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Stereochemical investigation of cationic olefin complexes of platinum(II) containing chiral diamines: a sequence of four asymmetric centres (N, C, C and N) in the chelate ring [☆]

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Abstract

The platinum(II) salts $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_2dab)](ClO_4)$, Me_2dab = *N,N'*-dimethyl-2,3-diaminobutane with *R,S*, *R,R* and *S,S* configurations at the asymmetric carbons, have been prepared. When coordinated to platinum, the nitrogens of Me_2dab also become stable chiral centres and in the chelate ring a sequence of four asymmetric atoms (N, C, C and N) is established. Because of the *trans*-labilizing effect of the ethene ligand, equilibration of different diastereomeric species takes place in solution under ambient conditions. Their relative stability proved to be dependent not only upon the 1,3-diaxial repulsions within the chelate ring of the diamine but also upon the flexibility of the ring puckering and the interligand steric repulsions. Therefore, in the case of Me_2dab with *R,S* configurations at the carbons, the complexed isomer with *R,S,R,S* configurations at the four asymmetric centres (N, C, C and N, respectively), which has no preference for either λ or δ conformation of the chelate ring and interconverts rapidly, is preferred over the *S,S,R,S* and *R,S,R,R* isomers which, although having smaller 1,3-diaxial repulsions, have a rigid puckering of the ring (λ and δ, respectively). In the case of Me_2dab complexes with *R,R* and *S,S* configurations at the carbons the puckering of the five-membered chelate ring is static (λ and δ, respectively) and the configurations with least possible 1,3-diaxial repulsions are *S,R,R,S* and *R,S,S,R*, respectively. However these configurations have both N–Me groups in quasi-equatorial position and protruding towards the *cis* ligands, as a consequence the *S,R,R,R* and *S,S,S,R* isomers, having slightly greater 1,3-diaxial repulsions but a 'quasi-axial' N–Me on one end of the diamine that can better accommodate in *cis* position a sterically demanding ethene ligand, also gain stability.

Keywords: Stereochemistry; Olefin complexes; Platinum complexes; Chiral diamines

1. Introduction

Coordinated amines can have asymmetric nitrogen donor atoms and, if one of the N-substituents is chiral, a certain degree of asymmetric induction can be expected. In the case of monodentate amines, however, the inversion at nitrogen can be quite rapid and although different isomers can be observed, equilibration among them is rather fast [1–3]. In the case of chelating diamines the rate of inversion at the coordinated nitrogen atoms can be rather low and different diastereoisomers can be separated by conventional techniques [4]. The presence of a chiral centre in the carbon chain linking the two nitrogens of a diamine is the most favourable situation for inducing asymmetry on the coordinated nitrogens [5]. Literature data, however, do not give clear indications of the interdependences between chiralities on the carbon skeleton and configurations on the coordinated nitrogens [6,7].

We are currently investigating the effect of configurations of platinum bonded diamines upon the chemistry and biochemistry of complexes of formula $[Pt(diamine)Cl_2]$ [8,9]. In these species (chlorine ligands *trans* to the amine groups) the nitrogen configurations are very stable and the type and abundance of isomers obtained in a given preparation depend upon the experimental conditions used and do not reflect their relative thermodynamic stability.

In order to evaluate the real conformational preference of the diamine ligand we planned to prepare complexes of the type $[Pt(\eta^2\text{-}C_2H_4)Cl(diamine)]^+$. The presence of a strong *trans*-labilizing ligand such as ethene should promote a configurational lability on the opposite

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[☆] This paper is dedicated to Professor György Bor on the occasion of his 70th birthday.

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nitrogen so that the isomeric composition should be determined by thermodynamic rather than kinetic factors.

The preparation of olefin complexes of platinum(II) of the type discussed above is rather challenging. Their thermodynamic stability resides on the chelating ability of the diamine which must balance the *trans*-labilizing effect of the olefin [10]. The best established complex of this type contains *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen) [11] having the five-membered chelate ring stabilized by the Thorpe–Ingold effect of the methyl substituents [12].

N,*N*′-Dimethyl-2,3-diaminobutane (Me_2dab) was chosen for the present study. The presence of a methyl substituent on each atom of the skeleton should create the conditions for a Thorpe–Ingold effect. Moreover, when coordinated to platinum, the nitrogens also become stable chiral centres and in the chelating ring a sequence of four asymmetric atoms (N, C, C and N) is established. Cationic complexes of this type should have additional interest since the chiral diamine could exert a stereocontrol on the addition of prochiral nucleophiles to the olefin.

