

## Complexes of the 4d- and 5d-Groups

## III. Absorption Spectra of Marcel Delépine's Rhodium(III) and Iridium(III) Complexes

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Professor M. Delépine has kindly furnished the octahedral complexes of rhodium(III) and iridium(III) with pyridine, oxalate, chloride, bromide, ammonia and water. In the *cis*-isomers of rhodium(III), the first transition to a singlet level is observed approximately at the position interpolated from the complexes with six equal ligands, while the first strong band is split into two bands of *trans*-isomers. However, it is difficult to describe this behaviour quantitatively by the ligand field theory for tetragonal symmetry without assuming interaction with higher  ${}^1T_6$  levels. In iridium(III), the electron transfer bands of oxalate groups and the ultraviolet absorption of pyridine render the observation of singlet bands difficult, while the triplet bands are rather strong due to the intermediate coupling. The *trans*-isomer of  $\text{Ir py}_2\text{Cl}_4^-$ , but not of  $\text{Ir ox}_2\text{Cl}_2^{3-}$ , has the triplet band at a lower wavenumber than the *cis*-isomer. The acidity of water in iridium(III) complexes is remarkably low, thus  $\text{p}K = 5.1$  of *trans*- $\text{Ir py}_2(\text{NH}_3)_3\text{H}_2\text{O}^{+3}$ , 6.7 of *cis*- $\text{Ir py}_2\text{Cl}_3(\text{H}_2\text{O})$  and  $\sim 10.1$  of  $\text{Ir Cl}_5(\text{H}_2\text{O})^-$ .

In the first paper of this series <sup>1</sup>, the absorption spectra of several rhodium(III) and iridium(III) complexes were interpreted as transitions to one of the two triplet levels  ${}^3T_4$  and  ${}^3T_5$  and to the two singlet levels  ${}^1T_4$  and  ${}^1T_5$  of the excited configuration  $\gamma_5^5\gamma_3$  while the groundstate is  ${}^1T_1$  of  $\gamma_5^6$ . This notation <sup>2</sup> is only meaningful for complexes of perfect cubic symmetry, e.g. with six equal ligands in equal distances from the central ion. Most complexes  $\text{M A}_n\text{B}_{6-n}$  with two different ligands A and B arranged in a regular octahedron have tetragonal symmetry <sup>3</sup>, of these *trans*- $\text{M A}_4\text{B}_2$  has a centre of inversion as also  $\text{M A}_6$ , while the other complexes have no centre of inversion. In some cases, the Jahn-Teller effect produces tetragonal symmetry by distortion of  $\text{M A}_6$ , e.g. copper(II)<sup>4-7</sup>. While these effects are conspicuous in the absorption spectra, the regular octahedral  $d^3$ -,  $d^8$ - and diamagnetic  $d^6$ -systems without Jahn-Teller effect <sup>3,8,9</sup> exhibit only small effects of tetragonal splitting with mixed sets of ligands, e.g. nickel(II) complexes <sup>10-12</sup>. Mr. C. E. Schäffer will later demonstrate that the absorption bands of chromium(III) complexes of tetra-

gonal symmetry generally are only slightly widened, but do not always exhibit the splitting, predicted from the ligand field theory by Hartmann and Kruse<sup>13</sup>; Linhard and Weigel<sup>14</sup> found that pentamine complexes of cobalt(III) in most cases exhibit a broadening or a splitting of the first singlet band, which is even more evident in *trans*-substituted cobalt(III) tetramine ions<sup>15</sup>. This led Orgel<sup>16</sup> to apply the ligand field theory on the case, and Basolo, Ballhausen and Bjerum<sup>17</sup> have later given more evidence, while Yamada, Nakahara, Shimura and Tsuchida<sup>18</sup> investigated the dichroism\* of *trans*-Co en<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and *trans*-Co en<sub>2</sub>Br<sub>2</sub><sup>+</sup> in crystals.

Professor Marcel Delépine of Collège de France has kindly placed at my disposal samples of the highly robust *cis*- and *trans*-isomers of rhodium(III) and iridium(III) complexes, which allow a comparison with the behaviour of cobalt(III).

Table 1. Absorption bands of M. Delépine's rhodium(III) complexes.  $\lambda_n$  is the wavelength,  $\sigma_n$  the wavenumber,  $\epsilon_n$  the molar extinction coefficient of each maximum.  $\delta(-)$  is the halfwidth towards smaller and  $\delta(+)$  towards larger wavenumbers. The ligand field quantum numbers of the excited levels are discussed in the text.

	$\lambda_n$ m $\mu$	$\sigma_n$ K	$\epsilon_n$	$\delta(-)$ K	$\delta(+)$ K
<i>cis</i> -Rh ox <sub>2</sub> Cl <sub>2</sub> <sup>-3</sup>	435	23 000	190	1 900	—
	352	28 400	275	2 500	—
	285	35 100	1 900	1 900	—
<i>trans</i> -Rh ox <sub>2</sub> Cl <sub>2</sub> <sup>-3</sup>	470	21 300	54	1 500	2 100
	398	25 100	38	—	—
	285	35 100	1 300	1 800	—
<i>cis</i> -Rh py <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	448	22 400	91	1 800	—
	348	28 700	118	—	—
	270	37 000	8 300	1 100	—
	263.5	38 000	11 800	—	—
	257.0	38 900	14 500	—	—
	222	45 000	36 000	4 800	—
<i>trans</i> -Rh py <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	500	20 000	39	1 600	—
	431	23 200	92	1 500	1 600
	269	37 200	11 600	1 200	—
	261	38 300	14 600	—	—
	256	39 100	14 400	—	—
	216	46 400	36 000	4 000	—
1,2,6-Rh py <sub>3</sub> Cl <sub>3</sub> Rh py <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	422	23 700	76	2 500	—
	411	24 300	70	1 300	1 900
	268	37 300	7 700	500	—
	261.5	38 200	11 300	—	—
	255	39 200	12 100	—	—
	228	43 900	33 000	2 900	—

#### DICHLORO BIS(OXALATO)RHODIUM(III) IONS

Fig. 1 and Table 1 give the absorption spectra of *cis*- and *trans*-Rh ox<sub>2</sub>Cl<sub>2</sub><sup>---</sup> prepared by Delépine<sup>19</sup>. The two bands of the *cis*-isomer are situated nearly as interpolated between the cubic Rh Cl<sub>6</sub><sup>---</sup> and Rh ox<sub>3</sub><sup>---</sup>, given in Ref. 1:

\* Recently, Ballhausen and Moffitt<sup>20</sup> applied the selection rules for transitions, coupled with one quantum of odd vibration, to these dichroic effects, supporting the identification of the first band as  ${}^1A_{1g} \rightarrow {}^1E_{1g}$ .

