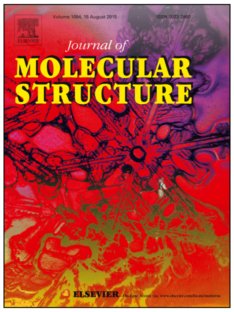

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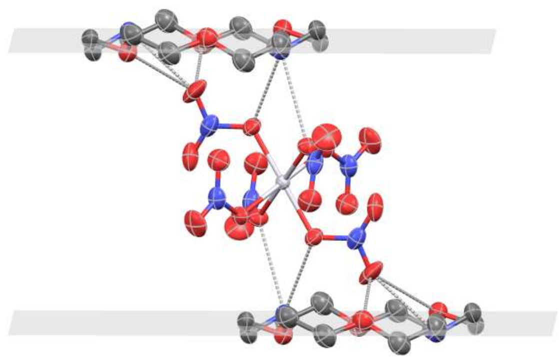

Isolation of Homoleptic Platinum Oxyanionic Complexes with Doubly Protonated Diazacrown Cation.

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Abstract

Doubly protonated diazacrown ether cation (1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane **DC**H_2^{2+}) was used for the efficient isolation of the homoleptic platinum complexes $[Pt(NO_3)_6]^{2-}$ and $[Pt(C_2O_4)_2]^{2-}$ to crystalline solid phases from solutions containing mixtures of related platinum complexes. **DC**H_2^{2+} molecules in nitric acid solution were shown to prevent the condensation of mononuclear $[Pt(H_2O)_n(NO_3)_{6-n}]^{n-2}$ species.

Keywords

Platinum, *O*-ligands, diazacrown, crystal structure, NMR

Introduction

The formation and reactivity of platinum complexes with small oxygen donor ligands (*O*-ligands) are an area of coordination chemistry with a considerable practical value. Complexes of platinum with oxygen donor ligands like nitrate and oxalate represent good thermolabile starting compounds for the preparation of supported catalytic systems based on highly dispersed metallic platinum or its oxide [1,2]. From this point of view, the solution chemistry of such complexes is of significant interest, especially for the elaboration of new techniques for the isolation of the individual complex species.

Multinuclear NMR spectroscopy has been used to demonstrate the variety of chelated and monodentate complexes formed between platinum(II) and oxalate ligands during the reaction of K_2PtCl_4 and oxalic acid [3,4]. In addition, as was reported for the first time by Krogmann and Dode [5], partial oxidation of platinum(II) oxalato complexes occurs in air, resulting in the formation of an interesting series of one-dimensional conductors [6–8]. Platinum nitric acid solutions represent even more complex mixtures of mononuclear and polynuclear species existing in dynamic equilibrium [9,10].

The diversity of possible complex forms that a platinum cation can adopt in a solution containing these ligand molecules ($C_2O_4^-$, NO_3^-, H_2O and OH^-) has a hampering effect on the detailed study of such systems and the isolation of individual metal complexes in the solid phase. Molecular recognition technology, based on supramolecular interactions, is of use in the industrial practices of the separation and selective isolation of platinum-group metals by the ion-exchange technique. For example, the SuperLig@ family of ion-exchange resins, based on macrocyclic ligands anchored to a silica gel support, is used for the selective removal of platinum, palladium and rhodium from solutions [11]. On the other hand, the selective isolation of metal complexes is also possible by the electrostatic interaction of metal complexes with a cation of appropriate size.

In this work we used doubly protonated diazacrown ether dication (1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane – **DC**H_2^{2+}) for the efficient isolation of the homoleptic platinum complexes $[Pt(NO_3)_6]^{2-}$ and $[Pt(C_2O_4)_2]^{2-}$ from solutions containing mixtures of related platinum complexes. The combination of positive charge, structural flexibility and the presence of H-bond donor groups (NH_2^+) provides **DC**H_2^{2+} molecules the ability to form complementary pairs with the mentioned platinum oxyanionic complexes.

