The first experimental evidence for the *cis–trans* isomerism of metal chelates with oxyazo ligands

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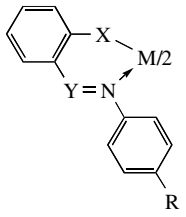
The *cis*- and *trans*-isomers of the metal chelate bis(2-hydroxy-4′-methylazobenzenato)platinum(II) were preparatively isolated and identified for the first time, and the *cis*-isomer was characterised by X-ray diffraction.

The structure of metal chelates **1** with azo and azomethine ligands depends on the nature of the metal (M), the donor atom (X) of the ligand and the steric effect of the substituent R. The diversity of structural forms results in various types of isomerism: *cis–trans*, square–tetrahedron and valence isomerism.[1–7]



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1a R = Me
X = O
Y = N
M = Pt^{II}

Stable but sterically hindered planar *cis* structures are most typical for the metal chelates **1** with X = S. In the azo complexes (Y = N), both five- and six-membered chelate rings can be formed because of the ambident character of the azo group.[3,4,6,7] Unusual structures with five- and six-membered chelate rings in a single molecule were found for the palladium complexes.[3,4]

At the same time, since the studies[8–10] in which the planar *trans* structure was found by the X-ray diffraction and dipole moment methods for oxygen-containing azo complexes **1** (Y = N, X = O), none of these compounds exhibited the *cis* structure. However, theoretical concepts[4] concerning the occurrence of *cis* structures in complexes **1** as a result of the -acceptor *trans* influence of the donor X atom in these metal chelates do not rule out the occurrence of *cis* structures in metal chelates **1** with X = O.

In this paper, we report the experimental data on the synthesis† and identification of the *cis*- and *trans*-isomers of platinum complexes **1a**.

The complexes were identified by elemental analysis and IR spectroscopy. The purity was checked by TLC (silica gel chromatoplates from Merck). With the use of toluene as the eluent, a blue spot with R_f = 0.8–0. 9 (*trans*-) and a cherry-violet spot with R_f = 0.5–0. 6 (*cis*-) were detected.

A special feature of the separation of the isomers is that the *cis* form should be rapidly separated from solutions because it spontaneously converts into the *trans* form. It is likely that for this reason the *cis*-isomers of chelates **1a** were not detected up to the present. However, our preliminary data indicate that the *cis*- and *trans*-isomers of palladium(II) and nickel(II) complexes **1** can be obtained by purification using a properly chosen sequence of operations. We measured the dipole moments (μ) in benzene (25 °C). The μ values are equal to 5.40 and 2.25 D for the *cis*- and *trans*-isomers, respectively. The dipole moment of the *trans*-isomer is consistent with the corresponding values for planar *trans* structures.[10]

The existence of the *cis* structure was conclusively proved by X-ray diffraction analysis‡ (Figure 1).

The platinum atom with two ligands forms a planar *cis* configuration. Thus, the molecule is very sterically hindered, and this fact is primarily responsible for the molecular structure. The coordination unit is somewhat tetrahedrally distorted; the O(2)Pt(1)N(3) plane is turned through 7.9° with respect to O(1)Pt(1)N(1), and the metal rings are crimped and exhibit two bends at N(1)–O (1) and N(1)–C(1) of 29° and 16°, respectively, which turn the Pt atom by 0.68 Å and the N(2) atom by 0.17 Å on different sides of the N(1)C(1)C(6)O(1) plane. In the second metal ring, the bends at N(3)–O(2) and N(3)–C(14) are 33° and 27°, respectively. The Pt and N(4) atoms are out of the

† Synthesis of bis(2-hydroxy-4′-methylazobenzenato)platinum(II) was performed by mixing a 2-hydroxy-4′-methylazobenzene (0.42 g, 2 mmol) solution in methanol, a KOH (0.14 g, 2.5 mmol) solution in methanol and a K_2PtCl_4 (0.42 g, 2 mmol) solution in DMSO. The complex was precipitated after boiling the mixture. The precipitate (a mixture of *cis*- and *trans*-isomers) was dissolved in a minimally possible volume of toluene, and the hot solution was filtered through a thin bed of silica gel for column chromatography (Merck). The adsorbed product was eluted with 50–80 ml of hot toluene. After evaporating and cooling the filtrate and the eluate, crystals of the *trans* complex of platinum were formed (mp 254–2 55 °C), yield 40-4 5%. Subsequent elution from the sorbent with hot chloroform (80–120 ml) followed by evaporation of the collected fraction to 20 ml and the addition of 5 ml of methanol resulted in the precipitation of crystals of the *cis* complex [mp 243–2 44 °C (decomp.)], yield 4–6%.

For *cis*-bis(2-hydroxy-4′-methylazobenzenato)platinum(II), found (%): C, 50.65; H, 3.40; N, 9.00; Pt, 31.65. Calc. for $C_{26}H_{22}N_4O_2Pt$ (%): C, 50.57; H, 3.50; N, 9.07; Pt, 31.59.

For *trans*-bis(2-hydroxy-4′-methylazobenzenato)platinum(II), found (%): C, 50.70; H, 3.26; N, 8.95; Pt, 31.59.

