Journal of Organometallic Chemistry, 220 (1981) 271—276
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

FORMATION OF ANIONIC σ-ARYL COMPLEXES OF PLATINUM (IV) IN THE REACTION OF H_2PtCl_6 WITH AROMATIC COMPOUNDS. THE CRYSTAL AND MOLECULAR STRUCTURES OF PLATINUM (IV) COMPLEXES OF NAPHTHALENE AND *ortho*-NITROTOLUENE

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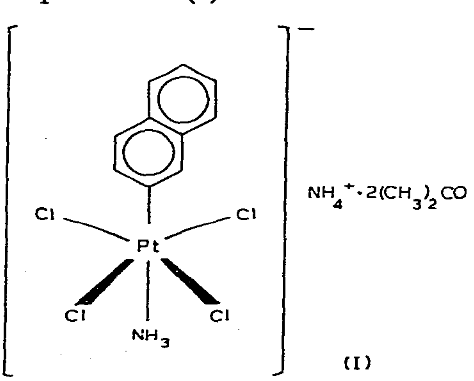
(Received May 19th, 1981)

Summary

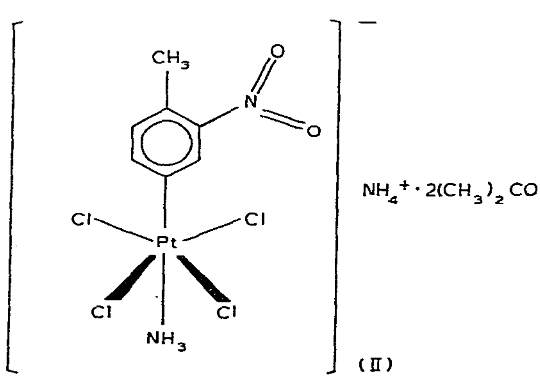
The crystal and molecular structures of anionic platinum(IV) complexes of naphthalene (I) and *ortho*-nitrotoluene (II) have been determined by X-ray diffraction. The structures of both complexes are similar. The platinum atom is octahedrally coordinated with four chlorine atoms occupying the equatorial positions and σ-bonded aryl and neutral ammonia ligands situated in the axial positions.

Introduction

We have shown previously [1—4] that hexachloroplatinic acid reacts with aromatic compounds in a CF_3COOH/H_2O mixture to give novel anionic σ-aryl complexes of platinum(IV). The complexes of naphthalene [1], benzene, alkyl benzenes and chlorinated benzenes [2], benzenes containing electron-withdrawing substituents (nitrobenzene, acetophenone, benzoic acid etc.) [3] and fluorinated benzenes [4] have been prepared by this method. In the present paper we describe the crystal and molecular structures of platinum(IV) complexes of naphthalene (I) and *o*-nitrotoluene (II).



(I)



(II)

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TABLE 1

CRYSTAL DATA FOR COMPLEXES I AND II

	Complex I	Complex II
Formula	$C_{16}H_{26}Cl_4N_2O_2Pt$	$C_{13}H_{25}Cl_4N_3O_4Pt$
Crystal size (mm)	0.15 × 0.20 × 0.55	0.9 × 0.5 × 0.4
Mol. wt.	615.30	624.30
a(Å)	15.95(2)	16.29(3)
b(Å)	18.78(6)	18.02(1)
c(Å)	7.531(9)	7.684(8)
V(Å^3)	2257	2256
Space group	*Pnam*	*Pnam*
d_{calc} (g cm^{-3})	1.82	1.85
μ (Mo-K_α) (cm^{-1})	70.2	70.4
Z	4	4

Experimental

Complexes I and II were prepared as described previously [1,3]. Crystals of the complexes were grown at 0°C by slow evaporation of an acetone solution. All work was carried out in air.

Some crystal data are given in Table 1. Intensities ($I \geqslant 2\sigma$) of 1021 independent reflections in the range $(\sin\theta/\lambda)_{max} = 0.696$ for complex I and 1165 reflections in the range $(\sin\theta/\lambda)_{max} = 0.697$ for complex II were measured (Syntex PI diffractometer, λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan, no absorption correction). The structures were solved by the heavy atom method and refined by a least-squares procedure using full matrix refinement with anisotropic temperature factors for all non-hydrogen atoms. The final R indexes were 0.084 for I and 0.067 for II. All calculations were performed with a BESM-6 computer using the "Roentgen-75" program [5].

