1,3-Diphenylpropane-1,3-diamines, V[1,2]:

^{1}H-NMR- and IR-Spectroscopic Data of 1,3-Diphenylpropane-1,3-diamines and their Pt(II) Complexes: Stereochemical Assignments and Binding Mode of the Non-amine Ligands

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The ^{1}H-NMR spectra of some 1,3-diacetamino-1,3-diphenylpropanes and of the dichloro-Pt(II) complexes of the corresponding diamines are compared with their simulated spectra leading to the stereochemical assignments *meso* / *rac* and *erythro*/*threo*, respectively.- IR-spectra data of our "diaqua/sulfato complexes" indicate coordinated as well as free (counterionic) sulfate.

^{1}H-NMR- und IR-spektroskopische Untersuchungen an 1,3-Diphenylpropan-1,3-diaminen und ihren Pt(II)-Komplexen: Stereochemische Zuordnung und Bindung der nicht-aminischen Liganden

Die ^{1}H-NMR-Spektren einiger 1,3-Diphenylpropan-1,3-diamine und ihrer Dichlor-Pt(II)-Komplexe wurden mit den berechneten Spektren verglichen und führten so zu den stereochemischen Zuordnungen *meso* / *rac* bzw. *erythro*/*threo*.- Die IR-spektroskopischen Daten unserer "diaqua/sulfato Komplexe" weisen auf koordiniertes und freies (gegenionisches) Sulfat in diesen Verbindungen hin.

In part III[1)] of this series we have reported on the syntheses of the title ligands, while part IV[2)] deals with the preparation of their Pt(II) complexes with Cl^-, I^-, SO_4^{2-}, and water as additional ligands.- The ^{1}H-NMR spectra of the ligands and their Pt complexes have been compiled in the Experimental Parts of these publications, and the ligands were assigned *meso* / *rac*, and *erythro*/*threo*, respectively, without giving an explanation for these indications.

Here we describe the arguments of these assignments based on ^{1}H-NMR measurements. Because we are dealing with complicated spin systems with various nuclei, the assignment of the protons by conventional methods is difficult in most cases. Therefore, we have simulated the spectra with the help of a Comparex 8/85 computer (system VM/CMS 5.0) using the program LAME (**LAOCOON** with **M**agnetic **E**quivalence). This is a variation of LAOCOON[3)] modified by *Haigh*, Swansea College, *Knorr*, München, and *Poppinger* and *Vollmerhaus-Koschnik*, Regensburg (unpublished). LAME considers nuclei of spin 1/2 only and maximally accepts seven groups of magnetically equivalent spins. If one or several of these groups contain more than one spin, there are additional limitations.

At first LAME calculates a theoretic spectrum with line frequences and line itensities in a non-iterative run, using a set of estimated chemical shifts and J-values. In most cases this spectrum does not yet fit the observed one. So, in an iterative run the frequence of a line of the experimental spectrum is attributed to the number of each calculated line. This step is decisive for a good result and, therefore, the lines are attributed according to *Hoffmann et al.*[4)]. The subsequent calculation is based on the assumption, that the set of parameters is the best one "which make the sum of the squared residuals of the observables (in this case, transition frequencies) a minimum"[3)].

$$\sum_{i=1}^{k} (f_{exp} - f_{ber})_i^2$$

k: number of observed lines

$(f_{exp} - f_{calc})$: difference of frequencies between observed and calculated transition

LAME then looks for alterations of those parameters in order to fit the observed and calculated data by indicating a new set of chemical shifts and J-values corresponding to the newly calculated frequencies, combined with a calculus of error. At the end various iterative cycles converge to the correct result.

The diastereomers of the title ligands are separated as their bisacetamides[5)] which in addition allow the attribution *meso* / *rac* to the stereomers. Here we discuss the ^{1}H-NMR spectra of *meso*-1,3-diacetamino-1,3-bis-(3,4-dimethoxyphenyl)propane (**1**) and of the *rac*-diastereomer **2**, exemplary of the situation in all the other *meso* / *rac*-forms described in part III[1)]. Both compounds show a doublet ($J \approx 7.5$ Hz) for the NH group. The chemical shift of this signal strongly depends on the solvent: in $CDCl_3$ (as in our example) it resonates at 6.0-6.3 ppm, whilst on account of reasons which are still unknown to us (H-bridges?) in DMSO it is shifted to 8.0-8.5 ppm. This solvent dependence was found in all cases checked.- The NH-signal of the *meso*-diastereomer is always found at lower field strength than that of the *rac*-form. The protons of the phenyl-, the methoxy-, and the acetyl-groups, resonating as one signal group each, differ only insignificantly. The methin-H's of both

*) Dedicated to Prof. Dr. *H. J. Roth*, Tübingen, on the occasion of his 65th birthday.

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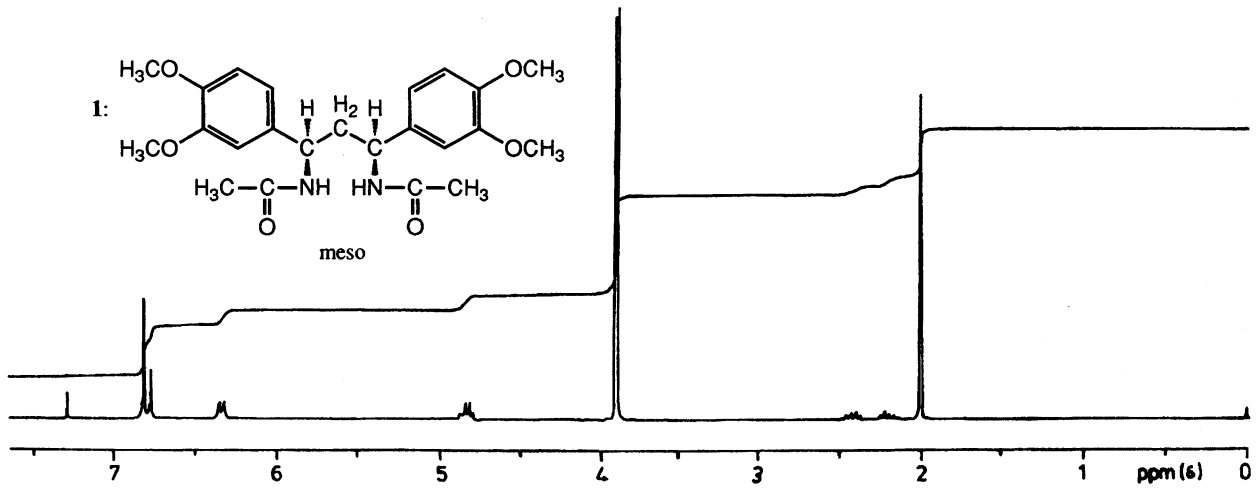


Fig. 1: 250 MHz-^{1}H-NMR spectrum of *meso*-1,3-diacetamino-1,3-bis-(3,4-dimethoxyphenyl)propane (**1**).- For enlargement see Fig. 4.

