Inorganic Chemistry
Article
pubs.acs.org/IC

Polynuclear Hydroxido-Bridged Complexes of Platinum(IV) with Terminal Nitrato Ligands

Danila Vasilchenko,*[†,‡] Semen Berdugin,[‡] Sergey Tkachev,[†] Iraida Baidina,[†] Galina Romanenko,[§] Olga Gerasko,[†] and Sergey Korenev[†,‡]

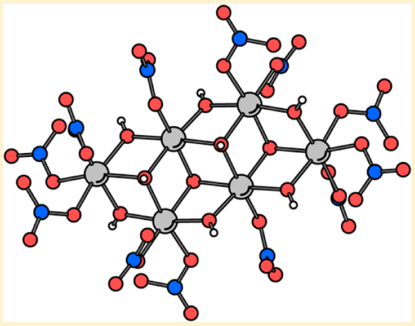
[†]Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Science, 630090 Novosibirsk, Russian Federation

[‡]Novosibirsk State University, 630090 Novosibirsk, Russian Federation

[§]International Tomography Centre, Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation

S *Supporting Information*

ABSTRACT: For the first time the polynuclear hydroxido-bridged platinum(IV) nitrato complexes with nuclearity higher than two were isolated from nitric acid solutions of $[Pt(H_2O)_2(OH)_4]$ and crystallized as supramolecular compounds of macrocyclic cavitands cucurbit[*n*]uril (CB[*n*], *n* = 6,8) and 18-crown-6 ether: $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]\cdot CB[6]\cdot 25H_2O$ (**I**), $[Pt_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_6(NO_3)_{12}](NO_3)_2\cdot CB[8]\cdot 50H_2O$ (**II**), and $[H_3O{\subset}18\text{-crown-6}]_2[Pt_2(\mu_2\text{-}OH)_2(NO_3)_8][Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]$ (**III**). The isolation of the compounds in the single crystalline state allows the determination of the structure of the tetranuclear and hexanuclear complexes $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]$ and $[Pt_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_6(NO_3)_{12}]^{2+}$, which have been previously unknown in the solid state. Stability of $Pt_x(OH)_y$ cores of the polynuclear nitrato complexes toward alkaline hydrolysis was verified by ^{195}Pt NMR spectroscopy. Analysis of ^{195}Pt NMR spectra of the compound **III** reveals that addition of every $Pt(\mu\text{-}OH)_2Pt$ ring results in ~260 ppm downfield shift relative to the mononuclear form, which allows the prediction of signal positions for complexes of higher nuclearity.



INTRODUCTION

Nitric acid solutions of Pt(IV) ("platinum nitrate solution" ≡ PNS) obtained from $[Pt(H_2O)_2(OH)_4]$ are useful precursors for preparation of heterogeneous Pt-containing catalyst by impregnation technique.[1−6] As it was demonstrated earlier mono- and polynuclear nitrato complexes of Pt(IV) are the form of existence of platinum in nitric acid solutions.[7−12] From a practical point of view, such solutions are free from halide and sulfate ions that are important to prevent catalyst corrosion, poisoning, and platinum leaching.[10] On the other hand, mono- and polynuclear nitrato complexes of Pt(IV) in the solutions are suitable precursors for creation of $Pt{-}O_x(OH)_y$ species and are known to be active sites for the low-temperature Pt-catalyzed water gas shift reaction[13−15] and methanol oxidation.[16] Heteropolymetalates containing platinum metals are considered as potential models of active sites in noble-metal-based heterogeneous catalytic oxidation systems.[17,18] Polynuclear structure of the Pt(IV) nitrato complexes supposedly remains even after interaction with the carrier surface and calcination of the catalyst.[10] Unfortunately, the detailed structure and properties of such complexes of platinum in nitric acid solutions were unknown.

In our recent work we explored Pt(IV) speciation in nitric acid by ^{195}Pt NMR and Raman spectroscopy and found a diversity of polynuclear species equilibrating with mononuclear aquahydroxidonitrato complexes.[9] Evaporation of these solutions with addition of organic cation (PyH^+, Me_4N^+) nitrates yields crystalline salts containing $[Pt(NO_3)_6]^{2-}$ and $[Pt_2(\mu\text{-}OH)_2(NO_3)_8]^{2-}$ anions. Species with four and more nuclei were detected by NMR spectroscopy, but all attempts to isolate such molecules in crystalline phase for gathering of direct structural information were unsuccessful.

A survey of the literature reveals several methods for crystallization of polynuclear complexes in similar (acidic) conditions. The supramolecular approach based on a combination of nonvalent interactions (hydrogen bonding, electrostatic, p-stacking, and van der Waals) is one of the most successful methods for crystallization of polynuclear complexes. Self-assembly of the p-sulfonatocalix[4]arene and 18-crown-6 ether, or related macrocycles, gives globular superanions or ionic capsules, which can crystallize, often selectively, the polynuclear hydrolytic metal(III) cations.[19−23]

Earlier, we and others have successfully used organic macrocyclic molecules, cucurbit[*n*]urils, for the isolation of polynuclear aqua complexes of different metals (Zr, Hf, V, Mo, W, U, Al, Ga, and Cr) in the solid phase from aqueous solutions.[24−29] Also, the cucurbit[*n*]uril macrocycles have been shown to form host−guest complexes with platinum-based anticancer drugs such as cisplatin and oxaliplatin.[30,31] The

