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The Hydrothermal Preparation and Characterization of Platinum Metal Complexes with Ethylenediaminetetraacetic Acid and Propylenediaminetetraacetic Acid

Masami SAITO, Takashi UEHIRO,** and Yukichi YOSHINO*

Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

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A new method for hydrothermal syntheses of osmium(III), ruthenium(III), iridium(III), and rhodium(III) complexes with ethylenediaminetetraacetic acid (EDTA) and propylenediaminetetraacetic acid (PDTA) has been developed. More than ten new complexes have been obtained in good yields and characterized by measuring their magnetic susceptibilities, infrared and electronic spectra, and acid-base properties. The stereochemical behavior of the iridium(III) and rhodium(III) complexes has also been described.

It is well known that most of the platinum metal ions are kinetically inert in aqueous solution,[1] that the preparation of their complexes with ethylenediaminetetraacetic acid and propylenediaminetetraacetic acid is not always reproducible, and that the yields are generally low. In order to improve this, the present authors have tried to prepare these complexes at temperatures higher than 100 °C using a Teflon bucket with a stainless-steel holder.[2]

In the present study attention was focused on the complexes of the less familiar platinum metals, *i.e.*, osmium, ruthenium, iridium, and rhodium, and efficient methods of the hydrothermal preparation of their EDTA and PDTA complexes involving some new complexes have been developed. The complexes thus obtained were characterized by measurements of their magnetic susceptibilities, infrared and electronic spectra, and acid-base properties.

Experimental

Materials. Osmium(VIII) oxide from Degussa, ruthenium(IV) oxide from the Japan Engelhard Co., iridium(IV) chloride from the Tanaka Noble Metals Co. and rhodium(III) chloride trihydrate from the Koso Chemicals Co. were employed. The other chemicals were of a reagent grade from the Wako Pure Chemicals Co. and were purified by recrystallization or distillation when necessary. Twice-distilled water was used throughout the experiment. For the hydrothermal preparation, a "Uniseal" with capacity of 23 ml from Uniseal Decomposition Vessels, Ltd., was used.

Physical Measurements. The infrared spectra were recorded on a JASCO Model 403G spectrophotometer, using the nujol or hexachlorobutadiene mull technique. The electronic spectra were obtained on a Hitachi Model 124 spectrophotometer, and the CD spectra, on a JASCO Model J-20 recording spectropolarimeter. The optical rotations were measured by means of a Yanaco Model OR-50 photoelectric polarimeter, and the NMR spectra, on a JEOL JUN-MH-100 spectrometer (100 MHz) at an ambient temperature (*ca.* 20 °C). The magnetic measurements were carried out with a Gouy balance at room temperature. Toa Dempa Digital pH-meters, Types HM-8 and HM-20B, were used for the acid-base titrations.

Preparation of Complexes. The general scheme of hydrothermal syntheses was as follows: the platinum metal halide or halogeno complex (1—4 mmol) and EDTA or PDTA (free acid or disodium salt) were mixed in a ratio of 1 : 1.05 in a bucket. To the mixture we then added 15 ml of water, and the resulting mixture was stirred for a while. Then, the bucket and the sealing lid were set in a stainless-steel holder, and the assembly was heated in an electric oven at temperatures from 100 to 150 °C for several hours or overnight. After the vessel has been cooled, a small amount of insoluble matter was filtered off, and the filtrate was evaporated to a small volume on a water bath. The addition of ethanol is often effective for crystallization.

*$NH_4[OsCl_2(H_2edta)]$ (**1a**).* The starting material, $(NH_4)_2[OsCl_6]$ was prepared by the reduction of OsO_4 with iron(II) in a methanol–HCl solution.[3] A mixture of 1.8 g of $(NH_4)_2[OsCl_6]$ (4 mmol) and 1.2 g of H_4edta (4.1 mmol) was suspended in 15 ml of water in a Teflon bucket, and the apparatus was heated at 150 °C for 5 h. Then, the filtrate was evaporated to a smaller volume. The crystals thus deposited were washed with ethanol and air-dried. Yield, 1.5 g.

*$H[OsCl_2(H_2edta)]\cdot 2.5H_2O$ (**1b**).* The filtrate obtained by the hydrothermal reaction in **1a** was directly passed through a column of cation-exchange resin in the hydrogen form (Dowex 50W, X8, 50—100 mesh). The effluent was concentrated by evaporation on a water bath, and the deposited crystals were washed with cold ethanol. Yield, 1.7 g.

