ChemComm
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1D silver(I) complex of nitronyl nitroxide with strong spin–spin interaction through silver(I) ion

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Received (in Cambridge, UK) 18th October 2001, Accepted 19th November 2001

First published as an Advance Article on the web 4th December 2001

A 1D silver(I) complex of nitronyl nitroxide was prepared and its structure was determined by X-ray diffraction analysis; magnetic studies indicate that the spin–spin interaction of nitronyl nitroxides through silver(I) ions along the chain are fairly strong ($J/k_\mathrm{b} = -84$ K).

Paramagnetic metal complexes of nitronyl nitroxides and imino nitroxides have been extensively studied,[1] and large spin clusters, magnetic chains and even bulk ferromagnetism have resulted from these studies. Meanwhile, the research on diamagnetic metal complexes of imino nitroxides and semiquinones has also attracted great attention, since this is an interesting reversal on the more usual situation where paramagnetic metal ions show superexchange through a bridging ligand. For example, metal complexes with semiquinones[2] show a variety of magnetic interactions depending on the metal ion and coordination geometry, and the magnitude of the magnetic interactions through diamagnetic ions depend strongly on the energy of d_π orbitals. Cu(I) complexes of imino nitroxides show fairly strong ferromagnetic interactions between imino nitroxides through the diamagnetic Cu^+ ion,[3] while Pd(II) complexes of imino nitroxides exhibit a substantial antiferromagnetic interaction through the Pd^{2+} ion.[4] However, for discrete silver(I) complexes of imino nitroxides, the corresponding spin–spin interactions of imino nitroxides mediated by silver(I) ions have been found to be very small and even negligible in some cases.[5] Up to now, to the best of our knowledge, no silver(I) complexes of nitronyl nitroxides have been described. Here, we report the synthesis, structure and magnetic property of a novel one-dimensional silver(I) complex (complex **1**) of nitronyl nitroxide derived from *m*-*N*-methylpyridinium nitronyl nitroxide iodide (Scheme 1) and silver nitrate. A fairly strong antiferromagnetic interaction between nitronyl nitroxides was observed for complex **1**.

Complex **1** was prepared starting from *m*-*N*-methylpyridinium nitronyl nitroxide iodide[6] and silver nitrate. After removal of the yellow precipitate, the solution was slowly evaporated to yield black crystals of complex **1**.† Its structure was established by X-ray diffraction analysis.‡

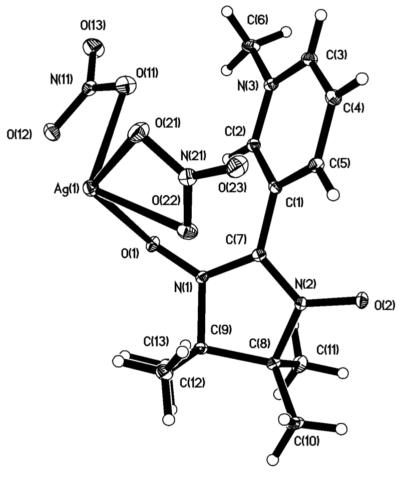
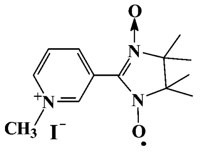


Fig. 1 The asymmetric unit of complex **1** together with selected bond lengths (Å) and angles (°): N(1)–O(1) 1.281(3), N(1)–C(7) 1.342(3), N(2)–O(2) 1.284(3), N(2)–C(7) 1.339(3), Ag(1)–O(1) 2.4452(19), Ag(1)–O(2)$^{\mathrm{i}}$ 2.3706(19), Ag(1)–O(11) 2.459(2), Ag(1)–O(21) 2.480(2), Ag(1)–O(22) 2.540(2); N(2)–C(7)–N(1) 109.6(2), N(1)–O(1)–Ag(1) 120.74(14), N(2)–O(2)–Ag(1)$^{\mathrm{i}}$ 123.51(15), O(1)–Ag(1)–O(11) 89.58(7), O(1)–Ag(1)–O(21) 125.91(7), O(11)–Ag(1)–O(21) 81.82(8), O(11)–Ag(1)–O(22) 108.19(7), O(21)–Ag(1)–O(22) 51.23(7) [symmetrical operation:$^{\mathrm{i}}$ x, $y - 1$, z].

