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A Tetra-nitrato Complex of Platinum(II). Synthesis and Crystal Structure of $K_2[Pt(NO_3)_4]\cdot\frac{1}{2}H_2O$[†]

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Abstract

$K_2[Pt(NO_3)_4]\cdot\frac{1}{2}H_2O$ was prepared from *ca.* 0.4 M solutions of platinum(II) perchlorate in perchloric acid by addition of $KHCO_3$ and KNO_3. Its crystal structure was determined from X-ray intensity data collected with a CAD-4 diffractometer. Monochromatic MoKα-radiation was used. The space group is $I4/m$ with $Z = 4$; $a = 7.5277(4)$ and $c = 20.470(3)$ Å. The refinement converged to $R = 0.036$. The structure contains discrete complexes, $[Pt(NO_3)_4]^{2-}$, with symmetry $C4$. Pt coordinates four O from different unidentate nitrato groups. The Pt–O distance is 2.010(5) Å. The coordination around Pt is distorted square-planar, with Pt situated 0.14 Å above the plane formed by four O, so that a very flat, square pyramid is formed. Two such pyramids on each side of the mirror plane are packed together with their bases facing each other. The closest O–O distance between them is 3.29(1) Å and the Pt–Pt distance is 3.590(1) Å. The potassium ions are located between the pairs of complexes so that a three-dimensional packing of K^+ and $2x[Pt(NO_3)_4]^{2-}$ is formed.

Introduction

In general, unidentate nitrato complexes are not common. The nitrato group has a tendency to form bridges and to act as a bidentate ligand [2, 3]. With the d^8-metals, particularly palladium(II), platinum(II) and gold(III), nitrate forms very weak complexes compared to most other ligands. Thus, in aqueous solution, nitrato complexes undergo a very rapid aquation. Not many square-planar nitrato complexes have been reported [4, 5].

$K_2[Pd(NO_3)_4]$ is formed by action of concentrated nitric acid on the tetranitrito complex [6]. Attempts to synthesize the corresponding platinum(II) compound by the same method resulted in oxidation to platinum(IV) nitro–nitrato complexes [6], and it was assumed that the tetranitrato complex $Pt(NO_3)_4^{2-}$ was probably unstable [2, 6]. The gold compound $K[Au(NO_3)_4]$ has been prepared [7] and its crystal structure determined [8]. Some other complexes of palladium(II) and platinum(II) containing one or two monodentate nitrato groups have also been synthesized [9–14] and – in a few cases – crystal structures have also been determined [9–12]. Some of those complexes are important in anti-cancer treatment [10].

Dilute solutions of tetra-aquaplatinum(II) can be obtained in perchloric acid solution [15, 16]. The complex $Pt(H_2O)_4^{2+}$ is a versatile starting material for synthesis of other platinum complexes with weak donor ligands, such as oxygen. Thus, squarato and acetylacetonato complexes have recently been prepared [17–20]. We report here the use of relatively concentrated solutions of $Pt(H_2O)_4^{2+}$ in the synthesis of the novel compound $K_2[Pt(NO_3)_4]\cdot\frac{1}{2}H_2O$, together with a determination of its crystal structure.

Experimental

Stock Solutions of $Pt(H_2O)_4^{2+}$

A *ca.* 10 mM solution of tetraaqua platinum(II) perchlorate in aqueous perchloric acid (1.00 M, Baker's p.a.) was prepared from potassium tetrachloroplatinate(II) (Johnson and Matthey) and anhydrous silver perchlorate (G. F. Smith, reagent quality) as described elsewhere [15, 16]. This solution was concentrated by a factor of *ca.* 40 by repeated evaporation, partial neutralization of excess perchloric acid with potassium hydrogen carbonate (Merck, p.a.), and separation of excess perchlorate as the sparingly-soluble potassium salt. The procedure is described in detail elsewhere [16]. It gave

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a 0.44 M stock solution of platinum(II) perchlorate in 1.8 M perchloric acid.

Synthesis of $K_2[Pt(NO_3)_4]\cdot\frac{1}{2}H_2O$

To 4.0 ml 0.44 M platinum(II) perchlorate in 1.8 M perchloric acid under nitrogen was added a calculated quantity (0.66 g) of $KHCO_3$ (Merck p.a.) suspended in 2.0 ml water. This decreased the perchloric acid concentration to 0.10 M and precipitated $KClO_4$(s). The addition was made slowly (dropwise from a pipette) and the solution was stirred magnetically to prevent local excess of base. It was flushed with nitrogen. The $KClO_4$-precipitate was separated by centrifugation, after which the volume of the solution (3.7 ml) and the concentrations of perchloric acid (0.10 M) and platinum (0.28 M) were determined.