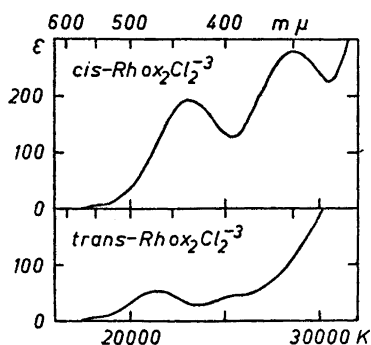


Fig. 1. Absorption spectra of rhodium(III) dichlorodioxalate complexes. 0.006 M *trans*-K<sub>3</sub>[Rhox<sub>2</sub>Cl<sub>2</sub>], 4H<sub>2</sub>O and 0.005 M *cis*-K<sub>3</sub>[Rhox<sub>2</sub>Cl<sub>2</sub>], H<sub>2</sub>O in aqueous solution.

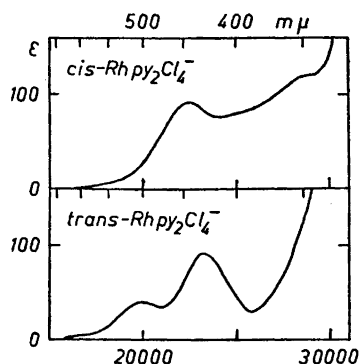


Fig. 2. Absorption spectra of rhodium(III) dipyridentetachloro complexes. 0.014 M *cis*-K<sub>3</sub>[Rhpy<sub>2</sub>Cl<sub>4</sub>], H<sub>2</sub>O and 0.016 M *trans*-K<sub>3</sub>[Rhpy<sub>2</sub>Cl<sub>4</sub>], H<sub>2</sub>O in aqueous solution.

	$\sigma_1$	$\sigma_2$
Rh Cl <sub>6</sub> <sup>---</sup>	19 300 K	24 300 K
Rh ox <sub>3</sub> <sup>---</sup>	25 100	30 000
<i>cis</i> -Rh ox <sub>2</sub> Cl <sub>2</sub> <sup>---</sup>	23 000	28 400
$\frac{1}{3} \sigma_{\mathbf{n}}(\text{RhCl}_6^{---}) + \frac{2}{3} \sigma_{\mathbf{n}}(\text{Rh ox}_3^{---})$	23 170	28 100

In the place of  $\sigma_1$ , the *trans*-isomer gives two weak bands at 21 300 and 25 100 K. These bands<sup>17</sup> are caused by transitions to the levels  ${}^1T_{t_5}$  and  ${}^1T_{t_2}$ , which have the degeneracy numbers 2 and 1, respectively. The weighted average of the two wavenumbers is then 22 600 K.

#### DIPYRIDINE TETRACHLORO RHODIUM(III) IONS

Fig. 2 and Table I give the absorption spectra of *cis*- and *trans*-Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup> studied by Delépine<sup>20</sup>. While *trans*-Rh ox<sub>2</sub>Cl<sub>2</sub><sup>---</sup> is tetragonal in the same way as copper(II) complexes, *viz.* with less crystal field strength along one axis than along the two equivalent axes in a plane, *trans*-Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup> is »compressed« tetragonal<sup>3</sup>, since the order in the spectrochemical series is:



The Rh py<sub>6</sub><sup>+++</sup> is regrettably not known, but its first singlet band can be assumed<sup>1</sup> to be  $\sim 30\,000$  K. The cubic contribution<sup>3</sup> of Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup> is thus 22 900 K. *cis*-Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup> has the first singlet band at 22 400 K. In *trans*-Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup>, two bands are observed at 20 000 and 23 200 K. In this case the second band is stronger than the first, agreeing with the degeneracy numbers 1 and 2. The weighted average is 22 200 K.

## DICHLORO TETRAPYRIDINE RHODIUM(III) IONS

The pale yellow  $\text{Rh py}_4\text{Cl}_2^+$  was first prepared by S. M. Jørgensen<sup>21</sup>. Recently, Delépine<sup>22</sup> discovered the strong catalytic influence of even 1 % of alcohols on the reaction between pyridine and a concentrated aqueous solution of  $\text{Na}_3\text{RhCl}_6$ , forming  $[\text{Rh py}_4\text{Cl}_2]\text{Cl}\cdot 6\text{H}_2\text{O}$ .

The spectrum (Table 1) has a band at 24 400 K, which is so low a wavenumber that it presumably is due to  ${}^1T_{15}$  of a *trans*-complex, which here is analogous to copper(II). The *trans*-configuration is also supported by the formation<sup>21</sup> of  $[\text{Rh py}_4\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$  analogous to the similar *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ . Steric reasons seem to prevent pyridine from using the two perpendicular places.

When  $\text{Rh py}_4\text{Cl}_2^+$  is boiled for some minutes with dilute  $\text{Na}_2\text{CO}_3$ , the band is shifted to 358  $m\mu$  (28 000 K) and by acidification with  $\text{HClO}_4$ , it is shifted to 384  $m\mu$  (26 000 K). This behaviour can be interpreted by the formation of hydroxo- and aquo-complexes, of which the spectra are analogous to  $\text{Co en}_2(\text{OH})_2^+$  and *trans*- $\text{Co en}_2(\text{H}_2\text{O})_2^{+3}$  studied by Bjerrum and Rasmussen<sup>23</sup>. Analogously when *cis*- $\text{Rh py}_2\text{Cl}_4^-$  is boiled with water, or with  $\text{Na}_2\text{CO}_3$  and subsequently with  $\text{HClO}_4$ , the first maximum is shifted to 421  $m\mu$  (23 700 K) corresponding to *cis*- $\text{Rh py}_2\text{Cl}_3(\text{H}_2\text{O})$ . If *trans*- $\text{Rh py}_2\text{Cl}_4^-$  is analogously treated, an orange precipitate<sup>20</sup>, *trans*- $\text{Rh py}_2\text{Cl}_3(\text{H}_2\text{O})\cdot\text{H}_2\text{O}$  is formed, which on heating polymerizes<sup>20</sup> to a completely insoluble pink product,  $\text{Rh py}_2\text{Cl}_3$ . Only one ligand field band has been observed of 1,2,6- $\text{Rh py}_3\text{Cl}_3$  (dissolved in  $\text{CHCl}_3$ ) at 23 700 K. This seems somewhat less than the probable cubic contribution  $\sim 24\,600$  K and may be ascribed to rhombic splitting of  ${}^1F_4$ . However, the larger number of interactions possible between levels in low symmetry may systematically depress the wavenumber of the first band.

