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Solution and solid state coexistence of head–head and head–tail isomers in dimeric Pd(II) and Pt(II) complexes of the type $[M_2(a–a)_2(\mu\text{-}L\text{-}N^3N^4)_2]^{2+}$ with a bridging triazolopyrimidine ligand and chelating bidentate diamines

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Six palladium and one platinum compound containing dimeric dinuclear cations of the type $[M_2(a–a)_2(\mu\text{-}7tpO\text{-}N^3,N^4)_2]^{2+}$ are presented, a–a representing a bidentate chelating amine and $7tpO^-$ being the anionic form of the ligand 4,7-dihydro-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine, which bridges the metal atoms through its nitrogen atoms in positions 3 and 4. Two linkage isomers are possible for such complexes, so called head–head and head–tail. According to ^{1}H- and ^{195}Pt-NMR data, both isomers are present in dmso-d^6 solution and display analogous stability. An exhaustive assignment of the ^{1}H signals has been made. The crystal structure of three of these compounds has been determined by single-crystal X-ray diffraction. For two of them, those with bispyrimidine as auxiliary ligand, the head–head and head–tail isomers coexist even in the solid state, both being present in the same crystal in a disordered scheme. This situation is explained by the almost symmetric external shape of the bridging ligand, which is expected to interact with neighbouring species in a similar way even if rotated 180 degrees.

Introduction

In any metal complex containing two equal (or similar) planar ligands occupying contiguous (*cis*) coordination positions, we may expect that the steric repulsion between the ligands is a minimum when the ligand planes are perpendicular to the coordination plane. If the ligands are not symmetric, there are two different situations that obey the previous condition: one of them with the analogous portion of both ligands pointing in the same direction and the other, pointing to the opposite direction. These two possibilities are usually referred to as "head–head" (HH) and "head–tail" (HT) respectively. If the rotation is hindered for some reason, we can look at this situation as a special kind of isomerism, so-called rotation isomerism or atropisomerism.

A common example of this are square planar complexes of the type *cis*-$[MX_2L_2]$, with X being a simple ligand such as halide or ammonia and L being a heterocyclic planar moiety. NMR is probably the best technique to study this subject and the observed spectrum will be influenced by the energy rotation barrier, an averaged single spectrum being observed if the rotation is faster than the NMR time scale or two species in equilibrium if the interconversion is slow enough for the NMR time scale but fast enough to quickly reach an equilibrium state. If the rotation is even slower we can expect a spectrum that changes with time until equilibrium is reached or even the fixed spectrum of the initial situation for a completely hindered rotation.

In the solid state, there is usually a single species, since we can expect for this a more efficient crystal packing. In most cases (but, of course, not necessarily always), we may expect that this species is representative of the situation in solution. Generally speaking, the steric repulsion between substituents of the same nature will likely make the HH atropisomer less stable than the HT and most crystal structures of *cis*-$[MX_2L_2]$ compounds are found in the head–tail form.[1,2] For the few cases in which the head–head isomer shows up in the crystal structure, it can be explained by the interaction with another species in the structure (such as a water molecule) that keeps the two "heads" together.[3] An interesting case is the complex *cis*-$[PtCl_2(9\text{-metiladenine})_2]$, for which the linkage isomers with the base coordinated *via* N7 and *via* N1 have been characterized:[4] the arrangement is HT when the ligand is N7-linked and HH when it is N1-linked, the latter supported by hydrogen bonding.

A different situation arises if we are dealing with dimeric species of the type *cis*-$[M_2X_4(\mu\text{-}L)_2]$, with the planar ligand L bridging both metal atoms. In this case, the interconversion between both dispositions implies the cleavage and restoration of the M–L bonds and it is likely to be more difficult than in the mononuclear case. HH and HT arrangements for these compounds are not rotation isomers but linkage isomers.

If the kinetics of the formation is slow (*i.e.*, Pt) and one of the binding sites of the bidentate ligand is occupied first (either due to the nature of the ligand or to the synthetic procedure), the HH isomer is usually the obtained product.[5] Nevertheless, it is expected that the HT arrangement is still thermodynamically more stable in most cases for the same reason mentioned above for monomeric compounds and it is found in systems with faster kinetics (*i.e.*, Pd) or when there is no reason for occupying one of the binding positions of L before the other.[6] The transformation in solution from kinetically favoured HH to thermodynamically more stable HT has been followed by NMR.[7]

From the above, it seems that the preference for the HH or HT isomer is always explainable either through kinetic reasons, steric repulsions or hydrogen bonding but no evidence has been found that one of the arrangements could be more stable than the other due to different intrinsic bonding stability. In seeking to identify whether the internal electronic nature of the compounds may play a role in creating a stability difference between the isomers, the present work deals with a number of Pd(II) and Pt(II) dinuclear complexes of the type $[M_2(a–a)_2(\mu\text{-}7tpO\text{-}N^3,N^4)_2]^{2+}$, a–a representing a bidentate chelating amine and $7tpO^-$ being the anionic form of the ligand 4,7-dihydro-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine. This ligand has an interest-

