Structural Characterization by *X*-Ray Absorption Spectroscopy (EXAFS/XANES) of the Vanadium Chemical Environment in Boscan Asphaltenes †

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X-Ray absorption spectroscopies, EXAFS (extended *X*-ray absorption fine structure) and XANES (*X*-ray absorption near-edge structure), were used for probing the structural and chemical environment of vanadium in two different asphaltenic fractions of a Boscan crude oil. Although the level of porphyrins detectable by u.v.–visible spectrophotometry was substantially reduced (*i.e.* <15% from the 4 000 p.p.m. of metal) due to successive solvent extractions, the EXAFS spectra of these fractions were still largely dominated by the typical pattern of vanadyl porphyrins, whereas the intense prepeak observed in the XANES spectra also clearly supported the presence of quite large amounts of porphyrins in these fractions. We thus suggest that the u.v.–visible spectrophotometric analyses tend systematically to underestimate the porphyrinic content in these heavy fractions, probably due to some hardly detectable microheterogeneity of the test solutions. E.s.r. spectra are produced which clearly support these various conclusions. Much more elaborate separation procedures are required in order to isolate and identify any ' non-porphyrinic vanadium fraction ' from Boscan crudes.

Since the pioneering work of Treibs [1] who isolated and identified about forty years ago the vanadyl porphyrin [VO(L^1)], many other metalloporphyrins have been extracted from petroleum and shale.[2] As many industrial processes in oil production or advanced coal conversion techniques are more or less critically affected by trace amounts of vanadium and nickel,[3] hydrodemetallization processes are thus often required for upgrading heavy crude oils. For a better understanding of the mechanisms involved in the latter processes, it would be highly desirable to check if the metal environment in these heavy fractions is purely of a porphyrinic nature and to learn some more about the so-called ' non-porphyrinic fraction ' *i.e.* the non-volatile fraction which does not exhibit any detectable Soret band in visible absorption spectroscopy.[4]

Extended *X*-ray absorption fine structure (EXAFS) together with *X*-ray absorption near-edge structure (XANES) spectroscopies are valuable new tools for structural investigations of chemical or biological systems where only the local arrangement of the atoms surrounding an *X*-ray absorbing element can be probed.[5] Recently, Wong and co-workers [6,7] reported XANES/EXAFS experiments carried out at the vanadium *K*-edge on pulverized coal samples and gave rather significant arguments discarding the presence of vanadyl porphyrins in these systems. In this paper we wish to show that even for asphaltenic fractions for which the level of u.v.–visible detected porphyrins is quite low, the EXAFS spectra remain obviously dominated by the typical pattern of vanadyl porphyrins. On the other hand, the presence of quite large amounts of porphyrins in these samples is also to be inferred from the characteristic prepeak observed in the detailed structure of the vanadium *K*-edge.

Experimental

Materials.—For the present study, a Boscan n-C5 asphalt (Elf-France, serial no. 15790) was selected because of its rather large metal content (~ 2 420 p.p.m. of vanadium). Another Boscan vacuum residue (Elf, no. 15787: Ni, 187 p.p.m.; V, 2 010 p.p.m.) was also retained. For the present EXAFS/XANES investigations, our strategy has been (*i*) to study various relevant synthetic model compounds, (*ii*) to extract from the Boscan asphalt the major series of petroporphyrins (metalloporphyrins extracted from petroleum) and record the EXAFS spectra of their natural mixture, and (*iii*) to compare the latter reference data with the EXAFS spectra of various asphaltenic fractions.

(*i*) *Model compounds.* For the sake of brevity, we shall restrict here our discussion to two porphyrin compounds (2,3,7,8,12,13,17,18-octaethylporphyrinato)-oxo- and -thio-vanadium(IV), [VO(L^2)] and [VS(L^2)]. Details of their structure and preparation have been published.[8,9] Very thin pellets of the pure powdered materials were prepared for the *X*-ray absorption measurements whereas a rather dilute solution of [VO(L^2)] in toluene ($\lesssim$3 300 p.p.m. of vanadium) was used for testing the *X*-ray fluorescence EXAFS set-up.

(*ii*) *Extraction of pure petroporphyrins.*‡ The Boscan vacuum (Elf-15787; 150 g) was dissolved in CH_2Cl_2 (3 × 250 cm^3) and the solutions were submitted to a number of successive chromatographic separations. A first separation was achieved on an aluminium oxide column using CH_2Cl_2–hexane (3 : 7) as eluant. The metalloporphyrin fractions were detected by absorption spectrophotometry and after evaporation of the

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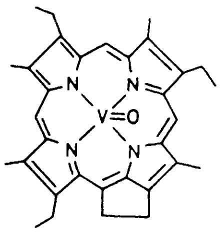
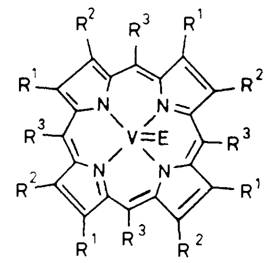
† *Non-S.I. units employed:* eV = 1.60 × 10^{-19} J; G = 10^{-4} T.

* *Work also carried out at:* L.U.R.E.: Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Laboratoire Propre du C.N.R.S. associé à l'Université de Paris-Sud, Bât. 209C–91405-Orsay, France.

‡ Carried out by Drs. J. L. Poncet and R. Guilard (Dijon).



[VO(L^1)]

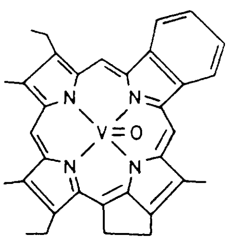


[VO(L^2)]; R^1 = R^2 = Et, R^3 = H, E = O

[VS(L^2)]; R^1 = R^2 = Et, R^3 = H, E = S

[VO(L^3)]; R^1 = Me, R^2 = Et, R^3 = H, E = O

[VO(L^5)]; R^1 = R^2 = H, R^3 = Ph, E = O



[VO(L^4)]

