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Palladium (II) and Platinum (II) aqueous solutions. Evidence for the solvation of the $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ ions

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Abstract

The isomorphic substitution applied to solutions of NH_4PtCl_4 and NH_4PdCl_4 allows to show the existence of 2 bound water molecules at the apical sites of PtCl_4^{2-} and PdCl_4^{2-} ions. The Pt(Pd)- H_2O distance results equal to 2.77 Å. © 1998 Elsevier Science B.V.

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1. Introduction

It has been shown that potassium chloropalladate (II) and chloroplatinate (II) are isomorphous and have a square-planar configuration of chlorine atoms around the metal ion¹. The geometry of the complex PtCl_4^{2-} is reported in literature for solid compounds²⁻⁸. The same square-planar arrangement has been verified by X-ray structure determination on a number of Pt complexes⁹.

Elding has studied Pd(II) and Pt(II) in aqueous solution¹⁰⁻¹² showing the existence of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$, $\text{Pt}(\text{H}_2\text{O})_4^{2+}$. Also the existence of PdCl_4^{2-} and PtCl_4^{2-} complexes has been assessed¹³. NMR studies of aqueous solutions of $\text{Pd}^{2+}(\text{aq})$ and $\text{Pt}^{2+}(\text{aq})$ show that these cations coordinate four H_2O ligands, with observable ligand-water exchange rates¹⁴⁻¹⁷. A square-planar coordination geometry is compatible with the experimental data reported in literature^{8,10-12,18-24}.

Solutions of the solvated dimethyl sulfoxide of both Pd(II) and Pt(II) have been studied^{10,11,12} showing that Pd(II) and Pt(II) contain two oxygen and two sulphur-bonded ligands. Crystallographic studies²⁸⁻³⁰ as well as a proton-NMR study of the solvent exchange on $\text{Pt}(\text{Me}_2\text{SO})_4^{2+}$ confirm the structure previously proposed²⁶⁻²⁸.

Four recent papers^{8,31-33} presented X-ray Diffraction studies on Pd(II), Pt(II) aqueous solutions.

Solutions of solvated cations of Pd(II) and Pt(II) in dimethyl sulfoxide and acetonitrile have been studied by EXAFS (Extended X-ray Absorption Fine Structure) and LAXS (Large Angle X-ray Scattering) and in all cases it was shown that Pt(II) and Pd(II) cations are four-coordinated. Both EXAFS and LAXS techniques did not give support for axially bound solvent molecules in addition to the four ligands in the assumed square-planar coordination. However, weaker bonds may be formed in the apical sites to give a distorted octahedral configuration, with four equivalent planar bonds and two apical longer bonds. There is evidence that these apical positions may be occupied by solvent molecules^{34,35}. In a spectrometric study of halogenopalladate (II) and halogenoplatinate (II) ions in various polar solvents, Harris *et al.*³⁴ correlated the change of absorption wavelength of Pd (II) complexes in more polar solvents to the expansion of the metal valence from 4 to 6, though they found no evidence for the valence expansion of Pt complexes. They hypothesized that the Pd (II) central ion can form two extra apical bonds using *5p5d* orbitals, though at a larger distance than the planar ones, because of the repulsion of the filled non-bonding $4d_{z^2}$ ($5d_{z^2}$) orbital. They also concluded that polar solvents, such as water, favour the valence expansion.

In a previous paper³³ we used the method of the difference radial distribution functions in a study the NH_4PdCl_4 and NH_4PtCl_4 aqueous solutions in order to isolate the coordination of the cation from the solvent contribution. In the data we presented a hump was also present in the difference radial distribution function at about 2.8\AA .

In this paper we present a more accurate analysis of the data previously reported in order to establish whether the hump at $\sim 2.8\text{\AA}$ can account for the solvation of the Pd and Pt chloride complexes in aqueous solution.

2. Experimental

The investigated Pd(II) and Pt(II) aqueous solutions are the ones reported in Ref. 33 and labelled D and E.

We report here how they were prepared and we keep in this paper the same notation for the different solutions.

$(\text{NH}_4)_2\text{PtCl}_4$ (sol. D) was prepared by dissolving a weighed amount of $(\text{NH}_4)_2\text{PtCl}_4$ in HClO_4 and H_2O . Also $(\text{NH}_4)_2\text{PdCl}_4$ (sol. E) was prepared by dissolving the corresponding salt to get a solution with same concentrations as in solution D.