Analysis for platinum was made spectrophotometrically at 275 nm, where the molar absorptivitiy of $Pt(H_2O)_4^{2+}$ is 56.5 cm^{-1} M^{-1} [15]. 100 to 200 μl samples of the solution were mixed with 1 ml 1 M perchloric acid. Perchloric acid was determined potentiometrically by use of a glass electrode and a standard calomel reference electrode. 100 μl samples of the solution were diluted to 100 ml with 0.5 M sodium chloride.

A calculated quantity of KNO_3(s) (4 mol/Pt + 1 mol/$HClO_4$; in this case 0.47 g; Merck p.a.) was added to the solution. It was flushed with nitrogen and stirred for 0.5 h to ensure complete dissolution of the nitrate and precipitation of $KClO_4$(s). After cooling on ice for 0.5 h the perchlorate precipitate was separated by centrifugation, and the *ca.* 2.8 ml solution was left for evaporation at ambient temperature. It had the approximate concentration ratios platinum:potassium:nitrate of 1:2.1:4.5. The perchlorate concentration was very low. After a couple of days, brown crystal needles were formed. They were stable for a couple of weeks when kept in a desiccator protected from light.

Single Crystal Work

The intensity data were collected at room temperature with the aid of a CAD-4 diffractometer. Laue class and systematic extinctions were consistent with the space groups $I\bar{4}$, $I4$ and $I4/m$. Cell dimensions were obtained from a least-squares calculation of 25 θ-values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$ (Table I). The diffractometer with $\omega_{\bar{h}\bar{k}\bar{l}}$ measured at negative θ-angle was used. During the intensity data collection three standard reflections were measured at regular intervals. No systematic variations of their intensities were observed. Information on the collection and reduction of the data is given in Table I. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration ($\sigma_c(I)$ is based on counting statistics). Reflections with $I < 3\sigma_c(I)$ were considered insignificantly different from the background and were excluded from all subsequent calculations.

TABLE I. Crystal Data, Collection and Reduction of Intensity Data and Least-Squares Refinement.

Crystal size (mm)	0.25 × 0.11 × 0.12
a(Å)	7.5277(4)
c(Å)	20.470(3)
D_x (g cm^{-3})	3.04
Z	4
MoKα, $\bar{\lambda}$ (Å)	0.7093
μ (cm^{-1})	130.0
Range of transmission factor	0.254–0.347
θ-interval (°)	3–30
$\omega-2\theta$ scan width ($\Delta\omega$/°)	1.1 + 0.5 tan θ
$\sigma_c(I)/I$ requested in a scan	0.028
Maximum recording time (s)	150
Number of reflexions measured	989
Number of reflexions with $I > 3\sigma(I)$, m	846
Number of parameters refined, n	51
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.036
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.048
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$	1.04

TABLE II. Atomic Coordinates.

Atom	x	y	z
Pt	0.0	0.0	0.08770(2)
K(1)	0.0	0.0	0.27145(23)
K(2)	0.1258(11)	0.4472(9)	0.0
O(1)	0.2462(7)	0.1013(8)	0.08030(24)
O(2)	0.2498(10)	0.1564(11)	0.18544(28)
O(3)	0.4749(8)	0.2185(10)	0.1253(4)
N	0.3259(8)	0.1589(8)	0.1343(3)
O(4) (water)	0.0	0.0	0.5

The structure was solved by vector and difference Fourier methods assuming the space group $I4/m$. The structure was refined by a full-matrix least-squares calculation. The function minimized was $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ with empirical weights $w = [(\sigma_c^2/4\lvert F_o\rvert)^2 + (0.03\lvert F_o\rvert)^2 + 6.0]^{-1}$. Scattering factors with corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography [21]. Details of the refinement are given in Table I. The final positional and thermal parameters are given in Tables II and III. A list of structure factors may be obtained through the authors.

