Inorganica Chimica Acta, 102 (1985) 39–43

Oxidation of a Platinummacrocycle by Iodine: Crystal Structures of the Platinumdibenzo[b,i]-1,4,8,11-tetraaza[14]annulene Iodides [Pt(IV)-(dbtaa)$I_{2.0}$] and [Pt(II)(dbtaa)]$(I_3)_{0.67}$

M. HUNZIKER* and G. RIHS

Zentrale Funktion Forschung, CIBA-GEIGY A.G., CH-4002 Basle, Switzerland

Received October 15, 1984

Abstract

The structures of two oxidation products of the title platinum macrocycle with the same analytical iodine content are reported. One is an electrically-insulating Pt(IV)-complex, while the other is a highly-conducting ligand oxidized species. Crystal data are as follows: [Pt(IV)(dbtaa)I_2]: space group = $P2_1/c$, a = 7.533 Å, b = 16.841 Å, c = 7.548 Å, β = 109.47°, Z = 2, R = 4.4% for 2446 reflections. [Pt(II)(dbtaa)]-$(I_3)_{0.67}$: space group = I_{bam} a = 20.712 Å, b = 13.369 Å, c = 6.349 Å, Z = 4, R = 9.8% for 472 reflections. The conducting phase can only be produced by a co-sublimation technique.

Introduction

Oxidation of metallomacrocycles (*e.g.* phthalocyanines (Mpc), porphyrins (Mp), tetraaza[14]-annulenes (Mtaa)) by iodine is a viable method for the preparation of electrically-conducting charge-transfer (CT) complexes [1, 2]. Owing to the difficulties in growing single crystals, only limited structural data on well-defined CT-complexes are available and most are concerned with metallomacrocycles of the first row transition elements, especially nickel. Only one structure of a highly conducting palladium macrocycle has been reported so far [3], and till now no structures of partially oxidized platinum macrocycles were known. While oxidation of nickel macrocycles by iodine leads to ligand oxidized species of the type $Ni(II)L^{+\bullet}$ (cation-radical), oxidation of palladium and especially platinum macrocycles by iodine may lead to both metal-centered and ligand-centered oxidation, since the higher oxidation states of these metals are more easily accessible than those of Ni. We have already reported the structures of the partially-oxidized complexes [Ni(II)(dbtaa)]$(I_3)_{0.67}$ and [Pd(II)(dbtaa)]$(I_3)_{0.67}$ which both show ligand-centered oxidation by iodine [3]. Here we report the structures of the highly-conducting partially-oxidized platinum macrocycle, [Pt(II)(dbtaa)]-$(I_3)_{0.67}$, and the insulating counterpart, showing metal centered oxidation [Pt(IV)(dbtaa)I_2].

Experimental

Pt(dbtaa)

The macrocycle was prepared by a modified literature procedure [4]. Thus, K_2PtCl_4 (5 g) was reacted with o-phenylenediamine (2.6 g) at 60 °C in 40 ml of 50% aqueous ethanol for 30 min. Acetic acid (2 ml) and tetraethoxypropane (6 ml) were added and the mixture refluxed for 2 h. Sodium acetate (2 g) was added and refluxing continued for 16 h. The precipitate was filtered while hot, washed with water, ethanol and ether, yielding crude macrocycle (5.3 g, 91%) which was purified by multiple sublimations *in vacuo* at 300 °C, 0.01 Torr. UV-Vis spectrum in DMF, λ_{max} [nm], (log ϵ): 542 (4.07), 506 (3.84), 406 (4.82), 395 (4.40), 384 (4.45), 376 sh, 356 (4.01).

