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Studies on Mixed Valence Complexes of Platinum and Palladium. II.[1] The Crystal Structures of $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$, $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$, and $[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$

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The crystal structures of Pt(II)–Pt(IV) complexes, $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$ (**1**), $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$ (**2**), and $[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$ (**3**) have been determined by the single-crystal X-ray diffraction method, where tn denotes trimethylenediamine. The crystals of these complexes are isomorphous with one another and the space group is A222 with $a=10.790(2)$, $b=13.872(2)$, $c=10.287(1)$ Å for **1**, $a=11.003(6)$, $b=13.979(6)$, $c=10.355(4)$ Å for **2**, and $a=10.925(3)$, $b=13.862(3)$, $c=10.291(1)$ Å for **3**. The structures were determined by the heavy atom method and refined by the block-diagonal least-squares method to give the disagreement factor 0.082, 0.089, and 0.086 for **1**, **2**, and **3**, respectively. Each crystal comprises infinite $Pt^{II}\cdots X–Pt^{IV}–X\cdots$ chains running parallel to the a-axis. In the chain, tetragonal bipyramidal $[Pt^{IV}X_2(tn)_2]^{2+}$ (X=Cl or Br) and square planar $[Pt^{II}(tn)_2]^{2+}$ units are stacked alternately. Two of the fluorine or oxygen atoms of the counter anion are hydrogen-bonded to the nitrogen atoms of the ligand, contributing to the formation of an infinite chain.

In the preceding paper,[1] we reported the preparation of a number of mixed-valence complexes, $[Pt(AA)_2][PtX_2(AA)_2]Y_4$, $[Pd(AA)_2][PtX_2(AA)_2]Y_4$, and $[Pd(AA)_2][PdX_2(AA)_2]Y_4$, (AA = ethylenediamine(en), propylenediamine(pn), trimethylenediamine(tn); X= Cl, Br, I; Y=ClO_4, BF_4). In the visible region, the complexes show a characteristic broad band assigned to the charge-transfer transition from Pt(II) to Pt(IV). They are of interest in connection with the oxidation states of the platinum atoms and the charge-transfer mechanism between platinum atoms.

In this work, the crystal structures for three complexes, $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$, $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$, and $[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$ have been determined by the single-crystal X-ray diffraction method in order to verify the mixed valence state and to discuss the oxidation state of each platinum atom in more detail.

Experimental

Single-crystals for X-ray work were obtained by recrystallization from a dilute perchloric acid or tetrafluoroboric acid solution at room temperature. Red needle crystals of $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$ show remarkable dichroism; they are dark-red for polarized light along the needle axis and almost colorless for polarized light perpendicular to the axis. $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$ and $[Pt(tn)_2][PtBr(tn)_2](BF_4)_4$ are lustrous dark-green needle crystals, and also show strong dichroism; they are dark-green parallel to, and light-green perpendicular to the needle axis.

Rotation and Weissenberg photographs about the needle axis (a-axis) were taken for each compound. In contrast to the even layer lines, the odd layer lines are weak in intensity. Similar phenomena were found in Wolffram's red salt,[2] $PtBr_3en$,[3] and related compounds,[4–7] consisting of infinite chains, $\cdots Pt^{II}\cdots X–Pt^{IV}–X\cdots$.

Approximate unit-cell parameters were obtained from the Weissenberg photographs, and refined later by a least-squares procedure using 2θ values of 15 high-angle reflections ($25° < 2\theta < 45°$) measured on a Syntex P$\bar{1}$ diffractometer. Bond's method[8] was applied to ground the crystals. However, no spherical crystals favorable for X-ray work could be obtained owing to the brittleness of the crystals. Hence, a nearly cubic crystal with dimensions *ca.* 0.3×0.3×0.3 mm was used for the intensity measurement. Intensity data were collected on a Syntex P$\bar{1}$ automated four-circle diffractometer by the 2θ-θ scan technique with a variable scan rate in the range 4.0°—24.0°/min using Mo $K\alpha$ radiation monochromoated by a

