

ATTEMPTS TO EFFECT EXCHANGE AND DISPLACEMENT REACTIONS WITH COBALT(II) MESOPORPHYRIN*

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There is ample evidence that divalent metal atoms, such as those of Zn, Cu, Ni, Co, Fe, and Mn, can be introduced directly into the centre of the tetrapyrrolic ring system of many porphin derivatives and that under appropriate conditions these metal atoms can be equally readily removed from metal porphin complexes. In this respect metal porphin complexes differ from those of phthalocyanine from which it is extremely difficult if not impossible to remove these metal atoms without destruction of the molecule. To introduce metal atoms into phthalocyanine it is necessary to do so during the synthesis of the phthalocyanine ring system itself. In these circumstances no exchange of metal ions between metal phthalocyanine complexes can be expected. The object of this note is to describe experiments made in the attempt to discover whether cobalt ion can exchange with cobalt(II) mesoporphyrin and whether cobalt can be displaced from cobalt(II) mesoporphyrin by copper ion which would be expected to form a more stable complex with mesoporphyrin.

The exchange experiments were carried out in carefully dried pyridine,‡ one of the few solvents in which mesoporphyrin was sufficiently soluble for this work. Equimolar solutions of cobalt(II) mesoporphyrin and cobalt(II) acetate were made up in pyridine and equal volumes (25 ml.) of each were mixed together and allowed to stand in a thermostat at 25 °C. for varying periods of time. Throughout the period of possible exchange, a stream of dry nitrogen

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‡ In this solvent the exchange would, if it occurred, take place between Co(py)_4^{++} and the dipyridine cobalt(II) mesoporphyrin.

was bubbled through the solution to prevent aerial oxidation. In one set of experiments ^{60}Co was incorporated in the mesoporphyrin and, in the other, with the cobalt(II) acetate.

After the lapse of the period of time decided upon for the exchange, the separation of cobalt(II) mesoporphyrin and cobalt(II) acetate was carried out as follows. To the pyridine solution were added 50 ml. of water and 50 ml. of chloroform. After thoroughly shaking the mixture and allowing it to stand 5 minutes, two layers separated; the lower, pyridine-chloroform layer containing cobalt(II) mesoporphyrin was then run off. The remaining water-pyridine layer containing the cobalt(II) acetate was washed four times with 25 ml. of chloroform each time. The combined chloroform-pyridine extractions were then similarly washed with 25 ml. of water and the washings added to the water-pyridine layer. The two soluble chemical compounds thus separated were then precipitated to determine their radioactivity. The cobalt(II) acetate was precipitated as cobalt(II) dipyridine thiocyanate by means of ammonium thiocyanate. Because of the relative difficulty of removing cobalt from cobalt(II) mesoporphyrin, its chloroform-pyridine solution was evaporated almost to dryness and a little water added. The remaining chloroform was boiled off leaving cobalt(III) mesoporphyrin suspended in water. The precipitate was filtered off and washed with water. A blank experiment with cobalt(II) acetate showed that 98–99 per cent. of the substance was extracted in the water-pyridine solution. With ^{60}Co in the mesoporphyrin, there was within the limits of experimental error, even over a long period of time, practically no exchange (Table 1).

TABLE 1
EXCHANGE OF ^{60}Co MESOPORPHYRIN WITH Co^{++} AT 20 °C.

Time (hr.)	Activity of Co^{II} Mesoporphyrin	Activity of Co^{II} Acetate	Exchange (%)
0	11241	62	1
1	8216	67	1
$3\frac{1}{2}$	7142	65	1
24	11061	108	1

Activities are given in counts per minute (corrected for background). When the exchange conditions were reversed, with ^{60}Co present as cobalt(II) acetate, there appeared to be an exchange that reached about 20 per cent. instantaneously and did not increase thereafter. This spurious result may have been due to the occlusion of free mesoporphyrin in the cobalt(II) mesoporphyrin in spite of every effort to prevent this. A more likely explanation of the effect is that cobalt(II) ion combined with the two adjacent propionic acid groups on the mesoporphyrin molecule, a probable reaction, especially in alkaline solution.

Attempts to carry out an exchange in glacial acetic acid solution failed owing to the low solubility of cobalt(II) mesoporphyrin in that solvent. Experiments in which pyridine was used as solvent were made to see whether copper

could replace cobalt in cobalt(II) mesoporphyrin. Even after 100 hours at 25 °C. the displacement amounted to not more than 10 per cent. (Table 2).

TABLE 2
REPLACEMENT OF CO FROM Co^{II} MESOPORPHYRIN BY CU

Time (hr.)	Activity of Co^{II} Mesoporphyrin	Activity of Co^{II} Acetate	Replacement (%)
0	6742	60	1
24	8417	134	2
100	7922	689	9

In these experiments the copper concentration greatly exceeded that of the cobalt compound, the concentration of which was approximately 10^{-5}M . Attempts to detect the replacement of cobalt with copper spectroscopically were unsuccessful. Barnes and Dorough (1950) were able completely to displace zinc from α , β , γ , δ tetraphenylporphin by copper only after 48 hours at the boiling point of pyridine.

From these experiments and those of other authors (Ruben *et al.* 1942) on similar compounds it must be concluded that metal atoms, such as Cu, Co, and Ni, are very firmly bound to the porphin nucleus being neither readily exchanged nor displaced by other metal atoms.*

References

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