

Complexes of the 4d- and 5d-Groups

II. Crystal Field and Electron Transfer Spectra of Ruthenium(II) and (III), Iridium(IV) and Platinum(IV)

CHR. KLIXBÜLL JØRGENSEN

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

The octahedral complexes of the platinum metals often exhibit relatively strong absorption bands. The electron transfer bands with the lowest wavenumbers are assumed to be due to π -electrons from the ligands, which are transferred to holes in the 4d- and 5d-shells. In the halido complexes of ruthenium(III) and platinum(IV), the crystal field bands of d^5 - and d^6 -systems, respectively, can be observed. The acidity of $\text{Pt}(\text{NH}_3)_6^{+4}$ and $\text{Pt}(\text{NH}_3)_5\text{Cl}^{+3}$ is measured; the formations of the monoamido complexes have $\text{p}K = 7.75$ and 8.7 , respectively. The theory of molecular orbitals is compared to the explanation by the crystal field theory of the energy difference between γ_2 - and γ_5 -electrons. Probably, it will be necessary to consider the interaction between different configurations of molecular orbitals.

In the first paper¹ of this series, the regularly octahedral complexes of the d^6 -systems rhodium(III) and iridium(III) were studied. Their absorption spectra can be explained as the crystal field bands, also found of the complexes of cobalt(III). However, this proves by no means that the electrostatic model of the crystal field, acting on the d-electrons² is a very good approximation for the actual states of the transition group complexes. Van Vleck³ has pointed out that the theory of molecular orbitals of Mulliken⁴ gives several of the results of the crystal field theory, thus the 10-fold degenerate d-shell in an octahedral complex is split to four γ_3 -electrons with higher energy and six γ_5 -electrons with lower energy. This analogy has been extended further by Hartmann⁵, Orgel^{6,7}, Owen⁸, Tanabe and Sugano⁹. Experimental evidence for the intermixing of molecular orbitals with the γ_5 -electrons was found by paramagnetic resonance measurements of IrCl_6^{3-} and IrBr_6^{3-} by Owen and Stevens¹⁰ and Griffiths and Owen¹¹. The present paper is a contribution to the discussion of molecular orbitals, applied to the electron transfer spectra.

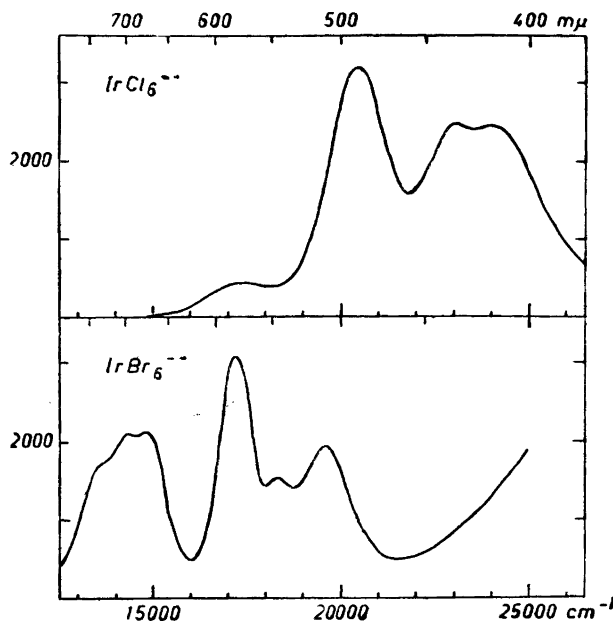


Fig. 1. Absorption spectra of hexachloro- and hexabromo-iridium(IV) ions.

0.0005 M Na_2IrCl_6 , measured in different solutions in water and dilute hydrochloric acid, which was not changed by addition of free chlorine, and from $\text{K}_3\text{IrCl}_6 + \text{Cl}_2$. 0.0005 M IrBr_6^{3-} from Na_2IrCl_6 in 0.1 M HBr.

HEXACHLORO- AND HEXABROMO-COMPLEXES OF IRIDIUM(IV).

The absorption spectra of the red-brown IrCl_6^{3-} and violet-blue IrBr_6^{3-} are given in Fig. 1 and Table 1. The band maxima of IrCl_6^{3-} have been found by Babaeva¹² at 490, 424 and 286 $m\mu$. The doublet structure of the second band was found by Inamura and Kondo¹³. The complex IrBr_6^{3-} is only stable under special conditions of temperature and concentrations. Thus, the dark-blue crystals of tetramethylammonium hexabromo iridate(IV) dissolves under complete decomposition in 6 M hydrobromic acid, which contains some free bromine. Only quite dilute solutions of HBr do not favorize the trivalent anion IrBr_6^{3-} so much, and IrBr_6^{3-} has been measured here. Therefore, the values of ϵ in Table 1 may be uncertain minimum values, but the relative height of the peaks is reproducible in many different solutions, since the decomposition product IrBr_6^{3-} is much less coloured¹.

There are six discernible absorption bands in the visible range of IrBr_6^{3-} , but only four of IrCl_6^{3-} . This can be ascribed to the larger energy differences between the two lowest levels $^2P_{3/2}$ and $^2P_{1/2}$ in the free halogen atom (404 cm^{-1} in F, 881 cm^{-1} in Cl, 3 685 cm^{-1} in Br and 7 603 cm^{-1} in I¹⁴) *i. e.* increasing ζ_{np} with increasing principal quantum number n ¹. This was early found by Scheibe¹⁵ from the double absorption band in the far ultraviolet of Br^- and I^- , compared to Cl^- .

Table 1. Absorption bands of iridium(IV) 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 band ²⁷.

	λ_n m μ	ν_n cm ⁻¹	ϵ_n	$\delta(-)$ cm ⁻¹	$\delta(+)$ cm ⁻¹	$P \cdot 10^{-5}$
IrCl ₆ ⁻	575	17 400	460	1 200	—	500
	489	20 450	3 200	900	—	2 600
	431	23 200	2 540	—	—	4 000
	414	24 200	2 480	—	1 400	
IrBr ₆ ⁻	737	13 600	1 550	600	—	2 000
	698	14 300	2 050	—	—	
	675	14 800	2 100	—	—	
	583	17 200	3 070	500	500	1 400
	544	18 400	1 500	—	—	1 500
	511	19 600	1 800	—	800	

The absorption spectrum of IrCl₆⁻ (Fig. 1) resembles much the spectrum of IrCl₆⁻ (Ref. 1, Fig. 2) multiplied in height by 40 and displaced 4 000 cm⁻¹ towards the red. This might perhaps suggest that iridium has the oxidation state +3 in IrCl₆⁻, involving as ligands the resonance structure of five chloride ions and one chlorine atom. However, this is impossible, since Owen and Stevens¹⁰ found the magnetic hole (the missing electron in the γ_5^5 -shell) is on an average, to 80 % near the iridium nucleus and to 3 % near each of the six chloride nuclei, *i. e.* about 20 % intermixing of the molecular orbitals with symmetry γ_5 . The question may be raised whether the oxidation state of Ir is an integral number, *e. g.* +3 or +4. In the author's opinion it is not deciding that the number of electrons within a volume defined as "the central atom" is some decimal fraction. Rather, the oxidation state of the central ion can be defined from the number of electrons in the highest γ_3 - and γ_5 -orbitals, which would have been pure d-electrons, if no intermixing occurred. *E. g.*, iridium is trivalent with γ_5^5 and quadrivalent with γ_5^6 as groundstate. This has nearly an exact meaning, since the interaction between different electron configurations is small in strong crystal fields, and since by chance the groundstates in weak crystal fields often contain an integral number of γ_3 - and γ_5 -electrons (*cf.* Santen and Wieringen¹⁶). It is known from applications of molecular orbital theory that the electron configurations can be highly intermixed by increasing nuclear distances and correspondingly weaker bonding, as pointed out by Slater⁵³ and Mc Weeny⁵⁴.

