# Tetrahedral Distortion in Palladium(II) Macrocyclic Complexes: The Single Crystal *X*-Ray Structure of [Pd(tbc)]$(PF_6)_2 \cdot 0.4MeNO_2$ (tbc = 1,4,8,11-tetrabenzyl-1,4,8,11-tetra-azacyclotetradecane)

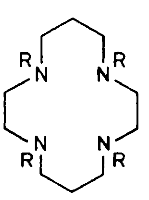
**Alexander J. Blake, Robert O. Gould, Timothy I. Hyde, and Martin Schröder***

*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland*

The single crystal *X*-ray structure of [Pd(tbc)]$(PF_6)_2 \cdot 0.4MeNO_2$ shows a tetrahedrally distorted square-planar stereochemistry around $Pd^{II}$; this distortion accounts for the anodic shift of the $Pd^{II}/Pd^{I}$ redox couple for the cation.

The modification of tetra-aza macrocyclic ligands to control and tune the redox properties of co-ordinated metal centres has been the subject of much interest. Meyerstein and co-workers have shown[1,2] that *N*-permethylation of $[M(cyclam)]^{2+}$ (M = Ni, Cu; cyclam = 1,4,8,11-tetra-azacyclotetradecane) leads to an overall net stabilisation of the monovalent species $[M(tmc)]^{+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane). The anodic shift in the $Ni^{II}/Ni^{I}$ redox couple on introduction of *N*-alkyl groups into the macrocycle has been correlated with the greater length of the Ni–N (tertiary) bonds relative to the Ni–N (secondary) bonds in these systems.[3] We wished to probe this theory further, particularly in view of the observation that increased alkylation of simple amines leads to an increase, rather than a decrease, in their basicity and donor properties.[4] Clearly, the cyclic nature of the tetra-aza ligands is a key factor in the redox behaviour of these systems.

Previously, we have observed increased redox stabilisation of monovalent palladium centres on alkylation of a tetra-aza co-ordination sphere, *e.g.* $E_{\frac{1}{2}} = -1.53$ and $-2.10$ V *vs.* $Fc/Fc^{+}$ (Fc = ferrocene) for $[Pd(tmc)]^{2+}$ and $[Pd(cyclam)]^{2+}$ respectively.[5] We were interested in trying to increase the stability of $Pd^{I}$ and $Pd^{0}$ species using tetra-aza macrocyclic ligands, and have therefore undertaken a study of Pd complexes of derivatised ligands. Since $Pd^{II}$ is much less susceptible to five and six co-ordination than $Ni^{II}$, $Pd^{II}$ systems would be expected to act as a clearer indicator of the electronic and stereochemical features of four co-ordinate tetra-aza complexes. Barefield and co-workers have shown[3] that benzyl functions lead to a greater anodic shift in the $Ni^{II}/Ni^{I}$ couple than methyl groups. We therefore undertook a synthesis of the $[Pd(tbc)]^{2+}$ cation.



R = H : cyclam
R = Me : tmc
R = $CH_2Ph$ : tbc

Reaction of tbc with $Pd(OAc)_2$ in $CH_2Cl_2$ (20 °C, 24 h) gave a pale yellow solution of the $[Pd(tbc)]^{2+}$ cation. Addition of $NH_4PF_6$ afforded a pale yellow precipitate which was recrystallized from $MeNO_2$ to give crystals of $[Pd(tbc)](PF_6)_2$.† $^1H$ and $^{13}C$ N.m.r. data indicated the presence of a single symmetrical isomer in solution. Cyclic voltammetry of $[Pd(tbc)](PF_6)_2$ in MeCN (0.1 M $Bu^n{}_4NPF_6$) at platinum electrodes shows a reversible reduction at $E_{\frac{1}{2}} = -1.27$ V *vs.* $Fc/Fc^{+}$. Controlled potential electrolysis of $[Pd(tbc)]^{2+}$ at a platinum gauze in MeCN at −1.45 V under a stream of Ar at 20 °C affords a highly air-sensitive, reactive species, the e.s.r. spectrum of which, at 77 K as a frozen glass, shows an anisotropic signal with axial symmetry, $g_{\parallel} = 2.320$, $g_{\perp} = 2.086$, $A_{\parallel} = 51$ G ($^{105}Pd$, $I = 5/2$). These spectral features are consistent with the formation of a $d^9$ palladium(I) species $[Pd(tbc)]^{+}$.[5] Coulometric measurements confirm the reduc-

