

Metalloporphyrins in Coal. 1. Gallium Porphyrins in Bituminous Coals

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The isolation and characterisation of a homologous series of gallium polyalkylporphyrins from a large scale extraction of a bituminous coal (Daw Mill) from the Carboniferous is described. About 0.2 $\mu\text{g/g}$ of metalloporphyrin fraction is obtained. The homologous series extends from C_{26} to C_{32} . It is proposed that the homologues arise by fragmentation (thermal cracking, protodesubstitution on a mineral surface) of etioporphyrin III or its metal complexes during the coalification process.

Evidence in support of this is provided by a survey of bituminous coals of increasing rank, where the predominating carbon number decreases in the range C_{30} to C_{26} as rank increases. The amount of metalloporphyrins extracted also decreases with increasing rank: only traces are detected in anthracites.

In the mid 1930's, Alfred Treibs founded the branch of chemistry which has now become known as organic geochemistry. He did this with some simple but incisive experiments on asphalts, crude oils, oil shales, and coals. He showed that such materials often contained porphyrins and metalloporphyrins, and he proposed that these originated from haems and chlorophylls set down in the original sedimentary deposit.¹ These porphyrins are thus to be regarded as biological markers, that is, substances which because of their structural affinities with the specialised components of living things are taken to indicate a biological origin. Such an origin is sufficiently obvious with the coals, but has not always been so with the other deposits.

Treibs paid most attention to crude oil and its relatives, and so have subsequent investigators. Metalloporphyrins, and particularly vanadyl and nickel porphyrins, have been repeatedly detected in such sources.² It is difficult to understand why the early indications³⁻⁵ of porphyrins in coal have received so little subsequent support.^{6,7} Treibs^{4,5} had made structural assignments and metal identifications for the coal porphyrins on the basis of correlations with basicity and visible absorption spectroscopy. Although the methods then available were not up to the complexities of the job in hand, remarkable progress was made. According to Treibs' findings, etioporphyrin was the most abundant component but other porphyrins ('deuteroetioporphyrin', desoxophylloerythroetioporphyrin)[†] corresponding respectively to lower homologues and to cyclo derivatives were also detected. Metal complexes were also found: specifically, in coal, vanadyl and iron porphyrins were reported, identifications resting on visible spectroscopy. The situation became obscured when Glebovskaia and Volkenshtein,⁸ again using visible spectroscopy but working with material obtained from crude oil and bitumen, reassigned to nickel porphyrins the visible absorption which Treibs had attributed to haems. Subsequent work with the oil-related materials has supported this reassignment.² There appears to have been no further work on this aspect of coal chemistry.

However, the presence of metal complexes in coal has recently become of importance in relation to extraction processes designed to produce liquid fuels and chemical feedstocks from coal.^{10,11} In these the coal is treated with an organic

solvent at high temperature and the liquid extract is subsequently hydrocracked. It has been observed that the catalyst in the latter process becomes deactivated due to the accumulation of metal-containing impurities.^{11,12} These have presumably been extracted from the coal, and hence it is postulated that co-ordination complexes or organometallic compounds are present in coal and can be extracted from it with organic solvents.

We have recently shown that lignites and lower ranking bituminous coals contain small amounts of gallium, iron and (in one case) manganese porphyrins.^{13,14} In this paper we describe in detail the isolation and identification of a mixture of gallium porphyrins from a large sample of a British bituminous coal.

A low rank bituminous coal (Daw Mill Colliery, South Midlands, National Coal Board rank code 902) was selected, and extracted on a ca. 100 kg scale with 7% sulphuric acid in methanol. This acidic medium was chosen because it was considered that it would cleave bonds where the axial ligand was the coal matrix, and so facilitate the liberation of metal complexes (including metalloporphyrins). At the same time acidic methanol is a *poor* solvent for coal, so that the complexity of the subsequent separation would be somewhat minimised. Indeed less than 0.05% of the coal was extracted into chloroform after neutralisation (see Experimental section). The neutral organic extract was submitted to column chromatography on silica gel. Those fractions which gave a positive indication for metalloporphyrin (Soret band, fluorescence) were combined and submitted to repeated preparative-scale thin layer chromatography. At this stage the metalloporphyrin component was strikingly evident as an orange red band with a bright orange fluorescence in u.v. (365 nm) light, although brown-black impurities were also present. The red substance extracted from the final batch of plates was dissolved in dichloromethane, filtered, and the metalloporphyrin was precipitated with petroleum, to give 17.8 mg (0.19 $\mu\text{g/g}$ of original coal) of metalloporphyrin concentrate as a dark red solid.

