May, 1994] © *1994 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **67**, *1281—1285(1994)* 1281

# Intercalation of $[Pt(en)_2]^{2+}$ and $[PtCl_2(en)_2]^{2+}$ Ions by Na-Montmorillonite

Tsuyoshi KIJIMA,* Kenji SAKAGUCHI, and Kaoru OHE
Department of Materials Science, Faculty of Engineering, Miyazaki University, Miyazaki 889-21

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The individual and mixed uptakes of $[Pt(en)_2]^{2+}$ and $[PtCl_2(en)_2]^{2+}$ ions by Na-montmorillonite have been studied at 25 °C. In the individual uptakes, the Pt(IV) complex ions are intercalated beyond the cation exchange capacity of the host, which is in striking contrast to the Pt(II) complex ions which are taken up through the capacity. Both complex ions are arranged as a monolayer in which their square-planar $Pt^{II}(en)_2$ and $Pt^{IV}(en)_2$ planes are parallel and perpendicular to the silicate layers, respectively. The uptake reaction with an equimolar solution of both complexes results in the predominant intercalation of the Pt(II) complex ions, while that with a Pt(IV)-riched mixed solution yields a co-intercalated monolayer in which the Pt(IV) complex ions are held with their square-planar planes tilted by ca. 52° with respect to the silicate layer.

The clay mineral montmorillonite consists of negatively charged layeres with a typical composition of $(Al, Mg)_{2-3}$ $(Si, Al)_4O_{10}(OH)_2$ and interlayer cations compensating the positive charge deficiency of the silicate layers.(1) Due to the weakly coupled layered structure, the interlayer cations can be easily ion-exchanged with a variety of inorganic and organic cations. This ion-exchange property of the clay mineral has been applied to obtaining new families of functional materials by the pillaring of the layered mineral with bulky inorganic or oraganic species.(2) Square-planar $[Pt(en)_2]$ and octahedral $[PtX_2(en)_2]$ (X=Cl, Br, and I) complex ions are bonded alternately to form linear $-Pt^{2+}-X^{-}-Pt^{4+}-X^{-}-$ chains which have such optical properties as large third-order electric susceptabilities.(3,4) This arouses our interest in an attempt to constitute a two-dimensional arrangement of the mixed-valent complexing chains in layered compounds, such as montmorillonite.

A preliminary study was thus made to examine the individual and mixed intercalation behavior of two platinum complexes, bis(ethylenediamine)platinum(II) chloride $[Pt(en)_2]Cl_2$ (**1**) and diclorobis(ethylenediamine)platinum(IV) clrolide $[PtCl_2(en)_2]Cl_2$ (**2**) by Na-montmorillonite.

## Experimental

The Na-montmorillonite sample used was the same as that used in previous studies.(5) The two platinum complexes (**1** and **2**) were prepared using platinum (II) pottassium chloride and ethylenediamine as starting materials in a manner similar to that described by Basolo et al.(6) The compositions of the resulting complexes were confirmed by a combined use of thermogravimetry (t.g.) and C, H, N elemental analysis. The montmorillonite sample was soaked in an aqueous solution containing various amounts of **1**, **2** or their mixture at 25 °C for 2 d, centrifuged, fully washed with water, and air-dried at 35 °C. The resulting solids were characterized by t.g. and X-ray diffraction. T.g. was carried out at a heating rate of 10 $°C\,min^{-1}$ in air. X-ray diffraction measurements for powdered samples were conducted with Cu $K\alpha$ radiation using 1-tetradecanol as an external standard.

## Results and Discussion

**$[Pt(en)_2]^{2+}$.** Figure 1A shows X-ray diffraction patterns of the resulting solids in the Na-montmorillonite–$[Pt(en)_2]Cl_2$ system. As a result of adding the Pt(II) complex, the diffraction peaks attributable to the host phase disappeared, while a new (001) diffraction peak appeared at $2\theta=6.74°$ ($d=13.1$ Å) along with its 3rd ($d=4.38$ Å) and 4th ($d=3.25$ Å) order harmonics of reflection. This indicates that the mineral phase is converted into an intercalated phase with an interlayer spacing of 13.1 Å. The thickness of the intercalated layer ($\Delta$) is estimated to be 3.6 Å by subtracting 9.5 Å,(7) the thickness of the silicate layer, from the observed *d*-spacings.