2. Results and discussion

2.1. Preparation of the complexes

The complexes $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_2dab)]^+$ were prepared by reaction of the diamine with Zeise's anion in methanol. Generally this reaction leads to the formation of a five-coordinate trigonal bipyramidal complex having axial chlorines and equatorial olefin and diamine ligands. The size of the substituents on the amine nitrogens plays an important role in the stability of the five-coordinate complex [13]. Bulky substituents (such as Bu^t and Pr^i) stabilize the five-coordinate species, in contrast small groups (such as Me) render the five-coordinate complex rather labile and promote its rapid decomposition to a square planar four-coordinate species by loss of either a chloride ion or the ethene molecule, the loss of chloride being favoured by polar solvents [14]. In the present case (Me_2dab ligand) the five-coordinate complexes were very labile even at a temperature as low as −15 °C and decompose directly to the desired cationic species. These were isolated as perchlorate salts performing the reaction at 0 °C in methanol solution in the presence of an excess of lithium perchlorate.

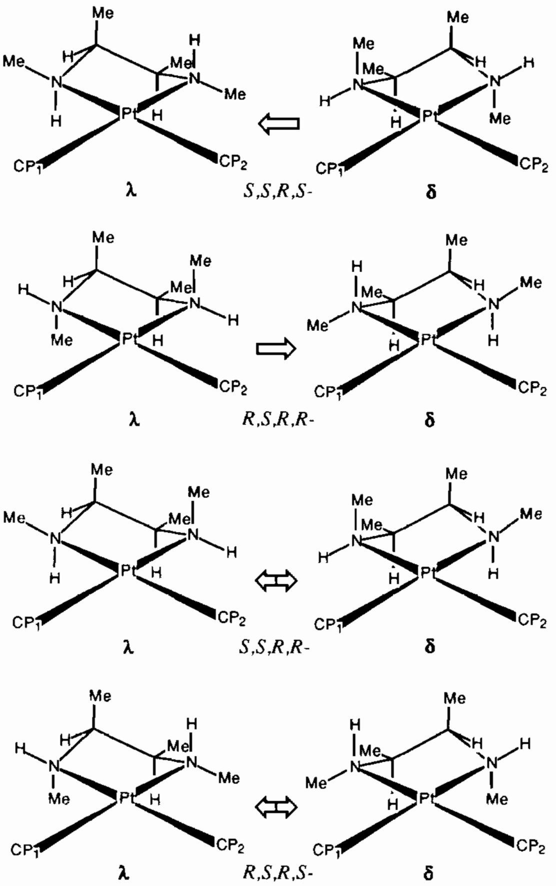
The solubility of the cationic species depends upon the configuration of the diamine. In the case of *R*,*S*-Me_2dab (when only two absolute configurations are given they pertain to the two asymmetric carbons; when four configurations are given they pertain to the four N, C, C and N asymmetric centres, respectively) the cationic species precipitates directly from the methanol solution. In the case of *R*,*R*- and *S*,*S*-Me_2dab the compounds are more soluble and crystallization was performed at −20 °C.

In the case of the tmen ligand a dimeric species, $[(tmen)ClPt\text{–}CH_2\text{–}CH_2\text{–}NH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2\text{–}CH_2\text{–}CH_2\text{–}PtCl(tmen)]^{2+}$, formed by nucleophilic addition of a diamine molecule on the ethene moieties of two cationic units, precipitated from solution [15]. Such a dimeric species was formed also in the presence of substoichiometric quantities of tmen with respect to Zeise's anion indicating that the diamine reacts faster with the olefin of two cationic units to give the dimer than with Zeise's anion to give the cationic complex. The monomeric cationic complex could be recovered from the dimeric salt by treatment with acid. Analogous dimeric salts were not isolated, under similar conditions, in the case of the Me_2dab ligand, the reason for the different behaviour being the greater solubility of the dimeric species which remains in solution giving the possibility to the bridging diamine to react with Zeise's anion which is left in solution to form the cationic species.

2.2. Stereochemistry

Me_2dab ligands with a given configuration at the carbon atoms, once coordinated to the metal atom, can give rise to formation of several stereoisomers depending upon the stable chiralities born on the coordinated nitrogen atoms.