The electronic absorption spectrum, with a Soret band at 405 nm, and visible bands at 532 and 570 nm (Figure 1), was clearly that of a metalloporphyrin: the metal evidently had a filled d shell, since the complex was fluorescent. Metals analysis was carried out by two independent methods (atomic absorption, thermal neutron activation, both at Harwell) and indicated that gallium was the principal metal present. Small amounts of sodium, iron, potassium, magnesium, and aluminium were present as impurities. Nickel and vanadium were present in negligible quantity in this fraction.

The nature of the ligand was examined in the following way. The mass spectrum revealed a mixture of gallium poly-

[†] The first name is no longer used, and the second, although used, has obvious disadvantages as a trivial name. The first name is intended for didemethyletioporphyrin. A simpler name for the second compound is cycloetioporphyrin (locants added where known with certainty: see IUPAC-IUB Joint Commission on Biochemical Nomenclature, 'Nomenclature of Tetrapyrroles,' *Pure Appl. Chem.*, 1979, 51, 2251).

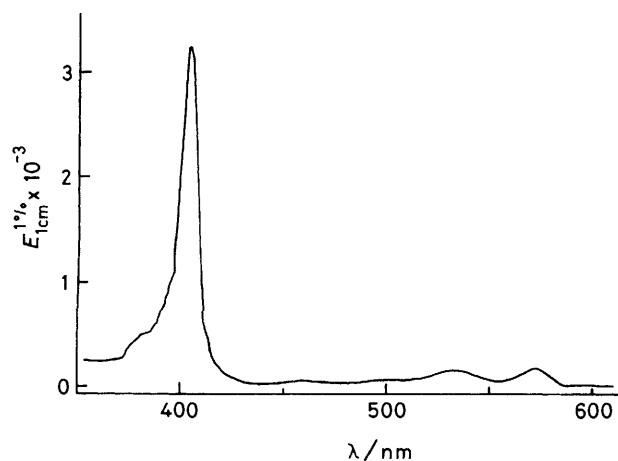


Figure 1. Metalloporphyrin fraction from Daw Mill coal: electronic spectrum in chloroform

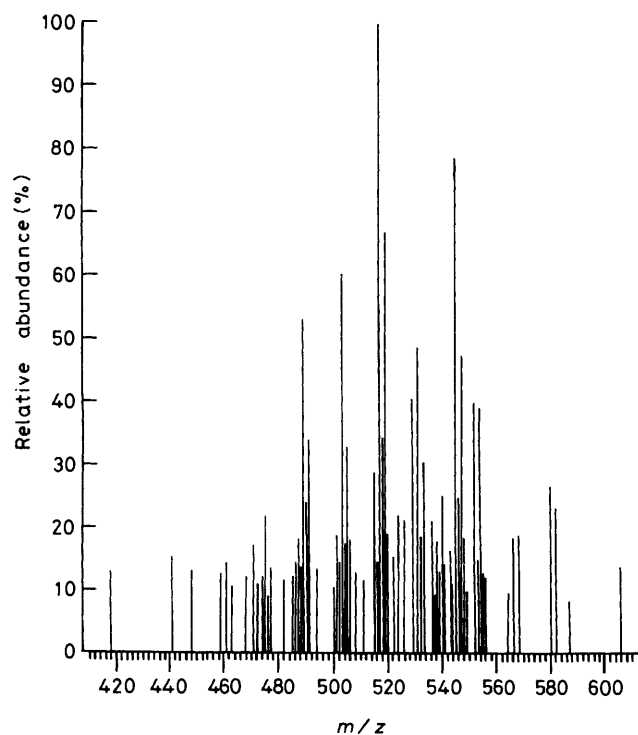


Figure 2. Metalloporphyrin fraction from Daw Mill coal: mass spectrum, direct insertion at 300 °C

alkylporphyrins as determined by accurately measured molecular ions (see Experimental section). Two series of ions were observed (Figure 2): a major series representing C_{26} – C_{32} complexes without the axial ligand occurred as doublets ($461 + 14n$, $463 + 14n$, $n = 0$ – 6 ; $^{69}\text{Ga} : ^{71}\text{Ga}$ relative isotopic abundance = 3 : 2); and a minor series clearly seen at higher m/z as a series of roughly equal doublets representing the chlorides of the C_{30} , C_{31} , and C_{32} complexes ($552 + 14n$, $554 + 14n$, $n = 0$ – 3 ; $^{71}\text{Ga}^{37}\text{Cl} : ^{69}\text{Ga}^{37}\text{Cl} + ^{71}\text{Ga}^{35}\text{Cl} : ^{69}\text{Ga}^{35}\text{Cl} = 1 : 9 : 9$). The main homologues in both series were the C_{30} and C_{32} porphyrins, the former predominating (Table 1).

