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Crystal and Molecular Structure of [2-(2-Benzoxazolyl)phenolatotetrachloroplatinum]·[2-(2-Benzoxazolyl)phenol]·Ethanol, [$PtCl_4$-($C_{13}H_8O_2N$)]·($C_{13}H_9O_2N$)·C_2H_5OH: Possibly a Stable New Pentavalent Platinum Complex

Akiko FURUHASHI,* Isao ONO, Akira OUCHI,† and Akira YAMASAKI††
Department of Chemistry, Aoyama Gakuin University, 1-1, Morinosato-Aoyama, Atsugi-shi, Kanagawa 243-01
† Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
†† Department of Applied Chemistry and Physics, The University of Electro-Communications, 1-5-1, Chofugaoka, Chofu-shi, Tokyo 182
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The crystal and the molecular structures of the title complex were determined by means of the single-crystal X-ray diffraction method. The crystal of $PtC_{28}H_{23}O_5N_2Cl_4$, F. W. 804.40, (black-violet in color) is monoclinic, with the space group of $P2_1/a$, a=18.293(4), b=9.682(2), c=15.797(3) Å, β=96.55(2)°, U=2779.6(9) Å^3, Z=4, D_m=1.90, D_x=1.92 g cm^{-3}, and μ (Mo $K\alpha$)=57.37 cm^{-1}. The platinum atom is in a hexa-coordinated octahedral geometry, where one 2-(2-benzoxazolyl)phenolate (bxp$^-$) ion is chelated with its N and phenolato O atoms. The bxp$^-$ ligand as well as the free Hbxp molecule are both approximately planar, and their planes are approximately in parallel: They are arranged alternately and are laid roughly along the a-axis. Although the overlappling areas of the neighboring rings are only 23 and 13% respectively of the whole ring area, the interplane distances are 3.42 and 3.49 Å.

The 2-(2-benzoxazolyl)phenol (Hbxp) is known to make chelates with many kinds of metal ions, where the ligand acts as the uninegative ion, bxp$^-$. Among these, the structures of its copper(II),[1] cadmium(II),[1] and iron(III),[2] chelates have already been elucidated. In these complexes, the benzoxazolyl (bxz) and the phenolate (pho) rings of the chelating ligand are approximately on the same plane. In the iron(III) complex, the bxp$^-$ rings of the neighboring complexes are approximately in parallel and they are partly overlapped with each other, so some π–π interaction between them is expected.[2] On the other hand, the platinum(II) cmplex, [$PtCl_2(Hbxp)_2$]·C_2H_5OH (**2**), on which the present authors recently reported, has unidentate non-charged Hbxp ligands, and the bxz and Hpho planes of each ligand are not in parallel.[3,4] During the process of synthesizing this platinum(II) complex, it was found unexpectedly that the title complex crystals, black-violet in color, were deposited together with the yellow platinum(II) crystals from the mother liquor, and in some cases they also precipitated from the filtrate of the main product. Although efforts to synthesize this complex separately have not yet been successful, its crystals have a characteristic color and shape different from the yellow platinum(II) complex **2**, so they can easily be separated by hand. Its crystal and molecular structures have been determined by the single crystal X-ray diffraction method.

Experimental

Growth of the Crystals of the Title Complex. The mother liquor used to obtain the title complex, [2-(2-benzoxazolyl)phenolatotetrachloroplatinum]·[2-(2-benzoxazolyl)phenol]·ethanol (**1**), has the same composition as that used to synthesize the Pt(II) complex **2**:[3,4] A solution of platinum(IV) chloride pentahydrate (1 g, 2 mmol in 15 cm^3 of ethanol) was mixed with a solution of Hbxp (1.5 g, 7 mmol in 300 cm^3 of ethanol), and the mixture was stirred, and left standing at room temperature for one month or longer. By this procedure, the yellow platinum(II) complex **2** crystals[3,4] can be reliably obtained, but the black-violet crystals of the title complex have appeared only in a few cases, always coprecipitated as a minor component with **2**. All attempts to precipitate only the black-violet crystals including addtion of some oxydizing agents, or changing the composition of the mother liquor, have ended in failure so far. In the best results to date, the amount of the obtained title complex, which appeared as the minor component of the bivalent complex, is approximately 0.02 g (1.1%) from the starting materials of the above mentioned quantities. Found: C, 40.87; H, 2.76; N, 3.39%. Calcd for $PtC_{28}H_{23}O_5N_2Cl_4$: C, 41.79; H, 2.88; N, 3.48 %.