Fig. 1 shows the asymmetric unit of complex **1** together with selected bond lengths and angles. There are two nitrate ions, one silver(I) ion and one *m*-*N*-methylpyridinium nitronyl nitroxide group (MPYNN), and thus the asymmetric unit is neutral as a whole. For the MPYNN unit, the bond lengths of N(1)–O(1) and C(7)–N(1) are almost identical to those of N(2)–O(2) and C(7)–N(2), respectively (see the caption of Fig. 1); the pyridinium and imidazoline rings are not coplanar, and they form a dihedral angle of 43.3°. Five oxygen atoms O(11), O(21), O(22), O(1) and O(2)$^{\mathrm{i}}$ (not shown in Fig. 1) are coordinated to silver(I). The bond lengths of Ag(1)–O(1) and Ag(1)–O(2)$^{\mathrm{i}}$, which are formed between the silver(I) ion and nitronyl nitroxide units, are comparable to those of bonds linking silver(I) and nitrate ions [Ag(1)–O(11), Ag(1)–O(21) and Ag(1)–O(22)].

Atoms O2 and Ag1 shown in Fig. 1 are further linked to another silver(I) ion and MPYNN unit, respectively, and the structure is extended in this manner to generate a one dimensional chain as clearly indicated in Fig. 2. Interestingly, despite the steric hindrance the *m*-*N*-methylpyridinium ring and the nitrate ions are arranged on one side of the chain, which is



Scheme 1 Chemical structure of *m*-*N*-methylpyridinium nitronyl nitroxide iodide.

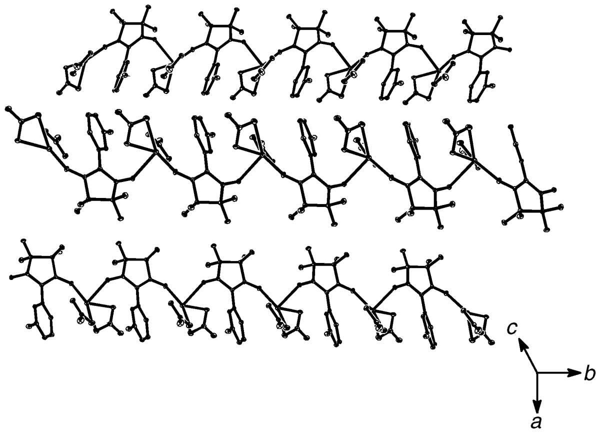


Fig. 2 The 1D structure and inter-chain arrangement of complex **1**.

DOI: 10.1039/b109354a

very likely due to electrostatic attraction interactions among the *m-N*-methylpyridinium and the nitrate ions. The inter-chain arrangement of complex **1** is also shown in Fig. 2. Besides the short contacts among the hydrogen atoms of *m-N*-methylpyridinium ring and oxygen atoms of nitrate ions, no short interatomic distances are found among the neighboring chains. According to previous studies,[7] for nitronyl nitroxide derivatives most of the spin density is distributed onto the atoms of the imidazoline ring, and the spin densities carried by other atoms, in particular hydrogen atom attached to *m-N*-methylpyridinium ring, are negligible. Thus, each of the one-dimensional chains in the crystal lattice of complex **1** can be treated independently from the magnetic point of view. Preliminary theoretical investigations were performed for a "dimer" of the asymmetrical unit.[8] The calculation results show that the electron densities ρ_b for the bonds of silver(I) ions and oxygen atoms of nitronyl nitroxide units are only about 0.004, indicating that these bonds are not typical covalent ones but electrovalent bonds. The electron density distribution around the silver(I) ions are spherical, from which it can be inferred that only the s orbitals of silver(I) ions are involved in the formation of the bonds of silver(I) ions with oxygen atoms of MPYNN units and nitrate ions.

Fig. 3 shows a plot of the χT *vs.* T for complex **1**, where χ is the molar magnetic susceptibility in terms of the asymmetric unit formula $C_{13}H_{19}AgN_5O_8$. The room temperature value of χT is 0.330 emu K mol^{-1}, smaller than 0.375 emu K mol^{-1}, the theoretically expected value for a one spin ($S = 1/2$) system. By lowering temperature, χT is reduced gradually from 300 to 100 K, and then it decreases more sharply reaching 0.014 emu K mol^{-1} at 5 K. Such temperature dependent behavior of χT indicates the presence of antiferromagnetic spin–spin interaction in complex **1**.