TABLE 1. CRYSTAL DATA

Compound	$[Pt(tn)_2]\ [PtCl_2(tn)_2]\ (BF_4)_4$	$[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$	$[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$
Formula	$Pt_2Cl_2F_{16}N_8C_{12}B_4H_{40}$	$Pt_2Br_2Cl_4O_{16}N_8C_{12}H_{40}$	$Pt_2Br_2F_{16}N_8C_{12}B_4H_{40}$
M.W.	1103.9	1244.2	1193.6
Color	Red-needle	Dark green needle	Dark green needle
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	A222	A222	A222
a(Å)	10.790(2)	11.003(6)	10.925(3)
b(Å)	13.872(2)	13.979(6)	13.862(3)
c(Å)	10.287(1)	10.355(4)	10.291(1)
V(Å^3)	1539.8(5)	1572.8(14)	1558.5(6)
D_{cal}(g cm^{-3})	2.382	2.594	2.543
Z	2	2	2
μ(cm^{-1})(Mo $K\alpha$)	107.0	132.1	132.0
F(000)	984	1180	1116
$2\theta_{max}$	60	54	60
N ref(obsd)	1260	1034	1287

graphite plate. Three standard reflections were monitored after each measurement of 50 reflections, their intensities showing good stability. The Lorentz and polarization corrections were applied to the intensity data. Since the present structure analysis was focussed on the determination of the arrangement of heavier atoms and their interatomic distances, no correction was made for absorption. The crystal data are given in Table 1.

Structure Determination and Refinement

The structures were determined by the heavey-atom method, and refined by the block-diagonal least-squares method. The function minimized was $\sum\omega(|F_o|-k|F_c|)^2$, where k is a scale factor and $\omega=1$ for $|F_o|>5.0$ and $\omega=0$ for $|F_o|<5.0$. The space group, in each case, was determined as A222 unequivocally based on the Patterson maps. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[9] Anomalous dispersion corrections were applied to Pt and Br atoms. All calculations were carried out on a FACOM 230-75 computer in the Computer Center of Kyushu University, the UNICS Program System being used.[10] The final positional and thermal parameters with their estimated standard deviations are given in Table 2. The tables of observed and calculated structure factors are deposited in the office of the Chemical Society of Japan as a Document No. 7842.

$[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$. The Patterson function gave the positions of platinum and chlorine atoms. The minimum function based on the platinum and chlorine positions revealed the positions of the nitrogen and boron atoms. In this stage the space group was unequivocally determined to be A222 on the basis of restrictions on crystal packing of the counter ions. Successive Fourier synthesis revealed all the remaining non-hydrogen atoms. The atomic positions and isotropic temperature factors were refined by the block-diagonal least-squares method, the disagreement factor (R) being reduced to 9.3%. Refinement was carried out with anisotropic temperature factors for the Pt and Cl atoms and isotropic ones for all the remaining non-hydrogen atoms, the final R value being 8.2%.

Table 2. Positional and thermal parameters with their estimated standard deviations in parentheses($\times 10^4$) (Anisotropic thermal parameters are expressed in the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.)

$[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$

	x/a	y/b	z/c	B(Å^2)
Pt(1)	0	0	0	—
Pt(2)	1/2	0	0	—
Cl	2870(7)	0	0	—
N(1)	171(26)	1076(16)	1393(22)	3.8(4)
N(2)	5169(33)	1062(15)	1403(21)	3.1(4)
C(1)	546(24)	928(19)	2609(28)	2.5(4)
C(2)	0	0	3291(63)	6.8(9)
C(3)	5557(38)	920(34)	2614(53)	6.0(8)
C(4)	1/2	0	3320(53)	6.8(11)
B	2548(42)	3052(27)	793(35)	3.7(6)
F(1)	1471(23)	2539(22)	510(24)	7.2(6)
F(2)	3578(22)	2601(20)	233(31)	8.1(6)
F(3)	2597(20)	3885(14)	−133(26)	6.2(4)
F(4)	2390(29)	3264(19)	2025(26)	8.1(6)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt(1)	37(1)	22(0)	44(1)	0	0	0
Pt(2)	39(1)	20(0)	39(1)	0	0	0
Cl	55(5)	21(2)	42(4)	0	0	−26(15)