---

† Characterised by elemental analysis, $^1H$ and $^{13}C$ n.m.r., u.v.–visible, i.r., and fast-atom bombardment mass spectroscopy, and conductivity measurements.

**Table 1.** Stereochemical parameters for palladium(II) complexes of tetra-aza macrocyclic ligands.

| Complex | $E_{\frac{1}{2}}$/V[a] | Site symmetry at Pd | Pd–N distances/Å | Pyramidal distortion /Å[b] | Tetrahedral distortion /Å[c] | Ref. |
|---|---|---|---|---|---|---|
| (*R*,*S*,*R*,*S*)-$[Pd(tbc)]^{2+}$ | −1.27 | $C_1$ | 2.105(8), 2.079(8)<br>2.098(7), 2.104(7) | 0.098 | −0.212(8), −0.210(7)<br>+0.211(8), +0.211(7) | This work |
| (*R*,*S*,*R*,*S*)-$[Pd(tmc)]^{2+}$ | −1.53 | $C_s$ | 2.051(11), 2.066(11) | 0.082 | zero | 5 |
| (*R*,*S*,*S*,*R*)-$[Pd(cyclam)]^{2+}$ | −2.10 | $C_s$ | 2.044(7), 2.057(7) | 0.004 | zero | 8 |

[a] Referenced *vs.* $Fc/Fc^+$. [b] Measured as distance of Pd out of the least-squares $N_4$ plane. [c] Measured as distance of each N above and below the least-squares $N_4$ plane.

