

Rhodium and Iridium Porphyrins

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WE have synthesized and characterized some new metalloporphyrins, the rhodium(III) and iridium(III) porphyrins. To our knowledge these two compounds have not been prepared and reported previously. Quite recently the chromium(II) mesoporphyrin IX dimethyl ester has been prepared by treating chromium hexacarbonyl and porphyrin in *n*-decane.¹ We have generated the reactive metal carbonyls, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $[\text{Ir}(\text{CO})_3\text{Cl}]$ and allowed them to react with the porphyrins in acetic acid to form the respective metalloporphyrin complexes.

To an excess of a freshly prepared solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in absolute alcohol² was added mesoporphyrindiethylester (MesoPDEE) (500 mg.), glacial acetic acid (200 ml.), followed by anhydrous sodium carbonate or sodium acetate (500 mg.). The mixture was then refluxed for $1\frac{1}{2}$ –2 hr. The initially dark brown mixture gradually turned light brown and finally maroon (pink when dilute). The solvents were then removed under reduced pressure.* The residue was digested in chloroform and the insoluble acetates and metallic residues were filtered off. The chloroform extract

* Caution should be used with these compounds as we have had two explosions with rhodium-tetraphenyl- and rhodium-tetrapyrrolyl-porphyrin complexes while pumping off the solvent.

thus obtained was chromatographed on an alumina column. The second chloroform fraction on evaporation yielded dark violet microcrystals of the rhodium porphyrin complex.

The infrared spectrum of the rhodium porphyrin showed no N-H absorptions. In addition no band assignable to a CO group bound to rhodium were observed in the 1800–2500 cm^{-1} region. The visible absorption spectrum in chloroform showed λ_{max} at 544 $m\mu$ ($\epsilon 8.0 \times 10^3$) and 512 $m\mu$ ($\epsilon 5.84 \times 10^3$). The Soret band appeared at 398 $m\mu$ ($\epsilon 3.6 \times 10^4$). The mass spectrum showed the most intense peak at m/e 723. The magnetic susceptibility of the rhodium porphyrin, after diamagnetic correction, was 0.5 B.M.†

Iridium hæmatoporphyrin diethyl ester was prepared and purified in a similar manner to the rhodium porphyrin, using a freshly prepared solution of $[\text{Ir}(\text{CO})_3\text{Cl}]$ in ethylene glycol monomethyl ether³ and hæmatoporphyrin diethyl ester (HemPDEE). On evaporating the chromatographed chloroform solution a dark powdery compound, the iridium hæmatoporphyrin diethyl ester, was obtained.

The infrared spectrum of the iridium porphyrin showed no N-H absorptions but exhibited a strong CO band at 2060 cm^{-1} indicating the presence of CO group bound to the metal atom. The visible absorption spectrum in chloroform showed λ_{max} at 548 $m\mu$ ($\epsilon 6.0 \times 10^3$), 517 $m\mu$ ($\epsilon 5.2 \times 10^3$) and the Soret band at 398 $m\mu$ ($\epsilon 4 \times 10^4$). The magnetic susceptibility of the iridium porphyrin was 0.4 B.M.†

From the above data these new metalloporphyrins can be formulated as the $[\text{Rh}^{\text{III}} \text{MesoPDEE}][\text{X-L}]$ and $[\text{Ir}^{\text{III}} \text{CO-HemPDEE}][\text{X}^-]$, where X^- can be an anion (acetate or chloride), and L a neutral ligand such as acetic acid, water, or methanol. Both the metals have d^6 electronic configurations. The small residual magnetic susceptibility could be due to several causes which have not as yet been determined. It could be due to the inherent residual susceptibility of $d^6 \text{Co}^{\text{III}}$, Rh^{III} , and Ir^{III} systems⁴ or to a small amount of impurity. All these complexes gave an e.s.r. signal with a g -value of 2.00, but the signal was due to less than 0.1% of sample.‡ The visible absorption spectra of these complexes show two characteristic bands of comparable intensity. This also indicates that the metal ion is in the +3 oxidation state.⁵ The formation of these compounds from the Rh^{I} and Ir^{I} carbonyls proceeds through the intermediate Rh^{I} and Ir^{I} porphyrin complexes. We have spectral evidence⁶ that the Rh^{I} porphyrin is formed and then oxidized to the Rh^{III} by oxygen. It is of interest that in the metalloporphyrins prepared by this method the iridium porphyrin retains the carbon monoxide ligand while rhodium and other metals¹ do not. We have also prepared the ruthenium hæmatoporphyrin diethyl ester by similar methods. The carbon monoxide is very tightly bound to the iridium porphyrin moiety. Heating, pumping, boiling in pyridine, or reprecipitating from concentrated sulphuric acid solution does not remove the CO from the complex.

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