and recrystallized from dry ethanol. M. p. 136—146°. (Found: N 13.92. Calc. for $C_{30}H_{30}O_{18}N_8$: N 14.10.)

a - Methyl - β - diethylaminoethyl phthalate (III). The ester III was prepared from 26.2 g (0.2 mole) of 1-diethylamino-2-propanol and 16.2 g (0.08 mole) of phthalyl chloride following the same procedure as for I. The ester seemed to be partly decomposed by distillation. It was a yellow oil. B.p. 145—147°/0.05 mm. The dipicrate was recrystallized from absolute ethanol. M. p. 148—149.5°. (Found: N 13.50 and 12.73. Calc. for $C_{34}H_{42}O_{18}N_8$: N 13.18.)

Bis-methiodides and bis-ethiodides of I, II and III. The bis-quaternary alkyliodides of I, II and III were prepared in an acetone solution. The alkyliodides formed were dissolved in hot methanol and ethyl acetate was added slowly until a precipitate appeared. The solution was then chilled overnight in a refrigerator. For the preparation of the compounds IV, V and VI a solution of the tertiary amine and excess of methyl iodide or ethyl iodide in acetone was left overnight at room temperature. Compound VII was formed when a solution of II in acetone was heated with ethyl iodide under reflux for 3 h. In preparing the ethiodide of III (VIII), the reaction mixture was left at room temperature for eight days, and the methiodide of III (IX) was prepared by keeping the reaction mixture at 37° for three days. All the quaternary compounds (IV—IX) prepared, decomposed on melting. They were analysed for iodine by potentiometric titration with silver nitrate.

Melting points and analytical data of the bis-quaternary compounds are listed in Table 1.

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M. Delépine's Nitrido-Iridium(III,IV) Sulphate Complexes with Nitrogen Bound to Three Iridium Atoms

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Delépine[1] prepared green salts from $(NH_4)_3IrCl_6$ boiled with concentrated sulphuric acid. These salts are aquo acids, forming red-brown hydroxo complexes in alkaline solution by a reversible reaction, consuming one OH^- per Ir. They are distinctly different from Lecoq de Boisbaudran's blue-green sulphates,[2] formed by boiling, *e.g.*, K_3IrCl_6 with H_2SO_4 without the presence of NH_4^+. The latter salts can have the composition $K_{10}Ir_3(SO_4)_9O,H_2O$ (private communication from Professor Delépine) and may have further H_2O of crystallization. Delépine[3] found later that the green salts, prepared in the presence of NH_4^+, contain one nitrogen atom for each three iridium atoms. Then, he proposed one of two formulae:

I. $K_4[N\{Ir(H_2O)(SO_4)_2\}_3]$
II. $K_4H_2[N\{Ir(H_2O)(SO_4)_2\}_3]$

I contains two tetravalent and one trivalent iridium atom, while II assumes that all three iridium atoms are trivalent. Since Pascal and Pacault found that the nitrogen salts are diamagnetic, while Lecoq de Boisbaudran's salts are paramagnetic and according to the analysis contains one Ir(IV) and two Ir(III), it was concluded that II was probably true. During the study of the absorption spectra of Delépine's many interesting complexes,[4] the present author was surprised by the strong colour of a pure Ir(III) salt as II, and further by the presence of two hydrogen ions even in the hydroxo salts $K_7H_2[N\{Ir(OH)(SO_4)_2\}_3]$. This note shall present evidence that I is correct. The magnetochemical criterion is not very certain; even compounds with an odd number of electrons may be diamagnetic in certain cases (*e.g.* NO at low temperatures) where the gyromagnetic factor g accidentally is zero. But the case of I with an even number of electrons has a great chance for being diamagnetic; the platinum group complexes with bridge atoms between the heavy atoms seem to utilize all possibilities of spin-pairing.[5]

The green salts do not react with most reducing agents. However, the present author found that vanadous ions (prepared from NH_4VO_3 and Zn in HCl) reduces the green solution to a straw-yellow colour, having only a weakly increasing absorption in the ultraviolet. Metallic zinc may act directly on the green solution in H_2SO_4. Uranium(III) in 2 M HCl reduces also quantitatively, and H_2O_2 restores at least 90 % of the original green colour, as measured on a recording Cary MS-11 spectrophotometer. The band maxima (shoulders in parenthesis) are at wavelengths in mμ with the extinction coefficients ε given per iridium atom present:

Green aquo form		Red-Brown hydroxo form		Blue-green Lecoq de Boisbaudran's salt	
(661)	$\varepsilon =$ 450	653	$\varepsilon =$ 470	(800)	$\varepsilon =$ 350
582	530	562	910	701	770
439	1 260	452	1 500	306	1 250
(356)	465	335	710		
(311)	850	(298)	1 300		
(276)	1 220	269	1 850		

The special type of absorption bands in polynuclear complexes with the same metal in different oxidation states have often smaller wavenumbers than the electron transfer bands of mononuclear complexes.[4] The bands of the iridium complexes given above, are more narrow than the bands of iron(II,III) cyanides or molybdenum-(V,VI) blue. This may simply be connected with the fact that we have well-defined iridium compounds. The wavenumbers of the first bands are smaller [6] than of $IrCl_6^{--}$ and resemble those of $IrBr_6^{--}$. The absorption spectra are probably related to the formation of molecular orbitals of the nitrogen lone-pair (mainly a p_z-orbital) interacting with some of the iridium d-electrons, as will be discussed later.

