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Synthesis, characterization and crystal structure of $[(Hdmpz)\{HB(dmpz)_3\}VO(\mu\text{-}\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]$ (Hdmpz = 3,5-dimethylpyrazole)

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The complex $[(Hdmpz)\{HB(dmpz)_3\}VO(\mu\text{-}\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]$ **1** (Hdmpz = 3,5-dimethylpyrazole) has been synthesized and its spectroscopic properties and crystal structure determined. It crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.563(2)$, $b = 12.460(4)$, $c = 13.028(5)$ Å, $\alpha = 95.16(3)$, $\beta = 98.93(2)$, $\gamma = 99.59(2)^\circ$ and $Z = 2$. The vanadium(IV) ion is in a distorted-octahedral environment with nitrogen atoms of the borate ligand occupying three facial sites and the other sites by an oxo group, an oxygen atom from the ferrocenecarboxylate, and a nitrogen atom from a neutral Hdmpz. The cyclic voltammogram in CH_2Cl_2 showed two oxidations at +0.70 and +1.41 V *vs.* Ag–AgCl, which are completely reversible at −30 °C. The first corresponds to oxidation of the ferrocenecarboxylate moeity, giving $\mathbf{1}^+$. The reversibility of $\mathbf{1} \longrightarrow \mathbf{1}^+$ has also been demonstrated by electronic absorption and EPR resonance spectroscopies. Complex **1** is EPR active giving spectra as expected from an isolated vanadium(IV) centre, whilst $\mathbf{1}^+$ is EPR silent.

An understanding of magnetic interactions in polynuclear co-ordination complexes for the purpose of designing molecular scale devices is currently of much interest.[1–3] Kahn and others[4–7] have concentrated on the 'irregular spin state' approach, Miller and co-workers[8,9] have had some success using organometallic and organic charge-transfer compounds, whilst Gatteschi and co-workers[10,11] have used metal complexes of 'nitronyl nitroxide' radicals. We are also studying the means whereby unpaired electron density is transmitted between paramagnetic centres causing magnetic interactions in a co-operative manner. As an extension of work[12–15] on the magnetic behaviour of compounds containing the {LMo(NO)} moiety, where L = tris(3,5-dimethylpyrazolyl)hydroborate, we are also investigating how the {LVO} unit can form magnetic interactions. Previously we have studied,[16–18] mainly by single-crystal EPR spectroscopy, weak extended exchange interactions between monomeric $\{VO^{2+}\}$ units in the solid state. In these systems the magnitude of the exchange interaction is comparable to the metal hyperfine splitting, and computer simulation of the spectra coupled to variable-temperature measurements was needed to obtain the magnitude of the exchange interaction (*ca.* 3 cm^{-1}). The use of the sterically demanding tris(3,5-dimethylpyrazolyl)hydroborate ligand enables isolated $\{VO^{2+}\}$ centres to be studied, and also control of the substitution at the metal centre which permits control of the extent of oligomerization when polyfunctional ligands are in the co-ordination environment. Using carboxylates as the bridging moieties, because of their structural flexibility and potential variety of bridging modes,[19] we have previously reported homometallic carboxylate-bridged dimers containing the $\{LVO^+\}$ moiety[20] and their unusual EPR properties.[21] In this paper we report the preparation and characterization of a heterometallic complex involving the $\{LVO^+\}$ moiety and ferrocenecarboxylate. Although no exchange interaction is expected in this compound because of the diamagnetism of the ferrocene group, it was chosen because of its potential redox activity. Thus oxidation of the ferrocene moiety will produce a one-unpaired-electron centre which could, and as we demonstrate does, interact with the oxovanadium(IV) centre.

Experimental

Materials

Dichloromethane and toluene were dried by standard techniques and distilled prior to use. Potassium tris(3,5-dimethylpyrazolyl)hydroborate[22] and $[VO(Cl)L(Hdmpz)]\cdot 2MeCN$ (Hdmpz = 3,5-dimethylpyrazole) were prepared as reported previously.[20] Ferrocenecarboxylic acid (Fluka) and triethylamine (Aldrich) were used without further purification.