Although the mass spectrum showed that chloride was present as an axial ligand in the isolated material, the chlorine analysis showed that it was not the only axial ligand present. It is possible that the halide complex occurs as such in the coal:

Table 1. Relative abundances of major metalloporphyrin ions in the mass spectrum of gallium porphyrin fraction from Daw Mill coal

(a) Ions without axial ligand			(b) Ions with chloride ligand
C_{32}	20.7	33.9	30.1
C_{31}	13.0	21.2	22.5
C_{30}	27.3	44.9	47.4
C_{29}	15.2		
C_{28}	14.3	100.0	100.0
C_{27}	5.7		
C_{26}^a	3.8		
	100.0		

^a Ions at m/z 461, 463 not accurately mass measured

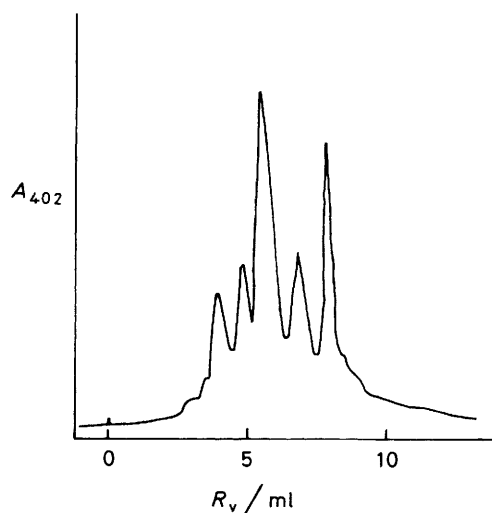


Figure 3. Reverse phase h.p.l.c. of metalloporphyrin fraction from Daw Mill coal. The system separates homologues, but not isomers. The component with a retention volume of 7.7 ml did not separate from authentic chlorogallium(III) etioporphyrin I

but coals frequently contain free halide ion and it seems likely that this axial ligand may have been introduced during the extraction with acidic methanol.

Comparisons with authentic samples of chlorogallium etioporphyrin I¹⁵ were made by chromatographic methods (t.l.c., h.p.l.c.) and showed considerable similarities. H.p.l.c. on a reverse phase column proved useful for the separation of homologues of gallium porphyrins (Figure 3). Co-injection showed that, under the conditions of the column, the least mobile component ($R_v = 7.77$ ml) of the coal porphyrin sample was indistinguishable from gallium etioporphyrin I. The relative abundances of the homologues as estimated by h.p.l.c. (see Experimental section) were in accord with the values from the mass spectrum (Table 1). Spectroscopic comparisons are summarised in Table 2: again there are general similarities between the coal metalloporphyrin fraction isolated here and the authentic gallium complex.

The n.m.r. spectrum of a specially purified sample of the gallium porphyrin from coal is shown in Figure 4. The spectrum is remarkably clean, although there remain small signals at δ 0.8 and 1.25 which are attributed to unknown substances: probably these are due to hydrocarbon/plasticizer impurities. The methyl (δ 3.60) and ethyl (δ 4.05, 1.90) groups appear at chemical shifts expected for a polyalkyl-

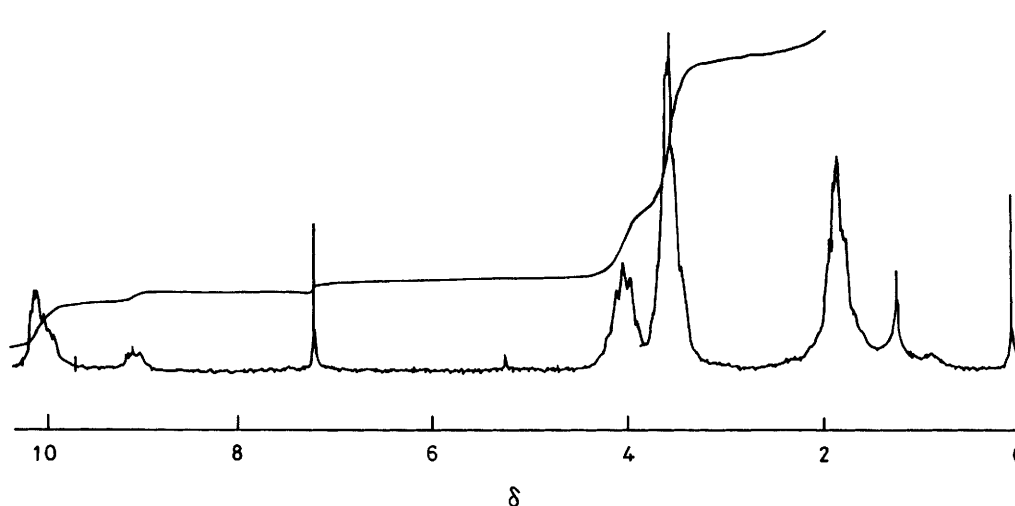


Figure 4. Metalloporphyrin fraction from Daw Mill coal: n.m.r. spectrum in $[^2\text{H}]$ chloroform

