Five-membered metal chelate rings in complexes of palladium with 2-mercaptomethylazobenzene

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The palladium atom is coordinated by ligands in the chelate manner forming two five-membered rings, in contrast to known palladium(II) complex with 2-mercapto-2′-methylazobenzene, containing five- and six-membered rings.

It was found that a variation of the position of the methyl substituent in the benzene ring in the azo-component substantially changes the structure of mercaptoazoaryl complexes of palladium, *i.e.* the complex under consideration exists as a *cis*-planar structure with two five-membered metal-containing rings rather than as a *cis*-planar chelate with five- and six-membered coordination units as has been the case with the previously obtained complex based on 2-mercapto-4′-methylazobenzene.

It has been found previously[1] that metallochelates of type **1** with azo- (X = N) and azomethine (X = CH) ligands containing sulfur atoms directly coordinated to the metal in a conjugated ring form sterically strained *cis*-structures. In the case of type **1** chelates (X = N) this strain is partially removed, but quite substantially, on going from six-membered rings to five-membered metal-containing rings **2** as shown in Figure 1.

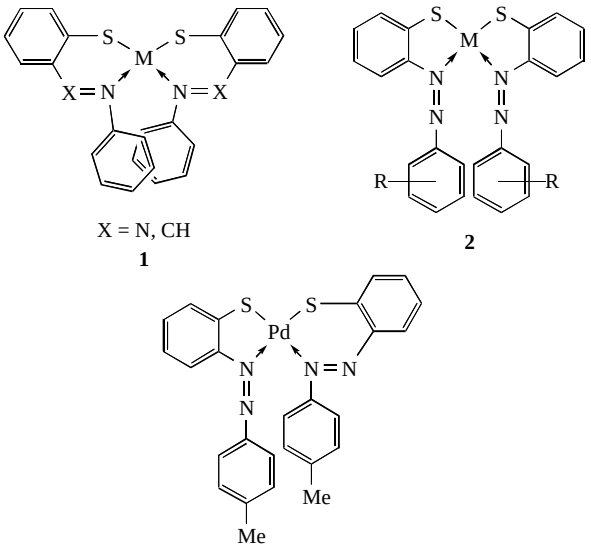

Figure 1

Nickel(II) chelates of type **1** with five-membered rings have been described previously.[2–4] In addition, it has been shown[1,4] that, depending on the stereochemical conditions, both five- and six-membered metal-containing rings can be formed upon variation of the radius of the complex-forming metal or the steric influence of the substituent R.

In particular, this situation is observed in the case of nickel(II) chelates of type **2**.[1,3] However, for the palladium(II) complex based on the same ligand, an interesting structure of type **3** was obtained. This structure contains both five- and six-membered metal-containing rings. In this case, the steric strain decreases somewhat due to the increase in the radius of the metal atom on passing from nickel to palladium. In addition, it has been suggested previously[1] that the variation in the size of the chelate ring may be due to the steric influence of bulky substituents (R) in the aryl nucleus of the azo moiety of the mercaptoaryl ligand.

Direct evidence for this assumption is presented in this study in which the synthesis† and structure‡ of a palladium chelate of type **1** (R = 2-CH_3) are reported for the first time. In this case, the stereochemical conditions for complex formation have been changed owing to the methyl groups introduced in the *ortho*-positions of the benzene rings of the ligand.

The structural units of the crystals of these compounds are complex molecules PdL_2 where LH is 2-mercapto-2′-methylazobenzene (Figure 2).

The central palladium atom in this unit is bound to two ligands thus forming the *cis*-planar configuration of the complex with the following bond lengths: Pd–S 2.265(2) Å, Pd–N(1) 2.125(6) Å.

The palladium atom is located on a second-order axis directed along the crystallographic axis *Z*. The coordination square is not completely planar; the angle between the PdSN fragments of the two ligands is 8°. The S··S′ distance is 3.097 Å.

The *cis*-structure of the MN_2S_2 coordination unit (M = Ni, Pd, Pt), unlike *trans*-MN_2O_2, is typical of metal with a d^8 electron configuration and has been proved by structural studies.[1]

In the compound under consideration, the palladium atom is coordinated by the ligands in a chelate manner forming two envelope-shaped five-membered rings with a bent palladium atom [the folding angle along the N(1)··S line is 31.2°]. The other four atoms of the metal-containing ring lie in the same plane to within ±0.015 Å. The (C1–6) benzene ring conjugated with the N(1)C(1)C(2)S tetraatomic group is bent in the opposite direction with respect to the Pd atom by 2.3°. The C(1–7) tolyl group is rotated by 38.8° with respect to the SPdN(1) plane.

The chelation of L to Pd in this compound (**2**; M = Pd, R = 2-Me) occurs in such a way that the azo-group remains outside the metal-containing ring. A similar situation, *i.e.* formation of two five-membered rings (with external azo-groups), has been observed in the Ni complex (**2**; M = Ni, R = 4-Me).[3] The folding angle of the Ni-containing ring along the N(1)··S line, equal to 30.9°, and the S··S′ distance, equal to 3.097(3) Å, coincide almost exactly with the corresponding values for compound **2** (M = Ni, R = 4-Me).[2,3] However, the NiN_2S_2

† *Synthesis of bis*(2-*mercapto*-2′-*methylazobenzolato*)*palladium*(II). Crystalline sodium sulfide (0.530 g, 2.1 mmol) was added to *o*-rhodanomethylazobenzene (0.0506 g, 2 mmol) in 20–30 ml of ethanol. The mixture was refluxed until the precipitate dissolved. The resulting red solution of the sodium salt was filtered, and a solution of K_2PdCl_4 (0.326 g, 1 mmol) in 5–7 ml of water was added to it dropwise. The solution was refluxed for 30–40 min. The crystalline precipitate of palladium complex was filtered off, washed successively with water and with hot ethanol and dried in air. The complex was recrystallised from a chloroform–ethanol or toluene–hexane mixture, yield 50–60%, dark green crystals, not melting below 350 °C. Found (%): C, 55.95; H, 3.54; N, 10.21; S, 11.20; Pd, 19.02. Calc. for $C_{26}H_{22}N_4PdS_2$ (%): C, 55.66; H, 3.95; N, 9.98; S, 11.43; Pd, 18.97.

fragment is distorted more substantially. The angle determining the extent of tetrahedrisation of the square is 12.9° (while that in PdN_2S_2 is only 8°).

