

# Strong ferromagnetic metal–ligand exchange in a nickel bis(3,5-dipyridylverdazyl) complex†

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**A new 1,5-dipyridyl verdazyl, synthesized from the corresponding dipyridyl hydrazone, coordinates nickel(II) to form a structurally characterized, pseudooctahedral complex analogous to Ni(terpy)<sub>2</sub><sup>2+</sup>. The unusually short Ni–verdazyl distance results in strong ferromagnetic exchange ( $J_{\text{Ni-rad}} = +300$ ,  $J_{\text{rad-rad}} = +160 \text{ cm}^{-1}$ ) between all three paramagnetic species along with a metal–ligand charge transfer band in the electronic spectrum.**

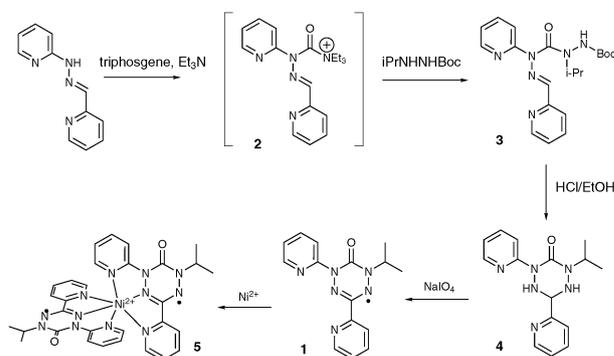
Verdazyl free radicals are an appealing building block for the synthesis of complex magnetic nanostructures as a result of their stability, strong magnetic exchange with coordinated metal ions,<sup>1</sup> and structural similarity to aromatic azine ligands such as pyridine and pyrimidine. Self-assembling systems based on polypyridines are well known and form a large variety of structures such as grids, cylinders and coordination polymers;<sup>2</sup> however, though a series of polytopic verdazyl ligands were reported in 2004<sup>3</sup> there have been no reports of self-assembled structures using these ligands. Clues to this somewhat surprising lack come from examining other reported verdazyl coordination compounds. For the most part they can be divided into two categories—coordination compounds with copper(I)<sup>4–7</sup> and coordination compounds with transition metals with hexafluoroacetylacetonate (hfacac) ancillary ligands.<sup>8–11</sup> This suggests that the verdazyl is a weakly basic,  $\pi$  acceptor ligand (consistent with the tetrazine core). Verdazyls interact strongly with Cu(I) as a result of significant  $\pi$  back bonding but coordination to harder metal ions requires the hfacac ligands to enhance the metal ion acidity.

An exception to these observations is the bipyridyl substituted verdazyl first reported in 2000 where an extra pyridine ring is the ‘glue’ that keeps the verdazyl coordinated.<sup>12,13</sup> Even in this case, metal–ligand bond lengths suggest that the verdazyl is the most weakly bound part of the ligand, and the low basicity of the ligand is compounded by the steric requirements of the 1 and 5 methyl substituents on the verdazyl ring. Replacement of one (or both) of the methyl groups in the verdazyl system with a group that could itself bind a metal ion should give a less sterically encumbered ligand while more effectively ‘clamping’ the weakly basic verdazyl nitrogen to the

metal center. The resulting ligand should show enhanced metal–ligand interaction and also provide a basis for the synthesis of more complex, self-assembled systems.