Experimental materials

1. Starting reagents and physical measurements

All the reactants were purchased from commercial suppliers and used as received. $[Pt(H_2O)_2(OH)_4]$ was prepared from hexachloroplatinic acid ("The Gulidov Krasnoyarsk Non-Ferrous Metals Plant" Open Joint Stock Company, 39.1% of platinum) as described previously [12]. Nitrate salt **DC**$H_2(NO_3)_2$ was precipitated from ethanol solution of **DC** (Alfa Aesar, 96%) by an excess of concentrated nitric acid, filtered off and dried in air stream.

^{195}Pt NMR spectra were recorded at 107.5 MHz using an Avance III 500 Bruker spectrometer with a 5 mm broad-band probe. A 90° excitation pulse of 15 µs was applied. All spectra were recorded at 24℃. δ^{195}Pt (ppm) values are reported relative to the external reference – a 2 M solution of $H_2[PtCl_6]$ in 1 M hydrochloric acid. The usual spectral window of 67 kHz (620 ppm) was used with an acquisition time of 0.1 s and pulse delay of 0.7 s to allow the ^{195}Pt nuclei to relax completely. A line-broadening factor of 1 Hz was applied in the processing of all experimental FID data.

X-ray powder diffraction analysis of the polycrystalline samples was carried out on a DRON-RM4 diffractometer (Cu Kα radiation, graphite monochromator in the reflected beam, scintillation detector with amplitude discrimination). The samples were prepared by deposition of a suspension in hexane on the polished side of a cell made of fused quartz. A sample of polycrystalline silicon (a = 5.4309 Å), prepared similarly, was used as an external standard.

Raman scattering spectra were measured on a Triplemate SPEX spectrometer with CCD camera and microscope for the detection of the backscattering spectra with excitation by a 488 nm laser line.

The simultaneous TG–DSC/EGA–MS measurement was performed in an apparatus consisting of an STA 449 F1 Jupiter thermal analyser and a QMS 403D Aëolos quadrupole mass spectrometer (NETZSCH, Germany). The spectrometer was connected online to a thermal analyser (STA) instrument by a quartz capillary heated to

280℃. The QMS was operated with an electron-impact ionizer with an energy of 70 eV. The ion currents of the selected mass/charge (m/z) numbers were monitored in multiple-ion detection (MID) mode with a collection time of 1 s for each channel. The measurements were made in a helium flow in the temperature range of 30–700℃ using a heating rate of 10℃ min $^{-1}$, a gas flow rate of 30 mL min $^{-1}$ and open Al_2O_3 crucibles. The sample mass was 20 mg. Analysis of the thermal data was performed with Proteus analysis software [13].

2. Preparation of solutions

2.1. Solution NT (nitric acid solution)

A sample of $[Pt(H_2O)_2(OH)_4]$ (150 mg, 0.5 mmol) was dissolved in 1 mL of nitric acid (15.7 M) and allowed to equilibrate for 5 days at room temperature in a dark place.

2.2. Solution NT1 (diluted solution of nitric acid)

A sample of $[Pt(H_2O)_2(OH)_4]$ (30 mg, 0.1 mmol) was dissolved in 1 mL of nitric acid (15.7 M) and the resulting solution was transferred to an NMR tube. The ^{195}Pt NMR spectrum of the solution was recorded immediately after the preparation and then after 7 days, 30 days and 90 days. Between measurements the solution was stored in the NMR tube at room temperature (20 ± 2℃) in a dark place.

2.3. Solution NT2 (diluted solution of nitric acid with addition of DC)

A sample of $[Pt(H_2O)_2(OH)_4]$ (30 mg, 0.1 mmol) and 0.2 mmol of **DC**$H_2(NO_3)_2$ were dissolved in 1 mL of nitric acid (15.7 M). The resulting solution was transferred to an NMR tube and the ^{195}Pt NMR spectrum of the solution was recorded immediately after the preparation and then after 7 days, 30 days and 90 days. Between measurements the solution was stored in the NMR tube at room temperature (20 ± 2℃) in a dark place.

2.4. Solution OX (oxalic acid solution)

A sample of $[Pt(H_2O)_2(OH)_4]$ (150 mg, 0.5 mmol) was boiled in 10 mL of oxalic acid water solution until fully dissolved, and the volume was reduced to 5 mL. The resulting solution was allowed to equilibrate in a closed container for 5 days at room temperature in a dark place.

