Synthesis and Crystal Structure of Potassium Tetranitrato Palladate(II)

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Abstract

$K_2[Pd(NO_3)_4]$ has been prepared and its crystal structure determined by use of a CAD-4 diffractometer with monochromatic Mo $K\alpha$ radiation. The space group is $P2_1/c$ with $Z = 4$; $a = 7.940(2)$; $b = 15.469(4)$; $c = 9.453(2)$ Å; $\beta = 91.10(3)°$. The refinement converged to $R = 0.023$. The structure contains discrete complexes of $[Pd(NO_3)_4]^{2-}$ with pseudosymmetry $C4$. Pd coordinates four oxygens from different unidentate nitrato groups. The average Pd–O distance is 2.000(7) Å. The coordination around Pd is distorted square-planar, with Pd situated 0.139 Å above the plane through the four coordinated oxygens. Similar to $[Pt(NO_3)_4]^{2-}$, but in contrast with $[Au(NO_3)_4]^-$, all four nitrato ligands are situated on the same side of the coordination plane forming a basket-like structure. This is probably due to interactions between the non-coordinated oxygens of the nitrato ligands and suitably located potassium ions. Comparison with the structure of *cis*-[Pd-$(NO_3)_2(DMSO)_2$] indicates strong ground-state *trans*-influence of dimethyl sulfoxide in palladium complexes.

Introduction

Nitrato complexes with d^8-metal ions, particularly Pd(II), Pt(II) and Au(III), are weak, compared to nitrato complexes with most other ligands, and have been little studied. The compounds $K[Au(NO_3)_4]$ [1] and $K_2[Pt(NO_3)_4] \cdot 0.5H_2O$ [2] have been synthesized and their crystal structures determined. They contain discrete tetranitrato ions in which the metal coordinates the four unidentate nitrato ligands in an (approximately) square-planar configuration.

Neither of these complexes adopts the D_{2d}-symmetry with the nitrato groups located alternately above and below the square plane, which would be the most efficient in reducing the mutual repulsions between the ligands. $[Au(NO_3)_4]^-$ has approximately C_{2h}-symmetry with two *cis*-ligands on the same side of the plane through the four coordinated oxygens, and the other two on the opposite side [1]. [Pt-$(NO_3)_4]^{2-}$, on the other hand, has C_4-symmetry with all four nitrato ligands situated on the same side of the coordination plane, forming a basket-like structure [2]. The coordination geometry obtained is probably due to forces between the complexes and the other units in the crystal, although a weak intramolecular interaction between Au(III) and the non-coordinated oxygens of the nitrato ligands has also been suggested [1]. We describe here the structure of $K_2[Pd(NO_3)_4]$, which offers a third example of a tetranitrato complex with a d^8-metal.

There is only one previous report on the structure of a palladium(II) nitrato complex, *viz. cis*-[Pd(NO_3)_2(DMSO)_2] [3]. A comparison with the present compound offers a possibility to study the ground-state *trans*-influence of dimethylsulfoxide in palladium complexes.

Synthesis

$K_2[Pd(NO_3)_4]$ was first prepared in 1962 by action of concentrated nitric acid on the tetranitrito complex [4]. We have used the following procedure instead.

153.5 mg (1.44 mmol) palladium sponge (Johnson and Matthey, spec. pure) was heated with 25 ml fuming nitric acid (Merck p.a.) in a 100 ml beaker for 0.5 h (Caution!). After cooling and sedimentation (0.5 h), the clear solution was decanted. An additional 12.5 ml fuming nitric acid was added to the remaining precipitate which dissolved almost completely after heating for 15 min. The two solutions were joined and mixed with 75 ml 2 M nitric acid (Merck p.a.). After filtration through an acid resistant Millipore filter, the clear, orange-coloured solution was transferred quantitatively by means of 25 ml 2 M nitric acid to an evaporation dish. 298.8 mg (2.96 mmol) solid potassium nitrate (Merck p.a.)

