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SYNTHESIS AND CHARACTERISATION OF A NEW O,N,O-TRIDENTATE LIGAND AND ITS Cu(I), Cu(II), Ag(I), Cd(II), Zn(II) AND Re(II) COMPLEXES

Nabila EL AZZOUZI,[a,*] Yassmina BAKHTAOUI,[b] Fatimezzahra DARHMAOUI,[b] Abdelkader ZARROUK,[c] Jaouad BENSALAH,[b] Maryem El ABBOUDI,[b] Ali OUMIRDINE[b] and El Housseine RIFI[b]

[a]Laboratory of Advanced Materials and Process Engineering, Higher School of Education and Formation, University Ibn Tofail, P.B. 242-14000, Kenitra, Morocco
[b]Laboratory of Advanced Materials and Process Engineering, Department of Chemistry, Faculty of Sciences, Ibn Tofaïl University, B.P. 133, Kenitra 14000, Morocco
[c]Laboratory of Materials, Nanotechnology and Environment, Faculty of Sciences, Mohammed V University, Av. Ibn Battouta, P.O. Box. 1014, Agdal-Rabat, Morocco

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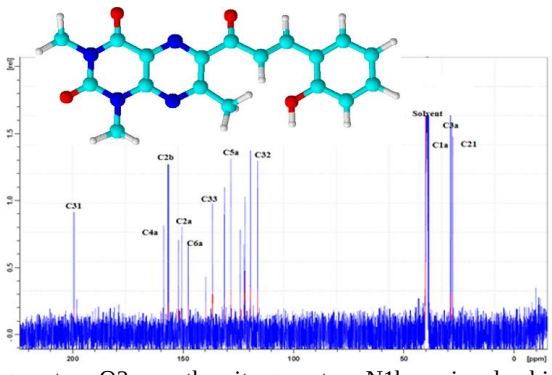
A novel pteridine-hydroxyphenyl-chalcone ligand (HPCLMH = hydroxyphenyl chalcone of 6-acetyl-1,3,7-trimethyllumazine) was synthesized and, once it was spectroscopically characterized, its behavior as a ligand was studied by the synthesis of a series of Cu(I), Cu(II), Ag(I), Cd(II), Zn(II) and Re(II) complexes. Once the metallic complexes have been synthesized and their purity was been established, they were characterized by means of analytical techniques (elemental analysis and TG) and spectral methods (IR, MS and RMN (^{1}H, ^{13}C, DEPT, HSQC)). The molecular structure of the ligand was designed such that the coordination ability through 6- acetyl-1,3,7-trimethyllumazine atoms was enhanced with a new O31 base atom of the keto-ethylene group -CO-CH=CH-. Thus, the coordination of this organic ligand can occur via the five heteroatoms N1b, N4b, O2a, O4a, and O31. Experimental data indicate that neither the carbonyl oxygen atom O2a nor the nitrogen atom N1b are involved in the coordination to the metal.



INTRODUCTION

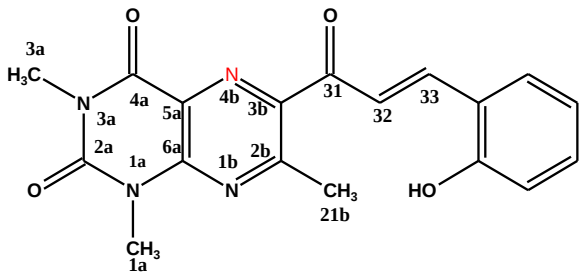
Pyrimidine has attracted great interest from its discovery as an important constituent of nucleic acids to its current use in chemotherapy. In this context, ligands containing the pyrimidine ring and their metal complexes demonstrated an unexpected variety of chemistry, biological, and pharmacological properties. These properties include anticancer, antiprotozoal, antibacterial, antiviral, antimicrobial, antihypertensive, antihistaminic and anti-inflammatory properties.[1–12]

Additionally, pyrimidine derivatives are an important commercial fungicide that has been used in agriculture, as an example, 4,6-diméthyl-N-phénylpyrimidin-2-amine.[2–4] Furthermore, it has

* Corresponding author: nabila.elazzouzi@uit.ac.ma

been shown that introduction of an additional ring to the pyrimidine core display better novel biological activities in these molecules.[16–18] It has also been noticed that metal complexes formed with these ligands and transition or non-transition metal ions display better properties as compared to the free ligand.[19–20] It is also noteworthy that many drugs possess modified toxicological and pharmacological properties when taken as mineral complexes.[21–22]

Moreover, the pteridine derivative, 6-carboxy-1,3,7-trimethylpteridine-2,4(1*H*,3H)-dione, substituted in position 6 is a biologically relevant heterocycle that occurs as a natural product. For example, it plays a role in the biosynthesis of flavin coenzymes. Effectively, because of their structural similarities with the flavins, lumazine, derivates, and metal complexes are biologically, photobiologically, photochemically, and photophysically relevant. Besides, they are present in pigments of certain insects and as cofactors in luminescence proteins.[23] On the other hand, chalcones are used nowadays for the treatment of stomach cancer, cardiovascular diseases, viral disorders, pain, gastritis, and parasitic infections.[24–27] These properties are due to the presence of the α, β-unsaturated ketone moiety of the reactive keto-ethylenic group -CO-CH=CH-, which belongs to the flavonoid family.[28–29] The introduction of various substituents into the particular structure of chalcones is also a subject of interest as it leads to a useful structure-activity relationship and gives them great therapeutic value. Based on a review of the literature, chalcone-heterocycle derivatives are future new medicinal agents with improved potency, lower toxicity and good pharmacological actions.[30]



Scheme 1. – Numbering scheme of the studied ligand (HPCLMH).