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Table 1 Elemental analysis data (calculated values in parentheses) for the compounds described in this article

Compound	Formula	%C	%H	%N
1	$[Pd_2(7tpO)_2(bpy)_2](ClO_4)_2\cdot H_2O$ $(C_{30}H_{24}Cl_2N_{12}O_{11}Pd_2)$	35.9 (35.65)	2.4 (2.40)	16.5 (16.64)
2	$[Pd_2(7tpO)_2(phen)_2](NO_3)_2\cdot 4H_2O$ $(C_{34}H_{30}N_{14}O_{12}Pd_2)$	39.4 (39.31)	2.8 (2.91)	18.3 (18.89)
3	$[Pd_2(7tpO)_2(phen)_2](ClO_4)_2\cdot 2H_2O$ $(C_{34}H_{26}Cl_2N_{12}O_{12}Pd_2)$	38.3 (37.92)	2.4 (2.44)	15.8 (15.62)
4	$[Pd_2(7tpO)_2(bpm)_2](NO_3)_2\cdot 9H_2O$ $(C_{26}H_{36}N_{18}O_{17}Pd_2)$	28.7 (28.78)	3.1 (3.35)	23.3 (23.25)
5	$[Pd_2(7tpO)_2(bpm)_2](ClO_4)_2\cdot 6H_2O$ $(C_{26}H_{30}Cl_2N_{16}O_{16}Pd_2)$	28.0 (28.26)	2.8 (2.74)	20.1 (20.30)
6	$[Pd_2(7tpO)_2(bpm)_2](H_5O_2)(ClO_4)_3\cdot 3H_2O$ $(C_{26}H_{29}Cl_3N_{16}O_{19}Pd_2)$	26.2 (26.31)	2.6 (2.46)	18.8 (18.89)
7	$[Pt_2(7tpO)_2(bpm)_2](NO_3)_2\cdot 6H_2O$ $(C_{26}H_{30}N_{18}O_{14}Pt_2)$	25.4 (25.82)	1.9 (2.50)	21.0 (20.86)

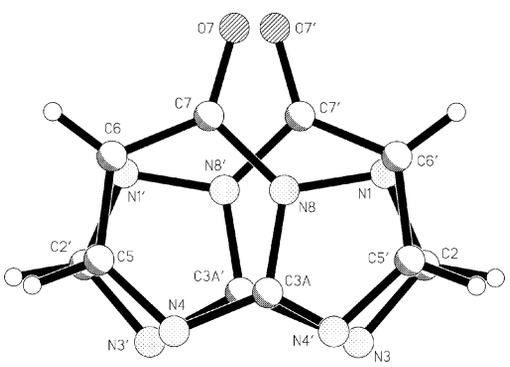

Fig. 1 Two images of the ligand $7tpO^-$ rotated 180° with respect to each other, showing that both positions are expected to interact in a similar way with neighbouring species.

ing feature: it is not symmetric but its external shape is almost symmetric. Fig. 1 displays two images of this anion, rotated 180° with respect to each other; it is expected that both positions interact with the surrounding species in a similar way. With this, HH–HT stability differences due to steric effects or hydrogen bonding are hopefully minimized and those due to intrinsic electronic stability may be evidenced.

Results and discussion

Seven compounds, containing dinuclear cations with general formulae $[M_2(a–a)_2(\mu\text{-}7tpO\text{-}N^3,N^4)_2]^{2+}$ are described in this article, where $7tpO^-$ represents the anionic form of the ligand 4,7-dihydro-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine and a–a represents a chelating bidentate diamine (bipyridine = bpy, phenanthroline = phen, bispyrimidine = bpm). The central cation is Pd(II) for six of the compounds and Pt(II) for the other. Table 1 collects the formulae of the isolated compounds and their elemental analysis data.

Description of the structures

The structure of three of the compounds described in this article, namely **3**, **6** and **7**, has been determined by single crystal X-ray diffraction. Table 4 (see Experimental) collects their crystallographic data whereas some selected bond distances and angles are collected in Table 2.

The three structures are made up of discrete dinuclear $[M_2(7tpO)_2(a–a)_2]^{2+}$ cations, the charge of which is balanced by perchlorate (**3** and **6**) or nitrate (**7**) anions. Perchlorate ions in **6** lie in positions of crystallographic *m* and *mm* symmetry, whereas the nitrate ions in **7** lie completely in mirror planes. Interstitial water molecules, some of them with partial occupancy, complete the structures.