Received: December 7, 2014
Published: April 24, 2015

DOI: 10.1021/ic502896s

Table 1. Crystal Data and Experimental Details for Compounds I, II, and III

compounds	I		II		III	
stoichiometric formula	$C_{36}H_{92}N_{34}O_{73}Pt_4$		$C_{24}H_{79}N_{24}O_{62}Pt_3$		$C_{24}H_{62}N_{18}O_{76}Pt_6$	
formula weight	2949.79		2281.38		2989.33	
temperature (K)	296(2)		150(2)		296(2)	
wavelength (Å)	0.710 73					
crystal system	triclinic					
space group	$P\bar{1}$		$P\bar{1}$		$P\bar{1}$	
unit cell dimensions (Å, deg)	a = 11.130(2)	α = 66.238(5)	a = 13.1408(7)	α = 70.471(2)	a = 12.303(8)	α = 82.03(2)
	b = 14.730(3)	β = 71.669(5)	b = 14.8737(8)	β = 72.032(2)	b = 12.691(9)	β = 76.28(2)
	c = 15.637(3)	γ = 79.704(5)	c = 17.9670(9)	γ = 88.713(2)	c = 18.188(9)	γ = 81.99(2)
volume ($Å^3$), Z	2223.3(7), 1		3135.5(3), 2		2716(3),1	
absorption coefficient (mm^{-1})	6.419		6.839		7.804	
D_{calc} ($g{\cdot}cm^{-3}$)	2.203		2.416		1.819	
$F(000)$	1442		2242		1394	
θ range for data collection (deg)	1.51–29.88		1.46–30.97		2.27–30.77	
limiting indices	$-15 \le h \le 15$		$-18 \le h \le 18$		$-17 \le h \le 17$	
	$-20 \le k \le 20$		$-21\le k \le 20$		$-18\le k \le 17$	
	$-21 \le l \le 21$		$-24 \le l \le 24$		$-25 \le l \le 14$	
reflections collected	45 421		45 342		26 247	
independent reflections	12 523 [R(int) = 0.0688]		17 177 [R(int) = 0.0416]		16 186 [R(int) = 0.0361]	
completeness (%)	99.7		99.2		97.7	
max. and min transmission	0.740 and 0.513		0.448 and 0.357		0.5360 and 0.1390	
refinement method	full-matrix least-squares on F^2					
data/constraints/parameters	12 523/0/550		17 177/6/829		16 186/72/694	
goodness-of-fit on F^2	0.906		1.101		1.010	
final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0362, $wR2$ = 0.0743		$R1$ = 0.0660, $wR2$ = 0.1914		$R1$ = 0.0570	$wR2$ = 0.1645
R indices (all data)	$R1$ = 0.0668, $wR2$ = 0.0791		$R1$ = 0.1062, $wR2$ = 0.2039		$R1$ = 0.0955	$wR2$ = 0.1824
CCDC No.	1036821		1036820		1037012	

cucurbit[n]uril molecule (CB[n], $C_{6n}H_{6n}N_{4n}O_{2n}$ (n = 5—8)) has a barrel-like shape containing polarized carbonyl groups (portals) in the planes of the lid and the bottom.[32,33] As a rule, the polynuclear species were isolated from aqueous or diluted acidic solutions as supramolecular products where the complexes were linked to CB[n] by hydrogen bonding between their hydroxido and aqua ligands and the portal oxygen atoms of cucurbit[n]urils. The packing of large cucurbit[n]uril molecules also plays the structuring role; the size of the cavities between them allows the encapsulation of polycations. Cucurbit[n]urils of larger size, correspondingly, form the larger cavities, which can encapsulate higher-nuclearity polycations.[26] An increase in acid (HCl) concentration, as was shown for molybdenum and tungsten cluster aqua complexes, leads to the replacement of the aqua ligands (responsible for binding to the CB[n] portals) by the halide ligands, and the packing factor becomes the main building principle for such structures.[24] Rigid structure and chemical stability make cucurbit[n]urils and crown ether molecules very attractive for crystallization of polynuclear complexes in concentrated acidic solutions.

In the present study, we applied the supramolecular approach to the isolation of polynuclear Pt(IV) complexes from concentrated nitric acid solutions with the use of the organic macrocycles cucurbit[n]uril and 18-crown-6. We report the synthesis and structural characterization of three new platinum polynuclear complexes as supramolecular compounds with CB[n] and 18-crown-6: tetranuclear $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]\cdot CB[6]\cdot 25H_2O$ (**I**), hexanuclear $[Pt_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_6(NO_3)_{12}](NO_3)_2\cdot CB[8]\cdot 50H_2O$ (**II**) complexes, and a compound with the composition $[H_3O{\subset}18\text{-crown-}6]_2[Pt_2(\mu_2\text{-}OH)_2(NO_3)_8][Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]$ (**III**), containing both bi- and tetranuclear Pt(IV) complexes in the structure. ^{195}Pt NMR spectral analysis of the Pt(IV) polynuclear complexes was performed to find a correlation of their nuclearity with the signal positions.

EXPERIMENTAL SECTION

General Procedures. Hexachloroplatinic acid produced at The Gulidov Krasnoyarsk Non-Ferrous Metals Plant Open Joint Stock Company with platinum content of 39.1% was used as starting reagent. Nitric acid (15.8 M concentration was determined by acid–base titration) and sodium hydroxide were of reagent grade quality and used without further purification. Cucurbit[n]urils (CB[6], $C_{36}H_{36}N_{24}O_{12}\cdot 10H_2O$ and CB[8], $C_{48}H_{48}N_{32}O_{16}\cdot 20H_2O$) were synthesized according to a known procedure.[31] $H_2[Pt(OH)_6]$ was prepared as described previously.[9]

Preparation of $H_2[Pt(OH)_6]$ Nitric Acid Solution. $H_2[Pt(OH)_6]$ (150 mg, 0.5 mmol) was dissolved in 1 mL of 15.8 M HNO_3 at 20 °C. Two-week aging of the resulting PNS was performed in a close flask at 20 °C in the darkness.

Preparation of Alkali-Treated Platinum Nitrate Solution. The aged PNS, prepared as mentioned above, was added dropwise and with constant stirring into 5 M solution of KOH (5 mL) in an ice bath. Resulting solution was boiled for 30 min and then cooled to room temperature. A precipitate of KNO_3 was removed by filtration, and the solution (C(Pt) = 0.08 M, C(KOH) = 1.5 M) was used to obtain ^{195}Pt NMR spectrum.

Preparation of $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]\cdot CB[6]\cdot 25H_2O$ (I). Solution of CB[6] (0.120 mg) in 2 mL of 15.8 M HNO_3 was mixed with freshly prepared PNS containing 0.5 mmol of Pt. The resulting clear yellow solution was allowed to stand in a desiccator over solid KOH at room temperature. After 3 d the pale yellow prisms were removed by filtration, washed with minimal volume of 15.8 M HNO_3 and then acetone, and dried in an air stream. Yield: 55%. Anal. Calcd (Found) for $C_{36}H_{92}N_{34}O_{73}Pt_4$: C, 14.66 (15.1); H, 3.14 (3.0); N, 16.15 (16.5)%. Single crystals for X-ray analysis were picked from the mother liquor.

Preparation of $[Pt_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_6(NO_3)_{12}](NO_3)_2\cdot CB[8]\cdot 50H_2O$ (II). Solution of CB[8] (0.105 mg) in 2 mL of 15.8 M HNO_3 was mixed with freshly prepared PNS containing 0.5 mmol of Pt. The resulting clear yellow solution was allowed to stand in a desiccator over solid KOH at room temperature. After 3 d the pale yellow prisms were removed by filtration, washed with minimal volume of 15.8 M HNO_3 and then acetone, and dried in an air stream. Yield: 42%. Anal. Calcd (Found) for $C_{48}H_{158}N_{48}O_{124}Pt_6$: C, 12.64 (12.3); H, 3.49 (3.1); N, 14.74 (15.0)%. Single crystals for X-ray analysis were grown from 10-fold diluted mother liquor.

