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Vanadium(IV) Porphyrins: Synthesis and Spectrochemical Characterization of Dihalogenovanadium(IV) Porphyrins. Extended X-Ray Absorption Fine Structural Study of Dibromo(2,3,7,8,12,13,17,18-octaethylporphyrinato)vanadium(IV)

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The action of SOX₂ or (COX)₂ on oxovanadium(IV) porphyrin complexes $[V^{IV}L(O)]$ (L = porphyrinate) under mild conditions affords the corresponding dihalogenovanadium(IV) porphyrins $[V^{IV}LX_2]$ (X = Cl or Br). These very reactive complexes are remarkable precursors to low-valent vanadium porphyrins. Extended X-ray absorption fine structure spectroscopy at the Br K edge confirms the *trans* configuration and INDO/S calculations suggest that the absence of an e.s.r. signal is due to an orbitally degenerate ground state.

FORTY years ago Treibs isolated and identified vanadyl deoxophylloerythroetioporphyrin, the major metalloporphyrin in petroleum and shale.¹ More recently the interfacial properties of petroporphyrins (*i.e.* porphyrins co-ordinated to V and Ni) at water-oil interfaces have been investigated.² Many processes in oil production or advanced coal-conversion techniques may be critically affected by the presence of trace amounts of vanadium.³ Moreover, vanadium in combination with sulphur compounds causes a significant number of problems in oil hydroprocessing. Curiously, the manner in which the vanadium atom is held in coal, oil, or bitumen is largely unknown. The poor reactivity of oxovanadium(IV) complexes has restricted co-ordination chemistry to that of the VO²⁺ unit.⁴

We report here a convenient procedure for the isolation of dihalogenovanadium(IV) porphyrins $[V^{IV}LX_2]$ (1) (L = oep, tpp, tmtp, or tptp).† These compounds are extremely reactive and may act as precursors in the synthesis of complexes formed during the conversion of oil or shale. Extended X-ray absorption fine structure (EXAFS) spectroscopy is a valuable new tool for structural analyses of chemical or biological systems where only the *local* arrangement of atoms surrounding an absorbing element is to be determined. This paper presents a typical application of this technique in order to discriminate between two possible structures. The absence of a detectable e.s.r. signal down to 77 K will also be discussed in the light of INDO/S calculations.

EXPERIMENTAL

Synthesis and Spectroscopic Measurements.—All experimental procedures were performed under an argon atmosphere using dry oxygen-free solvents. The oxo-complexes of vanadium(IV) porphyrins were prepared by standard methods.⁵ Preparation of the dihalogenovanadium(IV) complexes (1). Three typical preparations of compounds (1) are illustrated below.

Method (a) (with thionyl chloride). The compound $[V^{IV}(oep)O]$ (1 g, 1.7 mmol) was dissolved in toluene (80 cm³). On addition of SOCl₂ (1 cm³, 14 mmol) the colour of the solution immediately turned from red to maroon. The resulting mixture was maintained at room temperature with stirring for 24 h and then placed in a refrigerator. The precipitate was filtered off, washed with hexane, and dried {1.03 g, 93% yield of $[V^{IV}(oep)Cl_2]$ (1a)}.

Method (b) (with oxalyl chloride). The compound [VIV-(oep)O] (1 g, 1.7 mmol) was dissolved in toluene (100 cm³) and (COCl)₂ (1.5 cm³, 17 mmol) added. The reaction mixture was maintained at room temperature with stirring for 12 h. The precipitate was then treated as described in method (a) {98% yield of $[VIV(oep)Cl_2]$ (1a)}.

Method (c) (using $[V^{IV}LCl_2]$ and gaseous HBr as reagents). Dry HBr gas was passed through $[V^{IV}(oep)Cl_2]$ (1a) (596 mg, 1 mmol) in dry degassed toluene (300 cm³) at room temperature for 1 h. The reaction mixture was evaporated, heptane (60 cm³) was added, and the solid residue stirred. The heptane solution was filtered and the precipitate washed with heptane and then toluene {99% yield of $[V^{IV}(oep)Br_2]$ (1b)}.

The reaction conditions, yields, and elemental analyses for all the compounds are summarised in Table 1.

Analyses. Elemental analyses were performed by the Service de Microanalyses du C.N.R.S.

Mass spectrometry. Mass spectra were recorded in the electron-impact mode with a Finnigan 3300 spectrometer at an ionizing energy of 30-70 eV, ionizing current of 0.4 mA, and a source temperature of 250-400 °C.