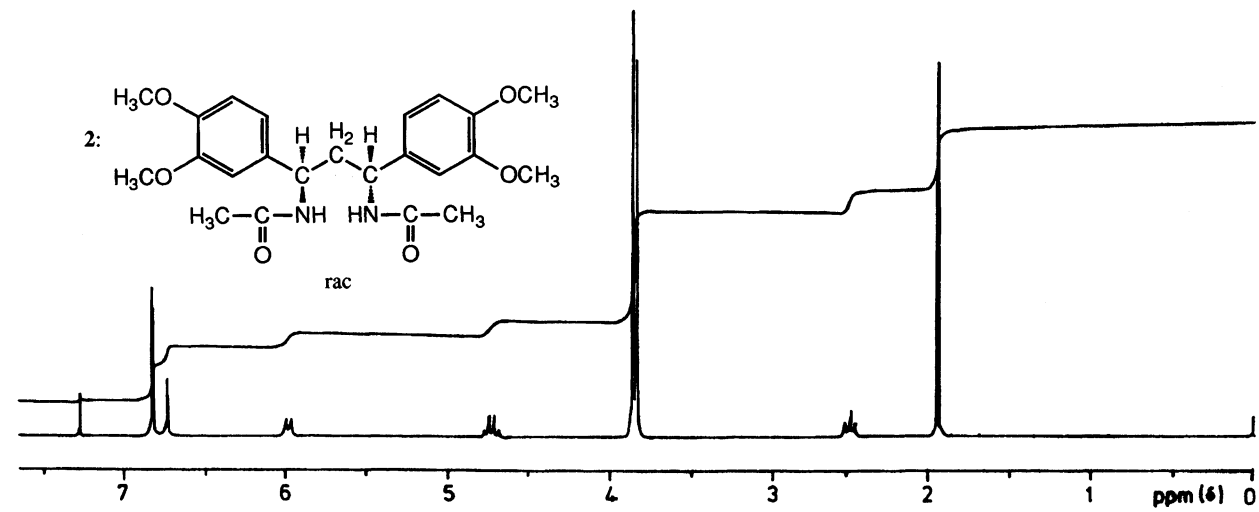


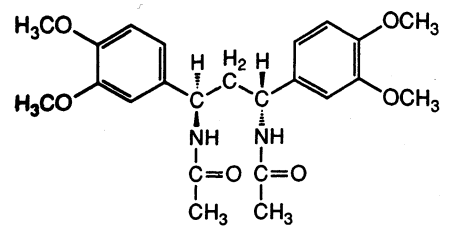
Fig. 2: 250 MHz-^{1}H-NMR spectrum of *rac*-1,3-diacetamino-1,3-bis-(3,4-dimethoxyphenyl)propane (**2**).- For enlargement see Fig. 4.

diastereomers result in one signal only (*meso*: m at 4.86-4.78 ppm, 2H; *rac*: m at 4.76-4.67 ppm, 2H, cf. Part I, ref.[5], compounds 5b in that publication), consisting of four symmetrically arranged lines. The diastereomers **1** and **2** can be distinguished, however, on account of the characteristic differences of the methylene protons: in the *rac*-form **2** they lead to a triplet at 2.47 ppm, whilst in the *meso*-form each H of the CH_2-group forms a multiplet of five lines which are arranged mirror-invertedly (δ = 2.41 and 2.18 ppm, respectively). This is due to the fact that the methylene-H's are diastereotopic in the *meso*-form, whilst they are chemically equivalent (homotopic) in the *rac*-form (for arguments see ref.[5]). Therefore, they resonate as an ABX_2 system in the *meso*-stereomer and as an A_2X_2 spin system in the *rac*-form.

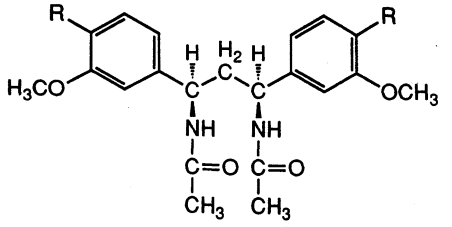
Bovey et al.[6] have demonstrated this assignment for *meso*- and *rac*-2,4-diphenylpentane, *Doskočilová et al.*[7] for 2,4-pentanediol-diacetate, *Pritchard et al.*[8] for pentane-2,4-diol, *Fujiwara et al.*[9] for pentane-2,4-diol and its diacetate, *McMahon et al.*[10] for 2,4-dichloro-, 2,4-dibromo-, and 2,4-dicyanopentane and for pentane-2,4-diol, *Meier*[11] for 2,4-diaminoglutaric acid, and *Murano et al.*[12] for pentane-2,4-diamine and its diacetate.

We had expected an ABXY system for the *meso*-form **1**, but the spectrum is reduced to the ABX_2 spin system as in all the spectra cited in part III[1], probably on account of rapid interconversion of the two "low energy rotational isomers" as formulated by *McMahon*[10]. This is proven by comparison of the observed data and the simulated ones for the methin- and methylene-protons of *meso*-1,3-diacetamino-1,3-bis-(3-methoxyphenyl)propane (**3**) (Fig. 3).

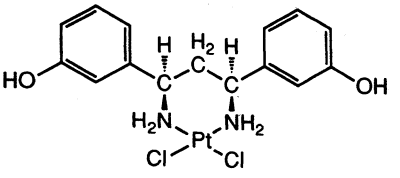
For the *rac*-diastereomer of pentane-2,4-bisacetamide *Murano*[12] found two triplets for the CH_2-protons (AA'XX' system), as did *Bovey*[6], *Doskočilová*[7], and *McMahon*[10] for their molecules (*vide supra*). For pentane-2,4-diamine and for pentane-2,4-diol, however, one triplet was found only[8-10]. The authors substantiate this difference by assuming that in the diamine and in the diol the two most frequently occuring conformations are of equal probability,



2 (rac)



meso: 1: R = OCH_3
3: R = H



4 (meso)

Scheme 1

whilst in the bisacetamide, *e.g.*, one conformation is prevailing on account of steric hindrance. Fig. 2 does not show such a hindrance for the racemate **2**, *e.g.*: there is only one triplet, and - curiously enough - the bulky phenyl- and acetamido-groups do not cause steric hindrance and a dominating conformation. Therefore, this situation is regarded to be an A_2X_2 system.- Fig. 4 shows the observed and calculated spectra for the methin- and methylene-protons of **1** and **2**.

The assignments *meso* and *rac* for the diastereomers **1** and **2** is proven by the separation of **2** on a chiral column, whilst **1** could not be resolved under identic conditions[5].

Pt(II) complexes of *meso*- and *rac*-configurated ligands

In general 6-membered chelate rings are more flexible than 5-membered ones. These 6-membered rings can adopt chair-, δ- and λ-skew boat-, and boat conformation. According to ^{1}H- and ^{13}C-NMR-results[13], confirmed by calculations of the conformation energies[14], the chair conformation is the most stable one. One chair conformation is transformed to the other one *via* a skew boat conformation. For our compounds we expected a restriction of the conformational mobility of the 6-membered chelate ring on account of the bulky phenyl groups. *Noji et al.*[15a] have investigated *meso*- and *rac*-1,3-diphenylpropane-1,3-diamino-diammine-Pt(II) dichlorides by ^{13}C-NMR techniques. The coupling constant of ^{195}Pt with C-1 of the phenyl ring ($^3J_{Pt\text{-}N\text{-}C\text{-}C\text{-}1}$) depends on the dieder angle between Pt-N-C and N-C-C-1, as shown by results also obtained with Pt(II) complexes of other ligands[16-18]. Then, ^{195}Pt satellites occur in the ^{13}C-NMR spectrum. For their *meso*-stereomer, *Noji*[15a] found both phenyl rings to be arranged equatorially, indicating a chair conformation. Contrary to the λ-skew boat conformation with equatorial-axial position of the phenyl rests, this is the stable conformation[15a]. For the R,R-form, having the phenyl rings axial-equatorial in the chair-conformation and diequatorially arranged in the λ-skew boat conformation[15b], the authors found a rapid interchange of the possible conformations in spite of the bulky phenyl groups[15a].