In compound **6**, the number of perchlorate ions exceeds that required for balancing the charge of the dinuclear cations: this is explained by the presence of an oxygen atom with occupancy 1/2 close to a *mm* axis, thus defining a rectangle of such half occupancy O atoms, which has been interpreted as a $H_5O_2^+$ cation disordered over two positions. The O–O distance (diagonal of the rectangle) in this species is 2.39(3) Å, analogous to that found in other compounds with this cation.[8]

The dimeric cations are built up by two metal atoms (Pd or Pt) in a square-planar environment, two of the positions being occupied by the auxiliary ligand coordinated through two nitrogen atoms closing a five-membered chelate ring. The other twopositionsareoccupiedbytwo4,7-dihydro-7-oxo[1,2,4]triazolo-[1,5-*a*]pyrimidinate ($7tpO^-$) bridging ligands which are linked to both metal atoms through their nitrogen atoms in positions 3 and 4. Such a binding mode is rather common for triazolopyrimidine ligands and has been found for Cu(I),[9] Cu(II),[10] Ag(I),[11] Pd(II),[12] Pt(II)[13] and for heterometallic compounds.[14,15]

In compound **3**, the bridging ligands are oriented in a head-to-tail disposition (Fig. 2) so each metal atom is linked to N(3)

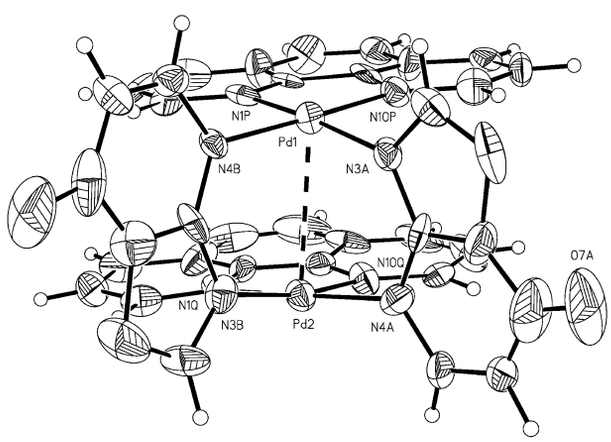

Fig. 2 View of the $[Pd_2(7tpO)_2(phen)_2]^{2+}$ cation in compound **3**. Non-hydrogen atoms are represented as thermal ellipsoids at the 30% probability level. Only selected atom labels are shown for clarity.

of one of the $7tpO^-$ moieties and to N(4) of the other. The situation is more complex in compounds **6** and **7**, for which there is a crystallographic mirror plane relating both metal atoms. Such a mirror plane is not compatible with the structure of the $7tpO^-$ ligands perpendicular to it, which appear in the difference Fourier synthesis as sets of peaks which do not define any reasonable molecular structure. These sets of peaks have been rationalized as a disordered situation, with two over-lapping images of the triazolopyrimidine anion, each of half occupancy, related by the mirror plane. In **6**, there is a second mirror plane, perpendicular to the former and containing the Pd–Pd bond.

Table 2 Selected bond distances (Å) and angles (°) for compounds **3**, **6** and **7**

	3			
	Pd1	Pd2	**6**	**7**
M ⋯ M	2.986(2)		3.1760(17)	3.1612(14)
M–N3	1.968(16)	1.996(16)	1.964(10)	1.92(2)
				1.94(3)
M–N4	2.001(14)	2.015(17)	2.095(11)	2.12(2)
				2.14(3)
M–Nm[a]	1.994(16)	1.977(16)	2.004(6)	2.000(12)
	2.009(16)	1.995(16)		2.027(11)
N3–M–N3	—	—	87.9(9)	89.2(13)
N4–M–N4	—	—	90.8(9)	88.9(12)
N3–M–N4	88.0(6)	89.3(7)	90.0(3)	91.9(12)
				87.2(12)
N3–M–Nm[a]	94.7(7)	93.2(7)	95.4(5)	94.5(9)
	173.1(6)	170.4(7)	170.2(4)	170.6(8)
				94.0(10)
				171.7(7)
N4–M–Nm[a]	95.1(6)	95.5(7)	94.7(5)	93.0(8)
	177.3(6)	177.3(7)	174.5(5)	174.1(8)
				96.9(10)
				177.7(9)
Nm–M–Nm[a]	82.3(7)	81.9(7)	79.9(4)	81.2(5)

[a] Nm = nitrogen atom of the diamine.

