Double helical assembly of imino nitroxyl diradicals by silver(I) ions

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The co-ordination of imino nitroxyl diradicals to diamagnetic silver(I) ions led to the self-assembled double helical dimer [Ag₂(bisimpy)₂][PF₆]₂ 1 (diradical bisimpy = 2,6-bis(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl 1-oxyl)-pyridine). The diradical has two imino nitroxyl groups linked by the pyridine group at its *meta* positions and acts as a tridentate ligand. In the double helicate two bisimpy bridge two silver(I) ions in a {4 + 2} connectivity, and the silver(I) ions have a very short contact of 2.8943(5) Å. Magnetic susceptibility measurements and crystal structure analysis revealed that the two radical moieties in bisimpy are ferromagnetically coupled ($J = 17.4(8)$ cm^{-1}; $H = -2J\Sigma S_i \cdot S_j$) through the pyridine group, and imino nitroxyl overlaps between adjacent molecules result in an intermolecular antiferromagnetic interaction ($-52.3(7)$ cm^{-1}).

Introduction

Supramolecular chemistry of co-ordination compounds is a subject of intense research interest,[1] of which self-assembled helicates have been one focus. Co-ordination sites of metal ions give helical formation of oligo-pyridyl strands and well organized molecular architectures like double[2]- and triple[3]-stranded metal helicates including inorganic grids[4] have been reported. On the other hand, compounds formed by metal co-ordination of organic radicals have large potential for expansion to cluster and infinite structures, and a variety of multi-radical ligands with multi-co-ordination ability has been designed toward assembled magnetic materials.[5] The number of radical helicates are, however, limited. In this paper, we report the structure and magnetic properties of a new double helicate of a silver(I)-imino nitroxide (bisimpy).

bisimpy
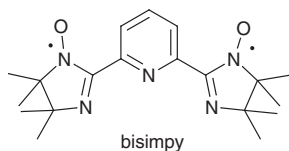
Experimental

Chemicals were obtained from standard sources and used as received. Magnetic susceptibility data were collected in the temperature range 2.0 to 300 K and in an applied 10 kG field with the use of a Quantum Design model MPMS SQUID magnetometer. Pascal's constants[6] were used to determine the constituent atom diamagnetism.

Preparation of [Ag₂(bisimpy)₂][PF₆]₂ 1

Ligand bisimpy (178 mg, 0.5 mmol), prepared by the reported method,[7] was added to a methanol solution (50 ml) of AgPF₆ (125 mg, 0.5 mmol). After standing overnight the resulting dark red microcrystals were filtered off. Recrystallization in methanol gave dark red tablets, one of which was subjected to X-ray structural analysis (Found: C, 36.96; H, 4.81; N, 11.06. C₁₉H₂₇AgF₆N₅OP requires C, 37.39; H, 4.46; N, 11.48%).

X-Ray crystallography

Crystal data for complex 1. C₃₈H₅₄Ag₂F₁₂N₁₀O₂P₂, $M = 1188.59$, monoclinic, space group $P2_1/n$, $a = 13.4333(7)$, $b = 20.8362(11)$, $c = 18.5916(10)$ Å, $\beta = 99.729(1)°$, $U = 5128.9(5)$ Å^3, $T = -70$ °C, $Z = 4$, μ(Mo-Kα) = 0.912 mm^{-1}, 27089 reflections measured, 11712 unique, R(int) = 0.0282, which were used in all calculations. The final R1 ($I > 3\sigma I$) was 0.0733 (0.0530), $wR2 = 0.1621$ (0.1471).

A single crystal was mounted on the tip of a glass fiber with epoxy resin. Diffraction data were collected on a Bruker SMART 1000 diffractometer fitted with a CCD-type area detector and a full sphere of data was collected by using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). At the end of data collection the first 50 frames of data were recollected to establish that crystal decay had not taken place during the data collection. The data frames were integrated using SAINT and merged to give a unique data set for the structure determination. Face-indexed (Gaussian) absorption correction was carried out and minimum and maximum transmissions were 0.7397 and 0.9419, respectively. The structures were solved by direct methods and refined by full-matrix least squares on all F^2 data using the SHELXTL 5.1 package (Bruker Analytical X-ray Systems). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. One of the PF₆$^-$ anions was found to be disordered around the F–P–F axis and a split-atom model with 1:1 occupancy was applied. The maximum residual electron-density peaks are close to the metal ion.