[Pt(II)(dbtaa)]$(I_3)_{0.67}$

Single crystals could only be grown by a co-sublimation technique, described in detail elsewhere [5]. A major problem was the facile formation of [Pt(IV)(dbtaa)I_2] which accompanied the growth of the conducting phase. Often, fine needle-like single crystals of [Pt(II)(dbtaa)]$(I_3)_{0.67}$ were covered by tile-like layers of plates of the Pt(IV) compound. Suppression of Pt(IV) formation was finally achieved by successive variation of the various growth parameters. Here we give a set that proved successful for our apparatus and geometry (different geometries will need different growth parameters): iodine source: 47 °C, annulene source 240 °C, mixing chamber 270 °C, growth area 15–20 °C, Argon carrier gas partial pressure, 9–10 mbar.

---

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

© Elsevier Sequoia/Printed in Switzerland

TABLE I. Crystal Data and Refinement of [Pt(IV)(dbtaa)I_2] and [Pt(II)dbtaa]$(I_3)_{0.67}$.

Compound	$Pt(C_{18}H_{14}N_4)I_2$	$Pt(C_{18}H_{14}N_4)(I_3)_{0.67}$
Molecular weight	735.3	735.3
Space group	$P2_1/c$	I_{bam}
Cell: a, Å	7.533	20.712
b, Å	16.841	13.369
c, Å	7.548	6.349
β, °	109.47	–
V, Å^3	903	1758
Z	2	4
Density, g/cm^3, calcd.	2.705	2.778
found	2.678	2.75
Radiation	MoK_α	MoK_α
Unique data with $I > I\sigma(I)$:	2446	472
Final R-factor	0.044	0.098
Final number of variables	118	42

[Pt(IV)(dbtaa)I_2]

As mentioned above this compound can be obtained from the vapor phase. However, the single crystals used in the X-ray structure determination were grown by slow diffusion of the components in chloroform solution in an H-tube. Typical dimensions of the intransparent platelets with metallic lustre: 0.25 X 0.15 X 0.05 mm^3.

Electrical conductivities, Resonance Raman and ESR-spectra were determined as described previously [3].

Structure Determination of [Pt(IV)(dbtaa)I_2]

Weissenberg and precession photographs revealed the crystals to be monoclinic, space group $P2_1/c$. Cell constants (Table I) were obtained by the usual procedures on a Philips PW1100 diffractometer with MoK_α-radiation. In the range $6° \leqslant 2\theta \leqslant 60°$ a total of 2879 reflections were collected, 2446 of which showed $I > 2\sigma(I)$ and were therefore used for the structure solution and refinement. The structure was solved by direct methods (MULTAN 77). Block-diagonal least-squares refinements with anisotropic temperature factors for the 13 non-hydrogen atoms converged at $R = 0.044$. The hydrogen atoms could not be located.

Refinement of the [Pt(II)(dbtaa)]$(I_3)_{0.67}$-structure

Weissenberg and precession photographs showed the crystals to be isomorphous with the corresponding nickel and palladium complexes [3], with only slightly different cell constants. Data were collected as above, on a crystal with a very small cross section (0.024 X 0.020 mm^2) yielding only 472 reflections with $I > 2\sigma(I)$. Refinement started at the positional parameters of the nickel complex, [Ni(II)(dbtaa)]$(I_3)_{0.67}$, and with anisotropic temperature factors for Pt and I only led to a R-value of 0.098. A better refinement would demand crystals with a larger cross section which, however, are very difficult to obtain owing to the strongly one-dimensional nature of the compound (strongly anisotropic crystal growth).

Results and Discussion

Bond lengths and angles are given in Table II for both [Pt(IV)(dbtaa)I_2] and [Pt(II)(dbtaa)]$(I_3)_{0.67}$. The atom labelling scheme valid for both structures is shown in Fig. 1 (omitting the iodine atoms for the Pt(II) compound).

