Inorg. Chem. **1999,** *38,* 2750−2752

Radical Double Helicates of Silver Imino Nitroxides, $[Ag_2(pyrd\text{-}im2)_2](PF_6)_2 \cdot 2CH_3OH$ and $[Ag_2(bpy\text{-}im2)_2](PF_6)_2 \cdot CH_3OH$

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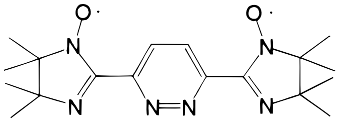
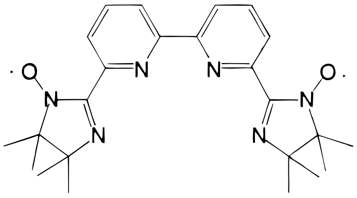
Received November 24, 1998

Introduction

Supramolecular chemistry of coordination compounds is the subject of intense research interest.[1] It has been known for several years that self-assembly of oligopyridyl strands with Ag^I and Cu^I ions gave well-organized molecular architectures such as an inorganic grid[2] and double-[3] and triple-stranded[4] metal helicates. A general feature of such diamagnetic metal ions as components of the self-assembled system is that the tetrahedral coordination algorithm can give helicate formation of the oligopyridyl strands. If the organic radicals are introduced into such oligopyridyl strands, the radicals are self-assembled to form radical supramolecules. Diradicals pyrd-im2 (3,6-bis(1′-oxyl-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-2′-yl)-pyridazine) and bpy-im2 (2,2′-bis(1′-oxyl-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-2′-yl)bipyridine)) used in this work have disparate coordination sites in close proximity and two imino nitroxides are linked by pyridazine and bipyridine moieties. Here we report double-stranded radical helicates with four imino nitroxides assembled by silver(I) ions.



pyrd-im2



bpy-im2

Experimental Section

General. Chemicals were obtained from standard sources and were used as received. Magnetic susceptibility data were collected in the temperature range of 2.0−300 K and in an applied 10 000 G field with the use of a Quantum Design model MPMS SQUID magnetometer. Pascal's constants[5] were used to determine the constituent atom diamagnetism.

Table 1. Crystallographic Data

	1	2
empirical formula	$C_{38}H_{60}Ag_2F_{12}N_{12}O_6P_2$	$C_{49}H_{64}Ag_2F_{12}N_{12}O_5P_2$
fw	1286.84	1406.80
T (°C)	−80	−80
space group	*Cc* (No. 9)	*Pbca* (No. 61)
a (Å)	13.688(5)	26.844(5)
b (Å)	32.668(8)	29.650(5)
c (Å)	13.718(4)	14.509(5)
β (deg)	119.95(2)	
V (Å^3)	5315(3)	11548(5)
Z	4	8
λ (Å)	0.710 73	0.710 73
ρ_{calc} (g/cm^3)	1.648	1.618
μ(Mo Kα) (cm^{-1})	8.96	8.28
R1[a]	0.0428	0.0620
wR2[b]	0.1088	0.1474

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$; for **1**, $w = 1/[\sigma 2(F_o^2) + (0.0679P)^2 + 7.1421P]$ and for **2**, $w = 1/[\sigma^2(F_o^2) + (0.0891P)^2 + 10.3209P]$, where $P = (F_o^2 + 2F_c^2)/3$.

3,6-Bis(*N,N′*-dihydroxy-4′,4′,5′,5′-tetramethylimidazolidyl)-pyridazine. A solution of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (1.3 g, 9.0 mmol) and 3,6-diformylpyridazine (0.51 g, 3.0 mmol), which was prepared by ozonolysis of distyrylpyridazine,[6] in 150 mL of *i*-propyl alcohol was stirred at room temperature for 3 days. The resulting precipitate was filtered and washed with methanol.

