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Article

Versatile Coordinative Abilities of a New Hybrid Pteridine–Thiosemicarbazone Ligand: Crystal Structure, Spectroscopic Characterization, and Luminescent Properties

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The synthesis and characterization of the first thiosemicarbazone–lumazine (TSCLMH = the thiosemicarbazone of 6-acetyl-1,3,7-trimethyllumazine) hybrid ligand is reported. The influence of the conformation of this compound on its energy and the atomic contribution to the molecular orbitals have been theoretically investigated. Ni(II), Cu(I), Zn(II), and Cd(II) complexes of this ligand have been synthesized and characterized by elemental analysis, thermogravimetric studies, IR, ^{1}H, ^{13}C, and ^{15}N NMR, and UV–vis–NIR spectroscopy, magnetic measurements, and X-ray crystallography. Four types of coordination modes for the ligand may be predicted: (a) double bidentate; (b) tetradentate; (c) tridentate; (d) bidentate. Structures of representative complexes of types a, b, and d have been determined by X-ray crystallography. In the $[Cu(TSCLMH)]_2(ClO_4)_2$ complex, TSCLMH acts as a doubly bidentate bridging ligand forming a dimer with a Cu···Cu distance of 2.876 Å. The geometry around the metal ion is trigonally distorted tetrahedral with a relatively long (four-atom) bridge between the metal centers instead of the shorter, mainly single atom, bridges present in other thiosemicarbazone derivatives complexes. In the $[Cd(NO_3)_2(TSCLMH)(EtOH)]$ complex, the metal ion displays eight-coordinated geometry with the TSCLMH ligand acting in a tetradentate planar fashion and two nitrate anions, one monodentate and the other bidentate. The coordination polyhedron in $[Cd(TSCLM)_2(H_2O)]\cdot MeOH\cdot 2H_2O$ is a square pyramid with two monoanionic ligands acting as bidentate NS donors and a water molecule completing the coordination sphere. Fluorescence spectroscopic properties of TSCLMH have been studied as well as the changes in position and intensity of fluorescence bands caused by the complexation with different metal ions (Ni^{2+}, Cu^{+}, Zn^{2+}, Cd^{2+}).

Introduction

The synthesis of ligands and relative complexes with architectures and properties analogous to natural systems or anticancer agents is one of the most fruitful areas of coordination chemistry in the context of designing systems for drug discovery and/or explaining the biosynthesis, metabolism, and activity of these molecules. It has been stated that pteridine and thiosemicarbazone derivatives are biochemically important molecules that have attracted continuous scientific interest due to their wide range of biological and pharmacological properties, which confer numerous applications.[1] The design of a hybrid ligand containing both moieties could increase the coordination capability and the versatility of these ligands.

Substantial effort has been devoted to synthesize model complexes that would permit the reliable simulation of experimental enzyme behaviors to better understand their

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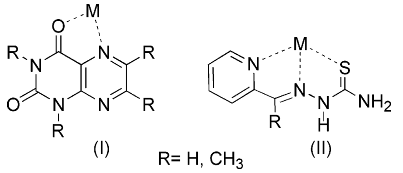
Chart 1



function. There are several enzymes involved either in folate biosynthesis or in pteridine metabolism that conceivably might be therapeutic targets.[2] In general, the role developed by these heterocycles is directly related with the establishment of coordinative bonds to biologically essential metal ions in some metalloenzymes.[3] Lumazine (2,4-(1*H*,3*H*)-pteridinedione) is a naturally occurring pteridine derivative known as a substrate in the oxidative hydroxylation reaction catalyzed by xanthine oxidase resulting in the product violapterin (2,4,7-(1*H*,3*H*,8*H*)-pteridinetrione).[4] A large number of complexes of different metals with the methylated lumazine derivatives (Chart 1) ligands have been studied, and the biological activity of some of them has been explored.[1] The structures and spectral properties of several metal complexes of lumazine derivatives, which usually coordinate to the metal ions in a bidentate pattern with N(5) and O(4) atoms (Chart 1), have been already studied by our group.[5]

Thiosemicarbazones (Chart 1.II) and their metal complexes are well-known by their anticarcinogenic, antibacterial, and antifungal properties.[6] In the past, it has been shown that the metal derivatives are more effective than the free ligands in anticancer activity.[7] One of the many reasons is that the binding affinity of metals to proteins or enzymes will change the interaction process of them with DNA, thereby affecting the DNA replication and cell proliferation.[8] This observation further encouraged the synthesis and characterization of a vast number of transition-metal and main-group metal complexes containing these ligands and their derivatives.[9]

In this context, hybrid chelate ligands containing mixed functionalities are widely used in both organic chemistry and in coordination chemistry as ligands for the isolation of interesting and important metal complexes.[10] In particular, thiosemicarbazone usually coordinates metal ions through the imine nitrogen and the sulfur atom in a bidentate mode[11] and can increase the coordination mode to tridentate with additional donor groups as heterocyclic substituents at the N(4) atom of the thiosemicarbazone.[12] The most popular donor set involves ONS or NNS atoms (Chart 1) displaying versatile coordination behavior like monomers, with one or two ligands attached to the metal ion, or dimmers, in which the metal centers can be bridged through either the thiolate sulfur or the non-thiosemicarbazone coligand (i.e., Cl^-, N_3^-, NCS^-, CH_3COO^-, etc.).[13] Biological studies have shown the type of substitution in the terminal N(4) atom influences crucially the antifungal effects, and an enhancement of the biological activity of the complexes has been also observed.[14]

In this context, we have designed of a new hybrid ligand in which a 6-acetyl-1,3,7-trimetillumazine was introduced into the backbone of thiosemicarbazone or vice versa, to further investigate the chemistry of thiosemicarbazones and lumazine derivatives and their potential usefulness as therapeutic agents. Moreover, the interest in the 6-substituted lumazine derivatives compounds has been increased since new coordination position pathways and new chemical and biological properties are provided while keeping the similarity to natural pterines.

In addition to the synthesis of the new hybrid ligand TSCLMH (thiosemicarbazone of 6-acetyl-1,3,7-trimethyl-

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lumazine), we report its characterization by spectral and structural properties and theoretical studies. Its binding ability toward nickel, copper, zinc, and cadmium ions was evaluated by elemental analysis, thermogravimetric studies, IR, ^{1}H, ^{13}C, and ^{15}N NMR, and UV−vis−NIR spectroscopy, and magnetic measurements. Structural XRD characterization of [Cu(TSCLMH)]$_2$(ClO$_4$)$_2$, [Cd(NO$_3$)$_2$(TSCLMH)(EtOH)], and [Cd(TSCLM)$_2$(H$_2$O)](MeOH)·2H$_2$O displays different coordination modes for neutral or anionic TSCLMH and provides bond length and angle distributions which reflect the steric demands and the degree of coordinative flexibility of this new ligand. Also, a preliminary study of the luminescence properties of the ligand and complexes has been carried out.

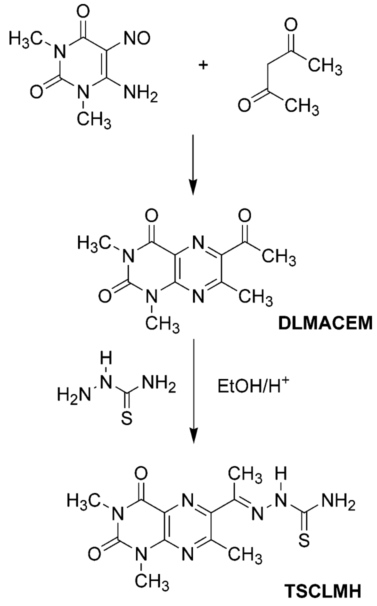
Experimental Section

Materials and Instrumentation. All starting materials were purchased from standard commercial sources and used without further purification. Solvents were reagent-grade commercial materials and were used as received. Nickel, cadmium, and zinc for the electrochemical synthesis were purchased from Aldrich and Alfa-Aesar and used as 0.5 mm thick sheets. Metals were cleaned of oxide in dilute hydrochloric acid prior to electrolysis. Elemental analyses were performed on a Fison Carlo Erba EA 1108 CHNS-O microanalyzer. The mass spectrum of the ligand was recorded on a Hewlett-Packard HT5989B spectrometer (electron ionization, 70 eV). IR spectra were measured over the range 4000−400 cm^{-1} on a Perkin-Elmer FT-IR 1760-X spectrometer with samples prepared as KBr pellets. Thermogravimetric measurements and the differential scanning calorimetry were done on Mettler Toledo TGA/SDTA851 and DSC822 equipment, respectively. ^{13}C, ^{1}H, and ^{15}N NMR spectra were recorded in DMSO-d_6 solutions on a Bruker DPX-300 spectrometer using TMS or nitromethane (^{1}H−^{15}N HMBC) as the internal standard. The UV−vis spectra were recorded between 1200 and 250 nm with solid samples on a Perkin-Elmer Lambda 19, while fluorescence excitation and emission spectra were measured with a Cary Elipse fluorescence spectrophotometer in DMSO.

