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## Molecular building blocks for magnetic spin chains

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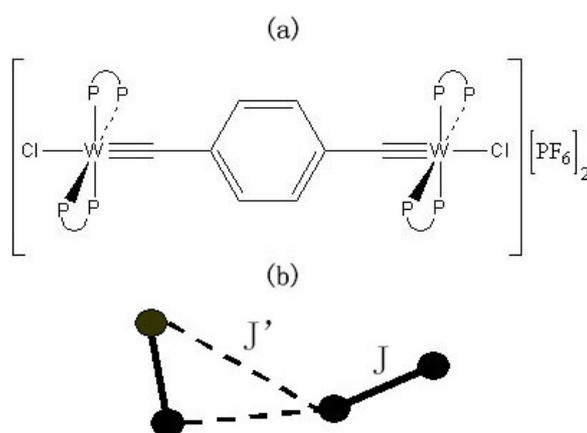
### Abstract

The paramagnetic di(metalloethynyl)benzene ion  $[1,4\text{-C}_6\text{H}_4\{\text{CW}(\text{depe})_2\text{Cl}\}_2]^{2+}$  was synthesized from diamagnetic  $1,4\text{-C}_6\text{H}_4\{\text{CW}(\text{depe})_2\text{Cl}\}_2$  (depe = 1,2-bis(diethylphosphino)ethane). Systematic measurements of magnetic susceptibility for both crystalline and powder-formed compounds indicate a predominant super-exchange coupling between the magnetic tungsten centres. We provide a quantitative description of the observed susceptibility using a decoupled Heisenberg dimer model, and find that all the complexes exhibit a robust antiferromagnetic coupling between spins,  $J \sim 38$  K. We note their potential use as building blocks for one-dimensional spin chains—with or without disorder—and describe possible synthetic routes to these architectures.

(Some figures in this article are in colour only in the electronic version)

Strong electron–electron correlations occur naturally in small-molecule systems [1]. Coulomb blockades [2] appear at ambient temperatures at energies of the order of electron volts. In simple pi-conjugated systems, surmounting the Coulomb gap is related directly to conduction through the pi system. This insight has motivated the development of hybrid organic/transition metal conjugated building blocks containing function-rich  $L_n\text{M}\equiv\text{C}$  units, which can be assembled into wires [3, 4]. Protonation, oxidation, or photoexcitation of the metal centres in these materials induces large changes in the electron–electron interaction that then can be used to control coupling across the pi-conjugated chain.

The transition metal components of these hybrid molecular building blocks are  $\text{Mo}^{\text{IV,V}}$  or  $\text{W}^{\text{IV,V}}$ , both of which can interact magnetically as well as electronically. Electron–electron exchange interactions between  $d^1$  metal centres can be controlled effectively by the bridging ligand structure, conformation [5, 6] and length [7]. If the magnetic spin arising from the 4d or 5d orbital of one metal atom couples sufficiently strongly to another, then the same design features that make these complexes attractive for molecular electronics make them attractive for designing new magnetic architectures in reduced dimension [8]. In particular, one can imagine purely one-dimensional spin chains [9, 10] where interchain coupling cannot

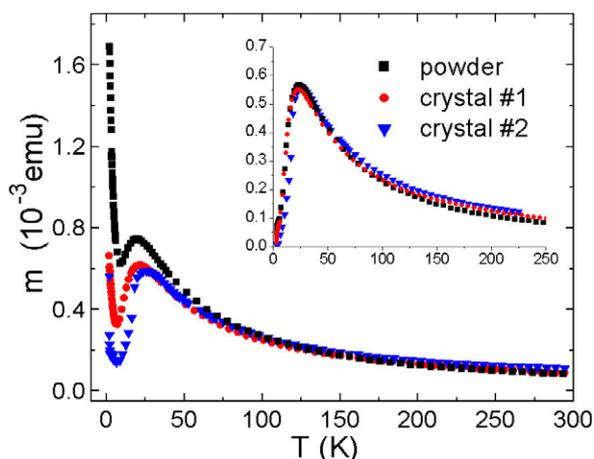


**Figure 1.** (a) Schematic diagram of the dimetallo-diethynylbenzene complex. (b) Possible intramolecular,  $J$ , and intermolecular,  $J'$ , magnetic couplings.

cut off intrinsic quantum effects at low temperature, and two-dimensional spin ladders of Mott–Hubbard character [11]. Moreover, these are molecular devices that permit the manipulation of both coupling strengths and spin disorder.

