

Complexes of the 4d- and 5d-Groups

I. Crystal Field Spectra of Rhodium(III) and Iridium(III)

CHR. KLIXBÜLL JØRGENSEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

In octahedral complexes with six d-electrons and singlet (*i. e.* diamagnetic) ground state, the crystal field theory predicts transitions to two singlet and two triplet levels. Several authors have studied the case of cobalt(III), and in this paper the four bands are found in rhodium(III) and iridium(III) complexes, *e. g.* with six bromide or chloride ligands. The slow aquation of these complexes in HCl and HClO₄ is studied, and rhodium(III) aquo ions prepared in HClO₄. The solutions of Rh(OH)₃ in acids show a high ultraviolet absorption, which disappears slowly, presumably owing to acidolysis of polymer hydroxo complexes. The hexammine and nitro-, iodo-, bromo-, chloro-, hydroxo-, and aquo-pentammine rhodium complexes of S. M. Jørgensen and the oxalato and ethylenediamine complexes exhibit the shifts predicted from the spectrochemical series, as also Ir(NH₃)₆Cl⁺⁺⁺ and Ir en₃⁺⁺⁺. The relative intensities of singlet and triplet transitions are explained by the deviations from the Russell-Saunders coupling, which are important in the heavy atoms. Later papers of the series will discuss why the concept of molecular orbitals is compatible with the approximate validity of the electrostatic model using ($E_1 - E_2$) as empirical parameter.

Nearly all the applications of the crystal field theory¹⁻¹⁷ to the absorption spectra of the complexes with partly filled d-shells have concerned the first transition group with 3d-electrons. The 4d³-system molybdenum(III) in MoCl₆³⁻ was investigated by Schmidt¹⁸ who found that the energy differences in the 4d-case are *inter alia* larger than in the 3d-case. Similar conclusions were drawn by Orgel¹³ from qualitative observations of the colours of the platinum group complexes, compared to cobalt(III). In the present paper the complexes of rhodium(III) and iridium(III) will be compared to the diamagnetic cobalt(III) complexes, which are all regularly octahedral. The ground state^{6, 9-11} is 1A_1 from the closed shell configuration γ_5^6 , and the next electron distribution $\gamma_5^5\gamma_3$ has the four levels 3A_4 , 3A_5 , 1A_4 and 1A_5 . All authors agree that the two relatively strong bands with $\epsilon \sim 100$ are due to the transitions to 1A_4 and 1A_5 . It is not yet certain which of the bands corresponds to 1A_4 , but the theory of Tanabe and Sugano¹⁰ with pure 3d-configura-

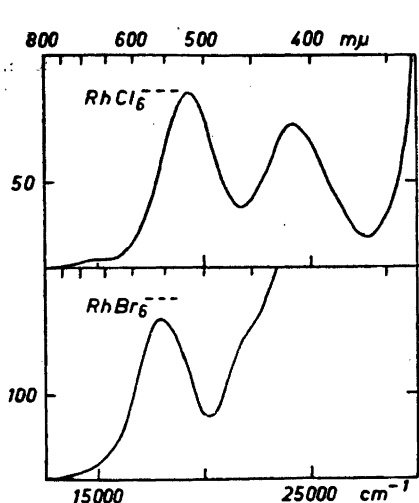


Fig. 1. Absorption spectra of hexachloro- and hexabromo-rhodium(III) ions.

From 0.01 M to 0.3 M Na_3RhCl_6 in 4 M HCl and H_2O , immediately measured. 0.01 M RhBr_6^{3-} in 4M HBr.

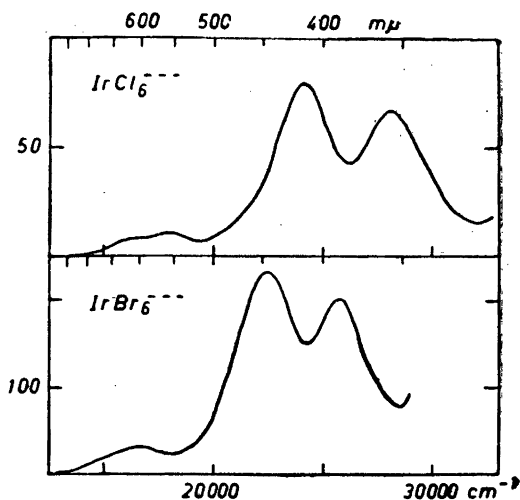


Fig. 2. Absorption spectra of hexachloro- and hexabromo-iridium(III) ions.

From 0.01 M to 0.1 M K_3IrCl_6 in 4 M HCl and H_2O , immediately measured. 0.005 M to 0.015 M IrBr_6^{3-} in 4 M HBr.

tions imply that it is the band with lowest wavenumber. The present author⁸ and Kondo¹⁰ have found a weak band with $\epsilon \sim 0.4$ of $\text{Co}(\text{NH}_3)_6^{+3}$ and Co en_3^{+3} in the far red. This must be due to either 3T_4 (which has the lowest energy¹⁰) or 3T_5 . This band is found here with relatively higher intensity in rhodium(III) and iridium(III) complexes.

HEXACHLORO- AND HEXABROMO-COMPLEXES

Fig. 1 gives the absorption spectra of RhCl_6^{3-} and RhBr_6^{3-} , and Fig. 2 those of IrCl_6^{3-} and IrBr_6^{3-} , while Tables 1 and 2 give the wavenumbers, wavelengths, and molar extinction coefficients of the maxima¹⁹ and the half-widths and oscillator strengths of the bands^{16,19}.

Samuel and Uddin²⁰ have measured RhCl_6^{3-} in H_2O (partly aquated, with maxima at 503 and 393 $m\mu$), in a saturated solution of NaCl (at 520 and 409 $m\mu$, nearly as here) and in saturated KBr (at 540 and 420 $m\mu$) probably transformed into bromo complexes. Babaeva²¹ has found maxima at 499 and 390 $m\mu$ of RhCl_6^{3-} and at 480, 418 and 359 $m\mu$ of IrCl_6^{3-} . The first complex must be aquated, while the second is slightly oxidized. As discussed in the next paper of this series, IrCl_6^{3-} has 40 times higher bands than IrCl_6^{4-} . Inamura and Kondo²² have measured IrCl_6^{3-} and several other iridium(III) complexes.

It is seen from Figs. 1 and 2 that the second band is lower than the first in all four complexes. According to C. E. Schäffer of this laboratory, similar be-

Table 1. Absorption bands of rhodium(III) complexes.

Wavelength λ_n wavenumber ν_n and molar extinction coefficient ϵ_n of each maximum, halfwidths $\delta(-)$ towards smaller and $\delta(+)$ towards higher wavenumbers, and the oscillator strength P of each band¹⁹. Transitions from 1A_1 to one of the levels 3T_4 or 3T_2 are marked (a) and (b) and from 1A_1 to 1T_4 and 1T_2 is marked (c) and (d).

