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# pH-Induced switching of metal ion co-ordination: the structure of $[Pd([18]aneN_2S_4{\cdot}2H^+)][BF_4]_4{\cdot}2H_2O$ from a twinned crystal ($[18]aneN_2S_4$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane)

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Treatment of $[Pd([18]aneN_2S_4)][BF_4]_2$ ($[18]aneN_2S_4$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane) with $HBF_4$ led to a marked structural change at Pd(II) from distorted octahedral $[N_2S_2 + S_2]$-donation to a square-planar $S_4$-donor co-ordination *via* protonation of the secondary amine functions; this pH-induced re-arrangement is accompanied by a reversible colour change from purple to yellow in MeCN solution.

The chemistry of macrocyclic ligand complexes has been an area of considerable interest for some years.[1] This is mainly due to the increased stability imparted by the macrocyclic effect and also the conformational flexibility of saturated ring systems which can accommodate a range of metal stereochemistries and oxidation states.[2] We have been interested in the interaction of transition metal centres with mixed thia/aza macrocycles since these ligands combine soft thioether donors of low basicity capable of binding transition metal ions, and harder, more basic amine functions within a cyclic configuration.[3] We have reported previously the preparation, structural characterisation and redox properties of Pd(II) and Pt(II) complexes involving the macrocyclic ligand $[18]aneN_2S_4$ (1,4,10,13-tetrathia-7,16-diazacyclooctadecane) and its di-*N*-methylated derivative $Me_2[18]aneN_2S_4$ (7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane).[4] Metal(II) complexes of these ligands exhibit strikingly different electrochemical properties, and these differences were traced back to the very different structures adopted by the Pd(II) complexes of these two ligands. Thus $[Pd([18]aneN_2S_4)]^{2+}$ shows a distorted square planar $N_2S_2$-co-ordination with additional, long-range interactions to two apical S donor atoms, $Pd\cdots S = 2.954(4)$, 3.000(3) Å, and exhibits a reversible Pd(II)/Pd(III) redox couple at +0.57 V *vs.* $Fc/Fc^+$. In contrast, $[Pd(Me_2[18]aneN_2S_4)]^{2+}$ shows a distorted square-planar $S_4$-co-ordination with the tertiary amine functions directed away from the metal centre. This complex exhibits a reversible Pd(II)/Pd(I) redox couple at −0.74 V *vs.* $Fc/Fc^+$, with no oxidative activity observed by cyclic voltammetry.

In view of these unexpected differences in redox behaviour and their correlation with the differing stereochemistries adopted by the complexes, we wished to establish whether stereochemical switching of co-ordination of $[18]aneN_2S_4$ to Pd(II) might be induced by changes in pH. Thus, addition of 40% aqueous $HBF_4$ to a MeCN solution of $[Pd([18]aneN_2S_4)][BF_4]_2$†

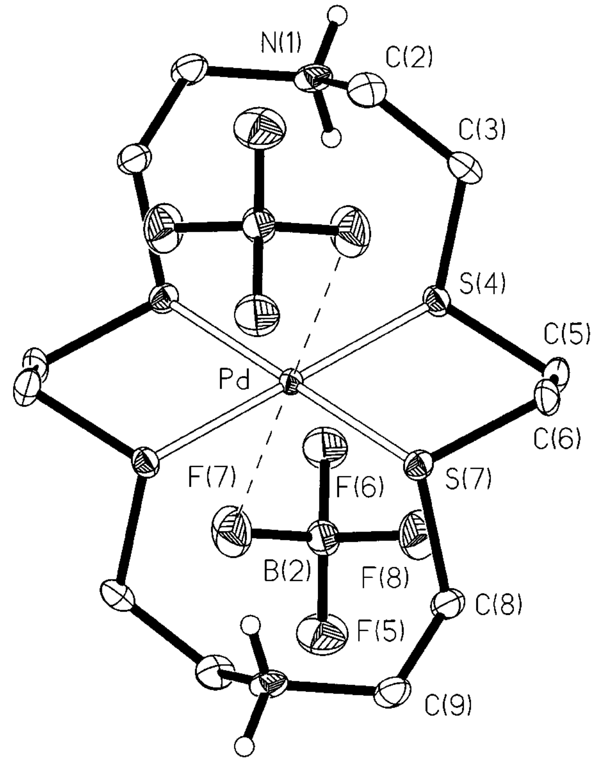
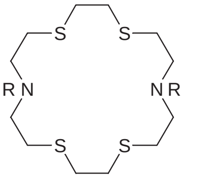


