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$[V(\eta^5\text{-}C_5H_5)]_2C_8H_6$: a bimetallic pentalene-bridged complex with multiple bonding between the metal atoms

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The bimetallic complex $[V(Cp)]_2Pn$, containing a V–V triple bond, has been synthesised; the vanadium centres adopt a *syn*-coordination and the complex exhibits a high-spin/low-spin equilibrium in both solution and the solid-state.

Bimetallic compounds have attracted considerable interest due to the possibility of direct[1] or indirect[2] metal–metal electronic interactions, and of cooperative catalytic effects.[3] Although the pentalene ligand (Pn = C_8H_6) has been found to form a range of dinuclear organometallic complexes, some of which show very strong ligand-mediated M–M interactions,[4,5] it still remains a rather underexploited ligand system.[6] Here we report on a dinuclear vanadium derivative of pentalene in which the ligand supports a direct M–M interaction, specifically a rare example of a V–V triple bond.

Reaction of $Li_2Pn \cdot x$DME (DME = 1,2-dimethoxyethane) with 2 equiv. of the 'half-sandwich' V(II) complex $[V(Cp)Cl \cdot THF]_n$ (Cp = η^5-C_5H_5)[7] gives, after work-up, $[V(Cp)]_2Pn$ as dark green, air-sensitive crystals. A single crystal X-ray diffraction study reveals the complex to have *syn*-geometry with regard to the pentalene ligand and a bond between the V atoms (Fig. 1).†

syn-Coordination of two metal centres is unusual in organometallic pentalene chemistry; coordination of two groups to the same face requires a fold of the ligand away from planarity.[5,8] For $[V(Cp)]_2Pn$ the hinge-angle between the two five-membered rings of the pentalene unit about the bridgehead C–C bond is 13°; this is in contrast to the molecular structure of isoelectronic *syn*-$[V(Cp)]_2$COT (COT = cyclooctatetraene), where the lack of a central carbon–carbon bond allows greater ligand flexibility and a hinge-angle of 56°.[9] The V–V distance is significantly shorter than a typical V–V single bond.‡ V–V multiple bonds are relatively scarce compared to the host of examples found for dichromium species.[1] Density functional calculations performed for $[V(Cp)]_2Pn$ suggest the ground state molecule has a V–V triple bond§ and that this bond is of $\sigma^2\pi^2\delta^2$ configuration; a triplet excited state exists corresponding to occupation of the low-lying δ* orbital.[10] Variable-temperature magnetic data (*vide infra*) are consistent with this description of the metal–metal bonding, demonstrating thermal population of this triplet state from a diamagnetic ground state.

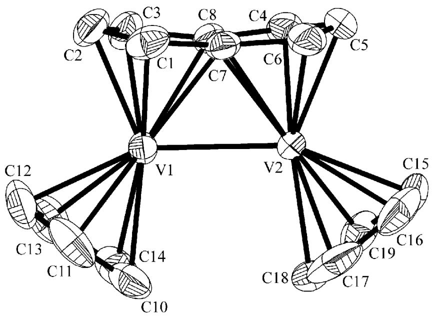

Fig. 1 Molecular structure of $[V(Cp)]_2Pn$ with thermal ellipsoids at 50% probability and all H atoms omitted for clarity. Selected bond distances (Å): V(1)–V(2) 2.5380(5); V(1)–C(1) 2.239(2); V(1)–C(2) 2.245(2);V(1)–C(3) 2.212(2); V(1)–C(7) 2.315(2); V(1)–C(8) 2.291(2);V(2)–C(4) 2.239(2); V(2)–C(5) 2.227(2); V(2)–C(6) 2.195(2); V(2)–C(7) 2.294(2); V(2)–C(8) 2.321(2); V(1)–Cp(centroid) 1.950; V(2)–Cp(centroid) 1.954.

$[V(Cp)]_2Pn$ is weakly paramagnetic in solution at room temperature; only two of the expected three peaks are observed in the ^{1}H NMR spectrum and these are broad (the Cp–*H* peak having a linewidth of *ca.* 30 Hz). The peaks sharpen on cooling and the third proton resonance (the pentalene *H*1 peak) becomes visible around 0 °C; this is broadened into the baseline at higher temperatures. Variable-temperature NMR experiments show that the chemical shift of each resonance is a function of temperature (Fig. 2). The shifts do not vary linearly with T^{-1} (as would be expected from the Curie law); such behaviour is typical of a spin-equilibrium between an $S = 0$ ground state and an $S = 1$ thermally populated excited state, as has been observed for *syn*-$[V(Cp)]_2$COT species.[11] The equilibrium can be modelled as a Boltzmann distribution of spin-states with the observed chemical shift of a nucleus given by the sum of the contributions from diamagnetic and paramagnetic terms [eqn. (1)]:

$$\delta_{\text{obs}} = \delta_{\text{LS}} + \frac{C}{T\left[1 + e^{(\Delta H - T\Delta S)/RT}\right]} \qquad (1)$$

where δ_{LS} is the limiting shift value for the pure diamagnetic (low-spin) form of the molecule, C is a constant related to the magnetic susceptibility of the high-spin species and the isotropic hyperfine coupling constant for the nucleus of interest, while ΔH and ΔS are the thermodynamic values for the spin-equilibrium. The Cp–*H* resonances of $[V(Cp)]_2Pn$ in d_8-toluene and d_8-THF were fitted to eqn. (1);¶ values for δ_{LS}, C, ΔH and ΔS were obtained by a least-squares analysis of the data and are given in Table 1.