3. Isolation of solid phases

3.1. $(DCH_2)[Pt(NO_3)_6]$ (1)

Solid diazacrown was added to Solution **NT**. This mixture was allowed to stand in a desiccator under solid KOH at room temperature. After 5 days yellow prisms were filtered out, washed with a minimal volume of 15.8 M HNO_3 and acetone, and dried in an air stream. Yield: 65%. Analysis calculated (found) for $C_{12}H_{28}N_8O_{22}Pt$: C, 17.33 (17.3); H, 3.39 (3.4); N, 13.48 (13.6). Single crystals for X-ray analysis were collected from the mother liquor.

3.2. $(DCH_2)[Pt(C_2O_4)_2]$ (2)

Solid diazacrown was introduced into Solution **OX**, resulting in the deposition of a fine pale orange precipitate, which was filtered out, washed with water, ethanol and ether and then dried in a stream of air. Yield: 70%. Analysis calculated (found) for $C_{16}H_{28}N_2O_{12}Pt$: C, 30.24 (30.1); H, 4.44 (4.4); N, 4.41 (4.2). Single crystals for X-ray analysis were obtained by recrystallization of the product from hot water.

The powder diffraction patterns of polycrystalline powders of compounds **1** and **2** were completely indexed using single-crystal data; no additional reflections were revealed.

4. X-ray crystallographic data collection and refinement

Crystal data and experimental details for **1** and **2** are given in **Table 1S**. Experimental data for the determination of the crystal structure of **1** were collected on a Bruker APEX-II CCD diffractometer at 240 K using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). Experimental data for the determination of the crystal structure of **2** were collected on a Bruker-Nonius X8 APEX CCD diffractometer at 296 K using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). All calculations were carried out with the SHELX-97 crystallographic software package [18]. The structure was solved by the standard heavy-atom method and refined by the anisotropic approximation. The H atoms were refined in their geometrically calculated positions; a riding model was used for this purpose. Absorption corrections were applied empirically using the SADABS software [14].

CCDC 1491951 (**1**) and 1491954 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Solutions containing mixtures of nitrato or oxalato complexes of platinum were obtained from $[Pt(H_2O)_2(OH)_4]$ (often referred to as $H_2Pt(OH)_6$) by interaction with nitric or oxalic acid, respectively. The resulting solutions (**Solution NT** and **Solution OX**, see Experimental Section for details) were characterized by ^{195}Pt NMR spectroscopy to describe the platinum speciation. As is clearly seen from the spectra (Figures 1 and 2), platinum was distributed in these solutions over several complex forms. The nitric acid solution (**Solution NT**) contained a mixture of mononuclear species $[Pt(H_2O)_n(NO_3)_{6-n}]^{n-2}$, including the $[Pt(NO_3)_6]^{2-}$ anion, whose signals were located in the range 3500–3950 ppm, and polynuclear hydroxo-bridged nitrato complexes of platinum(IV) with resonance lines in a weaker field range [9,10].