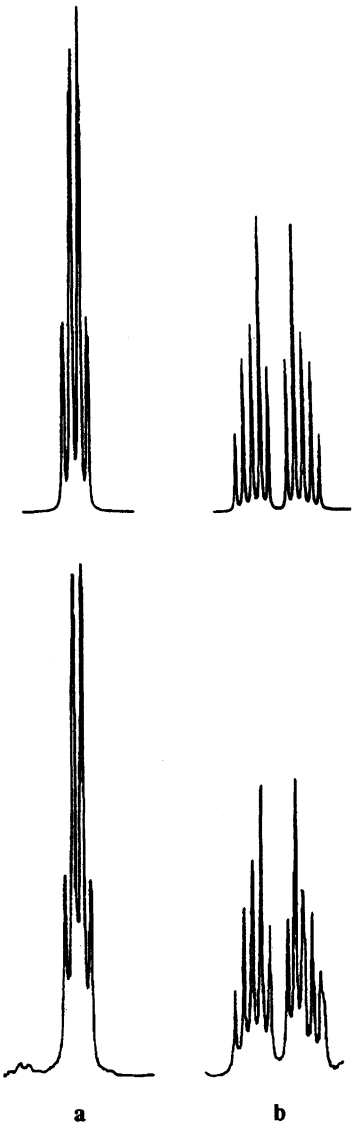


Fig. 3: Comparison of observed (top) and calculated (bottom) ^{1}H-NMR spectra of the methin-(**a**) and methylene-(**b**) protons of *meso*-1,3-diacetamino-1,3-bis-(3-methoxyphenyl)propane (**3**).

In our compounds there was no coupling between C-1 (aromat.) and ^{195}Pt, so excluding pertinent analyses. This may be due to the fact that dichlorides, *id est* charged complexes, have been investigated by *Noji*[15a], *Erickson*[16], and *Yano*[17] in D_2O, whilst our complexes are not charged and were measured in [D7]DMF. An assignment on the basis of $^3J_{Pt\text{-}N\text{-}C\text{-}H}$ is not possible in DMF because the signals of the ^{1}H-NMR-spectrum are broadened only, but there are no sharp ^{195}Pt satellites as in acetone or D_2O.

As an outlet we determined the dominant conformation of our complexes using the J-value of the methylene- and methin-protons. The ^{1}H-NMR spectra of the complexes **4** (*meso*) and **5** (*rac*) are distinctly different (Fig. 5 and 6),

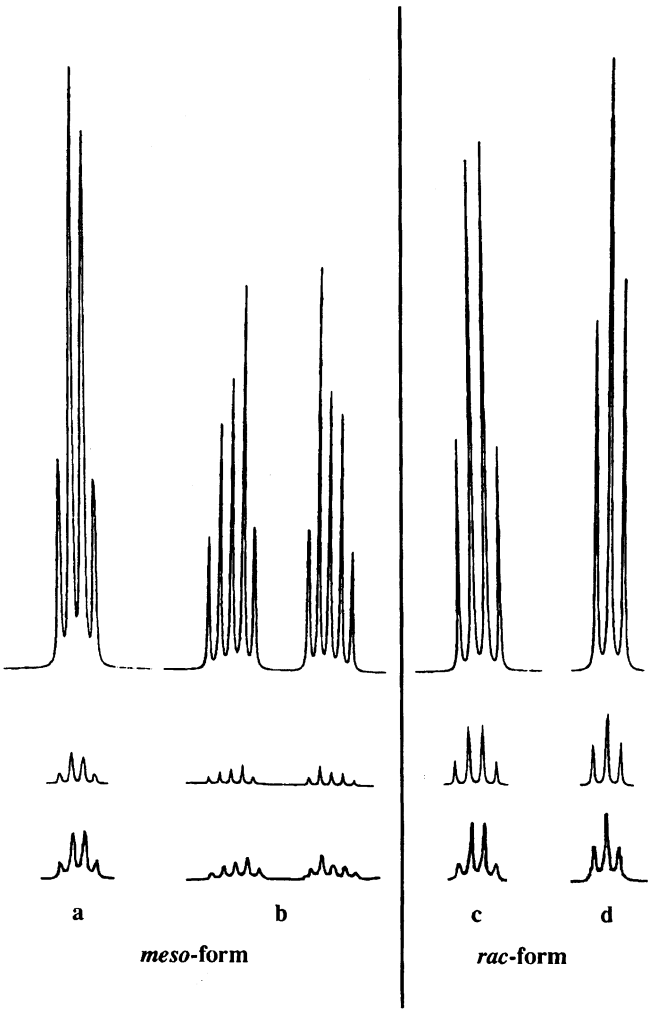
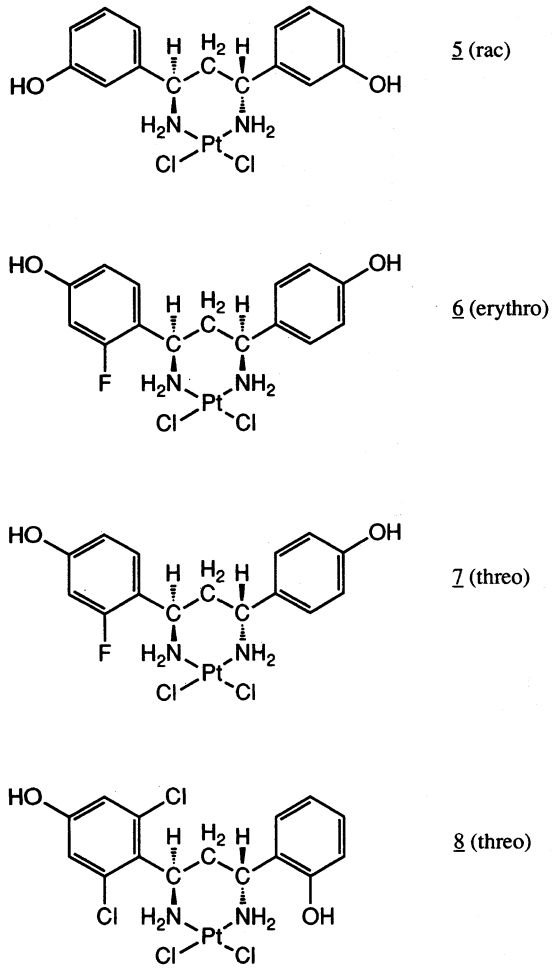


Fig. 4: **1** (*meso*)- and **2** (*rac*)-compounds: comparison of the observed (bottom) and calculated ^{1}H-NMR spectra (middle) of the methin-(**a**;**c**) and methylene-(**b**;**d**) protons. Top: calculated spectra with enlarged amplitude.