The $[Pt(en)_2]^{2+}$ complex ion contents in the intercalated solids were evaluated by the thermogravimetric method. As shown in Fig. 2, the t.g. curves for the intercalated solids showed two steps, one at below 100 °C and the other in the temperature range of 200—600 °C. The former weight loss was due to the desorption of water. The latter is attributable to a loss of the organic moiety of the intercalant species, accompanied by a weight loss due to condensation of the hydroxyl groups in the host phase. This second weight loss is plotted against the amount of Pt(II) complex added in Fig. 3A. Assuming that the Pt(II) complexes are taken up in the divalent cationic form ($[Pt(en)_2]^{2+}$), the Pt(II) complex ion content per gram of clay can be evaluated from the second weight loss, as indicated on the right ordinate in Fig. 3A. At addition levels of greater than 5 $mmol\,g^{-1}$ the Pt(II) complex uptake, thus obtained, reaches a constant value of 0.45 $mmol\,g^{-1}$. This value is in good agreement with 0.455 $mmol\,g^{-1}$ expected for an ion exchange of the $[Pt(en)_2]^{2+}$ ion with 0.91 mmol of the interlayer $Na^+$ ion per gram of the host phase.(5)

Referring to the structural data for $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$,(8) as well as the van der Walls radii of the constituent atoms or ions, the Pt(II) complex ion has a square-planar form with a van der Waals dimension of $5.8\times10.1\times3.6$ Å$^3$. The $\Delta$ value of 3.6 Å observed for the Pt(II)-based intercalate is in good agreement