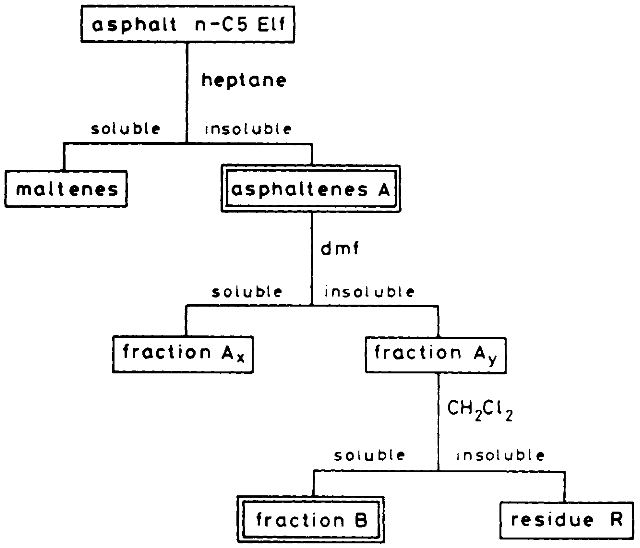


Figure 1. Synopsis of the separation procedures carried out at the University of Metz, on the Boscan asphalt ELF-15790 (dmf extractions were carried out by J. F. Tonnelier)

solvent, the corresponding oily residue was reinjected into another aluminium oxide column, using the same CH_2Cl_2–hexane mixture as eluting agent: a now rapidly moving red band containing the major portion of the metalloporphyrins was observed. Next, this metalloporphyrin concentrate was submitted to two successive chromatographic separations on active silica-gel columns; the eluants were various CH_2Cl_2–hexane mixtures made of purified solvents, 1 : 1 for the first column, 3 : 7 and then 1 : 1 again for the second column. The solvent was removed under vacuum and the solid was recrystallized from toluene–hexane (1 : 1). We obtained finally 300 mg of pure petroporphyrin dried *in vacuo* at 250 °C. According to our mass spectrometric measurements, porphyrins of type [VO(L^1)] were the major products present in our sample among the three classical series expected: [VO(L^1)], [VO(L^3)], and [VO(L^4)]. Also consistent with a large proportion of [VO(L^1)] is the α/β ratio of the intensities of the Q bands (α, 572 nm; β, 532 nm), usual companions of the Soret B band (407 nm). The apparent absorption coefficient measured for the Soret band ($\varepsilon = 0.3755$ l mg^{-1} cm^{-1}) was used hereafter for the calculation of the porphyrin concentrations in the Boscan asphalt or asphaltenes. E.s.r. spectra do indeed exhibit the typical hyperfine signal of VO^{2+} and were perfectly simulated with the following set of parameters: $g_{\text{iso.}} = 1.980_3$, $g_{\parallel} = 1.9618$, $g_{\perp} = 1.9838 \pm 0.0001$, $A_{\text{iso.}} \simeq 89.7 \times 10^{-4}$ cm^{-1}, $A_{\parallel} = 157.5 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 54.6 \times 10^{-4}$ cm^{-1}. The i.r.-active stretching mode of VO^{2+} was observed at *ca.* 995 cm^{-1}.

(*iii*) *Asphaltenic fractions.* The preparation of asphaltenic samples was conducted by the group at the University of Metz, according to the sequence shown in Figure 1. Starting from the n-C5 asphalt (Elf-15790), the heptane-insoluble asphaltenic fraction n-C7 was obtained following the standardized procedure AFNOR NFT 60—115, after elimination of maltenes containing a large amount of vanadyl porphyrins. The metal content of this asphaltenic fraction A was found to be of the order of 4 200 ± 200 p.p.m. A further extraction by *NN*-dimethylformamide (dmf) was then tentatively made according to the procedure suggested by Cagniant[10] and Mouchot:[11] the dmf-insoluble fraction was partially dissolved in CH_2Cl_2 and a powdered sample B could be prepared after evaporation of the latter solvent. The metal content of fraction B was measured both by atomic absorption (3 000 ± 200 p.p.m.) and by atomic plasma emission spectroscopy (3 500 ± 100 p.p.m.). On the basis of visible absorption spectrophotometry carried out by integration of area under the Soret band at 410 nm, the content of metal porphyrin in fractions A and B was found to be respectively 640 ± 50 and 475 ± 50 p.p.m. (*i.e.* 15% and 13% of the total amount of vanadium), using the experimentally determined absorption coefficient of the pure petroporphyrins. Therefore these fractions were good candidates for trying to elucidate the nature of the so-called ' non-porphyrinic fractions '.

Physical Methods.—General. Visible and u.v. spectra were recorded on a Perkin-Elmer 559 spectrometer using solutions in dry toluene (*ca.* 10^{-6} mol dm^{-3}). Mass spectra were obtained in the electron-impact mode with a Finnigan 3300 spectrometer (ionizing energy 30—70 eV; $i \approx 0.4$ mA; $250 < T < 400$ °C). Metal analyses were performed by atomic absorption and X-ray fluorescence. E.s.r. spectra were recorded on a Varian E4 spectrometer operating in the X-band (9.2 GHz) with 100 kHz modulation and phase-sensitive detection. I.r. spectra were recorded on a Perkin-Elmer 580B spectrometer using samples dispersed in CsI pellets.

X-*Ray absorption spectroscopy.* Our experiments were carried out at L.U.R.E. (the French national synchrotron radiation facility) using the X-ray emission of a positron beam (1.72 GeV, 200 mA) in the e^+/e^- storage ring DCI (' Double Collision dans l'Igloo '). The EXAFS-II spectrometer has already been described elsewhere.[12] The key component was a two-separated-crystal monochromator: with a pair of Si 311 monocrystals [cut parallel to the (311) planes], the third order harmonics are a problem which can however efficiently be rejected by slightly mistuning the parallelism of the reflecting planes.[13] This procedure was of special relevance here, as the vanadium K-absorption edge lies at rather low energy ($E_0 \simeq 5.5$ keV) with respect to the spectral range of emission of the machine under the present operating conditions. In the conventional absorption experiments (*e.g.* used for the study of model compounds), the detectors were two He/Ne-filled

