New Hydrogen Peroxide Adducts of Alkali Metal Tetracyanoplatinates $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs)

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The title compounds have been synthesized by adding hydrogen peroxide to an aqueous solution of $A_2[Pt(CN)_4]$ (A = K, Rb, Cs). They grow as yellow needles after concentrating and cooling to 4 °C. The structures were elucidated from single crystal analysis. The isostructural compounds crystallize monoclinically, in space group $C2/c$ with $Z = 4$. $K_2Pt(CN)_4 \cdot H_2O_2$: a = 13.3751(7), b = 11.2713(6), c = 6.5461(3) Å, β = 105.432(1)°, V = 951.3(3) Å^3. $Rb_2Pt(CN)_4 \cdot H_2O_2$: a = 13.6103(2), b = 11.6759(1), c = 6.5683(7) Å, β = 106.588(2)°, V = 1000.3(2) Å^3. $Cs_2Pt(CN)_4 \cdot H_2O_2$: a = 13.9569(2), b = 12.2023(2), c = 6.5857(9) Å, β = 107.590(3)°, V = 1069.1(2) Å^3. As a remarkable feature, the hydrogen bonds O–H···N vary significantly with the cation size: in the Cs compound the O–H bonds are weakest, and the N···H interactions are strongest. All three compounds were characterized by differential thermal analysis, thermogravimetry and infrared spectroscopy.

Key words: Crystal Structure, Alkali Metal Tetracyanoplatinate, Hydrogen Peroxide, Infrared Spectroscopy

Introduction

Substantial progress in the cyanoplatinate chemistry has been marked by the structural characterization of partially oxidized salts by Krogmann in the 1960ies [1]. He revealed a significant contraction of the Pt–Pt distances in the oxidized products $K_2[Pt(CN)_4]X_{0.33} \cdot y\ H_2O$ (X = Cl, Br) to distances as short as 2.88 Å [1], which is only slightly longer than in metallic platinum (2.77 Å), suggesting significant bonding interactions between the partially filled Pt d_{z^2} orbitals. The oxidized cyanoplatinates thus can be considered as one-dimensional metals, in accordance with their relatively high electron conductivity. The first experiments to obtain partially oxidized potassium cyanoplatinates by adding hydrogen peroxide and sulfuric acid to respective aqueous solutions were performed by Levy [2] at the beginning of the 20th century. In 1968, Krogmann [3] solved the structure and determined the composition of the product to be $K_{1.74}[Pt(CN)_4] \cdot 1.8\ H_2O$, exhibiting a Pt–Pt distance of 2.96 Å. Since Krogmann's pioneering work the amazing structure-property correlations in this class of compounds have been treated in a huge number of publications. A comprehensive review has been given by Williams in [4], including reports on $Rb_{1.6}[Pt(CN)_4] \cdot 2\ H_2O$ [5] and $Cs_{1.75}[Pt(CN)_4] \cdot y\ H_2O$ [4]. We have continued in this field [6, 7] focusing on getting more information about the partially oxidized cyanoplatinates, in particular how they form. Our attempts to synthesize the rubidium-deficient cyanoplatinate following the conventional route suggested by Levy [2] and Williams [5] sometimes resulted in the formation of yellow needles of an unknown phase. We found out that hydrogen peroxide in such instances did not oxidize platinum at neutral conditions, instead yellow needles form which are hydrogen peroxide adducts of the formula $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs). Here we report on their structure analyses by X-ray crystallography, and characterization of the new adducts by infrared spectroscopy (IR), thermogravimetry (TG) and differential thermal analysis (DTA).

Experimental Section

Synthesis

$K_2[Pt(CN)_4] \cdot 3\ H_2O$ was obtained from $K_2[PtCl_4]$ (Chempur, 99.9 %) and KCN as described previously [6, 8]. This salt was recrystallized three times from water to re-

Table. 1. Crystallographic data of $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs).

