DALTON

Preparation and structural characterization of a series of ternary palladium(II) binuclear complexes containing triazolopyrimidinate bridges

Jorge A. R. Navarro, M[a] Angustias Romero and Juan M. Salas*

Departamento de Química Inorgánica, Av. de Fuentenueva S/N, Universidad de Granada, 18071 Granada, Spain

The reaction of the $[Pd(H_2O)_2(L–L)][NO_3]_2$ electrophiles (L–L = ethane-1,2-diamine **1**, propane-1,3-diamine **2**, or 2,2′-bipyridine **3**) with 4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine (Hmtpo) in 1 : 1 molar ratio, in aqueous media (pH 7–8), yielded palladium(II) binuclear complexes of general formula $[Pd_2(\mu\text{-mtpo-}N^3,N^4)_2(L–L)_2][NO_3]_2$. The compounds have been structurally characterized by one- and two-dimensional ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction (**1** and **3**). The crystal structures of both compounds show that the Pd atoms are located in nearly square-planar PdN_4 environments. Two mtpo ligands arranged in a head-to-tail orientation bridge the two metal centres, giving rise to short intermetallic contacts. The Pd · · · Pd separation appears to be modulated by the interactions between the auxiliary ligands L–L in adjacent co-ordination planes. Thus, substitution of ethane-1,2-diamine by planar 2,2′-bipyridine is responsible for a shortening of the intermetallic separation from 3.225(1) Å in compound **1** to 3.034(1) Å in **3**. The NMR data suggest that the structures are preserved in solution.

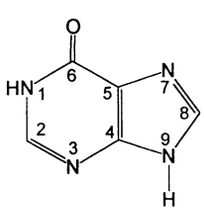
There is much interest in the study of the co-ordination chemistry of palladium(II) analogues of cisplatin *cis*-$[PtCl_2(NH_3)_2]$ to nucleobases because they usually reproduce adequately the binding of the latter but with a faster kinetics.[1] On the other hand, nucleobases and related heterocyclic compounds, in spite of their simplicity, are rather versatile multidentate ligands suitable for research on metal–metal interactions,[2] platinum polynuclear mixed-valence complexes,[2] and homo-[3] and heteropolynuclear[4] palladium complexes with the Pd in rare oxidation states such as +3, or compounds showing extraordinarily short $Pt^{II}\rightarrow Pd^{II}$ dative bonds.[5] However, metal–metal interactions in diplatinum(II) and dipalladium(II) complexes at distances in the range 3.0–3.3 Å are still ambiguous. Thus, while some authors regard these contacts as direct intermetallic bonding interactions,[6] even in solution,[7] others consider them non-bonding.[8] To clarify this controversy it should be noted that, apart from weak direct intermetallic interactions,[9] it is necessary to take into account possible interactions between the ligands in the adjacent co-ordination planes, which may contribute to the association, such as hydrogen bonding,[6,10] stacking[11] or dissociation (steric interligand interactions[12]).

Herein we present results concerning the preparation and structural characterization of a group of dimeric palladium(II) complexes of general formula $[Pd_2(\mu\text{-mtpo-}N^3,N^4)_2(L–L)_2][NO_3]_2$ {mtpo = 4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo-[1,5-*a*]pyrimidinate; L–L = ethane-1,2-diamine (en) **1**; propane-1,3-diamine (tn) **2** or 2,2′-bipyridine (bipy) **3**}. The Hmtpo can be considered an analogue of the natural occurring nucleobase hypoxanthine. Also, it is ideally suited for the study of metal–metal interactions due to its multiple donor positions, which give rise to homo- and hetero-dinuclear complexes of Pt^{II} and Pd^{II} with metal–metal separations ranging from 2.744(2)[13] to 3.337(1) Å.[14] Finally, the influence of the nature of the auxiliary ligands L–L on the possible Pd · · · Pd interaction is discussed.

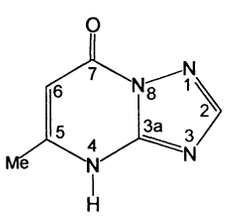
Experimental

Reactants and methods

The complexes $[PdCl_2(en)]$, $[PdCl_2(tn)]$ and $[PdCl_2(bipy)]$ were synthesized and converted into their corresponding aqua species, after treatment with $AgNO_3$, according to literature methods.[15] The compound Hmtpo was obtained from Aldrich Chem. Co. and used as received. Other chemical reagents and solvents were supplied from commercial sources. All experiments were performed in air.



