOH \cdot H_2O$ in 40 mL of the same solvent. The mixture was stirred under reflux for 6 h. Then the orange solid was filtered off, washed with methanol, and vacuum-dried (95%). (Anal. Found: C, 45.34; H, 3.60; N, 19.88; S, 14.98. Calcd for $ZnC_{16}H_{14}N_6S_2$: C, 45.78; H, 3.34; N, 20.03; S, 15.26.) MALDI-TOF+ (*m/z*): 419.1, $[ZnLH_4 + 1]^+$. ^1H NMR (DMSO-d_6): δ 7.5−6.9, m. ^{13}C NMR (DMSO-d_6): δ 179.7 (CS); 144.4 (CN); 134.5, 129.7, 129.6, 129.0, 128.5, 128.3, 127.8, 127.5 (CPh). IR (KBr) (ν_{max}/cm^{-1}): 3499, 3328, 3270, 3156, ν(NH), 1586, 1566, 1516, $\delta(NH_2)$, 1593, ν(C═N), and 844, ν(CS).

Recrystallization in ethanol gave orange crystals suitable for X-ray crystallography.

[$CdC_{16}H_{14}N_6S_2]_2$, 2. The procedure was the same as for complex **1** but using $Cd(NO_3)_2 \cdot 4H_2O$ (96%). (Anal. Found: C, 40.89; H, 3.16; N, 17.68; S, 13.24. Calcd for $CdC_{16}H_{14}N_6S_2$: C, 41.16; H, 3.00; N, 18.01; S, 13.72.) FAB+ (*m/z*): 467.8 ($Cd[LH_4 + 1]^+$, 15%). MALDI-TOF (*m/z*): 468.1 ($[CdLH_4 + 1]^+$), 935.1 ($[CdLH_4]_2 + 1]^+$. ^1H NMR (DMSO-d_6): δ 7.5−6.8, m. ^{13}C NMR (DMSO-d_6): δ 177.1 (CS); 146.4 (CN); 135.6, 129.7, 127.5, 127.4 (CPh). ^{113}Cd NMR (DMF, 213 K): δ 229. ^{113}Cd CP MAS NMR: δ 267. IR (KBr) (ν_{max}/cm^{-1}): 3467, 3428, 3349, 3158, ν(NH); 1616, 1581, 1513, $\delta(NH_2)$, 1596, ν(C═N), and 840, 813, ν(CS).

Recrystallization in a dimethylformamide/chloroform (9:1) solution gave orange crystals suitable for X-ray analysis.

[$NiC_{16}H_{14}N_6S_2$], 3.[38] A solution of 0.244 g (0.84 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 10 mL of ethanol was added over a suspension of 0.300 g (0.84 mmol) of LH_6 and 0.071 g (0.84 mmol) of $LiOH \cdot H_2O$ in 40 mL of the same solvent. The mixture was stirred for 3 h at room temperature. The reddish solid was filtered off, washed with methanol, and vacuum-dried (87%). (Anal. Found: C, 46.41; H, 3.42; N, 20.20; S, 15.46. Calcd for $NiC_{16}H_{14}N_6S_2$: C, 46.52; H, 3.39; N, 20.30; S, 15.53.) FAB+ (*m/z*): 412.9 ($[NiLH_4 + 1]^+$, 30%). ^1H NMR (DMSO-d_6): δ 7.6 (4H NH_2, s), 7.1−7.3 (10H Ph, m). ^{13}C NMR (DMSO-d_6): δ 179.7 (CS); 153.8 (CN); 131.6, 129.4, 128.8, 127.7 (CPh). IR (KBr): (ν_{max}/cm^{-1}): 3456, 3273, 3124, ν(NH), 1625, 1576, 1557, $\delta(NH_2)$, 1615, ν(C═N), and 852, ν(CS).

Recrystallization in dimethylformamide gave red crystals suitable for X-ray crystallography

Crystallography. Crystals of compounds were mounted on a glass fiber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd., rotating anode (Cu Kα radiation, λ = 1.541 78 Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data were collected at 296 K, with a combination of six runs at different φ and 2θ angles, 3600 frames. The data were collected using 0.3° wide ω scans (10 s/frame at $2\theta = 40°$ and 20 s/frame at $2\theta = 100°$ for LH_6, 30 s/frame at $2\theta = 40°$ and 60 s/frame at $2\theta = 100°$ for complex **1**, 1 s/frame at $2\theta = 40°$ and 3 s/frame at $2\theta = 100°$ for complex **2**, and 20 s/frame at $2\theta = 40°$ and 50 s/frame at $2\theta = 100°$ for complex **3**), with crystal-to-detector distance of 4.0 cm.

The substantial redundancy in data allows empirical absorption corrections (SADABS)[39] to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission: 0.836211 for LH_6, 0.862650 for complex **1**, 0.352243 for complex **2**, and 0.905221 for complex **3**). The unit cell parameters were obtained by full-matrix least-squares refinements of 1239 reflections for LH_6, 5227 reflections for complex **1**, 8961 for complex **2**, and 2969 for complex **3**.

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Table 1. Crystallographic Data for the Compounds

	LH_6	**1**	**2**	**3**
formula	$C_{16}H_{16}N_6S_2$	$C_{16}H_{14}N_6S_2Zn$	$C_{22}H_{28}N_8CdO_2S_2$	$C_{19}H_{21}N_7NiOS_2$
M	356.47	419.82	613.04	486.26
cryst system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$
a/Å	9.6364(4)	12.7945(2)	19.7587(3)	10.2602(4)
b/Å	9.9275(4)	9.0831(2)	12.32270(10)	10.5285(5)
c/Å	10.2686	14.9600(3)	22.4943(3)	11.2091(5)
α/deg	86.179(3)	90	90	98.070(3)
β/deg	70.671(3)	97.0220(10)	101.6190(10)	108.113(3)
γ/deg	71.795(2)	90	90	105.883(3)
V/Å^3	879.84(7)	1725.52(6)	5364.69(12)	1072.72(8)
Z	2	4	8	2
D_c/Mg m^{-3}	1.346	1.616	1.518	1.505
abs coeff/mm^{-1}	2.825	4.339	8.266	3.344
F(000)	372	856	2496	504
goodness of fit on F^2	1.043	1.051	1.050	1.018
reflcns collcd	5685	3141	16 449	6968
Indpndnt reflcns	2949	3141	4923	3574
final R1 and wR2 [$I > 2\sigma(I)$]	0.0427, 0.1111	0.0323, 0.0847	0.0409, 0.1205	0.0359, 0.0920
R indices (all data)	0.0633, 0.1232	0.0384, 0.0886	0.0428, 0.1226	0.0460, 0.0986

The raw intensity data frames were integrated with the SAINT[40] program, which also applied corrections for Lorentz and polarization effects.

