Crystal Structure Elucidation of Anhydrous $Rb_2[Pt(CN)_4]$ from X-Ray Powder Diffraction Data

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The title compound has been synthesized by metathesis of $Ba[Pt(CN)_4] \cdot 4\ H_2O$ with Rb_2SO_4, in aqueous solution. Its crystal structure was solved from X-ray powder diffraction data using the simulated-annealing approach, and refined by Rietveld's method. The compound crystallizes in space group *Imma*, $a = 11.1432(2)$, $b = 7.4382(1)$, $c = 11.1896(2)$ Å, $V = 927.45(3)$ Å^3, $Z = 4$, $R_p = 0.0402$, $R_w = 0.0247$ ($N_{hkl} = 173$). Square-planar tetracyanoplatinate groups stack in an unprecedented eclipsed conformation, forming one-dimensional linear chains of Pt-atoms with Pt–Pt separations of 3.719 Å. $Rb_2[Pt(CN)_4]$ was characterized by differential thermal analysis, thermogravimetry and infrared spectroscopy.

Key words: Cyanoplatinate, Rubidium, IR Spectroscopy, X-Ray Powder Diffraction

Introduction

Since the discovery of the platinum cyanocomplexes by Leopold Gmelin at the beginning of the 19th century [1], this class of compounds has continued to attract attention. First, the emphasis was put on their chemical characterization [2], and the investigation of chemical [3] as well as optical properties [4]. The first crystal structure determination was performed by Bozorth and Pauling on single crystals of $MgPt(CN)_4 \cdot 7\ H_2O$ in 1932, documenting the presence of linear stacks of $[Pt(CN)_4]^{2-}$ units [5]. A milestone in cyanoplatinate chemistry is marked by the structural characterization of oxidized salts by Krogmann in the 1960ies [6]. He revealed a significant contraction of the Pt–Pt distances in the oxidized products to a value as short as 2.8 Å and proposed 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. Since Krogmann's pioneering work a huge number of publications has revealed amazing physical-structural correlations in this class of compounds. A comprehensive review is given *e. g.* by Williams in [7].

Anhydrous unoxidized cyanoplatinates are important precursors for the preparation of these 1D metals. But only recently the first crystal structure of such a compound, $K_2Pt(CN)_4$, was clarified [8]. The main difficulties, at an earlier stage, were probably due to a lack of suitable single crystals combined with a deficit of powerful structure solution methods from powder X-ray diffraction data.

Herein we report on the synthesis of $Rb_2Pt(CN)_4$ and its crystal structure determination from powder X-ray diffraction data. The compound was investigated by differential thermal analysis (DTA), thermogravimetry connected with a mass spectrometer (TG-MS), and infrared spectroscopy (IR).

Experimental Section

Synthesis

A concentrated aqueous solution of $Ba[Pt(CN)_4] \cdot 4\ H_2O$ (Chempur, 99.9%) was mixed with a stoichiometric amount of an aqueous solution of Rb_2SO_4 (Sigma-Aldrich, 99.8%) as described in [9]. After removing $BaSO_4$ by filtrating, the clear residual solution was concentrated at 60 °C and then cooled to 4 °C in a refrigerator. The colorless crystals of $Rb_2[Pt(CN)_4] \cdot 1.5\ H_2O$ were filtered and dehydrated at 100 °C under vacuum. The as obtained anhydrous $Rb_2[Pt(CN)_4]$ is a pale pink powder, sensitive to moisture.

Crystal structure determination

The powder X-ray diffraction pattern of $Rb_2[Pt(CN)_4]$ was collected from a sample sealed in a 0.3 mm glass capillary on a D8 Advance diffractometer (Bruker-AXS, Germany) in the Debye-Scherrer geometry (Cu-$K_{\alpha 1}$, $\lambda =$

Table 1. Crystallographic data and details of the powder structure refinement of $Rb_2[Pt(CN)_4]$.

Formula	$Rb_2[Pt(CN)_4]$
Formula weight /g·mol^{-1}	470.09
Crystal system	orthorombic
Space group	*I m m a* (No. 74)
Z (formula units)	4
a/Å	11.1432(2)
b/Å	7.4382(1)
c/Å	11.1896(2)
V/Å^3	927.45(3)
T/K	295
ρ_{calc}/g·cm^{-3}	3.366
Radiation, wavelength λ/Å	Cu-K$_{\alpha 1}$, 1.5406
Capillary diameter/mm	0.3
2θ-Range, step/°	8 to 80, 0.017207
Number of points	4142
Number of Bragg reflexes	173
Number of profile parameters	37
Number of structural parameters	15
R_p/%[a]	4.02
R_{wp}/%[a]	5.06
R_w (all)/%[a]	2.47
GOF[a]	1.58

[a] R_p, R_{wp}, R_w and GOF as defined in JANA2000.

