First-row Transition-metal Complexes of Corroles: Synthesis and Characterization of Oxotitanium(IV) and Oxovanadium(IV) Complexes of β-Alkylcorroles†

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Oxotitanium and oxovanadium β-alkylcorrolates have been synthesized by reaction of corroles H_3L with different metal carriers. These complexes retain an aromatic π-electron system and exist as mononuclear species [MO(HL)] containing a M=O double bond. Optical and NMR spectroscopy indicated reaction with base leading to the formation of anionic species $[MOL]^-$. Titanyl corrolates represent the first examples of diamagnetic neutral complexes where the corrole acts as a dianionic ligand. Spectral characterization reveals that the location of the proton of HL is at the N^{22} or N^{23} inner nitrogen atoms and that the complexes are present in two tautomeric forms. In contrast to derivatives of Cr or Mo where the metals are in the +5 oxidation state, the EPR spectra of the vanadyl corrolates confirm the +4 oxidation state for the co-ordinated metal. These new complexes complete the series of first-row transition-metal derivatives of corrole.

Metal complexes of tetrapyrrolic macrocycles play an important role in life because of their implications in the activity of several enzymes. Their chemistry has been intensively studied during the last decades to gain better insights on the mechanism of the reactions occurring at metal centres in enzymes and to develop possible applications in different fields, such as medicine, biology, catalysis or technology.[1,2]

Our interest in tetrapyrrolic macrocycles other than porphyrins led us to study in detail the chemistry of corrole (see Fig. 1). Its preparation was reported for the first time by Johnson *et al.*[3] during their studies on the biosynthesis of the corrinoid structure.[4]

Despite its peculiarities, the chemistry of corrole and its metal complexes has not been extensively studied and, after an initial period, in which several reports were published by different authors,[5] this macrocycle has been almost forgotten by scientists. Such lack of interest might be ascribed to the idea that steric constraints, introduced by the direct link between pyrrole rings A and D, would cause severe limitations on the chemistry of corrole and by the fact that the synthetic procedures leading to the macrocycle and its metal complexes are rather long and complicated.

In the last few years we have developed several synthetic procedures leading to metallocorrolates[6-8] and the different methods that can be followed are outlined in Table 1 where the state of the art of the co-ordination chemistry of this macrocycle is illustrated. Structural and spectroscopic studies carried out on paramagnetic iron derivatives[9,10] and the synthesis of *meso*-substituted cobalt corrolates[11,12] evidenced several significant and interesting differences in the electronic and steric behaviour of corroles with respect to other macrocycles such as porphyrins.

Corroles have been demonstrated to have excellent chelating properties and it is possible to build up a 'Periodic Table of metallocorrolates' analogous to that of metalloporphyrinates: with the synthesis of titanyl and vanadyl complexes we have now completed the series of first-row transition-metal derivatives of corrole.

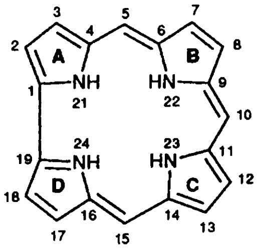

Fig. 1 Structural formula of corrole with the atom numbering scheme

Table 1 Synthesis of metallocorrolates

Reagent (solvent)[a]	Precursor[b]	Axial ligand	Metal inserted
MX_n (MeOH)	bd	–	Mn, Fe, Sn, Ge, In, Ni, Cu
	bd	PPh_3	Co, Rh
$M_x(CO)_y$ (toluene, benzene)	H_3L		Cr, Mo, Mn, Fe, Rh
MX_n (pyridine)	H_3L	—	Pd, Zn, Co
$[Mo(acac)_n]$ (phenol)	H_3L	—	Ti, V
$Co(acac)_2$ (MeOH)	L′	PPh_3	Co

[a] X = Halide, acac = acetylacetonate. [b] bd = 2,3,7,8,12,13,17,18-octaalkylbiladiene-*ac*, H_3L = 2,3,7,8,12,13,17,18-octaalkylcorrole, L′ = 2-(α-hydroxybenzoyl)-3,4-dimethylpyrrole.