Spectroscopic studies. Proton n.m.r. spectra were obtained on a JEOL FX 100 spectrometer. Samples (10 mg) were dissolved in CDCl_3 (0.4 cm³) with SiMe_4 as internal reference. Infrared spectra were recorded on a Perkin-Elmer 580 B instrument. Samples were 1% dispersions in Nujol. Visible and u.v. spectra were recorded on a Perkin-Elmer 559 spectrometer for 10^{-6} mol dm⁻³ solutions of compound in dry oxygen-free toluene or tetrahydrofuran.

Magnetic measurements. The magnetic susceptibility of

 $[\]uparrow$ Abbreviations used: oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2-); tpp = 5,10,15,20-tetraphenylporphyrinate-(2-); tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate(2-); and tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2-).

 $[\]ddagger$ Throughout this paper: 1 eV \approx 1.60 \times 10^{-19} J; 1 Oe \approx 79.58 A m^{-1}.

 $[V^{IV}(tptp)Cl_2]$ (1g) was measured on a powdered sample using a vibrating sample magnetometer, a cryostat between 4.2 and 200 K, and a field of 20 kOe.

Molecular-weight determination. The molecular weight of $[V^{IV}(tmtp)Cl_2]$ (1e) was determined by cryoscopy in benzene $[22.43 \times 10^{-3} \text{ g of (1e) per l g of solvent}]$.

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pounds.¹¹ The Debye–Waller parameter, σ_j , of each shell was allowed to vary, being fitted for an ultimate evaluation of the number of scatterers, N_j .

Quantum Chemistry Calculations.—All these calculations were run on the C.I.I. I.R.I.S. 80 computer of the Institut Universitaire de Calcul Automatique de Nancy. A rough

TABLE 1 Reaction conditions and yields

		Reaction				Analysis (%)	,	
Complex	Reagent *	solvent ^b	Yield (%)	C	н	Ň	X ª	
$(1a) [V^{IV}(oep)Cl_{oep}]$	Ă	F	93	65.6	6.50	8 60	10 7	7 70
	Α	G	75	(66.05)	(5.80)	(8.55)	(10.85)	(7.80)
	в	F	95	()	(0.00)	(0.00)	(10.00)	(1.00)
(1b) $[V^{IV}(oep)Br_{s}]$	С	F	71	57.3	5.80	7.70	21.1	6.60
	E	F	99	(58.15)	(5.95)	(7.55)	(21.5)	(6.85)
	D	F	79	()	()	()	(=1:0)	(0.00)
(lc) $[V^{IV}(tpp)Cl_2]$	Α	G	72	71.1	3.80	7.50	9.40	6.80
	в	G	75	(71.95)	(3.85)	(7.65)	(9,65)	(6.95)
(1d) $[V^{IV}(tpp)Br_2]$	D	G	50	65.1	`3.30 ´	6.90	19.9	6.30
				(64.15)	(3.45)	(6.80)	(19.4)	(6.20)
(le) $[V^{IV}(tmtp)Cl_2]$	Α	F	78	`71.6 ´	`4.70 ´	6.80	9.20	6.30
	в	G	93	(72.9)	(4.60)	(7.10)	(8.95)	(6.45)
(lf) $[V^{IV}(tmtp)Br_{g}]$	E	F	99	65.8	`4.30 ´	`6.10 ´	18.6	5.50
				(65.55)	(4.15)	(6.35)	(18.15)	(5.80)
$(lg) [V^{IV}(tptp)Cl_2]$	Α	G	40	72.4	4.50	`7.10	` 8.90 ´	6.40
	в	F	77	(72.9)	(4.60)	(7.10)	(8.95)	(6.45)
	в	\mathbf{F}	87		, , ,	· · ·	, ,	```
(1h) $[V^{IV}(tptp)Br_2]$	E	F	99	65.6	4.30	6.50	18.1	5.50
				(65.55)	(4.15)	(6.35)	(18.15)	(5.80)
	T (22.21)							•

^a Reagents: A, SOCl₂; B, (COCl)₂; C, SOBr₂; D, (COBr)₂; E, HBr. ^b Reaction solvents: F, toluene; G, methylene chloride. ^c Calculated values are given in parentheses. ^d X = Cl or Br.

