Palladium(II) and Platinum(II) Polyamine Complexes: X-Ray Crystal Structures of (*SP*-4-2)-Chloro{*N*-[(3-amino-κ*N*)-propyl]propane-1,3-diamine-κ*N*,κ*N*′}palladium(1+) Tetrachloropalladate (2–) (2:1) and (*R*,*S*)-Tetrachloro[μ-(spermine)]dipalladium(II) (= {μ-{*N*,*N*′-Bis[(3-amino-κ*N*)propyl]butane-1,4-diamine-κ*N*:κ*N*′}}tetrachlorodipalladium)

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The reactivity of the polyamines L, *i.e.*, *N*-(3-aminopropyl)propane-1,3-diamine (**1**), spermidine (= *N*-(3-aminopropyl)butane-1,4-diamine; **2**), and spermine (= *N*,*N*′-bis(3-aminopropyl)butane-1,4-diamine; **3**) *vs.* palladium(II) and platinum(II) salts is studied. These reactions allowed us to prepare and characterize a wide variety of Pd^{II} and Pt^{II} complexes containing the polyamines. Compounds of the general formula $[MCl(L)]_2[MCl_4]$ (L = **1**; **1a**: M = Pd; **1b**: M = Pt) or [MCl(L)]Cl (L = **1**; **1′a**: M = Pd; **1′b**: M = Pt) were isolated after treatment of $K_2[MCl_4]$ or *cis*-$[MCl_2(dmso)_2]$ respectively, with **1**. The reaction of $K_2[MCl_4]$ with **2** led to $[MCl(L)]_2[MCl_4]$ (L = **2**; **2a**: M = Pd; **2b**: M = Pt), while that with **3** gave the neutral dinuclear compounds $[M_2Cl_4(L)]$ (L = **3**; **3a**: M = Pd; **3b**: M = Pt). A comparative study of the results obtained in these reactions allowed us to evaluate the influence of *i*) the number of N-atoms in the polyamine, *ii*) their basicity, and *iii*) the palladium or platinum salt, upon the nature of the final product. Compounds **1a** and (*R*,*S*)-**3a** were characterized by their X-ray crystal-structure analysis. Both exhibited the monoclinic crystal system, **1a** the space group $P2_1/c$, and **3a** the space group $P2_1/n$.

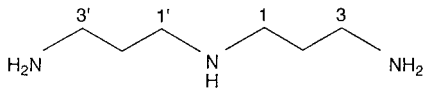
1. Introduction. – *cis*-Diamminedichloroplatinum(II) (cisplatin or CDDP) is an agent of established efficacy against a wide variety of human tumors, such as testicular, ovarian, and bladder cancers [1][2]. However, its utility is limited due to the toxic side effects, the narrow spectrum of responsive tumors, and the development of resistance in tumor cells.

For more than two decades, a great effort has been made not only to enhance the antitumor activity of cisplatin but also to widen the spectrum of drug-response by lowering its toxicity. Meanwhile, various clinical strategies have been used to reduce the toxicity of cisplatin. One of these strategies is based on the synthesis of new compounds capable of reducing toxicity [3][4]. In the last years, some dimeric platinum and palladium complexes have been synthesized, and their biological activity and DNA-binding properties have been studied [5–7].

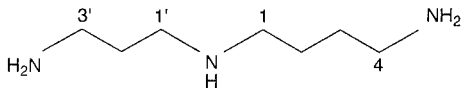
On the other hand, it is well known that polyamines, *e.g.*, spermine (= *N*,*N*′-bis(3-aminopropyl)butane-1,4-diamine; **3**) and spermidine (= *N*-(3-aminopropyl)butane-1,4-diamine; **2**) play an important role in the syntheses of nucleic acids and in the structure of the cell membrane [8][9].

Thus, it seemed interesting to study the reactivity of palladium(II) and platinum(II) salts *vs.* three different polyamines L, *i.e.*, *N*-(3-aminopropyl)propane-1,3-diamine (**1**;

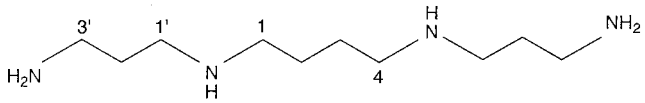
dipn), spermidine (**2**; spd), and spermine (**3**; spn), which contain three (in **1** or **2**) or four (in **3**) amine N-atoms able to coordinate one or more metal atoms. Moreover, in the case of the two triamine ligands **1** and **2**, the length of the parent alkane chain $-(CH_2)_n-$ ($n=3$ in **1** or 4 in **2**) may determine the nature and structure of the palladium and platinum complexes, as well as their interaction with DNA.



1 dipn



2 spd (spermidine)

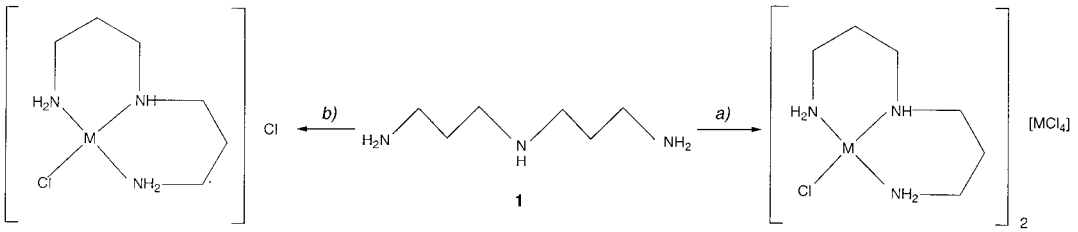


3 spn (spermine)

In this paper, we present the synthesis, characterization, and study of coordination compounds containing palladium(II) and platinum(II) and the polyamines **1**–**3**.

2. Results and Discussion. – When aqueous solutions of *N*-(3-aminopropyl)propane-1,3-diamine (**1**) and $K_2[MCl_4]$ ($M=Pd^{II}$ or Pt^{II}) were mixed, orange ($M=Pd$) or brown ($M=Pt$) solids were formed (*Scheme 1*). Elemental analyses of these products (see *Exper. Part*) were consistent with those expected for $[MCl(L)]_2[MCl_4]$ **1a** ($M=$ Pd) or **1b** ($M=Pt$), in which the cation contains a triamine ligand acting as a neutral terdentate group. The most relevant features observed in the IR spectra of **1a** and **1b** are the stretching bands of the M–Cl and M–N bonds (see *Exper. Part*) and the bendings of the NH_2 groups (at *ca.* 1600 cm^{-1}). The ^1H- and ^{13}C-NMR signals were assigned on the basis of two-dimensional NMR experiments. The number of signals detected in the NMR spectrum is in agreement with the proposed formula.