Experimental

Electronic spectra were recorded on a Philips PU8700 spectrophotometer. Fast atom bombardment (FAB) and electronic impact (EI) mass spectra were recorded on a VG Quattro spectrometer; 3-nitrobenzyl alcohol (noba) or PhSMe were used as matrixes for the FAB spectra. A

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† *Non-SI unit employed:* G = 10^{-4} T.

Bruker AM 400 spectrometer was used to obtain ^{1}H NMR spectra as $CDCl_3$ solutions. All chemical shifts are given in ppm from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer as Nujol mulls. EPR spectra were recorded on a Bruker ESP 300 spectrometer; g values were calculated using diphenylpicrylhydrazyl (dpph) as calibrant. All solvents (Farmitalia) were reagent grade and were used without further purification.

The free-base corroles 2,3,7,8,12,13,17,18-octamethylcorrole, H_3L^1; 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole, H_3L^2; 2,3,7,12,13,17,18-heptamethylcorrole, H_3L^3; 2,3,7,8,12,13,17,18,21-nonamethylcorrole, H_3L^4 and 2,3,7,8,12,13,17,18,22-nonamethylcorrole, H_3L^5, were synthesized according to published procedures.[7,13]

Synthesis of [MO(HL^1)] (M = Ti *or* V).—*Route* (*a*). Corrole H_3L^1 (0.1 g, 0.25 mmol) and a small excess of the corresponding metal acetylacetonate [MO(acac)$_2$] (M = Ti or V, 0.3 mmol) were suspended in diethylene glycol (10 cm^3) under nitrogen. The mixture was refluxed and the reaction was monitored by UV spectroscopy. When the characteristic absorptions of H_3L^1 had disappeared (after 6–8 h), the solution was allowed to cool to room temperature and dichloromethane (20 cm^3) was added. The mixture was extracted three times with acidified water (HCl, pH $\approx$ 4) and then several times with dilute alkali. The organic phase was dried over anhydrous Na_2SO_4 and then evaporated under vacuum: the residue was dissolved in dichloromethane (10 cm^3) and filtered. Addition of *n*-hexane (10 cm^3) afforded [MO(HL^1)] as dark red crystals.

When 1,2,4-trichlorobenzene was used as solvent instead of glycol, at the end of the reaction the solvent was evaporated under vacuum without performing extraction. However when the solid thus obtained was redissolved with dichloromethane, a large amount of insoluble tar was present.

Yields were always lower than 5%.

Route (*b*) Corrole H_3L^1 (0.1 g, 0.25 mmol), [MO(acac)$_2$] (M = Ti or V, 0.3 mmol) and phenol (0.5 g) were heated in an open tube at 450 K. The reaction was monitored by optical spectroscopy: in the case of the vanadyl derivative the free ligand absorptions disappeared after 5 min while for the titanyl derivative the reaction required 30 min for completion. The mixture was then allowed to cool to room temperature and addition of methanol (15–20 cm^3) afforded the products.

For the oxotitanium derivatives the NMR spectrum of the product showed the presence of phenol as crystallization solvent: exchange with methanol was observed after recrystallization from CH_2Cl_2–MeOH (1 : 3). Both crystallization solvents can be eliminated and [TiO(HL^1)] was afforded by drying the sample in vacuum overnight, or upon standing for several days. Yields were in the range 60–70%.

The compounds [TiO(HL^2)] and [TiO(HL^3)] were synthesized following the same procedure. [VO(HL^1)] (82 mg, 70%) (Found: C, 68.50; H, 5.40; N, 11.75. $C_{27}H_{25}N_4OV$ requires C, 68.65; H, 5.35; N 11.85 %); EI-MS *m/z* 472 (M^+), 456 (M – O) and 236 (M^{2+}). [TiO(HL^1)] (75 mg, 64%) (Found: C, 69.25; H, 5.45; N, 12.00. $C_{27}H_{25}N_4OTi$ requires C, 69.10; H, 5.35; N, 11.95%); EI-MS *m/z* 469 (M^+), 453 (M – O) and 234 (M^{2+}). [TiO(HL^2)] (81 mg, 65%) (Found: C, 69.50; H, 5.65; N, 11.45%. $C_{29}H_{29}N_4OTi$ requires C, 70.00; H, 5.90; N 11.25 %); EI-MS *m/z* 497 (M^+), 481 (M – O) and 248 (M^{2+}). [TiO(HL^3)] (70 mg, 61%) (Found: C, 68.75; H, 5.20; N, 12.15. $C_{26}H_{23}N_4OTi$ requires C, 68.55; H, 5.10; N, 12.30%); EI-MS *m/z* 455 (M^+), 439 (M – O) and 227 (M^{2+}).