		λ_n m μ	ν_n cm ⁻¹	ϵ_n	$\delta(-)$ cm ⁻¹	$\delta(+)$ cm ⁻¹	$P \cdot 10^{-5}$
RhBr ₆ ³⁻	(c)	553	18 100	190	1 500	1 400	250
	(d)	450	22 200	180	—	—	250
RhCl ₆ ³⁻	(a)	680	14 700	3	1 200	—	3
	(c)	518	19 300	102	1 500	1 500	140
Rhox ₆ ³⁻	(d)	412	24 300	82	1 600	1 900	130
	(a)	520	19 200	8	1 000	—	8
	(c)	398	25 100	290	2 000	—	540
	(d)	333	30 000	—	—	—	—
Rh(H ₂ O) ₆ ³⁺	(c)	393	25 500	47	2 600	—	110
	(d)	305	32 800	55	3 000	—	140
Rh(NH ₃) ₆ I ³⁺	(c ₁)	416	24 100	270	2 100	—	700
	(c ₂)	388	25 800	230	—	—	
Rh(NH ₃) ₆ Br ³⁺	(d?)	278	36 000	3 200	2 500	—	7 400
	(a)	424	23 600	25	1 100	—	25
	(c)	359	27 800	122	2 000	2 600	260
	(c)	349	28 700	100	2 000	2 600	210
Rh(NH ₃) ₆ Cl ³⁺	(d)	277	36 100	103	2 800	2 900	270
	(c)	321	31 200	124	2 800	—	500
	(d)	278	36 000	108	—	—	
Rh(NH ₃) ₆ H ₂ O ³⁺	(c)	316	31 600	105	2 800	—	260
	(d)	263	38 100	89	—	2 800	230
Rh(NH ₃) ₆ ³⁺	(c)	306	32 700	135	2 300	—	300
	(d)	256	39 100	100	—	2 700	250
Rhen ₆ ³⁺	(c)	301	33 200	210	2 400	—	480
	(d)	253	39 600	190	—	—	460
Rh(NH ₃) ₆ NO ₃ ³⁺	(c)	296	33 800	330	3 000	—	900
	(d?)	246	40 600	1 030	3 400	—	3 200

Table 2. Absorption bands of iridium(III) complexes. Nomenclature as in Table 1.

		λ_n m μ	ν_n cm ⁻¹	ϵ_n	$\delta(-)$ cm ⁻¹	$\delta(+)$ cm ⁻¹	$P \cdot 10^{-5}$
IrBr ₆ ³⁻	(b)	597	16 800	27	2 200	1 500	43
	(c)	447	22 400	232	1 800	1 700	370
	(d)	387	25 800	198	1 500	2 000	320
IrCl ₆ ³⁻	(a)	615	16 300	7.5	1 200	800	7
	(b)	560	17 900	10	900	1 500	11
	(c)	415	24 100	76	1 800	—	125
Ir(NH ₃) ₆ Cl ³⁺	(d)	356	28 100	64	—	2 100	120
	(b)	360	27 800	10	1 800	—	17
	(c)	286	35 000	71	3 500	—	230
	(b)	302	33 100	28	2 200	—	57
Iren ₆ ³⁺	(c)	249	40 200	170	2 800	—	400

haviour is found for nearly all chromium(III) and cobalt(III) complexes except the aquo ions and a few others. The small, spin-forbidden bands are discussed below in a special section. In the tables, the two transitions to the triplet levels are denoted a and b, while the stronger transitions to singlet levels are denoted c and d with increasing wavenumber.

THE AQUATION OF HEXACHLORO-COMPLEXES

It has been known for many years that rhodium(III) occurs in brownish-red and orange complexes containing less chloride than the raspberry-red RhCl_6^{3-} . Thus, Meyer and Kawczyk²³ recognized the non-ionized red $\text{RhCl}_5(\text{H}_2\text{O})$ and the yellow ion $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ in solutions of $\text{Rh}(\text{OH})_3$ in HCl , and these authors stressed the analogy with the chromium complexes $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{CrCl}(\text{H}_2\text{O})_5^{2+}$, and $\text{CrCl}_2(\text{H}_2\text{O})_4^+$ investigated by N. Bjerrum²⁴. Delépine^{25, 26} studied the reversible transformations of RhCl_6^{3-} to $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ and IrCl_6^{3-} to $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$.

The chloro complexes of the platinum metals are often assumed to have high formation constants²⁷. Even if they are robust, *i. e.* their reaction velocities are very low, they seem to have rather small formation constants, at least for the last chloride ligands. The latter effect is partly due to statistical reasons and to the electrostatic part of the residual effect²⁸.

Table 3 gives the wavelengths of the maxima, as well as points with half the maximum value of ϵ , and minima of the absorption spectra of RhCl_6^{3-} in 1 M HCl and 1 M HClO_4 as function of time at room temperature $18 \pm 2^\circ \text{C}$. It is seen that the two absorption bands move towards shorter wavelengths, corresponding to the exchange of chloride with water. In 1 M HCl , a steady state seems to be reached within some weeks, while the reaction continues in 1 M HClO_4 where the total chloride concentration is due only to the original

Table 3. The aquation of RhCl_6^{3-} .

	$\lambda(\epsilon = \frac{\epsilon_1}{2})$	λ_{max}	ϵ_1	λ_{min}	λ_{max}	ϵ_2	$\lambda(\epsilon = \frac{\epsilon_2}{2})$	λ_{min}
6 M HCl :								
immediately	561	518	100	460	412	81	381	361
7 days after	560	519	100	460	411	81	382	362
60 days after	560	518	100	459	411	81	382	360
4 M HCl :								
9 months after	559	513	101	457	410	90	380	360
1 M HCl :								
2 minutes after	559	513	105	453	405	99	376	355
4 minutes after	556	510	104	453	406	101	376	357
12 minutes after	554	508	103	451	402	105	375	354
2 days after	545	495	92	441	392	101	362	346
14 days after	541	494	90	439	391	99	361	348
28 days after	541	494	89	441	391	98	362	347
57 days after	541	495	90	440	392	97	362	348
1 M HClO_4 :								
2 minutes after	559	513	102	457	410	95	379	360
8 minutes after	555	510	101	452	404	102	375	355
10 minutes after	552	508	101	451	403	104	375	355
120 minutes after	548	500	94	414	396	101	368	350
2 days after	537	490	89	438	390	100	361	344
14 days after	529	481	79	431	384	90	351	341
28 days after	525	478	79	426	380	90	349	339
57 days after	526	477	79	425	379	89	—	344

Table 4. The aquation of IrCl_6^{--} .

	$\lambda\left(\varepsilon = \frac{\varepsilon_1}{2}\right)$	λ_{max}	ε_1	λ_{min}	λ_{max}	ε_2	$\lambda\left(\varepsilon = \frac{\varepsilon_2}{2}\right)$
1 M HCl:							
2 hours after	448	413	79	383	356	66	330
4 days after	444	403	87	374	346	91	320
20 days after	440	398	83	360	340	87	316
1 M HClO_4 :							
10 minutes after	449	415	76	380	355	64	331
4 days after	445	402	85	372	344	90	—
30 days after	438	395	79	366	338	85	—

0.018 M Na_3RhCl_6 . In 6 M HCl, there seems to be no change in a month, and a stock solution in 4 M HCl, which has been stored for nine months, is not more aquated than the solution in 1 M HCl after 3 minutes. The reciprocal process of $\text{Rh}(\text{OH})_3$ dissolved in 1 M HCl is extremely slow at room temperature, and even by boiling with 4 M HCl the colour is only changed from yellow to orange after 10 minutes.

It is seen from Table 3 that by the aquation the second maximum increased strongly, while the first is somewhat decreased. It is interesting to note that the halfwidths of the bands are not greatly increased. Generally, a mixture of several complexes tends to have higher halfwidths, *i. e.* the bands are blurred out. In this particular case, the reaction rates for expelling chloride ions, k_{-6}, k_{-5}, \dots seem to be highly decreasing with decreasing number of chloride ligands at constant pH. Thus, the system may contain mainly two complexes at the same time, as it gives not so levelled a spectrum as a mixture of many components. Definite maxima of $\text{RhCl}_n(\text{H}_2\text{O})_{6-n}^{3-n}$, have not yet been assigned but if the maxima are a linear function of n , *e. g.* their wavenumber

$$\nu = \frac{n}{6} \nu(\text{RhCl}_6^{--}) + \frac{6-n}{6} \nu(\text{Rh}(\text{H}_2\text{O})_6^{+++}) \quad (1)$$

then the steady state obtained in 1 M HCl corresponds to $n = 4.4$ from the first band and 4.5 from the second, while the state in 1 M HClO_4 after four weeks corresponds to $n = 3.5$ and 3.7.