Scheme 1



1'a M=Pd
b M=Pt

a) K_2MCl_4 in H_2O *b)* *cis*-$[MCl_2(dmso)_2]$ in MeOH

1a M=Pd
b M=Pt

Compound **1a** was also characterized by X-ray diffraction. The structure consists of two independent cations **I** and **II** of $[PdCl(dipn)]^+$ and of the anion $[PdCl_4]^{2-}$. The structures of the two cations **I** and **II** of **1a**, together with the atom-numbering scheme are presented in *Fig. 1*. A selection of bond lengths and angles is given in *Table 1*.

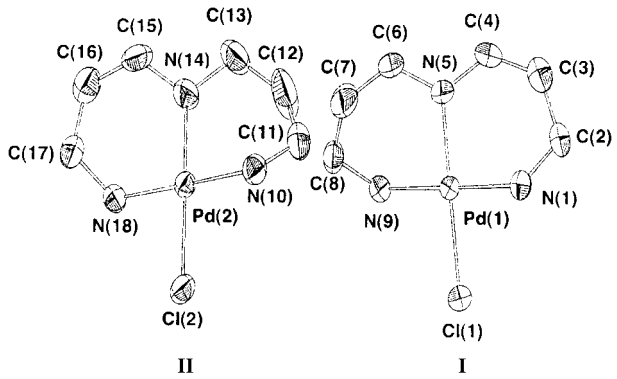


Fig. 1. *Molecular structure of [PdCl(dipn)]$_2$[PdCl$_4$]* (**1a**) *consisting of two independent cations* **I** *and* **II**. Arbitrary numbering. The anion $[PdCl_4]^{2-}$ is not shown.

Table 1. *Bond Lengths* [Å] *and Angles* [°] *for [PdCl(dipn)]$_2$[PdCl$_4$]* (**1a**). E.s.d. values in parentheses

Bond lengths:					
Pd(1)–N(5)	2.045(5)	Pd(1)–N(9)	2.063(4)	Pd(1)–N(1)	2.052(4)
Pd(1)–Cl(1)	2.3108(14)	Pd(2)–N(14)	2.041(5)	Pd(2)–N(10)	2.049(5)
Pd(2)–N(18)	2.051(5)	Pd(2)–Cl(2)	2.318(2)	Pd(3)–Cl(32)	2.289(2)
Pd(3)–Cl(32)[a])	2.289(2)	Pd(3)–Cl(31)	2.3020(14)	Pd(3)–Cl(31)[a])	2.3020(14)
Pd(4)–Cl(42)	2.293(2)	Pd(4)–Cl(42)[b])	2.293(2)	Pd(4)–Cl(41)	2.297(2)
Pd(4)–Cl(41)[b])	2.297(2)	N(1)–C(2)	1.466(8)	C(2)–C(3)	1.433(11)
C(3)–C(4)	1.403(10)	C(4)–N(5)	1.395(8)	N(5)–C(6)	1.405(8)
C(6)–C(7)	1.369(11)	C(2)–N(9)	1.466(79	C(8)–C(7)	1.447(10)
N(10)–C(11)	1.443(9)	C(11)–C(12)	1.460(12)	C(12)–C(13)	1.449(14)
C(13)–N(14)	1.459(9)	N(14)–C(15)	1.452(9)	C(15)–C(16)	1.449(10)
C(16)–C(17)	1.488(10)	C(17)–N(18)	1.470(8)		
Bond angles:					
N(5)–Pd(1)–N(1)	89.1(2)	N(5)–Pd(1)–N(9)	90.3(2)	N(1)–Pd(1)–N(9)	178.3(2)
N(5)–Pd(1)–Cl(1)	177.1(2)	N(1)–Pd(1)–Cl(1)	88.76(14)	N(9)–Pd(1)–Cl(1)	91.96(13)
N(14)–Pd(2)–N(10)	92.1(2)	N(14)–Pd(2)–N(18)	87.5(2)	N(10)–Pd(2)–N(18)	179.0(2)
N(14)–Pd(2)–Cl(2)	178.4(2)	N(10)–Pd(2)–Cl(2)	89.4(2)	N(18)–Pd(2)–Cl(2)	91.10(14)
Cl(32)[a])–Pd(3)–Cl(32)	180.0(1)	Cl(32)[a])–Pd(3)–Cl(31)	90.83(6)	Cl(32)–Pd(3)–Cl(31)	89.17(6)
Cl(32)[a])–Pd(3)–Cl(31)[a])	89.17(6)	Cl(32)–Pd(3)–Cl(31)[a])	90.83(6)	Cl(31)–Pd(3)–Cl(31)[a])	180.0
Cl(42)–Pd(4)–Cl(42)[b])	180.0	Cl(42)–Pd(4)–Cl(41)[b])	89.24(7)	Cl(42)–Pd(4)–Cl(41)	90.76(7)
Cl(42)[b]–Pd(4)–Cl(41)[b])	90.76(7)	Cl(42)[b])–Pd(4)–Cl(41)	89.24(7)	C(2)–N(1)–Pd(1)	115.7(4)
Cl(41)[b])–Pd(4)–Cl(41)	179.998(1)	C(3)–C(2)–N(1)	113.6(6)	C(4)–C(3)–C(2)	129.2(7)
N(5)–C(4)–C(3)	125.1(7)	C(4)–N(5)–C(6)	123.0(6)	C(4)–N(5)–Pd(1)	116.4(4)
C(6)–N(5)–Pd(1)	117.5(4)	C(7)–C(6)–N(5)	126.1(7)	N(9)–C(8)–C(7)	115.6(5)
C(6)–C(7)–C(8)	126.1(8)	C(8)–N(9)–Pd(1)	117.6(4)	C(11)–N(10)–Pd(2)	118.2(4)
N(10)–C(11)–C(12)	115.1(6)	C(11)–C(12)–C(13)	121.2(9)	N(14)–C(13)–C(12)	116.5(8)
C(15)–N(14)–C(13)	115.1(7)	C(15)–N(14)–Pd(2)	114.5(4)	C(13)–N(14)–Pd(2)	116.3(5)
C(16)–C(15)–N(14)	118.4(6)	C(15)–C(16)–C(17)	120.1(6)	N(18)–C(17)–C(16)	112.4(5)
C(17)–N(18)–Pd(2)	114.6(4)				

[a]) Symmetry transformation used to generate equivalent atoms: $-x+1,\ -y+1,\ -z+2$. [b]) Symmetry transformation used to generate equivalent atoms: $-x,\ -y+2,\ -z+2$.