Attempts have been made to refine these structures in spatial subgroups for which the offending mirror plane does not exist (see Experimental) but no ordered solution has been found in any case. The mirror plane and the disorder are always reproduced, so the disordered solutions in the groups with the mirror plane have been taken as the best representation of the samples. As there does not appear to be any correlation between the positions of both 7tpO$^-$ anions within the dimeric unit, it seems that both head–head and head–tail dispositions are present in the crystals in a random distribution. Figs. 3 and 4 display both isomers for compounds **6** and **7** respectively. This supposition is supported by the NMR data for compound **7** (see below), in which both isomers are present even in fresh solutions (due to the slow kinetics of Pt(II), we expect that the spectrum of a fresh solution is quite representative of the solid).

Final *R*-indices of compound **3** are quite high and this cannot be attributed only to decomposition of the crystal (only 7.5% during data collection) or poor definition of perchlorate groups (see Experimental). Thermal motion of some of the more external atoms of the cluster (C(7) and O(7) of the triazolopyirimidine ligands, some of the external carbon atoms of phen and, to a lesser extent, N(1) and C(6)) are abnormally high (see the ellipsoids in Fig. 2), which may suggest the existence of some extra degree of freedom in the structure, such as rotation around the Pd–Pd bond or even the presence of a small proportion of the HH isomer (for which there is not however any further evidence). Possibly, the sum of all these factors contributes to a decrease in the crystallinity of the sample.

The interaction between the auxiliary ligands clearly influences the geometry of the cluster, as has been previously shown.[12] Thus, the phenanthroline moieties in **3** are stacked with an angle between them of only 1.6(3)°, which is much closer than the angle between the PdN_4 planes (19.2(5)°), and an average interplanar distance of 3.36 Å. In this situation, the atoms of one of these ligands do not exactly fall over the atoms of the other but rather they fall over the centre of the aromatic rings; this implies that both PdN_4 units are slightly rotated with respect to each other, torsional angles N–Pd–Pd–N ranging from −13.3(7) to −10.0(6)°. This removes the possibility of a mirror plane analogous to that in **6** and **7** and probably favours the ordered head–tail disposition over the disordered head–head/head–tail in the solid state.

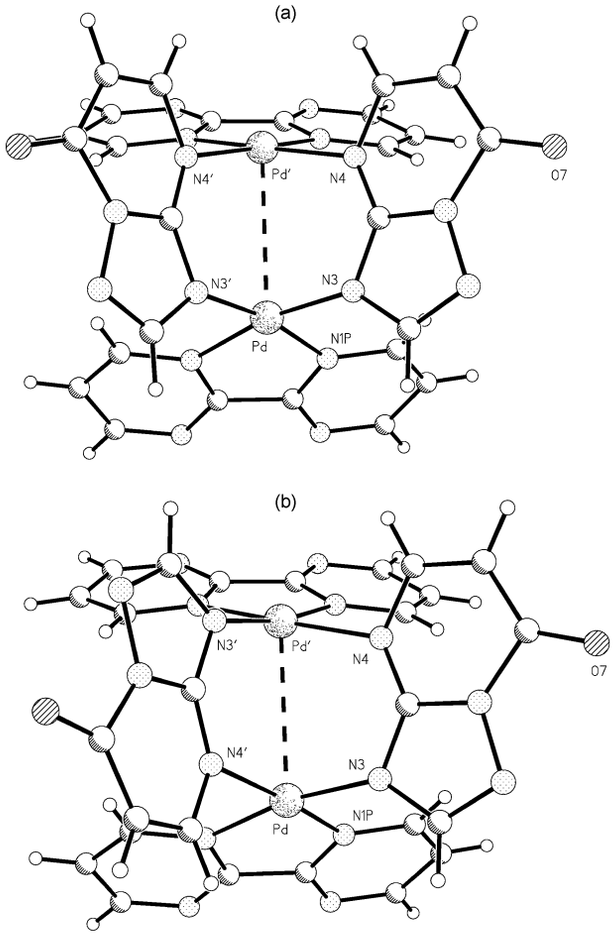

Fig. 3 Head–head (a) and head–tail (b) isomers of the $[Pd_2(7tpO)_2(bpm)_2]^{2+}$ cation which are present in the crystal structure of compound **6**. Only selected atom labels are shown for clarity.

On the other hand, the bispyrimidine auxiliary ligands (related by a crystallographic mirror plane) clearly repel each other, the external nitrogen atoms seeming to prevent the stacking interaction, the dihedral angle between the corresponding planes being quite large (62.1(3) for **6** and 52.9(4)° for **7**), much wider than the angle between the MN_4 planes (36.8(2) and 35.1(5)°, respectively, virtually identical for HH and HT arrangements). It is clear that the interaction between the auxiliary ligands is stabilizing for phenanthroline and destabilizing for bispyrimidine, which is also reflected by the intermetallic distances (Table 2). M–N(3) and M–N(4) distances for compounds **6** and **7** displayed in Table 2 are noticeably different. Nevertheless, as the ligands have been refined with severe geometrical constraints (see Experimental), standard deviations for these data are probably underestimated, so this dissimilarity could either be real or an artifact, and no safe conclusion should be taken from it.