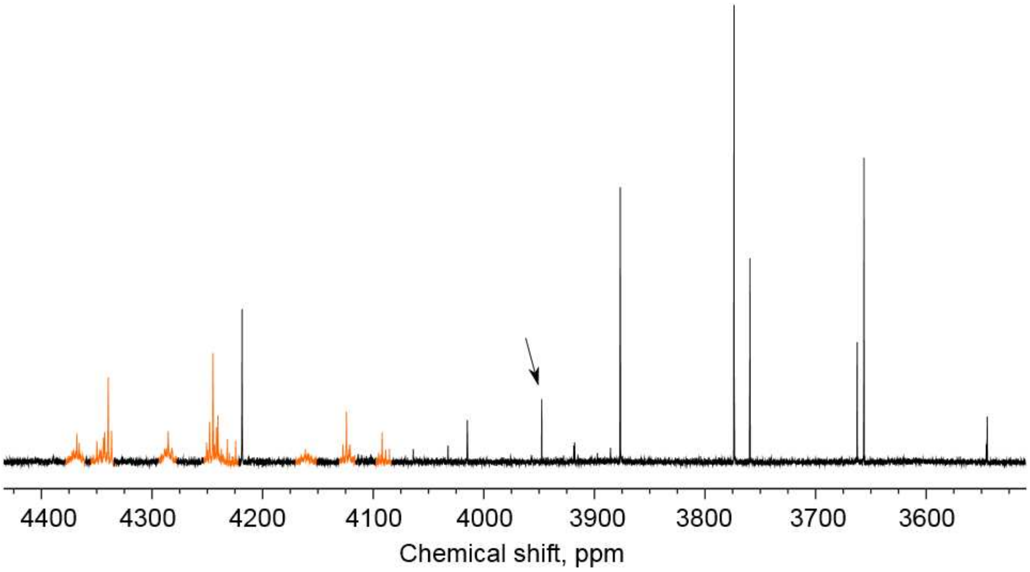

Figure 1. NMR spectrum of $[Pt(H_2O)_2(OH)_4]$ solution in nitric acid (**Solution NT**). Signals of polynuclear (tetranuclear) species are marked with an orange colour. The $[Pt(NO_3)_6]^{2-}$ signal is pointed out with an arrow.

The oxalic acid solution of $[Pt(H_2O)_2(OH)_4]$ (**Solution OX**) comprised both Pt(IV) and Pt(II) complexes due to the reduction of tetravalent platinum by oxalate ions. The signal in the high-field range of the ^{195}Pt NMR spectrum of this solution (-540 ppm) corresponds to the $[Pt(C_2O_4)_2]^{2-}$ anion (with a fraction of about 50%), while the two signals around 2600–2900 ppm are resonances of the $[Pt(H_2O)_2(C_2O_4)_2]$ and $[Pt(H_2O)_4(C_2O_4)]^{2+}$ species [3,4]. Prolonged standing of **Solution OX** resulted in a deepening of its blue colour, which originates from the formation of polynuclear Pt(II)/Pt(IV) clusters with an intense charge transfer [15].

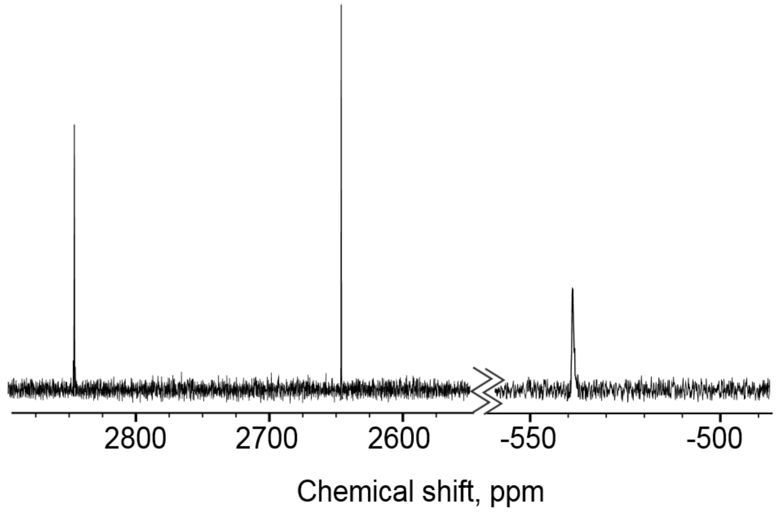

Figure 2. NMR spectrum of $[Pt(H_2O)_2(OH)_4]$ solution in oxalic acid (**Solution B**).

Since the homoleptic Pt complexes ($[Pt(NO_3)_6]^{2-}$ in **Solution NT** and $[Pt(C_2O_4)_2]^{2-}$ in **Solution OX**) were not the only form of platinum in the given solutions (their mole fractions were about 5% and 50%, respectively), attempts to crystallize these species in the form of solid salts by evaporation with alkali metal salts were unsuccessful. It has been reported that protonated diazacrown (**DC**H_2^{2+}) appeared to be a suitable cation to isolate anionic aquafluorocomplexes of germanium [16]. We adopt this approach to crystallize the platinum complexes from **Solution NT** and **OX** and have founded that **DC**H_2^{2+} selectively isolates homoleptic complexes ($[Pt(NO_3)_6]^{2-}$ and $[Pt(C_2O_4)_2]^{2-}$ correspondingly) from such multispecies solutions.