In the new calculations solution D has been normalized for the Pt concentration and solution E for the Pd concentration.

The scattered intensity data were handled by means of the KURVLR program^{37,38}. Normalization to a stoichiometric unit of volume containing one Cl atom was done by comparing the observed and calculated intensities in the high angle region of an intensity curve. The experimental structure function was obtained according to the expression $i(s) = I_{e.u.}(s) - \sum n_i f_i^2$ where $s = (4\pi/\lambda)\sin\theta$, n_i = number of atoms "i" in the stoichiometric volume, f_i = scattering factor of the i atom and $I_{e.u.}$ is the intensity in electron units.

The radial distribution functions were then calculated according to the expression:

$$D(r) = 4\pi r^2 \rho_0 + 2\pi r^{-1} \int_0^{s_{\max}} s i(s) M(s) \sin(rs) ds \quad (1)$$

where $\rho_0 = (\sum n_i f_i(0))^2 V^{-1}$, with V = stoichiometric unit of volume chosen.

The upper integration limit, s_{\max} was 15.5 \AA^{-1} .

Since it was our goal to evidence the interaction between the solvent and the metal, which is likely to occur in the range 1-3 Å, we used different sharpening factors in the calculation of the radial distribution function:

$$\{f^2 P_t(0)/f^2 P_t(s)\} \cdot \exp(-0.01s^2) \quad (2)$$

$$\{f^2 P_d(0)/f^2 P_d(s)\} \cdot \exp(-0.01s^2) \quad (3)$$

$$\{f^2 Cl(0)/f^2 Cl(s)\} \cdot \exp(-0.01s^2) \quad (4)$$

The sharpening factor M(s) influences the amplitude of the oscillations of the scattered intensities and, consequently, the radial distribution function, after performing the Fourier Transform. Since we are interested in small peaks of the radial distribution function, it is important to choose the proper sharpening factor in order to avoid artefacts.

Theoretical peaks were calculated by Fourier Transform of the theoretical intensities of pair of interactions (Debye functions):

$$i_{pq}(s) = \sum f_p f_q f \sin(r_{pq} s) (r_{pq} s)^{-1} \cdot \exp(-1/2 s p q^2 s^2) \quad (5)$$

using the same sharpening factors and the same s_{\max} values of the experimental data.

3. Data Analysis

In the previous investigation on NH_4PdCl_4 and NH_4PtCl_4 we applied the difference method in order to single out peaks in the radial distribution function which could be unambiguously assigned to the metal-chlorine interaction. In particular, both the PdCl_4^{2-} and the PtCl_4^{2-} complexes were found to be square-planar with 4 equal M-Cl distances, at 2.315 Å. A complete analysis of the D(r) function allowed us to determine the Cl-Cl interaction between ligands with cis configuration (3.274 Å), and with trans configuration (4.630 Å), in agreement with the proposed square-planar model. However, this model leaves the problem of the interaction between the complex and the solvent open. The solubility of PdCl_4^{2-} and PtCl_4^{2-} complexes in aqueous solutions suggests an interaction between the complex and the solvent. The previous assignment rules out a solvation by ligand exchange, with replacement of one or more Cl ions

with water molecules. The possible solvation mechanisms of the square-planar complexes implies ligand-solvent interaction and/or metal-solvent interaction.

Our hypothesis is that PdCl_4^{2-} and PtCl_4^{2-} are not perfectly square-planar and that an interaction between the metal and two water molecules occurs at apical positions, though at larger distances with respect to the chlorine ligands. A better insight of the X-ray scattering data can possibly give better information on the nature of the PdCl_4^{2-} and PtCl_4^{2-} solvent interaction.

The experimental curves show a hump at larger-distance side of the main peak at $\sim 2.3\text{\AA}$. The theoretical peak shape, where the only metal-ligand interactions have been included, fits the main experimental peak rather well, though no peak shape was calculated to fit the hump at larger distance.

In the present paper we focused our attention to the difference radial distribution function in the region 1-3 \AA , in order to establish the nature of the interaction which results in the hump at 2.8 \AA . Particularly we investigated the effects of different sharpening factors on the scattered intensity and as a consequence on the radial distribution function.

