

(PdCl₄)²⁻ Inclusion into the Deca-charged Polyammonium Receptor (H₁₀[30]aneN₁₀)¹⁰⁺ ([30]aneN₁₀ = 1,4,7,10,13,16,19,22,25,28-deca-azacyclotriacontane)**Andrea Bencini,^a Antonio Bianchi,^{*a} Paolo Dapporto,^b Enrique Garcia-España,^{*c} Mauro Micheloni,^{*a} Piero Paoletti,^{*a} and Paola Paoli^a**^a *Chemistry Department, University of Florence, Via Maragliano 75, I-50144, Italy*^b *Department of Energetics, University of Florence, Italy*^c *Inorganic Chemistry Department, University of Valencia, Spain*

The title deca-protonated deca-azamacrocyclic receptor encapsulates the tetrachloropalladate(II) anion forming a 'super complex' whose crystal structure has been determined.

Second-sphere co-ordination is a new area of co-ordination chemistry whose development is largely due to the increasing availability of synthetic macrocyclic molecules.¹ The interaction of both neutral and charged second-sphere ligands with cationic, anionic, as well as neutral transition metal complexes has been studied and it has been recognised that non-covalent interactions provide the main contributions to the stability of the supramolecular species.²⁻⁶ Polyammonium macrocyclic receptors form adducts with anionic complexes.^{2-4,7} The chemical and/or physico-chemical properties of the new species have been studied in an attempt to understand whether the co-ordination of the complexed anions takes place inside or outside the macrocyclic cavity.^{2,6} In some cases the inclusion of the complexed anions into the polyammonium receptors has been proposed⁶ although until now no molecular structure describing this co-ordination mode has been reported. Very few examples of crystal structures showing the outer co-ordination are available.^{2,3}

Crystals of [(PdCl₄)(H₁₀L)](PdCl₄)₂Cl₄ (L = [30]aneN₁₀)

suitable for X-ray analysis, were obtained by slow evaporation, at room temperature, of a solution containing L·10HCl (1 mmol) and K₂PdCl₄ (3 mmol) in 50 cm³ of HCl 2 mol dm⁻³. The crystal structure (triclinic, space group $P\bar{1}$) consists of [(PdCl₄)(H₁₀L)]⁸⁺ cations, where the (PdCl₄)²⁻ anion is enclosed in the (H₁₀L)¹⁰⁺ cavity, and of isolated (PdCl₄)²⁻ and Cl⁻ counterions (Figure 1).[†] Both the tetrachloropalladate(II)

[†] *Crystal data:* triclinic, space group $P\bar{1}$, $a = 7.760(3)$, $b = 11.448(4)$, $c = 13.399(11)$ Å, $\alpha = 96.31(8)$, $\beta = 104.50(6)$, $\gamma = 92.30(3)^\circ$, $Z = 1$. A total of 4061 reflections ($5 \leq 2\theta \leq 50^\circ$, Mo-K α radiation) were collected on an Enraf-Nonius CAD4 automatic diffractometer of which 2956 having $I > 3\sigma(I)$ were used in the structure solution and refinement. The structure was solved by the heavy atom technique. Final refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.046$ and $R_w = 0.039$. 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.