Spectral data of the complexes are reported in Table 2 together with those relative to analogous complexes of octaethylporphyrin (H_2oep).

Results and Discussion

Syntheses.—Titanium and vanadium porphyrinates are generally synthesized by reacting the ligand with the corresponding acetylacetonato complexes in a high-boiling solvent.[15] The synthesis of metallocorrolates can also be achieved by metallation of the preformed macrocycle but an easier route is that involving the cyclization of a linear tetrapyrrolic precursor, biladiene-*ac* dihydrobromide, carried out in buffered methanolic solution in the presence of an appropriate metal carrier. The resulting products largely depend on the metal used and the reaction affords either metal complexes or the corrole free base.[7] When possible this route should be the method of choice to synthesize metallocorrolates, because it involves a single reaction and affords higher yields.

Unfortunately, our attempts to prepare titanium or vanadium corrolates following this procedure were unsuccessful. Different metal carriers, [MO(acac)$_2$], MCl_3 (M = Ti or V), V(acac)$_3$ and titanocene, were used, but in all cases a

Table 2 Spectral properties of titanyl and vanadyl corrolates and porphyrinates

Complex	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})[a]	IR[b]/cm^{-1}	^{1}H NMR[c] (δ)
[TiO(HL^1)]	409 (40.0)	965	8.85 (2 H, s, H^5, H^{15}), 8.87 (1 H, s, H^{10}), 3.31 (12 H, s, Me of C^3, C^7, C^{13}, C^{17}), 3.28 (6 H, s, Me of C^8, C^{12}), 3.19 (6 H, s, Me of C^2, C^{18}), –3.48 (1 H, s, NH)
[TiO(HL^2)]	410 (36.3)	970	8.91 (2 H, s, H^5, H^{15}), 8.83 (1 H, s, H^{10}), 3.88–3.76 (4 H, m, CH_2CH_3 of C^8, C^{12}), 3.40 (6 H, s, Me of C^3, C^{17} or C^7, C^{13}), 3.31 (6 H, s, Me of C^3, C^{17} or C^7, C^{13}), 3.28 (6 H, s, Me of C^2, C^{18}), 1.51 (6 H, t, J = 7.5 Hz, Me of C^8, C^{12}), –3.42 (1 H, s, NH)
[TiO(HL^3)]	408 (37.6)	970	8.96, 8.92 (2 H, 2s, H^5, H^{15}), 8.88, 8.85 (1 H, 2s, H^{10}), 8.39 (1 H, s, H^8), 3.40, 3.37, 3.25 (21 H, s, Me), –3.54, –3.57 (1 H, 2s, NH)
[VO(HL^1)][d]	412 (35.8)	970	
[TiO(oep)][e]	406 (363) 536 (17.4) 574 (33.9)	960	10.48 (4 H, s, *meso*-H), 4.18 (16 H, q, CH_2CH_3), 1.99 (24 H, t, CH_2CH_3)
[VO(oep)][e,f]	407 (331) 533 (16.2) 572 (31.6)	990	

[a] CH_2Cl_2 Solutions. [b] ν(M=O), Nujol mull. [c] $CDCl_3$ Solution. [d] g_{iso} = 1.990. [e] Data taken from ref. 14. [f] g_{iso} = 1.979.

mixture of octamethylcorrole and octamethylporphyrin in very low yields was obtained.

The fourth *meso*-carbon atom necessary for the formation of the porphyrin structure is not present in the starting tetrapyrrole. The porphyrin is then probably obtained through a fragmentation of biladiene, catalysed by the metal ion, followed by a subsequent recombination of the resulting pyrrolic units. A similar result was previously observed in the case of the cyclization of 1,8,12,19-tetraethyl-2,3,7,13,17,18-hexamethylbiladiene-*ac* dihydrobromide, catalysed by transition metals, which yielded etioporphyrin I (2,7,12,17-tetraethyl-3,8,13,18-tetramethylporphyrin) *via* the fragmentation of the linear tetrapyrrole.[16]

The direct metallation of the preformed macrocycle is then the route that it is necessary to follow in order to achieve co-ordination of Ti and V. Thus, corroles were treated with acetylacetonato derivatives of the two metals in 1,2,4-trichlorobenzene or diethylene glycol. Evidence of metallation of the macrocycle was obtained by monitoring the electronic spectra of the reaction mixture and although it was possible to isolate the products the final yields of the reactions were very poor.