Synthesis. Synthesis of the Thiosemicarbazone of 6-Acetyl-1,3,7-trimethyllumazine (TSCLMH) (1). The proligand 6-acetyl-1,3,7-trimethyllumazine (DLMACEM) was prepared by standard Timmis reaction between 6-amino-5-nitrosopyrimidines and 1,3-dicarbonylic derivatives (Scheme 1) by the method described by Kim et al.[15]

The hybrid ligand thiosemicarbazone of 6-acetyl-1,3,7-trimethyllumazine (TSCLMH) (**1**) was obtained by reacting equimolar amounts of thiosemicarbazide (1.8 g, 20 mmol) with the lumazine derivative (DLMACEM) (5 g, 20 mmol) in ethanol (30 cm^3). Acetic acid was used as catalyst (ca. 1 cm^3). The mixture was refluxed for 8 h at 85 °C. The ligand was filtered off and isolated in high yield (75−80%). Anal. Calcd for $C_{12}H_{16}N_7SO_{2.5}$: C, 43.5; H, 4.8; N, 29.6; S, 9.6. Found: C, 43.1; H, 5.1; N, 29.3, S, 9.5. ^{1}H, ^{13}C, and ^{15}N NMR studies gave well-resolved resonances for all proton and carbon environments, while elemental analysis indicated that the compound was formed in good purity. The slow evaporation of the ethanolic solution allowed obtention of single crystals suitable for X-ray diffraction. Mass spectrum: *m*/*z* 321 (M$^+$, 28%); *m*/*z* 246 (M$^+$ − NH − CS − NH$_2$, 94%). Main IR peaks (KBr, cm^{-1}): 3430, 3146 (ν(N−H), m), 3244, 3212 (ν(N−H)$_{\text{hydrazonic}}$, m); 1720, 1685 (ν(C=O), vs), 1599 (ν(N=C−CH$_3$), w), 1553 (ν(C−N), m), 1458, 1287 (ν(C=C) + ν(C−N), m, w), 948 (ν(N−N), w), 847 (ν(C=S), w). ^{1}H NMR data (δ, ppm, DMSO-d_6): 10.46 (1H, s, N(62)H); 8.42−7.68 (2H, s, N(63)H$_2$), 3.54 (3H, s, N(1)Me), 3.32 (3H, s, N(3)Me), 2.83 (3H, s, C(7)Me), 2.40 (3H, s, C(61)Me). ^{13}C NMR data (δ, ppm, DMSO-d_6): 179.47 (s, C(63)), 159.12 (s, C(4)), 156.70 (s, C(7)), 150.33 (s, C(2)), 147.32 (s, C(6)), 145.59 (s, C(1A)), 144.79 (s, C(61)), 123.68 (s, C(4A)), 28.70 (s, C(1)), 28.17 (s, C(3)), 24.89 (s, C(71)), 14.83 (s, C(62)). ^{13}C NMR data (δ, ppm, solid): 173.97 (s, C(63)), 155.80 (s, C(7)), 154.56 (s, C(2)), 146.25 (s, C(6)), 141.74 (s, C(1A)), 138.56 (s, C(61)), 119.53 (s, C(4A)), 24.53 (s, C(3)), 10.08 (s, C(62)). ^{1}H−^{15}N HMBC data (δ, ppm, DMSO-d_6): 119.80 (N(1)), 153.97 (N(3)), 295.55 (N(61)), 319.96 (N(5) + N(8)). UV−vis [H$_2$O/DMSO, λ (nm) (log ϵ)]: 298 (4.0); 349 (3.9).

Scheme 1. Synthesis of TSCLMH



Caution! Perchlorate salts are potentially explosive and should only be used in small quantities and handled with the necessary precautions.

Synthesis of [Cu(TSCLMH)]$_2$(ClO$_4$)$_2$ (2). An ethanolic solution (10 cm^3) containing 160 mg (0.5 mmol) of the ligand was dropped into a solution (10 cm^3) of Cu(ClO$_4$)$_2$·6H$_2$O (185 mg, 0.5 mmol) in EtOH at room temperature. Brown crystals were formed after several days in a closed container with the solution. They were filtered off, washed with ethanol, and air-dried. Yield: 35−40%. Anal. Calcd for $C_{12}H_{15}N_7O_6SClCu$: C, 29.7; H, 3.1; N, 20.2; S, 6.6. Found: C, 29.5; H, 3.1; N, 19.9; S, 6.4. Main IR peaks (KBr, cm^{-1}): 3407, 3110, 3319, and 3203 (ν(N−H)), 1716, 1665 (ν(C=O)), 1600 (thioamide I), 952 (ν(N−N)), 802 (thioamide IV), and 1176, 1108, 1045, 626 (perchlorate vibrations). ^{1}H NMR data (δ, DMSO-d_6; Me$_4$Si): 2.49 (3H, s, C(61)−Me), 2.68 (3H, s, C(7)-Me), 3.33 (3H, s, N(3)Me), 3.58 (3H, s, N(1)Me), 7.41, 8.91 (2H, s, N(63)H), and 10.46 (H, s, N(62)H). ^{13}C NMR data (δ, ppm, DMSO-d_6): 179.32 (s, C(63)), 159.28 (s, C(4)), 156.73 (s, C(7)), 153.22 (s, C(2)), 146.65 (s, C(6)), 145.51 (s, C(1A)), 123.83 (s, C(4A)), 29.04 (s, C(1)), 28.68 (s, C(3)), 23.05 (s, C(71)), 18.25 (s, C(62)).

Synthesis of [Cd(NO$_3$)$_2$(TSCLMH)(EtOH)] (3). To a refluxing suspension of TSCLMH (160 mg, 0.5 mmol) in ethanol (20 cm^3) was added a solution of cadmium(II) nitrate tetrahydrate (0.5 mmol, 154 mg) in ethanol (10 cm^3). The resulting yellow solution was stirred for 15 min and cooled to room temperature. The resulting

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Table 1. Crystal and Structure Refinement Data

param	TSCLMH·1/2H$_2$O	[Cu(TSCLMH)]$_2$(ClO$_4$)$_2$	[Cd(NO$_3$)$_2$(TSCLMH)(EtOH)]
empirical formula	$C_{12}H_{16}N_7O_{2.5}S$	$Cu_2C_{24}H_{30}Cl_2N_{14}O_{12}S_2$	$CdC_{14}H_{21}N_9O_9S$
fw	330.38	484.35	603.83
T (K)	293(2)	293(2)	290(3)
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/c$
a (Å)	19.372(3)	23.754(4)	12.8903(6)
b (Å)	9.6280(5)	12.5640(2)	13.1999(7)
c (Å)	18.364(3)	14.043(2)	14.7455(7)
β (deg)	120.127(8)	116.657(1)	117.673(1)
V (Å^3)	2962.5(8)	3745.5(9)	2222.0(2)
Z	8	8	4
D_x (Mg/m^3)	1.481	1.718	1.805
μ (mm^{-1})	0.243	1.467	1.144
F(000)	1384	1968	1216
cryst size (mm)	0.55 × 0.50 × 0.42	0.30 × 0.20 × 0.10	0.35 × 0.30 × 0.20
reflcns collcd (R$_{int}$)	17 103 (0.0368)	13 528 (0.0766)	25 308 (0.0313)
goodness-of-fit on F^2	1.053	1.022	0.997
R1/wR2 ($I > 2\sigma(I)$)	0.0550/0.1527	0.0683/0.1736	0.0485/0.1437