Hypoxanthine



Hmtpo

Preparation of the complexes

The complexes were obtained by reaction of a warm solution of $[Pd(H_2O)_2(L–L)]^{2+}$ (2 mmol) in water (40–80 cm^3) with another Hmtpo (2 mmol) in water (20 cm^3). The resulting solution was adjusted to pH 7–8 after addition of 1 mol dm^{-3} NaOH. Some hours later yellow crystalline precipitates of the complexes $[Pd_2(\mu\text{-mtpo})_2(en)_2][NO_3]_2\cdot 2H_2O$ **1** and $[Pd_2(\mu\text{-mtpo})_2(tn)_2][NO_3]_2\cdot xH_2O$ **2** were recovered, rinsed with water and air dried, the respective yields being 44 and 46%. In the case of $[Pd_2(\mu\text{-mtpo})_2(bipy)_2][NO_3]_2\cdot 5H_2O$ **3** the reaction mixture was kept at 45 °C for 48 h in order to ensure complete reaction. From the resulting solution yellow single crystals of **3** were recovered in 65% yield. A common feature in this set of complexes is their loss of crystallinity on exposure to air, due to facile dehydration. Microanalytical and IR data are given in Table 1.

Instrumentation

Microanalyses of C, H and N were performed with a Fisons-Instruments EA-1008 apparatus by the Instrumentation Center of the University of Granada, whereas Pd was determined thermogravimetrically by means of Mettler TA-3000 equipment provided with a TG-50 thermobalance at a heating rate of 20 K min^{-1},

using an atmosphere of pure air (100 $cm^3\ min^{-1}$). Infrared spectra were recorded in the 4000–180 cm^{-1} range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets, NMR spectra in D_2O on a Bruker AM-300 Fourier-transform spectrometer and using sodium 3-(trimethylsilyl)tetradeuteriopropionate as internal standard in the Instrumentation Center of the University of Granada. The pD of the samples was calculated by adding 0.4 units to the pH meter reading.

Crystallography

Crystallographic data and details of refinement for compounds **1** and **3** are presented in Table 2. The crystals were mounted on a four-circle Stoe-Siemens AED-2 diffractometer. In the case of **3** its facile dehydration made it necessary to seal the crystal in a Lindemann capillary with some drops of mother-liquor. The intensity data were corrected for Lorentz-polarization effects, and empirically for absorption (ψ scans). The structures were solved by the heavy-atom and Fourier methods applying the SHELXTL PLUS program package.[16] Full-matrix least-squares refinement on *F* was performed. Non-hydrogen atoms were assigned anisotropic thermal parameters with the exception of those of the nitrate groups which were found to be disordered in both structures. The disorder was modelled by considering three different orientations with respective occupations of 0.5, 0.3 and 0.2 for compound **1** and two with occupations of 0.75 and 0.25 for **3**. The hydrogen atoms of the organic ligands were idealized and those of water molecules refined with fixed O–H distances (0.85 Å).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/395.

Table 1 Analytical and IR data for the complexes

	Analysis (%)*				IR/cm^{-1}
Compound	C	H	N	Pd	IR/cm^{-1}
1	24.2 (24.3)	3.7 (3.8)	24.0 (24.7)	25.0 (26.9)	3430s, 3110s, 3050s, 1650vs, 1575s, 1540vs, 1385vs, 1250m, 1195m, 1150m, 1060m
2	26.4 (26.4)	4.2 (4.2)	23.1 (23.9)	24.1 (26.0)	3425s, 3180s, 3095s, 1675vs, 1585s, 1540vs, 1420s, 1380vs, 1260m, 1150m, 1040m, 830m
3	40.0 (39.8)	2.7 (2.9)	20.4 (20.3)	21.6 (22.1)	3430m, 3050m, 1695vs, 1590s, 1535vs, 1410s, 1355vs, 1250m, 1190m, 1105m, 1075m, 1025m, 770s, 645m

* Calculated values in parentheses.