**Fig. 1** View of the structure of the $[Pd([18]aneN_2S_4{\cdot}2H^+)]^{2+}$ cation showing the numbering scheme adopted. The two weakly interacting $BF_4^-$ anions and the N-based protons are also included while the other two $BF_4^-$ anions, the methylene protons and $H_2O$ solvent molecules are omitted for clarity. Ellipsoids are shown at 40% probability. Selected bond lengths (Å) and angles (°): Pd–S(4) 2.3159(7), Pd–S(7) 2.3432(6), $Pd\cdots F(7)$ 3.122(2); S(4)–Pd–S(7) 88.52(3), $F(7)\cdots Pd$–S(4) 92.85(4), $F(7)\cdots Pd$–S(7) 112.07.



R = H: $[18]aneN_2S_4$
R = Me: $Me_2[18]aneN_2S_4$

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† Preparation of $[Pd([18]aneN_2S_4{\cdot}2H^+)][BF_4]_4$. An analytically pure sample of $[Pd([18]aneN_2S_4)][BF_4]_2$ (0.020 mg, 0.033 mmol) was dissolved in MeCN (2 $cm^3$) giving a purple solution. Aqueous $HBF_4$ (40%, 1 drop) was then added giving an immediate colour change to yellow. Upon standing for several days, yellow crystals were obtained in quantitative yield which were filtered and dried *in vacuo*. This product is very stable in the presence of $HBF_4$, but the starting material is readily regenerated in the absence of acid, and this hampered our efforts to obtain pure samples for microanalysis. Electrospray mass spectrum (MeCN): found $m/z = 433$; calculated for $[^{106}Pd([18]aneN_2S_4 + H)]^+$ $m/z = 433$. UV/VIS spectrum $[MeCN–HBF_4(aq)]$: $\lambda_{max} = 274$ nm ($\varepsilon_{mol}$ *ca.* 11 300 $dm^3\ mol^{-1}\ cm^{-1}$), 311 (sh) (*ca.* 3950). IR spectrum (CsI disk): 3400vs (br), 3220s, 2960w, 1635s, 1436m, 1386m, 1198m, 1072s (br), 884w, 795m, 646w, 549m, 527w, 502w $cm^{-1}$.

leads to an immediate colour change from red-purple of the parent 2+ cation to yellow suggesting that indeed a significant stereochemical rearrangement is occurring. This is a totally reversible process with the red-purple solution being readily regenerated near neutral pH. Slow evaporation of a solution of the protonated complex in MeCN and aqueous $HBF_4$ over several days furnished golden yellow, columnar crystals. A single crystal X-ray structure determination ‡ of this protonated complex confirms (Fig. 1) a centrosymmetric 4+ cation in which the Pd(II) ion is co-ordinated to a distorted square-planar array of four thioether donors, Pd–S(4) = 2.3159(7), Pd–S(7) = 2.3432(6) Å, with each of the secondary amine centres protonated and directed away from the metal centre. In addition, there are long-range, apical interactions between the Pd(II) ion and one F atom of each of two $BF_4^-$ anions, Pd · · · F(7) = 3.122(2) Å. The other two $BF_4^-$ anions are non-co-ordinating, although they are involved in significant H-bonding interactions with the protonated amine groups and $H_2O$ solvent molecules within the lattice. This H-bonding leads to an intricate network with N(1) · · · F(1) = 2.868, N(1) · · · O(1W) = 2.797, O(1W) · · · F(2) = 2.976, O(1W) · · · F(5) = 3.231, O(1W) · · · F(6) = 2.918 Å. The primary co-ordination at the metal centre in this species is very similar to that in $[Pd(Me_2[18]aneN_2S_4)]^{2+}$ with similar Pd–S bond distances [2.3261(22), 2.3239(21) Å].[4]

The electrospray mass spectrum of the yellow product (MeCN solution) shows peaks with the correct isotopic distribution at $m/z$ = 433, consistent with $[^{106}Pd([18]aneN_2S_4 + H)]^+$. The IR spectrum shows peaks associated with co-ordinated $[18]aneN_2S_4$ and $BF_4^-$ anion, and strong absorptions due to $H_2O$ are also apparent and mask the N–H stretching region. The UV/VIS spectrum of $[Pd([18]aneN_2S_4)][BF_4]_2$ in MeCN solution shows transitions at $\lambda_{max}$ = 514 nm ($\varepsilon_{mol}$ 124 $dm^3\ mol^{-1}\ cm^{-1}$), 322 (2815), 266 (9420) and 233 (12 140), and addition of a single drop of 40% aqueous $HBF_4$ leads to the loss of these absorptions, with a new band appearing at 274 nm (*ca.* 11 300 $dm^3\ mol^{-1}\ cm^{-1}$) together with a shoulder at 311 (*ca.* 3950) corresponding to $[Pd([18]aneN_2S_4{\cdot}2H^+)][BF_4]_4{\cdot}2H_2O$.