solid was filtered off and washed with ethanol and ether. After several days, yellow crystals suitable for X-ray diffraction were obtained from the mother liquor. Analytical and spectral data indicate both solid and crystals are the same material. Yield: 80%. Anal. Calcd for $C_{14}H_{21}N_9O_9SCd$: C, 26.6; H, 3.5; N, 21.4; S, 5.3. Found: C, 27.0; H, 3.4; N, 21.3; S, 5.1. Main IR peaks (KBr, cm^{-1}): 3415, 3300, 3187 (ν(N−H)), 1713, 1657 (ν(C═O)), 1609 (thioamide I), 952 (ν(N−N)), 753 (thioamide IV), and 1385 (nitrate vibration). ^{1}H NMR data (δ, DMSO-d_6; Me$_4$Si): 2.41 (3H, s, C(61)-Me), 2.83 (3H, s, C(7)Me), 3.32 (3H, s, N(3)Me), 3.54 (3H, s, N(1)-Me), 7.76, 8.47 (2H, s, N(63)H), and 10.51 (H, s, N(62)H). ^{13}C NMR data (δ, ppm, DMSO-d_6): 179.02 (s, C(63)), 159.47 (s, C(4)), 156.07 (s, C(7)), 150.52 (s, C(2)), 147.86 (s, C(6)), 145.86 (s, C(1A)), 28.97 (s, C(1)), 28.45 (s, C(3)), 25.14 (s, C(71)), 15.34 (s, C(62)). ^{1}H−^{15}N HMBC data (δ, ppm, DMSO-d_6): 122 (N(1)), 155 (N(3)), 295 (N(61)), 379 (N(5) + N(8)).

Synthesis of Ni(TSCLM)$_2$·2H$_2$O (4), Zn(TSCLM)$_2$·5H$_2$O (5), and Cd(TSCLM)$_2$·MeOH·3H$_2$O (6). The compounds were obtained using an electrochemical procedure.[16] A solution of the ligand (30 cm^3), containing about 10 mg of tetraethylammonium perchlorate as supporting electrolyte, was electrolyzed using a platinum wire as the cathode and a metal foil as the anode. The cell can be summarized as Pt(−)|HL + MeCN|M(+), where M = Ni, Zn, and Cd. The synthesis is typified by the preparation of M(L$^-$)$_2$(H$_2$O)$_n$. The insoluble products obtained were washed with acetonitrile and diethyl ether to remove any excess ligand and vacuum-dried.

Synthesis of Ni(TSCLM)$_2$·2H$_2$O (4). A solution (0.33 g, 1 mmol) of the ligand in acetonitrile (30 cm^3), containing 10 mg of tetraethylammonium perchlorate, was electrolyzed for 90 min using a current of 10 mA: brown solid; yield 70%. Anal. Calcd for $C_{24}H_{34}N_{14}O_7S_2Ni$: C, 38.3; H, 4.5; N, 26.1; S, 8.5. Found: C, 38.7; H, 4.3; N, 26.4; S, 8.4. Main IR peaks (KBr, cm^{-1}): 3431, 3328, 3156 (ν(N−H)), 1720, 1668 (ν(C═O)), 1629 (thioamide I), 960 (ν(N−N)), 809 (thioamide IV). ^{1}H NMR data (δ, DMSO-d_6; Me$_4$Si): 2.40 (3H, s, C(61)Me), 2.83 (3H, s, C(7)Me), 3.32 (3H, s, N(3)Me), 3.55 (3H, s, N(1)Me), 8.45, 7.70 (2H, s, N(63)H). ^{13}C NMR data (δ, ppm, DMSO-d_6): 179.35 (s, C(63)), 159.45 (s, C(4)), 156.98 (s, C(7)), 150.59 (s, C(2)), 147.32 (s, C(6)), 145.81 (s, C(1A)), 144.98 (s, C(61)), 123.94 (s, C(4A)), 28.96 (s, C(1)), 28.44 (s, C(3)), 25.17 (s, C(71)), 15.23 (s, C(62)). ^{13}C NMR data (δ, ppm, solid): 181.12 (s, C(63)), 162.09 (s, C(4)), 152.46 (s, C(2)), 149.12 (s, C(6)), 126.20 (s, C(4A)), 30.67 (s, C(1)), 23.13 (s, C(3)), 20.88 (s, C(71)), 15.75 (s, C(62)). ^{1}H−^{15}N HMBC data (δ, ppm, DMSO-d_6): 120 (N(1)), 155 (N(3)), 295 (N(61)), 322 (N(5) + N(8)).

Synthesis of Zn(TSCLM)$_2$·5H$_2$O (5). This complex was prepared by following the same procedure as described above: yellow solid; yield 55%. Anal. Calcd for $C_{24}H_{38}N_{14}O_9S_2Zn$: C, 36.2; H, 4.8; N, 24.6; S, 8.0. Found: C, 36.3; H, 4.6; N, 24.3; S, 7.6. Main IR peaks (KBr, cm^{-1}): 3443, 3328, 3198 (ν(N−H)), 1720, 1666 (ν(C═O)), 1620 (thioamide I), 964 (ν(N−N)), 808 (thioamide IV). ^{1}H NMR data (δ, DMSO-d_6; Me$_4$Si): 2.09 (3H, s, C(61)Me), 2.50 (3H, s, C(7)Me), 3.30 (3H, s, N(3)Me), 3.60 (3H, s, N(1)-Me). ^{13}C NMR data (δ, ppm, solid): 172.65 (s, C(63)), 168.67 (s, C(4)), 156.65 (s,C(7)), 153.08 (s, C(2)), 147.80 (s, C(6)), 145.00 (s, C(1A)), 142.98 (s, C(61)), 122.79 (s, C(4A)), 28.65 (s, C(1)), 26.40 (s, C(3)), 18.08 (s, C(71)), 15.40 (s, C(62)). ^{1}H−^{15}N HMBC data (δ, ppm, DMSO-d_6): 126 (N(1)), 153 (N(3)), 295 (N(61)), 317 (N(5) + N(8)).

Synthesis of [Cd(TSCLM)$_2$(H$_2$O)](MeOH)·2H$_2$O (6). This complex was prepared by following the same procedure as described above. A powdery product was readily isolated from the electrolysis solution by filtration. The solid was recrystallized in DMSO, and after several weeks we obtained a few orange crystals suitable for X-ray diffraction with low quality but enough to study the complex geometry. Orange solid, yield 65%. Anal. Calcd for $C_{25}H_{38}N_{14}O_8S_2$-Cd: C, 35.7; H, 4.8; N, 23.3; S, 7.6. Found: C, 35.6; H, 4.6; N, 23.3; S, 7.9. Main IR peaks (KBr, cm^{-1}): 3444 (ν(N−H)), 1718, 1667 (ν(C═O)), 1129 (ν(N−N)), 750 (thioamide IV). ^{1}H NMR data (δ, DMSO-d_6; Me$_4$Si): 2.49 (3H, s C(61)Me), 2.82 (3H, s C(7)Me), 3.31 (3H, s N(3)Me), 3.52 (3H, s N(1)Me). ^{13}C NMR data (δ, ppm, DMSO-d_6): 159.55 (s, C(4)), 156.72 (s, C(7)), 150.55 (s, C(2)), 146.45 (s, C(1A)), 144.95 (s, C(61)), 123.95 (s, C(4A)), 28.85 (s, C(1)), 28.28 (s, C(3)), 25.91 (s, C(71)), 15.24 (s, C(62)). ^{1}H−^{15}N HMBC data (δ, ppm, DMSO-d_6): 126 (N(1)), 164 (N(3)), 241 (N(61)).