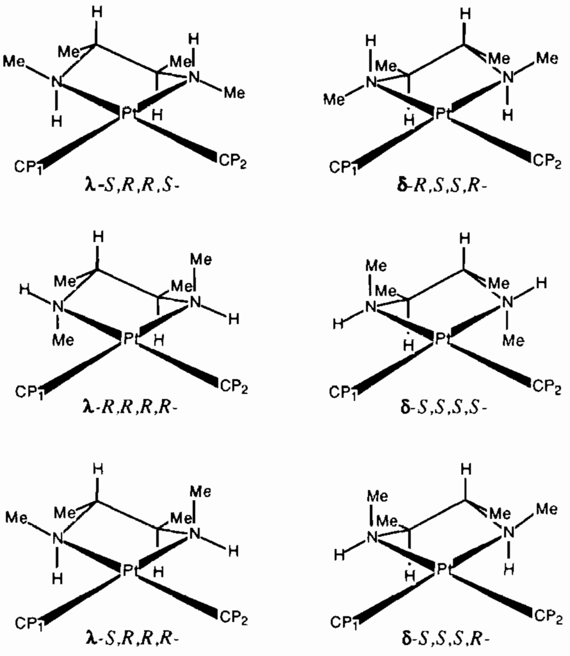
The *R*,*S*-Me_2dab ligand can lead up to four stereochemically distinct isomers (Scheme 1). In all four isomers one of the C–Me groups on the diamine ring is equatorially disposed while its adjacent counterpart occupies an axial position. The equitable axial–equatorial distribution of the C–Me groups within the chelate ring remits any internal conformational preference to the steric disposition of the nitrogen substituents. Given the choice of the eight conformers shown in Scheme 1, Dreiding models clearly indicate that the 1,3-diaxial repulsion between C–Me and N–Me groups will preclude the δ conformation for the *S*,*S*,*R*,*S* and the λ conformation for the *R*,*S*,*R*,*R* isomers. The sterically more favoured λ-*S*,*S*,*R*,*S* and δ-*R*,*S*,*R*,*R* isomers are enantiomers and have the two coordination positions (CP_1 and CP_2) for the Cl^- and C_2H_4 ligands, non-equivalent so that they admit positional isomers. For the *S*,*S*,*R*,*R* and *R*,*S*,*R*,*S* species there is no preference for either λ or δ conformation and the chelate ring averages to a planar geometry with the C–Me groups on one side of the coordination plane and the N–Me groups either on the same side as the C–Me groups (*S*,*S*,*R*,*R* isomer) or on the opposite side (*R*,*S*,*R*,*S* isomer). In both isomers the two coordination positions for Cl^- and C_2H_4 are equivalent so that each of them gives only one positional isomer.



Scheme 1.

In the case of either *R*,*R*- or *S*,*S*-Me_2dab, the five-membered chelate ring always adopts a single static chiral conformation with the C–Me groups equatorially disposed which ensures the lowest 1,3-diaxial repulsions within the chelate ring (Scheme 2) [16]. Therefore the conformation of the ring is λ in the isomers with *R*,*R* configurations at the carbons and δ in the isomers with *S*,*S* configurations at the carbons. The disposition of the neighbouring N–Me groups determines the absolute configurations of the N atoms which can be the same for both nitrogens (either *R* or *S*) or different for the two nitrogens (*R* for one nitrogen and *S* for the other). In the latter case (isomers *S*,*R*,*R*,*R* and *S*,*S*,*S*,*R*) the coordination positions for the Cl^- and C_2H_4 ligands are non-equivalent and positional isomers are allowed.

It becomes evident that not all the allowable diastereoisomers have equal stability, the steric demand being different from case to case. In particular, for the species drawn in Scheme 1, the enantiomeric configurations λ-*S*,*S*,*R*,*S* and δ-*R*,*S*,*R*,*R* (in which there is only one 1,3-diaxial repulsion involving C–Me and N–H groups within the diamine ring) should have the greatest stability. The lowest stability should be associated with the δ,λ-*S*,*S*,*R*,*R* configuration for which there is a 1,3-diaxial repulsion between two methyl groups. An intermediate situation would be that of δ,λ-*R*,*S*,*R*,*S* for which there are two 1,3-diaxial repulsions between Me and H groups. In the last case the less favourable enthalpy associated with the 1,3-diaxial repulsions could be compensated by a more favourable entropy associated with a greater degree of flexibility of the chelate ring in δ,λ-*R*,*S*,*R*,*S* with respect to that of either λ-*S*,*S*,*R*,*S* or δ-*R*,*S*,*R*,*R*.