We chose the 1,3-dipyridyl substituted verdazyl **1** as a suitable target ligand for such an approach. Milcent and Barbier reported a synthesis of 1,3-diaryl substituted 6-oxoverdazyls in 1994<sup>14</sup> in which reaction of a hydrazone with phosgene gave a chloroformamide that was subsequently reacted with a second hydrazine to give a precursor tetrazane. Because of the instability of the chloroformamide intermediate and current limitations on the commercial availability of phosgene we have been unable to directly apply this procedure. Instead we have developed a one-pot synthesis of the protected hydrazide **3** using triphosgene and a protected hydrazine (Scheme 1). We reasoned that by adding excess triethylamine to the reaction mixture, the initial reaction of hydrazone and triphosgene would be driven to the acyl ammonium ion **2** which could then be trapped *in situ* by the protected hydrazine. Deprotection with HCl results in ring closure to give the tetrazane **4**. Unlike our earlier isopropyl tetrazanes,<sup>15</sup> oxidation of **4** with benzoquinone only gives tarry mixtures. Aqueous sodium periodate, however, gave the verdazyl as an orange-red solid which was characterized by UV-vis, EPR, IR and MS. The EPR in degassed toluene shows coupling to four nitrogens and a single hydrogen consistent with a verdazyl structure. An additional small hyperfine coupling to the nitrogen of the 1-(2-pyridyl) group is also observed indicating some spin density on the 1-aryl ring similar to that observed in other *N*-aryl verdazyls.<sup>16</sup> The EPR spectrum and simulation is shown in Fig. 1. The UV-vis of **1** shows absorbance maxima at 410 and 480 nm similar to other 6-oxoverdazyls<sup>17,18</sup> (Fig. 2).

Addition of **1** to a solution of nickel triflate in acetonitrile results in the formation of a dark red solution of the nickel

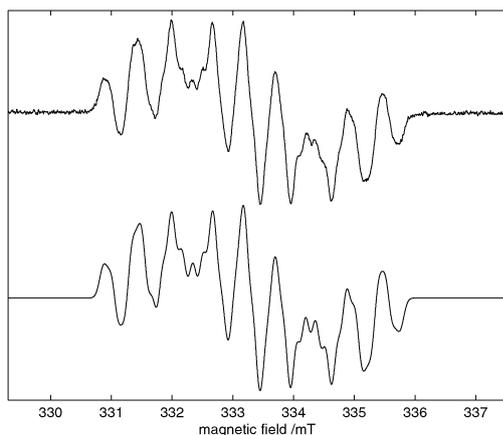


Scheme 1 Synthesis of ligand **1** and nickel complex **5**.

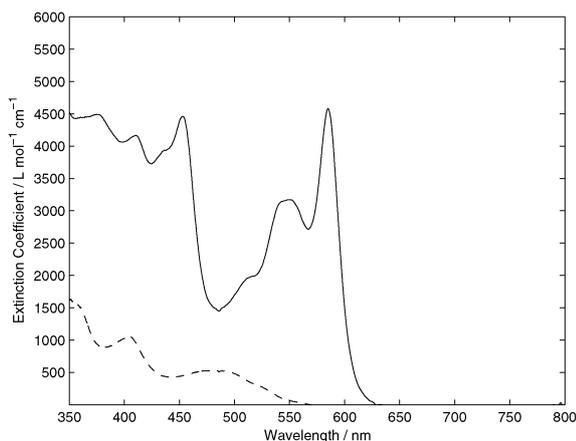
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† Electronic supplementary information (ESI) available: Experimental details of the synthesis of **1** and **5** including <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** and **4**. CCDC 753408. For ESI and crystallographic details in CIF or other electronic format see DOI: 10.1039/c0cc02233k

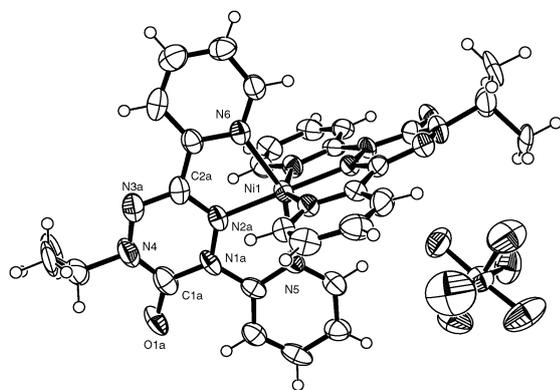


**Fig. 1** X band EPR spectrum of **1** in toluene (top) and simulation (bottom) with parameters  $a_{N2,4} = 0.66$ ,  $a_{N1} = 0.49$ ,  $a_{N5} = 0.43$ ,  $a_H = 0.15$ ,  $a_{N(\text{pyridyl})} = 0.074$  mT,  $g = 2.0034$ , linewidth = 0.075 mT.



