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MARCEL DELÉPINE'S RESEARCH ON COORDINATION COMPOUNDS

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CONTENTS

A. INTRODUCTION

In the same way that Alfred Werner's name is inextricably linked with cobalt and James Lewis Howe's name is similarly connected with ruthenium, mention of the name of Stéphane-Marcel Delépine (1871—1965) [1—6] immediately invokes the response "Iridium" among inorganic chemists. The qualification "among inorganic chemists" is necessary, for more than three-fourths of Delépine's publications dealt with organic themes, especially amines and their preparation by the so-called Delépine reaction, organic sulfur compounds, acetals, catalytic hydrogenation, terpenes, heterocyclic compounds, pyridine derivatives, alkaloids, and aminonitriles [7].

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Like a number of other leading coordination chemists, such as Sophus Mads Jørgensen [8], Alfred Werner himself [9], Lev Aleksandrovich Chugaev [10], James Lewis Howe [11] and John C. Bailar, Jr., Delépine began his long and fruitful career as an organic chemist. His first article was published in 1892 [12], his last in 1964 [13] – a span of almost three-quarters of a century. His retirement in 1941 as Professor of Chemistry at the Collège de France, the chair once held by his mentor, the distinguished French chemist and statesman Marcellin Berthelot, did not decrease his prolific scientific productivity, for during his retirement he added some seventy publications to his preceding two hundred or so articles. In fact, this indefatigable and long-lived pioneer in coordination chemistry continued to work in his laboratory with the aid of an assistant until a scant six weeks before his death at the age of ninety-four! Although he inspired a number of students including Raymond Charonnat, whose promising career in the chemistry of ruthenium was cut short by a tragic accident, and Alain Horeau, Delépine's successor at the Collège de France, Delépine preferred to do most of his own laboratory work, and with but few exceptions his publications bear his name alone.

In the field of inorganic chemistry, this man, whom Raleigh Gilchrist called "the one dominant figure among. . . French contributors [to the chemistry of the platinum metals]" [14], from the very beginning adopted Werner's then controversial views, and his numerous studies of coordination compounds, particularly those of the platinum metals, confirmed their geometric and optical isomerism and verified Werner's coordination theory [15]. For example, his preparation of the *cis* or *facial* (1, 2, 3) and *trans* or *meridional* (1, 2, 6) isomers of $[\mathrm{Irpy_3Cl_3}]$ (where py = C_5H_5N) constituted the first well-established case of geometric isomerism among compounds of the MA_3B_3 type, whose isomerism had been predicted by Werner in his first paper on the coordination theory [16]. Delépine's classical work on iridium, especially the sulfato, chloro, pyridine and oxalato complexes, placed the stereochemistry of this relatively neglected element on a firm basis, just as Werner's work had done for the complexes of cobalt. Delépine was a true master in the field of stereochemistry and crystallography, and his method of "active racemates" for resolving coordination compounds and determining their configurations provided the stereochemist with a valuable weapon in his arsenal of structure-proof methods.

Most of Delépine's work appeared in the Annales de Chimie (of whose editorial board he was a member for more than a quarter of a century), the Comptes rendus hebdomadaires de l'Académie des Sciences, Paris, and the Bulletin de la Société Chimique de France (de Paris before 1907). As in my four reviews of Werner's research [17], the viewpoint of this review is largely "historical", in the sense that no pretence is made to cover the contemporary literature. Although in some cases Delépine's results have been related to later developments, this article is in no way intended to compete with recent reviews of the topics discussed here. For summaries of the literature on specific compounds the reader is referred to Gmelins Handbuch [18—20] and Pascal's

Nouveau Traité [21—23], of which the section on iridium was written by Delépine himself [22].

B. PLATINUM COMPLEXES

During the earliest years of his career Delépine displayed in the platinum metals an interest that remained with him throughout his life. His interest in these metals arose from an apparently unrelated observation. In the well-known Kjeldahl method, nitrogen in organic and biological materials is converted into ammonium ion on boiling with concentrated sulfuric acid, yet heating the materials in platinum crucibles was found to give values of nitrogen that are slightly too low. Before Delépine's work, the dissolution of platinum in sulfuric acid was doubtful — denied by some and affirmed by others. In 1895 Delépine showed that the Kjeldahl method, when applied to the determination of nitrogen in such chloroplatinates as $[N(CH_3)_3H]_2[PtCl_6]$ and $(NH_4)_2[PtCl_6]$ likewise gives low results [24]. A decade later he demonstrated that metallic platinum placed in sulfuric acid in the presence of ammonium salts likewise results in a loss of nitrogen [25]. He later showed that an appreciable amount of metallic platinum is dissolved by boiling sulfuric acid [26] with formation of two compounds of tripositive platinum [27] — orange-red $H[Pt(SO_4)_2H_2O] \cdot 4\frac{3}{4} H_2O$ (written as $H_2[Pt_2(SO_4)_4(H_2O)_2] \cdot 9\frac{1}{2} H_2O$ by M. Blondel [28],) and brown $H[Pt(SO_4)(OH)_2H_2O]$ (written as $H_2[Pt_2(SO_4)_2(OH)_4(H_2O)_2]$ by Blondel) (ref. 18, p. 110). Delépine also studied the dehydration of the 6- and 12-hydrates of sodium and lithium hexachloroplatinates(IV), hexachloroiridates(III) and (IV) and hexachlororhodates(III), and he failed to verify Rosenstiehl's view that water of hydration is removed from salts containing $n \times 3$ H_2O in groups of 3 H_2O [28a]. Many years later, Delépine devised procedures for converting the platinum metals into compounds by chlorinating them by means of heating with ammonium chloride [29] or carbon tetrachloride [30].

C. IRIDIUM COMPLEXES

(i) Sulfato complexes

In his early investigation of the cause for the low values of nitrogen obtained by the Kjeldahl method with platinum ware, Delépine suspected that the low values might be due, not only to loss of elemental nitrogen, but also to the formation of iridium complexes from the platinum—iridium alloy. Therefore, in his work on the dissolution of platinum in sulfuric acid, he also employed platinum alloyed with 10% iridium, which dissolves more rapidly in the presence of potassium sulfate [31] with formation of a complex salt $K_3[Ir(SO_4)_3] \cdot H_2O$ (ref. 19, p. 107; ref. 22, p. 520) [32]. Thus began Delépine's extensive series of researches on iridium, the element with which his name is so closely identified.

Actually, Lecoq de Boisbaudron [33], one of Delépine's teachers, in 1883 had prepared this green compound which he considered to be a double sulfate $Ir_2(SO_4)_3 \cdot 3\,K_2SO_4$, by fusing an iridium(IV) compound with $KHSO_4$ and treating the cooled melt with aqueous K_2SO_4. Delépine [32] showed the compound to be a complex salt in which the SO_4 radical does not give any of its usual ionic reactions. Although it is very stable in acidic solution, alkalies and alkaline carbonates precipitate the iridium in the form of a violet oxide. Reducing agents change the color of its solution from blue to yellow. Part of its iridium content is in the tetrapositive oxidation state.

Delépine investigated two other series of complex sulfates of iridium, his so-called "iridodisulfates," over a period of more than half a century, (ref. 19, pp. 107,120; ref. 22, p. 521). In 1909 he treated ammonium hexachloroiridate(III) with boiling sulfuric acid. On adding water to the mixture, he obtained a dark green crystalline deposit, while the supernatant liquid contained an olive brown salt [34,35]. The two series of salts are isomeric, containing Ir and SO_4 in a 1 : 2 ratio. Their tautomeric parent acids are interconvertible according to the following reversible acid–base equilibrium reaction [36] in the

$$\underset{\text{Green acid}}{H_2[Ir^{III}(SO_4)_2(H_2O)OH]} \underset{\text{Acid}}{\overset{\text{Base}}{\rightleftharpoons}} \underset{\text{Reddish brown acid}}{H_3[Ir^{III}(SO_4)_2(OH)_2]}$$

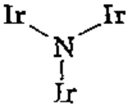
same way that pentachloroaquoiridic(III) and pentachlorohydroxoiridic(III) acids are interconvertible [37–39]

$$H_2[Ir(H_2O)Cl_5] \rightleftharpoons H_3[Ir(OH)Cl_5]$$

In the green salts, since the water molecule can be replaced by pyridine [40], Delépine concluded that a water molecule is actually present as such in this series. The pyridine complex can no longer be converted into the reddish brown complex.

Delépine (ref. 22, p. 521) [41] later found that the green salts, prepared in the presence of NH_4^+, contain nitrogen in the ratio N : Ir = 1 : 3, and he reformulated the acids as $H_6[N\{Ir^{III}(H_2O)(SO_4)_2\}_3]$ (green) and $H_7[N\{Ir^{III}(H_2O)(SO_4)_2\}_2\{Ir^{III}(OH)(SO_4)_2\}]$ or $H_9[N\{Ir^{III}(OH)(SO_4)_2\}]$ (reddish brown). Because of the intense dark color of these salts, Jørgensen suspected that they might contain iridium(IV), a possibility which Delépine had considered in April 1946, but which he had discarded because the compounds are diamagnetic [42]. During a study of the absorption spectra of a number of Delépine's complexes, Jørgensen [43] noted the persistent presence of two hydrogen ions even in the hydroxo salts $K_7H_2[N\{Ir(OH)(SO_4)_2\}_3]$.

Jørgensen [44] showed that strong reducing agents such as $V(H_2O)_6^{2+}$, metallic Zn or U(III) in 2 *M* HCl, reduce the green complex to the pale yellow color expected for iridium(III). The reduced form can be reoxidized with H_2O_2 to the green form, which Jørgensen formulated as $[N\{Ir^{III}Ir^{IV}Ir^{IV}(H_2O)(SO_4)_2\}_3]^{4-}$. He attributed the diamagnetism to strong coupling between the two Ir(IV) atoms, each having $S = \frac{1}{2}$. Together with Orgel, Jørgensen [45] discussed the molecular orbital formulation for a planar

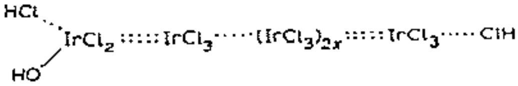


cluster containing the mixed oxidation state $3\frac{2}{3}$ delocalized on the three iridium atoms. In a publication [46] appearing fifty years after his early work on these compounds [34,35] Delépine subsequently produced analytical data supporting Jørgensen's formula for the green ion. He formulated the parent acids as $H_{4+n}[N\{Ir^{III}Ir^{IV}Ir^{IV}(H_2O)_{3-n}(OH)_n(SO_4)_6\}]$ [46].

Indeed, during his last years Delépine occupied himself with problems related to his green salts of 1909. For example, in 1959, he devised a new synthesis for the green potassium ammonium iridodisulfate [47]. In 1960 he prepared $(NH_4)_4[NIr^{III}Ir^{IV}Ir^{IV}(NH_3)_3(SO_4)_6] \cdot 4\ H_2O$ by the action of ammonia on $NH_4Ir(SO_4)_2$ and converted the new compound to the less soluble Rb, Cs, Ag, Hg(I), Tl(I), Sr, Ba and Pb salts by metathesis [48]. He also prepared the compound $K_4[NIr^{III}Ir^{IV}Ir^{IV}(\text{3-picoline})_3(SO_4)_6] \cdot 4\ H_2O$ by substituting 3-picoline for ammonia and by starting with $KIr(SO_4)_2$ [48].

(ii) Chloro complexes

Most of the work on the chlorides of iridium was incomplete or inexact when Delépine began his investigations. He examined the four chlorides then known (ref. 19, pp. 56, 63; ref. 22, p. 495) — $IrCl_4$, $IrCl_3 \cdot 4\ H_2O$ and the anhydrous iridium(III) chlorides described by Carl Ernst Claus [49] and E. Leidié [50], respectively. Delépine showed the first compound, commercial "iridium tetrachloride", to be more or less hexachloroiridic(IV) acid, $H_2[IrCl_6] \cdot 6\ H_2O$ [51], while he showed that pure crystalline $IrCl_3 \cdot 4\ H_2O$ does not exist. Reduction of $H_2[IrCl_6]$ gives only yellow, hygroscopic, amorphous products of variable composition $IrCl_3 \cdot m\ HCl \cdot n\ H_2O$ where $m < 1$, which on heating below 200°C lose water and hydrogen chloride and become increasingly insoluble. Heating to 500°C in a stream of HCl gives products approaching the composition $IrCl_3$. Delépine assigned the initial product the constitution



$$\overset{HCl}{\underset{HO}{}}\!\!\rangle IrCl_2 :::: IrCl_3 \cdots\cdots (IrCl_3)_{2x} :::: IrCl_3 \cdots\cdots ClH$$

Loss of H_2O from the left and HCl from the right would close the chain and result in an anhydrous $IrCl_3$ which would thus be a condensation compound similar to condensed metal oxides such as ZnO [52]. Delépine found Claus' so-called anhydrous $IrCl_3$, obtained by heating hexachloroiridates(III) with concentrated sulfuric acid, to be a yellow powder containing widely variable amounts of Ir, Cl, HCl, H_2SO_4 and H_2O [39]. He found the anhydrous trichloride obtained by Leidié by passing chlorine over $(NH_4)_3[IrCl_6]$ at 500°C to be actually $IrCl_{3+X}$ where X is small; only at 600°C is $IrCl_3$ formed.

