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Reactivity of the Pyrazolatopalladium(II) Complexes $[Pd(dmpz)_2(Hdmpz)_2]$ and $[Pd_2(\mu\text{-}dmpz)_2(dmpz)_2(Hdmpz)_2]$ towards Carboxylic Acids: Hydrogen Bonds as the Driving Force That Determines the Nature of the Final Products

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The compound $[Pd(Hdmpz)_4](O_2CCH_2NHCOCH_3)_2$ (**1**; (Hdmpz = 3,5-dimethylpyrazole) has been obtained by treatment of $[Pd(dmpz)_2(Hdmpz)_2]$ (**A**) with two equivalents of *N*-acetylglycine ($HO_2CCH_2NHCOCH_3$). The X-ray study on a crystal of **1** revealed that the *N*-acetylglycinate anion links to the cationic complex $[Pd(Hdmpz)_4]^{2+}$ through the carboxylate group by charge assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds. Additionally, the remaining N–H and C=O groups allow the *N*-acetylglycinate anions to self-assemble through N–H···O hydrogen bonds to generate infinite chains. The compounds $[Pd_2(\mu\text{-}dmpz)_2(O_2CCH_2NHCOCH_3\text{-}\kappa O)_2(Hdmpz)_2]$ (**2**) and $[Pd_2(\mu\text{-}dmpz)_2(O_2CC_6H_4\text{-}R\text{-}\kappa O)_2(Hdmpz)_2]$ [R = *m*-NO_2 (**3a**), *p*-$N(CH_3)_2$ (**3b**), *p*-NH_2 (**3c**), *p*-OCH_3 (**3d**), *p*-OH (**3e**)] have been obtained by treatment of $[Pd_2(\mu\text{-}dmpz)_2(dmpz)_2(Hdmpz)_2]$ (**B**) with two equivalents of the monocarboxylic acids *N*-acetylglycine ($HO_2CCH_2NHCOCH_3$) and the benzoic derivatives $HO_2CC_6H_4R$ [R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH] respectively. The X-ray study on complexes **3d** and **3e** shows that in these complexes the carboxylate anion bonded to one Pd atom and the terminal Hdmpz group bonded to the other one have the right arrangement to establish an N–H···O hydrogen bond. The H···O and N···O distances are in the range of those corresponding to charge-assisted $N–H^{(+)}\cdots O^{(-)}$ interactions. In complexes **3a**–**3e**, the H atoms of the terminal Hdmpz groups can be replaced by Ag^+ to give the mixed-metal complexes $[Pd_2Ag_2(\mu\text{-}dmpz)_4(\mu\text{-}O_2CC_6H_4\text{-}R\text{-}\kappa O)_2(Hdmpz)_2]$ [R = *m*-NO_2 (**4a**), *p*-$N(CH_3)_2$ (**4b**), *p*-NH_2 (**4c**), *p*-OCH_3 (**4d**), *p*-OH (**4e**)]. Compounds **4a**–**4e**, which exhibit a transoid conformation of the carboxylate groups with respect to the Pd···Pd line, isomerise to the cisoid species (**4a′**–**4e′**). The X-ray structure of the DMSO adduct of **4d′** is also reported.

Introduction

The coordination chemistry of neutral pyrazole (HRpz) or anionic pyrazolate (Rpz) ligands has been intensively developed over many years[1] and has been thoroughly reviewed.[2–5] Recently, unprecedented compounds showing new bonding modes for pyrazolate ligands have been reported.[6–10] In spite of this, the number of palladium and platinum compounds is rather low. Only a few examples of mono- ($[Pt(pz)_2(Hpz)_2]$,[11,12] $[Pt(Hpz)_4]Cl_2$,[11] $[Pd(Hpz)_4]Cl_2$,[12] $[Pd(dmpz)_2(Hdmpz)_2]$[13]), di- {$[Pd_2(\mu\text{-}dmpz)_2(dmpz)_2(Hdmpz)_2]$,[14] $[Pd_2(\mu\text{-}3\text{-}t\text{Bupz})_2(3\text{-}t\text{Bupz})_2(H_3\text{-}t\text{Bupz})_2]$,[12] $[Pd_2(\mu\text{-}pz)_2(Hpz)_4](BF_4)_2$[15]} or trinuclear ($[\{Pt(\mu\text{-}pz)_2\}_3]$,[12,16] $[\{Pd(\mu\text{-}pz)_2\}_3]$,[12] $[\{Pd(\mu\text{-}4\text{-}Mepz)_2\}_3]$,[12] $[\{Pd(\mu\text{-}3\text{-}Phpz)_2\}_3]$[17]) compounds containing only pyrazoles (HRpz) and/or pyrazolates (Rpz) as ligands have been reported up to now, one of them, $[Pd_2(\mu\text{-}dmpz)_2(dmpz)_2(Hdmpz)_2]$ having been published recently by us.[14] This kind of compound often contains inter-[11–13] or intramolecular[12,14] N–H···N hydrogen bonds involving neutral pyrazole (HRpz) and anionic pyrazolate (Rpz) groups, and the protons of the coordinated pyrazoles can be replaced by metal ions as Cu^I, Ag^I and Au^I to give heterometallic polynuclear complexes.[12–14]

The mono- and dinuclear complexes $[Pd(dmpz)_2(Hdmpz)_2]$ (**A**)[13] and $[Pd_2(\mu\text{-}dmpz)_2(dmpz)_2(Hdmpz)_2]$ (**B**)[14] have terminal dmpz and Hdmpz ligands bonded to each palladium centre, that is, on each side of both complexes there is a dmpz group, which is a hydrogen-bond acceptor, and an Hdmpz ligand, which is a hydrogen-bond donor. We therefore considered it of interest to use these compounds as starting materials to obtain organic–organometallic hydrogen-bonded networks by reaction of both complexes with carboxylic acids. A carboxylic acid group (COOH) can form complementary hydrogen bonds with the dmpz and Hdmpz ligands on the same side of each complex (Figure 1a) or transfer its proton to the dmpz ligand. Should this be the case, charge-assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds would be formed between complex cations and

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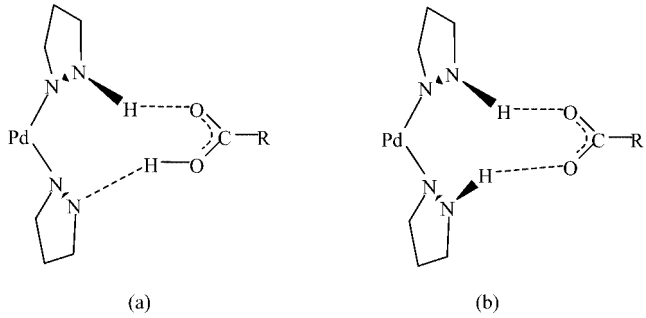
carboxylate anions yielding a heteromeric synthon of type $R_2(10)$[18,19] (Figure 1b). Additionally, the substitution of dmpz by carboxylate groups could also take place.



(a) (b)

Figure 1. a) Complementary hydrogen bonds between the neutral carboxylic group and the "*cis*-Pd(dmpz)(Hdmpz)" fragment. b) Charge-assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds between a carboxylate anion and the cationic "*cis*-$Pd(Hdmpz)_2$" fragment.

In this paper we report the reactivity of complexes $[Pd(dmpz)_2(Hdmpz)_2]$ (**A**) and $[Pd_2(\mu\text{-}dmpz)_2(dmpz)_2(Hdmpz)_2]$ (**B**) towards monocarboxylic acids such as *N*-acetylglycine ($HO_2CCH_2NHCOCH_3$) and benzoic acid derivatives [$HO_2CC_6H_4$-R, R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH]. Some of these carboxylic acids contain an additional functional group that is able to form an extra molecular hydrogen bond. As a result, a new mononuclear complex and new dinuclear heteroleptic compounds containing pyrazolate and carboxylate ligands in the same molecule have been obtained. Replacement of the protons of coordinated Hdmpz in the dinuclear complexes by Ag^I gives new heteropolynuclear Pd-Ag ones.