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See http://www.rsc.org/suppdata/dt/1999/2641/ for crystallographic files in .cif format.

Results and discussion

Structure

Complex [Ag₂(bisimpy)₂][PF₆]₂ 1 crystallizes in the monoclinic space group $P2_1/n$. Fig. 1 shows an ORTEP[8] diagram of the complex cation and Table 1 lists selected bond lengths and angles. In the complex molecule silver(I) ions and diradical ligands comprise the dimer [Ag₂(bisimpy)₂]²⁺ in which two of the diradicals are assembled as a double-stranded helicate twisted around the Ag(1)···Ag(2) axis. Complex 1 has a centrosymmetric space group, hence there are both plus and minus (clockwise and counterclockwise) helicates in the crystals.

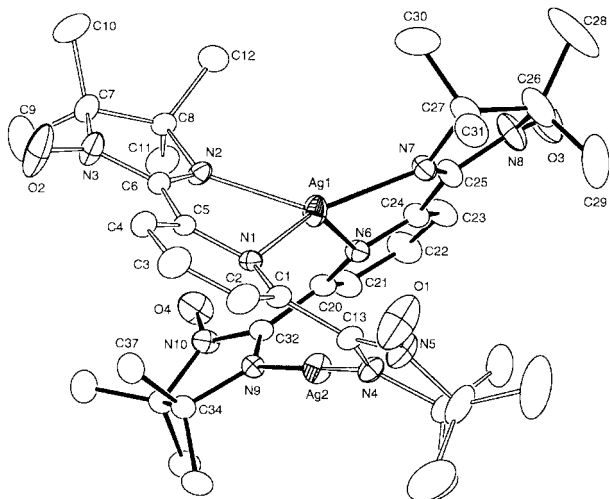The silver(I) ions in the {4 + 2} helical structure[9] have either

Fig. 1 An ORTEP diagram of complex **1**.

Fig. 2 Plot of $\chi_m T$ *vs.* T for complex **1**. Solid line corresponds to the theoretical curve, for which parameters are given in the text.

Table 1 Selected bond lengths (Å) and angles (°) for [Ag₂(bisimpy)₂]-[PF₆]₂

Ag(1)–N(7)	2.182(3)	Ag(1)–N(2)	2.206(3)
Ag(1)–N(1)	2.504(3)	Ag(1)–N(6)	2.587(3)
Ag(2)–N(9)	2.112(3)	Ag(2)–N(4)	2.112(3)
Ag(1)···Ag(2)	2.8943(5)	O(2)···O(3)*	3.239(8)
O(1)–N(5)	1.267(5)	O(2)–N(3)	1.265(5)
O(3)–N(8)	1.272(6)	O(4)–N(10)	1.262(5)
N(7)–Ag(1)–N(2)	139.25(13)	N(7)–Ag(1)–N(1)	133.77(12)
N(2)–Ag(1)–N(1)	71.63(10)	N(7)–Ag(1)–N(6)	70.42(11)
N(2)–Ag(1)–N(6)	111.82(11)	N(1)–Ag(1)–N(6)	140.59(9)
N(4)–Ag(2)–N(9)	173.09(13)		

Key to symmetry operation: $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

distorted tetrahedral or bent-bidentate co-ordination geometry, when the long interatomic contacts of the Ag(2) ions with pyridyl nitrogen atoms (Ag(2)···N(1) 3.135(3) and Ag(2)···N(6) 3.211(3) Å) are taken into account. Four co-ordination sites of the Ag(1) ion were occupied by the four nitrogen atoms from imino nitroxyl and pyridyl groups, where the Ag(1)–N (imino nitroxyl) bonds are much shorter (2.182(3) and 2.206(3) Å) than the Ag(1)–N (pyridine) bonds (2.504(3)–2.587(3) Å). Ion Ag(2) has two imino nitrogen atoms with co-ordination bond lengths of 2.112(3) and 2.112(3) Å and a bond angle N(4)–Ag(2)–N(9) 173.09°. Two silver(I) ions in the molecule have a very short contact of 2.8943(5) Å, which is slightly shorter than the metal–metal distances in open-shell metallic silver (2.899 Å) and in the helical complex [Ag₂L₂][PF₆]₂ (L = 2,2′:6′,2″-terpyridine) (Ag···Ag 2.914–2.940 Å).[10] In **1** the number of silver ions in the full turns of the helix is 8.6 and the helical pitch (length per turn) is very small (25 Å).