For the platinum metals, the complex chloro salts are more important than the simple chlorides, and for iridium most of the former were poorly described and understood in the first decade of the present century, largely because of the great variations in color depending upon the size of the crystals. Delépine first prepared the alkali metal salts of both the hexachloroiridates(IV) and hexachloroiridates(III), $M_2[IrCl_6]$ and $M_3[IrCl_6]$ (ref. 19, pp. 91, 100, 115; ref. 22, p. 498), where M = K, Rb, Cs, NH_4, Li and Na [37, 53, 54]. He employed oxalates to reduce hexachloroiridates(IV) to hexachloroiridates(III)

$$M_2[IrCl_6] + M_2C_2O_4 \rightarrow 2\ M_3[IrCl_6] + 2\ CO_2\uparrow$$

in what he mistakenly considered to be a new method [37], which, however, had been used previously by Vèzes [55]. In the course of this work he discovered a new series of salts, the pentachloroaquoiridates(III), formed from the hexachloroiridates(III) by the following reversible reaction (ref. 19, pp. 105, 117; ref. 22, p. 498)

$$M_3[IrCl_6] + H_2O \rightleftharpoons M_2[Ir(H_2O)Cl_5] + MCl \text{ (except Li and Na)}$$

Delépine also prepared the hexachloroiridate(III) of thallium for the first time and reinvestigated that of silver, which is formed under conditions where one would expect the formation of the hexachloroiridate(IV), which, however, is unstable [38]. Delépine systematically summarized his previously published work on chlorides and chloro salts of iridium in a lengthy 63-page paper [39]. In 1935 his older daughter Mme. Madeleine Delépine-Tard [56] prepared several hexabromo and pentachloro salts of tripositive iridium.

(iii) Pyridine complexes

Most of Delépine's research on the complexes of iridium involves coordination compounds containing pyridine as a ligand. As we have seen (Section C (i)), he early obtained deep green salts of general formula $M_xH_y[Irpy(OH)(SO_4)_2]_2$ (where $M_xH_y = Na_4H_2, K_4H_2, Ba_2H_2, Ag_4H_2$) either by the action of pyridine on the corresponding hydroxoaquosulfates or by metathesis of the ammonium salt, $(NH_4)_3H[Irpy(OH)(SO_4)_2]_2 \cdot 10\ H_2O$ (obtained by heating aqueous $(NH_4)_3H[Ir(H_2O)(OH)(SO_4)_2]_2$ with pyridine), with the corresponding metal salts [40]. The weakly acidic solutions are stable at room temperature. In contrast to the hydroxoaquosulfates, the color of the solutions and the compositions of these compounds are not altered by addition of alkali. In the course of this research, Delépine developed a method for the separation and quantitative determination of both ammonia and pyridine in iridium complexes [57].

Delépine's research on the pyridine complexes of iridium spanned more than half a century, from 1911 to 1964 — 53 years to be exact, slightly longer than Alfred Werner's entire life! During this time, Delépine methodically investigated the effect of the partial and progressive substitution of pyridine for chlorine in various hexachloroiridates(III) and thus obtained numerous stable complexes — cationic, neutral and anionic — e.g., $M_2[IrpyCl_5]$, $M[Irpy_2Cl_4]$, $[Irpy_3Cl_3]$ and $[Irpy_4Cl_2]X$. He also synthesized pyridine derivatives of tetrapositive iridium, such as $M[IrpyCl_5]$ and $[Irpy_2Cl_4]$. In the course of this extensive work, he obtained a number of geometric isomers, together with optical isomers of oxalato complexes of iridium(III), which served to provide additional verification for Werner's coordination theory. In Delépine's own words. "To summarize, in the field of iridium complexes — and iridium is perhaps the metal that forms the most stable complexes — Werner's theory of the octahedron continually finds its confirmation" [58b]. Elsewhere, along the same lines, Delépine wrote, "Not a single formula has been encountered that could not be written correctly by Werner's theory of the octahedron" (ref. 59, p. 178). We shall now briefly examine Delépine's most important work on the pyridine complexes of iridium.

(a) Monopyridine complexes

(1) $M_2[Ir^{III}pyCl_5]$ (ref. 19, p. 188; ref. 22, p. 559). Having noted, as we have already seen, that pyridine can be easily substituted for water in the "iridodisulfates" [40], Delépine attempted to carry out the same substitution with the water molecule in the pentachloroaquoiridates(III). Not only did this reaction occur as expected to yield pentachloropyridineiridates(III) but also a similar substitution of pyridine for MCl in the hexachloroiridates(III) was found to produce the same salts. Although the reactions occur only slowly at room temperature, they take place at 100° C in several minutes [60]

$$M_2[Ir(H_2O)Cl_5] + py \rightarrow M_2[IrpyCl_5] + H_2O$$

$$M_3[IrCl_6] + py \rightarrow M_2[IrpyCl_5] + MCl$$

In addition to these two methods of synthesis, the pentachloropyridineiridates(III) can also be prepared by the action of pyridine on hexachloroiridates(IV) [61]

$$M_2[IrCl_6] + py \rightarrow M_2[IrpyCl_5] + \tfrac{1}{2} Cl_2\uparrow$$

Delépine prepared the pure K, NH_4, Na, Tl(I), Pb(II), Hg(I), Ag and $AgNH_3$ salts, and the Rb and Cs salts in impure form. More than a decade later, he and his student, Jean Pineau [64a], prepared the dark chamois colored salt $[Ir(NH_3)_4pyCl][IrpyCl_5]$ by metathesis [62]. Delépine prepared the parent acid $H_2[IrpyCl_5]$ in solution but, on concentrating, it decomposes with formation of $H[IrpyCl_5]$ [60]. E. Ogawa [63] later obtained a solid mixture of the acid (80%) along with the salt $(pyH)_2[IrpyCl_5]$ by evaporating a solution of pyridine and $H_2[Ir(H_2O)Cl_5] \cdot 6\ H_2O$ at room temperature in vacuo over sulfuric acid.

The alkali metal pentachloropyridineiridates(III) range in color from pale orange-yellow to garnet-red and are very soluble in water. The pyridine is strongly bonded in these very stable salts, which are unaffected by warming with dilute acids or bases. On boiling for two hours with sodium sulfide all the pyridine is liberated [60]. Their behavior toward chlorine (pink to red coloration) may be used to differentiate them from hexachloroiridates(III) (reddish brown coloration) [61]. Heating the potassium salt with aqueous ammonia produces $[Ir(NH_3)_4pyCl]Cl_2$ along with a little $[Ir(NH_3)_5Cl]Cl_2$ (ref. 62; ref. 64a, p. 18). The photochemical and thermal hydrolysis of the $[IrpyCl_5]^{2-}$ ion has been studied by Delépine's student, Mlle. Fernande Larèze [64].

(2) $M[Ir^{IV}pyCl_5]$ (ref. 19, p. 193; ref. 22, p. 561). Oxidizing agents such as chlorine, nitric acid or aqua regia transform the yellow pentachloroiridates(III) into pink pentachloroiridates(IV) [60,61]

$$M_2[IrpyCl_5] + \frac{1}{2}Cl_2 \rightarrow M[IrpyCl_5] + MCl$$

a color change which is detectable in dilutions as low as 1 part in 100,000. The iridium(IV) salts are related to the iridium(III) salts in the same manner as the $M_2[IrCl_6]$ salts are related to the $M_3[IrCl_6]$ salts, but they cannot be formed by substitution of pyridine for MCl in the $M_2[IrCl_6]$ salts because pyridine acts as a reducing agent on the $M_2[IrCl_6]$ or the "pyridinated" chloroiridate(IV), giving rise to $M_2[IrpyCl_5]$. Similarly the pentachloropyridineiridates(IV) cannot be prepared by Anderson's reaction

$$(pyH)_2[Ir^{IV}Cl_6] \rightarrow (pyH)[Ir^{IV}pyCl_5] + HCl$$

but only by the oxidation of the corresponding pentachloroiridates(III) as shown above. Delépine [61] prepared the Na, K and NH_4 salts in this manner, and from these, he prepared the Rb, Cs, Ag, Tl(I), Hg(I) and Hg(II) salts by metathesis. The colors range from deep red or deep violet to black. Delépine obtained the parent acid $H[IrpyCl_5]$ by concentrating a solution of $H_2[IrpyCl_5]$ (ref. 60, p. 717) by acidifying the salts with strong acids, or by decomposing $Ag[IrpyCl_5]$ with water (ref. 61, p. 775). He also later claimed to have obtained the acid in crystalline condition but gave no details [58b].

Aqueous solutions of the pentachloropyridineiridates(IV) are much more intensely colored than those of the pentachloropyridineiridates(III) (detectable at a dilution of 1 : 100,000), and dilute solutions decolorize by reduction, slowly at room temperature, quickly on heating. On recrystallization from boiling water, the salts are reduced unless chlorine water is added. The pyridine is strongly bonded, and the compounds are very stable toward acids. The K or NH_4 salt is unchanged on boiling for several hours with aqueous hydrochloric or nitric acids, but heating in a sealed tube causes the reaction

$$2\,M[IrpyCl_5] + 2\,HCl \rightarrow M_2[IrCl_6] + (pyH)_2[IrCl_6]$$

The salts are reduced by alkalies, ammonia, nitrites, bromides, iodides, sulfides, sulfites, hyposulfites, hypophosphites, arsenites, oxalates and organic substances. In solution this change from red to yellow indicates the greater stability of the pentachloropyridineiridates(III). The reaction with iodides

$$2\ M[Ir^{IV}pyCl_5] + 2\ MI \rightarrow 2\ M_2[Ir^{III}pyCl_5] + I_2$$

occurs instantaneously and can be used for their quantitative determination. Unlike the pentachloropyridineiridates(III), they do not yield a precipitate with lead salts, and their precipitation with CsCl and $TlNO_3$ can be used to differentiate them from hexachloroiridates(III).

(3) Miscellaneous monopyridine complexes. Together with Jean Pineau [64a], Delépine prepared eight salts of the chloropyridinetetraammineiridium(III) ion, $[Ir(NH_3)_4pyCl]X_2$ (ref. 19, p. 160; ref. 22, p. 572) [62]. By heating potassium pentachloropyridineiridate(III) (See Section C (iii)(a)(1)) with aqueous ammonia in a sealed tube for 15 h at 100° C. Delépine and Pineau obtained a concentrated solution of the chloride (ref. 62, p. 231)

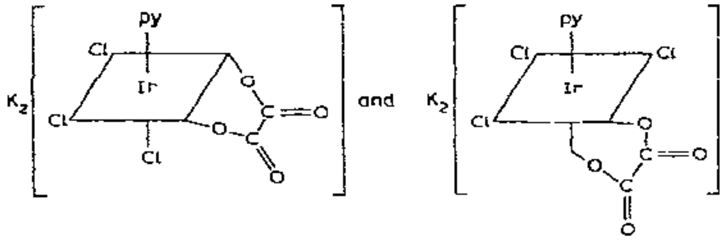
$$K_2[IrpyCl_5] + 4\ NH_3 \rightarrow [Ir(NH_3)_4pyCl]Cl_2 + 2\ KCl$$

They removed the potassium chloride by addition of ethanol, then evaporated the solution, and by addition of mercury(II) chloride precipitated the pale yellow double salt, $[Ir(NH_3)_4pyCl]Cl_2 \cdot 2\ HgCl_2$. The chloride was obtained by precipitation of the mercury(II) with hydrogen sulfide. From the chloride they prepared the sulfate, dichromate, picrate, pentachloropyridineiridate(III) and the *cis*- and *trans*-tetrachlorodipyridineiridates(III) by metathesis.

By refluxing a solution of potassium tetrachlorooxalatoiridate(III) on a water bath with pyridine, Delépine [59,65] obtained orange-yellow potassium trichlorooxalatopyridineiridate(III) 1½ hydrate (ref. 19, p. 191; ref. 22, p. 560)

$$K_3[Ir(C_2O_4)Cl_4] + py \rightarrow K_2[Irpy(C_2O_4)Cl_3] + KCl$$

The crystals are orthorhombic [66]. The salt can occur in two isomeric forms [59].



Inamura [67] later prepared the following salts of the new anion: Rb, Cs, Tl, Ba, Ag and KAg. He also obtained the corresponding iridium(IV) salt by bubbling chlorine through a concentrated solution of the potassium salt

$$\underset{\text{orange}}{K_2[Ir^{III}py(C_2O_4)Cl_3]} + \tfrac{1}{2}\ Cl_2 \rightarrow \underset{\text{very dark violet}}{K[Ir^{IV}py(C_2O_4)Cl_3]} + KCl$$

The iridium(III) salt is formed again on boiling the solution of the iridium(IV) compound.

(b) Dipyridine complexes

(1) $M[Ir^{III}py_2Cl_4]$ (ref. 19, p. 182; ref. 22, p. 562). We have already seen that one molecule of pyridine reacts almost immediately at 100° C with $M_3[IrCl_6]$ or $M_2[Ir(H_2O)Cl_5]$ to form pentachloropyridineiridates(III), $M_2[IrpyCl_5]$ [60,61] (Section C(iii)(a)(1)). By increasing the reaction time to one hour Delépine produced tetrachlorodipyridineiridates(III) [68]

$$M_3[IrCl_6] + 2\ py \rightarrow M[Irpy_2Cl_4] + 2\ MCl$$

$$M_2[Ir(H_2O)Cl_5] + 2\ py \rightarrow M[Irpy_2Cl_4] + H_2O + MCl$$

Only after long refluxing the aquo complex with excess pyridine did Delépine [59] succeed in coordinating the third pyridine molecule to form the non-electrolytic complex $[Irpy_3Cl_3]$ (Section C(iii)(c)).

Since hexacoordinate iridium has an octahedral configuration, the tetrachlorodipyridineiridates(III) should occur in two geometrically isomeric forms. Delépine's isolation of two isomeric series in almost equivalent amounts — orange (*cis*) and red (*trans*) — thus provided additional verification for Werner's theory [58b]. He established the structures by oxidizing the orange salts [59]

$$cis\text{-}M[Ir^{III}py_2Cl_4] + \tfrac{1}{2}\ Cl_2 \rightarrow cis\text{-}[Ir^{IV}py_2Cl_4] + MCl$$

and syncrystallizing the $[Irpy_2Cl_4]$ (See Section C (iii)(b)(2)) thus obtained with Anderson's salt, *cis*-$[Ptpy_2Cl_4]$ [69], whose configuration was already known. It should be emphasized that reliance on color alone as evidence of configuration is extremely risky. Thus, by analogy with Delépine's observations on iridium(III) isomers, Rây et al. [70] concluded that of the two isomers that they obtained of empirical formula $Ir\{(C_2H_5)_2S\}_3Cl_3$ [70—73] the yellow compound was the *cis* or *facial* (1, 2, 3) isomer and the red compound, the *trans* or *meridional* (1, 2, 6) isomer. Thirty years later Kauffman et al. [74] confirmed their structure for the yellow isomer but showed that the red compound is an electrolytic polymerization isomer, *trans*-$[Ir\{(C_2H_5)_2S\}_4Cl_2]$ *trans*-$[Ir\{(C_2H_5)_2S\}_2Cl_4]$.