Synthesis of $[(Hdmpz)LVO(\mu\text{-}\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]$ 1

Triethylamine was added dropwise to a mixture of ferrocenecarboxylic acid (0.283 g, 1.23 mmol) and CH_2Cl_2 (10 cm^3) until the acid dissolved to give a clear brown solution. This solution was added to a blue solution of $[VO(Cl)L(Hdmpz)]\cdot 2MeCN$ (0.711 g, 1.23 mmol) in CH_2Cl_2 (20 cm^3) to give a green solution which changed to red-brown on stirring at ambient temperature for 1 h. It was then evaporated to dryness, *in vacuo*, to give a mixture of a dark brown solid and colourless needles ($NHEt_3Cl$). The mixture was washed with ice-cold water (2 × 10 cm^3) to remove the colourless needles, and the remaining brown solid was dried, *in vacuo*, for 2 d. Successive recrystallization from CH_2Cl_2–toluene (1 : 1 v/v) gave red-brown block-shaped crystals suitable for structure determination. Yield 69%, based on vanadium (Found: C, 54.3; H, 5.9; Fe, 7.9; N, 16.1; V, 6.9. Calc. for $C_{31}H_{39}BFeN_8O_3V$: C, 54.0; H, 5.7; N, 16.3; Fe, 8.1; V, 7.4%).

Physical methods

Infrared spectra were obtained as Nujol mulls between CsI plates using a Perkin-Elmer 1710 FT-IR spectrometer, electronic absorption spectra in the range 300–900 nm from CH_2Cl_2

solutions using either a Shimadzu UV260 or a Perkin-Elmer Lambda 9 spectrometer and EPR spectra at room temperature and 77 K at X-band, and at 150 K at Q-band frequencies, using a Bruker ER200D-SCR and a Varian E112 spectrometer, respectively. Cooling at X-band was *via* an Oxford Instruments ESR9 continuous-flow cryostat. Mass spectra of samples dispersed in *m*-nitrobenzyl alcohol, glycerol, or tetraethylene glycol {2,2′-[oxybis(ethane-1,2-diyloxy)]bisethanol} were obtained by positive-ion fast atom bombardment using xenon and a Kratos Concept IS instrument. Electrochemical measurements were made using an Autolab PSTAT10 potentiostat and General Purpose Electrochemical System 3.2 software. Cyclic voltammetric studies were conducted in a conventional cell with a platinum-disc working electrode of diameter 1 mm, a large-surface-area platinum counter electrode, and a Ag–AgCl reference electrode (the ferrocene–ferrocenium couple was measured at +0.55 V). Scan rates were in the range 50–500 mV s^{-1}. Electrosynthetic experiments were performed in an H-type cell, where the working and counter electrode compartments were separated by a glass frit. The working and counter electrodes were of platinum gauze with large surface areas. The solutions were purged with dinitrogen for 20 min prior to study. Elemental analyses were performed by the staff of the microanalytical laboratory of the Department of Chemistry of the University of Manchester.

Crystallography

Crystals of complex **1** were mounted in Lindemann capillaries, containing mother-liquor, which were flame-sealed. Measurements were taken on a Siemens R3m/v diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) monochromated with a highly oriented graphite crystal. Intensity data were collected at room temperature using ω scans. There was no variation of the intensities of two standard reflections measured every 50. Lorentz-polarization corrections were made but no correction for absorption was applied. 6516 Reflections were collected, of which 6140 were unique ($R_{int} = 0.0142$), with 4315 considered observed [$F > 6\sigma(F)$]. Crystal data and data-collection parameters are in Table 1.