Crystallography. Details of the crystallographic data collection and refinement parameters are given in Table 1. The data were collected on a Nonius Kappa CCD diffractometer (graphite-monochromated Mo Kα radiation, ψ-scan technique, λ = 0.710 73 Å) at room temperature. An empirical absorption correction

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(SADABS[17]) was applied. The structures were solved by SIR-04, expanded by Fourier-difference syntheses, and refined with SHELXL-97 and incorporated in the WinGX 1.64 crystallographic collective package.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures on F^2. Hydrogen atoms from methyl groups were placed in idealized positions and treated using riding models; N−H hydrogens were found from difference map and refined isotropically. Graphics were obtained with PLATON.[19]

Special Features of Refinement. For compound $[Cu(TSCLMH)]_2(ClO_4)_2$ (**2**), the perchlorate ions are disordered over two positions with a relative occupancy of 0.5. In the complex $[Cd(TSCLM)_2(H_2O)]\cdot MeOH\cdot 2H_2O$ **(6)**, the poor data quality has limited the accuracy of the refinement. Two crystals were used to try improve the accuracy of the results, but both sets of data were equally poor. However, H atoms were placed in calculated positions "riding" on their C or N atoms. After anisotropic refinement, some unassigned electron density peaks were observed in the final difference Fourier map the highest being 7.54 e Å^3 at 1.324 Å from cadmium atom and the solvent molecules are disordered. CCDC 653993−653995 and 663028 contain supplementary crystallographic data for the structures described in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. Theoretical calculations were carried out on thiosemicarbazone of 6-acetyl-1,3,7-trimethyllumazine (TSCLMH) by using ab initio methods with GAUSSIAN03 program package.[20] In a first step, the calculation consisted on the optimization of the geometries of these species in the isolated approach to test the reliability of the procedure on comparing the theoretical results with XRD ones. Geometry optimizations were accomplished with the DFT-B3LYP approach using the 6-31G* basis set, as implemented in the GAUSSIAN03 suite. This program was run until the default convergence criteria were satisfied. For these calculations, the XRD structure were used as starting point and the corresponding vibrational frequencies for the ab initio optimized geometries were calculated to check they are true potential energy minima and not saddle points. The residual charges of the atoms were obtained by Mulliken's population analysis, as well as the contributions of atomic orbitals of each atom to the border molecular orbitals from LUMO to HOMO-8.

Results and Discussion

Ligand Synthesis. The new hybrid ligand TSCLMH was synthesized in two steps starting with the synthesis of the lumazine derivative using a known procedure (Scheme 1). So, the reaction of 6-amino-1,3-dimethyl-5-nitrosouracil in 2,4-pentanedione gave the proligand 6-acetyl-1,3,7-trimethyllumazine (DLMACEM)[15] in 75%. The available acetyl group allows for a classic condensation to isolate new multifunctional ligands containing the azomethinic C═N bond. DLMACEM was condensed with thiosemicarbazide in refluxing absolute ethanol for 8 h with addition of a small quantity of acetic acid as an acid catalyst on an oil bath at 85 °C. The yield of the reaction was ca. 80%. The TG and DSC studies of TSCLMH indicate a dehydration process in one step between 50 and 220 °C, the anhydrous compound being stable at temperatures up to 240 °C. In the DSC plot, a narrow endothermic peak appears at 275 °C assigned to the melting of the compound.

In the ^{1}H NMR spectrum of TSCLMH in DMSO-d_6 the amino group protons (N(63)H) appear as two signals at 7.68 and 8.42 ppm due to an intramolecular hydrogen bond. The ^{13}C NMR and the ^{1}H−^{13}C NMR spectra allow us to assign unequivocally all carbon signals. Only four signals were observed in the ^{1}H−^{15}N NMR spectrum, at 119, 154, 295, and 320 ppm. The first three have been assigned to N(1), N(3), and N(62) since they correlate with the hydrogen methyl groups C(1), C(3), and C(62), respectively, whereas the latter is explained by the overlapping of N(5) and N(8), which experiment a similar environment in the pteridine moiety.

The FT-IR spectrum shows bands of medium intensity in the 3400−3100 cm^{-1} range assignable to ν(N−H) of the amino and hydrazonic groups of the ligand. The characteristic bands of the lumazine derivative are two absorptions observed at 1720 and 1685 cm^{-1} assignable to the coupling of the ν(C═O) of both carbonyl groups, the band at 1553 cm^{-1} attributed to ν(C═N) of the pyrazine ring, and the two bands at 1450 and 1290 cm^{-1} assignable to ν(C═C) + ν(C−N) vibrations.[21] For the thiosemicarbazone moiety, thioamide bands I−IV are found at 1600, 1484, 1345, and 847 cm^{-1}. The sharp band at 1599 cm^{-1} was assigned to ν(C═N) of azomethine group, and the band at 948 cm^{-1} is assigned to ν(N−N) hydrazonic.[22] UV−vis experiments were performed at different pH values to obtain information about the ligand deprotonation. All the spectra are identical in the pH range studies showing two bands at 298 ($\log \epsilon = 3.99$) and 349 nm ($\log \epsilon = 3.90$) assignable to $\pi \rightarrow \pi^*$ transitions.[23]

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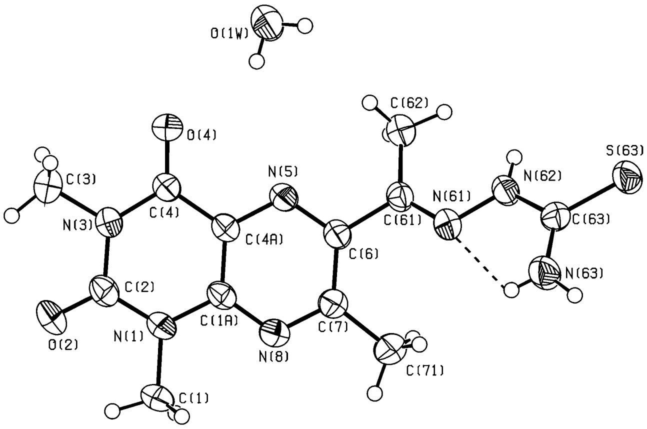


Figure 1. ORTEP plot of the TSCLMH ligand **1** showing the intramolecular H-bonding. Thermal ellipsoids are drawn at the 50% probability level.

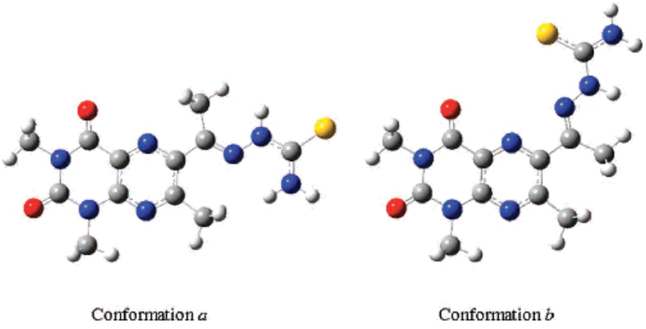
Table 2. Main Structural Parameters of **1** (Lengths in Å and Angles in deg)

S(63)−C(63)	1.673(3)	N(61)−C(61)	1.279(3)
O(2)−C(2)	1.210(3)	N(62)−N(61)	1.375(3)
O(4)−C(4)	1.222(3)	N(62)−C(63)	1.356(3)
C(6)−C(61)	1.489(3)	C(63)−N(63)	1.314(3)
C(61)−C(62)	1.487(4)		
C(6)−N(5)−C(4A)	117.8(2)	N(61)−C(61)−C(62)	126.2(2)
C(7)−C(6)−C(61)	124.7(2)	C(62)−C(61)−C(6)	118.1(2)
N(5)−C(6)−C(61)	114.1(2)	C(63)−N(62)−N(61)	119.1(2)
N(5)−C(6)−C(7)	121.2(2)	N(62)−C(63)−S(63)	120.3(2)
N(8)−C(7)−C(6)	120.2(2)	N(63)−C(63)−N(62)	117.4(3)
N(61)−C(61)−C(6)	115.6(2)	N(63)−C(63)−S(63)	122.3(2)
C(61)−N(61)−N(62)	117.7(2)		

For an unambiguous characterization of the ligand TSCLMH, its structure was also determined by X-ray crystallography. Figure 1 shows the molecule with the numbering scheme used. The main bond lengths and angles are listed in Table 2. The ligand crystallized as hemihydrate. The lumazine skeleton displays a roughly planar geometry like related ligands,[5,21] so the pyrimidine and pyrazine rings exhibit a dihedral angle of 1.6(1)°. The bond lengths of the carbonyl groups are slightly different (C(2)═O(2), 1.210(3) Å; C(4)═O(4), 1.222(3) Å)[5,21] whereas bond lengths at the thiosemicarbazone moiety indicate an extensive delocalization as usual on the thiosemicarbazone derivatives which is clearly reflected in the C−S distance at 1.673(3) Å intermediate between a single and double bond character (1.82 and 1.56 Å, respectively) and the N−N (1.375(3) Å) distance, less than the 1.44 Å accepted as typical of single bonds.[24] The chain exhibits an *EEE* isomeric conformation with C(61)−N(61), N(61)−N(62), and N(62)−C(63) bonds placed in trans disposition. This conformation favors the formation of an intramolecular hydrogen bond N(63)−H(632)···N(61) [*d*(N(63)···N(61)) = 2.630 Å, −(N(63)−H(632)···N(61)) = 110°].

