Polyhedron 50 (2013) 10–15

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Re(I) and Ag(I) complexes containing the polydentate symmetric diazine derived from 6-acetyl-1,3,7-trimethylpteridine-2,4(1*H*,3*H*)-dione in two different binuclear modes

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ARTICLE INFO

Article history:
Received 18 June 2012
Accepted 5 October 2012
Available online 2 November 2012

Keywords:
Azines
Crystal structure
Pteridines
Rhenium complexes
Silver complexes

ABSTRACT

The symmetric diazine derived from 6-acetyl-1,3,7-trimethylpteridine-2,4(1*H*,3*H*)-dione, (6,6′,1,1′-(hydrazine-1,2-diylidene) *bis* (ethan-1-yl-1-ylidene) *bis* (1,3,7-trimethylpteridine-2,4(1*H*,3*H*)-dione), DHzD) has been prepared and reacted with $ReCl(CO)_5$ and $AgClO_4$ to give binuclear complexes with formula $[Re_2Cl_2(CO)_6(DHzD)]\cdot 2CH_3CN$ and $[Ag_2(DHzD)_2](ClO_4)_2\cdot 7H_2O$. The XRD single-crystal results indicate two quite different binuclear modes depending on the number of ligands and the counteranion coordinative capacities. Thus, the dirhenium complex consists in two *fac*-$ReCl(CO)_3^+$ units attached to the N5–O4 bidentate sites from both pteridine moieties of the *Z,Z*′ isomer of the ligand (Re–O, 2.185(5) and Re–N5, 2.225(6) Å). The disilver complex displays two crystallographically independent but practically equivalent 3 + 3-coordinated silver centers to N61, N5 and O4 atoms from both DHzD ligands (*E,E*′ isomer); distances Ag–N range between 2.31 and 2.48 Å, whereas oxygen atoms are weaker bonded (2.65–2.82 Å). In the molecular units there are not M–M bonds, both metal atoms lying farther than the sum of Van der Waals' radii (Re–Re, 7.959(5) Å; Ag–Ag, 4.073(5) Å).

1. Introduction

Diazines, N–N linked diimines, exhibit a number of interesting properties from both biological and technological points of view; thus, they have recently attracted growing attention due to their activity as anticonvulsant, antidepressant, antiinflammatory, antiviral or antitumor agents [1], the design of liquid crystals [2,3], as non-linear optical materials [4,5], their utility as sensors for several metal ions [6–8] and their luminescent properties [9]. The flexibility of these ligands around the N–N single bond offers several possible mono- and binuclear binding modes which can give rise complexes having different geometries [10–18]. Most of the diazine ligands are symmetric and the bis-Schiff bases derived from hydrazine are one of the most important families of organic molecules designed for the assembly of helicates [13,15,16] or intercalating ligands to achieve site-specific DNA recognition [12].

Only a paper focused on the structural data of metal-containing Schiff bases diazines derived from 6-acetyllumazines has been previously reported [19]; in this paper, a number of asymmetric diazine ligands derived from 6-acetyl-1,3,7-trimethylpteridine-2,4(1*H*,3*H*)-dione and either hydrazine or several aromatic aldehydes and their Re(I) complexes were isolated and characterized. Different metal–ligand binding modes were found depending on the potential donor atoms supplied by the aldehyde moiety. The study of the effects of the compounds on the growth of several human tumor cell lines suggested a modulator behaviour, according to the concentration, of cell growth due to the estrogen-like characteristics of the compounds. Furthermore, in this paper, the possibility of isolation of symmetric diazines controlling the aldehyde/hydrazine stoichiometric ratio in the synthetic method was also pointed out. Now, the present paper is devoted to report the synthesis and structural study of the symmetric diazine (hereafter denoted as DHzD, Fig. 1) and its Re(I) and Ag(I) compounds, which, in accordance with the molecular structure of the ligand and the flexibility around the –C = N–N = C– segment bridging both pteridine moieties, are dinuclear complexes, but showing different metal-binding patterns as function of the stoichiometry of the reaction and the coordinative capacities of the counteranions used.

