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LETTER

Unusual *trans*-planar structure of the PdN_2S_2 coordination sphere with essential tetrahedral distortion. X-ray study of bis(1-isopropyl-3-methyl-4-cyclohexylaldimine-5-thiopyrazolato)-palladium(II)

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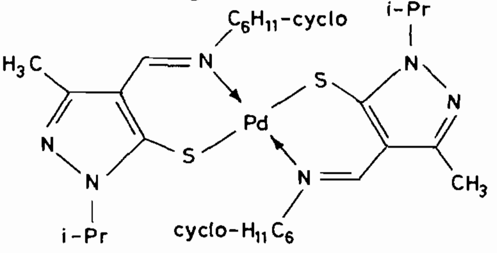
It is well known that the Pd^{II} ion conventionally forms bis-chelate complexes with near-planar configuration as its crystal field energy is very high [1]. Nevertheless, in principle it may be expected that an appropriate ligand environment could force a rather large tetrahedral distortion. It has been established earlier that the pyrazole ring annelating to metallocycles in tetracoordinated Schiff base complexes of 3d metals with a MN_2X_2 (X = S, Se) coordination sphere leads to the significant stabilization of tetrahedral structures [2–7]. For example, bis(4-*N*-alkyl(aryl)aldimine-5-pyrazolethion(seleno)ato)-Ni^{II} complexes possess a tetrahedral structure both in solid and solution [2, 3, 5–7]. We assumed the tendency towards tetrahedral torsion of these Ni^{II} complexes to be in line with that of similar Pd^{II} species. Another approach for creating tetrahedral structures includes the increase in steric volume of the substituent attached to the coordinated nitrogen atom which may introduce additional steric strains in favour of tetrahedral torsion [8–10].

In the present work we prepared the bis(1-isopropyl-3-methyl-4-cyclohexylaldimine-5-pyrazolethionato)Pd^{II} complex (**I**), which carries bulky N-C_6H_{11}-cyclo substituents and performed its X-ray structural investigation.



I

Crystal data for **I**: monoclinic; $a = 28.242(8)$, $b = 6.996(2)$, $c = 21.184(5)$ Å, $\beta = 132.29(2)°$, space group $C2/c$, $Z = 4$, $V = 3096(2)$ Å^3, $D_{calc} = 1.36$ g cm^{-3}. The unit cell parameters and intensities of 3630 reflections were recorded on a SYNTEX $P2_1$ automatic diffractometer (Mo Kα radiation with 0.71069 Å wavelength, graphite monochromator, $\theta/2\theta$-scan, $2\theta \leqslant 60°$). Intensity data from 3116 independent non-zero ($I \geqslant 3\sigma(I)$) reflections were collected. The structure was solved by the heavy-atom method and refined by full-matrix least-squares technique anisotropically (for non-hydrogen atoms) and isotropically to $R = 0.039$, $R_w = 0.032$. The molecule has a crystallographic C_2 axis along the b axis of the crystal lattice. Selected bond distances and valence angles are given in Table 1. A view of the molecule is shown in Fig. 1.

The bis-chelate complex **I** contains a tetracoordinated Pd atom bonded to two sulfur and two nitrogen atoms. The four metal–ligand bonds form near the square polyhedron with palladium as the central atom, in which the sulfur atoms lie in a *trans* position. Probably this particular structure, similar to that of the bis(8-mercaptoquinoline)ato Pd^{II} complex [11], represents the first example of the *trans*-form occurring among the thoroughly studied Schiff base complexes bearing a MN_2S_2 coordination unit which prefer the *cis*-form [8]. The *trans* isomers dominate ordinarily only in the case of Schiff base complexes with an MN_2O_2 coordination site [8–10].