Thus, the absorption spectra of IrCl₆⁻ and IrBr₆⁻ must be interpreted as transitions of one electron from the ligands to the central ion, which achieve the oxidation state +3, as defined above. The orbitals between which the electron moves, will be discussed below in a special section. The bathochromic effects of chloro-, bromo- and iodo-complexes (*cf.* platinum(IV) below) is qualitatively well understood. Thus, by a constant electron affinity of Ir⁺⁴, less energy is necessary to remove an electron from the most reducing ligand¹⁷, *i. e.* the heaviest halide ion. But the effect is larger than expected (one electron

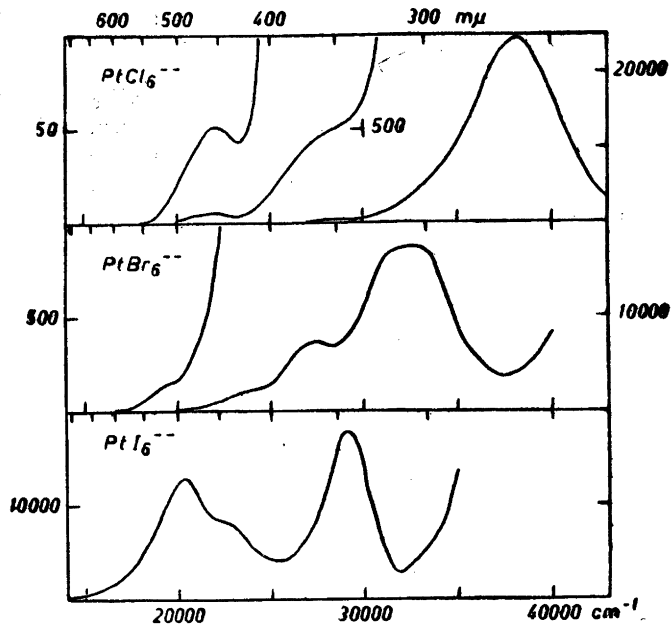


Fig. 2. Absorption spectra of hexachloro-, hexabromo- and hexaiodo-platinum(IV) ions.

0.0001 M to 0.05 M $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{PtCl}_6$ in 1 M HCl.

0.0001 M to 0.05 M $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{PtBr}_6$ in 0.1 M HBr.

0.0001 M PtI_6^{4-} from PtCl_6^{4-} in 0.1 M KI.

volt corresponds to 8067 cm^{-1}). However, the electron affinities of free halogen atoms are not easily compared with the conditions in aqueous solution, and are further influenced by the stabilization by resonance of the excited state of the iridium(IV) complexes.

Table 2. Absorption bands of platinum(IV) complexes. Notation as in Table 1.

	λ_n m μ	ν_n cm $^{-1}$	ϵ_n	$\delta(-)$ cm $^{-1}$	$\delta(+)$ cm $^{-1}$	$P \cdot 10^{-5}$
PtCl_6^{4-}	453	22 100	50	1 900	—	90
	353	28 300	490	1 700	—	700
	262	38 200	24 500	2 750	2 300	57 000
PtBr_6^{4-}	525	19 100	140	—	—	~150
	435	23 000	1 500	—	—	~2 000
	364	27 500	7 400	2 200	—	15 000
	311	32 200	17 800	2 800	2 600	44 000
PtI_6^{4-}	494	20 250	12 800	1 700	—	20 000
	446	22 400	8 300	—	—	12 000
	343	29 150	17 700	1 600	1 350	24 000

HEXACHLORO-, HEXABROMO-, AND HEXAIODO COMPLEXES
 OF PLATINUM(IV)

The colourless PtF_6^- , yellow PtCl_6^- , red-orange PtBr_6^- , and dark purple-red PtI_6^- was already measured by Schlesinger and Tapley¹⁸, and Wheeler, Perros and Naeser¹⁹ have later re-examined the two weak bands ($\epsilon \sim 50$) of PtF_6^- at 318 and 275 $m\mu$. Babaeva¹² has found bands of PtCl_6^- at 440, 348 and 254 $m\mu$. Fig. 2 and Table 1 give the measurements by the present author of PtCl_6^- , PtBr_6^- and PtI_6^- .

Platinum(IV) is a d^6 -system with strong tendency of forming diamagnetic complexes with regularly octahedral configuration. Thus, the crystal field bands analogous to these of cobalt(III), rhodium(III) and iridium(III)¹ may be predicted. They are present as the relatively weak shoulders in the spectra of PtCl_6^- and PtBr_6^- . The weakest bands at 453 and 525 $m\mu$, respectively, are identified as the transition from 1G_1 (γ_5^6) to one of the triplet levels 3G_4 or 3G_5 ($\gamma_5^5\gamma_3$); and the stronger bands at 353 and 435 $m\mu$, respectively, with the lowest singlet level, *viz.*⁹ 1G_4 ($\gamma_5^5\gamma_3$). The ratio between the wave-number of this band and the corresponding band in the iridium(III) complexes¹ will then have the values:

	$\text{PtCl}_6^-/\text{IrCl}_6^-$	$\text{PtBr}_6^-/\text{IrBr}_6^-$
Triplet level	1.24	1.14
Singlet level	1.17	1.03

This is reasonable evolution for two isoelectronic species with increasing oxidation state. The energy difference ($E_1 - E_2$) between γ_3 - and γ_5 -electrons is thus at least double as large in platinum(IV) complexes as in cobalt(III) complexes *inter alia* as discussed earlier¹. This explains the high tendency of magnetic anomaly in the platinum metal complexes ($S = 0$ for even and $S = \frac{1}{2}$ for odd number of electrons) since the distances in the free ion of terms with different S in the heavy elements is either less or equal to the distances in the first transition group, and they seem decreased in the complexes, relative to gaseous ions^{7,8,9}.

The two bands in PtF_6^- are presumably the transitions to the two singlet levels of $\gamma_5^5\gamma_3$. The three electron transfer bands in PtI_6^- are superposed the predicted places of the crystal field bands, which may show some intermixing effects.

AMMINE PLATINUM(IV) COMPLEXES

Like other d^6 -systems, platinum(IV) forms very robust hexammine complexes. They have been difficult to prepare before Tronev and Shumilina²⁰ recently demonstrated that $\text{Pt}(\text{NH}_2)(\text{NH}_3)_5\text{Cl}_3$ is formed by the action at room temperature of liquid NH_3 on $(\text{NH}_4)_2\text{PtCl}_6$. This base reacts with hydrogen ions and forms the normal "luteo" ion:



The titration curve, Fig. 3, shows that pK for this process is 7.75. Grünberg and Faerman⁵⁵ determined $pK = 8.9$ by the more uncertain method of dis-

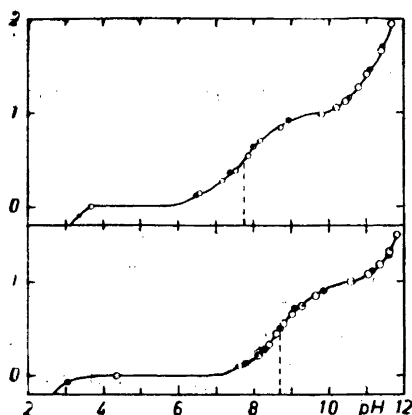


Fig. 3. Titration curve of hexammine and chloropentammine complexes of platinum(IV) at 20°C.

pH as function of consumed hydrogen ions per platinum atom. 0.02 M $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ and 0.025 M $[\text{Pt}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_3$ in H_2O titrated with 0.1 M NaOH (empty circles) and titrated backwards with 0.1 M HCl.