2. Experimental

2.1. Materials and instrumentation

The metallic sources $ReCl(CO)_5$ and $Ag(ClO_4)_2\cdot H_2O$, the organic reactants and solvents are commercially available and were used without purification. Microanalyses were carried out with a Ther-

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http://dx.doi.org/10.1016/j.poly.2012.10.033

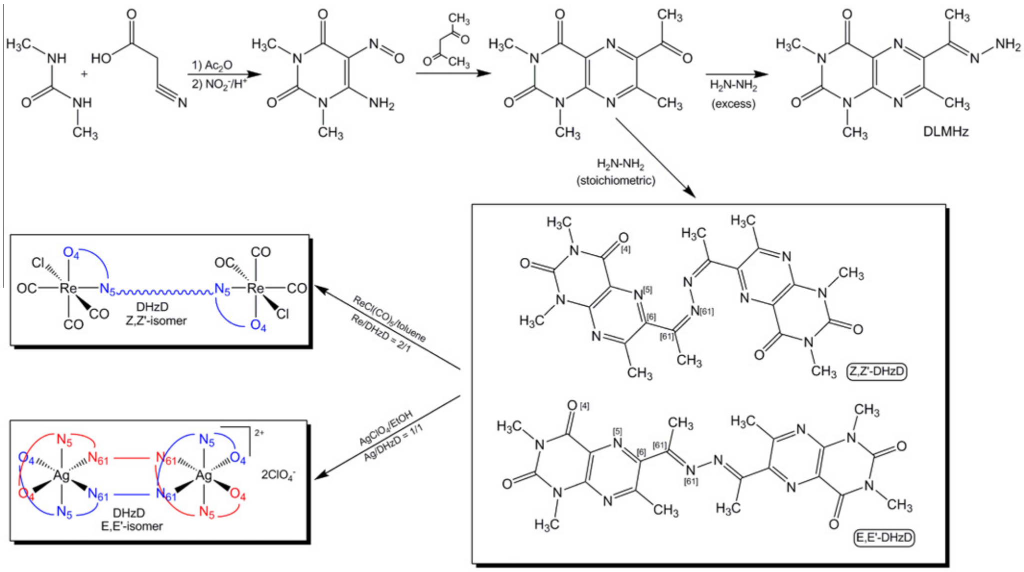

Fig. 1. Synthesis of the DHzD symmetric diazine and the Re(I) and Ag(I) dinuclear compounds. In the free ligand, significant atoms are labelled.

mo Finnigan Flash EA 1112. Mass spectrum of the ligand DHzD was run on a Thermo DSQ II spectrometer equipped with a direct inlet probe, operating at 70 eV. The ESI-MS (electrospray ionization mass spectrometry) spectra of the complexes were recorded in an ion-trap mass spectrometer Esquire 6000 Bruker Daltonics equipped with an electrospray interface operating in positive ion mode (4000 V) in the range m/z 50–3000; the samples were dissolved in methanol and analyzed by direct injection. The IR spectra were recorded on a IR Bruker Tensor 27 apparatus (KBr pellet, 4000–400 cm^{-1}). ^{1}H and ^{13}C NMR spectra of the ligand were recorded on a Bruker DPX-400 instrument in CDCl$_3$ and DMSO-d$_6$ at room temperature. For the complexes, the solubility in CDCl$_3$ and DMSO-d$_6$ is not too high and the NMR experiments were made at room temperature and 120 °C. Only the ^{1}H NMR spectra in CDCl$_3$ show quality enough to make some assignments, whereas the ^{13}C NMR spectra of the complexes show no clear resonances; then, reported data were obtained by simulation on a ^{1}H/^{13}C HMBC-custom (heteronuclear multiple bond correlation) experiment.

2.2. Synthesis of the ligand and complexes

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

The synthetic pathway used to isolate the symmetric diazine DHzD used as ligand is briefly outlined in the Fig. 1.

