

2D and 3D supramolecular assemblies of double cyclopalladated azobenzenes realized by C–H···Cl–Pd, π ··· π and C–H··· π interactions

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Received 21 March 2007; received in revised form 10 May 2007; accepted 16 May 2007

Available online 2 June 2007

Abstract

The double cyclopalladated complex with azobenzene, μ -[(*E*)-1,2-diphenyldiazene-*C*^{2,8}, *N*^{1,2}]-di-[chloro(dimethylsulfoxide)palladium(II)]; (DMSO)PdCl(μ -C₆H₄N=NC₆H₄)(DMSO)PdCl (**1**) and its analogous complex with DMF as ancillary ligand, (DMF)-PdCl(μ -C₆H₄N=NC₆H₄)(DMF)PdCl; μ -[(*E*)-1,2-diphenyldiazene-*C*^{2,8}, *N*^{1,2}]-di-[chloro(dimethylformamide)palladium(II)] (**2a**) were synthesized and the function of cyclopalladated moiety in molecular assembling in the solid state is illustrated by their crystal packings. The polymorphism of **2a** and **2b** is discussed. The crystal structures reveal assemblies with molecular components self-organized by C–H···Cl–Pd hydrogen bonds, π ··· π , and C–H··· π interactions. The double cyclopalladated complexes of azobenzene, with two Pd–Cl moieties participating in the hydrogen bond formation and π -conjugated system involved in the π ··· π or C–H··· π interactions, represent a new class of building blocks for construction of solid state supramolecular assemblies.

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Keywords: Palladium; Azobenzenes; Double cyclopalladation; X-ray structure; Supramolecular assemblies

1. Introduction

Cyclopalladated compounds have been extensively studied over the last four decades due to their wide application in organic and organometallic synthesis [1], catalysis [2], photochemistry [3] and in the design of new metalomesogens [4]. One of the most common ligands is azobenzene which readily reacts with variety of transition metals to form cyclometallated complexes *via* C(sp²)–H bond cleavage [5]. We have recently reported the preparation of double cyclopalladated complexes comprising two phenyl rings and two five-membered metallocycles [6]. The coordination sites occupied by solvent molecules are susceptible to modifications without any extra energy cost. Therefore, these double cyclopalladated analogues can be used as molecular building blocks in design and synthesis of coordination polymers and solid state supramolecular assemblies orga-

nized through metal-assisted hydrogen bonds and π ··· π or C–H··· π interactions [6]. The well-defined coordination geometry of metal–ligand system can be used to control the network topology and the crystal structure [7,8]. The hydrogen bonds are considered as the strongest and the most directional intermolecular interactions [9]. Ligands present in the double cyclopalladated complexes of azobenzene (azobenzene, DMF, DMSO and chlorides) can act as hydrogen bond donors and/or acceptors (Fig. 1) [10]. In recent years, it has been demonstrated that the high polarity of the M–Cl bond can result in hydrogen bonds with the strong hydrogen bond donors like N–H and O–H groups as well as the weaker donors like C–H bonds (present in azobenzene, and in solvent molecules such as DMF and DMSO) [11]. In our complexes Pd–Cl bonds can participate in the formation of intermolecular hydrogen bonds with two C–H bonds of azobenzene or solvent ligands.

Due to the presence of π -conjugated system, azobenzene ligands have ability to form other type of non-covalent interactions such as π ··· π and C–H··· π interactions. Although their importance is well established for biological

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systems, there is a limited information on their role in organometallic compounds [3c,12]. The role of these interactions in formation of supramolecular assemblies of cyclopalladated complexes of azobenzene $\{\text{PdCl}(\text{DMSO})\}_2(\mu\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4)$, (**1**) and two polymorphic forms of $\{\text{PdCl}(\text{DMF})\}_2(\mu\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4)$ (**2a** and **2b**) is presented in this work.

