Studies on Mixed Valence Complexes of Platinum and Palladium. I. Preparation and Characterization of Pt(II)-Pt(IV), Pd(II)-Pt(IV), and Pd(II)-Pd(IV) Complexes of the General Formula, $[M(AA)_2][M'X_2(AA)_2]Y_4$

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A series of deeply colored mixed valence complexes of the general formula $[M(AA)_2][M'X_2(AA)_2]Y_4$ were prepared and characterized, where M-M′=Pt(II)-Pt(IV), Pd(II)-Pt(IV), and Pd(II)-Pd(IV); (AA)=ethylenediamine, propylenediamine, and trimethylenediamine; X=Cl, Br, and I; Y=ClO_4, BF_4. The relationships between the reflection spectra and the nature of the constituents (X, (AA), Y and M-M′) of the compounds were studied. The value of $\bar{\nu}_{max}$ of the main absorption band in the visible region decreases in the order: Cl→Br→I, pn→tn→en, ClO_4→BF_4, Pd(II)-Pt(IV)→Pt(II)-Pt(IV)→Pd(II)-Pd(IV). On the basis of dichroism of the crystals, it can be predicted that the X-M′(IV)-X···M(II) atoms in these complexes are arrayed in a straight line parallel to the crystal needle.

Of a group of platinum compounds which appear to contain Pt(III), the most typical ones are PtA_2X_3 and PtA_4X_3, where A represents ammonia or organic monoamine, and X halogen or other monovalent anions.[1)] These compounds are not simple Pt(III) compounds, but mixed valence compounds containing Pt(II) and Pt(IV) in 1:1 ratio, since they are diamagnetic and display strong color.[2)] This was verified by sigle-crystal X-ray analysis.[3–8)] It was found that they consist of square planar Pt(II) and tetragonal bipyramidal Pt(IV) complexes arrayed in lines as shown in Fig. 1.

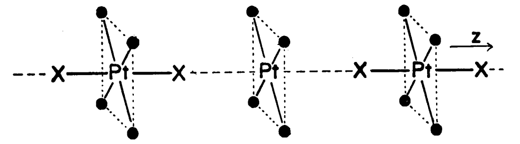

Fig. 1. The skeletal structure of Pt(II)-Pt(IV) mixed-valence complexes.

Yamada and Tsuchida studied the polarized single-crystal spectra of these compounds and attributed the strong absorption to the charge transfer transition from Pt(II) to Pt(IV), assuming a considerable electron exchange interaction between Pt(II) and Pt(IV) through the intervening halogen atom.[9)] Recently, Clark *et al.* have shown on the basis of resonance Raman study that such an interaction actually exists between Pt(II) and Pt(IV) through the halogen atom.[10)]

In spite of an increasing interest in the Pt(II)-Pt(IV) mixed valence compounds,[11)] only a limited number of such compounds are known so far. Wolffram's red salt $[Pt(ea)_4][PtCl_2(ea)_4]Cl_4\cdot 4H_2O$ (ea=ethylamine) is known to be of the PtA_4X_3 type. However, no other homologs were known except the bromo derivative,[1)] until Kida reported the synthesis of $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$, suggesting the possibility of the synthesis of other homologous compounds.[12)]

We have synthesized numerous Pt(II)-Pt(IV) compounds of the type, $[Pt(AA)_2][PtX_2(AA)_2]Y_4$ (AA=ethylenediamine(en), propylenediamine(pn), or trimethylenediamine(tn); X=Cl, Br, or I; Y=ClO_4 or BF_4). We have succeeded in the preparation of Pd(II)-Pt(IV) and Pd(II)-Pd(IV) compounds of similar type. We measured powder reflectance spectra of the compounds in order to elucidate the relationship between the band positions and the constituents of the compounds such as diamine, halogen, counter ion, and metal ion.

Experimental

Starting Materials. $[Pt(AA)_2]Cl_2$,[13)] $[Pd(AA)_2]Cl_2$,[14)] and $[PtX_2(AA)_2]X_2$[15)] (AA=en, pn, tn; X=Cl, Br) were prepared according to the reported methods.