Results and discussion

As we showed earlier [2—4], platinum replaces only *m*- and *p*-hydrogen atoms of monosubstituted benzenes, and only the β-isomer of the naphthalene complex is formed. The data from the X-ray analysis of complex I are consistent with an *ortho*-deactivation effect. In the case of *ortho*-nitrotoluene there are two possibilities for substitution. ^{1}H NMR spectra showed [3] that the two isomers of the complex were formed in the reaction of H_2PtCl_6 with *o*-nitrotoluene corresponding to a Pt atom in *meta*- and *para*-positions relative to the nitrogroup. X-ray analysis indicates that the crystal used for the structure determination corresponds to the first isomer of II. Thus, it may be concluded that during slow crystallization crystals of the separate isomers are formed. The crystallization conditions also affect the amount of acetone present in the crystal.

Atomic coordinates and their anisotropic temperature factors for complexes I and II are listed in Tables 2 and 3, respectively.

The projection of the structure of I on the *ab* plane is shown in Fig. 1. In the crystal of complex II the molecules are packed in the same manner. Unit cell

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND THEIR ANISOTROPIC THERMAL PARAMETERS [a] ($\times 10^4$) FOR COMPLEX I

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	0.5609(1)	0.3926(1)	0.25	32	14	172	0	0	0
Cl(1)	0.4668(4)	0.3561(3)	0.471(1)	42	20	216	−1	52	13
Cl(2)	0.6507(4)	0.4340(3)	0.033(1)	46	23	224	−13	3	17
O(1)	0.119(2)	0.355(1)	0.75	79	37	272	−71	0	0
O(2)	0.293(3)	0.182(3)	0.75	102	73	718	17	0	0
N(1)	0.498(2)	0.498(2)	0.25	57	28	359	8	0	0
N(2)	0.121(2)	0.208(2)	0.75	56	58	355	−10	0	0
C(1)	0.620(2)	0.296(2)	0.25	20	19	180	21	0	0
C(2)	0.703(2)	0.289(2)	0.25	54	24	132	28	0	0
C(3)	0.745(2)	0.224(2)	0.25	35	11	427	3	0	0
C(4)	0.698(2)	0.162(2)	0.25	8	31	500	31	0	0
C(5)	0.612(2)	0.167(2)	0.25	17	18	267	15	0	0
C(6)	0.575(2)	0.234(2)	0.25	36	14	313	24	0	0
C(7)	0.563(3)	0.101(2)	0.25	73	14	216	−44	0	0
C(8)	0.601(3)	0.036(2)	0.25	57	36	274	41	0	0
C(9)	0.688(3)	0.033(2)	0.25	94	11	302	−1	0	0
C(10)	0.736(2)	0.086(2)	0.25	50	23	243	52	0	0
C(11)	0.176(3)	0.404(2)	0.75	47	19	323	−7	0	0
C(12)	0.265(3)	0.381(3)	0.75	51	43	311	15	0	0
C(13)	0.149(3)	0.479(2)	0.75	44	32	442	23	0	0
C(14)	0.371(2)	0.169(2)	0.75	2	29	182	2	0	0
C(15)	0.413(2)	0.163(2)	0.589(2)	150	85	717	−7	804	259

