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The Preparation and Crystal Structure of *cis* and *trans* Potassium Tetrachlorodinitroplatinate(IV)

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The complex cis-$K_2PtCl_4(NO_2)_2$ *was prepared by reacting* $K_2Pt(NO_2)_4$ *with 50%* H_2SO_4 *at 100 °C and passing the resulting solution through a column of anion-exchange resin in the chloride form. The product that resulted from the initial reaction with sulfuric acid was* cis-$K_2Pt(NO_2)_2(SO_4)_2$ *which is an intermediate in the formation of the platinum(III) dimer* $K_2[Pt_2(SO_4)_4(H_2O)_2]$. *Crystals of* cis-$K_2PtCl_4(NO_2)_2$ *were obtained by evaporation and crystallized in a unit cell with parameters* $a = 6.438(2)$ Å, $b = 7.458(2)$ Å, $c = 10.984(2)$ Å, $\alpha = 89.66(2)°$, $\beta = 99.08(2)°$, $\gamma = 92.06(3)°$, $V = 520$ Å^3, $Z = 2$, *space group* $= P\bar{1}$. *The previously reported preparation of this* cis *isomer produced the* trans *isomer which crystallized in the orthorhombic space group Fddd with unit cell constants* $a = 15.356(3)$ Å, $b = 18.431(4)$ Å, $c = 7.361(2)$ Å, $V = 2083$ Å^3, $Z = 8$.

Introduction

In 1958, Babaeva and Ushakova reported the synthesis of both the *cis* and *trans* isomers of $K_2PtCl_4(NO_2)_2$ [1]. The *cis* complex was prepared by the oxidation by chlorine of *cis*-$K_2PtCl_2(NO_2)_2$ which was prepared by the reaction of equimolar amounts of K_2PtCl_4 and $K_2Pt(NO_2)_4$. The *trans* isomer was prepared by the reaction of chlorine with *trans*-$Pt(NO_2)_2(NH_2OH)_2$. However, in a later study it was determined that the Pt–Cl stretching frequencies of these two isomers were identical and it was suggested that both complexes actually had the *trans* geometry [2].

From the reaction of $K_2Pt(NO_2)_4$ with sulfuric acid at 100 °C followed by reaction with chloride ion, a yellow-green crystalline product was obtained. Structural characterization proved this to be the *cis* isomer of $K_2PtCl_4(NO_2)_2$. This material was physically different from the previously reported *cis* isomer. Therefore, it was decided to also structurally characterize the previously prepared complex. In this paper we report the synthesis and crystal structure of both the *cis* and *trans* isomers of $K_2PtCl_4(NO_2)_2$.

Experimental

Synthesis of trans-$K_2PtCl_4(NO_2)_2$

The previously reported synthesis for *cis*-$K_2PtCl_4(NO_2)_2$ was used [1]. Equal molar amounts of K_2PtCl_4 and $K_2Pt(NO_2)_4$ were dissolved in the minimal amount of water. The solution was placed in an oven at 80 °C and taken to dryness. Chlorine was bubbled through a solution of the resulting yellow powder. Yellow crystals of *trans*-$K_2PtCl_4(NO_2)_2$ were obtained by evaporation.

Synthesis of cis-$K_2PtCl_4(NO_2)_2$

A solution of 0.1 g of $K_2Pt(NO_2)_4$ in 10 ml of 50% H_2SO_4 was kept at 95–100 °C for 3–4 hours. The solution was cooled and any $K_2[Pt_2(SO_4)_4(H_2O)_2]$ formed was filtered off. The solution was diluted with water and passed through a DOWEX 1X-8 anion exchange resin column about 4 cm long. The resin was in the chloride form. The column was washed with water and then eluted with 0.5 *M* H_2SO_4. Evaporation of this solution resulted in the formation of large yellow-green crystals of *cis*-$K_2PtCl_4(NO_2)_2$.

