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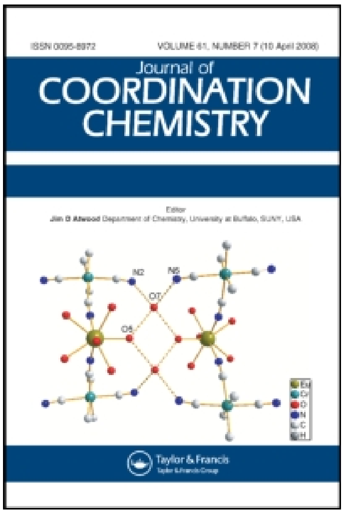

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Synthesis, crystal structure and ferromagnetic interactions of a silver(I) complex with imizadolyl-substituted nitroxide radicals

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Synthesis, crystal structure and ferromagnetic interactions of a silver(I) complex with imizadolyl-substituted nitroxide radicals

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A silver(I) complex with nitronyl nitroxide, $[Ag_2(NIT\text{-}R)_4(NO_3)_2]\cdot CH_3OH$ [NIT-R = 2-(5-methylimidazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxide], has been prepared and characterized by magnetic and single-crystal X-ray diffraction studies. In the complex, the silver(I) ion is coordinated with two monodentate nitronyl nitroxide radicals by the nitrogen of the imizadole ring. The silver(I) ion is two-coordinate and forms a dimer through $Ag\cdots Ag$ weak metal bonding interactions. The magnetic properties for the title complex have been investigated in the temperature range $2\sim 300\,K$ showing ferromagnetic interactions between the coordinated nitronyl nitroxides ($J = 3.64\,cm^{-1}$) and intermolecular antiferromagnetic interactions.

Keywords: Silver(I) complex; Crystal structure; Nitronyl nitroxide; Ferromagnetic interactions

1. Introduction

Engineering of molecular magnets constitutes a major research goal and has spawned interest in organic radicals as building blocks for construction of new materials [1, 2]. Nitronyl nitroxide radicals, stable organic radicals, have been widely employed as molecular units in the design and synthesis of molecular magnetic materials. There have been many magnetic studies on transition metal complexes with nitronyl nitroxide and imino nitroxide radicals [3–10] and paramagnetic metal complexes of nitronyl nitroxide radicals have been extensively studied [11–18]. However, reports of diamagnetic metal ions with radicals are much fewer. Some complexes such as Cu(I) and Ag(I) have shown that ferro or antiferromagnetic interactions between the radicals were operative through the diamagnetic metal ions. Combinations of organic radicals and diamagnetic Cu(I) and Ag(I) ions gives a variety of molecular based assemblies, with interesting structures and magnetic properties [19–22]. Few reports of two-coordinate silver complexes with nitroxide nitronyl radicals have been described. We report the synthesis, structure, and magnetic properties of a new silver(I) complex, $[Ag_2(NIT\text{-}R)_4(NO_3)_2]\cdot CH_3OH$ with

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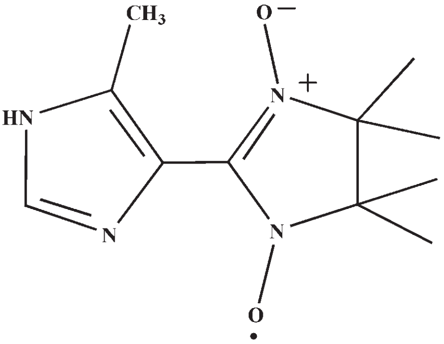

Scheme 1. $[Ag_2(NIT\text{-}R)_4(NO_3)_2] \cdot CH_3OH$ with nitronyl nitroxide radicals.

nitronyl nitroxide radicals (scheme 1). In addition, we observe intramolecular ferromagnetic interactions between nitronyl nitroxide radicals, while the intermolecular magnetic interaction is weakly antiferromagnetic.

