Research Article

The First Metal Complexes of 4,6-diamino-1-hydro-5-hydroxy-pyrimidine-2-thione: Preparation, Physical and Spectroscopic Studies, and Preliminary Antimicrobial Properties

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The new complexes \([M_2O_5L_2(H_2O)_2]\) \(\cdot\) \(H_2O\) \((M = Mo, 1; M = W, 2)\), \([RuL_2(H_2O)_2]\) \(\cdot\) \(H_2O\) \(3\), \([ML_3]\) \(\cdot\) \(xH_2O\) \((M = Rh, x = 2, 4; M = Ir, x = 1, 5)\), \([RhL_2(PPh_3)_2](ClO_4)\) \(\cdot\) \(2H_2O\) \(6\), \([PdL_2]\) \(\cdot\) \(2H_2O\) \(7\), \([PdL(Phe)Cl]\) \(\cdot\) \(H_2O\) \(8\), \([ReOL_2(PPh_3)]Cl\) \((9)\) and \([UO_2L_2]\) \((10)\) are reported, where \(L^-\) is in its thione form and behaves as a bidentate chelate with the deprotonated (hydroxyl) oxygen and the nitrogen of one amino group as donor atoms. Oxobridged dinuclear \((1, 2)\) and various mononuclear \((3–10)\) structures are assigned for the complexes in the solid state. The metal ion coordination geometries are octahedral \((1–6, 9, 10)\) or square planar \((7, 8)\). The free ligand \(LH\) and complexes \(1, 4, 7,\) and \(8\) were assayed in vitro for antimicrobial activity against two bacterial and two fungal cultures.

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1. INTRODUCTION

2-Mercaptopyrimidine nucleotides have been detected in Escherichia Coli sRNA and yeast tRNA; it has been found that they inhibit the synthesis of tRNA, thus acting as antitumour and antithyroid agents [1]. A similar inhibitory effect has been observed for pyrimidine-2-thione (I in Scheme 1) and its derivatives, which also show pronounced in vitro bacteriostatic activity [1]. Metal complexes of pyrimidine-2-thione or its pyrimidine-2-thiol tautomeric form [1, 2] and its amino [2, 3] or hydroxy [4–6] derivatives have been prepared and studied (for representative ligands see Scheme 1). Such complexes exhibit rich structural chemistry, and interesting thermal, magnetic, sorptive, and biological properties. However, the coordination chemistry of ligands based on the 2-mercaptopyrimidine moiety and containing both hydroxy and amino substituents on the pyrimidine ring is completely unknown.

We now describe here the preparation and characterization of the first metal complexes of 4,6-diamino-5-hydroxy-2-mercaptopyrimidine (LH, Scheme 2). We also report the antimicrobial activity of the free ligand and four representative complexes against two bacteria and two fungi. This work can be considered as a continuation of our interest on the coordination chemistry of derivatized pyrimidines [7].

2. EXPERIMENTS

All reagents were purchased from Merck and Alfa/Aesar. \(Na_2[ICl_6]\) is commercially available. \([PdCl_2(Phe)]\) was prepared by the reaction of \(K_2[PdCl_4]\) and 1,10-phenanthroline...
in H₂O/EtOH. [ReOCl₃(PPh₃)₂] was synthesized as previously reported [8]. DMSO used in conductivity measurements was dried over molecular sieves. The DMSO-d₆ protons (NMR) were referenced using TMS. Warning: perchlorate salts are potentially explosive; such compounds should be used in small quantities and treated with utmost care at all times. Elemental analyses (C, H, N, S) were performed by the University of Ioannina (Greece) Microanalytical Unit with an EA 1108 Carlo-Erba analyzer. The water content of the complexes was also confirmed by TG/DTG measurements performed on a Shimadzu Thermogravimetric Analyzer TGA-50. IR spectra were recorded on a Matson 5000 FT-IR spectrometer with samples prepared as KBr pellets. Far-IR spectra were recorded on a Bruker IFS 113 v FT spectrometer with samples prepared as polyethylene pellets. FT Raman data were collected on a Bruker IFS 66 v interferometer with an FRA 106 Raman module, a CW Nd: YAG laser source, and a liquid nitrogen-cooled Ge detector. Solution electronic spectra were recorded using a Unicam UV-100 spectrophotometer. Solid-state (diffuse reflectance, DRS) electronic spectra in the 300–800 nm range were recorded on a Varian Cary 3 spectrometer equipped with an integration sphere. ¹H NMR studies were performed on a Varian Gemini WM-200 spectrometer. ³¹P{¹H} NMR spectra were recorded with a Varian Mercury equipment [ref. 85% H₃PO₄ (ext.)]. Mass spectra were recorded on a Matson 5988 MS spectrometer. Conductivity measurements were carried out at room temperature on a YSI, model 32 conductivity bridge using 10⁻³ M solutions. Room temperature magnetic susceptibility measurements were performed using a Johnson Matthey magnetic balance standardized with HgCo(NCS)₄; diamagnetic corrections were estimated using Pascal’s constants.