EXAFS Spectroscopy.—Data collection. The KRONIG oscillations of the X-ray absorption spectrum of the dibromo-complex were recorded at the bromine (Br^*) K edge and at low temperature (25 K). A pellet of appropriate geometry was prepared from the powdered complex and held in the sample holder by air-tight Kapton windows. The data were collected at the EXAFS-I station ⁶ at Lure (the French Synchrotron Radiation facility) under the standard operating conditions of the storage ring DCI (1.8 GeV). Six successive scans were accumulated for a particular sample.

Data reduction. Analysis of the spectra is detailed elsewhere,' but it should be noted here that the Fouriertransformed spectra, $\tilde{\chi}(R)$, are corrected for the amplitudes and phase shifts of an absorbing back-scattering pair jaccording to equation (1) where g(k) is a Kaiser window

$$\tilde{\chi}_{j}(R_{j}) = \int_{0}^{\infty} dk g(k) \chi(k) [kR_{j}^{2}/N_{j}] F_{j} [A_{j}(k)] \\ \exp[2\sigma_{j}^{2}k^{2} - 2ikR_{j} - i\psi_{j}(k)] \quad (1)$$

minimizing the side lobes of the Fourier-transform spectra, and $F_j(k)$ and $\psi_j(k)$ denote respectively the back-scattering function and the total phase shift relative to the *j*th shell.⁶ These functions were numerically calculated using the simple parametrization suggested by Teo *et al.*⁸ which proved to be reliable in a number of cases if the energy offset, E_o , is properly selected. This parameter which is required for the evaluation of the photoelectron wave vector, $k = [(2m_e/\hbar^2)(E_{\rm RX} - E_o)^{\frac{1}{2}}]$, was adjusted according to the Lee-Beni criterion of coincidence of the maxima of $|\tilde{\chi}(R)|$ and ${\rm Im}\tilde{\chi}(R)$ (Im = imaginary part).⁹ Hence, E_o had a value of 13 468.0 eV for the Br-V signal and of 13 474.0 eV for the Br · · · N shell. The correction factor, $A_j(R_j,k)$, which accounts for the loss of coherence of the photoelectron ¹⁰ was crudely calculated by reference to the data of relevant model comestimate of the electronic structure of a *trans*-dichlorovanadium(IV) complex was made by intermediate neglect of differential overlap (INDO) calculations ¹² an option available in the latest version of the program GEOMO.^{13,*} No optimization of the geometry of the complex was undertaken, the V-Cl distance being arbitrarily fixed at 2.3 Å. A planar symmetrical structure of the metalloporphyrin similar to that of the well resolved dibromotitanium(IV) compound ¹⁴ was assumed. Besides the classical hypothesis of any INDO/S calculations,^{15, 16} the extended set of atomic parameters proposed by Zerner *et al.*¹² for the evaluation of the core and Coulombic interaction integrals was incorporated. Within the unrestricted Hartree-Fock (UHF) theory,¹⁷ the α - and β -spin functions require separate calculation, their energy levels usually being different.

RESULTS AND DISCUSSION

Synthesis and Physical Measurements.—Oxoporphyrinatovanadium(IV) complexes react under mild conditions with SOX_2 or $(COX)_2$ in methylene chloride (or toluene) to yield the dihalogenovanadium(IV) complexes (1), equation (2) (L = porphyrinate, X = Cl or Br). While

$$[V^{IV}L(O)] \xrightarrow{SOX_2 \text{ or } (COX)_a}_{CH_aCl_a \text{ or } C_sH_aCH_a} [V^{IV}LX_2]$$
(2)

the reaction of SOX_2 with metal oxides to produce anhydrous metal chlorides is a classic method in inorganic chemistry,¹⁸ the oxo(phthalocyaninato)vanadium(IV) complex is not deoxygenated even under drastic conditions.^{19,20} Results suggest that the factor controlling the deoxygenation of oxo-complexes is not steric.

^{*} The latest version of GEOMO is available upon request from the authors.