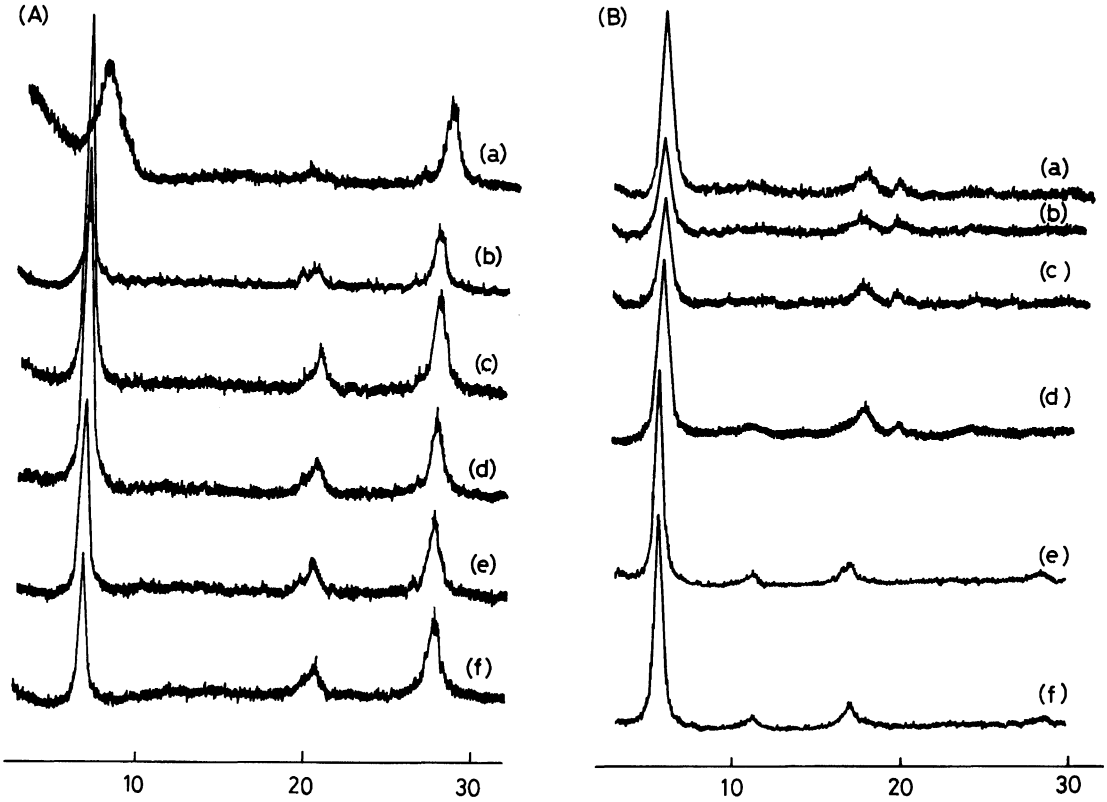

Fig. 1. X-Ray diffraction patterns of the reaction products of Na-montmorillonite with $[Pt(en)_2]Cl_2$ (A) and $[PtCl_2(en)_2]Cl_2$ (B) (Cu $K\alpha$ radiation). Amount of Pt complex added (mmol per gram of clay): (A) 0 (a), 0.225 (b), 1.0 (c), 3.0 (d), 5.0 (e), and 8.0 (f); (B) 1.0 (a), 3.0 (b), 5.0 (c), 8.0 (d), 12.0 (e), and 15.0 (f).

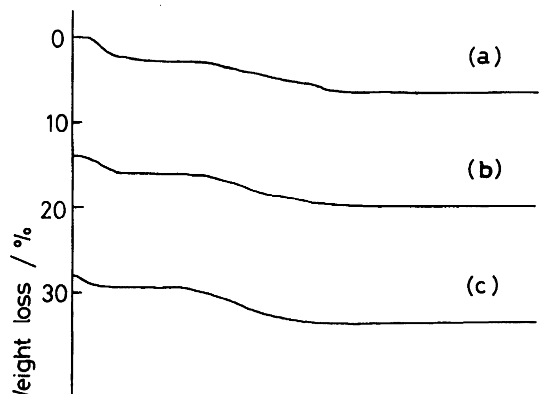

Fig. 2. T.g. curves for the reaction products of Na-montmorillonite with $[Pt(en)_2]Cl_2$. Amount of Pt complex added (mmol per gram of clay): 0.225 (a), 1.0 (b), 3.0 (c), 5.0 (d), and 8.0 (e).

with the thickness of the square-planar form. This suggests that the Pt(II) complex ions are intercalated as a monolayer with their square planes parallel to the silicate layers. The effective area per complex ion was evaluated to be 5.8×10.1 or 58.6 Å$^2$. The unit-cell weight of Na-montmollironite is 744,[5] and the surface area of one face of the unit cell is estimated to be 46.8 Å$^2$.[7] Hence, the Pt(II) complex ion content should be limited geometrically to below (46.8/58.6)/744 or 1.07 mmol g$^{-1}$; the observed value is within this limit. Thus, a model is proposed for the arrangement of the Pt(II) complex ions intercalated in montmorillonite, as shown in Fig. 4A. A similar structure was observed for an intercalate of Na-montmorillonite with $[Cu(en)_2]^{2+}$ ions.[9]

**$[PtCl_2(en)_2]^{2+}$.** As shown in Fig. 1B, the addition of $[PtCl_2(en)_2]Cl_2$ to Na-montmorillonite resulted in the occurrence of a diffraction peak at $2\theta=5.81°$ ($d$=15.2 Å) in the X-ray diffraction patterns, indicating the formation of an intercalated phase with a $\Delta$ value of 5.7 Å. The t.g. curves for the Pt(IV)-based intercalate samples were similar to those for the Pt(II)-based intercalate ones. The weight loss attributable to a weight loss due to the desorption of the non-metallic moiety of the intercalated Pt(IV) complex ion, as well as that due to the hydroxyl condensation, is plotted as a function of the Pt(IV) complex added in Fig. 3B. The right-hand ordinate in Fig. 3B indicates the Pt(IV) complex content obtained by assuming that the Pt(IV)