The presence of a high boiling solvent is crucial for the reaction, but the long and tedious purification procedures necessary to obtain analytically pure products drastically decreased the final yields. The problem was overcome by using phenol as solvent: in this case the minimum amount of solvent necessary to dissolve the macrocycle and the metal carrier is much smaller and at the end of the reaction titanyl and vanadyl corrolates can be precipitated in high yields simply by adding methanol to the reaction mixture.

Also, no variations in the reaction pathway were observed by varying the metal carrier, and $\mathrm{V(acac)_3}$, titanocene or $\mathrm{MCl_3}$ (M = Ti or V) afforded, under the same conditions, the corresponding oxometal derivatives. To help clarify the structure of the products the synthesis of titanium complexes of N-methyl derivatives of corrole was attempted but whilst the peripheral substitution pattern of the macrocyclic ligand does not seem to influence the fate of the reaction, both 2,3,7,8,12,13,17,18,21-nonamethyl- and 2,3,7,8,12,13,17,18,22-nonamethyl-corrole failed to give the corresponding complexes. Methylation of the preformed $[\mathrm{TiO(HL^1)}]$, following a literature method,[14] was also unsuccessful: the steric crowding present in the core of the corrole probably does not allow co-ordination of the metal.

The complexes gave satisfactory elemental analyses and have been characterized by electronic, IR, NMR, EPR and mass spectra as oxotitanium(IV) and oxovanadium(IV) complexes of the corrolate dianion. Purification procedures modify the nature of oxotitanium derivatives: crude precipitates, obtained following route (b) (see Experimental section), contained phenol as crystallization solvent and substitution with methanol was observed after recrystallization from dichloromethane–methanol, while the oxotitanium corroles were obtained by heating the samples under vacuum or by standing in air for several days.

The high stability of the vanadyl ion within the corrole ligand reflects that observed with porphyrins[14,15] for which reduction to $\mathrm{V^{3+}}$ only occurs under strongly acidic conditions and causes destabilization of the complex resulting from the increased radius of the metal ion. Although corroles are known to act as trianionic ligands and to favour in several cases the formation of metal(III) complexes, the reduced size of its chelating cavity with respect to other macrocycles would inhibit the formation of vanadium(III) corrolates which are expected to be even less stable than the corresponding porphyrinates.

Recently, Vogel *et al.*[9] confirmed the ability of corroles ($\mathrm{H_3L}$) to stabilize central metal atoms in higher oxidation states than those observed in analogous porphyrinates, and this should be a factor favouring the formation of neutral complexes [VOL]. Also, for both oxochromium and oxomolybdenum derivatives of corroles the metals are in the +5 oxidation state,[17–19] whereas in the corresponding porphyrinates the lower +4 oxidation state is the stable form for chromium and is easily obtained for molybdenum.[16] No evidence however suggests formation of $[\mathrm{VOL^1}]$: the corrole cavity appears unable to contract sufficiently to co-ordinate to the very small $\mathrm{V^{5+}}$ ion.

Spectral Properties and Reactivity.—The electronic spectra of all $[\mathrm{MO(HL^n)}]$ complexes are characterized by strong absorptions in the visible region which can be attributed to transitions within the π system of the macrocycle.[20] Fig. 2 shows the spectra of $[\mathrm{TiO(HL^1)}]$ and $[\mathrm{VO(HL^1)}]$: both complexes present similar spectra with an intense Soret-like band centred around 400 nm. When crystallization solvents complete the co-ordination sphere of titanium the appearance of Q bands in the low-energy region of the spectrum and a broadening of the Soret band is observed. Such broadening seems to indicate the presence of more than one species in solution, probably generated by a co-ordination equilibrium of PhOH or MeOH with the complex.

