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Synthesis, spectral properties and redox behaviour of oxovanadium(IV) complexes with tetraaza[14]annulenes

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Abstract

The preparation of a number of new oxovanadium(IV) complexes of γ-substituted tetraaza[14]annulenes using a template synthesis is reported. The relative merits of this method compared to previously reported methods for related compounds are discussed. The oxovanadium(IV) complexes show FAB mass spectra with prominent parent peaks as the only ions and a V=O stretching band is observed around 950 cm^{-1} in the IR spectra. The electronic spectra show two peaks in the range 500–400 nm attributed to CT and π–π^* transitions. Cyclic voltammetry studies, concentrating on the oxidative behaviour of the complexes, show at least one reversible oxidation for each of the derivatives.

Key words: Vanadium complexes; Oxo complexes, Macrocyclic ligand complexes

Introduction

It is almost sixty years since Treibs [1, 2] isolated and identified vanadyl deoxyphylloerythroetioporphyrin as the major metalloporphyrin in petroleum and shales. It was also Treibs [3, 4] who developed a detailed scheme to show that this vanadium complex was formed from chlorophyll. The presence of vanadium in fossil fuels has led to the element becoming of interest environmentally since problems occur in refining and burning high vanadium content fuels. Vanadyl porphyrins are also important as geochemical tracers when present in fossilised plant material and provide fundamental information to geochemists [5]. Vanadyl phthalocyanine complexes have been the subject of a series of patents [6–9] concerning their use in photoelectrophoretic and xerographic imaging. The similarity in terms of structure, physical and chemical properties of the tetraaza[14]annulenes to the porphyrins and phthalocyanines ensures that the synthesis and characterisation of these complexes is of interest.

With the exception of the 7,16-dihydro-6,8,15,17-tetramethyl-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato (TMTAA) oxovanadium(IV) complex, which has been studied in some depth by Goedken *et al.* [10, 11] and Sakata *et al.* [12], relatively little has been published concerning vanadium tetraaza[14]annulenes. Vanadium complexes of the flat tetraazaannulenes have been particularly neglected. The work of Sakata *et al.* on the unsubstituted 7,16-dihydro-dibenzo[*b,i*][1,4,8,11] tetraazacyclotetradecinato (TAA) oxovanadium(IV) complex [13] as well as reports of the γ-substituted (ethyl substituents in the 7,16 positions of the framework) complexes containing pyridine rings [14] represent the only examples of flat tetraazaannulene complexes of vanadium in the literature. Previous work on the electrochemical oxidation of metal complexes with antiaromatic tetraazamacrocyclic ligands suggests that these are oxidised to the corresponding aromatic compounds [15, 16]. This is the case for [Mn(TMTAA)Cl] where a one-electron oxidation leads to a monomeric cation radical and a second oxidation leads to the formation of the Hückel aromatic compound [17]. The nickel(II) complex of TMTAA when oxidised displays reversibility in its first oxidation followed by a rapid dimerisation through the γ position of the diiminate framework [18]. This dimerisation allows film growth by repetitive scanning in the oxidative region enabling TMTAA complexes to be used in electrocatalysis [19] via surface modified electrodes. Abelleira and Walsh [20] have shown that this dimerisation following the one-electron oxidation depends on the presence and structure of the γ substituent. In this work we have prepared a number of oxovanadium(IV) complexes of

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substituted tetraazaannulenes and characterised their spectral properties with the aid of mass, vibrational and electronic spectroscopy. Preliminary electrochemical studies of these complexes are reported using cyclic voltammetry, concentrating on the oxidation process to extend the work of Abelleira and Walsh to the early transition metal complexes and relating any difference in potential to the effect of the γ or benzenoid substituent.