Table 2. Spectroscopic comparisons between the gallium porphyrin fraction from Daw Mill coal and chlorogallium(III) etioporphyrin

	Gallium porphyrin fraction from coal	Chlorogallium(III) etioporphyrin I
1. Electronic spectrum		
$\lambda_{\text{max.}}$ (CHCl_3)	405, 532, 570 nm	403, 532, 570 nm
$\epsilon_{\text{Soret}}/\epsilon_{\beta}$	29.5	31.8
$\epsilon_{\beta}/\epsilon_{\alpha}$	6.9	7.6
2. ^1H N.m.r. spectrum ^a (90 MHz, C^2HCl_3)		
<i>meso</i> H	10.14, 10.11, 10.04, 9.94, 9.85 (bm)	10.14 (bs)
βH	9.11 (bm)	—
CH_2Me	4.05 (m)	4.06 (bq)
ArMe	3.60 (m)	3.61 (bs)
CH_2CH_3	1.90 (m)	1.87 (t)
i	1.25 (s)	—
i	0.86 (b)	—

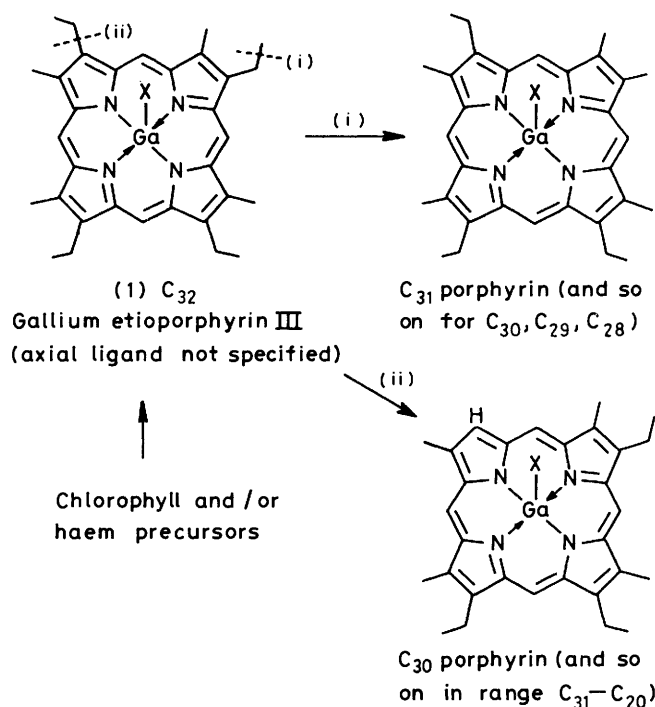
^a On sample subjected to further purification.

i = presumed impurity peak.

porphyrin, and compare well with the model compound (Table 2). The signal at δ 9.11 is assigned to an unsubstituted β -position on a pyrrole ring, with the *meso* signals further downfield (*ca.* δ 10). All these signals are broad and structured, consistent with a complex mixture of porphyrin homologues.

Demetallation of the gallium porphyrin mixture required treatment with concentrated sulphuric acid. The free base showed a typical four banded absorption spectrum of the etio type. T.l.c. separated three components, one of which was indistinguishable from etioporphyrin I in the solvent system employed.

It is concluded that the metal complex isolated from Daw Mill coal is a homologous series of gallium polyalkylporphyrins. The main components are C_{30} and C_{32} : on geobiogenetic grounds ¹ we formulate the C_{32} component as gallium etioporphyrin III (1) although the presence of isomeric C_{32} compounds is not excluded at this stage. We propose that the porphyrins with carbon numbers lower than this arise during the coalification process by thermal cracking (particularly at



Scheme. Proposed dealkylation processes for metalloporphyrins during coalification (see text)

pseudo-benzylic bonds) and protodealkylation processes (leading to β -hydrogens, as detected by n.m.r. spectroscopy), as shown in the Scheme. Such cleavage reactions would plausibly be assisted by a mineral surface.

We have uncovered evidence for such geochemical changes by examining a series of bituminous coals of increasing rank (*i.e.* degree of coalification). The samples were all selected from the British Carboniferous (Table 3). Two effects were apparent. First, as the degree of coalification increased, the amount of extractable gallium porphyrin decreased, so that with anthracite (sample 9) porphyrin components were scarcely detectable. Second, as coal rank increased, the average carbon number of the extracted metalloporphyrin decreased. Thus, in moving from Daw Mill coal (NCB coal

Table 3. Survey of gallium porphyrins in some British bituminous coals of differing rank