In the presence of strong bases, such as triethylamine or $\mathrm{OH^-}$ spectral changes are observed for both complexes. The variation can be ascribed to an acid–base reaction that leads to the formation of anionic species according to equation (1) (B =

$$[\mathrm{MO(HL^1)}] + \mathrm{B} \rightleftharpoons [\mathrm{MOL^1}]^-\mathrm{BH^+} \qquad (1)$$

$\mathrm{NEt_3}$ or $\mathrm{OH^-}$). It is relevant that the formation of metallocorrole anions leads to spectral changes similar to those observed in the first reduction of the oxochromium and

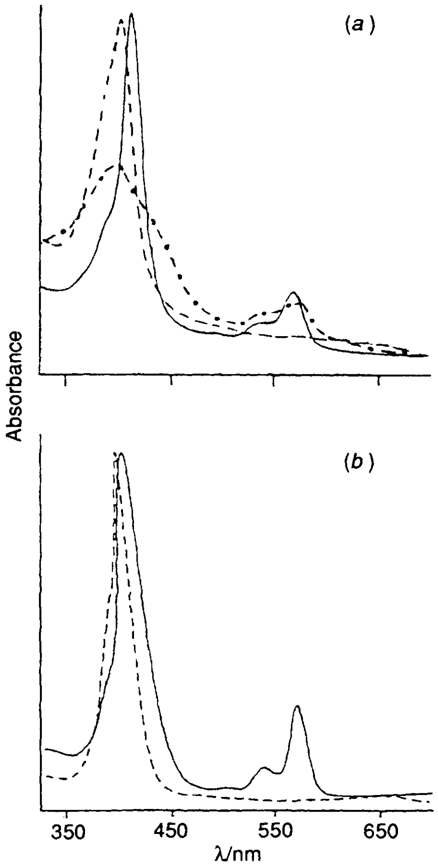

Fig. 2 Electronic spectra of $[\mathrm{TiO(HL^1)}]$ (*a*) and $[\mathrm{VO(HL^1)}]$ (*b*) in dichloromethane (——); spectra in the presence of an excess of $\mathrm{NEt_3}$ (– – – –); spectrum of $[\mathrm{TiO(HL^1)}]$ in the presence of phenol or methanol (— · — · —)

oxomolybdenum corrolate derivatives, which affords complexes of general formula $[MOL]^-$ where the metals have a formally similar +4 oxidation state.[18,19] Similar spectral variations have also been reported in the base-induced formation of corrolato anions of Cu and Ni.[20]

The observed acid-base reactivity was confirmed by NMR spectroscopy. The 400 MHz ^1H NMR spectrum of $[TiO(HL^1)]$ is shown in Fig. 3(*a*). All resonances, for which assignments are straightforward, show strong shifts generated by the macrocycle ring current.[6] Addition of NEt_3 to the solution leads to the spectrum shown in Fig. 3(*b*) where the peak due to the inner NH at δ −3.48 has disappeared with the concomitant appearance of a broad signal centred at δ 9.5 which can be attributed to the $NHEt_3^+$ ion. No significant shifting of any of the other resonances was observed.

The ^1H-NMR spectra of oxotitanium derivatives are not influenced by the presence of phenol or methanol, in contrast to the electronic spectra, however it is possible to observe resonances characteristic of these solvents, as shown in Fig. 3 (phenol) and Fig. 4 (methanol). The dissociation equilibrium of the co-ordinated phenol or methanol suggested by the electronic spectra and confirmed by their exchange in solution upon crystallization is too fast to be observed on the NMR time-scale. Similar results have been observed with $[Co^{III}L^1(PPh_3)]$ in the presence of an excess of phosphine.[21]

Titanyl corrolates represent the first examples of complexes where corrole behaves as a dianionic ligand that can be spectroscopically characterized *via* NMR spectroscopy as neutral compounds. Other derivatives where only two of the three inner NH protons were substituted upon co-ordination have been reported in the literature: among them a palladium(II) derivative the neutral form of which was too unstable to allow its isolation and which was characterized as its pyridinium salt.[22] Nickel(II) corrolates are non-aromatic, with one of the potentially tautomeric hydrogens displaced from nitrogen to carbon in such a way to interrupt the chromophore[5] whilst in a aromatic paramagnetic copper(II) complex the proton was postulated to be located on one of the inner nitrogen atoms on the basis of the electronic spectrum of the complex which was reported to be analogous to that of the fully conjugated N^{21}-methyl derivatives.[5]

For oxotitanium corrolates spectral properties clearly indicate the presence of the residual hydrogen on one of the inner nitrogen atoms. In order to define its exact location an analysis of the NMR spectra of derivatives with different peripheral substitution patterns has been carried out.