*$NH_4[OsBr_2(H_2edta)]$ (**2a**).* OsO_4 was converted to $(NH_4)_2[OsBr_6]$ by Dwyer's method.[4] Then, a suspension of 2.8 g of $(NH_4)_2[OsBr_6]$ (4 mmol) and 1.2 g of H_4edta (4.1 mmol) in 15 ml of water was heated at 150 °C for 5 h. From the filtrate, yellowish brown crystals were obtained. Yield, 1.0 g.

*$H[OsBr_2(H_2edta)]$ (**2b**).* The above-mentioned filtrate containing **2a** was passed through a column of cation-exchange resin (H^+-form). Yield, 1.0 g.

*$H[RuCl_2(H_2edta)]\cdot 3.5H_2O$ (**3**).* One gram of $RuO_2\cdot nH_2O$ (n=3—4) was dissolved in 20 ml of concd HCl by heating. After repeated heating to dryness, the residue was dissolved in 15 ml of water. To this we added 1.7 g of H_4edta (5.7 mmol), after which the mixture was heated on a water bath to give a clear solution. The resulting solution was heated at 120 °C for 5 h. The filtrate was cooled in an ice bath to give yellow crystals. The crystals were washed with a small amount of cold ethanol and acetone successively. Yield, 2.5 g.

*$Na[RuCl(Hpdta)]\cdot 3H_2O$ (**4**).* To a $RuCl_3$ solution (5.5 mmol) obtained from $RuO_2\cdot nH_2O$ and concd HCl, 5.8 mmol of NaH_3pdta was added. The mixture was heated at 120 °C for 10 h. The filtrate from the reaction mixture was then concentrated to *ca.* 10 ml, and twice the volume of ethanol was added. The fine crystals thus obtained were

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** Present address: National Institute for Environmental Studies, Yatabe, Tsukuba-gun, Ibaraki 305.

washed with ethanol. Yield, 1.5 g.

$\mathrm{Na[IrCl(Hedta)]\cdot 2H_2O}$ (5). A suspension of 0.68 g of $\mathrm{IrCl_4}$ (2 mmol) and 0.75 g of $\mathrm{Na_2H_2edta\cdot 2H_2O}$ (2 mmol) in 15 ml of water was heated at 150 °C for 24 h. The filtrate from the reaction mixture was evaporated to *ca.* 5 ml. When the solution was cooled, yellow crystals separated out. Yield, 0.7 g.

$\mathrm{Na[IrCl(Hpdta)]\cdot 3H_2O}$ (6). A procedure similar to that described in **5** was applied, using $\mathrm{Na_2H_2pdta}$ in place of $\mathrm{Na_2H_2edta}$. Yield, 0.7 g.

$\mathrm{NH_4[RhCl_2(H_2edta)]}$ (7). An aqueous suspension of 1.3 g of $\mathrm{RhCl_3\cdot 3H_2O}$ (5 mmol) and 2.0 g of $\mathrm{Na_2H_2edta\cdot 2H_2O}$ (5.4 mmol) was heated at 120 °C for 5 h. To the filtrate we then added 8 ml of concd HCl, and the solution was evaporated to 10 ml. In this solution, 0.5 g of $\mathrm{NH_4Cl}$ was dissolved, after which the solution was cooled in an ice bath. Yellowish brown crystals were collected and washed with 50% ethanol and diethyl ether successively. Yield, 2.1 g.

$\mathrm{[Os(edta)(H_2O)]\cdot H_2O}$ (8). An aqueous solution (20 ml) containing 1.5 g of $\mathrm{H[OsCl_2(H_2edta)]\cdot 2.5H_2O}$ (**1b**) was aerated for 20 h. The black, lustrous crystals thus deposited were collected and washed with water until free from chloride ions, and then with diethyl ether. Yield, 1.1 g.

$\mathrm{H[OsI(Hedta)]\cdot 2.5H_2O}$ (9a). One gram of **8** was added to 10 ml of concd HI (7.5 mol $\mathrm{dm^{-3}}$), after which the mixture was stirred for 1 h. The $\mathrm{I_2}$ liberated during the procedure was removed by extraction with diethyl ether. The crystals thus deposited were filtered and washed with a small amount of ethanol. Yield, 1.0 g.

$\mathrm{NH_4[OsI(Hedta)]}$ (9b). One gram of **9a** (1.5 mmol) was dissolved in 10 ml of warm water (*ca.* 40 °C). To this we then added 1.5 g of $\mathrm{NH_4I}$. The crystals thus obtained were washed with a small amount of cold water and with ethanol successively. Yield, 0.9 g.