Ligand: the proligand 6-acetyl-1,3,7-trimethyllumazine (DLMAceM) was synthesized from 6-amino-1,3-dimethyl-5-nitrosouracil and acetylacetone following a reported method [20]. The title symmetric diazine (hereafter denoted as DHzD) was prepared by reacting dropwise an ethanolic solution (5 mL) of hydrazine monohydrate (5 mmol) with the lumazine derivative (DLMAceM) (10 mmol) in ethanol (25 mL). Acetic acid was used as catalyst (*ca.* 1 mL). The mixture was refluxed for 5 h until the yellow product precipitates. Note that hydrazine must be added in stoichiometric ratio, not in excess, to avoid the appearance of the previously reported azine DLMHz [19] containing only one pteridine moiety. The ligand was filtered off and recrystallized in CH$_2$Cl$_2$ (yield *ca.* 75%). *Anal.* Calc. for $C_{22}H_{24}N_{10}O_4{\cdot}2CH_2Cl_2$ (M = 660.10): C, 43.52; H, 4.26; N, 21.15. Found C, 43.65; H, 4.40; N, 21.18%. MS (m/z, abundance): 492, 5%; 247, 20%; 246, 100%; 206, 5%; 177, 3%; 146, 4%; 107, 11%. IR bands (cm^{-1}): 1723vs, 1676vs, 1555vs, 1487s, 1456m, 1403w, 1373m, 1348m, 1287m, 1260m, 1228m, 1119m, 1053w, 1033w, 1008w, 969w, 810w, 750m. ^{13}C NMR (CDCl$_3$; δ, ppm): 158.4 (C4), 157.3 (C7), 156.7 (C2), 149.3 (C6), 144.6 (C8A), 144.1 (C61), 122.2 (C4A), 27.8 (C1), 27.4 (C3), 24.4 (C71), 15.0 (C62). ^{1}H NMR (CDCl$_3$; δ, ppm): 3.75 (s, 3H, N1–CH$_3$), 3.55 (s, 3H, N3–CH$_3$), 3.02 (s, 3H, C7–CH$_3$), 2.45 (s, 3H, C61–CH$_3$).

[Re$_2$Cl$_2$(CO)$_6$(DHzD)]: ReCl(CO)$_5$ (0.5 mmol) and DHzD (0.25 mmol) were put into a flask containing hot toluene (20 mL) and refluxed for 12 h; a orange powdered compound was isolated (yield referred to DHzD, *ca.* 35%). *Anal.* Calc. for $C_{14}H_{12}ClN_5O_5Re$ (M = 551.93): C, 30.47; H, 2.19; N, 12.69. Found: C, 30.21; H, 2.14; N, 12.24%. ESI-MS (m/z, abundance): 1127, 18%; 821, 100%; 515, 45%. IR bands (cm^{-1}): 2032vs, 1919vs, 1899vs, 1731s, 1680s, 1561s, 1532m, 1451w, 1398w, 1374w, 1300w, 1246w, 1190w, 1139w, 1082w, 1007w, 807w, 748w. ^{13}C NMR (CDCl$_3$; δ, ppm): 171.3 (C4), 165.9 (C7), 163.4 (C61), 149.3 (C6), 148.4 (C2). ^{1}H NMR (CDCl$_3$; δ, ppm): 3.83 (s, 3H, N1–CH$_3$), 3.71 (s, 3H, N3–CH$_3$), 2.86 (s, 3H, C7–CH$_3$), 2.53 (s, 3H, C61–CH$_3$). The recrystallization from acetonitrile afforded red crystals of $[Re_2Cl_2(CO)_6(DHzD)]{\cdot}2CH_3CN$.

[Ag$_2$(DHzD)$_2$](ClO$_4$)$_2$: AgClO$_4$·H$_2$O (0.25 mmol) and DHzD (0.25 mmol) were refluxed in hot EtOH (20 mL) during 24 h; a yellow solid precipitates (yield referred to DHzD, *ca.* 55%). *Anal.* Calc. for $C_{22}H_{24}ClN_{10}O_8Ag$ (M = 699.81): C, 37.76; H, 3.46; N, 20.02. Found: C, 37.87; H, 3.45; N, 20.23%. ESI-MS (m/z, abundance): 599, 85%; 393, 100%; 260, 55%. IR bands (cm^{-1}): 1722s, 1678vs, 1553s, 1489m, 1456w, 1406w, 1373w, 1348m, 1288w, 1260w, 1231w, 1142m, 1120s, 1086m, 952w, 809w, 749w. ^{13}C NMR (CDCl$_3$; δ, ppm): 164.9 (C7), 160.1 (C61), 150.2 (C2), 142.2 (C6), 29.8 (C1), 29.3 (C3), 25.3 (C71), 20.0 (C62). ^{1}H NMR (CDCl$_3$; δ, ppm): 3.73 (s, 3H, N1–CH$_3$), 3.41 (s, 3H, N3–CH$_3$), 2.87 (s, 3H, C7–CH$_3$), 2.62 (s, 3H, C61–CH$_3$). Some days later, from the mother liquor, orange crystals of the compound $[Ag_2(DHzD)_2(ClO_4)_2]{\cdot}7H_2O$ can be isolated.