Preparation of $[H_3O\subset 18\text{-crown-6}]_2[Pt_2(\mu_2\text{-}OH)_2(NO_3)_8][Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]$ (III). Solution of 18-crown-6 (0.130 mg) in 2 mL of 15.8 M HNO_3 was mixed with freshly prepared PNS containing 0.5 mmol of Pt. The resulting clear yellow solution was allowed to stand in a desiccator under solid KOH at room temperature. After 3 d the pale yellow prisms were removed by filtration, washed with minimal volume of 15.8 M HNO_3, and dried in an air stream. Yield: 40%. Anal. Calcd (Found) for $C_{24}H_{62}N_{18}O_{76}Pt_6$: C, 9.64 (9.2); H, 2.09 (2.3); N, 8.43 (8.1)%. Single crystals for X-ray analysis were picked from the mother liquor.

Deviations of analytical data from the calculated values for the synthesized complexes correspond to the easily reversible uptake of water molecules. Purity of **I** and **III** was additionally checked by comparison of XRD patterns of the complexes with those calculated from crystallographic data (Supporting Information, Figures S1 and S2).

NMR Data Collection. ^{195}Pt NMR spectra were recorded at 107.5 MHz using an Avance III 500 Bruker spectrometer with 5 mm broadband probe. A 90° excitation pulse of 15 μs was applied. All spectra were recorded at 24 °C. The shift δ ^{195}Pt (ppm) are reported relative to the external reference −2 M solution of $H_2[PtCl_6]$ in 1 M hydrochloric acid. 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 ^{195}Pt nuclei to relax completely. A line-broadening factor of 1 Hz was applied in processing of all experimental FID data.

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

Crystal Structure Determination. Crystal data and experimental details for **I**, **II**, and **III** are given in Table 1. Experimental data for determination of the crystal structures were collected on a Bruker-Nonius X8 APEX CCD diffractometer at 150 K (**II**) and 296 K (**I** and **III**) using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). All calculations were performed with SHELX-97 crystallographic software package.[34] The structure was solved by the standard heavy atom method and refined in 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 SADABS software.[35]

Structures of **I** and **II** contain a number of disordered water molecules with low occupancy, which could not be adequately modeled. Omission of these solvent molecules does not affect the general structural motif, so the SQUEEZE function from PLATON crystallographic tool was used for this purpose.[36] Refinements for **I** and **II** were performed using the adjusted reflection file from SQUEEZE, and all necessary information was added in the resulting .cif files. The content of water molecules in **I** and **II** was measured using thermogravimetric analysis (Supporting Information, Figure S3) and was found to be in agreement with crystallographic data (15.2 and 19.7%). Hydrogen atoms of $[H_3O\subset 18\text{-crown-6}]^+$ fragments in the structure of **III** were not included in the model due to disorder of the fragments.

■ RESULTS AND DISCUSSION

Polynuclear Nitrato Complexes of Pt(IV) in Solid Phase. Dissolution of $[Pt(H_2O)_2(OH)_4]$ in nitric acid yields a series of aquahydroxidonitrato complexes $[Pt(L)_x(NO_3)_{6-x}]$ (L = H_2O or OH^-; x = 0···6).[9] These mononuclear species participate in condensation process and form polynuclear nitrato complexes of Pt(IV) with OH-bridges. In our previous work we successfully used small organic cations PyH^+ and NMe^{4+} to isolate two nitrato complexes $[Pt(NO_3)_6]^{2-}$ and $[Pt_2(\mu\text{-}OH)_2(NO_3)_8]^{2-}$ from the PNS.[9] As a consequence of these findings, we focused our attention on the searching of methods for crystallization of individual polynuclear Pt(IV) complexes with a higher nuclearity from PNS using bulk organic molecules (stable in concentrated nitric acid) as appropriate companions to form crystalline phases. Both cucurbit[n]urils (n = 6,8) and the 18-crown-6 ether are uncharged molecules and represent good companions to crystallize bulk polynuclear complexes with low delocalized charge or the uncharged ones.

Evaporation of PNS with addition of CB[6] yields yellow crystals of **I** consisting of tetranuclear $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(NO_3)_{10}]$ (**Pt_4**) complex, CB[6] molecules, and water molecules of crystallization. The single-molecule view of the **Pt_4** complex is given in Figure 1; Table 2 lists the selected interatomic distances and interbond angles. Structure of the **Pt_4** complex represents two edge-shared incomplete cuboidal $\{Pt_3O_4\}$ cores decorated with 10 terminal nitrato ligands. Platinum(IV) centers in **Pt_4** molecule occupy two different, slightly distorted, octahedral positions with two and three terminal NO_3^- ligands. For the first time such double cuboidal

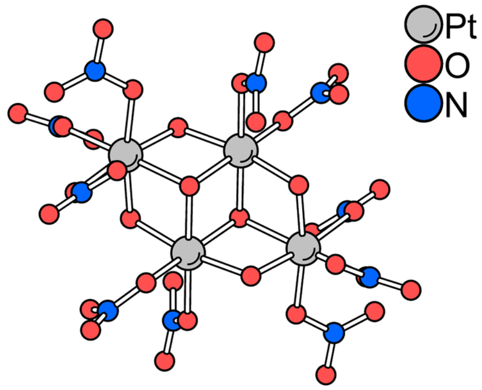


Figure 1. Structure of **Pt_4** complexes in **I**. Hydrogen atoms are omitted for clarity.

Table 2. Selected Geometric Parameters for Pt_4 Complexes in I

distances, Å	
Pt–O (NO_3^-)	2.007–2.020
Pt–O (μ^3-OH)	2.026–2.045
Pt–O (μ^2-OH)	1.990–2.017
Pt···Pt (shortest)	3.077–3.100
angles, deg	
(H)O–Pt–O(H)	78.79–92.82
(NO_2)O–Pt–O(NO_2)	87.88–101.78
(NO_2)O–Pt–O(H)	85.78–101.29
Pt–O(H)–Pt	98.83–101.72

DOI: 10.1021/ic502896s
Inorg. Chem. 2015, 54, 4644−4651

fragment $Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4$, unique for Pt(IV) chemistry, was found in organometallic compound $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(Me)_{10}]$ obtained by oxidation of platinum(II) methyl complex with hydrogen peroxide.[37] In the organometallic compound, trans influence of the CH_3 ligand results in an elongation of Pt−OH bonds and two different Pt−O bond lengths (2.2 Å for Pt−O in trans positions to methyl ligands and 2.0 Å for Pt−O in trans position to μ-OH groups) are in the structure. On the contrary, in the $\mathbf{Pt_4}$ complex all Pt−O distances are almost equal (Table 2) and close to Pt−O distances in $[Pt_2(\mu_2\text{-}OH)_2(NO_3)_8]^{2-}$ and $[Pt(OH)_6]^{2-}$ ions.[9,38] It corresponds to a weak structural trans influence of NO_3^- groups.