Scheme 2.

For the species drawn in Scheme 2 the least hindered situation should be that of the *S*,*R*,*R*,*S* and *R*,*S*,*S*,*R* enantiomers for which all methyl substituents are in equatorial positions; on the other hand the most hindered situation should be that of the *R*,*R*,*R*,*R* and *S*,*S*,*S*,*S* isomers for which two 1,3-diaxial repulsions between C–H and N–Me groups are present. Finally an intermediate situation should be that of the *S*,*R*,*R*,*R* and *S*,*S*,*S*,*R* isomers for which there is only one 1,3-diaxial repulsion between C–H and N–Me groups.

2.3. ^1H NMR spectroscopy

The ^1H NMR spectrum of $[Pt(\eta^2\text{-}C_2H_4)Cl(R,S\text{-}Me_2dab)]^+$ shows only one set of signals indicating that the diamine adopts essentially only one of the possible four configurations (Table 1). The non-equivalence of the two coordination positions for Cl^- and C_2H_4 rules out configurations *S*,*S*,*R*,*S* and *R*,*S*,*R*,*R* since they should give two distinct positional isomers. Between the two remaining *S*,*S*,*R*,*R* and *R*,*S*,*R*,*S* configurations, both having equivalent coordination positions for Cl^- and C_2H_4, steric considerations discussed above favour the latter (*R*,*S*,*R*,*S*) with respect to the former (*S*,*S*,*R*,*R*).

Table 1
Proton chemical shifts (δ, downfield from $SiMe_4$ or TSP; *J*(Pt–H) in parentheses) in Hz are given when assignable) of complexes $[PtCl(Me_2dab)Y]$. For each complex the configuration of the four asymmetric centres of the diamine (N, C, C and N) and the Y ligand is given

Config.	Y	Solvent	CMe	CH	NMe	NH	Y
R,S,R,S	Cl	[a]	1.14	2.72	2.56	5.74	
	C_2H_4	[b]	1.36	3.14	2.68	5.84[c]	4.73[d]
			1.37	3.41	2.86	6.80	
	DMSO	[a]	1.18	2.72	2.60	6.31	
			1.27	2.94	2.86	6.54	
S,S,R,S/	Cl	[a]	1.14	2.62	2.25	5.78	
R,S,R,R			1.18		2.50	6.40	
	DMSO[e] A	[a]	1.19	[f]	2.59	6.25	
			1.28		2.85	6.5	
	B	[a]	1.21	[f]	2.55	6.5	
			1.25		2.67	7.1	
S,R,R,S	Cl	[a]	1.08	2.30	2.56	5.92	
	C_2H_4	[b]	1.27	2.70	2.43(41)		[g]
			1.34		2.90(37)		
	DMSO	[a]	1.12	[f]	2.57	6.66	
			1.20		2.92	6.90	
S,R,R,R/	Cl	[a]	0.97	2.63	2.43	5.90	
R,S,S,S			1.04		2.59	6.28	
	C_2H_4[e] A	[b]	1.21	3.18	2.59(41)		[g]
			1.30		2.87(37)		
	B	[b]	1.24	3.10	2.49(41)		[g]
			1.27		2.62(37)		
	DMSO[e] A	[a]	1.06	3.05	2.62	6.50	
			1.12		2.65	6.65	
	B	[a]	1.06	2.71[h]	2.42	[f]	
			1.16		2.90		

[a] DMSO-d_6.
[b] CD_3OD.
[c] Values taken in the presence of 10^{-4} M $HClO_4$.
[d] Centre of an AA'BB' multiplet.
[e] Two positional isomers are obtained, they are indicated A and B.
[f] Overlapped by other signals.
[g] One of the three overlapping AA'BB' multiplets in the range 4.5–4.9 δ.
[h] Tentative assignment.

Although the asymmetry introduced by the Cl^- and C_2H_4 ligands makes non-equivalent the two halves of the diamine ligand, the two C–Me groups are nearly chemically equivalent. The olefin signals appear as an AA'BB' multiplet in the expected region.