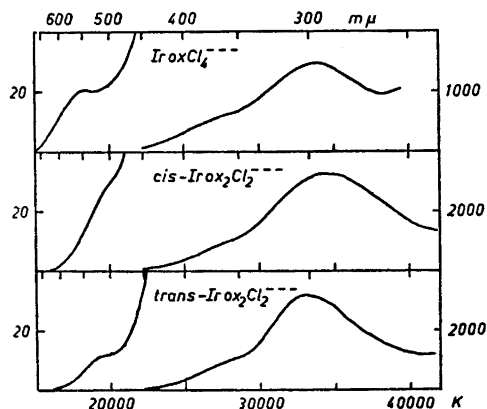


Fig. 3. Absorption spectra of iridium(III) chloro-oxalate complexes. 0.001 M to 0.014 M  $\text{K}_3[\text{Ir oxCl}_4]$ ,  $\text{H}_2\text{O}$ , 0.0006 M to 0.011 M *cis*- $\text{K}_3[\text{Ir ox}_2\text{Cl}_2]$ ,  $\text{H}_2\text{O}$  (racemic form), and 0.0006 M to 0.011 M *trans*- $\text{K}_3[\text{Ir ox}_2\text{Cl}_2]\cdot 5\text{H}_2\text{O}$  in aqueous solution.

Table 2. Absorption bands of M. Delépine's iridium(III) complexes. Notation as in Table 1. In the column "Excited level", triplet and singlet denote ligand field levels, Ir py the transition of an electron from the central ion to pyridine, redox the usual electron transfer spectra in the opposite direction, and py 0, py 1, . . . the vibrational structure of the pyridine band (py broad denotes the actual maximum, when this structure is blurred out), while "oxalate" denotes the ligand transition, polarized by the iridium ion.

	Excited level.	$\lambda_n$ m $\mu$	$\sigma_n$ K	$\epsilon_n$	$\delta(-)$ K
Ir oxCl <sub>4</sub> <sup>-3</sup>	triplet	550	18 200	21	1 700
	(singlet)	~375	26 600	500	—
	oxalate	298	33 600	1 450	4 400
<i>cis</i> -Ir ox <sub>2</sub> Cl <sub>2</sub> <sup>-3</sup>	triplet	510	19 600	27	1 300
	(singlet)	~360	27 800	~1 100	—
	oxalate	294	34 000	3 100	4 200
<i>trans</i> -Ir ox <sub>2</sub> Cl <sub>2</sub> <sup>-3</sup>	triplet	508	19 700	12	1 800
	(singlet)	~368	27 200	~800	—
	oxalate	303	33 000	3 200	3 100
IrCl <sub>5</sub> (H <sub>2</sub> O) <sup>-2</sup>	triplet	550	18 200	12	2 400
	singlet	405	24 700	110	2 200
	singlet	347	28 800	110	—
	triplet	540	18 500	11	1 600
Ir pyCl <sub>5</sub> <sup>-2</sup>	(singlet)	~420	23 800	100	2 000
	Ir py	329.5	30 400	2 250	1 800
	py broad	279	35 800	5 100	1 900
	triplet	464	21 600	20	2 000
<i>cis</i> -Ir py <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	Ir py	313	32 000	4 700	2 000
	(py 0)	267.5	37 400	9 600	—
	(py 1)	263	38 000	9 600	—
	triplet	515	19 400	8.8	1 600
<i>trans</i> -Ir py <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	(singlet)	~395	25 300	~80	—
	Ir py	316	31 600	4 400	1 500
	py 0	273	36 600	8 700	—
	py 1	267	37 400	9 300	—
1,2,3-Ir py <sub>3</sub> Cl <sub>3</sub>	Ir py	326.5	30 600	—	1 700
	py 0	276	36 200	—	—
	py 1	265	37 700	—	—
	triplet	432	23 100	53	2 000
1,2,6-Ir py <sub>3</sub> Cl <sub>3</sub>	Ir py	319	31 400	1 600	2 800
	py broad	265	37 700	—	—
	triplet	404	24 800	25	2 000
	Ir py	284	35 200	7 000	2 400
Ir py <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	py 0	271	36 900	11 400	—
	py 1	264.5	37 800	14 700	—
	py 2	257.5	38 900	16 400	—
	py 3	250	40 000	18 000	—
	py 4	245.5	40 800	—	—
	triplet	455	22 000	23	1 300
	(singlet)	~378	26 500	~150	—
<i>cis</i> -Ir py <sub>2</sub> Cl <sub>3</sub> (H <sub>2</sub> O) Sun-isomer	Ir py	304.5	32 800	5 000	2 000
	py 0	265.5	37 700	9 700	—
	py 1	260	38 500	10 300	—
	Ir py	326	30 700	4 500	2 200
<i>cis</i> -Ir py <sub>2</sub> Cl <sub>3</sub> OH <sup>-</sup> Sun-isomer	(py 0)	275	36 400	8 600	—
	py 1	267	37 400	9 100	—
	triplet	~445	22 500	28	2 800
<i>cis</i> -Ir py <sub>2</sub> Cl <sub>3</sub> (H <sub>2</sub> O) autoclave-isomer	Ir py	304	32 900	5 600	2 000
	(py 0)	265	37 800	10 300	—
	py 1	259	38 600	11 700	—
	triplet	~475	21 000	38	—

autoclave-isomer	Ir py	317.5	31 500	5 300	2 700
	(py 0)	276	36 300	7 800	—
	py 1	268	37 300	8 100	—
<i>trans</i> -Ir py <sub>2</sub> Cl <sub>3</sub> (H <sub>2</sub> O)	triplet	~475	21 000	17	—
	Ir py	307	32 600	4 900	1 800
	(py 0)	271	36 900	8 500	—
	py 1	265	37 800	10 300	—
<i>trans</i> -Ir py <sub>2</sub> Cl <sub>3</sub> (OH) <sup>-</sup>	py 2	260	38 500	10 000	—
	triplet	~488	20 500	~18	—
	Ir py	329.5	30 400	3 900	2 400
	py broad	284.5	35 200	7 200	—
Ir py(NH <sub>3</sub> ) <sub>4</sub> Cl <sup>++</sup>	(triplet)	~365	27 400	30	1 100
	Ir py	290	34 500	2 040	2 000
	py 0	271	36 900	3 400	—
	py 1	265	37 800	3 870	—
	py 2	258.5	38 700	4 060	—
	py 3	251.5	39 800	4 230	—
	py 4	246	40 700	4 350	—
	py 5	239	41 900	4 410	—
	(Ir py?)	282	35 400	5 700	1 400
	py 0	269.5	37 100	8 700	—
Ir py <sub>2</sub> (NH <sub>3</sub> ) <sub>3</sub> H <sub>2</sub> O <sup>+3</sup>	py 1	263.5	38 000	9 700	—
	py 2	256.5	39 000	9 600	—
	py 3	251	39 900	8 700	—
	py 4	245	40 900	8 200	—
	Ir py	304	32 900	4 500	2 600
	py 0	271	36 900	7 200	—
Ir py <sub>2</sub> (NH <sub>3</sub> ) <sub>3</sub> OH <sup>++</sup>	py 1	263	38 000	8 800	—
	py 2	258	38 800	8 800	—
	(triplet)	~370	27 000	~24	700
	Ir py	285.5	35 000	6 600	2 400
	py 0	270.5	37 000	7 600	—
	py 1	264	37 900	9 600	—
Ir py <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> Cl <sup>++</sup>	py 2	258	38 800	10 200	—
	(triplet)	~380	26 300	38	1 300
	Ir py	295	33 900	6 200	2 000
	py 0	272	36 800	8 800	—
	py 1	265	37 700	10 500	—
	py 2	260	38 500	10 400	—
IrBr <sub>3</sub> <sup>-3</sup>	py 3	254	39 400	8 900	—
	triplet	645	15 500	12	—
	triplet	585	17 100	16	—
	singlet	442	22 600	175	1 900
	singlet	380	26 300	145	—
	redox	270	37 000	12 000	2 200
IrBr <sub>3</sub> (H <sub>2</sub> O) <sup>--</sup>	redox	241	41 500	20 000	—
	redox	271	36 900	10 500	2 600
	redox	239.5	41 800	17 500	—
Ir py <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	triplet	515	19 400	17	1 400
	singlet	388	25 800	230	2 200
	Ir py	319	31 400	4 300	2 200
	py broad	270	37 000	11 500	2 700
	redox	~220	45 500	~25 000	—
	Ir py	335	29 800	~5 000	1 600
1,2,3-Ir py <sub>3</sub> Br <sub>3</sub>	py broad	284	35 200	~9 000	—
	triplet	471	21 200	36	1 900
1,2,6-Ir py <sub>3</sub> Br <sub>3</sub>	Ir py	321	31 200	~5 300	2 600
	py broad	269	37 200	~10 000	—