$[Pt(tn)_2][Pt\ Br_2(tn)_2](ClO_4)_4$

	x/a	y/b	z/c	B(Å^2)
Pt(1)	0	0	0	—
Pt(2)	1/2	0	0	—
Br	2686(7)	0	0	—
Cl	2518(12)	3055(7)	738(10)	—
N(1)	−139(24)	1045(19)	1432(23)	1.3(5)
N(2)	4976(61)	1055(29)	1363(36)	4.1(7)
C(1)	636(38)	937(32)	2624(42)	2.3(7)
C(2)	0	0	3343(82)	9.8(21)
C(3)	5362(68)	923(61)	2701(65)	7.5(18)
C(4)	1/2	0	3273(60)	4.2(11)
O(1)	1487(43)	2522(38)	503(43)	8.6(11)
O(2)	3610(40)	2561(35)	−87(62)	7.4(9)
O(3)	2802(29)	3902(22)	126(40)	4.3(7)
O(4)	2379(50)	3167(34)	2066(42)	7.4(9)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt(1)	17(1)	21(1)	37(2)	0	0	0
Pt(2)	22(1)	18(1)	28(1)	0	0	0
Br	132(8)	37(2)	49(4)	0	0	5(12)
Cl	59(8)	32(4)	100(11)	1(20)	−46(23)	8(13)

$[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$

	x/a	y/b	z/c	B(Å^2)
Pt(1)	0	0	0	—
Pt(2)	1/2	0	0	—
Br	2674(5)	0	0	—
N(1)	191(27)	1068(18)	1426(24)	2.1(4)
N(2)	5226(28)	1072(21)	1459(29)	2.8(5)
C(1)	600(32)	890(31)	2646(43)	3.1(6)
C(2)	0	0	3252(61)	4.6(10)
C(3)	5569(35)	923(36)	2662(50)	3.9(8)
C(4)	1/2	0	3335(46)	3.1(7)
B	2557(28)	3077(28)	776(42)	3.1(7)
F(1)	1520(28)	2588(23)	637(32)	6.1(7)
F(2)	3548(21)	2569(25)	240(43)	7.2(8)
F(3)	2626(30)	3887(18)	−82(50)	6.9(6)
F(4)	2291(41)	3264(29)	2026(29)	7.9(9)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt(1)	18(1)	12(0)	32(1)	0	0	0
Pt(2)	19(1)	11(0)	29(1)	0	0	0
Br	121(4)	24(1)	55(3)	0	0	−30(7)

$[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$. The structure was determined by a procedure similar to that for $[Pt(tn)_2]$-$[PtCl_2(tn)_2](BF_4)_4$, the final R value being 8.9%.

$[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$. Since this compound was thought to be isomorphous with $[Pt(tn)_2]$-$[PtBr_2(tn)_2](ClO_4)_4$, the positional parameters of the perchlorate and the over-all temperature factor calculated from Wilson's plot were used as the initial parameters of the refinement. After 5 cycles of the refinement, the R value was reduced to 10.5%. Refinement was then