**Fig. 2** Electronic spectrum of **1** (dashed line) and **5** (solid line) in acetonitrile.

complex **5** which can be purified as the hexafluorophosphate salt. Dark red needles suitable for X-ray crystallography were grown from ethanol/acetone.† A thermal ellipsoid plot is shown in Fig. 3. The molecule is located on a twofold axis that relates the two ligands. In addition, the molecule is



**Fig. 3** Thermal ellipsoid plot of compound **5**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths Ni–N(2a) 1.979(5), Ni–N(5) 2.106(5), Ni–N(6) 2.113(5).

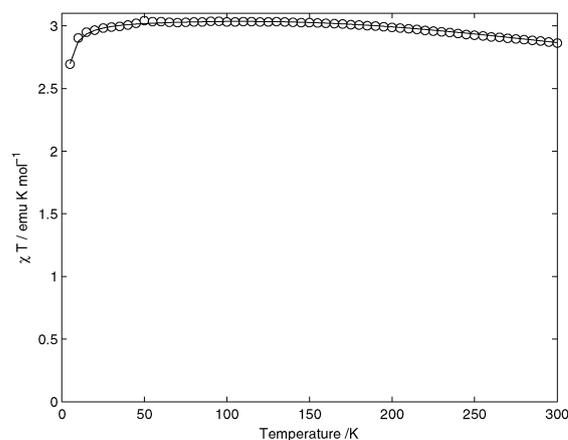
disordered about a non-crystallographic twofold axis passing through the two verdazyl rings. The latter disorder prevents accurate determination of the geometry of the verdazyl ring, however the coordination geometry is unambiguous. In particular, the verdazyl–nickel distance (1.98 Å) is significantly shorter than that for any other verdazyl–nickel complex—previously reported verdazyl–nickel distances vary between 2.19 and 2.23 Å.<sup>9,10,13,19</sup>

Unlike most transition metal verdazyl complexes, the electronic spectrum of **5** in acetonitrile (Fig. 2) shows significant perturbation of the verdazyl chromophore. The long wavelength band increases in intensity and is red shifted to 638 nm. Furthermore it shows well-resolved vibronic structure consistent with the formation of a rigid cyclic system.

Magnetic susceptibility of **5** was recorded in a 5000 G field from 5 K to 300 K and corrected for diamagnetism using Pascal's constants. Data are shown in Fig. 4 as a plot of the product of magnetic susceptibility and temperature,  $\chi T$  vs.  $T$ . At 300 K,  $\chi T = 2.86$  emu K mol<sup>-1</sup> which is significantly above the value expected for non-interacting spins ( $\chi T = 1.75$  emu K mol<sup>-1</sup>) and close to the spin only value expected for a quintet ( $\chi T = 3.0$  emu K mol<sup>-1</sup>). As the temperature drops,  $\chi T$  increases to a plateau value of 3.04 emu K mol<sup>-1</sup> at 130 K, then drops sharply below 10 K. This is consistent with a ground state quintet ( $S = 2$ ) separated from the magnetic excited states by a significant energy gap such that below 130 K the high spin state is the only populated state. The drop in  $\chi T$  below 10 K may be a result of intermolecular antiferromagnetic exchange or zero field splitting. Following the model of Kahn<sup>20</sup> and of Barclay and co-workers<sup>12,13</sup> we fitted the data to a three spin, two exchange model with Hamiltonian:

$$\hat{H} = -J_{\text{Ni-Vd}} (\mathbf{S}_{\text{Ni}} \mathbf{S}_{\text{Vd}_1} + \mathbf{S}_{\text{Ni}} \mathbf{S}_{\text{Vd}_2}) - J_{\text{Vd-Vd}} \mathbf{S}_{\text{Vd}_1} \mathbf{S}_{\text{Vd}_2}$$

We also included an arbitrary antiferromagnetic term  $zJ'$  to fit the low temperature data. The best fit (solid line in Fig. 4) gives  $J_{\text{Ni-Vd}} = +300$  cm<sup>-1</sup>,  $J_{\text{Vd-Vd}} = +160$  cm<sup>-1</sup>,  $zJ' = -1.21$  cm<sup>-1</sup>,  $g_{\text{Ni}} = 2.035$ ,  $R = 0.0011$  with  $g_{\text{Verdazyl}}$  fixed at 2.00; however the two exchange constants are highly correlated and fits of



