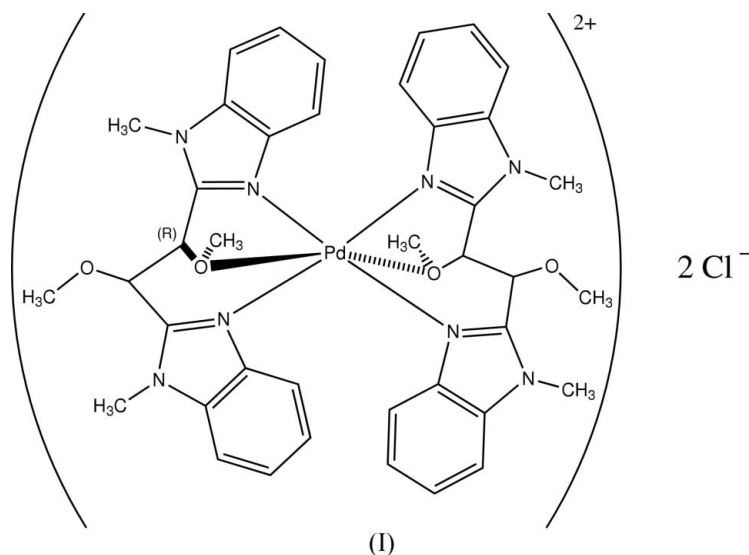


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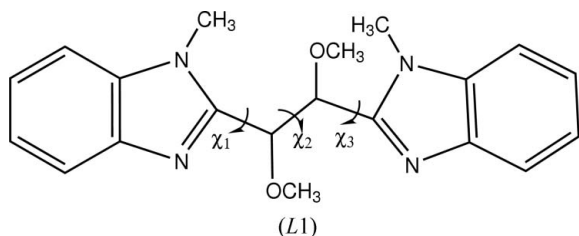
Key indicators

Single-crystal X-ray study
 $T = 297$ K
Mean $\sigma(\text{C}-\text{C}) = 0.010$ Å
Some non-H atoms missing
Disorder in solvent or counterion
 R factor = 0.051
 wR factor = 0.156
Data-to-parameter ratio = 13.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis[(*S,S*)-1,2-dimethoxy-1,2-bis(1-methyl-1*H*-
benzimidazol-2-yl)ethane]palladium(II) dichlorideChiral crystals of the title salt, $[\text{Pd}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2)_2]\text{Cl}_2$, contain $[\text{Pd}(\text{L}1)_2]^{2+}$ cations [$\text{L}1$ is (*S,S*)-1,2-dimethoxy-1,2-bis(1-methyl-1*H*-benzimidazol-2-yl)ethane] separated by disordered Cl^- anions. Two geometrically constraining $\text{L}1$ ligands coordinate each Pd^{II} ion facially to yield a distorted tetragonal $\text{N}_4(\text{imine})+\text{O}_2(\text{methoxy})$ coordination geometry.Received 30 August 2005
Accepted 8 September 2005
Online 17 September 2005

Comment

Our continuing effort to explore the chemistry of bis(imidazole) and bis(benzimidazole) compounds bridged by alkyl or aryl groups has led to their use as geometrically constraining ligands (Knapp *et al.*, 1990; Stibrany, Lobanov *et al.*, 2004). With several first-row transition metal ions, for example, we have found that certain of these ligands yield mononuclear complexes which are remarkably similar in coordination number and coordination geometry (Stibrany, Lobanov *et al.*, 2004; Stibrany *et al.*, 2004*b*). Ligands of this type have also been used to prepare several polynuclear complexes with Cu^{II} , all of which contain planar Cu_2O_2 groups (Isele *et al.*, 2005). Recently, we reported the structure of the chiral facially coordinated tetragonal 4+2 Cu^{II} complex, $[\text{Cu}(\text{L}1)_2]^{2+} \cdot 2\text{BF}_4^-$ bis(acetonitrile) solvate (Stibrany *et al.*, 2004*a*), where $\text{L}1$ is (*S,S*)-1,2-bis(1-methylbenzimidazol-2-yl)-1',2'-bis(methoxy)ethane. Here, we report the structure of the title compound, (I), $[\text{Pd}(\text{L}1)_2]^{2+} \cdot 2\text{Cl}^-$, which extends our exploration of these geometrically constraining ligands to metals in the second-row transition series.

