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Polymorphism in Coordination Chemistry. Selective Syntheses and *ab Initio* X-ray Powder Diffraction Characterization of Two New Crystalline Phases of Solid [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ (Hdmpz = 3,5-Dimethylpyrazole)

Norberto Masciocchi,*[,†] G. Attilio Ardizzoia,*[,‡,§] Girolamo La Monica,[‡,§]
Massimo Moret,[†] and Angelo Sironi*[,†]

Dipartimento di Chimica Strutturale e Stereochimica Inorganica and Dipartimento di Chimica
Inorganica, Metallorganica ed Analitica e Centro CNR, Università di Milano, via Venezian 21,
20133 Milano, Italy

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[Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$, which is known to crystallize in the monoclinic system (α phase), possesses two polymorphs which could only be produced as microcrystalline powders. Selective syntheses of these new (β and γ) polymorphs and their structural characterization from X-ray powder diffraction data have been successfully accomplished by *ab initio* methods and Rietveld refinement. β-[Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ is tetragonal, space group $I422$, a = 13.1342(7) Å, c = 13.7920(9) Å, Z = 2; R_p, R_{wp}, and $\mathrm{R_F}$ being 0.106, 0.143, and 0.075, respectively. γ-[Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ is triclinic, space group $P\bar{1}$, a = 11.470(1) Å, b = 11.619(2) Å, c = 19.221(2) Å, α = 80.928(6)°, β = 81.434(7)°, and γ = 69.033(5)°, Z = 2; R_p, R_{wp}, and R_F being 0.104, 0.136, and 0.085, respectively. In all three phases the identity of the [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ dimer, containing four strong intramolecular N−H···N bonds, is retained. The α and γ phases are a racemate of chiral molecules, while during the formation of the β phase, spontaneous resolution of chiral molecules occurs, thus generating a conglomerate of enantiomeric crystals.

The phenomenon of polymorphism, i.e., the ability of a compound to crystallize in more than one distinct crystal structure, has been extensively observed in both the inorganic and mineralogic fields and, more recently, in the organic and macromolecular ones.[1] Polymorphism, while affecting all possible categories of compounds, has been particularly studied in the realm of commercially relevant materials[2] (starting from silica, alumina, and metals (or alloys) up to complex molecular compounds such as drugs, dyes, and plastics), since different polymorphs, differing in their physical properties, might have different performances when used as drugs, catalysts, precursors, etc.[3] Two recent review articles give introductory, but excellent, comments and insights to the field.[4,5]

However, since the mainstream of organometallic chemistry deals with solution behavior and reactivity, it is customary for many structural chemists to assess stoichiometry, shape, and conformation of the molecules under study disregarding their packing environment.[6] In particular, once the structural characterization of a given compound has been performed, it is rare that further studies on the existence of polymorphs are undertaken.[7]

After having started a project on the *ab initio* X-ray powder diffraction (XRPD) structure determination of coordination chemistry materials, which only appear as powdered, but microcrystalline, samples,[8] we soon realized that polymorphism is a very annoying phenomenon, because the procedures of indexing and of integrated intensity extraction, which are at the very basis of the method, can be extremely hampered by the presence of a multiphase diffraction pattern. However, if suitable synthetic procedures leading to single phase specimens can be devised (for example, by employing different crystallization techniques or by applying suitable high-temperature or high-pressure environments[9]), the newly emerging technique of *ab initio* structure determination from powder diffraction data of a standard laboratory equipment becomes a viable tool for structural studies; in particular, for molecules of moderate or high complexity, the stereochemical information obtained from a previously characterized polymorphic structure can be of

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[†] Dipartimento di Chimica Strutturale e Stereochimica Inorganica.

[‡] Dipartimento di Chimica Inorganica.

[§] On leave from the Istituto di Scienze Matematiche, Fisiche e Chimiche, Università di Milano, via Castelnuovo 7, 22100 Como, Italy.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

(1) Bernstein, J. In *Organic Solid State Chemistry*; Desiraju, D. R., Ed.; Elsevier Science Publishers: Amsterdam, 1987; p 471.

(2) Indeed, according to W. C. McCrone: "the number of polymorphic forms for a given compound is proportional to the time and *money* spent in research on that compound." In *Physics and Chemistry of the Organic Solid State*; Fox, D., Labes, M. M., Weissberger, A., Eds.; Interscience: New York, 1965; Vol. 2, p 726.

(3) For instance, the effectiveness of drugs is often dependent on the kinetics of their dissolution in the human body liquids and tissues; extreme care is therefore given to the existence of polymorphs or amorphous phases in the pharmacological chemistry field, as doses and therapies can be highly influenced by their appearance. See: Burger, A. In *Topics in Pharmaceutical Sciences*; Breimer, D. D., Speiser, P., Eds.; Elsevier Science Publishers: Amsterdam, 1983; p 347.

(4) Threlfall, T. L. *Analyst* **1995**, *120*, 2435.