$\mathrm{[Ir(Hedta)(H_2O)]\cdot 1.5H_2O}$ (10). To an aqueous solution containing 3 mmol of **5** (10 ml) we added 3.1 mmol of $\mathrm{AgNO_3}$ dissolved in 10 ml of water; the excess $\mathrm{Ag^+}$ in the filtrate was removed by passing the solution through a column of hydrogen-form cation-exchange resin. After the effluent had been concentrated by evaporation, ethanol was added to give a precipitate. The precipitate was washed with ethanol and diethyl ether. Yield, 1.4 g.

$(-)_{589}$- and $(+)_{589}$-$\mathrm{Na[IrCl(Hedta)]\cdot 2H_2O}$ (11a). One millimole of **5** was dissolved in 10 ml of a warm solution containing 0.5 mmol of $(+)_{589}$-*cis*-$\mathrm{[Co(NO_2)_2(en)_2]Cl}$. When the solution was cooled, yellowish brown crystals of the diastereoisomer separated out, the molar rotion being $[M]_{589}=-84°$. The diastereoisomer was mixed with 1 g of NaI paste and then minimum amount of water was added and filtration was done. The addition of ethanol led to the crystallization of $(-)_{589}$-$\mathrm{Na[IrCl(Hedta)]\cdot 2H_2O}$; $[M]_{589}=-350°$. The $(+)_{589}$-isomer was obtained similarly by using $(-)_{589}$-*cis*-$\mathrm{[Co(NO_2)_2(en)_2]Cl}$; $[M]_{589}=+350°$.

$(+)_{589}$- and $(-)_{589}$-$\mathrm{Na[Ir(Hedta)(H_2O)]\cdot 1.5H_2O}$ (11b). These were prepared by treating **11a** with $\mathrm{AgNO_3}$ in the way described earlier for **10**. $[M]_{589}=\pm 526°$.

$(+)_{589}$- and $(-)_{589}$-Na[IrCl((S)-Hpdta)]$\cdot 3\mathrm{H_2O}$ (12). These complexes were obtained in the same way as in the case of the active $\mathrm{Na[IrCl(Hedta)]\cdot 2H_2O}$ (**11a**) except that the molar ratio of the racemate to the resolving agent was 1 : 1. $[M]_{589}=\pm 380°$. The optically active complex $(-)_{589}$-Na[IrCl((*R*)-pdta)]$\cdot 3\mathrm{H_2O}$ could be prepared directly by using (*R*)-PDTA under somewhat milder conditions, *i.e.*, 120 °C and 20 h. $[M]_{589}=-380°$.

$(-)_{589}$-$\mathrm{[Rh(Hedta)(H_2O)]}$ (13). The reacmic $\mathrm{Na[RhCl(Hedta)]\cdot 2H_2O}$ was resolved by using $(+)_{589}$-*cis*-$\mathrm{[Co(NO_2)_2(en)_2]Br}$; the resulting $(-)_{589}$-$\mathrm{[RhCl(Hedta)]^-}$ was converted into $(-)_{589}$-$\mathrm{[Rh(Hedta)(H_2O)]}$ by treating it with $\mathrm{AgNO_3}$. $[M]_{589}=-260°$.

Results and Discussion

Hydrothermal Preparation. The analytical data for the complexes are presented in Table 1. In Table 2, the results of the hydrothermal preparation of the EDTA and PDTA complexes of osmium(III), ruthenium(III), iridium(III), and rhodium(III) are summarized. Of these, the osmium(III) complexes of EDTA were synthesized for the first time.[5] As may be seen from the table, the yields of the known complexes increased remarkably; for example, the yield of the iridium(III) complex (**5**) increased from 35% to 60%.[6] In the case of rhodium(III), both EDTA and PDTA complexes were obtained nearly quantitatively. As for ruthenium(III), the PDTA complex was obtained for the first time. It is noteworthy that, in the case of the iridium(III)-PDTA complex, $(-)_{589}$-Na[IrCl((*R*)-Hpdta)]$\cdot 3\mathrm{H_2O}$ can be prepared hydrothermally using optically active (*R*)-PDTA as a ligand, without any accompanying