2. Experimental

The dicyclopalladated complexes with azobenzene were prepared as previously described by Ćurić et al. [6]. The single crystals of complex **1** suitable for X-ray structure analysis were grown from DMSO solution at 30 °C. Crystals of both polymorphs of complex **2** were grown from DMF solutions at ambient temperature. Data collections were performed on an Enraf–Nonius CAD-4 diffractometer, using a graphite monochromated Cu K α (1.54179 Å) radiation at room temperature [293(2) K]. The WinGX standard procedure was applied for data reduction [13]. Three standard reflections were measured every 120 min as an intensity control. The absorption correction, based on eight Ψ -scan reflections, was performed for structures of **1** and **2a** [14]. The structures were solved by SHELXS97 [15] and refined by SHELXL97 [16]. The models were refined using the full matrix least squares refinement. Hydrogen atoms were refined as riding entities. The atomic scattering factors were those included in SHELXL97 [16]. Molecular geometry calculations were performed by PLATON98 [17], and molecular graphics were prepared using ORTEP-3 [18], and CCDC-Mercury [19].

CSD (version 5.27, November 2005 and updates 2006) [20] was searched for palladium-containing structures with C–H \cdots Cl–Pd fragment and H \cdots Cl distance less than 4 Å. Only single-crystal structures with $R < 5\%$, no disorder and no errors and with defined H-positions were considered; 2000 such structures with terminal Cl and 250 with bridging Cl were found.

3. Results and discussion

The molecular architecture of **1** and **2** (Figs. 1 and 2) reveals dinuclear planar coordination with azobenzene bridging ligand resulting in double cyclopalladation. The chlorine atoms are *trans* disposed with respect to the azo-bond and act as the terminal ligands.

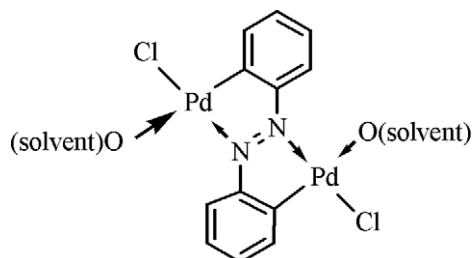


Fig. 1. Double cyclopalladated complexes of azobenzene.

