Porphyrin Metallation by Graphite–Metal Intercalates: a Model for the Occurrence of Metalloporphyrins in Coal

Gadi Lipiner, Itamar Willner,* and Zeev Aizenshtat*

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Metal–graphite intercalates effect the metallation of planar porphyrins.

Metalloporphyrins are widely distributed in fossil fuels, sediments, crude oil, and coals. In the organic matter of sediments VO^{2+}, Ni^{2+}, and Cu^{2+} porphyrins[1,2] are the most abundant, while Ga^{2+}, Al^{2+}, and Fe^{2+} porphyrins are distributed in coals.[3] Although the porphyrin ligands in these environments are evidently of plant origin, the metals introduced into the metalloporphyrins are often inconsistent with the natural abundance of the metals. It has been suggested that ingredients present in crude oil and coals, such as 1,2-dihydroxy aromatic compounds or amino acids, can have a sequestering effect in removing metal ions from ground water with some degree of selectivity.[4] Recently, we have shown that porphyrins are metallated in water–oil two-phase systems that include cation carriers such as long-chain carboxylic acids, thiols, and hydroxy-aromatic compounds.[5,6] These systems exhibit selectivity towards various metal ions and might offer a model for the formation and occurrence of metalloporphyrins in crude oil. Intercalated compounds of metals in graphite are well known.[7] Here we report on the metallation of porphyrins in the presence of metal–graphite intercalates. We believe that the metallation of the porphyrins by the intercalation media might suggest a model for the formation of metalloporphyrins in coals.

We have studied the metallation of mesoporphyrin IX dimethyl ester (MPDE) and of octaethylporphyrin (OEP), in the presence of $CuCl_2$, $AlCl_3$, $FeCl_3$, and $GaCl_3$ graphite intercalation compounds. The metallation experiments were performed by suspending the metal intercalate (3 mg) in a stirred toluene solution heated to 80 °C with OEP or MPDE (1×10^{-4} M). Uptake of the toluene-solubilized porphyrins by the graphite intercalate powder was observed implying that the ligands are adsorbed on the intercalation matrix. After 3 h of stirring, only *ca.* 10% of the porphyrin remained solubilized in the toluene phase. The intercalation graphite powder was then centrifuged and resuspended in chloroform. The chloroform solution became coloured and the absorption spectra of the supernatant solution revealed that metalloporphyrins had been formed.

Figure 1 shows the absorption spectra of OEP, and $Cu^{II}(OEP)Cl$ ($\lambda_{max.}$ 399 nm) and $Fe^{III}(OEP)Cl$ (382 nm) formed in the presence of the metal intercalates. Similarly, MPDE is metallated and forms $Cu^{II}(MPDE)Cl$ ($\lambda_{max.}$ 399 nm), $Fe^{III}(MPDE)Cl$ (385 nm), $Al^{III}(MPDE)Cl$ (400 nm), and $Ga^{III}(MPDE)Cl$ (404 nm). Control experiments suggest that the metal–graphite intercalates are the active media inducing the metallation process. The various metal salts were homogenized physically with graphite powder in the same ratios as in the intercalation compounds. These powders were suspended in toluene solutions of OEP and MPDE and the metallation processes examined. Interestingly, no metallation of the porphyrins occurred with $FeCl_3$, $AlCl_3$, and $GaCl_3$ while

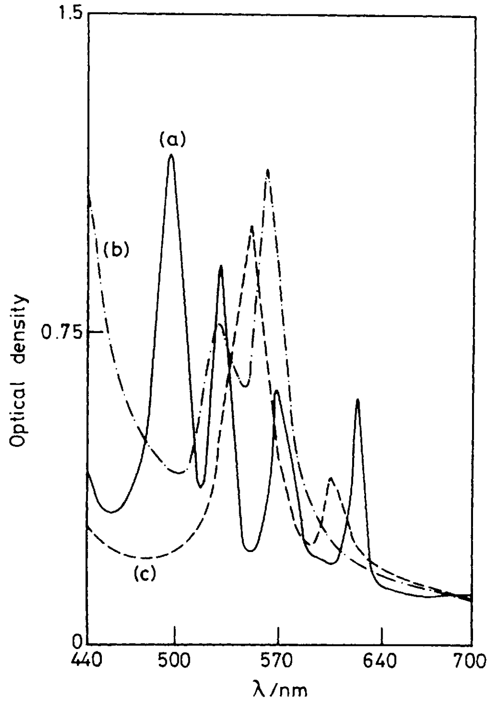

Figure 1. Absorption spectra of the metalloporphyrins formed in the reaction between the free porphyrin (OEP; spectrum a) and the metal–graphite intercalates: (b), Cu–OEP; (c), Fe–OEP.

the metallation in the presence of $CuCl_2$ was *ca.* 10 times slower than the corresponding reaction with $CuCl_2$–graphite intercalate.

These results imply that the metal intercalate matrix is essential for inducing metallation. Furthermore, it is interesting that mesotetraphenylporphyrin (TPP) is not metallated by the various metal intercalates. The steric differences between TPP and OEP or MPDE, and the structural relations between the porphyrin and the layered intercalate are probably the reasons for the inertness of TPP towards metallation. While OEP and MPDE are flat planar ligands capable of entering into the graphite layers, where metallation occurs, the bulky perpendicular substituents in the *meso* positions of TPP prohibit its penetration into the matrix layers and metallation is prevented.

In conclusion, we have demonstrated that metal–graphite intercalates act as an effective matrix that effects metallation of planar porphyrins. These reactions proceed *via* penetration of the porphyrin ligand into the layered structure of graphite, where metallation occurs. Thus, the association of inorganic minerals to coals *via* the formation of intercalation compounds might have a sequestering effect in the metallation of porphyrins and their consequent occurrence in coals. In addition, the formation of metalloporphyrin intercalation compounds suggest the potential application of these solid supports in metalloporphyrin catalysed processes.[8,9] Such systems might reveal selectivity[10] and means for the regeneration of the catalysts.

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