Solution and refinement of the structure. The structure was solved and refined using the SHELXTL PLUS (VMS) package.[23] The metal atoms were located from the Patterson map and all non-hydrogen atoms were located after successive cycles of full-matrix least-squares refinement (based on F) and assigned anisotropic thermal parameters. The H atoms, which could be observed in difference maps, were fixed to their parent atoms using a riding model with fixed isotropic thermal parameters. The refinement converged to a conventional R value of 0.038, R' of 0.055 for 413 parameters. The largest shift/e.s.d. was 0.004 with a mean value of 0.001. No peaks outside the range ±0.36 e $Å^{-3}$ were observed in the final difference map. Selected bond lengths and angles are in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/385.

Results and Discussion

Molecular structure of complex 1

Heterometallic compounds of iron and vanadium are rare[24] and **1** represents one of the few which have been crystallographically characterized. This dinuclear compound is formed by bridging *via* the carboxylate residue of the ferrocenecarboxylate group. Similar bridging arrangements between a ferrocene moiety and other d-transition-metal centres have previously been reported.[25–28]

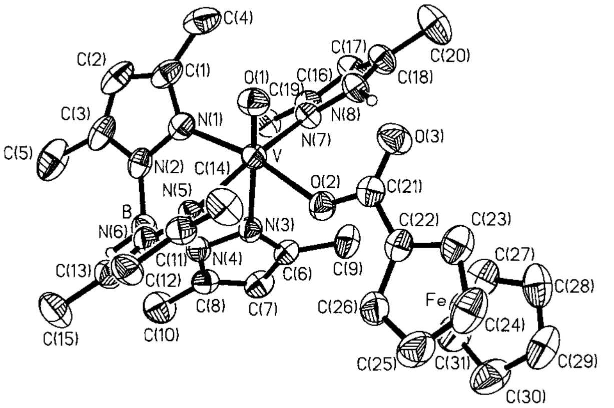


Fig. 1 An ORTEP[29] diagram of complex **1** showing 50% probability thermal ellipsoids and the atom numbering scheme

Table 1 Summary of crystal data and data-collection parameters for complex **1**

Empirical formula	$C_{31}H_{39}BFeN_8O_3V$
M	689.3
Colour, habit	Red, blocks
Crystal dimensions/mm	0.30 × 0.30 × 0.40
Crystal symmetry	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	10.563(2)
b/Å	12.460(4)
c/Å	13.028(5)
α/°	95.16(3)
β/°	98.83(2)
γ/°	99.59(2)
U/Å³	1658.9(9)
Z	2
T/K	294 ± 1
D_c/g cm^{-3}	1.380
R, R'*	0.038, 0.055
μ/mm^{-1}	0.752

* $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$ where $1/w = \sigma^2F + 0.000\,005F$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

V–O(1)	1.598(3)	V–N(3)	2.318(4)
V–N(7)	2.127(4)	V–N(1)	2.121(4)
V–N(5)	2.120(4)	V–O(2)	2.004(3)
O(1)–V–N(1)	95.4(2)	O(1)–V–N(3)	177.6(2)
O(1)–V–N(5)	96.5(2)	O(1)–V–N(7)	95.9(2)
O(1)–V–O(2)	98.6(1)	V–O(2)–C(21)	131.7(3)
N(1)–V–N(3)	82.8(1)	N(1)–V–N(5)	85.7(1)
N(1)–V–N(7)	90.1(2)	N(3)–V–N(5)	82.0(1)
N(3)–V–N(7)	85.6(1)	N(5)–V–N(7)	167.3(2)
N(1)–V–O(2)	165.7(1)	N(3)–V–O(2)	83.2(1)
N(5)–V–O(2)	89.5(1)	N(7)–V–O(2)	91.7(1)

