Structural control of ferromagnetic interactions in nickel(II) complexes based on a tetradentate biradical

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Complexation of a bipyridine-based nitronyl nitroxide biradical with nickel(II) affords two complexes that differ by the nature of one axial ligand and by their magnetic behaviour: in both cases ferromagnetic interactions between high-spin nickel(II) and the radicals are observed.

A key concept for the design of molecular ferromagnets involves the pre-programmed overlap of magnetic orbitals.[1] Thus far interest has focused on the preparation of multi-dimensional inorganic assemblies,[2,3] hybrid inorganic/organic systems[4] and organic radicals.[5] Coordination of nitroxide radicals to acidic paramagnetic metal centres provides valuable magnetic properties and, in certain cases, ferromagnetic ordering has been attained.[6,7] Surprisingly, chelating radicals have received scant attention despite the fact that they introduce important stereochemical constraints concerning the overlap of magnetic orbitals while favouring utilization of metal centres that are not strongly acid.[8,9] Here we report on the preparation, crystallographic analysis and magnetic properties of two nickel(II) complexes obtained from NIT-bpy, these being the first complexes to exhibit ferromagnetic Ni^{II}–radical inter-actions.

Complexes **1** and **2** were synthesised (Scheme 1), respectively, by mixing NIT-bpy with [Ni(H$_2$O)$_6$][ClO$_4$]$_2$ in methanol or in a mixture of dichloromethane–ethyl acetate.†

