

Fig. 1. $-\Delta h_v$ vs \bar{n} for the Pd(II)—chloride system. The curve has been calculated from the values in Table 2. The signs refer to Table 1.

a computer, using the program Letagrop Kalle,⁶ and a graphical method.⁴ The stability constants determined by Elding³ were used in the calculations (Table 2). The ΔH_1° value of the palladium(II) bromide complex was calculated directly from the heat evolved at each titration step.

The stepwise changes in free energy and entropy were determined from $\Delta G_j^\circ = -RT \ln \beta_j / \beta_{j-1}$ and $\Delta G_j^\circ = \Delta H_j^\circ - T \Delta S_j^\circ$.

The results are given in Table 2. A plot of $-\Delta h_v$ versus \bar{n} (Fig. 1) shows that $-\Delta h_v(\bar{n})$ is independent of C_M . Hence no polynuclear palladium chloride complexes are needed to describe the results.

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The Crystal Structure of *o*-Phenylenediamine Hydrochloride

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In order to study the packing of *o*-phenylenediamine molecules together with different halide ions the crystal structures of *o*-phenylenediamine hydrochloride,¹ *o*-phenylenediamine dihydrochloride,¹ and *o*-phenylenediamine dihydrobromide² have been determined. *o*-Phenylenediamine hydrochloride, isostructural with *o*-phenylenediamine hydrobromide,³ crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with four formula units $C_6H_4(NH_2)_2 \cdot HCl$ in a unit cell with the dimensions $a=9.312$, $b=4.920$, and $c=16.155$ Å. X-Ray intensity data were collected with an integrating Weissenberg camera using $CuK\alpha$ radiation. In the layers $h0l-h4l$ 488 independent reflexions were observed.

The coordinates of the chlorine atom were obtained from a sharpened three-dimensional Patterson function. The carbon and nitrogen atoms were located from three-dimensional electron density maps. Difference syntheses indicated positions for seven of the nine hydrogen atoms in the protonated molecule. A least-squares full matrix refinement was performed including positional parameters of the non-hydrogen atoms, anisotropic temperature factors for the chlorine atom, isotropic ones for the carbon and nitrogen atoms, and an overall scale factor. The refinement resulted in an R -value of 0.07, when only observed reflexions were used. The final atomic parameters with standard deviations obtained from the last cycle of the refinement are listed in Table 1 together with possible hydrogen atom positions.

The crystal structure of *o*-phenylenediamine hydrochloride consists of chloride ions and cations of the formula $C_6H_4N_2H_5^+$. One $-NH_2$ and one $-NH_3^+$ group are included in each cation. The hydrogen atoms of the $-NH_3^+$ group are tetrahedrally oriented with respect to the C-N bond. The distances and angles in the protonated aromatic molecule (Fig. 1)

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Table 1. Final positional parameters with standard deviations for the non-hydrogen atoms and possible positional parameters for the hydrogen atoms. The numbering of the hydrogen atoms, cf. Fig. 1.

Atom			
Cl	0.0647(2)	0.0094(4)	0.4981(2)
N(1)	0.2475(8)	0.5123(15)	0.4345(4)
N(2)	0.4122(9)	0.9458(17)	0.3678(5)
C(1)	0.2441(9)	0.5712(15)	0.3450(5)
C(2)	0.1587(12)	0.4190(19)	0.2942(6)
C(3)	0.1505(12)	0.4790(23)	0.2099(6)
C(4)	0.2301(13)	0.6893(22)	0.1794(7)
C(5)	0.3194(12)	0.8447(21)	0.2305(6)
C(6)	0.3290(11)	0.7853(17)	0.3153(6)
H(2)	0.097	0.235	0.312
H(3)	0.110	0.393	0.184
H(4)	0.211	0.704	0.114
H(5)	0.380	1.008	0.221
H(11)	0.185	0.320	0.448
H(12)	0.222	0.637	0.460
H(13)	0.340	0.482	0.450
H(21)	0.445	0.854	0.421
H(22)	0.496	1.082	0.343

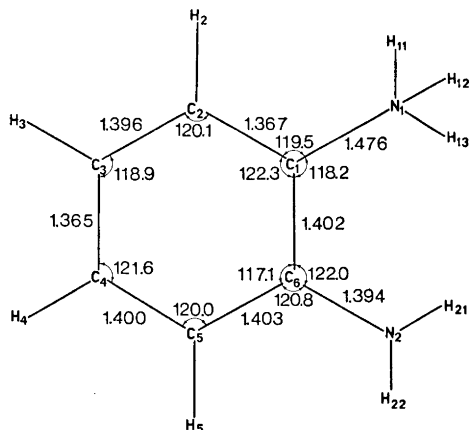


Fig. 1. Bond lengths (Å) and angles (°) in the aromatic molecule. The mean standard deviations are 0.013 Å and 0.8°, respectively.

are normal with carbon-nitrogen distances (C-NH₂) of 1.39(1) Å and (C-NH₃⁺) of 1.48(1) Å. The chloride ion is surrounded by three cations (Fig. 2). Each cation is coordinated *via* the -NH₃⁺ group through hydrogen bonds N-H...Cl. The N-Cl distances are 3.15(1) Å, 3.15(1) Å, and 3.17(1) Å. The shortest N-Cl distance from an -NH₂ group is 3.43(1) Å.

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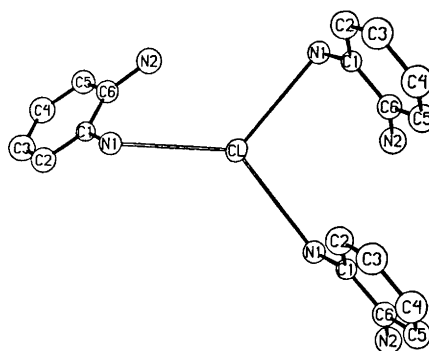


Fig. 2. The three cations C₆H₄N₂H₅⁺ hydrogen bonded to the chloride ion.

In order to obtain a more detailed information of the hydrogen bonding system a neutron diffraction study of the compound has been started. A full report of this work will be published later. A list of observed and calculated structure factors is available on request to the author.

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Studies on Orchidaceae Alkaloids. XXXV.* Alkaloids from *Hammarbya paludosa* (L.) O.K. and *Liparis keitaoensis* Hay.

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Recently the isolation of two alkaloids from *Hammarbya paludosa* (L.) O.K.

* For paper XXXIV, see Ref. 1.