The vanadium(IV) ion is in a distorted-octahedral environment with the L ligand occupying three facial sites. The other three sites are occupied by a terminal oxo group, an oxygen atom from the ferrocenecarboxylate, and a nitrogen atom of a neutral Hdmpz, see Fig. 1. The V=O(1) distance [1.598(3) Å] is typical of a terminal group in the {LVO^+} moiety.[20,30,31] The *trans* effect of this terminal oxo group is responsible for the increased length of the V–N(3) bond [2.318(4) Å] compared with V–N(1), V–N(5), V–N(7), which are 2.121(4), 2.120(4) and 2.127(4) Å, respectively, and are *cis* to this terminal oxo group. As observed[20] in [LVO{μ-$CH_2(CO_2)_2$}OVL(Hdmpz)] and [VO(CO_2CPh)L(Hdmpz)], the Hdmpz group is oriented about the V–N(7) bond such that the hydrogen atom attached to N(8) forms a hydrogen bond to the unco-ordinated carboxylate oxygen atom O(3). The co-ordination about the iron(II) ion is typical of that in ferrocene and its derivatives,[25–27] with Fe–C distances in the range 2.027(6)–2.047(4) Å.

Table 3 Selected spectroscopic properties of complex **1**

Infrared ν/cm^{-1}	Electronic absorption $\lambda/nm(\varepsilon/dm^3\ mol^{-1}\ cm^{-1})$	Mass m/z (assignment, relative intensity)[a]	EPR[b]
		1043 (unassigned, trace)	
		947 (unassigned, trace)	
3150 (−H)	766 (86)	689 (*P*, trace)	
2522 (B−H)	558 (sh, ≈63)	593 (*P* − Hdmpz, 0.8)	g_{iso} 1.972, $10^4A_{iso}/cm^{-1}$ −93.7
1606 (O−C−O)	444 (412)	460 [LVO(Hdmpz), 0.6]	$g_{\parallel}$ 1.953, $10^4A_{\parallel}/cm^{-1}$ −160.9
1578 (C=N, Hdmpz)		443 [LV(Hdmpz), 0.5]	$g_{\perp}$ 1.982, $10^4A_{\perp}/cm^{-1}$ −59.9
1542 (C=N, dmpz)		364 (LVO, 1.0)	
971 (V=O)			

[a] *P* = Parent ion. [b] Average of X- and Q-band measurements; values are ±0.002 for *g* and ±0.4 × 10^{-4} cm^{-1} for *A*.

Physical and spectroscopic properties

Selected physical and spectroscopic properties are summarized in Table 3. The Nujol mull infrared spectrum displays the characteristic frequencies for ν(V=O), ν(B−H) and asymmetric ν(OCO) at 971, 2522 and 1606 cm^{-1}, respectively. In addition the two different types of 3,5-dimethylpyrazole ring systems can be identified in the ν(C=N) region (*ca.* 1530–1600 cm^{-1}). The band at higher wavenumber, 1578 cm^{-1}, is assigned to the neutral pyrazole ligand.[20]

As we have previously observed[20,32] for other neutral compounds containing the {LMO^{n+}} moiety, the present compound was amenable to characterization by positive-ion FAB mass spectrometry. The peak corresponding to the parent ion appears only weakly; the dominant peak corresponds to {LVO}.

The electronic absorption spectrum recorded in CH_2Cl_2 solution shows three bands. The two at lowest energy have energies and absorption coefficients almost the same as those found[20] for the homometallic compound, [LVO{μ-$CH_2(CO_2)_2$}OVL(Hdmpz)], and they are therefore assigned to d–d transitions within the oxovanadium(IV) moiety. The third band, at *ca.* 444 nm, which has a significantly larger absorption coefficient, and is at the same wavelength as for a solution containing ferrocenecarboxylate, is assigned to the ferrocene moiety.

The fluid and frozen-solution EPR spectra of complex **1** are as expected for non-interacting monomeric oxovanadium(IV) centres. The spin-Hamiltonian parameters, which were obtained *via* spectrum simulation,[33] are comparable with those which we have observed for other {LVO(carboxylate)} compounds.[20,21] These observations, coupled with the similarity of the electronic spectra of the oxovanadium(IV) part of these molecules to those in known monomeric {LVO(carboxylate)}-containing compounds, are compatible with negligible electronic interaction between the metal centres in **1**.

