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Solid Solutions of Ammonium Salts of Chloro Complexes of Pt^{IV}, Rh^{III} and Rh^{IV}

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The formation of solid solutions of ammonium salts of chloro complexes of Pt^{IV} and $Rh^{III,IV}$ are observed under equilibrium coprecipitation.

Platinum has been isolated from hydrochloric acid solutions in the form of $(NH_4)_2[PtCl_6]$. Hence, investigation of the coprecipitation of rhodium with ammonium hexachloroplatinate(IV) in a limited range of compositions is of interest. In the present work the simultaneous crystallization of salts of Pt^{IV} and Rh^{III} complexes has been considered.

Products of variable composition containing Pt 43.3–43.9%, Rh 0.03–0.18%, NH_4^+ 8.0–8.2% have been obtained by equilibrium recrystallization of a mixture of salts with various ratios of $(NH_4)_2[PtCl_6]$, $(NH_4)_3[RhCl_6]\cdot H_2O$ and NH_4Cl from 0.1 mol dm^{-3} HCl aqueous solution at 25 ± 0.1 °C. Yellow tetrahedrons and truncated octahedrons resulted as the major crystalline phase. In these crystals the Rh content was determined by atomic absorption spectrometry, Pt was determined by the difference from the gravimetrically obtained sum of Pt and Rh, while NH_4^+ ion was determined by coulometry. In all the samples as impurity of green octahedral crystals at a level of approximately 0.3% (one crystallite per 330 crystallites of the major phase on average) was detected.

Microcrystals of the major phase were investigated using an analytical electron microscope and the elements Pt, Rh and Cl were detected. Using the 'COMPO' (phase contrast) regime for the electron microscopy (twinned detector) the crystals were shown to be single phase.[†] The $(NH_4)_2[PtCl_6]$ structure[1] was found using X-ray powder diffraction and electron microdiffraction.[‡] Microinclusions of ammonium salts of rhodium chloro complexes have been found in the crystal line phase. The crystals of the major phase show no EPR signal at 77 K, hence, they do not contain Rh^{IV}.

A solubility diagram of the system of Pt^{IV} and Rh^{III} chloro complexes in an aqueous solution of NH_4Cl (1.50–1.84 mol dm^{-3}) and HCl (0.1 mol dm^{-3}) has been obtained. It was found that the amount of rhodium in the solid phase decreases with decrease of rhodium content in the mother liquor. The cocrystallization coefficient (D) of Pt and Rh was calculated after 10 runs, using eqn. (1), where c is the

$$D = c^S_{Rh} c^L_{Pt} / c^L_{Rh} c^S_{Pt} \qquad (1)$$

metal concentration in g dm^{-3}, the upper index S the concentration in the solid phase and L the concentration in the mother liquor. The value of this coefficient, $(5.0\pm0.8)\times10^{-5}$, is constant in all runs within the error of confidence probability $P=0.95$. The contribution of adsorption and capture of rhodium during the crystallization processes can be neglected owing to the consistency of the values obtained for the coefficient.

The net results can be explained by the formation of solid solutions of complex Pt^{IV} and Rh^{III} compounds in the system. Other conclusions contradict to one or more of the experimental results. According to refs. 2–4, the dominant complex species at equilibrium over the investigated range of chloride ion concentrations (1.60–1.94 mol dm^{-3}) are $[PtCl_6]^{2-}$ and $[Rh(H_2O)Cl_5]^{2-}$. The contribution of hydroxo complexes in a 0.1 mol dm^{-3} HCl medium is negligible. Therefore, it is suggested that the solid solutions also contain dominant $[PtCl_6]^{2-}$ and $[Rh(H_2O)Cl_5]^{2-}$ complex species of the same charge. The similar ionic radii of Pt^{4+} and Rh^{3+} suggest that the $[PtCl_6]^{2-}$ ion may be substituted by $[Rh(H_2O)Cl_5]^{2-}$ in the crystal lattice, giving rise to the formation of solid solutions with isomorphous replacement into the $(NH_4)_2[PtCl_6]$ structure.

Selected microcrystals of the impure phase showed the presence of Pt, Rh and Cl upon scanning with an analytical electron microscope. Microdiffraction electron microscopy showed that the crystals of the impure phase were formed with the $(NH_4)_2[PtCl_6]$ structure.[§]

It is known that the Rh^{IV} salt $Cs_2[RhCl_6]$[5–7] and solid solutions of $A_2[(Pt^{IV}_{1-x}, Rh^{IV}_x)Cl_6]$ ($A = K^+, Cs^+$)[7] are green in colour. It appears that the impure phase is a solid solution of $(NH_4)_2[(Pt^{IV}_{1-x}, Rh^{IV}_x)Cl_6]$, with a number of $[RhCl_6]^{2-}$ ions substituting for $[PtCl_6]^{2-}$ ions.