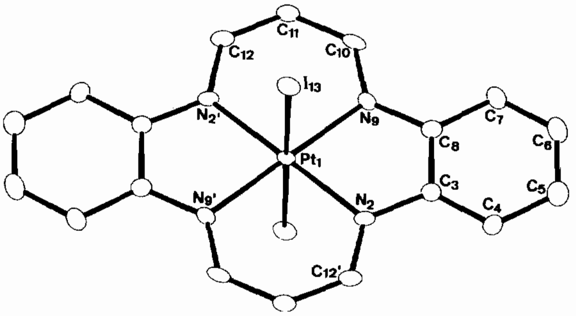

Fig. 1. Atom labelling scheme for [Pt(IV)(dbtaa)I_2] and [Pt(II)(dbtaa)]$(I_3)_{0.67}$ (omit the iodine atoms for the latter). Hydrogen atoms not shown.

Figure 2 shows the packing of the Pt(IV) complex molecules in a projection on the bc-plane. The packing is essentially controlled by van der Waals contacts. The shortest I···I distance is 4.39 Å, still slightly longer than the sum of the van der Waals radii.

TABLE II. Bond Lengths and Angles, Å and deg.

Atoms	$[Pt(C_{18}H_{14}N_4)I_2]$	$[Pt(C_{18}H_{14}N_4)](I_3)_{0.67}$
$Pt-N_2$	1.983(8)	1.97 (2)
$Pt-N_9$	2.005(8)	1.98 (2)
N_2-N_3	1.39(2)	1.42 (4)
C_3-C_4	1.39(2)	1.41 (4)
C_4-C_5	1.43(3)	1.38 (4)
C_5-C_6	1.40(3)	1.41 (4)
C_6-C_7	1.37(3)	1.42 (4)
C_7-C_8	1.42(2)	1.38 (5)
C_3-C_8	1.40(2)	1.45 (5)
C_8-N_9	1.39(2)	1.45 (6)
N_9-C_{10}	1.32(2)	1.36 (5)
$C_{10}-C_{11}$	1.40(3)	1.37 (6)
$C_{11}-C_{12}$	1.38(3)	1.42 (6)
Pt–I	2.678 (1)	
N_2-Pt-N_9	81 (1)	83 (3)
N_2-Pt-N_9'	99(1)	96 (3)
$Pt-N_2-C_3$	115(1)	114 (2)
$N_2-C_3-C_8$	115(1)	114 (3)
$C_4-C_3-C_8$	121 (2)	119 (3)
$C_3-C_4-C_5$	119(2)	119 (3)
$C_4-C_5-C_6$	119(2)	122 (3)
$C_5-C_6-C_7$	122(2)	120 (3)
$C_6-C_7-C_8$	119 (2)	119 (3)
$C_7-C_8-C_3$	120 (1)	121 (4)
$C_3-C_8-N_9$	116 (1)	115 (3)
C_8-N_9-Pt	113 (1)	113 (2)
$Pt-N_9-C_{10}$	119 (1)	121 (2)
$N_9-C_{10}-C_{11}$	127 (2)	128 (3)
$C_{10}-C_{11}-C_{12}$	129 (2)	128 (4)
$C_{11}-C_{12}-N_2'$	126 (2)	123 (4)
N_2-Pt-I	91.3(2)	
N_9-Pt-I	89.8(2)	

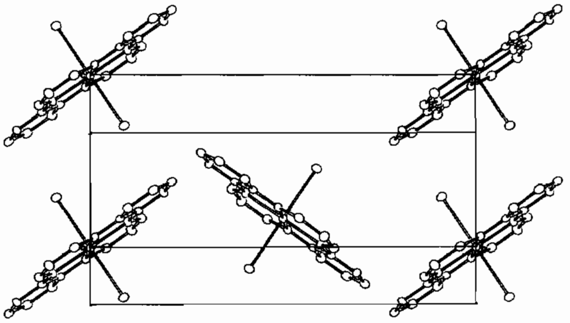

Fig. 2. Packing of the [Pt(IV)(dbtaa)I_2] molecules.