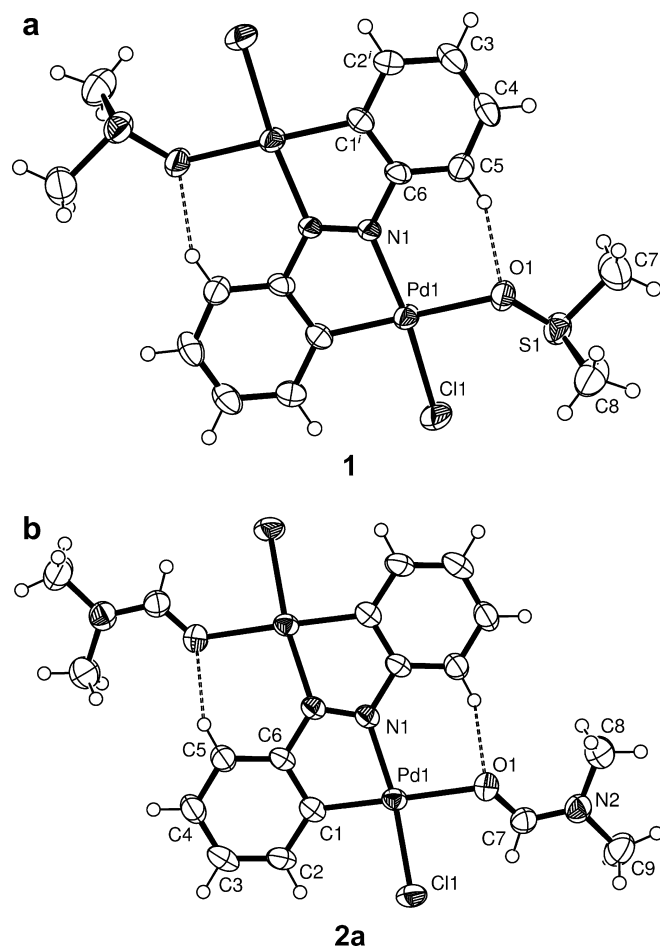


Fig. 2. Molecular structure of **1** and **2a**. Displacement ellipsoids are drawn at the 50% probability and hydrogen atoms are depicted as spheres of arbitrary radii. Intramolecular hydrogen bonds are depicted as dashed lines. Atom numbering schemes are the same for structures **2a** (present work) and **2b** [6]. Geometric parameters of Pd-coordination sphere in **1** are: $d(\text{Pd1}-\text{Cl1}) = 2.305(2)$ Å, $d(\text{Pd1}-\text{N1}) = 2.063(8)$ Å, $d(\text{Pd1}-\text{C1}) = 1.944(8)$ Å, $d(\text{Pd1}-\text{O1}) = 2.157(7)$ Å, $\text{Cl1}-\text{Pd1}-\text{N1} = 172.6(2)^\circ$, $\text{Cl1}-\text{Pd1}-\text{C1} = 94.4(2)^\circ$, $\text{Cl1}-\text{Pd1}-\text{O1} = 87.5(2)^\circ$, $\text{N1}-\text{Pd1}-\text{C1} = 79.3(3)^\circ$, $\text{N1}-\text{Pd1}-\text{O1} = 99.4(2)^\circ$, $\text{C1}-\text{Pd1}-\text{O1} = 169.4(3)^\circ$. Symmetry code: (i) $-x, -y, -z$.

The complex **1** is of C_i molecular symmetry (Fig. 2); the crystallographic inversion centre is located in the middle of the azo-bond. The geometric parameters of the Pd-coordination spheres for **1** and **2** are similar and they are in agreement with the results of *ab initio* calculations preformed for

Solvent = dimethyl sulfoxide (DMSO) in **1**
dimethylformamide (DMF) in **2**

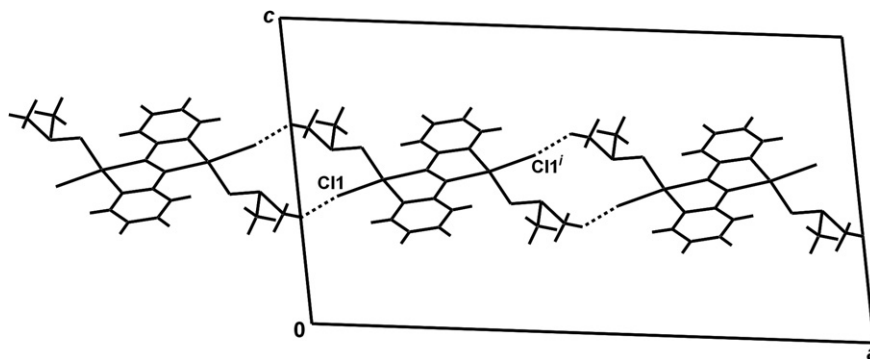


Fig. 3. The crystal packing of **1** viewed along *b*: the basic unit is the centrosymmetric dimer formed by a pair of C8–H8···Cl1 hydrogen bonds connected into infinite chain. Symmetry code: (i) $-x, -y, -z$.

1 [6]. The intramolecular hydrogen bonds C–H···O in **1** and **2** support the planar coordination (Fig. 2, Table 2). They are also maintained in the solution as revealed by the ^1H NMR spectra; the phenyl protons H5 of complexes are shifted downfield by 0.85 ppm, relative to the free ligand signal.

The C–H···Cl–Pd and π ··· π interactions dominate in the crystal packing of **1** and **2**. The molecules of **1** self-assemble through a pair of centrosymmetric C–H···Cl–Pd hydrogen bonds (Table 2) generating infinite chain extended in [110] direction (Fig. 3). These infinite chains are cross-linked into layers parallel to the plane (001) by π ··· π interactions between phenyl–phenyl rings and phenyl–Pd(II) chelate rings, (Table 3, Fig. 4). Thus, the crystal packing of **1** represents hydrogen-bonded assembly which is completed by π ··· π stacking interactions in *b* direction into 2D network.

The crystal packing of **2a** reveals also C–H···Cl hydrogen bond (Table 2) of topology different to that observed in **1**: it connects molecules into corrugated layers parallel to $[-103]$ (Fig. 5). These layers are further stacked in a herring-bone pattern by π ··· π interactions between phenyl groups and DMF molecules (separation distance of the

ring centroid and C7 atom is 3.36 Å) and C–H··· π interactions between the phenyl rings and DMF methyl moieties (the separation distance between the methyl carbon C9 and the centre of C4–C5 bond of the phenyl ring is 3.36 Å) (Fig. 6).