Results and Discussion

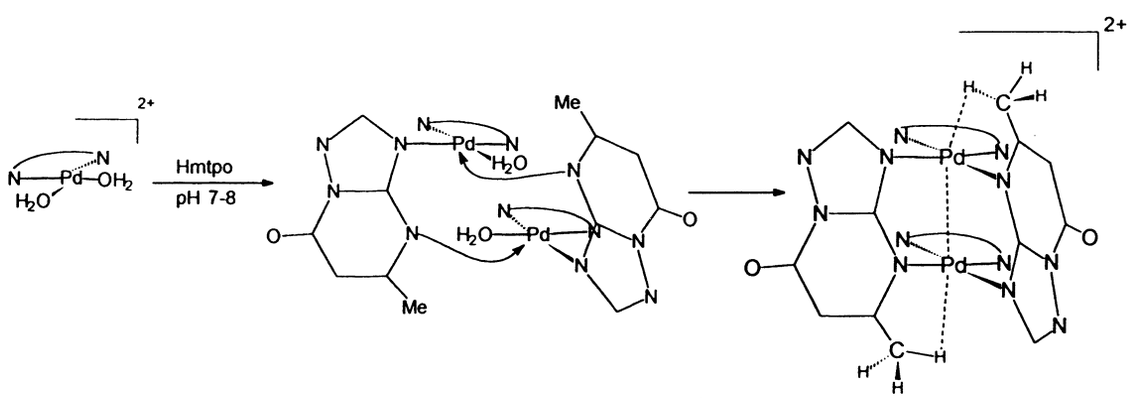
The reaction of $[Pd(H_2O)_2(L–L)][NO_3]_2$ with Hmtpo in 1:1 molar ratio in aqueous media (pH = 7–8) yields palladium(II) binuclear complexes of general formula $[Pd_2(\mu\text{-mtpo-}N^3,N^4)_2(L–L)_2][NO_3]_2$ (L–L = en, tn or bipy), in which the mtpo ligand shows a bidentate bridging mode *via* N^3 and N^4. Scheme 1 shows a possible mechanism of formation of the binuclear species according to that previously reported by Micklitz *et al.*[17] The mtpo ligands always appear to show a head-to-tail arrangement, which is favoured by the minimum steric inter-ligand interactions.

Structure of $[Pd_2(\mu\text{-mtpo-}N^3,N^4)_2(en)_2][NO_3]_2\cdot 2H_2O$ 1

The structure of compound **1** comprises isolated binuclear $[Pd_2(\mu\text{-mtpo-}N^3,N^4)_2(en)_2]^{2+}$ cations, disordered nitrate anions and interstitial water molecules. A view of the asymmetric unit is depicted in Fig. 1. Table 3 lists selected bond distances and angles. The Pd atoms are located in a nearly square-planar environment with respective deviations of 0.0311(8) and 0.0483(8) Å for Pd(1) and Pd(2) towards each other. The palladium atoms bind to two nitrogen-donor atoms from the en ligands and nitrogens N^3 and N^4 from two different mtpo entities, which bridge the two co-ordination planes, arranged in a head-to-tail fashion. The two co-ordination planes are tilted by 38.6°, giving rise to a Pd(1)···Pd(2) separation of 3.225(1) Å. Bond distances and angles around the metal atoms are in the same range as those found in other palladium(II) compounds with similar environments.[1a,18] The intermetallic separation in the cation is in the same range as the van der Waals radii sum[19] but considerably longer (0.15–0.3 Å) than those found in other similar palladium(II)[18,20] or mixed platinum(II)–palladium(II)[14] binuclear complexes containing two analogous bridges. Steric interactions between the en ligands in adjacent metal co-ordination planes appear to be responsible for the long Pd···Pd separation and the possible lack of a considerable metal–metal interaction. Thus, the substitution of the en ligands by planar bipy in **3** causes a considerable shortening in the intermetallic distance to 3.034(1) Å and the consequent diminution in the dihedral angle, between the co-ordination planes, to 19.1°. Thus, in other similar complexes, this steric interaction between the en ligands is regarded as responsible for the isomerization of head-to-head binuclear $[Pt_2(L_2)(en)_2]^{2+}$ species (L = pyridin-2-onate) to its head-to-tail isomer *via* cleavage of an inert Pt–N (heterocycle) bond *trans* to an amine[12] and also for the difficult isolation of a yet unknown $[Pd_2L_2(en)_2]^{2+}$ species (L = 1-methyluracilate).[17] In our case, the head-to-tail isomer appears to be favoured since this arrangement avoids the steric interaction between the mtpo methyl groups.