(5) Dunitz, J.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193.

(6) There are, however, a few notable exceptions. See for instance: Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51 and references therein.

(7) Normally, after a good-looking single crystal is randomly picked out of a bunch of crystals, or, more frequently, from a complex mixture containing also (morphologically) amorphous, microcrystalline, or powdered material, no scattering measurements characterizing the nature of the bulk are routinely performed, thus overlooking the possibility of finding coexistence of different crystalline phases of the same composition in the same sample.

(8) Masciocchi, N.; Moret, M.; Cairati, P.; Ragaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, *471*. Li, J.; McCulley, F.; McDonnell, S. L.; Masciocchi, N.; Proserpio, D. M.; Sironi, A. *Inorg. Chem.* **1993**, *32*, 4829. Masciocchi, N.; Cairati, P.; Ragaini, F.; Sironi, A. *Organometallics* **1993**, *12*, 4499. Masciocchi, N.; Cairati, P.; Carlucci, L.; Ciani, G.; Mezza, G.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1994**, 3009. Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1995**, 1671.

(9) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G. *J. Am. Chem. Soc.* **1994**, *116*, 7768.

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enormous help in solving tasks that otherwise would be impossible to challenge.

In this paper we report on the existence of three different polymorphic phases of $[Pd(dmpz)_2(Hdmpz)_2]_2$[10] (Hdmpz = 3,5-dimethylpyrazole) and on their structural relationships, selective syntheses, and thermal properties.

Experimental Section

Materials. 3,5-Dimethylpyrazole, COS (Aldrich), $PdCl_2$, and K_2PdCl_4 (Metalli Preziosi SpA) were used without further purifications. Solvents were distilled by standard methods and stored under nitrogen. All preparations were performed using usual Schlenk techniques.

Physical Measurements. Infrared spectra were measured on a BIORAD FRS 7PC FTIR instrument. DSC traces were obtained with the aid of a Perkin-Elmer DSC 7 calorimeter. Chemical analyses (C, H, N) were performed by the staff at the Microanalytical Laboratory of this University.

Synthesis of α-$[Pd(dmpz)_2(Hdmpz)_2]_2$. The monoclinic (α) phase can be obtained as macroscopic single crystals and/or microcrystalline samples by following the synthetic procedure described in ref 10, starting from $[Pd(CH_3CN)_2Cl_2]$,[11] $PdCl_2$, or K_2PdCl_4, in the presence of Hdmpz and a noncoordinating base such as Et_3N. Note, however, that the raw material obtained just after filtering of the mother liquor contains variable amounts of the triclinic (γ) phase, roughly estimated to be below 10%, which can be removed by recrystallization from hot 1,2-dichloroethane. On changing the solvent and the precipitation temperature (−70 to +50 °C), a mixture of the α and γ phases is typically obtained, with increasing amounts of the α phase at higher temperatures.

Synthesis of β-$[Pd(dmpz)_2(Hdmpz)_2]_2$. COS (2 mL) was condensed over solid α-$[Pd(dmpz)_2(Hdmpz)_2]_2$ (400 mg) at −78 °C. The resulting suspension was stirred for 24 h, and then liquid COS was removed by slowly raising the temperature to 0 °C. At this stage, the formation of the transient $[Pd(dmpz)_2(Hdmpz)_2]_2$·COS species[12] was evidenced. The white solid was then pumped under vacuum (10^{-2} Torr, 60 °C) for ∼8 h, causing the complete loss of clathrated COS (as monitored by IR spectroscopy) and the quantitative formation of the β phase.

Synthesis of γ-$[Pd(dmpz)_2(Hdmpz)_2]_2$. To a suspension of $[Pd(Hdmpz)_3Cl]Cl$[10] (400 mg, 0.87 mmol) in CH_3OH, triethylamine (300 μL) was added. The suspension was stirred for 2 h and the solid was filtered off, washed with methanol, and dried under vacuum. This procedure gives 199 mg (47% yield) of pure γ-$[Pd(dmpz)_2(Hdmpz)_2]_2$. If the preparation is carried out in the presence of excess of free 3,5-dimethylpyrazole, a mixture of the α and γ phases (∼50% each) was isolated.

Single-Crystal X-ray Analysis of α-$[Pd(dmpz)_2(Hdmpz)_2]_2$ (1). All relevant information is supplied in ref 10.