[a] $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

TABLE 3

FRACTIONAL ATOMIC COORDINATES AND THEIR ANISOTROPIC THERMAL PARAMETERS [a] ($\times 10^4$) FOR COMPLEX II

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	0.5611(1)	0.3893(1)	0.25	36	21	139	3	0	0
Cl(1)	0.4728(3)	0.3476(3)	0.4652(7)	41	36	165	2	33	7
Cl(2)	0.6475(3)	0.4368(3)	0.0377(7)	53	28	170	−4	18	35
O(1)	0.629(2)	0.144(2)	0.75	82	68	442	−3	0	0
O(2)	0.796(2)	0.326(2)	0.75	80	106	1193	−15	0	0
O(3)	0.598(3)	0.033(2)	0.314(6)	152	50	811	−9	−16	100
O(4)	0.507(2)	0.98(2)	0.198(8)	83	76	749	−54	−121	12
N(1)	0.493(2)	0.495(2)	0.25	71	21	216	49	0	0
N(2)	0.627(2)	0.301(2)	0.75	50	44	249	2	0	0
N(3)	0.572(2)	0.090(2)	0.25	103	38	457	40	0	0
C(1)	0.622(2)	0.289(1)	0.25	34	13	110	21	0	0
C(2)	0.708(2)	0.290(2)	0.25	39	38	212	31	0	0
C(3)	0.746(2)	0.217(2)	0.25	64	50	205	37	0	0
C(4)	0.710(2)	0.153(2)	0.25	75	33	258	37	0	0
C(5)	0.623(2)	0.155(2)	0.25	88	3	203	−8	0	0
C(6)	0.576(2)	0.225(2)	0.25	76	29	216	40	0	0
C(7)	0.756(2)	0.084(2)	0.25	103	51	204	−2	0	0
C(8)	0.681(2)	0.098(2)	0.75	109	52	219	57	0	0
C(9)	0.656(3)	0.019(2)	0.75	141	1	611	−17	0	0
C(10)	0.772(3)	0.114(3)	0.75	71	77	338	−27	0	0
C(11)	0.860(3)	0.342(3)	0.75	42	69	251	18	0	0
C(12)	0.900(2)	0.352(2)	0.582(6)	208	99	202	−28	16	−173

[a] $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^3 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