The presence of the direct link between pyrrole rings A and D on the corrole skeleton makes atoms N^{21} and N^{24} inequivalent with respect to N^{22} and N^{23}. X-Ray single-crystal analysis was attempted but failed to give good results because the presence of molecular disorder prevented good refinement of the data. Important information, however, was obtained from this analysis: the molecular disorder, present only on pyrrole rings B and C can be reasonably attributed to the presence of two different arrangements of these pyrrole units, *i.e.* above and below the macrocycle plane. This result strongly suggests that the location of the residual hydrogen is on N^{22} or N^{23}, giving two non-interconverting tautomers that are superimposed on the molecular structure.

The presence of two distinct resonances for the β-methylenic protons in the NMR spectrum of $[TiO(HL^2)]$ can be ascribed either to the rigidity of the molecule which would make protons located on the two sides of the macrocycle plane inequivalent as already observed for a cobalt complex,[23] or to the lack of interconversion between the two possible tautomeric forms with the inner hydrogen located on N^{22} or N^{23}.

The presence of a single NH resonance in the ^1H NMR spectra of corroles with a symmetrical arrangement of β-pyrrole substituents, such as H_3L^1 or H_3L^2, would then not be due to the time averaging of two resonances but can be explained considering that the deviations of the β-positions of pyrroles B and C from the plane of the macrocycle would not be reflected by the position of the relative inner nitrogens generating the magnetic equivalence of the N^{22} and N^{23} positions even in the case of an equilibrium that is slow at room temperature on the NMR time-scale. An asymmetrical corrole was synthesized and its spectral properties investigated to confirm to this hypothesis: the ^1H NMR spectrum of $[TiO(HL^3)]$ (Fig. 4) shows two set of resonances, thus revealing the presence of two non-interconverting tautomers in a 1 : 1 ratio.

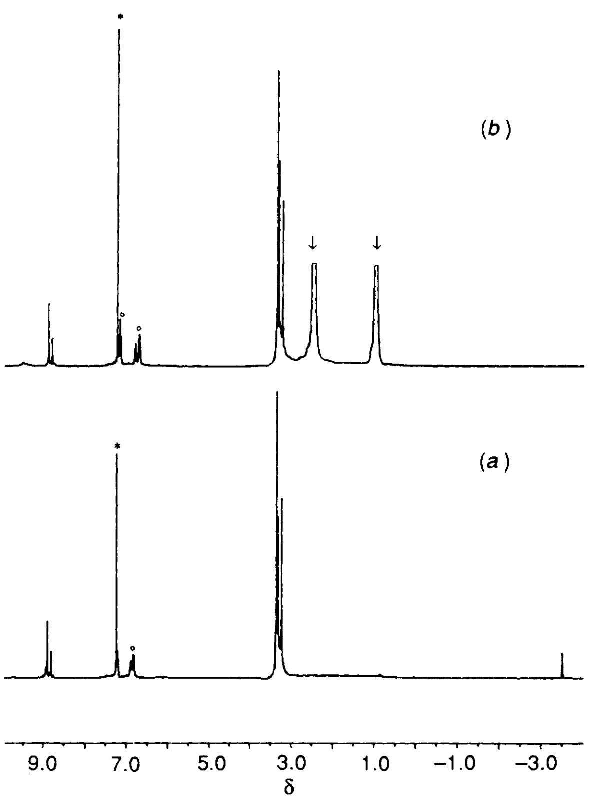

Fig. 3 The 400 MHz ^1H NMR spectrum of $[TiO(HL^1)]$ (*a*) in $CDCl_3$ and in the presence of an excess of NEt_3 (*b*); asterisks denote residual solvent signals; circles denote resonances due to phenol present as crystallization solvent; arrows denote signals due to excess NEt_3