X-Ray Crystallography

The data for the crystallographic experiments are given in Table I. The crystallography on each isomer was conducted using similar procedures. All measurements were made on an Enraf-Nonius CAD-4 diffractometer using Mo-K_α radiation. The procedures and programs used have been previously reported [3]. The unit cells were determined from the least squares fit of twenty-five accurately centered reflections. Absorption corrections were made using the empirical correction method and Flack's Camel Jockey with Three Humps [4].

Results and Discussion

The *cis* isomer of $K_2[PtCl_4(NO_2)_2]$ was prepared accidentally during the preparation of the platinum(III) dimer $K_2[Pt_2(SO_4)_4(H_2O)_2]$. This dimer is prepared by the reaction of $K_2Pt(NO_2)_4$ with 50% H_2SO_4 at 120 °C. During the reaction the solution turns dark blue, then green, and finally produces the dark yellow-orange precipitate which is the product [5]. Copious amounts of NO_2 are given off during the reaction. If the reaction is heated to temperatures greater than 120 °C, the final product is a red solu-

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TABLE I. Crystallographic Data for $K_2PtCl_4(NO_2)_2$.

	cis isomer	*trans* isomer
A (Å)	6.438(2)	15.356(3)
B (Å)	7.458(2)	18.431(4)
C (Å)	10.984(2)	7.361(2)
α (deg)	89.66(2)	90.0
β (deg)	99.08(2)	90.0
γ (deg)	92.06(3)	90.0
Space group	$P\bar{1}$	Fddd
Volume $Å^3$	520	2083
Z	2	8
Crystal dimensions (mm)	0.38 × 0.16 × 0.09	0.48 × 0.4 × 0.4
Molecular weight (AMU)	507.1	507.1
ρ_{calc} (g/cm^3)	3.22	3.23
μ (cm^{-1})	159.6	159.3
Maximum 2 θ	50°	50°
Number of unique data	1994	538
Number of data with $I > 3\sigma(I)$	1835	412
Final value R	0.059	0.043
Final value R_w	0.076	0.061

tion which presumably contains polymeric complexes.

Because of the great temperature sensitivity of this reaction, it was decided to run the reaction at 100 °C. At first, the reaction proceeded identically to that of the synthesis of the dimer. However, after 15–20 minutes the evolution of NO_2 ceased but little or no precipitate was obtained. Holding the reaction at 100 °C for periods as long as 24 hours did not result in the formation of the dimer. However, if the solution was heated to 120 °C, NO_2 gas was again produced and the dimer precipitated out after several minutes. This suggests that the yellow solution resulting from the reaction at 100 °C must contain an intermediate in the dimer formation.

In order to isolate this intermediate, ion exchange chromatography was used. First, the sulfuric acid solution was diluted with water. This must be done carefully because the heat evolved can warm the solution above 100 °C and restart the reaction. The diluted solution was then passed over a 4 cm long column of DOWEX 1X-8 anion exchange resin in the chloride form. Usually, not all the platinum complex adhered to the column. If an extremely long column was used, the entire product could be removed from solution. However, then it was extremely difficult to elute the platinum complex from the column. After washing, the column was eluted with 0.5 M H_2SO_4 to yield a dilute solution of *cis*-$K_2PtCl_4(NO_2)_2$. Crystals were obtained by evaporation of these solutions. Attempts to isolate and elute the original product from resin in the sulfate form were only partially successful. Evaporation of the resulting solutions yielded only amorphous powders and K_2PtCl_6.

One of the important features of this reaction appears to be the fact that sulfate is a poor ligand and will not directly displace nitrite from the platinum coordination spheres. When any of the above reactions were attempted using hydrochloric acid in place of sulfuric acid, the only product obtained was K_2PtCl_6. This appears to be the result of displacement of the nitrite ligands by chloride. In acid solutions, the displaced nitrite ion forms NO and NO_2. Thus, the evolution of these gases is no proof of proton attack on a coordinated nitrite as previously suggested [5].

