

### 135. Complex Formation of Pd<sup>II</sup> Ion with the Tripodal Ligand Tris[2-(dimethylamino)ethyl]amine

by **Giorgio Anderegg\***

Laboratory of Inorganic Chemistry, ETH-Zentrum, Universitatstr. 6, CH-8092 Zurich

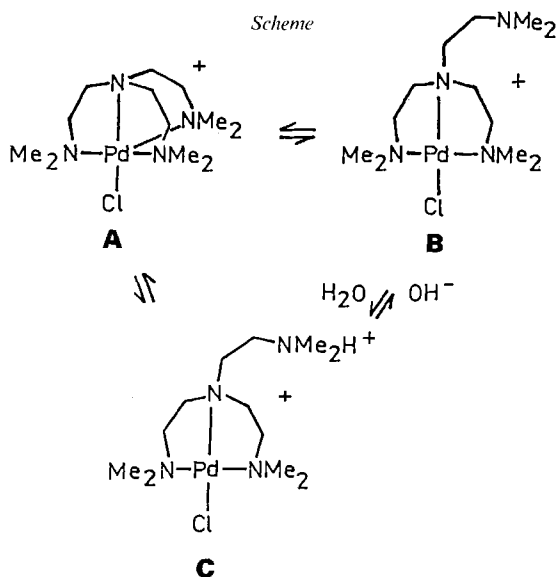
and **Zdenek Melichar**

Institute of Inorganic Chemistry, Czech Academy of Sciences, Pellaova 24,  
16000 Prague, Czech Republic

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The complex formation of Pd<sup>II</sup> with tris[2-(dimethylamino)ethyl]amine (N(CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, Me<sub>6</sub>tren) was investigated at 25° and ionic strength *I* = 1, using UV/VIS, potentiometric, and NMR measurements. Chloride, bromide, and thiocyanate were used as auxiliary ligands. The stability constant of [Pd(Me<sub>6</sub>tren)]<sup>2+</sup> in various ionic media was obtained: log β([Pd(Me<sub>6</sub>tren)]) = 30.5 (*I* = 1(NaCl)) and 30.8 (*I* = 1(NaBr)), as well as the formation constants of the mixed complexes [Pd(HMe<sub>6</sub>tren)X]<sup>2+</sup> from [Pd(HMe<sub>6</sub>tren)(H<sub>2</sub>O)]<sup>3+</sup>: log *K* = 3.50 (*X*<sup>-</sup> = Cl<sup>-</sup>) and 3.64 (*X*<sup>-</sup> = Br<sup>-</sup>) and [Pd(Me<sub>6</sub>tren)X]<sup>+</sup> from [Pd(Me<sub>6</sub>tren)(H<sub>2</sub>O)]<sup>2+</sup>: log *K* = 2.6 (*X*<sup>-</sup> = Cl<sup>-</sup>), 2.8(Br<sup>-</sup>) and 5.57 (SCN<sup>-</sup>) at *I* = 1 (NaClO<sub>3</sub>). The above data, as well as the NMR measurements do not provide any evidence for the penta-coordination of Pd<sup>II</sup>, proposed in some papers.

**Introduction.** – Five-coordinate complexes of the type [M(Me<sub>6</sub>tren)X]X (Me<sub>6</sub>tren = N(CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, X<sup>-</sup> = an anionic ligand) have been reported for the first-row transition metals [1–4]. Evidence for such five coordination by the metals of the second and third row is otherwise scarce. Senoff [5], studying the <sup>1</sup>H-NMR data of the system [Pd<sup>II</sup>(Me<sub>6</sub>tren)] under varying pH, postulates the equilibria shown in the *Scheme*.