The software package SHELXTL[41] version 6.10 was used for space group determination, structure solution, and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods (SHELXS-97),[42] completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97[43] minimizing $\omega(F_o^2 - F_c^2)^2$. Weighted *R* factors (R_w) and all goodness of fit *S* are based on F^2; conventional *R* factors (*R*) are based on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. The high quality of the data set allowed that all hydrogen atoms were located by difference maps and refined isotropically in all complexes, except in the solvent molecules and aromatic hydrogens of complexes **2** and **3**.

CCDC reference numbers: 190456 for complex **1**; 220143 for LH_6; 220144 for complex **2**; 220145 for complex **3**.

Results and Discussion

Complexes obtained present the same empirical formula [MLH_4].

Reactions between LH_6 and $Zn(NO_3)_2$·$6H_2O$ or $Cd(NO_3)_2$·$4H_2O$ depend on the working conditions; in the presence of a basic medium they give, with a quantitative yield, complexes **1** and **2**, respectively. In both of them, the ligand acts as dianion by the loss of the hydrogen of the secondary amine in contrast with the complexes previously prepared in absence of this medium.[32] The nickel complex **3** was obtained under the same conditions as the other and in the absence of basic medium.[38] FAB+ mass spectra of complexes **2** and **3** confirm the empirical formula; however the spectrum of complex **1** only shows a very weak peak. MALDI-TOF spectra of complexes **1** and **2** show a peak corresponding to the empirical formula, and the spectrum of the last complex shows an additional peak corresponding to the molecular mass. The different behavior observed could be explained probably because the Cd−S bond is stronger than the Zn−N bond, and while the first one remains, the second one is broken when the spectrum is carried out. Complexes **1** and **2** are only soluble in strongly donor solvents, as DMF and DMSO.

Crystallography. Crystallographic data of LH_6 and its complexes are summarized in Table 1.

Pale yellow crystals of LH_6 suitable for X-ray diffraction study were obtained by slow evaporation of an ethanol/water mixture. The structure determination shows (Figure 1; Table 2) that the free ligand exists in the thione form (supported by the presence of hydrazinic N−H and C−S distance of 1.67 Å, which is much shorter than a single C−S bond) and corresponds to a structure where the two thiosemicarbazone moieties are trans with respect to the single bond C(2)−C(3) and the phenyls are in a perpendicular disposition, thus minimizing the intramolecular interaction; both thiosemicarbazone branches are in a *E* disposition with respect to the CN double bond. The X-ray data confirm the proposed structure from a molecular modeling program (Hyperchem version 3) previously published by us.[44]The distances and bond angles of both thiosemicarbazone arms are very similar, and the molecular conformation of the atoms and the azomethine nitrogen atoms N(6) and N(3) is cis with respect to the C(4)−N(5) and C(1)−N(2) bonds. The N−N distances are shorter than 1.44 Å, accepted as typical for a single N−N bond, and agree well with those of similar thiosemicarbazones.[45] C−S bonds distances are intermediate between those of single and double bond (1.82 and 1.56, respectively),[46] showing the partial double bond character implied by the

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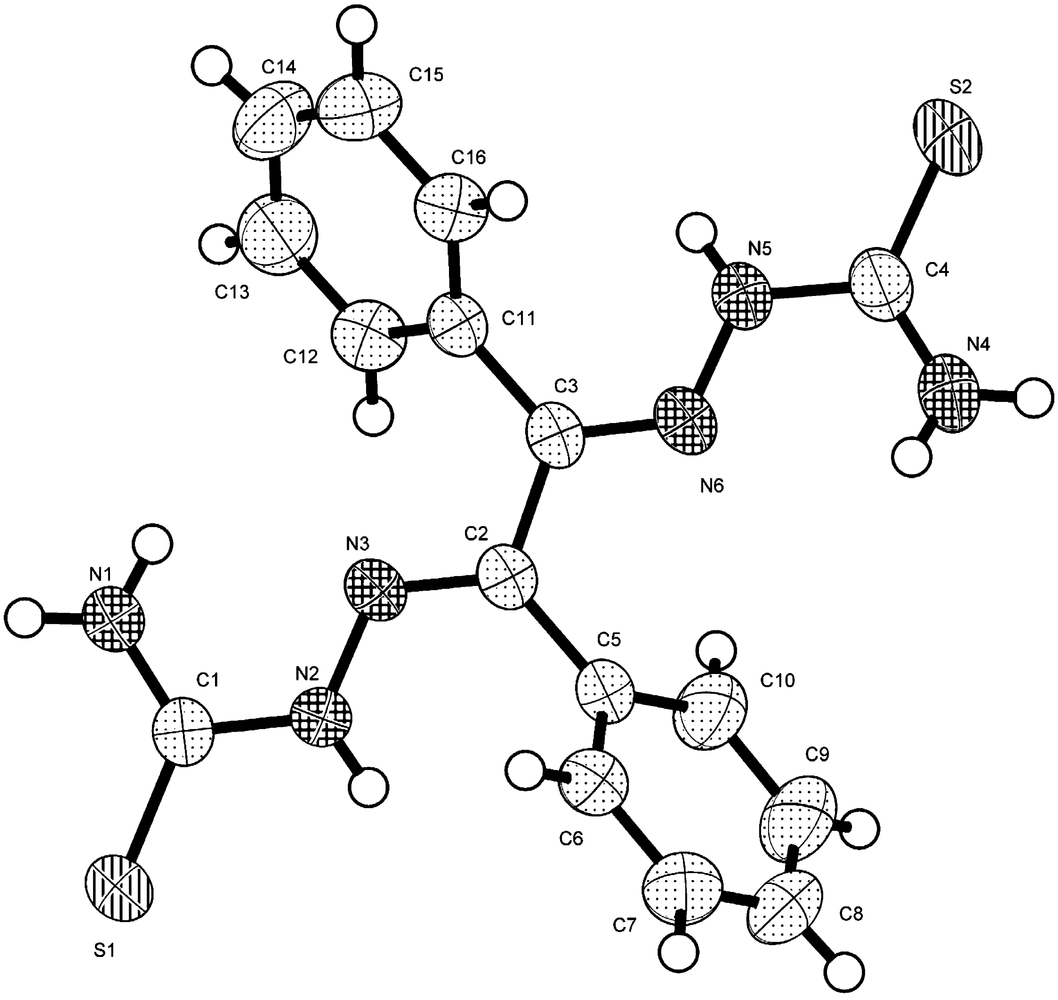