The crystal packing of compound **7** is quite remarkable. It crystallizes in the rather unusual hexagonal space group *P6*/*m*. Fig. 5 displays the projection of the structure on the plane perpendicular to the main axis, with *p*6 symmetry. Channels appear along this axis, partially occupied by water molecules which interact weakly with the dinuclear cations.

NMR results

The structures of **1**, **3**, **4** and **7** in dmso-d_6 solution have been analyzed by means of ^{1}H-NMR spectroscopy. In all cases, two sets of signals appear for the hydrogen atoms of 7tpO and four sets are present for the auxiliary ligand. This is explained by the presence in solution of both isomers, head–head (HH) and head–tail (HT). For the Pt compound (**7**), we expect that this is

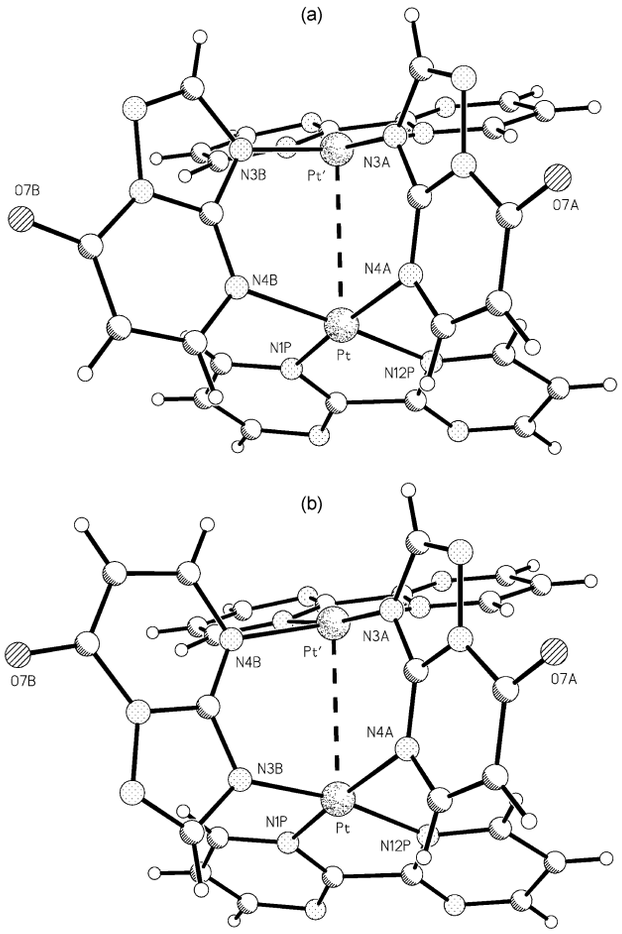

Fig. 4 Head–head (a) and head–tail (b) isomers of the $[Pt_2(7tpO)_2(bpm)_2]^{2+}$ cation which are present in the crystal structure of compound **7**. Only selected atom labels are shown for clarity.

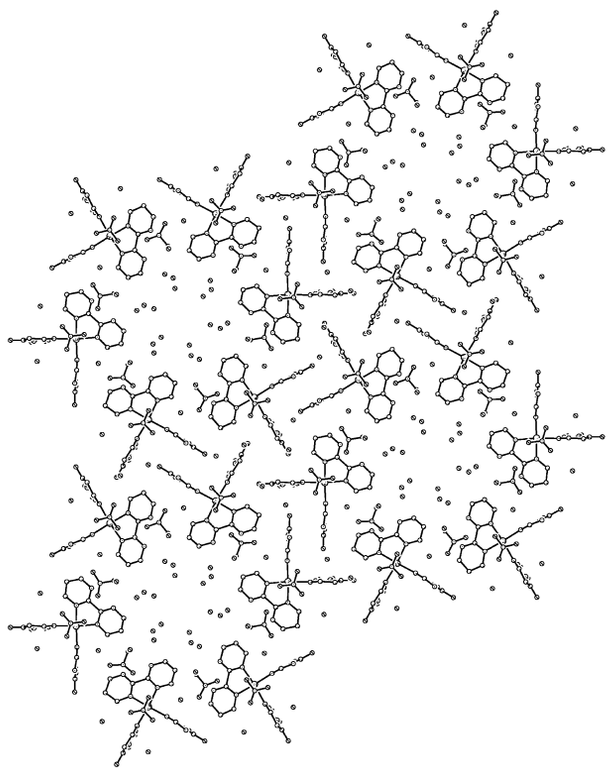

Fig. 5 Projection along the *c* axis of the crystal structure of compound **7** (*a* down, *b* in the plane at 120° from *a*). The channels around the six-fold axes are shown.