The species denoted by **A** is assumed to have a trigonal-bipyramidal symmetry with Pd<sup>II</sup> coordinated to one Cl<sup>-</sup> and four N-atoms, while the other two species **B** and **C** have a square-planar coordination around Pd<sup>II</sup>. The Me protons of the latter two species should give rise to NMR signals with intensity ratio 1:1:1 due to the diastereotopic Me groups bound to the N-atoms coordinated to Pd<sup>II</sup> and the Me groups of the uncoordinated amino group. On the other hand, all three Me groups of structure **A** should be magnetically equivalent, and thus give just one signal. While at pH < 7 three signals (at 3.27, 3.17, and 2.70 ppm) have been observed, at pH = 11.5, just one *singlet* at 2.6 ppm is present. However, the *Senoff's* experimental results do not provide unequivocal evidence for the existence of a compound with structure **A**. The NMR-spectral assignment to the latter species are also compatible with an other explanation: at higher pH, there might be fast exchange between one uncoordinated and two coordinated N-atoms of the ligand on the NMR time scale of the 60-MHz instrument used in that study.

There is also another report where five-coordination in a Pt<sup>II</sup> complex with a tripod N<sub>3</sub>O ligand with pida<sup>2-</sup> (pyridylmethylamine diacetate) was proposed on the basis of the NMR spectra in solution. However, the IR spectra of the solid complex support a square-planar arrangement around Pt<sup>II</sup> [6].

The present study was undertaken in order to obtain more information about the coordination of the tripod ligand Me<sub>6</sub>tren to Pd<sup>II</sup> as well as quantitative thermodynamic data, e.g., stability constants of the [Pd(Me<sub>6</sub>tren)]<sup>2+</sup> complex and its mixed complexes with halide or pseudo-halide ligands. These results can be compared with those already published for the tripod ligand (tris(2-aminoethyl)amine) (tren) [7]. New NMR results for its Pd<sup>II</sup> complex have also been included.

**Experimental.** – The ligand Me<sub>6</sub>tren was prepared as described in [1]. A stock soln. of [Pd(HMe<sub>6</sub>tren)]<sup>3+</sup> (3 · 10<sup>-3</sup> M) was prepared by dissolving PdCl<sub>2</sub> in an aq. soln. of Me<sub>6</sub>tren · 3 HClO<sub>3</sub> and precipitating the Cl<sup>-</sup> anions with an equivalent amount of AgNO<sub>3</sub>.

The chemicals used were of *p.a.* quality, supplied from *Merck* (HBr, HCl, HClO<sub>4</sub>, titrisol NaOH; NaBr, NaCl, AgNO<sub>3</sub>, NaClO<sub>3</sub>, NaClO<sub>4</sub> · H<sub>2</sub>O), *Fluka* (K<sub>2</sub>PdCl<sub>4</sub>), *Fisher Scientific Company*, U.S.A. (NaSCN), or *Engelhard* (PdCl<sub>2</sub>) and were employed without further purification. Deionized water was used for the preparation of solns.

For the pH measurements, a digital voltmeter SA 720 (*Orion*) and an automatic titrator *Dosimat 665* (*Metrohm*) were used. All equilibrium constants were obtained from measurements at constant ionic strength *I* = 1.00, using NaCl, NaBr, NaClO<sub>3</sub>, or NaClO<sub>4</sub> as inert salts. In each medium, at pH = 0, the corresponding strong acid was used, and, to increase the pH value, it was substituted by the corresponding Na salt, maintaining X<sup>-</sup> 1M, i.e., *I* = 1 (Na, H)X. The concentrations of the components investigated are so low (*c* ≈ 1 · 10<sup>-4</sup>–1 · 10<sup>-3</sup> M) that they do not alter the ionic strength by more than 1%.

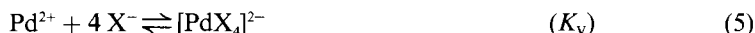
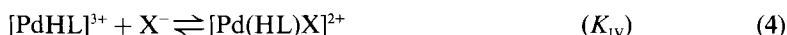
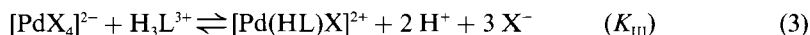
The UV/VIS spectra were measured with an *Uvikon 810* (*Kontron AG*) spectrophotometer. They allow, by taking into consideration the equilibria and their constants, to obtain those of the formed complexes (*Table*). The complex with diethylenetriamine [Pd(dien)OH]<sup>+</sup> was also characterized for comparison with [Pd(Me<sub>6</sub>tren)OH]<sup>+</sup>, in which the ligand acts as tridentate.