As mentioned earlier, polynuclear complexes of Pt(IV) with nuclearity higher than 4 are expected to exist in PNS. Isolation of such species requires bulkier companion molecules than CB[6]. Simple extension up to CB[8] gives positive result and evaporation of PNS with addition of CB[8] yields yellow crystal of **II** containing hexanuclear cationic complexes $[Pt_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_6(NO_3)_{12}]^{2+}$ ($\mathbf{Pt_6^{2+}}$). The complex is constructed of two separate incomplete cuboidal $\{Pt_3O_4\}$ cores connected by μ_3-OH and μ_2-OH groups (Figure 2).

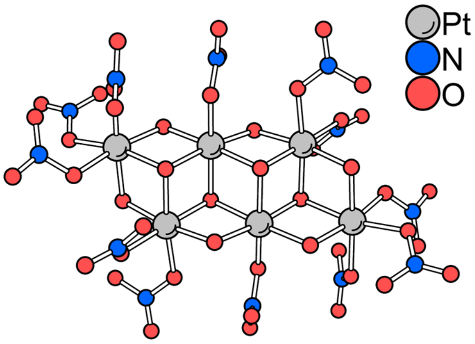


Figure 2. Structure of the $\mathbf{Pt_6^{2+}}$ complex in **II**. Hydrogen atoms are omitted for clarity.

Thereby in the $\mathbf{Pt_6^{2+}}$ complex, the Pt(IV) centers occupy three particular positions with one, two, and three terminal NO_3^- ligands. The remaining positions of the distorted octahedral environment of Pt(IV) ions are filled with μ_3-OH and μ_2-OH ligands. The geometric characteristics of the $\mathbf{Pt_6^{2+}}$ skeleton (Pt−O bond lengths and O−Pt−O angles) are almost identical to those of the $\mathbf{Pt_4}$ complex in **I** (Table 3). The Pt_2O_2 cycles with the smallest O−Pt−O angles of 78−79° appear as hard structural fragments in both $\mathbf{Pt_4}$ and $\mathbf{Pt_6^{2+}}$ structures despite sufficient PtO_6 polyhedron distortions.

The packing of CB[*n*] molecules in structures of **I** and **II** is not accompanied by the formation of any specific bonding with $\mathbf{Pt_4}$ and $\mathbf{Pt_6^{2+}}$ complexes (Figure 3) as was observed for a variety of supramolecular assemblies of CB[*n*] with aqua complexes.[24−30] Thus, the CB[*n*] molecules in the structures of **I** and **II** play only the role of template forming cavities of the appropriate size for the platinum complexes. Arrangement of CB[*n*]s is close to its columnar arrangements in structures of pure cucurbit[*n*]urils.[39] The space between them is occupied by the platinum complexes, crystallization water molecules, and nitrate anions (in **II**) connected together by an intricate network of hydrogen bonds.

Table 3. Selected Geometric Parameters for the $\mathbf{Pt_6^{2+}}$ Complex in II

distances, Å	
Pt−O (NO_3^-)	1.999−2.020
Pt−O (μ^3-OH)	2.005−2.072
Pt−O (μ^2-OH)	1.994−2.021
Pt···Pt (shortest)	3.079−3.134
angles, deg	
(H)O−Pt−O(H)	78.08−99.77
$(NO_2)O-Pt-O(NO_2)$	80.76−102.18
$(NO_2)O-Pt-O(H)$	81.69−107.64
Pt−O(H)−Pt	97.06−101.98

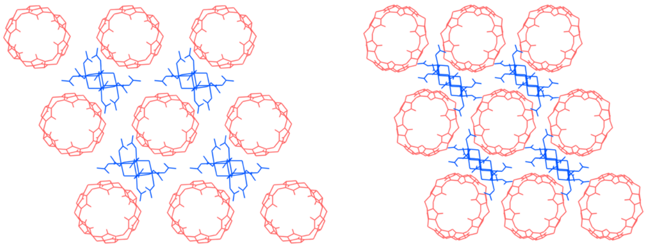


Figure 3. Mutual packing of $\mathbf{Pt_4}$ and $\mathbf{Pt_6^{2+}}$ complexes (blue) and cucurbit[*n*]urils molecules (red) in structures **I** (right picture) and **II** (left picture) along *a* axis. Water molecules and free NO_3^- ions are omitted for clarity.

The crystals of **I** and **II** are virtually insoluble in nitric acid, water, and common organic solvents. To further study the chemistry of polynuclear compounds in solution, it is important to find a route to soluble compounds. To prepare a soluble solid containing polynuclear Pt(IV) nitrato complexes we used $[H_3O\subset 18\text{-crown-6}]^+$ as bulk organic cation. The equimolar addition of 18-crown-6 to PNS with the consequent evaporation of the solution results in crystallization of a complex salt containing $[H_3O\subset 18\text{-crown-6}]^+$ cations, previously reported dimeric $[Pt_2(\mu_2\text{-}OH)_2(NO_3)_8]^{2-}$ anions ($\mathbf{Pt_2^{2-}}$), and neutral tetranuclear $[Pt_4(OH)_6(NO_3)_{10}]$ complexes ($\mathbf{Pt_4}$). The geometric characteristics of $\mathbf{Pt_2^{2-}}$ in the structure of **III** are identical to those reported earlier for this anion in the $(NMe_4)_2[Pt_2(OH)_2(NO_3)_8]$ salt;[9] the characteristics of $\mathbf{Pt_4}$ are close to those in crystal structure of **I**.

The extended structure of **III** represents a construction layered in *ac* plane where layers of $[H_3O\subset 18\text{-crown-6}]^+$ cations alternate with layers containing $\mathbf{Pt_2^{2-}}$ anions and $\mathbf{Pt_4}$ complexes (Figure 4). Fragments $[H_3O\subset 18\text{-crown-6}]^+$ are disordered over two pairs of positions (occupancy 0.3 and 0.2) where every pair consists of two crystallographic positions that differ by the angle of rotation around the axis of 18-crown-6 molecules. Such disorder pattern is not rare for crown ether,[19,40] but the presence of heavy metal atoms in the structure makes it complicated to find unambiguous solutions. Therefore, $[H_3O\subset 18\text{-crown-6}]^+$ molecules were modeled without hydrogen atoms and in an isotropic approximation.