The N(1)PdS intracyclic angle, equal to 83.5(2)°, and the SPdS′ external angle, 86.02(2)°, are markedly smaller than the corresponding angles in the nickel polyhedron [87.2(2) and 91.2(1)°, respectively], while the N(1)PdN(1)′ angle, 107.5(3)°, is larger than the N(1)NiN(1)′ angle, which is 98.4(3)°.

Thus, the introduction of a methyl substituent into an *ortho*-position of the benzene ring of the azo-constituent leads to appreciable changes in the structure of the complex **3**, *i.e.* to the occurrence of a structure of type **2** (M = Pd, R = 2-Me) with two five-membered metal-containing rings.

References

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‡ *Crystallographic data for bis*(2-*mercapto*-2′-*methylazobenzolato*)-*palladium*(II). The crystals of the prismatic habit are rhombic. The unit cell parameters: a = 15.947(2), b = 14.184(3), c = 10.515(3) Å, g = 2378(2), z = 4, space group *Pnca*, d_{calc} = 1.57 g cm^{-3}, μ = 1.0 cm^{-1}, F(000) 1136, M = 561.0. The data for the solution of the structure were obtained on a SYNTEX $P2_1$ diffractometer and included 3775 reflections measured by $\theta/2\theta$-scanning in the 2θ range 4–60° (Mo$K\alpha$ radiation, graphite monochromator). The structure was solved by the direct method over 2144 reflections, for which $I > 2\sigma(I)$. Hydrogen atoms were localised from the differential Fourier syntheses. The refinement was carried out by a full-matrix least-squares method in the anisotropic or isotropic (H atoms) approximation over 2138 reflections with $F > 4\sigma(F_0)$. The final R value was 0.044; for 2146 reflections 0.0509; wR^2 0.1103, G00F 1.30. WS = $1/\sigma^2$, (F_0^2). Full lists of bond lengths, bond angles, atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Communications*, 1997, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/22.

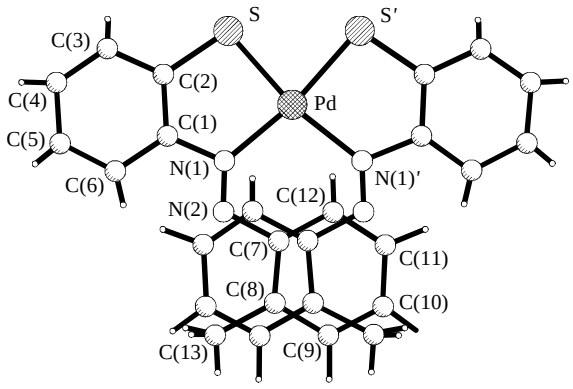

Figure 2 Crystal structure of bis(2-mercapto-2′-methylazobenzolato)-palladium(II). Bond lengths (Å) and bond angles (°): Pd–N(1) 2.125(6), Pd–S 2.265(2), S–C(2) 1.750(8), N(1)–N(2) 1.269(8), N(1)–C(1) 1.434(8), N(2)–C(7) 1.409(8), C(1)–C(6) 1.376(11), C(1)–C(2) 1.394(11), C(2)–C(3) 1.394(11), C(3)–C(4) 1.35(2), C(4)–C(5) 1.37(2), C(5)–C(6) 1.390(13), C(7)–C(12) 1.382(9), C(7)–C(8) 1.405(9), C(8)–C(9) 1.403(11), C(8)–C(13) 1.515(11), C(9)–C(10) 1.369(14), C(10)–C(11) 1.390(13), C(11)–C(12) 1.379(11); N(1)′–Pd–N(1) 107.5(3), N(1)–Pd–S′ 168.0(2), N(1)–Pd–S 83.5(2), S′–Pd–S 86.02(12), C(2)–S–Pd 96.2(2), N(2)–N(1)–C(1) 112.4(6), N(2)–N(1)–Pd 135.3(4), C(1)–N(1)–Pd 112.2(4), N(1)–N(2)–C(7) 118.8(5), C(6)–C(1)–C(2) 121.0(6), C(6)–C(1)–N(1) 122.7(7), C(2)–C(1)–N(1) 116.3(6), C(1)–C(2)–C(3) 117.9(8), C(1)–C(2)–S 120.4(5), C(3)–C(2)–S 121.7(7), C(4)–C(3)–C(2) 121.4(9), C(3)–C(4)–C(5) 120.0(8), C(4)–C(5)–C(6) 120.8(11), C(1)–C(6)–C(5) 118.8(10), C(12)–C(7)–C(8) 121.1(6), C(12)–C(7)–N(2) 125.1(6), C(8)–C(7)–N(2) 113.6(6), C(9)–C(8)–C(7) 116.9(7), C(9)–C(8)–C(13) 120.9(7), C(7)–C(8)–C(13) 122.2(7), C(10)–C(9)–C(8) 121.6(7), C(9)–C(10)–C(11) 120.7(8), C(12)–C(11)–C(10) 118.9(8), C(11)–C(12)–C(7) 120.7(7).

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