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Hydrolysis of Organonitriles and Carboxamides in Platinum(IV) Complexes. X-ray Structure Determination of the Crystalline Clathrate $\{(C_2H_5)_4N\}[Pt(NH_3)Cl_5]\cdot\frac{1}{6}NH_4Cl$

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Abstract

Complexes $[PtL(dmso)Cl_4]$ (L = MeCN, PhCN, $MeCONH_2$, $PhCONH_2$) are easily subject to hydrolysis at 20 °C and form a mixture of the ammine complexes Pt(IV) and corresponding carbonic acids.

As a result of hydrolysis of $[Pt(MeCN)(dmso)Cl_4]$ followed by addition of $(Et_4N)Cl$ to the mixture, the crystalline clathrate $(Et_4N)[Pt(NH_3)Cl_5]\cdot\frac{1}{6}NH_4Cl$ was obtained. The compound has the following X-ray structure: it crystallizes in the rhombohedric space group $R\bar{3}$; unit cell parameters: a = 25.050(3), c = 13.846(2) Å; Z = 18, ρ_{calc} = 2.09 g cm^{-3}. Bond lengths in the slightly distorted octahedric anion $[Pt(NH_3)Cl_5]^-$ are: Pt–N 2.065(10); Pt–Cl$_{cis}$ 2.331(3), 2.314(3), 2.327(3), 2.316(3); Pt–Cl$_{trans}$ 2.313(3) Å.

Introduction

The electrophilic behavior of organonitriles molecules is known to be strengthened due to their coordination to metal ions [1–3]. It accounts for higher bias toward the interaction with nucleophilic reagents. Therefore, hydrolysis of the coordinated RCN molecules proceeds fairly easy as compared to that of the same molecules in the free state. As repeatedly mentioned earlier, the interaction of organonitrilic complexes of different types with water results in the formation of carboxamides. It has been established that in Pt(IV) complexes, the hydrolysis process of organonitriles proceeds deeper with the formation of ammonia-containing complexes and acetic acid. The main purpose of this paper is to the study of the interaction between the complexes $[Pt(dmso)LCl_4]$ (L = MeCN, PhCN, $MeCONH_2$, $PhCONH_2$) and water.

Experimental

Materials and Apparatus

The *cis*-$[Pt(dmso)(MeCN)Cl_2]$ and $[Pt(dmso)(\mu\text{-}Cl)Cl]_2$ complexes were prepared by the methods described in refs. 4 and 5. Infrared spectra were recorded using a Perkin-Elmer model 983G spectrophotometer in pellets with potassium bromide. ^{1}H NMR spectra were recorded using Bruker model WP-80 (80.13 MHz) and Tesla model BS 497 (100 MHz) instruments. Molar conductivity was measured on an Impuls model KL2 conductometer at 20 °C with concentration of the complexes to $\sim 10^{-3}$ mol/l. Melting points were measured using Kofler tables. Elemental analysis was performed by the Chair of Analytical Chemistry at the Leningrad State University.

The identification of the products of hydrolysis of the complexes used was carried on a gas chromatograph–mass spectrometer model LKB-2091. A total of 1–2 microliters of the liquid phase was injected on a fiber glass layer in the initial part of the GC column at 160 °C (2 m × 2 mm with 3% OV-225 on chromatone N 0.16–0.20 mm) followed by separation at a temperature programmed between 50 and 200 °C (5 deg/min). The flow rate of the carrier gas (helium) was 20 ml/min. For the best detection of components overlapping with water

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(ionization energy 13.6 eV) the scanning energy for the chromatogram was chosen equal to 12 eV. Mass spectra were recorded at an ionization energy of 70 eV, an emission current of 25 mkA, and an acceleration voltage of 3.5 kV.