Formula	$K_2[Pt(CN)_4] \cdot H_2O_2$	$Rb_2[Pt(CN)_4] \cdot H_2O_2$	$Cs_2[Pt(CN)_4] \cdot H_2O_2$
Formula weight, g mol^{-1}	411.39	504.13	599.01
Crystal size, mm^3	$0.40 \times 0.15 \times 0.15$	$0.30 \times 0.15 \times 0.05$	$0.20 \times 0.08 \times 0.04$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)
Z (formula units)	4	4	4
a, Å	13.3751(7)	13.6103(2)	13.9569(2)
b, Å	11.2713(6)	11.6759(1)	12.2023(2)
c, Å	6.5461(3)	6.5683(7)	6.5857(9)
β, deg	105.432(1)	106.588(2)	107.590(3)
V, Å^3	951.3(3)	1000.3(2)	1069.1(2)
T, K	296(2)	296(2)	296(2)
ρ_{calc}, g cm^{-3}	2.87	3.35	3.72
Radiation; λ, Å	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073
μ(MoK_α), mm^{-1}	15.596	23.668	19.810
θ range for data collection, deg	2.40 – 37.02	2.34 – 37.35	2.26 – 27.50
Reflections collected	12789	12437	3977
Independendent reflections	2391	2532	1021
Goodness of fit on F^2	0.997	0.959	0.947
Final $R1$ / $wR2$ [$I \geq 2\sigma(I)$]	0.0131 / 0.0320	0.0222 / 0.0472	0.0305 / 0.0861
Final $R1$ / $wR2$ (all data)	0.0225 / 0.0355	0.02406 / 0.0529	0.0389 / 0.0974
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	1.81 / −1.11	1.19 / −2.06	2.33 / −1.68
Deposition number CSD	418913	418912	418911

Table 2. Selected interatomic distances (Å) and angles (deg) in $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs).

	A = K	A = Rb	A = Cs
Pt1 – Pt1	3.273(1)	3.284(1)	3.292(9)
Pt1 – C1	1.984(2)	1.987(3)	1.995(7)
Pt1 – C2	1.985(2)	1.988(3)	1.997(8)
C1 – N1	1.145(2)	1.147(4)	1.149(9)
C2 – N2	1.146(2)	1.144(4)	1.144(1)
A1 – N1	2.838(9)	3.004(6)	3.209(9)
A1 – N2	2.850(2)	3.075(8)	3.264(4)
A1 – O1	2.840(6)	2.980(3)	3.180(4)
N1 – H1	2.008(3)	2.083(1)	1.829(1)
O1 – N1	2.825(1)	2.836(5)	2.800(9)
O1 – N2	2.868(1)	2.942(7)	3.089(8)
O1 – O1	1.451(3)	1.444(5)	1.419(1)
O1 – H1	0.83(3)	0.79(4)	1.19(1)
C1 – Pt1 – C1	180	180	180
C1 – Pt1 – C2	90.2(1)	91.3(1)	92.0(3)
C2 – Pt1 – C2	180	180	180
N1 – A1 – C2	77.60(5)	75.18(7)	72.15(2)
N2 – A1 – C2	160.56(5)	161.90(7)	161.8(2)
O1 – A1 – C2	95.92(5)	96.89(7)	96.07(2)
O1 – A1 – N2	103.54(5)	105.17(8)	106.6(2)
O1 – O1 – H1	101.0(2)	99.0(3)	97.0(8)

move all traces of chloride. To a warm concentrated aqueous solution of 200 mg $K_2[Pt(CN)_4] \cdot 3\ H_2O$ 0.01 mL of 35 % H_2O_2 was added. Yellow crystals of $K_2[Pt(CN)_4] \cdot H_2O_2$ were formed after concentrating and subsequent cooling in a refrigerator at 4 °C.

A concentrated aqueous solution of $Ba[Pt(CN)_4] \cdot 4\ H_2O$ (Chempur, 99.9 %) was mixed with an excess of an aqueous solution of A_2SO_4 (A = Rb, Cs) as described in [9]. After separating $BaSO_4$ by filtrating, the clear residual solution was concentrated by heating, and 0.01 mL of 35 % H_2O_2 was added. Yellow needles of $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = Rb, Cs) were obtained by cooling to 4 °C in a refrigerator.