X-ray Powder Diffraction Analysis of β- and γ-$[Pd(dmpz)_2(Hdmpz)_2]_2$ (2 and 3). The white powders were gently ground in an agate mortar and then cautiously deposited in the hollow of an aluminium holder equipped with a zero background plate (supplied by The Gem Dugout, State College, PA) with the aid of glass slide. The sample was rotated at ∼60 rpm about the scattering vector, in order to minimize preferred orientation effects. Diffraction data (Cu Kα, $\lambda = 1.5418$ Å) were collected on a horizontal scan D III/Max Rigaku diffractometer, equipped with parallel (Soller) slits, a secondary beam curved graphite monochromator, a Na(Tl)I scintillation detector, and a pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. Slits used: divergence 1.0°, antiscatter 1.0°, and receiving 0.3°. Nominal resolution for the present setup is 0.14° 2θ (fwhm) for the Si(111) peak at 28.44° (2θ). Long overnight scans were performed with $5 < 2\theta < 95°$, with $t = 10$ s and $\Delta 2\theta = 0.02°$. Figure 1 shows the raw XRPD data for the three phases.

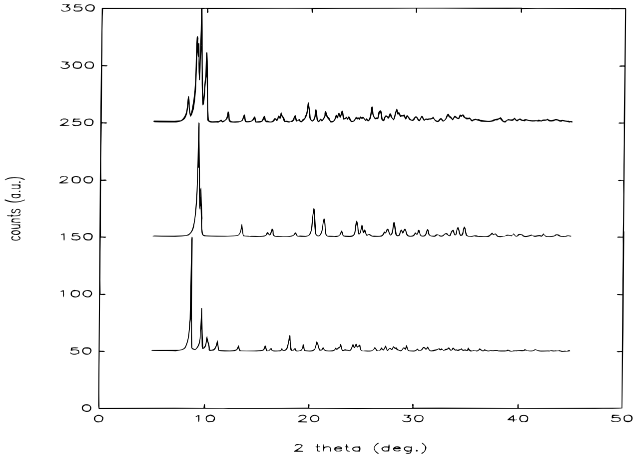

Figure 1. Raw XRPD data, in the $5 < 2\theta < 45°$ range, for $[Pd(dmpz)_2(Hdmpz)_2]_2$: α (bottom), β (middle), and γ (top) phases.

Indexing, using TREOR,[13] of the low-angle peaks for **2** and **3** suggested a tetragonal cell of approximate dimensions $a = 13.13$ Å, $c = 13.81$ Å for **2** [$M(20)$[14] = 34; $F(20)$[15] = 64 (0.006, 56)] and a triclinic cell of approximate dimensions $a = 11.44$ Å, $b = 11.60$ Å, $c = 19.18$ Å, $\alpha = 81.0°$, $\beta = 81.5°$, and $\gamma = 69.0°$ for **3** [$M(20) = 11$; $F(20) = 37$ (0.015, 37)], respectively.

Systematic absences for **2** indicated a probable body-centered tetragonal lattice, later confirmed by the successful refinement, in acentric $I422$, of the structural model of *idealized* 422 molecular symmetry detected in **1** and present in its direct precursor $[Pd(dmpz)_2(Hdmpz)_2$·COS.[12] Pawley's ALLHKL program[16] was used to extract 136 independent F_o's ($2\theta < 64°$), which afforded an easily interpretable Patterson map and the approximate location of the (crystallographically unique) Pd atom. Difference Fourier syntheses and geometrical modeling afforded approximate coordinates for the remaining non-hydrogen atoms.

ALLHKL has also been used to extract as many as possible reliable structure factors for the low-symmetry, high-volume unit cell of **3**. Data below 35° (2θ) afforded 272 independent reflections, which, in $P\bar{1}$, after interpretation of the Patterson map, unambiguously revealed the absolute location and orientation of the (nonbonding) Pd···Pd vector in the crystal lattice.

Completion of the model was only possible through the assumption of a local environment of each Pd atom (in terms of bond distances and fragment conformations) similar to those found in the α and β phases (as suggested, for example, by the similarities of the IR spectra and by the rather high stability experienced by a dimer possessing four strong *intra*molecular hydrogen bonds). Molecular mechanics within the crystallographic lattice, performed with a local modification[17] of Allinger's program,[18] capable of dealing with *concerted* motions within the space group constraints, has evidenced a rather deep local steric minimum for a (unique) molecular conformation which has been assumed as a starting model for Rietveld refinement (*vide infra*).

Final refinements were performed with the aid of the GSAS suite of programs,[19] by imposing steric constraints to chemically stiff and known fragments, such as the Hdmpz/dmpz ligands, for which ring bonds and C−CH_3 bonds were given literature values of 1.38 and 1.45 Å, respectively (internal ring angles being fixed at 108°, and external methyl atoms forced to be coplanar with the heterocyclic fragments). In order to limit the physically unsound scatter of equivalent Pd−N bond distances, if not restrained, a common value of 2.00 Å was imposed, on the basis of the values found in the α phase and in

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(10) Masciocchi, N.; Moret, M.; Ardizzoia, G. A.; Cenini, S.; La Monica, G. *J Chem. Soc., Dalton Trans.* **1996**, 1351.

(11) Doyle, J. R.; Stade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1969**, *6*, 216.

(12) Masciocchi, N.; Moret, M.; Sironi, A.; Ardizzoia, G. A.; Cenini, S.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1955.