Results and Discussion

The compound contains discrete complexes $Pt(NO_3)_4^{2-}$ with symmetry $C4$. The structure of

TABLE III. Anisotropic Thermal Parameters (exp – ($\beta_{11}h^2 + \beta_{22}k^2 + \ldots$).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.00711(6)	0.00711(6)	0.00100(6)	0.0	0.0	0.0
K(1)	0.0139(4)	0.0139(4)	0.0031(4)	0.0	0.0	0.0
K(2)	0.0336(18)	0.0166(11)	0.0015(1)	–0.0119(12)	0.0	0.0
O(1)	0.0085(8)	0.0169(11)	0.0014(1)	–0.0030(8)	0.0008(3)	–0.0006(3)
O(2)	0.0183(14)	0.0264(18)	0.0014(1)	–0.0065(13)	–0.0002(3)	–0.0010(4)
O(3)	0.0084(9)	0.0194(14)	0.0036(2)	–0.0039(9)	0.0004(4)	–0.0025(5)
N	0.0085(9)	0.0099(10)	0.0021(2)	–0.0010(8)	–0.0000(3)	–0.0010(3)
O(4)	0.0154(32)	0.0379(32)	0.0036(12)	0.0	0.0	0.0

the complex is shown in Fig. 1, and Table IV contains selected interatomic distances and angles. Table V compares the parameters of the present complex with those of previously studied d^8 unidentate nitrato complexes.

The platinum coordinates four oxygen atoms from different nitrato groups, which are equivalent to each other. The coordination around Pt is distorted square-planar, with the metal atom situated 0.14 Å above the plane formed by the four oxygen atoms O(1), which are separated 2.83 Å from each other. A very flat square pyramid is formed. The Pt–O(1) distance of 2.010(5) Å is in good agreement with those reported for the other nitrato complexes of platinum (Table V). It is also very similar to the Pt–O distances reported for oxalato complexes (2.007(5) Å) [22], squarato complexes (2.01(1) and 1.99(1) Å) [18]; and for some hydroxo-bridged platinum(II) complexes (2.07 to 1.99 Å) [23]. The sum of the covalent radii is 1.97 Å [24].

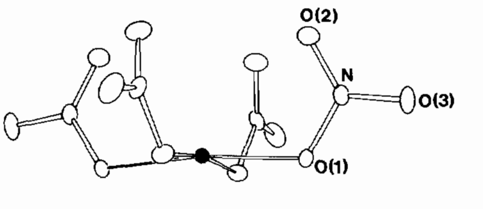


Fig. 1. Perspective view of the tetranitratoplatinate(II) ion.

TABLE IV. Selected Interatomic Distances (Å) and Angles (°) with e.s.d.s.

Pt–O(1)	2.010(5)	N–O(1)	1.330(8)
Pt–O(2)	2.988(7)	N–O(2)	1.194(9)
Pt–N	2.891(6)	N–O(3)	1.222(9)
Pt–Pt	3.590(1)	O(2)–O(2)^a	3.138(10)
K(1)–O(2)	2.832(7)		
K(1)–O(3)	2.999(8)	O(1)–N–O(3)	114.1(7)
K(2)–O(1)	2.813(8)	O(1)–N–O(2)	120.5(6)
K(2)–O(1)	2.839(7)	O(2)–N–O(3)	125.3(7)
K(2)–O(3)	2.722(8)	Pt–O(1)–N	118.5(1.1)
K(2)–O(4)	2.845(8)		

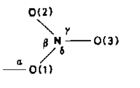
[a] Within the same complex.

The four equivalent oxygen atoms O(2) are separated by 3.14 Å and are situated in a plane which is parallel to the square plane through O(1). The distance between Pt and those oxygen atoms is 2.988(7) Å, which compares well with the corresponding distances in the other nitrato complexes of Table V. There is probably no strong mutual interaction between those oxygens or between them and Pt, in spite of the fact that all four nitrato ligands are situated on the same side of the square-plane through O(1). This is also supported by the fact that the angle Pt–O(1)–N is 118.5(1.1)°, very similar to the corresponding angle in other complexes containing only one or two nitrato groups with different configurations (Table V and Ref. [3]).

The planar configuration of the nitrato groups is preserved on coordination. The atoms O(1), O(2), O(3), N, and Pt are coplanar within 0.01 Å. This plane is inclined 80.0° from the square plane through O(1), so that a propeller-like arrangement of the four nitrato groups is obtained. Bond distances and angles of the nitrato groups agree well with those observed in other complexes with unidentate nitrato groups, Table V. As observed previously [3], both the angles and bond distances of the nitrato group are significantly changed on coordination. The distance to the coordinating oxygen N–O(1) is 1.330(8) Å, which is larger than the distance of 1.245(1) Å in a regular environment [3]. The other bond lengths N–O(2) and N–O(3) are similar to each other and are correspondingly shortened.

Two flat pyramids on each side of the mirror plane are packed together with the bases facing each other (Fig. 2). The closest O–O distance between the two polyhedra is 3.29(1) Å. The Pt–Pt distance, 3.590(1) Å, is far too long for a metal-metal bond. There are two crystallographically-different K$^+$ ions, which are located between the pairs of complexes in such a way as to form a three-dimensional

TABLE V. Interatomic Distances (Å) and Angles (degrees) for d^8 Unidentate Nitrato Complexes.