The annulene moiety is planar within experimental error. The Pt–I bond however is not perfectly vertical on the annulene plane (Table I). The Pt–I-bond length is 2.678(1) Å and thus close to the Pt–I-bond length in bis(1,2)benzoquinonedioximato)platinumiodide of 2.666(1) Å for modification I [6] and in the middle of the range of reported Pt(IV)–I bond lengths of 2.604 [7] to 2.771 Å [8]. The mean Pt–N-bond length of 1.994 Å is longer than in the parent unoxidized Pt(II)-(dbtaa), where it amounts to 1.968 Å*. The smaller ionic radius of Pt(IV) (0.65 Å) compared to that of Pt(II) (0.80 Å) imply a smaller Pt–N bondlength in the Pt(IV)-compound. The fact that the contrary is observed may be explained by the differences in the π-backbonding, which should be much stronger in the Pt(II) compound, resulting in a shortening of the Pt(II)–N-bond.

Figure 3 shows a projection of the [Pt(II)(dbtaa)]-$(I_3)_{0.67}$ structure on the *a,b*-plane. The macrocyclic molecules are stacked along the *c*-axis with their planes perpendicular to the stacking axis. Succeeding molecules along the stack are staggered by 54°.

---

*The structure of Pt(II)dbtaa has not been published yet. Our structure determination showed isomorphy with Ni(II)dbtaa [9] with the following data: monoclinic, $P2_1/c$, a = 19.368(3) Å, b = 5.341(1) Å, c = 14.772(3) Å, β = 112.01(1)°, Z = 4, V = 1417 Å^3, D_{calc} = 2.255 g/cm^3.

TABLE III. Cell Constants [Å] for $[M(II)(dbtaa)](I_3)_{0.67}$-complexes; Orthorhombic, I_{bam}.

M	*a*	*b*	*c*	M–M	Ref.
Ni	20.245	13.416	6.418	3.209	3
Pd	20.452	13.430	6.499	3.250	3
Pt	20.712	13.369	6.349	3.175	this work
Cu	20.45	13.48	6.46	3.23	this work

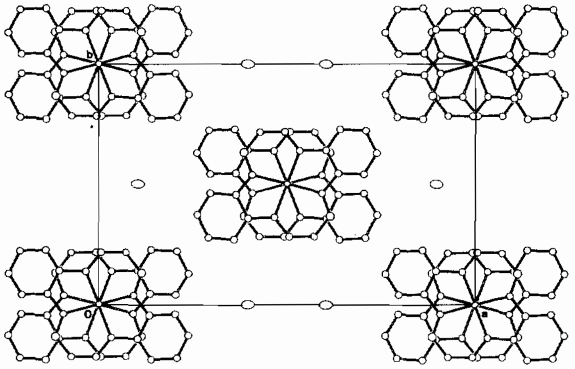

Fig. 3. Projection of the $[Pt(II)(dbtaa)](I_3)_{0.67}$ structure on the *ab*-plane.

The macrocycles are planar, within experimental error, and are separated by 3.175 Å. This is shorter than in the corresponding partially oxidized Cu-, Ni- and Pd-complexes (Table III) and shorter than the interplanar separation in the parent unoxidized Pt-macrocycle (3.257 Å and 3.299 Å) for the two types of crystallographically non-equivalent molecules A and B [9]. The iodine atoms are confined to the channels between the annulene stacks with two iodine chains per annulene stack. Resonance raman and X-ray analysis confirmed the presence of I_3^-. Thus 0.67 electrons are removed from each macrocycle on average.

Considering the ionic radius of Ni(II), Pd(II) and Pt(II) the short Pt–Pt-distance (Table III) in $[Pt(II)(dbtaa)](I_3)_{0.67}$ is surprising. Similarly short (3.173 Å) Pt–Pt-separations were observed in bis-(1.2-benzoquinonedioximato)platinum(II) [10] and may be explained by the 'nephelauxetic effect' of the electron-withdrawing ligand, causing a reduced electron density on the platinum atom and hence a smaller ionic radius allowing for a closer packing. In our example ligand oxidation should result in an enhanced withdrawal of electron density from the Pt(II)-ion through metal d and p - ligand π-orbital overlap, which is more effective here than for the less extended orbitals in Pd(II) and Ni(II).