Slow concentration of **Solution NT** (evaporation at room temperature) with the addition of diazacrown (**DC**) yielded yellow crystals of **1**. This compound was sparingly soluble in concentrated nitric acid, with the formation of the mononuclear aquanitrato Pt(IV) species, while in water it slowly decomposed to form hydrated platinum oxide ($PtO_2 \cdot 3H_2O$). The thermal decomposition of the complex **1** in inert atmosphere proceeded at about 150℃ as a one-stage process and resulted in the formation of metallic platinum with an admixture of amorphous carbon. The gaseous products escaping in this process were determined by mass spectrometry as CO, CO_2, N_2 and H_2O (Figure 1S).

The compound **1** crystallizes in monoclinic $P2_1/n$ space group. The asymmetric unit cell of **1** consists of one half of the protonated diazacrown molecule and half of the hexanitratoplatinate(IV) anion. The oxygen atoms of the nitrato ligands form a trigonal antiprismatic (D_{3d}) polyhedron around the platinum(IV) cations located on the axes or edges of the unit cell. The geometric characteristics of the PtO_6 polyhedron (see **Table 1** for details) and the mutual orientation of the nitrato groups are almost the same as reported earlier for a different salt of the $[Pt(NO_3)_6]^{2-}$ anion [1,9]. This fact indicates that the unusual trigonal antiprismatic shape of the PtO_6 polyhedron is not a result of packing effects but the stable form of the $[Pt(NO_3)_6]^{2-}$ anion. An analogous geometry was recently reported for the homoleptic nitrato complexes of tin(IV) [17], rhodium(III) [18] and chromium(III) [19] and interpreted (in the former work) as consequence of ligands crowding in coordination spheres. The Raman spectrum taken from solid **1** demonstrates two clearly resolved signals around 350 cm^{-1} corresponding to Pt-O stretching vibrations of the PtO_6 polyhedron also founded in the spectrum of **Solution NT** (Figure 2S). The coordination of the nitrate ion to the platinum centre causes substantial elongation of the N-O bonds by *ca.* 0.14 Å.

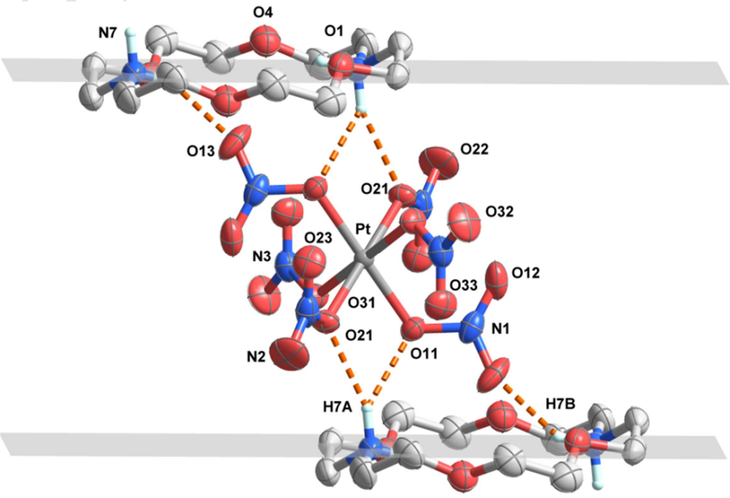

Figure 3. Mutual arrangement of species ($[Pt(NO_3)_6]^{2-}$ anion and two **DC**H_2^{2+} dications) in the crystal structure of **I**. The planes of **DC**H_2^{2+} molecules are marked with grey, H-bonds are shown as broken lines. Hydrogen atoms are omitted for clarity.