‡ *X-ray diffraction analysis of* **1a**. The crystals of **1** are dark brown, prismatic habit, 0.22×0 .16×0 .12 mm in size, monoclinic. The unit cell parameters: a = 9.089(2), b = 22.361(4), c = 11.619(4) Å β = 99.04(3)°, V = 2332.1(8) Å^3, d_{calc} = 1.759 g cm^{-3}, μ = 6.047 mm^{-1}, $F(000)$ = 1200, M = 617.57, space group $P2_1/n$, Z = 4.

The unit cell parameters were calculated from the setting angles of 25 reflections. Two reflections were chosen as intensity standards and were measured every 100 reflections.

The data for the solution of the structure were obtained on a SYNTEX $P2_1$ diffractometer and corrected for the Lorentz and polarisation effects. Equivalent reflections were merged. The intensity of 2635 reflections was measured (MoK radiation, graphite monochromator) by $\theta/2\theta$-scanning in the range $4° < 2\theta < 60°$, index ranges $0 < h < 12$, $0 < k < 28$, $-14 < l < 14$. The position of the platinum atom was determined by the heavy atom method over 2476 independent reflections for which $I \geq 2\sigma(I)$. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, which were refined with anisotropic thermal parameters by full-matrix least-squares procedures. Hydrogen atoms were placed in estimated positions (C–H = 0.96 Å) with common isotropic thermal parameters [U_H = 0.076, $U_{H(Me)}$ = 0.139 Å^2]. The final R and wR_2 values were 0.0494 and 0.1111, respectively; the number of parameters was 301; GOOF was 1.295. All crystallographic calculations were performed using SHELX-76 and SHELXL-93 programs.[11]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 1999. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/42.

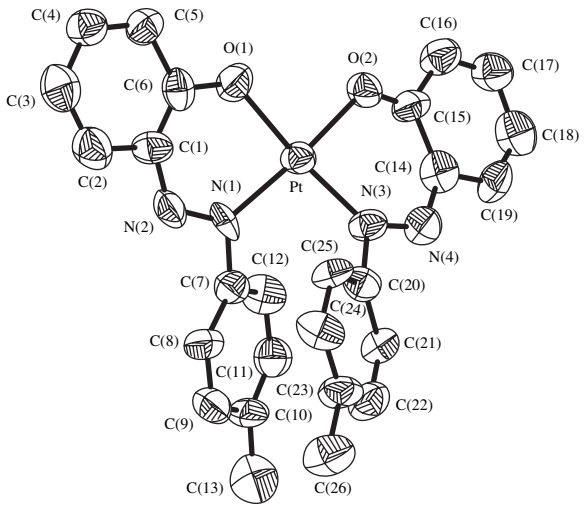

Figure 1 Crystal structure of *cis*-bis(2-hydroxy-4′-methylazobenzenato)-platinum(II). Selected bond lengths (Å): Pt–N(3) 1.95(2), Pt–N (1) 1.97(2), Pt–O(2) 1.98(2), Pt–O(1) 1.98(2), O(1)–C(6) 1.36(3), O(2)–C(15) 1.30(3), N(1)–N(2) 1.26(3), N(1)–C(7) 1.46(3), N(2)–C (1) 1.34(4), N(3)–N(4) 1.29(3), N(3)–C (20) 1.48(3), N(4)–C(14) 1.38(3), C(1)–C (6) 1.36(4), C(1)–C (2) 1.44(4), C(2)–C (3) 1.39(5), C(3)–C (4) 1.43(4), C(4)–C(5) 1.34(4), C(5)–C(6) 1.47(4), C(10)–C(13) 1.47(5), C(14)–C(15) 1.44(4), C(14)–C (19) 1.45(4), C(15)–C (16) 1.39(4), C(16)–C(17) 1.40(4), C(17)–C(18) 1.32(4), C(18)–C (19) 1.30(4), C(23)–C (26) 1.53(4); selected bond angles (°): N(3)–Pt –N(1) 96.4(9), N(3)–Pt–O(2) 88.4(8), N(1)–Pt –O(2) 172.0(8), N(3)–Pt– O(1) 172.8(9), N(1)–Pt–O(1) 89.7(9), O(2)–Pt –O(1) 86.1(8), C(6)–O(1)–Pt 118(2), C(15)–O(2)–Pt 11 8(2), N(2)–N(1)–Pt 126(2), N(1)–N(2)–C (1) 123(2), N(4)–N(3)–Pt 128(2), N(3)–N(4)–C (14) 119(2), N(2)–C(1)–C(6) 126(3), C(1)–C (6)–O(1) 126(2), N(4)–C(14)–C(15) 127(2), O(2)–C(1 5)–C(14) 122(2).

O(2)N(3)C(14)C(15) mid plane by 0.78 and 0.21 Å, respectively, on different sides. As a result of the interaction between phenyl nuclei, the C(7)–C(12) phenyl ring is turned through 124° with respect to the PtO(1)N(1) plane, and the C(20)–C(25) ring, through 122° with respect to PtO(2)N(3). The O(1)–O(2) distance is 2.70 Å.

The *cis*-isomer is closely similar to the *cis* complexes of palladium with 2-mercapto-4′(2″)-methylazobenzene (Y = N, X = S) in steric hindrance.[4,6] In the latter complexes, the coordination units are also tetrahedrally distorted by 12.2° and 8°, respectively, and the metal rings are crimped at the S–N line (from 24° to 32°). The difference is only in that six-membered metal rings are retained even in the sterically hindered *cis* structure of the platinum complex under study, whereas five-membered metal rings are formed in the sulfur-containing complexes of palladium.

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