Structure of $[Pd_2(\mu\text{-mtpo-}N^3,N^4)_2(bipy)_2][NO_3]\cdot 5H_2O$ 3

Fig. 2 shows a plot of the binuclear cation of compound **3**. Selected bond distances and angles are given in Table 4. The structure consists of binuclear $[Pd_2(\mu\text{-mtpo-}N^3,N^4)_2(bipy)_2]^{2+}$



Scheme 1 Proposed mechanism for the formation of the dimeric $[Pd_2(\mu\text{-mtpo})_2(L–L)_2]^{2+}$ species

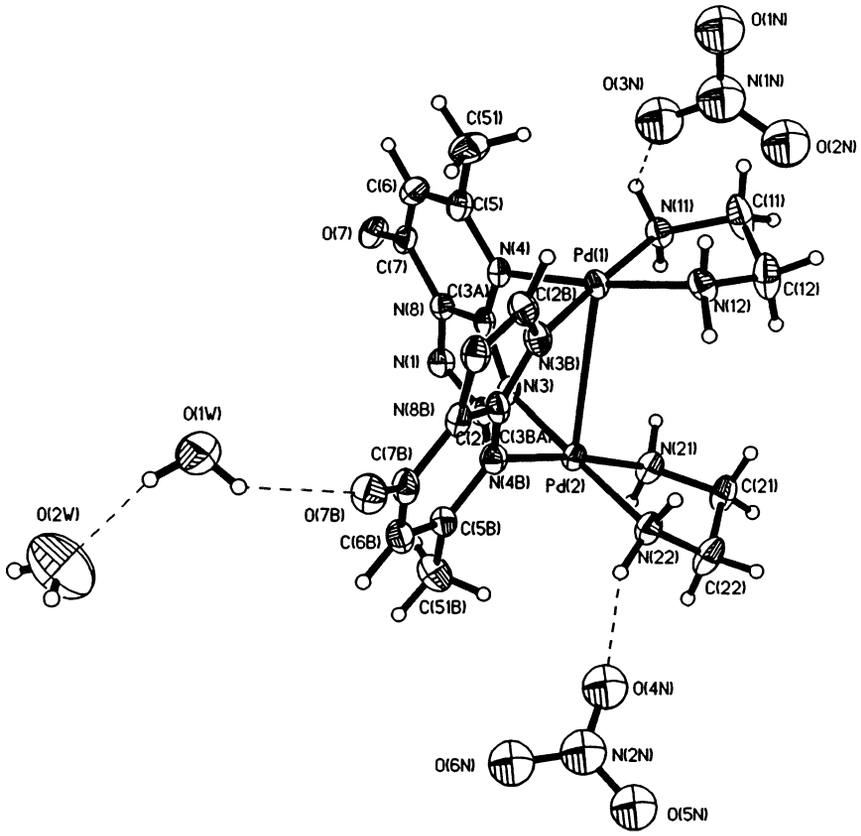


Fig. 1 Asymmetric unit and numbering scheme for $[Pd_2(\mu\text{-mtpo})_2(en)_2][NO_3]_2\cdot 2H_2O$. For clarity only one nitrate orientation is shown. The thermal ellipsoids are shown at the 30% probability level

Table 2 Crystallographic data and details of refinement for $[Pd_2(\mu\text{-mtpo})_2(en)_2][NO_3]_2\cdot 2H_2O$ **1** and $[Pd_2(\mu\text{-mtpo})_2(bipy)_2][NO_3]_2\cdot 5H_2O$ **3***

	1	**3**
Formula	$C_{16}H_{30}N_{14}O_{10}Pd_2$	$C_{32}H_{36}N_{14}O_{13}Pd_2$
M	792.0	1037.5
Crystal dimensions/mm	0.50 × 0.22 × 0.15	0.8 × 0.5 × 0.4
Space group	$P2_1/c$	$C2/c$
a/Å	12.135(2)	9.978(2)
b/Å	15.245(3)	23.803(5)
c/Å	16.126(3)	17.190(3)
β/°	111.85(3)	93.56(3)
U/ Å^3	2769.0(9)	4074.9(14)
D_m/g cm^{-3}	1.92	—
D_c/g cm^{-3}	1.90	1.69
μ(Mo-Kα)/cm^{-1}	13.8	9.6
F(000)	1584	2088
% Transmission, maximum, minimum	72, 61	45, 40
h, k, l Ranges	0–14, 0–18, −19 to 19	0–9, 0–28, −20 to 20
No. reflections measured	5306	3533
No. reflections independent (R_{int})	4839 (0.019)	3445 (0.020)
No. reflections observed [$F > 4.0\sigma(F)$]	3859	3175
Goodness of fit	1.47	0.97
Maximum, minimum in ΔF map/e Å^{-3}	0.94, −1.50	0.73, −0.93
No. parameters refined	393	278
R	0.058	0.041
R'	0.062	0.054

* Details in common: monoclinic; $Z = 4$; 295 K; $2\theta_{max}$ 50°. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \Sigma(||F_o| - |F_c||w^{\frac{1}{2}})/\Sigma(|F_o|w^{\frac{1}{2}})$, where $w^{-1} = \sigma^2(F_o) + 0.0018F_o^2$ for complex **1** and $\sigma^2(F_o) + 0.0058F_o^2$ for **3**.