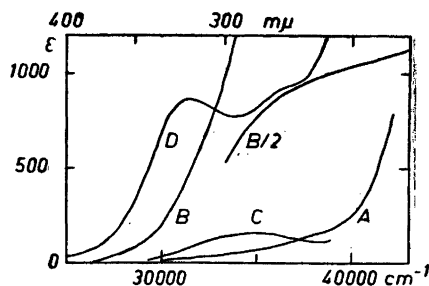


Fig. 4. Absorption spectra of hexammine-, amido- and chloropentammine-platinum(IV) ions.

- A. 0.01 M $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ in H_2O
- B. 0.001 M $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ in 1 M NH_3
- C. 0.01 M $[\text{Pt}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_3$ in H_2O
- D. 0.002 M $[\text{Pt}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_3$ in 1 M NH_3 .

solving the pure $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ in water and inserting the measured pH in Ostwald's square-root formula for the dissociation of a weak acid. Already Grünberg and Faerman⁵⁵ demonstrated the change of absorption spectrum of $\text{Pt}(\text{NH}_3)_6^{+4}$ by addition of one equivalent of OH^- , the absorption limit is displaced towards longer wavelengths. Fig. 4 gives the spectra of $\text{Pt}(\text{NH}_3)_6^{+4}$, $\text{Pt}(\text{NH}_3)_5\text{NH}_2^{+3}$, $\text{Pt}(\text{NH}_3)_5\text{Cl}^{+3}$ and $\text{Pt}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}^{+2}$. The spectrum of $\text{Pt}(\text{NH}_3)_5\text{NH}_2^{+3}$ is not further displaced in 1 M NaOH, and the titration curve Fig. 3 demonstrates that the next proton does not dissociate with $\text{p}K$ lower than 12. Thus there might be involved an electrostatic effect, which separates the two consecutive values of $\text{p}K$ by more than 5 units. However, $\text{Pt}(\text{NH}_3)_5\text{Cl}^{+3}$ is not a much weaker acid than $\text{Pt}(\text{NH}_3)_6^{+4}$. The titration curve in the lowest part of Fig. 3 gives $\text{p}K = 8.7$. The reversible titration demonstrates that the chloride ligand is not exchanged by OH^- during the measurements. Grünberg and Faerman⁵⁵ found $\text{p}K = 9.0$. Before this investigation was made, Professor F. Basolo informed me kindly that Pt en_3^{+4} is also a weak acid, forming amido complexes with the absorption band displaced towards lower wavenumbers.*

Sidgwick's concept of complexes as having "inert gas configurations" is in some way exemplified by the whitest of all ammonia complexes with partly filled d-shells $\text{Pt}(\text{NH}_3)_6^{+4}$. The characteristic property of an inert gas with

* Grünberg has later determined the consecutive values of $\text{p}K$ for Pt en_3^{+4} , viz. 5.5, 9.7, and 10.7; of $\text{Pt}(\text{NH}_3)_6^{+4}$, viz. 7.9 and 10.1; and of $\text{Pt}(\text{NH}_3)_5\text{Cl}^{+3}$, viz. 8.1 and 10.3.

a closed shell-groundstate is that the excited states have much higher energy than the ground-state. The singlet levels of $\gamma_2^2\gamma_3$ are hidden by the electron transfer band below 240 $m\mu$, but the triplet level can perhaps be observed as the shoulder at 300 $m\mu$.

RUTHENIUM(III) COMPLEXES

A most unusual discussion was once made of the oxidation states of ruthenium. Howe²³ prepared a rose-red isomer of the dark-brown $K_2RuCl_5 \cdot H_2O$, and maintained²³ that these two salts and the yellow-brown anhydrous K_2RuCl_5 do all contain trivalent ruthenium. Charonnat²⁴ demonstrated that the dark-brown salt really was $K_2RuCl_5(OH)$ with quadrivalent Ru, and finally Howe²⁵ agreed.

By a profound investigation, Charonnat²⁶ demonstrated the many analogies between ruthenium(III) and rhodium(III). Thus, two red complexes $RuCl_6^{3-}$ and $RuCl_5(H_2O)^{2-}$ are known, of which the first is only stable in very strong HCl, and the brownish green RuO_3^{2-} forms salts, which are isomeric with those of Rh Ox_3^{2-} and many other tris(oxalato) complexes of trivalent metals. The octahedral configuration of ruthenium(III) is thus evident, even though Charonnat²⁶ proposes octa-coordination in several complexes. Since the d^5 -systems with $S = \frac{1}{2}$ are liable to rhombic distortion²⁷ while d^6 -systems with $S = 0$ are regularly octahedral, a distortion is predicted as found²⁸ in the corresponding $Fe(CN)_6^{3-}$. Thus, the anhydrous K_2RuCl_5 and the orange pentanitrites as $K_2Ru(NO_2)_5$ may be penta-coordinated, but they are rather under suspicion for being dimeric with two anion bridges.

Wehner and Hindman²⁹ have later investigated the solutions of ruthenium (III) and (IV) in $HClO_4$, where hydroxo- and aquo-complexes are expected. Since the spectrum of the trivalent form is equal in 9 M and 1 M $HClO_4$ (one peak at 300 $m\mu$ with $\epsilon \sim 2000$), it is assumed to be due to the hexaaquo ion. This might very well have been a stronger acid; the tendency for deviation from regularly octahedral complexes gives higher affinity for the two first hydroxyl ions (*cf.* copper(II) and manganese(III) compared to the regular neighbors nickel(II), zinc(II), chromium(III) and iron(III))²⁷.

Fig. 5 and Table 3 give the spectra of ruthenium(III) in strong HCl and HBr, which can be assumed to contain $RuCl_6^{3-}$ and $RuBr_6^{3-}$. Mr. K. G. Poulsen has kindly pointed out to me that metallic silver is a good reducing agent in these media for providing the oxidation state +3; and even a green solution, containing a trace of +2 can be produced. However, upon standing in the air, a strawberry-red solution is obtained in HCl. This is slowly oxidized over a period of weeks to a yellow-brown solution with increasing amounts of +4. When the solution does not contain much ruthenium, less than 0.001 M, it is almost colourless in +3, while oxidation to +4 produces a strong colour. At this concentration, ruthenium(IV) has the same characteristic brownish orange colour as dilute $IrCl_6^-$ and nearly the same absorption spectrum, which is rather curious for this d^4 -system. The solution of ruthenium (III) in 4 M HBr is dark purple-brown.