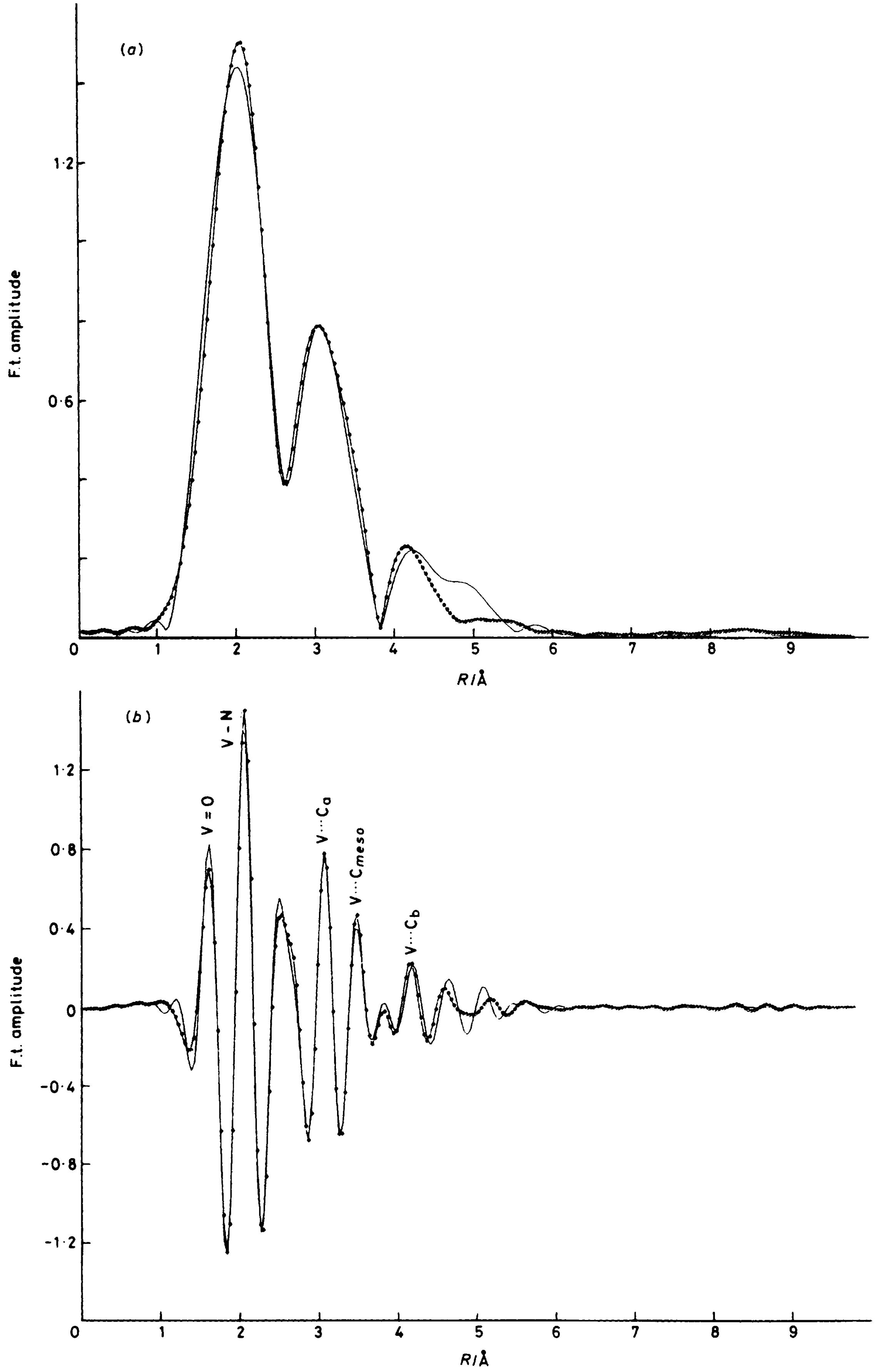


Figure 2. Comparison of the F.t. spectra derived from data recorded in the absorption mode on pure [VO(L^2)] (· · · ·) and in the *X*-ray fluorescence mode on a dilute solution (~3 000 p.p.m.) in toluene (—): (*a*) $|\tilde{\chi}_N(R)|$ *versus R*; (*b*) Im$\tilde{\chi}_N(R)$ *versus R*

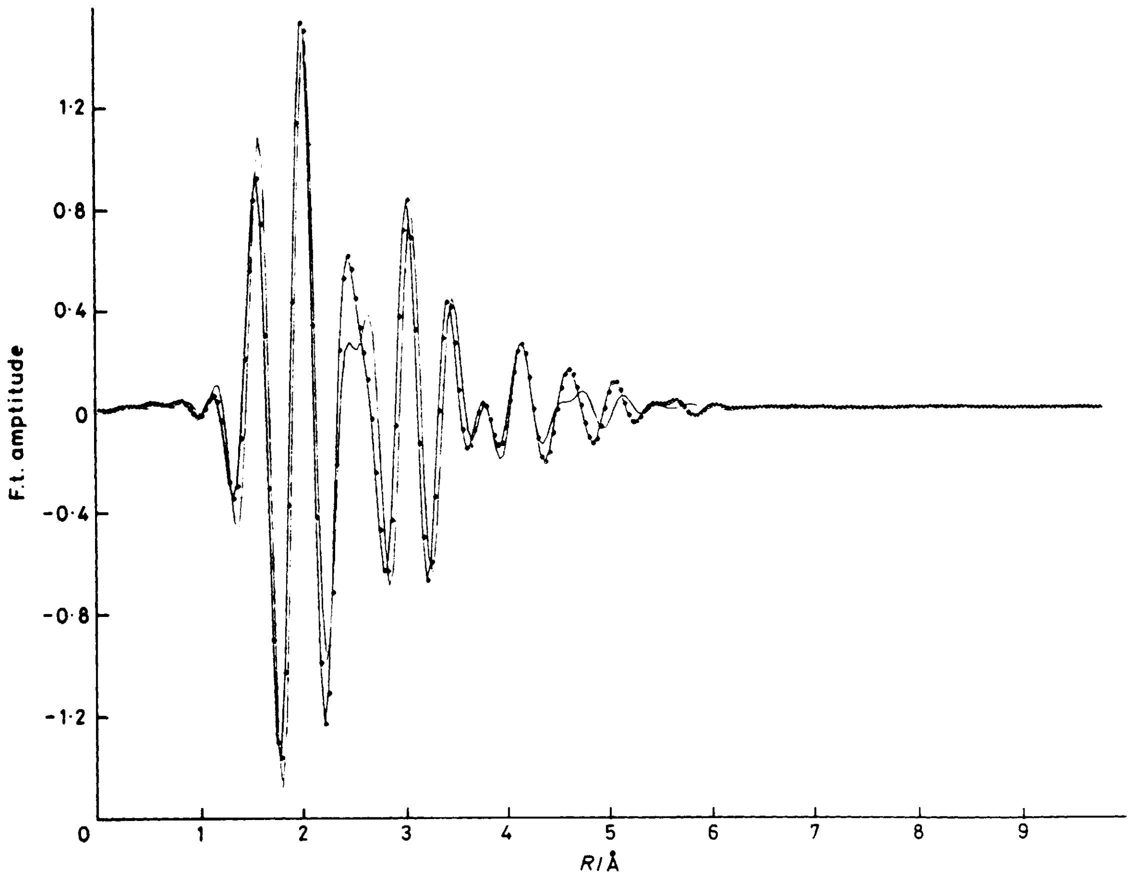


Figure 3. Comparison of the F.t. spectra Im$\tilde{\chi}_N(R)$ obtained for the extracted petroporphyrins (——) and the [VO(L^2)]-toluene solution (· · · ·). Both sets of data were recorded in the fluorescence mode

ion chambers incorporating home-made ultra-low noise preamplifiers. For more dilute samples, we used the *X*-ray fluorescence mode of detection on the EXAFS/XANES spectra.[14,15] The fluorescence detector was still an ion chamber but carefully designed in order to collect the fluorescent photons over a very large solid angle. The *X*-ray photons scattered by the sample were filtered out by a set of polyester membranes (3 μm thick) coated on both faces with a thin film (~2 μm) of vacuum-deposited titanium metal. Soller slits were also inserted in front of this ion chamber in order to reduce the fluorescence emission of these titanium filters themselves.[16] Sagittal focusing of the incident *X*-ray beam was also achieved by bending the first crystal of the monochromator in its meridian plane.[12]