In the TSCLMH crystal structure, the crystallization water and the N−H bonds are involved in hydrogen bonding. These lead to the formation of planes packed by van der Waals' interactions following the [10$\bar{1}$] direction.

Chart 2


Conformation *a*   Conformation *b*

Molecular Orbital Analysis of the Ligand. The ligand TSCLMH adopts two different conformations (Chart 2); that named "*a*" appears in the crystal structure of the free ligand whereas that named "*b*" is deployed in the structure of the complexes. In both modelized conformations, bond lengths and angles in the crystal structure of TSCLMH were reproduced with rms deviations of 0.002 Å and 1°, respectively. The conformation *a* is 106.5 kJ·mol^{-1} more stable than *b*, probably due to the establishment of the N(63)−H···N(61) intramolecular hydrogen bond in *a* and the steric hindrance between methyl groups attached at C(7) and C(61) atoms in *b*.

To analyze the symmetry of molecular orbitals, a σ character has been assigned when the contribution of orbitals with *z* component to the LCAO is less than 30%. The results indicate that in both conformations the most external occupied orbitals, HOMO and HOMO-1, are mainly localized over S(63) atom, whereas the O(4) and N(5) contribute to the HOMO-3−HOMO-5 orbitals. In the HOMO-7 for the conformation *b* and in the HOMO-8 for the conformation *a*, the main contribution is for the N(61) atom. So, the coordination capacity of the ligand via O(4), N(5), N(61), and S(63) is confirmed in both conformations although, in the complexes, the conformation *b* is most favorable probably due to the accumulate chelate effect.

Coordination Studies. Once TSCLMH was successfully prepared, we started to explore its coordination chemistry with particular emphasis on probing its possible ligating modes. Our initial efforts focused on whether it could behave as a mono-, bi-, tri-, or tetradentate ligand like other lumazine or thiosemicarbazone derivatives. Accordingly, when TSCLMH was reacted with $Cu(ClO_4)_2·6H_2O$ and $Cd(NO_3)_2·4H_2O$ in equimolar quantities, we isolated, as crystalline solids, the dinuclear brown $[Cu(TSCLMH)]_2(ClO_4)_2$ and the mononuclear yellow $[Cd(NO_3)_2(TSCLMH)(EtOH)]$ compounds, respectively. To study the coordination behavior of the deprotonated ligand, different classical synthetic procedures to obtain metalated species containing the monoanionic ligand (TSCLM$^-$) were carried out, all of them being unsuccessful probably due to the broad pH range of stability of neutral TSCLMH. Thus, direct electrochemical synthesis was attempted and we found that the anodic oxidation of nickel, zinc, and cadmium in the presence of TSCLMH is a route to isolate $M(L^-)_2·nH_2O$ complexes as $[Cd(TSCLM)_2(H_2O)]·MeOH·2H_2O$ (**6**).

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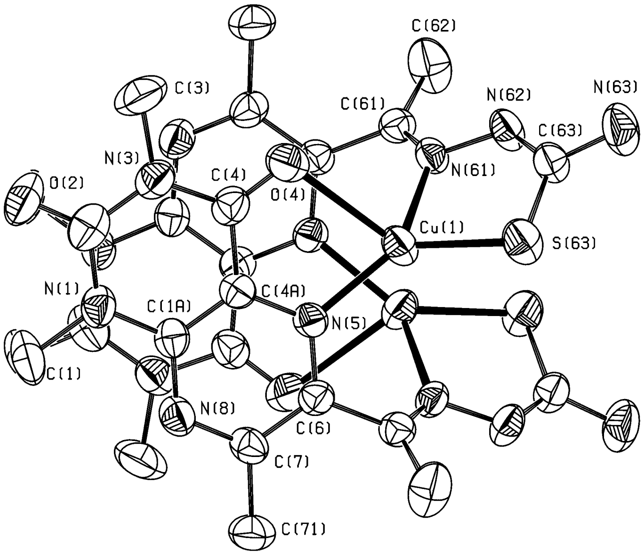

Figure 2. ORTEP drawing and relative disposition of the π interaction between the rings in the dimer cation $[Cu(TSCLMH)]_2^{2+}$ in complex **2** (ellipsoids at 50% probability; hydrogen atoms excluded for clarity).

Structure of $[Cu(TSCLMH)]_2(ClO_4)_2$ (2). A view of the dinuclear cation of this compound including the used numbering scheme is shown in Figure 2, and selected bond lengths and angles are listed in Table 3. The perchlorate anions are omitted for clarity. The dimeric units consist of two asymmetric $[Cu(TSCLMH)]^+$ portions related by a crystallographically imposed binary axis ($2 - x$, y, $1/2 - z$).

Previous structural studies on Cu(I) dinuclear complexes with heterocyclic thiosemicarbazone derivatives have found three different kinds of bridges between the metal atoms (Scheme 2) in $Cu(\mu\text{-}X)_2Cu$, where X is (a) halogen, (b) sulfur, or (c) non-thiosemicarbazone coligand bridged dimers like the propionate anion.[25] In complex **2**, each of the two TSCLMH ligands acts in doubly bidentate mode, forming one five-membered chelate ring with each of the metal atoms, through O(4) and N(5) atoms of the lumazine moiety for one of the Cu atoms and through N(61) and S(63) atoms of the thiosemicarbazone chain for the other. This coordination mode also implies a change the N−C bond conformation from the *E* configuration observed in the free ligand to *Z*. The geometries of Cu(I) complexes thiosemicarbazone derivatives present in the Cambridge Structural Database (CSD) have been analyzed. The observed stereochemistry of most four-coordinate copper(I) complexes is tetrahedral with distortions caused by the presence of chelating ligands or by the involvement of copper centers into dimeric or polymeric structures. There is no tendency to adopt a more planar configuration in the absence of large planar ligands, which are particularly subject to intermolecular interactions in the solid state. Some complexes exhibit a distortion toward a trigonal planar configuration, i.e., a C_{3v} [3 + 1] geometry.[26]

In our compound, the Cu(I) center has an very distorted tetrahedral to trigonal planar geometry, the M−N distances being similar to related compounds[27] (ca. 1.9−2.1 Å) while the Cu−S(63) bond is considerably shorter than that observed in the literature, longer than 2.27 Å.[25] The largest deviation from the ideal geometry is reflected by the S(63)−Cu−N(5) and O(4)−Cu−N(5) angles, whose values of 136.58 and 75.88°, respectively, are notably different from the tetrahedral value of 109.5°. The second angle corresponds to the bite angle of the rigid chelating lumazine moiety. The Cu−O(4) bond distance of 2.449 Å is much longer than the usual values in lumazine derivatives complexes,[5,21,37] which allows us to define the geometry as tetrahedral with considerable trigonal planar distortion ("3 + 1") with N(5), N(61), and S(63) in the basal plane and O(4) weakly coordinated in the apical position; in agreement with this, the sum of the angles S(63)−Cu−N(61), N(61)−Cu−N(5), and N(5)−Cu−S(63) (357.6°) is clearly closer to the expected value for a trigonal-planar configuration (360°) than the ideal value for a tetrahedron (328.5°). The Cu···Cu distance (2.876(2) Å) is almost equal to the sum of the van der Waals radius of copper (2.8 Å), indicating a minimum interaction between two copper atoms.[28]

It is usual that, upon complexation, the thiosemicarbazone moiety retains its planarity; however, in this complex the dihedral angle between it best plane and the lumazine plane is opened from the value of 40° in the free ligand to 56.1° in the complex. This change in the ligand geometry is caused by the breaking of the intramolecular hydrogen bond, which plays a key role in the ligand crystal arrangement, the most favorable disposition of the donor atoms to bind both copper ions, and mainly by the strong π interaction between the pyrimidine and pyrazine rings of the lumazine moiety.