In view of the data collected and in the continuity of our ongoing work, we have focused on the design of novel lumazine/chalcone derivative combining the properties of pyrimidine rings and the keto-ethylene group -CO-CH=CH-. As a result, Both the novel chalcone ligand [3-(2-hydroxyphenyl)prop-2-en-1-one] of the 6-acétyl-1,3,7-triméthyllumazine (HPCLMH) (Scheme 1) and some metal complexes were synthesized and studied through different analysis and spectroscopies methods.

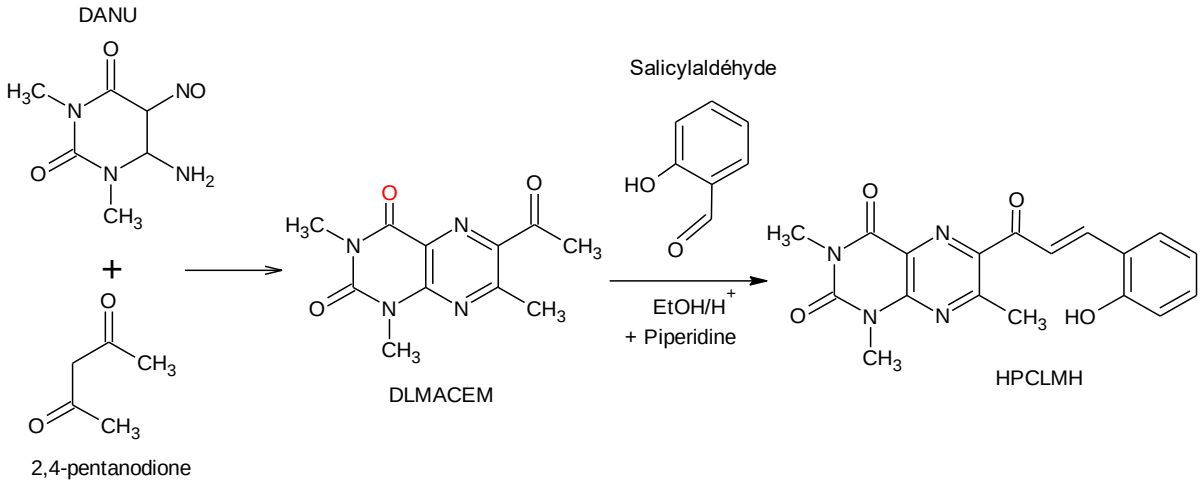
EXPERIMENTAL

Materials and instrumentation

Elemental analyses of the isolated compounds were carried out on the THERMO FINNIGAN flashEA 1112 apparatus. Conductivity measurements were carried out using 10 M^{-3} freshly prepared dimethylformamide solutions on a Hanna HI8820 instrument. The TG studies were recorded using METTLER TOLEDO Model TGA/SDTA851 equipment with a flow rate of 50 $mL \cdot min^{-1}$ and a sweep speed of 20 $°C \cdot min^{-1}$ in a pure air atmosphere. Infrared spectra were recorded on a PERKIN-ELMER mod.1760 FT-IR region (4000–400 cm^{-1}, KBr pellets). The ^{1}H and ^{13}C NMR spectra have been recorded in a BRUKER DPX-300 equipment, using DMSO-d_6 as solvents. Mass spectra were recorded using a Hewlett-Packard G1023B, employing an ionization energy of 70 eV. All reagents and solvents were purchased from commercial sources and used as received, without further purification.

Preparation of the ligand

This ligand is obtained from a non-commercial pro-ligand, 6-acetyl-1,3,7-trimethyllumazine (DLMACEM), obtained according to literature procedures.[31–32] After we synthesized the ligand by reflux condensation at 80 °C for 15h of equimolar amounts of the 6-substituted carbonyl group of DLMACEM with salicylaldehyde in ethanol (30 mL) and using as catalyst 5 drops of acetic acid and 1mL of piperidine (Scheme 2). The yellow precipitate formed in high yield (82%) was filtered and washed with ethanol and diethylether. Elemental analysis found (%), C, 61.55; H, 4.62; N, 15.05. Calc. For $C_{18}H_{16}N_6O_3$ (352.39): C, 61.35; H, 4.58; N, 15.9. MS (m/z) = 353 $[M+1]^+$; IR (KBr, cm^{-1}) : Main IR peaks (KBr, cm^{-1}) : 3260 (ν (OH)), 1716 (ν (C31=O)), 1694 (ν (C2a=O)),1667 (ν (C4a=O)), 1607 (ν (C=C) ketone), 1534 (ν (C=N)), 1459, 1294 (ν (C=C) + ν (C–N)). 1H NMR data (δ, ppm, DMSO-d6; Me4Si): 2.49 (3H, s, (21b)CH3), 2.66 (3H, s, (3a)CH3), 3.60 (3H, s, (1a)CH3), 8.10 (1H, d, C32-H), 8.26 (1H, d, C33-H), 6.86, 7.21, 7.51 (4H, m, C-H_{arom}), 10.15 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-d6): 199.00 (C31), 158.69 (C4a), 156.69 (C2b), 150.51 (C2a), 147.61 (C6a), 139.78 (C3b), 136.66 (C33), 124.05 (C5a), 116.19 (C32), 28.92 (C1a), 28.35 (C3a), 27.83 (C21), (119.44; 121.91; 122.32; 128.28; 131.18; 152.00 (C_{arom})).