Table 3 Selected bond distances (Å) and angles (°) for $[Pd_2(\mu\text{-mtpo})_2(en)_2][NO_3]_2\cdot 2H_2O$ **1**

Pd(1)–Pd(2)	3.225(1)	Pd(2)–N(21)	2.023(7)
Pd(1)–N(3B)	2.033(6)	Pd(2)–N(22)	2.040(7)
Pd(1)–N(4A)	2.056(6)	Pd(2)–N(4B)	2.071(6)
Pd(1)–N(11)	2.033(6)	Pd(2)–N(3A)	2.038(6)
Pd(1)–N(12)	2.020(6)		
N(11)···O(7A′)	3.002	O(1W)···O(7B)	2.908
N(11)···O(1W″)	2.964	O(1W)···O(2W)	2.724
N(3B)–Pd(1)–N(4A)	93.8(2)	N(21)–Pd(2)–N(22)	83.9(3)
N(3B)–Pd(1)–N(11)	175.6(2)	N(4B)–Pd(2)–N(22)	91.6(3)
N(3B)–Pd(1)–N(12)	91.9(2)	N(4B)–Pd(2)–N(21)	173.7(3)
N(4A)–Pd(1)–N(11)	90.5(2)	N(3A)–Pd(2)–N(22)	175.1(3)
N(4A)–Pd(1)–N(12)	173.5(3)	Pd(1)–N(4A)–C(3AA)	120.2(6)
N(11)–Pd(1)–N(12)	83.7(2)	Pd(1)–N(3B)–C(3AB)	128.3(5)
N(3A)–Pd(2)–N(4B)	93.2(3)	Pd(2)–N(3A)–C(3AA)	129.3(5)
N(3A)–Pd(2)–N(21)	91.2(3)	Pd(2)–N(4B)–C(3AB)	121.3(5)

Symmetry relations: $' -x - 1, -y, -z - 1$; $'' -x, y - \frac{1}{2}, -z - \frac{1}{2}$.

cations, two disordered nitrate anions and five lattice water molecules. The cation is very similar to that found in compound **1**, differing only in the presence of bipy ligands instead of en, and the presence of a two-fold axis relating both halves of the dimer. The geometry around the palladium nuclei is also nearly square planar with a deviation of 0.049(2) Å in the direction of the other metal nucleus. The bond distances and angles around the metal centres are similar to those found in other palladium(II) complexes with similar ligands.[17,21] The bipy ligands are stacked, being coplanar to within 4.6° and giving rise to a tilting angle between the metal co-ordination planes of 19.1° and an intermetallic separation of 3.034(1) Å. This shows the effect of the stacking interactions on the Pd···Pd distance, which is 0.19 Å shorter than that found in compound **1**. The strong π-acidic nature of the bipy ligands may also be considered as an additional contribution to the stabilization of a possible metal–metal interaction in **3**.[6] The fact that the metal centres in **3** appear to be slightly more displaced from the plane than those in **1** (see above) may be indicative of a pyramidalization of the co-ordination polyhedron and hence proof of an

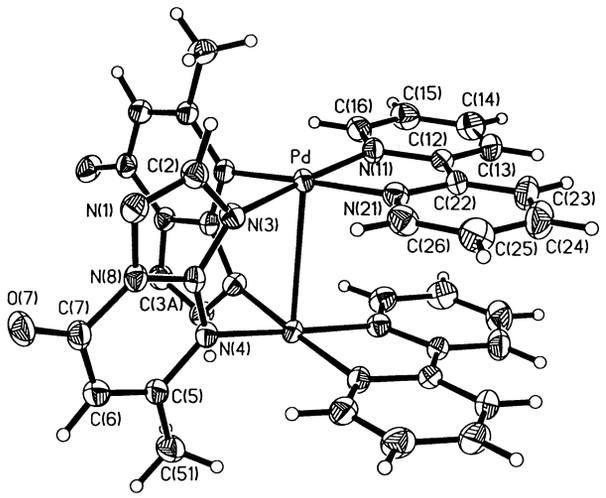


Fig. 2 Structure of cation **3** and the atomic numbering scheme. The thermal ellipsoids are shown at the 30% probability level