### 2.1. Preparation of the complexes

\([\text{Mo}_2\text{O}_5\text{L}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \) (1)

An aqueous solution (5 cm³) of (NH₄)₂[MoO₄] (0.24 g, 1.0 mmol) was added to a solution of LH (0.16 g, 1.0 mmol) in EtOH (25 cm³). The obtained slurry was heated and the resulting orange solution was refluxed for 4 hours, during which time an orange precipitate is formed. The solid was collected by filtration, washed with ethanol (2 cm³) and diethyl ether (2 × 5 cm³) and dried in vacuo. The yield was 35% (based on the metal). Elemental analytical calculation for C₈H₁₆N₈O₁₀S₂Mo: C, 15.00; H, 2.50; N, 17.50; S, 10.00% found that C, 14.98; H, 2.82; N, 17.51; S, 9.87%; Λ_M(DMSO): 3 S cm² mol⁻¹.

\([\text{W}_2\text{O}_5\text{L}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \) (2)

Using (NH₄)₂[WO₄] and following exactly the same procedure as that described for complex 1, a bright yellow material was isolated. The yield was 50% (based on the metal). Elemental analytical calculation for C₈H₁₆N₈O₁₀S₂W: C, 11.77; H, 1.96; N, 13.73; S, 7.85% found that C, 11.62; H, 1.90; N, 13.77; S, 7.95%; Λ_M(DMSO): 2 S cm² mol⁻¹.
[RuL2(H2O)2] · H2O (3)
Solid RuCl3 · 3H2O (0.12 g, 0.46 mmol) was added to a solution of NaO2CMe (0.62 g, 7.5 mmol) in water (30 cm3). Solid LH (0.24 g, 1.5 mmol) was then added and the resultant reaction mixture was refluxed for 12 hours. The deep brown solid formed was collected by filtration while the reaction mixture was hot, washed with hot water, and dried in vacuo. The yield was 30% (based on the metal). Elemental analytical calculation for C12H19N12O5S3Rh: C, 23.61; H, 3.23; N, 24.75; S, 13.64% found that C, 20.32; H, 3.05; N, 23.57; S, 13.21%; \( \Lambda_M \) (DMSO): 1 S cm−2 mol−1.

[RhL2] · 2H2O (4)
Using RhCl3 · 3H2O and following the same procedure as that described for complex 3, a reddish brown material was isolated. The yield was 60% (based on the metal). Elemental analytical calculation for C12H18N12O5S3Rh: C, 20.46; H, 3.12; N, 26.36; S, 14.98%; \( \Lambda_M \) (DMSO): 6 S cm−2 mol−1.

[IrL2] · H2O (5)
Using Na2[IrCl6] and following the same procedure as that described for complex 3, a yellow solid was isolated. The yield was 25% (based on the metal). Elemental analytical calculation for C12H18N12O5S3Ir: C, 21.14; H, 2.50%; N, 24.66; S, 14.09% found that C, 21.33; H, 2.64%; N, 24.75; S, 13.85%; \( \Lambda_M \) (DMSO): 5 S cm−2 mol−1.