Scheme 2. – Synthesis of HPCLMH.

Synthesis of the complexes

The complexes, from 1 to 7, were synthesized by the reaction of the ligand HPCLMH and the respective compound CuCl, CuI, $Cu(ClO_4)_2$, $AgClO_4$, $Re(CO)_5Cl$, $ZnSO_4$ and $Cd(ClO_4)_2$ in a 1:1 ratio in toluene at 50 °C, with magnetic stirring for 3 hours. The complexes 9, 10 and 11 were obtained by reacting the ligand, the corresponding compound CuCl, $AgClO_4$, and $AgNO_3$ respectively and triphenylphosphine in a 1/2:1/2:1/2 ratio in toluene at 50 °C with magnetic stirring. Complexes 12 and 13 were obtained by reaction of $Cu(ClO_4)_2$ and CuI with the ligand and triphenylphosphine in a 1/2:1/2:1/2 ratio and the reaction was carried out in a mixture of ethanol and dichloromethane (1:1) under magnetic stirring for 3h (50–60 °C). The last complex 14 was prepared by reacting a suspension of ligand (1/2 mmol) with a solution of metallic salt CuI (1/2 mmol) in a mixture of ethanol and dichloromethane (1:1). The reaction mixture was heated and stirred for 3h. In all cases, the resulting precipitates obtained were filtered off, washed with ethanol and diethyl ether and allowed to air dry. Yield: 60–70 %. Most of the compounds are non-electrolytes according to Greenwood,[33] with the exception of complexes 3 and 12 which give a conductivity characteristic of 1:1 electrolyte. From the TG diagrams, it can be seen that the ligand and metal complexes are anhydrous and do not undergo any dehydration process around 100ºC, the weight losses found are in good agreement with those calculated theoretically. The pyrolysis of the ligand does not leave any residue in the sample crucible.

***Cu(HPCLMH)Cl*.(1).** (light green, Λ_M =148 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 46.73; H, 3.56; N, 11.48; Calc. for $CuC_{18}H_{16}N_4O_4Cl$ (451.38) C, 47.89; H, 3.57; N, 12.40. Main IR peaks (KBr, cm^{-1}): 3262 (ν (O-H)), 1716 (ν (C31=O)), 1694 (ν (C2a=O)),1666 (ν (C4a=O)), 1606 (ν $(C=C)_{ketone}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b)CH_3), 2.64 (3H, s, (3a)CH_3), 3.58 (3H, s, (1a)CH_3), 7.90 (1H, d, C32-H), 8.25 (1H, d, C33-H), 6.26, 7.19, 7.49 (4H, m, C-H_{arom}) and 10.15 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 198 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 139 (C3b), 136 (C33), 123 (C5a), 115 (C32), 28.41 (C1a), 27.84 (C3a), 27.32 (C21).

***Cu_2(HPCLMH)$_3$.I_2*.(2).** (yellow, Λ_M =36 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 44.65; H, 3.33; N, 12.03; Calc. for $CuIC_{27}H_{24}N_6O_6$ (719.02) C, 45.09; H, 3.63; N, 11.69. Main IR peaks (KBr, cm^{-1}): 3262 (ν (O-H)), 1717 (ν (C31=O)), 1694 (ν (C2a=O)),1665 (ν (C4a=O)), 1606 (ν $(C=C)_{ketone}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b)CH_3), 2.67 (3H, s, (3a)CH_3), 3.60 (3H, s, (1a)CH_3), 8.13 (1H, d, C32-H), 8.25 (1H, d, C33-H), 6.89, 7.21, 7.53 (4H, m, C-H_{arom}) and 10.16 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 158 (C4a), 150 (C2a), 115 (C32), 28.59 (C1a), 27.99 (C3a), 27.50 (C21).

***Cu(HPCLMH)*$(ClO_4)_2$.(3).** (red-brown, Λ_M = 112 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 36.62; H, 3.62; N, 9.34; Calc. for $CuC_{18}H_{16}N_4O_{12}Cl_2$ (614.83) C, 35.16; H, 2.62; N, 9.11. Main IR peaks (KBr, cm^{-1}): 3261 (ν (O-H)), 1715 (ν (C31=O)), 1693 (ν (C2a=O)),1663 (ν (C4a=O)), 1611 (ν $(C=C)_{ketone}$), 1144, 1112, 1087, 627 (ν$(Cl–O)_{perchlorate}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.47 (3H, s, (21b)CH_3), 2.70 (3H, s, (3a)CH_3), 3.59 (3H, s, (1a)CH_3), 8.13 (1H, d, C32-H), 8.29 (1H, d, C33-H), 6.88, 7.22, 7.49 (4H, m, C-H_{arom}) and 10.18 (1H, s, O-H).