Magnetic properties

The temperature dependence of magnetic susceptibility for complex **1** was measured down to 2.0 K and a plot of $\chi_m T$ *vs.* temperature is depicted in Fig. 2. In **1** the two diradicals are assembled by the diamagnetic silver(I) ions, therefore the double helicate has four imino nitroxyl groups with $S = 1/2$. The $\chi_m T$ values showed a stepwise decrease as the temperature was lowered. The $\chi_m T$ value at 300 K is 1.50 K emu mol⁻¹, as expected for the isolated four spin system. The $\chi_m T$ values monotonously decreased down to 40 K and after a stationary region at 40–8 K showed a substantial decrease to 2.0 K.

There are two pathways responsible for intramolecular magnetic interactions: (i) through the silver(I) ions (reported to be very small);[11] (ii) through the pyridine group (two imino nitroxyl groups in bisimpy are linked by the pyridine ring in *meta* position, leading to ferromagnetic interaction between the
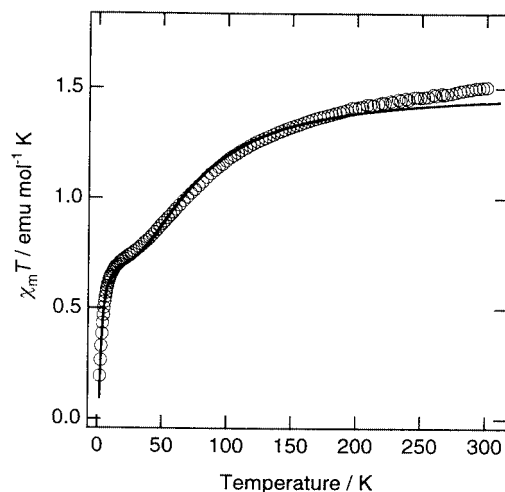
radicals by the spin-polarization mechanism[12]). When the substantially weak magnetic interaction through the silver(I) ion is taken into account, the magnetic system of **1** having four imino nitroxyls can be regarded as two magnetically isolated diradicals. However, the observed stationary temperature behavior of the $\chi_m T$ values cannot be explained in terms of a simple singlet–triplet model with one exchange parameter and this suggests an intermolecular magnetic interaction in the crystal. The structure analysis showed the imino nitroxyl oxygen atom O(2) has a close contact (3.239(8) Å) with the oxygen atom O(3)* in the adjacent molecule, which is related by the symmetry operation $(x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2})$ (Fig. 3), and the complex molecules form a one dimensional structure.

This close intermolecular contact of the imino nitroxyl groups leads to SOMO–SOMO (singly occupied molecular orbital) overlap, which results in an intermolecular antiferromagnetic interaction. In the radical chain the magnetic interactions between the radical centers are, however, broken at the silver(I) ions. Compound **1** can, therefore, be regarded as a tetraradical system composed of diradicals with an inter-ligand interaction and the magnetic data were analysed by a four spin model with two exchange coupling constants J_1 and J_2 representing intra- and inter-ligand magnetic interactions, respectively (Scheme 1). The exchange Hamiltonian has the form $H = -2J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - 2J_2(S_2 \cdot S_3)$.