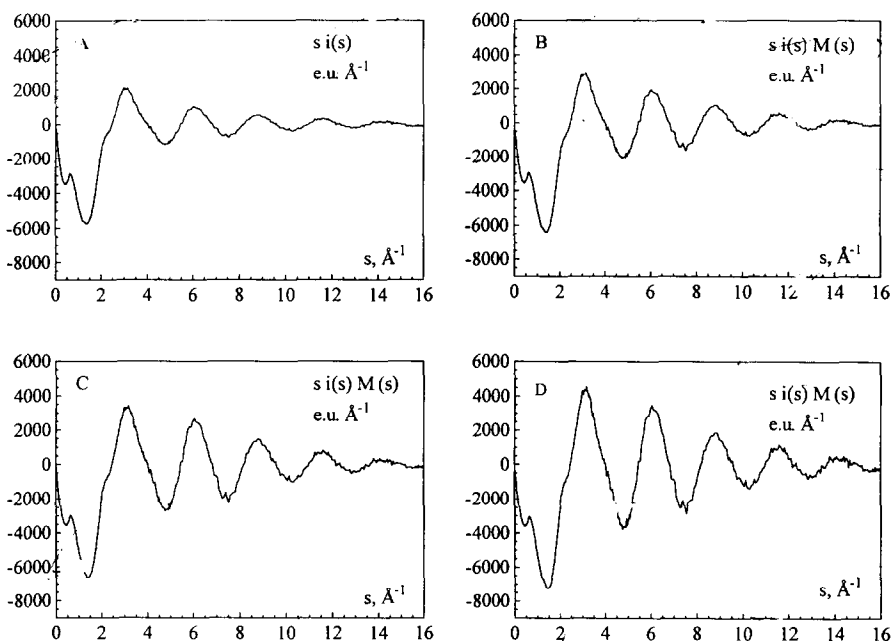


Fig. 1 Scattered intensities from sol. D, (Pt solution). In picture A no sharpening factor has been used, while in picture B, C and D respectively the sharpening factors (2), (3), and (4) (with the Pt, Pd and Cl scattering factors) have been used.

In Fig. 1 and 2 we reported the scattered intensities calculated with different sharpening factors for Pt and Pd solutions respectively.

From Fig. 1 it is evident that the amplitude of the oscillations of the scattered intensity of sol D is influenced by the use of different sharpening factors. The collected scattered intensity without

using any sharpening factor is shown in Fig. 1 A, while in Fig. 1 B, C and D three different sharpening factors have been used obtained respectively from Pt, Pd and Cl scattering factors. Curves 1B, 1C, 1D show wider amplitudes of the scattered intensity with respect to the curve 1A, though to a different extent. The sharpening factors (2) and (3) (obtained from Pt and Pd scattering factors respectively) slightly enhance the oscillations of the scattered intensity, while the use of the sharpening factor (4) (obtained from the chlorine scattering factor) causes, on the contrary, a larger enhancement of the oscillations. Different sharpening factors have been used also for sol. E and the resulting curves are reported in Fig. 2.

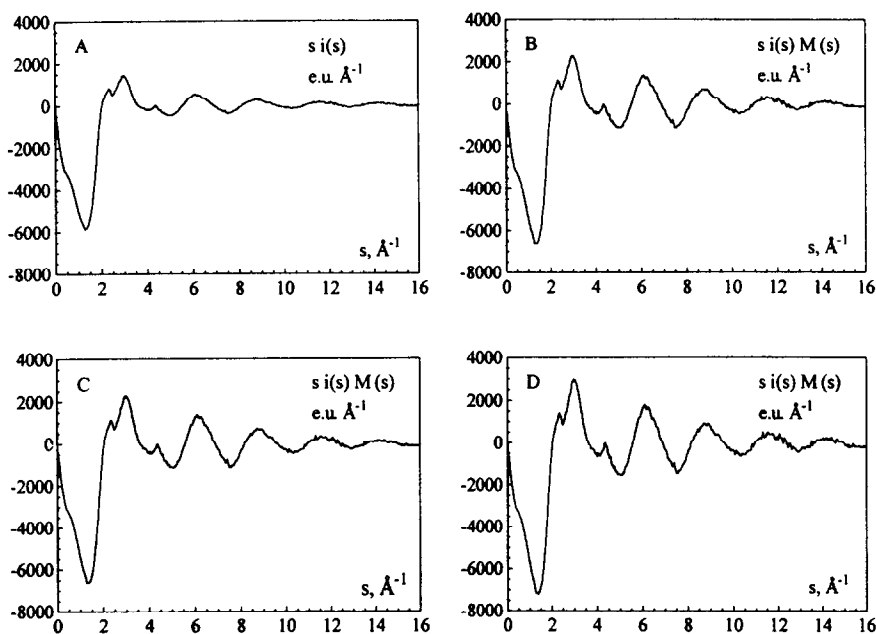


Fig. 2 Scattered intensities from sol. E (Pd solution). In picture A no sharpening factor has been used, while in picture B, C and D respectively the sharpening factors (2), (3), and (4) (with the Pt, Pd and Cl scattering factors) have been used.