X-Ray Crystal Structure Analysis. The black-violet crystal used for the structure determination was shaped into a sphere (ϕ=0.31 mm). The intensities of the range of $3<2\theta<55°$ (2θ) were collected on a Rigaku AFC-6A automated four-circle X-ray differactiometer using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å), by means of ω–2θ scan technique (scan speed, 4° min^{-1} (ω), scan width, 1.14+0.35 tan θ (ω/°)). The intensities were corrected for Lorentz and polarization factors, as well as for absorption. Of 6817 indenpendent intensities collected, 4217 with $|F_o|>3\sigma(|F_o|)$ were used for the structure calculation.

All the calculations were carried out on a HITAC M-682H computer at the Computer Centre of the University of Tokyo using a local version of UNICS program.[5] The scattering factors were taken from Ref. 6.

The structure was solved by the heavy-atom method. The positional and thermal parameters were refined by a block-diagonal least-squares method. At the final stage, all the non-hydrogen atoms were found and were refined anisotropically. All the hydrogen atoms were excluded from the structure calculations. The final R and R_w values obtained were reduced to 0.057 and 0.064, respectively.[7]

The proton nmr spectra were recorded using JEOL JNM-GX270 FT NMR Spectrometer.

Results and Discussion

The selected bond lengths and bond angles are tabulated in Table 1, the perspective view of the complex together with the numbering scheme of the atoms is shown in Fig. 1, the projection of the unit cell along b-axis in Fig. 2, and the projection of the atoms of the bxp$^-$ ring on both sides to a mean square plane of one Hbxp ring in Fig. 3.[8]

As shown in Fig. 1, the central platinum atom is in a 4Cl, N, O-hexa-coordinated octahedral geometry, where the bxp$^-$ ligand acts as a bidentate ligand forming a

Table 1. Selected Bond Lengths and Bond Angles of the Complex with Their Standard Deviations in Parentheses

Bond length	(l/Å)	Bond length	(l/Å)
Pt-Cl(1)	2.302(6)	Pt-Cl(2)	2.331(6)
Pt-Cl(3)	2.310(4)	Pt-Cl(4)	2.301(3)
Pt-O(1)	2.005(9)	Pt-N(1)	2.008(7)
O(2)-C(9)	1.352(18)	N(1)-C(1)	1.458(19)
N(1)-C(7)	1.327(16)	O(4)-C(29)	1.34(2)
N(2)-C(21)	1.47(2)	N(2)-C(27)	1.34(2)
O(4)···O(5)	2.501(19)		
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
Cl(1)-Pt-Cl(2)	177.4(2)	Cl(1)-Pt-Cl(3)	89.69(17)
Cl(1)-Pt-Cl(4)	90.59(17)	Cl(1)-Pt-O(2)	90.3(3)
Cl(1)-Pt-N(1)	88.8(3)	Cl(2)-Pt-Cl(3)	92.37(17)
Cl(2)-Pt-Cl(4)	91.04(16)	Cl(2)-Pt-O(2)	87.9(3)
Cl(2)-Pt-N(1)	89.4(3)	Cl(3)-Pt-Cl(4)	87.64(12)
Cl(3)-Pt-O(2)	173.7(3)	Cl(3)-Pt-N(1)	96.4(2)
Cl(4)-Pt-O(2)	86.1(3)	Cl(4)-Pt-N(1)	175.9(2)
O(2)-Pt-N(1)	89.9(3)	Pt-O(2)-C(9)	122.6(8)
Pt-N(1)-C(1)	133.4(8)	Pt-N(1)-C(7)	123.1(9)
O(2)-C(9)-C(8)	125.8(14)	O(2)-C(9)-C(10)	115.0(11)
O(4)-C(29)-C(28)	117.5(15)	O(4)-C(29)-C(30)	120.9(14)
C(1)-N(1)-C(7)	103.5(10)	C(21)-N(2)-C(27)	106.9(12)