Sundram and Sandell²⁹ have shown that the four first consecutive formation constants of palladium(II) with Cl^- are higher than 500, while the fifth and sixth constants are about 1. Palladium(II) is strongly tetragonal¹² analogously to Cu(II) and has probably anomalously high constants for the four first ligands, while the next two should be much more loosely bound. In the regular octahedral Rh(III), the constants were expected to be more nearly equal, but owing to the higher external charge, higher affinity for halide ions would be predicted than for Pd(II). However, the sixth formation constant in the rhodium(III)-chloride system cannot be larger than 0.5. The enhanced stability of RhCl_6^{--} in stronger HCl can be ascribed to the activity conditions in this medium³⁰. Mr. C. E. Schäffer has kindly pointed out to me that the crystal field stabilization¹² is negative for anion complexes with less crystal field strength than the aquo ions. Thus, each of the six consecutive

formation constants of RhCl_6^{3-} should be decreased by a factor 10^5 of this cause. However, this large effect is probably somewhat counter-acted by intermixing of other molecular orbitals than the 4d-electrons, *viz.* the 5s- and 5p-orbitals.

Table 4 shows that IrCl_6^{3-} is also slightly aquated in 1 M HCl or 1 M HClO_4 during some weeks. In stronger HCl, the ion is either stable or much more slowly reacting. In 10 M HCl, a 0.013 M K_3IrCl_6 was changed in five days from the pale olive-green colour to brownish red. This was due to oxidation to IrCl_6^- , the spectrum of which demonstrated the presence of 0.0001 M. As discussed in the experimental section, ascorbic acid reduces momentarily iridium(IV). The intensity of the second band of IrCl_6^{3-} increases also during the aquation, but here the formation of hydroxo complexes cannot be excluded as easily as in the case of rhodium(III). Delépine²⁵ described the curious change of visible colour of IrCl_6^{3-} with increasing concentration: from lemon yellow over olive-green and reddish brown to black. The spectra were measured of several concentrated solutions in H_2O , which are only slowly aquating. $\text{IrCl}_5(\text{H}_2\text{O})^-$ is more brownish yellow²⁵. A similar effect of the sensitivity of the eye is observed with RhBr_6^{3-} , which changes from greyish green to cherry red by increasing concentration or by use of tungsten light in the place of daylight. Two or more absorption bands of different intensity or with nearly complementary colours produce this type of dichroism.

THE HYDROXO AND AQUO COMPLEXES OF RHODIUM(III)

Analogously to the behaviour³¹ of chromium(III), the exchange reactions of rhodium(III) complexes are highly catalyzed by hydroxyl ions.* Thus, RhCl_6^{3-} and the other chloro complexes form purple intermediates and after some minutes a yellow precipitate of $\text{Rh}(\text{OH})_3$. This precipitate is weakly amphoteric and dissolves in NaOH with pale yellow colour. The weaker base BaCO_3 precipitates $\text{Rh}(\text{OH})_3$ quantitatively by boiling.

Moderately strong acids dissolve the hydroxide to yellow solutions, which can be assumed to contain the hexaquo ion. Fig. 3 shows a titration curve of a 0.01 M Rh(III) in 1 M NaClO_4 with NaOH and HClO_4 . This preliminary experiment shows that pH is a reversible function of added and consumed amounts of hydrogen ions per Rh. The hydroxide is seen to be soluble in one equivalent of hydrogen ions, as also found by Grube and Kesting³². The pK for this process is 5.0, and the acid product formed must be $\text{Rh}(\text{OH})_2(\text{H}_2\text{O})_4^+$ or some polymer with lower content of water. It cannot be seen from the curve whether the di-hydroxo complex takes up further hydrogen ions**, but in any case pK is less than 2.5.

Thus, it is useful to study the absorption spectra of rhodium hydroxide, dissolved in 0.01 M—10 M HClO_4 . A solution of 0.015 M Rh in 0.06 M HClO_4

* However, preliminary experiments seem to show that the aquation of RhCl_6^{3-} has the same velocity in 0.1 M as in 1 M HCl.

** The hexaquo ion does not seem to be a very strong acid, since the aqueous solution of $\text{CsRh}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ is only weakly acidic, according to Krauss and Umbach³². The electric conductance of the hexaquo ion is of the same magnitude²³ as that of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.

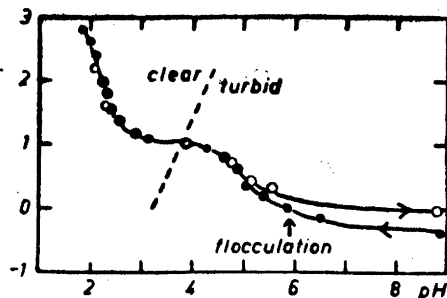


Fig. 3. Titration curve of rhodium (III) hydroxide in 1 M NaClO_4 at 20° C. 0.01 M Rh.

pH as function of added hydrogen ions (or consumed hydroxyl ions) per rhodium atom. Empty circles titration from acid range with NaOH and filled circles titration from alkaline range with HClO_4 . Turbidity appears at pH over 3.8 and disappears below this value, marked on the figure.

was measured and HClO_4 added in small quantities until a concentration of 0.4 M was reached. Fig. 4 gives the nearly identical absorption spectra of these two solutions. This might have been an argument for the two first pK -values of $\text{Rh}(\text{H}_2\text{O})_6^{+++}$ being less than 0.3. But when the spectrum was measured two days later (the original operations lasted two hours), the high absorption in the near ultraviolet was somewhat decreased, and much more so after 12 days. As seen in Fig. 4, a similar preparation from $\text{BaCO}_3 + \text{Rh}(\text{OH})_3$ exhibited similar properties. Since the reactions between monomeric hydroxo complexes and hydrogen ions presumably are very fast, the high absorption below 400 $m\mu$ is probably due to a hydroxo complex with at least two rhodium atoms. This can be compared with the dimeric $\text{Fe}(\text{OH})_2\text{Fe}^{+4}$ found by Mulay and Selwood³³, which also has a strong electron transfer spectrum at lower wavenumbers than $\text{FeOH}(\text{H}_2\text{O})_5^{++}$. Many rhodium(III) complexes have electron transfer spectra below 300 $m\mu$, e. g. RhCl_6^{3-} has a shoulder at 242 $m\mu$ with $\epsilon \sim 14\,000$ (it is decreased to 7 000 at 270 $m\mu$). In strongly alkaline solution, the polymer hydroxo complexes seem to disappear — two bands of ordinary intensity are observed at 415 and 326 $m\mu$.

The high absorption in the ultraviolet of hydroxo complexes can hardly be due to higher oxidation states of rhodium, since ascorbic acid has no influence, except reducing a trace of iridium(IV) with absorption at 480 $m\mu$. If rhodium (III) is oxidized in alkaline solution, blue solutions of Rh(VI) and green of Rh(IV) can be obtained, as studied by Grube and Autenrieth³⁴. The present author has measured the green solution in 1 M HClO_4 and found a broad absorption band around 770 $m\mu$. Cf. the measurements by Ayres⁶⁴.

If the solution in 0.4 M HClO_4 mentioned above is added to stronger HClO_4 , only small changes are observed, but the strong absorption limit decreases faster in 5 M HClO_4 . If the solutions are boiled, the second crystal field band appears as a shoulder $\sim 320 m\mu$. The best way found to eliminate the polymers is to boil $\text{Na}_3\text{RhCl}_6 \cdot 12 \text{H}_2\text{O}$ with 5 M HClO_4 for half an hour. The hydrochloric acid is evaporated, and the yellow solution exhibits two distinct

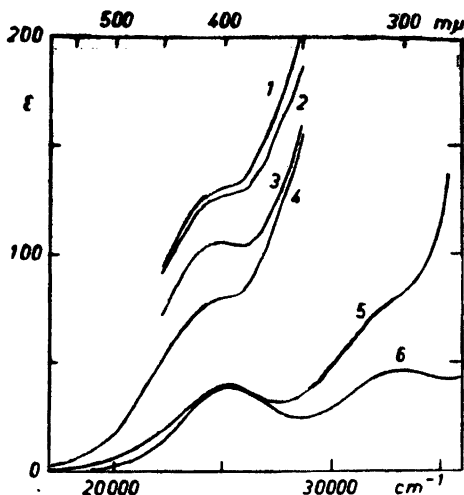


Fig. 4. Absorption spectra of aquo and hydroxo complexes of rhodium(III).