TABLE 3. INTERATOMIC BOND DISTANCES $[\mathrm{Pt(tn)_2}]$ (l/Å) AND ANGLES (ϕ/°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$[\mathrm{Pt(tn)_2}][\mathrm{PtCl_2(tn)_2}](\mathrm{BF_4})_4$			
Pt(1)–Cl	3.096(6)	N(2)–C(3)	1.33(5)
Pt(2)–Cl	2.299(6)	C(3)–C(4)	1.58(5)
Pt(1)–N(1)	2.07(2)	B–F(1)	1.39(5)
N(1)–C(1)	1.33(3)	B–F(2)	1.39(4)
C(1)–C(2)	1.58(4)	B–F(3)	1.49(4)
Pt(2)–N(2)	2.07(2)	B–F(4)	1.31(4)
N(1)–Pt(1)–N(1)$^{\mathrm{a)}}$	88.1(8)	N(2)–C(3)–C(4)	115(4)
N(1)–Pt(1)–N(1)$^{\mathrm{b)}}$	92.7(8)	C(3)–C(4)–C(3)$^{\mathrm{a)}}$	125(4)
Pt(1)–N(1)–C(1)	124(1)	F(1)–B–F(2)	110(3)
N(1)–C(1)–C(2)	111(4)	F(1)–B–F(3)	106(3)
C(1)–C(2)–C(1)$^{\mathrm{a)}}$	127(4)	F(1)–B–F(4)	103(3)
N(2)–Pt(2)–N(2)$^{\mathrm{a)}}$	89.2(8)	F(2)–B–F(3)	92(3)
N(2)–Pt(2)–N(2)$^{\mathrm{b)}}$	91.6(8)	F(2)–B–F(4)	126(3)
Pt(2)–N(2)–C(3)	125(2)	F(3)–B–F(4)	117(3)
$[\mathrm{Pt(tn)_2}][\mathrm{PtBr_2(tn)_2}](\mathrm{ClO_4})_4$			
Pt(1)–Br	2.955(7)	N(2)–C(3)	1.46(7)
Pt(2)–Br	2.546(7)	C(3)–C(4)	1.47(8)
Pt(1)–N(1)	2.08(2)	Cl–O(1)	1.37(5)
N(1)–C(1)	1.50(5)	Cl–O(2)	1.62(5)
C(1)–C(2)	1.66(5)	Cl–O(3)	1.37(3)
Pt(2)–N(2)	2.04(3)	Cl–O(4)	1.39(4)
N(1)–Pt(1)–N(1)$^{\mathrm{a)}}$	89.4(9)	N(2)–C(3)–C(4)	114(5)
N(1)–Pt(1)–N(1)$^{\mathrm{b)}}$	91.9(9)	C(3)–C(4)–C(3)$^{\mathrm{a)}}$	132(5)
Pt(1)–N(1)–C(1)	118(2)	O(1)–Cl–O(2)	106(2)
N(1)–C(1)–C(2)	102(3)	O(1)–Cl–O(3)	124(2)
C(1)–C(2)–C(1)$^{\mathrm{a)}}$	126(5)	O(1)–Cl–O(4)	98(2)
N(2)–Pt(2)–N(2)$^{\mathrm{a)}}$	87(1)	O(2)–Cl–O(3)	87(2)
N(2)–Pt(2)–N(2)$^{\mathrm{b)}}$	92(1)	O(2)–Cl–O(4)	130(3)
Pt(2)–N(2)–C(3)	124(4)	O(3)–Cl–O(4)	112(2)
$[\mathrm{Pt(tn)_2}][\mathrm{PtBr_2(tn)_2}](\mathrm{BF_4})_4$			
Pt(1)–Br	2.921(5)	N(2)–C(3)	1.31(5)
Pt(2)–Br	2.541(5)	C(3)–C(4)	1.59(5)
Pt(1)–N(1)	2.09(2)	B–F(1)	1.33(5)
N(1)–C(1)	1.35(5)	B–F(2)	1.40(5)
C(1)–C(2)	1.53(5)	B–F(3)	1.43(5)
Pt(2)–N(2)	2.12(2)	B–F(4)	1.34(5)
N(1)–Pt(1)–N(1)$^{\mathrm{a)}}$	90.0(9)	N(2)–C(3)–C(4)	115(4)
N(1)–Pt(1)–N(1)$^{\mathrm{b)}}$	91.0(9)	C(3)–C(4)–C(3)$^{\mathrm{a)}}$	126(3)
Pt(1)–N(1)–C(1)	123(2)	F(1)–B–F(2)	111(3)
N(1)–C(1)–C(2)	112(3)	F(1)–B–F(3)	111(3)
C(1)–C(2)–C(1)$^{\mathrm{a)}}$	131(4)	F(1)–B–F(4)	91(3)
N(2)–Pt(2)–N(2)$^{\mathrm{b)}}$	90(1)	F(2)–B–F(3)	96(3)
N(2)–Pt(2)–N(2)$^{\mathrm{b)}}$	91(1)	F(2)–B–F(4)	129(4)
Pt(2)–N(2)–C(3)	126(2)	F(3)–B–F(4)	116(3)

a) Key $\bar{x}, \bar{y}, z$. b) Key $\bar{x}, y, \bar{z}$.

TABLE 4. HYDROGEN BOND DISTANCES (Å)

Compound	A$^{\mathrm{a)}}$ N(2)–F(2) or (N(2)–O(2))	B$^{\mathrm{a)}}$ N(2)$^{\mathrm{b)}}$–F(2) (N(2)$^{\mathrm{b)}}$–O(2))	C$^{\mathrm{a)}}$ N(1)–F(1) (N(1)–O(1))
$[\mathrm{Pt(tn)_2}][\mathrm{PtCl_2(tn)_2}](\mathrm{BF_4})_4$	2.99(4)	3.03(4)	2.63(4)
$[\mathrm{Pt(tn)_2}][\mathrm{PtBr_2(tn)_2}](\mathrm{ClO_4})_4$	2.99(7)	2.93(7)	2.89(5)
$[\mathrm{Pt(tn)_2}]$ $[\mathrm{PtBr_2(tn)_2}](\mathrm{BF_4})_4$	3.03(4)	3.02(4)	2.68(4)

a) Hydrogen bonds depicted in Fig. 2. b) Key, $\bar{x}, y, \bar{z}$.

carried out with anisotropic temperature factors for the Pt and Br atoms, the final *R* value being 8.6%.