				Mass spectra			
I.r. (Nuiol)	Visible		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Relative	Fragmentation		
Complex	$\tilde{v}(V-X)/cm^{-1}$	λ/nm	10 ⁻⁴ ε/dm ³ mol ⁻¹ cm ⁻¹	m e	intensity (%)	pattern	
(la)	335	a		a			
(1b)	250	405 ^b	29.7	662	100	[V(oep)Br]+	
()		533	1.5	584	80	$[V(oep) + H]^+$	
		570	2.4				
(lc)	355	423 ^b	41	733	6	[V(tpp)Cl ₂]*+	
()		447	1.7	698	100	$[V(tpp)Cl]^+$	
(1d)	285	428 0	31.9	821	8	[V(tpp)Bra]+	
()		553	1.7	742	24	[V(tpp)Br]+	
				662	100	$[V(tpp) - H]^+$	
(le)	345	425 °	25.3	753	100	$[V(tmtp)Cl - H]^{+}$	
X ==7		546	1.4	718	50	$[V(tmtp) - H]^+$	
(1f)	270	424 °	54.5	800	14	$[V(tmtp)Br + H]^{+}$	
()		548	2.8	719	100	[V(tmtp)]+	
(lg)	350	426 °	24.5	754	100	[V(tptp)Cl]+	
(-8)		550	1.1				
(1h)	280	425 °	45.0	799	49	$[V(tptp)Br + H]^{+}$	
()		552	2.3	720	100	$[V(tptp) + H]^+$	
	Too inso	oluble to be	measured. ^b Tetrahydro	furan solu	tion. • Toluene solut	ion.	

TABLE 2 Infrared, visible, and mass spectral data of $[V^{IV}LX_2]$ (1)

Gaseous HBr bubbled through a toluene solution of $[V^{IV}LCl_2]$ affords $[V^{IV}LBr_2]$. Far-i.r. spectra in Nujol show the bands expected for vanadium-terminal halogen stretching vibrations $[v(V-Cl) 335-350, v(V-Br) 250-285 \text{ cm}^{-1}]$ (Table 2). In every case, the band at 1 000

mononuclear nature of these compounds was checked by a magnetic moment measurement²¹ and a molecularweight determination. The magnetic moment of $[V^{IV}(tptp)Cl_2]$ (lg) was found to be $\mu_{eff.} = 1.62 \ \mu_B$ (S = 0.45 calculated with a Lande factor of 2). This value is



			<u> </u>	-	
Compound	R ¹	R ²	х	Protons of R ¹	Protons of R ²
(l a)	н	$C_{2}H_{5}$	Cl	7.20 (s, 4)	1.88 (m, 24)
(11)	п	сч	D #	7 10 (2 4)	-0.62 (m, 16)
(10)	п	C2115	Ы	7.19 (5, 4)	-0.73 (m, 16)
(lc)	C _s H _s	н	Cl	6.75, 8.52, 9.62 (m, 20) ^b	20.60 (m, 8)
(1d)	C.H.	н	Br	6.75, 8.58, 9.64 (m, 20) ^b	19.70 (m, 8)
(le)	C, H, Me-m	н	Cl	2.84 (s, 12)	20.40 (m, 8)
				6.66, 8.40, 9.48 (m, 16) ^b	
(lf)	C _a H _a Me-m	н	Br	2.86 (s, 12)	19.48 (m, 8)
、 <i>i</i>	• •			6.52, 8.46, 9.63 (m, 16) ^b	
(lg)	C _s H _s Me-⊅	н	C1	1.51 (s, 12)	20.00 (m, 8)
				6.41, 9.69 (m, 16) °	
(1h)	C _s H _s Me-⊅	H	Br	1.41 (s, 12)	19.00 (m, 8)
				6.29, 9.88 (m, 16) ^e	• • •
				6.29, 9.88 (m, 16) °	

• Given as δ (p.p.m.), multiplicity, and intensity. δ Signals correspond to m-,p-, and o-protons of C_6H_6 respectively. • Signals correspond to m- and o-protons of C_6H_4 Me-p respectively.

cm⁻¹ assigned to the vanadium-oxygen stretching vibration of the oxo-products had disappeared. Highresolution ¹H n.m.r. spectra of $[V^{IV}LX_2]$ (X = Cl or Br) in CDCl₃ solution in the presence of an excess of SOX₂ exhibit the broad lines expected for paramagnetic porphyrin complexes (signals between 1 and 21 p.p.m., see Table 3); however, even at 77 K in toluene, no e.s.r. resonance corresponding to the hypothetical paramagnetic dihalogeno-complexes was found. The postulated consistent with a d^1 complex. The molecular weight of the complex (1e) determined by cryoscopy was 794 supporting a mononuclear formulation. These data are consistent with symmetrical axial ligation of two halogeno-ligands in either a *trans* or *cis* configuration. Structural data which allow a discrimination between these two configurations can be obtained from EXAFS spectroscopy.²²