Figure 1. Molecular structure of LH_6. Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for LH_6

C(1)−N(1)	1.305(3)	C(3)−C(11)	1.490(3)
C(1)−N(2)	1.369(3)	C(4)−N(4)	1.306(4)
C(1)−S(1)	1.667(3)	C(4)−N(5)	1.367(3)
C(2)−N(3)	1.298(3)	C(4)−S(2)	1.668(3)
C(2)−C(3)	1.478(3)	N(2)−N(3)	1.361(3)
C(2)−C(5)	1.490(3)	N(5)−N(6)	1.362(3)
C(3)−N(6)	1.294(3)		
N(1)−C(1)−N(2)	115.8(2)	N(4)−C(4)−S(2)	126.0(2)
N(1)−C(1)−S(1)	125.6(2)	N(5)−C(4)−S(2)	118.3(2)
N(2)−C(1)−S(1)	118.68(19)	C(6)−C(5)−C(2)	120.4(2)
N(3)−C(2)−C(3)	114.0(2)	C(10)−C(5)−C(2)	121.3(2)
N(3)−C(2)−C(5)	125.0(2)	C(16)−C(11)−C(3)	120.5(2)
C(3)−C(2)−C(5)	121.0(2)	C(12)−C(11)−C(3)	121.1(2)
N(6)−C(3)−C(2)	114.2(2)	N(3)−N(2)−C(1)	119.0(2)
N(6)−C(3)−C(11)	125.6(2)	C(2)−N(3)−N(2)	118.7(2)
C(2)−C(3)−C(11)	120.2(2)	N(6)−N(5)−C(4)	119.1(2)
N(4)−C(4)−N(5)	115.7(3)	C(3)−N(6)−N(5)	118.9(2)

canonical structures usually considered for thiosemicarbazones. Azomethine bond lengths are likewise short enough to imply a partial double bond. Formation of complexes, in which the ligand acts as a N_2S_2 chelate, takes place via three 180° rotations about C(2)−C(3), C(1)−N(2), and C(4)−N(5) bonds. The molecules are held together in the crystal packing through an extended network of intermolecular hydrogen bonds involving the amine nitrogen atoms N(1) and N(4) and the sulfur atoms S(1) and S(2) (Figure 2; Table 3).

Orange crystals of $[ZnLH_4]_\infty$, **1**, suitable for X-ray diffraction study were obtained by recrystallization in ethanol. Crystallographic data of complex **1** indicate that the Zn(II) ion is pentacoordinated in a distorted square-based pyramidal structure (Figure 3) and both thiosemicarbazone arms are in *E* disposition. Selected bond distances and angles are summarized in Table 4. The value of the parameter τ defined by Addison et al.[47] is 0.04 ($\tau = 0$ for a regular square-based pyramid). The coordination sphere of the zinc atom is formed by two sulfurs, two imine nitrogen atoms, and a nitrogen atom from a terminal amine group belonging to another ligand. To the best of our knowledge, this is the first time that a bis(thiosemicarbazonate) complex with this behavior has been crystallographically characterized. The N_2S_2 donor atoms of the tetradentate ligand define the base with a maximum deviation of 0.113 Å for N(5). The axial site is occupied by a NH_2 group. The zinc atom is displaced out of the basal plane by 0.412 Å toward the atom at the apex of the pyramid. The angle formed by the Zn−N(2A) bond with the normal to the basal plane is 10°. The pseudomacrocyclic

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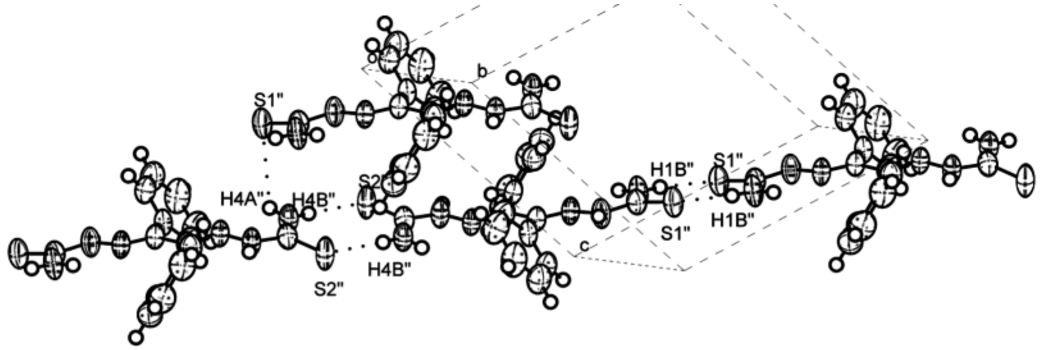

Figure 2. A plot including the hydrogen bonds in LH_6.