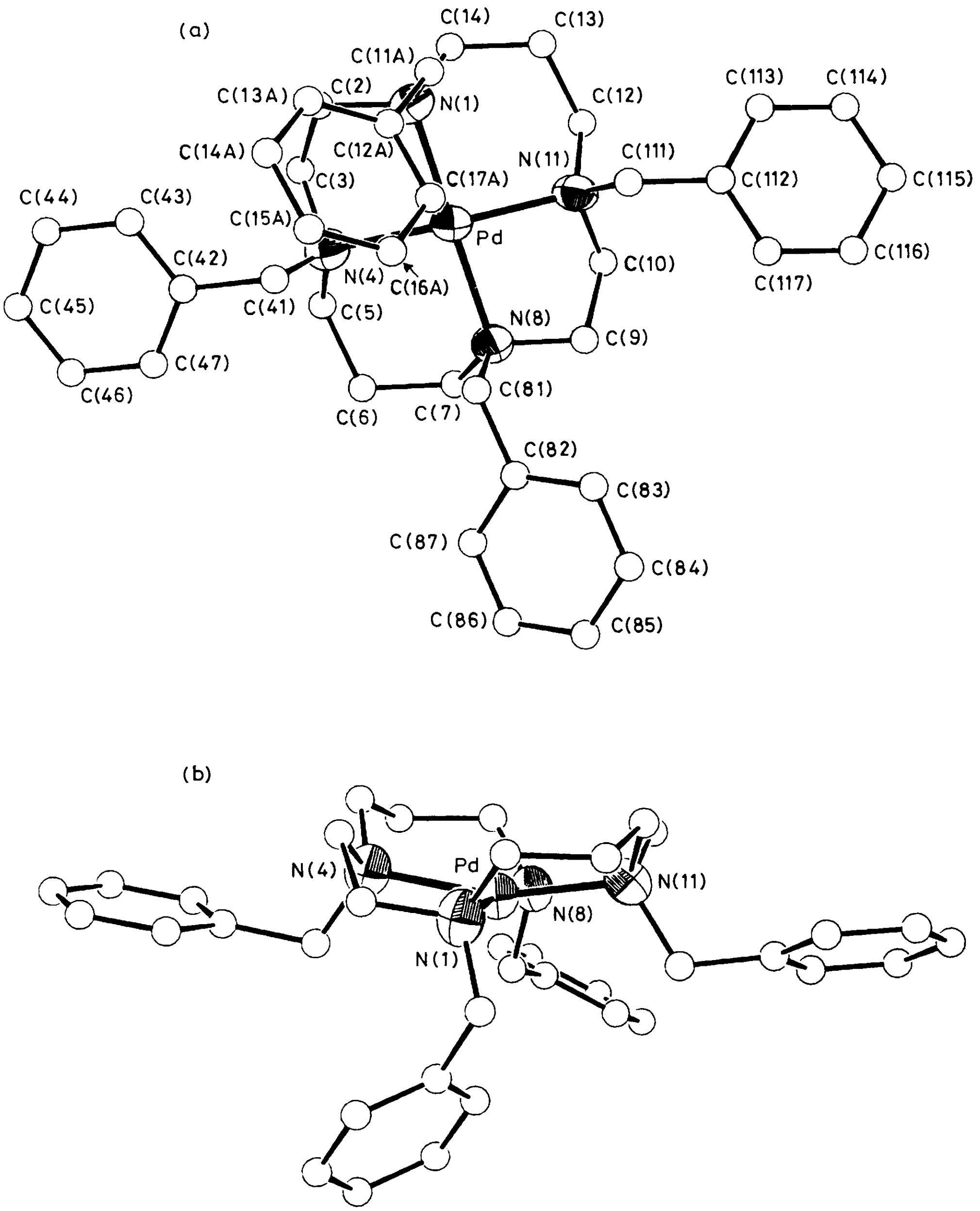


**Figure 1.** Two views of the single crystal *X*-ray structure of $[Pd(tbc)]^{2+}$.

tion to be a one-electron process. The electron transfer at $E_{\frac{1}{2}} = -1.27$ V is therefore assigned to a Pd$^{II}$/Pd$^{I}$ couple. This redox couple occurs at an appreciably less negative potential (by 260 mV) than for [Pd(tmc)]$^{2+}$.[5] We wished to monitor the stereochemical features of the Pd$^{II}$ precursor in an attempt to explain this phenomenon, and undertook a single crystal *X*-ray structural analysis of the tbc complex.

The single crystal *X*-ray structure of the [Pd(tbc)]$^{2+}$ cation (Figure 1a,b) shows‡ the Pd$^{II}$ ion co-ordinated to the tetra-aza ligand in an approximate square plane, Pd–N(1) 2.105(8), Pd–N(4) 2.079(8), Pd–N(8) 2.098(7), Pd–N(11) 2.104(7) Å, with the Pd atom lying 0.098 Å out of the least-squares $N_4$ plane towards the benzyl groups. The crystal structure confirms that all four benzyl groups lie on the same side of the co-ordinated macrocycle in an *R**,*S**,*R**,*S**-configuration (*trans*-I-isomer). Interestingly, one of the phenyl rings bends back in the solid state to lie over the Pd–N(1) bond (Figure 1a); in solution, the benzyl moieties are found to be equivalent by n.m.r. spectroscopy. The most important feature of the structure is that, in addition to a pyramidal distortion, there is also a marked tetrahedral distortion at the Pd$^{II}$ centre with N(1) and N(8) lying above, and N(4) and N(11) lying below the least-squares $N_4$ plane (Table 1). The tetrahedral distortion presumably minimises steric interactions between the benzyl side-chains and with the macrocyclic backbone,[6] and leads to the relatively anodic Pd$^{II}$/Pd$^{I}$ couple. Sauvage and co-workers have shown[7] that d$^9$ Ni$^{I}$ centres are highly stabilised by imposed tetrahedral co-ordination. Minimal distortions from square planarity are observed for [Pd(cyclam)]$^{2+}$,[8] and this complex shows the most cathodic Pd$^{II}$/Pd$^{I}$ couple;[5] [Pd(tmc)]$^{2+}$ shows a significant pyramidal distortion and a value of the Pd$^{II}$/Pd$^{I}$ couple intermediate between that for the cyclam and tbc complexes[5] (Table 1). These results suggest that tetrahedral and pyramidal distortions in d$^8$ metal complexes of tetra-aza macrocyclic complexes play a significant role in their reductive electrochemistry, and suggests that Pd$^{I}$ species might be even further stabilized by imposed tetrahedral co-ordination.