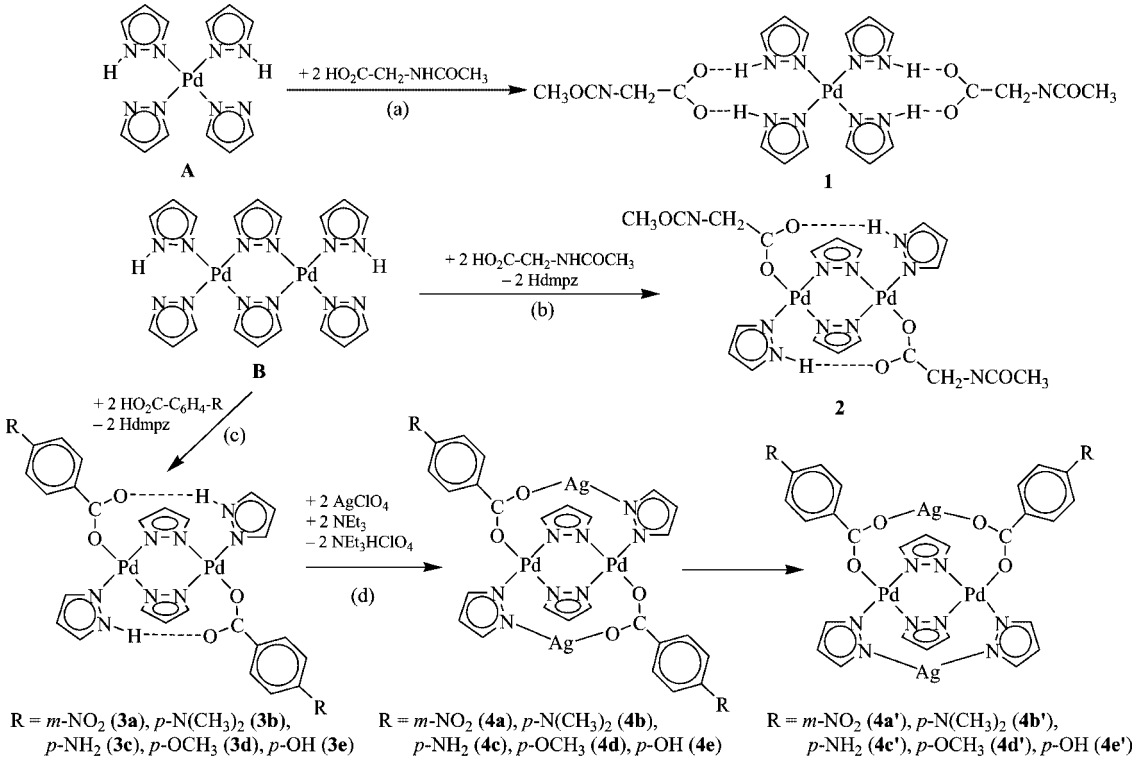
Results and Discussion

Reactivity of $[Pd(dmpz)_2(Hdmpz)_2]$ (A) towards the Monoprotic Weak Acids *N*-Acetylglycine and $HO_2CC_6H_4$-R [R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH]

$[Pd(dmpz)_2(Hdmpz)_2]$ (**A**) reacts with two equivalents of *N*-acetylglycine in dichloromethane/methanol solution to give $[Pd(Hdmpz)_4](O_2CCH_2NHCOCH_3)_2$ (**1**) as a pure compound in a very high yield (path a in Scheme 1) by selective protonation of the anionic monodentate dmpz ligands. The X-ray study of a crystal of **1** revealed that the *N*-acetylglycinate anion interacts with the cationic complex $[Pd(Hdmpz)_4]^{2+}$ through N–H···O hydrogen bonds.

The reactions of $[Pd(dmpz)_2(Hdmpz)_2]$ (**A**) with the benzoic derivatives $HO_2CC_6H_4$-R [R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH] under similar conditions do not give rise to pure compounds: their ^1H NMR spectra seem to indicate that species of stoichiometry $[Pd(Hdmpz)_4](O_2CC_6H_4\text{-}R)_2$ [R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH] could be present in all mixtures, but we have not been able to separate and characterise them.

Elemental analyses and the IR and ^1H NMR spectroscopic data of $[Pd(Hdmpz)_4](O_2CCH_2NHCOCH_3)_2$ (**1**) (see Experimental Section) are in agreement with this stoichiometry, which was confirmed later by an X-ray diffraction



(note: Me groups of the 3,5-dmpz or 3,5-Hdmpz have been omited for clarity)

Scheme 1.

study. The ^{1}H NMR spectrum of **1** in solution reveals the equivalence of the four Hdmpz ligands since only one set of signals is observed [δ = 15.45 (s, 4 H, N–H), 5.72 (s, 4 H, H^4), 2.49 (s, 12 H, CH_3), 2.25 (s, 12 H, CH_3) ppm]. The two *N*-acetylglycinate anions also give only one set of signals [δ = 6.56 (s, 2 H, N–H), 4.05 (d, $^3J_{H,H}$ = 3.74 Hz, 4 H, CH_2), 2.06 (s, 6 H, CH_3) ppm].

The molecular and supramolecular structures of compound **1** are shown in Figures 2 and 3, respectively. Table 1 lists a selection of intra- and intermolecular bond distances and angles.

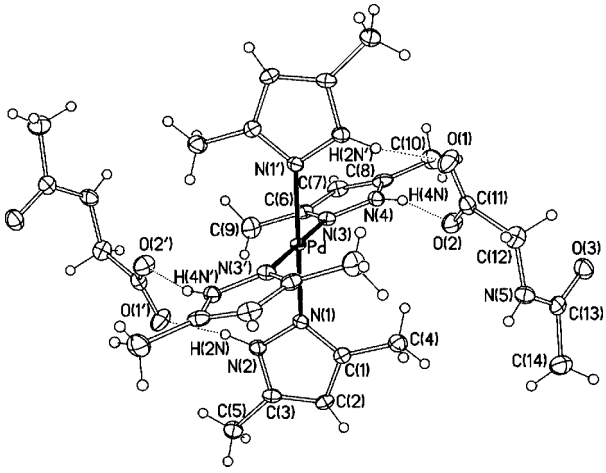


Figure 2. Molecular structure of **1** (50% probability ellipsoids).

In the $[Pd(Hdmpz)_4]^{2+}$ part of the complex the Pd centre shows an almost square-planar coordination environment with all the Pd–N bond lengths in the range of those found in palladium complexes with this kind of ligand.[6,11–13,15–17,20,21] Each pair of mutually *trans* Hdmpz groups are coplanar to each other (interplanar angle of 0° between planes 2 and 2′ and planes 3 and 3′. See Table 1 for the definition of the planes used in this discussion) and almost perpendicular to the other pair of Hdmpz groups [interplanar angle of 86.6(1)°]. All Hdmpz ligands are almost perpendicular to the best least-squares coordination plane of the metal centre (plane 1), since the interplanar angles are 80.9(1)° [planes 1 and 2 (2′)] and 76.7(1)° [planes 1 and 3 (3′)].[22] The Hdmpz groups are turned in such a way that the N–H bonds of the two Hdmpz ligands in the *cis* positions point roughly to the same side of the palladium coordination plane.

The *N*-acetylglycinate anions are bonded to the cation through hydrogen bonds. The two N–H groups pointing to the same side of the palladium coordination plane form N–H···O hydrogen bonds with the two oxygen atoms of the same carboxylate group. These N–H···O hydrogen bonds seem to be quite strong as the H···O and N···O distances are perceptibly shorter than those involved in neutral molecules[23,24] and are even at the lower end of the range observed for charge-assisted N–H$^{(+)}$···O$^{(-)}$ hydrogen bonds.[24–30] According to these structural data, the C–O distances within the COO^- moieties indicate that the carboxylic acid does not retain its acidic hydrogen, which has been transferred to the monodentate dmpz groups[31] such that the complex cations and the carboxylate anions are joined by a heteromeric synthon of type $R_2(10)$[18,19] (Figure 1b). Compound **1** is a new example in which the N–H···O interaction is reinforced by an electrostatic one, the