2. Experimental

2.1. *General*

The infrared spectra ($4000 \sim 600\,cm^{-1}$, KBr pellet) were recorded on an Avatar^{TM} 360 E.S.P. IR spectrometer. Elemental analysis for carbon, hydrogen and nitrogen was performed on a Vario EL III elemental analyzer. The variable temperature susceptibility measurements were carried out on a MPMS XL-7 magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms, and the magnetic moments were calculated based on the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

2.2. *Preparation of NIT-Rc*

NIT-R [NIT-R = 2-(5-methylimidazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxide] was prepared according to the literature method [23, 24].

2.3. *Preparation of the* $[Ag_2(NIT\text{-}R)_4(NO_3)_2] \cdot CH_3OH$

The complex $[Ag_2(NIT\text{-}R)_4(NO_3)_2] \cdot CH_3OH$ was synthesized by adding $AgNO_3$ (0.041 g, 0.125 mmol) to a 20 mL methanol solution of NIT-R (0.061 g, 0.25 mmol). The mixture was stirred for 14 h and then filtered, and the clear dark blue filtrate was diffused with diethyl ether vapor at room temperature in the dark for three weeks. Black crystals suitable for X-ray determination were obtained in a yield of 46%. Anal. Calcd for $C_{45}H_{72}Ag_2N_{18}O_{15}$. C 40.92, H 5.49, N 19.09; found C 40.76, H 5.37, N 19.27. The IR spectra of the complex show the N–O stretching vibration of the nitroxide radical at $1384\,cm^{-1}$.

Table 1. Crystallographic data for $[Ag_2(NIT\text{-}R)_4(NO_3)_2] \cdot CH_3OH$.

Empirical formula	$C_{45}H_{72}Ag_2N_{18}O_{15}$
Formula weight	1320.95
Temperature (K)	295(2)
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	12.8181(14)
b	26.786(3)
c	17.475(2)
β	107.185(2)
Volume ($Å^3$)	5732.1(11)
Z	4
Density (Calcd) ($g\,cm^{-3}$)	1.531
Absorption coefficient (mm^{-1})	0.762
$F(000)$	2728
θ Range for data collection (°)	2.25 to 27.50
Limiting indices	$-16 \le k \le 16$, $-34 \le h \le 33$, $-22 \le l \le 22$
Reflections collected	49,796
Independent reflections	13116 [$R_{int} = 0.0534$]
Observed reflections [$I > 2\sigma$ (I)]	7616
Data/restraints/parameters	3295/0/243
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0419$, $wR_2 = 0.0824$
R indices [all data]	$R_1 = 0.0945$, $wR_2 = 0.1028$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.474 and −0.489

2.4. *X-ray structure determination*

A single crystal with approximate dimensions of $0.18 \times 0.13 \times 0.06\,mm^{-3}$ was selected for data collection on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using the ω–2θ scan technique at room temperature. A total of 49796 reflections ($R_{int} = 0.0534$) were collected, of which 13116 were independent in the ω–2θ range of $2.25 \sim 27.50°$, and 7616 observed reflections with $I > 2\sigma(I)$ were employed for structure refinements for the complex.

The structure was solved by direct methods with SHELXS-97. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. The atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares using SHELXL-97. The final agreement factor values are $R = 0.0419$ and $wR = 0.0824$ ($w = 1/[\sigma^2(F_o)^2 + (0.0384P)^2]$, where $P = (F_o^2 + 2F_c^2)/3)$, $S = 0.998$ and $(\Delta/\sigma)_{max} = 0.002$. The residual peaks on the final difference Fourier map are 0.474 and $-0.489\,e\,Å^{-3}$ for the complex. Crystallographic data of the complex are listed in table 1 and selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure of the complex [$Ag_2(NIT\text{-}R)_4(NO_3)_2$] • CH_3OH*

An ORTEP drawing of the title complex is shown in figure 1. In the complex, the two silver ions with the four radicals have a peculiar coordination mode. Due to the distance

Table 2. Selected bond lengths (Å) and angles (°) for $[\mathrm{Ag_2(NIT\text{-}R)_4(NO_3)_2}]\cdot\mathrm{CH_3OH}$.