Similarly to sol. D, the use of the sharpening factors (2) and (3) affects only slightly the amplitude of the oscillations of the scattered intensity, while the sharpening factor (4) has a larger effect.

As previously described, differences of the radial distribution functions have been performed correspondingly to the three sharpening factors used.

The difference curves $(D(r))_{\text{DIFF}} = D(r)_{\text{Pt}} - D(r)_{\text{Pd}}$ isolate the contribution to the $D(r)$ of the metal-ligand, metal-solvent, metal-metal interactions, therefore the interactions such as ligand-ligand, ligand-solvent, solvent-solvent do not contribute to the difference curve. This is

particularly important since we are analyzing a peak at $\sim 2.8 \text{ \AA}$ corresponding to the water-water interactions.

The identification of the peak at $\sim 2.8 \text{ \AA}$ has been made by calculating separately the $D(r)_{\text{DIFF}}$ corresponding to four metal-chlorine and two metal-water interactions and by comparing their sum to the experimental curve for all the sharpening factors.

In Fig. 3 the curves calculated with sharpening factors (2) are reported.

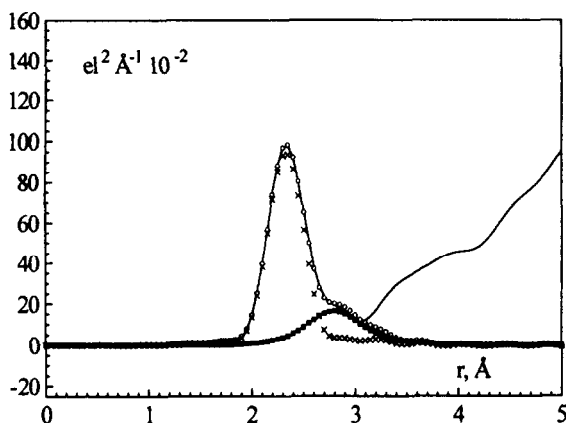


Fig. 3 Experimental and theoretical $D(r)_{\text{DIFF}}$ obtained using the sharpening factor (2). Solid line=experimental curve, crosses=theoretical $D(r)_{\text{DIFF}}$ calculated by introducing the metal-chlorine interactions in the Debye function, squares= $D(r)_{\text{DIFF}}$ function reproducing the metal-water interactions, open circles=total theoretical $D(r)_{\text{DIFF}}$ curve.

The two partial theoretical curves corresponding to the metal-chlorine and metal-water interactions reproduce rather well both the experimental peak at $\sim 2.3 \text{ \AA}$ (metal-chlorine interactions) and the hump at $\sim 2.8 \text{ \AA}$ (metal-water interactions). The total theoretical curves, sum of the two partial curves, fit well the experimental $D(r)_{\text{DIFF}}$, thus showing that the Pt-solvent and Pd-solvent interactions exist, although the Pt and Pd complexes are usually considered purely square-planar.

The metal-apical ligand distance is larger than the metal-planar ligand one, confirming then, the hypothesis made by Harris *et al.*³⁴ about the orbitals involved in the bonding of the complex.

In Fig. 4 the experimental and theoretical $D(r)_{\text{DIFF}}$ are calculated using the sharpening factor (3), while in Fig. 5 the curves are calculated with the sharpening factor (4). The structural parameters used in Fig. 4 and Fig. 5 are the same as in Fig. 3, but the agreement between experimental and theoretical curves is not of the same quality. The theoretical peak shapes are too low, particularly the theoretical $D(r)_{\text{DIFF}}$ which reproduces the metal-chlorine interactions shows negative values at the side of the peak.

This effect is larger for the curves calculated with the sharpening factor (4), obtained by using the Cl scattering factor already adopted in the previous paper³³.