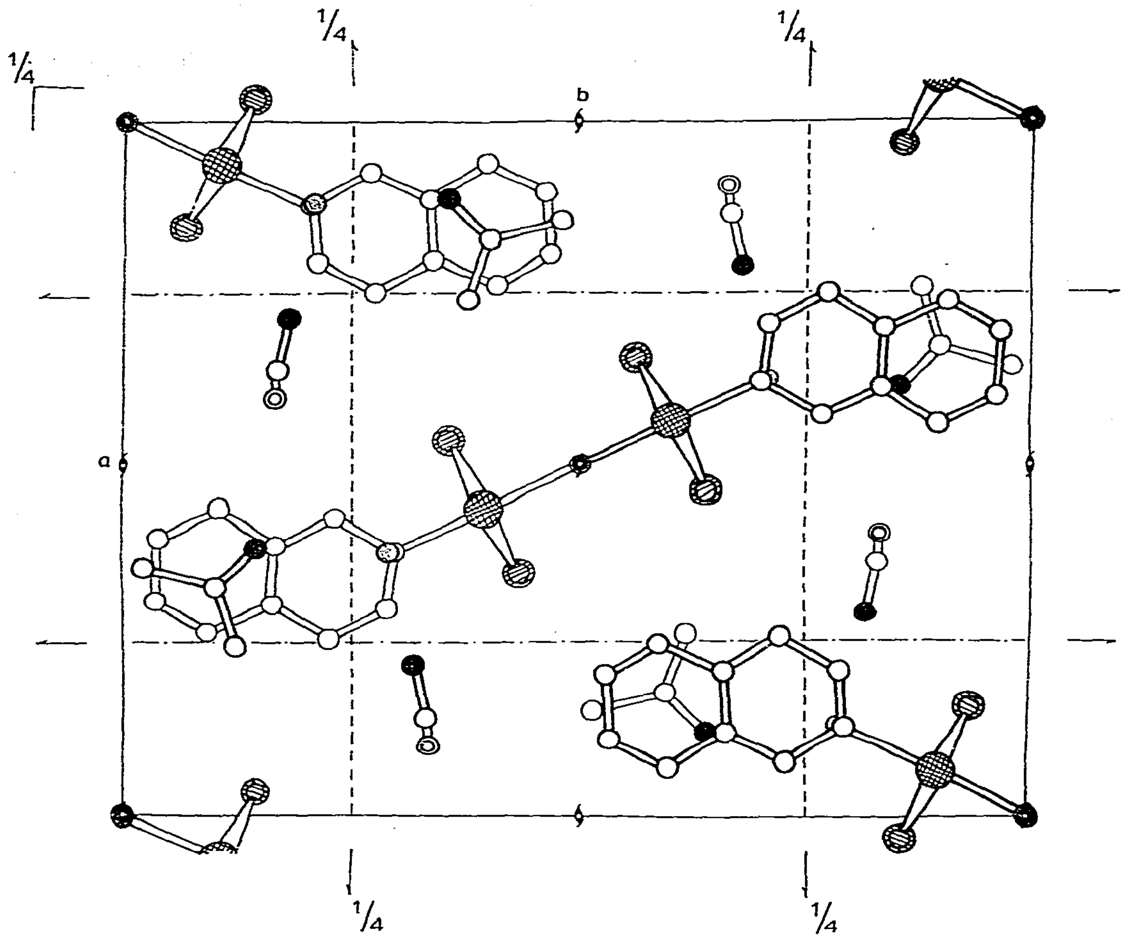

Fig. 1. The crystal structure of complex I projected along the c-axis.

parameters and the symmetry are similar for crystals of I and II. The platinum-(IV) complexes are in the following positions: the platinum atom, N atom, and naphthalene molecule in I, and the Pt atom, N atoms, carbon atoms of the benzene ring and the methyl group in II are located in the symmetry plane. The oxygen atoms of the NO_2 group in II occupy two positions of equal probability, the plane of the NO_2 group is twisted in both directions relative to the benzene ring plane and dihedral angles are 25.5°.

There are two types of acetone molecules in each crystal of I or II. Molecules of the first type occupy the position where all non-hydrogen atoms lie in the symmetry plane. Only the C=O group of the molecules of the second type lies in the symmetry plane (Fig. 1). There are shortened intermolecular distances between the latter acetone molecules and the NH_4^+ cation: the distances N(2)···O(1) and N(2)···O(2) are equal to 2.76 and 2.78 Å in I and 2.82 and 2.79 Å in II.

The main interatomic distances in complexes I and II are shown in Figs. 2 and 3, respectively. The interatomic angles around the platinum atom are listed in Table 4. The platinum atom exhibits octahedral coordination typical for Pt^{IV}: four chlorine atoms are situated in the equatorial plane of the octahe-

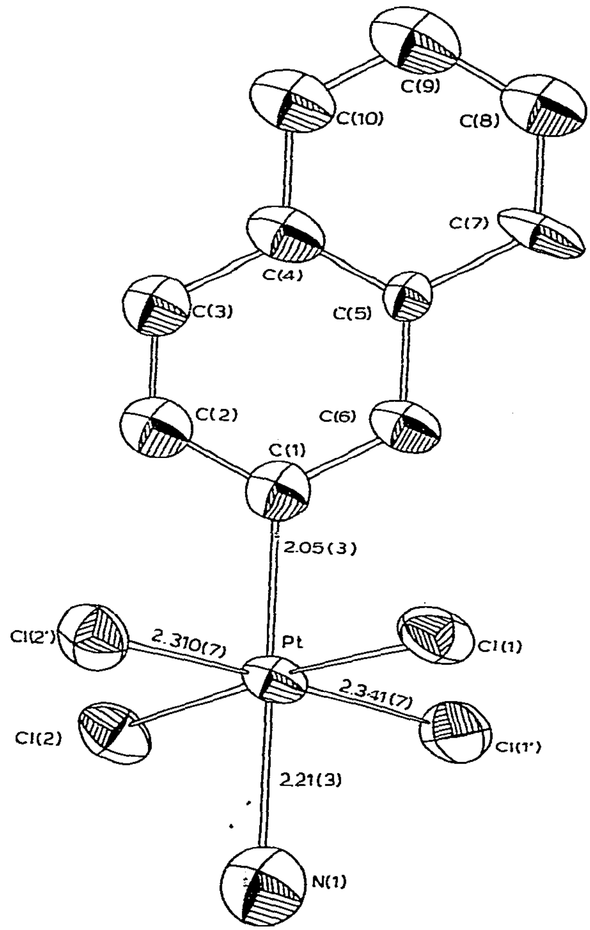

Fig. 2. The molecular structure of complex I (configuration and some important interatomic distances, Å).

dron, and molecules of ammonia and naphthalene in I or *o*-nitrotoluene in II lie on the axis of the octahedron and occupy *trans* positions. The platinum atom is not strictly in the plane of the four chlorine atoms, but is displaced from it towards atom C(1). This deviation is 0.056 Å in I and 0.053 Å in II.