Table. Spectral Data (wavelength, λ<sub>max</sub>, in nm, and molar absorptivity, ε<sub>mol</sub>, in cm<sup>-1</sup> M<sup>-1</sup>, of the maxima) of the Investigated Pd<sup>II</sup> Complexes

Complex	λ <sub>max</sub>	ε <sub>mol</sub>	Complex	λ <sub>max</sub>	ε <sub>mol</sub>
[Pd(HMe <sub>6</sub> tren)H <sub>2</sub> O] <sup>3+</sup>	333.8	1150	[Pd(HMe <sub>6</sub> tren)Cl] <sup>2+</sup>	356	850
[Pd(Me <sub>6</sub> tren)H <sub>2</sub> O] <sup>2+</sup>	328	850	[Pd(HMe <sub>6</sub> tren)Br] <sup>2+</sup>	370	740
[Pd(Me <sub>6</sub> tren)OH] <sup>+</sup>	316	710			
[Pd(dien)OH] <sup>+</sup>	312	480			

The NMR spectra were recorded at 200 and 500 MHz with *Bruker AC 200* and *AMX 500* spectrometers, respectively. The samples were prepared by dissolving weighed amounts of  $K_2PdCl_4$ ,  $Me_6tren \cdot 3 HClO_4$  and the salts providing the auxiliary ligand in  $D_2O$  (*Cambridge Isotope Laboratories*, U.S.A.) without addition of inert salt, in order to obtain solns. which were *ca.*  $1 \cdot 10^{-2}$  M in the  $Pd^{II}$  complex. Sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS; *Fluka*) was used as internal reference.

**Results and Discussion.** – Since the complex of  $Pd^{II}$  with  $Me_6tren$  is fully formed in 1M  $HClO_4$  solution, the constant  $\beta([Pd(Me_6tren)]) = [Pd(Me_6tren)]/([Pd][Me_6tren])$  cannot be measured directly. However, it can be determined using auxiliary ligands such as halide or thiocyanate ions. For the determination of  $\beta([Pd(Me_6tren)])$ , the following equilibria have to be studied:

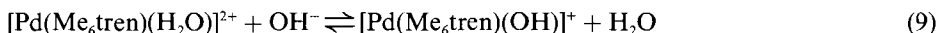
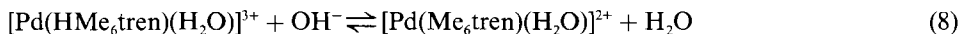


If the constants  $K_I, \dots, K_V$  of the equilibria defined above are known, the desired  $\beta([Pd(Me_6tren)])$  can be calculated as

$$\beta([Pd(Me_6tren)]) = [[Pd(Me_6tren)^{2+}]]/([Pd^{2+}][Me_6tren]) = K_I^{-1} \cdot K_{II} \cdot K_{III} \cdot K_{IV}^{-1} \cdot K_V \quad (6)$$

1. *Alkalimetric Titrations.* The constant  $K_I$  was obtained by titrating the protonated ligand with a strong base (0.1M NaOH + 0.9M  $NaClO_4$ ). The evaluation of the titration curve, using the program KONST [8], led to the following dissociation constants:  $pK_1 = 8.17 \pm 0.01$ ,  $pK_2 = 9.33 \pm 0.01$ ,  $pK_3 = 10.15 \pm 0.01$  and thus to  $-\log(K_I) = pK_1 + pK_2 + pK_3 = 27.65$ .

During the titration of 1:1 solution of  $Pd^{II}$  and  $Me_6tren \cdot 3 HClO_4$  with a strong base, the following processes are also taking place:



These reactions correspond to the neutralization of the two protons, liberated by the tri-protonated ligand, upon formation of the monoprotinated complex  $[Pd(HMe_6tren)(H_2O)]^{3+}$ . The latter subsequently loses two protons in steps (8) and (9). The corresponding  $pK$  values are  $6.58 \pm 0.01$  ( $= -\log(K_{II})$ ) and  $7.60 \pm 0.02$ . If halide ions  $X^-$  are present in solution, mixed complexes, in which the coordinated  $H_2O$  molecule is substituted by that anion, can be formed, *i.e.*,  $[Pd(HMe_6tren)X]^{2-}$  and  $[Pd(Me_6tren)X]^+$ . The following values were obtained from alkalimetric titrations for the latter species:  $\log([Pd(Me_6tren)X^+]/([Pd(Me_6tren)^{2+}][X^-])) = 2.6 \pm 0.1$  ( $Cl^-$ ),  $2.8 \pm 0.1$  ( $Br^-$ ), and  $5.57 \pm 0.05$  ( $SCN^-$ ) at  $I = 1$  Na( $ClO_4$ , X).

