Di- and Tri-palladium(II) Polyazacycloalkane Complexes. A Case of Deprotonated Secondary Nitrogen in Solution and in Solid State

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Crystal structures of di- and tri-nuclear palladium(II) complexes with the azamacrocycles[18]aneN_6 and [21]aneN_7 have been solved by X-ray analysis; in the case of the trinuclear complex deprotonation of a secondary amino group occurs, both in solution and in the solid state.

Pd^{2+} complexes of amine ligands have been studied instead of, or as well as, the analogous Pt^{2+} compounds, which exhibit some antitumour activity, in order to overcome the difficulties, owing to kinetic inertness, encountered in studying the Pt^{2+} complexes. However, thermodynamic data for the formation of Pd^{2+} complexes of amine ligands are rare because their very high stability complicates the determination of their equilibrium constants.

Polyazacycloalkanes of the series [3k]aneN_k ($7 \leq k \leq 12$) form polynuclear complexes with the metal ions Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}.[1-11] Prior to the present work the smallest ligand of this series able to include more than one metal ion was the heptadentate [21]aneN_7 which forms the dicopper(II) complex $[Cu_2([21]aneN_7)]^{4+}$.[2] While the other macrocycles of the series form dinuclear complexes, the largest elements [33]aneN_{11} and [36]aneN_{12} also form trinuclear species.[5] The equilibrium constants for the formation of these highly stable complexes have been determined.[1-11]

Consequently, polyazacycloalkanes of this series seem promising ligands to gain an insight into the coordination chemistry of the Pd^{2+} ion.

We have found that the Pd^{2+} ion, which presents rigid stereochemical requirements, can organize the cyclic ligands allowing the formation of polynuclear complexed systems with small macrocyclic ligands. Indeed $[18]aneN_6$ and $[21]aneN_7$ react in aqueous solution with $PdCl_4^{2-}$ to form the species $[Pd_2([18]aneN_6)Cl_2]^{2+}$ and $[Pd_3([21]aneN_7)Cl_3]^{2+}$, respectively. In the latter case, the inclusion of three Pd^{2+} ions into the macrocycle induced acidic dissociation of an amino group of the ligand. These polynuclear complexes have been isolated as the crystalline compounds $[Pd_2([18]aneN_6)Cl_2][ClO_4]_2$ and $[Pd_3([21]aneN_7)Cl_3][ClO_4]_2 \cdot H_2O$ and their crystal structures have been solved by X-ray analysis.

The structure of the compound $[Pd_2([18]aneN_6)Cl_2][ClO_4]_2$ consists of a dinuclear $[Pd_2([18]aneN_6)Cl_2]^{2+}$ cation and disordered uncoordinated perchlorate anions.† The complex cation (Fig. 1) possesses a $2/m$ symmetry. In the dinuclear complex each palladium ion is tetra-coordinated by three nitrogen atoms and one chloride ion in a distorted square geometry. Each metal ion lies 0.14 Å out of the plane identified by the donor atoms N(1), N(2), N(2′), Cl(1). The two palladium atoms are 3.04 Å apart and point towards each other with respect to the two planes containing the donor atoms. The overall macrocyclic conformation is S-like.

In $[Pd_3([21]aneN_7)Cl_3][ClO_4]_2 \cdot H_2O$ the $[21]aneN_7$ ligand and the chlorine atoms bind the three palladium atoms in square planar fashion (Fig. 2).† An amino group of the macrocyclic ligand, which undergoes deprotonation in the complex formation, bridges two palladium atoms. The coordi-

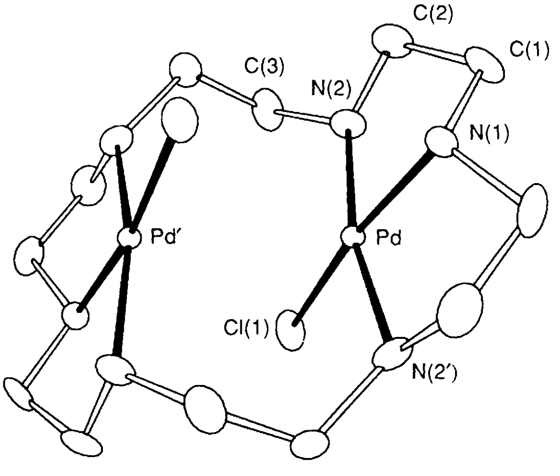

Fig. 1 ORTEP view of the complexed cation $[(Pd_2[18]aneN_6)Cl_2]^{2+}$; Selected bond distances (Å) and angles (°). Bond distances: Pd–N(1) 1.99(1), Pd–N(2) 2.049(9), Pd–Cl(1) 2.301(5). Bond angles (°): N(2)–Pd–N(2) 166.5(4), N(1)–Pd–N(2) 83.9(3), Cl(1)–Pd–N(2) 95.6(3), Cl(1)–Pd–N(1) 171.4(4).