***Ag(HPCLMH)*(ClO_4).(4).** (yellow-brown). Elemental analysis found, C, 40.11; H, 2.96; N, 9.74; Calc. for $AgC_{18}H_{16}N_4O_8Cl$ (559.67) C, 38.63; H, 2.71; N, 10.01. IR Main IR peaks (KBr, cm^{-1}): 3417 (ν (O-H)), 1722 (ν (C31=O)), 1666 (ν (C4a=O)), 1612 (ν $(C=C)_{ketone}$), 1140, 1121, 1091, 627 (ν$(Cl–O)_{perchlorate}$). 13C NMR data (δ, ppm, DMSO-*d*6): 199 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 136 (C33), 123 (C5a), 115 (C32), 28.83 (C1a), 28.56 (C3a), 27.87 (C21).

***Re_2(HPCLMH)$(CO)_6Cl_2$*.(5).** (garnet-red, Λ_M = 2 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 31.32; H, 1.99; N, 6.09; Calc. for $ReC_{12}H_8N_2O_5Cl$ (481.87) C, 29.91; H, 1.67; N, 8.71. Main IR peaks (KBr, cm^{-1}): 3417 (ν (O-H)), 1734 (ν (C31=O)), 1617 (ν $(C=C)_{ketone}$), 2041, 1921, 1090 (ν (C≡ O)). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b)CH_3), 2.67 (3H, s, (3a)CH_3), 3.61 (3H, s, (1a)CH_3), 8.13 (1H, d, C32-H), 8.31 (1H, d, C33-H), 6.86, 7.23, 7.57 (4H, m, C-H_{arom}) and 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 198 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 136 (C33), 123 (C5a), 115 (C32), 28.97 (C1a), 28.39 (C3a), 27.87 (C21).

***Zn(HPCLMH)*Ac_2.(6)**. (dark yellow, Λ_M = 1 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 46.92; H, 3.84; N, 10.09; Calc. for $ZnC_{22}H_{22}N_4O_8$ (535.8) C, 49.31; H, 4.13; N, 10.45. Main IR peaks (KBr, cm^{-1}): 3261 (ν (O-H)), 1717 (ν (C31=O)), 1699 (ν (C2a=O)), 1666 (ν (C4a=O)), 1601 (ν $(C=C)_{ketone}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b)CH_3), 2.67 (3H, s, (3a)CH_3), 3.60 (3H, s, (1a)CH_3), 8.10 (1H, d, C32-H), 8.33 (1H, d, C33-H), 6.83, 7.20, 7.51 (4H, m,

C-H_{arom}) and 10.20 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 199 (C31), 158 (C4a), 150 (C2a), 147 (C6a), 139 (C3b), 28.95 (C1a), 28.37 (C3a), 27.88 (C21).

***Zn_2(HPCLMH)$(SO_4)_2$*.(7).** (green yellow, Λ_M = = 0 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 33.45; H, 2.86; N, 8.12; S, 9.39; Calc. for $ZnC_{18}H_{16}N_4O_8S$ (337.60) C, 32.02; H, 2.39; N, 8.29; S, 9.50. Main IR peaks (KBr, cm^{-1}): 3423 (ν (O-H)), 1717 (ν (C31=O)), 1694 (ν (C2a=O)), 1665 (ν (C4a=O)), 1607 (ν (C=C)$_{ketone}$), 2924, 1115 (ν (SO_4)). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b) CH_3), 2.67 (3H, s, (3a)CH_3), 3.62 (3H, s, (1a)CH_3), 8.11 (1H, d, C32-H), 8.30 (1H, d, C33-H), 6.89, 7.25, 7.58 (4H, m, C-H_{arom}), 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 199 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 136 (C33), 124 (C5a), 28.96 (C1a), 28.30 (C3a), 27.86 (C21).

***Cd(HPCLMH)$(ClO_4)_2$*.(8)**. (dark yellow). Elemental analysis found, C, 32.88; H, 3.47; N, 8.10; Calc. for $CdC_{18}H_{16}N_4O_{12}Cl_2$ (663.7) C, 32.57; H, 2.43; N, 8.44. Main IR peaks (KBr, cm^{-1}): 3449 (ν (O-H)), 1718 (ν (C31=O)), 1665 (ν (C4a=O)), 1610 (ν (C=C)$_{ketone}$), 1140, 1121, 1087, 627 (ν(Cl–O)$_{perchlorate}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.52 (3H, s, (21b)CH_3), 2.67 (3H, s, (3a)CH_3), 3.63 (3H, s, (1a)CH_3), 8.13 (1H, d, C32-H), 8.29 (1H, d, C33-H), 6.89, 7.25, 7.58 (4H, m, C-H_{arom}), 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 199 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 136 (C33), 124 (C5a), 116 (C32), 29 (C1a), 28.41 (C3a), 27.89 (C21).

