= COORDINATION COMPOUNDS =

[Zn(NH₃)₄][PtCl₆] and [Cd(NH₃)₄][PtCl₆] as Precursors for Intermetallic Compounds PtZn and PtCd

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Abstract—Double complex salts (tetraamminezinc and tetraamminecadmium hexachloroplatinates) have been synthesized. Their thermal properties have been studied, as well as the products of their degradation in hydrogen and helium atmospheres. Optimal thermolysis schedules have been determined. Thermolysis under hydrogen yields intermetallic compounds PtZn and PtCd.

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Catalysis is now the most extensive application field of the platinum-group metals, consuming more than one-half of the world-wide production of platinum [1]. Catalysts are often supported nanosized platinum metals. A partial substitution of a nonprecious metal for a platinum metal significantly lowers the catalyst cost, and it is pertinent to search for new supported catalysts based on solid solutions of precious and nonprecious metals. In addition, multicomponent supported metal systems have several strengths over one-component systems due to synergism. In our earlier work [2], we showed for several double complexes of platinum metals that their reductive thermolysis under a hydrogen atmosphere, in many cases, yields metal solid solutions of various dispersions.

The goal of this work was to explore the feasibility of manufacturing fine-powdered intermetallic compounds PtZn and PtCd.

EXPERIMENTAL

The starting $K_2[PtCl_6]$ was prepared by a standard procedure [3] from hydrochloroplatinic acid (chemically pure grade).

The double complex salts (DCSs) were synthesized at room temperature. Solutions of tetraamminezinc and tetraamminecadmium were prepared by adding 25% aqueous ammonia to saturated aqueous solutions of zinc chloride or cadmium perchlorate until the nascent hydroxides completely dissolved. To the resulting solutions, a 0.02 M K₂[PtCl₆] solution was added so that the amount of zinc or cadmium was 10% over the 1 : 1 stoichiometry. Yellow precipitates appeared instantaneously; they were filtered off, washed with a minimal amount of cold water, and dried in air. The yield was 85–90% in both cases.

IR spectra were recorded as KBr pellets on a Scimitar FTS 2000 spectrometer in the wavenumber range of

| DCS | v(NH ₃) | $\delta_d(\mathrm{NH}_3)$ | $\delta_s(\mathrm{NH}_3)$ | $\rho_r(\mathrm{NH}_3)$ | v(M–N) |
|--|---------------------|---------------------------|---------------------------|-------------------------|--------|
| [Zn(NH ₃) ₄][PtCl ₆] | 3334, 3253 | 1683, 1607 | 1274, 1245, 1219 | 735, 714 | 427 |
| $[Zn(NH_3)_4]I_2*$ | 3290 | 1600 | 1242 | 693 | 410 |
| [Cd(NH ₃) ₄][PtCl ₆] | 3357, 3265 | 1674, 1599 | 1194 | 630 | 390 |
| $[Cd(NH_3)_4]Cl_2*$ | 3360, 3260 | 1608 | 1207 | 561 | 381 |

Table 1. IR vibration frequencies for DCSs (cm⁻¹)

* Data from work [4].

400–4000 cm⁻¹. Assignment was done with reference to work [4]. The assignment results are displayed in Table 1.

Chlorine was determined routinely according to Schoniger. Separate analyses of complexes and metal solid solutions for the metals were carried out by atomic absorption spectrometry (AAS) Zeeman background correction on a Hitachi Z 8000 spectrometer with after solubilizing the solid phases with aqua regia. Element interference was eliminated by buffering the solutions with LaCl₃.

For [Zn(NH₃)₄][PtCl₆] anal. calcd., %: Cl, 39.30; Zn, 12.08; Pt, 36.04.

Found, %: Cl, 39.1; Zn, 12.2; Pt, 36.1.

For [Cd(NH₃)₄][PtCl₆] anal. calcd., %: Cl, 36.16; Cd, 19.11; Pt, 33.16.

Found, %: Cl, 36.3; Cd, 19.3; Pt, 33.0.

Metal powders were prepared by reducing samples of the complexes (~100 mg) in flowing hydrogen at various temperatures and hearing rates. Figure 1 displays the weight of the residue (in percent of the starting weight) as a function of heating schedule for $[Zn(NH_3)_4][PtCl_6]$.

Thermoanalytical curves (Figs. 2, 3) were obtained on a Q-1000 derivatograph modified to operate in different gas atmospheres.