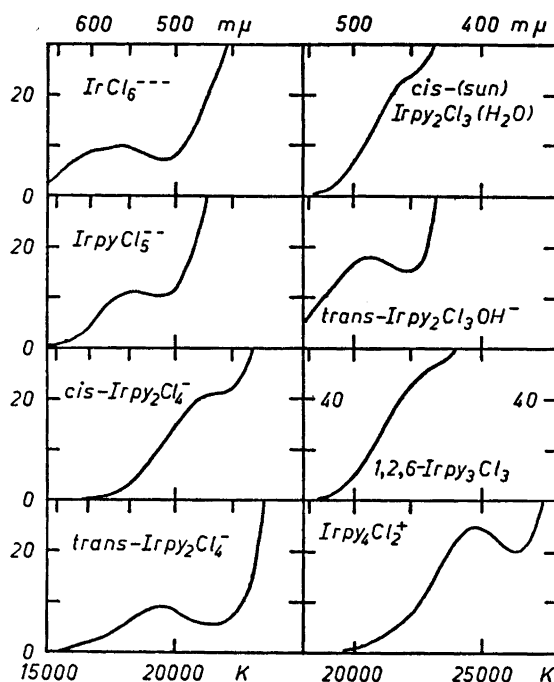


Fig. 4. The ligand field singlet  $\rightarrow$  triplet bands of iridium(III) complexes.

- 0.01 M to 0.2 M  $K_3IrCl_6 \cdot 3H_2O$  in 1 M HCl and pure  $H_2O$ , immediately measured.  
 0.014 M  $K_3[IrpyCl_6] \cdot 3H_2O$  in  $H_2O$ , immediately measured.  
 0.009 M *cis*- $K[Irpy_2Cl_4]$ ,  $H_2O$  in  $H_2O$   
 0.041 M *trans*- $K[Irpy_2Cl_3]$ ,  $H_2O$  in  $H_2O$   
 0.011 M *cis*- $[Irpy_2Cl_3(H_2O)]_2 \cdot 2H_2O$  (sun-isomer) in 0.1 M HCl.  
 0.005 M *trans*- $Irpy_2Cl_3OH^-$  from *trans*- $[Irpy_2Cl_3(H_2O)]$ ,  $H_2O$  in 1 M  $NH_3$ .  
 0.005 M 1,2,6- $Irpy_3Cl_3$  in  $CHCl_3$ .  
 0.005 M  $[Irpy_4Cl_2]Cl_6 \cdot 6H_2O$  in  $H_2O$ .

#### OXALATO- AND CHLORO-IRIDIUM(III) COMPLEXES

Vèzes and Duffour<sup>24</sup> studied the mixed chloro-oxalato complexes of iridium(III), and Delépine<sup>25</sup> later investigated the exact conditions for formation of  $IrOxCl_4^{3-}$ , *cis*- and *trans*- $IrOx_2Cl_2^{3-}$ . In these complexes, the triplet band<sup>1</sup> of  $IrCl_6^{3-}$  can be seen (Table 2 and Fig. 3) to be regularly shifted towards the higher wavenumbers with increasing number of oxalate groups, while the two singlet bands are hidden by the electron transfer band in the ultraviolet. This band has been found by Babaeva and Mosyagina<sup>26</sup> in all oxalate complexes. In iridium(III), the  $\epsilon_n$  of the maximum is 1 600 per oxalate group.

In  $IrOx_3^{3-}$ , all the crystal field bands are hidden<sup>1</sup>. The differences between *cis*- and *trans*- $IrOx_2Cl_2^{3-}$  are the intensity of the triplet band (which have the same position in the two complexes) and 3 % different wavenumbers of the electron transfer band (which perhaps is an internal transition in the oxalate group, analogous to the acetylacetonate<sup>7</sup> absorption.)

## PYRIDINE- AND CHLORO-IRIDIUM(III) COMPLEXES

Delépine<sup>27</sup> prepared the red-brown Ir pyCl<sub>5</sub><sup>−</sup>, and<sup>28</sup> the pink *trans*-Ir py<sub>2</sub>Cl<sub>2</sub><sup>−</sup> and orange *cis*-Ir py<sub>2</sub>Cl<sub>4</sub><sup>−</sup>, and the two yellow compounds<sup>25</sup> 1,2,3-Ir py<sub>3</sub>Cl<sub>3</sub> and 1,2,6-Ir py<sub>3</sub>Cl<sub>3</sub>. Finally, Professor M. Delépine has sent me the chloride of Ir py<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, which is not yet described in the literature, but is made by heating *cis*-Py H[Ir py<sub>2</sub>Cl<sub>4</sub>] with pyridine 1.5 h to 130°C.

As seen from Fig. 4 and Table 2, the triplet band is also here shifted from the place in IrCl<sub>6</sub><sup>−</sup> towards higher wavenumbers. But the triplet band of *trans*-Ir py<sub>2</sub>Cl<sub>4</sub><sup>−</sup> is shifted 2 200 K towards the red and is less intense, compared to the band of the *cis*-form. It might be argued that the weak band observed in Ir py<sub>4</sub>Cl<sub>2</sub><sup>+</sup> is the first singlet band as in the corresponding rhodium complex discussed above, but the extreme hypsochromy<sup>1</sup> of Mathieu's Ir(NH<sub>3</sub>)<sub>5</sub>Cl<sup>++</sup> and Ir en<sub>3</sub><sup>+++</sup> makes the triplet assignment more probable.