The analysis of the EXAFS spectra classically involves a number of preparative steps: pre-edge and post-edge continuous backgrounds were removed using standard numerical procedures [17–19] while the EXAFS oscillations were systematically normalized against the total edge jump.[17] A pseudo-radial distribution of the closest atoms surrounding each absorbing centre is thus achievable by Fourier-transforming the normalized EXAFS oscillations $\chi(k)$.[5] It is quite noteworthy that the Fourier-transformed (F.t.) spectra $\tilde{\chi}(R)$ discussed below were all corrected according to equation (1) in

$$\tilde{\chi}_N(R) = \int_0^\infty dk\; g(k)\; \chi(k)\, \frac{k\; R_N{}^2}{N_N|F_N|A_N} \exp\,[2\sigma^2{}_{VN}\, k^2 - 2ikR \quad - i\psi_{VN}(k)] \quad (1)$$

order to compensate for the total phase shift of the selected pair vanadium (absorber)/nitrogen (scatterer) and for the decay of the scattering amplitude of nitrogen. In this equation, $g(k)$ is a Kaiser window function minimizing side-lobe effects in the F.t. spectra, whereas F_N and $\psi_{VN}(k)$ are standard notations for the back scattering amplitude function of a nitrogen shell and the total phase-shift function of the V*–N pair (V* = vanadium as *X*-ray excited absorber). These functions were evaluated using the simple parametrization suggested by Teo *et al.*[5,20] which proved to be reliable as long as the energy offset E_0 involved in the definition of the photoelectron wavevector $k = [(2m\hbar^{-2})(E - E_0)]^{\frac{1}{2}}$ is kept as a freely adjustable parameter. The value of E_0 was thus fixed here according to the Lee–Beni criterion of coincidence of respective maxima of $|\tilde{\chi}(R)|$ and Im$\tilde{\chi}(R)$.[21] Standard values were also given to R_N (=2.09 Å) and N_N (=4) which are to be regarded as fixed, constant parameters. The Debye–Waller factor $\sigma^2{}_{VN}$ and the parameters involved for the determination of $A_N(k)$ [18,19] were also kept strictly unchanged over the whole study in order to make sense of direct comparisons of the spectra: their initial values were obtained by fitting the reference data on pure [VO(L^2)]. A package of efficient fitting routines was also available for refining the estimation of distances in multi-shell EXAFS spectra.[17]

Results and Discussion

EXAFS Spectra.—In order to assess the reliability and the sensitivity of the EXAFS experiments carried out in the fluorescence mode, we decided to compare first, for the same reference compound [VO(L^2)], the magnitude spectra $|\tilde{\chi}_N(R)|$ [Figure 2(*a*)] and the spectra of the imaginary (Im) parts Im$\tilde{\chi}_N$-(R) [Figure 2(*b*)] derived either from conventional absorption

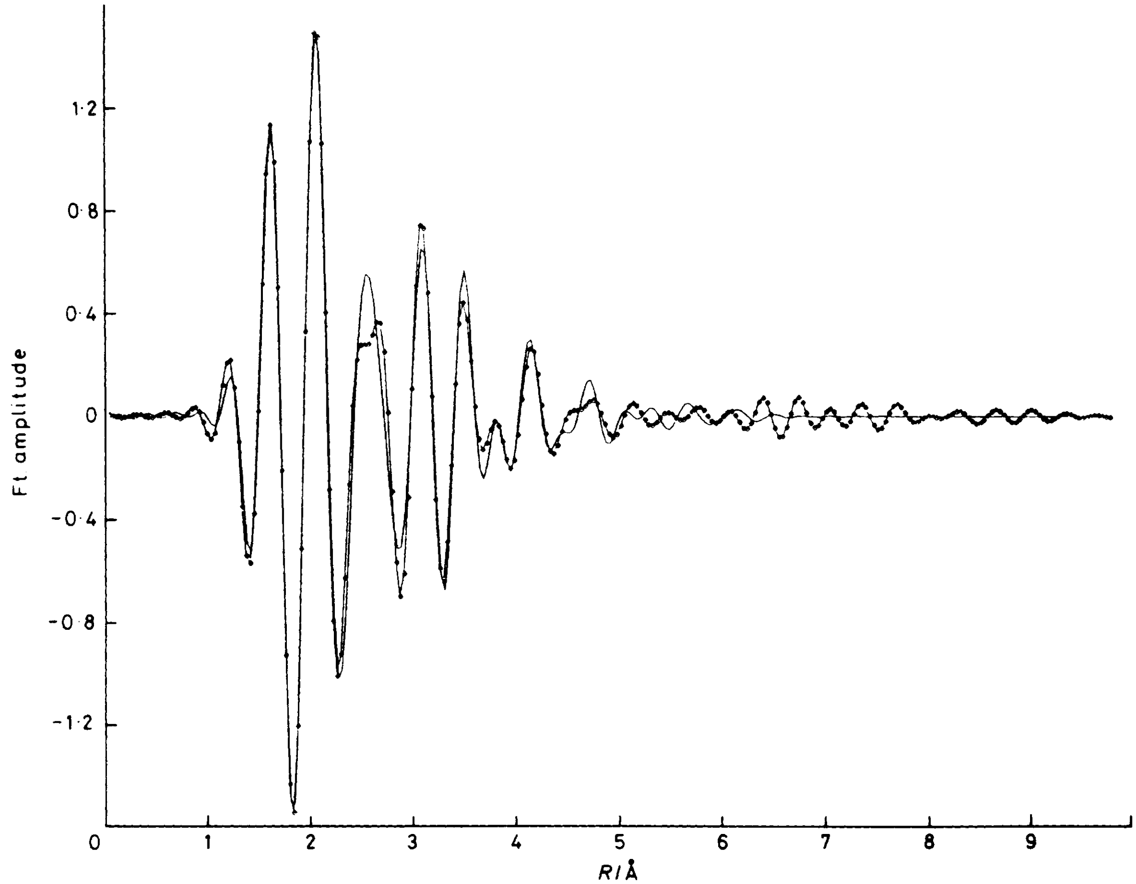


Figure 4. Comparison of the F.t. spectra Im$\tilde{\chi}_N(R)$ of the asphaltenic fraction A (——) and the petroporphyrins (····)