Experimental

Physical measurements

Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer using dichloromethane solutions at room temperature over the range 200–1100 nm. IR spectra were obtained as nujol mulls over the range 600–4000 cm^{-1} using a Perkin-Elmer model 580 IR spectrophotometer at room temperature. Fast atom bombardment (FAB) mass spectra using a NOBA or thioglycerol matrix were obtained from the SERC mass spectroscopy service centre at University College Swansea. Low resolution EI mass spectra were recorded on a VG micromass 16B instrument operating at 70 eV. Cyclic voltammograms were obtained using a Thompson Electrochem Ltd. Ministat Potentiostat together with a Miniscan 16 Bit potential sweep generator complemented by a digital multimeter and electrochemical cell. The electrochemical system was calibrated before each run using ferrocene in the electrochemical solvent (dichloromethane unless otherwise stated) with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The cell consisted of a platinum coil auxiliary electrode, a platinum wire working electrode and a calomel reference electrode.

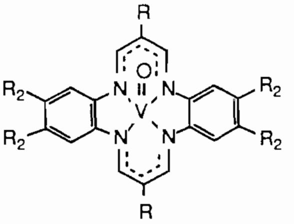
Preparation of complexes

All reactions were performed under an inert atmosphere of nitrogen but unless otherwise stated work up of reactions was done in air. Degassed solvents were used for reactions dried by distillation over the appropriate drying agent according to Perrin and Armarego [21]. All chemicals were obtained from the Aldrich Chemical Company except vanadyl acetate which was prepared following the method of Casey and Thackeray [22].

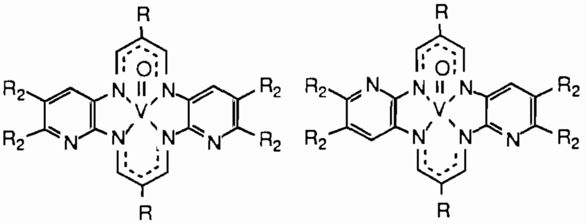
(7,16-dimethyl-dibenzo-[b,i][1,4,8,11]tetraazacyclotetradecinato) oxovanadium(IV) (1)

A mixture of vanadyl acetate (1.557 g, 8.4 mmol), *o*-phenylenediamine (1.82 g,16.8 mmol) and *N,N*-dimethylformamide (20 cm^3) was heated under reflux for 30 min. 2-Methyl-3-ethoxyacrolein (2 g, 16.8 mmol) was then added and the reaction mixture refluxed for a further 6 h. After cooling in ice the precipitate was filtered off and washed with methanol Recrystallisation from *N,N*-dimethylformamide gave a dark purple crystalline solid, 1.71 g, 53% yield. This was characterised as **1** on the basis of its IR, UV–Vis and mass spectra (Table 1).

Compound **2** was prepared as a brown crystalline solid on a similar scale, while compounds **3–6** were prepared as dark purple crystalline solids from *c* 0.2 g of vanadyl acetate using the same template method described above The *p*-tolyl γ-substituents in complexes **3**, **4** and **5** were provided by the reaction of 2-*p*-tolyl-3-dimethylaminoacrolein with the appropriate diamine. The methyl substituents on the benzenoid moiety in **2** and **4** were achieved by using 4,5-dimethyl-1,2-diaminobenzene as the amine precursor whereas the dipyrido derivatives **5** and **6** were synthesized using 2,3-diaminopyridine. Yields and spectroscopic data for these complexes are shown in Table 1.



1 R=Me, R_2=H
2 R=Me, R_2=Me
3 R=*p*-tolyl, R_2=H
4 R=*p*-tolyl, R_2=Me



5 R=Me, R_2=H
6 R=*p*-tolyl, R_2=H

Results and discussion

Synthesis of the macrocyclic complexes

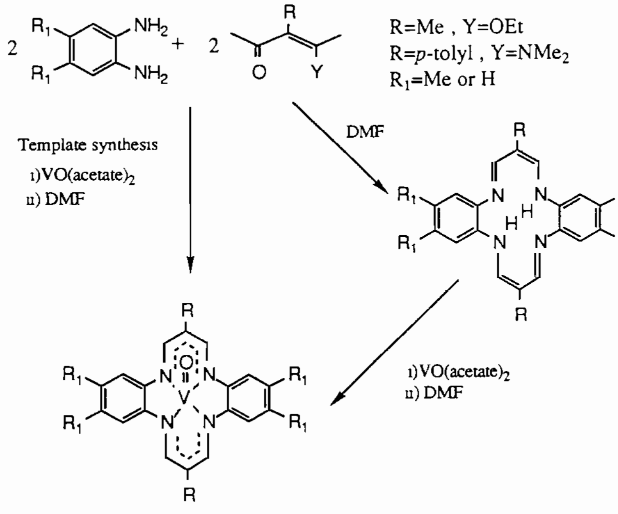
The template reaction of the appropriate acrolein and diamine precursors with vanadyl acetate in refluxing *N,N*-dimethylformamide gave the oxovanadium(IV) complexes **1–6** in the yields shown in Table 1. As with work by Mueller and Woehrle [23] no attempt was made to separate the *E* and *Z* isomers in the dipyridotetraazaannulene complexes **5** and **6**. Previous work