The overall packing of ions in the crystal structure of **1** presents columns running along the *a* axis (Figure 3S). These columns are constructed from alternate $[Pt(NO_3)_6]^{2-}$ anions and **DC**H_2^{2+} dications connected through a network of H-bonds. Two of the six NO_3^- ligands of the $[Pt(NO3)_6]^{2-}$ anion are directed to the **DC**H_2^{2+} dications in a column, and the oxygen atoms of these groups form H-bonds with the nitrogen centres of the macrocyclic cation. The remaining four NO_3^- ligands are oriented to the neighbouring columns and only weakly interact with the cationic species. The **DC**H_2^{2+} dications adopt a planar conformation, with distances between planes in the columnar structures **DC**H_2^{2+}–$[Pt(NO_3)_6]^{2-}$–**DC**H_2^{2+} of about 10 Å (Figure 3).

Table 1. Selected metal–ligand and intra-ligand bond lengths, metal-centred bond angles and related H-bonds parameters for compound **1**.

Bonds, Å		**Angles, °**	
Pt-O31	2.002(3)	O31^{1}-Pt-O31	180.0(2)
Pt-O11	2.007(5)	O31^{1}-Pt-O11	79.3(1)
Pt-O21	2.013(3)	O31-Pt-O11	100.7(1)
N1-O12	1.211(5)	O11-Pt-O11^{1}	180.0(1)
N1-O13	1.220(5)	O31^{1}-Pt-O21	80.2(1)
N1-O11	1.347(5)	O31-Pt-O21	99.8(1)
N2-O23	1.210(7)	O11-Pt-O21	77.7(2)
N2-O22	1.219(6)	O11^{1}-Pt-O21	102.3(2)
N2-O21	1.326(6)	O21-Pt-O21^{1}	180.0(1)
N3-O32	1.205(6)	N1-O11-Pt	121.4(3)
N3-O33	1.219(5)	N2-O21-Pt	120.7(3)
N3-O31	1.347(5)	N3-O31-Pt	122.3(3)
Hydrogen bonds			
O13…H7B…N7	2.14	0.91	150.7
O21…H7A…N7	2.25	0.91	158.1
O11…H7A…N7	2.36	0.91	135.1

^{1}-X,2-Y,1-Z; ^{2}1-X,2-Y,1-Z

According to the previously reported data [9,10], in a fresh nitric acid solution of $[Pt(H_2O)_2(OH)_4]$ only the mononuclear species $[Pt(H_2O)_n(NO_3)_{6-n}]^{n-2}$ is present. After standing of the solution at room temperature, the condensation of these complexes progressed to form polynuclear species, whose ^{195}Pt NMR signals appear in the low-field range 3900–4500 ppm. Because **DC**H_2^{2+} molecules show a unique complementarity with $[Pt(NO_3)_6]^{2-}$ anions in the solid state, we assumed that an analogous strong interaction of the macrocyclic cation with the anionic species $[Pt(H_2O)_n(NO_3)_{6-n}]^{n-2}$ in the nitric acid solution could prevent the condensation process. To verify this hypothesis, two nitric acid solutions of $H_2Pt(OH)_6$ were prepared: with (**Solution NT2**) and without (**Solution NT1**) the addition of **DC**$H_2(NO_3)_2$ (the nitrate salt was chosen instead of **DC** itself to avoid acidity changes). The solutions' compositions were monitored over the course of 3 months by ^{195}Pt NMR spectroscopy.

Inspecting Figure 4, one can see that the formation of polynuclear complexes was suppressed in **Solution NT2**, where diazacrown was added, in comparison with the intensive polycondensation process in **Solution NT1**. It should be noted that no solid **1** was formed during the standing of **Solution NT2** and evaporation was required up to [Pt] ≈ 1 M before **1** began to crystallize.