[RhL2(PPh3)2](ClO4) · 2H2O (6)
A hot ethanolic solution (20 cm3) of LH (0.25 g, 1.6 mmol) was added to a solution of RhCl3 · 3H2O (0.21 g, 0.8 mmol) in 6 M HClO4 (15 cm3). The resultant orange solution was refluxed for 4 hours and to this was added a solution of PPh3 (0.43 g, 1.6 mmol) in hot ethanolic solution (15 cm3). The new solution was refluxed for a further 3 hours and filtered, and its volume decreased in vacuo to give a red-brown solid. The solid was collected by filtration, washed with hot water (2 x 2 mL) and hot ethanol (2 x 3 cm3), and dried in vacuo. The yield was 25% (based on the metal). Elemental analytical calculation for C44H26N8O8S2P2Rh: C, 49.05; H, 4.09%; N, 10.41; S, 3.30% found that C, 48.79; H, 4.09%; N, 10.44; S, 3.46%; \( \Lambda_M \) (DMSO): 48 S cm−2 mol−1.

[PdL2] · 2H2O (7)
To a stirred slurry of LH (0.16 g, 1.0 mmol) in methanol (15 cm3) was added an aqueous solution (15 cm3) of K2[PtCl4] (0.16 g, 0.5 mmol). The resulting suspension was stirred at 40°C for 60 hours and the brown solid formed was collected by filtration, washed with warm water (5 x 3 cm3) and cold methanol (2 x 5 cm3), and dried in air. The yield (based on the metal) was 50%. Elemental analytical calculation for C8H16N8O4S2Pd: C, 21.23; H, 3.22%; N, 24.85; S, 14.02% found that C, 21.23; H, 3.22%; N, 24.85; S, 14.02%; \( \Lambda_M \) (DMSO): 9 S cm−2 mol−1.

[PdL(phen)]Cl · H2O (8)
To a stirred slurry of [PdCl2(phen)] (0.18 g, 0.5 mmol) in methanol/benzene solvent mixture (15 cm3, 3:2 v/v) was added a solution of KOH (0.055 g, 1.0 mmol) in methanol (15 cm3). Solid LH (0.08 g, 0.5 mmol) was added to the reaction mixture which soon dissolved. The solution was filtered and stirred for 48 hours at room temperature. During this time, a brown precipitate formed which was collected by filtration, washed with water (1 cm3) and methanol (2 x 3 cm3), and dried in air. The yield was 40% (based on the ligand). Elemental analytical calculation for C8H14N8O5S2Pd: C, 21.03; H, 3.07%; N, 24.54; S, 14.02% found that C, 21.23; H, 3.22%; N, 24.85; S, 14.21%; \( \Lambda_M \) (DMSO): 77 S cm−2 mol−1.

[ReOCl2(PPh3)]Cl (9)
To a stirred slurry of [ReOCl3(PPh3)]2 (0.25 g, 0.2 mmol) in ethanol (30 cm3) was added solid LH (0.057 g, 0.4 mmol). The solid soon dissolved and stirred at 40°C for 5 hours. The brown solution deposited a brown microcrystalline solid which was collected by filtration, washed with ethanol (3 x 3 cm3), and dried in vacuo. The yield was 65% (based on the metal). Elemental analytical calculation for C30H25N6O6S2Re: C, 38.37; H, 3.11%; N, 13.76; S, 7.86% found that C, 38.37; H, 3.11%; N, 13.87; S, 7.98%; \( \Lambda_M \) (DMSO): 46 S cm−2 mol−1.

[UO2L2] (10)
Solid LH (0.08 g, 0.5 mmol) was added to a stirred solution of [UO2(NO3)2] · 6H2O (0.25 g, 0.5 mmol) in methanol (10 cm3). The solid soon dissolved. The resultant yellow solution was filtered and refluxed for 4 hours, during which time a red microcrystalline solid was precipitated. The product was collected by filtration, washed with methanol (5 cm3) and diethyl ether (2 x 5 cm3), and dried in vacuo. The yield was 55% (based on the metal). Elemental analytical calculation for C26H25N6O6S2U: C, 16.44; H, 1.71%; N, 19.18; S, 10.96% found that C, 16.35; H, 2.02%; N, 18.98; S, 10.86%; \( \Lambda_M \) (DMSO): 11 S cm−2 mol−1.