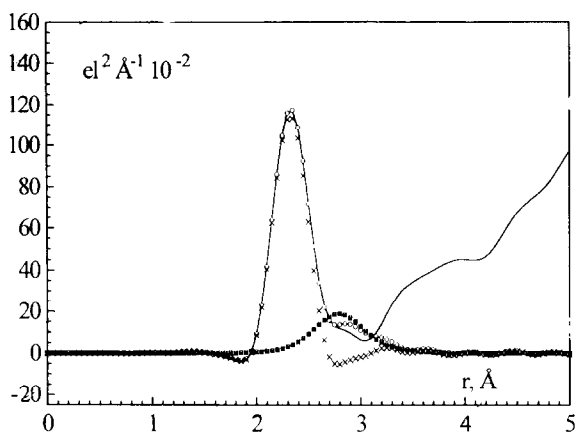


Fig. 4 Experimental and theoretical $D(r)_{\text{DIFF}}$ obtained using the sharpening factor (3). Solid line=experimental curve, crosses=theoretical $D(r)_{\text{DIFF}}$ calculated by introducing the metal-chlorine interactions in the Debye function, squares= $D(r)_{\text{DIFF}}$ function reproducing the metal-water interactions, open circles=total theoretical $D(r)_{\text{DIFF}}$ curve.

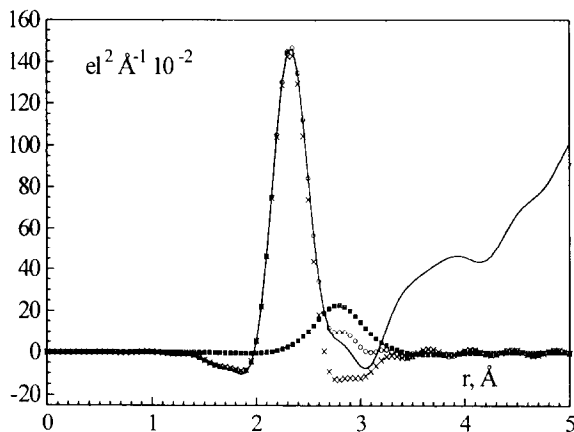


Fig. 5 Experimental and theoretical $D(r)_{\text{DIFF}}$ obtained using the sharpening factor (4). Solid line=experimental curve, crosses=theoretical $D(r)_{\text{DIFF}}$ calculated by introducing the metal-chlorine interactions in the Debye function, squares= $D(r)_{\text{DIFF}}$ function reproducing the metal-water interactions, open circles=total theoretical $D(r)_{\text{DIFF}}$ curve.

In Fig. 4 and 5, we can see how, not only a theoretical curve with metal-four chloride interactions is not sufficient to fit the experimental curve, but also that the proper choice of the sharpening factor may avoid artefacts such as the presence of negative peaks in the $D(r)_{\text{DIFF}}$. Furthermore, also the total theoretical $D(r)_{\text{DIFF}}$ does not fit the hump at the side of the main peak, since the contribution of the two metal-water interactions is not sufficient to compensate for the negative peak of the metal-chlorine interactions and the resulting curve is too low in this region. In all the calculations we have used the parameters reported in Table 1.

Distance	r	σ	n
Pt (Pd) - Cl	2.315(2)	0.075(4)	4
Pt (Pd) - H ₂ O	2.77(1)	0.155(7)	2

Table 1. Values of the structural parameters and standard deviations used in the models. r =distance (\AA), σ =root-mean-square deviation (\AA), n =frequency number.

In our calculation we assumed that both Pd (II) and Pt(II) expand their valence from 4 to 6. Harris *et al.*³⁴ had spectrometric evidence of the valence expansion for Pd, but not for Pt. Therefore in a first approach we have considered different coordination numbers for Pd and Pt. The difference method is, in fact very sensitive to the coordination number and it can be easily under or overestimated if too large or too small numbers are used.