The corrected pseudo-radial distributions $\tilde{\chi}_1(R)$ and



FIGURE 2 K Edge bromine EXAFS pseudo-radial distribution $\tilde{\chi}(R)$ of $[V^{Iv}(oep)Br_2]$. Phase-shift corrections are consistent with the parameters of a Br[•] · · · N shell ($E_o = 13\ 474.0\ eV$). (----), $Im\tilde{\chi}(R)$; (· · ·), $|\tilde{\chi}(R)|$

 $\tilde{\chi}_2(R)$ shown in Figures 1 and 2 were obtained by successively incorporating in equation (1) the phase shift/ amplitude parameters relevant for a Br*...V shell and a Br*...N shell. The interatomic distances Br-V 2.41₇ Å (first peak of Figure 1) and Br...N 3.18 Å (well resolved second peak of Figure 2) agree well with expectations judging by the crystallographic data of Lecomte ¹⁴ for a similar dibromotitanium(IV) porphyrin complex (Br-Ti 2.45₄, Br...N 3.20₅, Br...C_{α} 3.94₃ Å). A signal which may be assigned to the Br...C_{α} shell is to very short T_1 values and hence very broad absorption lines if the spectra are not recorded at very low (<10 K) temperature. Therefore the electronic ground states of the complexes were investigated for orbital degeneracy in the absence of spin–orbit coupling and Jahn–Teller effects. These sources of splitting would remove the orbital degeneracy but leave excited states only a few hundred cm⁻¹ away from the ground state. For simplicity INDO/S calculations were performed on an unsubstituted porphyrin ligand in a *trans*-dichloro-

TABLE 4

Nature and energy (a.u.) of highest occupied and lowest unoccupied molecular orbitals of a dichloroporphyrinatovanadium(iv) complex. Only those in which vanadium 3d atomic orbitals account for more than 5% are included α Spin

Orbital	Energy/a.u. "	Nature of atomic components ^b
23	-0.8619	$V[d_{x^2-y^2}]$ (5.5 ₂ %), N[s, p_x , p_y] (22.9%), C[s, p_x , p_y] (55.2 ₈ %)
47	-0.5377	$V[d_{x^{2}-y^{2}}]$ (24.6 ₂ %), N[s, $p_{x}, p_{y}]$ (34.4 ₁ %), C[s, $p_{x}, p_{y}]$ (37.5 ₈ %)
52	-0.4731	$V[d_{z^{1}}]$ (22.3 ₅ %), CI[s, p_{z}] (71.6 ₅ %)
53, 54	-0.4590	$V[a_{xx}, a_{yz}]$ (18.37%), $C[p_x, p_y]$ (49.44%), $C[p_z]$ (20.07%), $N[p_z]$ (11.08%)
00, 07	-0.1906	$v[u_{xz}, u_{yz}] (39.0_2/0), C1[p_z, p_y] (9.3_7/0), C[p_z] (31.1_1/0)$
68, 69	-0.0698	$V[d_{xz}, d_{yz}]$ (17.6 ₅ %), $Cl[p_x, p_y]$ (0.8 ₆ %), $C[p_z]$ (63.3 ₉ %), $N[p_z]$ (18.0 ₁ %)
70	-0.0653	$V[a_{xy}]$ (90.4 ₉ %), $N[p_x, p_y]$ (0.7 ₂ %), $C[s, p_x, p_y]$ (2.0 ₆ %)
73	+0.0459	$V[a_x^{a}_y^{a}]$ (30.37%), $IV[3, P_x, P_y]$ (32.48%), $C[3, P_x, P_y]$ (3.08%) $V[d_x]$ (57.5%) C[[5, d] (30.3%) C[5, d, d] (21.9%) N[5, d, d]
14	+0.0402	(1.7, 0)
		β Spin
Orbital	Energy/a.u.	Nature of atomic components ^b
23	-0.8620	$V[d_{x^2-y^2}]$ (5.1,%), N[s, p_x , p_y] (23.0,%), C[s, p_x , p_y] (55.4,%)
47	-0.5537	$V[d_{x^2-y^2}]$ (24.36%), N[s, p_x , p_y] (37.77%), C[s, p_x , p_y] (35.46%)
52	-0.4714	$V[d_{z^{*}}]$ (21.0 ₂ %), Cl[s, p_{z}] (74.35%)
54, 55	-0.4475	$V[d_{xz}, d_{yz}] (9.1_0\%), [Cl p_x, p_y] (54.6_4\%), C[p_z] (22.3_7\%), N[p_z] (13.5_8\%)$
66, 67	-0.0913	$V[d_{xx}, d_{yz}]$ (9.98%), $Cl[p_x, p_y]$ (1.72%), $C[p_z]$ (80.51%), $N[p_z]$ (7.69%)
68	-0.0476	$V_i[d_{xy}]$ (96.65%), $N[p_x, p_y]$ (0.64%), $C[s, p_x, p_y]$ (2.60%)
69, 70	-0.0208	$V[d_{xz}, d_{yz}]$ (74.6 ₆ %), $Cl[p_x, p_y]$ (4.3 ₄ %), $C[p_z]$ (14.9 ₈ %), $N[p_z]$ (5.4 ₃ %)
73	+0.0556	$V[d_{z^3}]$ (60.8 ₈ %), $Cl[s, p_z]$ (25.5 ₃ %), $C[s, p_x, p_y]$ (2.5 ₅ %), $N[s, p_x, p_y]$ (9.3 ₄ %)
74	+0.0576	$V[d_{x^{a}-y^{a}}]$ (60.44%), N[s, p_{x} , $p_{y}]$ (30.30%), C[s, p_{x} , $p_{y}]$ (8.19%)
	^a l a.u. = l Hartr	$ee = 4.359 \times 10^{-19}$ J. ^b No value below 0.5% is quoted.

