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Vanadium complexes of planar pentadentate macrocyclic ligands

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Abstract

Vanadium trichloride forms 1:1 adducts with 6,6′-bis(hydrazino)-2,2′-bipyridines, in which the metal is in a six-coordinate environment, with the two axial sites occupied by chloride ligands. These complexes are paramagnetic and ESR active. Condensation of these complexes with 2,6-pyridinedialdehyde leads to either vanadium(III) macrocyclic complexes or free macrocyclic ligands, depending upon the conditions of pH.

Introduction

Macrocyclic ligands and their complexes have been intensively investigated over the past three decades [1, 2]. The high stabilities and variable geometries associated with such compounds have allowed the preparation of complexes of metal ions in a wide range of unusual oxidation states and coordination geometries. We have been particularly interested in the preparation and coordination chemistry of planar pentadentate macrocyclic ligands incorporating 2,2′-bipyridine, 1,10-phenanthroline or 2,2′:6′,2″-terpyridine moieties within the macrocyclic framework [3–36]. Such macrocyclic ligand systems are conveniently prepared by template or transient template condensation reactions. Macrocyclic ligands containing a relatively rigid planar pentadentate donor set have been shown to form complexes with a number of differing coordination geometries about the central metal ion. The most common of these are a pentagonally-based pyramid and a pentagonal bipyramid, giving rise to six- and seven-coordinate complexes, respectively. In the course of our studies we have concentrated upon the coordination chemistry of the later first row transition metal ions, although we have also reported alkali metal [14, 24], rhodium [9, 26] and tin complexes [20, 21]. In the course of our investigations into the interactions of planar pentadentate macrocyclic ligands and their acyclic precursors with chromium(III) we discovered a transient template reaction which is a convenient method for the preparation of the metal-free ligands, and also described the preparation and structural characterisation of a seven-coordinate chromium(III) macrocyclic complex [13, 15]. These observations prompted us to investigate the behaviour of other early transition metal ions with planar pentadentate macrocyclic systems, and in this note we wish to report some vanadium complexes with such ligands.

Experimental

IR spectra were recorded in compressed KBr pellet on Perkin-Elmer FT 910 or Perkin-Elmer 983 spectrophotometers. ESR spectra were recorded using a Varian E109 spectrometer; *g* values were determined by reference to a 2,2-diphenyl-1-picrylhydrazyl hydrate standard ($g=2.0036$). Magnetic susceptibilities were measured using a Johnson Matthey susceptibility balance calibrated using copper sulfate pentahydrate and mercury cobalt thiocyanate. The ligand L^1 was prepared as described previously [13, 15]; L^2 was prepared in a precisely analogous manner to L^1 by the reaction of 6,6-dibromo-2,2′-bipyridine with 3-hydroxypropylhydrazine.

L^1 n = 2
L^2 n = 3

Synthesis of [VL^{1}Cl$_2$]Cl

Vanadium(III) chloride (0.6 g, 3.8 mmol) was added to a boiling degassed solution of [HL^1]Cl (1.0

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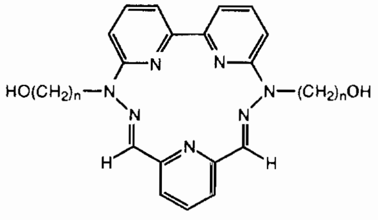
g, 3.3 mmol) in ethanol (500 cm^3) maintained under an atmosphere of dinitrogen. The resultant solution was heated to reflux for 2 h, and allowed to cool. The fine orange–yellow solid which was precipitated was collected by filtration and dried to yield [VL^{1}Cl$_2$]Cl·H$_2$O (1.20 g, 75%). *Anal.* Found: C, 35.4; H, 4.4; N, 17.5; Cl, 22.2. Calc. for $C_{14}Cl_3H_{22}N_6O_3V$: C, 35.0; H, 4.6; N, 17.5; Cl, 22.2%. μ_{eff} 2.96 BM.

Synthesis of [VL^{2}Cl$_2$]Cl

This was prepared in precisely the same manner as [VL^{1}Cl$_2$]Cl·H$_2$O, replacing the [HL^1]Cl by [HL^2]Cl, and the preparation yielded orange–yellow [VL^{2}Cl$_2$]Cl (70%). *Anal.* Found: C, 39.2; H, 4.9; N, 17.0; Cl, 21.8. Calc. for $C_{16}Cl_3H_{22}N_6O_2V$: C, 39.2; H, 4.9; N, 17.2; Cl, 21.8%. μ_{eff} 2.94 BM.