Sample	NCB coal rank code ^a	% C ^b	% Volatile ^c matter	Gallium porphyrin content $\mu\text{g/g}$ ^d	Gallium porphyrin fraction	
					Base peak in m.s.	Most abundant components ^e (h.p.l.c.)
1. Daw Mill (S.M.) ^f	902	81.5	40.6	0.90	C ₃₀	C ₃₀ , C ₃₂ , C ₃₁
2. Allerton (N.Y.)	802	81.8	38.2	0.58	C ₃₀	C ₃₀ , C ₂₉ , C ₃₁
3. Annesley (S.N.)	702	82.9	37.2	0.26	C ₂₉	C ₂₉ , C ₃₀ , C ₂₈
4. Hickleton (D)	602	83.7	38.1	0.46	C ₂₈ , C ₃₀	C ₂₉ , C ₃₀ , C ₂₈
5. Bersham (W)	502	85.8	38.0	0.09	C ₂₈	C ₂₉ , C ₃₀ , C ₂₈
6. Cortonwood (S.Y.)	401/2	87.2	35.5	0.11	C ₂₆ , C ₂₇	C ₂₇ , C ₂₈ , C ₂₆
7. Beynon (S.W.)	301a	89.5	27.2	0.002	g	g
8. Tymawr (S.W.)	204	90.8	18.7	Trace	g	g
9. Bettws (S.W.)	100	93.8	6.2	Trace	g	g

^a Data on rank, carbon, and volatile matter analyses were supplied by Mr. W. F. Wyss (Coal Research Establishment, Stoke Orchard) whom we thank. ^b Dry mineral-free matter. ^c Dry, ash-free. ^d Dried 105 °C, 4 h. ^e In order of decreasing abundance. ^f Location of collieries; S.M., South Midlands; N.Y., North Yorkshire; S.N., South Nottinghamshire; D, Doncaster; W, Western Region; S.Y., South Yorkshire; S.W., South Wales. ^g Insufficient material for study.

rank code 902) to Cortonwood coal (401/2) the most abundant molecular ion in the mass spectrum of the gallium porphyrin fraction had shifted from C₃₀ to C₂₆. This effect was supported by the h.p.l.c. separations. Although the mixtures are complex, and the components have not as yet been identified in chemical detail, it is evident that the samples which are most coalified have metalloporphyrin mixtures which are most degraded in the sense of the Scheme. It is of interest that there is some predominance of degraded porphyrins with an even number of carbon atoms (*e.g.* Figure 2): this may indicate a (surprising) preference for processes of type ii (see Scheme). In spite of the low abundance of metalloporphyrins in coal, we propose that the analysis of the metalloporphyrin fraction with respect to carbon number (*e.g.* by h.p.l.c./m.s., Table 3) offers a quantitative approach to the assessment of degree of coalification, which will be reported in detail elsewhere.

The possibility of contamination when manipulating such small amounts of material is a real one, and this especially so in a laboratory where porphyrins have been worked with for some years. However control experiments were negative (*e.g.* laboratory sand; and items 8 and 9 in Table 3), and the experiments could be reproduced, both at Queen Mary College and elsewhere.¹⁴ Gallium porphyrins had not been made previously in our laboratory. The possibility that gallium was introduced into the porphyrin under the extraction conditions was discounted by control experiments. In the presence of excess gallium salt, metallation of octaethylporphyrin was not observed under the conditions of the extraction in the presence or absence of powdered coal.

The presence of gallium as a porphyrin complex in coal was unexpected, although such a complex has been encountered in Nature once before, as a pigment in calcite.¹⁶ Although gallium is widely distributed, its abundance in the Earth's crust is only 15 $\mu\text{g/g}$,¹⁷ an order of magnitude less than vanadium, porphyrin complexes of which occur in crude oil.² However, during the process of coalification, various metals are known to be sequestered,¹⁸ and gallium is one of these. The association of gallium with the organic constituents of bituminous coals has been reported,¹⁹ and processes have been described for the isolation of gallium from coal.²⁰ Gallium porphyrins are not known in biological systems: although gallium is reported to be accumulated by some organisms,²¹ its metabolic function, if any, does not yet appear to have been recognised.

Finally it is important to note what appear at this stage to be distinctions between the metalloporphyrins detected in coals on the one hand and in crude oil and its relatives on the

other. (i) In the latter, vanadyl and nickel are the major porphyrin complexes.² Copper porphyrins have been detected in deep sea sediments.²² In coals, gallium porphyrins have been found as reported here, and iron and (in one case) manganese porphyrins have also been encountered.¹⁴ (ii) Crude oil and its relatives often contain much more metalloporphyrin than do coals. Thus for a number of bitumens Baker and his colleagues²³ report petroporphyrin contents such as 55 $\mu\text{g/g}$ (Eocene, Green River oil shale) and 145 $\mu\text{g/g}$ (Cretaceous, Athabasca tar sands). (iii) The homologous series of porphyrins found in crude oil often extends above C₃₂:² this has not been observed for the coal porphyrins so far studied. (iv) Although etioporphyrin and its homologues are encountered in crude oil, the porphyrins of the desoxyphyloerythroetioporphyrin (13²,15-cycloetioporphyrin III) type are often dominant in that source:² in coal the etio homologous series appears to be dominant. These distinctions presumably reflect differences in origin and diagenesis with respect to these substances in the two types of fossil fuel, and are clearly of considerable interest.

