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COORDINATION COMPOUNDS

Conversion of Magnus Salt into Diamminedichloroplatinum(II) Isomers in Aqueous Solution

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Abstract—The conditions inducing conversion of Magnus salt into diamminedichloroplatinum(II) isomers were studied. Syntheses of *cis*- diamminedichloroplatinum(II) and *trans*-diamminedichloroplatinum(II), which are used to prepare potassium or ammonium amminetrichloroplatinate(II), are described. The identity and structure of diamminedichloroplatinum(II) isomers were verified by elemental analysis, X-ray powder diffraction, and IR and UV spectroscopy. A workflow for preparing potassium or ammonium amminetrichloroplatinate(II) from diamminedichloroplatinum(II) isomers was developed. This workflow appreciably increases the product yield due to the return of unused Magnus salt to the main synthesis flow.

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Synthesis of potassium or ammonium amminetrichloroplatinate(II) meets several difficulties causing low yields. The use of these platinum(II) complexes as precursors for synthesis of the third generation of mixed platinum complexes, which have biological activity [1], suggests addition of tetramminedichloroplatinum(II) compounds and potassium tetrachloroplatinate(II); subsequently, these additives are removed from synthesis in the form of sparingly soluble Magnus salt. This additionally decreases the yield of the major products [2–5].

In this work, we develop a new approach to synthesis of potassium or ammonium amminetrichloroplatinate(II) with the goal of appreciably increasing the yield of these compounds via the use of Magnus salt [6].

EXPERIMENTAL

Magnus salt $[Pt(NH_3)_4] \cdot [PtCl_4]$ was prepared by the procedure described for the preparation of potassium or ammonium amminetrichloroplatinate(II) [7]. The identity of this compound was verified by elemental analysis, X-ray powder diffraction, and IR spectroscopy.

For $[Pt(NH_3)_4] \cdot [PtCl_4]$ anal. calcd., wt %: Pt, 65.01; Cl, 23.63; N, 9.33; H, 2.00.

Found, wt %: Pt, 65.07; Cl, 23.43; N, 9.22; H, 1.96.

Synthesis of diamminedichloroplatinum(II) isomers from Magnus salt includes the following procedures. To Magnus salt (3.0 g) suspended in water (20 mL), ammonium acetate (2 g) is added; solution pH is brought to 5.4 using acetic acid. The mixture in a flask equipped with a refluxer is heated on an electric plate for 1 h. When the precipitate dissolves and solution acquires a weak olive color, it is cooled and, when necessary, filtered. To the filtrate, strong hydrochloric acid (10 mL) is added; *cis*-diamminedichloroplatinum(II) (1.2 g) precipitates. After the precipitate is separated, the solution is continued to be heated at about 95°C for 1.5 h. Then, the solution is cooled and *trans*-diamminedichloroplatinum(II) (1.17 g) is isolated.

The resulting samples (samples **1** and **2**) of diamminedichloroplatinum(II) isomers were characterized by elemental analysis, X-ray powder diffraction, and IR and UV spectroscopy.

For *cis*-$[Pt(NH_3)_2Cl_2]$ anal. calcd., wt %: Pt, 65.01; Cl, 23.63; N, 9.3; H, 2.00

Found, wt %: Pt, 65.04; Cl, 23.53; N, 9.28; H, 2.08.

For *trans*-$[Pt(NH_3)_2Cl_2]$ anal. calcd., wt %: Pt, 65.01; Cl, 23.63; N, 9.33; H, 2.00

Found, wt %: Pt, 65.09; Cl, 23.47; N, 9.25; H, 1.96.

X-ray diffraction patterns for samples **1** and **2** were recorded on DRON-4-07 (CuK_α radiation, $\lambda = 1.5405$ Å). The measurement range was 2θ 4°–90° with 0.04° steps, and the accumulation (exposure) time was 10 s per point. Identification was carried out using software published in [8, 9].

IR spectra of solid samples were recorded as KBr disks on Specord IR-75 in the range 400–3800 cm^{-1}.

UV absorption spectra were recorded from aqueous solutions on Specord UV-Vis in the range 28000–48000 cm^{-1}.