2. *Spectrophotometry.* 2.1. *Exchange with Chloride.* The UV/VIS spectra of 1:1 solutions of  $Pd^{II}$  and  $Me_6tren \cdot 3 HClO_4$ , at constant ionic strength  $I = 1$  (Na, H)Cl, and varying pH values are shown in *Fig. 1*. These do not change in the pH-region 0–0.10 and agree well with those given by *Elding* [9] for the complex  $[PdCl_4]^{2-}$ . At  $pH > 0.10$ ,

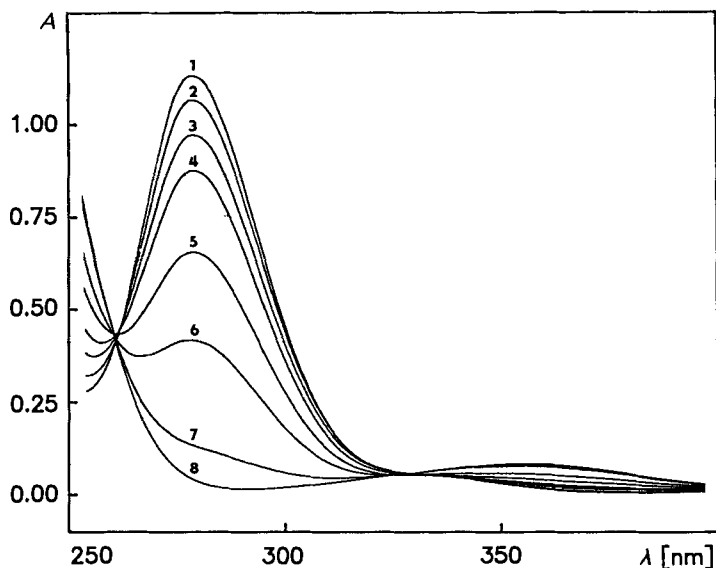


Fig. 1. The pH-dependence of the electronic spectra of  $[Pd(Me_6tren)Cl]^{2+}$ , at constant ionic strength  $I = 1$  ( $Na, H$ )  $Cl$ .  $[Pd] = 6 \cdot 10^{-4}$  M, 0.2 cm cells. The values of pH for indicated curves are: 0 for 1, 0.30 for 2, 0.52 for 3, 0.70 for 4, 1.00 for 5, 1.30 for 6, 2.00 for 7, and 4.63 for 8.

