

# Thermodynamic Properties of Palladium(II) Chloride and Bromide Complexes in Aqueous Solution

TORSTEN RYHL

Division of Physical Chemistry, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The enthalpy changes for palladium(II) chloride and bromide complex formation at 25.00°C and in a medium of 1 M HClO<sub>4</sub> have been determined calorimetrically. The medium was chosen so as to suppress hydrolysis.<sup>1</sup> By calorimetric titrations of palladium perchlorate solutions with perchloric acid it was verified that no hydrolysis occurs at [H<sup>+</sup>]=1.00. An isothermal-jacket calorimeter, (ac-

curacy 0.025 cal), of the type described by Gerding *et al.*,<sup>2</sup> was used.

Chloride-free palladium(II) perchlorate solutions were prepared as described by Elding.<sup>3</sup> The ligand solutions were prepared from hydrochloric acid, *p.a.*, and freshly distilled hydrobromic acid, *p.a.*

100.0 ml of a solution S, containing palladium(II) perchlorate, was titrated with increasing volumes, *v*, of a solution T, containing HA (A=Cl or Br). Each titration was performed at least twice. The solutions for the chloride system were (for all notations see Ref 4):

S: C<sub>M</sub> Pd(ClO<sub>4</sub>)<sub>2</sub>, C<sub>H</sub>=1.000 M HClO<sub>4</sub>  
T: C<sub>A</sub>=0.7298 M HCl, C<sub>H</sub>=0.2702 M HClO<sub>4</sub>

Owing to the rather low solubility of PdBr<sub>2</sub> only the enthalpy change for the first bromide complex could be determined. Then solutions S and T had the following compositions:

S: C<sub>M</sub>=0.01040 M Pd(ClO<sub>4</sub>)<sub>2</sub>, C<sub>H</sub>=1.000 M HClO<sub>4</sub>

T: C<sub>A</sub>=0.1000 M HBr, C<sub>H</sub>=0.900 M HClO<sub>4</sub>

The heats of dilution when these solutions were mixed with 1.000 M HClO<sub>4</sub> were zero within the experimental errors.

The computation of the enthalpy changes for the chloride system was made both by

Table 1. The calorimetric data for the palladium chloride and bromide systems at [H<sup>+</sup>]=1.00 M. The signs refer to Fig. 1.

Chloride:

○ S: C<sub>M</sub>=0.03976 M Pd(ClO<sub>4</sub>)<sub>2</sub>, C<sub>H</sub>=1.000 M HClO<sub>4</sub>. T: C<sub>A</sub>=0.7298 M HCl, C<sub>H</sub>=0.2702 M HClO<sub>4</sub>. V<sub>0</sub>=100.0 ml.

*v*/ml, *Q*/cal,  $\bar{n}$ : 1.00, 2.176, 0.184; 2.01, 2.185, 0.367; 3.01, 2.180, 0.550; 5.02, 4.244, 0.914; 7.03, 4.010, 1.274; 9.04, 3.780, 1.627; 11.05, 3.567, 1.964; 13.06, 3.361, 2.276; 15.07, 3.092, 2.553; 17.08, 2.739, 2.786; 19.09, 2.249, 2.980; 21.09, 1.782, 3.130.

● S: C<sub>M</sub>=0.03283 M Pd(ClO<sub>4</sub>)<sub>2</sub>, C<sub>A</sub>=0.1271 M HCl, C<sub>H</sub>=0.8729 M HClO<sub>4</sub>.

T: C<sub>A</sub>=0.7298 M HCl, C<sub>H</sub>=0.2702 M HClO<sub>4</sub>. V<sub>0</sub>=100.0 ml.

*v*/ml, *Q*/cal,  $\bar{n}$ : 2.01, 1.390, 3.254; 4.02, 1.038, 3.350; 6.03, 0.796, 3.427; 8.04, 0.586, 3.464; 10.05, 0.444, 3.531; 12.05, 0.387, 3.548; 14.06, 0.283, 3.560.

△ S: C<sub>M</sub>=0.01988 M Pd(ClO<sub>4</sub>)<sub>2</sub>, C<sub>H</sub>=1.000 M HClO<sub>4</sub>. T: C<sub>A</sub>=0.7298 M HCl, C<sub>H</sub>=0.2702 M HClO<sub>4</sub>. V<sub>0</sub>=100.0 ml.

*v*/ml, *Q*/cal,  $\bar{n}$ : 1.00, 2.190, 0.366; 2.01, 2.171, 0.728; 3.01, 2.080, 1.085; 4.02, 1.918, 1.433; 6.03, 3.496, 2.062; 8.04, 2.860, 2.551; 10.05, 2.004, 2.887.