Synthesis of [VL^{3}Cl$_2$]Cl

2,6-Pyridinedialdehyde (0.014 g, 0.11 mmol) was added to a solution of [VL^{1}Cl$_2$] (0.05 g, 0.11 mmol) in boiling degassed water (150 cm^3) and the solution heated to reflux for 4 h. The deep red–purple solution was concentrated *in vacuo* to about 2 cm^3 volume, and then filtered through celite. The complex [VL^{3}Cl$_2$]Cl·H$_2$O was obtained as a dark purple microcrystalline solid by the diffusion of acetone vapour into the solution (0.06 g, 60%). *Anal.* Found: C, 43.5; H, 3.9; N, 16.7; Cl, 18.2. Calc. for $C_{21}Cl_3H_{23}N_7O_3V$: C, 43.6; H, 4.0; N, 17.0; Cl, 18.4%. μ_{eff} 2.93 BM.



L^3 n = 2
L^4 n = 3

Synthesis of [VL^{4}Cl$_2$]Cl

This was prepared in precisely the same manner as [VL^{3}Cl$_2$]Cl·H$_2$O, replacing the [VL^{1}Cl$_2$]Cl by [VL^{2}Cl$_2$]Cl in 500 cm^3 of water, and the preparation yielded purple [VL^{4}Cl$_2$]Cl·H$_2$O (70%). *Anal.* Found: C, 43.92; H, 4.9; N, 15.6; Cl, 17.3. Calc. for $C_{23}Cl_3H_{29}N_7O_4V$: C, 44.2; H, 4.6; N, 15.7; Cl, 17.1%. μ_{eff} 2.90 BM.

Synthesis of [VL^{3}Cl$_2$]Cl in the presence of acid

2,6-Pyridinedialdehyde (0.014 g, 0.11 mmol) and hydrochloric acid (2.0 cm^3, 35%) were added to a solution of [VL^{1}Cl$_2$] (0.05 g, 0.11 mmol) in boiling degassed water (150 cm^3) and the solution heated to reflux for 4 h. The deep red solution was concentrated *in vacuo* to about 2 cm^3 volume, and then filtered through celite. The diffusion of acetone vapour into the solution initially yielded red crystals of [H$_2$L^3]Cl$_2$ (0.02 g, 40%) and later deposited purple crystals of [VL^{3}Cl$_2$]Cl (0.025 g, 43%).

Results and discussion

The addition of vanadium(III) chloride to an ethanolic solution of L^1 maintained under an inert atmosphere results in the formation of an orange–yellow solid. In principle, L^1 could act as a tetradentate ligand towards vanadium(III), or it could behave as a reducing agent and generate a vanadium(II) species. Partial microanalytical data for the orange–yellow compound are in accord with the formation of a 1:1 adduct, {VL^{1}Cl$_3$}. This is consistent with the formation of a vanadium(III) complex; further support for this formulation came from the observed magnetic moment of μ_{eff} 2.96 BM at room temperature, typical of a d^2 vanadium(III) compound. The complex is indefinitely stable in air. The orange–yellow compound is sparingly soluble in boiling water, but is insoluble in most other common solvents. Accordingly, we have been unable to determine the conductivity behaviour of solutions of the compound. The most likely structures for the compound contain a seven-coordinate vanadium centre in an N_4Cl_3 environment or a six-coordinate centre in an N_4Cl_2 environment. The IR spectrum of the complex is almost identical to that of [CrL^{1}Cl$_2$]Cl, which we have previously shown to contain a six-coordinate chromium(III) centre [13, 15]. We consider that the complex is best formulated as [VL^{1}Cl$_2$]Cl (Fig. 1).

Surprisingly, it was possible to measure an ESR spectrum of the solid product [VL^{1}Cl$_2$]Cl at 77 K, although the overall broadness of the signal means that further detailed analysis of the spectrum is not facile. Normally, d^2 ions in an octahedral field do not give detectable ESR signals, a combination of a short spin-lattice relaxation time and a large zero-field splitting [37]. Whilst it is possible that these

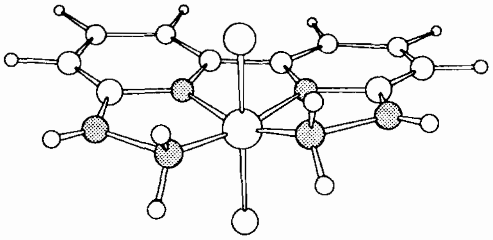


Fig. 1. Proposed structure for the vanadium(III) complexes of the open chain ligands.

signals are due to impurities, we merely wish to comment that the spectrum was reproducible with different samples on different occasions.

An analogous yellow–orange complex formulated as [VL^{2}Cl$_2$]Cl was prepared in a similar manner by the reaction of vanadium(III) chloride with L^2 in ethanolic solution. The product was very sparingly soluble in water and other solvents, and also exhibited a broad ESR spectrum.