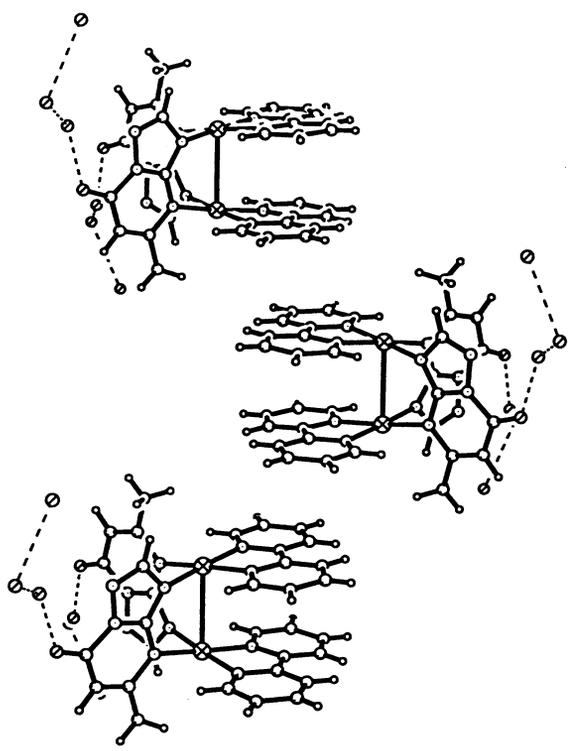


Fig. 3 Packing of complex **3** along the crystallographic *c* axis

Table 4 Selected bond distances (Å) and angles (°) for $[Pd_2(\mu\text{-mtpo})_2(bipy)_2][NO_3]_2\cdot 5H_2O$ **3**

Pd–Pd′	3.034(1)	Pd–N(21)	2.035(3)
Pd–N(3)	2.062(3)	Pd–N(4′)	2.053(3)
Pd–N(11)	2.047(3)		
O(1W)···O(3W)	2.837	O(3W)···O(7)	2.837
O(1W)···O(2W)	3.039	O(1W)···O(2″)	2.975
N(3)–Pd–N(4′)	88.1(1)	N(4)–Pd′–N(21′)	173.5(1)
N(3)–Pd–N(21)	96.7(1)	N(11)–Pd–N(21)	81.3(1)
N(3)–Pd–N(11)	177.7(1)	C(3A)–N(4)–Pd′	118.3(2)
N(11)–Pd–N(4′)	93.9(1)	C(3A)–N(3)–Pd	126.8(3)

Symmetry relations: ′ $-x, y, \frac{1}{2}-z$; ″ $1-x, y, \frac{3}{2}-z$.

attractive metal–metal interaction.[9,22] Therefore, the final conformation of the molecule must be the result of the sum of the different interactions.