measurements (dotted line) or from fluorescence data (full line). We should indicate here that the absorption measurements were performed on a powdered sample of pure [VO(L^2)] while the fluorescence data concerned the above-mentioned dilute solution in toluene. It is rather encouraging to observe that, as illustrated by Figure 2(*a*) and (*b*), the two sets of experiments led to nearly superimposed spectra up to R = 5 Å: beyond this limit, the data relative to the dilute solution become too noisy to make the difference really significant. As illustrated also by Figure 2, the F.t. spectra Im$\tilde{\chi}_N(R)$ offer an improved resolution of the structural information, as compared to the magnitude spectra $|\tilde{\chi}_N(R)|$. The ultimate resolution of the former spectra Im$\tilde{\chi}_N(R)$ is actually limited by negative side lobes inherent to a finite extent of the k-space data. Nevertheless, one may easily assign the major peaks of the typical porphyrinic pattern [22] shown in Figure 2(*b*) to the five successive shells of *light* scatterers expected in the vicinity of the absorbing vanadium atom: R_1(V=O) = 1.61 ± 0.01, R_2(V···N) = 2.08 ± 0.02, R_3(V···C$_a$) = 3.12, R_4(V···C$_{meso}$) = 3.49, and R_5(V···C$_b$) ≃ 4.20 Å. These distances derived from a refined analysis of the present EXAFS data are in good agreement with the known crystal structure of [VO(L^2)].[23] The high degree of symmetry of the porphyrinic structure and the presence of only light scatterers (C, N, O) were of considerable help for a direct assignment of the various signals resolved in Figure 2(*b*).

Figure 3 compares the F.t. spectrum Im$\tilde{\chi}_N(R)$ of the extracted petroporphyrins {mainly [VO(L^1)]} with the F.t. spectrum Im$\tilde{\chi}_N(R)$ of the above [VO(L^2)] solution, both sets of data being recorded in the fluorescence detection mode. Clearly, the spectrum of the extracted petroporphyrins is much less noisy as a consequence of the larger vanadium content of the sample. Only minor differences can be detected between the two samples. As far as their reliability can be ascertained, it is interesting to observe that these differences appear consistent with the distortions of the porphyrinic ring found in the crystal structure of [VO(L^1)].[23] Whereas three of the V···N distances in [VO(L^1)] average 2.10 Å, the fourth was found to be considerably shorter (1.96 Å), a probable consequence of the lateral substituents on the pyrrole ring.

In Figure 4, we compare the F.t. spectrum Im$\tilde{\chi}_N(R)$ of these extracted petroporphyrins with the F.t. spectrum Im$\tilde{\chi}_N(R)$ of the asphaltene fraction A, again derived from fluorescence data. Obviously, the two spectra exhibit such strong similarities that it must be concluded that large amounts of porphyrins are still present in fraction A (see below). It is also interesting to note small discrepancies in the relative amplitudes of the signals associated with the carbons C$_a$ and C$_{meso}$, while the amplitudes of the other major signals are not altered. Whatever the possible origins of this effect are, no significant alteration of the phase of the major signals can be detected.

In Figure 5, we extend the former comparison to fraction B. Again, the porphyrinic pattern still dominates the F.t. spectrum Im$\tilde{\chi}_N(R)$ of this sample, but it should be noted that the amplitude reduction of the signals associated with the carbons C$_a$ or C$_{meso}$ seems more pronounced thus suggesting either a lower concentration of porphyrins or their partial degradation.

XANES Spectra.—Other valuable structural indications are still to be extracted from the details of the X-ray absorption edge itself. However, in order to avoid any artefactual shift or distortion of these spectra (*e.g.* due to a slight difference in the

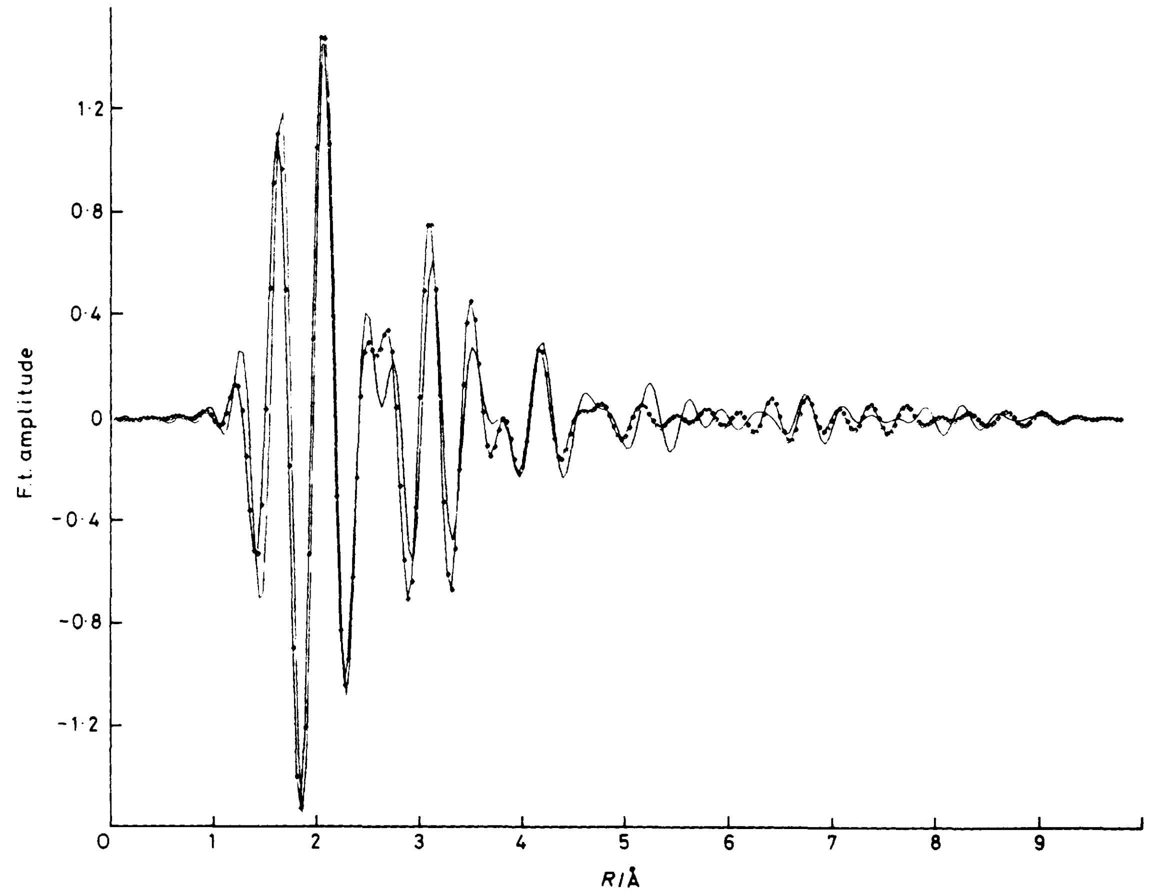


Figure 5. Comparison of the F.t. spectra Im$\tilde{\chi}(R)$ of the asphaltenic fraction B (——) and the petroporphyrins (····)

energy calibration of the monochromator, or due to a modification of the input/output slit widths), the various data shown below are systematically compared to the XANES spectrum of pure [VO(L^2)] recorded as a reference under most similar experimental conditions.