Scheme 2

and the CH- and CH_2-signals give decisive information about the conformation. We have analyzed these signals after H/D-exchange (simplification by abolishing the H-C-N-H-coupling): in the *meso*-complex **4** both CH-protons resonate at δ = 4.43 ppm as a "doublet" (ABX_2), followed by a mc for CHH at 2.44 ppm and a "doublet" for CHH at 1.98 ppm. According to computer simulation these "doublets" are non-resolved multiplets with a big and a small coupling constant each, resulting in a ^{3}J-value of about 1 Hz for the coupling of both CH-protons to CHH and of about 11.9 Hz to CHH. The methylene protons show ^{2}J = 14.8 Hz. In conclusion, we find an ABX_2 system. According to *Karplus'* equation the angle between the methin protons and one of the methylene-H's should be about 180°, that with the other methylene-H about 60°. This fits very well for the chair-conformation of the *meso*-form (both phenyl rings equatorially oriented) as observed by *Noji*[15a]. A diaxial arrangement of the phenyl groups is unlikely, because the phenyl rings hamper their free rotation reciprocally, as indicated by *Dreiding* models. The methylene-H leading to a "doublet" is, therefore, oriented equatorially, the methylene-H, forming a multiplet, stands axially. In conclusion: this *chair conformation with equatorial arrangement of the phenyl rings is the favoured one of the meso-form of our complexes.*

After H/D exchange, the spectrum of the *rac*-diastereomer **5** is very different from that of **4**. Both CH-protons and the methylene-H's resonate as broad "triplets" at 3.97 ppm and 2.41 ppm, respectively, with ^{3}J = 5 Hz. Obviously, there is no separation of the methylene-H's as it should result from a chair conformation with equatorial/axial phenyl rings. We see an A_2X_2 system indicating a rapid (NMR time scale) interconversion of the chelate ring with the intermediacy of a favoured δ-skew boat-conformation with both phenyl rings oriented equatorially. *On the whole there is no dominant conformation in the rac-stereomer.* This result coincides with those of *Noji*[15a]. We have tried to prove this conclusion by NMR measurements at low temp. which we expected to separate the signals of the methylene-H's, but even at -80°C we obtained broadening of the signals only. This points towards a slowed down but still existing change of conformations. Analogous results are reported by *Apple-*

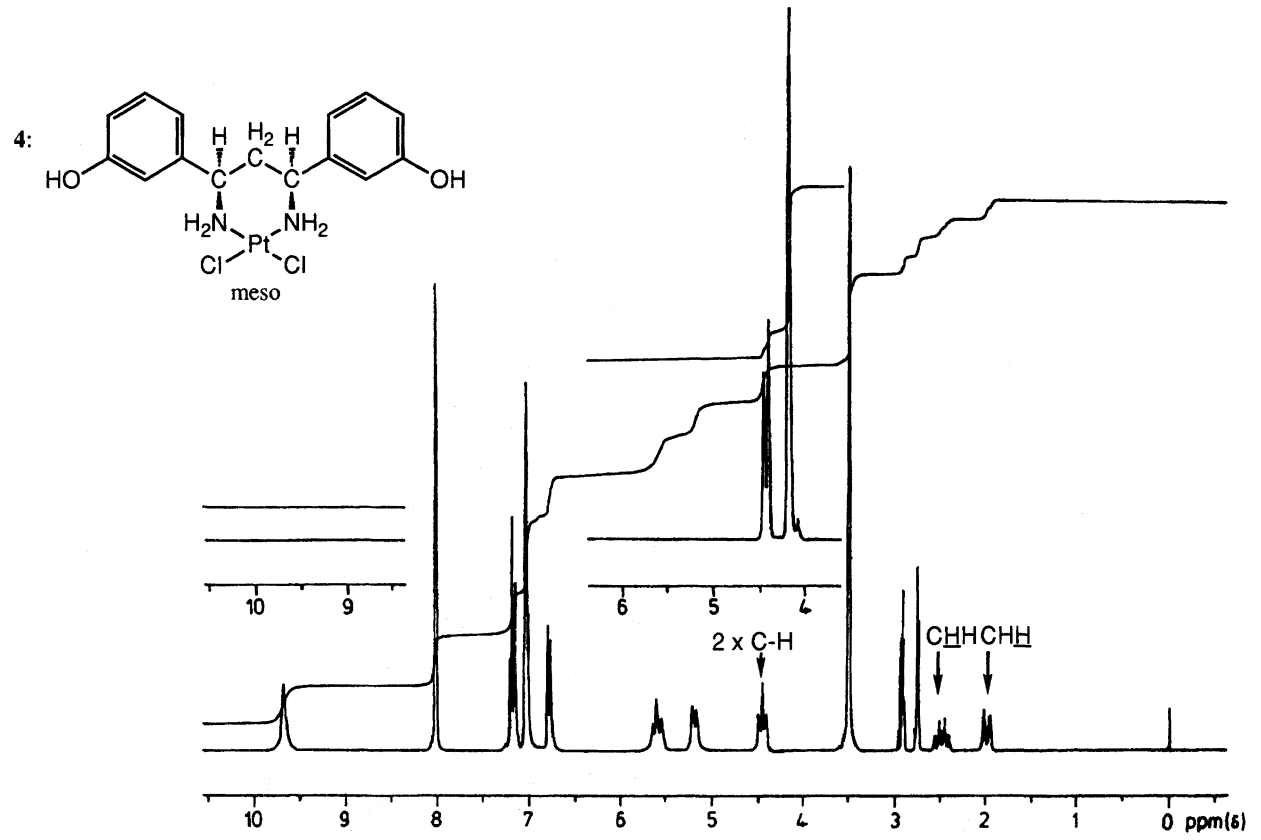


Fig. 5: 250 MHz-^{1}H-NMR spectrum of *meso*-dichloro-[1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (**4**). Upper scale after H/D exchange.