TABLE I. Atomic Coordinates and Isotropic Temperature Factors with Standard Deviations

Atom	x/a	y/b	z/c	U_{iso} $(Å^2)^a$
Pd	0.270072(28)	0.620241(15)	0.327474(25)	0.02402(7)
K1	0.254780(94)	0.906548(50)	0.448762(80)	0.03305(21)
K2	0.223420(91)	0.339569(53)	0.485622(79)	0.03458(22)
N1	0.57082(34)	0.69370(19)	0.21514(32)	0.0330(9)
O11	0.50946(27)	0.65947(16)	0.32881(25)	0.0325(7)
O12	0.48597(35)	0.69906(18)	0.10630(28)	0.0445(9)
O13	0.71651(32)	0.72002(20)	0.22757(33)	0.0505(10)
N2	0.10292(34)	0.76695(19)	0.20737(32)	0.0319(8)
O21	0.19794(30)	0.74394(15)	0.31579(26)	0.0343(7)
O22	0.07092(33)	0.71587(18)	0.11331(27)	0.0411(8)
O23	0.05033(39)	0.84110(18)	0.21040(35)	0.0557(10)
N3	−0.04662(34)	0.54074(18)	0.26097(31)	0.0320(9)
O31	0.03190(28)	0.58575(17)	0.36032(26)	0.0343(7)
O32	0.02925(34)	0.51740(18)	0.15671(28)	0.0440(9)
O33	−0.19440(30)	0.52522(19)	0.28238(33)	0.0474(9)
N4	0.43214(35)	0.46195(19)	0.26332(33)	0.0344(9)
O41	0.34431(31)	0.49779(16)	0.36296(26)	0.0351(7)
O42	0.45159(32)	0.49910(18)	0.15043(27)	0.0401(8)
O43	0.49082(41)	0.39073(17)	0.29056(35)	0.0543(10)

$^a U_{iso}$ is calculated from the average of the anisotropic temperature factors.

was added. The resulting *ca.* 125 ml solution was evaporated under a lamp for *ca.* 2.5 h to a volume of 15 ml. It was then transferred quantitatively by use of 2 ml 2 M nitric acid to a small evaporation dish (5 cm) and evaporated at ambient temperature to dryness (*ca.* 1 week). Brown—red single crystals separated. *Anal.* Calc. for $K_2[Pd(NO_3)_4]$: K, 18.1; N, 12.9; Pd, 24.6. Found: K, 17.4; N, 12.9; Pd, 23.7%.

Structure Determination

Unit cell dimensions were obtained from a least-squares treatment of 36 reflections registered with a Guinier—Hägg camera; $a = 7.940(2)$; $b = 15.469(4)$; $c = 9.453(2)$ Å; $\beta = 91.10(3)°$; $Z = 4$; $D_{exp} = 2.48(1)$ g cm^{-3}; $D_{calc} = 2.479$ g cm^{-3}. A single crystal (0.24 × 0.21 × 0.19 mm) was used for intensity data collection on a CAD-4 diffractometer employing monochromatized Mo Kα radiation (0.7093 Å). Laue class and systematic extinctions were consistent with the space group $P2_1/c$. The intensities in one quadrant of the reflection sphere ($3 \leqslant \theta \leqslant 27°$) were measured with ω–2θ scan ($\Delta\omega = 0.8 + 0.5 \tan \theta$). The ratio $\sigma(I)/I$ requested in a scan was 0.028 and the maximum recording time was 150 s. The variation in two standard reflections was less than 4%. I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects ($\mu = 23.7$ cm^{-1}, transmission factors 0.618–0.733). Only the 2510 reflections with $I \geqslant 3\sigma(I)$ were used in the calculations. The structure was solved by vector and Fourier difference

methods. The structure was refined using full-matrix least-squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = [\sigma^2/4|F_o|^2 + (0.01 \ F_o|)^2 + 0.75]^{-1}$. Anisotropic temperature factors (172 parameters refined totally) resulted in $R = 0.023$, $R_w = 0.028$ and $S = 0.98$. Scattering factors with corrections for anomalous dispersion were taken from ref. 5. Tables of $|F_o|$, $\sigma(F_o)$ and $|F_c|$ are available on request from the authors. Final positional and thermal parameters are given in Table I. Computer programs compiled and amended by Lundgren [6] were used for the calculations.