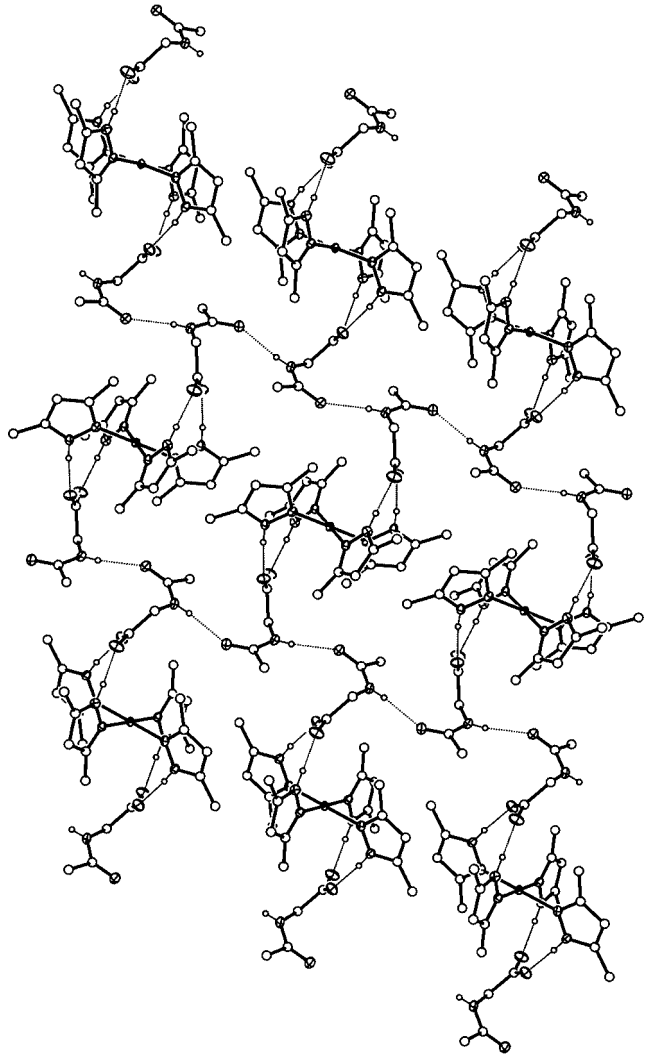


Figure 3. Supramolecular structure of **1**.

Table 1. Bond lengths [Å] and angles [°] for $[Pd(Hdmpz)_4](O_2CCH_2NHCOCH_3)_2$ (**1**).[a]

Pd–N(1)	2.029(2)	Pd–N(3)	2.018(2)	
C(11)–O(1)	1.252(4)	C(11)–O(2)	1.247(3)	
N(1)–Pd–N(3)	91.16(9)	N(1)–Pd–N(3′)	88.84(9)	
N–(H)···O	*d*(N–H)	*d*(H···O)	*d*(N···O)	<(NHO)
N(2)–(H2N)···O(1)	0.89(4)	1.76(4)	2.647(3)	166(3)
N(4)–(H4N)···O(2)	0.95(4)	1.73(4)	2.645(3)	164(4)
N(5)–(H5N)···O(3)	0.79(3)	2.16(3)	2.937(3)	168(3)
Plane1: Pd, N(1), N(3), N(1′), N(3′)				
Plane2: N(1), N(2), C(1), C(2), C(3)				
Plane2′: N(1′), N(2′), C(1′), C(2′), C(3′)				
Plane3: N(3), N(4), C(6), C(7), C(8)				
Plane3′: N(3′), N(4′), C(6′), C(7′), C(8′)				

[a] The symmetry transformation used to generate the equivalent primed atoms is $-x$, $-y + 1$, $-z + 1$.

H-bond acceptor being a carboxylate anion and the H-bond donor an organometallic cation containing N–H groups.

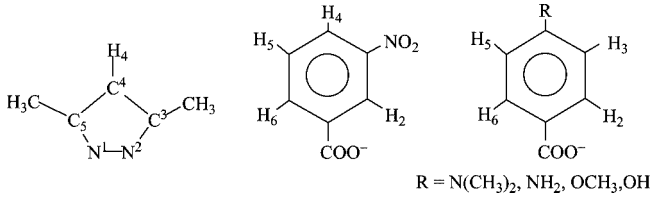
In addition, the *N*-acetylglycinate anions self-assemble through N–H···O links to generate infinite chains. The H···O and N···O distances are longer than those involving the carboxylate group, but within the range observed for this kind of interaction between neutral molecules.[23,25] The supramolecular architecture of compound **1** is a 2D network which can be described as being formed by infinite chains of *N*-acetylglycinate anions ($CH_3CONHCH_2COO^-$) linked through the carboxylate group (COO^-) to the $[Pd(Hdmpz)_4]^{2+}$ cations by charge-assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds.

Reactivity of $[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$ (B) towards the Monoprotic Weak Acids *N*-Acetylglycine and $HO_2CC_6H_4$-R [R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH]

$[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$ (**B**) reacts with the monocarboxylic acids *N*-acetylglycine and the benzoic derivatives $HO_2CC_6H_4$-R [R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH] in a 1:2 molar ratio, but in a different way to $[Pd(dmpz)_2(Hdmpz)_2]$ (**A**). In these cases selective protonation of the monodentate dmpz groups (one from each palladium atom), their elimination as Hdmpz, and their further displacement by the carboxylate anions generated takes place. These carboxylate groups interact with the palladium atoms in a monodentate way to give compounds $[Pd_2(\mu\text{-dmpz})_2(O_2CCH_2NHCOCH_3\text{-}\kappa O)_2(Hdmpz)_2]$ (**2**) and $[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4\text{-R-}\kappa O)_2(Hdmpz)_2]$ [R = *m*-NO_2 (**3a**), *p*-$N(CH_3)_2$ (**3b**), *p*-NH_2 (**3c**), *p*-OCH_3 (**3d**), *p*-OH (**3e**)] (paths b and c in Scheme 1).

The IR absorptions corresponding to the carboxylate groups (see Experimental Section) are in agreement with the monodentate coordination mode of these anions,[32] as confirmed by the X-ray structures of compounds **3d** and **3e**.

According to the symmetry of these compounds (C_2), their ^1H NMR spectra show a set of signals corresponding to one half of each complex, namely "Pd(μ-dmpz)($O_2CC_6H_4$-R-κ*O*)(Hdmpz)" (see Experimental Section, Scheme 2). The methyl signals corresponding to bridging dmpz or terminal Hdmpz groups were unambiguously assigned by NOE experiments.



Scheme 2.

A common way to synthesise pyrazolate complexes is by treating carboxylate derivatives with the neutral pyrazole (HRpz) in the presence of NEt_3. These reactions proceed with elimination of the carboxylic acid and coordination of the pyrazolate anion Rpz^- to the metal centre.[33,34] The substitution of Rpz^- anions by carboxylate groups has seldom been used as carboxylate complexes are much easier to make than pyrazolates. As far as we know, only $[Ru_2(\mu\text{-}O_2CR)_2(Hpz)_2(CO)_4]$ has been prepared in such a way;[35] the carboxylic acid is added in a large excess to induce protonation of all Rpz groups in the starting material. However, in the synthesis of complexes **2** and **3a**–**3e** the carboxylic acids are added to compound **B** in a stoichiometric manner (1:2) and selective protonation of the terminal dmpz groups takes place. Thus, the selectivity of this process is the key to synthesising mixed-ligand complexes.

An X-ray study was performed on complexes **3d** and **3e** to try to ascertain if the OH groups of the carboxylate anions of different complexes are involved in hydrogen-bonding interactions to generate supramolecular structures. Unfortunately, no supramolecular aggregates were found and both complexes show discrete dinuclear structures. The molecular structures of complexes **3d** and **3e** are shown in Figures 4 and 5, respectively, and a selection of bond lengths and angles is given in Tables 2 and 3.

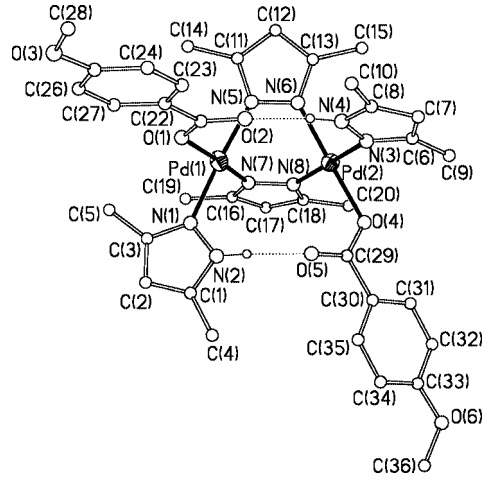


Figure 4. Molecular structure of **3d**.

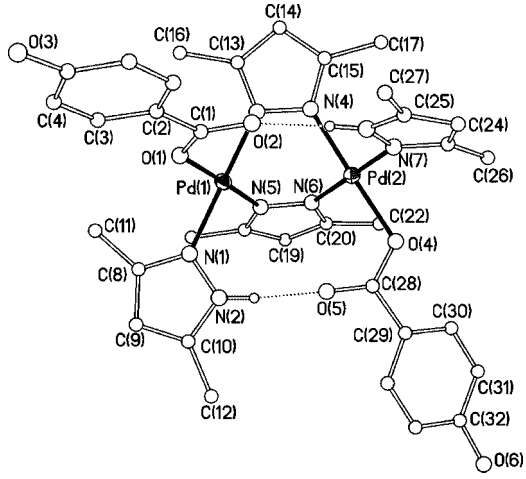


Figure 5. Molecular structure of **3e**.