by the imine N atoms of the planar benzimidazole fragments and by one of the methoxy O atoms from each of two *L1* ligands, to yield a distorted tetragonal N_4+O_2 coordination geometry, in which the N atoms form a nearly square-planar base (Table 1). The axial O atoms are displaced substantially from the axis normal to the PdN_4 plane towards the ligand to which they are attached. These geometric features of the coordination geometry are qualitatively similar to those observed for the $[Cu(L1)_2]^{2+}$ cation (Stibrany *et al.*, 2004a), the major differences being the $M-O$ distances, which are substantially longer in the Pd cation, and several of the $N-M-O$ angles, which indicate a greater deviation from regular tetragonal symmetry for the Pd species (Table 1). Similarities between the two cations extend to their X-shape in profile (Fig. 2), the V- or butterfly shape of the bound ligands, and the distorted-boat conformation of the seven-membered chelate rings (Stibrany *et al.*, 2004a). Comparable geometric features have also been observed in related bis(benzimidazole)copper(II) complexes (Isele *et al.*, 2002).



Ligand *L1*, with three torsional degrees of freedom, may be characterized by the torsion angles χ_1 , χ_2 , and χ_3 , which are shown in the scheme of *L1* and defined in the legend for Table

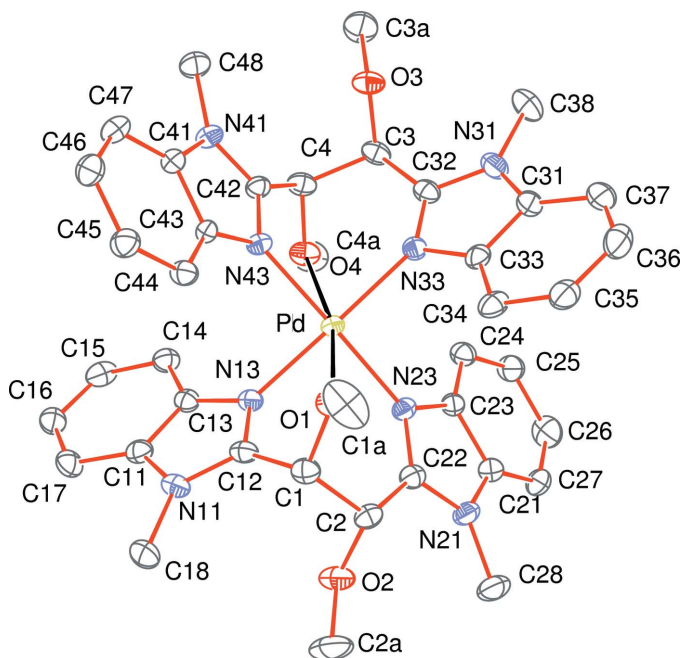


Figure 1
The structure of a cation in (I), showing 25% probability displacement ellipsoids. H atoms have been omitted for clarity.

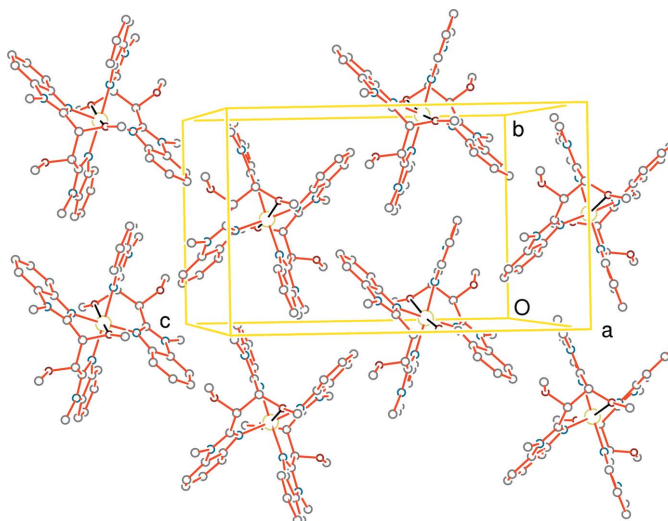


Figure 2
A view, approximately normal to (100), of a cation layer in (I). H atoms have been omitted for clarity.