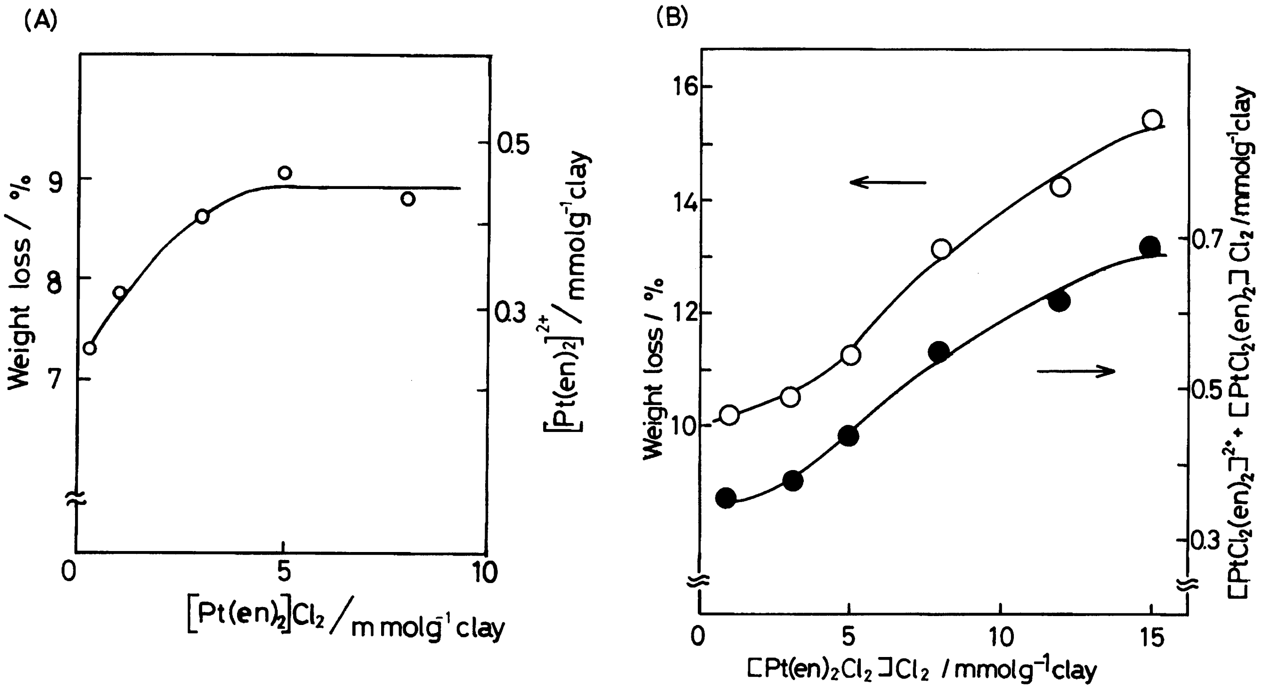

Fig. 3. Plots of the total weight loss observed at temperatures above 200 °C (left ordinate) against the amount added of $[Pt(en)_2]Cl_2$ (A) and $[PtCl_2(en)_2]Cl_2$ (B). The quantities on the right-hand ordinate are referred to the text.