For both the *cis* and *trans* series Delépine [68] prepared the following salts: Na, K [66], Rb, Cs, NH_4 [66], Tl, Ag, Pb and pyH; for the *trans* series he also prepared the Cd, $[Ir(NH_3)_4pyCl]^{2+}$ and $[Ir(H_2O)_2py_2Cl_2]^+$ salts. The *cis*- and *trans*-ammonium salts were also prepared by reduction of the corresponding tetrachlorodipyridineiridium(IV) compounds with ammonia

$$6[Ir^{IV}py_2Cl_4] + 8\ NH_3 \rightarrow 6\ NH_4[Ir^{III}py_2Cl_4] + N_2\uparrow$$

The sparingly soluble pyridinium salts [75] can readily be isolated and hence are convenient starting materials for the synthesis of other members of the series. Because of their widely differing solubilities in water (*cis*, 1 g in 65 ml at 18° C; *trans*, 1 g in 770 ml at 18° C), the isomeric pyridinium salts are easily separated. The coordinated pyridine in the tetrachlorodipyridineiridates(III) is strongly bonded; acids remove it only with the greatest difficulty; bases alone fail to expel it, and even in the presence of sodium sulfide they liberate it only slowly on long boiling, and then only from the *trans* salts.

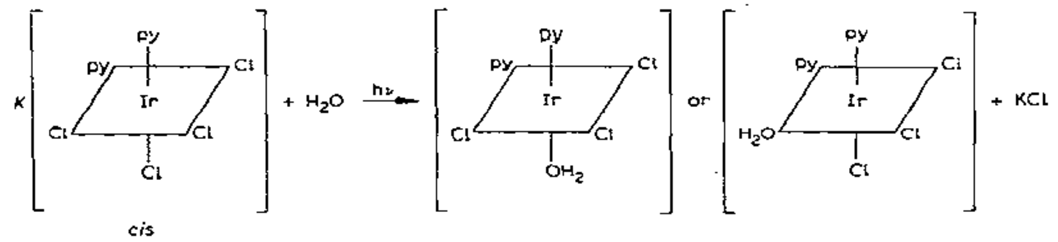
In 1940 Delépine [76] prepared the parent acids of the series — the orange pentahydrated *cis* acid by slow evaporation of the solution resulting from treatment of *cis*-Ag$[Irpy_2Cl_4]$ with H_2S or the solution resulting from treatment of *cis*-$[Ir(H_2O)py_2Cl_3]$ (prepared by boiling a solution of *cis*-K$[Irpy_2Cl_4]$) with concentrated HCl; the red dihydrated or tetrahydrated *trans* acid by treating *trans*-$[Ir(H_2O)py_2Cl_3]$ (prepared by boiling a solution of *trans*-K$[Irpy_2Cl_4]$) with HCl solution or better by treating *trans*-K$[Irpy_2Cl_4]$ with concentrated HCl. The *cis* acid is much more soluble than the *trans* acid. Both acids are strong, the *trans* being somewhat stronger than the *cis*. By treating $Na_3[IrBr_6]$ with pyridine in the presence of hydrobromic acid, Delépine-Tard [77,78], prepared pyH$[Irpy_2Br_4]$ and from it other tetrabromodipyridineiridates(III) — K, NH_4, Rb, Cs, Tl, Ag. She obtained only one series of salts — red (apparently *trans*) (ref. 19, p. 185; ref. 22, p. 565).

Delépine found that, when exposed to light, aqueous solutions of *trans*-K$[Irpy_2Cl_4]$ and *trans*-H$[Irpy_2Cl_4]$ decompose to the extent of more than 90% to form $[Ir(H_2O)py_2Cl_3]$

$$trans\text{-}K[Irpy_2Cl_4] + H_2O \xrightarrow{h\nu} [Ir(H_2O)py_2Cl_3] + KCl$$

$$trans\text{-}H[Irpy_2Cl_4] + H_2O \xrightarrow{h\nu} [Ir(H_2O)py_2Cl_3] + HCl$$

while in darkness the compounds are not decomposed even after 15 years [79,80]. Irradiation of the *cis*-potassium salt requires several days for the completion of the reaction, the product being an isomeric yellow-orange trichlorodipyridineaquo complex, $[Ir(H_2O)py_2Cl_3] \cdot 2\,H_2O$, which, assuming no rearrangement of the pyridine molecules, may have either of two configurations [80]



In the dark, even after twenty years, the solution of the *cis*-potassium salt remained almost completely unchanged. On March 4, 1963 Delépine presented to the Académie des Sciences the results of his student Mlle. Fernande Larèze [81], who by action of β-picoline (3-methylpyridine) on aqueous $K_3[IrCl_6]$ or $K_2[Ir(H_2O)Cl_5]$ obtained two series of salts, *cis*- and *trans*-M-$[Ir(\beta\text{-pic})_2Cl_4]$, in which M = pyH, K, Na, NH_4, Rb, Cs, Tl and Ag, as well as the *trans* acid. She found that the salts are analogous to the corresponding tetrachlorodipyridineiridates(III). Hydrolysis by irradiation of *cis*- and *trans*-K[Ir(β-pic)$_2$Cl$_4$] yields the corresponding isomers of [Ir(H$_2$O)(β-pic)$_2$Cl$_3$], while oxidation of the two salts yields the corresponding isomers of [Ir^{IV}(β-pic)$_2$Cl$_4$].

(2) [Ir^{IV}py$_2$Cl$_4$] (ref. 19, p. 192; ref. 22, p. 566). An impure substance with the reported composition Irpy$_2$Cl$_4$, prepared by the action of pyridine on an iridium(IV) chloride solution, was first described by Renz [82] and later investigated by Gutbier and Hoyermann [83,84]. Since the composition was based entirely on iridium content without any allusion to isomerism and since the color was inconsistent with his findings, Delépine [59,85] concluded that the product was not a pure substance.

The *cis* and *trans* forms of tetrachlorodipyridineiridium(IV) were first prepared in pure form by Delépine [59,85,86] by oxidation of the corresponding isomeric tetrachlorodipyridineiridates(III) (see Section C(iii)(b)(1)). Ogawa [63] later obtained them by oxidation of (pyH)$_2$[IrpyCl$_5$] and [Irpy$_3$Cl$_3$]. Delépine [59,87] also obtained the *trans* isomer by aqua regia oxidation of *trans*-[Irpy$_2$(C$_2$O$_4$)$_2$]. Kauffman [88] prepared both isomers by nitric acid oxidation of the tetrachlorodipyridineiridates(III) after conversion of the relatively water-insoluble pyridinium salts [75] (*cis*, 1 g/65 ml at 18°C; *trans*, 1 g/770 ml at 18°C) to the easily water-soluble ammonium salts (*cis*, 1 g/10 ml at 19°C; *trans*, 1 g/30 ml at 19°C)

$$cis\text{- or } trans\text{-pyH[Irpy}_2\text{Cl}_4] + \text{NH}_3 \rightarrow cis\text{- or } trans\text{-NH}_4[\text{Irpy}_2\text{Cl}_4] + \text{py}$$

$$cis\text{- or } trans\text{-NH}_4[\text{Ir}^{III}\text{py}_2\text{Cl}_4] + 4\ \text{HNO}_3 \rightarrow cis\text{- or } trans\text{-}[\text{Ir}^{IV}\text{py}_2\text{Cl}_4] + 4\ \text{NO}_2\uparrow + \tfrac{1}{2}\ \text{N}_2\uparrow + 4\ \text{H}_2\text{O}$$

The sensitivity of the isomeric tetrachlorodipyridineiridates(III) to oxidation differs markedly, the red *trans* salts being more easily oxidized than the orange *cis* salts. Thus the *trans* isomers are oxidized to *trans*-[Irpy$_2$Cl$_4$] almost immediately at room temperature by nitric acid, aqua regia, chlorine water or bromine water, whereas oxidation of the *cis* isomers to *cis*-[Irpy$_2$Cl$_4$] with nitric acid requires heating to dryness, and oxidation does not occur at all with bromine water. This difference in ease of oxidation between the isomeric tetrachlorodipyridineiridates(III) is reflected in the difference in ease of reduction between the corresponding tetrachlorodipyridineiridium(IV) compounds.

Both isomers of [Irpy$_2$Cl$_4$] are non-electrolytes, insoluble in water, ethanol and diethyl ether but slightly soluble in chloroform, yielding violet solutions. Both are deep violet, the *cis* compound being somewhat darker than the *trans* compound. Kauffman et al. have separated the isomers by column chromatography on silica gel [88a].

Both isomers behave as oxidizing agents; the *cis* compound is the stronger oxidant, falling between chlorine and bromine, whereas the *trans* isomer falls between bromine and iodine *cis*- or *trans*-$[\mathrm{Ir^{IV}py_2Cl_4}]$ + KI → *cis*- or *trans*-$\mathrm{K[Ir^{III}py_2Cl_4]} + \frac{1}{2}\,\mathrm{I_2}$

but $[\mathrm{Ir^{IV}py_2Cl_4}] + \mathrm{KBr} \rightarrow \mathrm{K[Ir^{III}py_2Cl_4]} + \frac{1}{2}\,\mathrm{Br_2}$ (*cis* only)

Similarly, the *cis* isomer dissolves in warm ethanol to form a yellow solution of *cis*-$\mathrm{H[Irpy_2Cl_4]}$, whereas the *trans* isomer is not reduced even by boiling ethanol. Both isomers oxidize aqueous NH_3 to elementary nitrogen and are reduced to the corresponding isomers of $\mathrm{NH_4[Irpy_2Cl_4]}$, but the reaction is more complex with the *trans* isomer. An interesting reaction illustrating relative oxidizing power occurs when the *cis* isomer is triturated with a solution of a *trans*-tetrachlorodipyridineiridate(III)

cis-$[\mathrm{Ir^{IV}py_2Cl_4}]$ + *trans*-$\mathrm{M[Ir^{III}py_2Cl_4]}$(red) → *trans*-$[\mathrm{Ir^{IV}py_2Cl_4}]$

+ *cis*-$\mathrm{M[Ir^{III}py_2Cl_4]}$ (orange)

Although the *trans* isomer is insoluble in boiling HNO_3, the *cis* isomer dissolves, giving a brown-violet solution. On evaporation the *cis* isomer is recovered as strongly dichroic green-violet rhomboids. The *trans* isomer is not dichroic.

Syncrystallization of the *cis* isomer with $[\mathrm{Ptpy_2Cl_4}]$ (Anderson's Salt) [69], which has been shown to possess the *cis* configuration [89,90] and with which it is isomorphous and to which it communicates its dichroism, enabled Delépine [59,85,86] to establish the configuration of not only the $[\mathrm{Ir^{IV}py_2Cl_4}]$ compounds but also the $\mathrm{M[Ir^{III}py_2Cl_4]}$ salts as well. The *trans* isomer, under the same conditions, forms no mixed crystals with *cis*-$[\mathrm{Ptpy_2Cl_4}]$ but crystallizes alone. Chemical reactions, sometimes effective in structure-proof, are uncertain in this case, for they are slow and require conditions that might lead to rearrangements.

From the very beginning and throughout his research on metallic complexes, Delépine encountered problems of fractionally separating crystalline substances, and the above application of the technique of syncrystallization was only one of several that he made [91–93]. As early as 1931 syncrystallization of the diethyldithiocarbamates provided the first real proof of the oxidation state (III) for polonium, which had hitherto been obtained in only almost immeasurably small quantities [91]. Similarly, the oxidation state (IV) was proven for the same element by syncrystallization of $\mathrm{(NH_4)_2[PoCl_6]}$ with the corresponding hexachloro complexes of platinum(IV), iridium(IV), tellurium(IV) and lead(IV) [91].

Of the three classically difficult fractionations in inorganic chemistry — K, Rb and Cs; Ba and Ra; and the lanthanides — Delépine utilized syncrystallization to attack the first [92]. Noticing that syncrystallization causes decreases in solubility in mixtures containing both rubidium and cesium salts from that of the pure salts, he followed the fractionation of K, Rb and Cs alums by measuring the density of the mother liquor. He also evaluated the use of $SbCl_3$ and $SnCl_4$ in the crystallization of Cs and Rb and the use of $H_2C_2O_4$ in the crystallization of Rb, the crystals formed being the hexachloroantimonates(III), the hexachloroplumbates(III) and the acidic double oxalates, respectively.

Tetrabromodipyridineiridium(IV), a brownish, violet-blue powder, was obtained by Delépine-Tard by oxidation of *trans*-$NH_4[Irpy_2Br_4]$ with nitric acid, bromine water, or best of all, chlorine water (ref. 19, p. 193; ref. 22, p. 567) [77,78]. This compound, the configuration of which has not been established as *cis* or *trans*, liberates iodine from potassium iodide and is reduced to iridium(III) by reducing agents.

Tetrachlorobis(α-picoline)iridium(IV), $[Ir(\alpha\text{-pic})_2Cl_4]$, a black-violet substance soluble in pyridine and picoline and analogous in its chemical behavior to *trans*-$[Irpy_2Cl_4]$, was prepared by oxidizing $[Ir(H_2O)(\alpha\text{-pic})_2Cl_3]$ with concentrated nitric acid or aqua regia (ref. 19, p. 193; ref. 22, p. 566) [94]. By heating α-picoline with $Na_2[IrCl_6]$, Gutbier and Hoyermann [84] obtained a yellow powder of the same composition, which, however, showed no analogy to the preceding compound.