TABLE 1. ANALYSES OF PLATINUM METAL COMPLEXES WITH EDTA AND PDTA

Complex	Found (%)					Calcd (%)				
	M	C	H	N	X	M	C	H	N	X
$\mathrm{NH_4[OsCl_2(H_2edta)]}$	33.97	21.06	3.21	7.47	12.31	33.41	21.08	3.19	7.38	12.45
$\mathrm{H[OsCl_2(H_2edta)]\cdot 2.5H_2O}$	31.73	20.03	3.37	4.69	11.99	31.81	20.11	3.38	4.63	11.57
$\mathrm{NH_4[OsBr_2(H_2edta)]}$	28.64	18.10	2.27	6.33	24.00	28.95	18.28	2.76	6.39	24.32
$\mathrm{H[OsBr_2(H_2edta)]}$	29.43	18.83	2.38	4.42	24.50	29.67	18.77	2.34	4.38	24.93
$\mathrm{NH_4[OsI(Hedta)]}$	28.39	18.19	3.16	6.34	19.20	28.64	18.20	3.21	6.37	19.11
$\mathrm{H[OsI(Hedta)]\cdot 2.5H_2O}$	29.23	18.35	3.06	4.32	19.36	29.17	18.42	2.94	4.30	19.46
$\mathrm{[Os(edta)(H_2O)]H_2O}$	36.92	23.29	3.14	5.54		36.98	23.35	3.14	5.45	
$\mathrm{H[RuCl_2(H_2edta)]\cdot 3.5H_2O}$		22.99	4.21	5.36	12.80		22.85	4.13	5.48	12.91
$\mathrm{Na[RuCl(Hpdta)]\cdot 3H_2O}$		25.63	3.81	5.46	6.98		25.58	3.68	5.42	6.87
$\mathrm{Na[IrCl(Hedta)]\cdot 2H_2O}$	33.09	20.88	2.77	4.93	6.53	33.38	20.85	2.97	4.89	6.15
$\mathrm{Na[IrCl(Hpdta)]\cdot 3H_2O}$		21.41	3.36	4.64	6.00		21.71	3.49	4.61	5.84
$\mathrm{[Ir(Hedta)(H_2O)]\cdot 1.5H_2O}$		22.43	3.41	5.38			22.79	3.45	5.32	
$\mathrm{NH_4[RhCl_2(H_2edta)]}$		24.79	3.69	8.61	14.49		24.90	3.76	8.72	14.73
$\mathrm{Na[RhCl(Hpdta)]\cdot 3H_2O}$		25.73	3.67	5.40	5.25		25.43	4.04	5.39	5.19

Table 2. Hydrothermal syntheses of platinum metal complexes

Metal	Complex	Temp/°C	Time/h	Yield/%
Os(III)	$NH_4[OsCl_2(H_2edta)]$	150	7	70
	$H[OsCl_2(H_2edta)]\cdot 2.5H_2O$	150	7	70
	$NH_4[OsBr_2(H_2edta)]$	150	7	70
	$H[OsBr_2(H_2edta)]$	150	7	70
Ru(III)	$H[RuCl_2(H_2edta)]\cdot 3.5H_2O$	120	5	85
	$Na[RuCl(Hpdta)]\cdot 3H_2O$	120	12	50
Ir(III)	$Na[IrCl(Hedta)]\cdot 2H_2O$	150	24	60(35)[a]
	$Na[IrCl(Hpdta)]\cdot 3H_2O$	150	24	60
Rh(III)	$NH_4[RhCl_2(H_2edta)]$	120	5	90(50)[a]
	$Na[RhCl(Hpdta)]\cdot 3H_2O$	120	5	90(50)[a]

a) Figures in parentheses are literature values.

racemization.

Osmium(III), (IV), and Ruthenium(III) Complexes. All the osmium complexes except **8** were found to be paramagnetic, with magnetic moments ranging from 1.73 to 1.82 B.M. which is to be expected for a spin-only atom with one unpaired electron spin. Hence, together with the analytical data in Table 1, the oxidation state of the osmium was presumed to be +3 with a low-spin $5d^5$ configuration. Some typical examples of the infrared spectra of the osmium-EDTA complexes in the region from 1200 to 1800 cm^{-1} are shown in Fig. 1. In the trivalent osmium complexes, there appear two characteristic CO stretching bands, one in the region of 1600 cm^{-1} and the other in the region higher than 1700 cm^{-1}. The former is assigned to the carboxylate coordinated to the metal, and the latter, to the free carboxylic acid. The frequencies of these bands are tabulated in Table 3. The appearance of these two bands indicates that, in all the complexes of osmium(III), the EDTA is bonded to the octahedral sites as a quinque- or quadridentate ligand. Such an interpretation may be supported by the examination of the pH-titration curves of the complexes with an alkali solution (Fig. 2). In the case of dihalogeno complex acid (**1b** or **2b**), 3 mol of alkali were consumed for 1 mol of osmium(III), indicating the presence of two carboxylic acid radicals. On the other hand, in the case of monohalogeno complex acid (**9a**), 2 mol of alkali were required for 1 mol of osmium(III), indicating the presence of one carboxylic acid radical.