Description of the Structure

The crystal structure of [Pt(tn)$_2$][PtCl$_2$(tn)$_2$](BF$_4$)$_4$ and the atom numbering systems are shown in Fig. 1. Bond distances and bond angles with their estimated standard deviations are given in Table 3, hydrogen bond distances in Table 4.

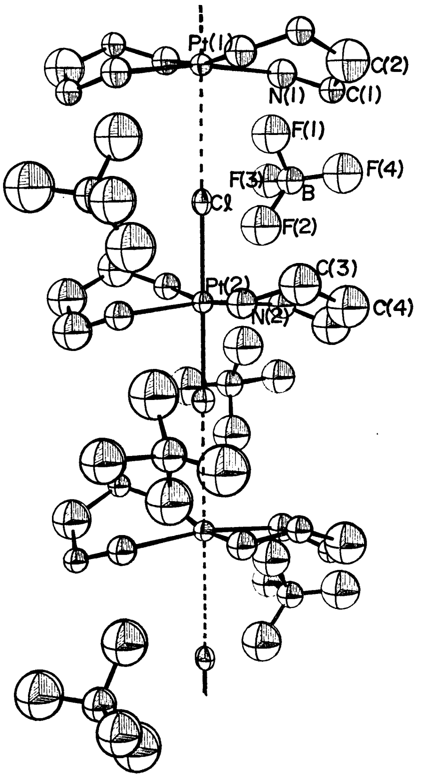

Fig. 1. A perspective view of [Pt(tn)$_2$][PtCl$_2$(tn)$_2$](BF$_4$)$_4$ and the numbering system of atoms. The vibrational spheres and ellipsoids are drawn at the 50% probability.[14]

[Pt(tn)$_2$][PtCl$_2$(tn)$_2$](BF$_4$)$_4$. The crystal contains infinite ···Pt(1)···Cl–Pt(2)–Cl··· chains running parallel to the a-axis. Pt(1) and Pt(2) occupy (0,0,0) and (1/2,0,0), respectively. Hence, the Pt(1)–Pt(1) and Pt(2)–Pt(2) distances correspond to the length of the a-axis.

Each platinum atom is coordinated with four nitrogen atoms of diamines in a square planar configuration with normal Pt–N distances of Pt(II) and Pt(IV) complexes. However, the Pt(1)–Cl (3.096(6) Å) and Pt(2)–Cl (2.299(6) Å) distances are quite different. The latter is close to the value (2.32 Å) of the Pt–Cl distance in *trans*-[PtCl$_2$(NH$_3$)$_4$]Cl$_2$,[11] which is a discrete Pt(IV) complex, and is also near the value (2.27 Å) calculated from atomic radii.[12] On the other hand, the former distance is greater than the normal covalent Pt–Cl distance, though it is still small enough to bring about some interaction between Pt(1) and Pt(2), as evidenced by the characteristic visible absorption.[13] Thus, the compound can be regarded to comprise square planar [Pt$^{\mathrm{II}}$(tn)$_2$]$^{2+}$ and tetragonal bipyramidal [Pt$^{\mathrm{IV}}$Cl$_2$(tn)$_2$]$^{2+}$ units which are stacked alternately in the chain.

The distances N(1)–F(1) (or –O(1)), N(2)–F(2) (or –O(2)), and N(2)$^{\mathrm{b)}}$–F(2) (or –O(2)) (Table 4 and Fig. 2) indicate that the atoms are hydrogen-bonded. These hydrogen bonds seem to serve for the formation of the complexes of this type.