In the solid state, the amino (N(63)) hydrogen atoms of thiosemicarbazone are involved in hydrogen bonds with the perchlorate ions and the O(2) atoms of the neighbor dimers, these being associated as tubular chains parallel to the *b*-axis. The π interactions also play an important role in the dimer structure, as shown in Figure 2 and Table 4, structural cohesion being achieved by π contacts between the Cu−O(4)−C(4)−C(4A)−N(5) (Cg(1)) chelate ring and the pyrazine ring (Cg(3)), both pyrimidine rings (Cg(2)), and the pyrimidine and pyrazine rings, respectively.[29]

Structure of $[Cd(NO_3)_2(TSCLMH)(EtOH)]$ (3). An ORTEP diagram of the molecular structure and the atom numbering system used is shown in Figure 3. The most relevant bond lengths and angles are given in Table 3. The structure of the complex **3** consists of discrete neutral monomeric units in which the cadmium atom is eight-coordinate with TSCLMH linked in a planar tetradentate

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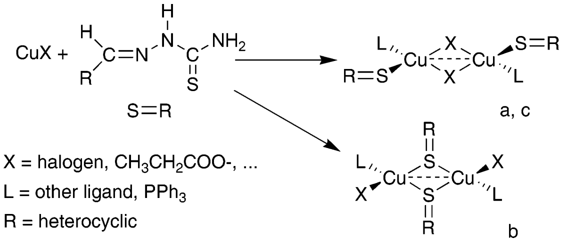
Table 3. Selected Bond Distances (Å) and Angles (deg) in the Complexes **2** and **3**

		[Cu(TSCLMH)]$_2$(ClO$_4$)$_2$ (**2**)			
Cu(1)−O(4)	2.449(5)	N(5)−Cu(1)−N(61)	134.1(2)		
Cu(1)−N(5)	1.978(5)	N(5)−Cu(1)−S(63)	136.6(1)		
Cu(1)−N(61)	2.099(5)	N(61)−Cu(1)−S(63)	86.9(1)		
Cu(1)−S(63)	2.215(2)	N(5)−Cu(1)−Cu(1)[a]	78.8(1)		
Cu(1)−Cu(1)[a]	2.8758(2)	N(61)−Cu(1)−Cu(1)[a]	71.6(1)		
		S(63)−Cu(1)−Cu(1)[a]	108.9(6)		
S(63)−C(63)	1.680(6)	C(63)−N(62)−N(61)	121.3(6)		
O(2)−C(2)	1.215(8)	C(61)−N(61)−N(62)	116.6(5)		
O(4)−C(4)	1.215(8)	N(61)−C(61)−C(62)	126.6(6)		
N(63)−C(63)	1.324(9)	N(61)−C(61)−C(6)[a]	114.5(5)		
N(62)−C(63)	1.331(8)	C(62)−C(61)−C(6)[a]	118.8(5)		
N(62)−N(61)	1.371(7)	N(63)−C(63)−N(62)	115.9(6)		
N(61)−C(61)	1.261(7)	N(63)−C(63)−S(63)	121.2(5)		
C(62)−C(61)	1.492(9)	N(62)−C(63)−S(63)	122.9(5)		
C(61)−C(6)[a]	1.495(8)	N(5)−C(6)−C(61)[a]	116.4(5)		
C(6)−C(61)[a]	1.494(8)	C(7)−C(6)−C(61)[a]	122.5(5)		
		[Cd(NO$_3$)$_2$(TSCLMH)(EtOH)] (**3**)			
Cd−S(63)	2.596(1)	S(63)−Cd−N(61)	71.53(7)	O(1E)−Cd−O(1N)	153.4(1)
Cd−O(1E)	2.314(4)	N(5)−Cd−N(61)	63.2(1)	O(1E)−Cd−O(4N)	72.4(1)
Cd−O(1N)	2.440(3)	O(4)−Cd−N(5)	67.9(1)	O(1E)−Cd−O(5N)	119.6(1)
Cd−O(4)	2.496(4)	O(4N)−Cd−O(5N)	47.7(1)	O(1E)−Cd−N(5)	77.1(1)
Cd−O(4N)	2.453(4)	S(63)−Cd−O(5N)	74.6(1)	O(1E)−Cd−N(61)	86.4(1)
Cd−O(5N)	2.691(5)	S(63)−Cd−N(5)	133.96(9)	O(1N)−Cd−O(4)	75.7(1)
Cd−N(5)	2.415(3)	S(63)−Cd−O(1E)	108.8(1)	O(1N)−Cd−O(4N)	114.1(1)
Cd−N(61)	2.547(4)	S(63)−Cd−O(1N)	97.7(1)	O(1N)−Cd−O(5N)	68.7(1)
		S(63)−Cd−O(4)	157.08(8)	O(1N)−Cd−N(5)	83.2(1)
		S(63)−Cd−O(4N)	82.2(1)	O(1N)−Cd−N(61)	100.6(1)
		O(4)−Cd−O(5N)	82.6(1)	O(4N)−Cd−N(5)	139.2(1)
		O(4)−Cd−O(4N)	80.6(1)	O(4N)−Cd−N(61)	138.9(1)
		O(4)−Cd−N(61)	131.0(1)	O(5N)−Cd−N(5)	143.5(1)
		O(1E)−Cd−O(4)	80.3(1)	O(5N)−Cd−N(61)	142.6(1)
S(63)−C(63)	1.683(5)	C(63)−N(62)−N(61)	120.1(4)		
O(2)−C(2)	1.218(6)	C(61)−N(61)−N(62)	117.1(4)		
O(4)−C(4)	1.214(5)	N(61)−C(61)−C(62)	123.5(4)		
N(63)−C(63)	1.329(6)	N(61)−C(61)−C(6)	113.0(4)		
N(62)−C(63)	1.350(5)	C(62)−C(61)−C(6)	123.2(4)		
N(62)−N(61)	1.368(5)	N(63)−C(63)−N(62)	114.5(4)		
N(61)−C(61)	1.284(5)	N(63)−C(63)−S(63)	120.6(3)		
C(62)−C(61)	1.494(7)	N(62)−C(63)−S(63)	124.9(4)		
C(61)−C(6)	1.488(6)	N(5)−C(6)−C(61)	115.4(3)		

[a] Symmetry transformation: $2 - x, y, 1/2 - z$.

Scheme 2



fashion, two nitrate ligands, one monodentate and the other bidentate, and one ethanol molecule. The bidentate nitrate group is asymmetrically coordinated [{Cd−O(4)}−{Cd−O(5)} = δ = 0.237 Å], as in other [Cd(NO$_3$)$_2$L$_2$] lumazine complexes, where the values of δ range from 0.108 Å (L = 1,3,6,7-tetramethyllumazine[30]) to 0.395 Å (L = 1,6,7-trimethyllumazine[31]).