Crystal structure determination

Single crystals of $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs) were selected under a microscope and sealed in Lindemann capillaries. All three compounds crystallize in space group *C*2/*c* (no. 15). The intensity data were measured on a Smart APEX CCD diffractometer (Bruker AXS) with a graphite monochromator using ω scans. Absorption corrections were done by the program SADABS [10]. The structures were solved and refined using the SHELXTL program system [11]. The atomic positions of the platinum and the alkali metals were found by Direct Methods, the positions of the cyanide and peroxide groups could be located from Difference Fourier maps. The hydrogen atoms have also been localized, and refined applying isotropic displacement parameters. Refinement was done by full-matrix least-squares methods on F^2. The crystallographic data are collected in Table 1, selected atomic distances and angles are given in Table 2.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers given in Table 1.

Physical properties

Simultaneous DTA/TG/MS was performed with a computer-controlled thermal analyzer (STA 409, Netzsch

GmbH, Germany). Samples of about 20 mg were placed in a corundum crucible, heated to 900 °C with a rate of 10 °C/min, and then cooled down to r. t. with the same rate. The whole process was run under argon.

The infrared spectra were recorded on an IR Spectrometer (113v, Bruker, Germany). About 2 mg of the samples were thoroughly mixed and ground with ∼400 mg of KBr (Aldrich, 99+ %, dried at 100 °C), and subsequently pressed into a pellet with a diameter of 10 mm. The frequencies of the main absorption bands are given in Table 3, a spectrum of $K_2[Pt(CN)_4] \cdot H_2O_2$ is shown in Fig. 3.

Results and Discussion

Crystal Structures

Up to now, only one previous report on a hydrogen peroxide adduct of a platinum salt, $[PtCl_2(NH_3)_2(OH)_2] \cdot 2\ H_2O_2$ [12], is documented. The new hydrogen peroxide adducts $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs), presented here, crystallize monoclinically in the space group $C2/c$, and the structures consist of square planar tetracyanoplatinate groups stacked in a staggered conformation along the c axis, thus forming one-dimensional chains of platinum atoms (Figs. 1 and 2). The same arrangement is observed in most hydrated and anhydrous cyanoplatinates [6, 7]. The platinum separations of 3.27 to 3.29 Å (Table 2) are in the range expected for non-oxidized cyanoplatinates, but significantly shorter than in the monohydrates (*c. f.* d(Pt–Pt) = 3.58 Å in $K_2[Pt(CN)_4] \cdot H_2O$ [6], d(Pt–Pt) = 3.42 Å in $Rb_2[Pt(CN)_4] \cdot 1.5\ H_2O$ [9] d(Pt–Pt) = 3.54 Å in $Cs_2[Pt(CN)_4] \cdot H_2O$ [13]), and pronouncedly larger than in the partially oxidized salt $K_{1.74}[Pt(CN)_4] \cdot 1.8\ H_2O$, d(Pt–Pt) = 2.96 Å [3] and in $A_{1.75}[Pt(CN)_4] \cdot y\ H_2O$ (A = Rb, Cs), d(Pt–Pt) = 2.88 to 2.94 Å [4], thus suggesting only weak direct interactions between the platinum atoms.

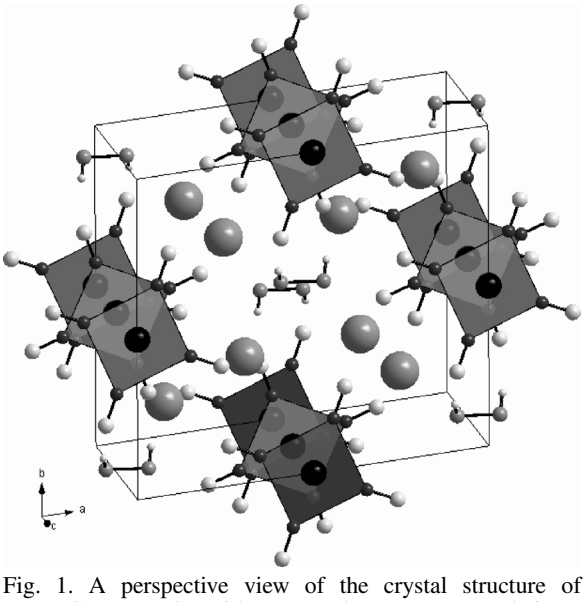

Fig. 1. A perspective view of the crystal structure of $K_2[Pt(CN)_4] \cdot H_2O_2$ with square planar tetracyanoplatinate groups. Black spheres represent platinum atoms, large grey spheres – potassium atoms, small black spheres – carbon atoms, light-grey spheres – nitrogen atoms, small grey spheres – oxygen atoms. The black lines mark the unit cell.