As discussed above, the spin–spin interaction among the one-dimensional chains (inter-chain interaction) in the crystal lattice of complex **1** should be rather weak. Therefore, the experimental magnetic data was fitted to a one dimensional antiferromagnetic model with eqn. (1):[9]

$$\chi = (Ng^2\beta^2/k_bT)(0.25 + 0.074975x + 0.075235x^2)/(1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3),\ x = |J|/k_bT \quad (1)$$

where J ($H = -J\Sigma S_1S_2$) is the spin–spin exchange constant and the other parameters have the conventional meanings. The best fit (see Fig. 3) gives $|J|/k_b = 84$ K, and J/k_b should be -84 K because of the antiferromagnetic interaction (The g factor was fixed to 2.0). Thus, the spin–spin interaction of the neighboring nitronyl nitroxides bridged by silver(I) ions in complex **1** is fairly strong albeit antiferromagnetic. By contrast, the spin–spin interactions of imino nitroxides through the silver(I) ion in the corresponding discrete silver(I) complexes were reported to be very weak.[5] Since the separation of nitronyl nitroxide units is rather large both along the one dimensional chain and among the neighboring chains, the spin–spin interaction of nitronyl nitroxides through space can be excluded. Therefore, the strong antiferromagnetic interaction exhibited by complex **1** is undoubtedly due to the bonds formed between the silver(I) ions and oxygen atoms of nitronyl nitroxide units. On the basis of the theoretical calculation as mentioned above, only the s orbitals of silver(I) ions contribute to the formation these silver(I)–oxygen bonds. Thus, it is probable that the indirect overlap of the SOMOs (spin occupied molecular orbital) through s orbitals of silver(I) ions leads to this strong antiferromagnetic interaction of nitronyl nitroxides. It should be mentioned that these silver(I)–oxygen bonds (formed between the silver ions and oxygen atoms of nitronyl nitroxides) display mainly ionic character. This is the first time it is shown that such non-typical covalent bonds with major ionic character can be used to mediate the spin–spin interaction of nitronyl nitroxides.

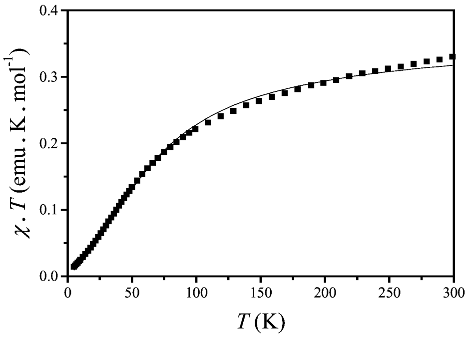


Fig. 3 Plot of χT product *vs.* T for complex **1**; the solid line represents the best theoretical fit (see text).

In summary, a novel silver(I) complex of nitronyl nitroxide with an extended 1D structure has been prepared and characterized. The spin–spin interaction of nitronyl nitroxides through the silver(I) ions along the chain is fairly strong with an exchange constant $J/k_b = -84$ K.

The present research work was supported by Chinese Academy of Sciences, NSFC (29972044, 90101025) and the Major State Basic Research Development Program (G2000077500). The authors also thank Prof. Xianglin Jin of Peking University for his kind help on crystal structural analysis.

Notes and references

† Yield, 40.9%; mp, 175–176 °C (decomp.); IR (KBr), 1384 (s), 1290 (w), 1215 (w), 1170 (w), 1137 (w) cm^{-1}; Anal. Calc. for $C_{13}H_{19}AgN_5O_8$: C, 32.50; H, 3.99; N, 14.59. Found: C, 32.25; H, 3.95; N, 14.60%.

‡ *Crystal data*: $C_{13}H_{19}AgN_5O_8$, $M = 481.20$, monoclinic, $C2/c$, $a = 28.278(6)$, $b = 7.0410(14)$, $c = 18.894(4)$ Å, $\beta = 112.55(3)°$, $V = 3474.3(12)$ Å^3, $Z = 8$, $D_c = 1.840$ g cm^{-3}; $F(000) = 1944$, μ(Mo-Kα) = 1.216 mm^{-1}. 16047 reflections of which 3956 are unique ($R_{\text{int}} = 0.0204$) were collected to a θ limit of 27.48° on a Rigaku RAXIS RAPID IP instrument at 293(2) K. The structure was solved by direct methods and refined by a least-squares matrix method. The final cycle of full-matrix least-square refinement was based on 3400 observed reflections [$I > 2\sigma(I)$] and 244 variable parameters and converged to $R_1 = 0.0292$, w$R_2 = 0.0775$. CCDC reference number 172993. See http://www.rsc.org/suppdata/cc/b1/b109354a/ for crystallographic data in CIF or other electronic format.

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