2.2. Antimicrobial activity
The bacterial strains (S. aureus and P. aeruginosa) were grown in Nutrient agar slants and the fungal strains (A. niger and C. albicans) were grown in Sabouraud dextrose agar slants. The viable bacterial cells were swabbed onto Nutrient agar plates, while the fungal spores onto Sabouraud dextrose agar plates. The free ligand and complexes 1, 4, 7 were dissolved in DMSO, while complex 8 was dissolved in H2O with 10, 20, 50, and 100 mg/mL concentrations. The blank was DMSO in saline buffer. The bacterial and fungal plates were incubated for 36 and 72 hours, respectively, and the activity of the compounds was estimated by measuring the diameter of the inhibition zone (the affected zone by the compounds) around the respective zone (the normal place in the agar). The incubation temperature was 27 ± 0.5°C.
3. RESULTS AND DISCUSSION

3.1. Synthetic comments and physical characterization

The preparative reactions for selected complexes can be represented by the stoichiometric equations (1)–(7); no attempts were made to optimize the yields,

\[2(NH_4)_2[MO_4] + 2LH \rightarrow \text{EtOH} / H_2O / T \rightarrow [M_2O_5L_2(H_2O)_2] + 4NH_3 + H_2O (1)\]

\[M = Mo(1), W(2), \text{RhCl}_3 \cdot 3H_2O + 3LH + 3NaO_2CMe \rightarrow \text{H}_2O / T \rightarrow [RhL_3(phen)] + 3NaCl + 3MeCO_2H + 3H_2O, \text{RhCl}_3 \cdot 3H_2O + 2LH + 2PPh_2 + HClO_4 \rightarrow \text{EtOH} / \text{MeOH} / \text{H}_2O \rightarrow [PdCl_2(phen)] + LH + KOH \rightarrow \text{MeOH/ benzene} \rightarrow [PdL_2](phen) + CL + KOH \rightarrow \text{[ReOCl}_3(PPh_3)_2] + 2LH \rightarrow \text{EtOH} \rightarrow [ReO_2(NO_3)_2] \cdot 6H_2O + 2LH \rightarrow \text{MeOH} / T \rightarrow [UO_2L_2](phen) + 2HNO_3 + 6H_2O. (7)\]

The metal is reduced (Ru\(^{III} \rightarrow \) Ru\(^{II}, \) Ir\(^{IV} \rightarrow \) Ir\(^{III}\)) during the preparation of complexes 3 and 5 although the reactions are performed in air. The redox reaction may be facilitated by the reducing character of LH, the products from the oxidation of the ligand remaining in the solution. Thus, LH possibly plays two roles in the reactions, that is, the role of the ligand and that of the reducing agent. It is well known that Ru(III) can undergo reduction reactions and that the [Ir\(^{IV}\)Cl\(_6\)]\(^{2-}\) ion is a convenient one-electron oxidant [9]. The use of a base (KOH) in the preparation of 8 is necessary to obtain the complex in pure form; otherwise, the produced aqueous HCl decomposes the compound.

Complexes 1–5, 7 and 10 are nonelectrolytes in DMSO [10]. Complexes 7 and 10 exhibit slightly increased molar conductivity values in DMSO. Since DMSO is a good donor solvent, this may be due to the partial displacement of one L\(^-\) ligand by two DMSO molecules. Assuming an equilibrium between the neutral and the resulting cationic complex, this displacement changes the electrolyte type of the compound explaining the increased AM value [10]. From the molar conductivities in DMSO (complexes 6 and 9) and DMF (complex 8), it is concluded that compounds 6, 8, and 9 behave as 1:1 electrolytes, supporting their ionic formulation [10]. All the complexes are diamagnetic, as expected [9]. It should be mentioned at this point that the \(\pi\) bonding in the {Re\(^{IV}\)O\(_2\)}\(^{2+}\) unit of 9 causes sufficient splitting of the \(t_{2g}\) (in \(O_6\)) set (5\(d_{yz}\), 5\(d_{x^2-y^2}\) \(\gg\) 5\(d_{xy}\)) that diamagnetism occurs through the configuration (5\(d_{xy}\))^2.

Complexes 1–10 are microcrystalline or powder-like, stable in the normal laboratory atmosphere, and soluble only in DMF and DMSO. We had hoped to structurally characterized one or two complexes by single-crystal X-ray crystallography (working mainly with DMF or DMF/MeCN), but were thwarted on numerous occasions by twinning problems or lack of single crystals. Thus, the characterization of the complexes is based on spectroscopic methods.