- Curve 1. 0.015 M Rh in 0.06 M HClO_4 .
 Curve 2. 0.015 M Rh in 0.4 M HClO_4 , immediately measured.
 Curve 3. The solution of curve 2 after two days.
 Curve 4. 0.01 M Rh in 2 M HClO_4 , from $\text{Rh}(\text{OH})_3$ precipitated by BaCO_3 .
 Curve 5. The solution of curve 4 after longer time of boiling.
 Curve 6. 0.015 M Rh in 1 M HClO_4 , from Na_3RhCl_6 boiled with HClO_4 .

crystal field bands at 393 and ~ 305 $m\mu$ (Fig. 4) when diluted to 1 M HClO_4 . It is highly probable that these maxima correspond to $\text{Rh}(\text{H}_2\text{O})_6^{+++}$. The half-width of the first band is not very large, and the position in the spectrochemical series is that predicted (Table 1) as compared to Rhox_3^{--} with the maximum at 398 $m\mu$; and the sulphato complexes (prepared from metal and $\text{HNO}_3 + \text{H}_2\text{SO}_4$ boiled nearly down) with maximum at 401 $m\mu$ and a shoulder ~ 320 $m\mu$.

It has not been possible by similar methods to find the crystal field bands of $\text{Ir}(\text{H}_2\text{O})_6^{+++}$, which most likely is a strong acid. If K_3IrCl_6 is boiled with HClO_4 , black-red K_2IrCl_5 precipitates at first, owing to oxidation. It redissolves with bluish purple colour, which does not change by dilution of the cooled solution to 1 M HClO_4 . This can be reduced by ascorbic acid, except for small precipitate of blue IrO_2 , to a straw-yellow solution. This solution has only steeply increasing absorption in ultraviolet, as Irox_3^{--} discussed below. Marino³⁵ prepared alums of iridium(III) and found yellow crystals and solutions. These are oxidizable by air to a purple colour, but can be reduced with H_2S . This reagent precipitates the solution in 1 M HClO_4 mentioned above.

TRIS(OXALATO) COMPLEXES

The orange Rhox_3^{--} and the yellow Irox_3^{--} have been much studied, owing to their optical activity and extreme robustness. Lifschitz and Rosenbohm³⁶ found that Rhox_3^{--} has a low band at 25 000 and a higher band at 35 000 cm^{-1} .

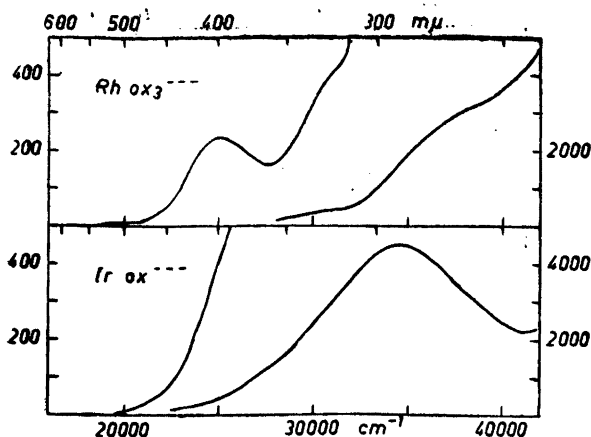


Fig. 5. Absorption spectra of tris-oxalato complexes of rhodium(III) and iridium(III).

0.1 M Rhox_3^{3-} in 0.6 M K_2ox , warmed at 100°C for 4 hours, and subsequently diluted. 0.01 M Irox_3^{3-} from similar method, and 0.0005 M to 0.02 M K_3Irox_3 from Professor Marcel Delépine.

Fig. 5 shows that the first band is the first crystal field band, while the other is a strong electron transfer band, as expected of an oxalato complex. The second crystal field band can be seen as a shoulder on the red side of this band. Delépine³⁷ has described the extremely slow reactions of IrCl_6^{3-} with one, two, and three oxalate ions. The third consecutive reaction takes ten hours at 130°C . Fig. 5 gives the spectrum of a solution which contains mainly Irox_3^{3-} . It has also high absorption in the ultraviolet, but a shoulder can be observed at $360\text{ m}\mu$. This is a very reasonable place for the first crystal field band estimated from the value for Rhox_3^{3-} and the hypsochromy of iridium(III) complexes compared to rhodium(III).

HEXAMMINE AND PENTAMMINE COMPLEXES

S. M. Jørgensen³⁸ found an analogy to the chromium(III) and cobalt(III) ammine complexes in the rhodium(III) complexes, and prepared the hexammine and iodo-, bromo-, chloro-, and nitro-pentammine complexes used for this study. Palmær³⁹ studied the similar iridium(III) complexes, of which only $\text{IrCl}(\text{NH}_3)_5^{2+}$ is examined here. The aquopentammine rhodium(III) salt, which with base gives the hydroxopentammine ion, was made from one of S. M. Jørgensen's preparations as a perchlorate by Brønsted and Volqvartz⁴⁰. These authors found $\text{p}K = 6.3$.

Fig. 6 gives the spectra of the rhodium(III) complexes. The hexammine is remarkable by its very deep minimum at $220\text{ m}\mu$, which shows the absence of both an electron transfer spectrum and of impurities. The two high bands resemble very much the spectrum of $\text{Co}(\text{NH}_3)_6^{3+}$, displaced towards higher wavenumbers, and the first band is highest as in RhCl_6^{3-} .

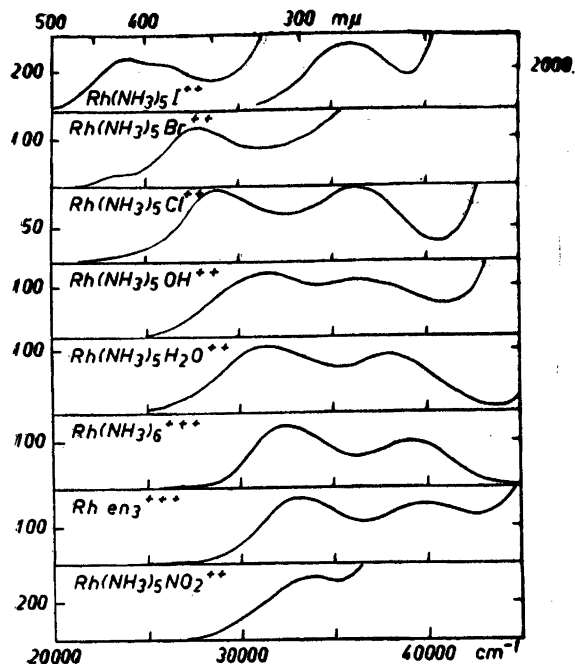


Fig. 6. Absorption spectra of hexammine and pentammine complexes of rhodium(III).

0.001 M to 0.01 M $[\text{Rh}(\text{NH}_3)_5\text{I}]\text{Cl}_2$ in H_2O .

0.01 M $[\text{Rh}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ in H_2O .

0.01 M $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in H_2O .

0.01 M $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ in 0.1 M Na_2CO_3 (forming $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$) and in 0.05 M HClO_4 .

0.01 M $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ in H_2O .

0.008 M Rh en_3^{3+} in 0.1 M en.

0.003 M $[\text{Rh}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and 0.06 M $[\text{Rh}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_3$ in H_2O .