Table 3. Hydrogen bonds for LH_6 (Å, deg)

D−H···A[a]	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
N(4)−H(4B)···S(2)$^{\#1}$	0.83(4)	2.57(4)	3.392(3)	172(3)
N(4)−H(4B)···S(1)$^{\#2}$	0.81(3)	3.01(3)	3.531(3)	125(3)
N(1)−H(1B)···S(1)$^{\#3}$	0.87(4)	2.48(4)	3.340(3)	171(3)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y + 2, -z + 1$; (#2) $x - 1, y, z$; (#3) $-x + 3, -y + 2, -z + 2$.

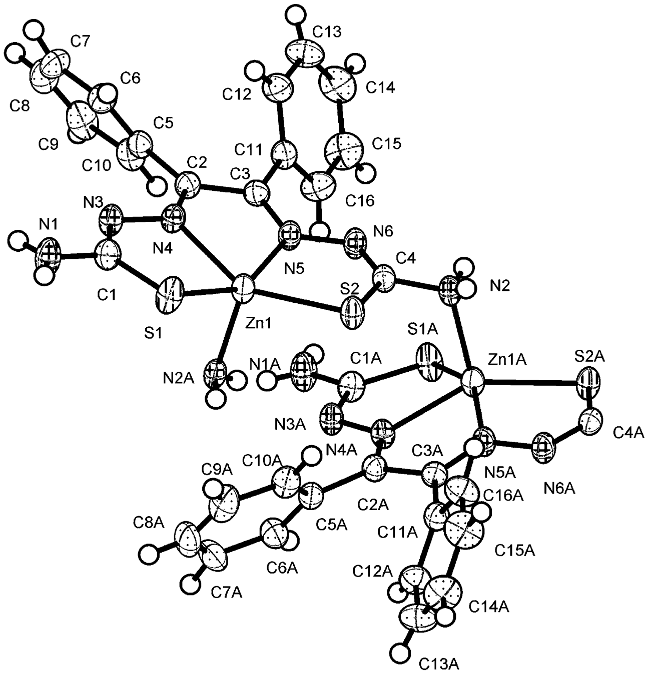

Figure 3. Molecular structure of $[ZnC_{16}H_{14}N_6S_2]_\infty$, **1**, with the atom labeling scheme. Thermal ellipsoids are shown at 40% probability.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **1**[a]

Zn(1)−N(5)	2.097(2)	C(3)−N(5)	1.293(3)
Zn(1)−N(4)	2.1393(19)	C(3)−C(11)	1.482(3)
Zn(1)−N(2)$^{\#1}$	2.170(2)	C(4)−N(6)	1.299(3)
Zn(1)−S(1)	2.3318(7)	C(4)−N(2)	1.401(3)
Zn(1)−S(2)	2.3621(7)	N(1)−H(1A)	0.80(3)
S(1)−C(1)	1.730(3)	N(1)−H(1B)	0.80(3)
S(2)−C(4)	1.732(2)	N(2)−Zn(1)$^{\#2}$	2.170(2)
C(1)−N(3)	1.334(3)	N(2)−H(2A)	0.64(3)
C(1)−N(1)	1.339(3)	N(2)−H(2B)	0.76(3)
C(2)−N(4)	1.301(3)	N(3)−N(4)	1.369(3)
C(2)−C(5)	1.485(3)	N(5)−N(6)	1.376(3)
C(2)−C(3)	1.494(3)		

N(5)−Zn(1)−N(4)	74.07(8)	N(6)−C(4)−N(2)	114.1(2)
N(5)−Zn(1)−N(2)$^{\#1}$	99.03(10)	N(6)−C(4)−S(2)	129.62(19)
N(4)−Zn(1)−N(2)$^{\#1}$	101.62(8)	N(2)−C(4)−S(2)	116.22(19)
N(5)−Zn(1)−S(1)	150.84(6)	C(1)−N(1)−H(1A)	118(2)
N(4)−Zn(1)−S(1)	81.16(6)	C(1)−N(1)−H(1B)	119(2)
N(2)$^{\#1}$−Zn(1)−S(1)	100.83(8)	H(1A)−N(1)−H(1B)	122(3)
N(5)−Zn(1)−S(2)	81.70(6)	C(4)−N(2)−Zn(1)$^{\#2}$	116.77(17)
N(4)−Zn(1)−S(2)	148.26(6)	C(4)−N(2)−H(2A)	109(3)
N(2)$^{\#1}$−Zn(1)−S(2)	102.17(6)	Zn(1)$^{\#2}$−N(2)−H(2A)	110(3)
S(1)−Zn(1)−S(2)	114.34(3)	C(4)−N(2)−H(2B)	112(3)
C(1)−S(1)−Zn(1)	94.86(9)	Zn(1)$^{\#2}$−N(2)−H(2B)	98(3)
C(4)−S(2)−Zn(1)	93.71(8)	H(2A)−N(2)−H(2B)	110(4)
N(3)−C(1)−N(1)	115.0(2)	C(1)−N(3)−N(4)	111.76(19)
N(3)−C(1)−S(1)	128.17(19)	C(2)−N(4)−N(3)	121.51(19)
N(1)−C(1)−S(1)	116.9(2)	C(2)−N(4)−Zn(1)	117.40(16)
N(4)−C(2)−C(5)	124.2(2)	N(3)−N(4)−Zn(1)	119.39(15)
N(4)−C(2)−C(3)	114.1(2)	C(3)−N(5)−N(6)	119.3(2)
C(5)−C(2)−C(3)	121.6(2)	C(3)−N(5)−Zn(1)	119.57(16)
N(5)−C(3)−C(11)	123.8(2)	N(6)−N(5)−Zn(1)	121.08(15)
N(5)−C(3)−C(2)	113.9(2)	C(4)−N(6)−N(5)	112.2(2)
C(11)−C(3)−C(2)	122.2(2)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1/2, y - 1/2, -z + 3/2$; (#2) $-x + 1/2, y + 1/2, -z + 3/2$.