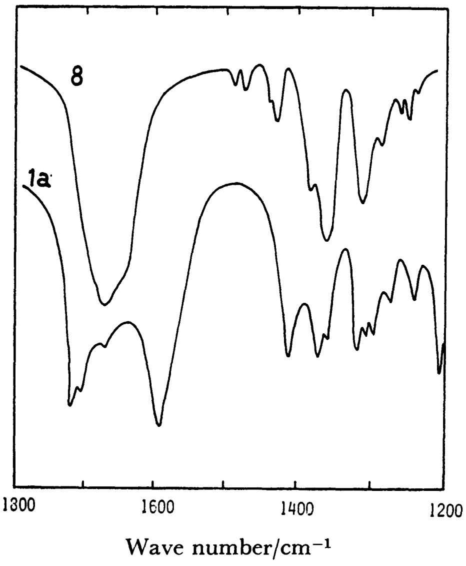

Fig. 1. Infrared spectra of osmium(III) and osmium(IV) complexes with EDTA.
1a: $NH_4[OsCl_2(H_2 edta)]$, **8**: $[Os(edta)(H_2O)]\cdot H_2O$.

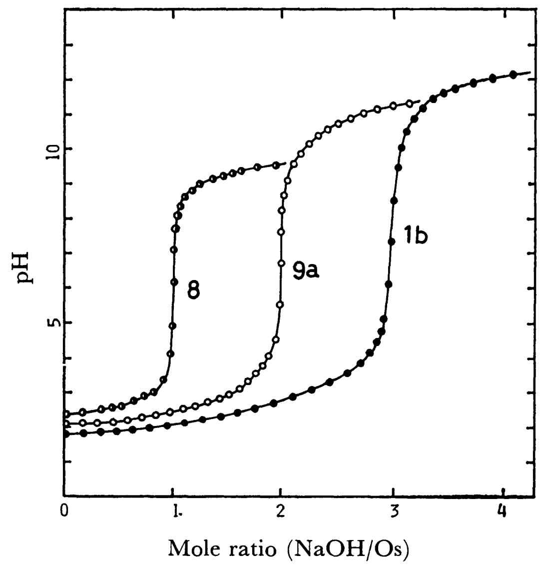

Fig. 2. Titration curves of osmium (III) and osmium (IV) complexes with EDTA at 20 °C.
1b: $H[OsCl_2(H_2edta)]\cdot 2.5H_2O$, 1.0×10^{-2} mol dm^{-3}, **8**: $[Os(edta)(H_2O)]\cdot H_2O$, 4.7×10^{-3} mol dm^{-3}, **9a**: $H[OsI(Hedta)]\cdot 2.5H_2O$, 5.6×10^{-3} mol dm^{-3}, NaOH, 1.2×10^{-1} mol dm^{-3}.

Figure 3 presents some typical examples of the electronic spectra of the osmium(III) complexes. Strong and broad absorption bands are seen in the ultraviolet region.

The **8** complex was found to react with potassium

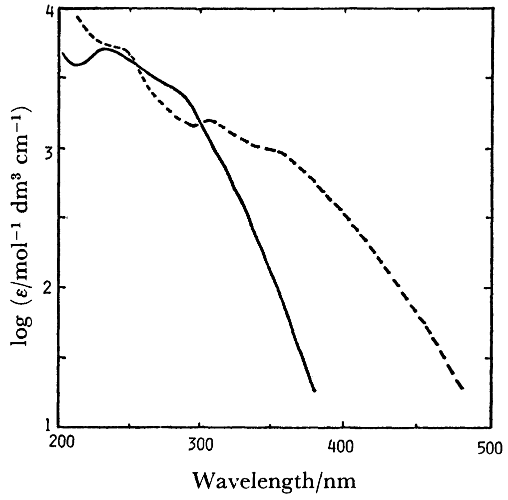

Fig. 3. Electronic spectra of osmium (III) complexes with EDTA.
——: $H[OsCl_2(H_2edta)]\cdot 2.5H_2O$, ------: $H[OsBr_2(H_2edta)]$.