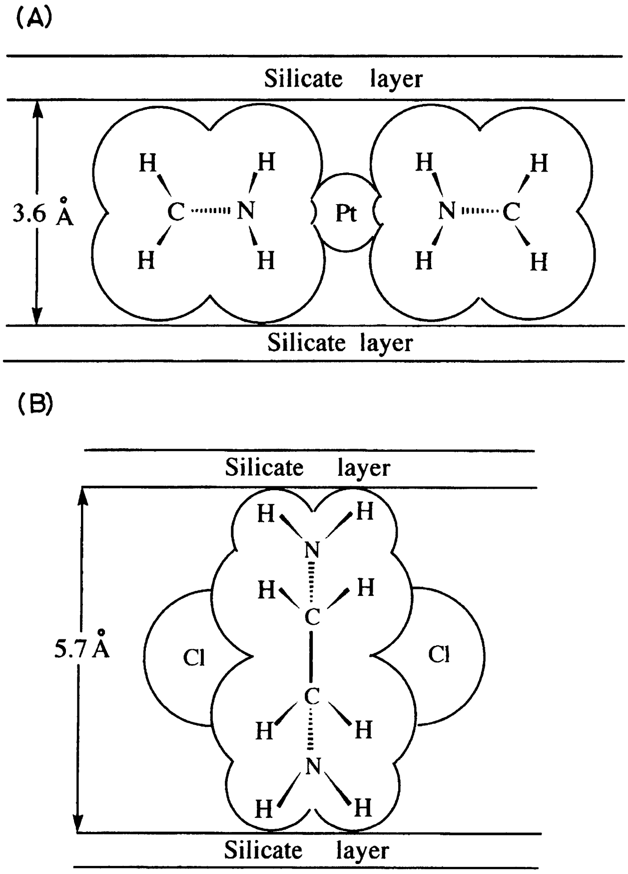

Fig. 4. Schematic representation of the probable orientation of Pt complex ions in the interlayer space of montmorillonite: $[Pt(en)_2]^{2+}$ (A) and $[PtCl_2(en)_2]^{2+}$ (B).

complexes are intercalated in the divalent cationic form of $[PtCl_2(en)_2]^{2+}$.

In contrast to the Pt(II) complex, the Pt(IV) complex uptake shows a remarkable increase with increasing amount added at intermediate addition levels until it exceeds the $Na^+$ ion exchange capacity to reach a value of as large as 0.81 $mmol\,g^{-1}$ at the highest addition level of 15 $mmol\,g^{-1}$. This indicates that the Pt(IV) complex uptake at the highest addition level would occur by an ion exchange of $[PtCl_2(en)]^{2+}/Na^+$ through 0.45 $mmol\,g^{-1}$ corresponding to the $Na^+$ ion exchange capacity, accompanied by an additional uptake of 0.24 $mmol\,g^{-1}$ of neutral $[PtCl_2(en)_2]Cl_2$ species.

Since the $[PtCl_2(en)_2]^{2+}$ ion is octahedral in the atomic configuration and its van der Waals dimension is 5.8×10.1×6.8 Å$^3$, the observed $\Delta$ value of 5.8 Å for the Pt(IV)-based intercalate corresponds to the width of the ethylenediamine ligand coordinating square-planarly to the central atom. This suggest that the Pt(IV) complex ions with or without counter ions are arranged as a monolayer with their square planes perpendicular to the silicate layers, as illustrated in Fig. 4B. Such an arrangement is also energetically favorable because the two $Cl^-$ anions bonded to the central atom would be more strongly repulsed by the negatively charged silicate layers than the ethylene group of the organic ligand. The effective areas of $[PtCl_2(en)_2]^{2+}$ and $Cl^-$ ions are 6.8×10.1 or 68.7 Å$^2$ and $\pi$ (1.8)$^2$ or 10.1 Å$^2$, respectively, which yields $(46.8—0.45\times10^{-3}\times68.7\times744)/\{(68.7+10.1\times2)\times744\}$ or 0.36 $mmol\,g^{-1}$ for the largest additional uptake of $[PtCl_2(en)_2]Cl_2$. This calculated value is slightly more than the 0.24 mmol $g^{-1}$ estimated for an additional uptake at the highest additional uptake at the highest addition level used in this work, which is in accordance with the assumption that any additional uptake is due to intercalation of neutral $[PtCl_2(en)_2]Cl_2$ species into a residual space between the $[PtCl_2(en)_2]^{2+}$ ions taken up by ion exchange with $Na^+$ ions. Such an additional uptake beyond the cation exchange capacity of a clay host was also observed for the uptake of racemic $M(phen)_3^{2+}$ (M=Fe, Co, Ni) by montmorillonite.[10,11] It is also noted that a significant diffraction peak attributable to the (004) reflection is observed for the Pt(II)-based intercalate, while that for the Pt(IV)-based intercalate is unobservable.