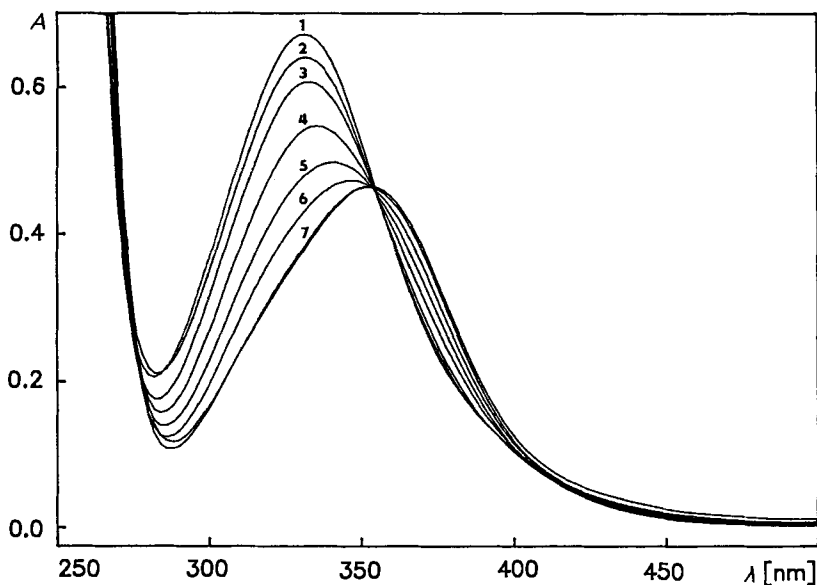


Fig. 2. The electronic spectra of  $[Pd(HMe_6tren)Cl]^{2+}$ , at constant ionic strength  $I = 1$  ( $Na$  ( $Cl, ClO_3$ )) and  $pH$  4.  $[Pd] = 6 \cdot 10^{-4}$  M, 1-cm cells. The chloride concentration varies as follows:  $[Cl^-] = 0$  for curve 1,  $1 \cdot 10^{-4}$  M for curve 2,  $2 \cdot 10^{-4}$  M for curve 3,  $5 \cdot 10^{-4}$  M for curve 4,  $1 \cdot 10^{-3}$  M for curve 5,  $2 \cdot 10^{-3}$  M for curve 6, and  $1 \cdot 10^{-2}$  M, resp.  $2 \cdot 10^{-2}$  M for curve 7 (the curves for both concentrations overlap).

exchange of  $\text{Cl}^-$  anions with  $\text{Me}_6\text{tren}$  takes place, as described by *Eqn. 3* giving the mixed complex  $[\text{Pd}(\text{HMe}_6\text{tren})\text{Cl}]^{2+}$ . At pH 3, the latter complex is fully formed, and the spectra do not show additional changes with increasing pH. The two isosbestic points at 265 and 330 nm confirm the occurrence of only two species containing  $\text{Pd}^{\text{II}}$ , *i.e.*,  $[\text{PdCl}_4]^{2-}$  and  $[\text{Pd}(\text{HMe}_6\text{tren})\text{Cl}]^{2+}$ .

This mixed complex shows absorbance maximum ( $\epsilon = 850 \text{ cm}^{-1} \cdot \text{M}^{-1}$ ) at  $\lambda = 356 \text{ nm}$  (see *Fig. 2*) where also the  $[\text{Cl}^-]$  dependence of UV/VIS absorption at constant ionic strength  $I = 1 \text{ Na}(\text{Cl}, \text{ClO}_3)$  and at constant pH 4 is shown. With increasing  $[\text{Cl}^-]$ , the  $\text{H}_2\text{O}$  molecule in the coordination sphere of  $\text{Pd}^{\text{II}}$  is replaced by a  $\text{Cl}^-$  anion; at  $[\text{Cl}^-]_{\text{tot}} = 0.01 \text{ M}$ , the mixed complex is already fully formed. The curve at  $[\text{Cl}^-] = 0$  corresponds to the spectrum of the  $[\text{Pd}(\text{HMe}_6\text{tren})(\text{H}_2\text{O})]^{3+}$  complex. It is evident from the isosbestic point at 355 nm that only one mixed complex is in equilibrium with  $[\text{Pd}(\text{HMe}_6\text{tren})(\text{H}_2\text{O})]^{3+}$ .

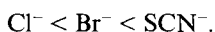
The values  $\log(K_{\text{III}}) = 1.41 \pm 0.08$  and  $\log(K_{\text{IV}}) = 3.50 \pm 0.05$  at  $I = 1$  ( $\text{NaClO}_3$ ) were obtained from the spectra discussed above. These logarithmic values, combined with those of  $K_{\text{I}}$ ,  $K_{\text{II}}$ , and the literature value of  $\log K_{\text{V}} = 11.54 \pm 0.09$  [9], give  $\log\beta([\text{Pd}(\text{Me}_6\text{tren})]) = 30.5 \pm 0.2$  for  $I = 1$  ( $\text{Na}, \text{H}$ )Cl.