Bond length			
Ag(1)–N(5)	2.143(3)	O(7)–N(15)	1.283(3)
Ag(1)–N(1)	2.163(3)	O(8)–N(16)	1.277(4)
Ag(1)–Ag(2)	3.2342(5)	O(9)–C(45)	1.300(5)
Ag(2)–N(9)	2.148(3)	O(9)–H(9)	0.8200
Ag(2)–N(13)	2.159(3)	O(10)–N(17)	1.231(4)
O(1)–N(3)	1.288(4)	O(11)–N(17)	1.222(4)
O(2)–N(4)	1.275(4)	O(12)–N(17)	1.227(4)
O(3)–N(7)	1.280(3)	O(13)–N(18)	1.218(4)
O(4)–N(8)	1.268(3)	O(14)–N(18)	1.237(4)
O(5)–N(11)	1.278(4)	O(15)–N(18)	1.208(4)
O(6)–N(12)	1.280(3)	N(1)–C(1)	1.318(4)
Bond angles			
N(5)–Ag(1)–N(1)	155.09(10)	C(13)–N(5)–Ag(1)	125.5(2)
N(5)–Ag(1)–Ag(2)	135.08(7)	C(11)–N(5)–Ag(1)	129.5(2)
N(1)–Ag(1)–Ag(2)	69.81(7)	C(1)–N(1)–Ag(1)	126.6(2)
N(9)–Ag(2)–N(13)	164.44(11)	C(3)–N(1)–Ag(1)	126.0(2)
N(9)–Ag(2)–Ag(1)	129.26(8)	C(1)–N(1)–C(3)	105.5(3)
N(13)–Ag(2)–Ag(1)	66.26(7)	C(45)–O(9)–H(9)	109.5

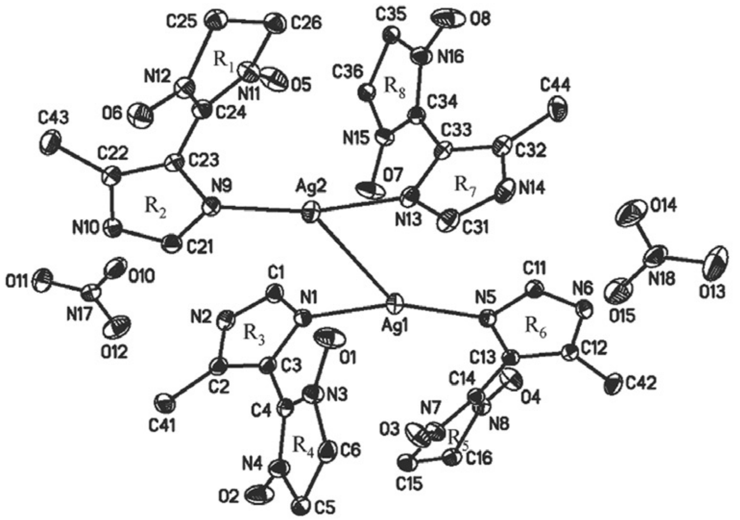

Figure 1. The structure of the title complex.

of silver ions and oxygen atoms of N–O group in the range 2.922–5.260 Å, there are no Ag–O bonds, so the silver ion is two-coordinate with two radicals coordinated through nitrogen atoms of imidazole rings of NIT-R with Ag1–N distances of 2.163(3), 2.143(3) Å and Ag2–N distances of 2.148(3), 2.159(3), where coordination around silver is approximately linear, ∠N1–Ag1–N5 = 155.09(10)°, ∠N9–Ag2–N13 = 164.44(11)°. The Ag–Ag distance in the crystal structure is 3.234 Å shorter than the sum of van der Waals' radii (3.4 Å) of silver [25], suggesting weak Ag···Ag bonding interactions, linking into a dimer. The nitroxide fragments and the imidazole rings are not coplanar and their dihedral angles are in the range 40.6 ~ 44.5°. The four nitroxide nitronyl radicals surround the two silver ions compactly, and the dihedral angles of five-membered rings are 5.1° (between C1–N1–C3–C2–N2

Table 3. The dihedral angles of two corresponding five-membered rings for the complex (°).