**Fig. 4** Plot of  $\chi T$  vs.  $T$  for compound **5**. Susceptibility measurements were made in a 5000 G external field. The solid line is the best fit to the data using the model described in the text.

only marginally lower quality were obtained with values ranging from  $J_{\text{Ni-Vd}} = +220 \text{ cm}^{-1}$ ,  $J_{\text{Vd-Vd}} = +510 \text{ cm}^{-1}$  to  $J_{\text{Ni-Vd}} = +350 \text{ cm}^{-1}$ ,  $J_{\text{Vd-Vd}} = +100 \text{ cm}^{-1}$ . Qualitatively the strong metal–radical coupling is consistent with the plateau value of  $\chi T$  noted above. Though the uncertainty in the exact magnitude of the exchange parameters is quite large, we can, at the least, conclude that exchange in this system is strongly ferromagnetic. In fact strong ferromagnetic exchange between all three components is consistent with orbital overlap models for exchange (*vide infra*).

Though strong ferromagnetic exchange between  $\text{Ni}^{2+}$  and coordinated verdazyls, and  $\text{Ni}^{2+}$  and iminonitroxides<sup>21–24</sup> has been previously observed, both exchange parameters are larger than those reported for any other comparable systems (earlier reported values range from  $+188 \text{ cm}^{-1}$  to  $+240 \text{ cm}^{-1}$  for  $J_{\text{Ni-Vd}}$ , while the only reported value for  $J_{\text{Vd-Vd}}$  mediated by  $\text{Ni}^{2+}$  is  $-8 \text{ cm}^{-1}$ ).

The short metal–radical distance alone would be expected to increase  $J_{\text{Ni-Vd}}$  exchange by increasing coulombic repulsion between the unpaired electrons. Further increase in metal radical exchange may result from delocalization of the radical spin onto the metal  $d_{\pi}$  orbitals. Evidence for such an interaction comes from the electronic spectrum. An increase in intensity and red shift of the verdazyl low energy band is associated with charge transfer into the verdazyl SOMO,<sup>18</sup> in this case most likely from the metal ion. Similar charge transfer bands were observed in nickel–iminonitroxide<sup>23</sup> and copper(i) verdazyl–phosphine complexes<sup>4</sup> and, more recently in a ruthenium verdazyl complex.<sup>25</sup> In the latter two cases, charge transfer bands could be directly correlated with an increase in spin density on the metal. Furthermore, spin delocalization onto the metal ion explains the strongly ferromagnetic radical–radical exchange as superexchange mediated by mutually orthogonal metal  $d_{\pi}$  orbitals. It is interesting to note that a recent computational study concluded that metal–ligand charge transfer was not significant in the verdazyl–nickel complexes known at the time.<sup>26</sup>

Together the electronic spectrum and magnetic properties of **5** show the dramatic effect that changes in geometry can have upon electronic structure and further illustrate the potential for synthesis of novel magnetic structures using verdazyls. To this end our new synthetic procedure for 1,5-bis(aryl)tetrazanes should be readily adapted to synthesis of polytopic ligands capable of self-assembly. These will be derived from the hydrazone ligands reported by ourselves and the research group of Lehn.<sup>27–29</sup> Further work toward this goal is underway in our laboratories.

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## Notes and references

‡ Crystal data:  $\text{C}_{30}\text{H}_{30}\text{F}_{12}\text{N}_{12}\text{O}_2\text{P}_2$ ,  $M = 939.26$ , tetragonal;  $a = 15.800(6) \text{ \AA}$ ,  $c = 15.227(6) \text{ \AA}$ ,  $V = 3810.17 \text{ \AA}^3$ ,  $T = 150 \text{ K}$ , space group  $P4_2(1)/c$  (No. 114).  $Z = 4$ , 18 198 reflections measured, 2419 unique ( $R_{\text{int}} = 0.076$ ). Solution and refinement gave  $R = 0.055$ ,  $wR(F_2) = 0.125$ ,  $S = 1.011$  (all data). The Flack parameter was 0.02(4). CCDC 753408.

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