In deuteriomethanol, because of H–D exchange of the amine hydrogens, NH signals are normally lost and NMe signals appear as singlets. However a different H–D exchange rate for the two amine functionalities was observed, the group having the methyl at lower field exchanging faster. Therefore soon after dissolution of the crystalline solid in deuteriomethanol containing 10^{-4} M $HClO_4$, both N–Me signals appear as doublets, after 24 h the signal at lower field becomes a singlet, while that at higher field still consists of a doublet due to the non-exchanged species together with a singlet due to the exchanged form. This observation allows the assignment of the more deshielded signal to the N–Me lying *trans* to the olefin which can undergo H–D exchange via Pt–N bond dissociation. The H–D exchange at the nitrogen atoms ensures that equilibration among the different diastereoisomers is attained. As far as the magnitude of vicinal *J*(Pt,H) coupling is concerned, we found 37 and 41 Hz for the N–Me signals at lower (*trans* to ethene) and higher (*trans* to chloride) field, respectively. The difference is rather small and does not fully account for the large difference in the *trans* influence between ethene and the chloride ion. On the other hand analogous complexes having ligands with a very similar *trans* influence, such as η^2-ethene and η^1-alkyl, exhibit very different coupling between N–Me and platinum (much greater in the η^2-ethene than in the η^1-alkyl case). The different type of metal–ligand bond can account for the observed differences. In particular the metal–alkene bond has a considerable π component which results in a large *trans* influence, but does not influence the σ component of the *trans*-ligand bond.

The ^1H NMR spectrum of a crystalline sample of $[Pt(\eta^2\text{-}C_2H_4)Cl(R,R,\text{-}Me_2dab)]^+$ (our discussion will be restricted to the *R*,*R*-Me$_2$dab case but it applies entirely also to the *S*,*S*-Me$_2$dab case) did show, right from dissolution, three sets of signals, two of comparable and one of lower intensity (Table 1).

The obtainment of three sets of signals indicates that the diamine ligand adopts only two of the three possible configurations. The *S*,*R*,*R*,*R* (which has non-equivalent coordination positions for Cl^- and C_2H_4 and admits two positional isomers) and one of the two symmetric configurations (either *R*,*R*,*R*,*R* or *S*,*R*,*R*,*S*). The latter (*S*,*R*,*R*,*S*) is favoured on the basis of smaller 1,3-diaxial steric interactions.

A complete assignment of the signals belonging to the same set was possible on the basis of intensity ratios and internal couplings (Fig. 1). The assignment of each set of signals to a given isomer was performed on the basis of trends in chemical shift values and of analogies with the data obtained for the corresponding complexes having dimethyl sulfoxide (DMSO) in place of C_2H_4. Of particular value were the chemical shifts of the CH protons of the skeleton which occupy static axial positions. Their chemical shifts appeared to vary little with the relative positions of the Cl^- and C_2H_4 ligands, but to change significantly with the stereochemistry of the adjacent nitrogens. Therefore one of the two more intense sets and the weakest set of signals, having both similar values of CH chemical shifts, belong to the two positional isomers originated by the *S*,*R*,*R*,*R* configuration, and the second more intense set of signals must belong to the isomer with *S*,*R*,*R*,*S* configuration of the diamine which is symmetric and admits only one positional isomer.