2.3. XRD experimental details

Details of the crystallographic data collection and refinement parameters are given in Table 1. The structures were solved by direct methods and refined using SHELXL97 program inside the WINGX package employing full-matrix least-squares methods on F^2 [21,22]. Lorentz, polarization and multi-scan absorption corrections

Table 1
Crystallographic and refinement data.

Compound	$Re_2Cl_2(CO)_6(DHzD){\cdot}2CH_3CN$	$Ag_2(DHzD)_2(ClO_4)_2{\cdot}7H_2O$
CCDC number	885224	885223
Empirical formula	$C_{32}H_{24}Cl_2N_{12}O_{10}Re_2$	$C_{44}H_{48}Cl_2N_{20}O_{23}Ag_2$
Formula weight (g mol^{-1})	1179.93	1511.66
Color, habit	red prism	orange prism
Crystal size (mm)	0.42 × 0.38 × 0.02	0.26 × 0.20 × 0.14
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/c$
Unit cell dimensions		
a (Å)	11.856(2)	26.156(2)
b (Å)	27.069(6)	14.785(5)
c (Å)	12.291(1)	15.895(3)
β (°)	90	101.130(8)
Volume (Å^3)	3944(1)	6031(2)
Z	4	4
D_{calc} Mg m^{-3})	1.987	1.655
Absorption coefficient (mm^{-1})	6.338	0.832
F(000)	2256	3056
Diffractometer	Bruker Nonius Kappa CCD	
Radiation	Graphite-monochromated Mo Kα (λ = 0.71073 Å)	
Temperature (K)	120(2)	120(2)
θ_{range} (°)	2.50 to 27.50	5.01 to 27.54
Index ranges	$-12 \leqslant h \leqslant 15$	$-33 \leqslant h \leqslant 33$
	$-35 \leqslant k \leqslant 34$	$-19 \leqslant k \leqslant 19$
	$-12 \leqslant l \leqslant 15$	$-20 \leqslant l \leqslant 20$
Reflections collected/independent reflections/$I > 2\sigma(I)$	42892/4525/2935	82491/13752/9470
R_{int}	0.0856	0.0865
Weighting scheme ($P = (F_o^2 + 2F_c^2)/3$)		
$w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$	$x = 0.0634/y = 24.0423$	$x = 0.0585/y = 62.9737$
Data/restraints/parameters	4525/0/257	13752/0/787
Goodness-of-fit on F^2	1.050	1.069
Final *R* indices [$I > 2\ (I)$] *R*/*wR*	0.0479/0.0919	0.0826/0.1861
R indices (all data) *R*/*wR*	0.1135/0.1353	0.1227/0.2098
Largest difference peak and hole (e Å^{-3})	3.395 and −1.802	2.089 and −1.359

were applied with SADABS [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms from methyl groups were put at calculated ideal positions following riding models. For the Ag compound, the final Fourier map shows eight main free peaks which were assigned to oxygen atoms from disordered water molecules. Graphics and calculations were performed with MERCURY [24] and PLATON [25].

3. Results and discussion

3.1. Synthesis

The reactions carried out to obtain the symmetric diazine DHzD and the Re(I) and Ag(I) complexes are depicted in the Fig. 1. The synthesis of the ligand was already somehow mentioned in a previous paper [19]; in the last step, it is a conventional carbonyl-primary amine condensation to afford the corresponding azomethine C═N bond. As the aim is to isolate the symmetric diazine, the use of a hydrazine/DLMAceM ratio near but slightly lower than 1/2 should be stressed. In view of the obtained results on preparing the metal complexes, it is clear that the DHzD is not isolated in a pure isomeric form. Therefore, it should be noted that the yields obtained in the synthesis of the complexes are limited by the both isomers abundance (*Z*,*Z*′ and *E*,*E*′) in the isolated product; in this way, the found yield for the Ag(I) compound (55%) is bigger than the Re(I) one (35%), in accordance with the lower steric impediments to build the E isomer if compared with the Z ones.

On the other hand, the structural results clearly reflect the influence of the used metallic starting material, the metal/ligand ratio for such synthesis as well as the higher coordinative capacity of the chloride if compared with the perchlorate counteranions. In this way, Ag(I) ions make available to the DHzD ligand their full coordinative capacity, perchlorate anions leaving outside the coordination sphere. By contrast, the presence in the starting Re(I) material of the very stable *fac*-$ReCl(CO)_3^+$ moiety leaves in the Re(I) only two *cis* unsaturated coordinative sites that are occupied by two pairs of donor atoms N5,O4 from bidentate lumazine fragments, which probably provides the sterically more favorable structural solution to the system.