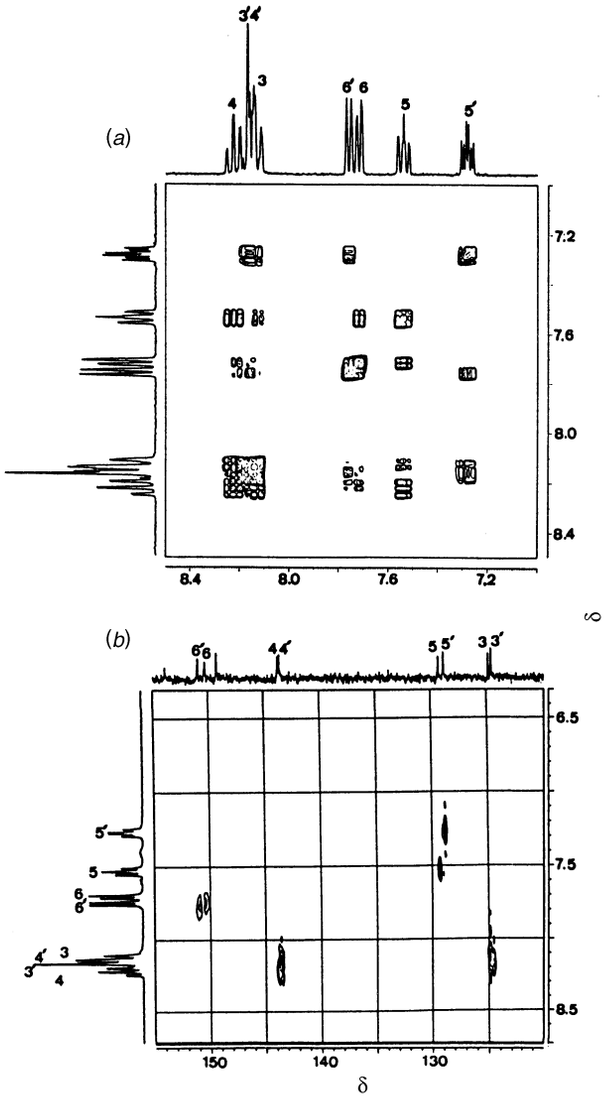


Fig. 4 The COSY ^1H–^1H (*a*) and ^1H–^{13}C (*b*) spectra of complex **3** in the bipy region

Table 5 Proton NMR data (δ) for $[Pd_2(\mu\text{-mtpo})_2(L\text{–}L)_2]^{2+}$ species in D_2O

		Hmtpo			
Compound	pD	Me	H^6	H^2	Auxiliary ligand
mtpo	7.0	2.37	5.93	8.14	
1	8.20	3.12	6.12	8.62	2.98 (en)
2	7.80	3.17	6.11	8.75	3.0 (H^2), 2.8 ($H^{2'}$), 2.2 (H^3), 1.9 ($H^{3'}$ of tn)
3	7.80	3.14	6.35	8.90	8.13 (H^3), 8.20 ($H^{3'}$), 8.23 (H^4), 8.18 ($H^{4'}$), 7.54 (H^5), 7.28 ($H^{5'}$), 7.72 (H^6), 7.76 ($H^{6'}$ of bipy)

In the crystal packing, the stacking interactions between the bipy ligands (separation between mean planes 3.36 Å) of different dimeric cations are responsible for the formation of a zigzag strand along the crystallographic *c* axis (see Fig. 3).Finally, the weak attachment of the water molecules to the dimeric cations and nitrate anions (see Fig. 3 and Table 4) explains their facile loss from the crystals on exposure to air.

NMR spectroscopy

Proton NMR spectroscopy confirmed the complex formation (see Table 5). The resonances of the deprotonated Hmtpo ligand ($pK_a = 6.3$, pD 7.0) occur as expected shifted downfield

after metal co-ordination (CH_3, 0.75–0.80; H^6, 0.19–0.42; H^2, 0.48–0.76 ppm). The bridging co-ordination mode of the mtpo ligand *via* N^3 and N^4 can be deduced from the large downfield shift of the H^2 and CH_3 protons. Thus, palladium binding to N^3 results in a downfield shift of H^2, in a similar way to H^8 of purine bases after metal binding to N^7.[2] On the other hand, the large downfield shift of the CH_3 group is a consequence of the methyl disposition over the palladium co-ordination plane after binding to N^4. This fact may be considered diagnostic of involvement of N^4 in the co-ordination of a d^8 metal ion,[13] and it may also be indicative of a weak Pd · · · H interaction,[23,24] the Pd–H separation being about 2.6 Å. On the other hand, the downfield shift of the mtpo signals increases in the order **1** < **2** < **3**. It appears that the charge withdrawal from the metal centres by the bipy ligands, due to their strong π-acid character, makes it possible for the mtpo ligands to act as better σ donors.[17] However, the increase in the ligand π-acid character does not appear to result in a significant *trans* influence, as can be deduced from the Pd–N (mtpo) bond distances. Furthermore, the ^1H resonances of the auxiliary ligands are also of great structural interest.

The assignments for bipy given in Table 5 were confirmed by a series of two-dimensional ^1H–^1H and ^1H–^{13}C correlation spectroscopy (COSY) experiments for complex **3** (see Fig. 4). The pronounced upfield shifts of the bipy proton resonances, if compared to those of the analogous compound $[(NH_3)_2Pt(\mu\text{-mtpo-}N^3,N^4)_2Pd(bipy)][NO_3]_2\cdot H_2O$,[14] suggest a stacking interaction of the two ligand planes. Also, it is possible to observe the loss of the original equivalence between the two halves of the tn and bipy auxiliary ligands as a result of the head-to-tail arrangements of the mtpo ligands in the complexes (see Fig. 4 and Table 5). This arrangement appears to be favoured in all cases since it minimizes the interligand steric interactions. Hence, it appears that the solid-state structures are clearly preserved in solution.