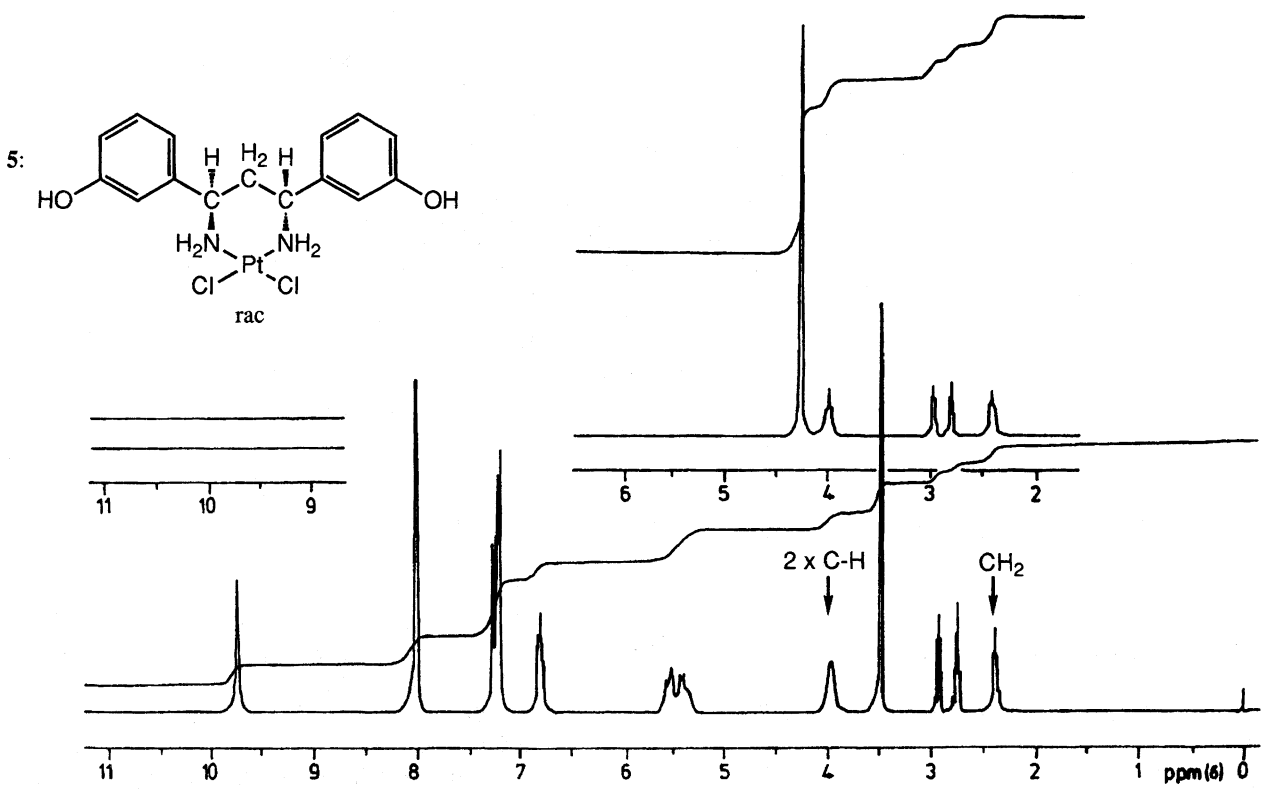


Fig. 6: 250 MHz-^{1}H-NMR spectrum of *rac*-dichloro-[1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (**5**). Upper scale after H/D exchange.

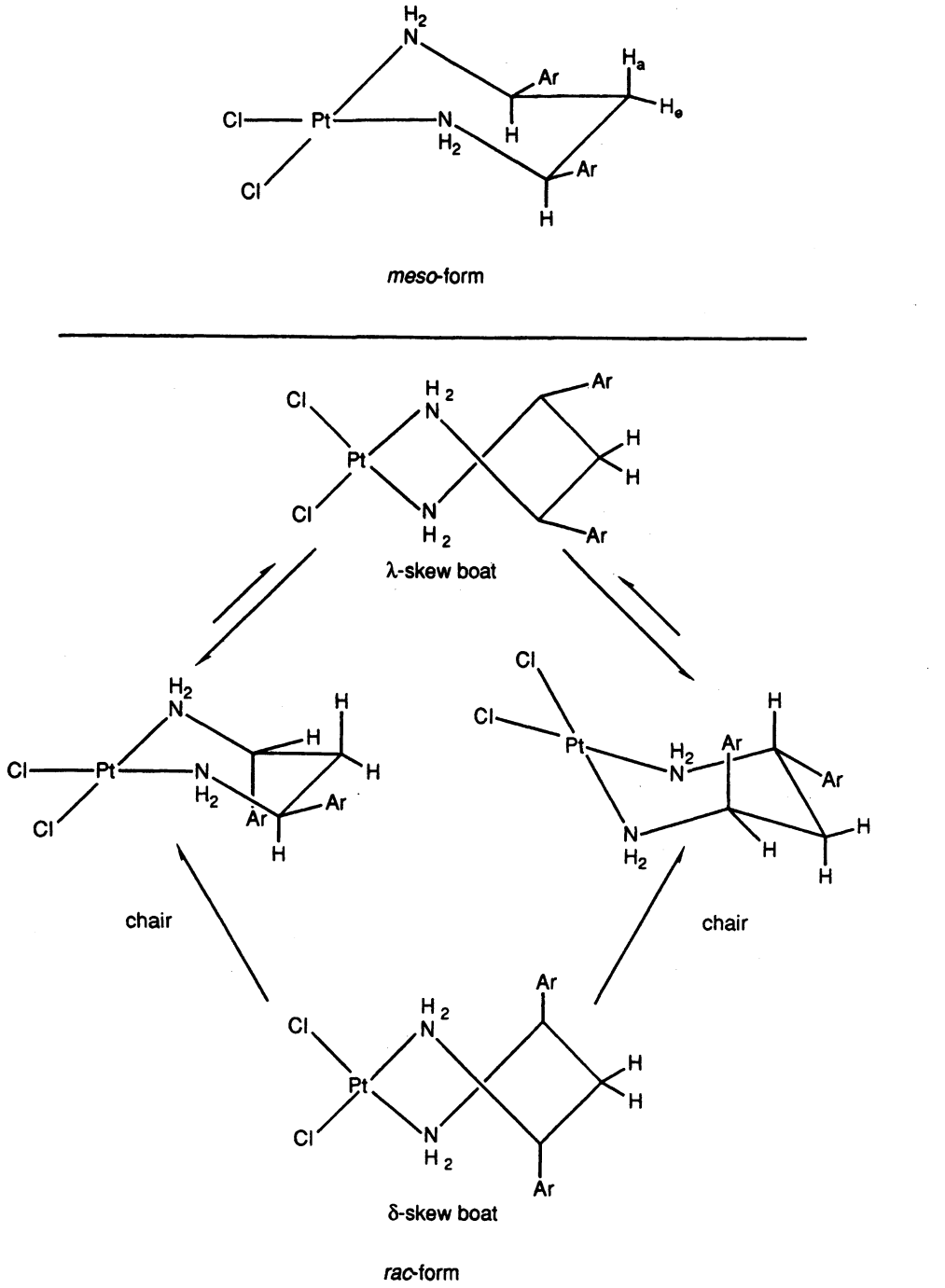


Fig. 7: Conformations of *meso*- and *rac*-dichloro-[1,3-diphenylpropane-1,3-diamino]-Pt(II) complexes.

ton[19] for the measurements of *rac*-pentane-2,4-diamine-Pt(II) complexes.

All our results coincide with those of *Appleton*[19] obtained for a related complex. The conformations of our complexes are given in Fig. 7, and Fig. 8 shows the observed signals of the methylene- and methin-protons of *meso*-(**4**) and *rac*-(**5**) dichloro-[1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino]-Pt(II) complexes in comparison with those of the simulation. The broadening of the experimentally obtained signals - due to the viscosity of DMF, which reduces the separation - can not be simulated in the computer (the broadening is probably also due to ^{195}Pt satellites laying underneath these signals).

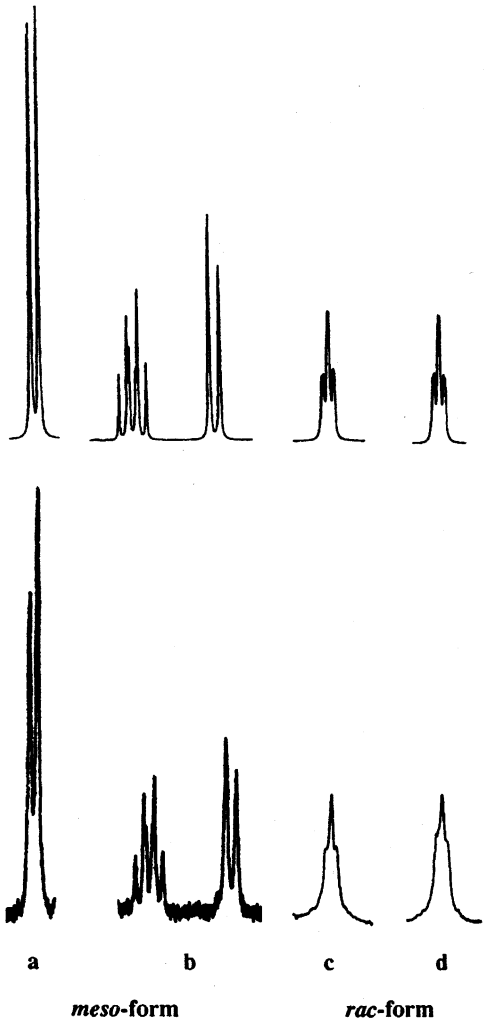


Fig. 8: Comparison of the observed (bottom) and calculated (top) ^{1}H-NMR spectra of **4** and **5**: methin-(**a**;**c**) and methylene-(**b**;**d**) protons.