In the two cations, the Pd-atom (Pd(1) and Pd(2)) is bound to one Cl-atom (Cl(1) or Cl(2)) and to the three N-atoms of the *N*-(3-aminopropyl)propane-1,3-diamine (N(1), N(5), and N(9) in cation **I**, or N(10), N(14), and N(18) in cation **II**). In each cation, the Pd-atom is in a slightly distorted square-planar environment[1]). Bond angles around the Pd-atoms range from 91.96(13)° (N(9)–Pd(1)–Cl(1)) to 88.76(14)° (N(1)–Pd–Cl(1)) in cation **I**, and from 91.10(14)° (N(18)–Pd(2)–Cl(2)) to 89.4(2)° (N(10)–Pd(2)–Cl(2)) in cation **II**.

The crystal structure of compound **1a** shows a bicyclic system arising from the fusion of the two six-membered rings of the two cations. The metallocycles have a chair conformation with the atoms Pd(1) and Pd(2) and the C-atom (C(3) and C(6) in cation **I** and C(13) and C(16) in cation **II**) out of the plane. The Pd-atoms are displaced from the mean planes by *ca.* – 0.99 and 0.79 Å in cation **I** and by 0.60 and 1.10 Å in cation **II**.

An interesting feature of the crystal structure of complex **1a** are the transannular Pd ··· H contacts involving the amine H-atoms, *i.e.*, Pd(1) ··· H(1A) 2.49(4) and Pd(1) ··· H(9A) 2.491(5) Å in cation **I**, and Pd(2) ··· H(10A) 2.48(5) and Pd(2) ··· H(18B) 2.489(5) Å in cation **II**. A similar kind of transannular contact has also been reported for *trans*-[Pd[R(Me)C=N–N(Me)(Ph)}$_2$Cl$_2$], with R = Me or ^{i}Pr [10–13], for *trans*-[Pd{(η^5-C$_5$H$_5$)Fe{(η^5-C$_5$H$_4$)C(Me)=N–N(Me)$_2$}Cl$_2$] [14], and for the dinuclear complex [Pd$_2$Cl$_4$}(Me)$_2$N–N=CH(CH$_2$)$_3$CH=N–N(Me)$_2$}] [15].

In contrast with the results mentioned above, when *N*-(3-aminopropyl)propane-1,3-diamine (**1**) was treated with equimolar amounts of the *cis*-[MCl$_2$(dmso)$_2$] complex [16] (M = Pd or Pt) (*Scheme 1*), no evidence for the formation of insoluble products was detected. The concentration of the resulting pale solutions followed by the addition of acetone produced a pale yellow (M = Pd) or a white (M = Pt) solid. Elemental analyses, IR, and NMR spectroscopic data of these materials were consistent with those expected for the coordination compounds [MCl(L)] **1′a** (M = Pd) or **1′b** (M = Pt), in which the amine is a neutral terdentate ligand. In 1994, *Rochon* and *Laperrière* [17] reported the preparation of the complex [PtCl(L)]Cl (**1′b**) from K$_2$[PtCl$_4$] as starting material. The use of *cis*-[PtCl$_2$(dmso)$_2$] as starting material has a few advantages over K$_2$[PtCl$_4$]. Fewer purification steps are needed since there are no by-products to remove (KCl), and the *cis*-[PdCl$_2$(dmso)$_2$] is insoluble in cold MeOH.

The action of aqueous solutions of K$_2$[MCl$_4$] (M = Pd or Pt) on spermidine (**2**) led to the formation of insoluble products (*Scheme 2*). Elemental analyses of these materials were consistent with those expected for [MCl(L)]$_2$[MCl$_4$] **2a** (M = Pd) or **2b** (M = Pt) with L = **2**. The IR spectra of **2a** and **2b** showed the typical bands of the [MCl$_4$]$^{2-}$ anions [18] at *ca.* 330 cm^{-1} for M = Pd or 320 cm^{-1} for M = Pt (also observed for **1a** and **1b**) and the absorptions due to the stretching of the M–N bonds and to the bending of the NH and NH$_2$ groups.

The binding of the secondary amine N-atom of **2** to M^{II} induces chirality, and since there is no any apparent source of chiral discrimination, the formation of a mixture of

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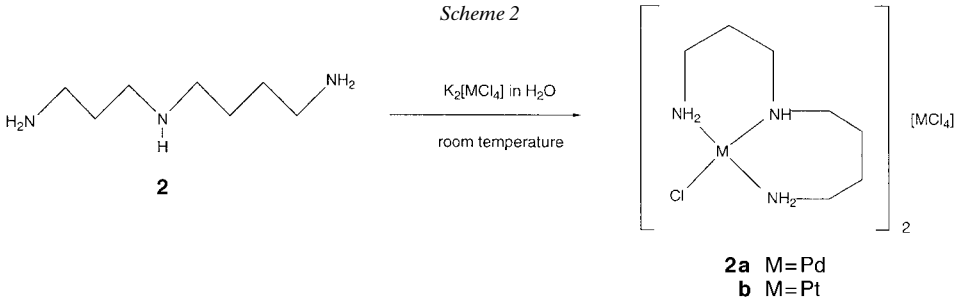
[1]) The least-squares equation of the plane defined by the atoms Cl(1), N(1), N(5), and N(9) in cation **I** is $(-0.6672)XO + (0.5416)YO + (0.5133)ZO = 2.4652$. The deviations from the mean plane are as follows: Cl(1) 0.03, N(1) – 0.03, N(5) 0.03, and N(9) – 0.03 Å. The least-squares equation of the plane defined by the atoms Cl(2), N(10), N(14) and N(18) in cation **II** is $(-0.4469)XO + (0.8616)YO + (0.2406)ZO = 9.3392$. The deviations from the mean plane are as follows: Cl(2) 0.01, N(10) 0.01, N(14) – 0.02, and N(18) – 0.01 Å.

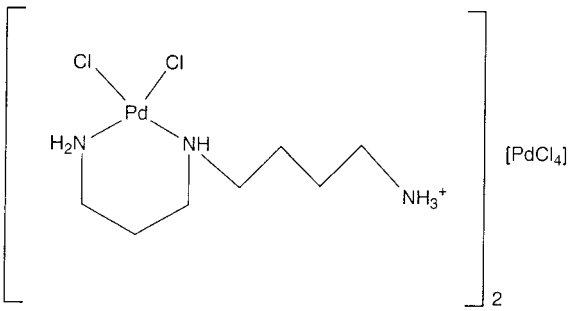
Scheme 2



2a M=Pd
b M=Pt

the two enantiomers (*R*) and (*S*) could be expected. These two enantiomers are not discriminated in NMR experiments, and only one signal is expected for each kind of proton and C-atom (see *Exper. Part*).