Although **2a** and **2b** are chemically identical species crystallizing in the same space group (Table 1, $P2_1/c$; $P2_1/n$ is an analogous setting) they reveal different structures representing two polymorphs. The polymorph **2b** reveals infinite chains extended in [100] direction which are formed by a pair of centrosymmetric hydrogen bonds C–H···Cl–Pd (Table 2). Topology of hydrogen-bonding pattern is analogous to that in **1** (Fig. 3), although space groups are different (Table 1). The chains are stacked into a herring-bone fashion by π ··· π interactions between phenyl rings and Pd(II) chelate rings (Table 4). The proton donor atoms in the two polymorphs are different: in **2a** the donor is an aromatic carbon while in **2b** the donor is a methyl carbon as in the compound **1**. Although no significant difference between the bond lengths (and, therefore, bond strengths) can be deduced from these crystal structures, however, according to the literature data [21] the aromatic carbon is a much stronger proton donor than the methyl one.

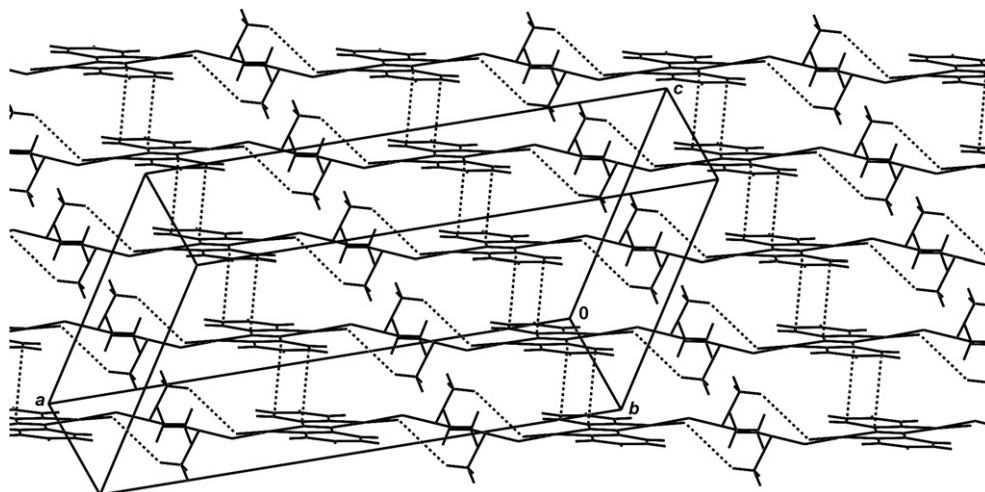


Fig. 4. In the structure of **1**, hydrogen-bonded chains are stacked into layers with π ··· π interactions involving phenyl rings.