1. In both the $[Cu(L1)_2]^{2+}$ and $[Pd(L1)_2]^{2+}$ species, the conformations of the individual ligands of a given cation are clearly distinguished by their χ_1 values, one of which is approximately 10° smaller than the other. However, the corresponding torsion angles for the Cu and Pd species differ on average by only about 2.5° , which gives an alternate measure of the degree to which *L1* is a geometrically constraining ligand.

Six-coordinate Pd^{II} species are uncommon and, based on a search of the Cambridge Structural Database (Version 5.25; Allen, 2002), compound (I) contains what is possibly the first structurally characterized example of a Pd^{II} complex with N_4+O_2 donation. The $Pd-O$ distances of 2.867 (4) and 2.871 (4) Å are long and there is some question regarding the extent to which these interactions are attractive. Thus, in two six-coordinate Pd^{II} complexes containing axial methoxy groups, linkages of 2.632 (7) and 2.671 (7) Å were considered bonding, while corresponding lengths of 2.887 and 3.025 Å were considered to be non-bonding (Sun *et al.*, 1998). However, with *S*(thioether) as an axial ligand in a tetragonally distorted Pd^{II} complex formed with two 10-crown-S3 thioether ligands, the axial S atoms were found to influence the electronic absorption spectrum of the complex, despite the relatively long $Pd^{II}-S$ (thioether) distance of 3.11 Å (Grant *et al.*, 1991).

$Pd^{II}-N$ (benzimidazole) linkages are rare: we are aware of only two examples, both in complexes with distorted square-planar coordination geometry. In these species, the $Pd^{II}-N$ (benzimidazole) distances of 2.151 (4) and 2.117 (4) Å (Figue *et al.*, 2002) are substantially longer than the corresponding linkages in (I), where the $Pd-N$ distances compare favorably with the $Pd^{II}-N$ (imidazole) distances, which range from 1.982 (4) to 2.029 (4) Å, reported for several square-planar complexes (Dahan, 1976; Liu *et al.*, 2001; Kurdziel & Glowiak, 2002). Lastly, we note that each cation contains three weak $C-H \cdots O$ interactions, two inter-ligand and one intra-ligand, between the methoxy O atoms and the H atoms of the

benzene rings of three of the four benzimidazole groups (Table 2).

In the crystal structure of (I), the cations form layers parallel to the (100) planes (Fig. 2) and centered about the plane $x = 0$. The planes of cations present hydrophobic surfaces, consisting largely of atoms from the methyl and phenyl fragments, to the Cl^- anions, which lie between them (Fig. 3). The relatively large size of the cations, coupled with their essentially non-polar surfaces, precludes strong Coulombic and/or ion-dipole interactions with the Cl^- anions, consistent with the observed disorder of the Cl^- layer. Within a given layer, the cations are linked by edge-over-edge π - π interactions along the b -axis direction, and by $\text{C}-\text{H}\cdots\pi$ interactions along both the b and c -axis directions. Packing of the cations may be visualized qualitatively by focusing on the relative orientation of the benzimidazole planes of adjacent cations, which vary from approximately parallel to approximately perpendicular (Fig. 2).

Experimental

Triethyl orthoformate (1 ml) was added to a 50 ml Erlenmeyer flask containing a yellow-orange solution of bis(acetonitrile)palladium(II) dichloride (30 mg, 0.12 mmol) and (*S,S*)-1,2-bis(1-methylbenzimidazol-2-yl)-1',2'-bis(methoxy)ethane (81 mg, 0.23 mmol) in acetonitrile (10 ml). After gentle warming of the solution for 5 min, slow evaporation afforded pale-yellow plates of (I) (yield: 71 mg, 67%). IR (KBr pellet, ν , cm^{-1}): 3435 (*br*), 2942 (*w*), 1645 (*w*), 1533 (*m*), 1477 (*m*), 1334 (*m*), 1155 (*w*), 746 (*m*).