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
R_1	–	41.9	116.5	119.8	2.2	43.6	113.3	116.1
R_2	41.9	–	84.2	77.9	40.5	4.1	83.4	74.1
R_3	116.5	84.2	–	40.6	116.5	85.4	5.1	39.9
R_4	119.8	77.9	40.6	–	118.2	76.3	45.3	3.9
R_5	59.7	20.1	116.5	118.2	–	41.9	113.5	114.5
R_6	43.6	4.1	85.4	76.3	41.9	–	85.0	72.6
R_7	113.3	83.4	5.1	45.3	113.5	85.0	–	45.5
R_8	116.1	74.1	39.9	3.9	114.5	72.6	45.5	–

and N13–C31–N13–C32–C33), 3.9° (between N3–C4–N4–C5–C6 and N15–C34–N16–C35–C36), 4.1° (between N5–C11–N6–C12–C13 and N9–C21–N10–C22–C23) and 2.2° (N7–C14–N8–C16–C15 and N11–C24–N12–C25–C26), respectively, almost co-planar. All the five-membered rings dihedral angles are listed in table 3. The dihedral angles of nitroxide fragments are 121.8° (between O6–N12–C24–N11–O5 and O7–N15–C34–N16–O8 for Ag2) and 124.6° (between O2–N4–C4–N3–O15 and O3–N7–C14–N8–O4 for Ag1).

There are two kinds of significant intermolecular hydrogen-bond interactions in the crystal structure. One occurs between one oxygen atom from uncoordinated NO_3^- and two nitrogen atoms of the neighboring imizadolyl-substituted radicals, while the other is the uncoordinated NO_3^- connecting two radicals with two oxygen atoms. The hydrogen bonding parameters are $O10A \cdots N2BA = 2.886$ Å, $O10A \cdots N6AA = 2.770$ Å, $O14A \cdots N14A = 2.842$ Å, $O15A \cdots N10B = 2.821$ Å, respectively. The dimer $[Ag_2(NIT\text{-}R)_4(NO_3)_2]$ was connected into a 1-D chain by intermolecular interactions ($N–H \cdots O$) (figure 2). The nearest intramolecular distances $O \cdots O$ of neighboring N–O groups within the molecules are 3.816 Å ($N7–O3 \cdots O1–N3$), 4.056 Å ($N11–O5 \cdots O8–N16$), while the shortest intermolecular $O \cdots O$ contact between N–O groups in the 1-D chain and in the dimer are 5.743 Å and 5.735 Å, respectively.

3.2. *Magnetic properties*

The magnetic susceptibility of the title complex was measured in the range 2–300 K at a magnetic field of 10,000 G. The variation of $\chi_M T$ and χ_M *versus* T are plotted in figure 3. The $\chi_M T$ value at room temperature is $0.75\,cm^3\,K\,mol^{-1}$, which is exactly equal to that expected for two $S_{rad} = 1/2$ uncoupled spin systems ($0.75\,cm^3\,K\,mol^{-1}$). By lowering the temperature, $\chi_M T$ increases approaching $0.85\,cm^3\,K\,mol^{-1}$ at 5 K. Thus, it is concluded that the magnetic behavior of the complex indicates an intramolecular ferromagnetic interaction between the nitronyl nitroxide ligands.

In order to understand quantitatively the magnitude of magnetic interaction, the magnetic susceptibility data were analyzed by using a Bleaney–Bowers equation ($H = -2JS_1S_2$), where J is the interaction parameter between two paramagnetic centers:

$$\chi_t = \frac{2Ng^2\beta^2}{KT}[3 + \exp(-2J/KT)]^{-1} \tag{1}$$

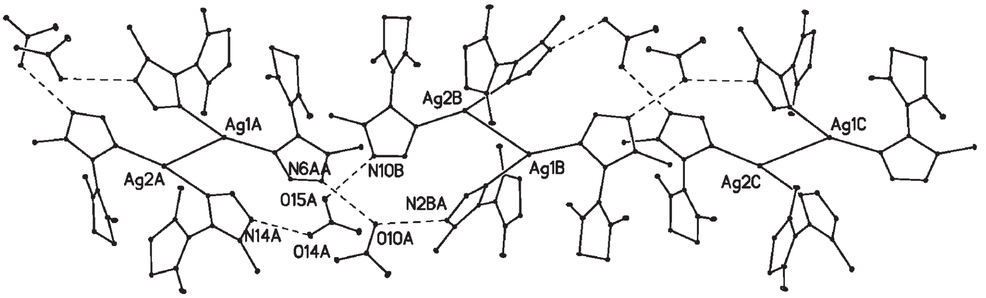

Figure 2. A sketch of the intermolecular interaction of the title complex (the methyl groups and hydrogen atoms are omitted for clarity).