3.2. Electronic spectra

The band at 335 nm in the DRS spectrum of 1 is assigned to an O\(^{2-}\) → Mo\(^{VI}\) p–d LMCT transition and is characteristic of the {MoO\(_2\)}\(^{2+}\) moiety [11] in octahedral complexes. The transition appears at 337 nm as a shoulder in solution (DMSO). The DRS spectrum of 3 is indicative of its low-spin octahedral structure. The ground term is \(1^A_g\) and the two spin-allowed transitions to \(1^T_{1g}\) and \(1^T_{2g}\) are observed at 565 and 420 nm, respectively [12]; the corresponding bands in DMSO are at 560 and 430 nm. The DRS spectra of the Rh(III) complexes 4 and 6 both exhibit bands at \(\sim 470\) and \(\sim 380\) nm; the spectra resemble those of other six-coordinate Rh(III) compounds and the bands are assigned as transitions from the \(1^A_{1g}\) ground state to the \(1^T_{1g}\) and \(1^T_{2g}\) upper states in octahedral symmetry in decreasing order of wavelength [12]. The lower wavelength band may also have a charge-transfer character. Both complexes exhibit an additional band in the blue region of the spectrum (\(\sim 520\) nm) which is responsible for their red-brown colors; a possible origin of this band is the singlet-triplet, spin-forbidden transition \(1^A_{1g} \rightarrow 3^T_{2g}\) [12]. The spectrum of the Ir(III) complex 5 shows two bands at 380 and 335 nm, which have a similar interpretation; the \(1^A_{1g} \rightarrow 3^T_{2g}\) transition is not observed. A weak shoulder in the spectrum of 9 is assigned to the \(3^T_{1g}(F) \rightarrow 3^T_{1g}\) transition in a \(d^2\) octahedral environment, while an intense band at 375 nm most probably has an LMCT origin [12]. The ligand-field spectra of 7 and 8 are typical of a square planar environment around pd\(^{11}\) with a mixed N\(_2\)O-ligation; the bands at 480, 375, and 330 nm are assigned [12] to the \(1^A_{1g} \rightarrow 1^A_{2g}, 1^A_{1g} \rightarrow 1^E_g,\) and \(1^A_{1g} \rightarrow 1^B_{1g}\) transitions, respectively, under \(D_4h\) symmetry. The spectra in DMSO exhibit only two bands at 480 and 330 nm.

3.3. NMR studies

Diagnostic \(^1H\) NMR assignments (in DMSO-d\(_4\)) for representative complexes are presented in Table 1. The study was based on comparison with the data obtained for diamagnetic complexes with similar ligands [7, 13, 14]. In all the spectra
studied, the integration ratio of the signals is consistent with the assignments.

The spectrum of LH exhibits two singlets at δ 6.07 and 6.18 assigned to the –N(4)H2/–N(6)H2 (for the numbering scheme see Scheme 2) amino hydrogens, respectively, and two relatively broad singlets at δ 7.43 and 9.13 due to the amide and hydroxyl protons –N(1)H– and –O(5)H, respectively. The appearance of these four peaks is consistent with the exclusive presence of the thione form of LH (Scheme 2) in solution. The proton of the hydroxyl group is not observed in the spectra of the complexes confirming its deprotonation and coordination to the metal ions. In the spectra of 1, 3, 4, and 6–8, the –N(1)H– signal undergoes a marginal shift to indicate the noninvolvement of this group in coordination; a relatively large downfield shift would be expected if coordination had occurred. In the same spectra, two signals appear for –NH2 protons, as expected. The most pronounced variation in chemical shift is the downfield shift of one signal. Since more specific assignments of these two signals seem impossible, it is difficult to conclude which amino nitrogen is coordinated. NMR evidence for the presence of thione –thiol tautomerism in the metal complexes in solution was not found.

The 1H NMR spectrum of 4 confirms that the three N,O-bidentate (vide infra) ligands are equivalent (C3 symmetry), and, therefore, the complex has the fac stereochemistry [15].

The spectrum of 8 is indicative of the presence of one solution species containing coordinated phen, consisting of four resonances [16]. Assignments are as follows (the numbers in parentheses are the positions of the protons in the classical numbering scheme of 1,10-phenanthroline; s = singlet, dd=doublet of doublets): 9.15 dd(2H; 2,9), 8.53 dd(2H; 4,7), 8.00 s(2H; 5,6), and 7.81 q(2H; 3,8). Considerable downfield coordination shifts are characteristic of coordinated phen [16].