***Cu(HPCLMH)ClPPh$_3$*.(9).** (clear green, Λ_M =22 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 58.09; H, 4.33; N, 7.46; Calc. for $CuC_{36}H_{31}N_4O_4PCl$ (713.67) C, 60.53; H, 4.38; N, 7.84. Main IR peaks (KBr, cm^{-1}): 3262 (ν (O-H)), 1719 (ν (C31=O)), 1696 (ν (C2a=O)), 1668 (ν (C4a=O)), 1608 (ν (C=C)$_{ketone}$), 3058, 1436, 1097, 524 (ν(PPH_3)). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.52 (3H, s, (21b)CH_3), 2.67 (3H, s, (3a)CH_3), 3.63 (3H, s, (1a)CH_3), 8.13 (1H, d, C32-H), 8.29 (1H, d, C33-H), 6.88, 7.22, 7.55 (4H, m, C-H_{arom}), 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 199 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 136 (C33), 124 (C5a), 116 (C32), 28.86 (C1a), 28.28 (C3a), 27.77 (C21).

***Ag(HPCLMH)(ClO_4)PPh$_3$*.(10).** (green yellow). Elemental analysis found, C, 51.80; H, 3.76; N, 7.76; Calc. for $AgC_{36}H_{31}N_4O_8PCl$ (882.00) C, 52.59; H, 3.80; N, 6.81. Main IR peaks (KBr, cm^{-1}): 3379 (ν (O-H)), 1713 (ν (C31=O)), 1657 (ν (C2a=O)), 1616 (ν (C4a=O)), 1607 (ν (C=C)$_{ketone}$), 3058, 1436, 1097, 522 (ν(PPH_3)), 1176, 1120, 1097, 621 (ν(Cl–O)$_{perchlorate}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.52 (3H, s, (21b)CH_3), 2.67 (3H, s, (3a)CH_3), 3.63 (3H, s, (1a)CH_3), 8.14 (1H, d, C32-H), 8.30 (1H, d, C33-H), 6.88, 7.20, 7.42 (4H, m, C-H_{arom}), 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 199 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 136 (C33), 124 (C5a), 115 (C32), 28.72 (C1a), 28.13 (C3a), 27.28 (C21).

***Ag(HPCLMH)(NO_3)PPh$_3$*.(11).** (dark olive green). Elemental analysis found, C, 53.98; H, 3.92; N, 8.30; Calc. for $AgC_{18}H_{16}N_4O_7N$ (784.55) C, 55.11; H, 3.98; N, 10.01. Main IR peaks (KBr, cm^{-1}): 3260 (ν (O-H)), 1717 (ν (C31=O)), 1693 (ν (C2a=O)), 1665 (ν (C4a=O)), 1606 (ν (C=C)$_{ketone}$), 3934, 1435, 1097, 523 (ν(PPH_3)), 1384 (ν (N–O)$_{nitrate}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b)CH_3), 2.67 (3H, s, (3a)CH_3), 3.63 (3H, s, (1a)CH_3), 8.14 (1H, d, C32-H), 8.30 (1H, d, C33-H), 6.88, 7.22, 7.42 (4H, m, C-H_{arom}), 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 199 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 136 (C33), 124 (C5a), 115 (C32), 28.99 (C1a), 28.40 (C3a), 27.88 (C21).

***Cu_2(HPCLMH)$(ClO_4)_2$PPh$_3$*.(12).** (red-brown, Λ_M = 148 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 46.91; H, 398.98; N, 6.24; Calc. for $Cu_2C_{36}H_{31}N_4O_{12}Cl_2$ (970.33) C, 45.96; H, 3.32; N, 5.95. Main IR peaks (KBr, cm^{-1}): 3442 (ν (O-H)), 1724 (ν (C31=O)), 1631 (ν (C4a=O)), 1606 (ν (C=C)$_{ketone}$), 2924, 1435, 1091, 542 (ν(PPH_3)), 1171, 1120, 1091, 624 (ν(Cl–O)$_{perchlorate}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b)CH_3), 2.63 (3H, s, (3a)CH_3), 3.57 (3H, s, (1a)CH_3), 8.12 (1H, d, C32-H), 8.24 (1H, d, C33-H), 6.88, 7.25, 7.57 (4H, m, C-H_{arom}), 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 198 (C31), 157 (C4a), 155 (C2b), 149 (C2a), 146 (C6a), 138 (C3b), 135 (C33), 125 (C5a), 115 (C32), 27.75 (C1a), 27.18 (C3a), 26.65 (C21).

***Cu_2(HPCLMH)I_2PPh$_3$*.(13).** (red, Λ_M =12 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 43.67; H, 3.21; N, 5.64; Calc. for $CuI(HCALMH)_{1/2}PPh_{1/2}$ (497.78) C, 43.39 ; H, 3.11 ; N, 5.62. Main IR peaks (KBr, cm^{-1}): 3417 (ν (O-H)), 1716 (ν (C31=O)), 1695 (ν (C2a=O)),1667 (ν (C4a=O)), 1607 (ν (C=C)$_{ketone}$), 3058, 1435, 1095, 519 (ν(PPH_3). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.47 (3H, s, (21b)CH_3), 2.70 (3H, s, (3a)CH_3), 3.59 (3H, s, (1a)CH_3), 8.29 (1H, d, C32-H), 8.13 (1H, d, C33-H), 6.88, 7.22, 7.54 (4H, m, C-H_{arom}), 10.18 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 198 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 135 (C33), 123 (C5a), 115 (C32), 28.43 (C1a), 27.48 (C3a), 27.33 (C21).