observed at ca. 3.85 Å but partially overlaps with the Br · · · N peak. A better signal-to-noise ratio at high kvalues would probably permit a better separation of these two shells. On the other hand, the intensity of the signals at ca. 4.85 Å strongly suggests a linear Br-V-Br sequence resulting from a typical enhancement of the signal assigned to the remote $Br \cdots Br$ shell.²³ An additional phase shift due to the forward scattering of the photoelectron by the intermediate vanadium atom explains why the apparent $Br \cdots Br$ distance is slightly shorter than twice the Br-V bond. EXAFS spectroscopy thus provides strong evidence in favour of an undistorted trans configuration. The hypothesis of a dimeric structure bridged by two bromine atoms is rejected since (i) the amplitude of the EXAFS oscillations of the first Br-V shell is consistent with the contribution of a single vanadium atom, and (ii) a dimeric structure would strongly distort the linear sequence Br -V-Br thus making the multiple scattering exaltation of the $Br \cdots Br$ signal unobservable.

However, it remains to explain why no e.s.r. signal was observed for these compounds. It has been recognized for a very long time that nearby excited states can lead vanadium(IV) complex. Since the complete density matrix obtained cannot be reproduced here, Table 4 summarizes the relevant data concerning the molecular orbitals to which the 3d atomic orbital of the vanadium atom contributes more than 5%. From these results it is apparent that the lowest occupied orbital (α spin functions 66,67) corresponds to a doubly degenerate state (E_q) . The upper half of Table 4 refers to occupied and the lower half to unoccupied electronic states (e.g. $d_{xy}, d_{x^2-y^2}, d_{z^2}$. Our results are consistent with an octahedral ligand field strongly distorted by a tetragonal perturbation. An alternative, but more expensive, approach to the present analysis would have been to use a scattered wave X- α method ^{24,25} based on Slater's transition theory.²⁶ Nevertheless, the prediction of an orbitally degenerate ground state in the absence of spinorbit coupling and Jahn-Teller distortion satisfactorily explains why no e.s.r. signal is detectable at room temperature. Further studies, probably at liquidhelium temperature, are now required.

Conclusion.—From a structural point of view, EXAFS spectroscopy provided an excellent opportunity for probing the *trans* configuration of dibromo(2,3,7,8,12,

13,17,18-octaethylporphyrinato)vanadium(IV). Noteworthy is the increase in intensity of the $Br \cdots Br$ signal resulting from the multiple scattering associated with the linear Br-V-Br sequence. The INDO/S calculations afforded an inexpensive explanation of the nonobservation at room temperature of an e.s.r. signal. A comparison between this approach and the more popular X- α method is presently under investigation.

As far as chemistry is concerned it should be noted that the dihalide complexes of vanadium(IV) porphyrins are remarkable precursors to low-valent vanadium porphyrins. Future studies on the interactions of the low-valent metalloporphyrins with sulphur compounds and catalysts used in the hydroprocessing of heavy oil are planned.

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