(13) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(14) De Wolff, P. M. *J. Appl. Crystallogr.* **1968**, *1*, 108.

(15) Smith, G. S.; Snyder, R. L. *J. Appl. Crystallogr.* **1979**, *12*, 60.

(16) Pawley, G. S. *J. Appl. Crystallogr.* **1981**, *14*, 357.

(17) Sironi, A.; Moret, M., to be published.

(18) Allinger, N. L.; Yu, Y. H.; Lii, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(19) Larson, A. C.; Von Dreele, R. B. *LANSCE*, MS-H805, Los Alamos National Laboratory, Los Alamos, NM, 1990.

Table 1. Crystal Data and Refinement Parameters for **2** and **3**

compound	$[Pd(dmpz)_z(Hdmpz)_2]_2$	$[Pd(dmpz)_1(Hdmpz)_2]_2$
formula	$C_{40}H_{60}N_{16}Pd_2$	$C_{40}H_{60}N_{16}Pd_2$
phase	β	γ
fw	1955.66	1955.66
crystal system	tetragonal	triclinic
space group	$I422$	$P\bar{1}$
ρ_{calc}, g cm^{-3}	1.365	1.382
μ_{calc}, cm^{-1}	65.97	66.79
$F(000)$	1008	1008
N_{obs}	3751	3701
N_{refl}	640	7889
2θ range, deg	17−92	18−92
N_{par}	37	194
$N_{restraints}$	21	168
R_p[a]	0.106	0.104
R_{wp}	0.143	0.136
R_F	0.075	0.085

[a] $R_p = \sum|y_i - y_{ci}|/\sum y_i$, $R_{wp} = [\sum w_i(y_i - y_{ci})^2/\sum w_i y_i^2]^{1/2}$, $R_F = \sum|F_o - F_c|/\sum F_o$, where y_i and y_{ci} are the observed and calculated intensities at the ith step, respectively, w_i is a weighting factor (taken as $w_i = 1/y_i$), and F_o and F_c are the observed and calculated structure factors for all the allowed reflections.

analogous compounds, such as $[Pd(dmpz)_2Cl_2]_2$.[20] The peak shapes were best described by the Thompson/Cox/Hastings formulations[21] and the pseudo-Voight function with GV and LY set to zero. The background functions were described by a cosine Fourier series, while systematic errors were corrected with the aid of a zero angle shift and, for the β phase, a preferred orientation parameter, which, in the formulation of March and Dollase,[22] was found to be best effective if the 00*l* pole vector was chosen. The contribution of the hydrogen atoms to the scattered intensity was neglected. Scattering factors, corrected for real and imaginary anomalous dispersion terms, were taken from the internal library of GSAS. Final R_p, R_{wp}, and R_F agreement factors, together with details of the data collections and analyses for the β and γ phases can be found in Table 1. Figures 2 and 3 show the final Rietveld refinement plots for the β and γ phases, respectively. Final fractional coordinates and full lists of bond distances and angles are supplied as Supporting Information.

Results and Discussion

Synthesis. When solid α-$[Pd(dmpz)_2(Hdmpz)_2]_2$ is suspended, at −78 °C, in liquid COS under magnetic stirring, it transforms quantitatively into the transient $[Pd(dmpz)_2(Hdmpz)_2]_2$·COS species,[12] which is stable, at room temperature, only for a few hours, and rapidly decays, by loss of carbonyl sulfide, to the starting material $[Pd(dmpz)_2(Hdmpz)_2]_2$. This transformation generates uniquely the new β phase, which is reminiscent of the tetragonal packing adopted by the $[Pd(dmpz)_2(Hdmpz)_2]_2$·COS clathrate, the structure of which was determined from powder diffraction also.[12] COS can also be quantitatively removed by vacuum pumping and/or moderate heating (60 °C) under nitrogen:

$$\alpha\text{-}[Pd(dmpz)_2(Hdmpz)_2]_2 \xrightarrow{COS} [Pd(dmpz)_2(Hdmpz)_2]_2\cdot COS \xrightarrow{-COS} \beta\text{-}[Pd(dmpz)_2(Hdmpz)_2]_2$$

Therefore, the formation and stability of the β phase can only be explained by the impossibility of a solid/solid transformation of the final product into the original α phase. Consistently, the formation of a conglomerate of acentric crystals of the $[Pd(dmpz)_2(Hdmpz)_2]_2$·COS species, starting from a racemate of chiral molecules of idealized 422 symmetry (*i*) cannot be explained by simple permeation of liquid COS into a preformed β phase lattice, (*ii*) excludes a simple liquid/solid reaction not involving a partial dissolution of α-$[Pd(dmpz)_2(Hdmpz)_2]_2$ into carbonyl sulfide and its subsequent recrystallization as a COS clathrate and, therefore, (*iii*) demonstrates the noninnocent nature of the solvent. After dissolution of β-$[Pd(dmpz)_2(Hdmpz)_2]_2$ in 1,2-dichloroethane and subsequent evaporation of the solvent, a mixture of the α and γ phases was quantitatively restored.