3.2. Spectroscopy

The analytical and spectral data of the free ligand are in accordance with the structure found in the title metal complexes. Mass spectrum shows the signal at $m/z = 492$ assignable to the molecular peak (M^+); the peak at $m/z = 246$ corresponds just to a half of the initial molecule $(M/2)^+$, broken through the N–N bond and, finally, the fragment at $m/z = 206$ may be assignable to the loss of the substituent in 6 position $(M/2\text{-}C(CH_3)N)^+$. The IR bands and NMR signals are in accordance with those published for related compounds [19,26].

ESI-MS spectrum of the Re(I) compounds shows the molecular peak at $m/z = 1127$ assignable to $(M + Na)^+$; other important peaks at $m/z = 821$ and 515 are assignable to the successive loss of two $ReCl(CO)_3^+$ fragments. In the spectrum of the Ag(I) compound, the molecular peak corresponding to the dimeric $[Ag_2(DHzD)_2]^{2+}$ cation does not appear and only the peak at $m/z = 599$ can be assigned to the monomer $(DHzD + Ag)^+$.

The tentative assignment of the infrared bands is not easy due to large number of bands shown in the spectrum of the ligand. Thus, upon complexation, some shifts are found in the stretching carbonyl range, two bands between 1730 and 1675 cm^{-1} due to the combination of ν(C2═O2) and ν(C4═O4) modes. The strong bands at *ca.* 1490–1560 cm^{-1} may be assigned to ν(C═N) vibration and a set of bands of medium-to-weak intensity ranging from 1460 to 1200 cm^{-1} are due to ν(C=C) + ν(C–N) mode. The vibrations ν(C=N–N=C) cannot be clearly identified because they are hidden by the C=O and C=N stretching vibrations (*ca.* 1600 cm^{-1}); due to the electronic delocalization with adjacent C=N double bonds, bands due to ν(N–N) vibrations become shifted to higher wavenumber than expected for a simple N–N bond (900–1000 cm^{-1}) and cannot be safely identified due to their weakness and the existence of bands assignable to ν(C=C) and ν(C–N). Finally, as typical features, three very strong bands (2032–1899 cm^{-1}) in the Re(I) spectrum from the *fac*-$Re(CO)_3^+$ moiety and a set of medium-to-strong bands (*ca.* 1120 cm^{-1}) in the Ag(I) spectrum due to the presence of free perchlorate anions can be cited.

More detailed information about the structure of ligand is provided by a series of 1D and 2D NMR experiments and specific assignments of protons and carbons are given in the experimental section. As it has been indicated in the Experimental part, the complexes are very soluble in neither $CDCl_3$ nor DMSO-d_6 and only spectra in $CDCl_3$ show quality enough to make some assignments. The signals for the protons C61–CH_3 and C7–CH_3 were shifted as consequence of the coordination from 2.45 and 3.02 in the ligand to 2.53 and 2.86 ppm in the Re(I) complex and 2.62 and 2.87 ppm in the Ag(I) complex. In the ^{13}C NMR spectrum of the free ligand, the signals at 144.1 ppm and 157.3 ppm were assigned to the C61 and C7 atoms, respectively. In the ^{13}C NMR spectra of the complexes, no resonances were found; for this reason, the reported data were obtained by simulation on a $^{1}H/^{13}C$ HMBC-custom spectrum. Although a general deshielding is observed, the main spectral change is found for the C61 signal which is downfield shifted to 163.4 ppm in the Re(I) complex and 160.1 ppm in the Ag(I) complex due to the coordination.

3.3. Structure of Re(I) and Ag(I) complexes

The molecular units of the title complexes are shown in Figs. 2 and 3. Distances and angles around the metal ions are given in Table 2.

The structure of the rhenium complex (Fig. 2) consists in centrosymmetric dinuclear units in which two *fac*-$ReCl(CO)_3$ fragments are attached in both N5,O4-bidentate cavities of the DHzD ligand (*Z*,*Z*′ isomer). To get this, the organic ligand rotates around the C6-C61 bond until the mean plane of each lumazine moiety becomes perpendicular to the azine bridge (C6–C61 = N61–N61′ = C61′–C6′) one. Then, both pteridine planes are parallel and distanced by 3.359 Å, but they cannot establish intramolecular π-stacking interactions because the mutual conformation of pteridine residues left as closest to both pyrazine rings with their centroids lying *ca.* 7 Å to each other; in the same way, the Re–Re distance is 7.959(5) Å. Consequently, the dimetallic molecule behaves as two independent octahedral $ReCl(CO)_3$(N5,O4-pteridine) centers linked by the diazine bridge.