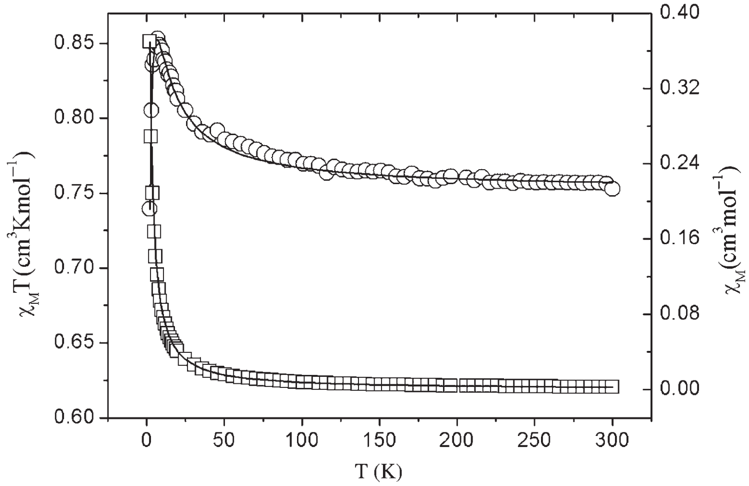

Figure 3. The plots of $\chi_M T$(○) and χ_M ( ) *vs.* T for the title complex. The solid line represents the best fit.

An additional coupling parameter, zJ', was introduced in equation (2) to take into account the magnetic interaction between $[Ag_2(NIT\text{-}R)_4(NO_3)_2]$ units in the 1-D chain and between the dimers, a weak intermolecular interaction based on the molecular field approximation. The total magnetic susceptibility is

$$\chi_M = \frac{\chi_t}{1-(2zJ'/N\beta^2 g^2)\chi_t} \tag{2}$$

The best-fit parameters were $J = 3.64\,\mathrm{cm^{-1}}$, $zJ' = -0.36\,\mathrm{cm^{-1}}$, $g = 2.00$, with $R = 1.00\times10^{-5}$, where R is defined as $R=\sum[(\chi_M)_{\mathrm{obs}}-(\chi_M)_{\mathrm{Calcd}}]^{2}/\sum(\chi_M)^2_{\mathrm{obs}}$. The solid lines in figure 3 show that the data in the 2–300 K range are accommodated by equations (1) and (2). These results indicate intramolecular ferromagnetic interactions between nitronyl nitroxide radicals resulting from the shortest intramolecular (N–O···N–O, 3.816 and 4.056 Å) contacts between molecules in the crystal as evidenced by the X-ray analysis. Between $[Ag_2(NIT\text{-}R)_4(NO_3)_2]$ units in the 1-D chain, the magnetic interaction is weakly antiferromagnetic.

According to previous studies, there are few complexes with such short intramolecular contacts between uncoordinated N–O groups. Such short N–O···O–N contact distance of about 4 Å allows intramolecular exchange interactions between the magnetic orbitals of the radicals, and the orthogonality of nitroxide radical magnetic orbitals leads to ferromagnetic interactions in the crystal [26–28]. In this article we showed that a near-linear arrangement of silver ions with two nitroxide radicals, precluding N–O coordination to Ag(I), results in ferromagnetic interactions between nitroxide radicals. According to the X-ray structure, the shortest intermolecular contact between the uncoordinated N–O groups in the 1-D chain and between the dimer is near 6 Å, so the intramolecular magnetic interactions play a dominant role.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 287256 for structure of the complex. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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