Description and Discussion of the Structure

Selected interatomic distances and angles are given in Table II. The compound contains discrete complexes $[Pd(NO_3)_4]^{2-}$, shown in Fig. 1. The coordination geometry is very similar to that observed for $[Pt(NO_3)_4]^{2-}$ although somewhat more distorted. For comparison, values for the platinum compound from ref. 2 are given within parenthesis below.

Pd coordinates four oxygens from different unidentate nitrato groups, with an average Pd—O distance of 2.000(7) Å (Pt: 2.010(5) Å). The coordination around Pd is distorted square-planar, with Pd situated 0.139 Å (Pt: 0.14 Å) outside the plane formed by the four coordinated oxygens, which are co-planar within 0.026 Å and separated from each other by 2.798(3) to 2.845(3) Å (Pt: 2.83 Å). A very flat pyramid of almost exactly the same size as that for the platinum complex is formed.

TABLE II. Selected Interatomic Distances (A) and Angles (°) with Standard Deviations

| Pd–O(11)	1.995(3)	Pd–O(11)–N(1)	119.37(19)
Pd–O(21)	2.000(2)	Pd–O(21)–N(2)	117.59(20)
Pd–O(31)	1.995(2)	Pd–O(31)–N(3)	117.89(19)
Pd–O(41)	2.010(2)	Pd–O(41)–N(4)	116.01(20)
N(1)–O(11)	1.301(4)	O(11)–N(1)–O(12)	120.93(27)
N(1)–O(12)	1.222(4)	O(12)–N(1)–O(13)	124.09(31)
N(1)–O(13)	1.230(4)	O(13)–N(1)–O(11)	114.98(29)
N(2)–O(21)	1.310(4)	O(21)–N(2)–O(22)	120.39(28)
N(2)–O(22)	1.213(4)	O(22)–N(2)–O(23)	124.21(31)
N(2)–O(23)	1.221(4)	O(23)–N(2)–O(21)	115.40(29)
N(3)–O(31)	1.317(4)	O(31)–N(3)–O(32)	119.91(27)
N(3)–O(32)	1.220(4)	O(32)–N(3)–O(33)	124.62(31)
N(3)–O(33)	1.218(4)	O(33)–N(3)–O(31)	115.47(28)
N(4)–O(41)	1.306(4)	O(41)–N(4)–O(42)	120.48(28)
N(4)–O(42)	1.224(4)	O(42)–N(4)–O(43)	123.57(32)
N(4)–O(43)	1.222(4)	O(43)–N(4)–O(41)	115.94(30)
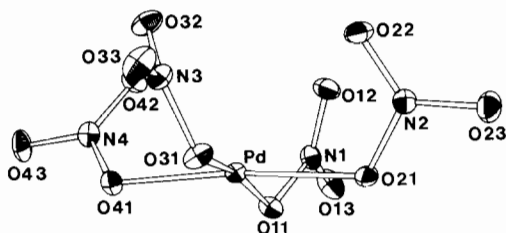
Fig. 1. Perspective view of the tetranitrato palladate(II) ion.

The four nitrato ligands are all situated on the same side of the coordination plane through O11–O41 so that a basket similar to that observed for $[Pt(NO_3)_4]^{2-}$ is obtained. They are planar within 0.004 Å, and, as expected, both angles and distances within the coordinated nitrato groups are significantly different from those of free nitrate, as observed previously ([2] and references therein).