As illustrated first by Figure 6(*a*) there is a nearly perfect reproducibility of the details of the edge if the solid-state data of [VO(L^2)] are compared with those of the former dilute solution in toluene recorded again in the fluorescence detection mode. As shown by Figure 6(*b*), the exact energy position and the relative amplitude of the prepeak usually assigned to $1s \rightarrow E$ type transitions are quite sensitive to a substitution of the vanadyl group by the thiovanadyl in [VS(L^2)]. On the other hand, the high-energy part of the spectrum associated with $1s \rightarrow np$ type transitions and the beginning of the EXAFS spectrum remain however quite similar. Thus the edge spectrum appears quite sensitive to the presence of a sulphur atom in the co-ordination shell of vanadium. If we further substitute the nitrogen atom by oxygens as in the 8-hydroxyquinoline complex mentioned above,[6] a strong shift of the prepeak towards higher energies and a marked distortion of the edge itself can be seen [Figure 6(*c*)], suggesting a lower intensity of the transitions towards excited states involving some contribution of 4*s* orbitals of the metal.[24] Also the near-edge EXAFS part of the spectrum becomes fully altered. These various effects are even more dramatic if we take the edge spectrum of V_2O_5 as a reference [Figure 6(*d*)]. Figure 7 shows the edge fine structure of the asphaltenic fraction A; the obvious similarity with the spectrum of [VO(L^2)] is further evidence for the presence in this fraction of large amounts of porphyrins but any quantitative estimation would be fairly difficult. The minor differences observed concern a small reduction of the amplitude of the prepeak and a slight difference in the slope of the edge. These details might reflect some small structural or electronic distortion of the vanadyl porphyrins due to the asphaltenic matrix effect but the contribution of a small amount of a non-porphyrinic species cannot be ruled out.

Table. E.s.r. spectral parameters of extracted petroporphyrins and of fraction B

	$g_{\parallel}$	$g_{\perp}$	$10^4A_{\parallel}/\text{cm}^{-1}$	$10^4A_{\perp}/\text{cm}^{-1}$
Petroporphyrins	1.9618	1.9838	157.5	54.6
Fraction B	1.962	1.985	156.4	54.6

Consistency with U.V.–Visible and E.S.R. Spectroscopic Data.—In discussing the present EXAFS/XANES study, it is helpful to keep in mind the rather important specificities of these methods.

(*i*) *X*-Ray absorption and emission spectroscopies are basically atomic spectroscopies dealing with inner-shell (not valence) electrons and thus *all* of the vanadium atoms are contributing with a comparable weight to the absorption edge or EXAFS spectra: there is no possibility of ' silent ' vanadium centres as in e.s.r. spectroscopy.

(*ii*) The usual normalization of the EXAFS oscillations with respect to the edge jump makes the F.t. spectra $\tilde{\chi}(R)$ really representative of an *average* atomic radial distribution around each contributing vanadium site. If we refer first more speci-

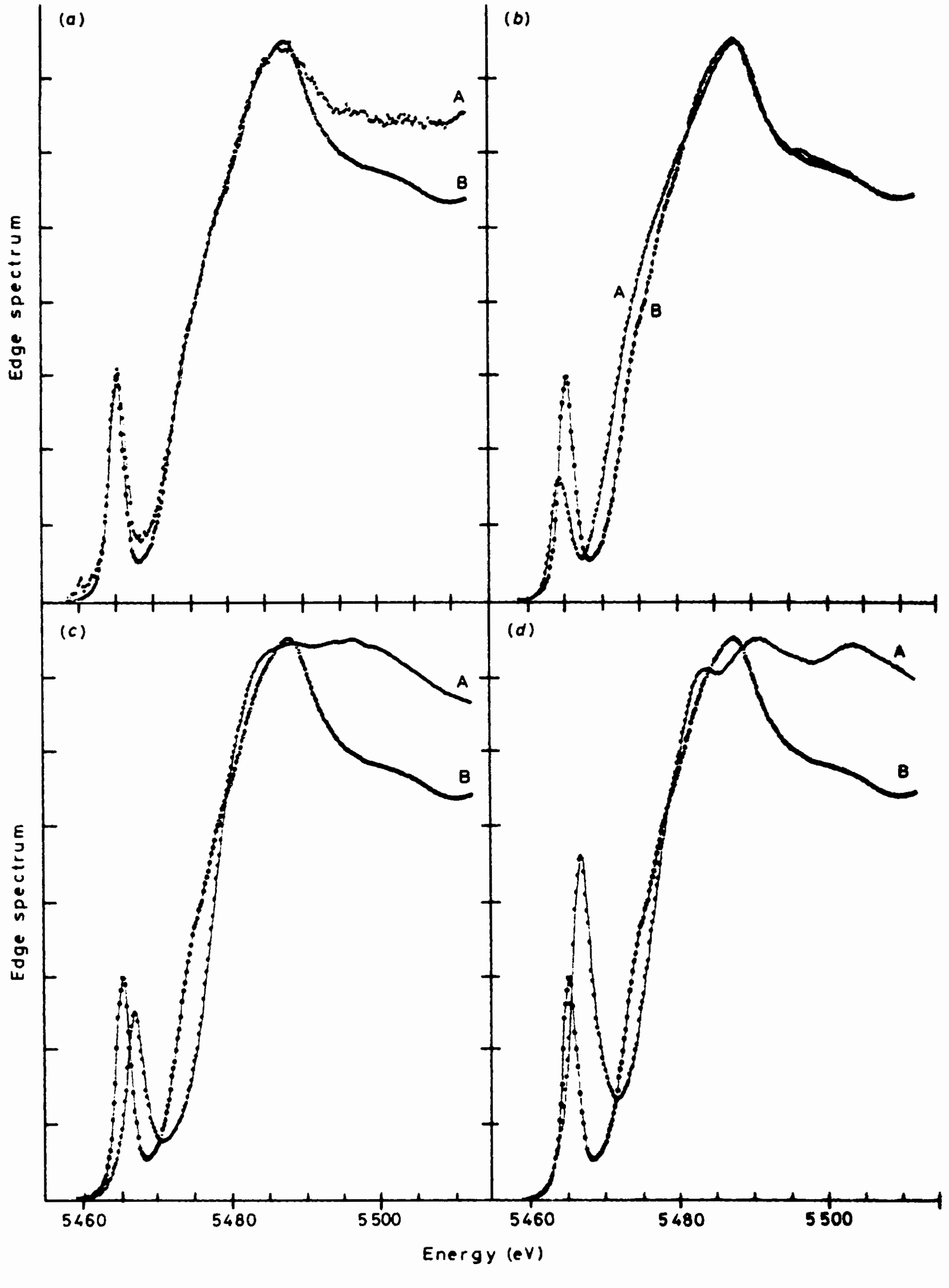


Figure 6. (*a*) Comparative display of the absorption edge spectra of pure [VO(L^2)] in the absorption mode (A) and of the latter solution in the fluorescence mode (B). (*b*) Comparative display of the absorption edge spectrum of pure [VS(L^2)] (A) with respect to pure [VO(L^2)] (B); note the amplitude reduction and the slight shift towards lower energy of the prepeak $1s \rightarrow E$ in [VS(L^2)] (A). (*c*) Comparative display of the absorption edge spectrum of a 8-hydroxyquinoline vanadyl complex (A) with respect to pure [VO(L^2)] (B). (*d*) Comparative display of the absorption edge spectrum of V_2O_5 (A) with respect to pure [VO(L^2)] (B)