3,6-Bis(1′-oxyl-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-2′-yl)pyridazine (pyrd-im2). 3,6-Bis(*N,N′*-dihydroxy-4′,4′,5′,5′-tetramethylimidazolidyl)pyridazine was oxidized to the biradical of pyd-im2 by using the same procedure as described for 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl by Ullman.[7]

2,2′-Bis(1′-oxyl-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-2′-yl)bipyridine (bpy-im2). This compound was synthesized by the reported method.[8]

$[Ag_2(pyrd\text{-}im2)_2](PF_6)_2 \cdot 2CH_3OH$ (1) and $[Ag_2(bpy\text{-}im2)_2](PF_6)_2 \cdot CH_3OH$ (2). Ligands pyrd-im2 (180 mg, 0.5 mmol) and bpy-im2 (217 mg, 0.5 mmol) were, respectively, added to the methanol solution (50 mL) of $AgPF_6$ (126 mg, 0.5 mmol). After standing overnight, the resulting dark red microcrystallines were filtered off. Recrystallization in methanol gave dark red tablets, one of which was subjected to the X-ray structural analysis. Elem. Anal. Found (calcd) for **1**: C, 35.92 (35.37); H, 4.37 (4.29); N, 13.72 (13.75). Found (calcd) for **2**: C, 42.14 (41.94); H, 4.48 (4.40); N, 12.17 (12.23).

X-ray Crystallography. Single crystals of **1** and **2** were mounted on the tips of glass fiber with epoxy resin. Diffraction data were collected at −80 °C on a Rigaku 7S four-circle diffractometer equipped with liquid nitrogen cryostream cooler (Oxford Cryosystream). Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used. Crystallographic data for the compounds are listed in Table 1. Cell constants were obtained from a least-squares fit of the setting angles of 20 carefully centered reflections in the range $25 < 2\theta < 30°$. The data using the $\omega-2\theta$ scan technique, were corrected for Lorentz and polarization effects. Empirical absorption corrections (ψ scans) were carried out and relative transmissions for **1** and **2** were 0.961−1.000 and 0.840−0.928, respectively. The structures were solved by direct method with SHELX-86 (G. M. Sheldrick, University of Göttingen, 1986) and Fourier techniques, and refined by full-matrix least squares on F^2 data by using SHELXL-93 (G. M. Sheldrick, University of

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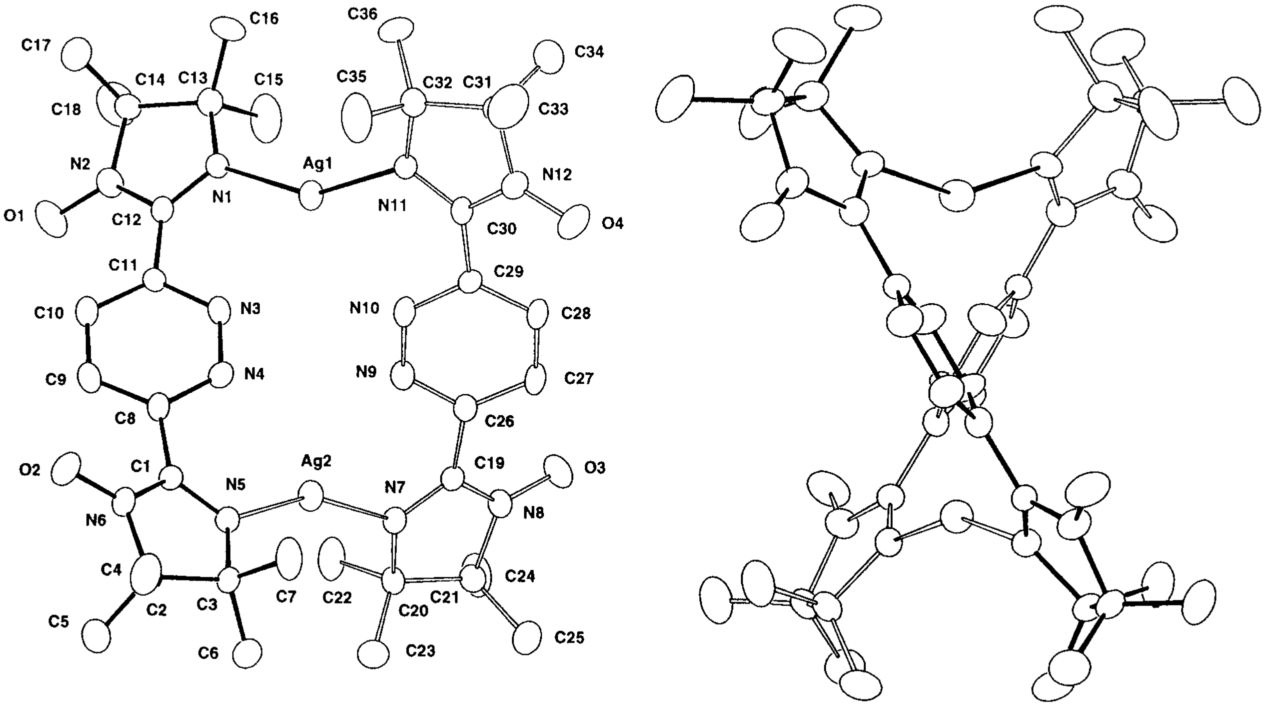

Figure 1. ORTEP diagram of **1** (ellipsoids at the 30% probability level).