TABLE 1 Yields and spectroscopic data for oxovanadium(IV) tetraazaannulene complexes

Complex	Yield (%)	FAB mass spectrum M^+ at m/z	ν(V=O) (cm^{-1})	Electronic spectra, peak position (nm) and (extinction coefficient (cm^{-1} M^{-1}))
1	53	381	965	483(23500), 415(50566), 317(11733), 255(29633)
2	60	438	955	494(21966), 424(44800), 347(16366), 245(35633)
3	51	533	975	481(19666), 423(39600), 292(68200), 250(29866)
4	68	589	985	491(22000), 428(43266), 301(65266), 252(32933)
5	66	384	970	487(33500), 400(36527), 298(4885), 242(7614)
6	51	536	975	488(31500), 413(28900), 290(74900), 239(25200)

by Reichardt and Scheibelein [24] and Sakata *et al.* [25] coupled with our own observations in preparing other metal complexes [26] lead us to suggest that there will be a mixture of isomers present.

Previous preparations of oxovanadium(IV) complexes of tetraaza[14]annulenes have involved reaction of a vanadium precursor such as vanadyl acetate or vanadium(III) chloride with the preformed macrocycle in *N*,*N*-dimethylformamide. However in this work a template method was used to synthesise these complexes. Scheme 1 compares and contrasts these two methods of synthesis. Sakata *et al.* [14] made the only other reported γ-substituted oxovanadium complexes which were synthesised in yields of 18–25% starting from the preformed macrocycle. The template method described in this work gives yields of over 50%. In comparing these yields it should be noted that synthesis of the macrocycles from its amine and acrolein precursors is also a low yield reaction. Thus, Sakata's overall yields from the organic precursors are less than 10% compared to greater than 50% via the template method. The FAB mass spectra of these complexes show only the molecular ion M^+ with no breakdown products. The absence of any other significant ions in the FAB mass spectra confirms the purity of the samples.



Scheme 1. Methods of synthesis for oxovanadium(IV) tetraazaannulene complexes

Vibrational spectra

The IR spectra of the oxovanadium(IV) complexes **1**–**6** show a strong absorption band in the range 950–1000 cm^{-1} due to the V=O stretching mode as illustrated in Table 1. The ν(V=O) for vanadyl acetate is 900 cm^{-1}, significantly lower than that of the complexes; this is because of the polymeric nature of the compound resulting in six-coordination being achieved by the vanadium through V—O—V bridging. Attempts to coordinate a donor ligand such as pyridine in the vacant axial coordination site, observed for instance with $VO(acac)_2$ [27], failed with no change in the position of the ν(V=O).

Electronic spectra

The spectra show two peaks in the region 400–500 nm in agreement with previous observations for similar complexes [19]. The absorption bands are credited to charge-transfer transitions from metal to ligand and π–π* transitions within the ligand molecule. The size of the extinction coefficients eliminates the possibility of the transitions as d–d*. The peak values and extinction coefficients are shown in Table 1. The oxovanadium(IV) complexes of the dibenzo- and dipyridotetraazaannulenes are slightly different in terms of the extinction coefficients for the two peaks in the region 400–500 nm. For the dibenzo derivatives **1–4** the λ_{max} peak has an extinction coefficient which is double that of the other peak in the region. However for the dipyrido derivatives **5** and **6** these two peaks have very similar extinction coefficients. The effect of methyl substitution on the benzenoid moiety causes a change in the λ_{max} value by 10 nm.