The formation of the γ-$[Pd(dmpz)_2(Hdmpz)_2]_2$ phase is more difficult to explain. The preparation methods of the α and γ phases are rather similar (the only difference being the presence of excess Hdmpz in the reaction medium; see Experimental Section), it is worth noting that fast crystallization (precipitation) of $[Pd(dmpz)_2(Hdmpz)_2]_2$ from chlorinated solvents always affords the α phase partially contaminated by variable amounts of the γ form. However, if a mixture of α and γ phases is suspended in hot (refluxing) 1,2-dichloroethane, it transforms quantitatively into α-$[Pd(dmpz)_2(Hdmpz)_2]_2$, which represents the thermodynamically stable phase; therefore, γ-$[Pd(dmpz)_2(Hdmpz)_2]_2$ might be described as the kinetically favorite (i.e., metastable) phase, which converts into α-$[Pd(dmpz)_2(Hdmpz)_2]_2$ only through a solvent-mediated process.

All three crystalline phases exhibit very similar IR spectra (Nujol mulls), as long as the general pattern of the absorption bands is concerned. However, slightly differences (a few wavenumbers) occur in the 1000−600 cm^{-1} frequency range, attributable to the ν_{C-H} of the pyrazole rings. Accordingly, these differences are diagnostic for the spectroscopical individuation of each phase (654, 768, 981, 1044 and 1145 cm^{-1} for α; 651, 762, 981, 1044, and 1147 cm^{-1} for β and 651, 761, 980, 1039, and 1148 cm^{-1} for γ; all these values are highly reproducible, the instrumental resolution being 1 cm^{-1}).

High-Temperature and High-Pressure Studies. All three polymorphic phases, which are indefinitely stable at room temperature, decompose to free Hdmpz and $[Pd(dmpz)_2]_n$ (previously suggested to be a trimeric species[10]) at similar temperatures (DSC peaks being observed at ∼270 °C, ΔH ∼130 kJ mol^{-1}). While the tetragonal (β) phase show a flat DSC trace below 250 °C, both α and γ phases possess a rather structured endothermic tail on the low-temperature side of the decomposition peak; these bumps, however, could not be further characterized, nor were they found to be related to transformations, detectable via XRPD, occurring in the solid state.

In search for other paths permitting the selective formation of a pure phase from another polymorph, we have tried a pressure-induced phase transformation, which has been shown on similar pyrazolato complexes to be a successful route.[9] Therefore, to pellets of all three polymorphs, a pressure of 0.7 GPa was applied for a few minutes, but resulted in structurally unmodified phases, as evidenced by subsequent XRPD analysis. While it is understandable that the formation of a racemate (α or γ) phase from the conglomerate (β) (which, *inter alia*, possesses the lowest density) is kinetically hindered, it was disappointing that, under the reported conditions, no α → γ nor γ → α transformation was observed.

Structural Relations. For molecules of high complexity, such as the β and γ phases described in the previous section, the XRPD structure determination is likely to afford only approximate atomic coordinates, obtained by imposing geometrical constraints from previous chemical knowledge, such as the complete single-crystal structural characterization reported in ref 10 (see Figure 4). However, when the lattice parameters and the space groups are well-defined, the analysis of the powder patterns affords reliable interatomic distances for heavy atoms[8]

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(20) Cheng, C.-H.; Lain, J.-S.; Wu, Y.-J.; Wang, S.-L. *Acta Crystallgr. Sect. C* **1990**, *46*, 208.

(21) Thompson, P.; Cox, D. E.; Hastings, J. B. *J. Appl. Crystallogr.* **1987**, *20*, 79.

(22) March, A. *Zeit. Kristallogr.* **1932**, *81*, 285. Dollase, W. A. *J. Appl. Crystallogr.* **1986**, *19*, 267.