The 31P{1H} NMR spectrum of the Re(V) complex 9 in DMSO-d6 consists of a sharp singlet at δ – 16.89, a value which is typical for PPh3-containing oxorhenium(V) species [17].

### 3.4. Vibrational spectra

Tentative assignments of selected IR ligand bands for complexes 1–10 and free LH are listed in Table 2. The assignments have been given by studying literature reports [3, 13, 14], comparing the spectrum of LH with the spectra of the complexes and by performing deuterium isotopic substitution experiments in few cases. As a general remark, we must emphasize that some stretching and deformation modes are coupled, so that the proposed assignments should be regarded as approximate descriptions of the vibrations.

In the ν(OH)water region, the spectra of complexes 1–3 show one medium-intensity band at ∼3420 cm⁻¹ attributed to the presence of coordinated water [13]. The same spectra exhibit, in addition to the relatively sharp band of coordinated water, a weaker broad continuous absorption covering the 3400–3200 cm⁻¹ region; this is apparently due to the simultaneous presence of crystal and coordinated water in these complexes [14]. In the spectra of 4–8, a medium broad absorption indicates the presence of exclusively crystal (lattice) water.

The absence of an IR or Raman band at ∼2600 cm⁻¹ in the spectrum of free LH suggests that the ligand exists in its thione form (see Scheme 2) [18]. This is corroborated by the appearance of the medium v(C=S) band at 1177 cm⁻¹ (this vibration appears as a strong peak at 1160 cm⁻¹ in the Raman spectrum) and the strong IR v(N–H) band at 2970 cm⁻¹ (this vibration appears as a medium peak at ∼3000 cm⁻¹ in the Raman spectrum); the broadness and low frequency of the latter IR band are both indicative of the involvement of the –NH– group in strong hydrogen bonding.

The medium IR band at 3305 cm⁻¹ in the spectrum of free LH is assigned to the ν(OH) vibration. This band does not appear in the spectra of the complexes indicating deprotonation of the –OH group and suggesting coordination of the resulting, negatively charged oxygen atom. The absence of large systematic shifts of the δ(N–H), δ(NH), ν(C=N), ν(C=O), ν(C–N1) and ν(C=S) bands in the spectra of the complexes implies that there is no interaction between the ring nitrogen atoms or the exocyclic sulfur atom and the metal ions. The νas(NH2) and νs(NH2) bands are doubled in the spectra of the complexes. One band for each mode appears at almost the same wavenumber compared with the corresponding band in the spectrum of free LH, whereas the other band of each pair is significantly shifted to lower wavenumbers. This fact is a strong evidence for the presence of one coordinated and one “free” (i.e., uncoordinated) amino group per L⁻ in the complexes [7].

The presence of coordinated PPh3 groups in 6 and 9 is manifested by the strong IR bands at ∼1100 and ∼750 cm⁻¹, attributed to the ν(P–C) and δ(CCH) vibrations, respectively [17]; the former band overlaps with the ClO4⁻ stretching vibration in the spectrum of the Rh(III) complex 6. In the spectrum of 8, the bands at 1627, 1591, 1510, 1485, and 1423 cm⁻¹ are due to the phen stretching vibrations [16]; these bands are at higher wavenumbers compared with the free phen indicating chelation. The bands at 854, 841, 743, and 725 cm⁻¹ are assigned to the γ(CH) vibrations of the coordinated phen [16].

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**Table 1: Diagnostic 1H NMR (δ, ppm) spectral data for LH and the representative complexes 1, 3, 4, and 6–8 in DMSO-d6.**

| Compound | –N(1)H– | –N(4)H2/–N(6)H2 | –O(5)H |
|----------|---------|----------------|--------|
| LH       | 7.43    | 6.07, 6.18     | 9.13   |
| 1        | 7.57    | 6.18, 6.55     | –      |
| 3        | 7.49    | 6.14, 6.47     | –      |
| 4        | 7.44    | 6.20, 6.49     | –      |
| 6        | 7.47    | 6.17, 6.48     | –      |
| 7        | 7.39    | 6.08, 6.46     | –      |

*The spectra were run 10–15 min after dissolution.