X-ray Structure Analysis

Experimental X-ray data were obtained on a Nicolet P3 diffractometer (λMo, Nb filter, $\theta/2\theta$ scanning to $2\theta_{max}$ = 45°) from a monocrystal (0.12 × 0.12 × 0.50 mm). X-ray absorption correction was made on the sample (μ = 96.0 cm^{-1}). The structure was solved using the heavy atom method and refined anisotropically to R = 0.034. Hydrogen atom coordinates in the ammonia molecule have not been localized. Crystals are rhombohedric, a = 25.050(3), c = 13.846(2) Å, ρ_{calc} 2.09 g cm^{-3}, space group $R\bar{3}$, Z = 18. Non-hydrogen atom coordinates, bond lengths and angles are shown respectively in Tables 1 and 2.

Preparation of the Complexes

cis-Dichloro(dimethyl sulfoxide)(benzonitrile)-platinum(II)

To a solution of K_2PtCl_4 (3.00 g, 7.23 mmol) in water (50 ml) was added dmso (0.54 ml, 7.60 mmol), and the mixture was kept at 15 °C for 12 h. Then a small amount of *cis*-$[Pt(dmso)_2Cl_2]$ was removed from the mixture by filtration, and benzonitrile (0.78 ml, 7.60 mmol) was added to the filtrate. After 24 h, needles began to be released from the solution, they were collected on a filter over seven days, washed with water (3 × 5 ml) and acetone (2 × 2 ml), and dried in air at 20 °C. Yield of *cis*-$[Pt(dmso)(PhCN)Cl_2]$ = 1.43 g, 44% based on Pt.

TABLE 1. Atomic parameters (×10^4) and temperature factors (Å^2 × 10^3)

Atom	*x*	*y*	*z*	*U*
Pt	4810(1)	1912(1)	55(1)	27(1)
Cl(1)	4253(1)	1766(1)	−1361(2)	40(1)
Cl(2)	4023(1)	1854(1)	1004(2)	42(1)
Cl(3)	5420(1)	2079(1)	1404(2)	43(1)
Cl(4)	5231(1)	2973(1)	−129(2)	43(1)
Cl(5)	4422(1)	861(1)	191(2)	41(1)
N(1)	5524(4)	1958(4)	−754(6)	46(4)
N(2)	7802(4)	350(3)	9127(6)	33(4)
C(1)	8425(4)	487(4)	9518(8)	39(5)
C(2)	8620(5)	20(5)	9268(9)	53(6)
C(3)	7795(5)	326(5)	8032(7)	40(5)
C(4)	8259(7)	919(7)	7550(11)	66(8)
C(5)	7292(5)	−285(5)	9462(8)	40(5)
C(6)	7234(6)	−372(7)	10546(9)	51(6)
C(7)	7697(5)	858(5)	9490(7)	43(5)
C(8)	7087(5)	797(5)	9179(8)	49(6)
N(3)	6667	3333	248(15)	89(8)

TABLE 2. Bond lengths (Å) and bond angles (°) for $(Et_4N)[Pt(NH_3)Cl_5]\cdot\frac{1}{6}NH_4Cl$

Bond lengths			
Pt–Cl(1)	2.327(3)	Pt–Cl(2)	2.313(3)
Pt–Cl(3)	2.316(3)	Pt–Cl(4)	2.331(3)
Pt–Cl(5)	2.314(3)	Pt–N(1)	2.065(10)
N(2)–C(1)	1.522(14)	N(2)–C(3)	1.517(13)
N(2)–C(5)	1.531(11)	N(2)–C(7)	1.507(17)
C(1)–C(2)	1.516(20)	C(3)–C(4)	1.508(17)
C(5)–C(6)	1.514(16)	C(7)–C(8)	1.522(20)
Bond angles			
Cl(1)–Pt–Cl(2)	92.5(1)	Cl(1)–Pt–Cl(3)	176.4(1)
Cl(2)–Pt–Cl(3)	91.0(1)	Cl(1)–Pt–Cl(4)	88.9(1)
Cl(2)–Pt–Cl(4)	91.1(1)	Cl(3)–Pt–Cl(4)	90.1(1)
Cl(1)–Pt–Cl(5)	90.7(1)	Cl(2)–Pt–Cl(5)	91.3(1)
Cl(3)–Pt–Cl(5)	90.2(1)	Cl(4)–Pt–Cl(5)	177.6(1)
Cl(1)–Pt–N(1)	89.3(3)	Cl(2)–Pt–N(1)	178.2(3)
Cl(3)–Pt–N(1)	87.2(3)	Cl(4)–Pt–N(1)	89.6(3)
Cl(5)–Pt–N(1)	88.1(3)	C(1)–N(2)–C(3)	110.8(8)
C(1)–N(2)–C(5)	110.8(9)	C(3)–N(2)–C(5)	106.0(7)
C(1)–N(2)–C(7)	106.4(7)	C(3)–N(2)–C(7)	111.3(9)
C(5)–N(2)–C(7)	111.6(8)	N(2)–C(1)–C(2)	115.7(8)
N(2)–C(3)–C(4)	114.6(8)	N(2)–C(5)–C(6)	114.9(8)
N(2)–C(7)–C(8)	114.3(8)		