***Cu_2(HPCLMH)I_2*.(14).** (orange, Λ_M =36 Ω^{-1} cm^2 mol^{-1}). Elemental analysis found, C, 27.13; H, 2.01; N, 6.78; Calc. for $CuIC_9H_8N_2O_2$ (366.63) C, 29.45; H, 2.18; N, 7.63. Main IR peaks (KBr, cm^{-1}): 3415 (ν (O-H)), 1716 (ν (C31=O)), 1693 (ν (C2a=O)),1665 (ν (C4a=O)), 1606 (ν (C=C)$_{ketone}$). 1H NMR data (δ, DMSO-*d*6; Me4Si): 2.49 (3H, s, (21b)CH_3), 2.66 (3H, s, (3a)CH_3), 3.59 (3H, s, (1a)CH_3), 8.24 (1H, d, C32-H), 8.12 (1H, d, C33-H), 6.87, 7.20, 7.52 (4H, m, C-H_{arom}), 10.15 (1H, s, O-H). 13C NMR data (δ, ppm, DMSO-*d*6): 198 (C31), 158 (C4a), 156 (C2b), 150 (C2a), 147 (C6a), 139 (C3b), 135 (C33), 123 (C5a), 115 (C32), 28.43 (C1a), 27.48 (C3a), 27.33 (C21).

RESULTS AND DISCUSSION

Mass spectra

The mass spectrum of HPCLMH (Fig. 1) shows that fragmentation occurs through the lumazine group. The molecular peak detected at *m*/*z* = 352 thus confirms the molecular formula as $C_{18}H_{16}N_4O_4$. We observe the appearance of the $[M+1]^+$ ion at *m*/*z* = 353, a unit higher than the molecular ion, following the capture of a hydrogen atom.[34] The fragmentation of the phenol group ($C_6H_4OH^+$) is found at *m*/*z* = 93.[35] For the remaining fragmentation that can be observed on the spectrum, it is worth noting that the base peak is detected at *m*/*z* = 309, corresponding to the deletion of -CH_3N- group in

the pyrimidine ring after the loss of -CH_3 from the pyrazine ring at *m*/*z* = 338. In addition, we can also affect the complementary pteridine moiety -$CONCH_3$ in the pyrimidine ring at *m*/*z* = 252, followed by the loss of carbon monoxide which reveals a signal around *m*/*z* = 224. The observation of the spectrum at m/z values lower than the loss of carbon monoxide indicates that there are other signals. As a simple hypothesis, we can attribute the resulting fragment to the removal of pyrazine at *m*/*z* = 148 and the one coming from the loss of a -CHCO group at *m*/*z* = 107.

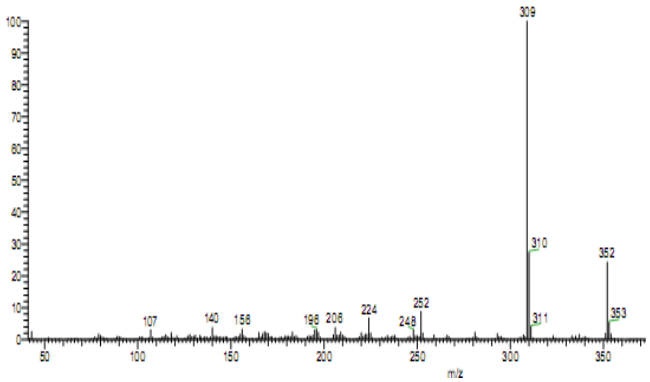


Fig. 1. – Mass spectrum of HPCLMH.

IR studies

The assignments given were established after careful comparative study of the infrared spectra of the complexes and the free ligand and were also made by comparing them with published data.[36–40]

Bands assignable to carbonyl group tension vibrations ν(C31=O), ν(C2a=O) and ν(C4a=O) appearing sharp and intense at 1717, 1694 and 1667 cm^{-1} respectively (Fig. 2). The vibrations corresponding to ν(C2a=O) and ν(C4a=O) remain practically unchanged for all the complexes except for 4, 5, 8 and 10 where they are shifted to a lower wave number from 28 to 77 cm^{-1} for C2a=O and from 51 to 98 cm^{-1} for C4a=O with a long and broad band. For compound 12, we note the of the of the ν(C2a=O) band and the presence of the corresponding C4a=O band at a lower value of 36 cm^{-1}. Nevertheless, the band corresponding to C31=O appears for values higher than 8 to 18 in compounds 4, 5 and 11.

The position of the (C=O) peak depends on the conjugation of the carbonyl group, the substituents, and the possible H-bonds. The displacement of its corresponding vibrations to lower frequencies is perhaps due to a retrodonation effect that causes an increase in conjugation in the chelate ring. This occurs as a result of the transfer of charge from the metal to the ligand, so that the metal electrons also participate in the conjugation a fact that supports the coordination of the ligand through this oxygen atom.[41] The ν(C=N) band is found at 1534 cm^{-1} and the strong coupling between the vibrational activities of C=C and C-N allows to find two bands ν(C = C) + ν(C-N), respectively at 1459, 1294 cm^{-1}. These are lower value than that of the ν(C=C) band which should appear at 1650 cm^{-1}, and remain unchanged for all complexes. A generally broad band associated with the ν(O-H) tension mode of the phenol group appears, for ligand and compounds, between 3260 and 3550 cm^{-1}. This variation, compared to the free ligand, is due to the coordination of the neighbouring atoms and to hydrogen bonds.