In compounds **2**, the cation $[MCl(L)]^+$ contains a [5.4.0]bicyclic metallacycle. Some examples of Pd^{II} and Pt^{II} compounds forming seven-membered chelate rings have been described [19][20]. In 1992, *Navarro-Ranninger et al.* [21] reported the synthesis, characterization, and X-ray crystal structure of $[PdCl_2(spdH)]_2[PdCl_4]\cdot 2\,H_2O$ (**2c**), which is closely related to **2a**. In compound **2c**, which was isolated after treatment of $K_2[PdCl_4]$ with spermidine trihydrochloride, the polyamine is a bidentate *N,N′*-donor ligand (forming a six-membered ring) and the terminal amine group is protonated. The comparison of the formation of **2c** with that of **2a** suggests that the coordination mode of the spermidine ligand is strongly affected by the experimental conditions, *i.e.* in acidic media, the formation of **2c** is strongly preferred. Under different conditions, the same authors obtained compounds with the same stoichiometry as **2a** [21] or **2b** [22], but they tentatively proposed a different structure.

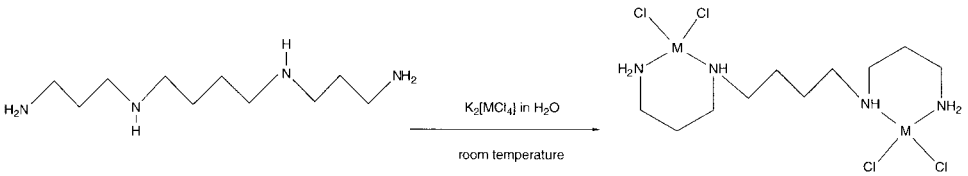


2c

More interesting are the results obtained when the reactions were carried out using spermine (**3**) as ligand (*Scheme 3*). When the $K_2[MCl_4]$ (M = Pd or Pt) salt was added to an aqueous solution of ligand **3** (in a 2 : 1 molar ratio) a yellow (M = Pd) or brown (M = Pt) solid formed immediately. Elemental analyses of these materials were consistent with those expected for the dinuclear compounds $[M_2Cl_4(spn)]$ **3a** (M = Pd) or **3b** (M = Pt) (*Scheme 3*). The data of **3a** and **3b** (see below) suggest that their structures have two *cis*-$[MCl_2(H_2NCH_2CH_2CH_2NHCH_2CH_2)]$ units connected by a

C–C bond. In each half of the molecule, the metal(II) is involved in a six-membered metallacycle, and the two remaining coordination sites are occupied by two Cl-atoms. Since the binding of the secondary amine NH to M^{II} induces chirality, and there is no any apparent source of chiral discrimination, a mixture of the two enantiomers (*R*,*R*)/(*S*,*S*) and the *meso* form (*R*,*S*) could be expected to form in the course of the reaction. Two superimposed sets of signals were detected in the NMR spectrum of **3a** (see *Exper. Part*), consistent with the presence of the isomers in solution.

Scheme 3



3 **3a** M=Pd **b** M=Pt

Good crystals of the *meso* form of **3a** were obtained by slow evaporation of the mother liquor. The molecular structure and the atom labelling scheme are presented in *Fig. 2*. A selection of bond lengths and angles is presented in *Table 2*.

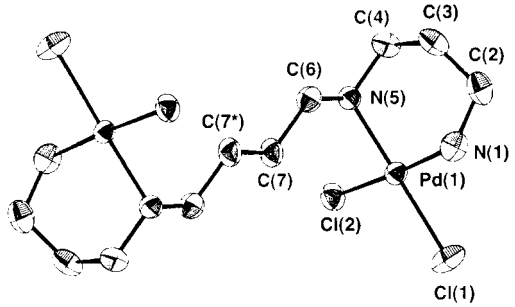


Fig. 2. *Molecular structure of [Pd_2Cl_4(spn)]* **3a**. Arbitrary numbering.

The structure of *meso*-**3a** consists of discrete molecules of [Pd_2($H_2NCH_2CH_2$-$CH_2NHCH_2CH_2$)$_2Cl_4$] separated by *van der Waals* contacts. The whole molecule can be visualized as being derived from the connection of two fragments *cis*-[$PdCl_2$(H_2NCH_2-$CH_2CH_2NHCH_2CH_2$)] linked by a crystallographic symmetry center located at the middle point of the segment C(7)–C(7*) (*Fig. 2*). In each fragment, the Pd-atom is in a slightly distorted square-planar environment[2]) coordinated to the atoms Cl(1), Cl(2), N(1), and N(5). Each half of the complex contains a six-membered palladacycle formed by the atoms N(1), N(5), C(2), C(3), and C(4). The metallacycle has a chair conformation with the Pd and the C(3) atoms out of the plane defined by N(1), C(2),

[2]) The last-squares equation of the plane defined by the atoms Cl(1), Cl(2), N(1), and N(5) is $(-0.1165)XO+(0.9024)YO+(-0.4148)ZO=-0.4727$. The deviations from the plane are as follows: Cl(1) 0.06, Cl(2) −0.06, N(1) −0.07, and N(5) +0.07 Å.

Table 2. *Bond Lengths* [Å] *and Angles* [°] *for [Pd_2Cl_4(spn)]* (**3a**). E.s.d. values in parentheses.

Bond lengths:		Bond angles:	
Pd(1)–N(1)	2.022(3)	N(1)–Pd(1)–N(5)	90.30(11)
Pd(1)–N(5)	2.041(3)	N(1)–Pd(1)–Cl(2)	175.02(9)
Pd(1)–Cl(2)	2.3143(8)	N(5)–Pd(1)–Cl(2)	87.47(8)
Pd(1)–Cl(1)	2.3158(9)	N(1)–Pd(1)–Cl(1)	88.49(9)
N(1)–C(2)	1.484(5)	N(5)–Pd(1)–Cl(1)	177.31(8)
C(2)–C(3)	1.505(6)	Cl(2)–Pd(1)–Cl(1)	93.91(4)
C(3)–C(4)	1.518(5)	C(2)–N(1)–Pd(1)	114.8(2)
C(4)–N(5)	1.486(4)	N(1)–C(2)–C(3)	1710.5(3)
C(2)–C(3)	1.505(6)	C(2)–C(3)–C(4)	115.6(3)
N(5)–C(6)	1.488(4)	N(5)–C(4)–C(3)	114.3(3)
N(6)–C(7)	1.520(5)	C(4)–N(5)–C(6)	113.1(3)
C(7)–C(7)[a])	1.531(6)	C(4)–N(5)–Pd(1)	113.9(2)
C(2)–C(3)	1.505(6)	C(6)–N(5)–Pd(1)	113.0(2)
		N(5)–C(6)–C(7)	112.3(3)
		C(6)–C(7)–C(7)[a])	111.3(4)

[a]) Symmetry transformation used to generate equivalent atoms: $-x+2,\ -y+1,\ -z$.