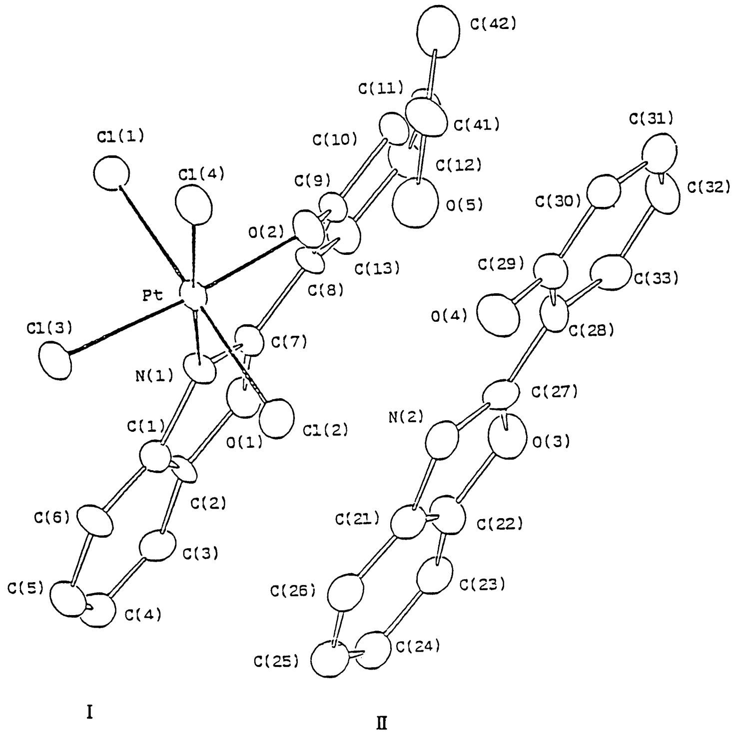

Fig. 1. Perspective drawing of the complex with the numbering scheme of the atoms.

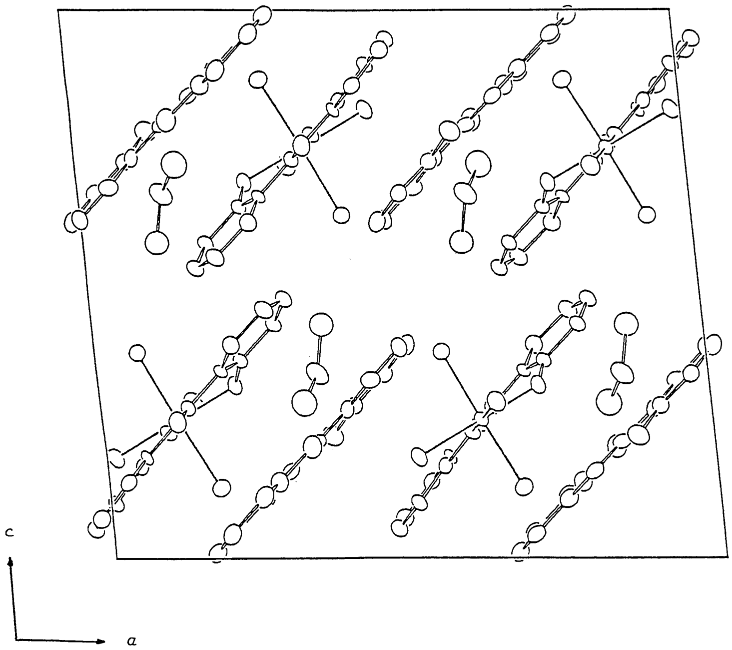

Fig. 2. A projection of the unit cell along c-axis. (i, 0.5+*x*, 1.5−*y*, *z*).