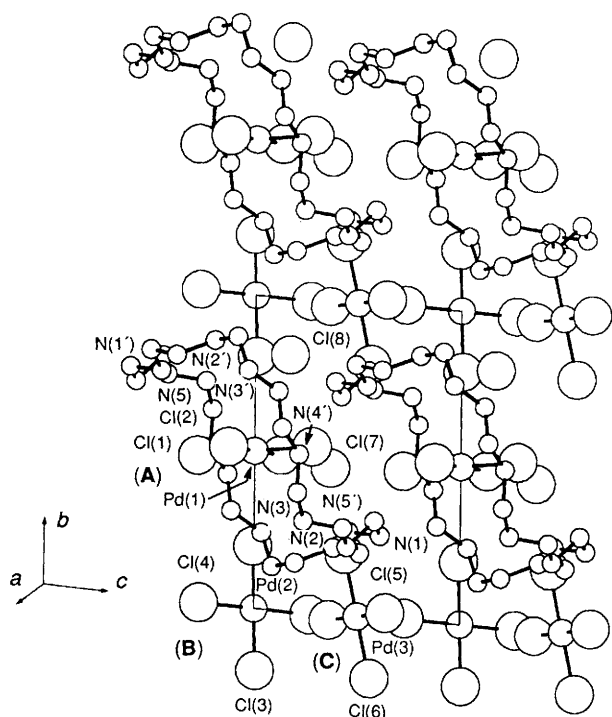


Figure 1. Crystal packing of the compound $[(\text{PdCl}_4)\text{-(H}_{10}\text{L})](\text{PdCl}_4)_2\text{Cl}_4$. The tetrachloropalladate(II) anions (A), (B), and (C) are located in the special WYCKOFF locations (c), (a), and (f) respectively.

anion (A) lying inside the macrocyclic framework, and the isolated (PdCl_4) anions [(B) and (C) in Figure 1] are centrosymmetric, the metal atom residing on an inversion centre in each case. Inclusion of $(\text{PdCl}_4)^{2-}$ into the deca-charged $(\text{H}_{10}\text{L})^{10+}$ macrocycle does not influence considerably the structural features of the anion, as shown by the small deviation from orthogonality of the $\text{Cl}(1)\text{-Pd}(1)\text{-Cl}(2)$ angle in (A). The Pd-Cl bond distances differ by less than 0.016 Å for the three anions. The decaprotonated macrocycle is centrosymmetric, the centre of symmetry being coincident with that of the $(\text{PdCl}_4)^{2-}$ anion (A). The macrocycle displays an S-shaped conformation (Figure 2) which produces an elongated macrocyclic cavity, of approximate dimensions 9×11 Å. The plane of the tetrachloropalladate(II) anion is perpendicular to the direction of main elongation of the cavity, with the chlorine atoms standing out of the macrocyclic frame. Such arrangement allows the chlorine atom Cl(2) of (A) to interact *via* a hydrogen bond with the N(4) protonated nitrogen atom of the receptor $[\text{Cl}(2) \cdots \text{HN}(4) 2.308(7)$ Å]. The $(\text{PdCl}_4)^{2-}$ anion (A) further interacts *via* hydrogen bonds with the nitrogen atoms of a symmetry related super-complexed species $[\text{Cl}(1) \cdots \text{HN}(4) 2.411(9)$ and $\text{Cl}(2) \cdots \text{HN}(1) 2.611(7)$ Å]. Hydrogen bond interactions with the macrocycle are also formed by the chlorine atoms of the $(\text{PdCl}_4)^{2-}$ anion (B) $[\text{Cl}(3) \cdots \text{HN}(1) 2.699(8)$ and $\text{Cl}(4) \cdots \text{HN}(1) 2.024(8)$ Å], as well as by those of (C) $[\text{Cl}(5) \cdots \text{HN}(2) 2.415(8)$, $\text{Cl}(6) \cdots \text{HN}(2) 2.399(8)$, and $\text{Cl}(6) \cdots \text{HN}(5) 2.589(8)$ Å]. The hydrogen bond framework is completed by several other interactions involving the chloride counterions Cl(7) and Cl(8). The reaction of $(\text{PdCl}_4)^{2-}$ with $(\text{H}_{10}\text{L})^{10+}$ has been followed by microcalorimetry[‡] in 2 mol dm^{-3} HCl

[‡] The calorimetric measurements were carried out on an LKB BATCH microcalorimeter, Model 10700-2. A 2 mol dm^{-3} HCl solution was used as solvent in all experiments.

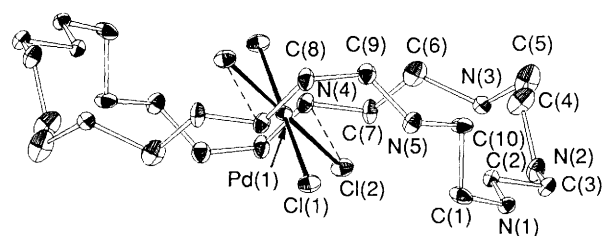


Figure 2. ORTEP drawing of the 'super complex' $[(\text{PdCl}_4)(\text{H}_{10}\text{L})]^{8+}$.