**Intercalation from Mixed Solution.** Mixed uptake experiments were carried out using an equimolar solution of **1** and **2** (case a) and varying amounts of **2** with respect to 0.225 mmol of **1** per gram of clay (case b).

In case a, and intercalated phase with an interlayer spacing of 13.1 Å, or $\Delta$=3.6 Å, formed at the initial uptake stage, and its interlayer spacing was little affected by any further addition of the 1:1 platinum complex (Fig. 5). The $\Delta$ value of 3.6 Å for the resulting solid is in good agreement with 3.6 Å for the Pt(II)-based intercalate obtained using the one-component solution of **1**, suggesting that the Pt(II) complex ions are intercalated in preference to the Pt(IV) complex ions. Two differences, however, are observed between the sample of Pt(II)-based intercalate formed from the solution of **1** and that formed from the equimolar solution of **1** and **2**. One is that the latter sample is more highly ordered, as inferred by a comparison of the intensities of the (001) diffraction peak for both samples. The other is that the Pt complex ion content for this sample (evaluate from the t.g. data) reaches a constant value of 0.56 mmol $g^{-1}$ at addition levels of as low as 1 mmol of 1:1 mixture of **1** and **2** per g of clay. Thus, it is most probable that the reaction of Na-montmorillonite with an equimolar mixture of **1** and **2** would occur preferentially through ion exchange with the Pt(II) complex ion, accompanied by a slight uptake of the Pt(IV) complex ion. Such a slight uptake of the Pt(IV) complex ion would serve to promote an uptake of the Pt(II) complex ion, but would not lead to an expansion of the intercalated layer.

The X-ray diffraction data for case b are shown in

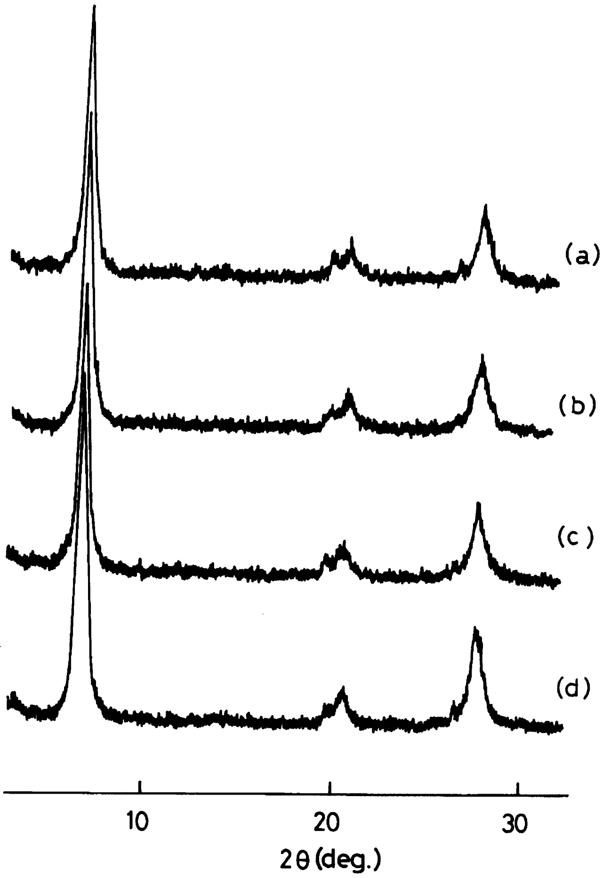

Fig. 5. X-Ray diffraction patterns of the reaction products of Na-montmorillonite with an equimolar mixed solution of $[Pt(en)_2]Cl_2$ and $[PtCl_2(en)_2]Cl_2$ (Cu $K\alpha$ radiation). Total amounts of $[Pt(en)_2]Cl_2$ and $[PtCl_2(en)_2]Cl_2$ (mmol per gram of clay): 1.0 (a); 3.0 (b); 5.0 (c); 8.0 (d).