coordination mode of the ligand affords three five-member chelate rings. The phenyl rings C(5)−C(10) and C(11)−C(16) form with respect to the basal plane dihedral angles of 54.81 and 52.64°, respectively. The angle between phenyl rings is 57.74°. In accordance with the symmetry of the ligand, bond distances and angles in both thiosemicarbazone moieties are similar. Bond lengths agree with a considerable electronic delocalization through the thiosemicarbazone backbone, enhanced upon deprotonation. Thus, the thione bond distances of ca. 1.73 Å are intermediate between a theoretical C−S single and double bond and longer than in the free ligand, as occurs with the N−N bonds (1.37 vs. 1.44 Å calculated for a single N−N). The different behavior of two thiosemicarbazone arms reflects on the values of 1.334(3) and 1.299(3) Å for the C(4)−N(6) and C(1)−N(3) bonds with respect to the free ligand [1.367(3) Å]. It can be pointed out that, owing to the dideprotonation, the C−S double bond character is smaller than in the complex $[Cd(NO_3)_2LH_6]$.[32] The bond N(2)−C(4) is larger than N(1)−C(1) because the N(2) is bonded to the zinc and then the delocalization is smaller than in the other amine group. The bond distance between the zinc atom and the amine nitrogen from the other ligand is slightly larger than the other Zn−N bonds, but it is close to those observed in some thiosemicarbazide complexes.[48] Furthermore the bond angles in the bis(thiosemicarbazone) ligand are also compatible with the electronic delocalization. Remaining bond distances and

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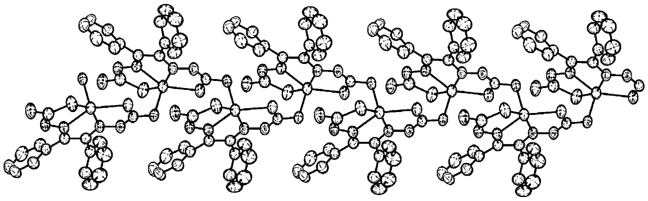

Figure 4. Formation of a 1D chain along the *b* direction based on the $ZnC_{16}H_{14}N_6S_2$ building unit.

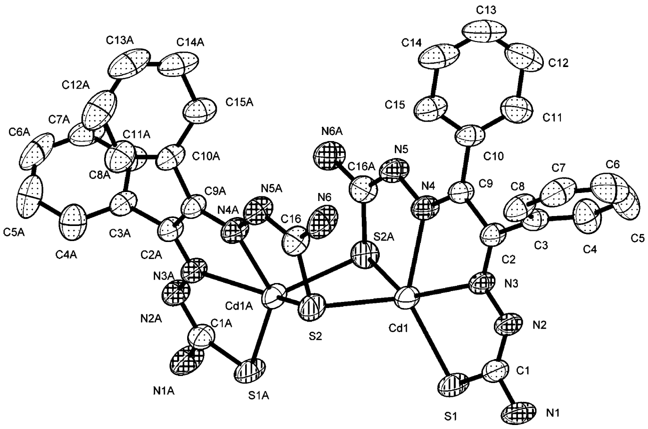

Figure 5. Molecular structure of $[CdC_{16}H_{14}N_6S_2]_2{\cdot}2DMF$ with atom labeling scheme. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[CdC_{16}H_{14}N_6S_2]_2{\cdot}2DMF^a$

Cd(1)−N(4)	2.308(3)	C(2)−N(3)	1.290(4)
Cd(1)−N(3)	2.329(3)	C(2)−C(3)	1.488(4)
Cd(1)−S(1)	2.4973(9)	C(2)−C(9)	1.493(4)
Cd(1)−S(2)$^{\#1}$	2.6128(9)	C(9)−N(4)	1.295(4)
Cd(1)−S(2)	2.6337(9)	C(9)−C(10)	1.491(4)
S(1)−C(1)	1.745(4)	C(16)−N(5)$^{\#1}$	1.319(5)
S(2)−C(16)	1.789(4)	C(16)−N(6)	1.327(5)
S(2)−Cd(1)$^{\#1}$	2.6128(9)	N(2)−N(3)	1.375(4)
C(1)−N(2)	1.318(5)	N(4)−N(5)	1.368(4)
C(1)−N(1)	1.338(5)	N(5)−C(16)$^{\#1}$	1.319(5)
N(4)−Cd(1)−N(3)	69.44(9)	N(3)−C(2)−C(3)	124.3(3)
N(4)−Cd(1)−S(1)	140.18(8)	N(3)−C(2)−C(9)	116.3(3)
N(3)−Cd(1)−S(1)	75.32(7)	C(3)−C(2)−C(9)	119.4(3)
N(4)−Cd(1)−S(2)$^{\#1}$	74.17(7)	N(4)−C(9)−C(10)	123.9(3)
N(3)−Cd(1)−S(2)$^{\#1}$	136.35(7)	N(4)−C(9)−C(2)	116.4(3)
S(1)−Cd(1)−S(2)$^{\#1}$	124.98(3)	C(10)−C(9)−C(2)	119.6(3)
N(4)−Cd(1)−S(2)	104.39(8)	N(5)$^{\#1}$−C(16)−N(6)	117.3(4)
N(3)−Cd(1)−S(2)	121.81(8)	N(5)$^{\#1}$−C(16)−S(2)	127.0(3)
S(1)−Cd(1)−S(2)	109.67(4)	N(6)−C(16)−S(2)	115.5(3)
S(2)$^{\#1}$−Cd(1)−S(2)	89.74(3)	C(1)−N(2)−N(3)	112.7(3)
C(1)−S(1)−Cd(1)	96.93(11)	C(2)−N(3)−N(2)	120.0(3)
C(16)−S(2)−Cd(1)$^{\#1}$	93.80(11)	C(2)−N(3)−Cd(1)	118.1(2)
C(16)−S(2)−Cd(1)	103.23(13)	N(2)−N(3)−Cd(1)	121.2(2)
Cd(1)$^{\#1}$−S(2)−Cd(1)	87.18(3)	C(9)−N(4)−N(5)	118.7(3)
N(2)−C(1)−N(1)	116.1(4)	C(9)−N(4)−Cd(1)	118.5(2)
N(2)−C(1)−S(1)	129.1(3)	N(5)−N(4)−Cd(1)	122.0(2)
N(1)−C(1)−S(1)	114.8(3)	C(16)$^{\#1}$−N(5)−N(4)	114.5(3)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x$, y, $-z + 1/2$.

angles are similar to those found in related complexes and do not deserve further comments.