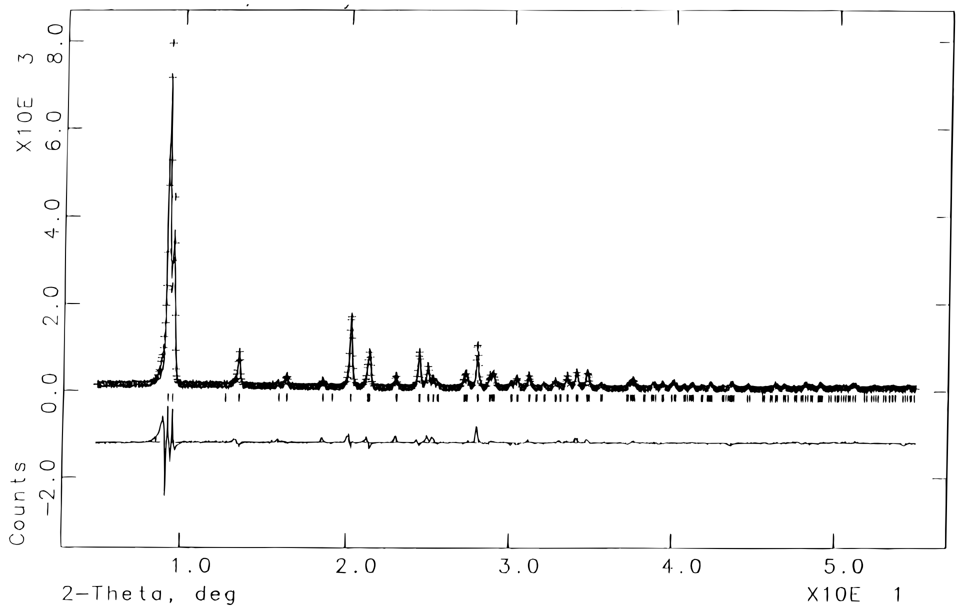

Figure 2. Final Rietveld plot for the β-[Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ powder pattern, with peak markers and difference plot at the bottom.

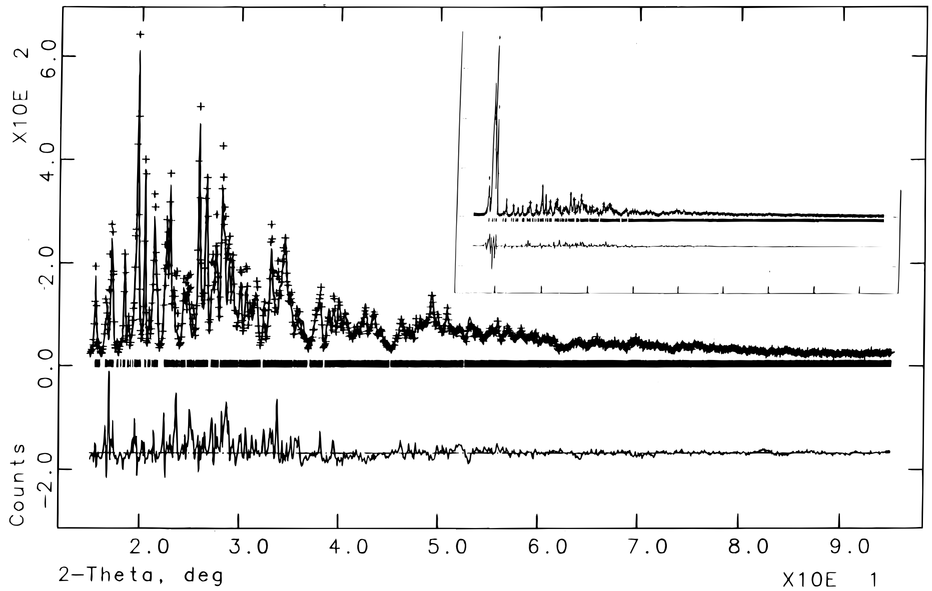

Figure 3. Final Rietveld plot for the γ-[Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ powder pattern in the $18 < 2\theta < 95°$ range, with peak markers and difference plot at the bottom. The inset shows the full data set on a reduced scale.

Table 2. Synoptic Collection of Lattice Parameters of Polymorphs α, β, and γ, with Their Relation to Each Other

phase	*a*	*b*	*c*	α	β	γ	*V*	*Z*	*V*/*Z*	space group
α	17.305(1)	15.737(3)	17.513(3)	90	100.11(1)	90	4695(1)	4	1174	*C*2/*c*
β	13.1342(7)	13.1342(7)	13.7920(9)	90	90	90	2379.2(4)	2	1184	*I*422
$\beta'^{a,b}$	19.045	13.134	19.045	90	92.80	90	4768	4	1184	pseudo *F*242
γ	11.470(1)	11.619(2)	19.221(2)	80.928(6)	81.434(7)	69.033(5)	2350.2(7)	2	1175	$P\bar{1}$
γ'^{b}	19.025	13.084	19.221	89.46	100.73	90.79	4700	4	1175	$C\bar{1}$

[a] $\beta' = [1,0,1; 0,1,0; -1,0,1]*\beta$; $\gamma' = [1,1,0; 1,-1,0; 0,0,-1]*\gamma$. [b] Primed phases refer to nonstandard settings of the unprimed ones.

(in the present case, palladium) and reliable information on the packing modes of the whole complexes.