The least squares calculation yielded the best fit parameters of $J_1 = +17.4(8)$ cm⁻¹ and $J_2 = -52.3(7)$ cm⁻¹, where the g value was fixed to 2.0 and the magnetic interactions through the silver(I) ions was included as a mean field approximation ($\theta = -0.3(1)$ K). The estimated intraligand ferromagnetic interaction J_1 (=+17.4(8) cm⁻¹) is in the range of reported ferromagnetic interactions in some alkylideneamine oxide and imino nitroxyl diradicals; *e.g.* 2,6- and 2,4-disubstituted phenylene and thiophene diradical derivatives showed ferromagnetic interactions of 1–57 cm⁻¹.[13] On the other hand, intermolecular imino nitroxyl–imino nitroxyl interactions give a variety of magnetic interactions and the sign and amplitude of the J values depend on stacking modes. 4,4,5,5-Tetramethyl-2-(5-pyrimidinyl)-4,5-dihydro-1*H*-imidazole 1-oxyl[14] has a substantial intermolecular antiferromagnetic interaction, $J = -54$ cm⁻¹ ($H = -2JS_iS_j$), where the close inter-imino nitroxyl contact (3.88 Å) is responsible for the antiferromagnetic interaction. It should be noted that the strength of the intermolecular magnetic interaction ($J_2 = -52.3(7)$ cm⁻¹) for **1** is the same as that for the imidazole radical in spite of the shorter inter-imino nitroxyl contact distance (3.239(8) Å) for **1**. The two imino nitroxyl groups in neighboring imidazole molecules have a parallel arrangement, while the adjacent radical moieties in **1** make a dihedral angle of 26.2(4) Å. The parallel arrange-
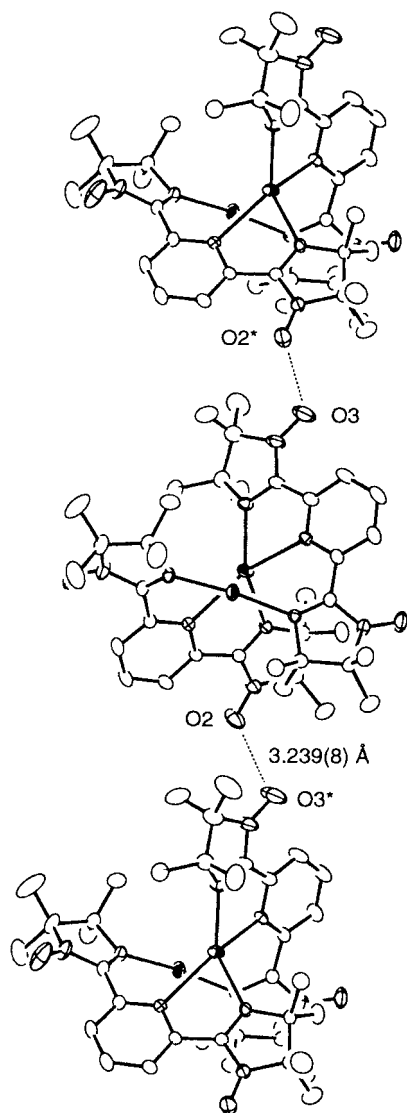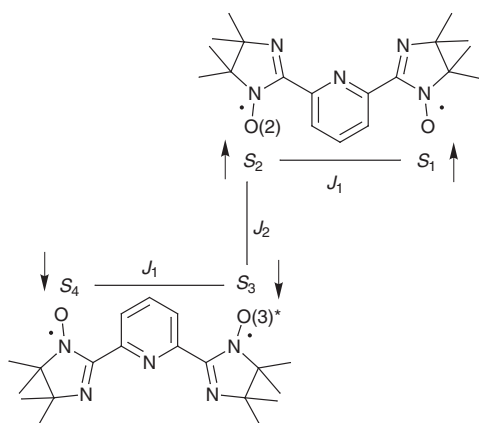
measurements showed that a spin polarization mechanism is operative for the two imino nitroxyls of bisimpy, while interradical overlap of adjacent molecules leads to antiferromagnetic interaction.

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Fig. 3 Chain structure of complex **1**.

Scheme 1

ment of the imino nitroxyl groups in imidazole prompts SOMO–SOMO overlap, which leads to a stronger antiferromagnetic interaction.

In summary, we have synthesized the double-stranded radical helicate of a silver aminyl oxide. Magnetic susceptibility

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