trans-Dichloro(dimethyl sulfoxide)(acetamide)-platinum(II)

Acetone (50 ml) was added to a mixture of $[Pt(dmso)(\mu\text{-}Cl)Cl]_2$ (3.95 g, 5.70 mmol) and acetamide (0.70 g, 11.80 mmol); the mixture was stirred and heated to 40 °C; after a complete homogenization, the solvent was removed *in vacuo*, the resulting precipitate was washed with toluene (20 ml) in flask. The material was collected and washed with ether (2 × 5 ml), then dried in air at 20 °C. Yield of *trans*-$[Pt(dmso)(MeCONH_2)Cl_2]$ = 3.95 g, 85% based on Pt.

trans-$[Pt(dmso)(PhCONH_2)Cl_2]$

This complex was prepared similarly to *trans*-$[Pt(dmso)(MeCONH_2)Cl_2]$, but nitromethane was used instead of acetone. This compound has not been released in the solid state. The interaction between the *trans*-$[Pt(dmso)(PhCONH_2)Cl_2]$ obtained *in situ* and Cl_2 in a mixture of $MeNO_2$ with toluene results in solid *trans*-$[Pt(dmso)(PhCONH_2)Cl_4]$.

$[Pt(dmso)LCl_4]$ *(L = MeCN, PhCN, MeCONH$_2$, PhCONH$_2$)*

The compounds were synthesized on oxidation of $[Pt(dmso)LCl_2]$ by Cl_2 in acetonitrile (L = MeCN), chloroform (L = PhCN, $MeCONH_2$), and in a mixture of toluene and nitromethane (L = $PhCONH_2$).

Results and Discussion

Oxidation of the earlier [4] prepared *cis*-[Pt(dmso)(MeCN)Cl_2] by Cl_2 in MeCN resulted in the formation of the *cis*-[Pt(dmso)(MeCN)Cl_4] complex. This material, like all other products of synthesis, was characterized by elemental analysis (Table 3), melting points, ^1H NMR (Table 4), and IR spectra (Table 5).

The ^1H NMR spectrum of the fresh prepared solution of the complex *cis*-[Pt(dmso)(MeCN)Cl_4] in acetonitrile-d_3 consists of two signal groups: 3.76 ppm (J_{PtH} 17.8 Hz) and 2.71 ppm (J_{PtH} 10.8 Hz) from dmso and MeCN molecules, respectively [6–8].

