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A copper(II) complex of a pentadentate ligand featuring large ferro- and antiferromagnetic interactions†

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A novel pentadentate ligand based on a 2,2'-bipyridine template and functionalized with two methylene bridged nitroxide arms provides mononuclear Cu(II) and Zn(II) complexes displaying a *facial* and *meridional* conformation, respectively; for Cu large intramolecular ferromagnetic (J/k_B = +173 K) and antiferromagnetic (J'/k_B = −170 K) exchange interactions are evidenced from magnetic measurements.

During the past decade, extensive studies have been carried out on organic and inorganic molecule-based magnets.[1] In most cases, the magnetism results from direct overlap between magnetic orbitals, a situation well correlated to structural factors.[2] However, the ability to have control over processes leading to ferromagnetic exchange interactions in spin-labelled molecules is one of the challenges facing the field of molecular magnetism. The engineering of coordination compounds from nitroxide ligands is especially attractive since ligation ensures significant magnetic interactions.[3] In particular, nitronyl nitroxide[4] radicals became popular because of their exceptional stability, chemical versatility and ability to act as bridging ligands. Many examples have been provided using acidic metal centres as a building block that results in the formation of pre-designed architectures.[5] However, the weakly basic character of these radicals makes coordination possible only if the metal centre is activated with electron withdrawing groups.

This major drawback could be overcome by incorporating into the ligand donor fragments such as a pyridine,[6] 2,2′-bipyridine,[7] 1,10-phenanthroline,[8] triazole[9] or imidazole and benzimidazole subunits.[10] Such a strategy offers the opportunity to use classical metal salts and to tune radical–metal interactions, giving rise to large magnetic interactions.[11] In some Cu(II) complexes the short linkage between the chelate and the radical forces the magnetic orbitals to adopt a non-ideal orthogonal conformation which minimises the magnetic exchange interactions. To overcome these difficulties it was necessary to develop more flexible platforms.[12]

In the present account we put together two ideas consisting of the design of a ligand bearing a chelating bipy template and two flexible spin-labelled antennas grafted on a single donor atom. The presence of methylene spacers is motivated by the possible coordination of the three N,N,N′ donor atoms to the metal (reminiscent of a terpyridine ligand, Chart 1), whereas the two free radicals display the possibility to coordinate apically or equatorially instead of in the basal plane of an octahedron. This situation is auspicious for very strong magnetic exchange interactions.

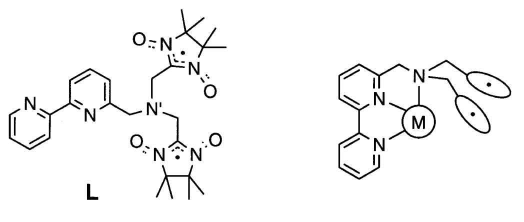

Chart 1

Ligand **L** was prepared by nucleophilic substitution of chloromethyl nitronyl nitroxide by aminomethyl-2,2′-bipyridine and shows the characteristic pink colour of an aminomethyl nitronyl nitroxide [FAB *m/z* = 524.2; ν_{NO} = 1369 cm^{-1}]. Mixing **L** with M(ClO$_4$)$_2$·6H$_2$O (M = Zn or Cu) is accompanied by a colour change from light pink to intense red. The FAB mass spectra of the resulting complexes show an intense molecular peak at 686.2 [(**L** + Zn)ClO$_4$]$^+$ and 685.6 [(**L** + Cu)ClO$_4$]$^+$ with the expected isotopomer distribution and the successive loss of a perchlorate and oxygen atoms. The only N–O stretching band observed is shifted to a lower value pointing to coordination of both radicals.‡

For Zn, the crystal structure§ reveals a unit cell containing a [Zn(**L**)·H$_2$O]$^{2+}$, two uncoordinated perchlorate and a CH$_2$Cl$_2$ (Fig. 1a). As previously found with related nitroxide radicals a disorder has been found for the methyl C24 to C27. The Zn atom is surrounded by the three N atoms of the aminomethyl-bipy fragment and a water molecule in its basal plane. The two nitroxide O atoms complete the coordination sphere providing an octahedral geometry, while the ON'O donor atoms lie in a *meridional* conformation. The dihedral angles between the two pyridine rings and the aminomethyl-pyridine fragment are 3.6 and 9.4°, respectively.