Complexes **3d** and **3e** are dinuclear species of Pd^{II} with two 3,5-dmpz groups bridging the two metal atoms, which

Table 2. Bond lengths [Å] and angles [°] for $[Pd_2(\mu\text{-dmpz})_2(O_2C\text{-}C_6H_4OCH_3\text{-}\kappa O)_2(Hdmpz)_2]$ (**3d**).

Pd(1)–O(1)	2.001(2)	Pd(1)–N(1)		2.016(2)
Pd(1)–N(5)	1.989(2)	Pd(1)–N(7)		1.994(2)
Pd(2)–O(4)	2.015(2)	Pd(2)–N(3)		2.011(2)
Pd(2)–N(6)	2.001(2)	Pd(2)–N(8)		1.989(2)
C(21)–O(1)	1.271(3)	C(21)–O(2)		1.234(3)
C(29)–O(4)	1.278(3)	C(29)–O(5)		1.232(3)
N(5)–Pd(1)–O(1)	92.74(8)	O(1)–Pd(1)–N(1)		86.06(9)
N(5)–Pd(1)–N(7)	89.04(9)	N(7)–Pd(1)–N(1)		92.64(9)
N(8)–Pd(2)–O(4)	89.90(8)	O(4)–Pd(2)–N(3)		90.26(8)
N(8)–Pd(2)–N(6)	89.97(9)	N(6)–Pd(2)–N(3)		90.00(9)
C(21)–O(1)–Pd(1)	122.89	C(29)–O(4)–Pd(2)		116.60
N–(H)···O	*d*(N–H)	*d*(H···O)	*d*(N···O)	<(NHO)
N(2)-(H2)···O(5)	0.88	1.85	2.725(3)	173.8(2)
N(4)-(H4)···O(2)	0.88	1.85	2.703(3)	163.3(2)

Table 3. Bond lengths [Å] and angles [°] for $[Pd_2(\mu\text{-dmpz})_2(O_2C\text{-}C_6H_4OH\text{-}\kappa O)_2(Hdmpz)_2]$ (**3e**).

Pd(1)–N(1)	2.017(2)	Pd(1)–N(5)		1.998(2)
Pd(1)–O(1)	2.004(2)	Pd(1)–N(3)		1.988(2)
Pd(2)–N(4)	1.986(2)	Pd(2)–O(4)		2.0098(17)
Pd(2)–N(6)	1.995(2)	Pd(2)–N(7)		2.014(2)
C(1)–O(1)	1.289(3)	C(1)–O(2)		1.239(3)
C(28)–O(4)	1.292(3)	C(28)–O(5)		1.234(3)
N(3)–Pd(1)–O(1)	91.72(8)	O(1)–Pd(1)–N(1)		88.06(8)
N(3)–Pd(1)–N(5)	89.76(8)	N(5)–Pd(1)–N(1)		90.48(8)
N(6)–Pd(2)–O(4)	89.92(8)	O(4)–Pd(2)–N(7)		90.03(8)
N(4)–Pd(2)–N(6)	89.75(8)	N(4)–Pd(2)–N(7)		90.39(8)
C(1)–O(1)–Pd(1)	124.29(16)	C(28)–O(4)–Pd(2)		118.23(16)
N-(H)···O	*d*(N–H)	*d*(H···O)	*d*(N···O)	<(NHO)
N(2)–(H2)···O(5)	0.88	1.827(2)	2.704(3)	174.26(18)
N(8)–(H8)···O(2)	0.88	1.852(2)	2.729(3)	174.47(18)

are located at 3.269 (**3d**) and 3.272 Å (**3e**). The Pd_2N_4 ring shows a typical boat-like conformation, the dihedral angle between both Pd–N–N–Pd fragments being 73.5(1)° (**3d**) and 72.9(1)° (**3e**).[22] In addition, each Pd atom is bonded to a nitrogen of a neutral, monodentate 3,5-dimethylpyrazole and to an oxygen of the carboxylate anion to complete a square-planar coordination environment. The angles defined by two ligands in *cis* positions and the metal centre are close to 90°. The Pd–N distances are in the range of distances found in other complexes with this kind of ligand.[6,11–17,20,21,36] No significant differences are observed in the Pd–N distances corresponding to terminal Hdmpz or bridging dmpz groups. The Pd–O bond lengths (ca. 2.00 Å) are similar to those observed in palladium complexes with monodentate carboxylate groups.[37–43] The two Pd–O–C angles are surprisingly different to each other: while one of them is smaller than 120° [C(29)–O(4)–Pd(2): 116.6° (**3d**); C(28)–O(4)–Pd(2): 118.2° (**3e**)] and similar to those found in other complexes with this type of ligand, such as $[Pd(phen)(MeCO_2)_2]$ (Pd–O–C: 114.3° and 118.5°),[37] $[Pd\{3,3'\text{-}[CH_2CH(COOEt)_2]\text{-}2,2'\text{-byp-}\kappa N,N'C^{\beta}\}(O_2CCH_3)]$ (Pd–O–C: 116.9°–119.9°),[38] the other is, unusually, greater than 120° [C(21)–O(1)–Pd(1): 122.9° (**3d**); C(1)–O(1)–Pd(1): 124.3° (**3e**)]. The C–O distances within the COO^- moieties (1.232–1.292 Å) indicate that the carboxylic acid molecules do not retain their acidic hydrogen, which has been transferred to the monodentate dmpz groups to generate Hdmpz ones.[31]

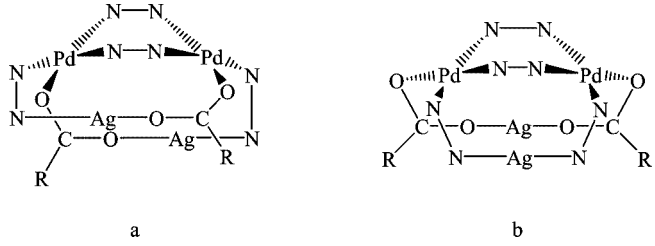
The monodentate carboxylate anion bonded to a Pd atom and the terminal Hdmpz group bonded to the other Pd atom have an adequate arrangement to establish an N–H···O hydrogen bond. The H···O and N···O distances are in the range of those corresponding to charge-assisted $N\text{–}H^{(+)}\cdots O^{(-)}$ bonds. In addition, the N–H···O angles are in the range observed for these kinds of interactions.[24–30]

Reactivity of $[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4\text{-R-}\kappa O)_2(Hdmpz)_2]$ [R = *m*-NO_2 (3a), *p*-$N(CH_3)_2$ (3b), *p*-NH_2(3c), *p*-OCH_3 (3d), *p*-OH (3e)] towards $AgClO_4$

The reactions of $[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4\text{-R-}\kappa O)_2(Hdmpz)_2]$ [R = *m*-NO_2 (**3a**), *p*-$N(CH_3)_2$ (**3b**), *p*-NH_2 (**3c**), *p*-OCH_3 (**3d**), *p*-OH (**3e**)] with $AgClO_4$ in a 1:2 molar ratio in the presence of NEt_3 produce the deprotonation of the terminal Hdmpz groups and formation of $[Pd_2Ag_2(\mu\text{-dmpz})_4(O_2CC_6H_4\text{-R-}\kappa O)_2]$ [R = *m*-NO_2 (**4a**), *p*-$N(CH_3)_2$ (**4b**), *p*-NH_2(**4c**), *p*-OCH_3 (**4d**), *p*-OH (**4e**)]. In these reactions the $NHEt_3ClO_4$ by-product is eliminated by washing with methanol, where compounds **4a**–**4e** are insoluble.

This method has previously been used in the synthesis of the Pd-Ag pyrazolate complexes $[Pd_2Ag_4(dmpz)_8]$[13] and $[Pd_2Ag_2(dmpz)_6]$[14] from $[Pd(dmpz)_2(Hdmpz)_2]$ and $[Pd(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$, respectively.

Elemental analysis and IR and ^1H NMR spectroscopic data (Experimental Section, Scheme 2) are in agreement with the stoichiometry proposed and presented in Scheme 1. With the exception of the signal corresponding to the acidic N–H protons, the number of signals observed in the ^1H NMR spectra of compounds **4a**–**e** is the same as that observed in the spectra of the starting complexes (**3a**–**3e**). We thus propose the molecular structure represented in Scheme 3a for compounds **4a**–**e**, in which the two acidic H atoms of complexes **3a**–**3e** have been replaced by Ag ones, keeping the carboxylate groups in a transoid conformation with respect to the Pd···Pd axis. If acetone solutions of compounds **4a**–**4e** are left at room temperature until the solvent has completely evaporated the resulting solids exhibit different ^1H NMR spectra (Experimental Section, Scheme 2) to those shown by the starting compounds (**4a**–**4e**), revealing a change in the molecular structure to give the isomers **4a′**–**4e′** (Scheme 3b). The ^1H NMR spectra of these complexes display two signals corresponding to the H^4 atoms



Scheme 3.

of the $Pd_2(\mu\text{-dmpz})_2$ groups. A cisoid arrangement of the carboxylate groups with respect to the Pd···Pd axis could account for these two signals.