Bromide:

S: C<sub>M</sub>=0.01040 M Pd(ClO<sub>4</sub>)<sub>2</sub>, C<sub>H</sub>=1.000 M HClO<sub>4</sub>. T: C<sub>A</sub>=0.1000 M HBr, C<sub>H</sub>=0.900 M HClO<sub>4</sub>. V<sub>0</sub>=100.0 ml.

*v*/ml, *Q*/cal: 1.00, 0.513; 2.01, 0.510.

Table 2. Thermodynamic functions for the stepwise formation of palladium chloride and palladium bromide complexes. The  $\Delta H_j^\circ$  values are given with their computed standard deviations whereas  $\Delta G_j^\circ$  and  $\Delta S_j^\circ$  are given with their estimated errors.

	<i>j</i>	Cl	Br
log β <sub><i>j</i></sub>	1	4.47 ± 0.01	5.17 ± 0.02
Ref. 3	2	7.76 ± 0.04	9.42 ± 0.04
	3	10.17 ± 0.07	12.72 ± 0.06
	4	11.54 ± 0.09	14.94 ± 0.08
- ΔG <sub><i>j</i></sub> <sup>°</sup>	1	6.10 ± 0.01	7.05 ± 0.03
kcal/mol	2	4.49 ± 0.05	5.80 ± 0.07
	3	3.28 ± 0.11	4.50 ± 0.11
	4	1.87 ± 0.16	3.03 ± 0.16
- ΔH <sub><i>j</i></sub> <sup>°</sup>	1	3.03 ± 0.03	5.10 ± 0.05
kcal/mol	2	2.59 ± 0.04	-
	3	2.56 ± 0.05	-
	4	3.41 ± 0.07	-
ΔS <sub><i>j</i></sub> <sup>°</sup>	1	10.3 ± 0.1	6.5 ± 0.3
cal/mol K	2	6.4 ± 0.3	-
	3	2.4 ± 0.6	-
	4	-5.2 ± 0.8	-

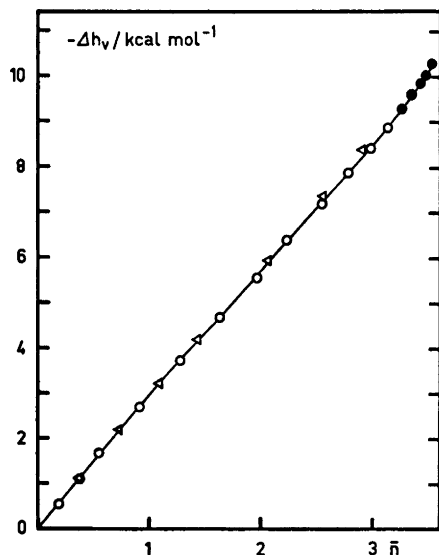


Fig. 1.  $-\Delta h_v$  vs  $\bar{n}$  for the Pd(II)—chloride system. The curve has been calculated from the values in Table 2. The signs refer to Table 1.

a computer, using the program Letagrop Kalle,<sup>6</sup> and a graphical method.<sup>4</sup> The stability constants determined by Elding<sup>3</sup> were used in the calculations (Table 2). The  $\Delta H_1^\circ$  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.

I should like to thank Docent Lars-Ivar Elding for useful discussions and Dr. R. E. Carter for revision of the English.

1. Nabivanets, B. I. and Kalabina, L. V. *Zh. Neorg. Khim.* **15** (1970) 1595.
2. Gerding, P., Leden, I. and Sunner, S. *Acta Chem. Scand.* **17** (1963) 2190.
3. Elding, L. I. *Inorg. Chim. Acta* **6** (1972). *In press.*
4. Leden, I. and Ryhl, T. *Acta Chem. Scand.* **18** (1964) 1196.
5. Arnek, R. *Arkiv Kemi* **32** (1970) 81.

Received August 2, 1972.

## The Crystal Structure of *o*-Phenylenediamine Hydrochloride

CLAES STALHANDSKE

Division of Inorganic Chemistry 2, The Lund Institute of Technology, Chemical Center, Box 740, S-220 07 Lund 7, Sweden

In order to study the packing of *o*-phenylenediamine molecules together with different halide ions the crystal structures of *o*-phenylenediamine hydrochloride,<sup>1</sup> *o*-phenylenediamine dihydrochloride,<sup>1</sup> and *o*-phenylenediamine dihydrobromide<sup>2</sup> have been determined. *o*-Phenylenediamine hydrochloride, isostructural with *o*-phenylenediamine hydrobromide,<sup>3</sup> 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)

*Acta Chem. Scand.* **26** (1972) No. 7