$\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ shows the same displacement towards lower wavenumbers as all "roseo" salts, compared to "luteo" salts, and $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$ has a smaller distance between the two bands, as usually found. The halidopentammine complexes were expected to have tetragonal splittings, since the two ligands are so distant in the spectrochemical series¹⁴. It cannot be excluded that the first band of $\text{RhCl}(\text{NH}_3)_5^{3+}$ is slightly split by tetragonal field effects, producing the flat minimum between the two bands as in $\text{Rh}(\text{NH}_3)_5\text{OH}^{2+}$. The second band is masked by the electron transfer spectrum in $\text{RhBr}(\text{NH}_3)_5^{3+}$ and $\text{RhI}(\text{NH}_3)_5^{3+}$. In the former ion, a weak shoulder is observed on the red side of the first band, while the shoulder is larger on the blue side in the latter case. The band in the bromo complex is presumably one of the triplet transitions which are intermixed with the strong singlet transitions¹⁶. If the double band in the iodo complex is not due to a similar intermixing, it is a

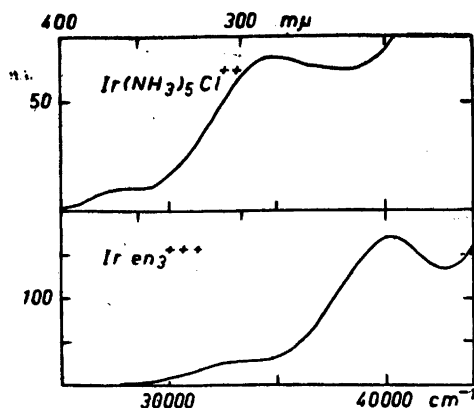


Fig. 7. Absorption spectra of chloropentammine- and tris(ethylenediamine)iridium(III) ions.

0.015 M $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, and 0.004 M $[\text{Iren}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ in H_2O , from J.-P. Mathieu's preparations.

genuine tetragonal splitting. But the theory for this splitting^{4, 7, 14, 17} is not easy to correlate with the observations.

The ammine complexes of rhodium(III) are exceedingly robust, as shown by Christiansen and Asmussen⁴¹, who in nearly all cases found the salts prepared fifty years before by S. M. Jørgensen undecomposed. The halide ions in the pentammine complexes exchange very slowly with water and even with hydroxyl ions, as found to a higher degree for iridium(III) pentammines by Palmær³⁹ and Lamb and Fairhall⁴².

It has been assumed by Grünberg⁴³ that $\text{Rh}(\text{NH}_3)_6^{3+}$ is a weak acid with $\text{p}K \sim 11.2$, forming the amidopentammine complex $\text{Rh}(\text{NH}_2)(\text{NH}_3)_5^{3+}$. The present author has measured $\text{Rh}(\text{NH}_3)_6^{3+}$ in 5 M and 1 M NaOH and Rh en_3^{3+} and $\text{Rh}(\text{NH}_3)_5\text{OH}^{3+}$ in 1 M NaOH and found no observable deviation from the ordinary spectrum; especially are the band maxima displaced less than 1 $m\mu$. Since the amido complexes presumably would be displaced much more towards the red, the $\text{p}K$ for their formation seems to be > 15 , *i. e.* they are not formed to a high degree in any aqueous solution. There is evidence⁴⁴ from reaction kinetics that the base hydrolysis of cobalt(III) complexes proceeds by an acid-base equilibrium followed by dissociation of the amido complex.

In the third paper of this series, which will concern the complexes prepared by M. Delépine, it will be shown that the base⁴⁵ assumed to be $\text{Ir}(\text{NH}_2)(\text{NH}_3)_3\text{py}_2^{3+}$ has the same $\text{p}K$, *viz.* 5.1, as $\text{Ir}(\text{OH})(\text{NH}_3)_3\text{py}_2^{3+}$ and thus probably does not have the presumed composition. Thus, Rh(III) and Ir(III) do not seem to exhibit amine acidity in aqueous solution contrary to Pt(IV) discussed in the second paper of this series.

In Figure 7, $\text{Ir}(\text{NH}_3)_5\text{Cl}^{3+}$ exhibits a rather narrow and weak band at 360 $m\mu$, which can be ascribed to the first transition to a triplet level, while the second band at 286 $m\mu$ is due to the first excited singlet level with some

evidence for tetragonal splitting. These two positions are displaced toward shorter wavelengths compared to $\text{Rh}(\text{NH}_3)_5\text{Cl}^{++}$ as can be extrapolated from the behaviour of IrCl_6^{--} and RhCl_6^{--} .

The first crystal field band can also be distinguished in $\text{Rh}(\text{NH}_3)_5\text{NO}_2^{++}$, while the second is hidden by or intermixed with electron transfer absorption. The intensity of the first band is not exceedingly large, as also observed in nitropentamminecobalt(III) ions. $\text{Rh}(\text{NO}_2)_6^{--}$ has a band at $270 \text{ m}\mu$ with $\epsilon \sim 17\,000$, which cannot reasonably be described as a crystal field band.

TRIS(ETHYLENEDIAMINE) COMPLEXES

The colourless Rh en_3^{+++} was studied by Werner⁴⁶ and Jaeger⁴⁷. Lifschitz and Rosenbohm³⁶ give the two absorption bands at $\sim 33\,000$ and $\sim 39\,500 \text{ cm}^{-1}$, as also Mathieu⁴⁸. The two crystal field bands are seen from Fig. 6 to be slightly hypsochromic, compared to $\text{Rh}(\text{NH}_3)_6^{+++}$.

The very robust Ir en_3^{+++} has according to Lifschitz and Bosenbohm³⁶, shoulders at $32\,500$ and $\sim 38\,000 \text{ cm}^{-1}$, while Mathieu⁴⁸ found a broad shoulder at $31\,000 \text{ cm}^{-1}$. Both bands are observed here in Mathieu's preparation, but with smaller intensity (Fig. 7 and Table 2). Thus, the first shoulder must be a triplet band. This band is $\sim 15\%$ singlet-like as in the other iridium(III) complexes and the distance between the first triplet and first singlet level of the configuration $\gamma_5^5\gamma_3$ seems to remain rather constant at increasing crystal field strength.

COMPARISON OF COBALT(III), RHODIUM(III) and IRIDIUM(III).

In Table 5 are given the evolution of the spectrochemical series and the distances between the two singlet levels of the electron configuration $\gamma_5^5\gamma_3$, represented by the two band maxima. The energy difference ($E_1 - E_2$) between

Table 5. Comparison of crystal field strength in nickel (II), chromium (III), cobalt (III), rhodium (III) and iridium (III) complexes.

ν/ν_{aq} is the wavenumber of the first band of the complex, divided with the wavenumber of the first band of the aquo ion. $\Delta\nu$ is the difference in wavenumber between the two first bands, which are not spin-forbidden. The measurements of Cr(III) and Co(III) are made by Mr. C. E. Schäffer, and those of Ni(II) taken from Ref. 16.

Complex	Ni(II)		Cr(III)		Co(III)		Rh(III)		Ir(III)	
	ν/ν_{aq}		ν/ν_{aq}	$\Delta\nu$	ν/ν_{aq}	$\Delta\nu$	ν/ν_{aq}	$\Delta\nu$	ν/ν_{aq}	$\Delta\nu$
Br_6	—	—	—	—	—	—	0.71	4 100	0.71	3 400
Cl_6	—	—	0.78	5 200	—	—	0.76	5 000	0.76	4 000
ox_3	—	—	1.00	6 600	0.99	7 300	0.98	$\sim 4\,900$	—	—
$(\text{H}_2\text{O})_6$	1.00	—	1.00	7 300	1.00	8 300	1.00	7 400	—	—
$(\text{NH}_3)_5\text{J}$	—	—	1.06	—	1.05	—	0.95	—	—	—
$(\text{NH}_3)_5\text{Br}$	—	—	1.10	7 400	1.11	—	1.09	—	—	—
$(\text{NH}_3)_5\text{Cl}$	—	—	1.12	7 200	1.15	8 500	1.13	7 400	1.11	—
$(\text{NH}_3)_5\text{OH}$	—	—	1.12	6 600	1.20	7 200	1.22	4 800	—	—
$(\text{NH}_3)_5\text{H}_2\text{O}$	—	—	1.19	6 900	1.24	8 800	1.24	6 500	—	—
$(\text{NH}_3)_6$	1.27	—	1.24	7 000	1.28	8 400	1.28	6 400	—	—
en_3	1.36	—	1.26	6 600	1.31	8 000	1.30	6 400	1.28	—
$(\text{NH}_3)_5\text{NO}_2$	—	—	—	—	1.32	—	1.32	—	—	—
$(\text{CN})_6$	—	—	1.51	5 900	1.95	6 600	—	—	—	—

a γ_3 - and a γ_5 -electron corresponds directly to the first band in octahedral d^3 - and d^8 -systems, therefore chromium(III) and nickel(II) complexes¹⁶ are also considered in Table 5. Since the distance between the two bands of the same first-order electron configuration has considerable interest for the theory of intermixing of molecular orbitals, *i. e.* beginning covalency, the wavenumber difference has been given not only for all three diamagnetic d^6 -systems, but also for $\gamma_5^2\gamma_3$ of chromium(III). Mr. C. E. Schäffer has kindly informed me about all his measurements of chromium(III) and cobalt(III) complexes.