(3) trans-[Ir(NH$_3$)$_2$py$_2$Cl$_2$]X (ref. 19, p. 172; ref. 22, p. 571). By the action of ammonia on *trans*-$[Irpy_2Cl_4]$ at room temperature, Delépine [86] obtained the red compound *trans*-dichlorodipyridinediammineiridium(III) *trans*-tetrachlorodipyridineiridate(III) dihydrate and *trans*-chlorodipyridinetriammineiridium(III) *trans*-tetrachlorodipyridineiridate(III) 5-hydrate. The latter compound is discussed in Section C(iii)(b)(4). The formation of the first compound may be represented by the overall redox reaction

$$6\ trans\text{-}[Ir^{IV}py_2Cl_4] + 14\ NH_3 \rightarrow 3\ trans\text{-}[Ir^{III}(NH_3)_2py_2Cl_2]\ trans\text{-}[Irpy_2Cl_4] + 6\ NH_4Cl + N_2\uparrow$$

The reaction probably occurs in the following steps

$$6\ trans\text{-}[Ir^{IV}py_2Cl_4] + 8\ NH_3 \rightarrow 6\ trans\text{-}NH_4[Ir^{III}py_2Cl_4] + N_2\uparrow$$

$$trans\text{-}[Ir^{IV}py_2Cl_4] + 2\ NH_3 \rightarrow trans\text{-}[Ir^{IV}(NH_3)_2py_2Cl_2]Cl_2$$

$$6\ trans\text{-}[Ir^{IV}(NH_3)_2py_2Cl_2]Cl_2 + 8\ NH_3 \rightarrow 6\ trans\text{-}[Ir^{III}(NH_3)_2py_2Cl_2]Cl + 6\ NH_4Cl + N_2\uparrow$$

$$trans\text{-}NH_4[Ir^{III}py_2Cl_4] + trans\text{-}[Ir^{III}(NH_3)_2py_2Cl_2]Cl \rightarrow trans\text{-}[Ir^{III}(NH_3)_2py_2Cl_2]\ trans\text{-}[Ir^{III}py_2Cl_4] + NH_4Cl$$

As the last of the reaction steps implies, the compound may also be prepared directly by metathetical reaction between *trans*-$[Ir(NH_3)_2py_2Cl_2]Cl$ and *trans*-$M[Irpy_2Cl_4]$. Addition of a *trans*-$[Ir(NH_3)_2py_2Cl_2]Cl$ solution to one of *cis*-$M[Irpy_2Cl_4]$ produces a yellow precipitate, which is apparently *trans*-$[Ir(NH_3)_2py_2Cl_2]$ *cis*-$[Irpy_2Cl_4]$ [86]. The chloride of the *trans* cation can be prepared by warming the initially obtained product with excess pyridinium chloride (ref. 86, p. 227) *trans*-[Ir(NH$_3$)$_2$py$_2$Cl$_2$] *trans*-[Irpy$_2$Cl$_4$] + pyHCl → *trans*-[Ir(NH$_3$)$_2$py$_2$Cl$_2$]Cl

+ *trans*-pyH[Irpy$_2$Cl$_4$]

From this Delépine prepared the bromide, iodide, sulfate and acid sulfate (ref. 86, p. 228).

By treating a solution of *trans*-[Ir(NH$_3$)$_2$py$_2$Cl$_2$]Cl with silver oxide and exposing the resulting strongly alkaline filtrate to atmospheric carbon dioxide, Delépine [86] obtained yellow crystals of [Ir(NH$_3$)$_2$py$_2$(H$_2$O)Cl]CO$_3$ · 6 H$_2$O, which on heating to 125°C loses CO$_2$ to form [Ir(NH$_3$)$_2$py$_2$(H$_2$O)Cl]O (ref. 19, p. 163; ref. 22, p. 572).

Treatment of the chloride with aqueous ammonia in a sealed tube at 100°C produces a basic salt of formula 2[Ir(NH$_3$)$_4$py$_2$]Cl$_3^{+}$[Ir(NH$_3$)$_4$py$_2$]Cl(O) + 9 H$_2$O(?) [86]. Crystallization of this salt in the presence of ammonia produces a substance [Ir(NH$_3$)$_4$py$_2$]Cl$_2$(OH) · 5 H$_2$O, which Delépine wrote as 2[Irpy$_2$(NH$_3$)$_4$]Cl$_3$ + [Irpy$_2$(NH$_3$)$_4$](O)Cl + 9 H$_2$O because its solution is basic to litmus and reacts readily with acids to form white [Ir(NH$_3$)$_4$py$_2$]X$_3$ (ref. 19, p. 152; ref. 22, p. 53) [86]. Such a reaction would be analogous to the better known reactions of platinum(IV) observed by Chugaev [95]

[Pt(NH$_3$)$_4$Cl(NH$_2$)]Cl$_2$ + HCl → [Pt(NH$_3$)$_5$Cl]Cl$_3$

and Grinberg [96]

[Pt(NH$_3$)$_5$NH$_2$]Cl$_3$ + HCl → [Pt(NH$_3$)$_6$]Cl$_4$.

However, Jørgensen [42,43], by means of spectral measurements and titrations of Delépine's compound, proved it to contain the [Ir(NH$_3$)$_3$py$_2$(OH)]$^{2+}$ ion.

(4) trans-[Ir(NH$_3$)$_3$py$_2$Cl]X$_2$ (ref. 19, p. 163; ref. 22, p. 572). As mentioned in Section C(iii)(b)(3) Delépine [86] obtained the *trans*-tetrachlorodipyridineiridate(III) 5-hydrate of this cation along with the corresponding salt of the *trans*-dichlorodipyridinediammineiridium(III) cation by the action of ammonia on *trans*-[Irpy$_2$Cl$_4$] at room temperature. The overall reaction for the formation of the former compound probably proceeds according to steps analogous to those given in the previous section. The overall reaction can be represented as

6 *trans*-[Ir^{IV}py$_2$Cl$_4$] + 14 NH$_3$ → 2 *trans*-[Ir^{III}(NH$_3$)$_3$py$_2$Cl] *trans*-[Ir^{III}py$_2$Cl$_4$]$_2$

+ 6 NH$_4$Cl + N$_2$↑

After mechanical separation of the accompanying *trans*-dichlorodipyridinediammineiridium(III) salt, the red salt is purified by repetitive recrystallization (ref. 59, p. 31) [86]. Delépine's student Jean Pineau also prepared it by concentrating an aqueous solution of *trans*-[Ir(NH$_3$)$_3$py$_2$Cl]Cl$_2$ and *trans*-M-[Irpy$_2$Cl$_4$] on the water bath (ref. 64a, p. 64). Treatment of the compound with pyridinium chloride results in formation of the tetrahydrated chloride [86]

trans-$[Ir(NH_3)_3py_2Cl]$*trans*-$[Irpy_2Cl_4]_2$ + 2 pyHCl → *trans*-$[Ir(NH_3)_3pyCl]Cl_2$
+ 2 *trans*-pyH$[Irpy_2Cl_4]$

from which the anhydrous chloride [86], dihydrated chloride (ref. 86, p. 234; ref. 64a, p. 34), bromide, iodide, anhydrous and trihydrated sulfate (ref. 86, p. 235), hexachloroiridate(IV) and hexachloroplatinate(IV) [86] and *cis*-tetrachlorodipyridineiridate(III) (ref. 64a, p. 64) may be prepared.

(5) $[Ir(H_2O)py_2Cl_3]$ (ref. 19, p. 177; ref. 22, p. 568). In his work on iridium and rhodium complexes Delépine made extensive use of the autoclave in order to force reactions to occur. By heating a solution of *cis*- or *trans*-potassium tetrachlorodipyridineiridate(III) for one hour in an autoclave at 130°C, he was able to replace one of the strongly bonded pyridine molecules by one of water resulting in a non-electrolyte in which the original configuration is preserved [97]

cis- or *trans*-$K[Irpy_2Cl_4] + H_2O \rightarrow$ *cis*- or *trans*-$[Ir(H_2O)py_2Cl_3] + KCl$

On cooling the resulting solutions, the less soluble products (*cis*, deep yellow, $1\frac{1}{2}$ H_2O; *trans*, orange-red, 1 H_2O) deposit. In the case of the *trans* compound, pink needles of $[Irpy_2Cl_3]_n$, insoluble in water, acids or dilute bases, but soluble in concentrated NaOH, are first deposited and separated from the *trans*-$[Ir(H_2O)py_2Cl_3]$, which is contained in the mother liquor (ref. 19, p. 181; ref. 22, p. 568) [97b,c]. On heating to 140—145°C both aquo isomers irreversibly lose all water, both inside and outside the coordination sphere to yield insoluble $[Irpy_2Cl_3]_n$. Although Kauffman et al. [88a] were unable to separate these isomers by column chromatography on silica gel because of limited solubility in non-polar or moderately polar solvents, they succeeded by use of thin-layer chromatography [97d].

The *cis* isomer is more soluble in water than the *trans*(*cis*, 4—5 parts at 100°C, 130 parts at 23°C; *trans*, 100 parts at 100°C, 900 parts at 25°C). Both isomers give acidic solutions. Both dissolve in bases to give salts of the tautomeric conjugate base $M[Irpy_2(OH)Cl_3]$ (ref. 19, p. 177). Acids reprecipitate the original aquo complexes. Delépine prepared the isomeric compounds $AgH[Irpy_2(OH)Cl_3]$ by reaction of the corresponding aquo compounds with silver nitrate in neutral or ammoniacal solution (ref. 19, p. 185) [97b]. If nitric acid is present, isomeric salts of formula $Ag[Irpy_2(NO_3)Cl_3] \cdot H_2O$ (*cis*, yellow; *trans*, pink) are formed (ref. 19, p. 185) [97b,c]. From the *trans* salt Delépine prepared the salt *trans*-$K[Irpy_2(NO_3)Cl_3]$ (ref. 19, p. 185) [97b,c].

The corresponding bromo derivatives, all apparently *trans* form only — $[Ir(H_2O)py_2Br_3] \cdot 3\ H_2O$ (ref. 19, p. 180; ref. 22, p. 568) [77,78], $Ag_2H[Irpy_2(OH)Br_3]_3$ (ref. 19, p. 186) [77,78] and $Ag[Irpy_2(NO_3)Br_3] \cdot 3\ H_2O$ (ref. 19, p. 186) [77,78] were prepared by Mme. Delépine-Tard. The corresponding α-picoline derivative, $[Ir(H_2O)(\alpha\text{-pic})_2Cl_3]$ (one form only) (ref. 19, p. 178; ref. 22, p. 569), was prepared by Guillot [94]. After Delépine's death, his former student Fernande Larèze [98] substituted for the water molecule in *trans*-$[Ir(H_2O)py_2Cl_3] \cdot H_2O$ the molecules CH_3OH, C_2H_5OH, $(CH_3)_2CO$

and $(CH_3)_2SO$ thermally or photochemically and for the water molecule in *cis*-$[Ir(H_2O)py_2Cl_3] \cdot 2\ H_2O$ the molecule CH_3OH photochemically.

(6) $M[Irpy_2(C_2O_4)_2]$ (ref. 19, p. 187; ref. 22, p. 564). By heating either *cis*- or *trans*-$K_3[Ir(C_2O_4)_2Cl_2]$ (for one hour) or $K_3[Ir(C_2O_4)_3]$ (for four hours) with pyridine in a sealed tube at 130° C, Delépine obtained sulfur yellow crystals of *trans*-$K[Irpy_2(C_2O_4)_2]$, while from the mother liquor he obtained an amorphous, yellow, easily soluble product that presumably contains the *cis* isomer (ref. 59, pp. 158, 171) [58b,87]. Since he was unable to resolve the strychnine salt obtained from the crystalline salt, Delépine assigned to the yellow crystals the *trans* configuration (ref. 59, p. 162). Crystallization of the *trans* salt from the warm solution yields a dihydrate, which on heating to 100° C forms the anhydrous salt. On standing in the air, the dihydrate is regenerated. A hexahydrate is also known. Heating with aqua regia causes oxidation to *trans*-$[Ir^{IV}py_2Cl_4]$, while heating with hydrochloric acid to 100—130° C yields a crystalline precipitate of *trans*-$[Ir(H_2O)py_2(C_2O_4)Cl]$ and *trans*-$[Ir(H_2O)_2py_2Cl_2]$*trans*-$[Irpy_2Cl_4]$ and a yellow solution containing *trans*-$[Ir(H_2O)py_2Cl_2]Cl$ and traces of $K_2[IrpyCl_5]$.

The non-electrolytic compound $[Ir(H_2O)py_2(C_2O_4)Cl]$ (ref. 19, p. 181; ref. 22, p. 569; ref. 59, p. 167) [87] consists of pale chamois yellow needles insoluble in water and organic solvents. It dissolves slowly in aqueous ammonia, quickly in lukewarm potassium hydroxide, apparently by forming salts of the acid $H[Irpy_2(OH)(C_2O_4)Cl]$. The products obtained on heating the non-electrolyte with 1 : 1 hydrochloric acid at 130° C led Delépine to assign it the *trans* configuration. Heating for $1\frac{1}{2}$ h yields *trans*-$[Ir(H_2O)_2py_2Cl_2]Cl$ along with traces of $K_2[IrpyCl_5]$, while heating for an additional 3 h yields *trans*-$[Ir(H_2O)_2py_2Cl_2]$*trans*-$[Irpy_2Cl_4]$.

(7) $[Ir(H_2O)_2py_2Cl_2]X$ (ref. 19, p. 173; ref. 22, p. 570) and *$[Ir(H_2O)(OH)py_2Cl_2]$* (ref. 19, p. 180; ref. 22, p. 570). Orange crystals of $[Ir(H_2O)_2py_2Cl_2]Cl$ were prepared by Delépine by dissolving $[Ir(H_2O)(OH)py_2Cl_2]$ in aqueous HCl and concentrating the solution (ref. 59, pp. 165, 171) [87]. Silver nitrate precipitates only $\frac{1}{3}$ of the chlorine. The compound is stable only in strong hydrochloric acid solution. In water it reverts to the compound from which it was prepared

$$[Ir(H_2O)_2py_2Cl_2]Cl + H_2O \rightleftharpoons [Ir(H_2O)(OH)py_2Cl_2] + H_3O^+ + Cl^-$$

On long heating at 130° C with hydrochloric acid, it first reacts according to the equation

$$[Ir(H_2O)_2py_2Cl_2]Cl + HCl \rightarrow trans\text{-}H[Irpy_2Cl_4] + 2\ H_2O$$

and then reacts according to the equation

$$[Ir(H_2O)_2py_2Cl_2]Cl + trans\text{-}H[Irpy_2Cl_4] \rightarrow [Ir(H_2O)_2py_2Cl_2]trans\text{-}[Irpy_2Cl_4] + HCl$$

Delépine also prepared the hydroxide (ref. 59, pp. 167, 170) [87] and the *cis*-

tetrachlorodipyridineiridate(III) (ref. 59, p. 171). Delépine obtained $[Ir(H_2O)(OH)py_2Cl_2]$ by the action of ammonia on $[Ir(H_2O)_2py_2Cl_2]$ *trans*-$[Irpy_2Cl_4]$ or by HCl splitting off from $[Ir(H_2O)_2py_2Cl_2]Cl$ when treated with water (ref. 59, pp. 167, 169, 171) [87].