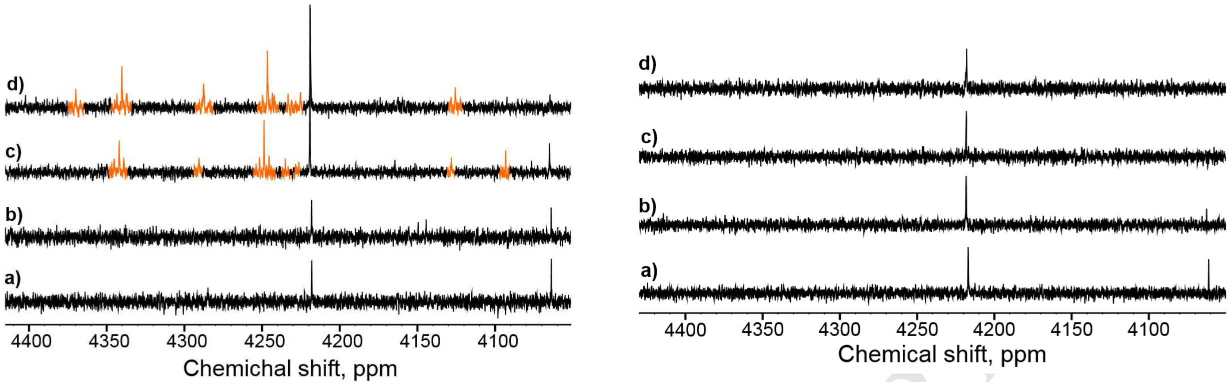

Figure 4 Evolution of ^{195}Pt NMR spectra obtained for nitric acid solution of $[Pt(H_2O)_2(OH)_4]$ with (Figure 4 right, **Solution NT1**) and without (Figure 4 left, **Solution NT2**) addition of solid diazacrown, [Pt] = 0.1 M for both solutions, [**DC**H_2^{2+}] = 0.2 M. a) – the spectra immediately after preparation of the solutions, b) – after 1 week, c) – after 1 month d) – after 3 months. Signals of polynuclear (tetranuclear) species are marked with an orange colour.

Contrary to an evaporation-induced growth of the crystals of **1** from **Solution NT**, the addition of solid **DC** or its water solution to **Solution OX** immediately deposited the pale yellow solid **DC**$\mathbf{H_2[Pt(C_2O_4)]}$ (**2**). Deposition of **2** prevented the formation of the mentioned polynuclear Pt(II)/Pt(IV) charge-transfer complexes by the Krogmann mechanism [4,15]; thus, the navy colour of the solution disappeared completely upon the addition of **DC**. Recrystallization of **2** was only possible from hot (boiling) water solution because of its low solubility.

Analogously to **1**, column-like cation–anion agglomerates can also be found in the crystal structure of **2** (Figure 5, Figure 4S). The platinum centre in the planar oxalato complex $[Pt(C_2O_4)_2]^{2-}$ is surrounded by four oxygen atoms at about 2 Å (Table 2) and has geometric characteristics similar to those reported previously for this anion [2]. Stretching Pt-O vibrations of this PtO_4 polyhedron are registered in Raman spectrum of solid **2** (Figure 5S) as a band at about 300 cm^{-1}.

The terminal oxygen atoms of the $[Pt(C_2O_4)_2]^{2-}$ anion form a network of H-bonds with the **DC**H_2^{2+} dications, which in this case adopt a chair conformation and envelop the oxalate ligands (Figure 5). The distances between the planes of **DC**H_2^{2+} dications in the column are 11.2 Å – slightly longer than such distances in **1**. The **DC**H_2^{2+} dications and $[Pt(C_2O_4)_2]^{2-}$ connect with each other through the system of H-bonds (2.80–3.00 Å) between the oxygen atoms of the oxalate ligands and the NH_2^+ groups of the macrocycle (Table 2).