It is interesting to note that octahedrally coordinated edge-linked PtO_6 units in polynuclear platinum complexes **I**−**III** (Figure 5) can be considered as fragments of α-PtO_2 structure that is formed by polymeric layers of edge-sharing PtO_6 octahedrons.[41,42] The identified structures of $\mathbf{Pt_2^{2-}}$, $\mathbf{Pt_4}$, and $\mathbf{Pt_6^{2+}}$ provide insights for further understanding of the nucleation processes in PNS, which are of great importance due to the high occurrence of the polynuclear PtO_x structures in Pt-based catalysts.[43,44]

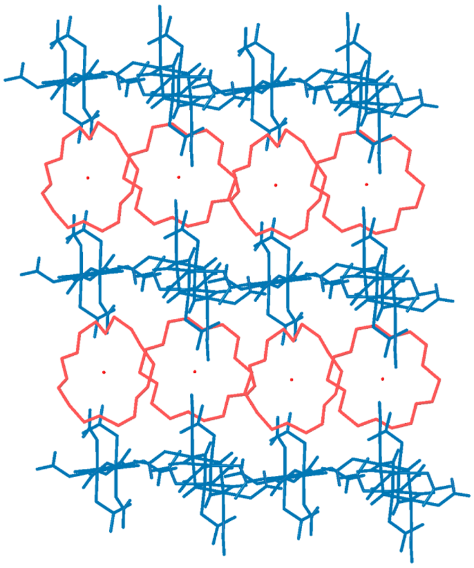


Figure 4. Mutual packing of $\mathbf{Pt_2}^{2-}$, $\mathbf{Pt_4}$ complexes (blue), and $[H_3O{\subset}18\text{-crown-}6]^+$ cations (red) in structure **III** along *c* axis.

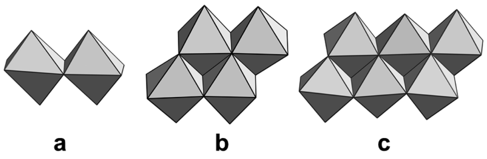


Figure 5. Polyhedron representation of $\mathbf{Pt_2}^{2-}$ (a), $\mathbf{Pt_4}$ (b), and $\mathbf{Pt_6}^{2+}$(c) complexes.

Polynuclear Nitrato Complexes of Pt(IV) in Solutions.

Unlike compounds **I** and **II**, the salt **III** has good solubility in acetone, diethyl ether, and water (with intensive hydrolysis). ^{195}Pt NMR spectrum of freshly prepared acetone solution of **III** demonstrates a singlet signal of the dimeric anions $\mathbf{Pt_2}^{2-}$ (3978 ppm), which is close to the earlier reported value (3970 ppm),[9] and two poorly resolved five-line sets of signals (4245 and 4347 ppm) corresponding to the tetranuclear complexes $\mathbf{Pt_4}$ (Figure 6b).

Platinum(IV) centers in the $\mathbf{Pt_4}$ complex occupy two different positions: $\{Pt(\mu\text{-}OH)_3(NO_3)_3\}$ and $\{Pt(\mu\text{-}OH)_4(NO_3)_2\}$. From the point of view of NMR spectroscopy, the $\mathbf{Pt_4}$ molecule represents an A_2X_2 system, where each A is connected with two X and vice versa (A and X magnetically nonequivalent Pt nuclei). Natural abundance of the only platinum NMR active isotope (^{195}Pt, $I = 1/2$) is 33.8%, therefore spectrum of A (or X) in A_2X_2 system represents the sum of three subspectra from the statistically possible isotopologues AX_2 (triplet), AX^*X (doublet), and AX^*_2 (singlet), where X* is a magnetically inactive Pt isotope. Result of the sum is the five-line set of signals with statistically expected ratio of 1:7.9:17.4:7.9:1 (Supporting Information, Figure S3). In the real spectrum only three central components of these sets are clearly visible due to the low intensity of the side signals. The least-squares fitting of the spectrum with Lorentzian functions gives good fit of experimental ratio of the central component (8.5:17.4:8.1 for $\{Pt(\mu\text{-}OH)_3(NO_3)_3\}$ and 8.3:17.4:7.8 for $\{Pt(\mu\text{-}OH)_4(NO_3)_2\}$) with statistically expected ones (Figure 6c).

Chemical shifts and $J(^{195}Pt{-}^{195}Pt)$ coupling constant of the $\mathbf{Pt_4}$ signals in acetone solution of **III** are close to those found for $\mathbf{Pt_4}$ complex in PNS, and that is surprising for ^{195}Pt NMR, which is known to be a strongly solvent-sensitive method (Figure 6a,b). On the other hand, the line width of the $\mathbf{Pt_4}$ NMR signals in acetone solution (160 Hz) is about 3 times greater than that in PNS. The signal line width grows with time (Supporting Information, Figure S4), indicating a certain process in the acetone solution of **III**. The generation of paramagnetic substance from **III** in acetone or other interaction with solvent can be responsible for this effect, but more detailed study is necessary to uncover the phenomenon.

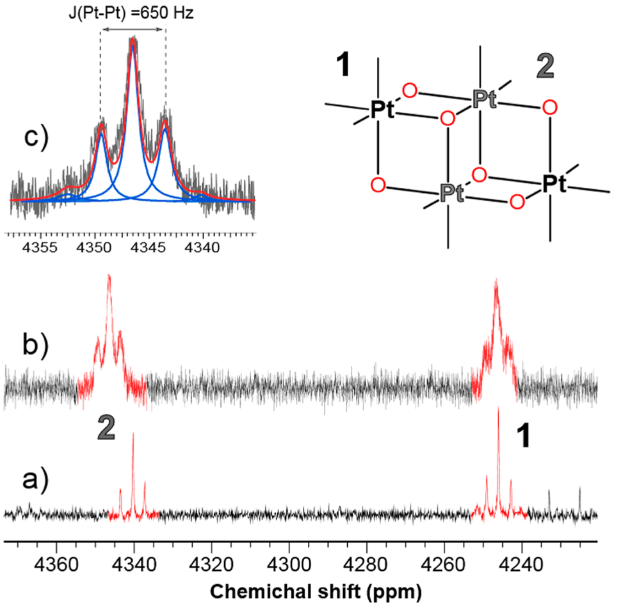
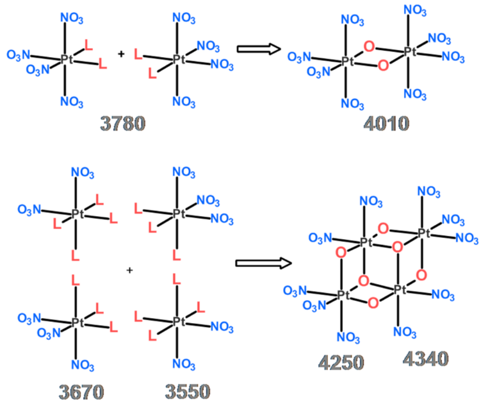