Table 3. Magnetic moments, IR absorption bands, and pK values of Os(III), Os(IV), and Ru(III) complexes with EDTA and PDTA

Complex		IR absorption bands		
	μ/B.M.	ν(COO$^-$)	ν(COOH)	pK_{av} at 20 °C
$NH_4[OsCl_2(H_2edta)]$	1.80	1590	1735	
$H[OsCl_2(H_2edta)]\cdot 2.5H_2O$	1.79	1590	1723	2.8
$NH_4[OsBr_2(H_2edta)]$	1.82	1585	1720	
$H[OsBr_2(H_2edta)]$	1.74	1600	1717	3.0
$NH_4[OsI(Hedta)]$	1.73	1620	1725	
$H[OsI(Hedta)]\cdot 2.5H_2O$	1.78	1620	1725	2.6
$[Os(edta)(H_2O)]\cdot H_2O$	dia	1675		2.6
$H[RuCl_2(H_2edta)]\cdot 3.5H_2O$	1.90	1590	1740	2.7
$Na[RuCl(Hpdta)]\cdot 3H_2O$	1.90	1635	1750	2.3[a]

a) The value for H[RuCl(Hpdta)] obtained by cation exchange.

iodide to give **1** equivalent of iodine per mole of osmium; this supports the idea that the oxidation state of the osmium atom is +4. As may be seen from Table 3 and Figs. 1, 2, and 3, the behavior of the tetravalent osmium complex is very different from that of the osmium(III) complexes described above. In the IR spectrum, a strong band was observed at 1675 cm^{-1}, too low to attribute it to a free COOH. In the acid-base titration (Fig. 2), the complex behaves as a rather strong monobasic acid, and deprotonation from a coordinated water molecule can be expected to take place. Furthermore, the magnetic susceptibility of the tetravalent osmium complex was determined to be -140×10^{-6} emu mol^{-1}. This observation seems rather unexpected because, in general, the tetravalent osmium complexes have been known to be paramagnetic, the magnetic moments ranging from 1.2 to 1.8 B.M. at room temperature.[7)]

The question was finally solved by the X-ray structure analysis of a single crystal of the complex. The results revealed that the osmium(IV) complex is seven-coordinate (one edta^{4-} and one water molecule), and so the diamagnetism of the complex could be interpreted in terms of the 18-electron rule.[8)]

The EDTA complexes of ruthenium(III) were prepared for the first time by Mukaida *et al.* in 1965;[9)] since they have been well characterized by other workers as well.[10,11)] In our study, we have attempted the hydrothermal preparation of other ruthenium complexes with EDTA and PDTA; two new complexes, $H[RuCl_2(H_2edta)]\cdot 3.5H_2O$ and $Na[RuCl(Hpdta)]\cdot 3H_2O$ were obtained in good yields. The characteristic properties of these complexes are shown in Table 3.

Iridium(III) and Rhodium(III) Complexes. The iridium complexes, **5**, **6**, and **10** were found to be diamagnetic. With reference to the analytical data (Table 1), the oxidation state of iridium was assumed as +3. In the IR spectra, besides ν_{asym}(COO$^-$) at 1650 cm^{-1}, ν_{asym}(COOH) in the region higher than 1700 cm^{-1} was observed in all the complexes. Therefore, in the solid states of these complexes, EDTA and PDTA may act as quinquedentate ligand, and one Cl$^-$ ion or H_2O molecule may occupy the sixth coordination site.

However, for the monochloro or monoaqua complex, two geometrical isomers are possible; the Cl$^-$ ion or the H_2O molecule may be *trans* to either a nitrogen or oxygen atom. In order to determine the structure, the deuteration of the acetate protons of [IrCl(Hpdta)]$^-$ in D_2O was studied by ^{1}H-NMR. It was observed that the only one AB-pattern with J=16.5 Hz survived after the other acetate signals had diminished upon deuteration. The remaining AB-pattern may be assigned to the in-plane acetate methylene protons.[12)] Therefore, in the present complex, Cl$^-$ ion should be *trans* to a nitrogen atom. This structure is the same as that of the result of the X-ray structure analysis of the corresponding [Rh(Hedta)(H$_2$O)].[13)]