fically to the signals associated with the co-ordination sphere ($R < 2.8$ Å) of the vanadium atoms, the quite remarkable superimposition of the spectra relative to fraction A and to the extracted petroporphyrins (Figure 4) thus definitively implies that the co-ordination sphere must be similar in both samples: it should include an oxygen atom at $R_1(V{=}O) = 1.61 \pm 0.01$ Å and four nitrogen (or perhaps oxygen) atoms at $R_2 = 2.08 \pm 0.02$ Å. Within the accuracy of the normalization procedure (~10%), there is little indication of additional or different signals due to other vanadium containing species, which should at least perturb the phase, intensity, or peak position of the observed porphyrin signatures ($R < 2.8$ Å). The complementary EXAFS study of [VS(L^2)] reported recently[9] provides a good illustration of such distortions of the signals of the four nitrogens by the presence of a sulphur atom.

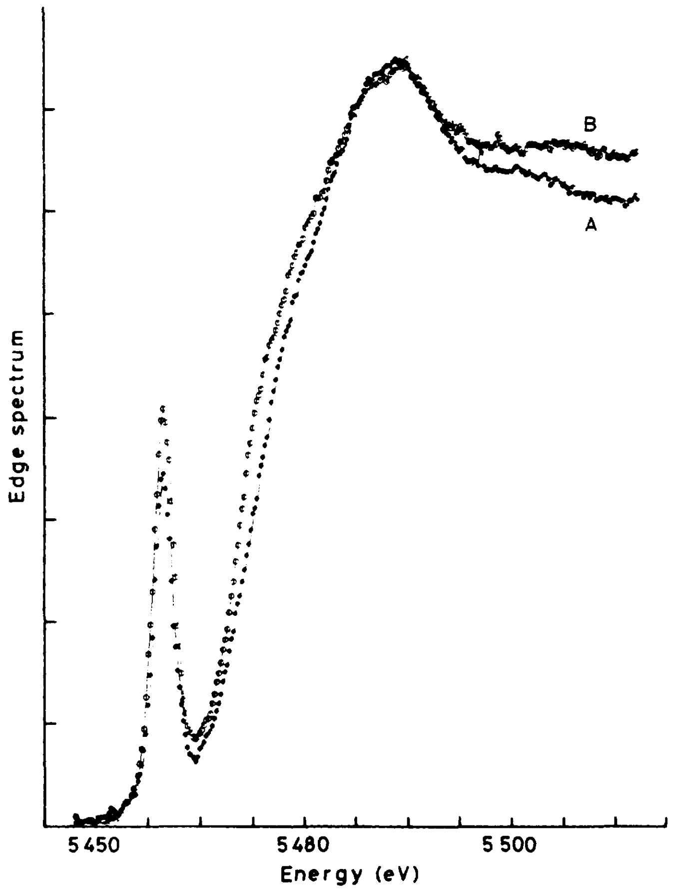


Figure 7. Comparative display of the absorption edge spectrum of the asphaltenic fraction A (A) with respect to pure [VO(L^2)] (B); both sets of data were obtained in the fluorescence mode

(*iii*) The relative interatomic distances V ··· C_a, V ··· C_{meso}, V ··· C_b, and also the relative intensities of the corresponding peaks, are most typical of a porphyrin ring. The presence of these signatures at the right distances is obvious in the spectra of fractions A or B, although we observed a slight alteration of the relative amplitudes of the signals V ··· C_a or V ··· C_{meso} compared to the amplitudes of either the V ··· N or V ··· C_b peaks. Such a slight alteration of the amplitudes might reflect either the presence of small, but hardly quantifiable (<20%), non-porphyrinic species, or the presence of additional interfering scattering centres in the close vicinity ($3 < R < 4$ Å) of the vanadium atom of vanadyl porphyrins, *e.g.* due to strong molecular interactions. These spectra however give a definitive indication that non-porphyrinic species cannot be the major components in fractions A or B.

(*iv*) The information given by the near-edge spectra displayed in Figures 6 and 7 is obviously qualitative. It establishes, however, that the average effective charge and valence state of all vanadium atoms in fraction A cannot be substantially different from the effective charge or valence state in the petroporphyrins. Similar conclusions also hold for the local symmetry of the ligand field. These results are fully consistent with the EXAFS data regarding the co-ordination sphere of the vanadium atoms. However, the lack of a perfect superimposition of the edge spectra in Figure 7, as observed in Figure 6(*a*), might again be indicative of either the contribution of small amounts of non-porphyrinic species, or specific matrix effects and/or molecular interactions affecting the electronic distribution.

