1,3-Diphenylpropane-1,3-diamines

Synthesis of 1,3-Bis(hydroxy-halogenophenyl)propane-1,3-diamines and their Pt(II) Complexes

Part B: Preparation of the Pt(II) Complexes

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The preparation of the Pt(II) complexes of the diamines described in Part A with Cl⁻, I⁻, SO₄²⁻, and water as additional ligands is reported.

Dichloro-platinum(II) complexes

The title complexes were prepared as described for the 1,2-diphenylethane-1,2-diamino-Pt(II) complexes. In brief, K₂PtCl₄ in water was added drop by drop to the dihydrochlorides of the ligands, dissolved in water or (lipophilic ligands) in water/tert. butanol at 40°C and pH 6.0-6.5. This range is important and was maintained by adding 0.1 N NaOH within small intervals. If the reaction mixture becomes too acidic the pertinent 1,3-diammoniumpropane-tetrachloro-Pt(II) derivative may come up. Basic conditions lead to exchange of Cl⁻ against OH⁻. Moreover Pt° may be formed by reduction. Analogously to the 1,2-diphenylethane-1,2-diamines the formation of the meso- and erythro-stereomeric Pt complexes need longer reaction times and the yields are lower in comparison with the rac- and threo-complexes which were obtained as analytically pure solids in most cases. On account of their sensitivity to oxygen, the ligands (Part A) with a catechol increment could not be obtained as bases. Therefore, their chloride-complexes could not be prepared directly.

As mentioned above, the o-methoxy-substituted ligands and (Part A) could not be converted to the corresponding phenols. Therefore, these ethers were reacted to the pertinent Pt(II) complexes directly. The complexes so obtained are shown in Table 1.

Although diaqua/sulfato-Pt(II) complexes can be prepared from the pertinent dichloro complexes - probably as a mixture with coordinated and counterionic sulfate ligands (this we want to indicate by our formulation "diaqua/sulfato", cf. the IR-spectra of the complexes as discussed in forthcoming Part V) - the formation via the diiodo complexes is favourable: I⁻ has a stronger trans-effect than Cl⁻. Therefore, the bond between Pt and the ligand arranged trans to I⁻ is weakened, resulting in a kinetically favoured substitution. Moreover, meso- and erythro-diastereomers precipitate as analytically pure diiodo complexes. Generally, the dihydrochlorides of the ligands were treated with K₂PtI₄ afford-

Tab. 1: Dichloro-platinum(II) complexes 114-139
ing complexes 140-151. In case of the catechol derivatives 92 and 93 (Part A) the dihydrobromides - resulting from Br2-induced ether cleavage - were used, needing longer reaction times than the dihydrochlorides as expected.

**Partial Chemistry**

Diaqua/sulfato-platinum(II) complexes

These complexes were obtained from the diodo-complexes by treatment with Ag₂SO₄/water in the dark, using a slight excess of the diiodo-complexes. The diaqua/sulfato-complexes are soluble in water and were obtained by freeze-drying. Again the bis-catechol complex 150 did not react properly. Special features of the NMR spectra of the ligands and the complexes cited here, establishing their stereochemistry, will be discussed with reference to Fig. 1 (Part III, preceding paper) in Part V of this series.

**Experimental Part**

**General remarks:** see preceding paper

**Dichloro-Pt(II) complexes**

The pertinent 1,3-diphenylpropane-1,3-diamines were liberated from 0.5 mmoles of the dihydrobromides (if not otherwise stated) by cc on silica with the solvents I or II as indicated. The solvent was removed in vacuo at 40°, the base was dried at the oil pump, suspended in 1 ml of water and dissolved by 1 ml of 2N HCl. After filtration this solution was warmed to 40° and the pH value was adjusted to 6.0-6.5 by 0.1N NaOH. In the cases of more lipophilic bases the solutions became turbid, and 10 ml of tert-butanol were added in order to improve solubility. Then 208 mg K₂PtCl₄ (0.5 mmoles) (Janssen) in 5 ml of water were added drop by drop with stirring. Stirring was continued for 12-14 h under light protection, whilst pH 6.5 was adjusted every 30-45 min by addition of 0.1N NaOH. After this time the pH-value did not change in most cases, so that the precipitated complex can be collected by suction filtration, washing with 2N HCl and water and drying at the oil pump for several days over P₂O₅ at 100°. In some cases the complexes had to be purified by dissolving in a very small quantity of DMF and precipitation with 5% NaCl solution.- Solvent I: MeOH/conc. ammonia 100/1.5 (v/v).- Solvent II: EtOH 96%/conc. amonia 100/1.5 (v/v).- The light-grey, non-crystalline complexes melt with decomposition.