Erythro- and *threo*-assignment of Pt complexes of ligands with different substitution patterns of the phenyl groups

The assignment *erythro* / *threo* at the stage of the bis-acetamides was not possible, because the ^{1}H-NMR-spectra of this highly mobile system are too complicated and, moreover, there are no reports on related compounds. After complexation of the bisamines, however, the spectra highly resemble those of the *meso*- and *rac*-complexes. So, stereochemical assignments become possible. This is illustrated by the 250 MHz-^{1}H-NMR-spectra of *erythro*-(**6**) (Fig. 9) and *threo*-dichloro-[1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (**7**) (Fig. 10).

In the spectrum of that compound which turned out to be the *erythro*-stereomer, a "doublet" at 4.57 ppm is found for one CH-proton; a "doublet" of the second CH-group at 4.51-4.35 ppm is overlapped by the water signal after H/D exchange. One of the methylene protons resonates as a multiplet at 2.54 ppm, the other one as a "doublet" at 1.99 ppm. The J-values correspond more or less to those of the *meso*-forms, indicating equatorial arrangement for both phenyl rings. We, therefore, conclude that complex **6** has the same chair conformation as the *meso*-form and consequently we have assigned the prefix *"erythro"* to the pertinent ligand. The only difference stems from the *separated* signals for the methin-H's (cf. Fig. 5: *one* signal at 4.43 ppm), but this was expected because their chemical environment is different.

The magnitude of the J-values in the spectrum of that diastereomer identified to be the *threo*-form -**7**- corresponds to that of the *rac*-form. Also here the non-equivalence of the methin-protons leads to two signals at 4.20 and 4.03 ppm, but in parallel to the *rac*-complex **5** (signal at 2.41 ppm) only one signal for the methylene-H's arises at 2.35 ppm. All these signals are broad "triplets". Analogously to the *rac*-forms this points towards a rapid interchange of chair-conformations. These findings suggest that the diastereomer **7** is the *threo*-form. Fig. 11 shows the observed and calculated data of the methin- and methylene-protons of diastereomers **6** and **7**. Here again the experimental signals are broadened by the solvent DMF.

These conclusions cannot be extended to compounds having a 2,6-dichloro-4-hydroxy-substituted phenyl ring. In this case the signals of the methin- and methylene-H's of the *erythro*-stereomer correspond to those of *erythro*-forms with a lower degree of substitution. We only observe a shift to lower field strength affording signals - not overlapped by solvent signals - for each methin proton.- On the other hand, however, the spectra of the *threo*-form - dichloro-[*threo*-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (**8**) *e.g.* - differ from those *threo*-forms of lower substitution grade: we see one signal for each methin-H, but only one is still a broad "triplet" (δ = 4.55 ppm) whilst the other one looks like a "doublet" (δ = 4.63 ppm). Here also the signals for the methin-H's are separated: one forms a multiplet at 2.86 ppm - mainly overlapped by solvent signals, cut off in Fig. 12 - the other one leads to a "doublet" at 2.33 ppm with small coupling constants. - According to the computer simulation the "doublet" at 4.63 ppm is a multiplet with a small and a big coupling constant (1.5 and 11.1 Hz, respectively), whilst the "triplet" at 4.55 ppm comprises a J-value of about 2 Hz. This points towards the fact that one methin-H shows an axial-axial- and axial-equatorial-coupling, indicating axial position, whilst the other methin-H is characterized by equatorial-equatorial- and equatorial-axial-coupling as it is expected for an equatorial position.

For the methylene-protons the "doublet" with two small coupling constants is attributed to the equatorial methylene-H, whilst the multiplet at 2.86 ppm is due to the axial methylene-H. From these results we conclude that - contrary to the *rac*- and *threo*-stereomers with phenyl rings of lower substitution pattern (*vide supra*) - the *threo*-diastereomers of our Pt(II) complexes highly substituted at their phenyl rings do not interchange their conformation at room temp. For these compounds a chair conformation with one phenyl ring in axial and the other phenyl ring in equatorial position

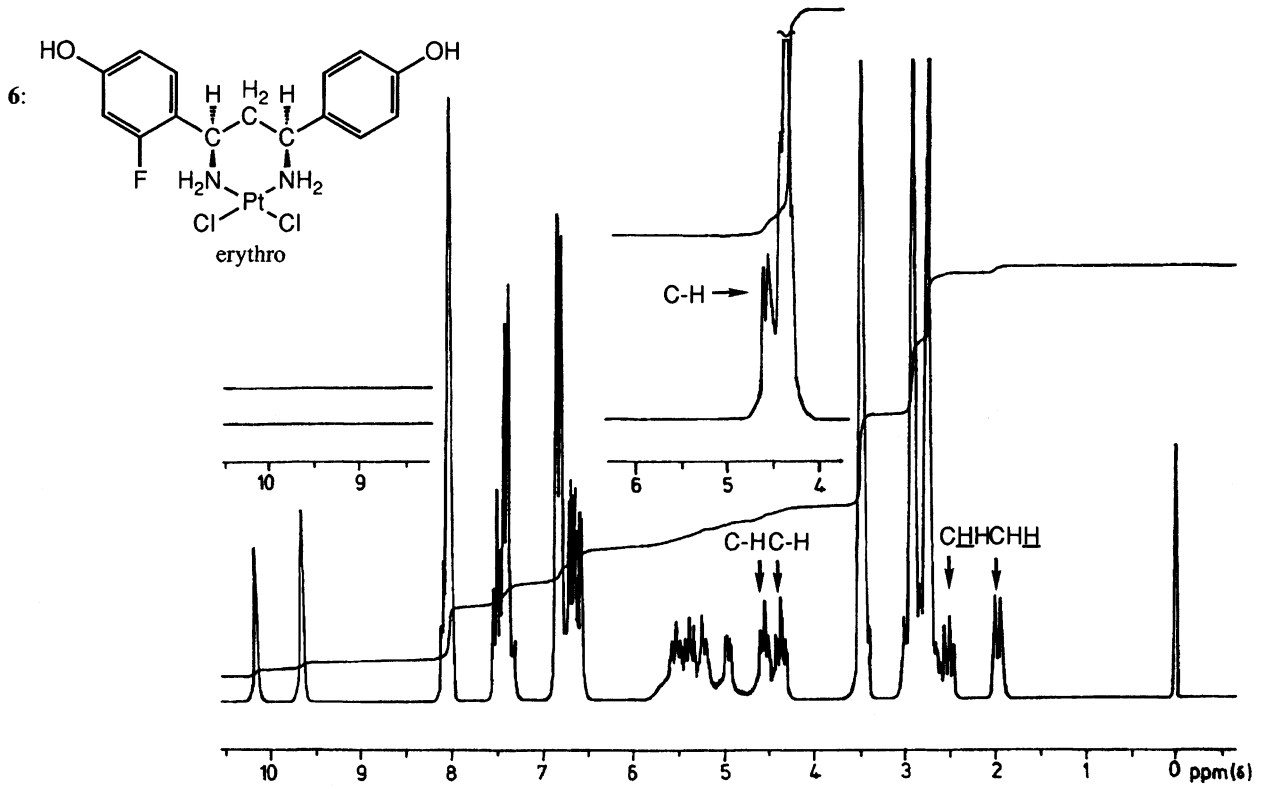


Fig. 9: 250 MHz-^{1}H-NMR-spectrum of *erythro*-dichloro-[1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (**6**). Upper scale after H/D exchange.