These results further exemplify the considerable chemical and structural diversity associated with metal complexes involving thia/aza macrocycles and the complex reported represents the first example of pH dependence in these systems. It suggests also that mixed thioether–aza macrocycles might be avid potential metal-ion extractors at low pH with the corresponding anion associated with the protonated amine function.

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‡ X-Ray crystallography and crystal data for $[Pd([18]aneN_2S_4{\cdot}2H^+)][BF_4]_4{\cdot}2H_2O$. The selected crystal was coated with mineral oil, mounted on a glass fibre and immediately placed under a stream of cold nitrogen. Data collection used a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat operating at 150 K, and graphite-monochromated Mo-K$\alpha$ radiation (0.710 73 Å) using $\omega$–2$\theta$ scans. $C_{12}H_{32}B_4F_{16}N_2O_2PdS_4$, $M$ = 818.28, monoclinic, space group $P2_1/c$, $a$ = 10.068(3), $b$ = 12.449(3), $c$ = 11.179(3) Å, $\beta$ = 106.20(2)° (cell 1), $U$ = 1345.5(6) $Å^3$, $Z$ = 2, $D_c$ = 2.020 g $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 11.30 $cm^{-1}$, $F(000)$ = 816. Yellow block (0.50 × 0.35 × 0.25 mm). 4751 Reflections were measured to $2\theta_{max}$ = 50° and absorption corrected ($\psi$ scans) on a monoclinic cell with $a$ = 11.179(3), $b$ = 12.449(3), $c$ = 20.154(6) Å, $\beta$ = 106.20(2)° (cell 2). These data could not be sensibly assigned to a space group. There were no significant data for $h,k,l$ with $h = 2n$, $l = 2n + 1$, and while data with $h$, $k$ and $l$ all even had a mean value of $E^2$ of 3.2, those with $h$, $k$ and $l$ all odd had $\langle E^2 \rangle = 2.4$ and other parity groups had mean values ranging between 0.2 and 0.9. The problem was resolved by treating the data as arising from a twinned crystal with dimensions of cell 1 above. This twinning arises because for this cell $|a| \approx |a + c/2|$, and both make the same angle with $c$. The two unequal components have the twin matrix $-1\ 0\ -\tfrac{1}{2}/0\ -1\ 0/0\ 0\ 1$. In terms of the cell used for data collection, $h,k,l$ combine the actual $-l'$, $k'$, $-2h'$ for one component with $l''$, $k''$, $2h'' + l''$ for the other. Consequently, the first component contributes only to data with $l = 2n$ and the second only to data with $h$ and $l$ either both even or both odd. The intensity distribution of the measured data clearly indicates that the structure contains a heavy atom on an inversion centre, and that the second component as described above is clearly predominant; the structure was solved roughly (direct methods)[5] by assuming that it was the entire structure and rejecting all other data. The accompanying computer program (deposited) was used to divide the data appropriately, giving 3272 unique reflections of which 2813 with $F > 4\sigma(F)$ were used in all calculations, and least-squares refinement proceeded smoothly using SHELXL,[6] the final contribution of the first component being 0.2809(11) of that of the second. One half cation, two $BF_4^-$ anions and one $H_2O$ solvent molecule were identified in the asymmetric unit. All non-H atoms were refined with anisotropic thermal parameters and H atoms associated with the C and N atoms were included in fixed, calculated positions, while those associated with the $H_2O$ molecules were located from the difference map, and included but not refined. At final convergence, $R1$ = 0.0292, $wR2$ = 0.0739 [$F > 4\sigma(F)$] and $R1$ = 0.0408, $wR2$ = 0.0863 (all data) (based upon least-squares refinement on $F^2$), $S$ = 1.088 for 91 parameters and the final $\Delta F$ synthesis showed $\Delta\rho$ in the range 0.53 to −0.55 e $Å^{-3}$. CCDC reference number 186/1080.