**meso-Dichloro-1,3-bis-(2-methoxyphenyl)propane-1,3-diamino-Pt(II) (114)**

From 60 x 2 HCl; solvent I; 25%; m.p. 205-208°.- C₁₇H₁₂Cl₂N₂O₂Pt (552.4) Calcd. C 37.0 H 4.01 N 5.1 Found C 37.4 H 4.09 N 4.8.- FT-IR (KBr): ν = 3258 s, 3195, 3120 m (NH₂); 2957 m, 2927 m (C-H aliph.); 2857 m (OCH₃); 1603 s, 1595 s (C=C and NH₂).- 1H-NMR ([D₆]DMSO): δ (ppm/250 MHz) = 7.52-6.82 (m; 8H aromat.), 5.53-5.09 (m; 4H, NH₂; H/D-exch.), 4.70-4.47 (m; 2H, CH; H/D-exch.); 4.59; ABX₂; Jₓₓ = 1.0 Hz, Jₓy = 1.04 Hz, 3.93 (s; 6H, OCH₃); 2.64-2.57 (ABX₂; Jₓy = 14.0 Hz, Jₓz = 10.4 Hz, 1H, CH₂, H₃), 2.30-2.13 (ABX₂; Jₓz = 14.0 Hz, 1H, CH₂, H₄).- PI-FAB-MS (glycerol/DMSO): m/z = 1065.1 ([(L₂PtCl₂H₂)⁺]; 629.2 ((M + H + DMSO)⁺); 593.3 ((M - Cl + DMSO)⁺); 515.3 ((M - Cl)⁺).

Dimers of the type [[(L₂PtCl₂)⁺] were also observed by Sperer in the PI-FAB-spectra of cis-dichloro-Pt(II) complexes of estradiol derivatives.

**rac-Dichloro-1,3-bis-(2-methoxyphenyl)propane-1,3-diamino-Pt(II) (115)**

From 61 x 2 HCl; solvent I; 11%; m.p. 209-211°.- C₁₇H₁₂Cl₂N₂O₂Pt (552.4) Calcd. C 37.0 H 4.01 N 5.1 Found C 36.4 H 3.94 N 5.0.- FT-IR (KBr): ν = 3258 s, 3195, 3120 m (NH₂); 2956 m, 2938 m (C-H aliph.); 2840 m (OCH₃); 1601 s, 1589 s (C=C and NH₂).- 1H-NMR ([D₆]DMSO): δ (ppm/250 MHz) = 8.47-6.91 (m; 8H aromat.); 7.56-7.50 (m; 2H, NH₃; H/D-exch.), 5.39-5.10 (m; 2H, NH₂; H/D-exch.), 4.38-4.17 (m; 2H, CH; H/D-exch.); 4.27; ABX₂; Jₓₓ = 5.1 Hz, Jₓy = 3.77 (s; 6H, OCH₃).- 2.38 (AₓX₂; Jₓy = 5.1 Hz, 1H, CH₂, H₄).- PI-FAB-MS (glycerol/DMSO): m/z = 1046.9 ([(L₂PtCl₂)⁺]; 643.1 ((M + H + glycerol)⁺); 629.1 ((M + H + DMSO)⁺); 593.2 ((M - Cl + DMSO)⁺); 515.2 ((M - Cl)⁺).

**meso-Dichloro-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (116)**

From 88; solvent I; 45%; m.p. 227-230°.- C₁₅H₁₃Cl₂N₂O₂Pt (524.3) Calcd. C 34.4 H 3.46 N 5.3 Found C 34.4 H 3.32 N 5.3.- FT-IR (KBr): ν = 3392 s, br (OH); 3266 s, 3201 s, 3185 s, 3133 s (NH₂); 2956 w, 2930 w (C-H aliph.).- 1393 s (C=C and NH₂).- CW-IR (KBr): ν = 330 sh, 320 m

*) For the sake of clearness only the ions for ³⁵Cl are cited in the mass spectra of Cl-containing compounds.
rac-Dichloro-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (117)

From 89; solvent I; 54%, m.p. 225-229°. C12H18Cl2N2O2Pt x H2O (542.3) Calcd. C 33.2 H 3.72 N 5.2 Found C 33.2 H 3.44 N 5.0.- FT-IR (KBr): v = 3424 s, 2925 s, 2912 s, 2850 s, 1609 s, 1520 s, 1471 s, 1390 s, 1359 s, 1171 s, 1070 s, 1030 s, 777 w (C-H aliph.).

three-Dichloro-1-(2-fluoro-4-hydroxy-phenyl)-3-(4-hydroxy-phenyl)propane-1,3-diamine-Pt(II) (122)

From 95; solvent I; 55%, m.p. 221-224°. C12H18Cl2FN2O2Pt (542.3) Calcd. C 33.2 H 3.16 N 5.2 Found C 33.2 H 3.44 N 5.1.- FT-IR (KBr): v = 3432 s, 2926 s, 2912 s, 2850 s, 1612 s, 1534 s, 1458 s, 1358 s, 1249 s, 1171 s, 1070 s, 1030 s, 777 w (C-H aliph.).