Acknowledgements

We thank Dirección General de Investigación Científica y Técnica for financial support (Grant No. PB94-0807-CO2-01).

References

1 (*a*) K. J. Barnham, C. J. Bauer, M. I. Djuran, M. A. Mazid, T. Rau and P. J. Sadler, *Inorg. Chem.*, 1995, **34**, 2826; (*b*) K. Uchida, A. Toyama, Y. Tamura, M. Sugimura, F. Mitsumori, Y. Furukawa, H. Takeuchi and I. Harada, *Inorg. Chem.*, 1989, **28**, 2067; (*c*) S. Schuvachittanont and R. van Eldik, *Inorg. Chem.*, 1994, **33**, 895; (*d*) T. G. Appleton, D. R. Bedgood and J. R. Hall, *Inorg. Chem.*, 1994, **33**, 3834.
2 B. Lippert, *Prog. Inorg. Chem.*, 1989, **37**, 1; O. Renn, A. Albinati and B. Lippert, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 84.
3 K. Umakoshi, A. Ichimura, I. Kinoshita and S. Ooi, *Inorg. Chem.*, 1990, **29**, 4005.
4 W. Micklitz, G. Müller, B. Huber, J. Riede, F. Rashwan, J. Heinze and B. Lippert, *J. Am. Chem. Soc.*, 1988, **110**, 7084.
5 M. Krumm, B. Lippert, L. Randaccio and E. Zangrando, *J. Am. Chem. Soc.*, 1991, **113**, 5129; M. Krumm, E. Zangrando, L. Randaccio, S. Menzer and B. Lippert, *Inorg. Chem.*, 1993, **32**, 700.
6 R. Cini, F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Am. Chem. Soc.*, 1993, **115**, 5123.
7 J. A. Bailey, M. G. Hill, R. G. Marsh, V. M. Miskowski, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1995, **34**, 4591.
8 T. Kawamoto, Y. Nagasawa, H. Kuma and Y. Kushi, *Inorg. Chem.*, 1996, **35**, 2427.
9 J. J. Novoa, G. Aullón, P. Alemany and S. Alvarez, *J. Am. Chem. Soc.*, 1995, **117**, 7169.
10 L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 1230.
11 M. Grehl and B. Krebs, *Inorg. Chem.*, 1994, **33**, 3877.
12 T. V. O'Halloran and S. J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 3342; *Inorg. Chem.*, 1989, **28**, 1289.
13 J. A. R. Navarro, M. A. Romero, J. M. Salas, M. Quirós, J. El Jaraoui Bahraoni and J. Molina, *Inorg. Chem.*, 1996, **35**, 7829.
14 J. A. R. Navarro, M. A. Romero, J. M. Salas and M. Quirós, unpublished work.
15 H. Hohmann and R. van Eldik, *Inorg. Chim. Acta*, 1990, **174**, 87.
16 G. M. Sheldrick, SHELXTL PLUS, Program for the solution of crystal structures, Release 34, Siemens Analytical X-Ray Instruments, Madison, WI, 1989.
17 W. Micklitz, W. S. Sheldrick and B. Lippert, *Inorg. Chem.*, 1990, **29**, 211.
18 M. Krumm, I. Mutikainen and B. Lippert, *Inorg. Chem.*, 1991, **30**, 884.
19 A. J. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
20 C.-L. Yao, L.-P. He, J. D. Korp and J. L. Bear, *Inorg. Chem.*, 1988, **27**, 4389.
21 H. Engelking, S. Karentzoupolos, G. Reusmann and B. Krebs, *Chem. Ber.*, 1994, **127**, 2355.
22 G. Aullón, P. Alemany and S. Alvarez, *Inorg. Chem.*, 1996, **35**, 5061.
23 R. G. Miller, R. D. Stauffer, D. R. Fahey and D. R. Parnell, *J. Am. Chem. Soc.*, 1970, **92**, 1511.
24 A. Albinati, P. S. Pregosin and F. Wombacher, *Inorg. Chem.*, 1990, **29**, 1812; G. Frommer, F. Lianza, A. Albinati and B. Lippert, *Inorg. Chem.*, 1992, **31**, 2434.

Received 10*th September* 1996; *Paper* 6/06257A