Structure and magnetic properties of a nickel(II) complex of a tridentate verdazyl radical: strong ferromagnetic metal-radical exchange coupling†

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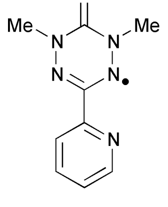
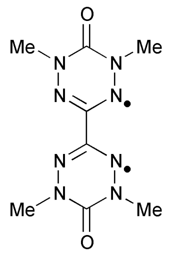
Magnetic susceptibility measurements on a structurally characterized nickel(II) complex of a tridentate verdazyl radical indicate very strong ferromagnetic Ni–verdazyl intramolecular exchange interactions ($J > +200$ cm^{-1}).

Metal complexes of coordinated radicals have been actively pursued as components of new molecular magnetic materials. A principal advantage of paramagnetic ligands is that direct magnetic exchange coupling between metal and ligand spins is possible. Although a large number of metal–radical systems have been studied, the *variety* of radical-based ligands is somewhat limited. Most work has been carried out with ligands based on the nitroxide family[1–3] and TCNE[4] and TCNQ[5] radical anions, although there has been a growing interest in exploring alternative radicals as ligands.[6] Derivatives of the verdazyl radical family[7] offer an attractive alternative to the conventional radical ligands because of their abundance of donor atoms. Verdazyls such as pyvd and bvd possess chelating environments that are excellent structural mimics of 2,2′-bipyridine and 2,2′-bipyrimidine, respectively, and transition metal complexes of both radicals have been reported.[8–11] Given the huge interest and success in employing oligopyridines as ligands in metallo-supramolecular chemistry,[12–14] it is appealing to consider creating oligopyridine analogues in which one or more of the heterocyclic rings is replaced by a verdazyl radical. The preservation of the chelating environment makes such systems attractive both for self-assembly processes and for the desirable metal–radical exchange coupling. As an initial foray in this direction, we present the synthesis, coordination chemistry, and magnetic properties of a nickel complex of the tridentate verdazyl 1,5-dimethyl-3-(2,2′-bipyridin-6-yl)-6-oxoverdazyl, bipyvd, a radical that possesses a coordination pocket analogous to that of 2,2′:6′,2″-terpyridine.


pyvd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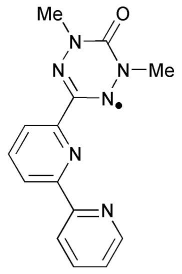
bipyvd

The bipyvd ligand was prepared[15] from 2,2′-bipyridine-6-carbaldehyde[16] using established procedures.[17,18] Reactions of bipyvd with $NiCl_2$ in the presence of $NaPF_6$ produced $Ni(bipyvd)_2^{2+}\cdot 2PF_6^-$ (**1**) which crystallized as an acetone solvate.‡ Fig. 1 shows the molecular structure of the cation of **1**, which consists of two tridentate bipyvd ligands surrounding the nickel ion in a pseudo-octahedral coordination sphere.§ The local geometry at the nickel is D_{2d} distorted from ideal octahedral geometry, as is also the case for structurally characterized $Ni(terpy)_2^{2+}$ complexes.[19,20] The six Ni–N bonds occur in three pairs with a distinct progression of bond lengths: two short bonds to each of the central pyridine nitrogens (N5 and N11, mean bond length 1.996 Å), two slightly longer bonds to the terminal pyridine nitrogens (N6 and N12, 2.098 Å) and two yet longer bonds to the verdazyl ring nitrogens (N1 and N7, 2.211 Å). The structural features of the verdazyl rings of the ligands are quite similar to other 1,5-dimethyl-6-oxoverdazyls, although there is a slight asymmetry in the bond lengths and angles induced by coordination to nickel (see supporting information). Each of the two bipyvd ligands are essentially planar and are oriented perpendicular to one another, with an interligand dihedral angle of 92.4°. Overall, the general structural features of this complex, particularly with respect to the local coordination environment at Ni, are strongly reminiscent of $Ni(terpy)_2^{2+}$-based systems,[19,20] further validating the *structural* analogy between oligopyridine-substituted verdazyls and the 'parent' oligopyridines.