Experimental

General.—*Thin layer chromatography.* Preparative: Merck silica gel 60H; 200 × 200 × 1 mm plates prepared in house, washed with methanol and reactivated (110 °C, 4 h) before use. Analytical: as before, but using 0.2 mm layers. The following solvent systems were employed (compositions by volume). A, petroleum: chloroform: acetone: ethyl acetate = 1:1:1:1; B, saturated NH₃ in methanol; C, ethyl acetate; D, benzene: saturated NH₃ in methanol = 19:1, 9:1, 4:1 in sequence. All solvents were redistilled.

Analytical h.p.l.c. Waters M6000A pump with a UK6 injector, and a Cecil CE212 variable wavelength detector set at 400 nm for metal-free porphyrins and 402 nm for gallium porphyrins. Column: Waters Bondapak C₁₈/Porasil B, i.d. 3.9 mm × 300 mm, eluted with methanol: water = 17:3 (proportion of water increased for aged columns), 0.001M in [Bu₄N][H₂PO₄], flow rate 0.8–1.5 ml/min.²⁴ Carbon numbers were assigned from a plot of log retention volume/carbon number using gallium complexes of porphyrin, octamethylporphyrin, etioporphyrin and octaethylporphyrin¹⁵ for calibration. Infrared spectra: Perkin-Elmer 225 KBr disc. Electronic spectra: Pye Unicam 8000, calibrated with holmium glass. Unknown porphyrins and metalloporphyrins were estimated spectroscopically from the electronic spectrum (Soret band) in chloroform, assuming a molecular mass of 600,

Table 4. Fractionation of extract on silica gel column chromatography

Fraction	% Methanol in benzene (v/v)	Colour of eluate	Weight (g)	Porphyrins present *
I	5—10	Black	17.81	—
II	10—20	Brown	9.25	—
III	20—30	Black	3.97	—
IV	30—50	Brown	0.41	+
V	50—70	Pink/brown	0.35	++
VI	70—90	Red	0.31	+++
VII	90—100	Pink	0.27	++

* As judged by fluorescence on analytical t.l.c. and presence of an inflection or peak at *ca.* 400 nm in the absorption curve.

m/z (300 °C) 582.186 (23.3, C₃₂H₃₆N₄⁷¹Ga³⁵Cl requires 582.188)
 580.184 (26.7, C₃₂H₃₆N₄⁶⁹Ga³⁵Cl requires 580.189)
 568.172 (19.0, C₃₁H₃₄N₄⁷¹Ga³⁵Cl requires 568.172)
 566.172 (18.5, C₃₁H₃₄N₄⁶⁹Ga³⁵Cl requires 566.173)
 554.155 (39.1, C₃₀H₃₂N₄⁷¹Ga³⁵Cl requires 554.156)
 552.157 (39.8, C₃₀H₃₂N₄⁶⁹Ga³⁵Cl requires 552.157)

547.220 (47.3, C₃₂H₃₆N₄⁷¹Ga requires 547.222)
 545.218 (78.7, C₃₂H₃₆N₄⁶⁹Ga requires 545.216)
 533.205 (30.3, C₃₁H₃₄N₄⁷¹Ga requires 533.207)
 531.200 (48.5, C₃₁H₃₄N₄⁶⁹Ga requires 531.196)
 519.188 (66.7, C₃₀H₃₂N₄⁷¹Ga requires 519.189)
 517.185 (100, C₃₀H₃₂N₄⁶⁹Ga requires 517.182)
 505.171 (32.8, C₂₉H₃₀N₄⁷¹Ga requires 505.171)
 503.169 (60.2, C₂₉H₃₀N₄⁶⁹Ga requires 503.173)
 491.157 (34.0, C₂₈H₂₈N₄⁷¹Ga requires 491.156)
 489.155 (53.0, C₂₈H₂₈N₄⁶⁹Ga requires 489.157)
 477.140 (13.6, C₂₇H₂₆N₄⁷¹Ga requires 477.140)
 475.137 (21.7, C₂₇H₂₆N₄⁶⁹Ga requires 475.141)

Grace Ltd., St. Neots, Hunts., 100—200 mesh, 6 cm diam. × 30 cm) which had been prepared in methanol and washed with benzene. The column was eluted with benzene-methanol, the proportion of methanol being gradually increased, and the solvent being 0.02—0.03 M in anhydrous ammonia. The eluates were collected in 350 ml portions, which were taken to dryness and the residues weighed. The results are summarised in Table 4.

(c) *Thin layer chromatography.* Analytical t.l.c. did not reveal fluorescent porphyrins in fractions I, II, and III.

