Highly-oxidised, sulfur-rich, mixed-valence vanadium(IV/V) complexes

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The reactions of $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]$ (R = alkyl) with $NOBF_4$ produce highly-oxidised, sulfur-rich, V(IV/V) complexes, $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]BF_4$, that exhibit 15-line EPR spectra and structures consistent with Class III mixed-valence behaviour.

The properties and reactions of sulfur-rich transition metal compounds are relevant to industrial processes such as hydroprocessing[1] and biological processes such as electron transfer, assimilation (*e.g.*, nitrogen fixation), metabolism and catabolism.[2] Mixed-valence species play a major role in many of these processes;[2] moreover, the electronic structures and applications of synthetic, mixed-valence complexes are of intrinsic, fundamental and technological interest.[3,4] Highly-oxidised, early transition metal, mixed-valence complexes are dominated by oxo complexes bearing hard-donor coligands. Only Mo and W form soft-donor, sulfur-ligand, mixed-valence complexes containing the metals in their highest oxidation states.[3] Metal–sulfur complexes, especially those containing dithiocarbamate (dtc) ligands, are also known to undergo unusual reactions with unsaturated organic molecules like alkynes. For example, $[Mo_2(\mu\text{-}S_2)_2(S_2CNR_2)_4](BF_4)_2$ (R = Me, Et) and related complexes react with dimethyl acetylenedicarboxylate to give complexes bearing novel organosulfur ligands.[5] Related vanadium complexes, $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]$ (R = alkyl),[6,7] do not undergo similar reactions. With the two-fold aim of producing a new class of highly-oxidised, sulfur-rich, early transition metal, mixed-valence complex and enhancing the reactivity of $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]$ towards alkynes, we have investigated the generation and reactivities of mixed-valence forms of the aforementioned dimer.

To date only one sulfur-donor, mixed-valence, vanadium complex has been reported;[8] however, this V(III/IV) complex, $NEt_4[V_2(\text{ethane-1,2-dithiolate})_4]$, does not contain the metal in its highest oxidation state. All previously reported V(IV/V) complexes contain oxo ligands and the most prevalent contain a $[V_2O_2(\mu\text{-}O)]^{3+}$ core.[3,4] These exhibit valence-localised or, to varying degrees, valence-delocalised structures characterised with 8- or 15-line EPR spectra, respectively. Here, we report the isolation of highly-oxidised, sulfur-rich V(IV/V) complexes of the type $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]BF_4$ (R = Et, ^{i}Pr, ^{i}Bu (**1**)) and spectroscopic and crystallographic evidence supporting their assignment as Class III[9] mixed-valence species at room temperature.

Electrochemical studies of $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]$ in dichloromethane showed a quasi-reversible, one-electron, oxidation at *ca.* 0.08 V *vs.* ferrocene followed by an irreversible oxidation at higher potentials (*ca.* 1.0 V *vs.* ferrocene); chemical generation of the V(IV/V) species was then pursued. Reaction of $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]$ with $NOBF_4$ in dichloromethane led to controlled evolution of NO gas and a colour change from brown to dark green. Removal of excess $NOBF_4$ by filtration and addition of hexane to the filtrate precipitated deep-green $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]BF_4$. The compounds were characterised by elemental analysis, mass spectrometry (*m*/*z* for $[V_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]^+$), and infrared spectroscopy (ν(CN) *ca.* 1520 cm^{-1} and $\nu(BF_4^-)$ *ca.* 1084 cm^{-1}).†

The room temperature, X-band EPR spectra of the complexes all exhibited a single 15-line signal centred around *g* 2.00, with A_{iso} *ca.* 29×10^{-4} cm^{-1} (Fig. 1). This is the *g* value and hyperfine pattern anticipated for coupling of a single, unpaired electron to two equivalent ^{51}V nuclei ($2nI + 1 = 15$ for two ^{51}V centres with $I = 7/2$). Thus, the spectra are indicative of complete delocalisation of the unpaired electron over both metal centres. Similar EPR spectra have been reported for a handful of $[V_2O_2(\mu\text{-}O)]^{3+}$ complexes, including $(NH_4)_3[V_2O_3\{N(CH_2CO_2)_3\}_2]$ (obtained from difference spectra)[10] and $[V_2O_3\{N(CH_2C_5H_4N)_3\}_2](ClO_4)_3$.[11] Interestingly, the A_{iso} parameters for the title compounds are just over half the magnitude of those reported for $[V_2O_2(\mu\text{-}O)]^{3+}$ complexes, a reflection of a highly covalent (V–V σ-bonding) magnetic orbital. Fifteen-line spectra with quite different hyperfine line intensity patterns are characteristic of species with temperature-dependent localised/hopping electronic structures.[12,13]