**2.2. Exchange with Bromide.** A solution of  $6 \cdot 10^{-4} \text{ M}$   $[\text{Pd}(\text{Me}_6\text{tren})]^{2+}$  in  $1 \text{ M}$  ( $\text{Na}, \text{H}$ )Br at  $\text{pH} \leq 1$ ,  $\text{Pd}^{\text{II}}$  is complexed exclusively with  $\text{Br}^-$  anions. The spectra of these solutions are in good agreement with those given by *Elding* [8] for the  $[\text{PdBr}_4]^{2-}$  complex ( $\lambda = 332 \text{ nm}$ ,  $\epsilon = 10500 \text{ cm}^{-1} \text{ M}^{-1}$ ). With increasing pH value, the exchange of  $\text{Br}^-$  with  $\text{Me}_6\text{tren}$  takes place and, at pH 3.50, only  $[\text{Pd}(\text{HMe}_6\text{tren})\text{Br}]^{2+}$  is present in solution, from these spectra, a logarithmic value of  $K_{\text{III}} = -1.55 \pm 0.05$  was obtained.

The mixed complex  $[\text{Pd}(\text{HMe}_6\text{tren})\text{Br}]^{2+}$  is characterized by maximum at 370 nm,  $\epsilon = 740 \text{ cm}^{-1} \text{ M}^{-1}$ . The exchange of  $\text{H}_2\text{O}$  molecules in  $[\text{Pd}(\text{H}_2\text{O})(\text{Me}_6\text{tren})]^{3+}$  with  $\text{Br}^-$  anions was studied at pH 4,  $[\text{Pd}^{2+}]_i = [\text{Me}_6\text{tren} \cdot 3 \text{ HClO}_4]_i = 6 \cdot 10^{-4} \text{ M}$ ,  $[\text{Br}^-]$  varying between 0–0.002M and  $I = 1 \text{ Na}(\text{ClO}_3)$  (at  $[\text{Br}^-]_i = 0.002 \text{ M}$  the mixed complex  $[\text{Pd}(\text{HMe}_6\text{tren})\text{Br}]^{2+}$  is fully formed). Well defined isosbestic points at 295 and 365 nm show, that only one mixed complex is in equilibrium with  $[\text{Pd}(\text{HMe}_6\text{tren})(\text{H}_2\text{O})]^{3+}$ . The logarithmic value of  $K_{\text{IV}}$ , obtained from these spectra, is  $3.64 \pm 0.02$ . This value, when combined with those of  $K_{\text{I}}$ ,  $K_{\text{II}}$ ,  $K_{\text{III}}$ , and that of  $\log K_{\text{V}} (= 14.95)$  taken from [8], gives  $\log\beta([\text{Pd}(\text{Me}_6\text{tren})]) = 30.8 \pm 0.2$  for  $I = 1$  ( $\text{Na}, \text{H}$ )Br.

**2.3. Exchange with Thiocyanate.** The exchange of  $\text{SCN}^-$  with  $\text{Me}_6\text{tren}$  was studied at constant ionic strength  $I = 1$  ( $\text{NaSCN}, \text{ClO}_3$ ),  $[\text{SCN}^-]_i$  varying between 0.001–0.1M and pH 5.8–6.9 ( $[\text{H}^+]$  was measured with a glass electrode). The spectral curves intersect at a well defined isosbestic point at 278 nm; the  $[\text{Pd}(\text{SCN})_4]^{2-}$  complex is thus in equilibrium with only one mixed complex, *i.e.*,  $[\text{Pd}(\text{HMe}_6\text{tren})(\text{SCN})]^{2+}$ .

The evaluation of the spectra gives  $\log(K_{\text{III}}) = -12.74 \pm 0.09$ . Attempts to estimate the constant  $K_{\text{IV}}$  for the exchange of  $\text{H}_2\text{O}$  molecule by the  $\text{SCN}^-$  anion in the  $\text{Pd}^{\text{II}}$  coordination sphere failed because of the formation of the strongly absorbing  $[\text{Pd}(\text{SCN})_4]^{2-}$  complex. Nevertheless, taking into account *Eqn. 6*, the known constants  $\beta([\text{Pd}(\text{Me}_6\text{tren})])$ ,  $K_{\text{I}}$ ,  $K_{\text{II}}$ ,  $K_{\text{III}}$ , and the literature value of  $K_{\text{V}}$  [9], the value of  $\log(K_{\text{IV}})$  can be estimated to be  $\sim 5.10$ . The constants  $K_{\text{IV}}$  thus follow the expected order