Single crystals of **1** were grown by slow evaporation of methanol.‡ Both the ORTEP view and the magnetic properties are shown in Fig. 1. It is seen that the NIT-bpy behaves as a pincer occupying the basal plane of the nickel octahedron. Two ancilliary ligands [H$_2$O molecules at a distance of 2.08(1) Å] complete the cation coordination sphere. Relevant structural features which have an impact on the magnetic properties are as follows: the O(1)N(1)C(1)N(2)O(2) mean plane containing one unpaired electron makes an angle of 14.07° with the equatorial plane N(5)N(6)O(1)O(3), 86.10 and 77.60°, respectively, with the N(5)O(w1)O(3)O(w2) and N(6)O(w1)O(1)O(w2) planes. The second O(3)N(3)C(12)N(4)O(4) mean plane exhibits an angle of 2.74° with the equatorial plane N(5)N(6)O(1)O(3), 89.50 and 88.97°, respectively, with N(5)O(w1)O(3)O(w2) and N(6)O(w1)O(1)O(w2) planes. The tilt angle about the exocyclic central C–C bond in the bpy subunit is 11.09°.
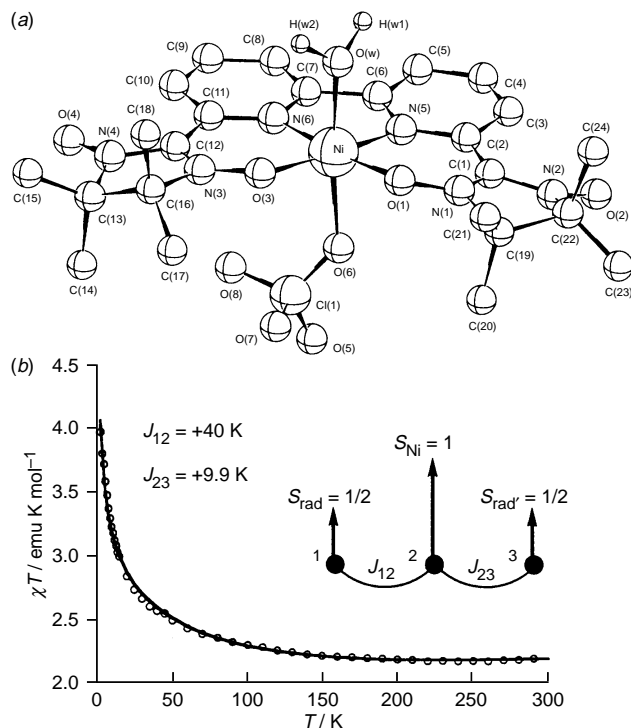
The magnetic properties of these two nickel(II) complexes were studied by use of a SQUID susceptometer. For **1**, the product of molar susceptibility and temperature (χT) at 300 K corresponds to the calculated value expected for three un-correlated spins (Ni^{II} $S = 1$ and two radicals $S = 1/2$) (Fig. 1). With decreasing temperature, χT shows a shallow decrease until a sharp breakdown occurs at around 220 K, presumably due to a phase transition. Then a continuous decrease is observed until a plateau is reached around 50 K, where $\chi T = 1.13$ emu K mol^{-1}. At still lower temperature an abrupt decrease occurs, indicating the onset of weak intermolecular antiferromagnetic interactions. A good fit of these experimental data could be obtained by allowing for the fact that coupling between each radical and the metal centre is different. One radical is coupled
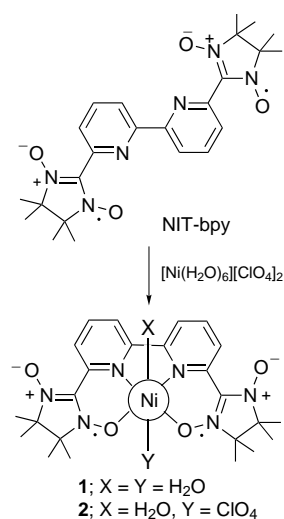
Scheme 1
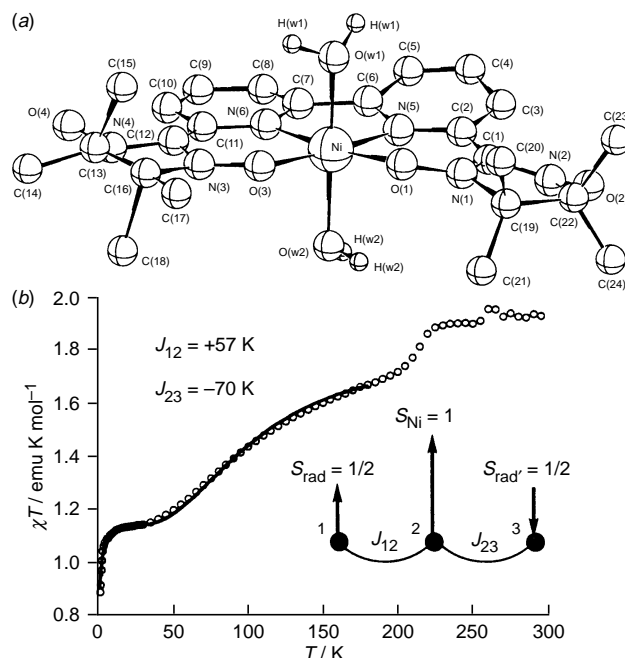
Fig. 1 (*a*) ORTEP view of the [Ni(NIT-bpy)·2H$_2$O]$^{2+}$ cation in complex **1** and (*b*) temperature dependence of the product of the magnetic susceptibility with temperature, χT *vs. T*, for **1**. The solid line represents the best-fit calculated values. Inset: magnetic interations network and values of the coupling constants.

(a)

(b)

Fig. 2 (*a*) ORTEP view of the [Ni(NIT-bpy)·H$_2$O·ClO$_4$]$^{2+}$ cation in complex **2** and (*b*) temperature dependence of the product of the magnetic susceptibility with temperature, χT *vs. T*, for **2**. The solid line represents the best-fit calculated values. Inset: Magnetic interactions network and values of the coupling constants.

ferromagnetically (J_{12} = +57 K) while the second interaction (J_{23} = −70 K) is antiferromagnetic. The value obtained for the plateau corresponds to the value calculated for an $S = 1$ ground spin state arising from antiferromagnetic coupling between a spin 3/2 and a spin 1/2 of the second radical. The best fit in the low temperature regime was obtained with a mean field approximation (zJ' = −0.47 K).

At a first glance the crystal structure of complex **2**‡ looks very close to that of **1** (Fig. 2). However, careful examination of these structures reveals some important differences concerning relevant angles. Indeed, for **2** the O(1)N(1)C(1)N(2)O(2) system containing one unpaired electron is planar and makes an angle of 14.20° with the equatorial plane N(5)N(6)O(1)O(3), 81.48 and 78.68°, respectively, with the N(5)O(w)O(3)O(6) and the N(6)O(w)O(1)O(6) planes. The O(3)N(3)C(12)N(4)O(4) plane makes an angle of 9.43° with the equatorial plane N(5)N(6)O(1)O(3), 78.20 and 84.44°, respectively, with the N(5)O(w)O(3)O(6) and the N(6)O(w)O(1)O(6) planes. The tilt angle between both pyridine rings in the bpy subunit is only 2.54°. The axial ligands in **2** comprise a water molecule, located at 2.085(4) Å, and a perchlorate anion located at 2.178(4) Å.