Electrochemistry

The cyclic voltammetry of complex **1** in 0.5 mol dm^{-3} $[NBu^n_4][BF_4]$–CH_2Cl_2 solution at room temperature reveals a chemically and electrochemically reversible one-electron oxidation at +0.70 V *versus* Ag–AgCl, followed by a second quasi-reversible one-electron oxidation at +1.41 V. The first process is assigned as the Fe^{II}–Fe^{III} oxidation by comparison with the oxidation potentials of ferrocenecarboxylic acid and tetraethylammonium ferrocenecarboxylate of +0.78 and +0.56 V, respectively, under the same conditions. The second oxidation is at a potential similar to those found previously for [VO(O_2CPh)L(Hdmpz)][20] and in a series of [VO(β-diket)L] compounds (β-diket = β-diketonate),[30] and is therefore assigned to the vanadium centre.

Bulk electrolysis of complex **1** at +1 V and room temperature resulted in decomposition. The EPR spectrum of the resulting solution at 77 K was typical of a monomeric vanadium(IV) species, but was different from that of **1**. Electrogeneration at 0 V failed to regenerate **1**, as shown by cyclic voltammetry. However, the oxidation of **1** to $\mathbf{1}^+$ was chemically reversible at −30 °C as shown by the identical cyclic voltammograms of these two species. The EPR spectrum of the resulting solution was identical to that of **1**, but with only *ca.* 1/5 of the original intensity. The residual EPR spectrum is attributed to incomplete oxidation of **1**. On regeneration of **1** at 0 V the original EPR spectrum was restored including the intensity. When **1** was oxidized chemically with an excess of $FeCl_3$ in CH_2Cl_2 solution at −30 °C the resulting species was EPR silent at 77 K. Chemical reduction of this solution with hydrazine hydrate restored the original EPR spectrum of **1**, including its intensity.

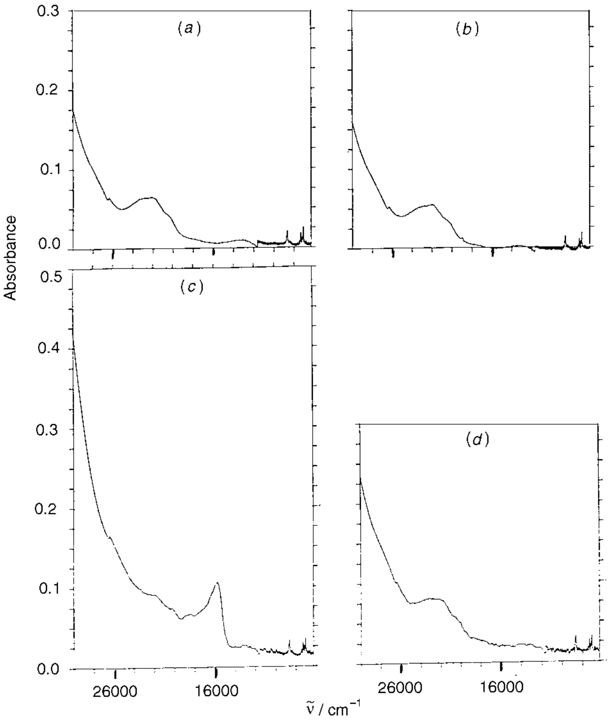


Fig. 2 Electronic absorption spectra of species **1** and $\mathbf{1}^+$ in CH_2Cl_2: (*a*) **1** at −30 °C, (*b*) **1** at 19 °C, (*c*) $\mathbf{1}^+$ at −30 °C, after electrogeneration at +1.0 V, (*d*) **1** at −30 °C, after electrogeneration from $\mathbf{1}^+$ at 0.0 V