Figure 6. Region of the $\mathbf{Pt_4}$ complex in the ^{195}Pt NMR-spectra of (a) PNS (C(Pt) = 0.5 M, C(HNO_3) = 15.8 M) and (b) freshly prepared acetone solution of **III** (C(Pt) = 0.04M); numbering scheme represents two different platinum positions in the $\mathbf{Pt_4}$ complex: $\{Pt(\mu\text{-}OH)_3(NO_3)_3\}$ (**1**) and $\{Pt(\mu\text{-}OH)_4(NO_3)_2\}$ (**2**). (c) Fitting of experimental NMR profile of the $\{Pt(\mu\text{-}OH)_4(NO_3)_2\}$ with Lorenzian curves showing good agreement with the five-line set of A_2X_2 structure.

The substitution of nitrato ligand by μ-OH ligand in the coordination sphere causes an essential deshielding of the Pt(IV) nucleus. For example, a gap between the signals of two different platinum(IV) centers of the $\mathbf{Pt_4}$ complex, $\{Pt(\mu\text{-}OH)_3(NO_3)_3\}$ (4250 ppm) and $\{Pt(\mu\text{-}OH)_4(NO_3)_2\}$ (4340 ppm), is ~100 ppm (Figure 6b). Analysis of the ^{195}Pt NMR spectra obtained for mononuclear and polynuclear complexes in PNS reveals that formation of every new $Pt(\mu\text{-}OH)_2Pt$ ring results in ~260 ppm downfield shift of the signals of corresponding Pt nuclei (230−290 ppm for different complexes) by comparison with mononuclear forms $[Pt(L)_x(NO_3)_{6-x}]$ (L = H_2O or OH^-; $x = 0\cdots6$; Scheme 1).

Bearing in mind that (a) maximum number of $Pt(\mu\text{-}OH)_2Pt$ rings is six for the octahedral complex, and (b) chemical shifts of mononuclear aquahydroxidonitrato complexes range from 3350 ($[Pt(L)_6]$) to 3950 ($[Pt(NO_3)_6]^{2-}$) ppm,[9] it is easy to calculate that signals of other possible polynuclear complexes with the same nature will be positioned not farther than ~5000 ppm. From this point of view, the poorly resolved sets of signals at 4130, 4270, 4350, and 4380 ppm observed previously in NMR spectra of ^{195}Pt-enriched PNS samples[9] can be attributed to the $\mathbf{Pt_6}^{2+}$ complex and its substituted analogues.

Scheme 1. Comparison of ^{195}Pt NMR Chemical Shift (ppm) of Mononuclear (L = H_2O or OH^-) and Corresponding Polynuclear Pt_2^{2-} and Pt_4 Complexes[a]



[a]The chemical shifts are given according to the spectrum of PNS ($C(Pt)$ = 0.5 M, $C(HNO_3)$ = 15.8 M).[9].

Alkaline Treatment of Platinum Nitrate Solution. During preparation of heterogeneous catalysts from PNS by impregnation technique, just alkaline conditions appear on oxide carriers (because of proton binding by the OH^- groups on the surface).[44] In addition, alkali-pretreated PNS was used as an active component precursor for preparation of methane oxidation catalysts.[11] Therefore, it is reasonable to study stability of the platinum(IV) polynuclear structures like **Pt_2^{2-}**, **Pt_4**, or **Pt_6^{2+}** in alkaline conditions for a better understanding of the catalyst active center formation.

Unique stability toward alkaline hydrolysis was postulated for OH-briged Pt(IV) complexes on the basis of extended X-ray absorption fine structure (EXAFS) study of alkali-treated PNS (ATPNS).[10] To check this hypothesis in detail by NMR spectroscopy we performed experiment with the sample of aged (two weeks, 20 °C) PNS; ^{195}Pt NMR spectrum of this initial solution is presented in Figure 7a. The solution of PNS (1 mL) was treated with 5 M KOH (5 mL), as described in Experimental Section, and the resulting clear yellow ATPNS was studied again with ^{195}Pt NMR-spectroscopy.

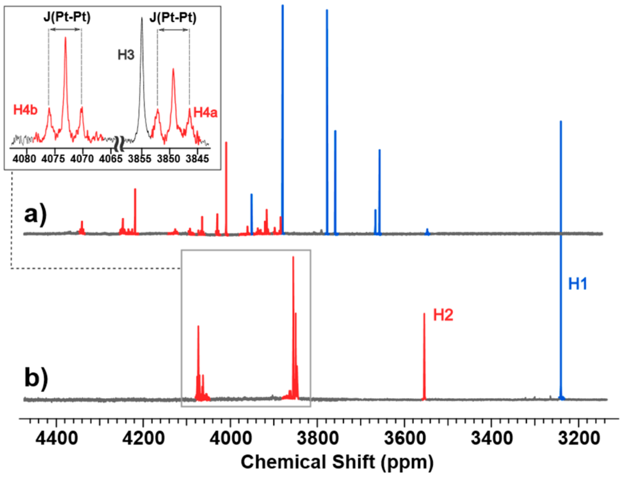
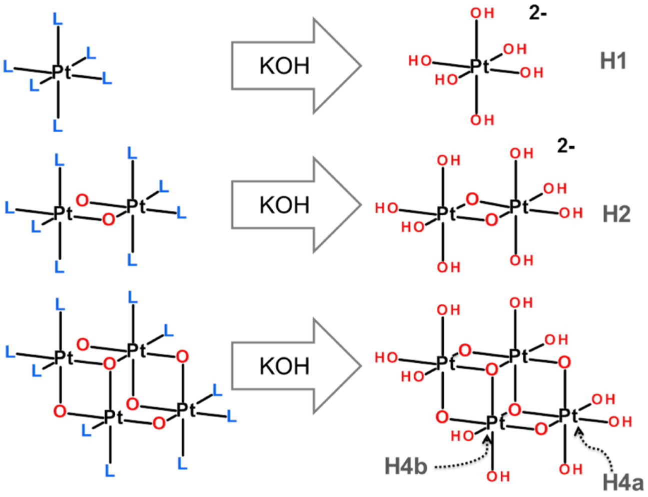


Figure 7. ^{195}Pt NMR-spectra of (a) original PNS ($C(Pt)$ = 0.5 M, $C(HNO_3)$ = 15.8 M) and (b) alkali-treated PNS ($C(Pt)$ = 0.08 M, $C(KOH)$ = 1.5 M). Designation of the species: $[Pt(OH)_6]^{2-}$ (H1, blue), $[Pt_2(\mu^2\text{-}OH)_2(OH)_8]^{2-}$ (H2, red), and $[Pt_3(\mu^3\text{-}OH)(\mu^2\text{-}OH)_3(OH)_9]^-$ (H3, black). (inset) The five-line sets of signals of $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(OH)_{10}]$ (H4a and H4b, red).