Complex **2** exhibits disparate magnetic properties when compared to **1** (Fig. 2). The χT product measured at 300 K is somewhat higher than that calculated for three uncorrelated spins. With decreasing temperature, χT continuously increases over the entire temperature range reaching a value of 3.96 emu K mol^{-1} around 1.8 K. This value is higher than that calculated for two radicals ferromagnetically coupled to Ni^{II} (3.63 emu K mol^{-1}). This reveals that intermolecular ferromagnetic interactions are effective in this complex. The experimental data could be well explained by taking into account two intra-molecular ferromagnetic interactions between the radicals and the Ni^{II} centre (J_{12} = +40 K and J_{23} = +9.9 K) as well as a weak intermolecular ferromagnetic interaction calculated by using a mean field approximation (zJ' = + 1.0 K). In **1** and **2**, as well as in the corresponding diamagnetic zinc(II) complex, intra-molecular spin coupling between the radicals is insignificant

since no sizeable magnetic interactions are observed when χ is measured in a frozen and dilute solution.

Analysis of the overlap between magnetic orbitals indicates that ferromagnetic interactions should be observed for the ideal case where the N$_2$O$_2$ ligand is planar. In fact, this conformation forces overlap between the π^* orbital of each radical and the magnetic orbitals of Ni^{II} to be orthogonal (for d$_{x^2-y^2}$) or symmetry forbidden (for d$_{z^2}$). However, slight deviation from orthogonality should induce the appearance of antiferromagnetic components. One radical in **1** is almost planar along the basal plane of the octahedron, thereby favouring ferromagnetic interaction. The second radical exhibits a prominent deviation from planarity, giving rise to strong antiferromagnetic interaction. Consequently, the overall magnetic behaviour of **1** is antiferromagnetic. The two radical centres in **2**, however, deviate only slightly from planarity and remain ferromagnetically coupled to the Ni^{II} centre.

This study has demonstrated that effective ferromagnetic coupling between Ni^{II} and nitronyl nitroxide radicals belonging to a tetradendate N$_2$O$_2$ tweezer ligand is possible. This is due to near orthogonality of the magnetic orbitals and was previously observed only for Cu^{II} complexes of nitronyl nitroxides in axial positions.[10] It is further shown that chelating ligands provide an excellent structural scaffold on which to assemble molecular ferromagnets. Future work will concentrate on the optimisation of these ligands both for their coordinative properties and for their ability to maintain strict orthogonality between the magnetic orbitals.

Notes and References

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† On the basis of spectroscopic evidence, including FAB$^+$ MS and elemental analysis, the structures of the new complexes were unequivocally authenticated.

‡ *Crystal data*: CAD4 Enraf-Nonius diffractometer (Mo-Kα), λ = 0.710 73 Å, graphite monochromator, T = 293 K. **1**, C$_{24}$H$_{30}$Cl$_2$N$_6$NiO$_{14}$, triclinic, space group $P\bar{1}$, a = 8.501(2), b = 12.815(3), c = 16.086(3) Å, α = 87.35(1), β = 84.86(1), γ = 71.18(1)°, Z = 2, V = 1651.8 Å^3, 2739 independent reflections with $F > 4\sigma(F)$, $R(F_o)$ = 0.0717, $R_w(F_o)$ = 0.0655. **2**, C$_{26}$H$_{35}$Cl$_2$N$_7$NiO$_{13}$, monoclinic, space group $P2_1/c$, a = 10.732(3), b = 20.823(3), c = 14.742(3) Å, β = 93.22(1)°, Z = 4, V = 3289.2 Å^3, 2780 independent reflections with $F > 4\sigma(F)$, $R(F_o)$ = 0.0417 and $R_w(F_o)$ = 0.0369. The structure was solved and refined on F factors using SHELX86[11a] and SHELX76[11b] packages, respectively. CCDC 182/746.

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