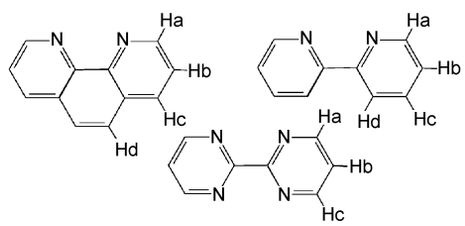

Fig. 6 Labelling scheme used in the ^{1}H-NMR discussion for the auxiliary ligands.

representative of the solid-state situation whereas for the Pd complexes, it seems that equilibrium between both isomers is quickly reached, regardless of the initial situation. The spectra do not change appreciably with time.

Both triazolopyrimidine ligands are equivalent in each isomer of the complex, related by a molecular two-fold axis (HT) or mirror plane (HH). The auxiliary ligands are also equivalent in the HT isomer but the two halves of the same ligand are not. In contrast, the two halves of the same ligand are equivalent in the HH isomer but the two ligands are different to each other. So, each isomer generates a set of signals for the triazolopyrimidine ligand and two sets of signals (two different halves or two different ligands) for the diamine.

The presence of both isomers is also supported by the ^{195}Pt-NMR spectrum of compound **7**. This spectrum displays three signals, a more intense one at −2424.4 ppm., assigned to the equivalent Pt atoms in the HT isomer, and the other weaker two at −2447.1 and −2407.2 ppm., assigned to the two non-equivalent metal atoms in the HH isomer. The use of ^{195}Pt-NMR has previously proved to be a good way of distinguishing the HH and HT isomers of platinum dimeric complexes and following their interconversion.[7] The area of the central peak is slightly higher than the sum of the areas of the other two, thus suggesting that the concentration of the HT isomer is slightly higher than that of the HH, in agreement with ^{1}H-NMR data (see below).

Seeking a complete assignment of the ^{1}H-NMR spectra, we have recorded bidimensional COSY (to reveal direct coupling) and NOESY (to reveal spatial proximity) spectra for compound **3**. This compound has been selected because it is the one with better separation among the signals. Also, the external hydrogen atom of phen is a good starting point for the assignment. Fig. 6 displays the labelling scheme used for the H atoms throughout the following discussion.

The easiest proton to assign is the most external one (Hd), since the two Hd of the same ligand are equivalent in the HH isomer whereas they are not in the HT. Thus, they appear as singlets in HH and as doublets, coupled with each other with a 8.9 Hz coupling constant, in HT. Once Hd is assigned, the Hc that corresponds to each Hd is clearly determined by the NOESY correlation between them.

Three double doublets appear for the Hb protons, the central one with a double integral. The COSY spectrum correlates the later with both HH Hc protons, showing that this signal corresponds to the two HH Hb protons that appear as if they were equivalent (though they are not). Each of the other Hb signals is easily correlated with one of the HT Hc signals as well as with one of the signals attributable to Ha, thus completing the Ha–Hb–Hc–Hd connection for each phen side of the HT isomer. For the HH isomer, the connection Ha–Hc cannot be established *via* COSY correlations through Hb but a weak NOESY direct Ha–Hc correlation lets us propose the connectivity indicated in Table 3.

In the NOESY spectrum, a weak but distinct correlation appears between the H2 signals and some of the Ha: this has

Table 3 ^{1}H-NMR data (δ/ppm) and assignments for **1**, **3**, **4** and **7** in dmso-d_6 solution [a]

Compound			H2	H5	H6	Ha	Hb	Hc	Hd
1	HH	h	8.57	8.21	6.17	7.81	7.35	8.26	8.33
		t				7.99	7.37	8.19	8.27
	HT	h	8.60	8.19	6.18	7.83	7.25	8.13	8.30
		t				7.97	7.46	8.19	8.28
3	HH	h	8.66	8.38	6.23	8.07	7.59	8.63	7.93
		t				8.28	7.59	8.53	7.79
	HT	h	8.70	8.30	6.24	8.10	7.41	8.48	7.83
		t				8.24	7.75	8.66	7.90
4	HH	h	8.51	8.16	6.16	8.50	7.78	9.28	
		t				8.68	7.79	9.27	
	HT	h	8.52	8.18	6.17	8.53	7.73	9.26	
		t				8.66	7.83	9.28	
7	HH	h	8.63	8.16	6.17	8.79	7.82	9.34	
		t				8.98	7.84	9.32	
	HT	h	8.61	8.19	6.16	8.83	7.78	9.31	
		t				8.95	7.88	9.34	

[a] HH = head–head. HT = head–tail. h and t denote the halves of the diamine ligand closer to N3 and N4 of 7tpO$^-$, respectively. For compounds **1**, **4** and **7**, assignments of Hc (also Hd of **1**) of both isomers and Hb of the HH isomer are only tentative. Coupling constants: J(H5–H6) = 7.3 Hz in all cases. J(Ha–Hb) = 5.8 (**1**); 5.3 (**3**); 4.9 Hz (**4** and **7**). J(Hb–Hc) = 7.6 (**1**); 8.3 (**3**); 5.9 Hz (**4** and **7**). J(Ha–Hc) = 1.7 Hz (**4** and **7**). J(Hc–Hd) = 8.0 Hz (**1**). J(Hd–Hd) = 8.9 Hz (HT isomer of **3**).