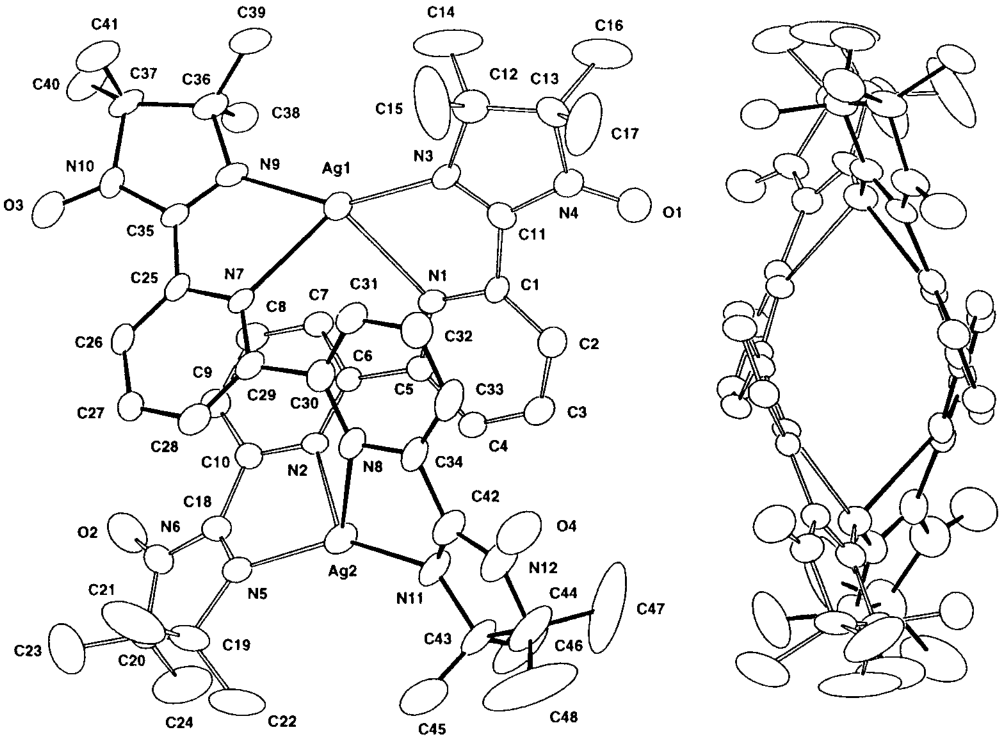

Figure 2. ORTEP diagram of **2** (ellipsoids at the 30% probability level)

Göttingen, 1993). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. On of the PF_6^- anion in **2** was found to be disordered around F−P−F axis and split-atom model with a 1:1 occupancy was applied.

Results and Discussion

Structures. Complexes $[Ag_2(pyrd\text{-}im2)_2](PF_6)_2\cdot 2CH_3OH$ (**1**) and $[Ag_2(bpy\text{-}im2)_2](PF_6)_2\cdot CH_3OH$ (**2**) crystallize in the monoclinic space group *Cc*, and orthorhombic space group *Pbca*, respectively. The absolute structure for **1** was determined by using the Flack's parameter,[9] which was estimated to be 0.08(3) for the presented structure. The crystal structure determinations for **1** and **2** show the compounds to be composed of a dimeric cation of $[Ag_2(pyrd\text{-}im2)_2]^{2+}$ (Figure 1) and $[Ag_2(bpy\text{-}im2)_2]^{2+}$ (Figure 2), respectively, which are best described as double-stranded helicates with the coordinated ligands being twisted around the Ag(1)−Ag(2) axis. Two silver ions doubly bridged by the diradicals in **1** and **2** are separated by 5.352(2) and 6.025(2) Å, respectively, and the dimeric molecules have