C(4), and N(5)[3]). The Pd-atom is displaced from the mean plane by *ca.* −1.02 Å towards the opposite side of the alkyl substituent at N(5). This arrangement provides less steric hindrance between the $PdCl_2$ moiety of *meso*-**3a** and the alkylic chain bound to N(5). As mentioned above, the binding of the Pd-atom to N(5) generates a chiral center, and the two halves of the molecule have different enantiomeric forms. The long distance between the two Pd-atoms (7.5074(8) Å) in *meso*-**3a** precludes the existence of direct interactions between Pd(1) and Pd(1*). In both structures **1a** and *meso*-**3a**, the Pd–N bond lengths are similar to those found for related palladium(II) compounds of the general formula *cis*-[Pd(N⋯N)Cl_2], where (N⋯N) represents a bidentate amine ligand (*Table 3*). In conclusion, the structure of complexes **3a**,**b** is markedly different from that of complexes **2a**,**b** and can be attributed to the presence of an additional N-atom, which is essential for the formation of the two six-membered rings.

As a result of the orientation of the alkylic chain at N(5) of *meso*-**3a** in relation to the $PdCl_2(H_2NCH_2CH_2CH_2NH)$ moiety there are Pd⋯H contacts similar to those found for complex **1a**. In addition, tiny rotations of the $PdCl_2(H_2N(1)CH_2CH_2CH_2$-NH(5)) moiety around the N(5)–C(6) bond would take the H(7A) further away from the Pd-atom, in which case the Pd⋯H(7A) contact would be avoided. This finding suggests that these interactions are attractive in nature.

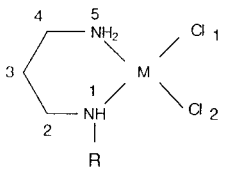
Although *Farrell* and coworkers [27] have recently reported a wide variety of dinuclear Pt^{II} complexes containing spermidine, spermine, and their derivatives with *tert*-butoxycarbonyl groups bound to the central amine N-atom (see **2d**,**e** and **3c**–**f**), these complexes are markedly different from **3a** and **3b** since *Farrell*'s complexes contain two $PdCl(NH_3)_2$ moieties linked by bridging spermidine and spermine groups. In addition, these authors reported that when complex **3d** was treated at 37° in D_2O (at

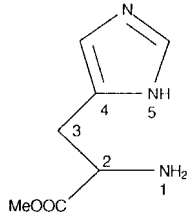
[3]) The least-squares equation of the plane defined by the atoms N(1), C(2), C(4), and N(5) is $(0.05061)XO + (0.8594)YO + (0.0723)ZO = 6.0374$. Deviations from the plane are as follows: N(1) +0.01, C(2) −0.02, C(4), +0.02, N(5) 0.02, Pd −1.02, and C(3) +0.074 Å.

Table 3. *Selected Bond Lengths* [Å] *and Angles* [°] *for Palladium(II) Compounds Containing* cis-*[PdCl$_2${N(1)···N(5)}] Cores, {N(1)···N(5)} Representing a Polydentate Amine Forming a Six-Membered Chelate Ring.* Arbitrary numbering of the ligands L_1, L_2 and L_3[a]).

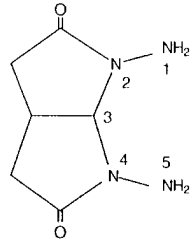
{N(1)···N(5)}	Pd–N(1)	Pd–N(5)	Pd–Cl(1)	Pd–Cl(2)	Cl(1)–Pd–Cl(2)	N(1)–Pd–N(5)	N(1)···N(5)	*b*	Ref.
dipn (**1**): cation **I**	2.052(5)	2.045(5)	2.3108(14)	–	–	89.1(2)	2.879(8)	1.405	
	2.063(4)	2.045(5)	–	–	–	90.3(2)	2.913(8)	1.418	this work
cation **II**	2.049(5)	2.041(5)	2.318(2)	–	–	92.1(2)	2.954(8)	1.444	
	2.051(5)	2.041(5)	2.318(2)	–	–	87.5(2)	2.829(8)	1.383	
spn (**3**)	2.022(4)	2.041(5)	2.3158(14)	2.318(2)	93.9(4)	90.30(11)	2.881(8)	1.418	this work
(2-OH–C_6H_4–CH_2NHCH_2CHMe–)$_2$	2.045(6)	2.056(6)	2.313(3)	3.311(3)	92.4(3)	93.4(4)	2.986(8)	1.460	[23]
L^1	2.043(3)	2.019(3)	2.306(1)	2.305(1)	91.40(0)	92.0(1)	2.939(5)	1.439	[24]
L^2	2.018(4)	2.073(3)	2.291(1)	2.300(2)	92.8(1)	94.7(1)	3.010(6)	1.472	[25]
L^3	2.116(3)	2.054(3)	2.309(1)	2.302(1)	88.0(1)	93.4(1)	3.036(5)	1.456	[26]

a)

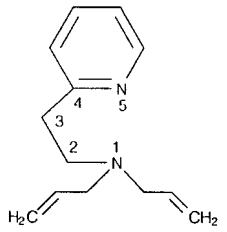




L^1

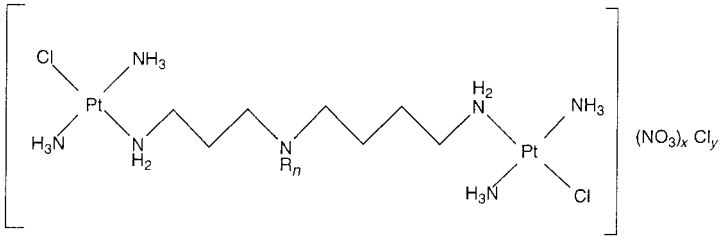


L^2

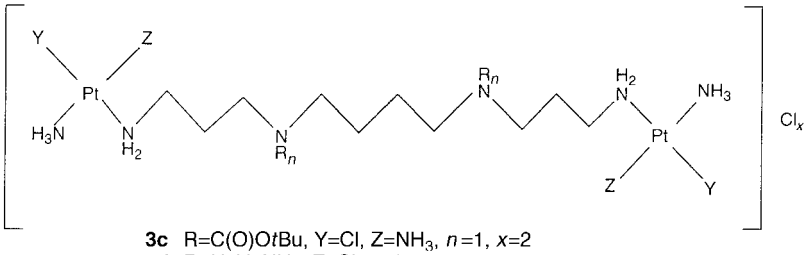


L^3

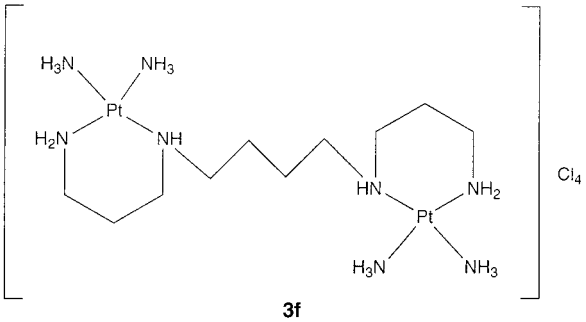
pD 7.3) for 2 days, its ^{1}H-NMR spectrum changed considerably. These variations were attributed to an elimination reaction followed by the subsequent change of coordination of the bridging ligand by binding of the central amine N-atoms to the Pt-atoms. The formation of complex $[Pt(NH_3)_2(H_2NCH_2CH_2CH_2NH_2CH_2CH_2)]_2Cl_4$ (**3f**) was postulated based on the NMR studies. It is interesting that in **3f**, the mode of coordination of the spermine is identical to those in **3a** or **3b**. However, in compound **3f**, the cation is a bis[(tetraamine)platinum(II)] derivative, which cannot bind to DNA. In contrast, in **3a** and **3b** each half of the molecule contains a di(amine)dichlorometal(II)] fragment which is formally identical to cisplatin.