While the exact nature of the intermediate in the original sulfuric acid solution is unknown, its structure can be surmised. Since the reaction at 100 °C produces NO_2, some of the nitrite ligands must be lost. However, some must also remain since further heating results in the evolution of more NO_2. The only other ligands present in the sulfuric acid solutions are sulfate or bisulfate ions. In addition, the complex must be anionic since it is removed from solution by ion exchange resin. Therefore, it appears likely that the yellow complex in solution is *cis*-$K_2Pt(SO_4)_2(NO_2)_2$. This product must have two chelating sulfate ligands. Therefore, it appears that the precursor to the platinum(III) dimers is a platinum(IV) intermediate and not a platinum(II) species. Thus the dimers are the result of a reduction reaction.

For several reasons, the preparation of *cis*-$K_2PtCl_4(NO_2)_2$ reported here is not a viable synthesis. The total yields were low. The biggest problem is getting the yellow product to bind to the ion exchange resin and then eluting it under mild conditions. Sulfuric acid was used because of the −2 charge on the sulfate. However, if concentrated acid was used, excess chloride was also eluted from the column resulting in the production of $PtCl_6^{2-}$. Attempts to obtain better yields were not successful.

The crystal structure of *cis*-$K_2PtCl_4(NO_2)_2$ is quite typical. The bond distances and angles are given in Table II and an ORTEP drawing of the anion is shown in Fig. 1. Table III provides the coordinates of the atoms. The anion is located at a general position in the triclinic unit cell. Therefore, there is no crystallographically imposed symmetry. In fact, there is a large variation in the Pt–Cl bond lengths. However, this variation is not a function of the position of the chloride with respect to the nitrite ligands. While the chlorides *trans* to the nitro ligands (Cl(2) and Cl(4)) are slightly longer, this result is not statistically meaningful. In fact, the interaction with the potassium cations (*vide infra* and Table VI) appears to be a more important factor. The shortest Pt–Cl distance is to Cl(1) which only weakly interacts with one potassium. On the other hand, the longest distance is

TABLE II. Bond Distances (in Å) and Angles (in Deg) for *trans*- and *cis*-$K_2PtCl_4(NO_2)_2$.

Cis			
Pt–Cl(1)	2.299(5)	N(1)–O(11)	1.21(1)
Pt–Cl(2)	2.329(4)	N(1)–O(12)	1.22(2)
Pt–Cl(3)	2.338(4)	N(2)–O(21)	1.17(2)
Pt–Cl(4)	2.362(4)	N(2)–O(22)	1.21(2)
Pt–N(1)	2.06(1)		
Pt–N(2)	2.07(1)		
Cl(1)–Pt–Cl(2)	89.3(2)	Cl(4)–Pt–N(1)	88.7(3)
Cl(1)–Pt–Cl(3)	177.4(1)	Cl(4)–Pt–N(2)	179.5(4)
Cl(1)–Pt–Cl(4)	89.2(2)	N(1)–Pt–N(2)	91.2(4)
Cl(1)–Pt–N(1)	91.1(4)	Pt–N(1)–O(11)	118.0(9)
Cl(1)–Pt–N(2)	91.3(4)	Pt–N(1)–O(12)	120.0(9)
Cl(2)–Pt–Cl(3)	88.7(1)	O(11)–N(11)–O(12)	122(1)
Cl(2)–Pt–Cl(4)	90.6(1)	Pt–N(2)–O(21)	118(1)
Cl(2)–Pt–N(1)	179.2(3)	Pt–N(2)–O(22)	120(1)
Cl(2)–Pt–N(2)	89.5(4)	O(21)–N(2)–O(22)	121(1)
Cl(3)–Pt–Cl(4)	89.2(1)		
Cl(3)–Pt–N(1)	90.9(4)		
Cl(3)–Pt–N(2)	90.4(4)		
Trans[a]			
Pt–Cl	2.319(3)	N–O	1.25(1)
Pt–N	2.09(2)		
Cl–Pt–N	89.11(9)	O–N–O′	121(2)
Cl–Pt–Cl′	178.2(2)		
Cl–Pt–Cl″	91.4(2)		

[a] Atoms designated by are related by the two-fold axis formed by Pt–N. Atom designated by ″ is related by a two-fold axis perpendicular to the Pt–N bond.

