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VANADIUM (IV) PORPHYRINS : SYNTHESIS AND SPECTRO-CHEMICAL CHARACTERIZATION OF THIOVANADYL PORPHYRINS. EXAFS STRUCTURAL STUDY OF THIO (2, 3, 7, 8, 12, 13, 17, 18 - OCTAETHYLPORPHYRINATO) VANADIUM (IV).

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Abstract - The action of elemental sulfur with vanadium (II) porphyrins complexes $\begin{bmatrix} V^{II}(por)(THF)_2 \end{bmatrix}$ (por • porphyrinate) affords the thiovanadyl porphyrins $\begin{bmatrix} V^{IV}(por)(S) \end{bmatrix}$. EXAFS spectroscopy at the V K-edge of $\begin{bmatrix} V^{IV}(oep)(S) \end{bmatrix}$ confirms the axial symmetry of these complexes.

Although complexes containing the vanadyl ion, $V=0^{2^+}$, are well known, there are very few studies of vanadium compounds in which the thiovanadyl ion is present^{1,2}. K.P. Callahan et al¹. recently have developed a synthetic route to the previously unknown thiovanadyl species, V=S Ln, which involves reaction of V=O Ln with B₂S₃. As such thiovanadyl species are of likely relevance to certain industrial catalysts in petrochemistry³, we report here a convenient procedure for the isolation of thiovanadium (IV) porphyrins $[v^{IV}(por)(S)]$ (por = oep, tpp, tmtp or tptp)⁺ by reaction of low-valent vanadium porphyrins with elemental sulfur. EXAFS spectroscopy at the V K-edge provides convincing evidence for the monomeric nature of the complexes, as well as the multiple V=S bond.

Reduction⁺⁺ by zinc amalgam (1g) of a dry oxygen

free tetrahydrofuran⁺⁺⁺ solution (60 cm³) containing $\begin{bmatrix} v^{IV} (tptp)(Cl_2) \end{bmatrix}^4$, (1d)(0.65g, 0.8 mmol) led to a brown solution of $\begin{bmatrix} v^{II}(tptp)(THF)_2 \end{bmatrix}^5$ after 24 h of vigourous stirring at room temperature. Excess of zinc amalgam was filtered and elemental sulfur (0.1g,3 mmol) was added to the filtrate. The mixture was then stirred for 5 h at room temperature and concentrated in vacuum. The excess sulfur was then sublimated (0.1mm Hg) at 110-120°C. The obtained residue was purified by chromatography on an aluminium oxide column (eluent : toluene) and recrystallized in a mixture of toluene-heptane (1/2) $\left(0.27 \text{ g}, 45\% \text{ yield of } \begin{bmatrix} v^{IV}(tptp)(S) \end{bmatrix}, (2d) \right)^6$.

The analytical results and the mass-spectral data agree perfectly with the proposed molecular formula $[V^{IV}(\text{por})(S)]$. The parent peak corresponds either to the molecular peak $[V^{IV}(\text{por})(S)]^{+}$ or to the recombination ion $[V^{IV}(\text{por})(S)+\text{H}]^{+}$. The IR spectra of these complexes show a medium to strong intensity band in the 550 - 565 cm⁻¹ range; this band corresponds to the V=S stretching vibration². The isotropic EPR spectral parameters g_{av} and A_{av} as well as the principal components of the <g> tensor and the hyperfine interaction tensor <A> for the thiovanadyl complexes (2) - are given in Table 1.

The complexes (2) exhibit eight-line isotropic solution spectra, indicative of a d¹ V(IV) nucleus. The tensor components calculated from spectra measured on frozen solutions correspond to axially symmetric compounds. EXAFS spectroscopy at the V K-edge confirms this square - plane pyramidal molecular structure.

For the sake of comparison we have reproduced on the same plots the FT-EXAFS spectra of both $[V^{IV}(oep)(0)]$ and $[V^{IV}(oep)(S)]$: the power spectra $|\tilde{\chi}_1(R)|$ and the imaginary part $Im \tilde{\chi}_1(R)$ being respectively displayed in figures 1a and 1b. It is worth mentioning here that according to a now standard procedure detailed elsewhere 4,7,8, these FT - spectra were corrected for both the amplitudes and phaseshifts of the V ... N shell which we expected to be the dominant signal of a typical porphyrinic pattern. As illustrated by figures la/lb the contributions of the carbons of the porphyrinic ring are fairly identical, for both compounds, whereas a strong destructive interference effect is clearly detected in the case of [V^{IV}(oep)(S)], as a direct consequence of the scattering phase shift difference between S and N. As the geometry of the porphyrinic ring remains identical, for both compounds a difference FT - spectrum gives (Fig 2) the negative contribution of the V=O shell $(R_1 \approx 1.6_1 \text{\AA})$ together with the unknown V=S signal $(R_2=2.0_6\pm0.02\text{\AA})$. The latter distance is in excellent agreement with the V=S distance reported for another compound¹.