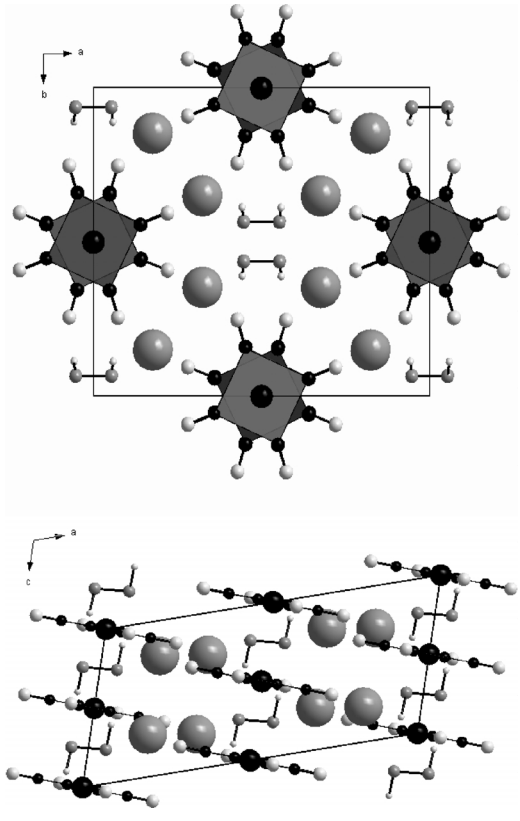

Fig. 2. A section of the crystal structure of $Cs_2[Pt(CN)_4] \cdot H_2O_2$. Top: view onto the crystallographic ab plane; bottom: view onto the ac plane. Black spheres represent platinum atoms, large grey spheres – caesium atoms, small black spheres – carbon atoms, light-grey spheres – nitrogen atoms, small grey spheres – oxygen atoms. The black lines mark the unit cell.

The alkali metal atoms are coordinated by six nitrogen atoms in the shape of a distorted trigonal prism with two of the faces capped by oxygen atoms raising the coordination number to eight. The distances d(A–N1) ranging from 2.84 to 3.21 Å (Table 2) grow as is to be expected from A = K to Cs, and are similar to those known for other non-oxidized cyanoplatinates [6, 7].

Table 3. IR absorption bands (cm^{-1}) of $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs)[a].

	A = K	A = Rb	A = Cs
δ(Pt–C≡N)	410 s	411 s	411 s
δ(Pt–C)	503 s	504 s	505 s
ν(O–O)	870 w	877 w	878 w
$\delta_{s/as}$(O–H)	1386 s	1398 s	1415 s
ν(C≡N)	2132 vs	2127 vs	2120 vs
ν_s(O–H)	2742 w	2758 w	2780 s
ν_{as}(O–H)	3229 s	3231 s	3204 s

[a] vs = very strong, s = strong, w = weak.

The symmetry-independent Pt1–C1, Pt1–C2 (1.984 – 1.997 Å) and C1–N1, C2–N2 bonds (1.144 – 1.149 Å) of the planar cyanoplatinate groups show a small spread over all compounds (Table 2). Along the *c* axis, the adjacent tetracyanoplatinate groups are rotated with torsion angles C–Pt–Pt–C different from 45°, decreasing from K (43.0°) and Rb (39.6°) to Cs (37.5°). This dihedral angle is regarded indicative of the degree of the platinum $5d_{z^2}$ orbital overlap [14]. Furthermore this rotation of the $Pt(CN)_4$ groups enables hydrogen peroxide to form hydrogen bonds to the nitrogen atoms with the characteristic distances of d(OH···N) = 2.8 to 3.1 Å and d(O–O) = 1.42 to 1.45 Å, similar to those observed for $[PtCl_2(NH_3)_2(OH)_2] \cdot 2\,H_2O_2$ [12].