bObscured by the signals of the aromatic protons.
The vibrational spectra of the inorganic “parts” of complexes 1, 2, 6, 9, and 10 are also diagnostic. The IR spectrum of 6 exhibits a strong band at ~1100 and a medium band at 624 cm⁻¹ due to the \( v_2(\text{F}_2) \) and \( v_1(\text{F}_2) \) modes of the uncoordinated \( \text{TaCl}_4^- \) ion [19], respectively, the former having also \( v(\text{P}–\text{C}) \) character [17]. In the 1000–750 cm⁻¹ region, the spectra of 1 and 2 show bands characteristic of the \( \text{cis-MO}_2^{2+} \) units and the \( \{\text{O}_2\text{M}–\text{O}–\text{MO}_2\}^{2+} \) core (M=Mo, W) [20, 21]. The IR bands at 930 and 912 cm⁻¹ in 1 are assigned to the \( v_1(\text{MoO}_2) \) and \( v_2(\text{MoO}_2) \) modes, respectively [19, 20]; the corresponding Raman bands appear at 910 and 896 cm⁻¹. As expected [19], the symmetric mode is weak in the IR spectrum and strong in the Raman spectrum, while the opposite applies for the asymmetric mode. The appearance of two stretching bands is indicative of the \textit{cis} configuration [19]. The strong IR band at 745 cm⁻¹ is assigned to the \( v_2(\text{Mo}–\text{O}–\text{Mo}) \) mode [20], indicating the presence of a \( \mu–\text{O}^2- \) group. The \( v_2(\text{WO}_2) \), \( v_2(\text{WO}_2) \), and \( v_2(\text{W}–\text{O}–\text{W}) \) bands appear at 945, 922, and 755 cm⁻¹, respectively, in the IR spectrum of complex 2 [19, 21]; the \( v_2(\text{WO}_2) \) and \( v_2(\text{WO}_2) \) Raman bands are at 940 and 917 cm⁻¹, respectively. The \( v_2(\text{WO}_2) \) and \( v_2(\text{WO}_2) \) modes are at higher wavenumbers when compared to those of the analogous Mo(VI) complex 1, suggesting [21] that the \textit{cis-WO}_2^{2+} group has some “triple” bond character [21]. In the spectra of 9, the band attributed to \( v(\text{Re}–\text{O}) \) appears at 956 (IR) and 968 (Raman) cm⁻¹ [17, 19]. The IR spectrum of the uranyl complex 10 exhibits only one \( \text{U}=\text{O} \) stretching band, that is, \( v_2(\text{UO}_2) \), at 940 cm⁻¹ (not observed in the Raman spectrum) indicating its linear transdioxo configuration [19]. The \( v_2(\text{UO}_2) \) mode appears as a strong Raman peak at 905 cm⁻¹, and, as expected, the corresponding IR band is very weak. The bands at 345 and 298 cm⁻¹ in the far-IR spectrum of 7 are assigned to the \( v(\text{Pd}–\text{NH}_2) \) and \( v(\text{Pd}-\text{O}) \) vibrations, respectively. The appearance of one band for

### Table 2: Diagnostic ligand IR bands (cm⁻¹) for LH and complexes 1–10.

| Compound | \( v_1(\text{NH}_2) \)^a | \( v_2(\text{NH}_2) \) | \( v(\text{N–H}) \) | \( v(\text{C}=\text{N}), v(\text{C}=\text{C}) \) | \( v(\text{C}_2–\text{N}_1), v(\text{C}_2–\text{N}_3) \) | \( \delta(\text{NH}) \) | \( v(\text{C}=\text{S}) \) |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| LH       | 3390            | 3185            | 2970            | 1652            | 1652            | 1455            | 1177            |
| 1        | 3377, 3330      | 3180, 3156      | 3005            | 1631            | 1553            | 1460            | 1155            |
| 2        | 3388, 3356      | 3188, 3160      | 3000            | 1633            | 1556            | 1465            | 1170            |
| 3        | 3399, 3343      | 3180, 3079      | 3010            | 1632            | 1558            | 1464            | 1157            |
| 4        | 3400, 3320      | 3160, 3105      | 3005            | 1642            | 1560            | 1460            | 1170            |
| 5        | 3387, 3320      | 3166, 3110      | 3010            | 1635            | 1556            | 1455            | 1177            |
| 6        | 3380, 3357      | 3170, 3095      | 3015            | 1641            | 1552b           | 1443b           | 1176            |
| 7        | 3395, 3357      | 3164, 3098      | 3010            | 1646            | 1550            | 1446            | 1170            |
| 8        | 3397, 3360      | 3165, 3100      | 3015            | 1640            | 1553            | 1450            | 1176            |
| 9        | 3400, 3355      | 3155, 3105      | 3012            | 1639            | 1555b           | 1460b           | 1170            |
| 10       | 3405, 3324      | 3180, 3100      | 3010            | 1641            | 1558            | 1462            | 1164            |