meso-Dichloro-1,3-bis-(4-hydroxy-phenyl)propane-1,3-diamino-Pt(II) (118)

From 90; solvent I; 33%, m.p. 216-219°. C12H18Cl2N2O2Pt (542.3) Calcd. C 34.4 H 3.46 N 5.3 Found C 34.6 H 3.85 N 4.9.- FT-IR (KBr): v = 3482 s, 2925 s, 2912 s, 2850 s, 1612 s, 1534 s, 1458 s, 1358 s, 1249 s, 1171 s, 1070 s, 1030 s, 777 w (C-H aliph.).

erythro-Dichloro-1-(2-chloro-4-hydroxy-phenyl)-3-(4-hydroxy-phenyl)propane-1,3-diamine-Pt(II) (122)

From 96; solvent I; 25%, m.p. 207-210°. C12H18Cl2N2O2Pt x 1.5 H2O (585.8) Calcd. C 30.8 H 3.44 N 4.8 Found C 30.8 H 3.22 N 4.7.- FT-IR (KBr): v = 3399 s, 2925 s, 2912 s, 2850 s, 1612 s, 1534 s, 1458 s, 1358 s, 1249 s, 1171 s, 1070 s, 1030 s, 777 w (C-H aliph.).

erythro-Dichloro-1-(2-fluoro-4-hydroxy-phenyl)-3-(4-hydroxy-phenyl)propane-1,3-diamine-Pt(II) (120)

From 94; solvent I; 48%, m.p. 207-210°. C12H18Cl2FN2O2Pt (542.3) Calcd. C 32.2 H 3.16 N 5.2 Found C 32.2 H 3.39 N 5.0.- FT-IR (KBr): v = 3407 s, 2925 s, 2912 s, 2850 s, 1612 s, 1534 s, 1458 s, 1358 s, 1249 s, 1171 s, 1070 s, 1030 s, 777 w (C-H aliph.).

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phenyl)propane-1,3-diamino-Pt(II) (H/D-exch.), 2.33 (AX, $J_{AX} = 5.0$ Hz, 4H), 4.07 (s, br; 1H, CH; partial overlap with solvent signals after H/D-exch.), 5.73-5.42 (m; 2H, NH; H/D-exch.), 4.28 (s, br; 1H, CH; partial overlap by solvent signals after H/D-exch.), 4.07 (s, br; 1H, CH; partial overlap with solvent signals after H/D-exch.).

**erythro-Dichloro-1-(2-bromo-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (125)**

From 99: solvent I, 15%; m.p. 211-215°. $C_{21}H_{17}BrCl_2N_2O_4Pt$ x H$_2$O (639.2) Calcd. C 28.2 H 3.31 N 4.44 Found C 28.2 H 3.36 N 4.4-. FT-IR (KBr): $\nu = 3394$ s, br (OH); 3239, 3201, 3132 s (NH$_2$); 2959 w, 2929 w (C-H aliph.). 1609 s, 1593 s (C=O and NH$_2$). $^{13}$C-NMR ([$\delta$ppm]): 156.0, 147.0, 137.3 (C); 5.95-5.79 (m; 2H, NH; H/D-exch.), 5.55-5.54 (m; 2H, NH; H/D-exch.), 5.37-5.24 (m, br; 1H, NH$_2$; H/D-exch.), 4.28 (s, br; 1H, CH; partial overlap by solvent signals after H/D-exch.).

**threeo-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (126)**

From 100; solvent II; 50%; m.p. 194-196°. $C_{23}H_{19}Cl_2N_2O_4Pt$ x H$_2$O (611.2) Calcd. C 29.5 H 2.97 N 4.66 Found C 29.6 H 2.95 N 4.6-. FT-IR (KBr): $\nu = 3394$ s, br (OH); 3239, 3201, 3132 s (NH$_2$); 2959 w, 2929 w (C-H aliph.). 1609 s, 1593 s (C=O and NH$_2$). $^{13}$C-NMR ([$\delta$ppm]): 156.0, 147.0, 137.3 (C); 5.95-5.79 (m; 2H, NH; H/D-exch.), 5.55-5.54 (m; 2H, NH; H/D-exch.), 5.37-5.24 (m, br; 1H, NH$_2$; H/D-exch.), 4.28 (s, br; 1H, CH; partial overlap by solvent signals after H/D-exch.).