Single crystals of $[Pd_2Ag_2(\mu\text{-dmpz})_4(p\text{-}O_2CC_6H_4OCH_3\text{-}\kappa O)_2(DMSO)]$ were obtained from a solution of **4d** in DMSO. Its ^1H NMR spectrum is similar to that of **4d′** in DMSO, indicating that the structure of the skeleton of both complexes is the same. The X-ray study of a single crystal allowed us to unambiguously establish the structure proposed for these compounds. The molecular structure of $[Pd_2Ag_2(\mu\text{-dmpz})_4(p\text{-}O_2CC_6H_4OCH_3\text{-}\kappa O)_2(DMSO)]$ is shown in Figure 6, and Table 4 contains a selection of bond lengths and angles in the complex.

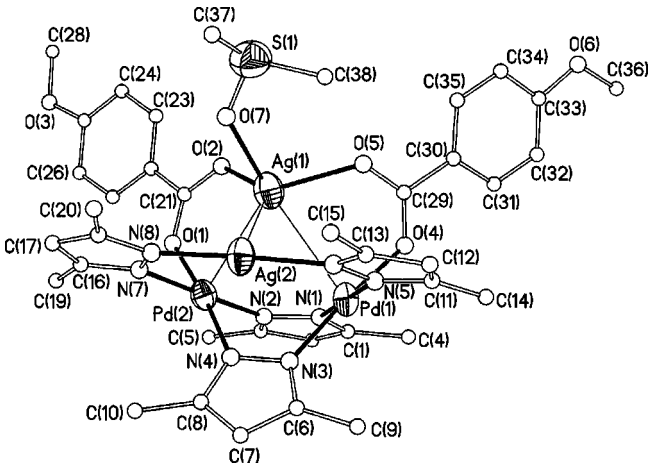


Figure 6. Molecular structure of $[Pd_2Ag_2(\mu\text{-dmpz})_4(\mu\text{-}O_2CC_6H_4OCH_3)_2(DMSO)]$.

Table 4. Bond lengths [Å] and angles [°] for $[Pd_2Ag_2(\mu\text{-dmpz})_4(O_2CC_6H_4OCH_3\text{-}\kappa O)_2(DMSO)]$ from **4d′**.

Pd(1)–N(1)	2.025(7)	Pd(1)–N(3)	2.002(6)
Pd(1)–N(5)	2.020(6)	Pd(1)–O(4)	2.007(6)
Pd(2)–N(2)	1.991(7)	Pd(2)–N(4)	1.994(6)
Pd(2)–N(7)	2.019(7)	Pd(2)–O(1)	2.008(6)
Ag(1)–O(2)	2.259(6)	Ag(1)–O(5)	2.262(6)
Ag(1)–O(7)	2.409(8)	Ag(2)–N(6)	2.069(7)
Ag(2)–N(8)	2.075(6)	Ag(1)···Ag(2)	2.9208(12)
Ag(1)···Pd(2)	2.9586(12)	Ag(1)···Pd(1)	3.0652(12)
O(4)–Pd(1)–N(5)	90.5(3)	N(5)–Pd(1)–N(3)	90.8(3)
N(3)–Pd(1)–N(1)	88.8(3)	N(1)–Pd(1)–O(4)	89.9(2)
O(1)–Pd(2)–N(7)	89.2(3)	O(1)–Pd(2)–N(2)	90.2(3)
N(7)–Pd(2)–N(4)	91.3(3)	N(4)–Pd(2)–N(2)	89.4(3)
O(2)–Ag(1)–O(7)	98.4(3)	O(2)–Ag(1)–O(5)	117.2(3)
O(5)–Ag(1)–O(7)	98.8(2)	O(2)–Ag(1)–Ag(2)	136.4(2)
O(5)–Ag(1)–Ag(2)	106.4(2)	O(7)–Ag(1)–Ag(2)	73.8(2)
O(2)–Ag(1)–Pd(2)	76.0(2)	O(5)–Ag(1)–Pd(2)	136.96(16)
O(7)–Ag(1)–Pd(2)	120.6(2)	Ag(2)–Ag(1)–Pd(2)	72.27(3)
O(2)–Ag(1)–Pd(1)	124.67(19)	O(5)–Ag(1)–Pd(1)	70.22(17)
O(7)–Ag(1)–Pd(1)	136.2(2)	Ag(2)–Ag(1)–Pd(1)	69.57(3)
Pd(2)–Ag(1)–Pd(1)	69.33(3)	N(6)–Ag(2)–N(8)	176.9(3)
N(6)–Ag(2)–Ag(1)	94.03(19)	N(8)–Ag(2)–Ag(1)	85.45(18)

$[Pd_2Ag_2(\mu\text{-dmpz})_4(p\text{-}O_2CC_6H_4OCH_3\text{-}\kappa O)_2(DMSO)]$ is a palladium/silver tetranuclear compound with both palladium atoms bridged by two 3,5-dmpz groups in such a way that the Pd_2N_4 ring shows a typical boat-like conformation, the dihedral angle between both Pd–N–N–Pd fragments being 70.5(2)°.[22] Both palladium atoms complete their square-planar coordination environments by bonding to one nitrogen of another 3,5-dmpz group and one oxygen of the carboxylate anion. In this complex the two 3,5-dmpz groups outside the Pd_2N_4 ring are in cisoid positions with respect to the Pd···Pd axis, as are both carboxylate groups, although in the starting complex $[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4\text{-}OCH_3\text{-}\kappa O)_2(Hdmpz)_2]$ (**3d**) transoid positions are observed. The Pd–N[6,11–17,20,21,36] and Pd–O[44,45]distances are in the range of those found in palladium compounds with the same kind of ligands.

One of the silver atoms, Ag(2), is bonded to two 3,5-dmpz groups in an almost linear coordination environment [N(8)–Ag(2)–N(6) = 176.9(3)°]. The 3,5-dmpz groups bridging Ag(2) and both palladium atoms are almost coplanar [interplanar angle of 4.7(3)°] and the dihedral angles between them and the coordination planes of the corresponding palladium atoms are 52.3(3)° [Pd(1)] and 51.5(3)° [Pd(2)].[22] The Ag–N distances are similar to those found in other silver pyrazolate complexes.[13]

The other silver atom, Ag(1), is coordinated to two oxygen atoms, one from each carboxylate group, which act as a bridge between this atom] and both palladium atoms. Ag(1) completes its coordination environment with the oxygen of one molecule of DMSO used as crystallisation solvent. All Ag–O distances are in the range of those observed in silver complexes with these kinds of ligands.[44–49] Ag(1) also contacts with Ag(2), the Ag(1)···Ag(2) distance being 2.9208(12) Å, which is similar to distances found in other complexes with Ag···Ag interactions.[50–53] In addition, Ag(1) contacts with Pd(1) [Ag(1)···Pd(1) = 3.0652(12) Å] and Pd(2) [Ag(1)···Pd(2) = 2.9586(12) Å] and the Ag–Pd vectors are nearly perpendicular to the square coordination planes of the Pd(1) and Pd(2) centres [9.2(1)° and 9.7(1)° respectively]. Both facts indicate weak Pd···Ag interactions.[54,55]

The planar "C–CO_2" fragment from the carboxylate group bonded to Pd(1) forms angles of 69.8(3)° and 72.3(4)° with the palladium coordination plane and the 3,5-dmpz group outside the Pd_2N_4 ring, respectively.[22] The same parameters for Pd(2) are 86.6(3)° and 87.1(4)°. The interplanar angle between both "C–CO_2" fragments is 68.1(4)°.