In the case of d^6 -systems, $(E_1 - E_2)$ is undoubtedly¹⁰ somewhat larger than the wavenumber of the first singlet band. This is due to different energies of electrostatic interaction between the electrons in the groundstate 1G_1 and the excited state, which according to Tanabe and Sugano¹⁰ is 1G_4 and not 1G_5 . But since the exact meaning of $(E_1 - E_2)$ in the diamagnetic d^6 -complexes is rather dispersed, owing to the interaction with other electron configurations, the wavenumber of the first band will be used as reference here.

The hexaquo ion is chosen as standard for each element with 8 500 cm^{-1} in nickel(II), 17 400 cm^{-1} in chromium(III), 16 600 cm^{-1} in cobalt(III), and 25 500 cm^{-1} in rhodium(III). Since $\text{Ir}(\text{H}_2\text{O})_6^{+++}$ is not known, it has been assigned the hypothetical value 31 500 cm^{-1} , which makes the ratios between the wavenumbers of hexachloro and hexaquo ions equal in rhodium(III) and iridium(III). As already proposed by Tsuchida⁴⁹, CrCl_6^{--} is represented by the anhydrous CrCl_3 , in which the environment of each chromium ion is a regular octahedron of six chloride ions⁵⁰.

While Table 5 illustrates the relative crystal field strengths of different ligands for the same ion, it is also possible to investigate the relative tendency of high crystal field strengths, *i. e.* hypsochromy, for the three related central ions, Co^{+3} , Rh^{+3} , and Ir^{+3} . Since the deviations of the ratios in Table 5 are rather small and scattered without a pronounced tendency, the assumed values of the hexaquo ions can be applied as constants: If a given ligand gives the crystal field strength 1.00 in a cobalt(III) complex, the same ligand will within a few per cent uncertainty give 1.54 in rhodium(III) and 1.90 in iridium(III). Since Ir^{+3} does not have a much larger ionic radius than Rh^{+3} , owing to the lanthanide contraction, there seems to be a specific difference between the 3d-, 4d-, and 5d-electrons, which probably evolves from the different interaction with the molecular orbitals. The purely electrostatic model with hydrogenic d-wave functions^{3,7} can hardly explain these facts and the strong increase of $(E_1 - E_2)$ with the external charge⁹.

THE INTERMIXING OF SINGLET AND TRIPLET LEVELS

In the pure Russell-Saunders coupling⁵¹, the levels of the free ions can be classified in the multiplet terms with a given combination of S (the total spin quantum number) and L (the total angular momentum quantum number). These are quantized vector sums of the quantum numbers of the individual electrons, denoted by small letters: s (always = $\frac{1}{2}$) and l (= 0 for s -, 1 for p -, 2 for d -, 3 for f -electrons . . .). In the heavy atoms, the levels deviate from the Russell-Saunders coupling, as shown *e. g.* by Rasmussen⁵² or by the author from the absorption spectra of lanthanide and actinide ions⁵³. The vector sum

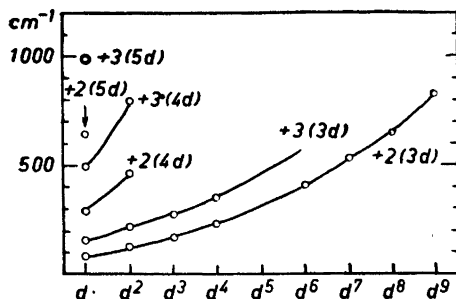


Fig. 8. Lande's multiplet splitting factor ζ_{nl} as function of the number of electrons in the partly filled nd -shell.

Divalent and trivalent ions of the 3d-, 4d- and 5d-groups⁵⁴. The steep increase of the curve for *e. g.* trivalent 4dⁿ-ions can be interpolated from the value $\zeta_{4d} = 2\ 325\text{ cm}^{-1}$ in Cd^{+++} , which has nine 4d-electrons,

J of L and S of each level is preserved when the q levels of a given electron configuration with the same J intermix, and the energy levels produced can be described by the eigen-values of a matrix of degree q . The elements of this matrix consist of the energies of the centres of the multiplet terms; and of constants multiplied by the Lande's multiplet splitting constant ζ_{nl} where n and l are the quantum numbers characteristic for each electron. The deviations from the Russell-Saunders coupling can be quantitatively described by increasing values of ζ_{nl} . For isoelectronic species, ζ_{nl} increases roughly proportionally to the square of Z_0^2 (the external charge is $= Z_0 - 1$), and varies much with the value of the principal quantum number n , *i. e.* in the second and third transition group compared to the first⁵⁴. Fig. 8 gives the values of ζ_{nl} , known from atomic spectroscopy, as function of the number of nd -electrons.

The crystal field theory, when applied to d^n -systems, assumes that the crystal field strength is much larger than ζ_{nl} . Then, the total spin S is "a good quantum number", and the levels can be described by the combination Γ_n and S in the theory of Bethe⁵⁵. The energies of the levels develop as a function of the crystal field strength as the q eigen-values of a matrix of q 'th degree, if q levels present the same combinations¹¹ of Γ_n and S . This matrix can have either as diagonal elements the weak-field energies^{1, 13, 15} with defined L from the free ion, or the strong-field energies^{6, 10, 14} with defined electron configurations $\gamma_5^a \gamma_3^b$. The final results are of course equal, but the former type of matrix has exclusively crystal field strengths in the non-diagonal elements, while the latter type has exclusively electrostatic interaction energies (from multiplet distances in the free ions) in the non-diagonal elements. In both types of matrices, the diagonal elements are linear combinations of electrostatic interactions and crystal field strengths.

But as seen from Fig. 8, the assumption of much larger $(E_1 - E_2)$ than ζ_{nl} is weakened in the ends of each transition group, and especially in the later groups with 4d- and 5d-electrons. Unfortunately, atomic spectroscopy has no information about Co^{+3} and most 4dⁿ- and 5dⁿ-systems, while most other

$3d^n$ -systems are well known⁵⁶. In Ni^{++} , the absorption spectra¹⁶ demonstrate an interaction of the level 1F_3 with 3F_5 and ${}^3F_4(F)$ with the non-diagonal elements 500 and 800 cm^{-1} , while $\zeta_{3d} = 600$ cm^{-1} . Generally, the intermixing in the squares of the wave functions is approximately $\left(\frac{k\zeta_{nl}}{E_a - E_b}\right)^2$, where k in the non-diagonal element $k\zeta_{nl}$ is a small number near 1, and $(E_a - E_b)$ is the energy distance between the two interacting levels. The selection rule that transitions are only allowed between levels with the same S , is weakened exactly to the extent, the two levels (originally with different S) have the same S , owing to intermixing effects. This is the explanation⁵ of the observation of spin-forbidden bands^{1, 8, 10, 53}. In cobalt(III) complexes, where the weak triplet bands⁸ demonstrate an intermixing ~ 0.005 , the value of $k\zeta_{nl}$ is thus 500 cm^{-1} , if the nearest singlet is the only cause of intermixing. From Fig. 8 ζ_{3d} can be extrapolated to 600 cm^{-1} . The groundstate 1F_1 is presumably intermixed with triplet states ~ 0.001 , which perhaps causes the temperature-independent paramagnetism of some cobalt(III) complexes⁵⁷. Sloth and Garner⁵⁸ have found relatively strong paramagnetism of $IrCl_6^{--}$ and $IrCl_5(H_2O)^-$, agreeing well with the large ζ_{5d} .