RESULTS AND DISCUSSION

Magnus salt $Pt(NH_3)_4] \cdot [PtCl_4$ is sparingly soluble in water, and it is difficult to convert it into other complexes. This salt is used to prepare tetraamminedichlo-

Table 1. X-ray diffraction data for precursor *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ and samples **1** and **2**

cis-$[Pt(NH_3)_2Cl_2]$ [12]		*trans*-$[Pt(NH_3)_2Cl_2]$ [13]		Sample 1		Sample 2	
d, Å	I/I_0, %	*d*, Å	I/I_0, %	*d*, Å	I/I_0, %	*d*, Å	I/I_0, %
6.35	100			6.35	100		
5.86	95	5.93	100	5.87	95	5.93	100
5.39	75			5.39	75		
		4.80	95			4.80	92
4.47	8			4.47	8		
4.39	10	4.23	35	4.39	9	4.23	35
3.68	20	3.44	40	3.68	20	3.44	40
3.32	35	3.39	10	3.32	35	3.39	10
3.13	30	3.26	60	3.14	29	3.26	60
		3.16	45			3.16	42
		3.09	12			3.09	10
2.92	20	2.96	8	2.92	20	2.96	6
2.88	16			2.88	16		
2.69	20			2.69	20		
2.57	10	2.58	8	2.57	9	2.58	7
2.48	16	2.48	40	2.48	16	2.48	40
2.43	12	2.40	25	2.43	12	2.40	23
2.35	16	2.30	8	2.35	16	2.30	7
2.26	8	2.17	20	2.26	8	2.17	20

roplatinum(II) and *trans*-diamminedichloroplatinum(II) complexes [10, 11]. There is no data on the preparation of diamminedichloroplatinum(II) isomers from Magnus salt. Therefore, we studied the conversion of $[Pt(NH_3)_4] \cdot [PtCl_4]$ into $[Pt(NH_3)_2Cl_2]$ isomers for various platinum, ammonium acetate, and hydrochloric acid concentrations. We determined that the *cis*-$[Pt(NH_3)_2Cl_2]$ yield drops with increasing ammonium acetate concentration, and the process produces complex $[Pt(NH_3)_4Cl_2]$. With decreasing hydrochloric cid concentration, the *trans*-$[Pt(NH_3)_2Cl_2]$ yield decreases and the process time increases. A decrease in the $[Pt(NH_3)_4] \cdot [PtCl_4]$ concentration reduces the yields of the major products. On the basis of these studies, we found the parameters for the preparation of diamminedichloroplatinum(II) isomers from Magnus salt. These optimal parameters were used in the synthesis described above. Samples **1** and **2** of $[Pt(NH_3)_2Cl_2]$ isomers were characterized by various physicochemical methods to judge their identity. Tables 1–3 display our results with reference to the related literature.

Table 2. Assignment of absorption frequencies (cm^{-1}) in the IR spectrum of precursor *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ and samples **1** and **2**

cis-$[Pt(NH_3)_2Cl_2]$ [14–17]	*trans*-$[Pt(NH_3)_2Cl_2]$ [14–17]	Sample 1	Sample 2	Assignment
3297	3300	3296	3300	ν(NH)
3232	3220	3231	3219	
1625	1635	1624	1635	δ(NH_3)
	1597		1597	
1544	1538	1543	1536	
1301	1294	1300	1296	δ(NH_3)
795	819	796	819	ρ(NH_3)
517	500	517	500	ν(Pt–N)

Table 3. Molar absorptivities ε of precursor $[Pt(NH_3)_2Cl_2]$ isomers and samples **1** and **2**

$\nu \times 10^{-3}$, cm	*cis*-$[Pt(NH_3)_2Cl_2]$ [18–20]	*trans*-$[Pt(NH_3)_2Cl_2]$ [18–20]	Sample 1	Sample 2
	ε, L/(mol cm)			
41	29.8	98.2	29.8	97.3
40	33.4	48.1	33.4	49.2
39	53.7	56.7	53.0	57.0
38	76.4	76.0	77.0	75.0
37	98.4	78.7	98.0	79.0
36	112.7	73.7	113.0	73.7
35	121.7	59.3	121.7	59.8
34	134.8	51.9	135.0	51.9
33	143.2	55.6	143.0	55.7
32	115.7	67.0	115.2	66.8
31	64.0	63.8	63.9	64.0
30	35.8	38.9	35.9	39.0

The results of physicochemical characterization indicate that sample **1** contains *cis*-$[Pt(NH_3)_2Cl_2]$ and sample **2** contains *trans*-$[Pt(NH_3)_2Cl_2]$. No foreign impurities were detected.

The complex *cis*-$[Pt(NH_3)_2Cl_2]$ is used for the production of first-generation antitumor drugs [21] and as a precursor for the synthesis of potassium or ammonium amminetrichloroplatinate(II). *trans*-$[Pt(NH_3)_2Cl_2]$ is used to prepare a tetraamminedichloroplatinum(II) salt, which is in turn used to prepare potassium or ammonium amminetrichloroplatinate(II).

Magnus salt contains complex species that are required for the synthesis of monoammineplatinum(II) complexes.

A workflow for the conversion of this salt is displayed on Fig. 1, together with the yields of the major products.