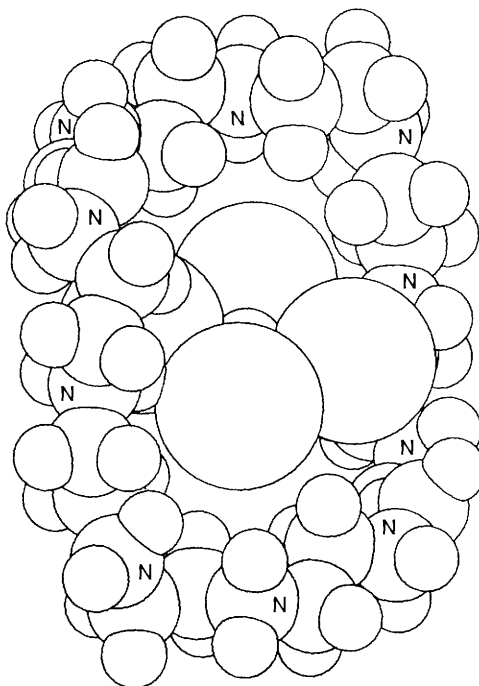


Figure 3. Space-filling representation of the X-ray structure of $[(\text{PdCl}_4)(\text{H}_{10}\text{L})]^{8+}$.

solution, the formation of palladium(II) polyamine complexes being strongly competitive with $(\text{PdCl}_4)^{2-}$ inclusion in less acid solutions. The reaction is exothermic and the heat evolution observed is typical of a slow reaction. The calorimetric measurements were carried out at different values (5–0.2) of the analytical concentrations ratio $R = [(\text{H}_{10}\text{L})^{10+}] / [(\text{PdCl}_4)^{2-}]$. In the range $1 \leq R \leq 5$ a constant value for the heat of reaction per mole of $(\text{PdCl}_4)^{2-}$ was observed $[\Delta H^\circ -16.3(4) \text{ kJ mol}^{-1}]$, indicating the formation of a stable 1:1 supercomplexed species. The slowness of this reaction may be rationalized assuming that part of the conformational energy of the receptor is devoted to accommodate the guest species inside the cavity so as to form a compact structure, like that observed in the solid state (Figure 3). Indeed the reactions of $(\text{PdCl}_4)^{2-}$ with the polyammonium macrocyclic receptors $(\text{H}_6[18]\text{aneN}_6)^{6+}$ and $(\text{H}_7[21]\text{aneN}_7)^{7+}$, whose cavities are too small to allow $(\text{PdCl}_4)^{2-}$ inclusive co-ordination, are fast.[§] For $1 \leq R \leq 0.2$ the heat of reaction per mole of $(\text{H}_{10}\text{L})^{10+}$ increases proportionally to the excess of $(\text{PdCl}_4)^{2-}$, in

[§] Fast exothermic reactions were observed for these two ligands with $(\text{PdCl}_4)^{2-}$ under the conditions reported.[‡]

agreement with the interaction of a further $(\text{PdCl}_4)^{2-}$ anion with the 1:1 supercomplexed species. Furthermore, the reaction of $(\text{PdCl}_4)^{2-}$ with $[(\text{PdCl}_4)(\text{H}_{10}\text{L})]^{8+}$ is fast.

The main conclusions drawn are: (i) the crystal structure of the $[(\text{PdCl}_4)(\text{H}_{10}\text{L})]^{8+}$ supercomplex shows a particular conformation of the $(\text{H}_{10}\text{L})^{10+}$ receptor which may be different from that expected for the isolated receptor; (ii) the thermodynamic measurements suggest that inclusive co-ordination of $(\text{PdCl}_4)^{2-}$ also takes place in solution and supercomplexed species in which more than one $(\text{PdCl}_4)^{2-}$ anion interact with one $(\text{H}_{10}\text{L})^{10+}$ polyammonium receptor molecule can be formed.

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