We synthesized [4] and studied both crystalline and powder-formed  $[1,4\text{-C}_6\text{H}_4\{\text{CW}(\text{depe})_2\text{Cl}\}_2][\text{PF}_6]_2$  (depe = 1,2-bis(diethylphosphino)ethane), with the goal of creating a new set of spin  $S = 1/2$  molecular dimers with prospective application as the building blocks for one-dimensional spin chains. Complex  $[1,4\text{-C}_6\text{H}_4\{\text{CW}(\text{depe})_2\text{Cl}\}_2][\text{PF}_6]_2$  exists as an orange powder and was synthesized in >90% yield by oxidizing diamagnetic  $1,4\text{-C}_6\text{H}_4\{\text{CW}(\text{depe})_2\text{Cl}\}_2$  with two equivalents of  $[\text{C}_7\text{H}_7][\text{PF}_6]$  in toluene/acetonitrile solution at  $-56^\circ\text{C}$  under nitrogen atmosphere. Its crystalline product was obtained by diffusion of diethyl ether into a concentrated acetonitrile solution of the complex at  $-33^\circ\text{C}$ , which provided crystals of composition  $[1,4\text{-C}_6\text{H}_4\{\text{C}\equiv\text{W}(\text{depe})_2\text{Cl}\}_2][\text{PF}_6]_2 \cdot 2\text{CH}_3\text{CN}$ . The synthesis of the starting material  $1,4\text{-C}_6\text{H}_4\{\text{CW}(\text{depe})_2\text{Cl}\}_2$  was accomplished in 70% yield by reducing  $1,4\text{-C}_6\text{H}_4\{\text{C}\equiv\text{WCl}_3(\text{dme})\}_2$  [12] (dme = 1,2-dimethoxyethane) with Na/Hg (0.4 wt%) in the presence of depe in tetrahydrofuran solution at room temperature.

X-ray crystallographic analysis of the sample shows an orthorhombic crystal system ( $Pbca$ ) with the molecular structure shown schematically in figure 1(a). The W ions are 9.35 Å apart. Counting a single alkyldyne ligand as a trianion, the metal centres are formally in the W(V) oxidation state, forming two localized  $S = 1/2$  dipole moments. On the basis of simple molecular orbital considerations [13], the ground and lowest-lying excited electronic states of  $[1,4\text{-C}_6\text{H}_4\{\text{C}\equiv\text{W}(\text{depe})_2\text{Cl}\}_2]^{2+}$  are expected to be closely analogous to those of quadruply metal–metal-bonded complexes. Taking the intermetallic axis as the reference, both types of compound can be described as consisting of a core  $\sigma^2\pi^4$  ( $\text{M}\equiv\text{M}$  or  $\text{M}\equiv\text{C}$ ) electron configuration, with two additional electrons occupying  $\delta$ -symmetry ( $d_{xy}$ ) orbitals that give rise to a singlet  $\delta^2$  ground state and triplet  $\delta^1\delta^{*1}$ , singlet  $\delta^1\delta^{*1}$  and singlet  $\delta^{*2}$  excited states. Theory and experiment place the splitting between the  $\delta^2$  ground state and triplet  $\delta^1\delta^{*1}$  excited state of quadruply bonded complexes (with ancillary ligands similar to those of the present ion) at about 4000–7000 K for M–M distances of about 2 Å [14]. At the 9.35 Å W–W distance of the  $[1,4\text{-C}_6\text{H}_4\{\text{C}\equiv\text{W}(\text{depe})_2\text{Cl}\}_2]^{2+}$  ion the  $\delta$  overlap is much less, substantially reducing the singlet–triplet energy gap. Although the dipolar interaction of two spin 1/2 moments at this distance has an energy scale less than 0.1 K, a magnetic pathway is available through the W–C bonds and phenylene ring. Such super-exchange coupling could permit the tungsten atoms to act as a magnetic dimer at more accessible temperatures.