It is seen from Fig. 5 and Table 3 that the chloro complex has much higher absorption in the near ultraviolet (as also has the aquo ion²⁹) and the bromo

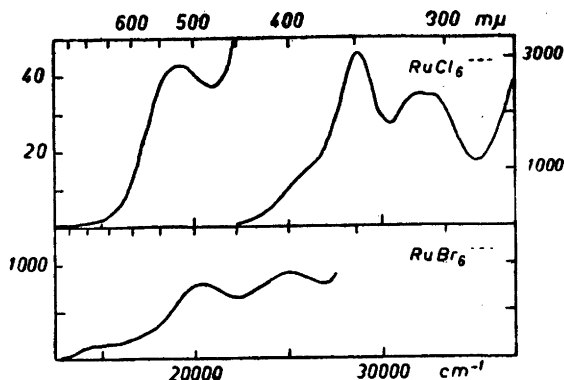


Fig. 5. Absorption spectra of chloro and bromo complexes of ruthenium(III).
 0.0005 M to 0.05 M ruthenium(III) in 10 M HCl, reduced with Ag powder.
 0.002 M to 0.05 M ruthenium(III) in 6 M HBr, reduced with Ag powder.

complex in the visible than found for rhodium(III)¹. These bands are undoubtedly due to electron transfer and will be discussed below. But there are also signs of crystal field bands: the relatively weak band at 521 mμ and the shoulder at 388 mμ in the chloro complex and perhaps also the shoulder at 653 mμ in the bromo complex. The intensity of these bands classify them as spin-allowed transitions from the groundstate ${}^2\Gamma_5(\gamma_5^5)$ to one of the doublet levels³⁰ of $\gamma_3^4 \gamma_3$. If they were spin-forbidden, the asymmetry of the ruthenium(III) complex must be so large that the hemiedric crystal field³¹ have made the spin-allowed crystal field bands nearly as allowed as electron transfer band. The present author has sought for spin-forbidden bands out to 1 100 mμ, but found at most a background with $\epsilon \sim 1$.

According to Tanabe and Sugano's calculation on pure d^2 -configurations⁹ the order of energy of $\gamma_3^4 \gamma_3$ -levels in strong crystal fields will be

$${}^4\Gamma_4, {}^4\Gamma_5, {}^2\Gamma_2, {}^2\Gamma_4, {}^2\Gamma_5, {}^2\Gamma_3 \dots \dots \quad (2)$$

Table 3. Absorption bands of ruthenium(III) and (II) complexes. Notation as in Table 1.

	λ_n mμ	ν_n cm ⁻¹	ϵ_n	$\delta(-)$ cm ⁻¹	$\delta(+)$ cm ⁻¹	$P \cdot 10^{-5}$
RuCl ₆ ³⁻ ?	521	19 200	43	2 000	—	70
	388	25 800	800	—	—	~1 000
	349	28 700	3 000	1 400	1 300	3 700
	313	32 000	2 300	—	—	} ~5 000
	307	32 600	2 300	—	—	
RuBr ₆ ³⁻ ?	655	15 300	130	1 500	—	180
	485	20 600	770	1 600	—	1 100
	400	25 000	900	—	—	—
Ru(II) in 2 M HCl	660	15 200	1 250	—	—	} ~5 000
	570	17 600	1 130	—	—	

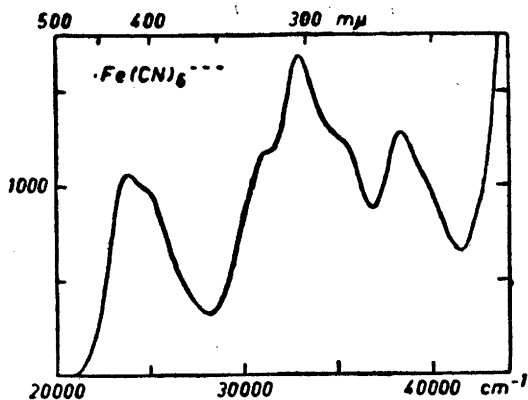


Fig. 6. Absorption spectrum of iron(III)hexacyanide ions.
0.001 M $K_3Fe(CN)_6$ in H_2O .

within a relatively narrow range of energy, about 50 B, where the Racah parameter B presumably is about $1\ 000\ cm^{-1}$ in the gaseous ion, but is decreased in complexes^{7,8,9}. Since the four bands in d^6 -systems should be placed⁹:

$$\begin{aligned}
 {}^3\Gamma_4 &: (E_1 - E_2) - 3 C \\
 {}^3\Gamma_5 &: (E_1 - E_2) + 8 B - 3 C \\
 {}^1\Gamma_4 &: (E_1 - E_2) - C \\
 {}^1\Gamma_5 &: (E_1 - E_2) + 16 B - C
 \end{aligned}
 \tag{3}$$

with $C \cong 4.5 B$, the first singlet band in $RhCl_6^{3-}$ corresponds to $(E_1 - E_2) = 21\ 000\ cm^{-1}$ and the distance between the two singlet bands*, which is somewhat less than 16 B due to the influence of non-diagonal elements, implies $B = 400\ cm^{-1}$ for $RhCl_6^{3-}$. If similar values are applied to $RuCl_6^{3-}$, Tanabe and Sugano's theory predicts the first quartet band at $11\ 800\ cm^{-1}$ and the first doublet band at $18\ 000\ cm^{-1}$.

For comparison with the electron transfer bands of ruthenium(III), Fig. 6 gives the spectrum of $Fe(CN)_6^{3-}$. The six strong bands agree with the measurements of Kiss, Abraham and Hegedüs³², and the present author has also found the very weak, broad band at $550\ m\mu$ with $\epsilon \sim 0.3$. This seems to be a spin-forbidden crystal field band, even if it is tempting to ascribe it to impurities of the Turnbull's blue type. Gleu *et al.*³³⁻³⁵ have prepared robust ruthenium(III) ammine complexes with nearly the same colours as the corresponding rhodium(III) ammines:

* It will be shown later that the values of B in d^n -complexes are only compatible with an average radius of the d-shell larger than the ionic radius. Thus, the partly occupied orbitals must be localized also on the ligands, eventhough a decreased central field relative to the gaseous ion (produced by the presence of some electrons donated from the ligands) co-operates in decreasing B.

$\text{Ru}(\text{NH}_3)_6^{+++}$	colourless
$\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$	colourless
$\text{Ru}(\text{NH}_3)_5\text{Cl}^{++}$	yellow
$\text{Ru}(\text{NH}_3)_5\text{Br}^{++}$	dark yellow
$\text{cis-Ru}(\text{NH}_3)_4\text{Cl}_2^+$	orange
$\text{trans-Ru}(\text{NH}_3)_4\text{Cl}_2^+$	red-orange
$\text{cis-Ru}(\text{NH}_3)_4\text{Br}_2^+$	red
$\text{trans-Ru}(\text{NH}_3)_4\text{Br}_2^+$	purple
$\text{Ru}(\text{NH}_3)_4\text{ox}^+$	yellow
$\text{Ru}(\text{NH}_3)_3\text{Cl}_3$	red

These colours demonstrate a bathochromic influence which is larger for bromide than for chloride, and which is slightly larger for *trans*- than for *cis*-complexes. The latter fact is of interest for the theory of tetragonal complexes. Since the spectrochemical series of crystal fields $\text{Br}^- < \text{Cl}^- < \text{ox}^{--} < \text{H}_2\text{O} < \text{NH}_3$ varies nearly as the decreasing tendency to give electrons off, it cannot be said with certainty if the colours are due to crystal field or electron transfer bands.

When sufficient ammonium chloride is added to prevent the precipitation of $\text{Ru}(\text{OH})_3$, solutions of RuCl_6^{--} in HCl reacts with concentrated ammonia water under formation of a clear, pink solution. It is difficult to separate the colourless hexammines and pentammines, probably formed in this reaction, from the traces of highly coloured ruthenium red. The constitution of the latter compound is not yet elucidated; it is diamagnetic³⁵ and probably a polynuclear complex with hydroxo bridges. Its formation in the solution mentioned above is reversible.