Cyclic voltammetry

The electrochemical data obtained for these oxovanadium(IV) complexes are shown in Table 2 and the cyclic voltammograms from complexes **4** and **6** are shown in Fig. 1. All these complexes show at least one reversible oxidation with the potential separation of the peaks ΔE_p having a value of approximately 80 mV. The theoretical value for a one-electron reversible oxidation is 59 mV, the higher value is due to uncompensated solution resistance since the well known reversible ferrocene–ferricenium couple also had a value of 80 mV under the same conditions. In addition, except for complex **5** a second oxidation wave is observed. For complexes **1** and **3** the shape of the voltammograms suggests that a phase transition process is occurring which is almost certainly electrocrystallisation of the dication on the electrode surface.

TABLE 2. Oxidation potentials for oxovanadium(IV) tetraazaannulene complexes

Complex	Half wave potential at 0.2 V/s (V)
1	0.74, 1.3[a]
2	0.6, 1.09
3[c]	0.85, 1.26[b]
4[c]	0.68, 1.13
5[d]	0.95
6[d]	1.12, 1.33

All potentials relate to reversible oxidation couples, with $E_{1/2}$ values given and $\Delta E_p = 80$ mV unless stated. The concentration of the complex in solution is 1.0 mM unless stated. [a]Non-reversible redox couple anodic peak at 1.3 V with the corresponding cathodic peak at 0.8 V. [b]Non-reversible redox couple anodic peak at 1.26 V with the corresponding cathodic peak at 0.89 V. [c]Concentration of complex 5.0 mM. [d]Concentration of complex 1.5 mM.

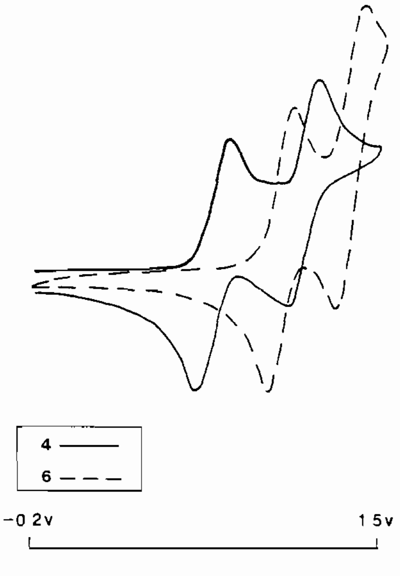


Fig. 1. Cyclic voltammograms for complexes **4** and **6**.

The oxidation potentials for the dipyrido oxovanadium(IV) complexes **5** and **6** are higher than for their dibenzo counterparts **1** and **3** consistent with the electron withdrawing effect of the nitrogen atom. Another interesting observation is the effect of substitution on the benzenoid moiety. The oxidation potentials for complexes **2** and **4** are both about 0.15 V less than the corresponding ones for **1** and **3**, respectively, presumably due to the inductive effect of the methyls on the benzene groups in **2** and **4**. In addition the second oxidation for complexes **2** and **4** is now electrochemically reversible, presumably the extra methyl groups mean that the dications for these complexes are soluble in dichloromethane unlike those for **1** and **3** mentioned above. This effect of methyl substituents on the benzene ring on the oxidation potentials has been noted previously for derivatives of the saddle-shaped Ni(TMTAA) complex [28]. Abelleira and Walsh have shown that the zinc complex of the 7,16-di-*p*-tolyl-substituted macrocycle undergoes two reversible oxidations which are assigned to ligand based processes. In the case of iron and cobalt complexes they found that the metals also underwent oxidation at potentials below those of the ligands as found for porphyrins and phthalocyanines. A recent report on the oxidation of vanadyl octaethylporphyrin [29] suggested two ligand based oxidations occurred (at 0.95 and 1.25 V versus SCE). Given the similarity between the electrochemistry of iron and cobalt complexes of γ-substituted tetraazaannulenes and those of porphyrins together with results on vanadyl porphyrins we feel the oxidations observed for complexes **1–6** are probably ligand based rather than involving the vanadium centre. Further work is in progress to verify this hypothesis and further investigate the electrochemistry of these compounds.

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