^aOverlapping with the \( v(\text{OH})_{\text{water}} \) band in the spectra of 1–8.

^bOverlapping with phenyl stretching vibrations of the coordinated PPh₃ ligands.

### Table 3: Diameters (mm) of growth inhibitions zones for the antibacterial activity of LH and complexes 1, 4, 7, and 8.

| Compound | \( S. \text{ aureus} \) (mg/cm²)^a | \( P. \text{ aeruginosa} \) (mg/cm²)^a |
|----------|-------------------------------------|-------------------------------------|
| LH       | 5                                  | 10                                  |
| 8        | 13                                 | 10                                  |
| 7        | 10                                 | 10                                  |
| 4        | 8                                  | 8                                   |
| 1        | 10                                 | 10                                  |

^amg/cm² represents the concentration of the reagent in the gel.

### Table 4: Diameters (mm) of growth inhibitions zones for the antifungal activity of LH and complexes 1, 4, 7, and 8.

| Compound | \( A. \text{ niger} \) (mg/cm²)^a | \( C. \text{ albicans} \) (mg/cm²)^a |
|----------|-------------------------------------|-------------------------------------|
| LH       | 5                                  | 10                                  |
| 8        | 15                                 | 10                                  |
| 7        | 10                                 | 10                                  |
| 4        | 0                                  | 10                                  |
| 1        | 6                                  | 10                                  |
| Nystatin | 17                                 | 10                                  |

^aA currently prescribed antifungal drug.

### Scheme 3: The proposed coordination mode of the anionic ligand \( \text{L}^- \) in complexes 1–10; \( \text{M} \)=metal ion.
molecules and counterions have been omitted for clarity. However, −N and O donor atoms of L = the pyrimidine ring; M′ (most probably) and the deprotonated oxygen of the position 5 of NO

Figure 1: Schematic structures proposed for the neutral complexes 1–5, 7, 10 and for the cations of complexes 6, 8, 9. Lattice H2O molecules and counterions have been omitted for clarity. However, N−O and N’ N’ represent the ligands L− and phen, respectively. The N and O donor atoms of L− are the amino nitrogen of the position 6 (most probably) and the deprotonated oxygen of the position 5 of the pyrimidine ring; M=Mo, W; M′ = Rh, Ir.

4. CONCLUSIONS

The M/LH general reaction system fulfilled its promise as a source of interesting complexes. From the overall evidence presented before, it seems that the ligand L− behaves as a bidentate chelate in all the prepared complexes with the deprotonated oxygen and most probably the amino nitrogen of the position 6 of the pyrimidine ring being the donor atoms, see Scheme. However, the participation of the amino nitrogen of the position 4 of the ring cannot be ruled out. The nonparticipation of the sulfur atom in coordination in complexes 7 and 8 may be seen as unusual given the soft character of Pd(II) in the context of the HSAB concept.

The chelate effect (a stable chelating ring with the participation of the sulfur atom cannot be formed due to the geometry of L−) seems to govern the thermodynamic stability of these complexes. The proposed gross schematic structures for 1–10 are shown in Figure 1. Due to the fact that single-crystal, X-ray crystallographic studies are not available, few structural features (e.g., the symmetric structures of 1–3, 6, 7, and 10) are tentative. The metal ions adopt octahedral (1–6, 9, 10) or square planar (7, 8) stereochemistries.

Finally, complexes 1, 4, 7, and 8 are new welcome additions in the growing family of metal complexes with antimicrobial activity.

The results described in this report represent the initial study of the coordination chemistry of LH and the biological activity of its complexes. Further studies with 3d-metal ions are in progress.

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