The crystal structures of two polymorphs of $[V_2(\mu\text{-}S_2)_2(S_2CN^iBu_2)_4]BF_4\cdot CH_2Cl_2$ were determined. The asymmetric unit for the first structure (**1a**) was comprised of one $[V_2(\mu\text{-}S_2)_2(S_2CN^iBu_2)_4]^+$ cation (Fig. 2), two half occupancy BF_4^- anions (one BF_4^- anion is disordered over two sites) and a lattice dichloromethane molecule.‡ The eight-coordinate vanadium atoms can be ascribed distorted octahedral coordination spheres if each μ-disulfido ligand is considered to straddle a single polyhedral vertex. The $V_2(\mu\text{-}S_2)_2$ core also exhibits a distorted octahedral geometry with short S–S (av. 2.01 Å) and long S···S

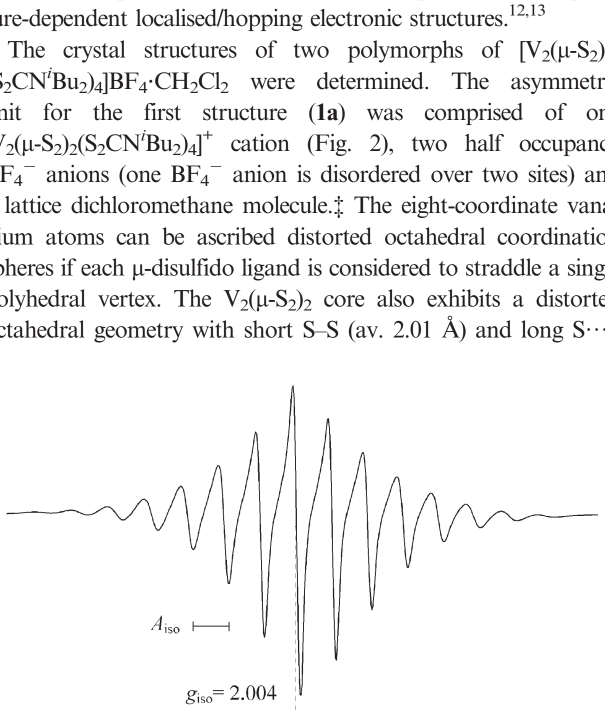

Fig. 1 The EPR spectrum of **1** in dichloromethane at 298 K.

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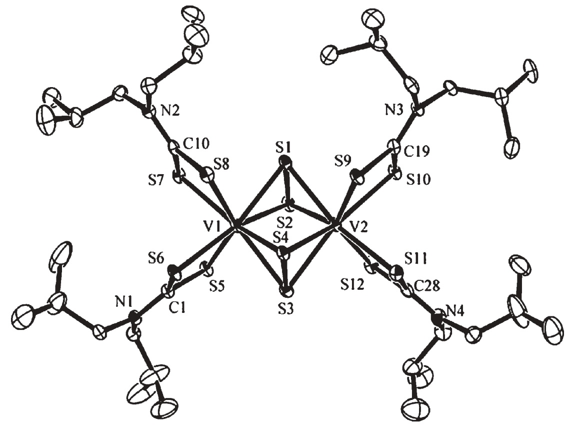

Fig. 2 Structure of the $[V_2(\mu\text{-}S_2)_2(S_2CN^iBu_2)_4]^+$ cation of **1a** drawn at the 30% probability level. Selected bond lengths (Å): V(1)–S(1–8) 2.3727(15), 2.4467(15), 2.4241(17), 2.4012(14), 2.4787(15), 2.4134(14), 2.4348(16), 2.5050(16), V(2)–S(1–4) 2.3837(17), 2.4486(15), 2.4217(16), 2.4033(14), V(2)–S(9–12) 2.4731(15), 2.4430(15), 2.4363(16), 2.4672(17). Selected bond angles (°): V(1)–S(1–4)–V(2) 76.20(5), 73.67(4), 76.20(5), 73.67(4).

(av. 3.26 Å) distances, with the V atoms an average of 1.467 Å either side of the S_4 plane. The average V–μ-S and $V\text{–}S_{dtc}$ distances are 2.413 and 2.456 Å, respectively. The metrical parameters associated with the two V centres are equivalent within experimental error. As expected,[14] the $V\text{–}S_{dtc}$ distances are statistically shorter (by 0.038 Å) than those observed in $[V_2(\mu\text{-}S_2)_2(S_2CN^iBu_2)_4]$.[6] However, there is a slight increase in the average V–μ-S distances (*cf.* 2.405 Å) and V–S–V angles (74.94° for **1a**, *cf.* 69.27°) upon oxidation of $[V_2(\mu\text{-}S_2)_2(S_2CN^iBu_2)_4]$; these increases are associated with the expected increase in the V–V distance (2.934(1) Å for **1a**, *cf.* 2.851(1) Å).