RUTHENIUM(II) COMPLEXES

Already Claus³⁶ observed a dark blue solution of ruthenium with strong reducing agents. This solution contains ruthenium(II) as shown by titrations with sodium amalgam (authors who assumed $\text{K}_2\text{RuCl}_5\text{OH}$ to be $\text{K}_2\text{RuCl}_6(\text{H}_2\text{O})$ found of course +1). The present author can add but a few new arguments to the vivid debate about the green colour formed, when yellow ruthenium solutions (with traces of +4?) are reduced with zinc amalgam or other metals, and which turn lavender blue with excess of reducing agent³⁷⁻⁴³. Grube and Nann⁴⁴ found that the actual oxidation state +1 in few minutes disproportionates to the metal and +2; and that +2 in 2 M HCl in two days is 5 % disproportionated to metal and +3. Grube and Fromm⁴⁵ later investigated RuCl_3 and its hydrates and found the emerald-green RuCl_3^+ , which may resemble the green isomer of $\text{RuCl}_4(\text{H}_2\text{O})_2^-$ (the other isomer is red) which Gall and Lehmann⁴¹ assume to be a mixture of +2 and +3.

The reaction between yellow +4 and blue +2 requires some minutes, so that a green intermediate colour can be observed. Besides this the blue solution has only been measured in solutions 1 M to 4 M in HCl. In stronger hydrochloric acid, the spectrum of the solution is displaced towards red with resulting green colour: The maximum at 660 μ to 710 μ and the shoulder at 568 μ to 578 μ . The influence of the halide ion was studied by reduction of a chloride-free ruthenium(III) solution in 4 M HBr (see experimental section). Similar blue and green solutions with broad bands in the red are obtained.

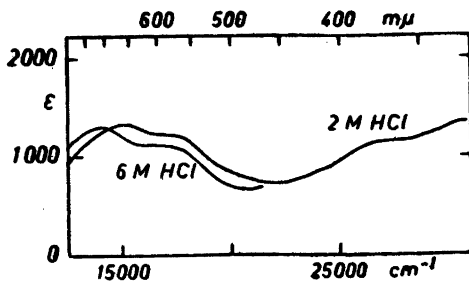


Fig. 7. Absorption spectra of ruthenium (II) complexes.

0.001 M ruthenium in 2 M and 6 M HCl, reduced with zinc amalgam.

The absolute extinction coefficients cannot be determined exactly, due to the impurities of +3 and the metal. But the value of $\epsilon \sim 1\ 100$ is too high for an ordinary crystal field band. Thus, it is probably an electron transfer band. It cannot be excluded *a priori* that ruthenium(II) is a stronger oxidizing agent, *i. e.* has larger electron affinity, than ruthenium(III). The disproportionation⁴⁴ supports this possibility, analogous to the behaviour of copper(I).

Ruthenium(II) is a d^6 -system and may thus be expected to form diamagnetic complexes ($S = 0$). But only the colourless $\text{Ru}(\text{CN})_6^{4-}$ and several sulphito-ammine complexes⁴⁶ are known to be six-coordinated, while the blue complexes are often assumed to be RuCl_4^- . If they have a planar configuration, they have probably the groundstate $\gamma_2^2 \gamma_3$ with $S = 1$. Even if Tanabe and Sugano⁹ have proven that no groundstate of an octahedral complex has $S = 1$ in d^6 and $S = \frac{3}{2}$ in d^5 -systems, tetragonal complexes may stabilize the intermediate values of S .

ELECTRON TRANSFER FROM MOLECULAR ORBITALS

In Mulliken's theory of molecular orbitals⁴, the symmetry of the distribution of atomic nuclei in the molecule determines the possible quantum numbers of the orbitals, analogous to the symmetry of the crystal field from the ligands, acting on the central ion². In this paper the notation of Bethe² will be used also for molecular orbitals of octahedral complexes. The translation table is:

Mulliken:	a_1	a_2	e	t_1	t_2	(4)
Bethe:	γ_1	γ_2	γ_3	γ_4	γ_5	

While small letters denote the states of electrons, the corresponding states of whole systems, here molecules, are denoted by capital letters $A_1 = \Gamma_1$. In a complex with a centre of symmetry, the states can further be divided into two classes with different parity: odd and even. This is denoted by the small letters *u* (ungerade) and *g* (gerade) after the numbers: γ_{1g}, Γ_{3u} . The parity of a system is equal to the sum of parities of the electrons, defined by the addition rules:

$$\begin{aligned}
 g + g &= g \\
 u + g &= g + u = u \\
 u + u &= g
 \end{aligned}
 \tag{5}$$

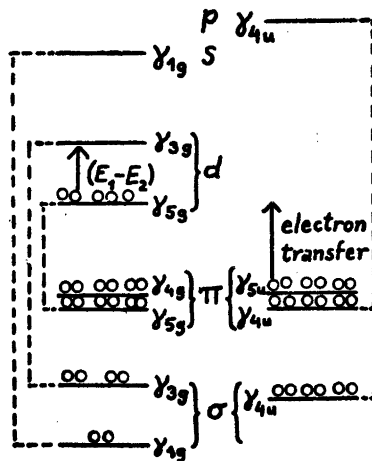


Fig. 8. Molecular orbitals of an octahedral complex MX_6 with partly filled d-shell in M . Even orbitals (g) at left-hand and odd (u) at right-hand side. Arrows denote possible interactions between orbitals with the same Γ_n and parity.

In a single atom or ion, an electron has the quantum number l , and the parity is g for even values of l , *i. e.* for s-, d-, g-electrons *etc.* and u for odd values of l , *i. e.* for p-, f-, h-electrons *etc.* Thus, all the values of γ_n and Γ_n encountered in the theory for pure d^n -configurations are even, and the "g" is often neglected in the quantum numbers.

The electrons of the six ligands of an octahedral complex can be classified as σ -electrons, π -electrons, *etc.* according to their angular momentum around the straight line connecting central ion-ligand's centre being 0 or 1, *etc.* The chemical bonds between the ligands and the central ion can be described by the intermixing of orbitals having the same γ_n and parity, from the ligands and the central ion. Thus, the chemical bonds can be classified as σ -bonds, π -bonds *etc.* according to the electrons, participating from the ligands.

Van Vleck³ pointed out the σ -bonds in an octahedral complex with an unfilled nd-shell is due to the three pairs of intermixing orbitals:

$$\begin{aligned} \gamma_{3g} & \text{ with } \gamma_{3g}(nd) \\ \gamma_{4u} & \text{ with } \gamma_{4u}(n + 1p) \\ \gamma_{1g} & \text{ with } \gamma_{1g}(n + 1s) \end{aligned} \quad (6)$$

The three types of orbitals can accumulate 4, 6, and 2 electrons, respectively, 12 bonding and 12 anti-bonding electrons (six electron-pairs in the localized valence picture). According to Hartmann⁵, the energy of the bonding orbitals decrease in the order, given in eqn. 6. It is evident that the d^2sp^3 -hybridization discovered by Pauling^{47,48} is equivalent to complete intermixing of the three pairs of orbitals. The molecular orbital theory has the advantage that the electrostatic crystal field model and Pauling's hybridization can be described as two limiting cases⁵ with, respectively, pure d^n -configurations and complete intermixing (which is 50% in the squares of the wavefunctions). Owen⁸ pointed out that the intermixing coefficients can be different for the three orbital types γ_{3g} , γ_{4u} and γ_{1g} . Thus, the evolution from the "ionic" to "co-

valent" structure⁴⁸ must be described by three independent parameters. In all cases of intermixing, the parameter may happen to exceed 50 % in the squares, corresponding in this case to higher energy of the original σ -electrons than of the electron of the central ion.