2d R=C(O)O*t*Bu, n=1, x=0.75, y=1.25
e R=H, n=2, x=0, y=3



3c R=C(O)O*t*Bu, Y=Cl, Z=NH_3, n=1, x=2
d R=H, Y=NH_3, Z=Cl, n=2, x=4
e R=H, Y=Cl, Z=NH_3, n=2, x=4



3f

3. Conclusion. – The results reported in this work reveal that the reaction of the polyamine ligands *N*-(3-aminopropyl)propane-1,3-diamine (**1**), spermidine (**2**), or spermine (**3**) with $K_2[MCl_4]$ (M = Pd or Pt) produces different kinds of coordination compounds (mono- or dinuclear), the nature of which mainly depends on the number

of N-atoms in the ligand (three for **1** or **2** and four for **3**). Thus, when **1** was treated with $K_2[MCl_4]$, $[MCl(H_2NCH_2CH_2CH_2NHCH_2CH_2CH_2NH_2)]_2[MCl_4]$ **1a** (M = Pd) or **1b** (M = Pt) were obtained, the structure of which contains cations with the metal atom involved in a bicyclic system derived from the fusion of two six-membered metallacycles. When the polyamine is spermidine (**2**), which has an additional CH_2 group between the primary- and secondary-amine N-atom, the reaction also produced compounds of formula $[MCl(L)]_2[MCl_4]$, *i.e.*, **2a**,**b**, but these are mixtures of the two enantiomers (*R*) and (*S*) in which the amine behaves as a *N*,*N*′,*N*″-terdentate group. In contrast, spermine (**3**) which has an additional $(CH_2)_3NH_2$ group, reacted with $K_2[MCl_4]$ (M = Pd or Pt) to give a mixture of the two enantiomers (*R*,*R*) and (*S*,*S*) and the *meso* form ((*R*,*S*)) of $[MCl_2(H_2NCH_2CH_2CH_2NHCH_2CH_2)]_2$, *i.e.* **3a**,**b**, which contain two units $[MCl_2(H_2NCH_2CH_2CH_2NHCH_2CH_2)]$ connected by a C–C bond.

The crystallographic studies on compounds **1a** and *meso*-**3a** allowed us not only to confirm the different type of binding of the ligands *N*-(3-aminopropyl)propane-1,3-diamine (**1**) and spermine (**3**) to Pd^{II}, but also to determine the absolute configuration of the two halves of the *meso* form of complex **3a**.

The most outstanding feature of the studies reported in this work is the environment of the metal(II) ions, which are basically a (triamine)chlorometal(II) unit in **1a**,**b** and **2a**,**b**, or two (diamine)dichlorometal(II) moieties in **3a**,**b**. The backbones in **1a**,**b** and **2a**,**b** are similar to those reported for $[\{cis\text{-}PtCl(NH_3)_2\}_2[\mu\text{-}H_2N(CH_2)_nNH_2]]^+$ or $[\{trans\text{-}PtCl(NH_3)_2\}_2\{\mu\text{-}H_2N(CH_2)_nNH_2\}]^{2+}$ ($n = 2-6$) [28][29], which are of particular interest because they show high activity against tumor-cell lines resistant to cisplatin *in vivo* and *in vitro*, and they cause an irreversible B → Z transition in poly(dG-dC)·poly(dG-dC). In addition, compounds **3a** and **3b** contain two *cis*-$[MCl_2(diamine)]$ moieties, which are formally identical to that of cisplatin.

Several factors are of crucial importance in the design of new antitumoral drugs [30], including the type of ligand, the coordination mode, and the arrangement of ligands around the metal centers. Polyamines, such as spermine (**3**), are effective inducers of DNA conformation and compound $[spnH_4][PtCl_4]_2$ tends to stabilize the DNA secondary structure [31]. Furthermore, some Pd^{II} putrescine complexes also introduce changes in the tertiary structure, and the antiproliferative effect of the putrescine complexes on cancer cells is higher than that of their analogues containing spermine [32]. Furthermore, the comparison of the toxicities of compounds **2d**,**e** and **3d**,**e** *in vitro* [27] reveals that slight modifications of the polyamine are enough to modify the activity of the platinum(II) compounds against tumor cell lines *in vitro*. Thus, the compounds reported here which contain polyamines bound to Pd^{II} or Pt^{II} appear to be excellent candidates for studies of their interaction with DNA, as well as their antitumoral activity. Further work in this area is currently under way.

Experimental Part

General. *N*-(3-Aminopropyl)propane-1,3-diamine (= bis(3-aminopropyl)amine; **1**; *Fluka*), spermidine (**2**) and spermine (**3**) (*Sigma*), dimethylsulfoxide (*Pancreac*), and $K_2[MCl_4]$ salts (M = Pd, Pt) (*Johnson Matthey*) were used as obtained without further purification. *cis*-$[MCl_2(dmso)_2]$ ($M = Pd^{II}$, Pt^{II}) was prepared as described in [16].

IR Spectra: *Nicolet-520-FTIR* spectrophotometer; KBr pellets; in cm^{-1}. ^1H- and $^{13}C\{^1H\}$-NMR Spectra: *Varian-Gemini-200* or *Varian-Unity-500* spectrophotometers; at 20° in $(D_6)DMSO$; δ in ppm; the spectra of

most of the Pt-complexes could not be recorded because of their low solubility in any deuterated solvent. $^1H,^{13}C$-2D-NMR Spectra: at 500 MHz with a *Varian-VXR-500* or *Bruker-Avance DMX-500* instrument; phase-sensitive heteronuclear single-quantum coherence $^1H,^{13}C$ (HSQC) spectra with gradient selection were recorded; a total of 2×128 increments of 2 *K* spectra (2 scans) were collected and zero-filled to 512 in *F*1 and 4096 in *F*2. Elemental analyses were carried out on a *Carlo Erba 1500* microanalyzer at the Serveis Ciéntífico-Tècnics de la Universitat de Barcelona.