TABLE 1. Selected bond lengths and valence angles for complex **I**

Bond lengths (Å)		Bond angles (°)	
Pd–S	2.324(1)	SPdS′	165.43(4)
Pd–N(1)	2.059(2)	SPdN(1)	88.0(1)
C(1)–S	1.717(3)	SPdN′(1)	93.0(1)
C(3)–N(1)	1.288(5)	N(1)PdN′(1)	171.8(1)
C(1)–C(2)	1.404(5)	PdSC(1)	100.2(1)
C(2)–C(3)	1.410(6)	PdN(1)C(3)	125.7(3)
		N(1)C(3)C(2)	126.6(4)
		C(3)C(2)C(1)	125.8(4)
		C(2)C(1)S	129.6(3)

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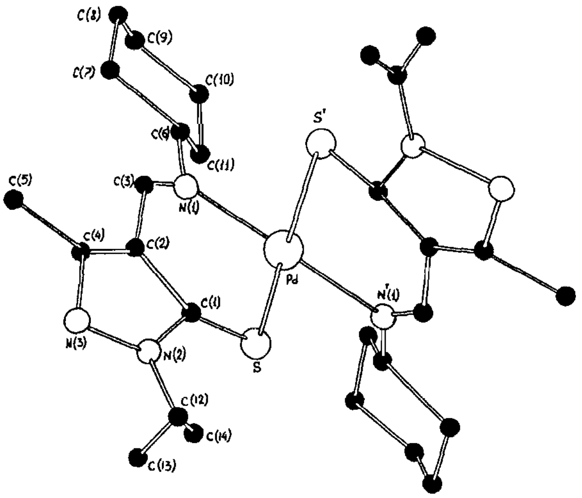

Fig. 1. The structure of complex I.

N-C_6H_{11}-cyclo substituents have a chair conformation. The angle between the planar pyrazole ring and N(1)C(3)C(2)S metallocyclic part is equal to 7.8°.

Another peculiarity that is characteristic of the type **I** structure is the essential tetrahedral distortion of square coordination achieving 17° (the angle between the NPdS and N'PdS' planes). This value may be regarded as a rather large distortion, since normally it does not exceed several degrees. Two exceptions are represented by bis(2-mercapto-4-methylazobenzolato)Pd^{II}, $\theta = 12.2°$ [12], and bis-(methyl-3-isopropylidenedithiocarbazato)Pd^{II}, $\theta = 10.7°$ [13]. The extremely high θ value of 25.6° was also found for bis[(phenylazo)acetaldoximato]Pd^{II} with a PdN_4 environment [14]. The value of $\theta \geqslant 85°$ was observed within the scope of isoligand pyrazoleato complexes of Ni^{II}, Zn^{II}, Cd^{II} and Hg^{II} of type **I** [5, 6].

The sum of the metallocyclic valence angles in **I** is equal to 696°. The rings are not planar being bent along the S···N axis by $\varphi = 40°$ so that the whole molecule has an umbrella conformation. This manner of planar structure distortion has been known so far only in a few cases of bridged Schiff base complexes derived from tetradentate ligands in contrast with well documented stepped displacement [9] as may be exemplified by the *trans*-planar bis(*N*-t-Bu-salicylaldiminato)Pd^{II} complex, $\varphi = 36°$ [15].

It is notable that structure **I** maintains some steric strains manifesting in the shortened C(6)···S contact of 3.18 Å, less than the sum of the van der Waals radii, 3.57 Å. If it had a strictly planar structure, this distance should be *c.* 2.4 Å. For planar bis(*N*-t-Bu-salicylaldiminato)Pd^{II} of type PdN_2O_2 no shortened contacts of the *N*-t-Bu substituent with ligand atoms were observed probably due to the difference between the sulfur, 1.85 Å, and oxygen, 1.40 Å, van der Waals radii. Therefore, it could be inferred that the C(6)···S repulsion is responsible for the tetrahedral torsion found in complex **I**. To check this suggestion a study of the thiosalicylaldiminato and pyrazoleato Pd^{II} complexes with various N–R substituents is now in progress.

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