From this workflow, 52% tetramminedichloroplatinum(II) is used in the synthesis of monoammineplatinum(II) complexes and 48% leaves to affinage, because a little more than one-half tetraamminedichloroplatinum(II) must be used in the synthesis of potassium or ammonium amminetrichloroplatinate(II).

Our workflow (Fig. 2) for the conversion of Magnus salt into diamminedichloroplatinum(II) completely makes it possible to use the major products completely in the synthesis of potassium or ammonium amminetrichloroplatinate(II). The synthesis of $[Pt(NH_3)_4] \cdot [PtNH_3Cl_3]_2$ consumes 22% tetramminedichloroplatinum(II). The main synthesis of Koss salt consumes the remaining 10%. The workflow in Fig. 2 appreciably increases the yield of potassium or ammonium amminetrichloroplatinate(II) due to the return of unused Magnus salt into the main synthesis.

Our study demonstrated that Magnus salt in aqueous solution can convert into diamminedichloroplatinum(II) isomers. These compounds are the major products in $[Pt(NH_3)_4] \cdot [PtCl_4]$ conversion. Our workflow

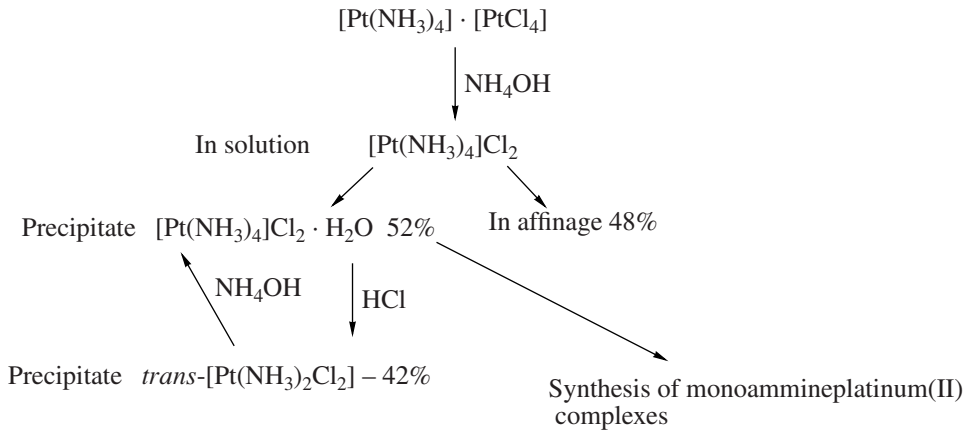

Fig. 1. Workflow for the conversion of Magnus salt $[Pt(NH_3)_4] \cdot [PtCl_4]$ into the reaction products $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and *trans*-$[Pt(NH_3)_2Cl_2]$.

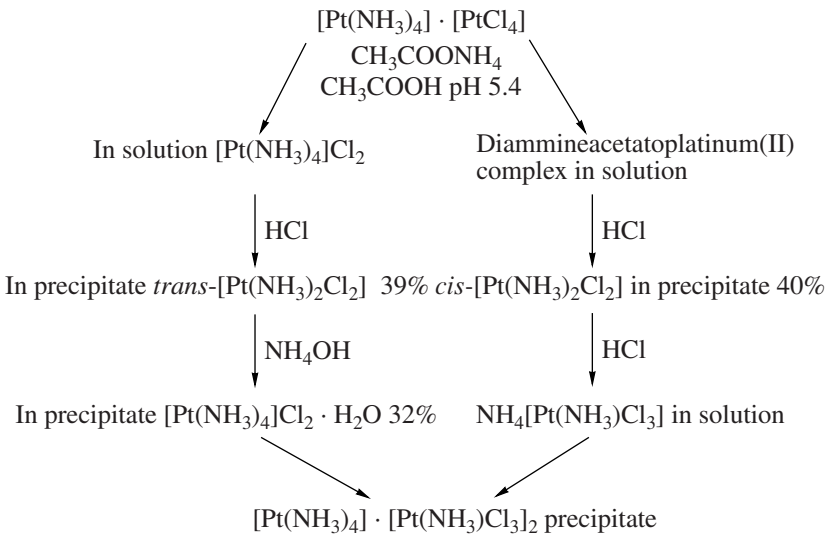

Fig. 2. Workflow for the conversion of Magnus salt $[Pt(NH_3)_4] \cdot [PtCl_4]$ into $[Pt(NH_3)_2Cl_2]$ isomers.

makes it possible to use them in the preparation of potassium or ammonium amminetrichloroplatinate(II), completely exclude the removal of platinum from the synthesis in the form of Magnus salt, and increases the yield of these compounds.

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