The values in the two solvents are very similar, ruling out a possible change in molecular conformation with temperature that could lead to the non-linear chemical shift dependence. The positive sign of ΔH demonstrates that the singlet is the ground state in solution; population of the triplet state requires

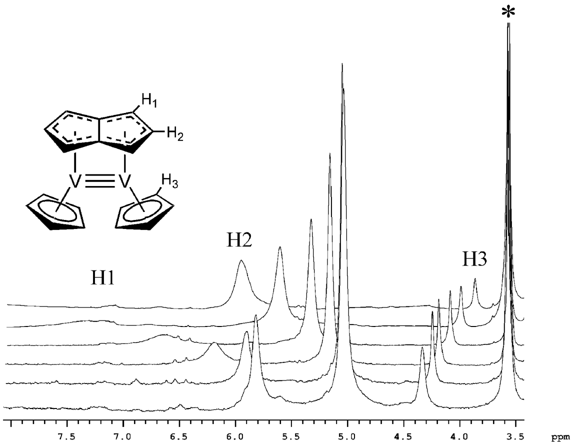

Fig. 2 Temperature variation of ^{1}H NMR chemical shift for the resonances of $[V(Cp)]_2Pn$ in d_8-THF; these are labelled according to the diagram. The peak labelled * is due to residual protio-solvent.

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Table 1 High-spin/low-spin equilibrium parameters obtained from ^1H NMR data for $[V(Cp)]_2Pn$

Solvent	*C*	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
d_8-Toluene	2820	+17.2	+34.9
d_8-THF	2744	+16.6	+33.1

occupation of the V–V δ* orbital. For a singlet–triplet process, the increase in electronic degeneracy upon attaining the high-spin state is calculated to give $\Delta S = 9.13$ J K^{-1} mol^{-1}; the greater entropy change observed experimentally may be qualified as due to an increase in the number of accessible vibrational degrees of freedom in the high-spin state.[12] At 300 K the triplet state has a population of *ca*. 6% and 7% in d_8-toluene and d_8-THF respectively. A similar NMR study[11] of *syn*-$[V(Cp)]_2COT$ in d_8-toluene found $\Delta H = 23.8$ kJ mol^{-1} and $\Delta S = 42.8$ J K^{-1} mol^{-1}. The smaller value of ΔH determined in this work for $[V(Cp)]_2Pn$ is consistent with the longer V–V distance found in its crystal structure when compared to *syn*-$[V(Cp)]_2COT$; a weaker metal-metal bond results from poorer δ-overlap (presumably due to the lower flexibility of pentalene compared to COT) and affords the pentalene complex a reduced HOMO–LUMO gap.

The magnetism of $[V(Cp)]_2Pn$ in the solid state was investigated by variable temperature SQUID magnetometry from 5–350 K. Plots of both molar susceptibility and effective magnetic moment (defined as $\mu_{\text{eff}} = \sqrt{(8\chi_m T)}\mu_B$) *vs*. *T* are shown in Fig. 3.

The solid state magnetism of $[V(Cp)]_2Pn$ clearly does not obey the Curie law; the effective magnetic moment is small and increases with temperature, consistent with the thermal population of a triplet excited state from a diamagnetic ground state as found in solution. This may be described as an antiferromagnetic interaction between two $S = \frac{1}{2}$ V centres. The data were fit to the Bleaney–Bowers expression including correction terms for temperature-independent paramagnetism (TIP) and a small amount of mononuclear V(II) impurity [eqn. (2)]:[13]

$$\chi_m = \left(\frac{5N_A g_1{}^2 \mu_B{}^2}{4k(T-\theta)}\right)(\rho) + \left(\frac{2N_A g_2{}^2 \mu_B{}^2}{3kT}\right)\left(\frac{1}{1+(1/3)e^{(-2J/kT)}}\right)(1-\rho) + \text{TIP} \qquad (2)$$

Analysis of the fit shows the triplet state 14.6 kJ mol^{-1} higher in energy than the ground state; the Boltzmann distribution gives a triplet population of around 1% at 300 K.

$[V(Cp)]_2Pn$ is unstable in solution, decomposing to the known monometallic V(III) η^8-coordinated complex V(η^8-Pn)(Cp)[14] over a period of days at room temperature (as established by ^1H NMR spectroscopy), presumably by a disproportionation process giving other unidentified V-containing species. Whilst *syn*-$[V(Cp)]_2COT$ readily forms a radical anion upon contact with potassium metal,[9] attempted chemical reduction of $[V(Cp)]_2Pn$ results in decomposition. Preliminary results show that $[V(Cp)]_2Pn$ binds carbon monoxide, as found for simple vanadocenes;[15] further investigations into this reactivity are in progress.