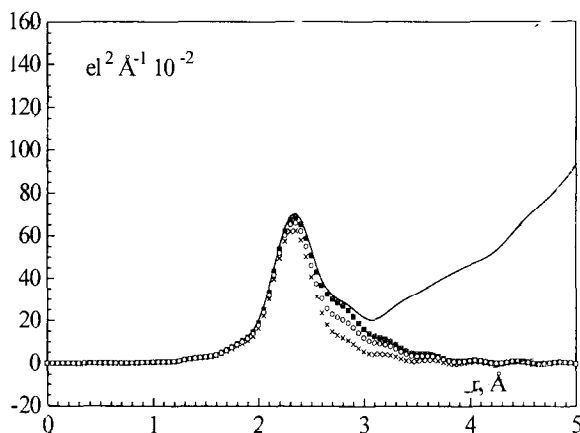


Fig. 6 Experimental and theoretical $D(r)_{\text{DIFF}}$ obtained without using any sharpening factor. Solid line=experimental curve, crossed squares=theoretical $D(r)_{\text{DIFF}}$ using 6 as coordination number both for Pd(II) and for Pt(II), open circles= $D(r)_{\text{DIFF}}$ using 5 as coordination number both for Pd(II) and for Pt(II), crosses= $D(r)_{\text{DIFF}}$ using 5 as coordination number for Pt(II) and 6 for Pd(II).

In Fig. 6 we reported some of the difference curves which have been calculated with different sets of coordination numbers: 6 for both cations (crossed squares), 5 for both cations (open circles) and 5 for Pt and 6 for Pd (crosses). The best fit corresponds to the use of the largest coordination number for both cations. A lower number for both cations results in an underestimated theoretical curve. The worst agreement between theoretical and experimental curve corresponds to the use of two different coordination number for the two cations. The theoretical curve would be even lower if we had used 4 as coordination number for Pt (pure square-planar complex) and 6 as coordination number for Pd (distorted octahedral). Therefore we can conclude that both Pd (II) and Pt (II) are hexacoordinated.

In these calculations we also whether the use of the sharpening factor can introduce itself any artefact. Therefore no sharpening factor has been used both for the experimental and for the theoretical data of Fig. 6.

It is important to notice that the hump at 2.8 Å is evident even without the use of any sharpening factor and that the analysis of this peak really leads to the evaluation of the solvent-metal apical distances.

4. Conclusions

A detailed analysis of the X-ray Scattering data of two NH_4PtCl_4 and NH_4PdCl_4 solutions has been performed in order to establish how the solvent-complex interaction occurs in the Pt and Pd square-planar complexes.

In a previous paper we had studied the Pt and Pd square-planar complexes³⁴ by the isomorphic substitution method. We had determined the metal-chlorine as well as the chlorine-chlorine distances. In the first approach nothing could be said about the complex-solvent interaction. However, the difference radial distribution function showed a hump at the side of the peak at ~ 2.3 Å not considered.

In the present study we used different sharpening factors in the calculation of the radial distribution function, in order to find out whether the hump at ~ 2.8 Å might be attributed to solvent apical ligands. Position and intensity of this peak can be fitted by theoretical peak shape including an interaction of the metal with two water molecules. It is important to notice that in this study we applied the isomorphic substitution method to solutions with equivalent concentration. Therefore, all the contributions of the solvent-solvent, ligand-ligand, ligand-solvent interactions have been deleted and the only contribution of interactions with the metal have been isolated. In this frame the peak at ~ 2.8 Å in the difference radial distribution function cannot be attributed to the $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions in the solvent (2.85 Å is the typical distance between two oxygen atoms in water). It was attributed to an interaction involving the metal in the complex.

Our hypothesis on the nature of this peak is that it involves a metal-oxygen interaction, with the water molecules at apical positions. In this way the coordination of the Pt and Pd in tetrachloride complexes in aqueous solution can no longer be defined pure square-planar, but it becomes a distorted octahedral, with apical distances longer (and different ligands) than the planar ones (similarly to the complexes of d^9 elements, distorted by Jahn-Teller effect).

The solvation of halogenopalladate (II) and halogenoplatinate (II) ions had been hypothesized by Harris *et al.* in a spectrophotometric study in several polar solvents³⁴. In their study they had correlated the decrease of the wavelength at the maximum in the absorption spectra to the metal-solvent interaction. They also hypothesized a distorted octahedral geometry for the solvated complexes.

The LAXS study we present in this paper can confirm the previous hypothesis made about the palladate (II) and platinate (II) ions and also provides the value of the metal -solvent distance in the distorted octahedral Pt and Pd chloride complexes.