The bite angles of the metallocycles, S(63)−M−N(61), N(61)−M−N(5), and N(5)−M−O(4), which depend on the electronic and steric hindrances of the ligand are lowered if compared with data found in bibliography for related compounds.[32] The greatest variation with respect to the usual value (68−85°) takes place in the N(61)−M−N(5) angle (63.2°); this can be due to the rough planarity of the

Table 4. Intermolecular π-Stacking Parameters for [Cu(TSCLMH)]$_2$(ClO$_4$)$_2$ (**2**)[a]

centroids	slippage (Å)	$d(c_1-c_2)$ (Å)	α (deg)	β (deg)	γ (deg)
Cg(1)−Cg(1)[b]	1.798	4.412(3)	0.03	24.06	24.06
Cg(2)−Cg(2)[c]	1.214	3.658(3)	7.54	19.39	19.39
Cg(3)−Cg(3)[c]	2.362	4.169(4)	9.12	39.14	39.14
Cg(1)−Cg(3)[c]	0.952	3.315(4)	12.93	10.10	21.35
Cg(2)−Cg(3)[c]	1.533	3.687(4)	8.33	27.97	20.69

[a] Terms: Cg(1) = centroid of quelate ring (Cu−O(4)−C(4A)−N(5)); Cg(2) = centroid of pyrimidine ring; Cg(3) = centroid of pyrazine ring; $d(c_1\text{-}c_2)$ = centroids of rings involved in π-interactions; α = angle between planes of both centroids; β and γ = slipping angles between the centroid−centroid vector and the normal to each stacked ring plane. [b] Equivalent position: $2 - x, -y, -z$. [c] Equivalent position: $2 - x, y, 1/2 - z$.

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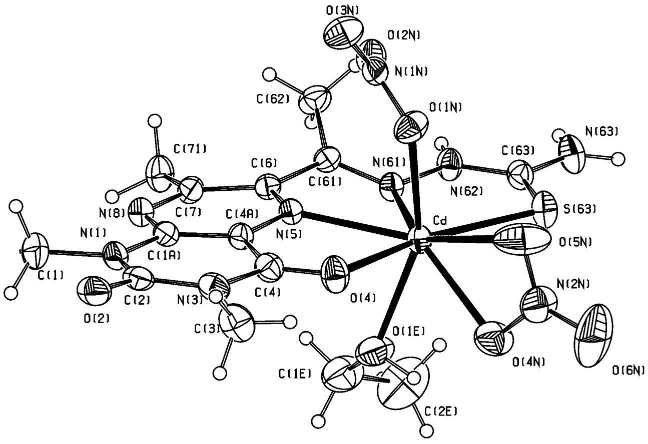

Figure 3. View of the complex **3**, with thermal ellipsoids drawn at the 30% probability level.

tetradentate ligand. In contrast, in the copper complex, the planarity of the ligand is lost as consequence the simultaneous binding ligand to two metallic ions in a doubly bidentate pattern.

In the cadmium complex (Figure 3), and following Kepert,[33] the presence of four vertices [N(5), N(61), O(4N), and O(5N)] which join four edges and another four vertices [S(63), N(5), N(61), S(63)] joined by five edges is indicative of a dodecahedron shape. An alternative useful way of viewing the different geometries has been explained by Drew[34] on the basis of the values of several angles calculated by using the "hard sphere model" (HSM) shape characteristics. The angles values calculated for complex **3**, compared with those for the ideal dodecahedron and square-antiprism, clearly indicate that the coordination polyhedron is best described as a distorted dodecahedron.

The pyrimidine and pyrazine rings of TSCLMH are almost coplanar with a dihedral angle of 4.8°, the thiosemicarbazone chain of the organic ligand exhibits a 19.9° angle between the $C-C(CH_3)=N$ and N−N−C(S)−N average planes, and the least-square planes of the lumazine moiety and the side chain define a dihedral angle of 5.5°. The chelate rings Cd−S(63)−C(63)−N(62)−N(61), Cd−N(61)−C(61)−C(6)−N(5), and Cd−N(5)−C(4A)−C(4)−O(4) are essentially planar and roughly coplanar with each other with angles ranging from 2.52 to 7.48° and are perpendicular to the chelate ring O(4N)−Cd−O(5N) (82−87°).

The monomers are associated by hydrogen bonds with the ethanolic (O1E−H1E), amino (H631−N(63)−H632), and imino (N(62)-H62) hydrogens as donors and the oxygen atoms of the lumazine (O(2)) and nitrate groups (O(1N), O(2N), and O(3N)) as acceptors. The intermolecular bonding leads to the formation of a tridimensional structure.

Structure of $[Cd(TSCLM)_2(H_2O)]\cdot MeOH\cdot 2H_2O$ (6). Unfortunately, we could not grow single crystals of this compound better than the one used for the present study; for this reason, the refinement did not reach a satisfactory level. X-ray crystallographic analyses show some degree of disorder in the solvent molecules, but the main moiety was unambiguously determinated (Figure 4).

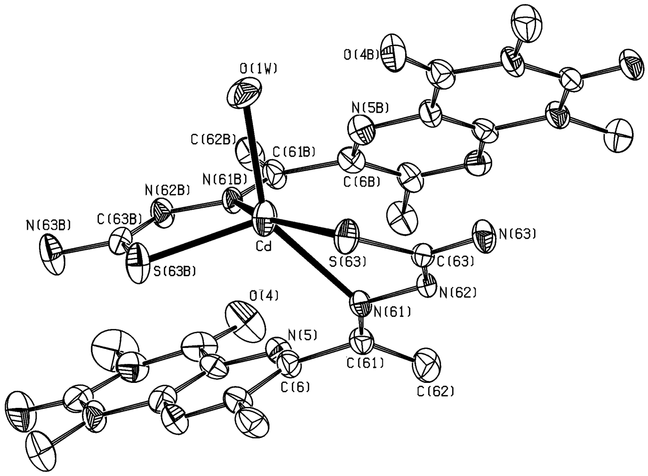

Figure 4. View of the molecular unit of $[Cd(TSCLM)_2(H_2O)]\cdot MeOH\cdot 2H_2O$ **(6)**, with thermal ellipsoids drawn at the 30% probability level. Uncoordinated solvent molecules are disordered and have been omitted for clarity.

The metal ion is surrounded by two TSCLMH ligands in a bidentate mode through the S(63) and N(63) atoms and the oxygen atom of a water molecule. The resulting geometry can be described as a distorted square pyramid [sp: τ^{35} index ca. 0.25] with S(63B) at the apex. Opposite to it, there is a distorted plane formed by the O(1W), S(63), N(61B), and N(61) atoms with the metal placed 0.6 Å above the plane. The two ligands exhibit different conformation, with one chelate ring N(61)−N(62)−C(63)−S(63)−Cd nearly planar and the other with an envelope conformation.

Unlike the above-described Cu(I) and Cd(II) complexes, the ligands are deprotonated, the loss of the protons originally bound to N(62) and N(62B) producing a negative charge delocalized toward S(63) and S(63B) atoms. The structural effects of deprotonation and coordination, if compared with free TSCLMH and the above-described complexes, clearly indicate the presence of a thiolato form.

The pyridine and pyrimidine rings of both lumazine moieties are almost perfectly planar, and the N(61)−N(62)−C(63)(S(63))−N(63) chain is planar too. However, like in the copper(I) dimer, the ligands do not display the planar conformation observed in the free TSCLMH and in the other Cd(II) complex, the lumazine heterocycle and the thiosemicarbazone chain being angled by ca. 45°.

As a concluding remark, crystallographic studies evidence the coordination versatility of the new hybrid ligand. This fact can be attributed to the nonrigidity of the thiosemicarbazone moiety with respect to the lumazine unit which permits an easier arrangement of the ligand donor sites to obtain structures with different nuclearity and coordination modes.

Spectroscopic Studies of the Complexes. The coordination behavior of TSCLMH toward the metal cations Ni(II), Cu(I), Zn(II), and Cd(II) has been studied. Before discussion

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of any results, it is necessary to have a clear understanding of the topology of the ligand, which consists of a new hybrid ligand between a lumazine derivative and a thiosemicarbazone moiety. The resulting molecule has three different kinds of donor atoms (O, N, S) which may lead to diverse coordination modes and species. Indeed, TSCLMH forms mono- and dinuclear species with bidentate, doubly bidentate, and tetradentate modes with Cu(I) and Cd(II) ions, as demonstrated by the above X-ray diffraction studies. IR, TG, DSC, NMR, reflectance diffuse, and magnetic susceptibility experiments were performed to obtain further information about the coordination environment for all the studied complexes.

The thermal stability of the new complexes has been investigated by thermogravimetric analysis. The TG curves of the aquo complexes show a first weight loss in one or two steps in the range 50−250 °C, and DSC curves show the corresponding endothermic peak appearing in the same temperature range which is attributed to the loss of the lattice and coordination water molecules. The pyrolysis of the anhydrous compounds finishes around 500−700 °C, leaving as final residue the corresponding metal oxide; this process is observed as a exothermic effect in the DSC curves.