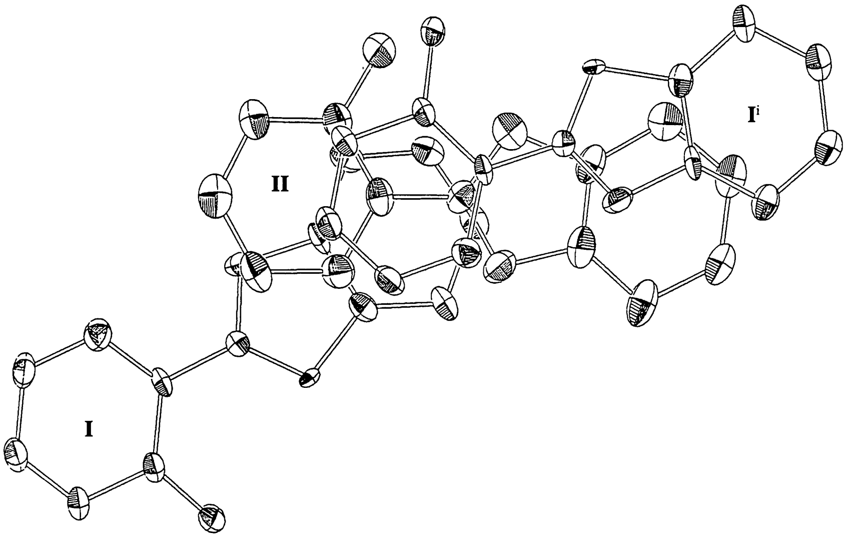

Fig. 3. A projection of the chelated ligand rings on the mean square plane of the non-coordinated Hbxp ring. (i, 0.5+*x*, 1.5−*y*, *z*).

five-membered ring chelate. The coordination geometry is not much deformed from the typical octahedron. As shown in Table 1, the average Pt–Cl, and Pt–N(1), and Pt–O(2) bond lengths are, 2.311 on the average (2.301(3)—2.331(6)), 2.008(7), and 2.005(9) Å, respectively.

The oxidation state of the central platinum seems to be somewhat peculiar, because the 2-(2-benzoxazolyl)-phenol ligand acts as a uninegative bxp$^-$ ion in these complexes. Considering the stoichiometry as well as the characteristically intense color of the crystals, the oxidation number of the central platinum can be expected to be +5. As the bond lengths are usually affected by the valence and coordination number of the bonding atoms, the bond lengths around the platinum atom were compared with the sum of the Shannon's ionic radii.[9] In the hexa-coordinated octahedral complexes, Pt–Cl, Pt–N, and Pt–O bond lengths estimated from the Shannon's ionic radii show clearly different values for Pt(V) and Pt(IV). For Pt(V) complexes, Pt–Cl, Pt–N, and Pt–O bond lengths are: 2.435, 2.085, and 1.975 Å, and for Pt(IV) complexes,

Table 1a. Positional Parameters ($\times 10^3$)