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ag(1)−N(11)	2.152(4)	Ag(1)−N(1)	2.163(5)
Ag(1)−N(3)	2.672(6)	Ag(1)−N(10)	2.680(7)
Ag(2)−N(7)	2.129(4)	Ag(2)−N(5)	2.138(4)
Ag(2)−N(4)	2.743(7)	Ag(2)−N(9)	2.750(6)
O(1)−N(2)	1.287(7)	O(2)−N(6)	1.262(6)
O(3)−N(8)	1.254(6)	O(4)−N(12)	1.280(6)
Ag(1)···Ag(2)	5.352(2)		
N(1)−Ag(1)−N(3)	68.9(2)	N(1)−Ag(1)−N(4)	85.6(2)
N(1)−Ag(1)−N(9)	120.0(2)	N(1)−Ag(1)−N(10)	136.7(2)
N(1)−Ag(1)−N(11)	152.5(2)	N(3)−Ag(1)−N(4)	16.9(2)
N(3)−Ag(1)−N(9)	66.2(2)	N(3)−Ag(1)−N(10)	78.9(2)
N(3)−Ag(1)−N(11)	136.7(2)	N(4)−Ag(1)−N(9)	56.2(1)
N(4)−Ag(1)−N(10)	66.1(1)	N(4)−Ag(1)−N(11)	119.9(2)
N(9)−Ag(1)−N(10)	16.7(2)	N(9)−Ag(1)−N(11)	85.4(2)
N(10)−Ag(1)−N(11)	68.9(2)	N(3)−Ag(2)−N(4)	16.7(2)
N(3)−Ag(2)−N(5)	84.0(2)	N(3)−Ag(2)−N(7)	117.6(2)
N(3)−Ag(2)−N(9)	64.5(2)	N(3)−Ag(2)−N(10)	54.7(1)
N(4)−Ag(2)−N(5)	67.5(2)	N(4)−Ag(2)−N(7)	134.3(2)
N(4)−Ag(2)−N(9)	77.2(2)	N(4)−Ag(2)−N(10)	64.6(1)
N(5)−Ag(2)−N(7)	156.7(2)	N(5)−Ag(2)−N(9)	134.1(2)
N(5)−Ag(2)−N(10)	117.6(2)	N(7)−Ag(2)−N(9)	67.6(2)
N(7)−Ag(2)−N(10)	83.9(2)	N(9)−Ag(2)−N(10)	16.5(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ag(1)−N(9)	2.174(6)	Ag(1)−N(3)	2.200(6)
Ag(1)−N(7)	2.508(6)	Ag(1)−N(1)	2.534(6)
Ag(2)−N(11)	2.213(7)	Ag(2)−N(5)	2.230(7)
Ag(2)−N(2)	2.477(6)	Ag(2)−N(8)	2.552(6)
Ag(1)···Ag(2)	6.025(2)		
O(1)−N(4)	1.272(8)	O(2)−N(6)	1.259(9)
O(3)−N(10)	1.270(9)	O(4)−N(12)	1.265(10)
N(9)−Ag(1)−N(3)	150.8(2)	N(9)−Ag(1)−N(7)	71.6(2)
N(3)−Ag(1)−N(7)	133.6(2)	N(9)−Ag(1)−N(1)	129.6(2)
N(3)−Ag(1)−N(1)	70.9(2)	N(7)−Ag(1)−N(1)	93.5(2)
N(11)−Ag(2)−N(5)	150.5(3)	N(11)−Ag(2)−N(2)	136.6(2)
N(5)−Ag(2)−N(2)	70.9(2)	N(11)−Ag(2)−N(8)	70.6(2)
N(5)−Ag(2)−N(8)	127.0(2)	N(2)−Ag(2)−N(8)	93.5(2)

four imino nitroxides (Tables 2 and 3). In **2**, the bipyridyl group of bpy-im2 adopts a trans conformation, contrary to what is shown in the previous scheme, and dihedral angles between pyridyl groups are 39.1(3) and 41.4(3)°. In **1**, the silver ions have two coordinated nitrogen atoms of the imino nitroxide groups. Bond lengths and angles of silver ions and coordinated nitrogen atoms are in the range of 2.129(4)−2.163(5) Å and of 152.5(2)−156.7(2)°, respectively, while each silver ion has close contacts (2.672(6)−2.750(6) Å) with nitrogen atoms of pyridazinyl groups. In **2**, coordination geometry about each silver ion is a distorted tetrahedron with four coordinated nitrogen atoms, where the Ag−N(imino nitroxide) bonds are much shorter (2.174(6)−2.230(7) Å) than the Ag−N(bipyridine) bonds (2.477(6)−2.552(6) Å). Bond angles of N(imino nitroxide)−Ag−N(imino nitroxide) are 150.8(2) and 150.5(3)°. Compounds **1** and **2** have a glide mirror plane and an inversion center, respectively; therefore, there are both plus and minus (clockwise and counterclockwise) helicates in the crystals. The angles of twist, that is, the angles of rotation of the helix, between two imino nitroxyl planes on the successive silver centers are 59° for **1** and 70° for **2**. This means the full turns of the helix for **1** and **2** would involve 6.1 and 5.1 silver ions, so the helical pitches (length per turn) is about 33 and 31 Å, respectively. It should be noted that there is no intermolecular close contact between imino nitroxyl groups in **1** and **2**, where the closest intermolecular atomic contact between radical moiety was observed for O(1)···O(3) contact with 3.657(9) Å in **2**.