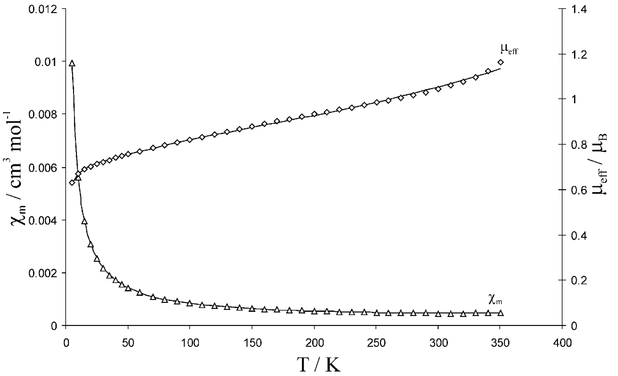

Fig. 3 Plots of χ_m (△) and μ_{eff} (◇) *vs*. T for $[V(Cp)]_2Pn$ in the solid state. The solid lines represent calculated values from a fit of the data using the expression in the text with $g_1 = g_2 = 2.00$; least-squares analysis gives $J = -610$ cm^{-1}, TIP $= 0.00023$ cm^3 mol^{-1}, $\rho = 0.0329$, $\theta = -1.5$ K.

In summary we have characterised an unusual example of a *syn*-metal–metal bonded bimetallic species.

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Notes and references

† All procedures were carried out under N_2 using standard Schlenk techniques in dry solvents. A solution of $Li_2Pn\cdot x$DME ($x = 1.14$) (0.49 g, 2.24 mmol) in 20 ml THF was added dropwise to a stirred solution of $[V(Cp)Cl\cdot THF]_n$ (1.00 g, 4.47 mmol) in 20 ml THF at −78 °C, affording a dark solution. This was warmed to room temperature and stirred for 1 h, after which volatiles were removed *in vacuo*. The dark residue was extracted with toluene (4 × 30 ml) and filtered through Celite to give a clear dark green solution. Toluene was removed *in vacuo* and the crude product recrystallised from the minimum volume of Et_2O at −35 °C. Yield: 0.30 g, 0.90 mmol, 40%. Selected analytical data: Calc. for $C_{18}H_{16}V_2$: C, 64.69; H, 4.83%; found C, 63.92; H, 4.88%. HRMS: Calc. *m/z* 334.0131; found *m/z* 334.0122. IR (KBr, cm^{-1}) 2924 (m), 1640 (w), 1430 (m), 1364 (w), 1256 (s), 1112 (m), 1096 (s), 1040 (m), 1014 (s), 890 (m), 802 (vs), 770 (vs), 656 (m), 622 (m), 450 (m). Cyclic voltammetry (THF, 0.1 M $[^nBu_4N][PF_6]$, values quoted *vs*. ferrocenium/ferrocene): $E_{1/2} = -1.12$ V (reversible), $E_{\text{red}} = -2.78$ V (irreversible).

Crystal data: $C_{18}H_{16}V_2$, $M = 334.19$, monoclinic, space group $P\,2_1/a$ (14), $a = 11.5324(3)$ Å, $b = 7.7618(2)$ Å, $c = 15.9992(5)$ Å, $\beta = 102.4650(10)°$, $V = 1398.36(7)$ Å^3, $T = 150(2)$ K, $Z = 4$, $F(000) = 680$, $\mu = 1.321$ mm^{-1}. Data were collected in the θ range 5.22–27.43°, 5330 reflections, 3146 unique ($R_{\text{int}} = 0.0262$), $R_1 = 0.0329$, $wR_2 = 0.0705$ for $I > 2\sigma(I)$ with allowance for thermal anisotropy of all non-hydrogen atoms. CCDC 212741. See http://www.rsc.org/suppdata/cc/b3/b306688f/ for crystallographic data in .cif or other electronic format.

‡ A search of the compounds listed in the Cambridge Structural Database uncovers a mean V–V single bond distance of 2.830 Å. V–V triple bonds reported in the literature range from 1.978(2) Å[16] to 2.462(2) Å;[17] isoelectronic *syn*-$[V(Cp)]_2COT$ has a V–V distance of 2.439(1) Å.[9]

§ Resonance forms for *syn*-$[V(Cp)]_2COT$ may be drawn whereby one V atom attains an 18-electron configuration if a V–V triple bond is understood.[9]

¶ Only the Cp–*H* resonance data were included in the fit as the pentalene *H*1 peaks were not resolvable over the full temperature range and the temperature dependence of the pentalene *H*2 resonance was considered too small (0.5 ppm) in relation to that expected for the *diamagnetic* shift over this temperature interval. For a discussion of the assumptions made in this magnetic fit see ref. 11.

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