The structure of $[ZnLH_4]_\infty$ is made up of $[ZnLH_4]$ units, which are connected by a NH_2 group acting as bridge between two units, leading infinite 1D chains running along the *b* direction (Figure 4).

Orange crystals of **2** were obtained in a dimethylformamide/chloroform solution. Discrete $[CdLH_4]$ entities form the crystal structure of the complex, linked through one sulfur atom of each thiosemicarbazonate ligand, which leads to the dinuclear centrosymmetric $[CdLH_4]_2$ species, with two crystallization molecules of DMF. The molecular structure of $[CdLH_4]_2{\cdot}2DMF$ is shown in Figure 5. Selected interatomic dimensions are given in Table 5. The cadmium(II) ions are five-coordinate with four positions occupied by two imine nitrogen and two sulfur atoms from the thiosemicarbazonate ligand and the five position occupied by the sulfur atom of the adjacent $[CdLH_4]$ entity. The distortion of the coordination polyhedron from square-pyramidal ($\tau = 0$) and trigonal-bipyramidal ($\tau = 1$) topologies has been analyzed.[47] The τ value obtained was 0.06, which clearly indicates that the environment of the cadmium(II) ion is close to a square-pyramidal geometry. The two cadmium atoms are separated by 3.613 Å, and the bridging sulfur atoms, by 3.703 Å. The mean deviation of N(3), N(4), S(1), and S(2) from the least-squares plane through the four is 0.061 Å for N(3) and N(4), and the cadmium atom lies 0.619 Å above this plane. The thiosemicarbazone backbone is pseudoplanar, with a maximum deviation of 0.191 Å for S(2A), the bridging sulfur. Bond distances and angles are compatible with electronic delocalization. Within $[CdLH_4]$, bond distances of both thiosemicarbazonate branches are quite similar (and similar to complex **1**), except those of C−S bonds, where the distance corresponding to the bridging sulfur is larger [1.788(4) Å] and closer to the value expected for a C−S single bond (1.82 Å), as could be expected. The Cd−N bond distances are similar [2.308(3) and 2.329(3) Å], but Cd−S distances involving the bridging sulfur [2.6337(9) and 2.6129(9) Å] are larger than the remaining Cd−S distance [2.4972(9) Å]. The Cd−N bond distances are shorter than in the complex $[Cd(NO_3)_2LH_6]$,[32] and there is one Cd−S bond distance shorter and one larger (with the bridging sulfur), as expected for the behavior of the ligand. The coordination mode of the ligand affords six five-member and one four-member chelate rings. There is an extended network of intermolecular hydrogen bonds with the DMF molecules and between the dinuclear units (Figure 6; Table 6).

Red crystals of **3** were obtained from a dimethylformamide solution. The crystal structure consists of two units of $[NiLH_4]$ and two dimethylformamide molecules, held together in the crystal packing by hydrogen bonds. A perspective view of $[NiLH_4]{\cdot}2DMF$ with the atom-labeling scheme is given in Figure 7, and selected bond angles and distances are given in Table 7. Crystallographic data of complex confirm the geometry predicted from spectroscopic data,[38] showing that the Ni(II) ion is tetracoordinate in a planar disposition. The coordination sphere of the nickel atom is formed by two sulfur and two imine nitrogen atoms as expected for this ligand. Bond distances Ni−L are in the range found for this kind of complex. Bond distances and angles are in accordance with electronic delocalization in the ligand. They are similar to those of complex **1**, although the C−S bond is slightly longer. The environment of the nickel ion is planar with a maximum deviation of 0.015 Å for N(1). Finally, the molecules are held together in the

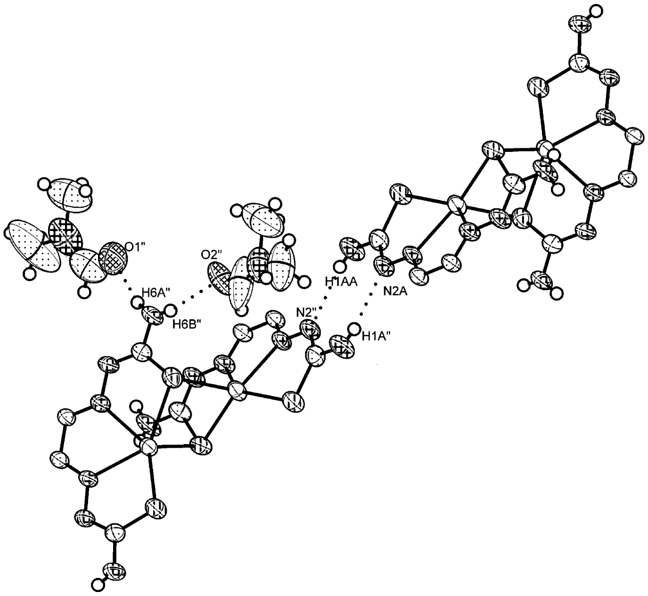

Figure 6. Plot of $[CdC_{16}H_{14}N_6S_2]_2 \cdot 2DMF$ including hydrogen bonds with the DMF molecules. Phenyl rings are omitted for clarity.