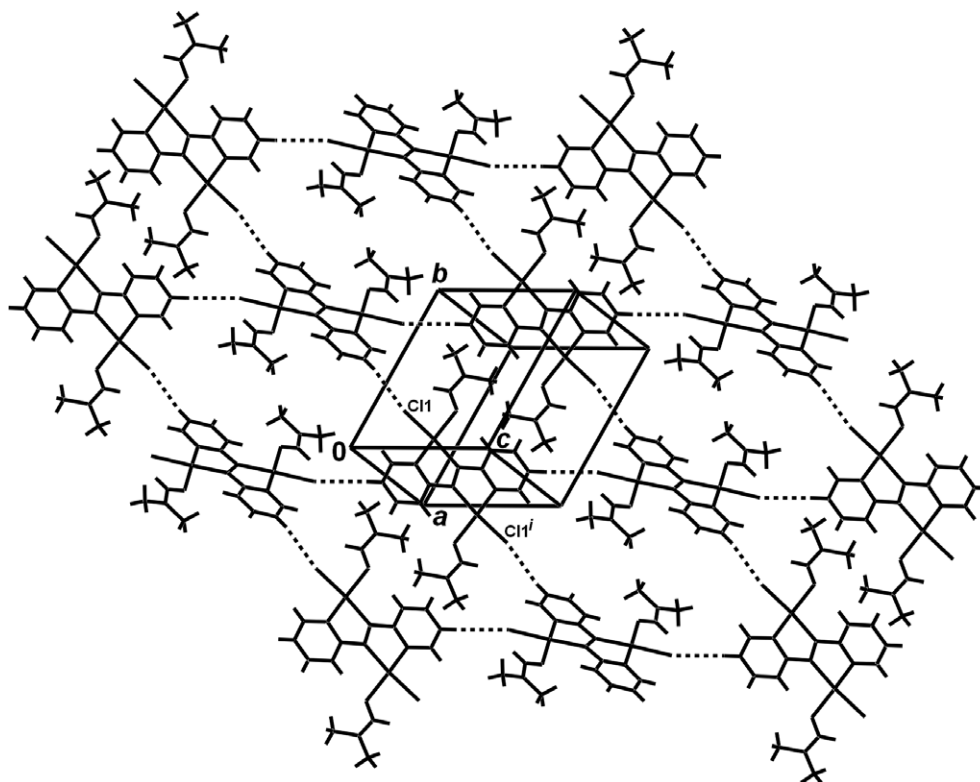


Fig. 5. 2D array of **2a** obtained by the C3–H3···Cl1 hydrogen bond. Symmetry code: (i) $-x, -y, -z$.

Reports [7d,11b,11c,21–24] on hydrogen bonds involving halogens as acceptors and C–H as donors reveal their characteristics and structural role. Halogens bonded to transition metals are particularly strong acceptors due to the polarized metal-halogen bond [25]. We focused on C–H···Cl–Pd interactions, dominating ones in the complexes

studied. Therefore, the CSD [20] (version 5.27, November 2005, updates 2006) was searched for the fragment C–H···Cl–Pd to perform geometric analysis of this interaction. The analysis reveals no significant differences of hydrogen bond strength with respect to hybridization of C donors: sp, sp² and sp³. However, the terminal and bridging chlorine atoms exhibit different geometric parameters (Fig. 7). Terminal chlorine atoms are stronger acceptors than bridging ones according to the values of H···Cl distances (Fig. 7a vs. b). An interaction C–H···Cl–Pd with the terminal Cl prefers angles larger than 100° (Fig. 8a) as shown by the results of Brammer and coworkers [27]. Bridging chlorines, however, form more bent hydrogen bonds with values from 60° to 160° (Fig. 8b) due to steric hindrances and/or electronic effects.

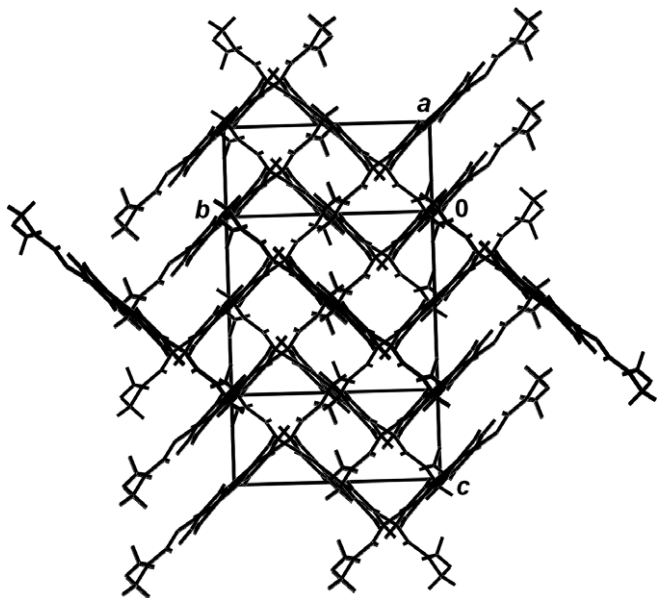


Fig. 6. Herring-bone pattern of corrugated hydrogen-bonded layers in **2a** results in 3D array, finally.

4. Conclusion

In the structures discussed, molecular components are organized *via* C–H···Cl–Pd hydrogen bonds and π ··· π or C–H··· π interactions. The weak intermolecular π ··· π interactions between phenyl rings and Pd(II) chelate rings in the crystal structures of **1** and **2a** suggest metalloaromaticity of five membered Pd(II) chelate rings [3c].