Powder X-ray diffraction analysis of polycrystalline samples of the complex salts and their thermolysis products was carried out on a DRON-Seifert RM4 diffractometer (Cu K_{α} radiation, graphite monochromator on a diffracted beam, scintillation detector with amplitude discrimination). Test samples were prepared by spilling an ethanol suspension onto the polished side of a fused silica cell. A polycrystalline silicon sample (a = 5.4309 Å) prepared in the same manner was used as an external reference. The X-ray diffraction patterns were recorded in a discrete mode in the 20 range from 5° to 60° for the complex salts and from 5° to 135° for thermolysis products.

RESULTS AND DISCUSSION

IR spectra. In the IR spectra of the DCSs, the bands of the bending vibrations of coordinated ammonia molecules shift toward higher wavenumbers compared to simple salts of zinc and cadmium tetraammines. The $\delta_d(NH_3)$ bands are split in both compounds. The $\delta_s(NH_3)$ and $\delta_r(NH_3)$ bands are split for the zinc compound. We observed split and shifted modes of coordinated ammonia molecules in DCSs in our previous work [5]; this was due to the distortion of the symmetry of complex ions in the crystal structure of DCSs. The nonappearance of the vibrations intrinsic to the ammonium ion and other complex cations ([Cd(NH₃)₆]²⁺ with the following wavenumbers (cm⁻¹): $\delta_s(NH_3)$, 1091; $\delta_d(NH_3)$ 1585; $\rho_r(NH_3)$ 613; ν_{MN} , 298



Fig. 1. Thermolysis of $[Zn(NH_3)_4][PtCl_6]$ in hydrogen. The weight of the residue (in percent of the starting weight) as a function of heating schedule (obs./calcd.).

[4]) in the spectra of the DCSs in question provides circumstantial evidence in favor of the individuality of the compounds.

Powder X-ray diffraction. We failed to grow DCS crystals suitable for a single-crystal X-ray diffraction experiment. We also failed to find compounds isostructural to our synthesized complexes in the JCPDS database [6]. The X-ray diffraction pattern for a polycrystalline sample of the complex was indexed assuming a monoclinic unit cell with the parameters a = 12.134(3) Å, b = 7.813(2) Å, c = 7.787(2) Å, $\beta = 119.4(2)^{\circ}$. The positions and intensities of X-ray diffraction reflections for this complex repeat from synthesis to synthesis. Reflections other than pertaining to the chosen unit cell were not found.

The X-ray diffraction pattern of the complex $[Cd(NH_3)_4][PtCl_6]$ differs strongly from that of the complex $[Zn(NH_3)_4][PtCl_6]$ in both the positions and intensities of the reflections. Broad, poorly resolved reflections did not allow us to index the unit cell.

Thermolysis in helium. The thermolysis of the DCSs under a helium atmosphere involves three stages. The weight loss at the first stage corresponds to ~17 amu in both cases. Powder X-ray diffraction shows that the intermediate produced at this stage is amorphous. There are low-intensity reflections, which are assigned to the $(NH_4)_2[PtCl_6]$ phase. This stage is accompanied by a noticeable exotherm in the DTA curve, which is characteristic of ligand exchange between the inner spheres of the complex ions in the DCS.

The second stage also produces a hygroscopic intermediate, which contains metallic platinum and zinc or cadmium chloride hydrates as shown by powder X-ray diffraction. Weight losses at this stage well match the stoichiometry of the PtMCl₂ residue, where M = Zn or Cd.



Fig. 2. Thermoanalytical curves for [Zn(NH₃)₄][PtCl₆] thermolysis in helium at 10 K/min.



Fig. 3. Thermoanalytical curves for [Cd(NH₃)₄][PtCl₆] thermolysis in helium at 10 K/min.

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The final stage involves the sublimation (vaporization) of zinc or cadmium chloride. The boiling temperatures are 733 and 975°C for ZnCl_2 and CdCl_2 , respectively. The final product of $[\text{Zn}(\text{NH}_3)_4][\text{PtCl}_6]$ thermolysis in helium is platinum metal as identified by powder X-ray diffraction; the weight of the residue (37%) matches the calculated platinum proportion in this salt (36.04%).

Thermolysis in hydrogen. When the DCSs degrade in hydrogen at temperatures above 500°C, the resulting metal phases are depleted in the nonprecious component (we called this phenomenon "oveheating" of the samples). Therefore, we had to choose optimal reduction parameters to ensure the 1 : 1 stoichiometry of the product.

Figure 1 displays several examples of the reduction of $[Zn(NH_3)_4][PtCl_6]$. Salt samples were heated at 10 or 20 K/min. Faster heating resulted in either incomplete reduction (in sample 1) or loss of zinc (in sample 2). Slower heating (5 K/min) to 400°C also did not ensure full reduction (in sample 3); however, subsequent exposure at this temperature (in sample 4) or slow cooling (in sample 5) diminished the deviation of the product weight from the value calculated for the sum of the metals. We believe that the schedule we employed for sample 6 is optimal: first, a DCS was heated at a rate of 10 K/min to 300°C; then, the heating rate was lowered; after reaching 400°C, the sample was exposed for at least 1 h.