TABLE 4

BOND ANGLES (deg.) IN THE COORDINATION SPHERE OF THE Pt ATOM FOR COMPLEXES I AND II

	Complex I	Complex II
Cl(1)PtCl(2)	177.2(2)	177.2(2)
Cl(1)PtCl(1')	90.4(2)	91.1(2)
Cl(1)PtCl(2')	89.6(2)	89.7(2)
Cl(2)PtCl(2')	90.2(2)	89.4(2)
Cl(1)PtN(1)	88.4(7)	88.1(6)
Cl(1)PtC(1)	92.1(6)	90.1(5)
Cl(2)PtN(1)	88.9(7)	89.3(6)
Cl(2)PtC(1)	90.7(6)	91.8(5)
N(1)PtC(1)	179(1)	178(1)

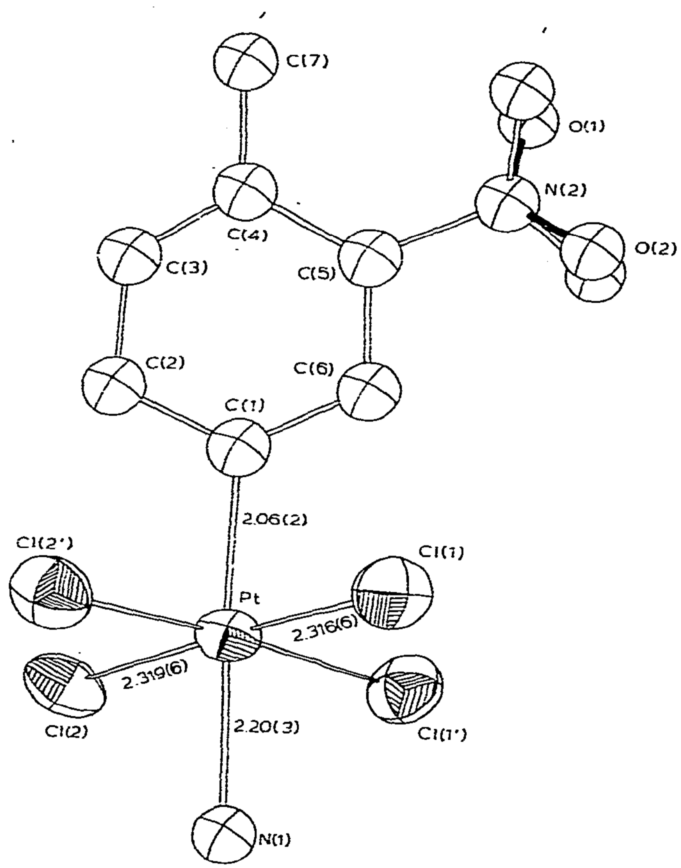

Fig. 3. The molecular structure of complex II (configuration and some important interatomic distances, Å).

The Pt—Cl and Pt—N interatomic distances are similar to those found in the structures of other platinum(IV) complexes [6,7].

The length of the Pt—C σ-bond is the same in both cases to within experimental error. The Pt—C distances are close to those determined for known Pt-σ-C_6H_5 complexes: *cis*-[$(Ph_3P)_2(\sigma$-Ph)Pt($PbPh_3$)] 2.06(2) Å [8], [Pt_3-(σ-Ph)($PPh_2)_3(PPh_3)_2$] 2.03(2) Å [9] and [$(PhCH_2)_2(C_6H_4)CH_2P]_2Pt$ 2.062(7) Å and 2.071(7) Å [10].

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