TABLE 3. Elemental analyses

Compound (no.)	Found (%)		Brutto-formula	Calculated (%)	
	Cl	Pt		Cl	Pt
cis-[Pt(dmso)(MeCN)Cl_2] (1)	18.1[a] 18.6[b]	50.8[a] 50.5[b]	$C_4H_9Cl_2NOPtS$	18.41	50.65
cis-[Pt(dmso)(MeCN)Cl_4] (2)	30.9	43.1	$C_4H_9Cl_4NOPtS$	31.09	42.78
trans-[Pt(dmso)(NH_2COMe)Cl_2] (3)	17.5	48.3	$C_4H_{11}Cl_2NO_2PtS$	17.58	48.39
trans-[Pt(dmso)(NH_2COMe)Cl_4] (4)	29.8	41.1	$C_4H_{11}Cl_4NO_2PtS$	29.91	41.15
[Pt(dmso)(NH_3)Cl_4] (5)	32.6[c]	45.3[c]	$C_2H_9Cl_4NOPtS$	32.82	45.15
cis-[Pt(dmso)(PhCN)Cl_2] (6)	16.0[d] 16.2[e]	43.5[d] 43.1[e]	$C_9H_{11}Cl_2NOPtS$	15.85	43.62
[Pt(dmso)(PhCN)Cl_4] (7)	27.6	37.7	$C_9H_{11}Cl_4NOPt$	27.37	37.65
[Pt(dmso)($PhCONH_2$)Cl_4] (8)	26.7	36.7	$C_9H_{13}Cl_4NO_2PtS$	26.45	36.39
(Et_4N)[Pt(NH_3)Cl_5]$\cdot\frac{1}{6}NH_4Cl$ (9)	33.9[f]	37.2[f]	$C_8H_{23}Cl_5N_2Pt\cdot\frac{1}{6}NH_4Cl$	34.65	36.91
(Et_4N)[Pt(dmso)Cl_5] (**10**)	30.2	33.5	$C_{10}H_{26}Cl_5NOPtS$	30.52	33.60
$(Et_4N)_2[PtCl_6]$ (11)	31.9[g]	28.7[g]	$C_{16}H_{10}Cl_6N_2Pt$	31.83	29.19

Elemental analyses for the complexes obtained by interaction of: [a]K[Pt(dmso)Cl_3] with acetonitrile in water. [b]*cis*-[Pt(dmso)(MeCN)Cl_4] with water. [c][Pt(dmso)(NH_2COMe)Cl_4] with water. [d]K[Pt(dmso)Cl_3] with benzonitrile in water. [e][Pt(dmso)(PhCN)Cl_4] with water. [f]Found: C, 18.59, 18.68; H, 3.89, 4.20; N, 5.35, 5.19. Calc. for $C_8H_{23}Cl_5N_2Pt\cdot\frac{1}{6}NH_4Cl$: C, 18.18; H, 4.51; N, 5.74%. [g]Found: C, 30.49, 30.31; H, 5.21, 6.01; N, 3.88, 4.14. Calc. for $C_{16}H_{40}Cl_6N_2Pt$: C, 28.75; H, 6.03; N, 4.19%.

TABLE 4. Physicochemical parameters for the identified complexes

Compound	Melting point (°C)	Color	^1H NMR spectrum		
			δ (ppm)	J_{PtH} (Hz)	Solvent/internal standard
1	[a]	light yellow	3.41 (SCH_3)	22.8	acetonitrile-d_3/TMS
			2.45 (CCH_3)	14.3	
			3.49 (SCH_3)	22.5	acetone-d_6/TMS
			2.68 (CCH_3)	14.2	
2	138–141	bright yellow	3.76 (SCH_3)	17.8	acetonitrile-d_3/TMS
			2.71 (CCH_3)	10.8	
3	119–123	pale yellow	3.46 (SCH_3)	24.5	DMF-d_7/HMDS
			1.81 (CCH_3)		
4	146–148	bright yellow	3.89 (SCH_3)	17.5	DMF-d_7/HMDS
			1.78 (CCH_3)		
trans-5	192	bright yellow	3.65	12.5	DMF-d_7/HMDS
cis-5	205	bright yellow	3.77	15.5	DMF-d_7/HMDS
6	183–186	light yellow	3.58	23.0	DMF-d_7/HMDS
7	146	bright yellow	3.71	14.0	DMF-d_7/HMDS
8	145–148	bright yellow	3.65	12.5	DMF-d_7/HMDS
9[b]	248–270	orange			
10[c]	236	orange yellow	3.58	13.5	acetone-d_6/TMS

[a]This complex has no pronounced melting temperature. At 145 °C the acetonitrile molecule is abstracted and the complex [Pt(dmso)(μ-Cl)Cl]$_2$ is formed. [b]Molar conductivity is 90 ohm^{-1} cm^2 mol^{-1} in nitromethane. [c]Molar conductivity is 140 ohm^{-1} cm^2 mol^{-1} in acetonitrile.