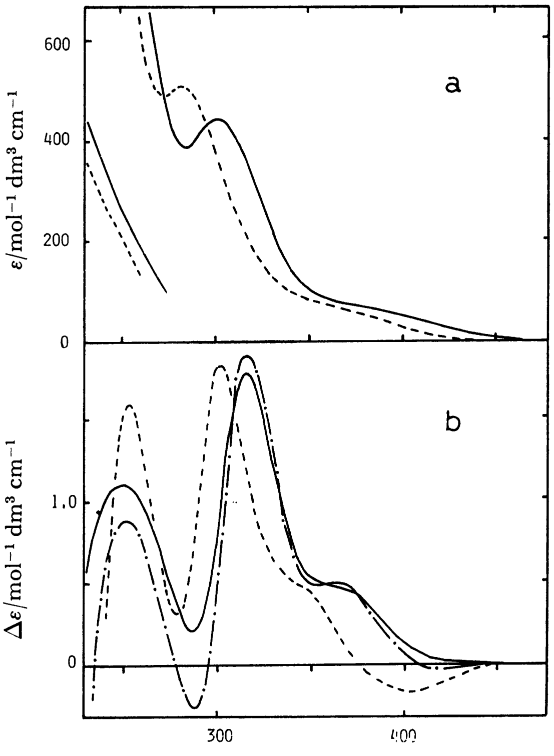

Fig. 4. Electronic and CD spectra of iridium(III) complexes with EDTA and PDTA.
(a): Absorption spectra. ——: Na[IrCl(Hedta)]·2H$_2$O or Na[IrCl(Hpdta)]·3H$_2$O, ------: [Ir(Hedta)(H$_2$O)]·1.5H$_2$O.
(b): CD spectra. ——: $(-)_{589}$-Na[IrCl(Hedta)]·2H$_2$O, —·—: $(-)_{589}$-Na[IrCl(Hpdta)]·3H$_2$O, ------: $(-)_{589}$-[Ir(Hedta)(H$_2$O)]·1.5H$_2$O.

Figure 4 shows the electronic spectra and CD curves. The aqueous solution of Na[IrCl(Hedta)]·2H$_2$O and Na[IrCl(Hpdta)]·3H$_2$O exhibited a very similar spectral pattern; ε=440 at 303 nm and a shoulder (ε=70) at *ca.* 385 nm. These peaks are tentatively assigned to the d-d transitions, though a possible overlapping of charge-transfer bands in the shorter-wavelength region must be taken into consideration. The spectrum of

$[Ir(Hedta)(H_2O)]$ shifts to shorter wavelengths as compared with that of the parent complex, $[IrCl(Hedta)]^-$, *i.e.*, from 303 nm (ε=440) for the monochloro complex to 290 nm (ε=510) for the monoaqua complex. This is consistent with the spectrochemical series.

Since the sexidentate (*R*)-PDTA complexes of cobalt(III) and rhodium(III) have the Δ configuration,[14,15] the corresponding complex of iridium(III) can be expected to have the same configuration. As may be seen from Fig. 4, the CD spectra of the $(-)_{589}$-isomer of EDTA- and PDTA complexes are quite similar. Therefore, it is presumed that $(-)_{589}$-$[IrCl(Hedta)]^-$ has the same structure as that of the sexidentate EDTA complex of the Δ configuration, in which one carboxyl group coplanar with the N–C–C–N chelate is free. This is consistent with the presumption presented by Ezerskaya *et al.* on the basis of the Cotton effects of the iridium(III)–EDTA complexes.[16]

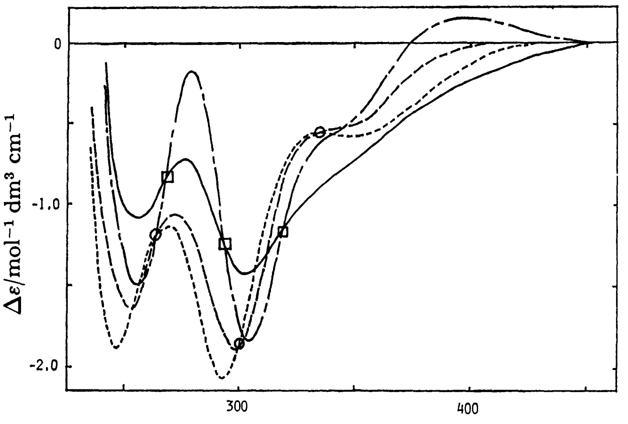

Fig. 5. pH dependence of CD spectra of $(+)_{589}$-$[Ir(Hedta)(H_2O)]\cdot 1.5H_2O$.
------: pH=1.6, ----: pH=2.6, —·—: pH=7.6, ——: pH=10.0.

