Synthesis, Structure, and Magnetic Properties of a 2,2-Dipyridyl-2,5-dihydroimidazole-1-oxyl-(L-)Bridged Disilver Complex $[Ag_2L_2](SbF_6)_2$: A Four-Membered Ring from two Ag(I) Ions and two Imine Nitrogen Atoms☆

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Received November 24, 1995

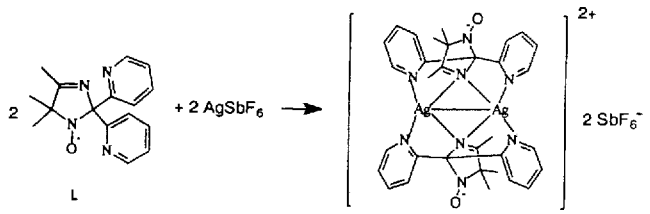
Key Words: Nitroxide radical / Silver(I) complex

The reaction of 2,5-dihydro-4,5,5-trimethyl-2,2-di-2-pyridyl-imidazole-1-oxyl (**L**) with $AgSbF_6$ gives the complex $[Ag_2L_2]^{2+}[SbF_6^-]_2$ which was characterized by X-ray diffraction. – The complex (a biradical) forms a four-membered ring with two Ag(I) ions and two imine nitrogen atoms of the imidazolines with a relatively short Ag–Ag distance [2.839(2) Å]. Magnetic measurements indicate that two nitroxide radicals are slightly coupled.

Complexes with nitroxide radicals are of current interest due to their magnetic properties and the possibility of forming molecular magnetic materials[1]. Recently, we reported on the preparation of the new nitroxide radical 2,5-dihydro-4,5,5-trimethyl-2,2-di 2-pyridylimidazole-1-oxyl (**L**)[2] and of some metal complexes thereof[3]. In this paper a silver(I) complex with this ligand is described.

Results and Discussion

The reaction of **L** with $AgSbF_6$ in methanol gives a complex of the composition $Ag(L)SbF_6$ (**1**).



L

1

The X-ray structural analysis of **1** shows that two Ag(I) ions form with two imine nitrogen atoms of the imidazolines a four-membered ring with a relatively short Ag–Ag distance of 2.839(2) Å. The molecule contains an inversion center. The Ag_2N_2 ring is planar and perpendicular to the two 3-imidazoline heterocycles. The Ag–N distances within the Ag_2N_2 ring are 2.50 and 2.65 Å. The length of the imine bond (N2–C2: 1.27 Å) is not affected by coordination and has the same value as found in the free ligand **L**[2], which is typical of C=N bonds[4]. Two pyridine nitrogen atoms of each ligand are also coordinated to an Ag(I) ion. The Ag–N(pyridine) distances are 2.22 and 2.25 Å and are similar to those in known Ag(I) complexes of N heterocycles[5]. The Ag–N1a and Ag–N2 (2.65, 2.50 Å) are significantly longer than the Ag–N3 and Ag–N4 bonds (2.25, 2.22 Å) which reflects the weak bridging effect of the imidazoline ring as was previously observed with pyridine bridges[7]. Additionally, a weak coordination of one fluorine atom (F2) of a SbF_6^- counterion is found (Ag–F: 3.09 Å). The nitroxide group of **L** has a N–O bond length of 1.26 Å as found in free nitroxides[6].

The interesting feature of this structure is the four-membered Ag_2N_2 ring. In accordance with the C=N bond length the IR spectrum shows that the C=N group of the imidazoline cycle is a typical imine group; the C=N absorption of **1** is shifted only by 9 cm^{-1} to lower wave numbers in comparison with the free ligand. This means that an ylidic C–N structure is not important, and coordination of the nitrogen atom to both Ag(I) ions occurs only by one electron pair.

A similar M_2N_2 diamond-type structure show Zn(II) and Cu(I) complexes in which two pyridine N atoms are bridging two d^{10} metal ions and in which the pyridine ligands have two coordinated imino groups in the position 2 and 6[7]. Like **1** these complexes show short M–M distances.