**3. NMR Measurements.** The Me protons in the NMR spectra of  $[\text{Pd}^{\text{II}}(\text{Me}_6\text{tren})]$  system, in presence of different auxiliary ligands  $\text{X}^-$  ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{SCN}^-$ ), and with

different  $[\text{Pd}^{2+}]_t : [\text{X}^-]_t$  ratios, always show three distinct *singlets* due to the three inequivalent types of Me groups, e.g., for  $\text{X}^- = \text{Cl}^-$  at 3.05, 2.97, and 2.66 ppm at pH 5, and 2.90, 2.53, and 2.31 ppm at pH 10. Increasing the pH up to 12 results in broadening of all signals. This is indicative of exchange between the free and coordinated arms of  $\text{Me}_6\text{tren}$  rather than evidence for the pentacoordination of  $\text{Pd}^{\text{II}}$ , as suggested previously [5]<sup>1)</sup>.

The spectra of a 0.1M  $[\text{Pd}(\text{tren})]^{2+}$  solution, at pH 12, show that Pd has a square-planar coordination geometry. However, these data do not allow an unambiguous distinction between monomeric and dimeric species as the appropriate ligand-coordination shifts are not known. Nevertheless, it should be noted that the UV characteristics [7] indicate the presence of a  $\text{PdN}_4$  chromophore and this, in combination with the NMR results, is only consistent with a dimeric structure.

**Conclusions.** – The two ligands tren and  $\text{Me}_6\text{tren}$  in acidic solutions form with  $\text{Pd}^{2+}$  a protonated complex  $[\text{Pd}(\text{HL})\text{H}_2\text{O}]^{3+}$ . Both complexes have one  $\text{H}_2\text{O}$  molecule bound to the central ion, which can be substituted by halides, forming complexes of similar stability [7]. Base addition causes deprotonation of the free N-atom which, in the case of tren, then binds to a second complex ion with formation of a dimeric species  $[\text{Pd}_2\text{L}_2]^{4+}$  and involvement of all N-donor atoms [7]. In the case of  $\text{Me}_6\text{tren}$ , for steric reasons, this is not possible, and further addition of base causes deprotonation of the coordinated  $\text{H}_2\text{O}$ . The  $\text{pK}$  value obtained is very near that of  $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$  (7.8 [7]; dien = diethylenetriamine). Also the spectral data (*Table*) show no particular change which would imply an increase in coordination number from 4 to 5. This is also in agreement with the results of the NMR measurements and accounts for the observation that solid crystalline  $[\text{Pd}^{\text{II}}(\text{Me}_6\text{tren})]$  complex salts contain square planar  $\text{Pd}^{\text{II}}$ .

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#### REFERENCES

- [1] M. Ciampolini, N. Nardi, *Inorg. Chem.* **1966**, 5, 41.
- [2] M. Ciampolini, N. Nardi, *Inorg. Chem.* **1966**, 5, 1150.
- [3] M. Ciampolini, N. Nardi, G. P. Speroni, *Coord. Chem. Rev.* **1966**, 1, 222.
- [4] R. Morassi, I. Bertini, L. Sacconi, *Coord. Chem. Rev.* **1973**, 11, 343.
- [5] C. V. Senoff, *Inorg. Chem.* **1978**, 17, 2320.
- [6] J. A. Winter, F. A. Lin, R. E. Shepherd, *Inorg. Chim. Acta* **1989**, 155, 155.
- [7] G. Anderegg, *Inorg. Chim. Acta* **1986**, 111, 25.
- [8] G. Anderegg, *Helv. Chim. Acta* **1961**, 44, 1673.
- [9] L. I. Elding, *Inorg. Chim. Acta* **1982**, 6, 647.
- [10] G. Anderegg, S. C., Malik, *Helv. Chim. Acta* **1976**, 59, 159.
- [11] G. Ferguson, H. Parvez, *Acta Crystallogr., Sect. B* **1979**, 35, 2207.
- [12] G. Ferguson, P. J. Roberts, *Acta Crystallogr., Sect. B* **1978**, 34, 3083.

<sup>1)</sup> The chemical-shift differences of the Me groups found in this study and expressed in Hz are ca. 180 and 110 Hz, which should be ca. 20 and 13 Hz at 60 MHz used by Senoff. The latter values are within the range of line broadening observed by us at pH 11.5.