**erythro-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (129)**

From 103; solvent II; 66%; m.p. 225-229°. $C_{21}H_{19}Cl_2N_2O_4Pt$ x 0.5 tert.-C$_4$H$_9$O (630.3) Calcd. C 32.4 H 3.66 N 4.4 Found C 32.1 H 3.22 N 4.5-. FT-IR (KBr): $\nu = 3395$ s, br (OH); 3276 s, 3230 s, 3131 s (NH$_2$); 3085 w (C-H aromat.), 2973 w (C-H aliph.). 1603 s, 1574 s (C=O and NH$_2$). $^{13}$C-NMR ([$\delta$ppm]): 156.0, 147.0, 137.3 (C); 5.95-5.79 (m; 2H, NH; H/D-exch.), 5.55-5.54 (m; 2H, NH; H/D-exch.), 5.37-5.24 (m, br; 1H, NH$_2$; H/D-exch.), 4.28 (s, br; 1H, CH; partial overlap by solvent signals after H/D-exch.).

**erythro-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (130)**

From 104; solvent II; 56%; m.p. 212-215°. $C_{21}H_{19}Cl_2N_2O_4Pt$ (593.2) Calcd. C 32.4 H 2.72 N 4.7 Found C 32.0 H 3.01 N 4.7-. FT-IR (KBr): $\nu = 3415$ s, br (OH); 3284 s, 3222 s, 3143 s (NH$_2$); 2963 w, 2915 w (C-H
phenyl)propane-1,3-diamino-Pt(II) (131) = 10.3 Hz), 4.99-4.79 (m; 1H, NH2; H/D-exch.), 4.42-4.23 (m; 1H, CH; H/D-exch.: 4.31; ABX, 3Jax = 3JAY = 1.5 Hz, 3Jay = 10.3 Hz). 3.00 (ABX; 3Jax = 15.5 Hz, 3Jay = 10.3 Hz, 1H, CH2, H6; partial overlap with solvent signals), 1.87 (ABX, 3Jax = 15.5 Hz, 3Jay = 1.5 Hz, 1H, CH2, H5; PI-FAB-MS (glycerol/DMSO)[8]: m/z = 1145.6 ([(LPtCl3)]; 683.0 (M + H + glycerol)*); 669.0 (M + H + DMSO)*); 647.0 (M - Cl + glycerol)*; 633.0 ((M - Cl + DMSO)*); 591.0 (M + H); 555.1 (M - Cl)).

three-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (131)

From 105; solvent II: 50%; m.p. 202-205°. C18H14Cl4N2O4Pt (593.2) Calcd. C 30.4 H 2.72 N 4.7 Found C 30.6 H 2.89 N 4.6. FT-IR (KBr); ν = 3413 s, br (OH); 3251 s, 3210 s, 3127 s (NH2); 2965 w, 2921 w (C-H aliph.); 1603 s, 1574 s (C=C and NH2). - H-NMR (D2O): δ (ppm/250 MHz) = 8.05, 6.93 (AA’BB’); 3Jab = 8.6 Hz, 4H aromatic), 6.85 (2H aromatic), 6.02-5.95 (m; 1H, NH2; H/D-exch.), 5.90-5.80 (m; 1H, NH2; H/D-exch.), 5.21-5.13 (m; 1H, NH2; H/D-exch.), 4.71-4.52 (m; 2H, CH and NH2; H/D-exch.: 4.65; ABX, 3Jax = 15.0 Hz, 3Jay = 10.9 Hz, 1H, CH2, H6; 4.36 (s; br, 1H, CH; H/D-exch.: 4.37); ABX, 3Jax = 2.0 Hz, 3Jay = 2.0 Hz, 1H, CH, H5; 2.98 (ABX; 1H, CH2, H5; overlap with solvent signals), 2.14 (ABX; 3Jax = 14.2 Hz, 3Jay = 2.0 Hz, 1Jax = 1.5 Hz, 1H, CH2, H5; PI-FAB-MS (glycerol/DMSO)[8]: m/z = 775.1 (M + H + 2 glycerol)*); 683.0 (M + H + glycerol)*; 669.0 (M + H + DMSO)*); 647.1 (M - Cl + glycerol)*; 633.1 ((M - Cl + DMSO)); 555.0 (M - Cl)).

diastereomeric-rac-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (112)

From 106; solvent II: 20%; m.p. 202-205°. C18H14Cl4F2N2O4Pt (578.3) Calcd. C 31.2 H 3.4 N 4.9 Found C 31.6 H 3.42 N 4.8. - FT-IR (KBr); ν = 3432 s, br (OH); 3210 s, 3137 s (NH2); 2965 w, 2921 w (C-H aliph.); 1628 s (NH); 1597 s (C=C). - H-NMR (D2O): δ (ppm/250 MHz) = 10.22 (s; 2H, OH; H/D-exch.), 7.52 (t; δ = 8.7 Hz, 3Jab = 8.7 Hz, 2H aromat.), 6.75-6.59 (m; 4H aromat.), 5.60-5.39 (m; 2H, NH2; H/D-exch.), 5.39-5.22 (m; 2H, NH2; H/D-exch.), 4.69-4.49 (m; 2H, NH2; H/D-exch.: 4.58; ABX, 3Jax = 1.0 Hz, 3Jay = 10.7 Hz). 2.78 (ABX; 3Jab = 15.1 Hz, 3Jax = 10.7 Hz, 1H, CH2, H5; 2.03 (ABX; 3Jab = 15.1 Hz, 3Jax = 1.0 Hz, 1H, CH2, H5; PI-FAB-MS (glycerol/DMSO)[8]: m/z = 1080.8 ([(LPtCl3)]; 743.2 (M + H + 2 glycerol)*); 651.0 (M + H + glycerol)*); 637.0 ((M - Cl + DMSO); 615.1 ((M - Cl + glycerol)*); 601.1 ((M - Cl + DMSO); 523.1 ((M - Cl)).