The asymmetric unit of the second crystal (**1b**) contained one complete molecule of the complex and two half molecules (each of half occupancy) for which the corresponding halves can be symmetry generated *via* crystallographic inversion centres. The asymmetric unit was completed by two BF_4^- anions and two lattice dichloromethane molecules.§ This gives an overall V : BF_4^- ratio of 2 : 1, consistent with an oxidation state of +4.5 for each vanadium. The V–S distances are comparable with those of the structure described above (**1a**), with average V–μ-S = 2.411 Å and $V\text{–}S_{dtc}$ = 2.455 Å. The structural equivalence of the vanadium centres in both structures is consistent with EPR results showing delocalisation of the unpaired electron over equivalent metal centres.

The complexes reported are the first dinuclear V(IV/V) complexes to be devoid of oxo ligation and in possession of a coordination sphere comprised entirely of sulfur donors. The EPR spectra and crystal structures support their assignment as Class III valence-delocalised species. The variable-temperature behaviour of the complexes is currently under investigation.

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Notes and references

† The following synthesis is typical (solvents were dried and deoxygenated and the reactions were performed under an atmosphere of nitrogen): Brown $[V_2(\mu\text{-}S_2)_2(S_2CN^iBu_2)_4]$ (0.25 g, 0.24 mmol) and $NOBF_4$ (0.10 g, 0.86 mmol) were stirred in dichloromethane (15 ml) for 30 min, with the occasional application of a slight vacuum to remove liberated NO gas. The resulting dark green solution was filtered to remove excess $NOBF_4$ and the filtrate was treated with hexane (15 ml). Removal of dichloromethane under vacuum yielded dark green product (**1**) (yield 0.26 g, 95%), which was collected by filtration and washed with hexane, then diethyl ether. Crystals suitable for X-ray diffraction were grown under anaerobic conditions by slow diffusion of hexane into a dichloromethane solution of the complex at −30 °C. For R = ^{i}Bu. Found: C, 38.0; H, 6.5; N, 4.8; S, 33.75; calc. for $C_{36}H_{72}BF_4N_4S_{12}V_2$: C, 38.1; H, 6.4; N, 4.9; S, 33.9%. ν_{max}(KBr)/cm^{-1}: 2960s, 2920w, 2871w, 1631w, 1520m, 1485m, 1465m, 1435m, 1386w, 1338w, 1248m, 1199w, 1151m, 1124m, 1084s and 1053m. EPR (CH_2Cl_2): g_{iso} 2.004, A_{iso} 29.3 × 10^{-4} cm^{-1}. ESI-MS: *m/z* 1047 (M^+). Echem (CH_2Cl_2, *vs.* ferrocene): $E_{1/2}$ +0.10 V (reversible), E_{pa} (irreversible) +1.06 V.

‡ *Crystallographic data* for **1a**: $C_{37}H_{74}BCl_2F_4N_4S_{12}V_2$, M = 1219.31, green block, 0.36 × 0.19 × 0.16 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 11.6884(8), b = 16.6907(11), c = 17.7774(11) Å, α = 105.7420(10), β = 95.2160(10), γ = 107.4620(10)°, V = 3127.7(4) Å^3, Z = 2, D_c = 1.295 g cm^{-3}, F_{000} = 1274, CCD area detector, Mo Kα radiation, λ = 0.71073 Å, T = 130(2) K, $2\theta_{max}$ = 55.0°, 19 387 reflections collected, 13 518 unique (R_{int} = 0.0334). Final GoF = 1.036, $R1$ = 0.0729, w$R2$ = 0.1791, R indices based on 8735 reflections with $I > 2\sigma(I)$ (refinement on F^2), 657 parameters, 62 restraints. Lorentz polarisation and absorption corrections were applied, with μ = 0.825 mm^{-1}.

§ **1b**: $C_{74}H_{148}B_2Cl_4F_8N_8S_{24}V_4$, M = 2438.62, green block, 0.31 × 0.17 × 0.15 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 14.7389(13), b = 20.7238(18), c = 21.4366(18) Å, α = 79.133(2), β = 76.828(2), γ = 73.115(2)°, V = 6047.8(9) Å^3, Z = 2, D_c = 1.339 g cm^{-3}, F_{000} = 2548, CCD area detector, Mo Kα radiation, λ = 0.71073 Å, T = 130(2) K, $2\theta_{max}$ = 53.0°, 35 554 reflections collected, 24 378 unique (R_{int} = 0.0427). Final GoF = 0.976, $R1$ = 0.0813, w$R2$ = 0.1991, R indices based on 13 383 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1158 parameters, 1 restraint. Lorentz polarisation and absorption corrections were applied, with μ = 0.853 mm^{-1}.

CCDC 614332 (**1a**) and 614333 (**1b**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610036h

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