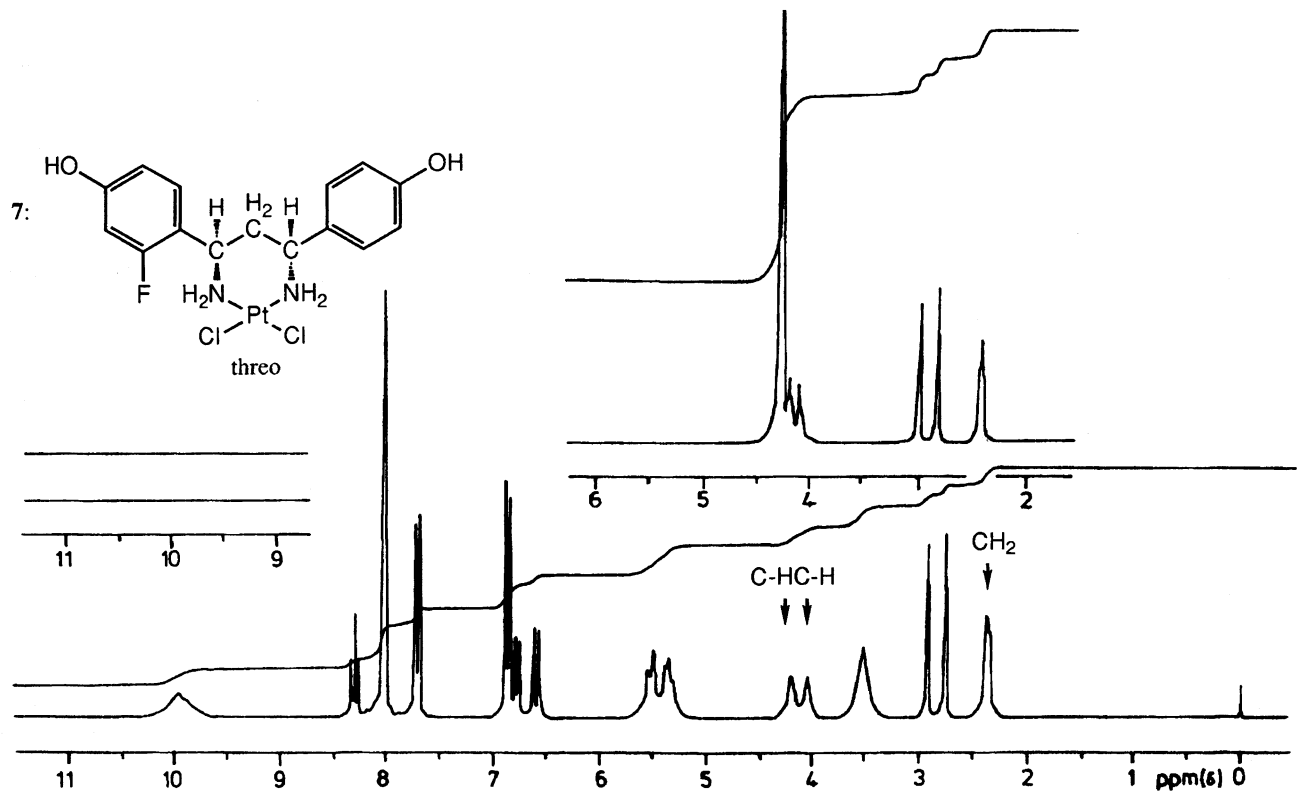


Fig. 10: 250-MHz-^{1}H-spectrum of *threo*-dichloro-[1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (**7**). Upper scale after H/D exchange.

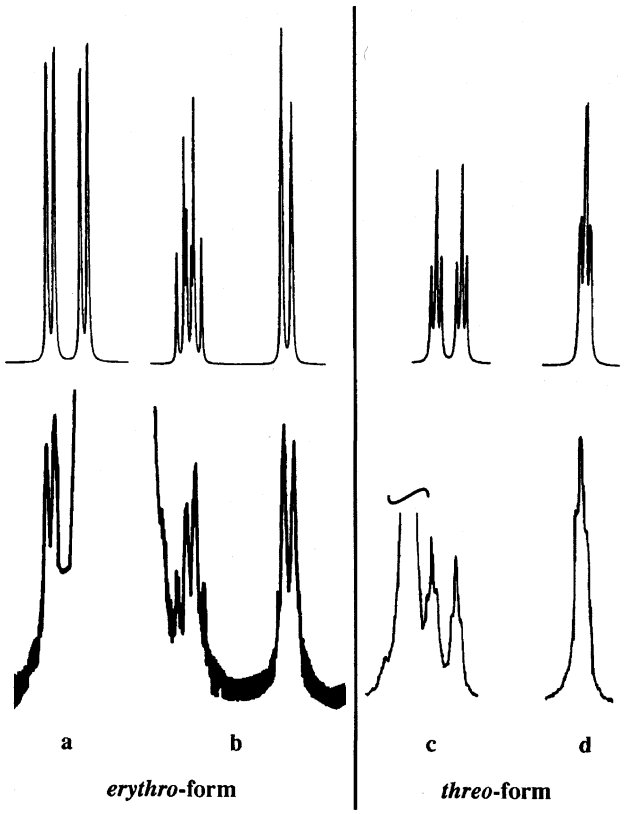


Fig. 11: **6** (*erythro*)- and **7** (*threo*)-complexes: comparison of the observed (bottom) and calculated (top) ^{1}H-NMR spectra of the methin-(**a**;**c**) and methylene-(**b**;**d**) protons after H/D exchange.

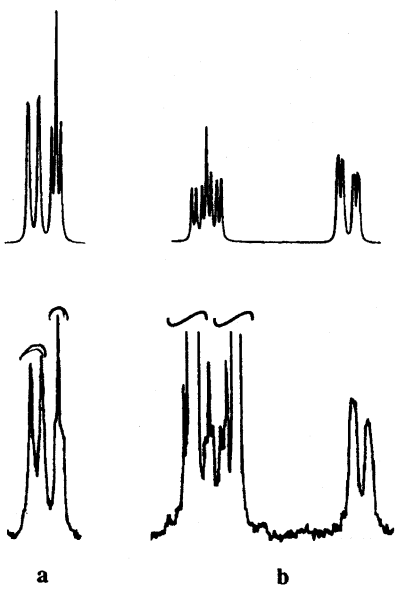


Fig. 12: Comparison of the observed (bottom) and calculated (top) ^{1}H-NMR spectra of the methin-(**a**) and methylene-(**b**) protons of *threo*-dichloro[-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (**8**) after H/D exchange.

looks favourable. On account of sterical reasons the 2,6-dichloro-4-hydroxy-phenyl ring most probably adopts the equatorial position, as it was found by *Gust et al.* for all the pertinently substituted 1,2-diphenylethane-1,2-diamino-Pt(II) complexes[20]. Fig. 12 shows the calculated and observed data for the methin- and methylene-H's for complex **8**.