rac-Dichloro-1,3-bis(2-fluoro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (133)

From 107; solvent II: 38%; m.p. 200-205°. C18H14Cl2F2N2O4Pt (560.3) Calcd. C 32.2 H 2.88 N 5.0 Found C 32.0 H 2.87 N 4.9. - FT-IR (KBr); ν = 3432 s, br (OH); 3268 s, 3249 s, 3199 s, 3132 s (NH2); 3052 w (C-H aromat.); 2967 w, 2938 w (C-H aliph.); 1624 s (NH); 1593 s (C=C). - H-NMR (D2O): δ (ppm/250 MHz) = 10.22 (s; 2H, OH; H/D-exch.), 8.45 (t; δ = 8.8 Hz, 3Jab = 8.8 Hz, 2H aromat.), 6.81-6.57 (m; 4H aromat.), 6.83-6.78 (m; 2H aromat.), 5.80-5.55 (m; 2H, NH2; H/D-exch.), 5.55-5.27 (m; 2H, NH2; H/D-exch.), 4.24 (s; br, 2H, CH; partial overlap with solvent signals after H/D-exch.). 2.29 (AX3, 3Jax = 5.0 Hz, 2H, CH2, Pt-PI-FAB-MS (glycerol/DMSO)[8]: m/z = 1181.4 ([(LPtCl3)]; 701.2 (M + H + glycerol)*); 687.1 ((M - Cl + glycerol)*); 665.2 ((M - Cl + DMSO); 651.3 (M - Cl + DMSO); 573.2 (M - Cl)).

diastereomeric-rac-Dichloro-1,3-bis(2-fluoro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (137)

From 111; solvent II: 65%; m.p. 196-199°. C18H14Cl2F2N2O4Pt (611.2) Calcd. C 29.5 H 2.84 N 4.6 Found C 29.8 H 2.92 N 4.4. - FT-IR (KBr); ν = 3378 s, br (OH); 3276 s, 3129 m (NH2); 3010 w (C-H aromat.); 2963 w, 2927 w (C-H aliph.); 1626 s, 1603 s (NH2); 1572 s (C=C). - H-NMR (D2O): δ (ppm/250 MHz) = 9.29 (t; δ = 8.8 Hz, 3Jab = 8.8 Hz, 1H aromat.). 6.93-6.63 (m; 2H aromat.), 6.86 (s; 2H aromat.), 6.27-6.08 (m; 2H, CH; H/D-exch.: 4.73; ABX, 3Jax = 1.0 Hz, 3Jay = 12.7 Hz). 2.44 (ABX; 3Jab = 15.2 Hz, 3Jax = 12.7 Hz, 1H, CH2, H5; 1.98 (ABX; 3Jab = 15.2 Hz, 3Jay = 1.0 Hz, 1H, CH2, H5; PI-FAB-MS (glycerol/DMSO)[8]: m/z = 1145.7 ([(LPtCl3)]; 682.9 ((M + H + glycerol)*); 669.0 (M + H + DMSO)*); 646.9 ((M - Cl + glycerol)*); 632.9 ((M - Cl + DMSO)*); 555.0 (M - Cl)).
1H, NH2), 6.08-5.90 (m; 1H, NH2), 5.28-5.03 (m; 1H, NH2), 4.78-4.57 (m; 2H, CH2, Hax overlapped with solvent signals), 2.01 (ABYX; JAB = 14.9 Hz, JAX = 2.0 Hz, JBX = 1.5 Hz, 1H, CH2, Hax). PI-FAB-MS (glycerol/DMSO/98%Pt): m/z = 1181.5 ([L2PtCl4]) + 793.3 (M + H + 2 glycerol); 701.1 (M + H + glycerol); 687.3 (M + H + DMSO); 659.3 (M + Cl + glycerol); 651.2 (M + Cl + DMSO); 609.1 (M + H); 573.1 (M + Cl).

eythro-Dichloro-1-[(2,6-dichloro-4-hydroxyphenyl)propane-1,3-diamino]Pt(II) (119)