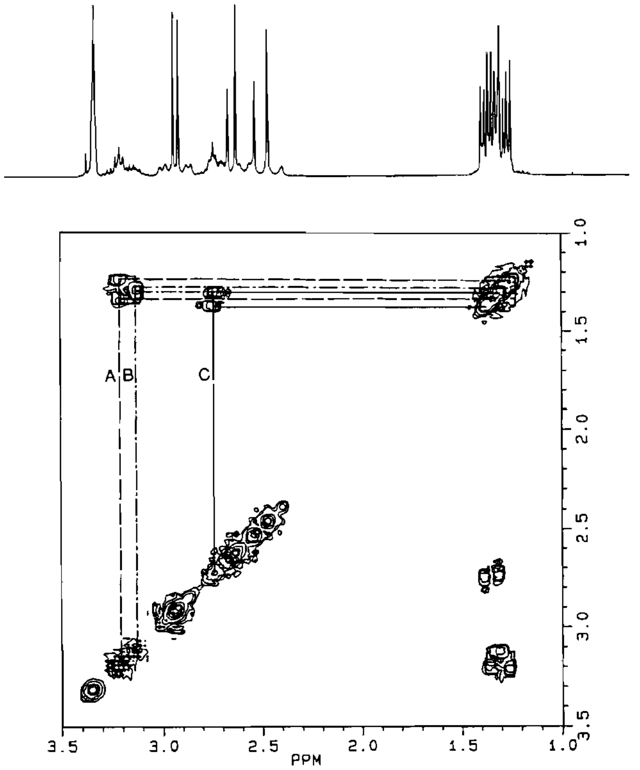


Fig. 1. COSY spectrum illustrating the scalar coupling between CH and CMe protons for the equilibrium mixture of the two positional isomers (A and B) of $[Pt(\eta^2\text{-}C_2\text{-}H_4)Cl(S,R,R,R\text{-}Me_2dab)]^+$ and of (C) $[Pt(\eta^2\text{-}C_2H_4)Cl(S,R,R,S\text{-}Me_2dab)]^+$.

The different yields of the two positional isomers (ratio A/B (see Table 1) ~2) originated by the *S*,*R*,*R*,*R* configuration are indicative of a steric control exerted by the asymmetric diamine on the sites of coordination of the monodentate Cl^- and C_2H_4 ligands. The N–Me on one end of the diamine is in 'quasi-equatorial' position while that on the opposite end is in 'quasi-axial' position. Dreiding models indicate that the 'quasi-equatorial' N–Me is protruding towards the *cis* ligand more that the 'quasi-axial' N–Me, therefore it is most likely that the more sterically demanding ethene ligand will occupy preferentially the coordination site *cis* to the 'quasi-axial' N–Me.

In all isomers with *R*,*R*-Me$_2$dab the rate of H–D exchange for NH in deuteriomethanol is much faster than that observed in the complex with *R*,*S*-Me$_2$dab. A not completely exchanged NH was observed only for one of the major species and solely for the amine functionality *trans* to the chlorine ligand.

2.4. Reaction with chloride supports the given assignment

In $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_2dab)]^+$ complexes the ethene ligand can be easily displaced by a chlorine ion, in methanol, leading to the formation of the corresponding neutral dichloro species which have a poor solubility in this solvent in contrast with the good solubility of the cationic complexes. Substitution of chloride for ethylene in the case of *R*,*S*-Me$_2$dab cationic species leads to formation of only one product having a symmetric ligand (only one ^1H resonance for each type of proton, Table 1) if the substitution is performed in rather concentrated solution (complex concentration $>5\times10^{-2}$ M). The symmetry of the molecule indicates that the configuration of the asymmetric centres can be either *S*,*S*,*R*,*R* or *R*,*S*,*R*,*S*; the former configuration is ruled out on the basis of steric considerations (see above). If, instead, the substitution reaction is performed in more dilute conditions ($<10^{-3}$ M) so that the neutral species crystallize slowly from the solution, in addition to the previous compound a second isomer crystallizes as long yellow needles. The latter species showed (^1H NMR, DMSO-d$_6$, Table 1) two distinct signals for each type of proton, thus indicating that the ligand molecule is asymmetric and can have either of the two enantiomeric configurations, *S*,*S*,*R*,*S* and *R*,*S*,*R*,*R*. These observations confirm that the preferred configuration of the diamine ligand found for [Pt(η^2-C_2H_4)Cl(*R*,*S*-Me$_2$dab)]$^+$ is the symmetric one (*R*,*S*,*R*,*S*), then follow the asymmetric configurations (*S*,*S*,*R*,*S* and *R*,*S*,*R*,*R*) and finally the second symmetric configuration (*S*,*S*,*R*,*R*) which is the least favoured. A small amount of the asymmetric species could be in equilibrium with the dominant species even in the cationic complex but could not be detected by NMR.

In the case of [Pt(η^2-C_2H_4)Cl(*R*,*R*-Me$_2$dab)]$^+$ the displacement of the ethene molecule by the chloride ion leads to a mixture of two species which were separated by fractional crystallization from DMF. One of them was the asymmetric [PtCl$_2$(*S*,*R*,*R*,*R*-Me$_2$dab)] complex, and the other was the symmetric [PtCl$_2$(*S*,*R*,*R*,*S*-Me$_2$dab)] species. This result buttresses the assignment given for the cationic species. The configurations of the Me$_2$dab ligands in the two isomers was also ascertained by NOESY/EXY and COSY spectra [17].