(c) Tripyridine complexes (ref. 19, p. 176; ref. 22, p. 567)

By refluxing pyridine for 50 h with orange (*cis*)$K[Irpy_2Cl_4]$ Delépine obtained both the *facial* or *cis* (1, 2, 3) and the *meridional* or *trans* (1, 2, 6) isomers of the non-electrolyte, trichlorotripyridineiridium(III), $[Irpy_3Cl_3]$ [58b] (ref. 59, pp. 172, 174). By using an autoclave at 130°C only 4 h are required. He separated the yellow isomers by extraction with boiling chloroform, in which the *trans* isomer is quite soluble. By starting with red (*trans*)$K[Irpy_2Cl_4]$ Delépine obtained only *trans*-$[Irpy_3Cl_3]$ together with an orange-red, chloroform-insoluble substance, the composition of which was close to $Irpy_3Cl_3$ and which was not investigated further. Delépine later obtained the *trans* isomer by heating *trans*-$[Ir(H_2O)py_2Cl_3] \cdot H_2O$ with pyridine for 1⅓ hours at 130°C [97c]. According to Ogawa [63], *cis*-$[Irpy_3Cl_3]$ is formed along with *cis*-pyH-$[Irpy_2Cl_4]$ by heating a solution of 1 mole of $H_2[Ir(H_2O)Cl_5] \cdot 6\,H_2O$ and 3 moles of pyridine. Kauffman et al. [88a] attempted to separate *cis*- from *trans*-$[Irpy_3Cl_3]$ by column chromatography but failed because of limited solubility in non-polar and moderately polar solvents.

More than thirty years after he had discovered the isomers of $[Irpy_3Cl_3]$, Delépine published several studies of the effect of light on these isomers (ref. 22, p. 569). He found that sunlight or diffuse daylight decomposes dilute solutions of *trans*-$[Irpy_3Cl_3]$ in chloroform rapidly — in a matter of minutes — while the same solutions can be preserved unchanged in the dark for five years [99]. The decomposition arises from the loss of a molecule of pyridine to give the radical *trans*-$Irpy_2Cl_3$ which then reacts to give a mixture of products — insoluble $Irpy_2Cl_3$ (by polymerization), *trans*-$[Ir(H_2O)py_2Cl_3]$ (by addition of water), *trans*-$pyH[Irpy_2Cl_4]$ (by addition of hydrogen chloride). Traces of $[Ir(H_2O)py_3Cl_2]Cl$ are also formed [100]. The ratio of the decomposition products obtained thus depends on whether the chloroform contains moisture (favors *trans*-$[Ir(H_2O)py_2Cl_3]$) or hydrogen chloride, also formed by irradiation of $CHCl_3$ (favors *trans*-$pyH[Irpy_2Cl_4]$). By irradiating solutions of *trans*-$[Irpy_3Cl_3]$ in solvents other than chloroform (CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CHCl_2, $Cl_2CHCHCl_2$, $Cl_2CHCO_2C_2H_5$, $C_6H_5CH_2Cl$) and obtaining the same products (as various solvates), Delépine showed that chloroform was not the cause of the reaction [101]. Furthermore, occurrence of the reaction in acetone and methyl ethyl ketone solutions showed that it is not restricted to chlorine-containing solvents. Acetone gave the compound *trans*-$Irpy_2Cl_3 \cdot C_3H_6O$, which can be viewed as *trans*-$[Ir(H_2O)py_2Cl_3]$ in which water has been replaced by acetone. In all these decompositions Delépine proved the presence of free pyridine as a product by precipitating it with *trans*-$H[Irpy_2Cl_4]$. He also found that irradiation of a dilute solution of *trans*-$[Irpy_3Br_3]$ in chloroform rapidly expels pyridine and yields an olive green crystalline precipitate of $(Irpy_2Br_3)_2 \cdot CHCl_3$ [102]. The compounds *cis*- and *trans*-$[Irpy_3Br_3]$ (ref. 22, p. 567) were prepared by Delépine-Tard [77,78]. The compound [Ir(α-picoline)$_3$Cl$_3$] (one form only, canary yellow) (ref. 19, p. 178; ref. 22, p. 567) was prepared by Guillot [94], while the corresponding compound of β-picoline was prepared by Delépine's student Larèze [103,104], who also prepared the compound $[Ir(H_2O)py_3Cl_2]Cl$ [105].

(d) Tetrapyridine complexes

Delépine isolated an amorphous yellow product of formula $[Irpy_4Cl_2]Cl$ (ref. 19, p. 173; ref. 59, p. 174) from mother liquor obtained in the preparation of *cis*- and *trans*-$[Irpy_3Cl_3]$ by heating *cis*-K$[Irpy_2Cl_4]$ with pyridine (Section C(iii)(c)). After separating the tripyridine complex, he evaporated the mother liquor to dryness, dissolved the residue in ethanol and after treatment with ether and filtration, he evaporated the solution to dryness. By heating *trans*-$[Irpy_3Cl_3]$ with aqueous pyridine he was unable to obtain compounds with a higher pyridine content.

Thirty years later, together with Mlle. Larèze, Delépine [106] obtained two apparently geometrically isomeric forms with the same composition. Heating a mixture of *trans*-K$[Irpy_2Cl_4]$, water, ethanol and pyridine on a water bath produced $[Irpy_4Cl_2][Irpy_2Cl_4]$ as a pink crystalline powder

$$trans\text{-}K[Irpy_2Cl_4] + 2\ py \rightarrow [Irpy_4Cl_2]Cl + KCl$$

$$[Irpy_4Cl_2]Cl + trans\text{-}K[Irpy_2Cl_4] \rightarrow [Irpy_4Cl_2]\ trans\text{-}[Irpy_2Cl_4]\downarrow + KCl$$

On heating this with additional pyridine and water at 130° C in an autoclave for $1\frac{1}{2}$ h they obtained a yellow solution which, after filtration and cooling, gave yellow lammelar crystals of $[Irpy_4Cl_2]Cl \cdot 6\ H_2O$ (Salt A)

$$[Irpy_4Cl_2]\ trans\text{-}[Irpy_2Cl_4] + 2\ py \rightarrow 2[Irpy_4Cl_2]Cl$$

They obtained chunky yellow isomeric tetrahydrated crystals (Salt B) by combining the filtrate from the crystallization with the unreacted material from the autoclave, reheating until all the material dissolved, and concentrating the solution. The first salt, on treatment with HNO_3, KI or NH_4SCN gave the corresponding nitrate, iodide or thiocyanate, whereas the second salt did not undergo such metatheses.

Later that same year Delépine and Larèze [107] reported an improved and simplified preparation for these isomers, involving refluxing a mixture of *trans*- or *cis*-trichlorodipyridineaquoiridium(III) (Section C(iii)(b)(5)), water, absolute ethanol (as an activator) and pyridine [108]

$$[Ir(H_2O)py_2Cl_3] + 2\ py \rightarrow [Irpy_4Cl_2]Cl + H_2O$$

The *trans* aquo complex gave good yields of both isomers A and B, while the *cis* isomer furnished a lesser yield of isomer A and a gummy mass which contained isomer B. Attempts to increase the number of molecules of pyridine beyond four were unsuccessful; $[Irpy_4Cl_2]Cl$ did not react with pyridine at

130°C and raising the temperature to 180°C yielded only [$Irpy_3Cl_3$]. The absorption spectrum of Delépine's [$Irpy_4Cl_2$]Cl obtained in 1923 [59] was measured by Jørgensen [43], who characterized it as the *trans* isomer, while the spectra of Delépine and Larèze's compounds [106,107] were measured by Schmidtke [109,110]. Mlle. Larèze also studied the effect of irradiation on [$Irpy_4Cl_2$]X and prepared the compounds [Ir(β-picoline)$_4Cl_2$]X, where X = Cl · 5 H_2O and NO_3 · 2 H_2O [103].

(iv) Oxalato complexes

The compounds M[$Irpy_2(C_2O_4)_2$] and [$Ir(H_2O)py_2(C_2O_4)Cl$] have already been discussed in Section C(iii)(b)(6). In general, the oxalato complexes of iridium are quite stable (ref. 22, p. 549). Of the three series investigated by Delépine that are discussed below, the first two were resolved into optically active isomers [58b].

(a) $M_3[Ir(C_2O_4)_3]$ (ref. 19, pp. 81, 109; ref. 22, p. 553)

The parent acid of this series, $H_3[Ir(C_2O_4)_3] \cdot XH_2O$ was first prepared by Gialdini [112,113] by the action of excess oxalic acid on freshly precipitated $IrO_2 \cdot 2\ H_2O$

$$2\ IrO_2 + 7\ H_2C_2O_4 \rightarrow 2\ H_3[Ir(C_2O_4)_3] + 2\ CO_2\uparrow + 4\ H_2O$$

Delépine prepared the orange-red potassium salt, $K_3[Ir(C_2O_4)_3] \cdot 4\ H_2O$, by the action of potassium oxalate on either aqueous potassium hexachloroiridate(III) or (IV) or on aqueous *trans*-potassium dichlorodioxalatoiridate(III) at 130°C in an autoclave for 8 h (ref. 59, p. 152) [65b,c]

$$2\ K_2[Ir^{IV}Cl_6] + 7\ K_2C_2O_4 \rightarrow 2\ K_3[Ir^{III}(C_2O_4)_3] + 12\ KCl + 2\ CO_2\uparrow$$

$$K_3[IrCl_6] + 3\ K_2C_2O_4 \rightarrow K_3[Ir(C_2O_4)_3] + 6\ KCl$$

$$trans\text{-}K_3[Ir(C_2O_4)_2Cl_2] + K_2C_2O_4 \xrightarrow{130°C} K_3[Ir(C_2O_4)_3] + 2\ KCl$$

A recent publication [114] criticizes both Gialdini's and Delépine's methods for giving low yields and presenting difficulties in separation. It modifies Gialdini's method by following it by passage of the solution through an ion exchange column in the calcium form. The method is based on the separation of soluble $Ca_3[Ir(C_2O_4)_3]_2$ from insoluble CaC_2O_4. On refluxing in an aqueous solution containing potassium chloride, the potassium salt is partially converted into the corresponding dichlorodioxalato salts in accordance with the following equilibrium reaction [65c]

$$K_3[Ir(C_2O_4)_3] + 2\ KCl \rightleftharpoons cis\text{- and } trans\text{-}K_3[Ir(C_2O_4)_2Cl_2] + K_2C_2O_4$$

On crystallizing an aqueous solution of $K_3[Ir(C_2O_4)_3]$ that is almost saturated with KCl, Delépine obtained yellow, strongly double-refracting rhombohedra of the composition $KCl \cdot 2\ K_3[Ir(C_2O_4)_3] \cdot 8\ H_2O$, which decompose in solution [65a,c]. He was able to syncrystallize $K_3[Ir(C_2O_4)_3] \cdot 4\frac{1}{2}\ H_2O$ with the triclinic rhodium(III) and ruthenium(III) potassium trioxalato salts, which also contain $4\frac{1}{2}$ H_2O.

Delépine confirmed his postulated octahedral configuration for iridium(III) by resolving $K_3[Ir(C_2O_4)_3]$ by fractional crystallization of the strychnine salt [65]. Additional confirmation was later obtained by resolutions of other compounds by Delépine, e.g., *cis*-$K_3[Ir(C_2O_4)_2Cl_2]$ (Section C(iv)(b)), and by others [115]. The optically active strychnine trioxalatoiridates(III) are differently hydrated and in the anhydrous state possess $[\alpha]_D$ values of +11.8° and −56.4°, respectively. From these by treatment with KOH solution, Delépine obtained (+)- and (−)-$K_3[Ir(C_2O_4)_3] \cdot 2\ H_2O$, $[\alpha]_D = \pm 82°$; by treatment with $Ba(OH)_2$ solution, he obtained (+)- and (−)-$Ba_3[Ir(C_2O_4)_3] \cdot 15\ H_2O$, $[\alpha]_D = \pm 62.5°$. He was able to obtain the optically active silver salts only as amorphous, granular masses.

The active salts can be heated to 100°—125°C without decrease in rotatory power. Their solutions exhibit no racemization even after 40 days at room temperature but at 100°C their rotations decrease by several percent per hour. They show the same anomalous rotatory dispersion [116,117] as the trioxalato compounds of chromium(III) [118], rhodium(III) and cobalt(III) [119]. The (+)-potassium salt exhibits circular dichroism and a positive Cotton effect [120—122]. The optically active racemate $K_3[Rh_{0.5}Ir_{0.5}(C_2O_4)_3] \cdot 4\frac{1}{2}\ H_2O$ is discussed in Section E.