REFERENCES

1. R.G. Dickinson, *J. Am. Chem. Soc.*, 1922, 44, 2404.
2. R.H.B. Mais, P.G. Owston and A.M. Wood, *Acta Cryst. Sect. B*, 1972, 28, 393.
3. B. Morosin, P. Fallon and J.S. Valentine, *Acta Cryst. Sect. B*, 1975, 31, 2220.
4. S. Ohba, S. Sato and Y. Saito, *Acta Cryst. Sect. B*, 1983, 39, 49.
5. D.H. Templeton and L.K. Templeton, *Acta Cryst. Sect. A*, 1985, 41, 365.
6. P.J.M. Delafontaine, P. Toffoli, P. Khodadad and N. Rodier, *Acta Cryst. Sect. C*, 1988, 44, 1376.
7. G.R. Clark and S.B. Hall, *Acta Cryst. Sect. C*, 1989, 45, 67.
8. L.A. Bengtsson and Å. Oskarsson, *Acta Chem. Scand.*, 1992, 46, 707.
9. Wells, "Structural Inorganic Chemistry" Eds. Oxford University Press, 1950, 645.
10. L.I. Elding, *Inorg. Chim. Acta*, 1972, 6, 647.
11. L.I. Elding, *Inorg. Chim. Acta*, 1972, 6, 683.
12. L.I. Elding, *Inorg. Chim. Acta*, 1976, 20, 65 and references therein.
13. L. Rosmussen and C.K. Jørgsen, *Acta Chem. Scand.*, 1968, 22, 2313.
14. Ö. Gröning, T. Drackenberg and L.I. Elding, *Inorg. Chem.*, 1982, 21, 1820.
15. L. Helm, L.I. Elding and A.E. Merbach, *Helv. Chim. Acta*, 1984, 67, 1453.
16. L. Helm, L.I. Elding and A.E. Merbach, *Inorg. Chem.*, 1985, 24, 1719.
17. Ö. Gröning, and L.I. Elding, *Inorg. Chem.*, 1989, 28, 3366.
18. L.I. Elding and L.F. Olsson, *J. Phys. Chem.*, 1978, 82, 69.
19. L.I. Elding, *Inorg. Chim. Acta*, 1978, 28, 255.
20. L.I. Elding and A.B. Gröning, *Inorg. Chim. Acta*, 1978, 31, 243.
21. L.I. Elding and A.B. Gröning, *Inorg. Chim. Acta*, 1980, 38, 59.
22. L.I. Elding and L.F. Olsson, *Inorg. Chim. Acta*, 1986, 117, 9.
23. Y. Ducommun, A.E. Merbach, B. Hellquist and L.I. Elding, *Inorg. Chem.*, 1987, 26, 1759.
24. B. Hellquist, L.I. Elding and Y. Ducommun, *Inorg. Chem.*, 1988, 27, 3620.
25. B.B. Wayland and R.F. Schramm, *Chem. Comm.*, 1968, 23, 1465.
26. B.B. Wayland and R.F. Schramm, *Inorg. Chem.*, 1969, 8, 971.
27. J.H. Price, A.N. Williamson, R.F. Schramm, and B.B. Wayland, *Inorg. Chem.*, 1972, 11, 1280.
28. B.F.G. Johnson, J. Puga and P.R. Raithby, *Acta Cryst. Sect. B*, 1981, 37, 953.
29. L.I. Elding and Å. Oskarsson, *Inorg. Chim. Acta*, 1987, 130, 209.
30. Y. Ducommun, L. Helm, A.E. Merbach, B. Hellquist and L.I. Elding, *Inorg. Chem.*, 1989, 28, 377.
31. G. Johansson, *Pure and Appl. Chem.*, 1988, 60, 1773.
32. B. Hellquist, L.A. Bengtsson, B. Holmberg, B. Hedman, I. Persson and L.I. Elding, *Acta Chem. Scand.*, 1991, 45, 449.
33. R. Caminiti, C. Sadun, M. Basanisi and M. Carbone, *J. Mol. Liquids*, 1996, 70, 55.
34. C.H. Harris, S.E. Livingstone and I.H. Reece, *J. Chem. Soc.* 1959, 2, 1505.
35. S.E. Livingstone and B. Wheelahan, *Austral. J. Chem.*, 1964, 17, 219.
36. G. Johansson and R. Caminiti, *Z. Naturforsch.*, 1986, 41a, 1325.
37. G. Johansson and M. Sandstrom, *Chem. Scr.*, 1973, 4, 195.
38. R. Caminiti and G. Johansson, *Acta Chem. Scand.*, 1981, A35, 373.