Sufficient simplification of the ^{195}Pt NMR spectrum is observed after alkaline treatment of the solution (Figure 7b). There are only five signals in the spectrum of ATPNS (instead of ~20 signals in the spectrum of initial PNS): three singlets (H1 and H2 in Figure 7b, H3 in the inset of Figure 7) and two five-line sets with equal intensity (H4a and H4b signals in the inset of Figure 7). Full substitution of terminal NO_3^- ligands by OH^- ions in all mono- and polynuclear platinum(IV) complexes is assumed to take place in ATPNS (Scheme 2).

Scheme 2. Transformation of the Aquahydroxidonitrato Complexes $[Pt(L)_x(NO_3)_{6-x}]$ (L = H_2O or NO_3^- or OH^-) under Alkaline Treatment[a]



[a]Hydrogen atoms of the OH-bridges are omitted. Designations H1, H2, H4a, and H4b correspond to the ^{195}Pt NMR signals of platinum centers in Figure 7.

According to the previously reported data, two singlet signals H1 at 3260 ppm and H2 at 3550 ppm were referred to $[Pt(OH)_6]^{2-}$ and $[Pt_2(\mu_2\text{-}OH)_2(OH)_8]^{2-}$ correspondingly.[45,10] The five-line sets of signals at 3849 and 4073 ppm (H4a and H4b), most probably, correspond to the A_2X_2 system mentioned above. The $^2J(^{195}Pt{-}^{195}Pt)$ coupling constants in the five-line sets of signals (about 620 Hz) are close to values observed for the Pt−Pt coupling in **Pt_4** molecule. As a result we ascribe the five-line sets of signals to tetranuclear $[Pt_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_4(OH)_{10}]$ complex containing Pt(IV) in two different environments (H4a and H4b, Scheme 2). Third singlet signal H3 (3850 ppm) may be attributed to trinuclear $[Pt_3(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3(OH)_9]^-$ symmetrical species (H3, Scheme 2), which should produce single signal in ^{195}Pt NMR spectrum.

As can be concluded from chemical shifts of $[Pt(OH)_6]^{2-}$ (3260 ppm) and $[Pt(NO_3)_6]^{2-}$ (3940 ppm),[9] an upfield chemical shift of all signals in the spectrum of ATPNS by comparison with spectrum of PNS reflects substitution of terminal NO_3^- ligands for OH^-. Therefore, our NMR data fully confirm the previous EXAFS-based suggestion about stability of Pt(IV) polynuclear complexes with OH bridges in alkaline solutions.[10] Initially obtained in nitric acid, these species can be transferred into a basic solution without destruction of their $Pt_x(\mu\text{-}OH)_y$ cores.

■ CONCLUSIONS

To conclude, we have demonstrated that the macrocyclic cavitands cucurbit[*n*]urils ($n = 6,8$) and 18-crown-6 ether can be used for solid-state isolation of polynuclear platinum(IV) complexes from nitric acid solution. We present the first examples of structurally characterized hydroxido-bridged tetranuclear and hexanuclear platinum(IV) nitrato complexes. The CB[*n*] molecules serve as bulk building blocks for creation of an appropriate framework where platinum complexes are localized. ^{195}Pt NMR spectral analysis reveals the stability of $Pt_x(OH)_y$ cores toward alkaline hydrolysis and a correlation of signal positions with nuclearity of species. Recently polynuclear $\mathbf{Pt_{14}}^{4+}$ and $\mathbf{Pd_{10}}^{4+}$ species were found to exist in perchloric acid solutions of Pt(II) and Pd(II) aqua ions, and similar structures with OH(O)-bridging cores were proposed for them by EXAFS and small-angle X-ray scattering.[46] Conceivably, the application of such acid-resistant bulk molecules like cucurbit[*n*]urils and crowns will make it possible to perform the solid-state isolation of polynuclear species, previously postulated to exist in acidic solutions, and also the new ones with structures still unknown.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculated and experimental XRD patterns for **I** and **III**; thermogravimetric analysis data for **I** and **II**; graphical clarification of the ^{195}Pt NMR spectrum of A_2X_2 system; ^{195}Pt NMR spectra of fresh and aged acetone solution of **III**, X-ray crystallographic data for **I**, **II**, and **III** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Further crystallographic details may be obtained from the Cambridge Crystallographic Data Center upon quoting depository numbers CCDC 1036821, 1036820, and 1037012. Copies of this information may be obtained free of charge from http://www.ccdc.cam.ac.uk.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vasilchenko@niic.nsc.ru.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Russian Academy of Sciences (program of the Division of Chemistry and Materials Science No. 5).

■ REFERENCES

(1) Foster, A. J.; Do, P. T. M.; Lobo, R. F. *Top. Catal.* **2012**, *55*, 118−128.

(2) Kalantar Neyestanaki, A.; Mäki-Arvela, P.; Backman, H.; Karhu, H.; Salmi, T.; Väyrynen, J.; Murzin, D. Y. *Ind. Eng. Chem. Res.* **2003**, *42*, 3230−3236.

(3) Arzumanov, S. S.; Stepanov, A. G. *J. Phys. Chem. C* **2013**, *117*, 2888−2892.

(4) Zhivonitko, V. V.; Kovtunov, K. V.; Beck, I. E.; Ayupov, A. B.; Bukhtiyarov, V. I.; Koptyug, I. V. *J. Phys. Chem. C* **2011**, *115*, 13386−13391.

(5) Huang, H.; Sun, D.; Wang, X. *J. Phys. Chem. C* **2011**, *115*, 19405−19412.

(6) Ahmadi, M.; Macias, E. E.; Jasinski, J. B.; Ratnasamy, P.; Carreon, M. a. *J. Mol. Catal. A: Chem.* **2014**, *386*, 14−19.

(7) Dou, D.; Liu, D.-J.; Williamson, W. B.; Kharas, K. C.; Robota, H. J. *Appl. Catal., B* **2001**, *30*, 11−24.