From 112; solvent II: 71%, m.p. 202-205°C. C17H12Cl2N2O2Pt x H2O (645.7). Calcld. C 27.9 H 2.65 N 4.3. Found C 27.8 H 2.82 N 4.1 FT-IR (KBr): ν = 3422 s, br (OH); 3284 s, 3224 s, 3139 s (NH2); 2929 w (C-H aliph); 1607 s, 1570 s (C=C and NH2). 1H-NMR ([D2]DMF): δ (ppm/250 MHz) = 10.29 (s, br; 2H, OH; H/D-exch.), 7.76 (d, J = 8.5 Hz, 1H aromat.), 7.01-6.86 (m; 2H aromat.), 6.93 s (2H aromat.), 6.23-6.06 (m; 1H, NH2; H/D-exch.), 5.90-5.71 (m; 1H, NH2; H/D-exch.), 5.50-5.34 (m; 1H, NH2; H/D-exch.), 5.31-5.01 (m; 1H, CH2; H/D-exch.): 5.11; ABXY; JAX = 2JAY = 3JAB = 13.2 Hz, 1H, CH2, Hax overlapped with solvent signals), 4.53 (ABYX; JAX = JAY = 15 Hz, JBX = 10 Hz). 2.93 (ABYX; 1H, CH2, Hax overlapped with solvent signals). From [ABXY; JAX = 14.7 Hz, JAB = 15 Hz, 1H, CH2, Hax]. PI-FAB-MS (glycerol/DMSO/98%Pt): m/z = 1213.6 ([L2PtCl4]); 703.1 (M + H + DMSO); 681.1 (M + Cl + glycerol); 667.1 (M + Cl + DMSO); 589.2 (M - Cl).
	hree-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)propane-1,3-diamino]Pt(II) (119)

From 113; solvent II: 68%, m.p. 216-220°C. C17H12Cl2N2O2Pt (627.6). Calcld. C 28.7 H 2.41 N 4.5. Found C 29.3 H 2.91 N 4.4 FT-IR (KBr): ν = 3340 s, br (OH); 3274 s, 3237 s, 3193 s, 3131 s (NH2); 2932 w (C-H aliph); 1609 s, 1574 s (C=C and NH2). 1H-NMR ([D2]DMF): δ (ppm/250 MHz) = 10.30 (s, br; 2H, OH; H/D-exch.), 9.56 d, J = 8.6 Hz, 1H aromat.), 7.10-6.91 (m; 2H aromat.), 6.87 s (2H aromat.), 6.54-6.11 (m; 1H, NH2), 6.11-5.97 (m; 1H, NH2), 5.34-5.07 (m; 1H, NH2), 4.82-4.50 (m; 3H, 2 CH and 1 NH2), 2.97-2.86 (m; 1H, CH2, Hax overlapped with solvent signals), 2.09 (ABXY; JAX = 13.2 Hz, JAX = JAY = 2.0 Hz, 1H, CH2, Hax). PI-FAB-MS (glycerol/DMSO/98%Pt): m/z = 1213.6 ([L2PtCl4]); 707.1 (M + H + glycerol); 703.0 (M + H + DMSO); 681.2 (M + Cl + glycerol); 667.2 (M + Cl + DMSO); 625.2 (M + H); 589.2 (M - Cl).

Diiodo-Pt(II) complexes

The title complexes were prepared from the 1,3-diphenylpropane-1,3-diamine-dihydrobromides (0.5 mmole), liberating the corresponding bases as described for the corresponding dichloro-Pt(II) complexes with the solvent indicated there. To the solution of the base (if necessary tert-butanol is added, see above) of pH 6.5 K2PtCl6 solution (prepared from 208 mg (0.5 mmole) K2PtCl6 and 0.750 g KI in 1.25 ml of water by stirring for 30 min in the dark at room temp.) was added drop by drop. The mixture was stirred at room temp. adjusting the pH-value to 6.5 until it does not change anymore. Then the precipitated analytically pure complex is filtered off by suction, washed with 2N HCl and water and dried at 100°C for several days over P2O5 in vacuo. All complexes are yellow to ochre coloured powders.

meso-Diiodo-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino Pt(II) (140)

From 88; 51%, m.p. 224-228°C. C17H12Cl2N2O2Pt (707.2). Calcld. C 25.5 H 2.37 N 4.0. Found C 25.4 H 2.76 N 4.0 FT-IR (KBr): ν = 3423 s, br (OH); 3257 s, 3187 s, 3121 s (NH2); 3052 s (C-H aromat); 2925 s (C-H aliph); 1603 s, 1591 s (C=C and NH2). 1H-NMR ([D2]DMF): δ (ppm/250 MHz) = 9.72 (s; 2H, OH; H/D-exch.), 7.25-6.80 (m; 8H aromat.), 5.65-5.49 (m; 2H, NH2), 4.89-4.64 (m; 2H, NH2), 4.53-4.36 (m; 2H, CH2); 2.55 (ABXY; JAX = 14.2 Hz, JAY = 11.4 Hz, 1H, CH2, Hax). PI-FAB-MS (glycerol/DMSO/98%Pt): m/z = 785.8 (M + H + DMSO); 749.0 (M + I + DMSO + glycerol); 761.0 (M + I + glycerol); 657.0 (M + I + DMSO); 579.0 (M - I).
three-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (149)