Table 6. Hydrogen bonds for $[CdC_{16}H_{14}N_6S_2]_2 \cdot 2DMF$ (Å, deg)[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(6)−H(6B)···O(2)	0.68	2.21	2.859	162
N(6)−H(6A)···O(1)	0.97	2.02	2.948	160
N(1)−(1A)···N(2)$^{\#2}$	0.74	2.39	3.125(5)	167

[a] Symmetry transformations used to generate equivalent atoms: (#2) $-x + 1/2, -y + 3/2, -z + 1$.

crystal packing through an extended network of intermolecular hydrogen bonds involving the amino groups, S(2) and N(5) atoms, and the oxygen atom from the DMF molecules (see Figure 8; Table 8).

Spectroscopy. The Experimental Section lists the main IR bands of the ligand and its complexes. In the complexes the number of bands corresponding to ν(N−H) vibrations have decreased due to deprotonation and the others appear at higher frequencies probably due to that the intermolecular hydrogen bonding has decreased. In the margin of the deformation modes of the primary amine groups, a different behavior is observed; the spectrum of nickel complex **3** shows two bands, and the spectrum of complex **1** presents double number of bands suggesting a different behavior for the two NH_2 groups. The ν(C═N) band are shifted to higher frequencies in all complexes, a clear sign of coordination via the azomethine nitrogen atom.

The values of the chemical shifts of the amine hydrogen atoms in the ^{1}H NMR spectrum of LH_6 depend on the donor character of the solvent. This fact is related to the grade of rupture of the intermolecular hydrogen bonds present in the solid state. ^{1}H NMR spectra of complexes **1** and **2** are very similar. In both of them the signal of hydrogen atoms of the secondary amine has disappeared and the signal corresponding to the terminal amine hydrogen atoms is shifted to high field, and it is inside the multiplet of the aromatic hydrogen atoms. In the spectrum of complex **3** the signal of the H(NH) has also disappeared, but a signal corresponding to the hydrogen of the terminal amine group is observed at higher field than in the free ligand. These facts agree with that, in all complexes, the ligand is dideprotonated.

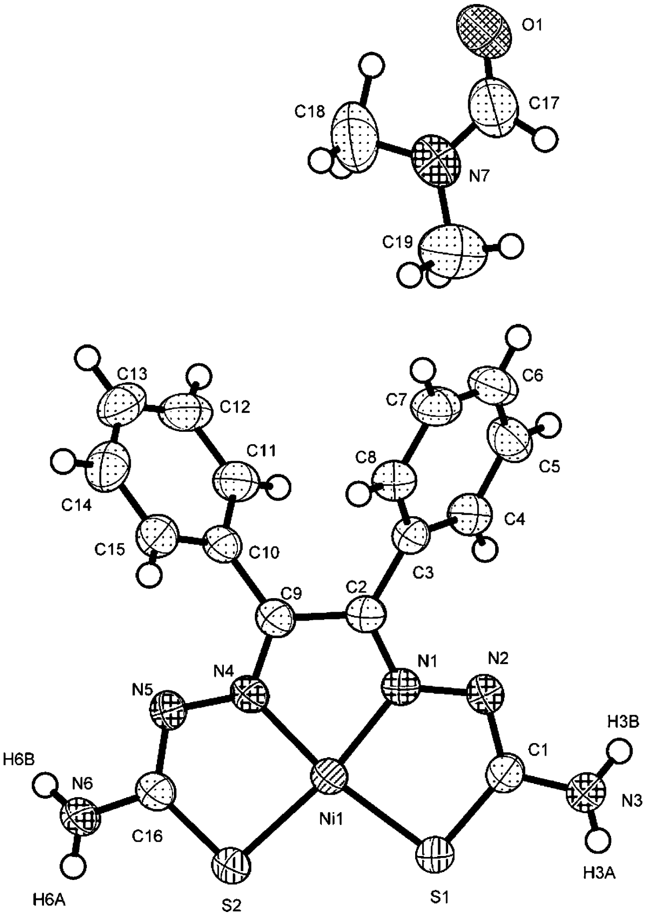

Figure 7. Molecular structure of $[NiC_{16}H_{14}N_6S_2] \cdot 2DMF$ with the atom labeling scheme. Thermal ellipsoids are shown at 40% probability.

Table 7. Selected Bond Distances (Å) and Angles (deg) for $[NiC_{16}H_{14}N_6S_2] \cdot 2DMF$

C(1)−N(3)	1.341(3)	C(16)−N(6)	1.330(3)
C(1)−N(2)	1.320(3)	C(16)−S(2)	1.745(3)
C(1)−S(1)	1.744(3)	N(1)−N(2)	1.371(3)
C(2)−N(1)	1.307(3)	N(1)−Ni(1)	1.862(2)
C(2)−C(3)	1.475(3)	N(4)−N(5)	1.372(3)
C(2)−C(9)	1.474(3)	N(4)−Ni(1)	1.861(2)
C(9)−N(4)	1.308(3)	Ni(1)−S(1)	2.1462(3)
C(10)−C(9)	1.474(3)	Ni(1)−S(2)	2.1572(3)
C(16)−N(5)	1.328(3)		
N(3)−C(1)−N(2)	117.9(2)	N(2)−N(1)−Ni(1)	123.88(16)
N(3)−C(1)−S(1)	117.3(2)	C(1)−N(2)−N(1)	109.4(2)
N(2)−C(1)−S(1)	124.81(19)	C(9)−N(4)−N(5)	120.5(2)
N(1)−C(2)−C(9)	113.1(2)	C(9)−N(4)−Ni(1)	116.08(17)
N(1)−C(2)−C(3)	124.1(2)	N(5)−N(4)−Ni(1)	123.42(16)
C(2)−C(9)−C(10)	123.2(2)	C(16)−N(5)−N(4)	110.0(2)
C(9)−C(2)−C(3)	122.7(2)	N(4)−Ni(1)−N(1)	83.31(9)
N(4)−C(9)−C(2)	111.9(2)	N(4)−Ni(1)−S(1)	170.68(6)
N(4)−C(9)−C(10)	125.0(2)	N(1)−Ni(1)−S(1)	87.39(7)
N(5)−C(16)−N(6)	117.3(2)	N(4)−Ni(1)−S(2)	87.62(6)
N(5)−C(16)−S(2)	124.48(19)	N(1)−Ni(1)−S(2)	170.87(7)
N(6)−C(16)−S(2)	118.3(2)	S(1)−Ni(1)−S(2)	101.68(3)
C(2)−N(1)−N(2)	120.7(2)	C(1)−S(1)−Ni(1)	94.26(9)
C(2)−N(1)−Ni(1)	115.43(17)	C(16)−S(2)−Ni(1)	94.08(8)