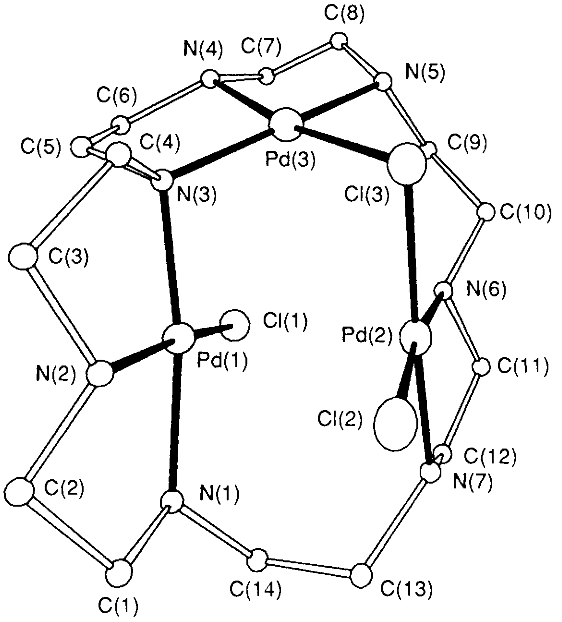

Fig. 2 ORTEP view of the complex cation $[Pd_3([21]aneN_7)Cl_3]^{2+}$. Selected bond distances (Å) and angles (°). The deprotonated nitrogen is N3. Bond distances (Å): Pd(1)–Cl(1) 2.3556(88) Pd(2)–N(6) 2.0422(254), Pd(1)–N(1) 2.0249(250) Pd(2)–N(7) 1.9887(243), Pd(1)–N(2) 2.0105(237) Pd(3)–Cl(3) 2.3407(89), Pd(1)–N(3) 2.0657(260) Pd(3)–N(3) 1.9521(263), Pd(2)–Cl(2) 2.2756(92) Pd(3)–N(4) 1.9769(277), Pd(2)–Cl(3) 2.3063(94) Pd(3)–N(5) 2.0874(299). Bond angles (°): N(2)–Pd(1)–N(3) 87.61(1.03) Cl(2)–Pd(2)–N(7) 92.84(0.74), N(1)–Pd(1)–N(3) 167.99(1.10) Cl(2)–Pd(2)–N(6) 173.04(0.75), N(1)–Pd(1)–N(2) 81.04(1.08) Cl(2)–Pd(2)–Cl(3) 83.15(0.33), Cl(1)–Pd(1)–N(3) 97.98(0.76) N(4)–Pd(3)–N(5) 81.83(1.20), Cl(1)–Pd(1)–N(2) 173.42(0.75) N(3)–Pd(3)–N(5) 168.78(1.17), Cl(1)–Pd(1)–N(1) 93.13(0.79) N(3)–Pd(3)–N(4) 88.88(1.13), N(6)–Pd(2)–N(7) 84.02(1.01) Cl(3)–Pd(3)–N(5) 94.65(0.89), Cl(3)–Pd(2)–N(7) 176.62(0.76) Cl(3)–Pd(3)–N(4) 171.18(0.83), Cl(3)–Pd(2)–N(6) 93.70(0.75) Cl(3)–Pd(3)–N(3) 95.42(0.80).

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† *Crystallographic data*: for $C_{12}H_{30}N_6Cl_4O_8Pd_2$: M = 741.01, monoclinic, space group $C2/m$, $a = 10.876(2)$, $b = 18.117(2)$, $c = 7.043(2)$ Å, $\beta = 113.78(2)°$, $V = 1270(12)$ Å^3, $Z = 2$, $D_{calc} = 1.92$ g cm^{-3}, $\mu = 16.94$ cm^{-1}, graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). A crystal of $(Pd_2[18]aneN_6)Cl_2(ClO_4)_2$ was mounted on a Enraf-Nonius CAD-4 X-ray diffractometer. 1272 Intensities were collected in the range $5 \le 2\theta \le 50°$ and corrected for Lorentz and polarization effects. An absorption correction was applied once the structure was solved.[13] The 1062 reflections having $I \ge 3\sigma(I)$ were considered observed and used in the structure analysis. The structure was solved by the heavy-atoms method, which gave the position of the palladium atom. Successive Fourier syntheses showed all non-hydrogen atoms. The refinement, performed by means of the full-matrix least-squares method, gave $R = 0.063$ and $R_w = 0.059$. Hydrogen atoms were included in calculated positions with an overall temperature factor U of 0.05. Anisotropic temperature factors were used for all non-hydrogen atoms except for the oxygen atoms of the perchlorate anion, which show some degree of disorder. Two different models were found for the perchlorate ion; therefore, populations parameters of 0.5 were used for these oxygen atoms.