From 105 76%, m.p. 172-174°.- C₇H₆Cl₂N₂O₇Pt x 2 H₂O (812.1) Calcd. C 22.2 H 2.84 N 3.4 Found C 21.9 H 2.26 N 3.1.- FT-IR (KBr): v = 3405 s, br (OH), 3247 s, 3139 s, 3129 m (NH₃); 2936 w (C-H aliph.); 1605 s, 1570 s (C=C and NH₂). ⁻¹-H-NMR (D₂DMF): δ (ppm/250 MHz) = 10.94 s (1H, OH; H-D exch.), 9.67 s (1H, OH; H-D exch.), 7.94, 6.91 (AA'BB'); 8.15 s (8.68 Hz, 4H aromat.), 6.88 s (2H, NH₂), 5.48-5.32 (m; 1H, CH, H₂.), 4.75 s (2H, NH₂), 4.73 s (2H, NH₂), 4.72 s (2H, NH₂), 4.67 s (2H, NH₂), 3.21 s (2H, NH₂), 2.04 s (2H, NH₂), 1.75 s (2H, CH₂), 1.71 s (2H, CH₂), overlap with solvent signals), 0.78 s (4H aromat.); 785.0 (M - I + DMSO + glycerol); 724.8 (M - I + DMSO); 646.9 (M - I°).

eythoro-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (150 and 151)

Diaqua/sulfato-1,3-diphenylpropane-1,3-diamino-Pt(II) complexes

Under light protection a suspension of 0.5 mmoles of the pertinent diiodo-1,3-diphenylpropane-1,3-diamino-Pt(II) complex and 148 mg (0.475 mmole) of Ag₂SO₄ in 20 ml of water was stirred for several days, until the reaction for Ag⁺ with 20% NaOH in the supernatant is negative. Then AgI was separated by millipore-filtration and the filtrate was freeze-dried. The complexes were obtained as colourless powders. Melting points cannot be determined.

eythoro-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3,4-dihydroxyphenyl)propane-1,3-diamino-Pt(II) (152)

From 140 54%. C₂H₆N₂O₇PtS x 3 H₂O (638.6) Calcd. C 28.2 H 4.42 N 4.4 Found C 28.1 H 4.32 N 4.4.- FT-IR (KBr): v = 3407 s, br (OH), 3240 s, 3134 m, 3125 s (NH₃); 2969 w (C-H aliph.); 1603 s, 1593 s (C=C and NH₂). ⁻¹-H-NMR (D₂DMF): δ (ppm/250 MHz) = 10.81 s (1H, OH; H-D exch.), 9.74 s (1H, OH; H-D exch.), 7.60-6.82 (m; 4H aromat.), 6.88 s (2H aromat.), 5.88-5.56 (m; 2H, NH₂), 5.30-5.12 (m; 1H, NH₂), 4.89-4.62 (m; 2H, 1H and 1NH₂), 4.58 s (br; 1H, CH, 2.96 (ABXY; 1H, CH₂, H₂), overlap by solvent signals), 2.23 s (ABXY; 1H, CH₂, H₂), 1.48 s (AA'BB'); 1.20 s (2H, NH₂), -1FAB-Ms (glycerol/DMSO)Pt; m/z = 835.1 (M + H + DMSO); 817.1 (M - I + DMSO + glycerol)*; 739.1 (M - I + glycerol)*; 667.2 (M - D°).

eythoro-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (153)

From 151 62%. C₂H₆N₂O₇PtS x 0.5 H₂O (626.5) Calcd. C 28.8 H 3.70 N 4.5 Found C 28.9 H 4.06 N 4.7.- FT-IR (KBr): v = 3401 s, br (OH and H₂O); 3214 s, 3112 m (NH₂); 2965 w, 1942 w (C-H aliph.); 1591 s (C=C and NH₂). ⁻¹-H-NMR (D₂DMF): δ (ppm/250 MHz) = 10.94 s (1H, OH; H-D exch.), 9.67 s (1H, OH; H-D exch.), 7.74, 6.86 (AA'BB'); 1.48 s (AA'BB'); 1.20 s (2H, NH₂), 6.94 s (2H aromat.), 5.50-5.77 (m; 1H, NH₂), 5.77-5.60 (m; 1H, NH₂), 4.94-4.75 (m; 1H, CH, 2 NH₂), 4.79-4.66 (m; 1H, CH, 2 NH₂), 3.23 (ABXY; 1H, CH₂, H₂), 2.84 (2H, NH₂), 1.54 (1H, CH₂, H₂), 0.78 (4H aromat.); 785.0 (M - I + DMSO + glycerol)*; 724.8 (M - I + DMSO)*; 646.9 (M - I°).