The Zn : Pt ratio in these products determined by AAS is displayed in Table 2. One can see that "overheated" samples are depleted in zinc. Powder X-ray diffraction shows that sample 2 (with the lowest zinc concentration) consists of pure platinum and intermetallic compound PtZn (JCPDS 6-604), which matches the phase diagram [7]. According to the phase diagram



Fig. 4. Fragment of the Pt–Zn phase diagram [7]. Dashed lines indicate the compositions of the metal phase as determined from TG data for the relevant sample (Fig. 1).

(Fig. 4), the homogeneous range of the PtZn phase at room temperature is 31–47.5 at. % Zn. As temperature increases, the homogeneous range widens to reach 31–51 at. % Zn at 900°C. Samples 4–6 have only reflections from the PtZn phase. The unit cell parameters of PtZn in all samples are practically the same; they do not differ from the parameters of the reference in the JCPDS database (Table 2). Reflections of the PtZn_{1.7} phase (JCPDS 6-619) are not found in equiatomic samples 5 and 6. The absence of this phase is likely due to nonequilibrium synthesis conditions. Sample 5 displays very weak (<5%) reflections of platinum, which is also because of its metastable state.

For $[Cd(NH_3)_4][PtCl_6]$, 400°C is also the optimal reduction temperature. However, despite several attempts, we failed to obtain the single-phase intermetallic compound. Powder X-ray diffraction shows

| Sample no. | M: Pt (AAS) | Phase | Percentage con- tent of the phase | <i>a</i> , Å | <i>c</i> , Å | MCS, Å |
|----------------------|-------------|-------|--------------------------------------|----------------|----------------|---------|
| 2 | 0.73 | PtZn | ~45 | 4.025(3) | 3.500(5) | 90-120 |
| | | Pt | ~55 | 3.919(2) | | 90-120 |
| 4 | 0.82 | PtZn | 100 | 4.030(3) | 3.500(3) | 120-170 |
| 5 | 1.00 | PtZn | >95 | 4.025(3) | 3.491(3) | 120-200 |
| | | Pt | <5 | Not determined | | |
| 6 | 1.00 | PtZn | 100 | 4.030(3) | 3.485(3) | 150-220 |
| Reference PtZn* | _ | — | - | 4.0247 | 3.491 | _ |
| Pt-Cd** | 0.995 | PtCd | >95 | 4.185(3) | 3.825(3) | |
| | | Pt | <5 | | Not determined | |
| Reference PtCd*** | _ | _ | _ | 4.174 | 3.817 | _ |

Table 2. Analytical data for the thermolysis products of DCSs in hydrogen

* Reference data for $Pt_{52.8}Zn_{47.2}$ (JCPDS 6-604) [6].

** Thermolysis product of [Cd(NH₃)₄][PtCl₆] in hydrogen.

*** Reference data fo Pt_{51.5}Cd_{48.5} (JCPDS 14-7) [6].



Fig. 5. Catalytic activity of the intermetallic compound PtZn in hydrogenation of butadiene. Selectivity is measured relative to butenes.

a PtCd phase in all runs and a minor amount of platinum (in all runs, less than 5 wt %). However, AAS (Table 2) shows insignificant sublimation of cadmium during the experiment, and the excess of platinum is ~0.5 at. %. In the Pt–Cd phase diagram, this composition falls in the field of PtCd-base solid solution. Thus, the presence of a platinum phase in the reduction products of $[Cd(NH_3)_4][PtCl_6]$ is due to incomplete equilibration in the mixture.

It is noteworthy that under the chosen conditions, hydrogen reduces active metals, such as zinc and cadmium, from similar compounds. To confirm the uniqueness of this preparation process of intermetallic compounds, we carried out the following experiments. First, zinc and cadmium chlorides were heated to 400° C in flowing hydrogen. As expected, reduction did not occur. We repeated the experiments adding a stoichiometric amount of K₂[PtCl₆] to zinc and cadmium chlorides and carefully stirring the blend. In this case, zinc and cadmium did not reduce either; disperse platinum was the only metallic product. The reason for this, as well as for the conservation of the PtZn structure at different zinc concentrations, is associated with the high thermodynamic stability of this intermetallic compound. The reduction of [Zn(NH₃)₄][PtCl₆] supported on γ -Al₂O₃ with hydrogen yielded a catalyst containing 2 wt % PtZn. Tests for butadiene hydrogenation (Fig. 5) showed that the activity of this catalyst is comparable with that of a pure platinum catalyst.

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