In the hexachloro complexes of rhodium(III) and iridium(III), the intermixing of singlet character in the triplet levels is about 0.03 and 0.12, corresponding to $k\zeta_{4d} = 900$ cm^{-1} and $k\zeta_{5d} = 2\,000$ cm^{-1} , respectively. The evolution

$$\zeta_{5d} \cong 2 \zeta_{4d} \cong 5 \zeta_{3d} \quad (2)$$

is predicted from Fig. 8, analogous to the relation $\zeta_{5f} = 2 \zeta_{4f}$ found in the actinides and lanthanides⁵³.

$IrCl_6^{--}$ has evidently two weak triplet bands with the distance 1 700 cm^{-1} (Table 2), and $RhCl_6^{--}$ seems also to have two triplet bands, since the shoulder towards the red is so broad (Fig. 1). The two bands are probably due to transitions to 3F_4 and 3F_5 with increasing energy¹⁰. It cannot be excluded that the splitting in the weak band of $IrCl_6^{--}$ is due to different levels of the Γ_j type discussed below, since their distance is not larger than ζ_{5d} ; but it is a quite paradoxical fact that such a splitting has never as yet been observed in a band with a defined Γ_n except in the tetrahedral $CoCl_4^{--}$ ⁵⁹.

Tanabe and Sugano¹⁰ pointed out that the quantum numbers of the levels must be written Γ_j , where the ordinary Bethe-level (S, Γ_n) split into the class of Γ_j given by the internal vector product¹⁴

$$C(\Gamma_j) = C(\Gamma_n) \times C(S) \quad (3)$$

For integral numbers of S , $C(S)$ is equal to the usual¹⁴ $C(L)$ with $S = L$, *e. g.* Γ_1 for $S = 0$; Γ_4 for $S = 1$; $\Gamma_3 + \Gamma_5$ for $S = 2$; *etc.* For half-numbered values of S , the double-groups Γ_6, Γ_7 , and Γ_8 must be used⁵⁵.

Thus¹⁶, the triplet levels 3F_4 and 3F_5 should each divide into four levels with distances which are of the order of magnitude ζ_{nl} , as calculated for γ_5^a by Kotani⁶⁰ and Griffiths, Owen and Ward⁶¹. Absorption bands due to transitions^{8, 10}, where one electron changes from γ_5 to γ_3 have a halfwidth between 1 000 and 2 000 cm^{-1} . Thus, it should be possible in many cases to distinguish the Γ_j components. Especially Mr. Schäffer has continued the investigations

of Gaussian shape of absorption bands¹⁹ and found no sign of extra bands, except those due to intermixing of other values of S . The two sharp lines of Cr^{+++} in the ruby are due to ${}^2\Gamma_3$ and the broader band groups with higher wavenumber due to ${}^2\Gamma_4$ in the red and ${}^2\Gamma_5$ in the blue. The two latter groups are perhaps each divided into two Γ_7 -bands, but it cannot easily be decided.

In the next paper of this series, the influence of other molecular orbitals than the γ_5 and γ_3 (from d-electrons) will be discussed for the octahedral complexes of the second and third transition groups.

EXPERIMENTAL

The measurements of absorption spectra were performed on a Cary spectrophotometer, $\sim 25^\circ\text{C}$. The titration curve of $\text{Rh}(\text{OH})_3$ was measured with a glass electrode pH-meter Radiometer M 22.

$\text{Na}_3\text{RhCl}_6, 12\text{H}_2\text{O}$. Rhodium metal from S. M. Jørgensen's collection (partly from Johnson and Matthew, London) was mixed with 10 moles sodium chloride per Rh and treated with chlorine for six hours at $600-700^\circ\text{C}$ in a pyrex tube, electrically heated. The cooled mass was perfectly soluble in 4 M HCl, except for a few per cent of anhydrous RhCl_3 formed. By addition of ethanol to such a solution, most rhodium crystallizes after some days as $\text{Na}_3\text{RhCl}_6, 12\text{H}_2\text{O}$. But this method is disadvantageous, since metal tends to precipitate from the filtrate when boiled. Rather, fractionated crystallization of the melted mass in dilute HCl can be recommended. $\text{Rh}(\text{OH})_3$ can be regenerated from the solutions with NaOH or BaCO_3 .

The iridium content was found to 0.4 % and 0.2 % in two samples, from the absorption spectra in HCl + Cl_2 . There were found 17 % Rh from precipitation of the metal by TiCl_3 and 37 % Cl from Mohr's titration of the filtrate from BaCO_3 (calc. 17.1 % Rh and 35.1 % Cl).

RhBr_6^{3-} was prepared in solution by prolonged boiling of $\text{Na}_3\text{RhCl}_6, 12\text{H}_2\text{O}$ with 6 M HBr till the spectrum of different solutions did not change. Even though Poulenc⁶³ has prepared solid salts of $\text{Rh}_2\text{Br}_8^{3-}$, RhBr_6^{3-} and $\text{Rh}_2\text{Br}_{11}^{3-}$, it is here assumed that these complexes with bromide bridges are not abundant in strong HBr.

$\text{Rh}(\text{H}_2\text{O})_6^{+++}$ was made by boiling 0.5 g $\text{Na}_3\text{RhCl}_6, 12\text{H}_2\text{O}$ with 50 ml 5 M HClO_4 in a 100 ml beaker, covered with a watch-glass. The dark-red colour turns first orange, then a red-brown precipitate is formed, which redissolves to a dark brown solution. By dilution of the residual 4 ml to 50 ml with water, a clear yellow solution is obtained.

Rh ox_3^{3-} was made by heating 4 hours to 100°C of a solution, originally 0.1 M RhCl_6^{3-} and 0.6 M K_2ox .

$\text{Rh}(\text{NH}_3)_6\text{Cl}_3$, $[\text{Rh}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$, $[\text{Rh}(\text{NH}_3)_5\text{I}]\text{Cl}_2$, $[\text{Rh}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ and $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were taken from the collection of S. M. Jørgensen. The last salt was prepared for the determination of the atomic weight of Rh.

$[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ of Brønsted and Volqvartz⁴⁰ was kindly furnished by Professor J. A. Christiansen. It was measured in 0.05 M HClO_4 and in H_2O , giving the aquo form, and in 0.1 M Na_2CO_3 and 1 M NaOH, giving the hydroxo ion. Further, it was compared with the solution of sodium aquopentammine rhodium(III) pyrophosphate (S. M. Jørgensen) in 1 M HCl and in 5 M NH_3 .

Rh en_3^{+++} was prepared by Werner⁴⁶ by reacting $\text{Na}_3\text{RhCl}_6, 12\text{H}_2\text{O}$ with 50 % ethylenediamine. If the solution is more dilute, a yellow precipitate ($\text{Rh}(\text{OH})_3$?) is formed by warming, and the quantitative reaction is slow. For the experiments, 0.5 g $\text{Na}_3\text{RhCl}_6, 12\text{H}_2\text{O}$ was dissolved in 2 ml H_2O and added a solution of 0.5 ml ethylenediamine hydrate (Merck's No. 946) in 10 ml 0.2 M HCl. The solution was evaporated cautiously to 1 ml under stirring.

In the next paper of this series the preparation of iridium compounds from the metal will be described. Here, it can be mentioned that IrCl_6^{3-} was reduced by H_2S or ascorbic acid for some repeated measurements. In most cases were used:

$\text{K}_3\text{IrCl}_6, 3\text{H}_2\text{O}$, supplied from Dansk Hollandsk Ædelmetal (H. Drijfhout and Zoon).

$IrBr_6^{3-}$, prepared by boiling this salt with 6 M HBr.