*(*SP*-4-2)-Chloro{*N*-[(3-amino-*κ*N)propyl]propane-1,3-diamine-*κ*N,*κ*N′}palladium(1+) Tetrachloropalladate-(2−)(2:1)* (**1a**) *and (*SP*-4-2)-Chloro{*N*-[(3-amino-*κ*N)propyl]propane-1,3-diamine-*κ*N,*κ*N′}platinum(1+) Tetrachloroplatinate(2−) (2:1)* (**1b**). An aq. soln. (5 ml) of **1** (1 mmol) was added to a mixture of $K_2[PdCl_4]$ (1.5 mmol) or $K_2[PtCl_4]$ (1 mmol) and H_2O (5 ml). The mixture was stirred at *ca.* 20° for 24 h. The solid formed was collected by filtration, washed in H_2O and Et_2O, and dried over SiO_2: 93.1% of **1a** or 20.4% of **1b**. Good-quality crystals of **1a** for X-ray analysis were obtained by slow evaporation of the mother liquor.

Data of **1a**: IR (selected data): 1602*m*, (NH_2), 1057*m*, (C−N), 498*w* and 456*w* (Pd−N), 337*m* and 330*m*, (Pd−Cl). ^{1}H-NMR: 4.20, 4.06 (2 NH_2); 2.42, 2.34 (CH_2(3), CH_2(3′)); 1.79, 1.60 (CH_2(2), CH_2(2′)); 2.60, 2.54 (CH_2(1), CH_2(1′)); 5.43 (NH). ^{13}C-NMR: 38.91 (C(3), C(3′)); 27.00 C(2), C(2′)); 51.06 (C(1), C(1′)). Anal. calc. for $C_{12}H_{34}Cl_6N_6Pd_3$: C 18.1, H 4.3, Cl 26.8, N 10.6; found: C 18.0, H 4.3, Cl 27.5, N 10.4.

Data of **1b**·*3 H_2O:* 1602 (br. NH_2), 1035*m* (C−N), 513*m* and 498*m* (Pt−N), 332*m* and 320*m* (Pt−Cl). Anal. calc. for $C_{12}H_{40}Cl_6N_6O_3Pt_3$: C 12.9, H 3.6, Cl 19.1, N 7.5; found: C 12.9, H 3.4, Cl 18.4, N 7.4.

*(*SP*-4-2)-Chloro{*N*-[(3-amino-*κ*N)-propyl]propane-1,3-diamine-*κ*N,*κ*N′}palladium(1+) Chloride* (**1′a**) *and (*SP*-4-2)-Chloro{*N*-[(3-amino-*κ*-N)propyl]propane-1,3-diamine-*κ*N,*κ*N′}platinum(1+) Chloride* (**1′b**). A suspension of *cis*-[MCl_2(dmso)$_2$] (M = Pd^{II}, Pt^{II}) [20] (1.0 mmol) in MeOH (40 ml) was refluxed to complete dissolution. Then a soln. of **1** (1.0 mmol) in MeOH (10 ml) was added, and the mixture was stirred at *ca.* 20° for 1 h. The resulting clear soln. was concentrated to *ca.* 5 ml, cooled to r.t., and filtered. Addition of acetone to the filtrate produced the precipitation of the complexes, which were removed by filtration, washed in acetone, and dried over SiO_2: 73.4% of **1′a** or 69.7% of **1′b**.

Data of **1′a**. IR (selected data): 1595*s* (NH_2), 1068*s* (C−N), 513*w*, 456*w* (Pd−N), 350*w* (Pd−Cl). Anal. calc. for $C_6H_{17}Cl_2N_3Pd$: C 23.4 (23.4), H 5.6, Cl 23.0, N 13.6; found: C 23.4, H 5.6, Cl 23.2, N 13.3.

Data of **1′b**·H_2O: IR (selected data): 1602*s* (NH_2), 1036*m* (C−N), 525*w* and 470*w* (Pt−N), 330*w* (Pt−Cl). Anal. calc. for $C_6H_{19}Cl_2N_3OPt$: C 17.4, H 4.6, Cl 17.1, N 9.9; found: C 17.6, H 4.4, Cl 18.0, N 10.1.

*(*SP*-4-2)-Chloro{*N*-[(3-amino-*κ*N)propyl]butane-1,4-diamine-*κ*N,*κ*N′}palladium(1+) Tetrachloropalladate-(2−) (2:1)* (**2a**) *and (*SP*-4-2)-Chloro{*N*-[(3-amino-*κ*N)propyl]butane-1,4-diamine-*κ*N,*κ*N′}platinum(1+) Tetrachloroplatinate(2−)*(**2b**). These compounds were prepared as described for **1a** and **1b**, except that the reaction mixtures were stirred at r.t. for 3 days: 87.5% of **2a** or 34.0% of **2b**.

Data of **2a**: IR (selected data): 1588*m* (NH_2), 1061*m* (C−N), 505*w* and 449*w* (Pd−N), 343*m* and 334*m* (Pd−Cl). ^{1}H-NMR: 4.14 and 4.05 (NH_2−C(3′)); 2.41 and 2.28 (CH_2(3′)); 2.60 and 2.02 (CH_2(2′)); 2.75 and 2.41 (CH_2(1′)); 6.74 (NH); 3.09 and 2.31 (CH_2(1)); 2.42 and 1.81 (CH_2(2)); 1.77 and 1.69 (CH_2(3)); 2.47 and 2.40 (CH_2(4)); 4.63 (NH_2−C(4)). ^{13}C-NMR: 40.62 (C(3′)); 27.05 (C(2′)); 49.50 (C(1′)); 52.94 (C(1)); 25.54 (C(2)); 24.30 (C(3)); 45.76 (C(4)). Anal. calc. for $C_{14}H_{38}Cl_6N_6Pd_3$: C 20.4, H 4.7, Cl 25.9, N 10.2; found: C 20.5, H 4.8, Cl 26.5, N 10.0.

Data of **2b**: IR (selected data): 1588 (br., NH_2), 1047*m* (C−N), 520*w* and 463*w* (Pt−N), 334*m* and 318*m* (Pt−Cl). Anal. calc. for $C_{14}H_{38}Cl_6N_6Pt_3$: C 15.5, H 3.5, Cl 19.5, N 7.7; found: C 15.5, H 3.8, Cl 19.6, N 7.6.