(8) Venediktov, A. B.; Korenev, S. V.; Vasil'chenko, D. B.; Zadesenets, a. V.; Filatov, E. Y.; Mamonov, S. N.; Ivanova, L. V.; Prudnikova, N. G.; Semitut, E. Y. *Russ. J. Appl. Chem.* **2012**, *85*, 995−1002.

(9) Vasilchenko, D.; Tkachev, S.; Baidina, I.; Korenev, S. *Inorg. Chem.* **2013**, *52*, 10532−10541.

(10) Beck, I. E.; Kriventsov, V. V.; Fedotov, M. A.; Bukhtiyarov, V. I. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2009**, *603*, 182−184.

(11) Beck, I. E.; Kriventsov, V. V.; Ivanov, D. P.; Zaikovsky, V. I.; Bukhtiyarov, V. I. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2009**, *603*, 108−110.

(12) Belyaev, A. V.; Fedotov, M. A.; Vorobieva, S. N. *Russ. J. Coord. Chem.* **2011**, *37*, 281−287.

(13) Zhai, Y.; Pierre, D.; Si, R.; Deng, W.; Ferrin, P.; Nilekar, A. U.; Peng, G.; Herron, J. A.; Bell, D. C.; Saltsburg, H.; Mavrikakis, M.; Flytzani-Stephanopoulos, M. *Science* **2010**, *329*, 1633−1636.

(14) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. *Science* **2003**, *301*, 935−938.

(15) Flytzani-Stephanopoulos, M.; Gates, B. C. *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 545−574.

(16) Merte, L. R.; Ahmadi, M.; Behafarid, F.; Ono, L. K.; Lira, E.; Matos, J.; Li, L.; Yang, J. C.; Roldan Cuenya, B. *ACS Catal.* **2013**, *3*, 1460−1468.

(17) Lee, U.; Joo, H.-C.; Park, K.-M.; Mal, S. S.; Kortz, U.; Keita, B.; Nadjo, L. *Angew. Chem., Int. Ed. Engl.* **2008**, *47*, 793−796.

(18) Izarova, N. V.; Pope, M. T.; Kortz, U. *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 9492−9510.

(19) Drljaca, A.; Hardie, M. J.; Ness, T. J.; Raston, C. L. *Eur. J. Inorg. Chem.* **2000**, *2000*, 2221−2229.

(20) Hardie, M. J.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **2000**, 2483−2492.

(21) Spiccia, L. *Inorg. Chim. Acta* **2004**, *357*, 2799−2817.

(22) Drljaca, A.; Hardie, M. J.; Raston, C. L.; Spiccia, L. *Chem.—Eur. J.* **1999**, *5*, 2295−2299.

(23) Atwood, J. L.; Barbour, L. J.; Hardie, M. J.; Raston, C. L. *Coord. Chem. Rev.* **2001**, *222*, 3−32.

(24) Gerasko, O. A.; Sokolov, M. N.; Fedin, V. P. *Pure Appl. Chem.* **2004**, *76*, 1633−1646.

(25) Gerasko, O. A.; Mainicheva, E. A.; Naumov, D. Yu.; Kuratieva, N. V.; Sokolov, M. N.; Fedin, V. P. *Inorg. Chem.* **2005**, *44*, 4133−4135.

(26) Gerasko, O. A.; Mainicheva, E. A.; Naumov, D. Yu.; Fedin, V. P. *Russ. Chem. Bull., Int. Ed.* **2007**, *56*, 1972−1977.

(27) Gerasko, O. A.; Samsonenko, D. G.; Sharonova, A. A.; Virovets, A. V.; Lipkowski, J.; Fedin, V. P. *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 346−349.

(28) Thuéry, P. *Cryst. Growth Des.* **2008**, *8*, 4132−4143.

(29) Fang, X.; Paul Kögerler, P.; Isaacs, l.; Uchida, S.; Mizuno, N. *J. Am. Chem. Soc.* **2009**, *131*, 432−433.

(30) Plumb, J. A.; Venugopal, B.; Oun, R.; Gomez-Roman, N.; Kawazoe, Y.; Sathiyamoorthy, N.; Venkataramanan, N. S.; Nial, J.; Wheate, N. J. *Metallomics* **2012**, *4*, 561−567.

(31) Jeon, Y. J.; Kim, S.-Y.; Ko, Y. H.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Org. Biomol. Chem.* **2005**, *3*, 2122−2125.

(32) Kim, J.; Jung, I.-S.; Kim, S.-Y.; Lee, E.; Kang, J.-K.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *J. Am. Chem. Soc.* **2000**, *122*, 540−541.

(33) Day, A.; Arnold, A. P.; Blanch, R. J.; Snushall, B. *J. Org. Chem.* **2001**, *66*, 8094−8100.

(34) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(35) Bruker. *SADABS;* Bruker AXS Inc.: Madison, WI, 2001.

(36) Spek, P. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, C34.

(37) Safa, M. S.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2009**, *12*, 1487−1489.

(38) Bugaris, D. E.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2013**, *52*, 3836−4384.

(39) Bardelang, D.; Udachin, K. A.; Leek, D. M.; Margeson, J. C.; Chan, G.; Ratcliffe, C. I.; Ripmeester, J. A. *Cryst. Growth Des.* **2011**, *11*, 5598−5614.

(40) Grassl, T.; Hamberger, M.; Korber, N. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2012**, *68*, o2933.

DOI: 10.1021/ic502896s
Inorg. Chem. 2015, 54, 4644−4651

(41) Mansour, A. N.; Sayers, D. E.; Cook, J. W., Jr. *J. Phys. Chem.* **1984**, *88*, 1778−1782.

(42) Nomiyama, R. K.; Piotrowski, M. J.; Da Silva, J. L. F. *Phys. Rev. B* **2011**, *84*, 100101.

(43) Pakharukova, V. P.; Pakharukov, I. Y.; Bukhtiyarov, V. I.; Parmon, V. N. *Appl. Catal., A* **2014**, *486*, 12−18.

(44) Mironenko, R. M.; Belskaya, O. B.; Talsi, V. P.; Gulyaeva, T. I.; Kazakov, M. O.; Nizovskii, A. I.; Kalinkin, A. V.; Bukhtiyarov, V. I.; Lavrenov, A. V.; Likholobov, V. a. *Appl. Catal., A* **2014**, *469*, 472−482.

(45) Appleton, T. G.; Hall, J. R.; Ralph, S. F.; Thompson, C. S. M. *Inorg. Chem.* **1984**, *23*, 3521−3525.

(46) Torapava, N.; Elding, L. I.; Mändar, H.; Roosalu, K.; Persson, I. *Dalton Trans.* **2013**, *42*, 7755−7760.