Conclusion

In summary, *N*-acetylglycine reacts with $[Pd(dmpz)_2(Hdmpz)_2]$ (**A**) in a 2:1 molar ratio to give $[Pd(Hdmpz)_4](O_2CCH_2NHCOCH_3)_2$ (**1**) by selective protonation of the anionic monodentate dmpz ligands. The cationic complex $[Pd(Hdmpz)_4]^{2+}$ is bonded to the *N*-acetylglycinate anion through charge-assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds. *N*-acetylglycine also reacts with $[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$ (**B**) in a 2:1 molar ratio, but in this case, the

selective protonation of the monodentate dmpz groups (one from each palladium atom) is followed by their displacement by the carboxylate anions generated and their elimination as Hdmpz. In the resulting compound, $[Pd_2(\mu\text{-dmpz})_2(O_2CCH_2NHCOCH_3\text{-}\kappa O)_2(Hdmpz)_2]$ (**2**), the monodentate carboxylate groups exhibit a transoid conformation with respect to the Pd···Pd axis. The benzoic derivatives, $HO_2CC_6H_4$-R [R = *m*-NO_2, *p*-$N(CH_3)_2$, *p*-NH_2, *p*-OCH_3, *p*-OH] react with **B** in the same way that *N*-acetylglycine does to give compounds $[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4\text{-R-}\kappa O)_2(Hdmpz)_2]$ [R = *m*-NO_2 (**3a**), *p*-$N(CH_3)_2$ (**3b**), *p*-NH_2 (**3c**), *p*-OCH_3 (**3d**), *p*-OH (**3e**)]. In the complexes **3a**–**3e**, the H atoms of the terminal Hdmpz groups can be replaced by Ag^+ to give $[Pd_2Ag_2(\mu\text{-dmpz})_4(\mu\text{-}O_2CC_6H_4\text{-R-}\kappa O)_2(Hdmpz)_2]$ [R = *m*-NO_2 (**4a**), *p*-$N(CH_3)_2$ (**4b**), *p*-NH_2 (**4c**), *p*-OCH_3 (**4d**), *p*-OH (**4e**)], keeping the carboxylate groups in a transoid conformation. Compounds **4a**–**4e** isomerise in acetone solution at room temperature to the cisoid species **4a′**–**4e′**.

Experimental Section

General Procedures and Materials: $[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$[14] and $[Pd(dmpz)_2(Hdmpz)_2]$[13] were prepared as described elsewhere. All reagents were commercially available and used as received from Aldrich. Elemental analyses were performed with a Perkin–Elmer 240-B microanalyser. IR spectra were recorded with a Perkin–Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 400–4000 cm^{-1}). NMR spectra were recorded with a Varian Unity-300 spectrometer using standard references.

$[Pd(Hdmpz)_4](O_2CCH_2NHCOCH_3)_2$ (1): *N*-acetylglycine (0.12 g, 1.0227 mmol) was added to a solution of $[Pd(dmpz)_2(Hdmpz)_2]$ (**A**; 0.250 g, 0.5113 mmol) in CH_2Cl_2/MeOH (25:5 mL). The mixture was stirred at room temperature for 2 h and then the solvent was evaporated to dryness. Addition of Et_2O (5 mL) to the residue yielded **1** (0.3436 g, 93%). $C_{28}H_{44}N_{10}O_6Pd$ (723.12): calcd. C 46.51, H 6.13, N 19.36; found C 46.63, H 5.90, N 19.07. IR: $\tilde{\nu}_{max}$ = 3450–3000 cm^{-1} (s, br), 1667 (m), 1628 (vs), 1583 (s), 1376 (s), 1287 (s), 1068 (m), 1035 (m), 783 (m, sh), 650 (m), 597 (m), 555 (m), 517 (m).

$[Pd_2(\mu\text{-dmpz})_2(O_2CCH_2NHCOCH_3)_2(Hdmpz)_2]$ (2): A solution of *N*-acetylglycine (0.06 g, 0.51 mmol) in methanol (10 mL) was added to a solution of $[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$ (**B**; 0.200 g, 0.2546 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at room temperature for 2 h and the solution was then filtered through celite and the solvent evaporated to dryness. Addition of Et_2O (5 mL) to the residue yielded **2** (0.110 g, 51%). $C_{28}H_{42}N_{10}O_6Pd_2$ (721.11): calcd. C 40.64, H 5.12, N 16.92; found C 40.71, H 5.08, N 16.60. IR: $\tilde{\nu}_{max}$ = 3450–3000 cm^{-1} (s, br), 1627 (vs), 1583 (vs), 1376 (s), 1282 (s), 1175 (m), 1035 (m), 814 (m), 775 (m), 660 (w). ^1H NMR (300 MHz, $CDCl_3$, 23 °C): δ = 1.80 (s, 6 H, CH_3, dmpz), 1.86 (s, 6 H, CH_3, *N*-acetylglycine), 2,18 (s, 6 H, CH_3, Hdmpz), 2.26 (s, 6 H, CH_3, dmpz), 2.64 (s, 6 H, CH_3, Hdmpz), 3.74 (ν_A, $^2J_{H,H}$ = 4.0 Hz, 2 H, CH_2, acetylglycine), 3.76 (ν_B, 2 H, CH_2, acetylglycine), 5.41 (s, 2 H, 4-H, dmpz), 5.80 (s, 2 H, 4-H, Hdmpz), 5.99 (s, 2 H, N-H, acetylglycine), 13.07 (s, 2 H, N-H, Hdmpz) ppm.

$[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4NO_2\text{-}\kappa O)_2(Hdmpz)_2]$ (3a): A solution of *m*-nitrobenzoic acid (0.1067 g, 0.638 mmol) in methanol (3 mL) was added to a yellow solution of **B** (0.2496 g, 0.318 mmol) in CH_2Cl_2 (35 mL). The mixture was stirred at room temperature for 2 h and the solvent was then evaporated to dryness. Addition of diethyl ether (12 mL) to the residue gave **3a** as a yellow solid, which was filtered off and dried (0.055 g, 32% yield). $C_{34}H_{38}N_{10}O_8Pd_2$ (927.54): calcd. C 44.03, H 4.13, N 15.09; found C 43.93, H 4.27, N 14.83. IR: $\tilde{\nu}_{max}$ = 1631 cm^{-1} (vs), 1586 (s), 1531 (s), 1378 (vs), 1348 (s), 1155 (m), 1072 (m), 820 (m), 782 (m), 760 (m). ^1H NMR (300 MHz, [D$_6$]acetone, 23 °C): δ = 1.94 (s, 6 H, CH_3, dmpz), 2.36 (s, 6 H, CH_3, Hdmpz), 2.40 (s, 6 H, CH_3, dmpz), 2.93 (s, 6 H, CH_3, Hdmpz), 5.47 (s, 2 H, 4-H, dmpz), 6.10 (s, 2 H, 4-H, Hdmpz), 7.70 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, 5-H), 8.33 (d, $^3J_{H6,H5}$ = 7.7 Hz, 2 H, 6-H), 8.40 (d, $^3J_{H4,H5}$ = 7.7 Hz, 2 H, 4-H), 8.80 (s, 2 H, 2-H), 13.78 (s, 2 H, N-H, Hdmpz) ppm.

$[Pd_2(\mu\text{-dmpz})_2\{O_2CC_6H_4N(CH_3)_2\text{-}\kappa O\}_2(Hdmpz)_2]$ (3b): Prepared similarly to **3a** from **B** (0.3000 g, 0.382 mmol) and *p*-dimethylaminobenzoic acid (0.1262 g, 0.764 mmol). Addition of methanol (7 mL) to the residue gave **3b** (0.2904 g, 82%). $C_{38}H_{50}N_{10}O_4Pd_2$ (923.68): calcd. C 49.41, H 5.46, N 15.16; found C 49.15, H 5.45, N 15.17. IR: $\tilde{\nu}_{max}$ = 1609 cm^{-1} (vs), 1589 (s), 1543 (s), 1525 (s), 1356 (vs), 1307 (s), 1230 (m), 1194 (vs), 1140 (m), 1063 (m), 946 (m), 837 (m), 810 (m), 778 (vs). ^1H NMR (300 MHz, [D$_6$]DMSO, 23 °C): δ = 1.83 (s, 6 H, CH_3, dmpz), 2.25 (s, 6 H, CH_3, Hdmpz), 2.30 (s, 6 H, CH_3, dmpz), 2.78 (s, 6 H, CH_3, Hdmpz), 2.92 (s, 12 H, NMe_2), 5.45 (s, 2 H, 4-H, dmpz), 6.07 (s, 2 H, 4-H, Hdmpz), 6.65 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.8 Hz, 4 H, 3-H, 5-H), 7.71 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.8 Hz, 4 H, 2-H, 6-H), 14.00 (s, 2 H, N-H, Hdmpz) ppm.