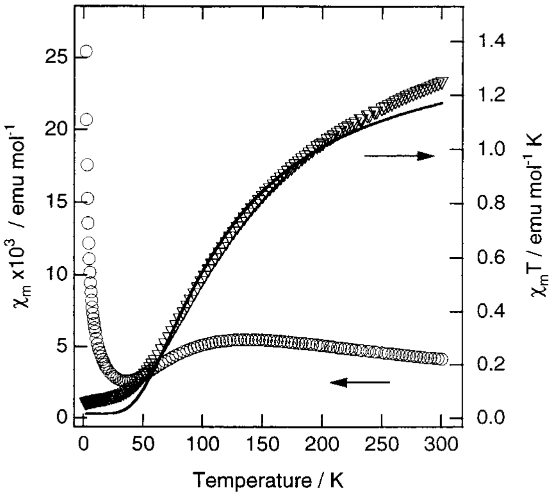

Figure 3. Plots of χ_m and χ_mT vs T for **1**. The solid line corresponds to the theoretical curves, parameters of which are given in the text.

Magnetic Properties. The temperature dependence of magnetic susceptibility of the compounds was measured down to 2.0 K. Room temperature χ_mT value of **2** is 1.49 emu^{-1} K mol^{-1}, which would be expected for the isolated four-spin system, and χ_mT remains at constant plateau down to 50 K, then decreases to a value of 0.7 emu K mol^{-1} at 2.0 K. Magnetic data of **2** was analyzed by the four spin model with two exchange coupling constants J_1 and J_2 representing magnetic interactions through the silver ions and bipyridyl groups ($H = -2J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - 2J_2(S_1 \cdot S_3 + S_2 \cdot S_4)$). The best fitting parameters of both J_1 and J_2 values are −1.4(1) cm^{-1}. The magnetic susceptibility data of **1** are shown in the form of χ_mT vs T and χ_m vs T plots (Figure 3). The χ_mT value of **1** steadily decreases as the temperature lowered, reaching a value of 0.005 emu K mol^{-1} at 2.0 K, which is indicative of intramolecular antiferromagnetic interactions. The closest intermolecular contact of nitroxyl groups is 4.3 Å, which exclude the presence of substantial intermolecular magnetic interactions. The two exchange parameters J_1 and J_2 through the silver ions and pyridazine groups, respectively, were used to analyze the magnetic data. The magnetic interaction of the imino nitroxides through the silver ions is considered to be the same order as that of **2**, because the coordination bond length and angles of the imino nitroxides in **1** are very similar to those of **2**. The exchange coupling constant through the silver ions was, therefore, fixed to −1.4 cm^{-1} in the analysis of the magnetic data of **1**.[10] The least-squares calculation, where the contribution of paramagnetic impurity (p) was included and the g value was fixed to 2.0, yielded the best fit parameters of $J_2 = -70.8(7)$ cm^{-1} and $p = 0.03(1)$. The significant antiferromagnetic interactions are propagated by the pyridazine ring, which can be understood by the spin-polarization mechanism.[11]

Acknowledgment. The authors thank Prof. T. Sakamoto and Dr. A. Yasuhara (Pharmaceutical Institue, Tohoku University) for their help to prepare 3,6-diformylpyridazine. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Listing of crystallographic data, fractional coordinates of non hydrogen atoms, bond lengths, bond angles, anisotropic parameters, and calculated hydrogen coordinates for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The least-squares calculation with the J_1 and J_2 values as variables for **2** gave unreasonable values of −86 and +45 cm^{-1}, respectively, despite fact that the amplitudes of the J_1 value should be close to −1.4 cm^{-1}.

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