We thank BP Chemicals and the S.E.R.C. for a CASE Award (to T. I. H.), the S.E.R.C. for support, and Johnson Matthey plc for generous loans of platinum metals.

*Received, 14th July 1987; Com. 1018*

---

‡ *Crystal data:* $C_{38}H_{48}N_4Pd^{2+}\cdot 2PF_6^{-}\cdot 0.4\ CH_3NO_2$, triclinic, $P\bar{1}$, $a$ = 9.870(3), $b$ = 14.995(5), $c$ = 18.233(5) Å, $\alpha$ = 107.95(2), $\beta$ = 103.99(2), $\gamma$ = 101.50(3)°, $U$ = 2379 Å$^3$, $D_c$ = 1.370 g cm$^{-3}$, $Z$ = 2, 6223 data measured to $\theta$ = 22.5° using Mo-$K_\alpha$ radiation; refinement based on 5189 data with $F \geqslant 6\sigma(F)$. At convergence, $R,R_w$ = 0.0822, 0.1177 respectively for 312 parameters. The Pd position was obtained from a Patterson synthesis and the remaining non-H atoms from iterative rounds of least-squares refinement and difference Fourier synthesis.[9] The structure exhibits disorder affecting the two $PF_6^-$ ions and solvent molecules. A well-defined solvent nitromethane molecule refined to a partial occupancy of 0.407(11); a solvent molecule that defied modelling is also present, and is the most likely cause of the relatively high *R* values. A minor component of the cation was found to have an alternative orientation of the phenyl ring C(42)–C(47), C(42′)–C(47′). Phenyl rings were refined as rigid hexagons. Hydrogen atoms were included in calculated positions and Pd, P, N, F, and O atoms were refined anisotropically.[9] At convergence, the difference map showed no feature above 1.06 e Å$^{-3}$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

## References

1 N. Jubran, G. Ginzberg, H. Cohen, and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1982, 517; N. Jubran, G. Ginzberg, H. Cohen, and D. Meyerstein, *Inorg. Chem.*, 1985, **24**, 251.

2 N. Jubran, H. Cohen, Y. Koresh, and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1984, 1683.

3 E. K. Barefield, G. M. Freeman, and D. G. Van Derveer, *Inorg. Chem.*, 1986, **25**, 552, and references therein.

4 E. M. Arnett, *Acc. Chem. Res.*, 1973, **6**, 404.

5 A. J. Blake, R. O. Gould, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 431.

6 N. W. Alcock, K. P. Balakrishnan, P. Moore, and G. A. Pike, *J. Chem. Soc., Dalton Trans.*, 1987, 889.

7 J. P. Sauvage, C. O. Dietrich-Buchecher, and J. M. Kern, *J. Chem. Soc., Chem. Commun.*, 1985, 760.

8 M. Yamashita, H. Ito, K. Toriumi, and T. Ito, *Inorg. Chem.*, 1983, **22**, 1566; K. Toriumi, M. Yamashita, H. Ito, and T. Ito, *Acta Crystallogr., Sect. C.*, 1986, **42**, 963.

9 SHELX76, G. M. Sheldrick, Program for Crystal Structure Refinement, University of Cambridge, 1976.