For Cu, the unit cell consists of a [Cu(**L**)·ClO$_4$]$^+$, an uncoordinated perchlorate and one acetonitrile. The Cu(II) is surrounded by one ligand and the O atom of a perchlorate (Fig. 1b). Interestingly, one radical is coordinated within the basal plane whereas the second radical lies in an apical position. In contrast with the Zn compound, the ON′O set of atoms provide a *facial* conformation. The basal plane is provided by the three N atoms of the aminomethyl-bipy ligand and a nitroxide O atom, with a Cu–O4 distance of 1.91 Å. In the apical position, the Cu–O2 distance is 2.43 Å, and the perchlorate O atom is loosely bonded with a distance of 2.47 Å. The dihedral angles between the two pyridine rings and between the aminomethyl-pyridine fragment and the adjacent pyridine are only 0.9 and 13.6°, respectively.

For both complexes the coordinated N–O (1.30 to 1.33 Å) and non-coordinated N–O distances (1.26 to 1.28 Å) deduced from X-ray data are in keeping with the radical nature of the five

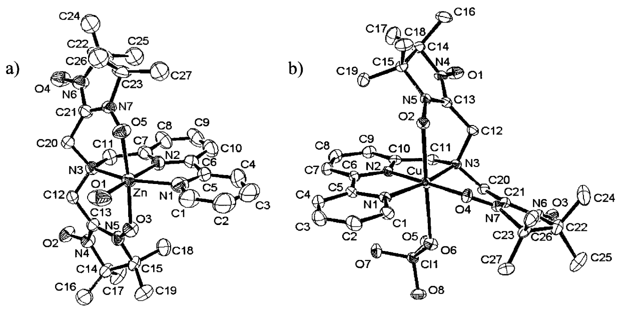

Fig. 1 (a) ORTEP view of Zn; (b) ORTEP view of Cu. Structures were drawn at the 30% probability level and hydrogen atoms have been omitted for clarity.

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† Electronic supplementary information (ESI) available: magnetic data. See http://www.rsc.org/suppdata/cc/b2/b204899j/

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membered rings. Further evidence is provided by EPR and susceptibility measurements and excludes any electron transfer processes during the complexation. The magnetic susceptibility (χ) *versus* temperature has been measured from 300 to 2 K for both complexes on microcrystalline materials. For Zn, the high temperature value is close to 0.8 emu K mol^{-1} and is in good agreement with two uncorrelated spins (χT = 0.75). It decreases by only 2% down to 30 K (Fig. 2a). A maximum is observed at 5 K in the susceptibility (χ *vs.* T) which fits very well to a Bleaney Bowers model for a dimer and a mean-field correction.[13] An antiferromagnetic intramolecular interaction of $J/k_B = -5.3$ K and a positive intermolecular interaction θ = 2.0 K were obtained. The first is reasonably explained by means of a superexchange mechanism through the diamagnetic zinc and it is likely that the weak ferromagnetic interaction is due to a favourable alignment of the nearest neighbour radicals. EPR measurements of dilute solutions confirm that only a weak antiferromagnetic interaction is operating at very low temperature.[14]

For the Cu, a very interesting magnetic behaviour is observed. Between 300 and 250 K, a constant χT value of 1.1 emu K mol^{-1} close to the expected value of three non-interacting S = 1/2 spins (χT = 1.12) was found. A gradual decrease of the χT value is observed down to a plateau of 0.63 emu K mol^{-1} at 40 K, followed by a further decrease below 20 K to a value of 0.55 emu K mol^{-1} at 3 K (Fig. 2b). The best fit was found using a triangle with three exchange interactions with an analytical expression previously described by Belorizky and coworkers.[15] Very strong couplings between the copper and the radicals are evidenced: J/k_B = +173 K and $J'/k_B = -170$ K, with a weaker radical–radical antiferromagnetic interaction of $J_{rad-rad}/k_B = -3$ K and a mean field interaction of $\theta = -0.4$ K (g_{Cu} = 2.21; g_{rad} = 2.01; g_{rad} = 2.04). The use of two different g values for the radicals is justified by the fact that they are not in the same environment and that one of these is involved in a short intermolecular interaction with the nearest neighbour (shortest distance at 3.70 Å) as deduced from the crystal packing. Uncertainties in the fitting parameters have been estimated to 10% in view of the variation of the J values by modifying the values of the g parameters.