(b) $M_3[Ir(C_2O_4)_2Cl_2]$ (ref. 19, pp. 82, 113, 141; ref. 22, p. 551)

Salts of this series, the longest known of all oxalato complexes of iridium, were first discovered by Vèzes [55b], investigated by Vèzes and his student Duffour [123] and then by Duffour alone [124,125]. The monohydrated potassium salt may be obtained by treating a boiling solution of either potassium hexachloroiridate(III) [123—125] or hexachloroiridate(IV) [55b] with potassium oxalate

$$\underset{\text{brownish green}}{K_3[IrCl_6]} + 2\ K_2C_2O_4 \rightarrow \underset{\text{red}}{K_3[Ir(C_2O_4)_2Cl_2]} + 4\ KCl$$

$$2\ \underset{\text{red}}{K_2[Ir^{IV}Cl_6]} + 5\ K_2C_2O_4 \rightarrow 2\ \underset{\text{red}}{K_3[Ir^{III}(C_2O_4)_2Cl_2]} + 2\ CO_2\uparrow + 8\ KCl$$

If iridium(III) possesses an octahedral configuration, compounds of type $M(\overline{AA})_2B_2$, where $\overline{AA}$ is a symmetrical bidentate ligand, should exist in two geometrically isomeric forms. Reasoning that, according to probability, the synthetic method of Vèzes and Duffour [123] should yield a mixture of *cis* and *trans* isomers in the ratio of 4 : 1, Delépine [126] repeated their work and found that potassium hexachloroiridate(III) reacts completely with potassium oxalate in 10 min at 130°C rather than the longer time required at 100°C [123,124]. In accordance with his expectations, Delépine obtained a 60% yield of the salt previously prepared by Vèzes and Duffour, which he considered the *cis* isomer, as well as 12—15% of a new salt, which he considered the *trans* isomer, from the mother liquor obtained from the crystallization of the *cis* salt. He also obtained 25—28% of an amorphous, orange-red, very soluble substance of composition $K_7Ir_3Cl_4(C_2O_4)_6 \cdot 5\ H_2O$ ($=3\ K_3[Ir(C_2O_4)_2Cl_2] - 2\ KCl$), which nitric acid first turns deep blue, then deep red as the *cis* and *trans* salts are formed. Delépine [65] also obtained the *trans* isomer by heating potassium trioxalatoiridate(III) solution with excess potassium oxalate at 130°C

$$K_3[Ir(C_2O_4)_3] + 2\ KCl \xrightarrow{130°C} K_3[Ir(C_2O_4)_2Cl_2] + K_2C_2O_4$$

The *cis* salt forms deep red, monoclinic, monohydrated prismatic crystals with imperceptible pleochroism. Delépine found the red *trans* salt to form both monoclinic needles and triclinic prisms, both tetrahydrated with a transition temperature >40°C, as well as a pentahydrated monoclinic form, which separates from solutions near 0°C (ref. 59, pp. 150, 157) [58b,127]. The aqueous solution of the *cis* salt, which is much more intensively colored than that of the *trans* salt, is so stable that evaporation to dryness yields the unchanged salt. Either isomer can be transformed into the other by heating to 130°C, but the *trans* to *cis* isomerization is slower than the reverse process (ref. 59, p. 152). Heating the *trans* salt with excess potassium oxalate at 130°C yields $K_3[Ir(C_2O_4)_3]$. Solutions of the two isomers behave differently with solutions of $AgNO_3$ and $TlNO_3$.

Delépine [58b,59,126] proved his assignment of configuration by resolving the less soluble *cis* isomer and failing to resolve the more soluble *trans* isomer. Resolution was accomplished by means of the *cis*-strychnine salts; the less soluble salt corresponds to the (—)-isomer and the more soluble one to the (+)-isomer. Treatment of the strychnine salts with potassium hydroxide or potassium iodide solutions yields (+)- or (—)-*cis*-$K_3[Ir(C_2O_4)_2Cl_2] \cdot 3\ H_2O$, the orthorhombic, prismatic crystals [127] of which are much larger and more soluble than those of the racemate. Although the single water molecule in the racemate is not lost at 100°C and only with great difficulty at much higher temperatures, the optically active salts lose their water easily at 100°C. Although their rotatory power is low ($[\alpha]_D = +20.8°$ and $-23.8°$ for the (+)- and (—)-salts, respectively), it is permanent; no noticeable racemization occurs in aqueous solutions at room temperature in the course of three years. However, racemization is complete after long heating at 130°C.

(c) $M_3[Ir(C_2O_4)_2(NO_2)_2]$

In 1962 Delépine and Larèze [128] reported that in trying to prepare $K_3[Ir(C_2O_4)(NO_2)_2Cl_2]$ (ref. 19, p. 115; ref. 22, p. 550) by heating aqueous $K_3[Ir(C_2O_4)_2Cl_2]$ (Section C(iv)(b)) with excess potassium nitrite according to the directions of Vèzes and Duffour [55b,123—125], they obtained instead clear yellow crystals of the new compound $K_3[Ir(C_2O_4)_2(NO_2)_2]$, which by analogy with other systems they assumed to possess the *cis* configuration [129], although they started with the *trans*-dichlorodioxalato salt.

They prepared the silver and thallium (I) salts of the new anion but failed to resolve it by means of the strychnine salt. They assumed that Vèzes and Duffour had used the compound $K_3[Ir(C_2O_4)Cl_4] \cdot H_2O$ (ref. 19, p. 114; ref. 22, p. 549) as starting material rather than $K_3[Ir(C_2O_4)_2Cl_2]$, a supposition confirmed by Mathieu's work [130].

D. RHODIUM COMPLEXES

The element rhodium [20,23] furnished Delépine with complexes that are often similar to those of iridium, both in formulas — chloro salts as well as pyridine and oxalato complexes — and in the types of isomerism encountered. The lesser strength of the rhodium—ligand bond compared to the iridium—ligand bond, however, makes the preparation of many rhodium compounds more difficult than that of their iridium analogues, and some iridium complexes have no rhodium counterparts. Delépine's work on rhodium was much less extensive than his work on iridium, but he also made a great contribution to the chemistry of rhodium through the varied research of his student Pierre Poulenc, who described more than forty rhodium complexes in his thesis of 1935 [131]. Poulenc carried out extensive research on bromo compounds as well as polynuclear complexes of rhodium such as $[Rh_2Br_9]^{3-}$, $[Rh_2Br_{10}]^{4-}$ and $[Rh_2Br_{13}]^{5-}$. In a similar manner Delépine exercised a profound influence on the chemistry of ruthenium through the work of his student Raymond Charonnat [132].

(i) Chloro complexes

Inasmuch as the chlorides and chloro complexes are probably the most convenient starting materials for the preparation of various rhodium compounds, it is not surprising that Delépine occupied himself with this important class of derivatives. In fact, his review of 1927, "Chlorures et chlorosels de rhodium" [133], summarizing both his work and that of others, fulfilled the same function for the chloro salts of rhodium as his review of 1917, "Sur les chlorures et les chlorosels de l'iridium" [39], had done for those of iridium. In fact, it might be mentioned in passing that Delépine's granddaughter, Mme. Claude Ouannès, née Catherine Tard, investigated the action of alcohol on the reactions of halogen salts of rhodium [134].

The chemistry of the chlorides of rhodium(III) is extremely complicated; both insoluble, anhydrous (ref. 20, p. 54; ref. 23, p. 325) and soluble, hydrated forms (ref. 22, p. 56; ref. 23, p. 327) [135—137] are known. The hydrated chloride, obtained by the action of hydrochloric acid on rhodium(III) oxide, is contaminated with alkaline chloride from the traces of alkali always contained in the oxide. Delépine [133] found that this solution does not initially contain $RhCl_3 \cdot n\ H_2O$ but a complex such as $[Rh(H_2O)_6]Cl_3$, which imparts to the solution a yellow color. Slowly in the cold, more rapidly on heating, the solution becomes red as atoms of chlorine replace the water molecules in the coordination sphere

$$[Rh(H_2O)_6]Cl_3 \rightarrow RhCl_3 + 6\ H_2O$$

Ammonia converts $RhCl_3 \cdot n\ H_2O$ into $[Rh(NH_3)_5Cl]Cl_2$, while alkali metal chlorides convert it into chloro salts such as $M_3[RhCl_6]$ and $M_2[Rh(H_2O)Cl_5]$. When Delépine [133a] heated $Na_3[RhCl_6] \cdot 12\ H_2O$ or $(NH_4)_3[RhCl_6] \cdot 1\frac{1}{2}\ H_2O$ for a long time with concentrated sulfuric acid, he obtained a brick red powder, which was not the anhydrous chloride as Claus had supposed, but instead a basic chloride of composition $RhCl_{2.88}(OH)_{0.12} \cdot 2.5\ H_2O$ (ref. 20, p. 59; ref. 23, p. 328), that was later also obtained by Grube and Autenrieth [138]. By heating this compound at 200°C with gaseous hydrogen chloride, Delépine obtained a water-soluble chloride of formula $RhCl_3 \cdot \frac{2}{3}\ H_2O$, which on heating to 360°C with gaseous hydrogen chloride yields a deliquescent substance, the composition of which is close to anhydrous $RhCl_3$ but which is easily soluble in cold water (ref. 20, p. 57) [133a].

The chloro salts of rhodium(III) (ref. 23, p. 334) are very similar to those of iridium(III) (Section C(ii)) and likewise exist as two types — the hexachlororhodates(III), $M_3[RhCl_6] \cdot n\ H_2O$, of which the Li (anhydrous and 12 H_2O; ref. 20, p. 72; ref. 23, p. 336; [133]), Na (anhydrous and 12 H_2O; ref. 20, p. 73; ref. 23, p. 335; [28a]), K (anhydrous, 1 H_2O and 2 H_2O; ref. 20, p. 79; ref. 23, p. 337; [133]), NH_4 (1 and $1\frac{1}{2}\ H_2O$; ref. 20, p. 87; ref. 23, p. 337; [133]), Rb (1 H_2O; ref. 20, p. 94; ref. 23, p. 338; [133]) and Cs (anhydrous; ref. 23, p. 338; [29]) salts are known, and the pentachloroaquorhodates(III), $M_2[Rh(H_2O)Cl_5]$, of which the K (anhydrous; ref. 20, p. 78; ref. 23, p. 336; [133]), NH_4 (anhydrous; ref. 20, p. 87; ref. 23, p. 337; [133]), Rb (anhydrous; ref. 20, p. 94; ref. 23, p. 338; [133]) and Cs (anhydrous; ref. 20, p. 95; ref. 23, p. 338; [133]) salts are known. As in the case of the iridium salts, evaporating the hexachloro salts in aqueous solution yields the pentachloroaquo salts in those cases in which the latter exist. It is only in the presence of high concentrations of alkali metal chlorides that hexachloro salts can be obtained in accordance with the equilibrium reaction [133]

$$M_2[Rh(H_2O)Cl_5] + MCl \rightleftharpoons M_3[RhCl_6] + H_2O$$

The parent acid $H_2[RhCl_5] \cdot 4\ H_2O$ or $H_2[Rh(H_2O)Cl_5] \cdot 3\ H_2O$ (the formula is not certain) has been obtained by evaporating a solution of rhodium(III) chloride in HCl solution in a hydrogen chloride atmosphere in a desiccator over sulfuric acid (ref. 23, p. 334) [138]. Just as silver nitrate reacts with a pentachloroaquoiridate(III) to yield $Ag_3[Ir(OH)Cl_5]$ (Section C(ii)), Delépine found that a pentachloroaquorhodate(III) reacts similarly to yield $Ag_3[Rh(OH)Cl_5]$ (ref. 20, p. 101; ref. 23, p. 339) [133a]

$$(NH_4)_2[Rh(H_2O)Cl_5] + 3\ AgNO_3 \rightarrow Ag_3[Rh(OH)Cl_5] + 2\ NH_4NO_3 + HNO_3$$

In the course of his research on the chloro salts of rhodium(III) [133], Delépine showed the striking similarity between these complexes and those of iridium(III) in crystalline form, solubility, behavior on heating, interaction with hydrogen on heating, etc. The red color of the rhodium salts in comparison with the greenish red color of the iridium compounds serves to distinguish the two series.

One of the problems in the practical synthetic chemistry of the platinum metals is how to produce compounds from the free metals. Rhodium, one of the rarest and most expensive of the platinum metals, is not attacked by acids or even aqua regia, and its dissolution in alkaline fusion mixtures (e.g., Na_2CO_3 and KNO_3) or in molten salts (e.g., $KHSO_4$) is inefficient and tedious. Delépine was able to produce rhodium chloride by heating the metal in the vapors of ammonium chloride in the presence of oxygen [29]. He also succeeded in preparing hexachlororhodates(III) by heating a mixture of the metal and an alkali metal chloride with carbon tetrachloride vapor at 550—600°C [30]. By employing high temperatures, excess sodium chloride and mechanical agitation of the reaction mixture, Kauffman and Tsai [139] were able to convert rhodium metal almost quantitatively to hexachlororhodate(III) in one chlorination step

$$2\ Rh + 6\ NaCl + 3\ Cl_2 \xrightarrow{900^\circ C} 2\ Na_3[RhCl_6]$$

Reaction of $Na_3[RhCl_6]$ solution with excess concentrated potassium chloride solution, followed by evaporation to incipient crystallization yields $K_3[RhCl_6]$ H_2O [133a]. Delépine obtained the anhydrous salt by heating the monohydrate to 100—120°C [133a].

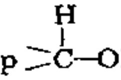
(ii) Pyridine complexes

During the late nineteenth century numerous complexes of the platinum metals with pyridine and other nitrogenous heterocyclic bases were studied in considerable detail. In particular, the extensive work on rhodium by Sophus Mads Jørgensen (1837—1914) [140—142], Alfred Werner's primary scientific adversary, deserves mention. But, as was the case with iridium (Section C(iii)), the most important series of compounds in the development of the stereochemistry of rhodium(III) from the viewpoint of Werner's coordination theory were the mixed pyridine—chlorine complexes [143]. When Delépine first began his systematic study of these compounds in 1929 [144], the most important pyridine complex of rhodium known was *trans*-$[Rhpy_4Cl_2]Cl$, first prepared in 1883 by Jørgensen (ref. 20, p. 142; ref. 23, p. 448) [145], from which Chugaev [146] had prepared the compound $[Rhpy_3(C_2O_4)Cl]$ (ref. 20, p. 149; ref. 23, p. 448). By the end of the 1930s, largely as a result of the work of Delépine and of Poulenc, the entire series: $M_2[RhpyX_5]$ (Br only), $M[Rhpy_2X_4]$, $M[Rh(H_2O)py_2X_3]$, $[Rhpy_3X_3]$, $[Rhpy_4X_2]X$, where X = an acid radical such as Cl or Br, had been well investigated [147]. By 1957, Jørgensen [43] had applied ligand field theory to rhodium(III)—pyridine complexes. As Delépine had noted [144], the rhodium(III)—pyridine complexes are completely analogous to the corresponding compounds of iridium(III); the most striking difference is in the rates of reaction.