Table 4 Crystallographic data for compounds **3**, **6** and **7**

	3	**6**	**7**
Formula	$C_{34}H_{26}Cl_2N_{12}O_{12}Pd_2$	$C_{26}H_{29}Cl_3N_{16}O_{19}Pd_2$	$C_{26}H_{30}N_{18}O_{14}Pt_2$
M	1078.37	1188.80	1208.86
Crystal size/mm	0.35 × 0.32 × 0.30	0.6 × 0.5 × 0.4	0.25 × 0.1 × 0.1
Crystal system	Orthorhombic	Orthorhombic	Hexagonal
Space group	*Pbca*	*Pmmn*	*P6/m*
a/Å	15.468(6)	11.1799(14)	26.509(2)
b/Å	20.652(10)	18.9400(18)	—
c/Å	25.162(5)	9.6374(8)	10.1184(13)
U/Å^3	8038(5)	2040.7(4)	6158.0(11)
Z	8	2	6
μ(Mo-Kα)/cm^{-1}	1.106	1.176	6.891
F(000)	4288	1184	3480
Independent reflections	7060	3193	2876
R ($F > 4\sigma(F)$)	0.1483	0.0821	0.0494
$wR2$ (all data)	0.2882	0.2107	0.1703

been explained by the vicinity of H2 with the Ha next to the phen N atom close to N3 of 7tpO$^-$ ("head"); assuming this, it is possible to completely assign the phen H atoms as indicated in Table 3.

For compounds **1**, **4** and **7**, Ha of both isomers and Hb of the HT isomer have been assigned by direct comparison with the spectrum of **3**. Hb protons of the HH isomer overlap with each other (but are not completely coincident as in **3**) and their assignments in Table 3 could possibly be interchanged. All Hc protons (and Hd of **1**) appear overlapped in a very narrow region and their assignments in Table 3 are only tentative.

Among all these signals, it is clear that those of Hb are possibly the only ones that can be regarded as diagnostic to determine the present isomer; they appear well separated in the HT isomer whereas they overlap in the HH. The compound analogous to **1** with a methyl group at position 5 of the triazolopyrimidine ligand,[12] with only the HT isomer present, displays two signals for Hb separated by 0.44 ppm.

A rough estimate of the proportion of HH and HT isomers can be inferred from the integrals of those protons that are well separated from others. In the four cases, there is a very slight preponderance of the HT isomer, the proportion of which is however not higher than 60% for any of the compounds. Then, both isomers present analogous stability in solution. This is in contrast to the results previously reported for the compound analogous to **1** with the 5-methyl derivative of 7tpO$^-$,[12] for which only the HT isomer is present, possibly due to steric repulsion between the neighbouring methyl groups that would take place in the HH isomer.

Conclusions

The dinuclear compounds included in this paper contain two 4,7-dihydro-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidinate (7tpO$^-$) bridging ligands. There are two possible relative dispositions for these bridging ligands (head–head, HH and head–tail, HT). Since the "external shape" of this ligand is almost symmetric even if the ligand itself is not, the possible stability differences between the isomers can safely be attributed to intrinsic bonding reasons instead of factors such as the interaction of these ligands with each other or with external species.

However, according to the NMR data, both arrangements are present in solution and display similar stability. So, we may deduce that such intrinsic electronic reasons do not exist or in any case, they play a minor role. For the compounds with bispyrimidine as auxiliary ligand, the coexistence of both isomers seems to occur even in the solid state, with a random disordered distribution across the crystals. This does not happen in the compound with phenanthroline; in this case, the stacking interaction between the aromatic rings possibly favours a crystal packing in which the head–tail isomer fits better.