Crystal data

$[\text{Pd}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2)_2]\text{Cl}_2$	D_m measured by flotation in CCl_4 -cyclohexane
$M_r = 878.15$	
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 13.0985$ (4) Å	Cell parameters from 1022 reflections
$b = 10.7801$ (4) Å	$\theta = 3.7$ – 24.8°
$c = 17.0783$ (6) Å	$\mu = 0.55$ mm^{-1}
$\beta = 102.440$ (3) $^\circ$	$T = 297$ (1) K
$V = 2354.89$ (14) Å 3	Cleaved plate, pale yellow
$Z = 2$	$0.44 \times 0.23 \times 0.14$ mm
$D_x = 1.238$ Mg m^{-3}	
$D_m = 1.25$ (1) Mg m^{-3}	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	7194 independent reflections
φ and ω scans	6863 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS, Blessing 1995)	$R_{\text{int}} = 0.025$
$T_{\text{min}} = 0.779$, $T_{\text{max}} = 0.926$	$\theta_{\text{max}} = 25.0^\circ$
16641 measured reflections	$h = -15 \rightarrow 15$
	$k = -11 \rightarrow 12$
	$l = -20 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.13P)^2 + 1.0352P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.157$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.97$ e \AA^{-3}
7194 reflections	$\Delta\rho_{\text{min}} = -0.47$ e \AA^{-3}
522 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	2799 Friedel pairs
	Flack parameter: -0.04 (4)

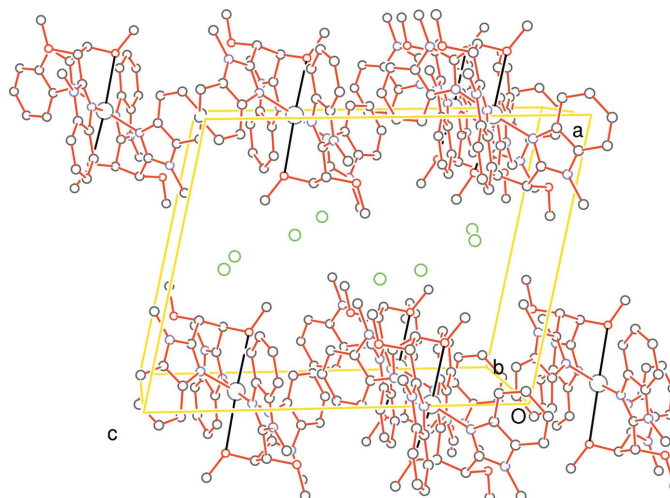


Figure 3
A view, approximately along the b axis direction, of the structure of (I). H atoms have been omitted for clarity.

Table 1

Comparison of selected bond lengths (Å), bond angles ($^\circ$) and torsion angles ($^\circ$) for $[\text{Cu}(L1)_2]^{2+}$ (Stibrany *et al.*, 2004a) and $[\text{Pd}(L1)_2]^{2+}$ cations (this work). The torsion angles χ_1 , χ_2 , and χ_3 correspond to $(\text{CH}_3)\text{N}-\text{C}-\text{C}-\text{O}(M)$, $\text{O}(M)-\text{C}-\text{C}-\text{O}$ and $\text{O}-\text{C}-\text{C}-\text{N}'(\text{CH}_3)$, respectively, where $\text{O}(M)$ is the O atom coordinated to the metal.

	$M = \text{Cu}^{\text{II}}$	$M = \text{Pd}^{\text{II}}$	$M = \text{Cu}^{\text{II}}$	$M = \text{Pd}^{\text{II}}$
$M-\text{N}43$	2.028 (6)	2.006 (5)	$M-\text{N}33$	2.006 (6)
$M-\text{N}13$	2.032 (5)	2.011 (5)	$M-\text{O}4$	2.520 (5)
$M-\text{N}23$	1.973 (6)	2.027 (5)	$M-\text{O}1$	2.483 (4)
$\text{N}43-\text{M}-\text{N}13$	92.2 (2)	90.4 (2)	$\text{N}23-\text{M}-\text{O}4$	99.9 (2)
$\text{N}43-\text{M}-\text{N}23$	177.4 (3)	177.27 (18)	$\text{N}33-\text{M}-\text{O}4$	73.9 (2)
$\text{N}13-\text{M}-\text{N}23$	89.7 (2)	89.2 (2)	$\text{N}43-\text{M}-\text{O}1$	106.24 (19)
$\text{N}43-\text{M}-\text{N}33$	90.3 (2)	87.8 (2)	$\text{N}13-\text{M}-\text{O}1$	81.39 (19)
$\text{N}13-\text{M}-\text{N}33$	177.4 (3)	176.39 (18)	$\text{N}23-\text{M}-\text{O}1$	72.4 (2)
$\text{N}23-\text{M}-\text{N}33$	89.8 (2)	92.8 (2)	$\text{N}33-\text{M}-\text{O}1$	98.4 (2)
$\text{N}43-\text{M}-\text{O}4$	81.15 (19)	66.92 (15)	$\text{O}4-\text{N}-\text{O}1$	169.55 (15)
$\text{N}13-\text{M}-\text{O}4$	106.05 (19)	102.79 (16)		
$\chi_1(\text{ligand } 1)$	-145.2 (7)	-140.9 (6)	$\chi_1(\text{ligand } 2)$	-134.9 (7)
$\chi_2(\text{ligand } 1)$	-177.3 (7)	-178.8 (5)	$\chi_2(\text{ligand } 2)$	-178.6 (5)
$\chi_3(\text{ligand } 1)$	-62.1 (8)	-59.8 (8)	$\chi_3(\text{ligand } 2)$	-56.0 (8)