Compound		Ref.	M–O(1)	M–O(2)	N–O(1)	N–O(2)	N–O(3)	α	β	γ	δ
$K_2[Pt(NO_3)_4]\cdot\frac{1}{2}H_2O$		a	2.010(5)	2.988(7)	1.330(8)	1.194(9)	1.222(9)	118.5(1.1)	120.5(6)	125.3(7)	114.1(7)
cis-$[Pt(NO_3)_2(NH_3)_2]$;	$(NO_3)_1$	b	1.99(1)	3.02	1.30(2)	1.22(2)	1.24(2)	120(1)	120(1)	123(2)	117(1)
cis-$[Pt(NO_3)_2(NH_3)_2]$;	$(NO_3)_2$	b	2.03(1)	3.02	1.28(2)	1.19(2)	1.22(2)	119(1)	116(2)	121(2)	123(2)
$[Pt(dien)NO_3]Cl$		c	2.030(8)	3.020(8)	1.31(1)	1.23(1)	1.25(1)	~118	120.4(9)	124.1(9)	115.5(9)
$C_{28}H_{45}NO_3P_2Pt^e$		d	2.17(1)	3.13(2)	1.35(2)	1.20(2)	1.24(2)	115(1)	122(1)	126(2)	112(2)
$K[Au(NO_3)_4]$	$(NO_3)_1$	d	2.02(2)	2.85(2)	1.34(2)	1.24(3)	1.14(3)	114(2)	118(2)	129(2)	114(2)
$K[Au(NO_3)_4]$	$(NO_3)_2$	d	1.99(1)	2.87(2)	1.39(3)	1.22(3)	1.20(2)	114(1)	118(2)	131(2)	112(2)

[a] This work. [b] Ref. [10]. [c] Ref. [11]. [d] Ref. [12]. [e] *trans*-nitrato[2-(di-tert-butylphosphino)phenyl]di-tert-butylphenylphosphineplatinum(II). [f] Ref. [8].

packing of K^+ and 2 × $[Pt(NO_3)_4]^{2-}$ units (Fig. 2). K(1) coordinates 8 O atoms (4 × 2.832(7) and 4 × 2.999(8) Å) forming a distorted square antiprism. K(2), which is statistically distributed in the position 8h [25], coordinates 6 oxygen from nitrato groups, 2.722(8) to 2.839(7) Å, and the water molecule, 2.845(8) Å. The water molecule does not participate in any hydrogen bonding, the closest approach of other oxygen atoms being 3.332(7) Å (nitrate oxygen).

The present compound was obtained in attempts to crystallize $Pt(H_2O)_4^{2+}$ from aqueous solutions. We have tried counterions such as perchlorate, nitrate, tetrafluoroborate and tosylate, without success. Similar attempts to crystallize aqua species like $Pt(NH_3)_2(H_2O)_2^{2+}$ and $Pt(dien)(H_2O)^{2+}$ have also been reported as unsuccessful [11].

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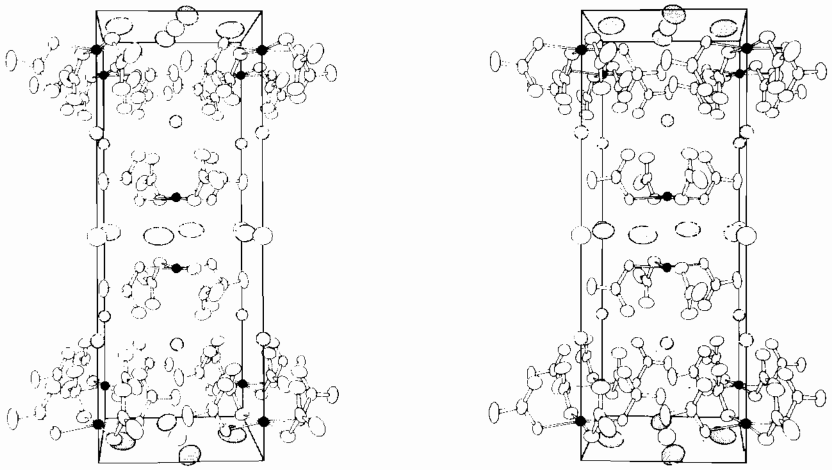

Fig. 2. Stereoview of the unit cell of $K_2[Pt(NO_3)_4]\cdot\frac{1}{2}H_2O$. Pt black, K shaded, O and N unfilled.

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