The top portion of the d_{z^2}-band in platinum chain compounds is largely antibonding in character [11, 12]. Electron withdrawal from d_{z^2}-orbitals will decrease the antibonding interaction in the *z*-direction (stacking axis) so that Pt–Pt-bonding is strengthened and separation is reduced. Whether this mechanism is of importance to explain the short Pt–Pt-distance in our example is unknown. ESR spectra gave no conclusive evidence. Close packing along *z* in this partially oxidized Pt-complex should result in high electric conductivity along the needle axis. However, the conductivity shows a maximum value of 12 Scm^{-1}, practically identical to the palladium complex and more than one order of magnitude smaller than the nickel complex [3]. The temperature behaviour is not metallic as in $[Ni(II)(dbtaa)](I_3)_{0.67}$, but semiconducting as for the palladium complex.

In addition to the two structurally characterized complexes there exist various other phases with unknown structures showing higher as well as lower iodine contents. All are electrically conducting. From reaction of a 10-fold excess of iodine with Pt(dbtaa) in hot 1,2,4-trichlorobenzene, Hatfield [4] obtained the stoichiometries $Pt(dbtaa)I_{1.35}$ (after 18 h) and $Pt(dbtaa)I_{1.5}$ (24 h) with pressed pellet conductivities of 0.12 and 0.03 Scm^{-1}, respectively. These stoichiometries probably resulted because the macrocycle was not fully dissolved and crystal needles were only doped to a certain degree. This is supported by the fact that the higher iodine content was found for the longer reaction time for otherwise identical reaction conditions. In our own experiments I_2-oxidation of Pt(dbtaa) fully dissolved in 1,2,4-trichlorobenzene or *o*-dichlorobenzene invariably produced the insulating Pt(IV) complex $[Pt(IV)(dbtaa)I_2]$, while solid state doping with iodine in organic solvents or *via* vapour phase resulted in a wide variety of stoichiometries from $Pt(dbtaa)I_1$ up to $Pt(dbtaa)I_{5.4}$. All phases showed electrical conductivities (pressed pellet) around 10^{-1} to 10^{-2} Scm^{-1}. Resonance raman spectra confirmed the presence of I_3^- and I_5^-. This behaviour is typical for this class of compounds and has been described earlier [3].

Acknowledgements

We thank Dr. B. Hilti for the provision of a co-sublimation apparatus and J. Pfeiffer for conductivity measurements.

References

1 B. M. Hoffman and J. A. Ibers, *Acc. Chem. Res., 16, 15 (1983) and refs. therein.*

2 M. Hunziker, H. Loeliger, G. Rihs and B. Hilti, *Helv. Chim. Acta, 64,* 2544 (1981).

3 M. Hunziker, B. Hilti and G. Rihs, *Helv. Chim. Acta, 64,* 82 (1981).
4 W. E. Hatfield, *U.S. Government Reports,* TR-10 and TR-12, AD 083765 and AD 089940, 1980.
5 *Ger. Offen.* 2 641 742, to B. Hilti and C. W. Mayer (Swiss Appl. 12230/57 (19.9.75).
6 H. Pritzkow, *Z. Naturforsch., Teil B:, 31,* 401 (1976).
7 K. D. Buse, H. J. Keller and H. Pritzkow, *Inorg. Chem., 16,* 1072 (1977).
8 G. Casalone and R. Mason, *Inorg. Chim. Acta, 7,* 429 (1973).
9 M. C. Weiss, G. Gordon and V. L. Goedken, *Inorg. Chem., 16,* 305 (1977).
10 M. Mégnamisi-Bélombé, *J. Solid State Chem., 27,* 389 (1979).
11 H. M. Whangbo and R. Hoffmann, *J. Am. Chem. Soc., 100,* 6093 (1977).
12 K. Krogmann, *Angew. Chem., Int. Ed. Engl., 8 (1),* 35 (1969).