For $C_{14}H_{36}N_7Cl_5O_9Pd_3$: M = 942.93, orthorhombic, space group $Pcab$, $a = 13.125(7)$, $b = 13.213(3)$, $c = 33.570(5)$ Å, $V = 5822(3)$ Å^3, $Z = 8$, $D_{calc} = 2.15$ g cm^{-3}, $\mu = 21.20$ cm^{-1}, graphite monochromated Mo-Kα ($\lambda = 0.7107$ Å) radiation. A crystal of $[Pd_3([21]aneN_7)]Cl_3(ClO_4)_2 \cdot H_2O$ was mounted on a Enraf-Nonius CAD-4 X-ray diffractometer. 4275 Reflections were collected in the range $5 \le 2\theta \le 45°$. The intensities were corrected for Lorentz and polarization effects, and an absorption correction was applied once the structure was solved.[13] The 1899 reflections having $I \ge 3\sigma(I)$ were considered observed and used in the structure analysis. The structure was solved by the heavy-atoms method, which gave the position of the palladium atoms. Successive Fourier syntheses showed all non-hydrogen atoms. Refinement was performed by means of the full-matrix least-squares method to obtain a final R factor of 0.074. Hydrogen atoms were included in calculated positions with an overall temperature factor U of 0.05. Isotropic temperature factors were used for all atoms except for the palladium and chlorine. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

nation planes of Pd(1) and Pd(2) are nearly parallel, the angle between being 1.0°. The third square plane containing N(3), N(4), N(5), Cl(3) and Pd(3) forms an angle of 92.0° with the others. The Pd(1) and Pd(2) atoms lie significantly out from their mean square coordination planes, 0.084 and 0.048 Å, respectively, pointing towards each other. The distance Pd(1)–Pd(2) [3.057(4) Å] is the shortest among the three contact interactions between the three metal atoms, the other being 3.232(4) Å for Pd(1)–Pd(3) and 3.478(4) Å for Pd(2)–Pd(3). The macrocyclic geometry is determined by the coordination spheres around the palladium atoms, which arrange the nitrogen donor atoms on the three different coordination planes.

The formation of these polynuclear complexes in solution has been followed by means of spectrophotometric and potentiometric techniques. Experimental results have also shown that mononuclear Pd^{2+}-[18]aneN_6 and both mono- and di-nuclear Pd^{2+}-[21]aneN_7 complexed species are formed by the macrocyclic ligands. Treatment of the potentiometric data by means of the computer program SUPERQUAD[12] allowed the calculation of the formation constants of the species $[Pd([18]aneN_6)]^{2+}$ [log K = 29.2(1)] and $[Pd([21]aneN_7)]^{2+}$ [log K = 24.5(1)]. The molar conductivity of a pure water solution containing $[Pd_2([18]aneN_6)Cl_2][ClO_4]_2$ in the dilution range 10^{-1}–10^{-4} mol dm^{-3} showed that no appreciable dissociation of the chloride ligands takes place, in the complexed cation $[Pd_2([18]aneN_6)Cl_2]^{2+}$, under the experimental condition employed. This result is in accord with the observation that the electronic spectra of solid $[Pd_2([18]aneN_6)Cl_2][ClO_4]$ and of its solution are essentially the same. The very high stability of the complex $[Pd_2([18]aneN_6)Cl_2]^{2+}$ [log K = 51.8(8)], which is formed in very acidic solutions, is accompanied by a marked kinetic inertness towards acid dissociation. Some months are required for the complete dissociation of $[Pd_2([18]aneN_6)Cl_2]^{2+}$ in 2 mol dm^{-3} HCl solution. Also [21]aneN_7 forms a very stable dinuclear Pd^{2+} species with estimated stoichiometry $[Pd_2([21]aneN_7)Cl]^{3+}$ (log $K > 52$). This complex can react with a further $PdCl_4{}^{2-}$ ion forming a trinuclear species the electronic spectrum of which is quite similar to the reflectance spectrum of $[Pd_3([21]aneN_7)Cl_3][ClO_4]_2 \cdot H_2O$ solid compound. As observed in the potentiometric study the binding of the third Pd^{2+} ion causes the release of one equivalent of H^+ ions. These results suggest that the overall structure of $[Pd_3([21]aneN_7)Cl_3]^{3+}$, observed in the solid state, in which an amino group of the ligand deprotonates bridging two Pd^{2+} ions, is also likely to be maintained in solution. The coordination of the three Pd^{2+} ions activates the ligand to such extent that its deprotonation occurs even in fairly acidic solutions.

As observed, combination of ligand molecular topology and metal stereochemical requirements can produce complexed species with unusual properties. Indeed, ligand activation, resulting in the deprotonation of a secondary nitrogen atom and bridging coordination of the same, both in solution and in the solid state is a rare chemical event.

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