Atom	x	y	z	$B_{eq}/\text{Å}^2$
Pt	1258.3(2)	3870.8(4)	2516.8(3)	2.44
Cl(1)	718 (2)	4113 (3)	3755 (2)	3.70
Cl(2)	1837 (2)	3715 (3)	1280 (2)	3.89
Cl(3)	150 (2)	3108 (4)	1827 (2)	4.03
Cl(4)	1534 (2)	1601 (3)	2845 (2)	3.95
O(1)	1249 (4)	8100 (7)	2484 (5)	3.53
O(2)	2244 (4)	4316 (8)	3148 (5)	3.17
O(3)	3386 (5)	8498 (9)	2021 (6)	4.56
O(4)	3751 (5)	4369 (10)	2222 (6)	4.92
N(1)	1082 (5)	5890 (7)	2286 (5)	2.29
N(2)	2991 (6)	6465 (12)	1576 (6)	4.21
C(1)	581 (6)	6648 (12)	1669 (7)	3.06
C(2)	680 (6)	7999 (13)	1834 (7)	2.86
C(3)	322 (7)	9070 (13)	1383 (8)	3.57
C(4)	−195 (7)	8642 (13)	722 (8)	3.82
C(5)	−309 (7)	7251 (14)	530 (8)	3.98
C(6)	74 (6)	6168 (14)	998 (7)	3.73
C(7)	1446 (6)	6881 (11)	2737 (7)	2.60
C(8)	2034 (5)	6771 (12)	3409 (6)	2.53
C(9)	2376 (6)	5495 (12)	3598 (7)	2.78
C(10)	2974 (6)	5428 (13)	4259 (7)	3.15
C(11)	3182 (6)	6596 (14)	4718 (7)	3.53
C(12)	2847 (7)	7862 (14)	4520 (8)	3.83
C(13)	2248 (7)	7935 (13)	3886 (8)	3.62
C(21)	2539 (7)	7495 (13)	1074 (8)	4.03
C(22)	2789 (7)	8719 (15)	1383 (9)	4.54
C(23)	2520 (7)	9969 (16)	1113 (9)	5.21
C(24)	1928 (7)	9854 (14)	439 (9)	4.51
C(25)	1660 (7)	8563 (15)	100 (9)	4.59
C(26)	1953 (7)	7303 (15)	424 (8)	4.22
C(27)	3478 (7)	7165 (13)	2111 (7)	3.36
C(28)	4035 (6)	6635 (15)	2705 (8)	3.76
C(29)	4161 (7)	5187 (14)	2771 (8)	3.79
C(30)	4716 (7)	4641 (15)	3347 (8)	4.18
C(31)	5133 (7)	5577 (17)	3871 (9)	5.09
C(32)	5009 (7)	7005 (17)	3831 (9)	4.78
C(33)	4472 (8)	7517 (13)	3239 (8)	4.15
C(41)	3601 (8)	1045 (15)	3359 (10)	5.28
C(42)	3752 (10)	1502 (21)	4248 (11)	7.49
O(5)	3335 (7)	2152 (12)	2824 (8)	7.53

2.38, 2.03, and 1.92 Å respectively. However, the observed bond lengths of Pt–Cl and Pt–N for our complex **1** were much shorter than those of these Pt(V) and Pt(IV) complexes, and Pt–O bond length was a little longer than the Shannon's values. Therefore, it cannot be decided whether the valence of the platinum ion in **1** is +5 or +4 from X-ray analysis. The relatively large covalent character of the Pt–Cl bond of **1** may decrease the bond length, and the steric effect of the large bxp$^-$ ligand may also affect the bond lengths of Pt–N and Pt–O.

Although there is a possibility that the chelating ligand is a non-changed Hbxp and that the central metal platinum ion has the oxidation number of +4, such type chelate ring of the bxp ligand has not yet been found in any metal complexes.

The benzoxazolyl (bxz) ring and the phenol (Hpho) or phenolato (pho) ring of a bxp$^-$ as well as of Hbxp in **1** are approximately planar: The average of the deviation of all the atomic positions from their respective ring planes (mean square planes of the bxz or the pho ring atoms) is only 0.016 Å (0.0018—0.0503 Å). The dihedral angles between the mean square planes of the whole ring atoms and the respective mean square planes of the bxz and pho or Hpho ring atoms are bxp$^-$=12.3°, and Hbxp=3.2°. This is much different from what was found in **2**, where the Hbxp act as unidentate ligands where the dihedral angle between the two ring planes in each ligand is much larger.[3,4] The dihedral angle between the mean square plane of the Hbxp(II) ring atoms and the bxp$^-$ ring atoms neighboring on both sides of the former plane (I, and I^i; i, $0.5+x$, $1.5-y$, z) are 3.7° and 4.5° respectively. As a result, in the crystal of **1**, bxp$^-$ and Hbxp rings are arranged approximately in parallel and are laid alternately along a-axis. The interplanar distances between the neighboring bxp$^-$