The UV–visible spectrum of **1** exhibits an absorption maximum at 438 nm (ε = 5700 L mol^{-1} cm^{-1}), which is slightly red shifted with respect to the spectrum of free bipyvd (λ_{max} = 400 nm, ε = 1900). The complex is therefore appropriately described as consisting of a nickel(II) center and two radicals. The temperature dependence of the effective

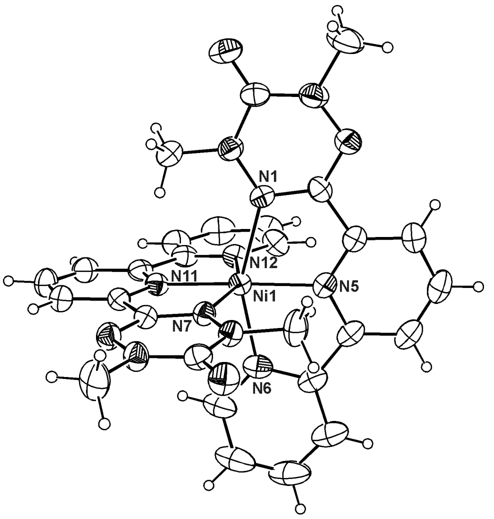

Fig. 1 Molecular structure of the $Ni(bipyvd)_2^{2+}$ dication of **1** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°) Ni(1)–N(1) 2.209(3), Ni(1)–N(5) 2.000(3), Ni(1)–N(6) 2.101(3), Ni(1)–N(7) 2.212(3), Ni(1)–N(11) 1.991(3), Ni(1)–N(12) 2.094(3); N(1)–Ni(1)–N(6) 154.59(12), N(7)–Ni(1)–N(12) 155.58(11), N(5)–Ni(1)–N(11) 175.08(11).

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† Electronic supplementary information (ESI) available: partial packing diagram for **1**. See http://www.rsc.org/suppdata/cc/b0/b006520j/

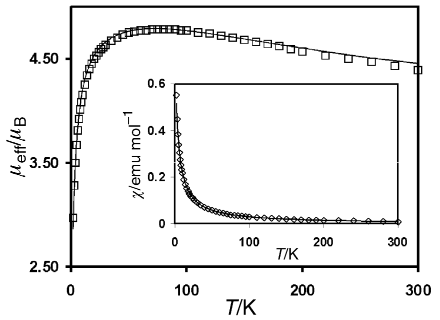

Fig. 2 Plot of μ_{eff} *vs.* *T* for **1**. The solid line corresponds the model fit according to parameters described in the text. The inset displays the corresponding χ *vs.* *T* profile.

magnetic moment of **1** is presented in Fig. 2.¶ The room temperature value (4.4 μ_B) is significantly higher than that expected for a non-interacting $S = 1$ Ni^{II} ion and two $S = \frac{1}{2}$ radicals (3.9 μ_B for $g = 2.1$). As the temperature decreases, μ_{eff} increases to a maximum value of 4.8 μ_B at 85 K and then rapidly decreases on further cooling. The high temperature behaviour provides evidence for strong ferromagnetic interactions between the Ni^{II} spins and each of the two radical centers. The magnetic data were fitted to a three-spin model in which the two radicals ($S_{A1} = S_{A2} = \frac{1}{2}$) are both ferromagnetically coupled to a nickel ion ($S_B = 1$) by exchange constant J_1 and coupled to each other with value J_2. Attempts to model the magnetic behaviour of **1** yielded several different solutions with essentially the same quality fits to the experimental data. In these various solutions, the radical–radical coupling J_2 varied from +40 to −70 cm^{-1}, precluding any firm conclusions regarding the nature of the magnetic interactions between coordinated radicals. The metal–radical exchange J_1 was also variable, although the *smallest* acceptable fitted value was +200 cm^{-1} (and values of up to +330 cm^{-1} were obtained in some solutions). This implies that the observed magnetic properties are largely determined by the very strong ferromagnetic metal–radical coupling. The uncertainty in the coupling parameters may be a reflection of the difficulties associated with quantifying exchange integrals in strongly ferromagnetically coupled systems.[21] We are currently preparing analogous bipyvd complexes of diamagnetic metal ions in order to explicitly determine the radical–radical coupling. In the absence of any knowledge regarding the true value of J_2 we arbitrarily set it equal to zero, producing the following parameters: $J_1 = +320$ cm^{-1}, $J_2 = 0$ cm^{-1}, $g = 2.11$, $\theta = -5$ K, TIP (temperature-independent paramagnetism) = 0.00022 cm^3 mol^{-1}, ρ (fraction of paramagnetic impurity) = 0.014 ($R = 0.0321$; $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2]^{1/2}$). The Weiss-like constant θ was employed as a pseudo-intermolecular exchange parameter necessary to model the low temperature magnetic behaviour; analysis of the molecular packing in **1** reveals neighbouring verdazyl rings in somewhat close proximity (ESI†). The overlap of adjacent verdazyl moieties offers a probable intermolecular exchange pathway, although zerofield splitting of the high-spin Ni^{II} ground state may also contribute to the low temperature behaviour.