2.5. Analogies with the [PtCl(DMSO)(Me$_2$dab)]$^+$ complexes

The complexes [PtCl(DMSO)(Me$_2$dab)]$^+$, having DMSO in place of C_2H_4, were also obtained by solvolysis in DMSO of the neutral dichloro species (Table 1).

Starting from the racemic mixture of [PtCl$_2$(*S*,*S*,*R*,*S*-Me$_2$dab)] and [PtCl$_2$(*R*,*S*,*R*,*R*-Me$_2$dab)] substitution of DMSO for Cl$^-$ doubles the number of isomers (two couples of enantiomers) in accord with non-equivalent coordination positions for the two chloride ions. On the contrary starting from [PtCl$_2$(*R*,*S*,*R*,*S*-Me$_2$dab)], having the two chlorides in equivalent coordination sites, only one isomer is obtained by substitution of one Cl$^-$ by DMSO, therefore confirming that the latter ligand configuration was also present in the ethene species.

In the case of [PtCl$_2$(*S*,*R*,*R*,*S*-Me$_2$dab)], substitution of DMSO for Cl$^-$ leads to the formation of only one isomer while in the case of [PtCl$_2$(*S*,*R*,*R*,*R*-Me$_2$dab)] two isomers are formed as observed in the ethene complex. Again the two isomers have different concentrations (ratio A/B (see Table 1) ~4) indicating that DMSO, like ethene, has a preference for the coordination position which does not suffer from the steric interaction with the protruding N–Me group.

3. Conclusions

This investigation has revealed that 1,3-diaxial repulsion within a five-membered chelate ring is not the only criterion for the relative stability of possible diastereoisomeric species, but, in addition to this, the flexibility of the puckered ring (that is the equitable λ/δ conformations) and the interligand steric repulsions play also a role. This is clearly shown by the different behaviour of the *meso* and racemic Me$_2$dab ligands. In the case of the *meso* form the preference for a flexible ligand puckering makes the *R*,*S*,*R*,*S* isomer preferred with respect to the *S*,*S*,*R*,*S* and *R*,*S*,*R*,*R* enantiomers which, although having smaller 1,3-diaxial steric repulsions, have a static puckering of the ring. In the case of the racemic ligand (we referred to the *R*,*R* isomer but the same applies to the *S*,*S* enantiomer) the chelate ring has always a static conformation and the *S*,*R*,*R*,*S* isomer is favoured on the basis of smaller 1,3-diaxial repulsions. However the interligand steric repulsion between one end of the diamine and the *cis* ethene ligand (which is rather sterically demanding) gives stability to the *S*,*R*,*R*,*R* isomer which is less favoured on the basis of 1,3-diaxial repulsions but has one end of the diamine with a 'quasi-axial' N–Me group and can better accommodate an ethene ligand in *cis* position. The interligand steric argument acts in favour of the observed isomer also in the case of the *meso* ligand.

In subsequent work, it will be shown that the information obtained in this study is crucial to the rational use of these substrates in stereochemically demanding organic reactions.

4. Experimental

4.1. Starting materials

R,*R*, *S*,*S* and *R*,*S* isomers of *N*,*N*′-dimethyl-2,3-diaminobutane were prepared by the method of Dickey et al. [18]. Zeise's salt was prepared according to well established procedures [19,20].

4.2. Preparations of compounds

4.2.1. [Pt(η^2-C_2H_4)Cl(R,S-Me$_2$dab)](ClO$_4$)

Zeise's salt (1 mmol) was dissolved in methanol (5 ml), and LiClO$_4$ (2.5 mmol) was then added. This operation induced quantitative precipitation of KClO$_4$ which was removed by filtration. To the solution, kept in an ice-cold bath, were added, in succession *R*,*S*-Me$_2$dab·2HCl (2 mmol) and LiOH (2 mmol). The addition of base produced a decolouring of the solution from bright to very palc yellow and the precipitation of a white compound. The solid was separated by filtration of the solution, washed with cold methanol and dried in vacuo; it proved to be the desired cationic species. From the solution, kept overnight in a deep freezer, another crop of product precipitated. The isolated yield, referred to platinum, was 65%. *Anal.* Calc. for $C_8H_{20}Cl_2N_2O_4Pt$: C, 20.3; H, 4.3; N, 5.9. Found: C, 20.4; H, 4.2; N, 5.7%.