For the case of Re(I) and Ir(I) compounds, in the literature, the ν(C≡O) band is observed in the vicinity of 2000 to 1900 cm^{-1}, characteristic of the carbonyl groups bound to the metal ion through the carbon atom.[42] Whereas for compound 5, $Re_2(CO)_6Cl_2L$, this vibration shows a considerable shift and appears at 2041, 1921 and 1901 cm^{-1}. The vibrations of the perchlorate group, for compounds 3, 4, 8, 10 and 12, appear clearly in the spectra and differ notably from the ligand bands. The vibration mode of the perchlorate ions appears divided into three bands between 1148 and 1079 cm^{-1}.[42-43] In the case of compound 7, two bands appear at 2924 and 1115, attributed to the vibration of SO_4^{2-}. Meanwhile, for complex 11, is observed, originating from (NO_3).

For complexes containing (PPh3) groups, four bands are observed at 3050, 1435, 1095, 690 cm^{-1},[44–47] all of which are of high intensity.

This is the case for compounds 9, 10, 11, 12, and 13, where these bands appear without remarkable change. In contrast, the vibration of the (P-M) bond is observed at 519–524 and 501–506 cm^{-1}, with the vibrational frequencies showing shifts indicative of the interaction between the ligand and the metal.[36]

The band shift is a result of coordination process, although it is less noticed in cases where the ligand remains in its molecular form; these shifts are consistent with those found in the literature for similar complexes.[48–51] The ν(M-Cl) and ν(M-I) bands appear in an area below 400 cm^{-1}, which is not covered by our spectra.

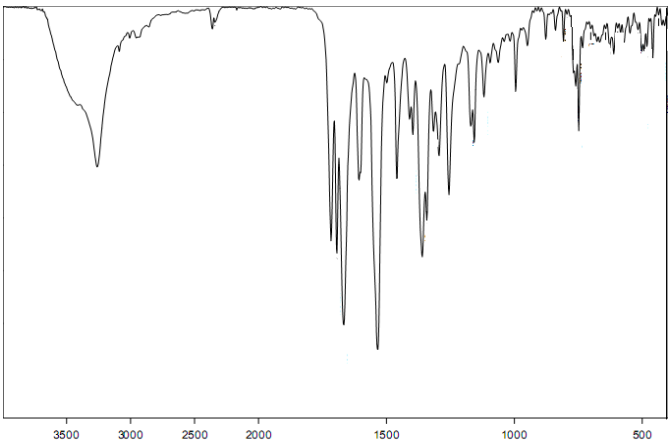


Fig. 2. – Infrared spectrum of HPCLMH.

^{1}H-NMR and ^{13}C-NMR Spectra

The ^{1}H-NMR spectrum of the ligand represents a broad singlet signal at 10.15 ppm, attributed to presence of one (–OH) group. Due to the two different substituents of the aromatic ring, the four protons of the latter are not isochronous, yielding a multiple between 6.88 and 7.51 ppm. The olefinic proton of α, β unsaturated ketone were distinctly observed, as a double doublet, at 8.12 and 8.26 ppm, corresponding to C32-H and C33-H, respectively. Three singlet signals resonating at 2.49, 3.29, and 3.60 ppm are attributed respectively to the three methyl protons. Moreover, it was difficult to allocate the signals of the quaternary carbons of pteridine through a simple analysis of the 13C-NMR spectrum. The study was completed with DEPT, COSY, HSQC and HMBC techniques. The initial attributions, without any ambiguity, were for the methyl carbons of pteridine C1a, C3a, C21b and the carbons of the double bond C32 and C33 which give rise to a positive signal in DEPT spectrum. In addition, the quaternary carbons were studied using HMBC ^{1}H-^{13}C. The most unshielded signal corresponding to carbon C31, correlated with the hydrogens of C33, appears at 199 ppm, while signals 116 and 136 ppm were unambiguously assigned to C32 and C33. C2a correlates with the protons of carbons C1a and C3a and its signal appears at 150 ppm, whereas the signal of carbon C4a is observed at a lower field, 158 ppm, correlated with the hydrogens of methyl C3a. Similarly, the C3b signal is correlated with the hydrogens of C32 and C21b, appearing particularly shielded at 139 ppm; however, this value is similar to existing data in the literature.[52–53]

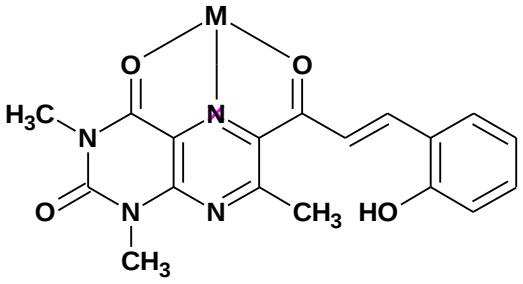
In general, a comparative study of the ^{13}C-NMR spectra of the metal complexes with that of the free ligand does not show appreciable variations, except for a few complexes, possibly due to the dissociation of these compounds in the solvent (DMSO-d6) used for the realization of ^{13}C-NMR spectra.[54] As an example, the ^{13}C-NMR spectrum of compound 12 shows a shift at all carbons except C6a, C3b and C5a and C33. The presence of new peaks between 135–127 ppm attributable to the aromatic carbons of the PPh_3, is also remarkable. This leads us to think of a possible coordination by atoms O31, N4b, O2a and O4a. Even this possible coordination to the metal via the O2a, atom could be deduced since this atom participates in the formation of hydrogen bonds in the free ligand, as observed in its X-ray structure of similar complexes.