Pt(II)-Pt(IV) Compounds. Compounds of this type were prepared by a procedure similar to that for $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$.[12)] The tetrafluoroborates were prepared by the same method as that for the perchlorate except for use of a 42% tetrafluoroboric acid solution instead of a 60% perchloric acid solution. Some typical examples are shown below. The procedure of Bekaroglu *et al.* was employed[16)] for iodo derivatives.

i) $[Pt(en)_2][PtBr_2(en)_2](BF_4)_4$: Equimolar amounts of $[Pt(en)_2]Cl_2$(386 mg) and $[Pt(en)_2Br_2]Br_2$(635 mg) were dissolved in 20 ml of water. To this solution was added dropwise a 42% tetrafluoroboric acid solution to yield dark green needles with metallic luster, which were filtered and then washed with a small amount of water and then acetone. Recrystallization was carried out from a dilute tetrafluoroboric acid solution.

ii) $[Pt(tn)_2][PtI_2(tn)_2](ClO_4)_4$: One millimole of $[Pt(tn)_2]Cl_2$(414 mg) was dissolved in 20 ml of water. To this solution was added an excess amount of I_2 dissolved in ethanol. The solution was evaporated almost to dryness in a rotary evaporator under reduced pressure in order to remove unreacted I_2. To this residue were added 414 mg (1 mmol) of $[Pt(tn)_2]Cl_2$, 440 mg of $NaClO_4$, and 5 ml of 42% tetrafluoroboric acid. Golden needles with metallic luster were separated from the solution. They were filtered and recrystallized from a dilute perchloric acid solution.

Pd(II)-Pt(IV) Compounds. The compounds were obtained by a procedure similar to that for the Pt(II)-Pt(IV) compounds using $[Pd(AA)_2]Cl_2$ instead of $[Pt(AA)_2]Cl_2$.

Pd(II)-Pd(IV) Compounds. $[PdX_2(AA)_2]X_2$ was not isolated because of its low stability. However, in the mixed valence state Pd(IV) is much stabilized. Hence, $[Pd(AA)_2]^{2+}$ was oxidized by X_2 to form $[PdX_2(AA)_2]^{2+}$, which immediately reacted with the remaining $[Pd(AA)_2]^{2+}$ in a perchloric acid solution. Preparation of iodo homologs of this series was not successful. Typical examples of the procedure are shown below.

i) *[Pd(en)$_2$][PdCl$_2$(en)$_2$](ClO$_4$)$_4$*: One half gram of [Pd(en)$_2$]Cl$_2$ was dissolved in 10 ml of water. Ten millilitres of 60% perchloric acid was added to this solution, and chlorine gas was passed into the solution under ice-cooling. Dark green fine needles with metallic luster immediately separated out. The crystals were dissolved in a small amount of cold water and filtered. To the filtrate was added 60% $HClO_4$ under ice-cooling in order to obtain the crystals, which were filtered and washed with water and acetone. It should be noted that the Pd(IV) oxidation state is stable only in the crystal lattice of the mixed valence compound. Thus, recrystallization was carried out as quikly as possible.

ii) *[Pd(en)$_2$][PdBr$_2$(en)$_2$](ClO$_4$)$_4$*: This was prepared by a procedure similar to that described above except for use of Br_2 instead of Cl_2.

Measurement. Powder reflectance spectra were obtained with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000.

Results and Discussion

The results of elemental analyses are given in Table 1. All the compounds crystallized from aqueous solutions forming strongly colored needles or long prisms, exhibiting remarkable dichroisms, *i.e.*, strongly colored for the