4.2.2. [Pt(η^2-C_2H_4)Cl(R,R-Me_2dab)](ClO_4) and [Pt(η^2-C_2H_4)Cl(S,S-Me_2dab)](ClO_4)

These compounds were prepared in an analogous way, but the cold bath was kept at −5 °C. A temperature lower than that used in the previous case was required in order to avoid the formation of neutral species formed by substitution of chloride for ethene. The cationic complexes containing the *R,R* and *S,S* forms of the ligand were more soluble than that containing the *R,S* form and crystallization from solution had to be performed at a deep freezer temperature (−20 °C). The isolated yields, referred to platinum, did not exceed 50%, but they were only limited by the solubility of the products. *Anal.* Calc. for $C_8H_{20}Cl_2N_2O_4Pt$: C, 20.3; H, 4.3; N, 5.9. Found: C, 20.4; H, 4.3; N, 5.9%.

4.2.3. [$PtCl_2$(Me_2dab)]

These compounds were prepared by reaction of a solution of the cationic complexes in methanol with an excess of LiCl (twice the stoichiometric amount).

In the case of *R,S*-Me_2dab two products can be obtained depending upon the experimental conditions. Using a concentrated solution of the reactants (~0.5 mmol of complex and 1.2 mmol of LiCl in 5 ml of solvent) at room temperature, a yellow compound began to form within a few hours from the mixing time. After 12 h the precipitation could be considered complete. The yellow solid was collected by filtration of the mother liquor, washed twice with methanol and dried. The yield, referred to platinum, was nearly quantitative. The solid proved to be a unique isomer having a symmetric ligand (*R,S,R,S* configuration at the N, C, C and N stereogenic centres). *Anal.* Calc. for $C_6H_{16}Cl_2N_2Pt$: C, 18.8; H, 4.2; N, 7.3. Found: C, 18.7; H, 4.1; N, 7.1%. Using a more dilute solution of the cationic complex ($\leqslant 10^{-3}$ M), a stoichiometric amount of LiCl and a temperature of 0 °C, the crystallization of the neutral species is much slower and leads to the formation of some long yellow needles. These proved to be a second isomer with a non-symmetric ligand (*S,S,R,S* and *R,S,R,R* configurations at the N, C, C and N stereogenic centres). *Anal.* Calc. for $C_6H_{16}Cl_2N_2Pt$: C, 18.8; H, 4.2; N, 7.3. Found: C, 18.9; H, 4.2; N, 7.3%.

In the case of *R,R*-Me_2dab (the same applies to *S,S*-Me_2dab) the reaction of the cationic species with LiCl leads to formation of a mixture of two isomers in comparable yields, one with a symmetric ligand (*S,R,R,S* isomer) and the other with an asymmetric ligand (*S,R,R,R* isomer). The two forms could be separated quantitatively owing to their different solubility in dimethylformamide (DMFA). In a typical experiment the product obtained from the above reaction was suspended in a small volume of DMFA (10 ml), kept under stirring on a steam bath for 10 min and the solution filtered. The procedure was repeated a few times until the DMFA remained colourless. The solid residue was washed with water and methanol and dried in vacuo and proved to be the pure symmetric isomer (*S,R,R,S*). *Anal.* Calc. for $C_6H_{16}Cl_2N_2Pt$: C, 18.8; H, 4.2; N, 7.3. Found: C, 19.0; H, 4.3; N, 7.3%. The DMFA solution, containing the second isomer, was treated with an excess of diethyl ether. A yellow precipitate separated out; this was collected and recrystallized from DMFA/diethyl ether. It proved to be the pure asymmetric isomer (*S,R,R,R*). *Anal.* Calc. for $C_6H_{16}Cl_2N_2Pt$: C, 18.8; H, 4.2; N, 7.3. Found: C, 19.1; H, 4.4; N, 7.4%.

4.3. Methods

IR spectra in the range 4000–400 cm^{-1} were recorded as KBr pellets; spectra in the range 400–200 cm^{-1} were recorded as polythene pellets on Perkin-Elmer 283 and FT 1600 spectrometers. ^1H NMR spectra were obtained with Varian XL 200 and Bruker AM 300 spectrometers. Two-dimensional ^1H correlation spectroscopy (COSY) was performed with the Bruker automation program COSY.

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