The 24 π -electrons from six monatomic ligands of the type Cl^- are distributed in the four orbitals (*cf.* Orgel⁷) of which two are intermixed⁸:

$$\begin{array}{ll} \gamma_{4u} & \text{--- with } \gamma_{4u} \text{ (n + 1 p)} \\ \gamma_{4g} & \text{---} \\ \gamma_{5u} & \text{---} \\ \gamma_{5g} & \text{--- with } \gamma_{5g} \text{ (nd)} \end{array} \quad (7)$$

There are no orbitals in the central ions of the type γ_{4g} and γ_{5u} , and the ligand orbitals are thus non-bonding (*cf.* Fig. 8).

The effect of intermixing of orbitals^{8,8} is to increase ($E_1 - E_2$) by σ -bonding (which increases the energy of $\gamma_{3g}(\text{d})$) and to decrease ($E_1 - E_2$) by π -bonding (which increases the energy of the relatively low $\gamma_{3g}(\text{d})$). This type of intermixing is connected with the non-orthogonality of the orbitals in the central ion and the ligands, which thus have "overlap" integrals contrary to the orbitals used in monatomic problems. Another type of intermixing can be found between two levels of the system with the same Γ_n , due to two configurations with a different distribution of electrons in the molecular orbitals. The latter type of intermixing gives generally smaller effects^{49,50}, but it must be realized that the molecular orbital theory does not give a detailed picture, when more levels are possible from a given configuration: the four levels ${}^3\Gamma_4$, ${}^3\Gamma_5$, ${}^1\Gamma_4$ and ${}^1\Gamma_5$ of the d^6 -systems $\gamma_3^2 \gamma_2$ have different energies even in a strong crystal field, while the distribution of electrons in the molecular orbitals is identical in the four levels. The concept of molecular orbitals is more distinct in the compounds outside the transition groups, where most configurations of interest do only contain one level.

The crystal field bands, which are characteristic for the complexes with partly filled d-shells are thus in the molecular orbital language due to transitions between the possible levels Γ_n of the electrons in γ_{5g} and γ_{3g} , while the other molecular orbitals are invariably filled or empty during the transition. The low intensities demonstrate³¹ that the parity "g" is at least a 99 % good quantum number; and the orbital quantum numbers γ_{5g} and γ_{3g} are only affected by relatively small intermixings with other configurations, while Γ_n is only intermixed by (L, S) coupling effects. But the orbitals γ_{5g} and γ_{3g} cannot be seen from the absorption spectra to be pure d-electrons; they may contain considerable amounts of π - and σ -antibonding character, respectively. Owen⁸ concludes from the decreased values of ζ_{3d} in the first transition group complexes, found by paramagnetic measurements, that the σ -intermixing of γ_{3g} varies between 17 % in $\text{Ni}(\text{H}_2\text{O})_6^{++}$ to 37 % in $\text{Cr}(\text{H}_2\text{O})_6^{+++}$. By the more direct method of measuring the contribution of nuclear fine-structure of Ir, Cl and Br to the paramagnetic resonance curves of IrCl_6^- and IrBr_6^- , Owen and Stevens¹⁹ found 20 % π -intermixing of γ_{5g} in these much more distinctly "covalent" complexes, while the σ -intermixing is assumed to be rather complete, *i. e.* 50 % in the platinum group complexes.

In d^5 -systems, the excited states of the electron transfer bands correspond presumably to the closed shell γ_5^6 , which can be only in one state, ${}^1\Gamma_{1g}$. Since $\gamma_{5g}^6\gamma_{3g}$ in iridium(III) is situated¹ about $25\,000\text{ cm}^{-1}$ above γ_{5g}^6 , the next type of excited state $\gamma_{5g}^6\gamma_{3g}$ will be far in the ultraviolet. Besides (L, S) coupling effects, each band should thus correspond to one type of hole in the molecular orbitals, which have lower energy than the partly filled γ_{5g} -shell (if this is not be case, the electron transfer would be spontaneous). It can be presumed that these orbitals of highest energy are of the π -electron type, while the stronger bonding σ -orbitals have lower energy. This is supported by the observed intensities in iridium(IV) and ruthenium(III) complexes (see Tables 1 and 3). The intensity of a transition is increasing with the coincident presence in space of the groundstate ψ_1 and the excited state ψ_2 , *i. e.* proportional to⁵¹:

$$\left(\int \psi_1 r \psi_2 dr\right)^2 \quad (8)$$

The π -electrons which are mainly removed from the central ion, has a relatively low value of this integral, corresponding to the oscillator strength $P \sim 0.02$. When the σ -electrons are excited to anti-bonding states, much higher values of P are expected at higher wavenumbers. Since γ_{4u} is weakly bonding, while γ_{5u} is not bonding at all, the configuration $\gamma_{5g}^6\gamma_{4u}^{-1}$ (π) has probably slightly higher energy than $\gamma_{5g}^6\gamma_{5u}^{-1}$ (π), when a hole in a molecular orbital is denoted $\gamma_u^{-1}(\pi)$ or (σ).

The two high bands with $\varepsilon \sim 2\,000$ in RuCl_6^{3-} , RuBr_6^{3-} and IrCl_6^{3-} should thus correspond to ${}^2\Gamma_{5u}$ at lower and ${}^2\Gamma_{4u}$ at higher wavenumber. By effects of intermediate coupling, the two bands should each divide into two bands:

$$\begin{aligned} {}^2\Gamma_5 \times \Gamma_6 &= \Gamma_7 + \Gamma_9 \\ {}^2\Gamma_4 \times \Gamma_6 &= \Gamma_6 + \Gamma_9 \end{aligned} \quad (9)$$

Due to deviations from the cubic symmetry, the band Γ_9 can further divide into two, but Kramer's degeneracy permits only three levels to be formed from the six states in ${}^2\Gamma_4$ or ${}^2\Gamma_5$. This accounts for IrBr_6^{3-} exhibiting six bands with a splitting, comparable to $\zeta_{4p} = 2\,458\text{ cm}^{-1}$ in atomic Br, while the smaller $\zeta_{3p} = 588\text{ cm}^{-1}$ in Cl is only indicated by the splitting in IrCl_6^{3-} at $23\,200$ and $24\,200\text{ cm}^{-1}$.

Since the even $\gamma_{4g}(\pi)$ and $\gamma_{5g}(\pi)$ presumably have similar energy as the odd π -orbitals, the observation of weak electron transfer bands from these states is not very probable. But the weak shoulder of IrCl_6^{3-} at $17\,400\text{ cm}^{-1}$ is not yet identified; it resembles very much a spin-forbidden band as discussed above, but quartet levels are only possible in configurations with at least two partly filled shells with each an electron or a hole. It may be a crystal field band ${}^2\Gamma_{2g}$ of the type discussed above for ruthenium(III) complexes, highly intermixed by hemiedric fields with the odd levels of electron transfer. However, this necessitates interactions between two levels, which are mainly different by two electrons.