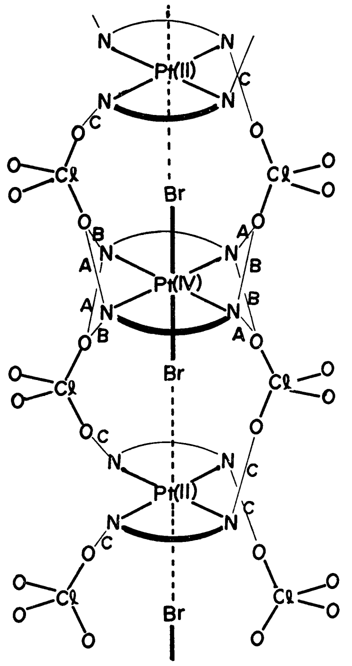

Fig. 2. A schematic representation of the hydrogen bonds. (A, B, and C refer to Table 4.)

[Pt(tn)$_2$][PtBr$_2$(tn)$_2$](ClO$_4$)$_4$ and [Pt(tn)$_2$][PtBr$_2$(tn)$_2$](BF$_4$)$_4$. The crystal structures are essentially the same as that of [Pt(tn)$_2$][PtCl$_2$(tn)$_2$](BF$_4$)$_4$. The Pt–Br distances are 2.546(7) and 2.955(7) Å for [Pt(tn)$_2$][PtBr$_2$(tn)$_2$](ClO$_4$)$_4$, and 2.541(5) and 2.921(5) Å for [Pt(tn)$_2$][PtBr$_2$(tn)$_2$](BF$_4$)$_4$, respectively. The Pt(2)–Br bond distances (2.546(7), 2.541(5) Å) are greater than the sum of the covalent bond radii 2.43 Å.[12] They are also greater than the corresponding distances in the related compounds, [Pt(ea)$_4$][PtBr$_2$(ea)$_4$]Br$_4$·4H$_2$O (2.447 Å)[5] and [Pt(ea)$_4$][PtBr$_2$(ea)$_4$]Br$_4$ (2.42 Å),[4] where ea denotes ethylamine. The Pt(1)–Br distances (2.955(7), 2.921(5) Å) are smaller than those in the related complexes [Pt(ea)$_4$][PtBr$_2$(ea)$_4$]Br$_4$·4H$_2$O (3.107, 3.139 Å)[5] and [Pt(ea)$_4$][PtBr$_2$(ea)$_4$]Br$_4$ (3.19, 4.07 Å).[4]

Discussion

The crystal structure is exactly in accord with what we had expected.[1] The fact that the ···Pt$^{\mathrm{II}}$···X–Pt$^{\mathrm{IV}}$–X··· chains array along the needle axis of crystal is also in line with our prediction deduced from the consideration of the polarization of the visible absorption.[1]

The relation between ν_{max} of the visible absorption and the Pt–halogen distances has not been clarified. The difference in Pt–Br distances between the per-

Table 5. Absorption maximum and platinum–halogen distances

Compound	ν_{max}(kcm^{-1})	Pt$^{\mathrm{IV}}$–X(Å)	Pt$^{\mathrm{II}}$–X(Å)	a(Å)	ρ=(Pt$^{\mathrm{IV}}$–X)/(Pt$^{\mathrm{II}}$–X)
$[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$	20.62	2.299(6)	3.096(6)	10.790(2)	0.74
$[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$	16.53	2.546(7)	2.955(7)	11.003(6)	0.86
$[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$	14.08	2.541(6)	2.921(5)	10.925(3)	0.87

chlorate and the tetrafluoroborate seems to be too small to account for the remarkable red-shift of the visible band (Table 5).

It is of interest to examine the oxidation states of the platinum atoms in the crystal in terms of the ratio of interatomic distances between platinum and halogen, ρ=(Pt(IV)–X)/(Pt(II)–X). In the case $\rho<1$, there is a difference in oxidation state between platinum atoms. When ρ approaches unity, the difference decreases to zero; the oxidation states of platinum atoms being leveled out at $\rho=1$. All the ratios are less than unity, and the ρ value of the bromo-complexes is larger than that of the chloro-complex (Table 5). This indicates that the extent of leveling of oxidation states of platinum atoms is greater in bromo-complexes than in the chloro-complex, as a result of the stronger Pt(II)⋯Br–Pt(IV) interaction. In this connection, it is of interest to consider the ρ value of the iodo-homologs expected to assume a value greater than that of bromo-homologs. The single-crystal X-ray analysis of $[Pt(tn)_2][PtI_2(tn)_2](ClO_4)_4$ is in progress, preliminary data showing $\rho \approx 0.91$.

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