$[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4NH_2\text{-}\kappa O)_2(Hdmpz)_2]$ (3c): Prepared similarly to **3a** from **B** (0.2027 g, 0.258 mmol) and *p*-aminobenzoic acid (0.071 g, 0.516 mmol). Yield: 0.2017 g (90%). $C_{34}H_{42}N_{10}O_4Pd_2$ (867.58): calcd. C 47.07, H 4.88, N 16.14; found C 46.76, H 4.72, N 15.83. IR: $\tilde{\nu}_{max}$ = 3386 cm^{-1} (m), 3329 (m), 3176 (m), 3125 (m), 1642 (m), 1600 (vs), 1548 (m), 1513 (m), 1376 (vs), 1297 (s), 1174 (s), 1066 (m), 849 (m), 813 (m), 782 (m), 649 (m), 505 (m). ^1H NMR (300 MHz, [D$_6$]acetone, 23 °C): δ = 1.94 (s, 6 H, CH_3, dmpz), 2.36 (s, 12 H, CH_3, dmpz, Hdmpz), 2.89 (s, 6 H, CH_3, Hdmpz), 4.98 (s, 4 H, NH_2), 5.41 (s, 2 H, 4-H, dmpz), 6.00 (s, 2 H, 4-H, Hdmpz), 6.60 (m, 4 H, 3-H, 5-H), 7.77 (m, 4 H, 2-H, 6-H), 14.34 (s, 2 H, N-H, Hdmpz) ppm.

$[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4OCH_3\text{-}\kappa O)_2(Hdmpz)_2]$ (3d): Prepared similarly to **3a** from **B** (0.2995 g, 0.381 mmol) and *p*-methoxybenzoic acid (0.1161 g, 0.763 mmol). The addition of methanol (8 mL) to the residue gave **3d** as a yellow solid (0.2165 g, 63%). $C_{36}H_{44}N_8O_6Pd_2$ (897.60): calcd. C 48.17, H 4.94, N 12.48; found C 47.87, H 4.82, N 12.35. IR: $\tilde{\nu}_{max}$ = 1609 cm^{-1} (vs), 1586 (s), 1570 (s), 1533 (s), 1509 (s), 1364 (vs), 1305 (s), 1253 (s), 1168 (s), 1031 (s), 851 (m), 819 (m), 778 (s). ^1H NMR (300 MHz, [D$_6$]acetone, 23 °C): δ = 1.94 (s, 6 H, CH_3, dmpz), 2.35 (s, 6 H, CH_3, Hdmpz), 2.36 (s, 6 H, CH_3, dmpz), 2.89 (s, 6 H, CH_3, Hdmpz), 3.81 (s, 6 H, OCH_3), 5.42 (s, 2 H, 4-H, dmpz), 6.02 (s, 2 H, 4-H, Hdmpz), 6.91 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.8 Hz, 4 H, 3-H, 5-H), 7.97 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.8 Hz, 4 H, 2-H, 6-H), 14.16 (s, 2 H, N-H, Hdmpz) ppm.

$[Pd_2(\mu\text{-dmpz})_2(O_2CC_6H_4OH\text{-}\kappa O)_2(Hdmpz)_2]$ (3e): Prepared similarly to **3a** from **B** (0.2120 g, 0.269 mmol) and *p*-hydroxybenzoic acid (0.0745 g, 0.539 mmol). Yield: 0.2211 g (94%). $C_{34}H_{40}N_8O_6Pd_2$ (869.54): calcd. C 46.96, H 4.60, N 12.89; found C 47.23, H 5.00, N 12.93. IR: $\tilde{\nu}_{max}$ = 3331 cm^{-1} (m), 1610 (vs), 1597 (vs), 1537 (vs), 1503 (vs), 1377 (vs), 1288 (vs), 1234 (vs), 1167 (vs), 1054 (m), 857 (m), 788 (s), 777 (s), 651 (m). ^1H NMR (300 MHz, [D$_6$]acetone, 23 °C): δ = 1.94 (s, 6 H, CH_3, dmpz), 2.35 (s, 12 H, CH_3, dmpz, Hdmpz), 2.88 (s, 6 H, CH_3, Hdmpz), 5.42 (s,

2 H, 4-H, dmpz), 6.00 (s, 2 H, 4-H, Hdmpz), 6.80 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.4 Hz, 4 H, 3-H, 5-H), 7.89 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.4 Hz, 4 H, 2-H, 6-H), 14.19 (s, 2 H, N-H, Hdmpz) ppm.

[Pd_2Ag_2(μ-dmpz)$_4$($O_2CC_6H_4NO_2$-κ*O*)$_2$] (4a): $AgClO_4$ (0.0663 g, 0.3198 mmol) and NEt_3 (0.5 mL) were added to a solution of **3a** (0.1412 g, 0.152 mmol) in acetone (12 mL). The resulting solution was stirred for 75 min and then filtered through celite to eliminate some impurities. The solution was evaporated to dryness and MeOH (15 mL) added to the residue. The yellow solid was filtered and washed with diethyl ether (6 mL). Yield of **4a**: (0.165 g, 74%). $C_{34}H_{36}Ag_2N_{10}O_8Pd_2$ (1141.3): calcd. C 35.78, H 3.18, N 12.27; found C 35.58, H 2.95, N 12.08. IR: $\tilde{\nu}_{max}$ = 1598 cm^{-1} (vs), 1564 (vs), 1399 (vs), 1349 (vs), 1160 (m), 1081 (m), 1050 (m), 780 (m), 654 (w). ^1H NMR (300 MHz, [D_6]acetone, 23 °C): δ = 2.17 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.52 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.60 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.85 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 5.64 [s, 2 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.74 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 7.80 (m, 2 H, 5-H), 8.43 (m, 4 H, 4-H, 6-H), 8.80 (m, 2 H, 2-H) ppm. Slow evaporation of a solution of **4a** in acetone at room temperature gave **4a′**. ^1H NMR (300 MHz, [D_6]acetone, 23 °C): δ = 1.90 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.22 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.58 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.66 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 5.62 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.64 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$],5.86 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 7.75 (m, 2 H, 5-H), 8.37 (ddd, $^3J_{H4,H5}$ = 8.2, $^4J_{H4,H2}$ = 2.4, $^4J_{H4,H6}$ = 1.2 Hz, 2 H, 4-H), 8.41 (dt, $^3J_{H6,H5}$ = 7.8, $^4J_{H6,H4}$ = $^4J_{H6,H2}$ = 1.2 Hz, 2 H, 6-H), 8.77 (m, 2 H, 2-H) ppm.

[Pd_2Ag_2(μ-dmpz)$_4${$O_2CC_6H_4N(CH_3)_2$-κ*O*}$_2$] (4b): Prepared similarly to **4a** from **3b** (0.2001 g, 0.202 mmol), $AgClO_4$ (0.0893 g, 0.431 mmol) and NEt_3 (0.7 mL). Yield of **4b**: 0.1753 g (79%). $C_{38}H_{48}Ag_2N_{10}O_4Pd_2$ (1137.4): calcd. C 40.06, H 4.24, N 12.29; found C 40.41, H 4.41, N 11.99. IR: $\tilde{\nu}_{max}$ = 1603 cm^{-1} (m), 1566 (m), 1512 (m), 1379 (s), 1366 (m), 1196 (m), 779 (m). ^1H NMR (300 MHz, CH_2Cl_2, 23 °C): δ = 2.04 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.21 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.51 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.53 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 3.02 (s, 12 H, NMe_2), 5.61 [s, 2 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.73 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 6.63 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 9.1 Hz, 4 H, 3-H, 5-H), 7.87 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 9.1 Hz, 4 H, 2-H, 6-H) ppm. Slow evaporation of a solution of **4b** in acetone at room temperature gave **4b′**. ^1H NMR (300 MHz, CD_2Cl_2, 23 °C): δ = 1.89 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.25 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.59 [s, 12 H, CH_3, Pd_2(μ-dmpz)$_2$, Pd_2Ag(μ-dmpz)$_2$], 3.02 (s, 12 H, NMe_2), 5.62 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.71 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.82 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 6.63 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.9 Hz, 4 H, 3-H, 5-H), 7.86 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.9 Hz, 4 H, 2-H, 6-H) ppm.