The pyridine-complexes of iridium(III) all have a broad band in the range 30 000—34 000 cm<sup>−1</sup> and a set of narrow bands, often four members of a vibrational structure 37 000—41 000 cm<sup>−1</sup> (*cf.* Fig. 5). The latter bands are nearly equal in different complexes and can be ascribed to the  $\pi$ -electron system of the heterocyclic pyridine-ring. The broad band at lower wavenumber is not observed in free pyridine or pyridinium salts with a comparable intensity. Further, Rh py<sub>2</sub>Cl<sub>4</sub><sup>−</sup> and Rh py<sub>4</sub>Cl<sub>2</sub><sup>+</sup> do not either exhibit this band, which must be due to some electron transfer process in iridium(III) which is not observed in pyridine-free complexes<sup>1</sup>.

In the fourth paper of the series, the latter band will be discussed. Its position is dependent on the other ligands and seems to follow the spectrochemical series. Actually, it has nearly the same wavenumber as predicted of the ligand field transition to the second singlet level <sup>1</sup>F<sub>5</sub>. However, it is not very likely that it is strongly intermixed with this Laporte-forbidden band, or that it is a triplet or weak singlet band otherwise known of pyridine: rather, it is probably due to transition of a  $\gamma_5$ -electron from iridium(III) to a  $\pi$ -anti-bonding orbital of pyridine.

## THE THREE ISOMERS OF DIPYRIDINO TRICHLORO AQUO IRIDIUM(III)

Delépine<sup>29,30</sup> has prepared three isomers of Ir py<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O): one with the pyridines in *trans*-position, and the two possible monomers with pyridine in *cis*-position and the water in *trans*-position to either pyridine or chloride. The two latter isomers can be made from an aqueous solution of *cis*-Ir py<sub>2</sub>Cl<sub>4</sub><sup>−</sup> by a photochemical reaction with sunlight, producing a relatively more water-soluble form, and by heating in an autoclave to 130°C, where polymerized by-products and a less soluble monomer is produced. The geometrical configuration of the "sun" and the "autoclave" isomer is not yet elucidated. *Cf.* the seven publications by Delépine<sup>29</sup>.

It is seen in Table 2 that while the absorption spectra of the three isomers of Ir py<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O) are not very different, the alkaline solutions, forming Ir py<sub>2</sub>Cl<sub>3</sub>(OH)<sup>−</sup>, have, *e.g.*, the iridium-pyridine band mentioned above at highly different wavenumbers. It is remarkable that the water group can be revers-



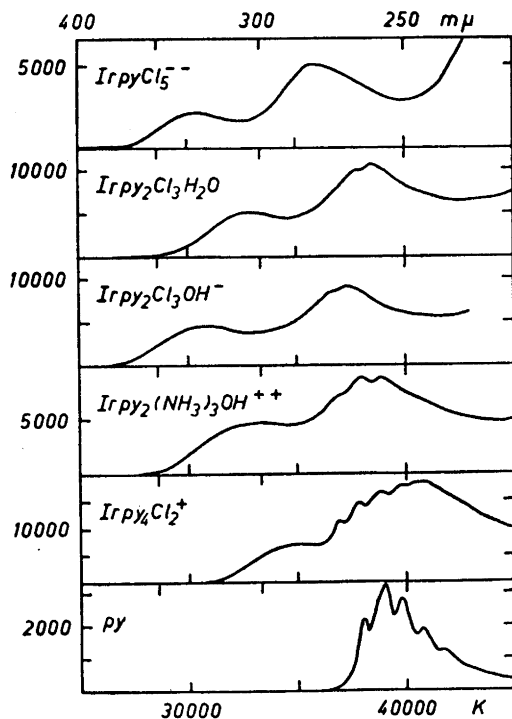


Fig. 5. The Ir-py and genuine pyridine bands of iridium(III) complexes.

0.0003 M  $K_2[Ir py Cl_5] \cdot 3 H_2O$  in  $H_2O$ , immediately measured.

0.0002 M *cis*- $[Ir py_2 Cl_3 (H_2O)] \cdot 2 H_2O$  (sun-isomer) in 0.1 M HCl.

0.0002 M *cis*- $[Ir py_2 Cl_3 OH]^-$  from sun-isomer in 0.1 M  $Na_2CO_3$ .

0.0002 M  $[Ir py_2 (NH_3)_3 OH]^{++}$  from  $[Ir py_2 (NH_3)_3 H_2O] Cl_3$  (pyridine in *trans*-position) in 1 M  $NH_3$ .

0.0001 M  $[Ir py_4 Cl_2] Cl \cdot 6 H_2O$  in  $H_2O$ .

0.0005 M py in  $H_2O$ .

ibly titrated without appreciable loss of chloride in alkaline solution for many hours at room temperature. Even the least robust iridium(III) pyridine complex with the highest number of chloride groups,  $[Ir py Cl_5]^{--}$ , aquates during several days with the result that the Ir-py band shifts monotonously towards higher wavenumbers of the aquo forms and towards lower wavenumbers of the hydroxo forms, as discussed in the next paper. It is necessary to boil the alkaline solution of  $[Ir py Cl_5]^{--}$  to efficiently destroy the binding between iridium and pyridine.

*trans*- and *cis*-(autoclave)  $[Ir py_2 Cl_3 (H_2O)]$  are so weakly soluble in water that it is difficult to observe the ligand field triplet transition. Similar remarks apply to the 1,2,3-isomers of  $[Ir py_3 Cl_3]$  and  $[Ir py_3 Br_3]$ , of which the best solvent known, chloroform, only dissolves a very small amount.

## PYRIDINE-, AMMONIA-, CHLORO-, AQUO-COMPLEXES OF IRIDIUM(III)

Delépine<sup>28</sup> has prepared yellow  $\text{Ir py}_2(\text{NH}_3)_2\text{Cl}_2^+$ , pale yellow  $\text{Ir py}_2(\text{NH}_3)_3\text{Cl}^{++}$ , and white  $\text{Ir py}_2(\text{NH}_3)_3\text{H}_2\text{O}^{+++}$ , all with the pyridines in *trans*-position, and Delépine and Pineau<sup>30</sup> the pale yellow  $\text{Ir py}(\text{NH}_3)_4\text{Cl}^{++}$ . In the chloro complexes, there are very weak traces of a shoulder corresponding to the triplet band at  $360 \text{ m}\mu$  of  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{++}$ . The wavenumber of the broad and strong Ir-py band increases with a decreasing number of chloride groups, but seems still to subsist in  $\text{Ir py}_2(\text{NH}_3)_3\text{H}_2\text{O}^{+++}$  superposed upon the narrow pyridine bands, while it is very evident in  $\text{Ir py}_2(\text{NH}_3)_3\text{OH}^{++}$  (see Fig. 5).