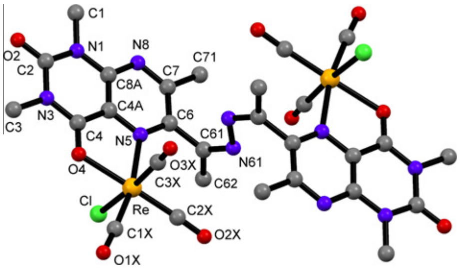

Fig. 2. Labelled ball-and-stick drawing for $[Re_2Cl_2(CO)_6(DHzD)]$ (hydrogen atoms and solvent molecules are omitted for clarity).

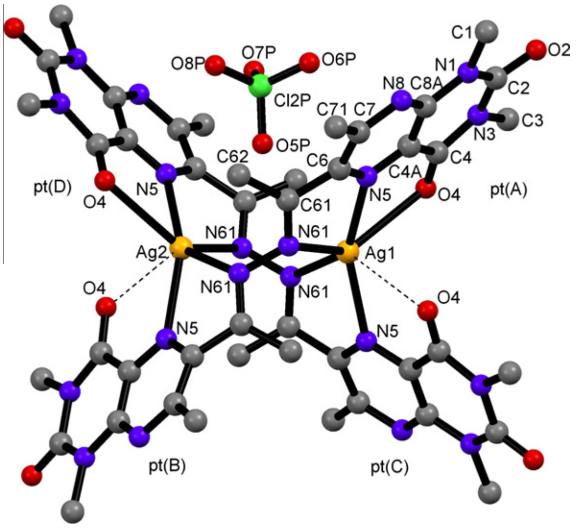

Fig. 3. Ball-and-stick picture for $[Ag_2(DHzD)_2]^{2+}$ unit, showing only the encapsulated perchlorate anion (the other perchlorate anion, hydrogen atoms and solvent molecules are omitted for clarity). The two DHzD ligands are built as *pte*(A) = N–N = *pte*(B) and *pte*(C) = N–N = *pte*(D). Atoms are labelled as *pte*(A) followed by the *pte*(X) corresponding letter.

Table 2
Bond lengths (Å) and angles (°) around the metal center.

$[Re_2Cl_2(CO)_6(DHzD)]$			
Re–C2X	1.892(9)	Re–O4	2.185(5)
Re–C1X	1.922(9)	Re–N5	2.225(6)
Re–C3X	1.971(9)	Re–Cl	2.448(3)
C2X–Re–C1X	87.7(4)	C3X–Re–N5	91.0(3)
C2X–Re–C3X	90.4(4)	O4–Re–N5	75.9(2)
C1X–Re–C3X	89.9(4)	C2X–Re–Cl	92.7(3)
C2X–Re–O4	177.8(3)	C1X–Re–Cl	93.8(3)
C1X–Re–O4	92.7(3)	C3X–Re–Cl	175.3(3)
C3X–Re–O4	91.8(3)	O4–Re–Cl	85.1(1)
C2X–Re–N5	103.7(3)	N5–Re–Cl	84.9(2)
C1X–Re–N5	168.6(3)		
$[Ag_2(DHzD)_2](ClO_4)_2$			
Ag1–N5A	2.323(6)	Ag2–N5D	2.310(5)
Ag1–N5C	2.371(6)	Ag2–N5B	2.348(6)
Ag1–N61C	2.374(5)	Ag2–N61B	2.391(6)
Ag1–N61A	2.453(6)	Ag2–N61D	2.479(6)
Ag1–O4A	2.649(6)	Ag2–O4D	2.656(6)
Ag1–O4C	2.816(6)	Ag2–O4B	2.791(6)
N5A–Ag1–N5C	151.9(2)	N5D–Ag2–N5B	152.5(2)
N5A–Ag1–N61C	140.0(2)	N5D–Ag2–N61B	139.0(2)
N5C–Ag1–N61C	67.8(2)	N5B–Ag2–N61B	68.3(2)
N5A–Ag1–N61A	66.6(2)	N5D–Ag2–N61D	67.3(2)
N5C–Ag1–N61A	115.9(2)	N5B–Ag2–N61D	108.6(2)
N61C–Ag1–N61A	106.9(2)	N61B–Ag2–N61D	105.1(2)
O4A–Ag1–N5A	66.5(2)	O4D–Ag2–N5D	67.0(2)
O4A–Ag1–N5C	106.3(2)	O4D–Ag2–N5B	112.3(2)
O4A–Ag1–N61C	107.2(2)	O4D–Ag2–N61B	108.2(2)
O4A–Ag1–N61A	133.1(2)	O4D–Ag2–N61D	134.2(2)
O4A–Ag1–O4C	88.8(2)	O4D–Ag2–O4B	92.7(2)
O4C–Ag1–N5A	88.7(2)	O4B–Ag2–N5D	88.6(2)
O4C–Ag1–N5C	63.5(2)	O4B–Ag2–N5B	63.9(2)
O4C–Ag1–N61C	131.3(2)	O4B–Ag2–N61B	132.2(2)
O4C–Ag1–N61A	92.1(2)	O4B–Ag2–N61D	87.5(2)