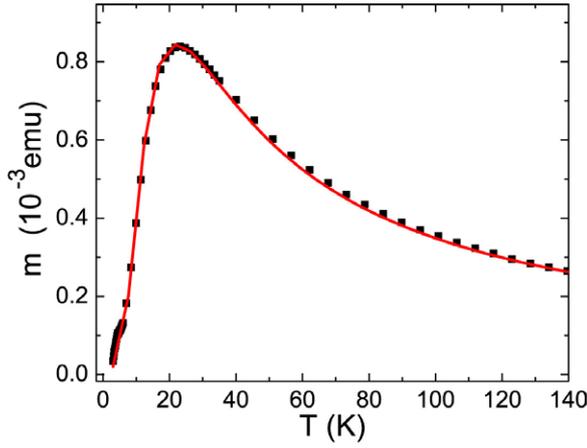


**Figure 2.** Magnetic moment per unit mass at a constant field of 4000 Oe for a powder-formed sample (black), crystal No 1 (red) and crystal No 2 (blue). The anomalies below 10 K are due to a small number of partially oxidized, paramagnetic dipoles and can be fitted well to a Curie law. Inset: when the free moment contribution is subtracted from the original data, the three curves collapse on top of each other, showing only magnetic signatures from molecular dimers.

Intermolecular coupling also may exist between the W ions of different molecules, depicted as  $J'$  in figure 1(b). This intermolecular coupling, if comparable in magnitude to the main coupling constant  $J$ , would make the system behave more like a random coupled spin chain or introduce frustration into the system. The presence of such effects can be investigated by comparing the magnetic response of crystalline and powder-formed samples, since the distribution of intermolecular couplings  $P(J')$  should have a sensitive dependence on molecular distance and lattice structure.

A few hundred single crystals of typical dimensions ( $0.45 \times 0.15 \times 0.10$ ) mm<sup>3</sup> and 0.01 mg weight were flame sealed inside thin (5 mm) quartz tubes after weighing and filling in a glove box, and then placed in a SQUID magnetometer for magnetic moment measurements. Similar quantities of powder samples were prepared for comparison. After cooling from 300 K to pumped helium temperature (2 K) in zero magnetic field (ZFC), the sample was warmed slowly in a constant field ranging from 100 to 4000 Oe, and the temperature dependence of the magnetic moment was recorded. The data also were collected following a field-cooled protocol (FC) where a constant magnetic field was applied while cooling. No difference was found between the magnetic responses measured using these two different methods of cooling, indicating the absence of glassy behaviour in the spin system [15].

We plot in figure 2 the temperature dependence of the magnetic moment in a constant field of 4000 Oe for three different samples, two crystalline and one powder-formed. When scaled with sample mass, the three curves essentially coincide from room temperature down to 50 K, but depart from one another at lower temperatures. The anomalies below 10 K have the typical  $1/T$  dependence of a free moment paramagnet and can be fitted well to a Curie law. When the free moment contribution is subtracted from the original data, one broad peak appears for each of the three samples (figure 2, inset). Within the error bars, this peak is in the same location for all three samples at  $T = 22 \pm 2$  K. Its magnitude lies more than an order of magnitude below the demagnetization limit and the extrapolation of the high temperature tail on a  $1/T$  plot intersects the abscissa at a negative temperature, thereby indicating a predominant antiferromagnetic coupling between W spins.



**Figure 3.** Fitting (solid line) of the 4000 Oe magnetization versus temperature curve for crystal No 1, using a model of antiferromagnetically coupled magnetic dimers. Only the intrachain coupling,  $J \sim 38$  K, is found to be important.