^{13}C NMR spectra of complexes **2** and **3** show four signals corresponding to phenyl carbon atoms. This fact indicates that complex **2** is symmetric in solution, so the sulfur bridge must be broken when the complex is dissolved in DMSO.

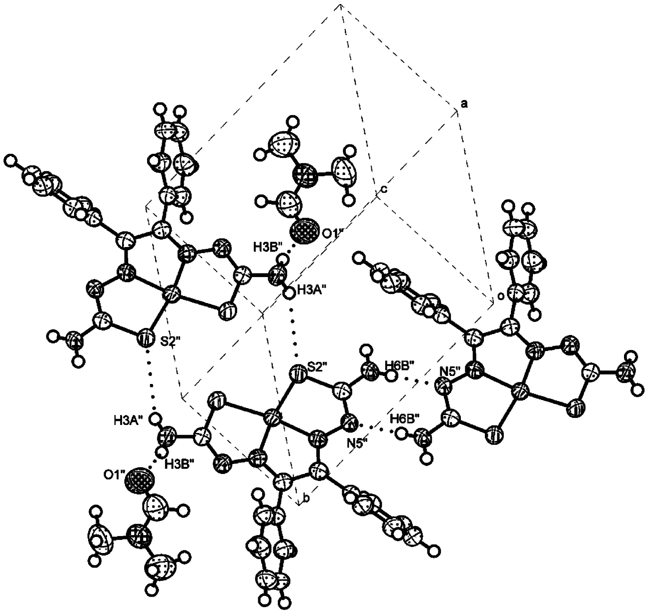

Figure 8. Plot of complex $[NiC_{16}H_{14}N_6S_2]\cdot 2DMF$ including the hydrogen bonds with the DMF molecules.

Table 8. Hydrogen bonds for $[NiC_{16}H_{14}N_6S_2]\cdot 2DMF$ (Å, deg)[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(6)−H(6B)···N(5)[#1]	0.84	2.17	3.000	172
N(3)−H(3B)···O(1)[#2]	0.87	2.01	2.867	167
N(3)−H(3A)···S(2)[#3]	0.79	3.03	3.735	150

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x - 1, -y, -z + 1$; (#2) $-x + 1, -y, -z + 1$; (#3) $-x, -y + 1, -z + 2$.

For complex **3** the number of signals agrees with the structure of the complex. In complex **1** the number of signals indicates asymmetry in the phenyl groups, induced by the nonsymmetric coordination mode of LH_4, as the crystal structure shows**.** From the signals attributed to the carbon bonded to the sulfur and the nitrogen atoms can be deduced that the imine and thio groups are bonded to the metal atom in all complexes.

The ^{113}Cd CP MAS NMR spectrum of complex **2** shows a signal at 267 ppm, which is broaden probably due to some heterogeneity in the solid state. This value is within the range expected for cadmium five-coordinate complexes.[49] The ^{113}Cd NMR of complex **2** in DMF at 213 K shows a signal at 229 ppm, which is in agreement with the value obtained in the solid state but more shielded, which could indicate the partial substitution of the atoms bonded to the cadmium by solvent molecules. Sulfur ligands are most strongly deshielding, while nitrogen and oxygen donor ligands have a weaker deshielding effect on the Cd(II) ion.[50] Moreover, increasing the coordination number tends to give more shielded values.[31] Taking into account both factors and for comparison with the complex $[Cd(NO_3)_2LH_6]$[32] and other compounds found in the literature, the value of the ^{113}Cd chemical shift in solution and in the solid state is in agreement with a N_2S_3 environment for cadmium ions.

Conclusions

We present the crystal structure of benzil bis(thiosemicarbazone), which confirms the structure previously proposed by us.[44] The structure shows a trans disposition of the thiosemicarbazone moieties, which changes to cis to form a N_2S_2 chelate in all complexes.

The results presented in this work are a good example to prove the importance of the working conditions and the coordination preferences for a metal ion in the structural characteristic of the complexes derived from a particular ligand. The presence of a basic medium decides the anionic behavior of benzil bis(thiosemicarbazone) in zinc and cadmium complexes, whereas in the case of nickel it is always the most favorable situation in all conditions. More important is the preference of the coordination number of the metal ion. The N_2S_2 planar disposition provided by LH_6 is adequate to the nickel ion yielding a planar structure for this complex. However, it forces the zinc and cadmium complexes (both show the same spectroscopic characteristics and are usually isostructural) to adopt an alternative structure, in the zinc one a monodimensional chain through a NH_2 group in a polymeric structure, observed for the first time in a bisthiosemicarbazone ligand, and a dinuclear complex with bridging sulfur atoms for the cadmium derivative, both with pentacoordinate geometry. To explain this different behavior, one should note that since cadmium(II) is a soft ion, it prefers to bond to sulfur instead of to nitrogen atoms, so the polymeric structure formed in complex **1** through an amine nitrogen atom is less favorable, and bonding to sulfur is preferred. It must be borne in mind that the two complexes are not strictly comparable: the Cd(II) derivative is a DMF solvate in which the solvent molecules interact with the NH_2 group, which must make the coordination of this group more difficult, so the formation of the polymeric structure should be less favorable than the dimeric one. The combination of both factors, geometry and softness of the metal ion, would permit one to design selective routes to get novel architectures.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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