Green crystals with not trace of the yellow phase were obtained by evaporation of salt solutions in 1–2 mol dm^{-3} HCl. Aqueous solutions of $(NH_4)_2[PtCl_6]$ and $(NH_4)_3[RhCl_6]\cdot H_2O$ in molar ratio 4.4 : 1 were mixed with varying amounts of hydrochloric acid and NH_4Cl, evaporated with a water bath and then crystallized for 2–3 days. It was noted that the intensity of the green tint of the crystals increased with increasing HCl concentration. Atomic absorption analyses of the substances obtained indicated 0.05–0.32% Rh and 42.0–45.2% Pt; NH_4^+ ion was determined by coulometry: 7.9–8.3%. The data obtained by phase contrast showed that all the samples were single phase, and an $(NH_4)_2[PtCl_6]$ structure for the samples was determined by X-ray powder diffraction and electron microdiffraction.[¶]

EPR spectra of the synthesized green crystals were recorded at 77 K. The spectrum is a singlet transition without anisotropy with linewidth $\Delta H = 200$ Oe.[‖] The signal shape is not essentially changed upon cooling to 16 K. This may be caused by both magnetic interactions between closely located Rh^{4+} ions and the high symmetry of the environment close to a rhodium ion. The value of g_0 is 1.765 ± 0.005, *i.e.*, consistent with $g_0 = 1.7545\pm0.0005$ determined for $[Rh^{IV}Cl_6]^{2-}$.[5] No EPR spectrum is observed at 300 K. A decrease of EPR signal amplitude was found for samples with a lower rhodium content. Hence, rhodium is mainly present in the +4 oxidation state.

The overall results allow us to consider the green phase which is formed during the coprecipitation of complex salts of platinum and rhodium as an isomorphic solid solution of $(NH_4)_2[PtCl_6]$ and $(NH_4)_2[RhCl_6]$. The appearance of Rh^{IV} can be explained as the result of a redox conversion in the system [eqn. (2)]. Pt^{II}, found by coulometric titration in the mother

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[†] A REMMA-202M high resolution scanning electron microscope with facilities for X-ray microanalysis was used for these measurements. The device has an electron probe 100 Å in diameter.

[‡] *Crystal data* for the major phase: face-centred cubic, space group F_{m3m}, $a = b = c = 9.86(1)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, reflections were measured using a DRON-3 diffractometer (graphite-monochromated Cu-K$_\alpha$ radiation, $\lambda = 1.5418$ Å). These data were confirmed by electron diffraction using an EMV-100BR electron microscope, $U = 100$ kV, $2\lambda L = 4.6$ cm Å [$a = b = c = 9.8(3)$ Å, $\alpha = \beta = \gamma = 90°$].

[§] *Crystal data* for the impure phase: face-centred cubic, space group F_{m3m}, $a = b = c = 9.9(4)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, reflections were measured with JEM-100C electron microscope in microdiffraction regime, $U = 80$ kV, $2\lambda L = 4.5$ cm Å.

[¶] *Crystal data* for the green crystals: face-centred cubic, space group F_{m3m}, $a = b = c = 9.843(7)$–$9.851(4)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, reflections were measured on a DRON-3 diffractometer. These data were confirmed by electron diffraction using an EMV-100BR electron microscope, $U = 100$ kV, $2\lambda L = 4.6$ cm Å [$a = b = c = 9.84(5)$ Å, $\alpha = \beta = \gamma = 90°$].

[‖] Oe $= 10^3$ A m^{-1}.

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$$PtCl_6^{2-} + 2RhCl_6^{3-} \rightleftharpoons PtCl_4^{2-} + 2RhCl_6^{2-} + 2Cl^- \qquad (2)$$

liquor of the heterogeneous system confirms this assumption. A distribution constant of Rh^{IV} of 1.6×10^9 between the liquid and solid phases has been estimated. Consequently, Rh^{IV} exists in the system only in the solid phase, where it is stabilized as a solid solution with $(NH_4)_2[PtCl_6]$. The distribution constant K of Rh^{IV} between liquid and solid phases was found using eqn. (3), where c is the concentration of Rh^{IV} (in g dm^{-3}). In the

$$K = c_{\text{green phase}}/c_{\text{mother liquor}} \qquad (3)$$

heterogeneous system which contained salts of Rh^{III} and Pt^{IV} in the mother liquor, Pt^{II} appeared over time. This Pt^{II} was quantitatively determined by coulometric titration. When multiplied by 2, the obtained number of moles of Pt^{II} gives the total quantity of Rh^{IV} which appeared in the heterogeneous system. The equilibrium constant of the redox reaction (2.5×10^{-18} mol^2 dm^{-6}) was estimated from the redox potentials of $E(Pt^{2+}/Pt^{4+})$ and $E(Rh^{3+}/Rh^{4+})$, then this constant was used to calculate the quantity of Rh^{IV} in the mother liquor. This quantity is 10^5 times less than that in the solid phase, hence, the quantity of Rh^{IV} in the solid phase is approximately equal to that in the system. The distribution constant of Rh^{IV} between the liquid and the solid phases (K) was then estimated using eqn. (3), taking into account the impurity of Pt^{II} in $(NH_4)_2[PtCl_6]$.

The data presented here provides evidence that the formation of solid solutions of complex compounds results in contamination of platinum by associated rhodium in affinage.

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References

1 *Powder Diffraction File*, ed. W. F. McClune, ICPDS International Centre for Diffraction Data, Pennsylvania, USA, 1977, data card 7-218.
2 E. Blasius, W. Preetz and R. Schmitt, *J. Inorg. Nucl. Chem.*, 1961, **19**, 115.
3 D. Cozzi and F. Pantani, *J. Inorg. Nucl. Chem.*, 1958, **8**, 385.
4 A. V. Belyaev, *Izv. Sib. Otd. Acad. Nauk SSSR. Ser. Khim. Nauk*, 1970, **4**(9), 11.
5 A. D. Westland, *Can. J. Chem.*, 1968, **46**, 3591.
6 C. K. Jorgensen, *Mol. Phys.*, 1961, **4**, 231.
7 I. Feldman, R. S. Nyholm and E. Watton, *J. Chem. Soc.*, 1965, 4724.

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