TABLE 5. Infrared spectra

Compound	Some bands in the IR spectrum (cm^{-1})
1	2339m and 2312mw (ν_{CN}), 1147vs (ν_{SO}), 439m (ν_{PtS}), 375m (γ_{CSO}), 359s and 336s (ν_{PtCl})
2	2252w (ν_{CN}), 1159vs (ν_{SO}), 428m (ν_{PtS}), 374m (γ_{CSO}), 343s and 317s (ν_{PtCl})
3	1662vs (ν_{CO}), 1114vs (ν_{SO}), 443m (ν_{PtS}), 380m (γ_{CSO}), 334s (ν_{PtCl})
4	1664vs (ν_{CO}), 1161vs (ν_{SO}), 428m (ν_{PtS}), 375m (γ_{CSO}), 343s (ν_{PtCl})
trans-5	3290m and 3252m (ν_{NH}), 1156vs (ν_{SO}), 432m (ν_{PtS}), 388m (γ_{CSO}), 351s (ν_{PtCl})
cis-5	3265m and 3179m (ν_{NH}), 1154vs (ν_{SO}), 430m (ν_{PtS}), 374m (γ_{CSO}), 349s and 318s (ν_{PtCl})
6	2292m and 2242vw (ν_{CN}), 1145vs (ν_{SO}), 439m (ν_{PtS}), 377m (γ_{CSO}), 323s (ν_{PtCl})
7	2299w and 2227m (ν_{CN}), 1167vs (ν_{SO}), 429m (ν_{PtS}), 375m (γ_{CSO}), 344s and 316ms (ν_{PtCl})
8	1659vs (ν_{CO}), 1173s and 1159vs (ν_{SO}), 429m (ν_{PtS}), 376m (γ_{CSO}), 354s and 314m (ν_{PtCl})
9	3300w, 3260w, 3188m (ν_{NH}) (in complex $(Et_4N)[Pt(ND_3)Cl_5]$ 2466w, 2324m, 2270w (ν_{ND})), 1563m (δ_{NH}), 336s (ν_{PtCl})
10	1172vs (ν_{SO}), 429m (ν_{PtS}), 374m (γ_{CSO}), 340s and 320s (ν_{PtCl})
11	327vs (ν_{PtCl})

Just after dissolution, the intensity of peaks from the coordinated acetonitrile molecule decreases to complete disappearance in 10–15 min after dissolution. At the same time, the signal at 1.97 ppm due to a free acetonitrile molecule appears and increases. These phenomena may be attributed to a fairly easy exchange of nitrile ligands

$$[Pt(dmso)(MeCN)Cl_4] + CD_3CN \rightleftharpoons [Pt(dmso)(CD_3CN)Cl_4] + MeCN$$

A much slower reaction, as compared to that of ligand exchange is *cis–trans* conversion of the complex $[Pt(dmso)(CD_3CN)Cl_4]$. The reaction proceeds within 1.5–2 h at 20 °C. The complex *trans*-$[Pt(dmso)(CD_3CN)Cl_4]$ differs from the *cis* form in ^1H NMR* spectra and in TLC on a Silufol UV 254**.

It was established that when the complex *cis*-$[Pt(dmso)(MeCN)Cl_4]$ is kept in undried acetonitrile the complexes *cis*- and *trans*-$[Pt(dmso)(NH_3)Cl_4]$ and acetic acid appear in the mixture apart from the ligand exchange reaction and *cis–trans* rearrangement. The authors believe that the formation of the above material may be attributed to the hydrolysis of acetonitrile intraspheric molecules.