Fractions IV to VII were individually dissolved in chloroform and submitted to preparative t.l.c. (16 plates developed with benzene : methanol = 4 : 1 *ca.* 0.1M in NH₃). Fluorescent components were observed under u.v. light, a typical separation being shown diagrammatically in Figure 5.

and a molecular extinction of 400 000 (for gallium porphyrins). N.m.r. spectra: Bruker WP90, with tetramethylsilane as internal reference. Mass spectra: A.E.I. MS902, ionising voltage 70 eV, direct insertion, probe temperature indicated, reported as *m/z* values with relative abundances in parentheses (%). Some mass spectra (particularly those with multiple measurement of accurate mass) were determined at P.C.M.U., Aldermaston, on the Kratos (A.E.I.) MS50 instrument. Metals analysis at A.E.R.E., Harwell.

Coal samples were supplied powdered (typically <0.2 mm) by the Coal Research Establishment, Stoke Orchard. Petroleum refers to that fraction of light petroleum, b.p. 60—80 °C; methanol was AnalaR grade.

Isolation of Gallium(III) Porphyrins from British Bituminous Coal.—(a) *Initial extraction.* Batches of a powdered sample (92 kg, *ca.* 9% moisture, average particle size 52 μm) from the Daw Mill Colliery were dried in air (105 °C, 4 h) and then continuously stirred with 7% (v/v) sulphuric acid in methanol at room temperature for 12 h (using 1.4 l of solvent/kg of coal powder). The slurry was filtered at the Buchner (Whatman No. 1 paper) and the residue was washed with methanol (0.5 l/kg, in portions) the washings being combined with the main filtrate.

To the acidic methanol extract was added one fifth of its volume of chloroform. The homogeneous solution was then diluted with ten volumes of distilled water. The chloroform layer was removed and neutralised with an excess of saturated sodium hydrogencarbonate and washed three times with distilled water before being dried (Na₂SO₄) and evaporated to dryness under reduced pressure to give 42.79 g (0.046%) of crude extract.

(b) *Column chromatography.* The extract (in two portions) was applied in chloroform to columns of silica gel (W. R.

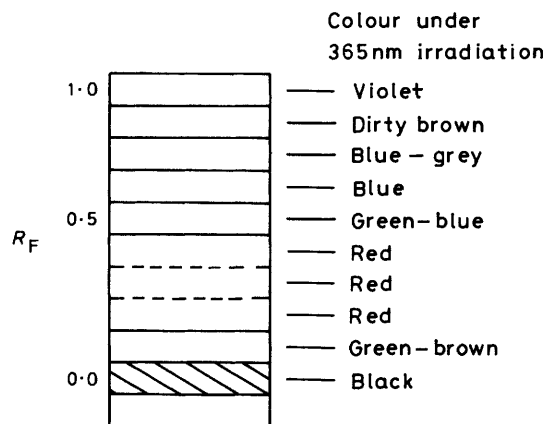


Figure 5. Diagram of a typical separation of components of Fraction IV by t.l.c. Fractions V, VI, and VII behaved similarly. The red fluorescent band corresponds to gallium porphyrins (iron polyalkylporphyrins have higher *R_F* in this system)

The red fluorescent bands were not clearly separated from one another, and the porphyrin material appeared to be similar in each of Fractions IV—VII. These porphyrin components were combined and subjected to a further t.l.c. purification (15 plates) using 4.15M-methanolic ammonia as developing solvent. The orange-pink components in the region *R_F* 0.5—0.8 were extracted with benzene-methanolic ammonia and the solution was filtered and taken to dryness to give 40.1 mg (4.3 × 10⁻⁵ %) of a crude mixture of porphyrins, which was reprecipitated as a purple amorphous solid (17.8 mg, 1.9 × 10⁻⁵ %, m.p. >320 °C) from dichloromethane-petroleum; λ_{max} (CHCl₃) (E₁^{1%}_{1cm}) 385sh (245), 405 (3 310), 532 (98), and 570 (137); ν(KBr) 3 380, 2 950, 2 910, 2 860, 1 640, 1 445, 1 370, 1 260, 1 145, 1 055, 1 030, 980, 928, and

835 cm^{-1} ; $\delta(\text{CDCl}_3)$ 10.14, 10.11, 10.04, 9.94, 9.85 (bm, arbitrarily set at 4 H, *meso*), 9.11 (m, 0.8 H), 4.05 (m, 6.0 H), 3.6 (m, 13.1 H), *ca.* 1.90 (m, bt, 12.4 H), 1.35 (s, 2.8 H), and 0.86 (m, 0.5 H). Metals analysis: by atomic absorption, Ga 5.3%; by thermal neutron activation analysis, Ga 5.7% (Cl, 1.3; Na, 0.49; Fe, 0.36; Br, 0.29; K, 0.2; Mg, 0.2; Al, 0.17; Ni, 0.05; V, <0.0006%).