Remarkably, in $Cs_2[Pt(CN)_4] \cdot H_2O_2$ the O–H bonds with 1.19 Å are significantly longer and weaker, than in the potassium and rubidium compounds, and the hydrogen atoms appear to be shifted towards the nitrogen atoms forming stronger N···H interactions. The O1–O1 distances and the O1–N1 separations in the cesium cyanoplatinate peroxide adduct clearly are shorter than in the other two compounds but do not induce a significant effect on the principal structural features.

Depending on the cation size, the unit cell varies only in the *a* and *b* axis but not significantly with respect to the *c* axis. Thus, only the hydrogen bonds were affected by the type of the alkali cation but not the Pt–Pt interactions of the platinum chains along the *c* axis.

Physical properties

The decomposition of $K_2[Pt(CN)_4] \cdot H_2O_2$, as measured by DTA and TG-MS, starts at 100 °C with loss of hydrogen peroxide. According to the MS the evolving entities are HO, H_2O and H_2O_2. At temperatures higher than 700 °C the CN groups are also leaving. Powder X-ray diffraction measurements of the solid residues confirm a decomposition to elemental platinum. The thermal decompositions of $Rb_2[Pt(CN)_4] \cdot H_2O_2$ and $Cs_2[Pt(CN)_4] \cdot H_2O_2$ proceed in a similar way.

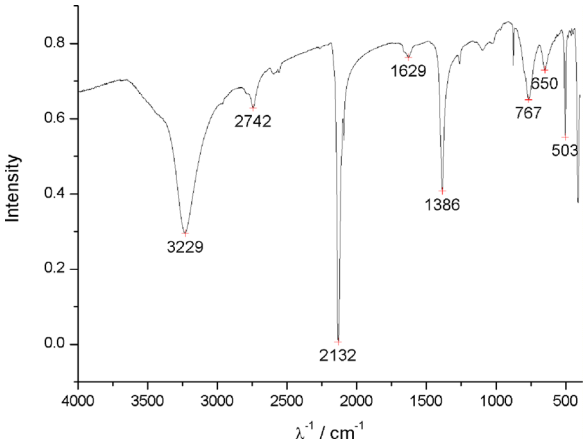

Fig. 3. Infrared spectrum of $K_2[Pt(CN)_4] \cdot H_2O_2$.

In all three infrared spectra (one is shown in Fig. 3, frequencies are given in Table 3) of $A_2[Pt(CN)_4] \cdot H_2O_2$ (A = K, Rb, Cs) the strong absorption bands at 2120 – 2132 cm^{-1}, which are associated with the valence vibrations of the cyanide groups [15], and correspond to the ν(C≡N) valence vibrations of anhydrous and hydrated alkali metal cyanoplatinates [6, 7], are similar in accord with the similar Pt–Pt distances in all three compounds. The frequencies of the vibration of coordinated C≡N groups in the tetracyanoplatinates are much higher than in KCN (2080 cm^{-1}) [6]. The strong bands at 503 – 505 cm^{-1} are assigned to the deformation vibrations of the Pt–C bonds [15, 16]. The absorption bands of the deformation vibrations of the Pt–C≡N groups occur at 410 – 411 cm^{-1} [6, 14]. The hydrogen peroxide can be identified by the weak ν(O–O) valence vibration at 870 to 878 cm^{-1} [17], the δ(O–H) deformation and the characteristic broad δ(O–H) valence vibrations. In the K and Rb compounds, the deformation vibration occurs at similar frequencies at $\delta_{s/as}$(O–H) = 1386 and 1398 cm^{-1} whereas in the Cs compound it is shifted to 1415 cm^{-1}. The symmetric valence vibrations ν_s(O–H) at 2742 (K), 2758 (Rb) or 2780 cm^{-1} (Cs) relate to the overtone of the deformation vibration with lower intensity and at lower frequency. The asymmetric valence vibrations ν_{as}(O–H) at 3229 (K), 3231 (Rb) and 3204 (Cs) occur at lower frequencies for hydrogen peroxide than for water molecules [18] and reflect the

longer and weaker O–H bonds in $Cs_2[Pt(CN)_4] \cdot H_2O_2$, as compared to the K and Rb analogs. Thus, the findings on the hydrogen bonding distances varying from the potassium and rubidium platinate to the cesium representative seem to be corroborated by infrared spectroscopy.

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