Table 2

Hydrogen-bond geometry (Å, $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}38-\text{H}38\text{C}\cdots\text{O}3$	0.96	2.60	3.012 (12)	106
$\text{C}34-\text{H}34\cdots\text{O}1$	0.93	2.46	3.342 (9)	158
$\text{C}14-\text{H}14\cdots\text{O}4$	0.93	2.51	3.387 (8)	157

Crystals of (I) were prepared using enantiomerically pure *L1* and are, therefore, of necessity chiral, excluding the possibility that the space group is $P2_1/m$. Initial solution of the structure clearly revealed the cation and four potential sites for Cl^- anions in the asymmetric unit. This structure was refined to convergence with four partially occupied Cl^- sites to yield 1.05 Cl^- anions per cation. Examination of the structure at this point using *PLATON* (Spek, 2003) revealed two voids per asymmetric unit, one of 87 Å 3 and one of 66 Å 3 , both located in the space between the cation layers and therefore likely to contain the missing electron density from any remaining Cl^- anions.

At this point, a modified data set was generated using the SQUEEZE algorithm (Spek, 2003; van der Sluis & Spek, 1990) to subtract the contribution of the electron density in the voids from the structure factors and, using the modified data set, the structure was re-refined to convergence. *PLATON* estimated a total integrated electron count of 19 for the two voids, which, when added to the 18.9 electrons corresponding to 1.05 Cl⁻ ions on the four disordered sites, accounts well for the electron count of 36 expected for two Cl⁻ ions. H atoms were positioned geometrically and refined using a riding model, with C–H distances in the range 0.93–0.98 Å, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for all others.

Data collection: *SMART-WNT/2000* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996) and *ORTEP32* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruker (2000). *SHELXTL* (Version 6.10), *SAINT-Plus* (Version 6.02) and *SMART-WNT/2000* (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Dahan, F. (1976). *Acta Cryst.* **B32**, 2472–2475.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Figge, A., Altenbach, H. J., Brauer, D. J. & Tielmann, P. (2002). *Tetrahedron Asymm.* **13**, 137–144.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Grant, G. J., Sanders, K. A., Setzer, W. N. & VanDerveer, D. G. (1991). *Inorg. Chem.* **30**, 4053–4056.
- Isele, K., Broughton, V., Matthews, C. J., Williams, A. F., Bernardinelli, G., Franz, P. & Decurtins, S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3899–3905.
- Isele, K., Franz, P., Ambrus, C., Bernardinelli, G., Decurtins, S. & Williams, A. F. (2005). *Inorg. Chem.* **44**, 3896–3906.
- Knapp, S., Keenan, T. P., Zhang, X., Fikar, R., Potenza, J. A. & Schugar, H. J. (1990). *J. Am. Chem. Soc.* **112**, 3452–3464.
- Kurdziel, K. & Glowiak, T. (2002). *J. Coord. Chem.* **55**, 327–334.
- Liu, H.-K., Hu, J., Wang, T.-W., Yu, X.-L., Liu, J. & Kang, B. (2001). *J. Chem. Soc. Dalton Trans.* pp. 3534–3540.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* **A46**, 194–201.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Stibrany, R. T., Lobanov, M. V., Schugar, H. J. & Potenza, J. A. (2004). *Inorg. Chem.* **43**, 1472–1480.
- Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2004a). *Acta Cryst.* **E60**, m1147–m1150.
- Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2004b). *Acta Cryst.* **E60**, m1836–m1840.
- Sun, J.-S., Uzelmeier, C. E., Ward, D. L. & Dunbar, K. R. (1998). *Polyhedron*, **17**, 2049–2063.