*{*μ*-[*N,N′*-Bis[(3-amino-*κ*N)propyl]butane-1,4-diamine-*κ*N:*κ*N′]}tetrachlorodipalladium* (**3a**) *and {*μ*-[*N,N′*-Bis[(amino-*κ*N)propyl]butane-1,4-diamine-*κ*N:*κ*N′]}tetrachlorodiplatinum* (**3b**). After complete dissolution of $K_2[MCl_4]$ (M = Pd^{II} or Pt^{II}; 1.0 mmol) in H_2O (5 ml), a soln. of spermine (**3**) in H_2O (5 ml) was added under continuous stirring. A yellowish (for **3a**) or brown (for **3b**) precipitate formed immediately after the mixing. The mixtures were stirred at *ca.* 20° for 24 h. The solid was collected by filtration, washed with H_2O and Et_2O, and finally dried over SiO_2: 74.3% of **3a** or 53.6% of **3b**. Good-quality crystals of **3a** for X-ray analysis were obtained by slow evaporation of the mother liquor.

Data of **3a**: IR (selected data): 1595*m* (NH_2), 1054*m* (C−N), 513*m* and 431*m* (Pd−N), 328*m* and 320*m* (Pd−Cl). ^{1}H-NMR[4]): (*R*,*R*)/(*S*,*S*) isomers: 2.44 (2 CH_2(3′))[5]); 2.53, 1.96 (2 CH_2(2′)); 2.77, 2.42 (2 CH_2(1′)); 3.10, 2.40 (CH_2(1), CH_2(4)); 1.73 (CH_2(2), CH_2(3)); *meso* form: 2.40 (2 CH_2(3′))[5]); 2.24, 1.71, 2.11, 1.77

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[4]) Moreover, all isomers showed the following signals: 6.66 (2NH); 4.41, 4.23 (2 H, NH_2); 5.11, 5.27 (2 H, NH_2).

[5]) Partially overlapped by the signal due to (D_6)DMSO.

(2 $CH_2(2')$); 2.77, 2.42 (2 $CH_2(1')$); 3.08, 2.24, 3.02, 2.33 ($CH_2(1)$, $CH_2(4)$); 1.76 ($CH_2(2)$, $CH_2(3)$). ^{13}C-NMR: (*R*,*R*)/(*S*,*S*) isomers: 39.80 ($C(3')9^5$); 25.74 ($C(2')$); 48.60 ($C(1')$); 52.44 ($C(1)$, $C(4)$); 23.14 ($C(2)$, $C(3)$); *meso* form: 40.60 (2 $C(3')^5$); 25.70 and 25.95 (2 $C(2')$); 48.60 (2 $C(1')$); 51.01 and 51.20 ($C(1)$, $C(4)$); 23.70 ($C(2)$, $C(3)$). Anal. calc. for $C_{10}H_{26}Cl_4N_4Pd_2$: C 21.6, H 4.7, Cl 25.5, N 10.1; found: C 21.9, H 4.6, Cl 25.5, N 9.7.

Data of **3b**·2 H_2O: IR (selected data): 1595*m* (NH_2), 1054*m* (C–N), 520*m* and 477*m* (Pt–N), 327*m* and 312*m* (Pt–Cl). Anal. calc. for $C_{10}H_{30}Cl_4N_4O_2Pt_2$: C 15.6, H 3.9, Cl 18.4, N 7.3; found: C 15.6, H 3.9, Cl 18.4, N 7.1.

X-Ray Diffraction Analysis of **1a** *and* meso-**3a**. Suitable crystals for X-ray diffraction experiments of **1a** and **3a** (see *Table 4*) were selected and mounted on an *Enraf-Nonius CAD4* four-circle diffractometer. Unit-cell parameters were determined from 25 reflections and refined by the least-squares method. Intensities were collected with graphite monochromated Mo$K\alpha$ radiation. Three reflections were collected every hour as intensity control, and no significant intensity decay was observed. *Lorentz*, polarization, and absorption (PSI scan method, max. and min. abs. corrections were 0.9994 and 0.9596 for **1a** and 0.9998 and 0.9469 for *meso*-**3a**) corrections were applied. The structures were solved by locating the Pd-atoms by direct methods using SHELXS-86 [33] for **1a** and MULTAN 11/84 [34] for *meso*-**3a**. The positions of the remaining non-H-atoms were determined by weighted *Fourier* synthesis. Refinement was carried out using the SHELXL-93 program [35] in both cases. The function minimized was $\Sigma w[|F_o|^2 - |F_c|^2]^2$, where $w = 1/(\sigma^2(F) + kF^2)$ and $k = 0.0682$ for **1a** and 0.0465 for *meso*-**3a**; f, f', f'' were taken from [36]. H-Atoms were located by difference *Fourier* syntheses and introduced in the refinement with a global isotropic temperature factor after the convergence of the anisotropic thermal parameters for non-H-atoms. The final R_1 and wR_2 values, as well as other details concerning the refinement of the crystal structures of **1a** and *meso*-**3a**, are summarized in *Table 4*. Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-116621 for $[PdCl(dipn)]_2[PdCl_4]$ (**1a**) and CCDC-116620 for $[Pd_2Cl_4(spn)]$ (**3a**). Copies of the data can be obtained, free of charge, on application to the *CCDC*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: #44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

We are grateful to *DGICYT* ref. PB94-0922-C02-01.

Table 4. *Crystal Data and Structure Refinement for Compounds* **1a** *and meso*-**3a**

	1a	*meso*-**3a**
Empirical formula	$C_{12}H_{34}Cl_6N_6Pd_3$	$[C_5H_{13}Cl_2N_2Pd]_2$
M_r	794.38	278.47
Crystal system	monoclinic	monoclinic
T/K	293(2)	293(2)
λ(Mo$K\alpha$)/Å	0.71069	0.71069
Space group	$P2_1/c$	$P2_1/n$
a/Å	14.670(2)	9.001(1)
b/Å	11.774(1)	8.028(2)
c/Å	14.944(2)	12.924(2)
β/°	105.03(9)	91.88(1)
U/Å^3	2492.9(3)	933.4(3)
Z	4	2
F(000)	1552	548
D_c/g·ml^{-1}	2.116	1.982
Crystal size/mm^3	0.30 × 0.29 × 0.39	0.30 × 0.20 × 0.18
μ/cm^{-1}	27.97	24.94
Θ Range for data collection/deg	from 2.45 to 30.44	from 2.99 to 30.40
Index ranges of (h,k,l)	(–20,0), (0,16), (–20,21)	(0,12), (0,11), (–18,18)
Reflections collected	7811	3117
Independent reflections	7548	2815
Method of refinement	Full-matrix least squares on F^2	
Data and parameters	7548 and 248	2815 and 92
Goodness of fit on F^2	1.126	0.829
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0426$, $wR_2 = 0.1346$	$R_1 = 0.0258$, $wR_2 = 0.0628$
R indices (all data)	$R_1 = 0.0559$, $wR_2 = 0.1412$	$R_1 = 0.0551$, $wR_2 = 0.0765$
Largest difference peak and hole/eÅ^{-3}	1.270 and –1.463	1.109 and –0.605

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