1.5406 Å, $8 < 2\theta < 80$ degrees in steps of 0.017207 degree). The diffraction pattern was indexed using the DICVOL91 algorithm [10] implemented in the DASH program package [11], and an orthorhombic cell was found. Then, the Bragg peak intensities were extracted using a Pawley fit, and the space group *Imma* was found to be the most likely as evaluated by the probabilistic approach [12]. This assumption was proved by the following successful structure determination. The formula unit number $Z = 4$ was deduced from volume considerations.

The structure was solved using the simulated-annealing approach embodied within the DASH program package. Tetracyanoplatinate (TCP) ions, constrained to their typical geometric parameters (a planar square with d(Pt–C) = 1.99 Å, d(C–N) = 1.16 Å [9], C–Pt–C = 90°, Pt–C–N = 180°), and rubidium atoms were used as building blocks. The resulting structural model was then refined applying Rietveld's method [13] with the JANA2000 program [14]. The peak profile and the lattice constants were fitted using Le-Bail's method. The background was modelled with a Legendre polynom of the 10th order. The $[Pt(CN)_4]$ group was described as a Rigid-Body with the displacement parameters of the Pt-atom refined anisotropically, and equal isotropic displacement parameters of the light elements. A free refinement of this group led to an unrealistic distortion originating from flat minima of the electron density around the light elements. A small amount of the Rb_2SO_4 impurity was included in the Rietveld refinement as a second phase, with four profile parameters (lattice constants plus the Lorentzian L_Y parameter) allowed to vary. The details of the structure refinement are given in the Table 1. The best Rietveld profile is shown in Fig. 1. The atomic parameters obtained, together with the respective displacement parameters, are listed in Table 2.

Table 2. Atomic positions and displacement parameters U_{eq}(isotropic)/U_{ij}(anisotropic) of $Rb_2[Pt(CN)_4]$.

Atom	Site	Occ.	x	y	z	U_{eq}/U_{ij} /Å^2
Pt	4*a*	1	0	0	0	$U_{11} = 0.0074(9)$; $U_{22} = 0.0172(8)$; $U_{33} = 0.0194(9)$; $U_{12} = U_{13} = 0$; $U_{23} = -0.007(1)$
Rb1	4*c*	1	1/4	1/4	1/4	0.0286(8)
Rb2	4*e*	1	0	1/4	0.5278(2)	0.0224(8)
C1	8*h*	1	0	0.0167(6)	0.1774(1)	0.008(1)
N1	8*h*	1	0	0.0270(9)	0.2807(1)	0.008(1)
C2	8*f*	1	0.1784(1)	0	0	0.008(1)
N2	8*f*	1	0.2824(1)	0	0	0.008(1)

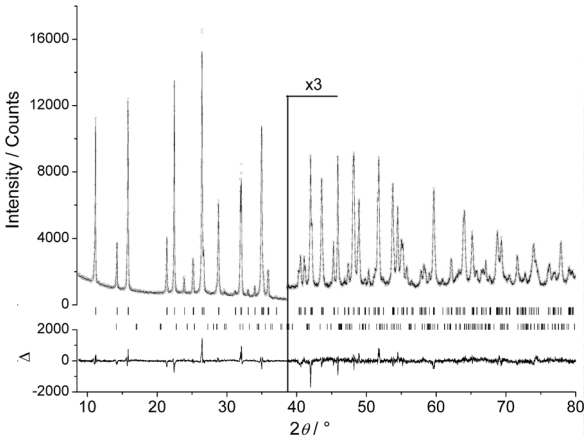

Fig. 1. Observed and calculated powder X-ray diffraction pattern for $Rb_2[Pt(CN)_4]$ at room temperature. Shown are the observed (circles) and calculated (solid line) data and the enlarged difference curve between observed and calculated profiles (below in an additional window). Vertical lines indicate the Bragg reflection positions for $Rb_2[Pt(CN)_4]$ (top) and Rb_2SO_4 (bottom). The high angle part is enlarged for clarity.

Physical properties

Differential thermal analysis (DTA), and thermogravimetry (TG) equipped with a mass spectrometer (MS) for analyzing the volatile decomposition products were performed with a computer-controlled thermal analyzer (STA 409, Netzsch GmbH, Germany). A powder sample (20 mg) was placed in a corundum crucible, heated to 800 °C with a rate of 10 °C/min, and then cooled down to room temperature with the same rate. The whole process was run under argon.

An IR spectrum was recorded on an IR-Spectrometer (113v, Bruker, Germany) from 2 – 3 mg of the sample thor-

Table 3. Selected atomic separations (/Å) and angles (/°) of $Rb_2[Pt(CN)_4]$.