High-pressure Liquid Chromatography of Gallium Porphyrins Fraction from Daw Mill Coal.—The sample was dissolved in the h.p.l.c. solvent system for injection. Seven components were revealed (Figure 3) the relative areas of the various peaks being as follows:

Retention volume (ml)	3.00	3.43	3.91	4.83	5.56	6.78	7.77
Relative abundance	(1.5)	(3.2)	12.1	14.0	30.7	17.9	20.6
Assignment C_x	26	27	28	29	30	31	32

The peak at 7.77 ml was not separated from gallium etiopyrin I on co-injection.

Demetallation of Gallium Porphyrin Fraction from Daw Mill Coal.—The metalloporphyrin fraction (*ca.* 1 mg) was heated with concentrated sulphuric acid (*ca.* 5 ml) on a steam-bath for 3 h. The cold mixture was diluted with water, chloroform was added, and the mixture was neutralised (saturated NaHCO_3). The chloroform layer was concentrated and submitted to t.l.c. purification (system D). The major product (visual estimation) was a red mobile component with a red fluorescence in 365 nm light. It was extracted and shown by electronic spectroscopy to consist of metal-free porphyrins [λ_{max} (CHCl_3) (relative extinctions) 397 (100), 497 (7.1), 530 (5.4), 565 (4.2), and 618 (2%) nm] and by t.l.c. (in benzene) to contain three components one of which did not separate from etiopyrin I.

Exhaustive Extraction Procedure: Kilogram Scale.—The powdered coal was dried at 105 °C for 2 h and a weighed amount (1–2 kg) was vigorously stirred with 5% (v/v) H_2SO_4 -MeOH (1.5 l/kg) for 30–100 h. The slurry was separated by filtration, the coal residue being returned for a repeated extraction. (Repeat extractions required less solvent—generally *ca.* 0.8 l/kg.) Extraction was continued until metalloporphyrin (see below) could no longer be detected as a weak inflection at 400 nm.

Each filtrate was diluted with chloroform (*ca.* 1/3 vol), and distilled water (*ca.* 5 vol) was added. The chloroform layer was removed and shaken with portions of saturated aqueous sodium hydrogencarbonate until neutral. The chloroform layer was separated. At this stage the absorption spectrum of the solution was measured in the 400 nm region, diluting or concentrating the solution as deemed appropriate. When an inflection could no longer be detected, or only appeared weakly on concentrating the solution, the extraction was stopped.

The chloroform solution was taken to dryness: as subsequent porphyrin-containing chloroform solutions were produced they were combined with this residue, and again taken to dryness on each occasion.

Where the amount of extracted material exceeded 1 g, it was subjected to a preliminary separation by column chromatography on Merck silica gel, 120–200 mesh. For 1 g of extract a column 20 cm \times 1.5 cm diameter was used, and in proportion. The column was packed as a methanol slurry, the column was washed with benzene, and the extract was applied as a concentrated solution in chloroform. The column was

developed with benzene and then with benzene containing a proportion of methanolic ammonia which was increased in a stepwise manner (10 to 100%). The eluate was monitored by electronic spectroscopy, and porphyrin-containing fractions indicated by an inflection or a peak at *ca.* 400 nm were combined and taken to dryness.

The red-black residue was dissolved in chloroform and submitted to preparative t.l.c., *ca.* 200 mg being applied to each plate. The plates were irrigated as follows: system A (to take non-polar materials to the top of the plate) followed by system B (to move a pink zone, fluorescent in 365 nm light, and of high mobility in this system, away from the base line). The development was stopped when the pink zone was clearly

defined. The pink zone was removed and extracted with methanolic ammonia, taken to dryness, and applied in chloroform to a second preparative plate. Development was carried out with system C followed by system D. To suit individual circumstances the proportion of methanolic ammonia in the latter was sometimes adjusted to maximise the separation of the pink-red component, which was extracted as before.

The amount of metalloporphyrin was estimated spectroscopically in chloroform.

The residue after removing solvent (chloroform) was dissolved in the minimum amount of dichloromethane, and the metalloporphyrin (gallium porphyrin) concentrate was obtained by precipitation with light petroleum.

Extraction of British Bituminous Coals.—A number of bituminous coals were examined and are listed, with the coal-field of origin and the NCB classifications of coal rank, in Table 3. The electronic spectra of the metalloporphyrin fractions isolated in each case were very similar; and they had similar t.l.c. behaviour. All these porphyrins were assessed to be gallium porphyrins: although a metals analysis was not carried out on each sample, the low resolution mass spectra accorded with the assignment of gallium porphyrin structures. However, both h.p.l.c. and mass spectra showed changes in the porphyrin ligand with increasing rank of the coal sample (Table 3).

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