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erythro-Diaqua(sulfato-1-(2-fluoro-4-hydroxyphenyl)-(4-hydroxyphenyl)propene-1,3-diamino-Pt(II)) (155)

From 142; 72%: C_{13}H_{30}F_{3}N_{2}O_{6}PtS x H_{2}O (639.5) Calcd. C 28.2 H 3.94 N 4.4 Found C 28.2 H 3.99 N 4.6 - FT-IR (KBr): \( \nu = 3422 \) s, br (OH and H_{2}O); 3206 s, 3125 m (NH_{2}); 2963 w, 2929 w (C-H aliph.); 1628 s (NH); 1597 s (C=C); 1223 s, 1178 s, 1032 m, 968 m, 617 m, 592 m (SO_{2}) \(-1\) H-NMR ([D_{2}]DMF): \( \delta \) (ppm/250 MHz) = 7.49-6.78 (m; 6H aromat.), 4.55 (ABXY; 1H, CH, overlap with solvent signals), 2.49 (A_{2}X_{2}; \( J_{AX} = 5.0 \) Hz, 2H, CH_{2}).

three-Diaqua(sulfato-1-(2-fluoro-4-hydroxyphenyl)-(4-hydroxyphenyl)propene-1,3-diamino-Pt(II)) (156)

From 143; 84%: C_{13}H_{27}F_{2}N_{2}O_{6}PtS (603.5) Calcd. C 29.9 H 3.51 N 4.6 Found C 29.8 H 3.37 N 4.7 - FT-IR (KBr): \( \nu = 3374 \) s, br (OH and H_{2}O); 3218 s, 3129 m (NH_{2}); 2967 w (C-H aliph.); 1628 s, 1616 s (NH); 1597 s (C=C); 1209 m, 1182 s, 1024 s, 588 m (SO_{2}) \(-1\) H-NMR ([D_{2}]DMF): \( \delta \) (ppm/250 MHz) = 8.05-6.82 (m; 6H aromat.), 4.69 (ABXY; 1H, CH), 4.42 (ABXY; 1H, CH, overlap with solvent signals), 2.95 (A_{2}X_{2}; \( J_{AX} = 5.0 \) Hz, 2H, CH_{2}).

erthro-Diaqua(sulfato-1-(2-chloro-4-hydroxyphenyl)-(4-hydroxyphenyl)propene-1,3-diamino-Pt(II)) (157)

From 144; 48%: C_{13}H_{18}ClN_{2}O_{6}PtS x 4 H_{2}O (690.2) Calcd. C 26.0 H 4.22 N 4.0 Found C 25.6 H 3.62 N 4.0 - FT-IR (KBr): \( \nu = 3407 \) s, br (OH and H_{2}O); 3210 s, 3116 m (NH_{2}); 2970 w (C-H aliph.); 1613 s, 1582 s (C=C and NH_{2}); 1178 s, 1115 m, 1030 m, 947 w, 592 m (SO_{2}) \(-1\) H-NMR ([D_{2}]DMF): \( \delta \) (ppm/250 MHz) = 7.49-6.78 (m; 6H aromat.), 4.68 (ABXY; \( J_{AX} = 5.0 \) Hz, 1H, CH), 4.34 (ABXY; \( J_{AX} = 5.0 \) Hz, 1H, CH), 5.16 (ABXY; \( J_{AX} = 5.0 \) Hz, 1H, CH), 2.50 (A_{2}X_{2}; \( J_{AX} = 5.0 \) Hz, 2H, CH_{2}).

three-Diaqua(sulfato-1-(2-chloro-4-hydroxyphenyl)-(4-hydroxyphenyl)propene-1,3-diamino-Pt(II)) (158)

From 145; 55%: C_{13}H_{20}ClN_{2}O_{6}PtS x 0.5 H_{2}O (629.0) Calcd. C 28.6 H 3.53 N 4.5 Found C 28.4 H 3.16 N 4.3 - FT-IR (KBr): \( \nu = 3424 \) s, br (OH and H_{2}O); 3260 s, 3120 m (NH_{2}); 2969 w (C-H aliph.); 1611 s, 1578 s (C=C and NH_{2}); 1209 s, 1113 s, 1036 m, 953 w, 592 m (SO_{2}) \(-1\) H-NMR ([D_{2}]DMF): \( \delta \) (ppm/250 MHz) = 7.98-6.83 (m; 4H aromat.), 4.28 (A_{2}X; \( J_{AX} = 5.0 \) Hz, 1H, CH), 4.00 (A_{2}X; overlap with solvent signals), 2.46 (A_{2}X; \( J_{AX} = 5.0 \) Hz, 2H, CH_{2}).

References


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