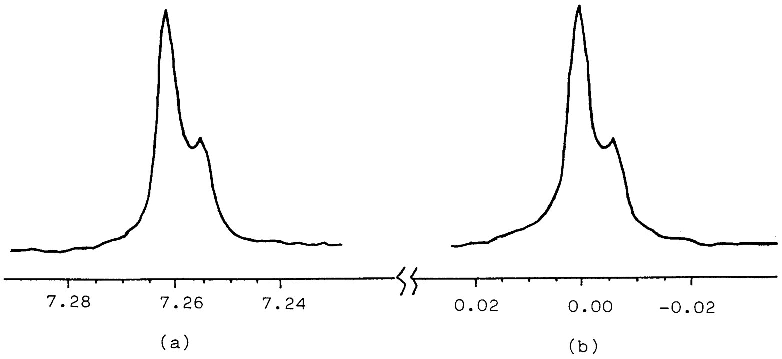

Fig. 4. 270 MHz proton NMR spectra of TMS-containing deuteriochloroform with centrally placed black-violet platinum complex (2.0 mg inserted in coaxially placed capillary of 1.0 mm outer diameter) in the ordinary 5 mm sample tube. (a) $CHCl_3$ (impurity in $CDCl_3$) (b) TMS. Paramagnetically shifted signals are clearly shown in both species.

(I) plane and a Hbxp (II) plane (calculated by the average distance between the bxp$^-$ ring atom positions and the mean square plane of the Hbxp) is 3.42 Å, while that of the Hbxp (II) and the other neighboring bxp$^-$ (I^i) ring is 3.49 Å. The overlapping of the rings II and I or I^i are calculated from the overlapping areas between the rings of II and the projection of the ring I or I^i on it as show in Fig. 3: They were 23% (I–II) and 13% (II–I^i) respectively. Consequently, the π-electron clouds of the neighboring bxp$^-$ and Hbxp rings are thought to be interacting by overlapping each other.

If the platinum ion has an oxidation number of +5, it must have unpaired electrons and should show clear paramagnetism due to these unpaired electrons.(10) Unfortunately the small quantity of the obtained sample prevented us from measuring the magnetic susceptibility by ordinary methods such as Gouy balances. Moreover, this complex is not readily soluble in appropriate solvents, or decomposes gradually by the reaction with solvents.

An attempt to detect paramagnetism with the highly sensitive customary NMR technique,(11–13) was carried out with slight modification.(14) A capillary containing about 2 mg of the sample was coaxially placed in an NMR tube filled with deuterio-chloroform with TMS as a standard of chemical shift. The two proton signals due to $CHCl_3$ (impurity in $CDCl_3$) and TMS were recorded by the usual procedure. The two chemical shift values of the main peak (bulk liquid) remained unchanged, and the smaller components of both signals showed a clear upfield shift (Fig. 4) which showed that the closely neighboring nuclei surrounding the capillary tube are affected by the paramagnetism.

As this signal splitting was observed only when the sample in the capillary is paramagnetic,(14) it may be safely concluded that the present complex is paramagnetic.

These rather queer characteristics of complex **1** suggest that there is some possibility of the existence of apparently pentavalent platinum in this complex.

Although more detailed studies would be needed to elucidate this peculiar oxidation state, it seems quite interesting to compare our complex with the other already-known Pt(V) complexes. Some Pt(V) complexes, mainly its fluoro complexes, have been already reported: For example, $XePt(V)F_6$,(15) and $(O_2)Pt(V)F_6$.(16) However, these compounds are not stable and are easily reduced. On the other hand, the obtained complex is stable in open air.

Probably the electrons of the complex are diffused, not only in the ligated bxp$^-$ ligand, but also all throughout the lined up complexes and Hbxp molecules via overlapping π-electron clouds. This delocalization of the electrons may be the cause of the extraordinary apparent valence of the metal ion in this complex.

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8) The final atomic positional as well as anisotropic thermal parameters, the structure factor table, and some additional bond lengths and bond angles of the complex are deposited as Document No. 9095 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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