Pt – Pt	3.719(0) 2×	Rb2 – N1	2.973(5) 2×
Pt – C1	1.989(1) 2×		3.224(4) 2×
Pt – C2	1.989(1) 2×	Rb2 – N2	3.072(1) 4×
C1 – N1	1.159(2)		
C2 – N2	1.159(2)	C1 – Pt – C2	90.0
Rb1 – N1	3.260 (3) 4×	Pt – C1 – N1	179.8(5)
Rb1 – N2	3.378 (1) 4×	Pt – C2 – N2	180.0

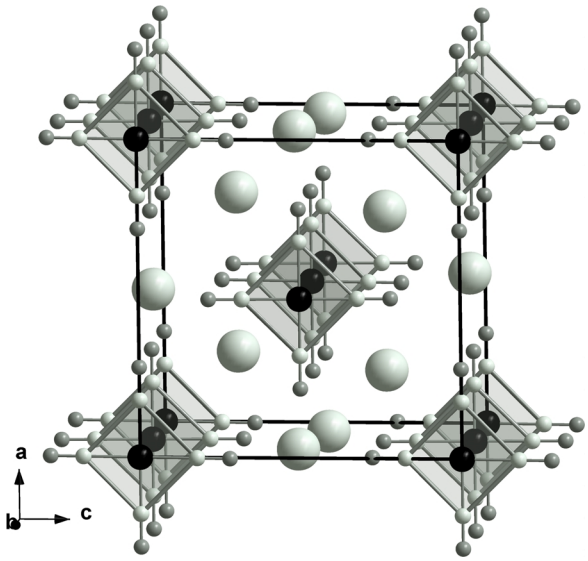

Fig. 2. A perspective view of the crystal structure of $Rb_2[Pt(CN)_4]$ with square planar tetracyanoplatinate groups emphasized. Black spheres represent platinum atoms, large light-grey spheres – rubidium atoms, small light-grey spheres – carbon atoms, dark-grey spheres – nitrogen atoms. Black lines mark the unit cell.

oughly mixed and ground with ∼ 400 mg of KBr (Aldrich, 99%, dried at 200 °C in vacuum) and subsequently pressed into a pellet with a diameter of 10 mm.

Results and Discussion

Crystal structure

The crystal structure of the compound consists of square planar TCP groups stacked in an eclipsed conformation to form one dimensional chains of platinum atoms (Fig. 2). The same (eclipsed) arrangement of anions is observed *e. g.* in alkali tetrachloroplatinates [15, 16]. Platinum separations (3.72 Å, Table 3) are in the range as expected for non-oxidized TCP compounds (*c.f.* d(Pt–Pt) = 3.52 Å in $K_2[Pt(CN)_4]$ [8], or d(Pt–Pt) = 3.42 Å in $Rb_2[Pt(CN)_4] \cdot 1.5\ H_2O$ [9]), and are significantly larger than in the Krogmann's salt (d(Pt–Pt) = 2.8 Å [6]), thus suggesting only weak or virtually no interactions between platinum d_{z^2} orbitals.

The eclipsed conformation of the TCP groups is quite unusual, and was not observed before. Two structural features may be related to this phenomena. (1) The large separation of the complex anions reduces the (CN)–(CN) repulsion, and favours van der Waals attraction, (2) the larger size of Rb as compared to K in $K_2[Pt(CN)_4]$ induces the eclipsed stacking in order to satisfy its coordination requirements. Both crystallographically different rubidium atoms are coordinated by eight nitrogen atoms in a shape of distorted cubes at distances ranging from 3.07 to 3.38 Å (Table 3), which are similar to other known rubidium TCP (d(Rb–N) = 3.00 – 3.28 Å in $Rb_2[Pt(CN)_4] \cdot 1.5\ H_2O$ [9], or d(Rb–N) = 3.03 – 3.30 Å in $Rb_2[Pt(CN)_4]Br_2$ [17]). Slightly shorter distances in the hydrate and bromide compounds are due to the more electronegative oxygen or bromine atoms, respectively.

Physical properties

The decomposition of $Rb_2[Pt(CN)_4]$, as measured by DTA and TG-MS, starts at temperatures above 700 °C. According to MS data, the evolving fragments are CN groups. Powder X-ray diffraction measurements on the solid residues confirm a partial decomposition of the TCP to elemental platinum. This thermal decomposition was also observed for $K_2[Pt(CN)_4]$ [8]. Any thermal effects up to the decomposition point have not been observed, thus ruling out phase transitions in the considered temperature region.

The infrared spectrum of anhydrous $Rb_2[Pt(CN)_4]$ shows a strong absorption band at $\nu = 2132\ cm^{-1}$ together with a weak band at $\nu = 2092\ cm^{-1}$, which are associated with the valence vibrations of the cyanide groups [8, 18]. The strong band at $\nu = 505\ cm^{-1}$ is assigned to the deformation vibration of the Pt–C bonds [18, 19]. The absorption band of the valence vibration of the Pt–C ≡ N group occurs at $\nu = 411\ cm^{-1}$ [8, 19].

Acknowledgements

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