The refined values for the Pd···Pd *intra*molecular vector as similar (3.746(1), 3.726(5), and 3.658(9) Å in the α, β, and γ phases, respectively), thus suggesting that the identity of the [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ molecules (accurately characterized in the α phase) is essentially retained also in the β and γ phases. The small differences among the three values may be attributed to the slightly different packing environments affecting the overall conformation of the dimer, with slightly different staggering of the PdN$_4$ moieties[10] or, more likely, to the error in estimating such parameters which, for the complexity of the γ phase, is intrinsic in the powder method. The choice of rather different site symmetries for the three polymorphs of such highly symmetric molecule reflects the recent observation[23] that, in search for different molecular arrangements, the compactness of a given packing (measured, for example, by the similar density values), rather than crystal symmetries suggested by the molecular symmetry, is preferred. While the least-squares stability of the Rietveld technique cannot allow a reliable

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(23) Gavezzotti, A.; Filippini, G. *J. Am. Chem. Soc.* **1995**, *117*, 12299.

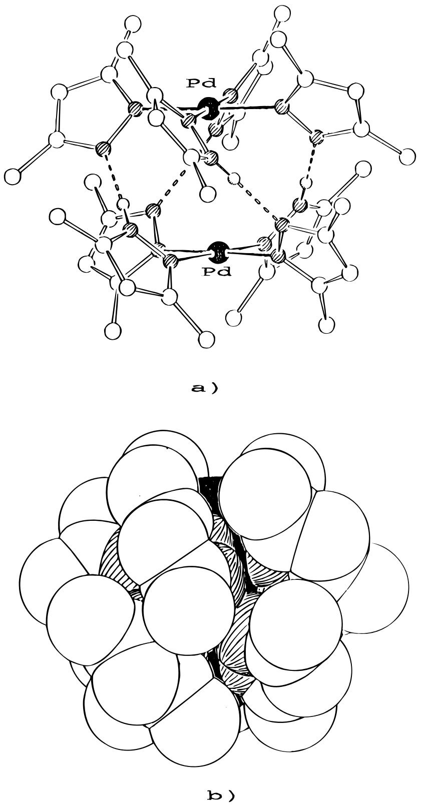

Figure 4. Molecular drawing (using SCHAKAL[27]) of the α-[Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ molecule, as determined from the coordinates published in ref 10: (a) Stick and balls model; (b) CPK model. At the drawing resolution, molecules of [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ in the β and γ phases look similar.

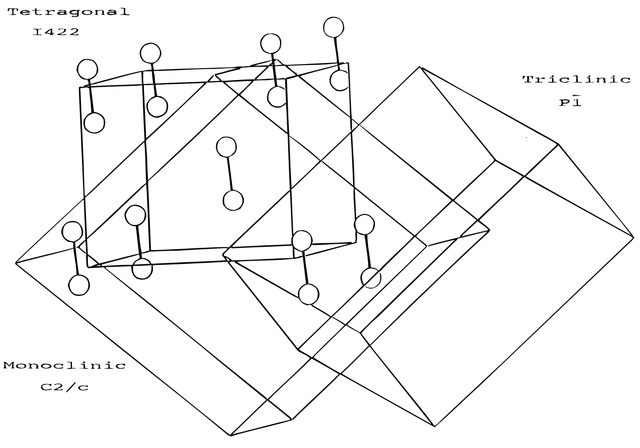

Figure 5. Geometrical relationships between the unit cell parameters of phases α, β, and γ. The phases possess rather similar packing modes. For the sake of simplicity, only the Pd$_2$ dumbbells (taken from the triclinic γ phase) are shown.

independent atoms model to be refined, the steric requirements imposed by the space group constraints act as an independent check for the validity of the proposed molecular model, in size, shape, and orientation, as large cavities or anomalously short contacts must be avoided. For all three phases, therefore, the size of the largest cavities has been computed using PLATON[24] and resulted, once hydrogen atoms were added in idealized positions about their ring or methyl atoms, in 60, 75, and 80 Å^3 mol^{-1} for the α, β, and γ phases, respectively (it is worth noting that the rather large value observed for the γ phase, which does *not* possess the lowest density, might be related to the *slightly shorter* Pd···Pd contact whose experimental determination can be flawed by the reasons discussed above). These values show that none of the three phases reaches a maximum of compactness (typical values found for such a method are below 5−10 Å^3 mol^{-1}), probably because of the pseudoglobular shape (with large bumps and holes) and high stiffness of the molecule; this holds both in the two racemates and in the conglomerate (β), where the hole lies exactly about 0,0,$^1/_2$ and is clearly reminiscent of the originally clathrated carbonyl sulfide[12] hosted in the lattice before vacuum pumping. The identical nature of the Pd dimers in the three polymorphs is also counterparted by the high stability of its solutions, which, followed by ^{1}H NMR spectra (CD$_2$Cl$_2$) in the −90/+20 °C range, did not show any tendency to fluxionality or dissociation; as already evidenced in ref 10, the "unbreakable" nature of the [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ dimer is probably attributable to the presence of four strong "*intra*molecular" hydrogen bonds (average N−H···N = 2.70 Å in the α phase).