Structural conclusions

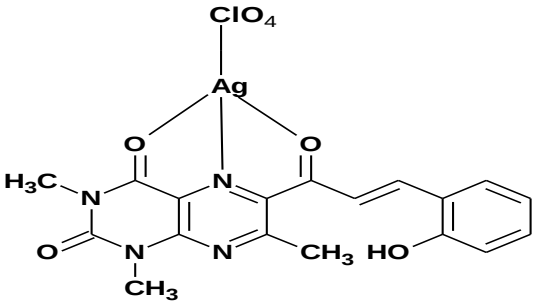
The slow crystallization did not result in any

single crystal, of the ligand or its complexes, and therefore no definitive structure has been described. However, considering the spectral data presented in this work and those collected from the literature for analogous compounds,[38,55–59] three different behaviors can be proposed for the PHCLMH ligand namely, a tridentate, bidentate or monodentate coordination via the O4a, N4b and O31 atoms around the metal ion. The remaining metal coordination positions would be occupied by a acetate, perchlorate or other anion as appropriate, which can be justified by infrared and NMR spectroscopic studies, in which we found a shift in the position of νas(COO), *νs* (COO) and the signal corresponding to C5a and C31. Complexes containing bidentate perchlorate groups generally exhibit four infrared bands, while, when the ν(Cl-O) vibrational mode is split into two bands, which is in agreement with the loss of T_d geometry of free perchlorate ions. This split may be caused by hydrogen bonding or coordination of the perchlorate group to the metal ion in a monodentate form.[32–33] Consequently, according to the obtained results, the following suggestions about the structure of some complexes could be made.

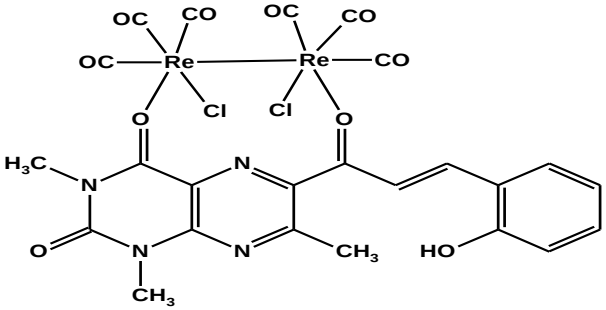
On the other hand, for complexes 1 and 4, CuClL and, $Ag(ClO_4)L$ respectively, the coordination to the metal is established by the atoms O4a, N4b and O31 and the anion. The geometry to be expected would be tetrahedral (Scheme 4). Finally, for the compound $Re_2(CO)_3ClL$ (Scheme 5), we can expect an octahedral coordination in which three face positions are occupied by the three carbonyl ligands and the fourth coordination position is occupied by the chloride ion. The TSCLMH ligand will likely behave in a bidentate manner, where the two Re atoms are each bonded to an oxygen atom of the same ligand, O4a and O31.



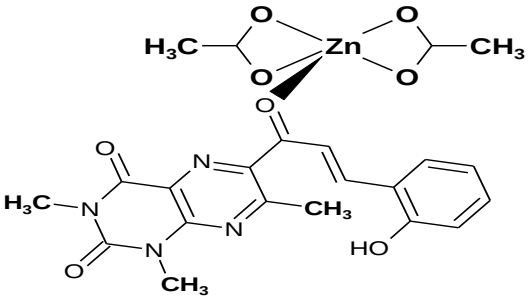
Scheme 3. – Possible tridentate behavior of the PHCLMH ligand.



Scheme 4. – Tridentate coordination in the $Ag(ClO_4)$(HPCLMH) complex.



Scheme 5. – Possible geometry of the compound $Re_2(CO)_3Cl$(HPCLMH).



Scheme 6. – Predicted geometry for the $ZnAc_2$(HPCLMH) complex.

CONCLUSION

In summary, a new pteridine derivative and its metal complexes were synthesized and characterized using various techniques to obtain information on the obtained compounds. The stoichiometry and composition of the organic ligand and its metal complexes are fully supported by elemental analysis, conductivity measurements, and mass spectrometry, while IR and NMR spectra data confirmed their binding characteristics. We can well suggest that the coordination of the ligand occurs through the O4a and N4b atoms of the pteridine, as it is usual for this type of compound and the O31 atom of the keto-ethylene group. Therefore, we can propose four different behaviors for this ligand: a tridentate (O4a, N4b and O31), bidentate (O4a,

N4b) (N4b, O31) and even monodentate coordination around the metal ion.

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