The above behaviour is very reminiscent of that which we have previously reported for reactions with chromium(III) chloride. In the reaction with kinetically inert d^3 chromium(III) chloride, the formation of [CrLCl$_2$]Cl ($L=L^1$ or L^2) is very slow, whereas in the case of the labile d^2 vanadium(II) ion the formation of the adducts is near-instantaneous. In view of the similarity in behaviour, we considered it would be instructive to investigate the reactions of the vanadium(III) complexes with 2,6-pyridinedialdehyde.

The reaction of the orange–yellow compounds [VLCl$_2$]Cl ($L=L^1$ or L^2) with 2,6-pyridinedialdehyde in dilute aqueous solution containing hydrochloric acid results in the formation of red–purple solutions. As in the case of the condensations in the presence of chromium(III) the reactions were sensitive to the presence and quantity of acid in solution. Concentration of these solutions resulted in the separation of microcrystalline products which could be seen to contain a mixture of red and purple components. The ratio of red to purple component varied according to the amount of hydrochloric acid which had been added to the solution. In the presence of high concentrations of hydrochloric acid, the sole products were the red compounds. These red compounds were shown by microanalysis, ^{1}H NMR and IR spectroscopy to be the salts of the free macrocyclic ligands [H$_2$L]Cl$_2$ ($L=L^3$ or L^4) which were identical in all respects to those obtained from the transient template reaction with chromium(III) chloride.

In the absence of added hydrochloric acid, the sole product of the reaction was, in each case, the purple compound. In general, the higher the concentration of acid in the solution, the greater an amount of red compound and the lesser an amount of purple compound was obtained. Treatment of aqueous solutions of the purple compounds with hydrochloric acid yielded red solutions from which the free ligand salts could be obtained. This behaviour strongly suggests that the purple compounds are vanadium complexes of the macrocyclic ligands L^3 or L^4. This behaviour is in very marked contrast to that observed with chromium(III); once the chromium(III) complexes of L^3 or L^4 are formed, they do not undergo demetallation reactions in the presence of acid. Similarly, the condensation of [CrLCl$_2$]Cl ($L=L^1$ or L^2) with 2,6-pyridinedialdehyde yields only the corresponding chromium(III) macrocyclic complexes.

The partial microanalytical results for these purple complexes suggested the formulations [VLCl$_2$]Cl·nH$_2$O ($L=L^3$ or L^4, $n=1$ or 2) to be appropriate. The IR spectra of the compounds very closely resembled those of the chromium(III) macrocyclic complexes which we have previously described [13, 15]. We propose that the purple compounds are seven-coordinate pentagonal bipyramidal vanadium(III) complexes of the pentadentate macrocyclic ligands, in which the two axial sites are occupied by chlorides (Fig. 2). The complexes are paramagnetic with $\mu_{\text{eff}}=2.9\pm0.05$ BM, as expected for a d^2 ion. The purple macrocyclic complexes exhibited no ESR spectra in the solid state or in frozen aqueous solution at 77 K. Although the purple compounds may be obtained in microcrystalline form, we have been unable to obtain any crystals of sufficient quality to perform an X-ray structural investigation.

The complexes are, however, electrochemically active. Although the compounds are not soluble in acetonitrile or dichloromethane, it was possible to investigate the electrochemical behaviour in dimethyl sulfoxide (dmso) solutions. The cyclic voltammogram of a purple solution of [VL^{3}Cl$_2$]Cl in dmso exhibited a single reversible reduction centred at −0.97 V (versus Ag/AgCl, E_a-E_c 70 mV). Controlled potential electrolysis at −1.0 V of such a solution only resulted in slight changes in the appearance of the solution. The ESR spectra of frozen dmso solutions at 77 K following controlled potential electrolysis were variable. In each case two overlapping sets of weak signals showing coupling to ^{57}V ($I=7/2$) were observed. However, the relative proportions of the two overlapping subspectra varied from compound and from experiment to experiment. We propose that this is due to the formation of variable amounts of complexes containing axial chloride and axial dmso ligands. The hyperfine couping constants to the ^{57}V nuclei ($A=150$–160 G) indicated that the electrogenerated species formed had the unpaired electron density associated primarily with the metal centre,

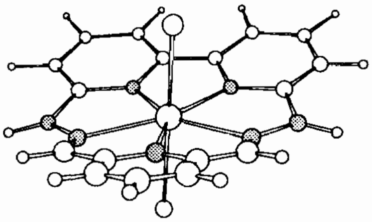


Fig. 2. Proposed structure for the vanadium(III) complexes of the macrocyclic ligands.

and that they are best formulated as vanadium(II) compounds.

In conclusion, the reactions of 6,6′-bis(hydrazino)-2,2′-bipyridines with vanadium(III) compounds very closely resemble the reactions with chromium(III) salts. The labile d^2 vanadium(III) ion undergoes reactions very much more rapidly than the inert d^3 chromium(III) ion. This is reflected in the ease of formation of the complexes, and in the lability complexes which may be prepared from them.

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