The four nitrogen atoms in the complex are coplanar within 0.015 Å, and the angle between this plane and the coordination plane through O11–O41 is only 0.7°. Similarly, the four oxygens O12–O42 which form the top of the basket are coplanar within 0.001 Å, and this plane is also approximately parallel (angle 0.6°) to the coordination plane.
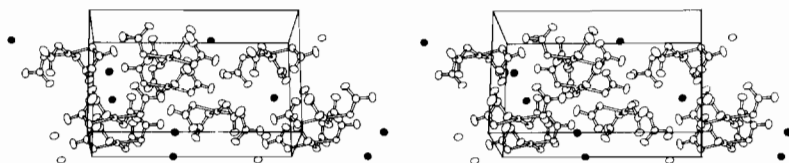
O12–O42 are separated by 3.070(4) to 3.254(4) Å from each other; this separation compares well with the corresponding distances in the platinum complex (3.14 Å).

The four nitrato ligands 1–4 are inclined at angles of 67.5(1.1), 65.8(1.1), 68.6(1.1) and 63.9(1.0)° respectively, from the coordination plane, so that a propeller-like arrangement is obtained. This tilt is larger and more irregular than in $[Pt(NO_3)_4]^{2-}$, where it is 80.0° for all four ligands. The slightly larger distortion in the case of Pd is also obvious from the fact that the metal atom is 0.10 to 0.21 Å outside the planes through the nitrato groups, whereas in the case of Pt, it is included in those planes. The palladium complex has the pseudosymmetry C_4.

The packing of the complexes is radically different in the two compounds. The Pd compound displays a three-dimensional packing of K⁺ and $[Pd(NO_3)_4]^{2-}$ units, while the Pt complexes are packed as dimers so that a three-dimensional network of K⁺ and $2 \times [Pt(NO_3)_4]^{2-}$ units is obtained [2]. However, in both cases, there are potassium ions (K1) situated close to the top of the basket. Most probably, interactions between those potassium ions and the four oxygens O12–O42 are responsible for the particular structure chosen by both $[Pd(NO_3)_4]^{2-}$ and $[Pt(NO_3)_4]^{2-}$. The distances between K1 and O12–O42 are 2.855(3), 2.868(3), 2.931(3), and 2.907(3) Å, respectively. For Pt, the corresponding K1–O2 distance is 2.832(7) Å [2]. Those distances are slightly shorter than the sum of the ionic radii of O^{2-} and ten (Pd)- and eight (Pt)-coordinated K⁺, which are 3.0 and 2.9 Å, respectively [7]. Intermolecular forces between the central metal ions and O12–O42 are less likely, as pointed out in ref. 2. The corresponding gold compound $K[Au(NO_3)_4]$, which has a different arrangement of the nitrato ligands [1], has no such ion-pair formation between the potassium ions and a particular complex. Instead, K⁺ is located at a center of symmetry, which means that it is surrounded by pairs of symmetrically equivalent complexes. The coordination around the potassium ions is somewhat irregular. K1 has 10 oxygen atom neighbours in the range of 2.844(3)–3.071(4) Å, and K2 has 6 in the range of 2.829(3)–3.149(3) Å.

It is astonishing that the palladium and platinum compounds are not isostructural, in spite of the fact

Fig. 2. Stereoview of the unit cell of K₂[Pd(NO₃)₄]. K1 black, other atoms unfilled.

that the coordination geometries and sizes of the complexes are very similar and the counterions identical. The packing in the Pt compound is somewhat more efficient. One formula unit of $K_2[Pt(NO_3)_4] \cdot 0.5H_2O$, including the $0.5H_2O$, occupies the same space (290 Å^3) as one formula unit of $K_2[Pd(NO_3)_4]$. One reason for these differences might be the experimental conditions used for the crystal growth, which were not the same in the two cases.

It is interesting to compare the Pd–O distance of the present compound, 2.000(7) Å, with that obtained by Langs, Hare and Little [3] for *cis*-[Pd(NO₃)₂(DMSO)₂], where two nitrates are coordinated to the palladium *trans* to sulfur-bonded dimethyl sulfoxides. The Pd–O distances for those nitrates are 2.066 Å. Thus, the Pd–O bond *trans* to DMSO is 0.066 Å longer than the bond *trans* to nitrate, which indicates a strong ground-state *trans*-influence for sulfur-bonded dimethyl sulfoxide in palladium complexes.

Acknowledgements

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