## THE ACIDITY OF WATER IN IRIDIUM(III) COMPLEXES

Reversible titration curves have been made with a glass electrode pH-meter of the following of Delépine's compounds:

*cis*- $\text{Ir py}_2\text{Cl}_3(\text{H}_2\text{O})$  (sun) has  $\text{p}K = 6.7$

*trans*- $\text{Ir py}_2(\text{NH}_3)_3\text{H}_2\text{O}^{+++}$  has  $\text{p}K = 5.1$

$\text{Ir Cl}_5(\text{H}_2\text{O})^{--}$  has  $\text{p}K \sim 10.1$ , however with some decomposition in alkaline solution.

Thus, the acidity of water increases with the positive external charge, but not to a larger extent than known of aquo complexes of cobalt(III) or chromium(III).

A sample of what was assumed to be  $\text{Ir py}_2(\text{NH}_3)_3\text{NH}_2^{++}$  exhibited the same absorption spectrum as  $\text{Ir py}_2(\text{NH}_3)_3\text{OH}^{++}$ , and by titration of a sample of assumed  $\text{Ir py}_2(\text{NH}_3)_4\text{Cl}_3$ , 80 % of the calculated stoichiometric amount titrated with a fine one-proton curve, corresponding to  $\text{p}K = 5.2$ . Thus, the latter sample contains at most 20 %  $\text{Ir py}_2(\text{NH}_3)_4^{+++}$ , and its acidity cannot be ascribed to formation of amido complexes. This is not in disagreement with the analyses of Delépine<sup>28</sup>, who determined only iridium and chloride but not nitrogen.

## PYRIDINE- AND BROMO-IRIDIUM(III) COMPLEXES

$\text{Ir Br}_6^{---}$  and  $\text{Ir Br}_5(\text{H}_2\text{O})^{--}$  have not very different spectra in aqueous solution, as seen from Table 2. The former ion aquates probably rather quickly in aqueous solution, explaining the slight deviation from the solution in HBr, described previously<sup>1</sup>. While most other iridium(III) complexes do not exhibit maxima of the electron transfer bands in the accessible range above  $205 \text{ m}\mu$   $\text{Ir Br}_6^{---}$  and  $\text{Ir Br}_5(\text{H}_2\text{O})^{--}$  have a double band with  $\epsilon_n \sim 11\,000$  and  $20\,000$ , resembling much the isoelectronic<sup>32</sup>  $\text{Pt Br}_6^{--}$ . The doublet structure and energy levels of halide complexes will be discussed in the fourth paper of this series.

In dilute solution, both  $\text{Ir Br}_6^{---}$  and  $\text{Ir Br}_5(\text{H}_2\text{O})^{--}$  form the same  $\text{Ir Br}_6^{--}$  by addition of bromine:



the total reaction thus being an addition of a bromine atom and not a simple electron transfer.

Madame Delépine-Tard<sup>37</sup> prepared dark red  $\text{Ir py}_2\text{Br}_4^-$ , which has the triplet at so high a wavenumber (compared to  $\text{Ir py}_2\text{Cl}_4^-$ ) that the *cis*-structure is most probable. Besides the Ir-py and the py-bands, this ion exhibits also a genuine redox band at a much higher wavenumber than  $\text{IrBr}_6^{3-}$ , as usually found for a decreasing number of halide ligands.

1,2,6-Ir  $\text{py}_3\text{Br}_3$  is sufficiently soluble<sup>29</sup> in  $\text{CHCl}_3$  to show the triplet band. The Ir-py band has a larger wavenumber in this isomer than in 1,2,3, as is also found for  $\text{Ir py}_3\text{Cl}_3$ .

Table 3. Absorption bands of iridium(IV) pyridine pentachloro complex.

	$\lambda_n$ m $\mu$	$\sigma_n$ K	$\epsilon_n$	$\delta(-)$ K	$\delta(+)$ K
Ir $\text{pyCl}_5^-$	625	16 000	400	900	—
	~503	19 900	2 450	1 300	—
	487	20 500	2 600	—	1 400
	405	24 700	1 500	1 700	2 000
	~344	29 100	~800	—	—
	~267	37 500	4 900	—	—

#### PYRIDINE- AND CHLORO-IRIDIUM(IV) COMPLEXES

Delépine<sup>27,33</sup> oxidized  $\text{Ir pyCl}_5^{2-}$ , *cis*- and *trans*- $\text{Ir py}_2\text{Cl}_4^-$  to the corresponding iridium(IV) complexes  $\text{Ir pyCl}_5^-$  and *cis*- and *trans*- $\text{Ir py}_2\text{Cl}_4$ . The two latter neutral compounds are nearly insoluble in any solvent.  $\text{Ir pyCl}_5^-$  and *trans*- $\text{Ir py}_2\text{Cl}_4$  are even stronger oxidizing agents than bromine<sup>27</sup>. Inamura and Kondo<sup>34</sup> have measured the spectrum of  $\text{Ir pyCl}_5^-$ , which is also given in Table 3 and can be compared with<sup>32</sup>  $\text{Ir Cl}_6^{3-}$ . While the maximum in the blue-green is nearly identical except for a shoulder at 502 m $\mu$  of  $\text{Ir pyCl}_5^-$ , the double maximum at 431 and 414 m $\mu$  of  $\text{IrCl}_6^{3-}$  is here shifted to 405 m $\mu$  and is single. Further,  $\text{Ir pyCl}_5^-$  has the first shoulder at 625 rather than at 575 m $\mu$ . Presumably, all the bands are mainly due to transfer of  $\pi$ -electrons<sup>32</sup>. If the band at 625 m $\mu$  of  $\text{Ir pyCl}_5^-$  was a ligand field band, it would probably be shifted towards the blue; it has rather another, mainly even excited state.

Table 4. Absorption bands of pyridine and pyridinium ion in aqueous solution. Notation as in Table 1.

	Band No.	$\lambda_n$ m $\mu$	$\sigma_n$ K	$\epsilon_n$
py	0	262.8	38 050	2 100
	1	256.6	38 970	3 130
	2	250.7	39 890	2 780
	3	245.1	40 800	1 900
	4	~239	41 840	1 200
py H <sup>+</sup>	0	262	38 170	3 600
	1	256	39 060	5 300
	2	251.5	39 760	4 700
	3	~245	40 820	2 900

Table 5. Absorption bands of S. M. Jørgensen's platinum(II) pyridine complexes. Notation as in Table 1.