IR-Spectra

a) *Dichloro-Pt(II) complexes*

All the dichloro complexes show similar FT-IR-spectra. That of complex **7**, *e.g.*, shows a weakly broadened OH valence vibration near 3400 cm^{-1}, followed by mostly four (in case of bad resolution occasionally only three) NH valence vibrations between 3300 and 3100 cm^{-1}. Near 1600 cm^{-1} the NH deformation vibrations come up, mostly coinciding with C=C stretching vibrations. The Pt-N- and the Pt-Cl-vibrations are considered to be characteristic for dichloro-diamino-Pt complexes, but the Pt-N-bands arise near 650-450 cm^{-1} in the region of the ring skeleton vibrations. Therefore, the pertinent indications in lit.[21,22] are contradictory and as a consequence we do not cite these absorp-tions of our complexes.- On the other side the localisation of the Pt-Cl vibration in the far IR-region near 320 cm^{-1} is unequivocal[22-24]. *cis*-Dichloro complexes should show two bands of medium intensity, because the vibrations are additive, but in a lot of cases, the second band is only a shoulder[24]. *trans*-Complexes show one band only[24]. For most of the 1,2-diphenylethane-1,2-diamine-Pt(II) complexes only one band was observed due to low resolution, independent from *cis*- or *trans*-configuration[25,26].

The IR-spectra of the diastereomeric pairs **4/5** and **6/7**, respectively, show the Pt-Cl band near 320 cm^{-1}, but the *rac*- and *erythro*-forms **5** and **6** show only one absorption on account of low resolution. In the *meso*-diastereomer **4**, however, the second band forms a shoulder, and the *threo*-stereomer **7** shows nicely separated absorptions at 330 and 320 cm^{-1}.

In conclusion the complexes show the expected IR-absorptions in the far IR-region characteristic for *cis*-configurated dichloro-Pt(II)-complexes.

b) *Diaqua/sulfato complexes*

As explained in part IV[2] of this series, we have chosen the term "diaqua/sulfato" in order to indicate that we cannot differentiate conclusively between free counterionic sulfate (**a**), a monodental- (**b**) and bidental (**c**) sulfate ligand in our water and sulfate containing complexes (the possible binding of two Pt atoms by one sulfate (**d**) was excluded for our complexes by PI-FAB, cf. part IV[2]).

The sulfate ion absorbs between 600 and 1300 cm^{-1}: ionic sulfate (**a**) shows only two absorptions at 1130 and 620 cm^{-1} on account of T_d-symmetry[27,28]. If sulfate is coordinated, the symmetry decreases from **b** to **d**, resulting in an increasing number of bands from **b** to **d**[29]. These rules were established with Co complexes, they were proved for

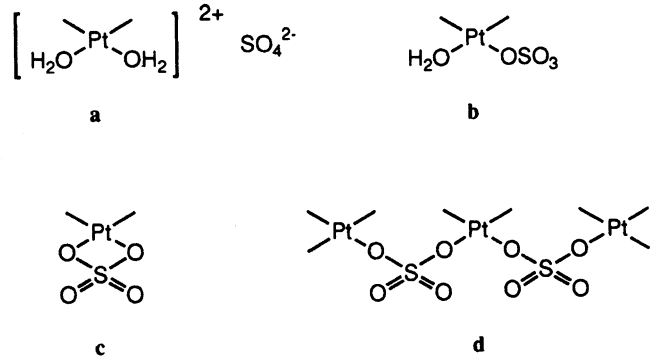


Fig. 13: Possible complexations of sulfate.

Pd complexes[30] and transfered to complexes of other metals[31].

Already in 1938, *King* regarded the sulfate ion in *cis*-diammine Pt complexes as a monodental ligand[32]. *Appleton et al.* have prepared the corresponding water free complex[33]. Both complexes are in agreement with the rules for the IR-spectra cited.- By X-ray analysis of aqua-*N,N'*-dimethylethylenediamine-sulfato-(Pt)II complex *Rochon et al.*[34] have shown that sulfate is bound as a monodental ligand in this quadratic planar complex, whilst water was bound at the fourth coordination place, stabilized by H-bridges to the sulfate ligand and to crystal water.

According to the lit. cited and on account of the IR-absorptions at 1140-1110; 1050-1030; and near 970 cm^{-1} *Gust et al.*[20,35] assumed the sulfate to be a monodental ligand in aqua-[1-(2,6-dichloro-4-hydroxyphenyl)-2-phenyl-ethylenediamine]-sulfato-Pt(II) accompanied by impurities. Later on *Schönenberger et al.* proposed that Pt(II) complexes of 1,2-diphenyl-ethylenediamines contain two molecules of water coordinated to Pt(II) with sulfate as the counterion. This was based on the elementary analyses always showing at least two water molecules. Also here, impurities with other coordination types could not be excluded[36-38].- Depending on the work-up procedure, *Müller*[39] found the diaqua species or the complex with chelated sulfate for *rac*-1,2-bis-(4-fluorophenyl)ethylenediamine-Pt(II). Comparison with a freeze dried complex indicated a mixture of ionic sulfate and ligandous sulfate[39].

Spiroplatin, a 6-ring Pt(II) complex, contains sulfate as a monodental ligand, the water is bound to the 4. coordination place (X-ray). The 2. water molecule is crystal water, but this complex was not freeze dried[40].

The FT-IR spectra of all our diaqua/sulfato complexes (part IV[2]) show strong absorption near 1120 cm^{-1} and a weak one near 590 cm^{-1}, pointing towards ionic sulfate, and a broad band near 3340 cm^{-1}, caused by water molecules. In addition we observe weak absorption near 950 and 1130 and between 1180 and 1220 cm^{-1} suggesting coordinated sulfate. In *threo*-diaqua/sulfato-[1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino]-Pt(II) (cf. **7**) we find a pronounced absorption at 839 cm^{-1}, indicating coordinated water.

In conclusion: the IR-spectra of our complexes give hints for coordinated as well as for ionic sulfate (the molecular formulas of the elementary analyses always contain two molecules of water; if additional water molecules are shown, this indicates a content of more than two molecules of water in the pertinent compounds). Therefore, we assume that our complexes are mixtures provoking our nomenclature "diaqua/sulfato complexes".

For the determination of their antitumor activity (part VI of this series, forthcoming paper) the binding state of the sulfate is not meaningful, because *Schönenberger et al.*[36] have shown by conductivity measurements that sulfate in 1,2-diphenylethylenediamine-Pt(II) complexes is substitued by water within a few min affording the biologically active diaqua species. Most probably this will happen also in the 1,3-diphenylpropane-1,3-diamino-Pt(II) complexes.

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Data

The preparation of the ligands discussed in this paper and their spectral data are described in part III[1], preparation and spectral data of the complexes in part IV of this series[2].

1 (*meso*) and **2** (*rac*): see cpds. 5b in ref.[5].- **3** (*meso*): see cpd. 34 in part III.- **4** (*meso*) and **5** (*rac*): see cpds. 116 and 117 in part IV.- **6** (*erythro*) and **7** (*threo*): see cpds. 120 and 121 in part IV.- **8** (*threo*): see cpd. 127 in part IV.

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