Experimental

Synthesis of the compounds

The starting reagents [Pd(bpy)Cl$_2$] and [Pd(phen)Cl$_2$] were synthesized following the literature procedure for [Pd(ethylendiamine)Cl$_2$][16] using the appropriate diamine. [Pd(bpm)Cl$_2$] was

prepared by refluxing 2 mmol of $PdCl_2$ and 4 mmol of bispyrimidine in 1 : 1 acetonitrile–methanol for eight hours; after this time, $PdCl_2$ dissolved and a precipitate of the desired product appeared, which was filtered off without cooling the solution and washed with ethanol. [Pt(bpm)Cl_2] was prepared according to the previously reported method.[17] 4,7-Dihydro-7-oxo[1,2,4]-triazolo[1,5-*a*]pyrimidine (7HtpO) was synthesized as indicated in a previous work.[18]

The compounds $[Pd_2(a–a)_2(7tpO)_2]X_2{\cdot}nH_2O$ were prepared by reacting 2 mmol of [Pd(a–a)Cl_2] with 4 mmol of $AgNO_3$ or $AgClO_4$ in 40 ml of water at 45 °C in the dark for one hour. The precipitated AgCl was filtered off and the resulting solution treated with 4 mmol of 7HtpO keeping the solution at 60 °C for four hours. The solution was then left to stand for several days, when the products appeared as microcrystalline solids, which were recrystallized in an acetonitrile–ethanol–water (2 : 2 : 1) mixture. Compounds **1**–**5** were obtained in this way: their formulae and elemental analysis data are listed in Table 1. The yields (after recrystallization) were: 20, 23, 18, 23 and 15% respectively for **1**–**5**. If the synthesis described for compound **5** is carried out adding the triazolopyrimidine ligand dissolved in 40 ml of 2 M $HClO_4$, crystals of the related compound **6** are obtained (no recrystallization in this case), yield 40%.

The platinum compound (**7**) was prepared as follows: 2 mmol of [Pt(bpm)Cl_2] was reacted with 4 mmol of $AgNO_3$ in 40 ml of water in the dark at 37 °C for 12 hours. The precipitated AgCl was removed by filtration and the solution was stirred at room temperature with 4 mmol of 7HtpO until the solid was completely dissolved. After 24 hours, a very small amount of very thin needles of a Pt–Ag heterometallic compound appeared, the structure of which has been published elsewhere.[15] From its mother liquor, hexagonal prismatic crystals of compound **7** appeared four days later (yield, 12%).

Microanalyses of C, H and N were performed in a Fisons Instruments EA-1008 analyser at the Centre of Scientific Instrumentation of the University of Granada.

Crystallography

X-Ray work was carried out at room temperature on a Stoe Stadi 4 (**3** and **6**) or Siemens P4 (**7**) at the Centre of Scientific Instrumentation of the University of Granada. The crystals needed to be covered with a drop of parafin oil to prevent their decomposition (possibly by dehydration). Data collections were performed in the $2\Theta/\omega$ scan mode. Data were corrected for Lorentz and polarization effects and empirically (psi-scans) for absorption. The structures were resolved by the heavy atom method; for compound **7**, due to the highly symmetric space group, several non-equivalent solutions are compatible with the Patterson map and some trial and error was necessary to find the right one. Full-matrix least squares refinement was carried out by means of the SHELXL 97 program.[19]

For compounds **6** and **7**, there is a crystallographic mirror plane which is the median plane of the M–M segment: such a plane is not compatible with the geometry of the bridging ligand, which appears in the difference maps as a number of peaks that cannot directly define any reasonable moiety. This has been rationalized supposing a disordered situation for $7tpO^-$ between two positions related by the symmetry plane. These ligands have been refined isotropically with fixed bond distances and for compound **7** it was also necessary to constrain the thermal parameters so that they are equal for the couples of atoms (N(1)–C(6), C(2)–C(5) and N(3)–N(4)) that overlap with the image of their counterparts through the symmetry plane. Attempts have been made for refining the structure in space subgroups for which the offending symmetry plane does not exist ($P2_1mn$ and $P2_12_12$ for **6** and $P6$ and $P\bar{3}$ for **7**) with different starting positions for the ligands but in all cases the disordered solutions with the symmetry plane are reproduced, so the solutions in $Pmmn$ and $P6/m$ have been taken as the best representations of the samples.

For compound **3**, perchlorate ions are poorly defined and they have been refined with a fixed geometry, since no rational disordered scheme has been found which yielded better results. In the three compounds, water molecules with partial occupancy isotropically refined were included. Non-disordered non-hydrogen atoms, except the perchlorate oxygens in **3**, were refined anisotropically. Hydrogen atoms of the organic moieties were included at ideal positions with thermal parameters 1.2 times those of their parent atoms. Crystal data are summarized in Table 4.

CCDC reference numbers 190494–190496.

See http://www.rsc.org/suppdata/dt/b2/b207263g/ for crystallographic data in CIF or other electronic format.

NMR studies

^{1}H-NMR spectra were recorded for dmso-d_6 solutions of the compounds on a Bruker AM-300 spectrometer at the Center of Scientific Instrumentation of the University of Granada. The ^{195}Pt-NMR spectrum of compound **7** was recorded in a Bruker AC-200 equipment at the Faculty of Chemistry of the University of Dortmund.

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