	Band No.	$\lambda_n$ m $\mu$	$\sigma_n$ K	$\epsilon_n$
Pt(NH <sub>3</sub> ) <sub>2</sub> py <sup>++</sup>	0	267.5	37 380	1 930
	1	260.6	38 380	2 980
	2	254.2	39 340	3 320
	3	248.2	40 290	3 300
	4	~243.5	41 060	2 920
Pt py <sub>4</sub> <sup>++</sup>	0	267	37 450	8 700
	1	260.2	38 430	13 600
	2	253	39 530	15 300
	3	243 broad	41 150	19 800
Pt(NH <sub>3</sub> ) <sub>2</sub> py <sub>2</sub> <sup>++</sup>	0	267.5	37 380	4 650
	1	260.3	38 410	7 800
	2	253.4	39 460	10 300
	3	249	40 160	10 100
<i>trans</i> -Pt(NH <sub>3</sub> )pyCl <sub>2</sub>	0	269.4	37 120	—
	1	262.2	38 140	—
	2	256.6	38 970	—

## THE PYRIDINE BANDS AND S.M. JØRGENSEN'S PYRIDINO PLATINUM(II) COMPLEXES

Table 4 gives the absorption bands of pyridine, which are very narrow ( $\delta = 300$  K) and are nearly equidistant with  $\sigma_c = 920$  K. This is evidently a vibrational structure, which is excited by a Franck-Condon mechanism. There is no sign of transitions from vibrationally excited levels of the electronic groundstate, and the bands can thus be numbered 0, 1, . . . according to the vibrational quantum number of the excited electronic state. In aqueous solution, there is no sign of weaker bands at smaller wavenumbers than those of the vibrational structure. Thus, the values of  $\epsilon$  are:

270	275	280	285	290	300 m $\mu$
150	27	3	0.5	0.1	0.02

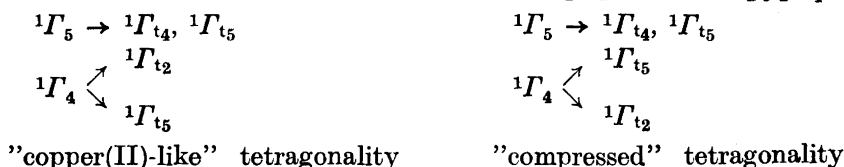
The pyridinium ion pyH<sup>+</sup> has bands at nearly the same wavenumbers as py, but they are blurred out ( $\delta \sim 500$  K) and have  $\sim 70$  % higher intensity. In rhodium(III) pyridine complexes, the bands have not much smaller wavenumbers than of py, and nearly the same intensity per pyridine molecule, as seen above. Some iridium(III) complexes have not very much larger bathochromic shifts of the py-bands, while other have very broad py-bands with vanishing vibrational structure at relatively low wavenumbers,  $\sigma \sim 4\ 000$  K below the centre of the bands of py (*cf.* Fig. 5). The latter behaviour of iridium(III) is enhanced by the presence of many anions (Cl<sup>-</sup>, Br<sup>-</sup>, OH<sup>-</sup>) among the ligands and a low number of pyridine molecules, suggesting an especially strong bonding of the pyridine with larger change of the  $\pi$ -electron system of this molecule than in most other complexes.

As discussed in the next paper, the electron transfer, producing the new Ir-py band may be expected to occur also in pyridine complexes of other metals with low oxidation states. Platinum(II) should have possibilities for exhibiting this effect, and therefore the absorption spectra were measured of

some of the pyridine complexes, prepared by S. M. Jørgensen<sup>35</sup>. As seen from Table 5, the py-bands are shifted towards lower wavenumbers to a remarkably low extent, and there is no sign of a Pt-py band in the complexes with neutral ligands, such as py and NH<sub>3</sub>. In the chloro complex, there may be distinguished an increasing background, but no certain conclusion can be drawn.

#### LIGAND FIELD QUANTUM NUMBERS IN COMPLEXES OF TETRAGONAL SYMMETRY

Qualitatively, the order of tetragonal levels<sup>3,16,17</sup> are supported by the measurements of *cis*- and *trans*-isomers of Rh ox<sub>2</sub>Cl<sub>2</sub><sup>-3</sup> and Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup>:



The result, derived by Tanabe and Sugano<sup>36</sup> for an electrostatic ligand field acting on pure d<sup>n</sup>-configurations, *viz.* that  ${}^1\Gamma_4$  is lower than  ${}^1\Gamma_5$  of  $\gamma_5^5\gamma_3$ , is highly supported, since  ${}^1\Gamma_{t_4}$  could hardly<sup>3</sup> take the place of  ${}^1\Gamma_{t_2}$  in the left-hand set of levels. But quantitatively, the results reported here cannot be explained without strong interactions between the electron configurations of tetragonal orbitals.

Thus, the ratio between the splitting of  ${}^1\Gamma_{t_2}$  and  ${}^1\Gamma_{t_5}$  and the differences of the cubic ligand field strength of the purely hexa-coordinated complexes should be a constant number<sup>3</sup>. However, this ratio is 0.65 for *trans*-Rh ox<sub>2</sub>Cl<sub>2</sub><sup>-3</sup>, but only 0.32 for *trans*-Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup>. This is a more fundamental difficulty than the problem of the value<sup>3</sup> of  $B_2/B_4$ , which may be solved by use of other d-wavefunctions than the hydrogen-like ones, *e.g.* the Hartree model discussed by Linn Belford<sup>7</sup>, and by consideration of the much stronger influence of charge distributions near to the surface of the central ion than the point charges and point dipoles assumed in early electrostatic theory<sup>6</sup>. According to calculations on strong tetragonal fields<sup>3</sup>, it is an almost paradoxical fact that  ${}^1\Gamma_{t_4}$  does not decrease much in energy, producing a larger splitting of the second band, if this is caused by  ${}^1\Gamma_5$  (the energy difference between  ${}^1\Gamma_4$  and  ${}^1\Gamma_5$  is explained as the correlation energy between d-electrons expressed in the Racah parameters *B* and *C*). An interaction between the two  ${}^1\Gamma_{t_5}$ , useful for explaining a part of the splitting of the first band, will further increase the distance between  ${}^1\Gamma_{t_4}$  and the second  ${}^1\Gamma_{t_5}$ , which actually have nearly the same energy. Among the tetragonal levels of  $\gamma_5^4\gamma_3^2$ , the lowest energy will probably be represented by  $\gamma_{t_5}^3\gamma_{t_4}\gamma_{t_1}^2$  in *trans*-Rh ox<sub>2</sub>Cl<sub>2</sub><sup>-3</sup> and  $\gamma_{t_5}^3\gamma_{t_4}\gamma_{t_3}^2$  in *trans*-Rh py<sub>2</sub>Cl<sub>4</sub><sup>-</sup>, both composed of  ${}^1\Gamma_{t_5}$  and  ${}^3\Gamma_{t_5}$ . Thus, the second  ${}^1\Gamma_{t_5}$  may be held in place besides  ${}^1\Gamma_{t_4}$  by the interaction from opposite directions. This can also explain, why the second cubic band in some few cases capriciously exhibits tetragonal splitting, *e.g.*<sup>11</sup> Co enta OH<sup>-</sup>. It may be noticed that the non-diagonal elements of energy between the two  ${}^1\Gamma_5$  of

$\gamma_5^4\gamma_3^2$  and the one  ${}^1\Gamma_5$  of  $\gamma_5^5\gamma_3$  are rather important<sup>36</sup>, explaining the decrease of the distance between  ${}^1\Gamma_4$  and  ${}^1\Gamma_5$  from the asymptotical strong-field value  $16B$  to  $10-12B$ .