By means of reactions corresponding to those that he had used with iridium(III), viz., the action of pyridine on the hexachloro salts (Section C(iii)), Delépine [144] obtained dipyridine and tripyridine chloro complexes of rhodium(III). In this case, however, the rates of reaction are much more rapid — so fast, in fact, that the monopyridine derivatives $M_2[RhpyCl_5]$ cannot be obtained (the compounds $M_2[RhpyBr_5]$ (M_2 = $(pyH)_2$, pyHCs and $[Rh(NH_3)_5Cl]$) were later prepared by Poulenc) (ref. 20, p. 152; ref. 23, p. 438) [131].

By heating $Na_3[RhCl_6] \cdot 12\ H_2O$ solution with pyridine (molar ratio 1 : 6) Delépine [144] obtained a yellow crystalline mixture, from which he extracted $[Rhpy_3Cl_3]$ with a $CHCl_3$—C_2H_5OH mixture (6 : 1), while the compound $[Rh_2(H_2O)py_4Cl_6]$ remained undissolved. The orange-yellow trichlorotripyridine derivative (ref. 20, p. 147; ref. 23, p. 446) corresponds to the analogous *trans*-iridium(III) compound; like the latter it crystallizes with the two molecules of chloroform. Heating it with ammonia or pyridine results in the formation of $[Rh(NH_3)_5Cl]Cl_2$ (ref. 20, p. 134; ref. 23, p. 372) or $[Rhpy_4Cl_2]Cl$ (ref. 20, p. 142; ref. 23, p. 448), respectively. Heating it with aqueous pyridine in sealed tubes at 130°C yields bright yellow leaflets of *trans*-$[Rhpy_4Cl_2]Cl \cdot 6\ H_2O$. *trans*-Trichlorotripyridinerhodium(III) in three different crystalline forms — octahedral, prismatic needles — can also be obtained by irradiating or heating a saturated solution of *trans*-$[Rhpy_4Cl_2]Cl$ [131].

Since Delépine's early experiments [144], $[Rhpy_3Cl_3]$ has been obtained in two geometrically isomeric forms — a red-orange *cis* or *fac* (1, 2, 3) isomer and a yellow *trans* or *mer* (1, 2, 6) isomer [148—150]. Recently Kauffman et al. were able to separate mixtures of the two isomers by adsorption chromatography on alumina [88a] and by thin-layer chromatography on silica gel [97d].

In his experiments of 1929 Delépine noted that the formation of *trans*-$[Rhpy_4Cl_2]Cl$ is greatly catalyzed by the presence of ethanol [144], and almost 25 years later he extended his observations to include a study of the action of many other organic species containing the group  $>\overset{\overset{\displaystyle H}{|}}{C}-OH$ on the pyridination of $Na_3[RhCl_6]$ [151]. In other reactions of platinum metal compounds, the methylene hydrogen atom in ethanol may serve as a two-electron reductant, and Gillard et al. [152] believed that the catalytic species is either a rhodium(I) complex or a rhodium(III) hydrido complex. Delépine's extensive works on catalytic hydrogenation of organic compounds [153—167] fall outside the scope of this article, but a brief discussion of catalytic hydrogenation using rhodium compounds can be found in Gillard's review article [143].

The *tetrachlorodipyridinerhodates(III)*, $M[Rhpy_2Cl_4]$ (ref. 20, p. 149; ref. 23, p. 440), like the corresponding iridium(III) compounds, occur in two isomeric forms, which, without exception, are similar to their iridium analogues — in color, solubility, hydration, metatheses, etc. [144]. The pyridinium salts are formed by the action of pyridine on $Na_3[RhCl_6]$ in the presence of pyridinium chloride at room temperature. Without pyridinium chloride, $[Rh(H_2O)py_3Cl_2][Rhpy_2Cl_4]$ is also formed. Extraction with hot water leaves the less soluble *trans* salt, while the *cis* salt hydrolyzes to form *cis*-$[Rh(H_2O)py_2Cl_3]$. The *trans*-pyridinium salt likewise forms *trans*-$[Rh(H_2O)py_2Cl_3]$ with boiling water (ref. 20, p. 147; ref. 23, p. 443). From *cis*- and *trans*-$pyH[Rhpy_2Cl_4]$, Delépine prepared the corresponding potassium, ammonium, and silver salts. The red *trans* salts are less soluble in water and less decomposable by boiling water than are the yellow-orange *cis* salts. However, both isomeric series are much less stable than their iridium analogues; their isolation is difficult because of their tendency to hydrolyze

$$M[Rhpy_2Cl_4] + H_2O \rightarrow [Rh(H_2O)py_2Cl_3] + MCl$$

The *cis*- and *trans*-trichlorodipyridineaquorhodium(III) compounds react with silver nitrate to form crystalline compounds *cis*- and *trans*-$Ag[Rhpy_2(NO_3)Cl_3]$ (ref. 20, p. 150; ref. 23, p. 440) [144], which act as weak pseudo-acids, dissolving in bases to yield *cis*- and *trans*-$M[Rhpy_2(OH)Cl_3]$ salts, which can react with acids to regenerate the neutral complexes.

Delépine [144] found that all the above di-, tri- and tetrapyridine compounds are rapidly decomposed by ammonia on heating, or even at room temperature after some time, with expulsion of the pyridine to yield $[Rh(NH_3)_5Cl]Cl_2$ although pyridine is not similarly displaced from the corresponding complexes of iridium (Section C(iii)). Furthermore Delépine was unable to prepare *cis*- and *trans*-$[Rh^{IV}py_2Cl_4]$, similar to *cis*- and *trans*-$[Ir^{IV}py_2Cl_4]$ (Section C(iii)(b)(2)).

Beginning in 1953 [168], almost a quarter of a century after his first work on the rhodium(III)—pyridine complexes, Delépine began a series of experiments on the effect of light on solutions of these compounds [79,80,102,168]. The results are similar to those obtained with the corresponding iridium complexes (Section C(iii)(c)). Solutions of *trans*-$[Rhpy_3Cl_3]$ in chloroform decompose in sunlight to lose one molecule of pyridine yielding polymeric $[Rhpy_2Cl_3]_n$. The presence of water leads to the formation of *trans*-$[Rh(H_2O)py_2Cl_3]$, while hydrochloric acid yields *trans*-$pyH[Rhpy_2Cl_4]$, $[Rhpy_2Cl_3]_n$, and *trans*-$[Rh(H_2O)py_2Cl_3]$. Pyridine retards the decomposition and leads to the formation of *trans*-$[Rhpy_4Cl_2]Cl$ and $[Rhpy_2Cl_3]_n$. Decomposition of *trans*-$[Rhpy_3Cl_3]$ in different solvents yields the following products: CH_2Cl_2—$[Rh_2(H_2O)py_4Cl_6]$ and $[Rhpy_2Cl_3]_n$; $CHCl_2CHCl_2$—$[Rhpy_2Cl_3] \cdot \frac{1}{2} C_2H_2Cl_4$ and $[Rhpy_2Cl_3] \cdot \frac{1}{4} C_2H_2Cl_4$; $(CH_3)_2CO$—$Rh\{(CH_3)_2CO\}py_2Cl_3$ and other products [168]. Delépine also found that a chloroform solution of *trans*-$[Rhpy_3Br_3]$ rapidly becomes turbid on exposure to light and forms a brown precipitate of the composition *trans*-$[Rhpy_2Br_3] \cdot CHCl_3$ [102].

On exposure to light, aqueous solutions of *trans*-$K[Rhpy_2Cl_4]$ decompose to the extent of more than 90% to yield *trans*-$[Rh(H_2O)py_2Cl_3]$ and KCl [79]. Similar irradiation of aqueous solutions of *cis*-$K[Rhpy_2Cl_4] \cdot H_2O$ yields *cis*-$[Rh(H_2O)py_2Cl_3]$ after two days. The same reaction occurs in the dark in the course of four months [80]. Mlle. Larèze studied the effect of irradiation on *trans*-$[Rhpy_4Cl_2]X$ where $X = Cl$ or NO_3 [111].

(iii) Oxalato complexes

The commonest trioxalatorhodate(III) is the potassium salt, $K_3[Rh(C_2O_4)_3] \cdot 4\frac{1}{2} H_2O$ (ref. 20, p. 83; ref. 23, p. 427), obtained by saturating a concentrated and boiling solution of potassium hydrogenoxalate with freshly hydrated rhodium(III) oxide [170—172]

$$3\ KHC_2O_4 + Rh(OH)_3 \rightarrow K_3[Rh(C_2O_4)_3] + 3\ H_2O$$

While the formation of $H_3[Ir(C_2O_4)_3]$ requires boiling $Ir(OH)_3$ in $H_2C_2O_4$ solution for 30—40 h [112,113] (Section C(iv)), the above reaction is rapid [170]. Delépine obtained $K_3[Rh(C_2O_4)_3] \cdot 4\frac{1}{2}\ H_2O$ by heating a solution containing $K_2C_2O_4$ and either $K_2[Rh(H_2O)Cl_5]$ or $K_3[RhCl_6]$ in a molecular ratio of 3 : 1 [169]. He found that the compound loses $3\frac{1}{2}$ molecules of water at 150°C and all its water at 190°C [169]. By crystallizing the salt in the presence of potassium chloride just slightly below saturation, Delépine [169] obtained crystals of the composition $KCl \cdot 2\ K_3[Rh(C_2O_4)_3] \cdot 8\ H_2O$, which are isomorphous with the corresponding iridium salt [127]. This salt loses 7 molecules of water at 130°C and 8 molecules at 150°C; with silver nitrate in nitric acid solution it yields a precipitate of silver chloride [169].

Werner and Poupardin [171] resolved potassium trioxalatorhodate(III) with strychnine nitrate and isolated the optically active sodium, rubidium and barium salts. Some question has risen about the number of molecules of water of crystallization contained in optically active $K_3[Rh(C_2O_4)_3]$. Whereas Werner and Poupardin [171] and Jaeger [173] claimed only one molecule, Delépine [174] and Charonnat [175], on the basis of isomorphism with the corresponding iridium salt whose water content was well established, claimed two molecules. Werner considered his resolution as evidence for an octahedral configuration for rhodium(III) with coordination number six, whereas Charonnat [175], on the basis of the formula $K_3[Rh(H_2O)_2(C_2O_4)_3]$, proposed a coordination number of eight, together with a structure that would require two additional isomers, which have never been found.

By treating a 10% aqueous solution of $K_3[Rh(C_2O_4)_3]$ with a 25% aqueous solution of $AgNO_3$ containing somewhat more than the equivalent amount of $AgNO_3$, Delépine obtained orange needles of the composition $KAg_5[Rh(C_2O_4)_3]_2 \cdot 6\ H_2O$, which lose the water of hydration at 110°C (ref. 20, p. 101; ref. 23, p. 429) [169]. Potassium trioxalatoiridate(III) and potassium trioxalatocobaltate(III) give similarly composed products on precipitation with $AgNO_3$. Recrystallization of the rhodium salt from warm water in the presence of $AgNO_3$ yields products poorer in potassium, which approach the composition $Ag_3[Rh(C_2O_4)_3]$.

The dichlorodioxalatorhodates(III) are strictly analogous to the corresponding iridium(III) salts and, like the latter (Section C(iv)(b)), occur in two geometrically isomeric forms (ref. 20, p. 86; ref. 23, p. 430). Both series were first discovered by Delépine in 1929 [169]. Boiling a solution of $K_2[Rh(H_2O)Cl_5]$ with KHC_2O_4 for half an hour and then concentrating the solution first yields orange-red *cis*-$K_3[Rh(C_2O_4)_2Cl_2] \cdot H_2O$, which may be recrystallized from hot water. It only partially loses its water of hydration at 150°C. Yellow *trans*-$K_3[Rh(C_2O_4)_3] \cdot 4\ H_2O$ is formed at the end of the crystallization of the *cis* salt. It may be obtained more easily by boiling a solution of the *cis* salt for a half hour with one-tenth its weight of potassium chloride. When the solution is concentrated, some *cis* salt is formed, followed by needles of *trans* salt, which, on recrystallization from cold water, are obtained in the form of brownish, orange-red prisms. The four molecules of water of hydration are lost at 100°C.

Although Delépine was able to resolve *cis*-$K_3[Ir(C_2O_4)_2Cl_2]$ with strychnine (Section C(iv)(b)), he was unable to resolve the corresponding rhodium salt. Like the corresponding iridium salts, the *cis* and *trans* rhodium compounds may be differentiated by the precipitates which they form with $AgNO_3$ and $TlNO_3$. With the first reagent, the *cis* salt yields orange-yellow crystals, while the *trans* salt changes gradually into pale red-orange parallelogram plates. The composition of the first product corresponds to $KAg_5[Rh(C_2O_4)_2Cl_2] \cdot 2\ H_2O$, while the second contains more silver [169]. With $TlNO_3$, the *cis* salt yields brown-orange needles, while the *trans* salt gives red parallelopiped crystals.

E. "ACTIVE RACEMATES"

Among the techniques available for the determination of absolute configuration of complexes may be listed "active racemates", the Cotton effect, stereospecificity and "anomalous X-ray diffraction" [176,177]. The first technique is associated with the name of Delépine, whose long years of experience with the formidable problems involved in the separation, differentiation and identification of very similar substances led him to devise this powerful method for resolving and determining the configuration of optically active homeomers. Since definitive proof of structure is usually based on more than one line of evidence, Delépine's development of the method of "active racemates" was a welcome and significant contribution to stereochemistry [178—181].