TABLE 1. ELEMENTAL ANALYSIS OF $[M(AA)_2][M'X_2(AA)_2]Y_4$

M	M′	(AA)	X	Y	%C		%H		%N	
					Found	Calcd	Found	Calcd	Found	Calcd
Pt	Pt	en	Cl	ClO_4	8.94	8.74	2.89	2.93	10.26	10.19
Pt	Pt	pn	Cl	ClO_4	12.40	12.47	3.48	3.49	9.68	9.70
Pt	Pt	tn	Cl	ClO_4	12.47	12.47	3.52	3.49	9.68	9.70
Pt	Pt	en	Cl	BF_4	9.16	9.16	2.96	3.08	10.66	10.69
Pt	Pt	pn	Cl	BF_4	12.95	13.05	3.75	3.65	9.92	10.14
Pt	Pt	tn	Cl	BF_4	13.13	13.05	3.74	3.65	10.17	10.14
Pt	Pt	en	Br	ClO_4	8.21	8.09	2.72	2.71	9.61	9.43
Pt	Pt	pn	Br	ClO_4	11.77	11.58	3.20	3.24	9.09	9.01
Pt	Pt	tn	Br	ClO_4	11.62	11.58	3.25	3.24	9.08	9.01
Pt	Pt	en	Br	BF_4	8.52	8.45	2.95	2.84	9.92	9.85
Pt	Pt	pn	Br	BF_4	12.01	12.08	3.44	3.38	9.30	9.39
Pt	Pt	tn	Br	BF_4	12.00	12.08	3.55	3.38	9.27	9.39
Pt	Pt	en	I	ClO_4	7.58	7.49	2.49	2.52	8.66	8.74
Pt	Pt	pn	I	ClO_4	10.73	10.77	2.94	3.01	8.30	8.37
Pt	Pt	tn	I	ClO_4	10.93	10.77	3.01	3.01	8.47	8.37
Pt	Pt	pn	I	BF_4	10.37	10.60	3.42	3.53	8.30	8.24
Pt	Pt	tn	I	BF_4	11.06	10.60	3.29	3.53	8.47	8.24
Pd	Pt	en	Cl	ClO_4	9.45	9.50	3.15	3.19	10.86	11.09
Pd	Pt	pn	Cl	ClO_4	13.38	13.50	3.75	3.78	10.47	10.51
Pd	Pt	tn	Cl	ClO_4	13.45	13.50	3.72	3.78	10.43	10.51
Pd	Pt	en	Cl	BF_4	10.14	10.00	3.34	3.35	11.42	11.67
Pd	Pt	pn	Cl	BF_4	14.11	14.18	4.02	3.96	10.97	11.03
Pd	Pt	tn	Cl	BF_4	14.27	14.18	3.93	3.96	10.96	11.03
Pd	Pt	en	Br	ClO_4	8.83	8.73	2.94	2.93	10.26	10.19
Pd	Pt	pn	Br	ClO_4	12.51	12.46	3.47	3.49	9.71	9.70
Pd	Pt	tn	Br	ClO_4	12.56	12.46	3.55	3.49	9.79	9.70
Pd	Pt	en	Br	BF_4	9.31	9.50	3.16	3.06	10.81	10.69
Pd	Pt	pn	Br	BF_4	13.17	13.03	3.70	3.65	10.29	10.14
Pd	Pt	tn	Br	BF_4	12.93	13.03	3.88	3.65	9.94	10.14
Pd	Pt	pn	I	ClO_4	11.12	11.53	3.05	3.23	8.62	8.97
Pd	Pt	tn	I	ClO_4	11.70	11.53	3.25	3.23	9.12	8.97
Pd	Pd	en	Cl	ClO_4	10.36	10.42	3.42	3.50	11.49	12.15
Pd	Pd	pn	Cl	ClO_4	14.68	14.74	4.07	4.12	11.49	11.46
Pd	Pd	tn	Cl	ClO_4	14.56	14.74	4.12	4.12	11.27	11.46
Pd	Pd	en	Cl	BF_4	10.92	11.03	3.71	3.70	12.65	12.86
Pd	Pd	pn	Cl	BF_4	15.35	15.54	4.34	4.35	11.88	12.08
Pd	Pd	tn	Cl	BF_4	15.44	15.54	4.52	4.35	12.05	12.08
Pd	Pd	en	Br	ClO_4	9.69	9.51	3.12	3.19	11.24	11.09
Pd	Pd	pn	Br	ClO_4	13.52	13.51	3.77	3.78	10.59	10.50
Pd	Pd	tn	Br	ClO_4	13.60	13.51	3.77	3.78	10.59	10.50
Pd	Pd	en	Br	BF_4	10.04	10.01	3.26	3.36	11.56	11.67
Pd	Pd	pn	Br	BF_4	14.24	14.18	4.02	3.97	10.74	11.03
Pd	Pd	tn	Br	BF_4	14.31	14.18	4.00	3.97	10.93	11.03

Table 2. Color and spectral data (10^3 cm^{-1})

	Pt(II)–Pt(IV)			Pd(II)–Pt(IV)			Pd(II)–Pd(IV)		
	ClO_4	BF_4	Color	ClO_4	BF_4	Color	ClO_4	BF_4	Color
en-Cl	22.73	20.00	red	24.69	23.81	yellow	15.63	15.04	dark green[a]
tn-Cl	22.96	20.62		24.69	23.81		16.39	15.34	
pn-Cl	23.53	21.51		26.32	25.64		19.42	17.30	
en-Br	15.15	14.08	dark green[a]	21.28	20.41	red	13.0[b]	13.0[b]	golden yellow[a]
tn-Br	16.53	14.08		20.83	19.61		13.0[b]	13.0[b]	
pn-Br	17.70	15.87		22.22	21.74		13.0[b]	13.0[b]	
en-I	12.3[b]	—	golden yellow[a]	—	—	golden yellow[a]	—	—	
tn-I	12.3[b]	12.3[b]		13.5[b]	—		—	—	
pn-I	12.3[b]	12.3[b]		13.5[b]	—		—	—	

a) With metallic luster. b) Broad band.