Synthesis of ammonia-containing complexes resulting from interaction of an acetonitrile derivative of platinum(IV) with water was obtained experimentally using preparative amounts of the complex $[Pt(dmso)(MeCN)Cl_4]$. This compound was put in a solid state into a desiccator filled with water vapor at 20 °C. In several days, the material 'ran' and an orange syrup-like mass with a strong smell of acetic acid was formed. After 14 days, the mixture was washed with water and the undissolved part was filtered (mixture of 'A' products). Tetraethylammonium chloride was added to the filtrate and this aqueous solution was evaporated via boiling till the solid began to crystallize. After cooling, the precipitate was filtered and the evaporation–cooling–filtration procedure was repeated twice. As a result three compounds were prepared, each of them was then recrystallized from hot water.

The chemical and physicochemical analysis of the products of the interaction of the complex *cis*-$[Pt(dmso)(MeCN)Cl_4]$ with water (see Tables 3–5) shows that the mixture of 'A' products contains the complexes *cis*-$[Pt(dmso)(MeCN)Cl_2]$ (about 30% based on Pt) and *cis*- and *trans*-$[Pt(dmso)(NH_3)Cl_4]$ (about 3–5%). Precipitates subsequently prepared from the filtrate provide the complexes $(Et_4N)[Pt(dmso)Cl_5]$ (~20%), $(Et_4N)_2[PtCl_6]$ (~10%), and $(Et_4N)[Pt(NH_3)Cl_5]\cdot\frac{1}{6}NH_4Cl$ (~10%).

The chromato-mass-spectrometric study of products of the interaction of the complex *cis*-$[Pt(dmso)(MeCN)Cl_4]$ with water allowed us to find apart from acetonitrile also products of its conversion: CH_3CO_2H, CH_3CONH_2 and $ClCH_2CONH_2$. The mixture contains also $(CH_3)_2SO_2$ and trace amounts of CH_3Cl, CH_2Cl_2, SO_2 and CO_2. The identification of the above materials was carried out by a comparison of their statistically treated mass spectra (based on results of multiple scannings) with the literature data [9]. Chloroacetamid has not been earlier characterized by its mass spectrum and we identified it using a set of fragment ions (Table 6).

Such an easy procedure and complete hydrolysis of the coordinated acetonitrile was quite a surprise. Therefore, to make the results more valid and to better substantiate the conclusions the complex $(Et_4N)[Pt(NH_3)Cl_5]\cdot\frac{1}{6}NH_4Cl$ resulting from the interaction of the complex *cis*-$[Pt(dmso)(MeCN)Cl_4]$ with water and $(Et_4N)Cl$ was subject to X-ray structure analysis.

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*The compound *trans*-$[Pt(dmso)(CD_3CN)Cl_4]$ in the ^1H NMR spectrum recorded in CD_3CN is marked by signals at 3.67 ppm (J_{PtH} 14.6 Hz).

**R_f = 0.68 and R_f = 0.43 are respectively for the *trans*-isomer eluted with acetone/chloroform mixture (1:2 in volume) and for the *cis*-isomer eluted with the same mixture.

TABLE 6. Main signals in mass spectra due to identified products

Component	m/z (I_{rel} (%))
CH_3CO_2H	60(86)M, 45(100), 43(98)
CH_3CONH_2	59(100)M, 44(96), 43(82), 42(32)
$ClCH_2CONH_2$	95(7), 93(18)M, 51(3), 49(7) $[CH_2Cl]^+$, 44(100) $[CONH_2]^+$, 43(27), 42(12)
$(CH_3)_2SO_2$	96(3), 95(3), 94(60)M, 81(6), 80(2), 79(100)
CH_3Cl	52(34), 50(100)M
SO_2	64(100)M
CO_2	44(100)M

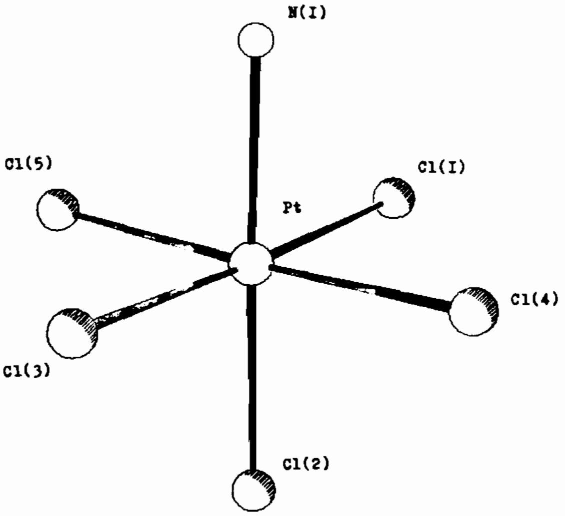

Fig. 1. View of the structure of the $[Pt(NH_3)Cl_5]^-$ ion.