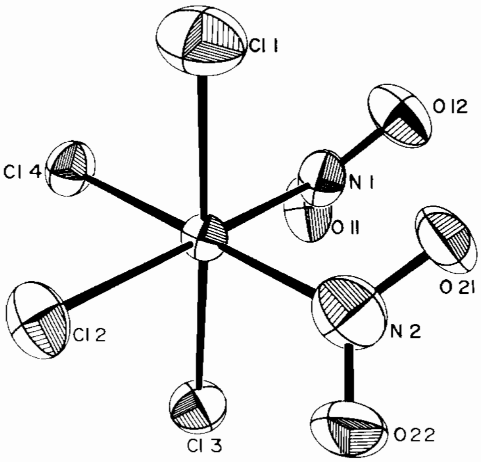

Fig. 1. An ORTEP diagram of *cis*-$[PtCl_4(NO_2)_2]^{2-}$ illustrating the numbering system used. The ellipsoids are drawn at the 50% probability level.

to Cl(4) which interacts strongly with two potassium cations. The angles between the planes of the nitrite ions and the platinum-chlorine planes are given in

TABLE III. Positional Parameters for the Atoms of *Cis*-$Pt_2Cl_4(NO_2)_2$, Fanwick and Evans, 1983.

Atom	X[a]	Y	Z
Pt	0.12003(6)	0.25767(5)	0.24860(4)
Cl1	−0.0561(9)	0.2259(8)	0.0505(4)
Cl2	−0.1231(6)	0.4658(5)	0.2866(4)
Cl3	0.2859(6)	0.2908(6)	0.4553(4)
Cl4	−0.0914(6)	0.0235(5)	0.3102(4)
K1	0.2172(6)	0.7435(5)	0.4673(3)
K2	0.6457(6)	0.7659(4)	0.1072(3)
N1	0.335(2)	0.071(1)	0.217(1)
N2	0.308(2)	0.463(2)	0.196(1)
O11	0.400(2)	−0.031(2)	0.301(1)
O12	0.394(2)	0.066(2)	0.1177(10)
O21	0.373(2)	0.450(1)	0.0987(9)
O22	0.352(2)	0.590(2)	0.259(1)

[a] Estimated standard deviations in the last figure(s) are given in parentheses in this and all subsequent tables.

Table IV. The planes defined by two nitrite ions make an angle of 68.8° with respect to each other. These planes also make an angle of ~53° with respect to the plane defined by the platinum and the two chlorines *trans* to these nitro ligands. Again, interactions with the cation play an important part in determining these angles.

The structure of *fac*-$K_2[PtCl_3(NO_2)_3]$ ·has been previously reported [6]. There are slight differences in the bond distances for this complex and *cis*-$K_2PtCl_4(NO_2)_2$. The greatest difference is for the Pt–N distances which average 2.07(1) Å in the structure reported here and 2.20 Å in the *fac* complex. In addition, the O–N–O angles average 122(1)° and 128° in the two respective structures. In KNO_2 this angle was 115.3° [7]. It was observed that the O–N–O angle always increases upon coordination [6]. However, the cause of this increase is not obvious. Clearly, it is not a function of the strength of the π-interaction, since the angles of the nitrite planes

TABLE IV. Interplanar Angles for *cis*-$K_2PtCl_4(NO_2)_2$.

Plane 1 – Pt, Cl(1), Cl(3)
Plane 2 – Pt, Cl(2), Cl(4)
Plane 3 – N(1), O(11), O(12)
Plane 4 – N(2),, O(21), O(22)

Plane	Angles
1–2	89.8
1–3	128.4
1–4	59.6
2–3	53.8
2–4	50.2
3–4	68.8

TABLE V. Positional Parameters for the Atoms of *Trans*-$Pt_2Cl_4(NO_2)_2$, Fanwick and Evans, 1983.