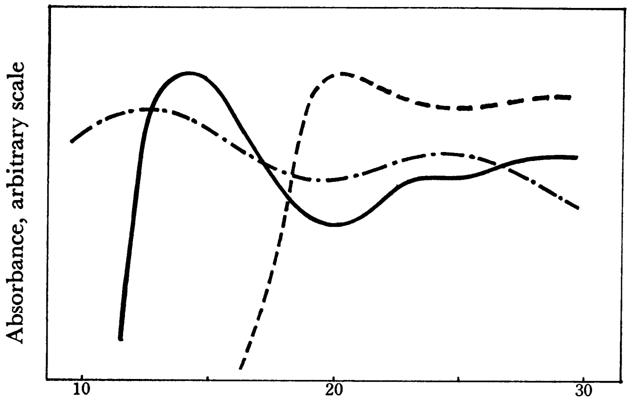

Fig. 2. Powder reflectance spectra of $[Pt(tn)_2][PtX_2(tn)_2](BF_4)_4$; ---- X=Cl, —— X=Br, -·-·- X=I.

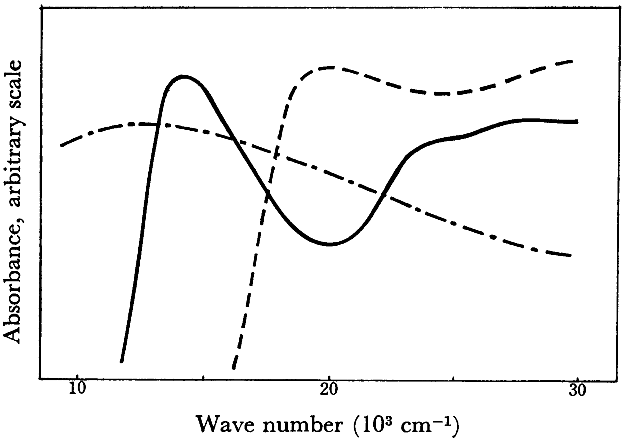

Fig. 3. Powder reflectance spectra of $[M(tn)_2][M'Br_2(tn)_2](BF_4)_4$; —— M–M'=Pt–Pt, ---- M–M'=Pd–Pt, -·-·- M–M'=Pd–Pd.

light polarized along the needle and only slightly colored for the light polarized perpendicular to the needle. The colors and band maxima of the powder reflectance spectra in the visible region are given in Table 2. Some spectra are shown in Figs. 2 and 3. Since no intense coloration of the crystals is observed in aqueous solutions and in either of the constituent complexes $[M(AA)_2]Y_2$ and $[MX_2(AA)_2]Y_2$, the strong absorption in the visible region should be attributed to the charge transfer transition from M(II) to M(IV) (M=Pt or Pd) effected by the interaction between M(II) and M(IV) through the halogen atom.[9] Thus, the band can be assigned to the transition from d_{z^2}\{M(II)\} to the molecular orbital consisting of p_z (halogen) and d_{z^2}\{M(IV)\}, assuming the model depicted in Fig. 1. Since this transition corresponds to the $^1A_1 \leftarrow {}^1A_1{}^*$ in the model (C_{2v} symmetry), it is only allowed for the z axis. Thus, from the fact that the crystals absorb light polarized along the crystal needle only, we can predict that the –Pt–X···Pt··· axis is arrayed parallel to the crystal needle.

On the basis of the theory of charge-transfer complex[2,17] we can assume that the position of the visible band is a measure of the interaction between M(II) and M(IV), *i.e.* the lower the wave-number of the band the stronger the interaction. From the data given in Table 2, it is seen that the $\bar{\nu}_{max}$ of the main absorption band decreases in the order: 1) Cl→Br→I, 2) pn→tn→en, 3) $ClO_4 \rightarrow BF_4$, 4) Pd^{II}-$Pt^{IV} \rightarrow Pt^{II}$-$Pt^{IV} \rightarrow Pd^{II}$-$Pd^{IV}$.

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