The electrogeneration experiments were also monitored *via* electronic absorption spectroscopy.[34] The spectrum of complex **1** in CH_2Cl_2 at −30 °C is shown in Fig. 2(*a*). The band centred at 22 990 cm^{-1} corresponds to that at 22 523 cm^{-1} in the room-temperature spectrum, see Fig. 2(*b*). The spectrum of the solution after bulk electrogeneration at +1.0 V is in Fig. 2(*c*). The band at 22 990 cm^{-1} was replaced by one at 16 000 cm^{-1}. This new band is attributed to an oxidized iron centre. Bulk electroregeneration of **1** at 0.0 V restores the original spectrum, see Fig. 2(*d*). Thus it seems that both electrochemical and chemical oxidation of **1** to $\mathbf{1}^+$ is reversible at −30 °C. The electronic absorption spectra of triethylammonium ferrocenecarboxylate and of triethylammonium ferrocenium carboxylate at −30 °C in

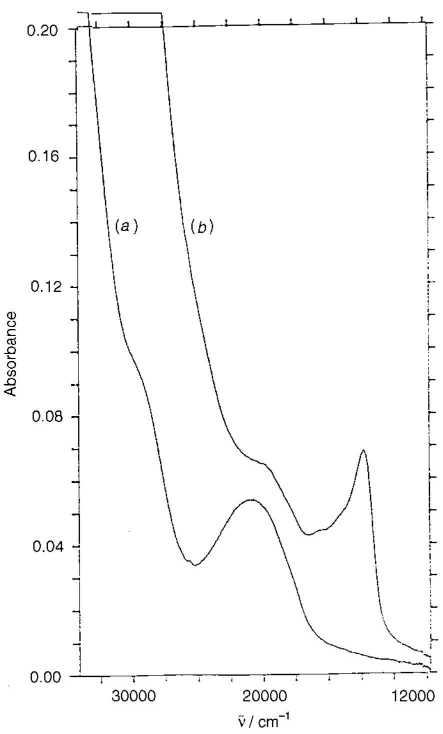
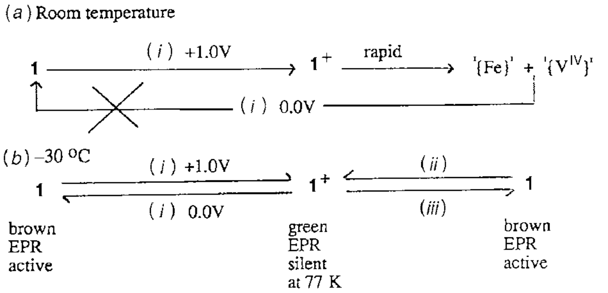


Fig. 3 Electronic absorption spectra of (*a*) ferrocenecarboxylate and (*b*) ferrocenium carboxylate in CH_2Cl_2 at −30 °C



Scheme 1 (*i*) Electrogeneration; (*ii*) $FeCl_3$; (*iii*) $N_2H_4{\cdot}H_2O$

0.5 mol dm^{-3} [$NBu^n{}_4$][BF_4]–CH_2Cl_2 are shown in Fig. 3. The band maxima are at 22 727 and 15 803 cm^{-1} for ferrocene carboxylate and for ferrocenium carboxylate, respectively. These spectra are similar to those of **1** and **1**$^+$ under similar conditions, see Fig. 2(*b*) and 2(*c*).

Both the electronic absorption spectra and the EPR observations, particularly on the chemically oxidized solutions which have been taken to completion, indicate a first oxidation localized on the iron moiety. The lack of an EPR spectrum at 77 K for species **1**$^+$ is indicative of either a strong antiferromagnetic interaction or mutual relaxation effects between iron(III) and vanadium(IV) centres in close proximity in **1**$^+$. These observations, and those at room temperature, are summarized in Scheme 1.

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