The geometry around the Re atoms are practically octahedral with the sterical restraints imposed by the *bite* O4–Re–N5 angle of the pteridine (75.9(2)°) which is quite far from the ideal 90° expected for a regular octahedron. The metal–ligand distances are in the ranges reported for Re–Cl (2.47 ± 0.02 Å), Re–N (2.18 ± 0.04 Å) and Re–O (2.18 ± 0.01 Å) distances in eight related mononuclear Re(I) compounds [19,27–29].

The structure of the silver compound (Fig. 3) also consists in dinuclear units, but due to the 1:1 M/L ratio employed in the synthesis and the low coordinative ability of the perchlorate counteranions, two Ag(I) ions are binucleated by two ligands (*E,E′* isomer). The whole set is arranged around a central Ag1–N61C–N61D–Ag2–N61B–N61A six-membered boat-shaped ring, the prow and poop sites being occupied by N61B and N61C atoms. Each metal ion is chelated by two tridentate N61,N5,O4-pteridine moieties, from different DHzD ligands, in a roughly perpendicular *mer*-conformation. In the dinuclear unit, the silver atoms are almost equivalent, being surrounded by four nitrogen atoms at 2.31–2.48 Å and two oxygens quite longer distanced at 2.64–2.82 Å (see Table 2), but shorter than the sum of the Van der Waals' radii (3.24 Å); the long Ag–O bonds are consistent with those found for other complexes of metals of the first and second transition rows [30,31]. Although the Ag(I) centers are nearer than in the Re(I) compound, the Ag1–Ag2 distance (4.073(5) Å) is longer than the sum of Van der Waals' radii (3.44 Å), thus preventing the existence of M–M bonds. Therefore, as in the Re(I) complex, the disilver unit also behaves as two independent 5 + 1-coordinated centers mutually assembled by two N61–N61 azine groups.

A closest view of the coordination environment around the silver atoms is shown in the Fig. 4. Both polyhedra are really distorted and can be described as square-based pyramids with one farther oxygen atom (O4C and O4B) capping the *quasi*-planar N61A–N5A–N5C–O4A (Ag1) and N61D–N5D–N5B–O4D (Ag2) faces. The analysis of five-coordination following Holmes [32] indicates that the pivot atoms that best describe a Berry pseudo-rotation are N61C (Ag1) and N61B (Ag2); in both polyhedra, the percentage along Berry pseudorotation coordinate D_{3h}(TBP) → C_{2v} → C_{4v}(SP) being *ca.* 54%, which indicates a just intermediate geometry between the extreme shapes. Furthermore, the Addison's τ parameter [33] (Ag1, $\tau = 0.20$; Ag2, $\tau = 0.22$) describes a more tetragonalized nearer-to-SP shape for both coordination polyhedra.

In both cases, the geometry of the pteridine moieties are in according with bibliographic data [19,21,30,31], although it is noteworthy that, in the Ag(I) compound, the endocyclic C4═O4 carbonyl groups are slightly shorter than in most of the examples previously reported. Also, the distances in the azine bridge (C6–C61, *ca.* 1.48 Å; C61═N61, *ca.* 1.26–1.29 Å; N61–N61′, *ca.* 1.39 Å) clearly denote only a little electron delocalization due to the lack of coplanarity between the bridge and the pteridine cores, the N5–C6–C61–N61 dihedral angles being about 90° (Re) and 33° (Ag).