It was observed that the molecule of the complex consists of discrete ions $(Et_4N)^+$ cation and $[Pt(NH_3)Cl_5]^-$ anion (Fig. 1). The coordinated polyhedron of the platinum atom is a slightly distorted octahedron with five Cl atoms and one N atom at the apexes. Valence angles are between 87.2–92.5 and 176.4–178.2°. Atoms Cl(1), Cl(3), Cl(4) and Cl(5) are coplanar within ±0.013 Å and Pt, N(1) and Cl(2) atoms are displaced from this plane by −0.059, 2.005 and −2.372 Å, respectively.

Bond lengths of Pt–N are 2.065(10) Å, i.e. within the estimated standard deviation, it corresponds to the bond length of Pt–N in other Pt(IV) complexes with N-donor ligands [10–17]. Bond lengths of Pt–Cl are inequivalent and fall between 2.313 and 2.331 Å. These interatomic distances correspond to bond lengths of Pt–Cl in different complexes with the $[PtCl_6]^{2-}$ anion (2.31–2.33 Å) [18–20] and also to those of Pt–Cl in the complexes $[PtBipyCl_4]$ (2.306–2.320 Å) [10], *mer*-$[Pt(NH_3)_2Cl_3L]$ (L = pyridone [11], 1-methyluracil [12]) (2.310–2.334 Å), *cis,cis,trans*- and *cis,trans,cis*-$[Pt(NH_3)_2Cl_2(OH)_2]$ (2.314–2.325 Å) [13–16] but slightly higher than in $^+NH_3C_2H_4NH_2PtCl_5$ (2.294–2.306 Å) [17] and *trans,trans,trans*-$[Pt(NH_3)_2Cl_2(OH)_2]$ (2.303 Å) [15].

The crystalline structure of the monoammine Pt(IV) complex is a clathrate (Fig. 2). The packing of the 'host' molecules, the complex $(Et_4N)[Pt(NH_3)Cl_5]$ in the unit cell, is such that hollow 'cylinders' ($\phi \sim 4.1$ Å) are coaxial to the third-order axes. 'Guest' molecules of ammonium chloride (N(3) 'atom') are arranged in them being statistically ordered. This 'guest' compound is also a product of hydrolysis of the complex *cis*-$[Pt(dmso)(MeCN)Cl_4]$.

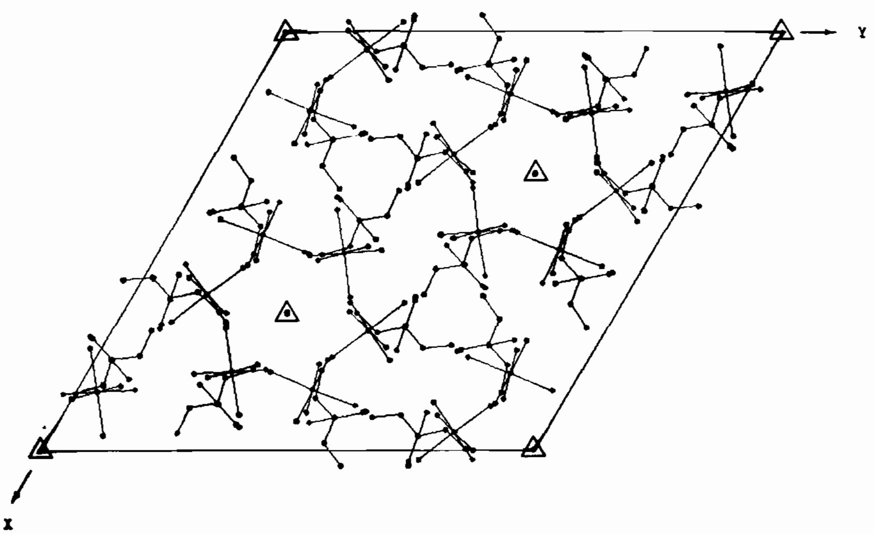

Fig. 2. Unit cell view of $(Et_4N)[Pt(NH_3)Cl_5]\cdot\frac{1}{6}NH_4Cl$.