In the platinum(IV) and other d^6 -systems, the excited configuration of an electron transfer band must be $\gamma_{5g}^6\gamma_{3g}$. The relatively high energy of this configuration explains very well the lower oxidizing character of platinum(IV),

compared to iridium(IV) and of rhodium(III), compared to ruthenium(III). The electron transfer bands seem to be about 10 times higher in the d^6 -systems than in the d^5 -systems, suggesting the transfer of $\gamma_{4n}(\sigma)$.

In the first transition group, the d^6 -systems of cobalt(III) exhibit similar very strong electron transfer bands, as shown by Linhard and Weigel⁵². Smaller bands with $\epsilon \sim 1000$ occur only in the case of ligands with internal transitions, *e. g.* SCN^- or NO_2^- . An analogy to ruthenium(III) and iridium(IV) with one hole in a closed shell, which moves by the transition, can be found in the d^9 -system copper(II). Besides the strong absorption in the far ultraviolet, a band of CuCl_4^{2-} can be distinguished at $26\,000\text{ cm}^{-1}$ with $\epsilon \sim 1\,500$. In the dark-red solutions of copper(II) in HBr, presumably containing CuBr_4^{2-} , a double band is found by the author at $588\text{ m}\mu$ ($\epsilon = 1\,000$) and $512\text{ m}\mu$ ($\epsilon = 2\,100$). These bands are probably due to transfer of a γ_{5n} electron. This level is the only tetragonal one, which can split due to intermediate coupling, maintaining Kramer's degeneracy. Belford⁵⁶ has recently applied the molecular orbital theory to copper(II) complexes, especially with two acetylacetonates in the plane and different solvents perpendicular to the plane. Ito and Kuroda⁵⁷ have published four papers on the molecular intermixing of d-orbitals in general. Only the Japanese text of the three first has been available to the present author, but Ito and Kuroda seem to place the bonding σ -orbitals γ_3 and γ_{4n} very close below γ_5 (3d), thus exaggerating their influence. Rather, the crystal field splitting must constitute roughly 50 % of ($E_1 - E_2$), as pointed out by Belford⁵⁶ who calculated the influence of the crystal field on a Hartree's self-consistent field copper ion, rather than the improbable hydrogen-like 3d-electron⁵ with $Z = 7.85$.

Fig. 6 gives the spectrum of $\text{Fe}(\text{CN})_6^{4-}$, one of the few $3d^5$ -systems with $S = \frac{1}{2}$. The six bands found may be compared to those of IrBr_6^{3-} . However, in this case the diatomic ligands have empty molecular orbitals to which γ_{5g} -electrons from the central ion can be excited. The triple bond between carbon and nitrogen in CN^- is equivalent to one σ - and two π -orbitals of anti-bonding type, which are empty in the ground-state. The excited states in this ion must have high energy, since ϵ first exceeds 1 at $265\text{ m}\mu$ and $\epsilon = 10$ at $215\text{ m}\mu$.

EXPERIMENTAL

The spectra were measured on a Cary spectrophotometer, furnished with a tungsten lamp in the range $800 - 325\text{ m}\mu$ and with a hydrogen lamp $400 - 220\text{ m}\mu$; 1 cm absorption cells were used. While the Beckman spectrophotometer has its optimum accuracy at optical densities in the range 0.3 to 0.6, the similar range seems to be 0.8 to 1.5 on the Cary.

Preparation of the solutions of ruthenium complexes. Ruthenium metal powder from "Dansk Hollandsk Ædelmetal" (H. Drijfhout and Zoon) was melted with the ten-fold weight of Merck's potassium hydroxide in a nickel dish. Air-oxidation produces K_2RuO_4 , but KNO_3 or KClO_3 , mixed with the metal finishes the reaction in ten minutes. For preparation of the ruthenium(III) bromide solution, KBrO_3 was used as oxidizing agent. In all cases the cooled, tomato-red mass was dissolved in water (small gas-bubbles were evolved) and a few ml 96 % ethanol was added. After some seconds, the ruthenium is quantitatively reduced and precipitated as a black tetrahydroxide from a greenish, intermediate colour. It was washed several times with water and soon (to evade ageing) dissolved by boiling for 30 minutes with 6 M HCl or HBr. The clear, dark-brown solution

in HCl can be reduced with excess of precipitated silver powder to a strawberry-red solution of RuCl_6^{3-} and $\text{RuCl}_5(\text{H}_2\text{O})^{2-}$, while further reduction with stronger reducing agents (Zn, Al) gives green and finally blue-violet ruthenium(II), as described above. $\text{Ru}(\text{OH})_4$ boiled with HBr liberates Br_2 and a dark purple-brown solution is formed.

Preparation of the solutions of iridium(IV) complexes. Iridium metal powder from "Dansk Hollandsk Edelmetal" was more difficult to oxidize. 3.3 g was mixed with 10 g NaCl and heated to 600–700° C in a vitreous tube in a stream of chlorine. The cooled mass yielded only 1.3 g Ir soluble in water as IrCl_6^{3-} . The coarse crystalline residue was melted six hours with NaOH + NaNO_3 in a nickel crucible; only 0.4 g was dissolved. Then, it was melted with 5 g BaO_3 + 5 g $\text{Ba}(\text{NO}_3)_2$, dissolving 0.5 g. The main portion of the rest was dissolved by melting with pure barium dioxide in the same crucible at 700° C for two hours. In all cases, the alkaline solutions precipitated, on boiling and dilution, most iridium as blue tetrahydroxide, which could be washed and dissolved in 10 M HCl. This gives a dark-blue colour, which after four days at room temperature or by boiling turns red-brown. The alkaline filtrate is pale lavender-blue and is unchanged by addition of acids. The absorption spectrum exhibits maxima at 575 $m\mu$ (very broad, often with a shoulder at 740 $m\mu$) and a shoulder at 356 $m\mu$. If boiled with BaCO_3 , the acid solution precipitates $\text{Ir}(\text{OH})_4$.

$\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$. A sample of fine quality from the laboratory's collection was used. K_2IrCl_6 of unknown origin was found to contain much Pt; "Crude IrO_3 " of S. M. Jørgensen had a high content of Os, etc.

The purple chloride-free solutions of iridium(IV) have been made¹ from Na_2IrCl_6 boiled with HClO_4 . Ayres and Quick⁵⁸ have investigated the solutions in mixtures of HClO_4 , H_3PO_4 , and HNO_3 and demonstrated the oxidation state to be +4. The maximum at 564 $m\mu$ has $\epsilon = 2650$ and is displaced, when pH increases over 3 to 584 $m\mu$ at pH = 5. The analytical method does not seem to be more advantageous than the determination of IrCl_6^{3-} in strong HCl + Cl_2 and seems to have the same drawbacks: Ru and Os interfere strongly, while Rh, Pd and Pt in both cases have ϵ only a few per cent of Ir. Although $\text{Ir}(\text{OH})_4$ forms blue and purple, colloidal solutions^{59,60}, it cannot be regarded as certain, if the purple solutions in strong acids (which already were discovered by Vauquelin⁶¹), are not simply monomer or dimer hydroxo-aquo complexes.

$[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{PtCl}_6$, K_2PtBr_6 and $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{PtBr}_6$ were taken from S. M. Jørgensen's collection. PtI_6^{3-} was prepared several times from different solutions of PtCl_6^{3-} and KI and always showed identical spectra.