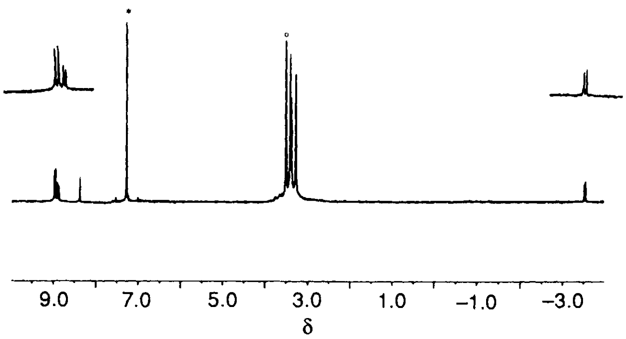

Fig. 4 The 400 MHz ^1H NMR spectrum of $[TiO(HL^3)]$ in $CDCl_3$; an asterisk denotes the residual signal, a circle denotes the resonance due to methanol present as crystallization solvent. Insets show magnification of the resonances due to the *meso* protons and inner NH protons

The very narrow signals observed in the NMR spectra of titanyl corrolates and the independence of both NMR and electronic spectra with concentration indicates the absence of aggregation and that the titanium complexes of corroles exist as mononuclear species. Titanyl porphyrins are reported[14] to be examples of very rare truly mononuclear complexes of the titanyl ion. The same behaviour is shown by titanyl corrolates as demonstrated by the presence of the Ti=O stretching vibrations

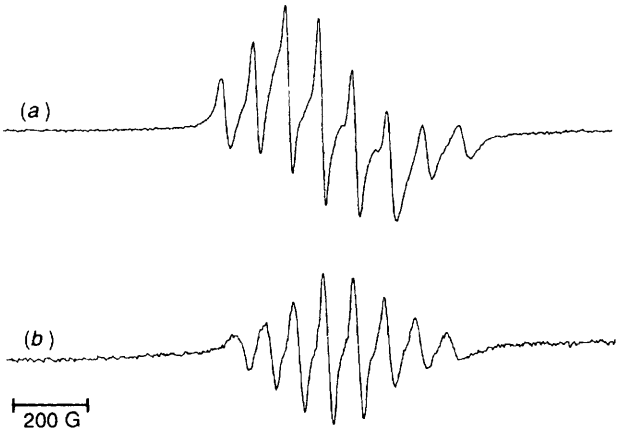

Fig. 5 The EPR spectrum of [VO(HL^1)] in chloroform (*a*) and in the presence of an excess of NEt$_3$ (*b*)

in their IR spectra. Analogous behaviour is shown by [VO(HL^1)]. The M=O absorption is centred for all complexes around 970 cm^{-1}, in good agreement with the previously reported data for derivatives of Cr and Mo.[17] For such complexes the M=O stretching vibration overlaps with bands due to ligand vibrations and the same observation has been made for the newly prepared vanadium and titanium derivatives. However, the significant increase of the relative intensity of this band, when compared with metal-free or non-oxo metal complexes (such as [Cu(HL)]), allows its attribution as an M=O stretching absorption.

The room-temperature EPR spectrum of [VO(HL^1)] is shown in Fig. 5(*a*). The spectrum is anisotropic and shows the presence of two different components that may be ascribed to the concomitant presence of the two tautomeric forms.

In the presence of base the spectrum shown in Fig. 5(*b*) is obtained. The complex exists in the anionic form, [VOL^1]$^-$ generated by removal of the inner hydrogen atom and is characterized by the following spectral values, determined directly from the spectrum: A_{iso} = 85 G, g_{iso} = 1.990, ΔH = 22 G.

Mass spectra recorded by electron impact ionization (EI) show for all complexes the parent peak corresponding to the molecular ion M^+. In addition a M^{2+} peak has been revealed, a feature characteristic of tetrapyrroles with an aromatic π system.

The presence of phenol as crystallization solvent was confirmed by the fast atom bombardment (FAB) mass spectra: although the peak corresponding to the species containing phenol has not been revealed, the C_6H_6O unit was observed in the fragmentation pattern. Another significant feature of the mass spectra is the presence of a peak corresponding to the [noba + M]$^+$ moiety, for both the titanium and vanadium derivatives, indicating a strong interaction with the matrix. Using a different matrix, such as PhSMe, which does not contain oxygen, spectra free of matrix ligated spacies were observed. In all the spectra a further significant peak was the [M − O]$^+$ ion, indicating loss of the oxo group.

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