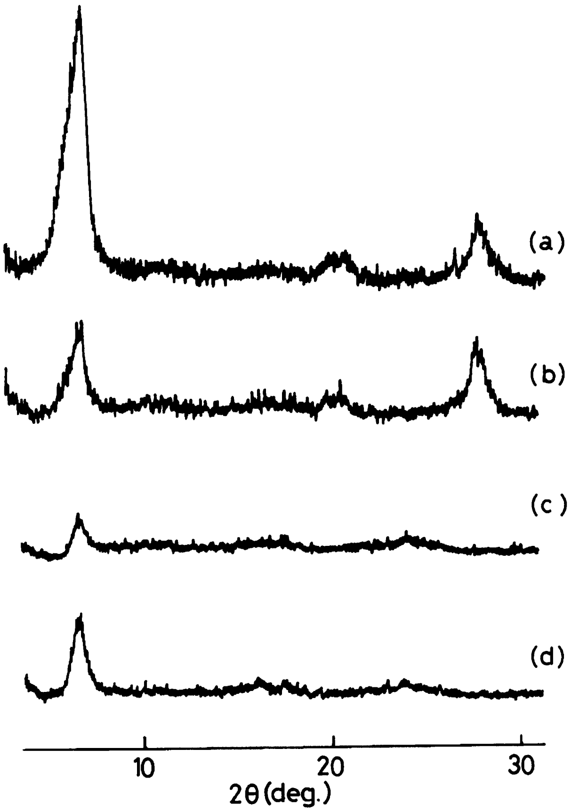

Fig. 6. X-Ray diffraction patterns of the reaction products of Na-montmorillonite with varying amounts of $[PtCl_2(en)_2]Cl_2$ with respect to 0.225 mmol $g^{-1}$ of $[Pt(en)_2]Cl_2$ (Cu$K\alpha$ radiation). Amount of $[PtCl_2(en)_2]Cl_2$ (mmol per gram of clay): 1.0 (a); 3.0 (b); 5.0 (c); 7.0 (d).

Fig. 6. At low uptakes the X-ray diffraction peaks of the resulting solids were identical with those of the Pt(II)-based intercalate, while at higher uptakes the 001 diffraction peak shifted in position from $2\theta=6.69^\circ$ ($d=13.1$ Å or $\Delta=3.6$ Å) to $2\theta=6.24^\circ$ ($d=14.1$ Å or $\Delta=4.6$ Å). The latter $\Delta$ value corresponds to an intermediate of 3.6 Å for the Pt(II)-based intercalate and 5.8 Å for the Pt(IV)-based analogue. This indicates that the Pt(IV) complex ions are co-intercalated with their square planes tilted by $\sin^{-1}(4.6/5.8)$, or 52°, with respect to the silicate layer, along with the Pt(II) complex ions with their square planes parallel to it. The difference in the thicknesses of the co-intercalated Pt(II) and Pt(IV) complex ions would modulate the distance between adjacent silicate layers, leading to the weak and broad X-ray diffraction peaks observed for the co-intercalated phase. Similarly to the individual uptake of Pt(IV) complex, the t.g. data for the mixed intercalated phase also suggested an accompanying uptake of neutral $[PtCl_2(en)_2]Cl_2$ species. It is thus concluded that linear chains or even oligomers of the $Pt^{2+}$–$Cl^-$–$Pt^{4+}$ type cannot be stably held in the interlayer electrostatic field of montmorillonite.

Although the arrangement of the Pt(II) and Pt(IV) complex ions intercalated in montmorillonite would be more exactly determinable by the method of one-dimensional Fourier synthesis, the present X-ray data are not available for such a structure analysis, because of insufficiency in both the number and intensity of the observed (00*l*) reflections.

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