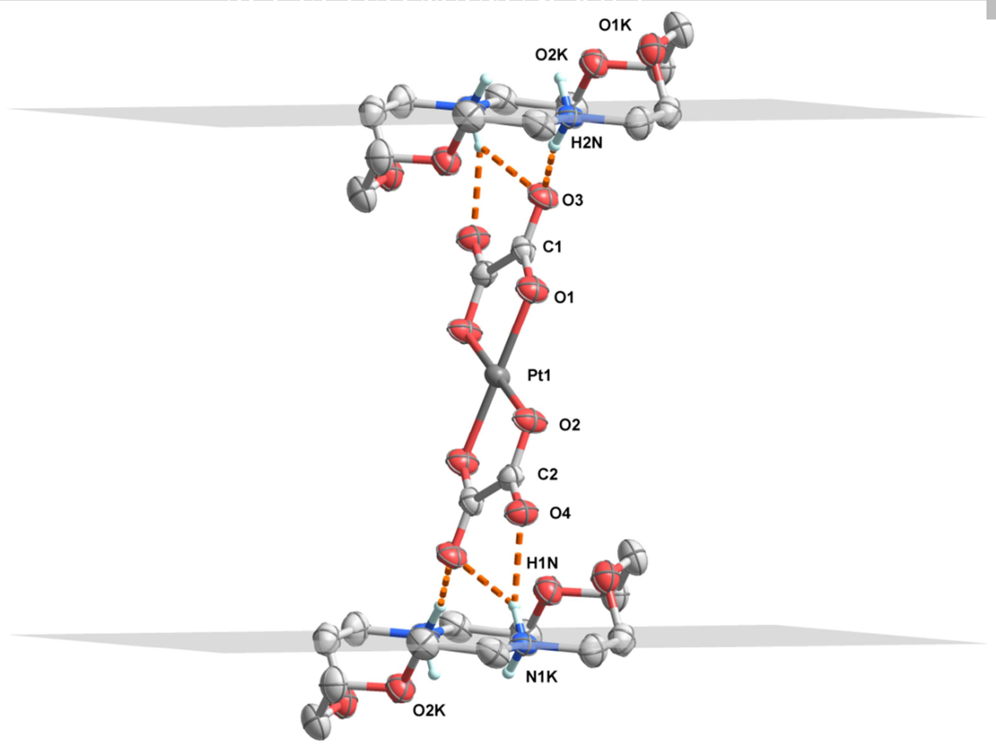

Figure 5. Mutual arrangement of $[Pt(C_2O_4)_2]^{2-}$ anion and two **DC**H_2^{2+} dications in the crystal structure of **II**. The planes of **DC**H_2^{2+} molecules are marked with grey, H-bonds are shown as broken lines. Hydrogen atoms of methylene groups are omitted for clarity.

Table 2. Selected metal–ligand and intra-ligand bond lengths, metal-centred bond angles and related H-bonds parameters for compound **1**.

Bonds, Å		**Angles, °**	
Pt1-O2	2.008(3)	O2-Pt1-O2^2	180.0
Pt1-O2^2	2.008(3)	O2-Pt1-O1^2	97.62(14)
Pt1-O1^2	2.020(4)	O2-Pt1-O1	82.4(1)
Pt1-O1	2.020(4)	O2^2-Pt1-O1	97.6(1)
O1-C1	1.264(6)	O1^2-Pt1-O1	180.0(1)
O2-C2	1.284(6)	C1-O1-Pt1	113.1(3)
O3-C1	1.222(6)	C2-O2-Pt1	113.2(3)
O4-C2	1.205(6)		
C1-C2	1.558(7)		

Hydrogen bonds

O3…H1N…N1K	2.24	0.90	142.5
O4…H1N…N1K	2.09	0.90	136.5
O3…H2N…N1K	1.98	0.90	160.7

^{1}-X,2-Y,-Z; ^{2}1-X,1-Y,1-Z

The powder of **2** was stable on heating in an inert atmosphere up to 250℃, upon which it decomposed in one stage to give the gaseous products CO, CO_2, H_2O and N_2 (Figure 6S) and metallic platinum (with an admixture of amorphous carbon). It should be noted that thermal decomposition of both **1** and **2** in a hydrogen stream yielded pure metallic platinum without a carbon admixture.

Conclusions

Homoleptic anionic complexes of platinum $[Pt(C_2O_4)_2]^{2-}$ and $[Pt(NO_3)_6]^{2-}$ were selectively isolated from solutions containing complicated mixtures of related complexes by using the macrocyclic cation **DC**H_2^{2+}. The structures of the salts and their properties were studied. For the aquanitrato complexes of platinum, **DC**H_2^{2+} was demonstrated to act as an effective suppressor of their polycondensation.

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Protonated diazacrown selectively isolates platinum(IV) homoleptic complexes.

Intensive H-bonding connects the macrocycle and platinum(IV) complexes.

Condensation of platinum nitrato complexes can be suppressed by diazacrown.