In the case of the first tetragonal level  ${}^1\Gamma_{15}$  the configurations  $\gamma_{t_5}^3\gamma_{t_4}^2\gamma_{t_1}$  and  $\gamma_{t_5}^2\gamma_{t_4}^2\gamma_{t_3}$  must be highly intermixed<sup>3</sup> at low values of the tetragonality. Actually, the intermixing does not need to produce a splitting, proportional to the tetragonality, but rather to the square. This would explain why the splitting of the first band of *cis*-complexes is not always half as large as in the corresponding *trans*-complex<sup>3</sup>. Figs. 1 and 2 show that the first band of *cis*-Rh  $\text{ox}_2\text{Cl}_2^{-3}$  and *cis*-Rh  $\text{py}_2\text{Cl}_4^-$  definitely do not exhibit splittings amounting to 1900 and 1600 K, respectively. Analogously, the first band<sup>1</sup> of Rh(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> is only split 1700 K, while the difference between the first band of Rh(NH<sub>3</sub>)<sub>6</sub><sup>+++</sup> and the hypothetical RhI<sub>6</sub><sup>-3</sup> must be over 15000 K (Rh(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> is remarkable by having a negative cubic contribution<sup>3</sup> of the iodide, since the wavenumber of the first band is less than 5/6 of that of Rh(NH<sub>3</sub>)<sub>6</sub><sup>+++</sup>). The tetragonality effect, calculated for *trans*-M A<sub>4</sub>B<sub>2</sub> is thus only  $\lesssim 0.22$  for Rh(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and 0.32 for *trans*-Rh  $\text{py}_2\text{Cl}_4^-$  multiplied by the differences in cubic ligand field strengths, while most electrostatic models would have presumed this ratio near to or above 1.

#### EXPERIMENTAL

The absorption spectra were measured at 25°C on a Cary recording spectrophotometer 11 MS-50. Since many of the measured compounds are so rare, several samples were weighed and transferred to the 1 cm absorption cell, which by weighing was found to contain 3.1 ml. Subsequent dilutions were performed with A. Krogh's syringe-pipettes. The high absorption bands ( $\epsilon_n \sim 10\,000$ ) were redetermined with solutions of weighed portions  $\sim 5$  mg in 50 ml or 250 ml measuring flasks.

The ligand field bands ( $\epsilon_n = 10-200$ ) were measured with solutions, 0.01-0.03 M. The aqueous solutions of chloro-complexes were measured twice within 10 min (as the other complexes) and one and four days later. Only during at least several days were aqution effects observed of complexes with at most four chloride ligands. The complexes Ir  $\text{py}_2(\text{NH}_3)_2\text{Cl}_2^+$ , Ir  $\text{py}_2(\text{NH}_3)_2\text{Cl}^{++}$  and Ir  $\text{py}(\text{NH}_3)_4\text{Cl}^{++}$  were measured in 2 M NH<sub>3</sub> without showing changes of spectra, which might be caused by acidity of the amine groups. The titration curves were measured on a Radiometer glass-electrode pH-meter M 22.

It was assumed that the crystalline compounds have the compositions, indicated by M. Delépine:

*cis*-K<sub>3</sub>[Rh ox<sub>2</sub>Cl<sub>2</sub>],H<sub>2</sub>O  
*trans*-K<sub>3</sub>[Rh ox<sub>2</sub>Cl<sub>2</sub>],4H<sub>2</sub>O  
*cis*-K[Rh py<sub>2</sub>Cl<sub>4</sub>],H<sub>2</sub>O  
*trans*-K[Rh py<sub>2</sub>Cl<sub>4</sub>],H<sub>2</sub>O  
 1,2,6-Rh py<sub>2</sub>Cl<sub>2</sub>  
 [Rh py<sub>2</sub>Cl<sub>4</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O  
 K<sub>3</sub>[Ir oxCl<sub>4</sub>],H<sub>2</sub>O  
*cis*-K<sub>3</sub>[Ir ox<sub>2</sub>Cl<sub>2</sub>],H<sub>2</sub>O (racemic)  
*trans*-K<sub>3</sub>[Ir ox<sub>2</sub>Cl<sub>2</sub>],6 H<sub>2</sub>O  
 K<sub>3</sub>[Ir ox<sub>2</sub>],4.5 H<sub>2</sub>O (racemic)  
 K<sub>3</sub>[Ir pyCl<sub>4</sub>]  
 K<sub>3</sub>[Ir pyCl<sub>4</sub>],3 H<sub>2</sub>O  
*cis*-K[Ir py<sub>2</sub>Cl<sub>4</sub>],H<sub>2</sub>O  
*trans*-K[Ir py<sub>2</sub>Cl<sub>4</sub>],H<sub>2</sub>O  
 1,2,3-Ir py<sub>2</sub>Cl<sub>2</sub>

1,2,6-Ir py<sub>2</sub>Cl<sub>2</sub>  
 [Ir py<sub>2</sub>Cl<sub>4</sub>]Cl<sub>2</sub>·6 H<sub>2</sub>O  
 Ir py<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2 H<sub>2</sub>O (*cis*, sun)  
 Ir py<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O) (*cis*, autoclave)  
 [Ir py<sub>2</sub>Cl<sub>2</sub>((H<sub>2</sub>O))<sub>2</sub>],H<sub>2</sub>O (*trans*)  
 [Ir py(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>·2 H<sub>2</sub>O  
 [Ir py<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>],H<sub>2</sub>O  
 [Ir py<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>Cl]Cl<sub>2</sub>·4 H<sub>2</sub>O  
 [Ir py<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl<sub>2</sub>·H<sub>2</sub>O  
 Na<sub>3</sub>[Ir Br<sub>4</sub>],12 H<sub>2</sub>O  
 K<sub>3</sub>[Ir Br<sub>4</sub>],4 H<sub>2</sub>O  
 K<sub>3</sub>[Ir Br<sub>4</sub>(H<sub>2</sub>O)]<sub>2</sub>·H<sub>2</sub>O  
 NH<sub>4</sub>[Ir py<sub>2</sub>Br<sub>4</sub>],H<sub>2</sub>O  
 1,2,3-Ir py<sub>2</sub>Br<sub>2</sub>  
 1,2,6-Ir py<sub>2</sub>Br<sub>2</sub>

*Cf.* also the review of the chemistry of iridium, written by Professor M. Delépine in Paul Pascal: *Traité de la Chimie Minérale*, Paris 1932, Vol. 11, p. 443–527.

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