It was demonstrated that in the solid state the double cyclopalladated complexes of azobenzene form extensive 2D arrays for **1** and **2b**, and 3D array for **2a**. The most important interactions in 2D arrays are C–H···Cl–Pd hydrogen bonds while the stacking *via* π ··· π and C–H··· π

Table 1
Crystallographic data and structure refinement data for compounds **1** and **2a**

Compound	1	2a	2b
Empirical formula	C ₁₆ H ₂₀ Cl ₂ N ₂ O ₂ PdS ₂ S ₂	C ₁₈ H ₂₂ Cl ₂ N ₄ O ₂ Pd ₂	C ₁₈ H ₂₂ Cl ₂ N ₄ O ₂ Pd ₂
Formula weight (g mol ⁻¹)	620.14	610.14	610.14
Crystal dimensions (mm)	0.35 × 0.05 × 0.05	0.33 × 0.10 × 0.08	
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> (Å)	25.530(3)	6.1221(6)	12.7700(10)
<i>b</i> (Å)	5.8808(6)	10.2795(6)	5.2796(6)
<i>c</i> (Å)	13.9556(12)	16.7424(10)	15.4190(8)
α (°)	90	90	90
β (°)	97.953(9)	100.198(6)	92.460(10)
γ (°)	90	90	90
<i>Z</i>	4	4	4
<i>V</i> (Å ³)	2075.1(4)	1036.99(13)	1038.60(15)
<i>D</i> _{calc} (g cm ⁻³)	1.985	1.954	
μ (mm ⁻¹)	18.356	16.55	
<i>T</i> _{min} , <i>T</i> _{max}	0.2347, 0.3987	0.1352, 0.2648	
θ Range (°)	3.5–76.06	5.07–75.89	
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 > <i>h</i> > 32, 0 > <i>k</i> > 7, -17 > <i>l</i> > 17	0 > <i>h</i> > 7, 0 > <i>k</i> > 12, -21 > <i>l</i> > 20	
Reflections collected	2211	2348	
Independent reflections	2163	2146	
Observed reflections (<i>I</i> ≥ 2σ)	1656	1767	
<i>R</i> _{int}	0.1239	0.0211	
<i>R</i> (<i>F</i>)	0.0754	0.0392	
<i>R</i> _w (<i>F</i> ²)	0.2286	0.1098	
Goodness-of-fit	1.049	1.029	
Number of parameters	119	128	
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	2.466, -2.183	0.668, -1.605	

Unit cell data for structure **2b** are listed to document polymorphism.⁶

Table 2
Geometric parameters of the hydrogen bonds

		<i>d</i> (<i>D</i> – <i>H</i>) (Å)	<i>d</i> (<i>H</i> ··· <i>A</i>) (Å)	<i>d</i> (<i>D</i> ··· <i>A</i>) (Å)	<i>D</i> – <i>H</i> ··· <i>A</i> (°)	Pd–Cl··· <i>H</i> (°)	Symm. operation on <i>A</i>
1	C8–H8···Cl1	0.96	2.89	3.726(6)	165	115	1 – <i>x</i> , – <i>y</i> , 1 – <i>z</i>
	C5–H5···O1	0.93	2.15	2.949(10)	142	–	<i>x</i> , <i>y</i> , <i>z</i>
2a	C3–H3···Cl1	0.93	2.89	3.800(8)	165	166	–1/2 – <i>x</i> , –1/2 + <i>y</i> , 1/2 – <i>z</i>
	C5–H5···O1	0.93	2.16	2.963(7)	144	–	1 – <i>x</i> , 2 – <i>y</i> , 1 – <i>z</i>
2b	C9–H9···Cl1	0.96	2.90	3.801(8)	156	140	– <i>x</i> , – <i>y</i> , 1 – <i>z</i>
	C5–H5···O1	0.93	2.09	2.956(7)	155	–	<i>x</i> , <i>y</i> , <i>z</i>

Table 3
Geometric parameters of the π ··· π interactions

	π ··· π	Cg ^a ···Cg (Å)	α ^b	β ^c	Cg···plane(Cg) (Å)
1	Cg(chelate ^d) → Cg(phenyl)	3.970(5)	4.89	28.91	3.475
	Cg(phenyl) → Cg(phenyl)	3.965(5)	0.00	32.18	3.356
2b	Cg(chelate ^d) → Cg(phenyl)	3.804(3)	2.42	27.72	3.292
	Cg(phenyl) → Cg(chelate ^d) ⁱ	3.746(3)	2.42	27.06	3.336

Symmetry code: (i) –*x*, –*y*, –*z*.

^a Cg = centre of gravity of the aromatic ring.

^b α = angle between planes of two aromatic rings.

^c β = angle between Cg···Cg line and normal to the plane of the first aromatic ring.