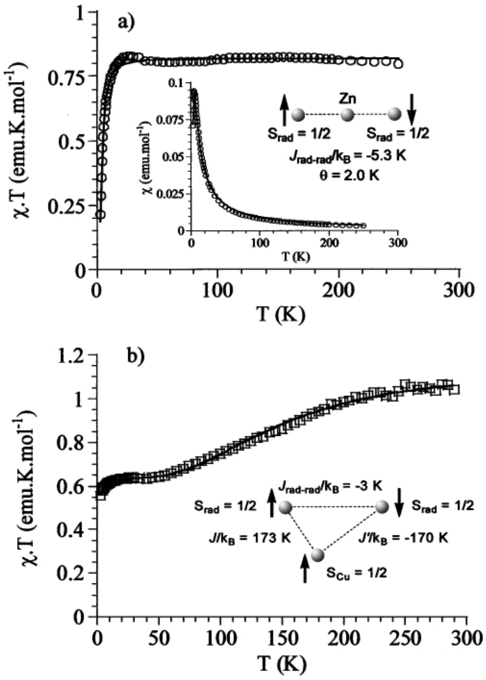

Fig. 2 (a) Temperature dependence of the product of the molar magnetic susceptibility with temperature (χT) for the Zn, $H = -2JS_{rad}S_{rad}$ (Inset: χ = f(T)) and (b) χT = f(T) for Cu, $H = -2JS_{Cu}S_{rad} - 2J'S_{Cu}S_{rad} - 2J_{rad-rad}S_{rad}S_{rad}$ (Inset shows the exchange interaction pattern and values of the calculated parameters). The solid line represents the best-fit.

In summary, we have developed an asymmetric pentadentate ligand using an aminomethyl-bipyridine skeleton which strongly binds divalent metals to form 1 : 1 (M : L) complexes. This model system is a case where the bipy fragment is strongly coordinated to the metal and the flexible arms accommodate almost perfectly in the first coordination sphere of the metal. The fact that the Cu(II) is Jahn–Teller distorted results in a *facial* conformation of the ON'O fragment *versus* the *meridional* arrangement found with Zn. This ensemble leads to large ferromagnetic and antiferromagnetic interactions, whereas the rad–rad interaction is antiferromagnetic due to the favourable orientation and spin polarization. The judicious balance provided during the ligand design between the rigidity of the chelating template and the flexibility of the spin-labelled arms favours a very good magnetic orbitals overlap which results in very high couplings.

Notes and references

‡ All products were characterized by EPR, MS, UV–vis, IR spectroscopies and elemental analysis and all data are consistent with the proposed structures. Note that perchlorate salts should be handled with care in low quantities as hydrated matter.

§ *Crystal data for* the Zn complex: $C_{27}H_{39}N_7O_5Zn{\cdot}2ClO_4{\cdot}CH_2Cl_2$, hexagonal, $P3_2$, a = 15.4545(3), b = 15.4545(3), c = 13.5594(3) Å, α = 90, β = 90, γ = 120°, V = 2804.7(2) Å^3, Z = 3, M = 890.86 g mol^{-1}, μ(Mo-Kα) = 1.028 mm^{-1}, D_c = 1.58 g cm^{-3} and GOF = 1.330, for 3174 observed reflections [$I > 3\sigma(I)$] and 438 variables. X-Ray diffraction data recorded using a KappaCCD diffractometer. The positions of the metal ions were found using the SHELX86 package.[16a] The remaining atoms were located in a succession of difference Fourier syntheses and were refined with anisotropic thermal parameters using the SHELX76 package[16b] to give R = 0.075, R_w = 0.096. Note that the disordered atoms and the solvent molecules were refined isotropically and no hydrogens were refined for the disordered atoms. CCDC reference number 186271.

Crystal data for the Cu complex: $C_{27}H_{37}N_7O_4Cu{\cdot}2ClO_4{\cdot}CH_3CN$, triclinic, $P1$, a = 11.8640(4), b = 13.2032(4), c = 13.2661(5) Å, α = 90.539(9), β = 104.983(9), γ = 113.252(9)°, V = 1829.7(5) Å^3, Z = 2, M = 827.13 g mol^{-1}, μ(Mo-Kα) = 0.811 mm^{-1}, D_c = 1.50 g cm^{-3}, and GOF = 1.556, for 5601 observed reflections [$I > 3\sigma(I)$] and 478 variables. R = 0.051, R_w = 0.078. CCDC reference number 186272. See http://www.rsc.org/suppdata/cc/b2/b204899j/ for crystallographic data in CIF or other electronic format.

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