We recently reported similarly strong coupling in a nickel complex of pyvd which contains two hfac ligands.[11] In this system the ferromagnetic verdazyl–nickel coupling was explained by invoking well-established orbital orthogonality arguments.[21] The intramolecular exchange coupling in compound **1** is similar in nature and establishes that verdazyl–nickel ferromagnetic coupling is a general phenomenon and is not dependent on the nature of the ancillary ligands. This stands out in sharp contrast to the behaviour of virtually all other metal-radical complexes described to date, in which strong *anti*-ferromagnetic or weak ferromagnetic coupling is the rule. The only other complexes which we are aware of with comparable ferromagnetic exchange properties are semiquinone complexes of Ni^{II} and Cu^{II}.[22] Moreover, the structural similarities of verdazyl–metal binding to that seen in complexes of oligopyridines brings a significant component of structural design into the construction of metal–radical assemblies because of the well-established binding modes of oligopyridines. We are enthusiastic about the prospects of making new high-spin clusters and solids based on nickel(I) and oligopyridine-based verdazyls.

Notes and references

‡ A solution of $NiCl_2 \cdot 6H_2O$ (103 mg, 0.433 mmol) in 5 mL of water was added to a slurry of bipyvd (240 mg, 0.853 mmol) in 5 mL of methanol, causing immediate dissolution of the ligand and formation of a deep cherry red solution. The mixture was stirred for 20 minutes and a solution of $NaPF_6$ (143 mg, 0.851 mmol) in 2 mL of water was added, giving a red precipitate. The reaction mixture was concentrated to about 3 mL and placed in an ice bath. The product **1** was vacuum filtered as a deep red powder and washed with cold distilled water. Yield: 290 mg (74%). The product was recrystallized by slow evaporation of a 1 : 1 acetone–ethanol solution, giving deep red plates. ν/cm^{-1} (KBr) 1709(s), 1602(m), 1574(m), 1496(m), 1460(s), 1437(m), 1359(w), 1306(m), 1275(s), 1216(w), 1177(w), 1158(w), 1090(w), 1057(w), 1037(m), 1012(m), 844(s), 777(s), 748(m), 713(m), 685(s), 643(w), 559(s), 503(w). UV–Vis (CH_3CN) λ_{max}(nm) (ε/M^{-1}cm^{-1}) 438 (5691). FAB-MS 764.9(22) [M − PF_6]$^+$. Anal. Calcd for $C_{28}N_{12}O_2H_{26}NiP_2F_{12} \cdot C_3H_6O$: C, 38.41; H, 3.33; N, 17.34. Found: C, 38.25; H, 3.18; N, 17.27.

§ *Crystal data* for **1**: $C_{31}H_{32}F_{12}N_{12}NiO_3P_2$, $M = 969.34$, monoclinic, $a = 11.2095(16)$, $b = 17.362(2)$, $c = 20.494(3)$ Å, $V = 3986.8(10)$ Å^3, $T = 293$ K, space group $P2_1/c$, $Z = 4$, λ(Mo-Kα) = 0.71073 Å, 20965 reflections measured, 7033 unique ($R_{int} = 0.026$). The final $wR(F^2)$ was 0.155 (all data). CCDC 182/1796. See http://www.rsc.org/suppdata/cc/b0/b006520j/ for crystallographic files in .cif format.

¶ Variable temperature magnetic data (2−300 K) were obtained with a Quantum Design MPMS5S Squid magnetometer operating at 0.1–0.5 T. Calibrations were carried out with a palladium standard cylinder, and temperature errors were determined with $[H_2TMEN][CuCl_4]$ (D. S. Brown, V. H. Crawford, J. W. Hall and W. E. Hatfield, *J. Phys. Chem.*, 1977, **81**, 1303). The spin Hamiltonian for **1** has the form $H = J_1(S_{A1}S_B + S_{A2}S_B) - J_2S_{A1}S_{A2}$.

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