^{*}Abbreviations used : por = porphinato ; oep = octaethylporphinato ; tpp = meso-tetraphenylporphinato ; tmtp = meso-tetra-m-tolylporphinato ; tptp = mesotetra-p-tolylporphinato.

^{***}All operations were carried in Schlenk tubes under purified argon and with dried oxygen free solvents.

⁺⁺⁺ THF = tetrahydrofuran.

	Table	- EPR	spectral para	meters of thic	vanadyl complexes	
Complex	A _{av} (10 ⁻⁴ cm ⁻¹)	A // (10 ⁻⁴ cm ⁻¹)	A L (10 ⁻⁴ cm ⁻¹)	8 av	// 8	Т 8
[v ^{IV} (oep) (S)]	79.76	143.40	51.50	1.9691	1.9635	1.9717
$\left[v^{IV}(t_{PP})(s)\right]$	80.31	142.10	50.88	1.9712	1.9651	1.9711
$\left[v^{IV}(t_{mtp})(s)\right]$	80.52	144.10	50.93	1.9727	1.9655	1.9732
$\left[v^{IV}(t_{ptp})(s)\right]$	80.71	141.50	51.83	1.9734	1.9656	1.9724



Fig. 1 a) comparison of the modulus of χ (R) for $[V^{IV}(oep)(0)]$ (dotted line) and $[V^{IV}(oep)(S)]$ (full line)

b) Imaginary parts $Im\tilde{\chi}_{1}(R)$ for $[V^{IV}(oep)(0)]$ (dotted line) and $[V^{IV}(oep)(S)]^{1}$ (full line)



Fig 2 Difference spectra $[V^{IV}(oep)(S)] - [V^{IV}(oep)(0)]$ $(|\tilde{\chi}(R)|$ dotted line ; Im $\tilde{\chi}(R)$ full line)

The reaction of elemental sulfur with low-valent organometallic systems led normally to chair-like metal pentasulfide molecules ; in contrast, reaction of the low-valent vanadium (II) porphyrins with excess sulfur led to the thiovanadyl complexes. We plan to report further studies on the catalyst deactivating agents during petroleum hydrodesulfurization ; these agents contain sulfur and vanadium, also, thiovanadyl petroporphyrins are very interesting models for the catalyst poisons. This study was supported by the "Direction du Développement Scientifique et Technique et de l'Innovation" (D.D.S.T.I.).

REFERENCES

- ¹K.P. Callahan, P.J. Durand and P.H. Rieger, J. Chem. Soc., Chem. Commun. 1980, 75; M. Sato, K.M. Miller, J.H. Enenark, C.E. Strouse and K.P. Callahan, Inorg. Chem. 1981, 20, 3571.
- ²V.L. Goedhen and J.A. Ladd, J. Chem. Soc., Chem. Commun. 1981, 910.

³B.G. Silbernagel, Journal of Catalysis 1979, 56, 315

- ⁴P. Richard, J.L. Poncet, J.M. Barbe, R. Guilard, J. Goulon, D. Rinaldi, A. Cartier and P. Tola, *J. Chem. Soc.*, *Dalton Trans.* 1982, 8, 1451.
- ⁵J.L. Poncet, J.M. Barbe, R. Guilard, H. Oumous, C. Lecomte and J. Protas, unpublished results.
- ⁶The other complexes $[v^{IV}(por)(S)]$ were prepared in a similar way (yield $\tilde{z} \approx 45$) : $[v^{IV}(oep)(S)](2a)$; $[v^{IV}(tpp)(S)](2b)$; $[v^{IV}(tmtp)(S)](2c)$.
- ⁷J. Goulon, C. Goulon, F. Niedercorn, C. Selve and B. Castro, *Tetrahedron* 1981, 37, 3707.
- ⁸J. Goulon, C. Goulon-Ginet, H. Chabanel, J. Sol. Chem. 1981, 10,9.