In his first publication on the subject [182], dating from 1921, Delépine discussed the previous literature and proposed a more general definition of a racemic compound. In his view, a crystalline racemic mixture composed of dextrorotatory molecules of one compound and levorotatory molecules of a compound isomorphous with it will usually exhibit optical activity because in most cases the rotatory powers of the different isomorphous species will not be the same and hence will not balance out by compensation. Delépine discussed a number of examples of such "active racemates" and concluded "that one can call racemic a crystalline structure composed of an equal number of dextro- and levorotatory molecules. Optical activity is only an accessory phenomenon depending upon the nature of the two kinds of molecules; it is zero in case these two are simply enantiomorphic" [182].

For the rotatory power of an "active racemate" Delépine derived the formula

$$[\alpha]_r = \frac{m_a[\alpha]_a - m_b[\alpha]_b}{m_a + m_b}$$

where $[\alpha]_r$, $[\alpha]_a$ and $[\alpha]_b$ are the specific rotations of the "active racemate", of component a and component b, respectively, and m_a and m_b are the molecular weights of components a and b, respectively. He verified his suppositions by preparing "active racemates" of the two following double pairs of enantiomorphs

$$(1)\ \begin{cases} (+)\text{- and } (-)\text{-}K_3[Ir(C_2O_4)_3] \\ (+)\text{- and } (-)\text{-}K_3[Rh(C_2O_4)_3] \end{cases}$$

$$(2)\ \begin{cases} (+)\text{- and } (-)\text{-}Ca(C_{10}H_{14}OCl.SO_3)_2 & \text{(chlorocamphorsulfonate)} \\ (+)\text{- and } (-)\text{-}Ca(C_{10}H_{14}OBr.SO_3)_2 & \text{(bromocamphorsulfonate)} \end{cases}$$

and measuring the optical activities. For example, from solutions of either (+)-$K_3[Ir(C_2O_4)_3] \cdot 2\ H_2O$ (1.59 g.) and (−)-$K_3[Rh(C_2O_4)_3] \cdot 2\ H_2O$ (1.35 g.) or of (−)-$K_3[Ir(C_2O_4)_3] \cdot 2\ H_2O$ (1.18 g.) and (+)-$K_3[Rh(C_2O_4)_3] \cdot 2\ H_2O$ (1.02 g.), he obtained orange crystals of $K_3[Rh_{0.5}Ir_{0.5}(C_2O_4)_3] \cdot 4\frac{1}{2}\ H_2O$, which, like the corresponding racemic orange-yellow iridium and red rhodium salts, belong to the triclinic system. For this "active racemate" he obtained the value of $[\alpha]_D = +39.9°\ (-39.5°)$, which agrees closely with the value of $[\alpha]_D = +(-)39.8°$ calculated from the rotations of the starting materials. With potassium chloride the aqueous solution forms rhombohedral crystals analogous to the salts $KCl \cdot 2\ K_3[Rh(C_2O_4)_3] \cdot 8\ H_2O$ and $KCl \cdot 2\ K_3[Ir(C_2O_4)_3] \cdot 8\ H_2O$ with somewhat changed crystal habit [182b].

According to Werner [183], optically active compounds which form salts with the same solubility relationships with the same optically active substances have the same configuration. In his second article on "active racemates" Delépine [184] together with Charonnat, declared that isomorphous compounds which form homogeneous mixed crystals have the same configuration. With such compounds, a racemate is formed, which is optically active because of the unequal rotatory powers of the components. Thus Delépine and Charonnat reported that (+)-$[Rh(en)_3]Cl_3$ and (−)-$[Co(en)_3]Cl_3$ are equally optically active but opposite in sign of rotation, and they form solid solutions; therefore they are isomorphous (ref. 20, pp. 104, 117; ref. 23, p. 389). On the other hand, (+)-$[Rh(en)_3]Cl_3$ and (+)-$[Co(en)_3]Cl_3$, having different rotatory powers, form an "active racemate" in agreement with Werner's solubility rule prediction [183] and contrary to Jaeger's prediction [185,186]. Delépine's results thus show that cobalt(III) and rhodium(III) complexes of the same sign of rotation have opposite generic configurations in the tris(ethylenediamine) series.

In 1934 Delépine [174] applied his concept of "active racemates" to provide a method for resolving racemates, for separating conglomerates or for determining the relative configurations of homeomers such as the active trioxalatocobaltates(III), trioxalatochromates(III) and trioxalatorhodates(III) compared to active compounds such as the trioxalatoiridates(III). Thus, if the "active racemate" a^+ and b^- can exist, the addition of active antipode a^+ to the unresolved racemic compound B (containing b^+ and b^-) will give a mixture of $[n(a^- + b^-) + (1 - n)B]$, where the + and − signs indicate the directions of rotation and *n* represents a fraction of the total amount of racemate. Analysis of the "active racemate" would then give data on the quantity and rotation of the fraction b^-. Since the mother liquor from these racemates contains excess b^+ it will also be optically active. The success of this method depends upon the racemate separating as a racemic compound rather than as a racemic mixture or solid solution.

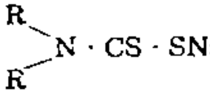
Delépine [174] verified his assumption by studying the following systems

(+)-$K_3[Rh(C_2O_4)_3]$	and (±)-$K_3[Ir(C_2O_4)_3]$
(+)-$K_3[Ir(C_2O_4)_3]$	and (±)-$K_3[Co(C_2O_4)_3]$
(—)-$K_3[Ir(C_2O_4)_3]$	and (±)-$K_3[Co(C_2O_4)_3]$
(+)-$K_3[Ir(C_2O_4)_3]$	and (±)-$K_3[Cr(C_2O_4)_3]$
(+)-$K_3[Ir(C_2O_4)_3]$	and (±)-$K_3[Al(C_2O_4)_3]$
(+)-$K_3[Ir(C_2O_4)_3]$	and (±)-$K_3[Fe(C_2O_4)_3]$
(—)-$[Co(en)_3]Br_3$	and (±)-$[Rh(en)_3]Br_3$

From his results he concluded that the syncrystallization of a racemic compound with an antipode (a^+ or a^-) of a homeomer A should be considered a sufficient reason for the existence of antipode B in the mixed crystal and therefore of the occurrence of B in the active forms b^+ and b^-, each enantiomorphic with a^- and a^+. The subsequent separation of b^+ from a^- or of b^- from a^+ results in the resolution of B. Of the racemic mixtures listed, Delépine was unable to resolve $K_3[Al(C_2O_4)_3]$ or $K_3[Fe(C_2O_4)_3]$, which have been subsequently resolved [187—190]. He demonstrated that the pairs (—)-$K_3[Ir(C_2O_4)_3]$ and (+)-$K_3[Rh(C_2O_4)_3]$, (+)-$K_3[Ir(C_2O_4)_3]$ and (+)-$K_3[Co(C_2O_4)_3]$ and (+)-$K_3[Ir(C_2O_4)_3]$ and (—)-$K_3[Cr(C_2O_4)_3]$ form "active racemates", and he therefore concluded that the generic configuration of the trioxalato complexes of these four metals are the same in (+)-$K_3[Co(C_2O_4)_3]$, (—)-$K_3[Cr(C_2O_4)_3]$, (+)-$K_3[Ir(C_2O_4)_3]$ and (—)-$K_3[Rh(C_2O_4)_3]$. In a lecture, "Sur quelques applications de l'isomorphisme", presented before the Swiss Chemical Society in March 1939, Delépine [91] reviewed the development of isomorphism from Mitscherlich's time (1821) to 1939 with special emphasis on his "active racemate" method. Recently Andersen et al. [191,192] have correlated the absolute configurations of tris(ethylenediamine) and tris(propylenediamine) complexes of cobalt(III), chromium(III) and rhodium(III) by means of X-ray powder photographs of "active racemates".

F. DITHIOCARBAMATE COMPLEXES

As we have mentioned in the Introduction, despite Delépine's great contributions to inorganic chemistry, the great majority of his research involved organic compounds. Of these, his voluminous work on organic sulfur compounds included studies of dithiourethanes, the discovery of the monomeric sulfides of ethylene (whose existence had been considered impossible), and the application of dithiocarbamates to analysis. It is the last of these topics that is of interest to us as coordination chemists.

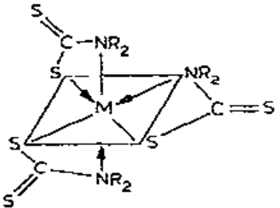
An article of 1956 entitled "Visuelle Titrationen unter Verwendung von Diäthyldithiocarbaminat" begins: "Diethyldithiocarbamates of general formula  $\genfrac{}{}{0pt}{}{R}{R}\!>\!N \cdot CS \cdot SNa$ were first recommended by M. Delépine about 50 years ago for research on copper and iron" [193]. In the paper referred to [194], Delépine reported that certain dialkyldithiocarbamates react with salts of metals like copper, iron, cobalt and nickel in solution, forming colored compounds which may be used to detect very small traces of the metallic salts (e.g., 1 p.p.m. for Cu), especially when the colored compound is extracted with ether or benzene. With his characteristic painstaking thoroughness, Delépine, in a review article of 1958 on the biological action and analytical and other applications of *N*-disubstituted metallic dithiocarbamates [195], traced his interest in these compounds to his early work on methylformothialdine $C_4H_9NS_2$, dimethylformocarbothialdine $C_5H_{10}N_2S_2$ and methyl methylimidodithiocarbonate $C_4H_9NS_2$, with which he dealt in his thesis for his degree of *pharmacien de première classe* (1896) [196—198].

Aliphatic isothiocyanates are usually prepared by Hofmann's method — treating an amine with carbon disulfide and then decomposing the dithiocarbamate formed with mercury(II) chloride [199,200] — a method which involves several operations and gives poor yields because one half of the amine used is recovered as its hydrochloride. In order to overcome these disadvantages, Delépine [201], in his first article on metallic dithiocarbamates (then called thiosulfocarbamates), used a synthetic method applied successfully in the aromatic series [202,203]. He reacted the aliphatic amine with carbon disulfide in the presence of sodium hydroxide, which forms a sodium salt of the dithiocarbamic acid. He then decomposed this salt with basic lead acetate instead of mercury(II) chloride and obtained good yields. In the course of this work he prepared water-insoluble diisobutyldithiocarbamates of the following metals: Ag, Tl, Zn, Cd, Hg(I), Hg(II), Pb, Sn, Cu, Fe(II), Fe(III), Ni, Co, Mn, UO_2, Au, Sb, Bi, Be, Al, Cr, Ce, Nd, MoO_3, Pt and Th. Several of these possess the unusual property of dissolving in benzene and carbon disulfide. All are soluble in ether and chloroform.

In his second article [204], Delépine described eighteen salts of substituted dithiocarbamic acids. He noted that the alkali metal and alkaline earth metal salts dissociate in solution like ordinary ionic salts, whereas the salts of cobalt(III), nickel, copper and iron are highly colored and act like organic substances in benzene solution, showing no trace of dissociation, i.e., they are "inner complex salts" [205], then a relatively new concept introduced by Heinrich Ley [206,207]. They are volatile without decomposition, and the metal ion in them is "masked". Thus the copper salts are not precipitated by hydrogen sulfide, nor are the nickel, cobalt [2[illegible]8] or iron salts precipitated by ammonium sulfide. Dubský later investigated these compounds [209].

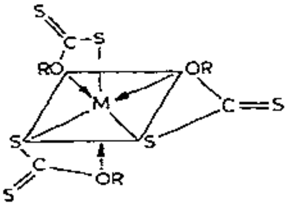
More than a decade later, together with his student Louis Compin [210], Delépine [211] made a careful study of nickel and cobalt xanthates, which they prepared by metathesis with alkali metal xanthates [209]. The nickel salts are black, the cobalt(III) salts deep green or black and the cobalt(II) salts brown. As with the dithiocarbamates [201,204], the cobalt(III) complexes are formed spontaneously from cobalt(II) salts, but, as is also true of the dithiocarbamates, there is some tendency to get some cobalt(II) salt along with the cobalt(III) salt, a tendency increasing with increasing molecular weight [208b].

In the xanthates, divalent oxygen plays the role of trivalent nitrogen in the dithiocarbamates, and the two series, which show a complete analogy in appearance and properties, were assigned the following similar inner complex formulations by Delépine and Compin [211]



Dithiocarbamates

and



Xanthates

As would be expected from the generally weaker combination of oxygen by secondary valence as compared with nitrogen, the xanthates are less stable than the dithiocarbamates and must be recrystallized in vacuo.

Delépine and Compin [212] made a detailed comparative study of the visible and ultraviolet spectra of the dithiocarbamates and xanthates of cobalt(III) and observed remarkable similarities. For example, the spectra for $[Co(S \cdot CS \cdot O \cdot CH_2C_6H_5)_3]$ and $[Co(S \cdot CS \cdot N(CH_3)_2)_3]$ are virtually identical, showing the dominating influence of the $Co(S \cdot CS—)_3$ grouping upon absorption.

Delépine's work on metallic dithiocarbamates and xanthates has had a great impact on analytical chemistry and theory of spectra of highly covalent complexes [213]. Several reviews of these compounds have appeared in the literature (ref. 16b, p. 136) [195,214]. Perhaps we can best conclude our discussion of these interesting complexes with Delépine's conclusion to his own review: "This account that one will certainly find too drawn out has no other purpose than to show that one observation, like that of the formation of dithiocarbamate, commonplace, so to speak, in its beginnings, can result in unexpected developments in the field of analysis as well as in special applications: fungicides, insecticides, vulcanizing agents and wetting agents" [195].

G. CONCLUSION

In these days of excessive specialization, the example of Marcel Delépine, perhaps one of the last generalists in chemistry capable of working with equal skill and productivity in a variety of different areas, is particularly inspiring. A contemporary of Alfred Werner (he was only five years younger than

Werner), he played a prominent role in the development of classical coordination chemistry. Yet he outlived Werner by almost half a century, and many of today's practicing chemists knew him personally (This author carried out a correspondence with Delépine during the early 1960s and separated several samples of iridium complexes kindly provided by the Master). Delépine's work on the stereochemistry of iridium, rhodium and platinum and his research on "active racemates" are considered true classics in the annals of coordination chemistry.

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