IrO_2 , made by warming 30 hours at 110° C of a solution 0.05 M $K_2IrCl_6 \cdot 3H_2O$ and 0.8 M K_2Ox , in a stoppered bottle. Professor Marcel Delépine, Collège de France, has kindly presented me with a series of iridium(III) and rhodium(III) complexes, which will be the subject of the third paper of this series. $K_3Irox_3 \cdot 4.5H_2O$ of this collection has a spectrum similar to that given in Fig. 5.

$[Ir(NH_3)_5Cl]Cl_2$ and $[Ir en_3]Br_3 \cdot 2H_2O$ (the l-form), kindly furnished by Professor Jean-Paul Mathieu. The spectrum of $Ir en_3^{3+}$ was also measured in 0.3 M NaOH and showed no change.

Acknowledgments. I am very much indebted to Professor J. Bjerrum for his interest in the work. Further, I thank Mr. C. E. Schäffer for interesting discussions and valuable information about his measurements of chromium(III) and cobalt(III) complexes, and Miss Bodil Friis for assistance with the preparation of $Na_3RhCl_6 \cdot 12H_2O$. Finally, I thank Professor Jean-Paul Mathieu of Université de Paris for the valuable samples of iridium(III) amine complexes.

REFERENCES

1. Finkelstein, R. and Van Vleck, J. H. *J. Chem. Phys.* **8** (1940) 790.
2. Abragam, A. and Pryce, M. H. L. *Proc. Roy. Soc. London* **206 A** (1951) 173.
3. Ilse, F. E. and Hartmann, H. *Z. physik. Chem.* **197** (1951) 239.
4. Hartmann, H. and Ilse, F. E. *Z. Naturforsch.* **6a** (1951) 751.
5. Hartmann, H. and Schläfer, H. L. *Z. Naturforsch.* **6a** (1951) 754.
6. Orgel, L. E. *J. Chem. Soc.* **1952** 4756.
7. Ballhausen, C. J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **29** (1954) No. 4 and **29** (1955) No. 8.
8. Jørgensen, C. *Klixbüll Acta Chem. Scand.* **8** (1954) 1502.
9. Owen, J. *Proc. Roy. Soc. London* **227 A** (1955) 183.
10. Tanabe, Y. and Sugano, S. *J. Phys. Soc. Japan* **9** (1954) 753 and 766.
11. Jørgensen, C. *Klixbüll Acta Chem. Scand.* **9** (1955) 116.
12. Jørgensen, C. *Klixbüll and Bjerrum, J. Acta Chem. Scand.* **9** (1955) 180.
13. Orgel, L. E. *J. Chem. Phys.* **23** (1955) 1004 and 1819.
14. Ballhausen, C. J. and Jørgensen, C. *Klixbüll Kgl. Danske Videnskab. Selskab, Mat. fys. Medd.* **29** (1955) No. 14.
15. Hartmann, H. and Fischer-Wasels, H. *Z. physik. Chem.* **4** (1955) 297.
16. Jørgensen, C. *Klixbüll Acta Chem. Scand.* **9** (1955) 717 and 1362.
17. Basolo, F., Ballhausen, C. J. and Bjerrum, J. *Acta Chem. Scand.* **9** (1955) 810.
18. Hartmann, H. and Schläfer, L. *Angew. Chem.* **66** (1954) 768.
19. Jørgensen, C. *Klixbüll Acta Chem. Scand.* **8** (1954) 1495.
20. Samuel, R. and Uddin, M. *Trans. Faraday Soc.* **31** (1935) 423.
21. Babaeva, A. V. *Bull. Acad. Sci. URSS Cl. Sci. Chim.* **1943** 171.
22. Inamura, Y. and Kondo, Y. *J. Chem. Soc. Japan* **72** (1951) 787.
23. Meyer, J. and Kawczyk, M. *Z. anorg. Chem.* **228** (1936) 297.
24. Bjerrum, N. *Z. physik. Chem.* **59** (1907) 336.
25. Delépine, M. *Ann. chimie* [9] **7** (1917) 277.
26. Delépine, M. *Bull. soc. chim. Belg.* **36** (1927) 108.
27. Charlot, G. and Gauguin, R. *Les methodes d'analyse des reactions en solution.* Paris. 1951.
28. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution.* Copenhagen 1941.
29. Sundram, A. K. and Sandell, E. B. *J. Am. Chem. Soc.* **77** (1955) 855.
30. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **22** (1946) No. 18.
31. Bjerrum, N. *Kgl. Danske Videnskab. Selskabs Skrifter, Nat. math. Afd.* [7] **4** (1907) No. 1.
32. Grube, G. and Kesting, E. *Z. Elektrochem.* **39** (1933) 948.
33. Mulay, L. N. and Selwood, P. W. *J. Am. Chem. Soc.* **77** (1955) 2693.
34. Grube, G. and Autenrieth, H. *Z. Elektrochem.* **43** (1937) 880 and **44** (1938) 296.
35. Marino, L. *Z. anorg. Chem.* **42** (1904) 213.
36. Lifschitz, J. and Rosenbohm, E. *Z. physik. Chem.* **97** (1920) 1.

37. Delépine, M. *Bull. soc. chim. France* [4] **21** (1917) 157.
38. Jørgensen, S. M. *J. prakt. Chem.* [2] **27** (1883) 461, **34** (1886) 440, and **44** (1891) 42 and 63.
39. Palmær, W. *Z. anorg. Chem.* **10** (1895) 320 and **13** (1897) 211.
40. Brønsted, J. N. and Volqvartz, K. *Z. physik. Chem.* **134** (1928) 97.
41. Christiansen, J. A. and Asmussen, R. W. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **12** (1934) No. 1.
42. Lamb, A. B. and Fairhall, L. T. *J. Am. Chem. Soc.* **45** (1923) 384.
43. Grünberg, A. A. and Faerman, G. P. *Z. anorg. Chem.* **193** (1930) 193.
44. Adamson, A. W. and Basolo, F. *Acta Chem. Scand.* **9** (1955) 1261.
45. Delépine, M. *Z. physik. Chem.* **130** (1927) 222.
46. Werner, A. *Ber.* **45** (1912) 1228.
47. Jaeger, F. M. *Rec. trav. chim.* **38** (1919) 171.
48. Mathieu, J.-P. *J. chim. phys.* **33** (1936) 85.
49. Tsuchida, R. *Bull. Chem. Soc. Japan* **13** (1938) 388 and 436.
50. Wooster, N. *Z. Kryst.* **74** (1930) 363.
51. Condon, E. U. and Shortley, G. H. *Theory of Atomic Spectra*. Cambridge 1953.
52. Rasmussen, E. *Serier i de cødle Luftarters Spektre*. Thesis. Copenhagen 1931.
53. Jørgensen, C. Klixbüll *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **29** (1955) No. 7 and 11.
54. Jørgensen, C. Klixbüll *J. Inorg. Nucl. Chem.* **1** (1955) 301.
55. Bethe, H. *Ann. Physik* [5] **3** (1929) 133.
56. Moore, C. E. *Nat. Bur. Stand. Circ. No. 467*, Vol. II, 1952.
57. Asmussen, R. W. *Magnetokemiske Undersøgelser*. Thesis. Copenhagen 1944.
58. Sloth, E. N. and Garner, C. S. *J. Chem. Phys.* **22** (1954) 2064.
59. Ballhausen, C. J. and Jørgensen, C. Klixbüll *Acta Chem. Scand.* **9** (1955) 397.
60. Kotani, M. *J. Phys. Soc. Japan* **4** (1949) 293.
61. Griffiths, J. H. E., Owen, J. and Ward, I. M. *Proc. Roy. Soc. London* **219 A** (1953) 526.
62. Krauss, F. and Umbach, H. *Z. anorg. Chem.* **182** (1929) 411.
63. Poulenc, P. *Compt. rend.* **190** (1930) 639.
64. Ayres, G. H. *Anal. Chem.* **25** (1953) 1622.

Received December 22, 1955.