[Pd_2Ag_2(μ-dmpz)$_4$($O_2CC_6H_4NH_2$-κ*O*)$_2$] (4c): Prepared similarly to **4a** from **3c** (0.08 g, 0.0922 mmol), $AgClO_4$ (0.0382 g, 0.1844 mmol) and NEt_3 (0.5 mL). Yield of **4c**: 0.009 g (9%). $C_{34}H_{40}Ag_2N_{10}O_4Pd_2$ (1081.3): calcd. C 37.77, H 3.73, N 12.95; found C 37.68, H 3.67, N 12.65. IR: $\tilde{\nu}_{max}$ = 3363 cm^{-1} (m), 1619(m), 1602 (m), 1584 (s), 1523 (m, sh), 1377 (s), 1299 (m), 1176 (m), 841 (w), 776 (m), 641 (w), 500 (w). ^1H NMR (300 MHz, $CDCl_3$, 23 °C): δ = 2.02 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.16 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.47 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.49 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 3.92 (s, 4 H, NH_2), 5.30 [s, 2 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.55 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 6.58 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.4 Hz, 4 H, 3-H, 5-H), 7.81 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.4 Hz, 4 H, 2-H, 6-H) ppm. Slow evaporation of a solution of **4c** in acetone at room temperature gave **4c′**. ^1H NMR (300 MHz, [D_6]acetone, 23 °C): δ = 1.87 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.21 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.57 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.63 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 3.92 (s, 4 H, NH_2), 5.60 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.63 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.81 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 6.60 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.4 Hz, 4 H, 3-H, 5-H), 7.75 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.4 Hz, 4 H, 2-H, 6-H) ppm.

[Pd_2Ag_2(μ-dmpz)$_4$($O_2CC_6H_4OCH_3$-κ*O*)$_2$] (4d): Prepared similarly to **4a** from **3d** (0.1810 g, 0.202 mmol), $AgClO_4$ (0.0836 g, 0.403 mmol) and NEt_3 (0.7 mL). Yield of **4d**: 0.165 g (74%). $C_{36}H_{42}Ag_2N_8O_6Pd_2$ (1111.3): calcd. C 38.91, H 3.81, N 10.08; found C 38.91, H 3.78, N 10.03. IR: $\tilde{\nu}_{max}$ = 1610 cm^{-1} (s), 1591 (s), 1546 (s), 1378 (s), 1260 (s), 1171 (m), 1032 (m), 848 (m), 778 (s), 765 (m), 642 (m), 628 (m). ^1H NMR (300 MHz, [D_6]DMSO, 23 °C): δ = 2.02 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.24 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.47 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.60 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 3.91 (s, 6 H, OCH_3), 5.70 [s, 2 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.83 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 7.09 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 9.1 Hz, 4 H, 3-H, 5-H), 7.99 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 9.1 Hz, 4 H, 2-H, 6-H) ppm. Slow evaporation of a solution of **4d** in acetone at room temperature gave **4d′**. ^1H NMR (300 MHz, [D_6] DMSO, 23 °C): δ = 1.77 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.18 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.46 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.59 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 3.80 (s, 6 H, OCH_3), 5.59 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.60 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.83 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 6.94 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.7 Hz, 4 H, 3-H, 5-H), 7.89 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.7 Hz, 4 H, 2-H, 6-H) ppm.

[Pd_2Ag_2(μ-dmpz)$_4$($O_2CC_6H_4OH$-κ*O*)$_2$] (4e): Prepared similarly to **4a** from **3e** (0.17 g, 0.196 mmol), $AgClO_4$ (0.0812 g, 0.392 mmol) and NEt_3 (0.75 mL). Yield of **4e**: 0.08 g (38%). $C_{34}H_{38}Ag_2N_8O_6Pd_2$ (1083.3): calcd. C 37.70, H 3.53, N 10.34; found C 37.39, H 3.16, N 10.51. IR: $\tilde{\nu}_{max}$ = 3606 cm^{-1} (m), 1610 (m), 1594 (s), 1538 (s, sh), 1377 (s), 1274 (m), 1236 (m), 1166 (m), 1095 (m), 848 (m), 780 (s), 768 (s), 643 (m). ^1H NMR (300 MHz, [D_6]acetone, 23 °C): δ = 2.04 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.16 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.51 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.57 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 5.60 [s, 2 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.72 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 6.87 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.9 Hz, 4 H, 3-H, 5-H), 7.93 (d, $^3J_{H2,H3}$ = $J_{H5,H6}$ = 8.9 Hz, 4 H, 2-H, 6-H) ppm. Slow evaporation of a solution of **4e** in acetone at room temperature gave **4e′**. ^1H NMR (300 MHz, [D_6]acetone, 23 °C): δ = 1.88 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.21 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 2.57 [s, 6 H, CH_3, Pd_2(μ-dmpz)$_2$], 2.64 [s, 6 H, CH_3, Pd_2Ag(μ-dmpz)$_2$], 5.61 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.64 [s, 1 H, 4-H, Pd_2(μ-dmpz)$_2$], 5.83 [s, 2 H, 4-H, Pd_2Ag(μ-dmpz)$_2$], 6.82 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.9 Hz, 4 H, 3-H, 5-H), 7.89 (d, $^3J_{H2,H3}$ = $^3J_{H5,H6}$ = 8.7 Hz, 4 H, 2-H, 6-H) ppm.

X-ray Structure Determination: Crystal data and other details of the structure analysis are presented in Table 5. Single crystals of **1** were obtained by slow diffusion of *n*-hexane into a solution of **1** in chloroform at room temperature. Single crystals of **3d** and **3e** were obtained by slow diffusion of *n*-hexane into their respective solutions in acetone at room temperature. Single crystals of **4d′** were obtained by slow diffusion of diethyl ether into a solution of **4d** in DMSO at room temperature. For **3d·Me_2CO**, the acetone solvent molecule was found to be disordered over two sets of positions that were refined with partial occupancy 0.50:0.50. A common set of anisotropic parameters was used for each pair of homologous atoms. For **3e·2Me_2CO**, one of the acetone solvent molecules was modelled as disordered over two positions with partial occupancy 0.75:0.25, with the central C atom (C38) being common for the two sets. For **4d′·0.7Me_2SO**, the sulfur atom of the Me_2SO molecule coordinated to Ag(1) was disordered over two positions [S(1)/S(1′)] refined with partial occupancy 0.80:0.20. For this molecule, all the

Table 5. Crystal data and structure refinement for complexes **1**, **3d**·Me_2CO, **3e**·2Me_2CO and **4d′**·0.7Me_2SO.

Complex	**1**	**3d**·Me_2CO	**3e**·2Me_2CO	**4d′**·0.7Me_2SO
Empirical formula	$C_{28}H_{44}N_{10}O_6Pd$	$C_{36}H_{44}N_8O_6Pd_2$·Me_2CO	$C_{34}H_{40}N_8O_6Pd_2$·2Me_2CO	$C_{38}H_{48}Ag_2N_8O_7Pd_2S$·0.7$Me_2SO$
Formula mass	723.13	955.67	985.7	1244.13
T [K]	150(1)	173(1)	100(1)	173(1)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	Cc	$P\bar{1}$
a [Å]	8.3462(6)	8.5194(6)	17.8303(7)	12.867(5)
b [Å]	9.4493(5)	22.1527(15)	12.8679(5)	13.823(5)
c [Å]	20.7037(15)	22.9327(16)	20.9510(9)	14.585(5)
α [°]	90	90	90	99.922(7)
β [°]	95.491(10)	96.938(1)	113.957(1)	101.816(8)
γ [°]	90	90	90	100.341(6)
V [Å^3]	1625.32(19)	4614.5(5)	4392.8(3)	2438.3(15)
Z	2	4	4	2
D_c [g cm^{-3}]	1.478	1.477	1.490	1.695
μ (Mo-K_α) [mm^{-1}]	0.628	0.892	0.877	1.643
θ range [°]	2.37–24.97	2.01–25.03	2.02–28.47	1.93–25.03
Data collected	3045	32062	19098	13477
Independent data (R_{int})	2835 (0.0222)	7570 (0.0336)	9547 (0.0232)	8529 (0.0330)
Goodness-of-fit on F^2[a]	1.050	1.010	1.030	1.032
Final R indices [$I > 2\sigma(I)$][b]	$R_1 = 0.0292$; $wR_2 = 0.0722$	$R_1 = 0.0305$; $wR_2 = 0.0687$	$R_1 = 0.0230$; $wR_2 = 0.0583$	$R_1 = 0.0589$; $wR_2 = 0.1344$
R indices (all data)[c]	$R_1 = 0.0438$; $wR_2 = 0.0782$	$R_1 = 0.0374$; $wR_2 = 0.0710$	$R_1 = 0.0234$; $wR_2 = 0.0585$	$R_1 = 0.0806$; $wR_2 = 0.1476$

[a] Goodness-of-fit = $[\Sigma w (F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{0.5}$. [b] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

S–C and S–O distances were restrained to be equal for both S atoms. No attempts were made to include the methyl hydrogen atoms of this molecule in the final model.

CCDC-271570–271573 (for **1**, **3d**, **3e** and **4d′**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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