**Table 1.** Fitting results.

	Crystal No 1	Crystal No 2	Powder
$J$ (K)	$37.0 \pm 0.6$	$40.2 \pm 0.6$	$35.4 \pm 0.5$
$N_{\text{free}}/N_{\text{dimer}}$	$0.066 \pm 0.001$	$0.014 \pm 0.004$	$0.166 \pm 0.005$

For a quantitative understanding of the data, we assume that our system can be treated as a mixture of antiferromagnetic dimers with Heisenberg coupling constant  $J$ , and a small number of partially oxidized molecules which act as free magnetic dipoles with  $S = 1/2$  (and give rise to the  $1/T$  behaviour at low temperatures). This simplification is made possible by our assumption that  $J'$  is negligible, consistent with the observed lack of glassy behaviour in both crystalline and powder samples. The temperature dependence of the magnetic moment under a given  $B$  field then can be explicitly shown as follows:

$$N_{\text{free}} \frac{\mu_B^2}{k_B T} B + \frac{N_{\text{dimer}} * 2\mu_B \sinh\left(\frac{2\mu_B B}{k_B T}\right)}{1 + e^{J/k_B T} + e^{2\mu_B B/k_B T} + e^{-2\mu_B B/k_B T}}.$$

Here  $\mu_B$  is the Bohr magneton and  $k_B$  is Boltzmann's constant. The coupling constant  $J$ , the number of dimers  $N_{\text{dimer}}$ , and the number of free moments  $N_{\text{free}}$  are left as fitting parameters. The solid line in figure 3 shows the fitting of the data for crystal No 1, from which we subtracted the low temperature Curie component for clarity. Good consistency was found between the decoupled dimer model and all the magnetic moment data, thus justifying our assumption that effects from the intermolecular coupling  $J'$  are negligible. The main coupling constant  $J$  and the ratio  $N_{\text{free}}/N_{\text{dimer}}$  were obtained for each of the three samples, and are displayed in table 1. Each result listed is the weighted average of the fitting results from several magnetic field strengths: 100, 250, 500, 1000, and 4000 Oe.

The ratio  $N_{\text{free}}/N_{\text{dimer}}$  differs by factors of 3–10 between the crystals and the powder-formed samples, consistent with the large difference between the magnetic moment curves at low temperature in the main part of figure 2. Hence, we believe that the free magnetic dipole component is not an intrinsic property of this system, presumably arising from unpaired W ions in partially oxidized molecules. However, a universal intramolecular coupling,  $J = 38 \pm 3$  K, was found for all three samples, consistent with the picture of decoupled antiferromagnetic dimers. The difference between the value of  $J$  obtained from the fitting and the actual peak

position at  $T = 22$  K reinforces the conclusion that there is no long range order in this dimer system.

We have shown that tungsten atoms bridged by ligands can retain their spin state and form a network of decoupled dimers. The remarkably strong antiferromagnetic coupling of  $[1,4\text{-C}_6\text{H}_4\{\text{C}\equiv\text{W}(\text{depe})_2\text{Cl}\}_2]^{2+}$  suggests that this complex and its relatives could be important molecular building blocks for a new class of  $S = 1/2$  spin chains at reasonably accessible temperatures. The building block complex  $\text{Cl}(\text{depe})_2\text{WCC}_6\text{H}_4\text{CW}(\text{depe})_2\text{Cl}$  has a functional group ( $\text{Cl}^-$ ) at both ends, which can be extended readily into low (1D and 2D) dimensional polymeric materials by reacting with different organic linker molecules [4]. Three-dimensional order is also achievable by the fine-tuning of interchain interactions to couple the chains together. The neutral precursor to this ion has been incorporated into pi-conjugated polymers of the type  $[1,4\text{-C}_6\text{H}_4\{\text{C}\equiv\text{W}(\text{depe})_2\}(\mu\text{-C}\equiv\text{CC}_6\text{H}_2\text{R}_2\text{C}\equiv\text{C})_n$  through substitution of the axial chloride ligand by diethynylene-arene bridging ligands [4]. Partial oxidation of these polymers should give rise to materials in which unoxidized domains would function as non-magnetic spacers to permit the manipulation of spin disorder [16]. In addition, it has been demonstrated that paramagnetic tungsten-containing building blocks of general form  $[\text{C}_6\text{H}_{6-x}\{\text{C}\equiv\text{W}(\text{depe})_2\text{Cl}\}_x]^{x+}$  with different substitution patterns (1,4-, 1,3- or 1,3,5-substituted benzene) can be synthesized, allowing high level control over the geometric arrangement of the metal centres. Preliminary measurements suggest different coupling strengths with various pattern derivatives.

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