The stability of the bonding of the nitrogen atom to the three iridium atoms, which even may survive the reduction to three Ir(III), is rather surprising. Werner prepared many cobalt (III) with NH- and NH_2-bridges, but the bonding of three metal atoms is rather exceptional. By X-ray crystallography, Scavnicar and Grdenic [7] found that $HgO,2HgCl_2$ contains oxygen atoms, surrounded in a plane by three rectilinear HgCl groups. The nitrogen-atom in Delépine's green salts may be nearly co-planar with the iridium atoms, forming a structure of the type of triphenylamine without tendency to co-ordinate a fourth group. That such »nitrido» complexes are formed in concentrated H_2SO_4, is rather remarkable. The oxygen atom (which also may be two OH^-) in Lecoq de Boisbaudran's salts may also co-ordinate three Ir. These salts are less stable; with alkalis or by standing with water, they precipitate violet, basic salts, and they are easily reduced by vanadium(II). On the other hand, the green nitride salt does not decompose to any great extent, if stored in aqueous solution at 25°C for 15 months.

Analysis. Since it is only possible to reduce the green nitrogen compound with ions, evolving hydrogen with water, it is not easy to make a direct titration, involving the reduction of iridium. However, the vanadium content [8] of the mixed $(NH_4)_2$ (V; Zn) $(H_2O)_6$ $(SO_4)_2$ was found by potentiometric titration with $KMnO_4$ in 1 M H_2SO_4 (showing distinct potential shifts at each of the oxidized forms (III), (IV), (V)) to have the effective molecular weight $M =$ 2 090 (while a pure V (II) salt would have $M = 387$). To each 1 ml of a solution, 0.5 M in HCl and 0.0150 M in total Ir from the green salt, was added 10, 15, 20, 25, and 30 mg of the V (II), Zn (II) salt, which is remarkably stable in air [8]. The solutions were diluted to 10 ml with 0.5 M HCl, and the decrease of ε at several wavelengths was found to be a linear function of the reducing agent added, corresponding to complete reduction for 20.5 mg. This is 98 % of the value expected for a Ir (III, IV, IV) compound, proving the formula I discussed above.

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Cuprous Chloride Catalysed Dimerisation of Methyl Propiolate

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In an attempt to prepare methyl deca-2:4-diynoate by the so-called Glaser coupling [1] of methyl propiolate with *n*-hept-1-yne, Christensen and Sörensen [2] were able to obtain only tetradeca-6:8-diyne and two crystalline substances which analysed for $C_8H_8O_5$ and $C_8H_8O_6$, respectively. In order to determine the structures of these two anomalous products the Glaser coupling of methyl propiolate was investigated.

The reaction of methyl propiolate in slightly acidic aqueous cuprous chloride-ammonium chloride solution, with air as the oxygen source, gave a crystalline compound in 36 % yield. The substance was obtained as colourless thick needles from ether-petroleum ether, m.p. 57°. (Found: C 57.40; H 5.04. Calc. for $C_8H_8O_4$; C 57.14; H 4.80). U.V.-absorption, in ethanol: $\lambda_{\max}$ 2 660, 2 540, 2 440 (inflexion) Å. ε 12 900, 17 500, 16 300. The infrared spectra showed the presence of acetylenic- and ethylenic bonds in addition to bands characteristic of an ester. A strong band at 958 cm^{-1} indicated that the double bond had the *trans* configuration. [3] On the basis of this evidence we concluded that the substance was dimethyl hex-2-en-4-yne-1:6-dioate (I). This compound has been reported in the literature.[4] There are, however, small discrepancies in the melting points and ultraviolet spectra of the two compounds, but these may be due to a difference in the configuration about the double bond.

$$\begin{array}{l} H_3COOC \cdot C \equiv C - H \\ \quad + HC \equiv C \cdot COOCH_3 \xrightarrow[NH_4Cl]{Cu_2Cl_2} H_3COOC \cdot C \equiv C \cdot CH = CH \cdot COOCH_3 \end{array}$$

(I)

The formation of the compound can be explained by addition of one molecule of methyl propiolate to another, thus being an example of a substituted acetylene undergoing the Nieuwland dimerisation.[5] Accordingly oxygen should not play any part in the reaction. This was confirmed by running the reaction under pure nitrogen, when practically the same yield of (I) was obtained.

Just after the completion of this work, Akhtar and Weedon [6] published a report on the reaction of substituted copper acetylides with oxygen in hot acetic acid. They obtained the corresponding vinyl acetylenic compounds in good yields.

Further work on this reaction is in progress.

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