It was found that the CD spectra of monoaqua complexes of iridium(III) and rhodium(III) shows a remarkable pH dependence, while those of monochloro complexes change little with the pH of the solution (Fig. 5 and Fig. 7). In the case of the iridium(III) complex, in the acidic region three isosbestic points appear at 335, 309, and 264 nm, while in the basic region they shift to 319, 294, and 268 nm. A plot of $\Delta\varepsilon$ values at 280 nm against the pH gives the curve in Fig. 6, while the curve in Fig. 8 was obtained by a similar plot at 315 nm for $(-)_{589}$-$[Rh(Hedta)(H_2O)]$. This behavior implies that there exist stepwise acid-base equilibria between species, I, II, and III, of the Ir(III)- and Rh(III) complexes:

$$\mathrm{I} \underset{pK_1}{\rightleftarrows} \mathrm{II} \underset{pK_2}{\rightleftarrows} \mathrm{III}$$

From the curves in Fig. 6 and Fig. 8, the p*K* values are evaluated as:

pK_1=2.5 and pK_2=9.1 for the Rh(III) complex, and pK_1=2.9 and pK_2=8.4 for the Ir(III) complex.
The p*K* values for the Rh(III)–EDTA complex may be

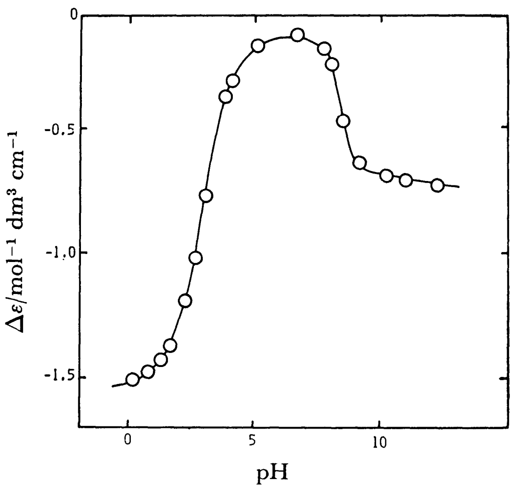

Fig. 6. The plot of $\Delta\varepsilon$ values for $(+)_{589}$-$[Ir(Hedta)(H_2O)]\cdot 1.5H_2O$ against pH at 280 nm.

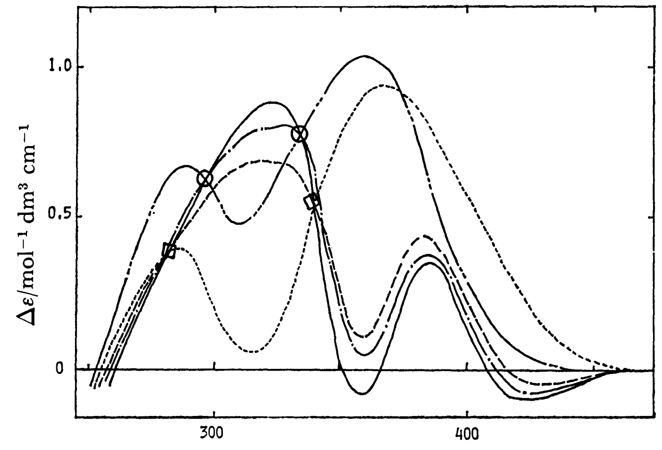

Fig. 7. pH dependence of CD spectra of $(-)_{589}$-$[Rh(Hedta)(H_2O)]$.
—··—: pH=0.8, —·—: pH=2.6, ——: pH=3.5, ----: pH=8.9, ------: pH=12.1.

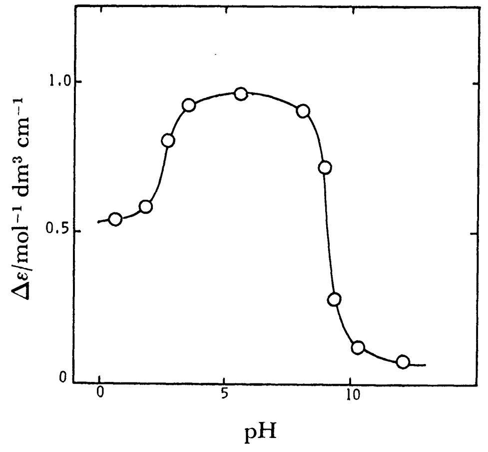

Fig. 8. The plot of $\Delta\varepsilon$ values for $(-)_{589}$-$[Rh(Hedta)(H_2O)]$ against pH at 315 nm.

compared with the values of pK_1=2.32 and pK_2=9.12 reported by Dwyer and Garvan.[17)] Furthermore, the remarkable pH dependence of the CD spectra of the Rh(III) complex may be responsible for the formation of a sexidentate complex, $[\mathrm{Rh(edta)}]^-$, in the intermediate pH region (pH=4—8), as has been suggested by Smith and Sawyer on the basis of their PMR study.[18)] A similar interpretation should be applicable to the pH dependence of the CD spectra of the iridium(III) complexes, but further study is necessary to elucidate the nature of this observation.

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