In the IR spectra of the complexes, some absorptions were tentatively assigned by comparing with those reported for several lumazine[21,37] and thiosemicarbazone derivative complexes[13,22] as well as with the IR spectra of the free TSCLMH ligand. Except in the complex **3**, the small down-wavenumber shifts (ca. 5−10 cm^{-1}) of the bands assignable to the carbonyl groups of the lumazine (1720 and 1685 cm^{-1} in the free TSCLMH) and the strong up-wavenumber shift (ca. 20−40 cm^{-1}) of the C═C and C═N stretching vibrations indicate the N(5)−metal ligation, whereas carbonylic O(4) atoms are weak or null coordinated.[5,21,36,37] In general, the greatest shifts take place in the bands related to the thiosemicarbazone moiety. Bands assigned to hydrazonic ν(N−H) do not appear in the NiL, ZnL, and CdL complexes indicating the deprotonation of the NH group and coordination via the thiolate sulfur. A small shift in the absorption bands due to the (N−N) stretching vibrations from 948 cm^{-1} to a higher region is a confirmation of the coordination of the ligand through the azomethine nitrogen atom. Coordination via the thiolate sulfur is also indicated by a decrease in the frequency of the thioamide bands (C═S), found at 1600 and 847 cm^{-1} in the uncomplexed thiosemicarbazone, by 20−100 cm^{-1} in the complexes. Hence, the infrared spectra indicate coordination of the thiosemicarbazones through the N−S chelating system.[36] The spectrum of complex **2** shows a strong multicomponent ν(Cl−O) band (1180−1045 cm^{-1}) and the δ(O−Cl−O) band (626 cm^{-1}) assignable to the perchlorate anions.[37] The appearance of a broadened ν(N−O) band at 1385 cm^{-1} indicates the presence of a bidentate nitrate anion[30,31] in the cadmium complex **3**.

We have also performed ^{1}H, ^{13}C, and ^{1}H−^{15}N HMBC NMR experiments in DMSO-d_6 solution and ^{13}C solid-state studies for the isolated complexes. ^{1}H NMR spectra of the complexes show different shifts of both amino protons with respect to the free ligand as consequence of the involvement in hydrogen bonding. The proton H62 signal does not appear in the spectra of the NiL, ZnL, and CdL with the deprotonated ligand, or it is downfield shifted in the other complexes by the coordination of the neighboring atoms to the metal. In the ^{13}C NMR solution experiments only the Cu/dimer complex shows significant shifts in the C(2), C(6), C(62), and C(71) signals due to the involvement of adjacent atoms in coordination and hydrogen bonding. The strong shifts observed in the C(4A), C(6), C(61), C(62), and C(63) atoms in the solid ^{13}C NMR spectra of the complexes can be justified by the coordination of N(5), N(61), and S(63) to the respective metal ion. The ^{1}H−^{15}N HMBC experiments allow us to assign the N1, N3, and N(5) + N(8) signals; however, only a strong shift in the CdL complex due to the loss of the planarity of the ligands as previously explain in the X-ray diffraction section can be observed.

The diffuse reflectance spectrum recorded for a powder sample of the $Ni(TSCLM)_2\cdot 3H_2O$ complex shows a broad band whose deconvolution from a simultaneous Gaussian fit indicates the presence of the absorptions centered at 21 900 ($^{1}E_g \leftarrow {}^{1}A_{1g}$), 15 900 ($^{1}A_{2g} \leftarrow {}^{1}A_{1g}$), and 11 600 ($^{1}B_{1g} \leftarrow {}^{1}A_{1g}$) cm^{-1}, assignable to a square-planar coordination of the nickel ion,[38] which is confirmed by the diamagnetic behavior of complex **4** in the 2−300 K range ($\mu_{eff} = 0.7\ \mu_B$ at 78 K).[39]

Luminescent Properties. Construction of transition-metal complexes containing rigid chromophoric ligands with a π-conjugation system can be an efficient method for obtaining new luminescent materials, due to the ability of the metal ion to enhance, shift, and quench luminescent emission of these organic ligands. In this work, we have tested the luminescent properties of the new ligand (TSCLMH) and its above-described complexes. It is important to bear in mind that the luminescent properties of lumazine and benzoylhydrazone ligands are very well-known and have been widely used to obtain fluorescent sensors.[40] Thus, we have borrowed this previous knowledge to study the luminescence of TSCLMH, a new lumazine derivative which incorporates the photochemically active thiosemicarbazone group that could enhance the delocalization of π electrons and increase the fluorescence intensity of lumazine due to the internal photoinduced thio−enol tautomerism.[41]

The luminescence spectra of free ligand **1** and its metal complexes **2**−**6** were registered using 10^{-3} M solutions in

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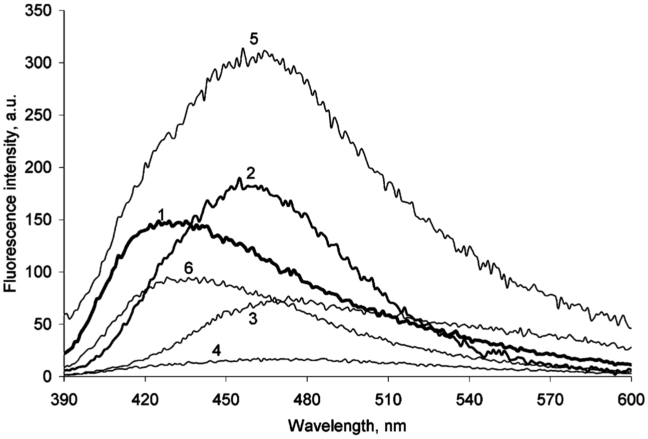

Figure 5. Luminescence spectra of TSCLMH (**1**), $[Cu(TSCLMH)]_2(ClO_4)_2$ (**2**), $[Cd(NO_3)_2(TSCLMH)(EtOH)]$ (**3**), $Ni(TSCLM)_2 \cdot 2H_2O$ (**4**), $Zn(TSCLM)_2 \cdot 5H_2O$ (**5**), and $Cd(TSCLM)_2 \cdot (MeOH) \cdot 3H_2O$ (**6**) at room temperature (10^{-3} M, DMSO).

DMSO. All fluorescence spectra were acquired by exciting at 370 nm (Figure 5).

The free ligand TSCLMH (**1**) shows a luminiscence band centered at 430 nm which can be assigned to the $\pi \rightarrow \pi^*$ transition, while in the complexes a red shift of this band (10−40 nm) is observed. The fluorescence intensity of the Ni complex (**4**) decreases, which could be explained by the occurrence of fluorescence quenching. In the other complexes, both conformational changes upon complexation, as it is evident in the X-ray studies, and formation of metal−ligand bonds promote the different behavior of luminescence intensity as shown in Figure 5.

Conclusion

This work highlights the versatile coordination behavior of a new hybrid ligand TSCLMH in which the properties of lumazine and thiosemicarbazones derivatives have been joined. In the light of the spectroscopic and structural studies reported here, three different ligating modes (bidentate, doubly bidentate, and tetradentate) have been recognized. This study has demonstrated the ability of TSCLMH to form mono- and dinuclear species with different coordination modes as consequence of the nonrigidity of the relative disposition of thiosemicarbazone and lumazine moieties. Furthermore, the compounds obtained exhibit luminescent properties at room temperature.

In view of the final results, in our future work we plan to study **1** not only as regards to the capacity to bind other metal ions but also as source of luminescent sensors. Also, we are currently pursuing other types of hybrid chelate ligands with different donor atoms combinations and so different possible coordination capabilities toward various metals. These results will be published in due course.

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Supporting Information Available: X-ray crystallographic files (CIF) and tables of (a) hydrogen bonds parameters, (b) quantification of the geometry of the coordination polyhedron in compound **3**, (c) atomic orbital contributions to the LUMO to HOMO-8 molecular orbitals of TSCLMH, and (d) infrared bands and tentative assignments. This material is available free of charge via the Internet http://pubs.acs.org.

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