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58. Stereochemistry from X-Ray Diffraction Studies of Three Palladium(II) Complexes with Terdentate Chelating Amines

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Summary. X-ray crystal structure analysis of three Pd(II) complexes with *cis*-3,5-diamino-piperidine (DAPI) shows that the metal ion has a square planar coordination. The DAPI groups are *trans* in the protonated and mixed complexes. Most surprisingly, the unprotonated complex has a basket-like structure with the DAPI groups *cis*.

The usual coordination geometry of divalent palladium or platinum is square planar. True octahedral complexes of Pd(II) and Pt(II) are rare [1] and, as far as the authors are aware, no octahedral complexes of Pd(II) with nitrogen donors have been reported in the literature. Attempts have recently been made by *Schwarzenbach et al.* [2] to force the Pd(II) ion into an octahedral coordination by employing the terdentate ligand *cis*-3,5-diaminopiperidine (DAPI), $C_5NH_9(NH_2)_2$, in the expectation that the three nitrogens of the ligand might coordinate to form one of the faces of the octahedron. With this object in view, complexes with the protonated (HDAPI$^+$) as well as with the unprotonated ligand have been prepared. The crystal structure analysis of these compounds has been undertaken to obtain the actual geometry of the complexes.

Intensity data for all the complexes were collected on a *Picker* FACS-1 automated X-ray diffractometer. They were corrected for absorption. The structures were solved by *Patterson* and *Fourier* techniques and refined by least squares [3].

1. $[Pd(HDAPI)_2]$ $(ClO_4)_4 \cdot 2H_2O$: Orthorhombic, Pbca, $\mathbf{a} = 14.575$ (14), $\mathbf{b} = 10.815$ (8), $\mathbf{c} = 16.176$ (15) Å, $Z = 4$; 2259 reflections measured; R = 0.046. The molecular structure is shown in Figure 1. Pd(II), which occupies a centre of symmetry, is coordinated by nitrogens of the four primary amino groups in a square planar arrangement at distances 2.072 (5) and 2.070 (6) Å. Two ring nitrogens at a larger distance of 3.358 (7) Å complete a highly distorted octahedron. The Pd-N(3) direction makes an angle of 40° with the normal to the square plane. The two DAPI groups

are *trans*. Both the piperidine as well as the chelate rings have the 'chair' conformation. The protonated nitrogens of the positively charged ammonium groups are certainly not coordinated. It would appear that they might become so on deprotonation. This, however, does not happen as seen below.
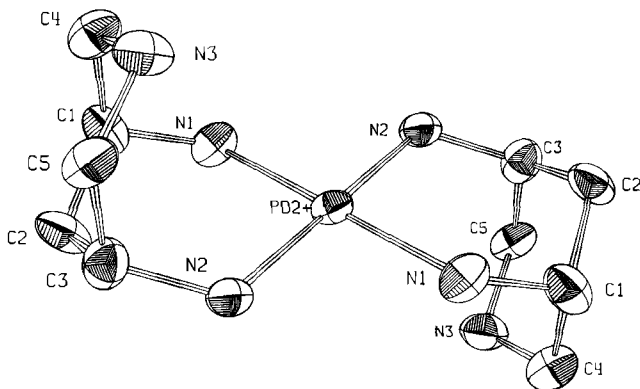

Fig. 1. *Molecular structure of Pd(HDAPI)$_2^{4+}$-Ion*

2. [*Pd(DAPI)$_2$*] (*ClO$_4$*)$_2$. Monoclinic, P2$_1$, **a** = 16.992 (7), **b** = 8.305 (3), **c** = 6.872 (3) Å, β = 98.57 (2)°; Z = 2; 3002 reflections measured; R = 0.052. The molecular structure is shown in Figure 2. Pd(II) is again coordinated by nitrogens of the four NH$_2$ groups in a square planar arrangement at distances 2.041 (7), 2.054 (7), 2.067 (7) and 2.077 (7) Å. The ring nitrogens have moved in slightly on deprotonation and are at distances of 3.084 (10) and 3.167 (7) Å. However, most surprisingly, the two DAPI groups are now *cis*. As before, the piperidine and the chelate rings have the 'chair' conformation. The N(5)–N(6) distance of 3.383 (11) Å between the piperidine nitrogens may suggest a stabilisation of this unusual structure by a weak hydrogen bond.
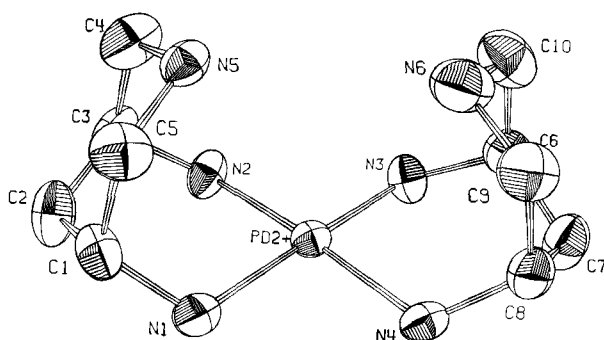

Fig. 2. *Molecular structure of Pd(DAPI)$_2^{2+}$-Ion*

3. [*Pd(DAPI)* (*HDAPI*)] (*NO$_3$*)$_3$. Monoclinic, P2$_1$/c, **a** = 9.663 (4), **b** = 12.978 (6), **c** = 9.727 (4) Å, β = 125.18 (2)°; Z = 2; 1314 reflections measured; R = 0.10. One of the nitrates in the structure is disordered. Three chemically unreasonable bond lengths

in the DAPI group and large temperature motions along **b** suggest either a lower symmetry or a partially disordered structure. Attempts to find a satisfactory model in the space group Pc failed. The salient features of the structure closely resemble those of (1), with four short Pd-N distances of 1.975 (21) and 2.019 (21) Å and two longer distances of 3.210 (14) Å. The direction from the palladium atom to the more distant nitrogen atom makes an angle of 29° with the normal to the square plane. Details of this work will be reported elsewhere.

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59. Thermodynamique des mélanges liquides binaires.
Volume de mélange et nombre moyen de configurations gauches des alcanes

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Summary. It is shown that there exists a fair correlation between the average number of 'gauche' conformations of normal and branched alkanes, and their volumes of mixing.

Introduction. – *Fernández-García et al.* [1] et *Steiger et al.* [2] ont mesuré précédemment les volumes de mélange d'alcanes normaux et ramifiés.

Le présent travail a pour objet de mettre en corrélation ces mesures avec une propriété conformationnelle de l'alcane, le nombre moyen Z_g de conformations gauches.

Nombre moyen Z_g de conformations gauches. – Dans une suite de travaux basés sur les théories conformationnelles de *Pitzer* [3], *Mann* [4] a introduit une relation entre les conformations stériques obtenues par rotation autour des liaisons $C - C$ des hydrocarbures, et les différences d'énergie interne des niveaux de rotation. Le nombre moyen de conformations gauches, tel qu'il ressort du travail de *Mann* [4] peut être écrit

$$Z_g = \frac{\sum z_i g_i \cdot \exp(-z_i U/RT)}{\sum g_i \cdot \exp(-z_i U/RT)}$$

où g_i est le nombre de manières d'obtenir une conformation i comprenant z_i formes gauches et où l'énergie U nécessaire pour passer d'une forme *trans* à une forme *gauche*