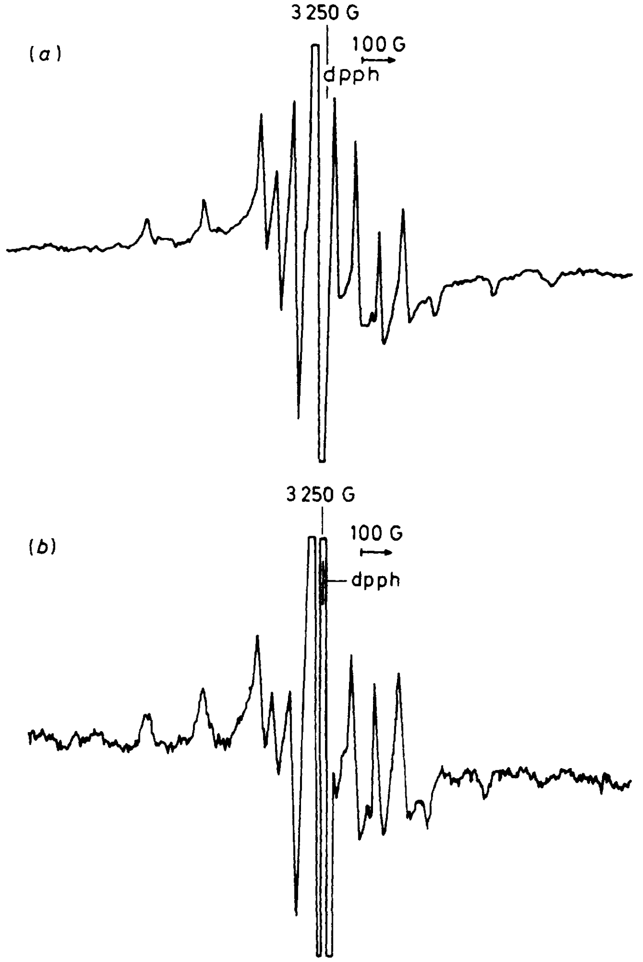


Figure 8. E.s.r. spectra (dpph = diphenylpicrylhydrazyl): (*a*) of the petroporphyrins in the solid state at − 150 °C; (*b*) of a clear solution of fraction B in CH_2Cl_2 at room temperature [scan range 2 000 G, field setting 3 250 G, time constant 1 s; modulation amplitudes 1 G (*a*) or 2.5 G (*b*); microwave attenuation 10 dB]

From the present *X*-ray study, it can therefore be concluded that vanadyl porphyrins are still the dominant components in the asphaltenic fractions A or B. However, if such a conclusion is accepted, the underestimated level of porphyrin deduced from u.v.–visible absorption spectrophotometry should be explained. A possible answer was found in questioning the homogeneity, on the microscopic scale, of the test solutions used for the u.v.–visible analysis of the asphaltenic fractions A or B. Indeed, it has been recognized for many years that, in microheterogeneous solutions, the measured absorption coefficient in the u.v.–visible region K_T (T referring to transmission) is a decreasing function of the dispersed particle size.[25–28] Following Felder [28] and restricting our discussion to the simplest case of monodisperse particles of diameter D and packing density $P = \frac{N}{V}\frac{\pi D^3}{6}$ (N = number of particles in volume V), K_T is thus given by equation (2), in which $\varphi(P_M)$ is a given function of the maximum packing P_M

$$K_T = -\frac{3}{2D}\cdot\varphi(P_M)\cdot\ln[1 - \frac{P}{\varphi(P)_M}(1 - T_D)] \quad (2)$$

defined by the limit to which the particles can approach each other: $\varphi(P_M) \simeq P_M$. In equation (2), T_D is the transmittance of a single particle,[27] defined in equation (3) where $k = 2.303\varepsilon$ denotes the natural absorption coefficient of the absorbing

$$T_D = \frac{2}{(kc_0D)^2}\left[1 - (1 + kc_0D)\cdot e^{-kc_0D}\right] \simeq e^{-2kc_0D/3} \quad (3)$$

species of concentration c_0. For a molecularly dispersed solution only, $K_{T(D\rightarrow 0)} = kc_0P$; while for $P/P_M \ll 1$, equation (4) applies.

$$\frac{K_T}{K_{T(D\rightarrow 0)}} \simeq \frac{3}{2kc_0D}\left[1 - e^{-2kc_0D/3}\right] \quad (4)$$

Equation (4) clearly predicts this effect to become most pronounced for absorbing species featuring very high absorption coefficients; it may be expected therefore, to be rather sensitive for the Soret band of metalloporphyrins ($\varepsilon > 10^5$ dm^3 mol^{-1} cm^{-1}). In order to give an experimental verification of the reality of this effect, we compared the *apparent* absorption coefficient of the Soret band (421 nm) of oxo(5,10,15,20-tetraphenylporphyrinato)vanadium(IV), [VO(L^5)], for both a perfectly homogeneous solution in CH_2Cl_2 (I) and a sonicated hyperfine dispersion of [VO(L^5)] in Nujol (II): $\varepsilon(I) = 45.1 \times 10^4$, $\varepsilon(II) = 3.3 \times 10^4$ dm^3 mol^{-1} cm^{-1}. The effect predicted by equation (4) is well illustrated by the inequality $\varepsilon(II) \ll \varepsilon(I)$, but a quantitative application of equation (4) would result in a clearly underestimated particle size ($D > 200$ Å) due to some partial solubility of [VO(L^5)] in Nujol. It is therefore our interpretation that the test solutions prepared with the asphaltenic fractions A and B were not molecularly dispersed, due to strong molecular associations: the apparent absorption coefficient K_T thus cannot be used for reliable estimation of the concentration of the porphyrinic species.

Further evidence about the microheterogeneity of the test solutions of asphaltenic fractions A or B was gained from e.s.r. spectroscopy. We have reproduced in Figure 8(*a*) the e.s.r. spectrum of the extracted petroporphyrins in the solid state ($T = -150$ °C) and in Figure 8(*b*) the e.s.r. spectrum of a clear solution of fraction B in CH_2Cl_2. We wish to emphasize that the spectrum displayed in Figure 8(*b*) is indicative of a solid dispersion of vanadyl porphyrins. Beyond a marked similarity with the reference spectrum shown in Figure 8(*a*), it exhibits the 16 anisotropic components to be observed only in the solid state for axially symmetrical vanadium(IV) d^1 complexes, while we had expected for a molecularly dispersed solution only a classical isotropic eight-line pattern. In fact, a careful inspection of the spectrum reproduced in Figure 8(*b*) also revealed very weak isotropic components associated with the probable limited solubility of these microscopic particles in CH_2Cl_2. The intensity of these isotropic components was, however, too low for any reliable evaluation of the relevant parameters. The obvious similarity of the spectra shown in Figure 8(*a*) and (*b*) can still be further quantified by comparing the e.s.r. parameters deduced from the anisotropic pattern (Table).

The values quoted in the Table give strong support to our presumed but rather unambiguous assignment of the major features of Figure 8(*b*) to vanadyl porphyrins, in perfect agreement with the conclusions of the present *X*-ray study. It is however not clear yet whether more elaborate and quantitative e.s.r. studies could really help to ascertain the exact concentration of porphyrinic species in these asphaltenic fractions and clarify the origin of the small differences observed in the EXAFS/XANES spectra of these fractions.

Conclusions

From these various pieces of information, we may conclude the following. (*i*) On the basis of EXAFS, XANES, and e.s.r. spectra, the chemical environment of vanadium in these Boscan asphaltenic fractions is predominantly, if not totally, porphyrinic in nature. (*ii*) The so-called ' non-porphyrinic fraction ' of vanadium in Boscan crudes is, by far, lower than originally reported (see, for example, ref. 4) on the basis of visible spectrophotometry. Microheterogeneity of the test solutions might well explain the underestimated results produced by the latter technique when the porphyrinic content of the samples is measured using the Soret band.

Further work is in progress in order to check if the same conclusions prevail for other crudes not so rich in porphyrins. Also, more elaborate extractions of the metalloporphyrins will be required before new structural investigations of ' non-porphyrinic ' metal fractions can be carried out.

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