Atom	X[a]	Y	Z
Pt	1/8	1/8	1/8
K	0.4797(3)	1/8	1/8
Cl	0.1273(2)	0.0372(2)	0.3504(5)
N	0.259(1)	1/8	1/8
O	0.2987(6)	0.1363(5)	0.270(2)

[a]Estimated standard deviations in the last figure(s) are given in parentheses in this and all subsequent tables.

TABLE VI. Bond Distances for Potassium Cations in *cis*-and *trans*-$K_2PtCl_4(NO_2)_2$ (in Å).

cis isomer			
K(1)–O(22)	2.83(1)	K(2)–O(12)	2.75(1)
K(1)–O(11)	2.84(1)	K(2)–O(21)	2.77(1)
K(1)–Cl(3)	3.197(5)	K(2)–O(12)	2.82(1)
K(1)–Cl(4)	3.229(5)	K(2)–O(21)	2.88(1)
K(1)–Cl(4)	3.235(5)	K(2)–O(22)	2.96(1)
K(1)–Cl(2)	3.241(6)	K(2)–Cl(4)	3.186(5)
K(1)–Cl(2)	3.373(5)	K(2)–Cl(2)	3.221(5)
K(1)–Cl(3)	3.426(5)	K(2)–Cl(1)	3.37(5)
K(1)–Cl(3)	3.477(5)	K(2)–Cl(1)	3.91(5)
trans isomer			
K–O	2.66(1)		
K–O	2.66(1)		
K–O	3.02(1)		
K–O	3.02(1)		
K–Cl	3.411(5)		
K–Cl	3.411(5)		
K–Cl	3.425(4)		
K–Cl	3.425(4)		
K–Cl	3.459(5)		
K–Cl	2.459(5)		

suggest π-bonding to the platinum is minimal. Similarly the shorter Pt–N distance observed for the *cis* complex should result in a greater O–N–O angle if the strength of the Pt–N bond was the cause. This is not the case. Again interaction with the cation may be the overriding factor.

The synthesis of *cis*-$K_2PtCl_4(NO_2)_2$ had been previously reported [1] but these results had been questioned because of spectroscopic evidence [2]. Since the crystals of *cis*-$K_2PtCl_4(NO_2)_2$ were not yellow as previously reported but greenish-yellow and since they were shaped like rhombs and not needles, it was decided to determine the structure of the previously reported material. The synthesis proceeded smoothly and produced large yellow needles which had the same morphology as previously reported for the *cis* isomer.

The unit cell of this compound was found to belong to the orthorhombic space group Fddd. This immediately suggested that this compound was the *trans* isomer. In the unit cell the platinum atom is located at the intersection of three perpendicular two-fold axes. Therefore, the molecule possesses D_2 symmetry. One two-fold axis runs through the Pt–N bonds. The other axes run between the Pt–Cl bonds. The potassium cation is located on the two-fold axis defined by the Pt–N bonds. The end result is that only one atom of each type present in the compound is crystallographically unique. The atomic coordinates are listed in Table V.

The structures of the *cis* and *trans* isomers of $K_2PtCl_4(NO_2)_2$ have a great many similarities. The volumes of a single unit of each isomer are nearly identical. The Pt–Cl and Pt–N distances are comparable. In fact, the Pt–Cl distance of 2.319(2) Å observed in the *trans* isomer is identical to the average distance found for the two chlorines *trans* to each other in the *cis* isomer. Lastly, the O–N–O angles in the two isomers are identical.

The bond distances to the potassium cations are given in Table IV. In the *cis* complex the two potassium cations are each nine-coordinate, while in the *trans* isomer the potassium is ten-coordinate. Since the potassium ion in the *trans* complex is located on a two-fold rotation axis, these coordinating atoms occur in pairs. Many of the K–O and K–Cl interactions are reasonably strong and appear to play an important part in determining the overall geometry of the anion in the solid state.

Acknowledgements

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Supplementary Materials

Tables of Thermal Parameters and Their Errors and Tables of Calculated and Observed Structure Factors for both *cis*- and *trans*-$K_2PtCl_4(NO_2)_2$ are available.

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