Data for intermolecular interactions, calculated by means of PLATON [25] and examined following the criteria reported by Janiak [34], are given in Table 3. In the crystal structure of Re compound, the molecules are placed with the pteridine planes normal to the [$\bar{1}$02] direction. There are no classical H-bonds and the molecules interact to each others mainly through C2X–O2X···pyz ($\frac{1}{2} + x, y, {}^3/_2 - z$) interactions, whereas the acetonitrile molecules occupy the solvent accesible voids of the cell in a *quasi*-perpendicular C–C≡N···pym arrangement.

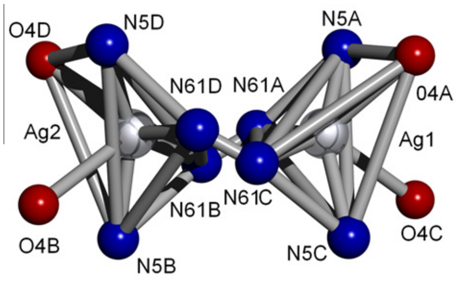

Fig. 4. Detailed view of the coordination polyhedra on the $[Ag_2(DHzD)_2]^{2+}$ cation. Dihedral angles: N61D–N5D–N5B–O4D, 163.5(7)°; N61A–N5A–N5C–O4A, 162.6(8)°.

Table 3
Geometrical details of Y–X anion···ring interactions.

	d(X···Cg) (Å)	δ (°)	∠Y–X···Cg (°)
$[Re_2Cl_2(CO)_6(DHzD)]$			
C2X–O2X···pyz ($\frac{1}{2} + x, y, {}^3/_2 - z$)	3.087(7)	14.1	110.4(5)
C1S–N1S···pym	2.924(9)	4.0	103.6(8)
$[Ag_2(DHzD)_2](ClO_4)_2$			
C2B–O2B···pymD ($2 - x, -y, 1 - z$)	3.076(8)	24.5	153.3(6)
C2C–O2C···pymA ($1 - x, -y, 1 - z$)	2.711(7)	8.8	173.5(6)
C2D–O2D···pymB ($2 - \times, \frac{1}{2} + y, {}^3/_2 - z$)	2.899(7)	18.6	157.7(6)
Cl1P–O3P···pyzB ($x, 1 + y, z$)	3.096(9)	15.0	109.1(5)
Cl1P–O3P···pyzC ($x, 1 + y, z$)	3.461(9)	25.5	101.9(5)
Cl1P–O4···pyzB ($x, 1 + y, z$)	3.432(9)	26.0	94.2(4)
Cl2P–O6P···pyzA	3.090(7)	9.0	117.2(3)
Cl2P–O7P···pyzD	3.045(6)	13.5	104.2(3)
Cl2P–O8P···chel2D	3.520(7)	18.7	90.3(3)
Cl2P–O8P···pymD	3.598(6)	20.3	111.6(3)
Cl2P–O8P···pyzD	3.768(7)	27.9	74.9(2)

Rings are labelled as follows: pym, pyrimidine; pyz, pyrazine; chel, Ag–O4–N5–C4–C4A. *d*(X···Cg): distance between the X atom and the centroid of the ring; δ: slipping angle between the X-centroid vector and the normal to the ring.

Despite the single-crystal XRD measurements have allowed a good knowledge of the disilver units and perchlorate counteranions, several disordered non-coordinated water molecules, which of course contribute to the crystal packing through H-bonds, have been found. In this way, the analysis with PLATON [25] indicates that the structure contains solvent accessible voids of 41 Å^3, as consequence of minor unassigned diffraction peaks. In addition to this, several Y–X···ring σ–π interactions have been also found (see Table 3), the most important being those encapsulating the perchlorate (Cl2P) between the pteridine moieties A and D as shown in Fig. 3.

Acknowledgements

Thanks are due to the Universidad de Jaén (Plan de Apoyo a la Investigación, al Desarrollo Tecnológico y a la Innovación de la Universidad de Jaén) and Junta de Andalucía (FQM-273) for financial support.

Appendix A. Supplementary material

CCDC 885223 and 885224 contain the supplementary crystallographic data for Ag and Re compounds. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.10.033. These data include MOL files and InChiKeys of the most important compounds described in this article.

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