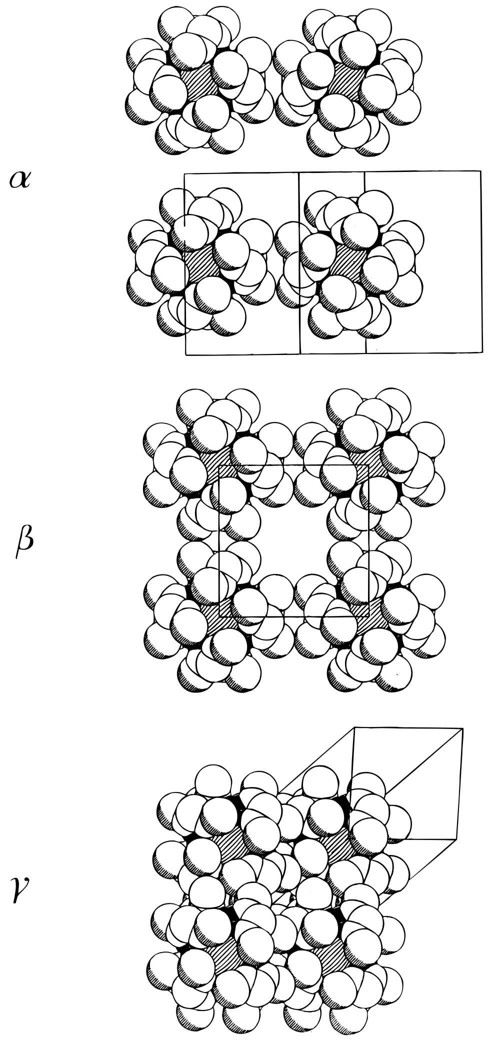

Figure 6. Packing modes of the [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$ molecules in the three polymorphs, viewed approximately down the (pseudo)fourfold axis. Note that in the β phase, only homochiral molecules are present.

Despite of the very different crystal systems, point group symmetry, and lattice parameters adopted by each of the three crystal phases, there is a strong structural relation between them. With reference to Table 2 and the matrix transformations reported therein, it is possible to see that the packing modes of the palladium dimers must be somewhat similar. This is best depicted in Figure 5, where a pictorial view of the unit cells and of their content, schematized as Pd$_2$ dumbbells, is presented.

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(24) Spek, A. L. *Acta Crystallogr*. **1990**, *A46*, C34.

Figure 6 shows the space-filling models of the three phases, viewed approximately down the (pseudo)fourfold axis. Quantitatively speaking, the shortest distances between the center of mass of neighboring dimers are 11.18, 11.57, and 11.05 Å, for the α, β, and γ phases, respectively. Note that within each polymorph the Pd···Pd vectors are by symmetry arguments collinear to each others.

In the realm of organic and organometallic compounds, polymorphism has bene often associated with the torsional degrees of freedom of fragments bound by single bonds, thus conformational in nature. In the present case, where the stiffness of the molecule and the rigid nature of the ligands is well documented, the existence of different polymorphs, which, in general, represent local minima in the (molecular) conformational space and in the packing constraints, cannot be attributed to internal degrees of freedom (other than methyl hydrogen torsional conformation) and is probably related to different interlocking of the corrugated van der Waals surface of a otherwise pseudospherical molecule, which is depicted in Figure 4b. A similar case of a rather stiff (organic) molecule crystallizing in different ways has been found for "lepidopterene".[25]

Conclusions

We have shown that, on using different synthetic approaches (not *merely* changing temperature and solvents), it is possible to selectively produce three different polymorphs of the title compound, which contain rather similar molecules that are not tautomers or conformational isomers.

It is worth noting that the discovery of similar polymorphic behavior can simply be done by recording fast (30 min) X-ray powder diffraction patterns as a routine control of the nature of the reaction products; the complete interpretation of the new β and γ phases, however, was only possible by a fruitful combination of (*i*) the newly emerging technique of *ab initio* structure solution from powder data, (*ii*) the detailed knowledge of the stereochemical features of a rather rigid molecule (obtained from the single-crystal determination of the α phase), (*iii*) the power of molecular building programs and (*iv*) the possibility of performing molecular mechanics computations within the crystallographic lattice, raising the present triclinic phase to the top of the list of coordination compounds of the highest complexity even characterized by XRPD.[26]

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Supporting Information Available: Final fractional coordinates and full lists of bond distances and angles (17 pages). See any current masthead page for ordering information.

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(25) Gauthier, J.; Hauw, C.; Bouas-Laurent, H. *Acta Crystallogr.* **1976**, *B32*, 1220. Becker, H. D.; Hall, S. R.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 1313.

(26) Masciocchi, N. In *Ricerca Scientifica ed Educazione Permanente* (*Scientific Research and Permanent Education*), University of Milano Ed.; Città Studi Printers: Milano, Italy, 1995; Vol. 98, p 115. Masciocchi, N.; Sironi, A. *Rigaku J.*, in press.

(27) Keller, E., SCHAKAL 92: a computer program for the graphical representation of crystallographic models. University of Freiburg, Freiburg, Germany, 1992.