The occurrence of the remnant electronic density peak of ~1.0 e/Å^3 in the difference synthesis implies the presence of the $NH_4^+Cl^-$ molecule. The N(3) 'atom' does not form any short intermolecular contacts with other atoms.

The interaction of the complex [Pt(dmso)(PhCN)Cl_4] with water was performed under conditions similar to those of the acetonitrile derivative. The authors obtained the same platinum-containing products as in the case of the hydrolysis reaction of the complex [Pt(dmso)(MeCN)Cl_4]. Benzoic acid was prepared in an individual state after its extraction with dichloromethane, removal of solvent *in vacuo* and subsequent sublimation. The identification of $PhCO_2H$ was performed by a comparison of melting points and R_f value on TLC with the same parameters in a commercial benzoic acid.

Thus, experimental data suggest that the reaction of organonitrile platinum(IV) complexes [Pt(dmso)(RCN)Cl_4] with water results in a mixture of products among which ammonia-containing platinum(IV) complexes and RCO_2H acids were observed.

The authors assumed that the formation of complexes with coordinated carboxamides is a transitional stage of hydrolysis. To check this assumption the *trans*-[Pt(dmso)($RCONH_2$)Cl_4] complexes were obtained and their interaction with water was studied. The synthesis of platinum(IV) complexes was performed after the following scheme

$$[\mathrm{Pt(dmso)(MeCN)Cl_2}] \xrightarrow[-\mathrm{MeCN}]{\Delta}$$

$$\tfrac{1}{2}[\mathrm{Pt(dmso)(\mu\text{-}Cl)Cl}]_2 \xrightarrow[\mathrm{MeNO_2}]{\mathrm{RCONH_2}}$$

$$trans\text{-}[\mathrm{Pt(dmso)(RCONH_2)Cl_2}] \xrightarrow{\mathrm{Cl_2}}$$

$$trans\text{-}[\mathrm{Pt(dmso)(RCONH_2)Cl_4}]$$

Hydrolysis of [Pt(dmso)($RCONH_2$)Cl_4] under conditions described for the complex *cis*-[Pt(dmso)(MeCN)Cl_4] proceeds within a matter of days and results in the formation of the complexes *cis*- and *trans*-[Pt(dmso)(NH_3)Cl_4], yield = 40–50%. CH_3CO_2H and small amounts of CH_3CONH_2, $(CH_3)_2SO_2$, CH_3Cl, CH_2Cl_2, and CO_2 were found in the mixture using the GC-MS method.

Conclusions

In the Pt(IV) complexes discussed the hydrolysis of organonitriles and carboxamides proceeds fairly easily to completion and as a result ammonia-containing complexes of platinum and RCO_2H are formed. Apparently, the reactions studied provide the first or at least one of the first examples of a complete hydrolysis of the RCN coordinated molecules. Here we should refer to the work [21] in which the interaction of the complex *cis*-[Pt(MeCN)$_2$$Cl_2$] with Br_2 in a undried ethanol was discussed. It resulted in the preparation of the complex $(NH_4)_2$[$PtBr_6$]. The presence of ammonium ions in this compound [21] is ascribed to the hydrolysis reaction of the acetonitrile molecules in a free state after their substitution by bromide ions.

It is noteworthy that easy hydrolysis of the RCN and $RCONH_2$ ligands may be attributed to a strong electrophilic activation of these molecules by Pt(IV). The complete hydrolysis of the coordinated RCN molecules had not been observed earlier, because only the reactions of complexes with an oxidation state not higher than three had been studied.

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