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ was prepared according to Tronev and Shumilina²⁰. $(\text{NH}_4)_2\text{PtCl}_6$ of the laboratory's collection was treated with liquid ammonia in a test tube, surrounded by a steel micro-autoclave. The pale yellow powder was extracted with water and made 5 M in HCl, which precipitated the white chloride. Since nearly all salts of $[\text{Pt}(\text{NH}_3)_6]^{4+}$ are feebly soluble, the ionic strength was maintained at only 0.1 during the titration with the glass-electrode pH-meter Radiometer M22.

$[\text{Pt}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_3$ was kindly furnished by Professor J. A. Christiansen. For study of the influence of nitrate ions the spectra were compared with $[\text{Pt}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]\text{Cl}_2$ dissolved in HCl, which exhibited also the weak band at 286 $m\mu$.

$\text{K}_3\text{Fe}(\text{CN})_6$ was recrystallized from "Anala R" by Miss Lene Rasmussen.

Acknowledgments. I am very much indebted to Professor J. Bjerrum for his interest in the work. Further, I thank Miss Bodil Friis for assistance with preparation of ruthenium complexes.

REFERENCES

1. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **10** (1956) 500.
2. Bethe, H. *Ann. Physik* [5] **3** (1929) 133.
3. Van Vleck, J. H. *J. Chem. Phys.* **3** (1935) 803 and 807.
4. Mulliken, R. S. *J. Chem. Phys.* **3** (1935) 375, 506, 517 and 586.
5. Hartmann, H. *Theorie der chemischen Bindung auf quanten-theoretischer Grundlage*. Springer Verlag 1954.
6. Orgel, L. *J. Chem. Soc.* **1952** 4756.
7. Orgel, L. *J. Chem. Phys.* **23** (1955) 1004, 1819 and 1824.

8. Owen, J. *Proc. Roy. Soc. London* **227 A** (1955) 183.
9. Tanabe, Y. and Sugano, S. *J. Phys. Soc. Japan* **9** (1954) 753 and 766.
10. Owen, J. and Stevens, K. W. H. *Nature* **171** (1953) 836.
11. Griffiths, J. H. E. and Owen, J. *Proc. Roy. Soc. London* **226 A** (1954) 96.
12. Babaeva, A. V. *Bull. Acad. Sci. URSS Cl. Sci. Chim.* **1943** 171.
13. Inamura, Y. and Kondo, Y. *J. Chem. Soc. Japan* **72** (1951) 840.
14. Landolt-Börnstein Tables Ed. Vol I, part 1, p. 165.
15. Scheibe, G. *Z. physik. Chem.* **5B** (1929) 355.
16. van Santen, J. H. and van Wieringen, J. S. *Rec. trav. chim.* **71** (1952) 420.
17. Jørgensen, C. Klíxbüll *Acta Chem. Scand.* **8** (1954) 1502.
18. Schlesinger, H. and Tapley, M. J. *Am. Chem. Soc.* **46** (1924) 276.
19. Wheeler, Th. E., Perros, Th. P. and Naesser, C. R. *J. Am. Chem. Soc.* **77** (1955) 3488.
20. Tronev, V. G. and Shumilina, M. E. *Doklady Akad. Nauk. SSSR* **101** (1955) 499.
21. Lifschitz, J. and Rosenbohm, E. *Z. physik. Chem.* **97** (1920) 1.
22. Howe, J. L. *J. Am. Chem. Soc.* **26** (1904) 543.
23. Howe, J. L. and Haynes, L. P. *J. Am. Chem. Soc.* **47** (1925) 2920.
24. Charonnat, R. *Compt. rend.* **180** (1925) 1271.
25. Howe, J. L. *J. Am. Chem. Soc.* **49** (1927) 2381.
26. Charonnat, R. *Ann. Chim.* [10] **16** (1931) 5 and 123.
27. Jørgensen, C. Klíxbüll and Bjerrum, J. *Acta Chem. Scand.* **9** (1955) 180.
28. Howard, J. B. *J. Chem. Phys.* **3** (1935) 813.
29. Wehner, P. and Hindman, J. C. *J. Am. Chem. Soc.* **72** (1950) 3911.
30. Jørgensen, C. Klíxbüll *Acta Chem. Scand.* **9** (1955) 116.
31. Jørgensen, C. Klíxbüll *Acta Chem. Scand.* **9** (1955) 405.
32. Kiss, A. v., Abraham, J. and Hegedüs, I. *Z. anorg. Chem.* **244** (1940) 98.
33. Gleu, K. and Rehm, K. *Z. anorg. Chem.* **227** (1936) 237.
34. Gleu, K. and Cuntze, W. *Z. anorg. Chem.* **237** (1938) 187.
35. Gleu, K. and Breuel, W. *Z. anorg. Chem.* **237** (1938) 197, 326, 335 and 350.
36. Claus, C. *J. prakt. Chem.* **34** (1845) 431.
37. Remy, H. *Z. anorg. Chem.* **113** (1920) 229.
38. Remy, H. and Lührs, A. *Ber.* **61** (1928) 917.
39. Remy, H. and Wagner, Th. *Ber.* **61** (1928) 151.
40. Zintl, E. and Zaimis, Ph. *Ber.* **60** (1927) 842.
41. Gall, H. and Lehmann, G. *Ber.* **59** (1926) 2856, **60** (1927) 2491; **61** (1928) 1573.
42. Krauss, F. and Kückenthal, H. *Z. anorg. Chem.* **137** (1924) 33.
43. Remy, H. *Angew. Chem.* **42** (1929) 289 and 291.
44. Grube, G. and Nann, H. *Z. Elektrochem.* **45** (1939) 874.
45. Grube, G. and Fromm, G. *Z. Elektrochem.* **46** (1940) 661 and **47** (1941) 208.
46. Gleu, K., Breuel, W. and Rehm, K. *Z. anorg. Chem.* **235** (1938) 201 and 211.
47. Pauling, L. *J. Am. Chem. Soc.* **53** (1931) 1367.
48. Pauling, L. *The Nature of the Chemical Bond*, Ithaca, 1944.
49. Jørgensen, C. Klíxbüll *Acta Chem. Scand.* **9** (1955) 717.
50. Jørgensen, C. Klíxbüll *Acta Chem. Scand.* **9** (1955) 1362.
51. Condon, E. U. and Shortley, G. H. *Theory of Atomic Spectra*. Cambridge 1953.
52. Linhard, M. and Weigel, M. *Z. anorg. Chem.* **266** (1951) 49.
53. Slater, J. C. *Electronic Structure of Atoms and Molecules*. Technical Report No. 3. Solid-State and Molecular Theory Group. Massachusetts Institute of Technology, 1953.
54. McWeeny, R. *Electronic Structure of Molecules. Some recent Developments*. Technical Report No. 7. Solid-State and Molecular Theory Group. Massachusetts Institute of Technology, 1955.
55. Grünberg, A. A. and Faerman, G. P. *Z. anorg. Chem.* **192** (1930) 193.
56. Belford, R. L. *Bonding and Spectra of Metal Chelates*. University of California. Radiation Laboratory. 1955. UCRL-3051.
57. Ito, K. and Kuroda, Y. *J. Chem. Soc. Japan* **76** (1955) 545, 762, 766 and 934.
58. Ayres, G. H. and Quick, Q. *Anal. Chem.* **22** (1950) 1403.
59. Wöhler, L. and Witzmann, W. *Z. anorg. Chem.* **57** (1908) 323.
60. Ruff, O. and Fischer, J. *Z. anorg. chem.* **179** (1929) 177.
61. Vauquelin, L. N. *Ann. Chim.* **90** (1814) 260.

Received December 22, 1955.

Acta Chem. Scand. **10** (1956) No. 4