^d 5-membered Pd-chelate ring abbreviated as “chelate”.

interactions complete packing to 3D array. The π ··· π stacking interactions are pronounced in double cyclopalladated complexes due to the extended aromatic system involving both phenyl rings and five-membered metallocycles. In

addition to classical non-covalent interactions used in molecular assemblies, π ··· π interactions involving metallocycles can be a good strategy in design of the new classes of organometallic supermolecules.

Table 4

Geometric parameters of the C–H··· π interactions

		H···Cg (Å)	γ (°) ^a	C–H···Cg (°)	C···Cg (Å)	Symm. operation on Cg
1	C4–H4···Cg(phenyl)	2.84	10.11	146	3.650(10)	$x, -y, -1/2 - z$
2b	C6–H6···Cg(phenyl)	2.97	16.27	141	3.739(7)	$x, 1/2 - y, -1/2 + z$

^a γ = angle defined by a line connecting centre of gravity of the aromatic ring with H atom and the normal to the aromatic ring.

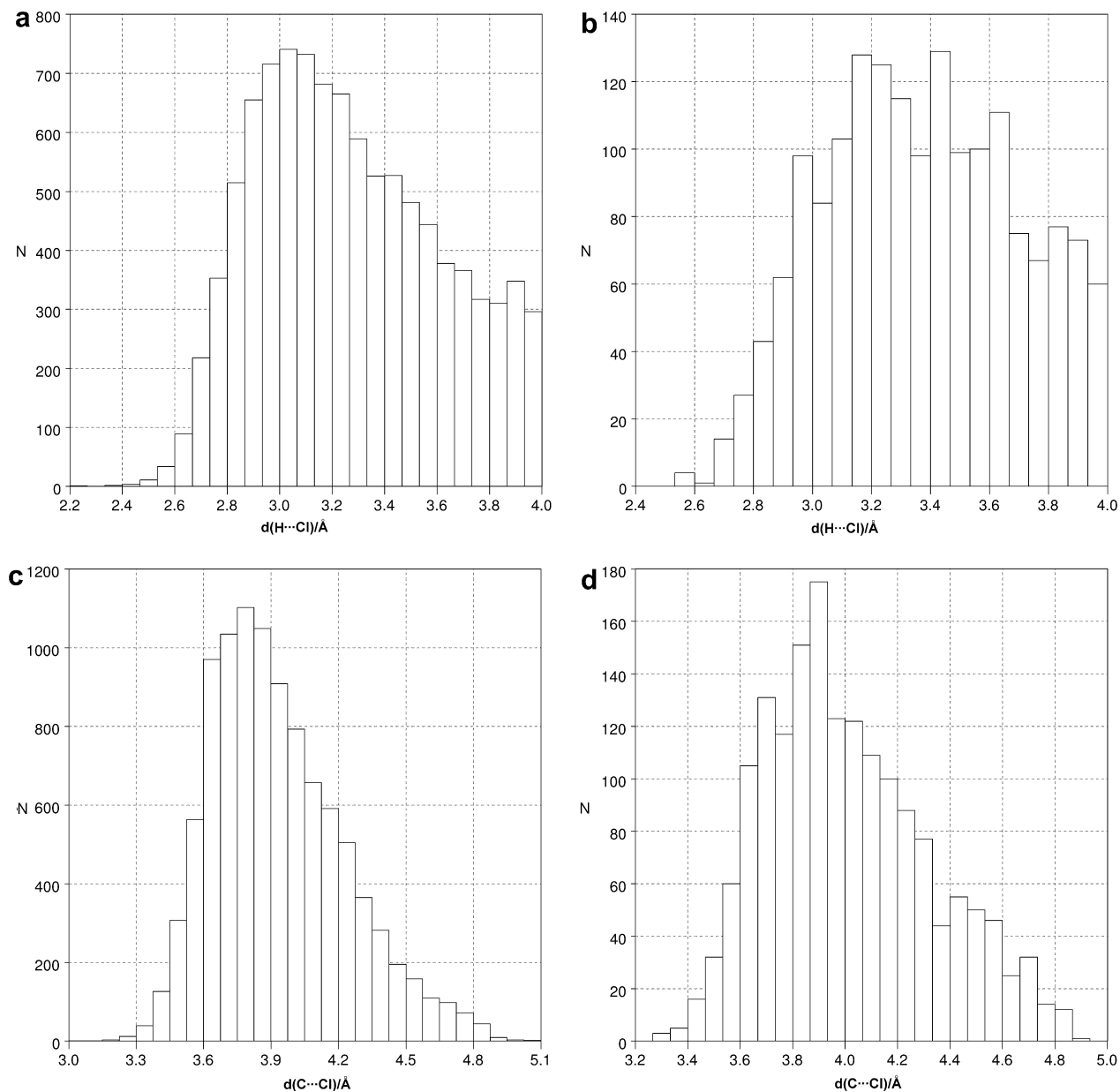


Fig. 7. Distribution of H···Cl distances for C–H···Cl–Pd hydrogen bonds with chlorine as (a) terminal ligand and (b) bridging ligand. Distribution of C···Cl distances for C–H···Cl–Pd hydrogen bonds with chlorine as (c) terminal ligand and (d) bridging ligand.

5. Supplementary material

CCDC 637353 and 637354 contain the supplementary crystallographic data for this paper. These data can be

obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

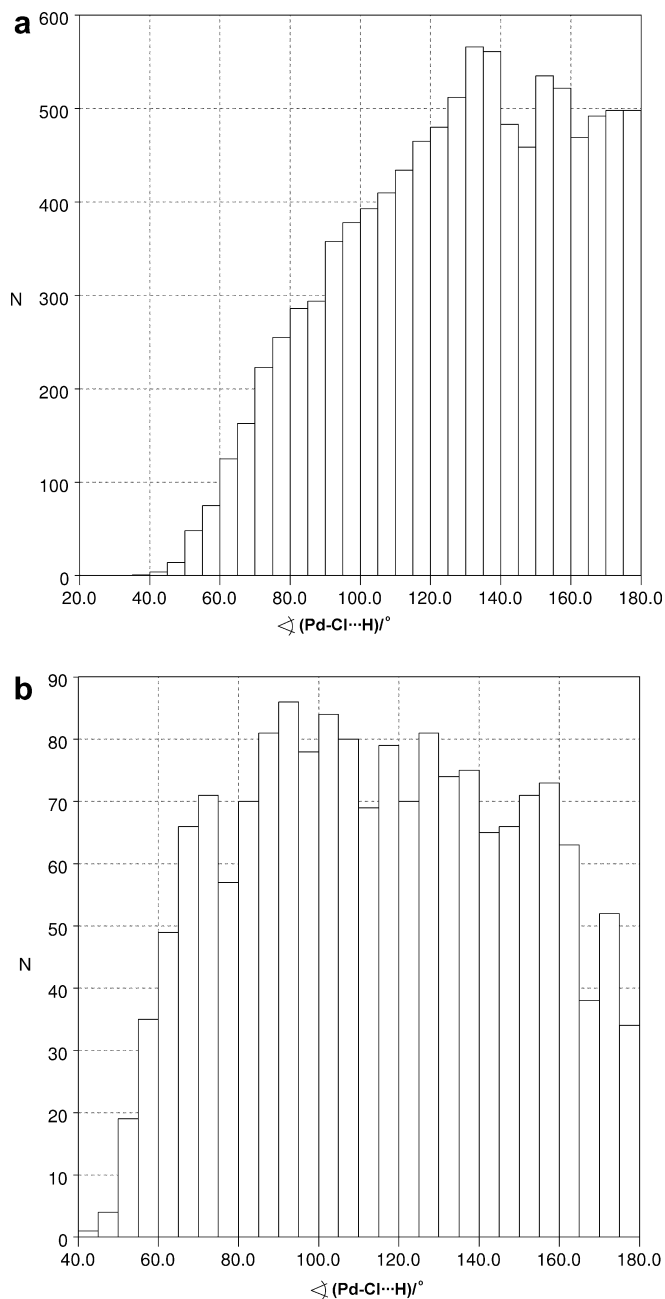


Fig. 8. Distribution of Pd–Cl···H angles for (a) terminal and (b) bridging chlorine ligands after conical correction [26].

Acknowledgements

The Ministry of Science, Education and Sports of The Republic of Croatia (Grant nos. 098-0982915-2950 and 098-1191344-2943) provided financial support for this research.

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