MO calculations of multinuclear ligand-bridged Cu(I) complexes by Hoffmann[8] indicate that the attractive Cu(I)–Cu(I) interaction is caused by s+p+d mixing. Alvarez[9] proposes that the bonding in M_2X_2 diamonds of tetrahedral d^{10} ions is 4-electron-4-center deficient as in other electron-deficient compounds, e.g. B_2H_6, and that d^{10}-d^{10} interaction occurs.

However, ab-initio calculation on Au(I)[10] and Cu(I)[11] clusters by Pykkö, Fenske, and Ahlrichs suggest that the

[+] X-ray structural determination. – [++] Magnetic properties.

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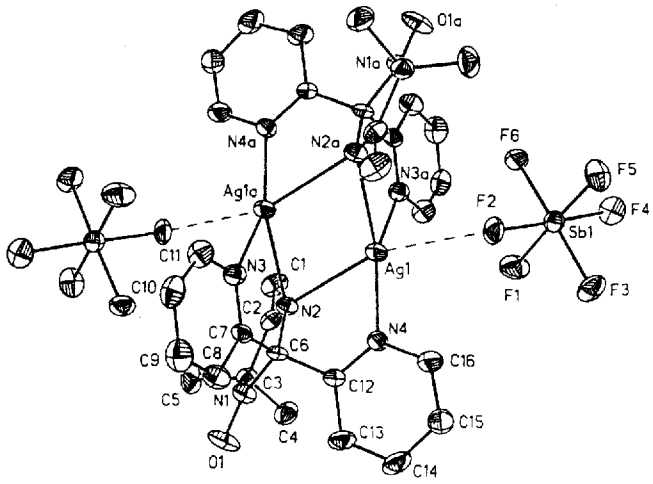
Figure 1. Molecular Structure of 1[a]



[a] Selected bond lengths [Å] and angles [°]: Ag1–Ag1a 2.839(2), Ag1–N2 2.646(7), Ag1–N2a 2.499(6), Ag1–F1 3.462(8), Ag1–F2 3.090(7), Ag1–N3a 2.253(7), Ag1–N4 2.220(6), Ag1a–N4a 2.220(6), N1–O1 1.264(8), N2–C2 1.269(10), N3–C7 1.323(9), N3–C11 1.333(11), N4–C12 1.326(9), N4–C16 1.334(10); N2–Ag1–N2a 113.1(2), Ag1–N2–Ag1a 66.9(2), N2–Ag1–Ag1a 54.07(14), N2a–Ag1–Ag1a 59.0(2), N4–Ag1–N3a 154.3(3), N3a–Ag1–N2a 69.2(2), N4–Ag1–N2a 134.6(2), N4–Ag1–Ag1a 108.0(2), C2–N2–C6 110.2(6), C2–N2–Ag1a 121.2(5), Sb1–F2–C13 115.9(3).

metal–metal attraction is a pure correlation effect. The origin of the thermodynamic formation of similar 2:2 complexes with rigid tridendate ligands in which no significative metal–metal bonds are involved has been discussed[12].

Even shorter Ag–Ag distances than in **1** were found in a series of Ag(I) complexes in which two Ag(I) ions are bridged by two bidentate ligands[13]. Relativistic effects which enhance Au(I)–Au(I) interactions seem to be negligible for Ag(I) compounds[14].

The magnetic susceptibility χ of **1** was determined by a SQUID magnetometer in the temperature range from 2 to 295 K. The magnetic moment found at 295 K is 2.45 μ_B, which is exactly the value expected for two independent NO radical spins ($S_1 = S_2 = 1/2$). Further analysis of the temperature dependence of χ, taking into account two independent radical spins and appropriate corrections for diamagnetism and temperature-independent paramagnetism, reveals that it does not fit the calculated magnetic moment at very low temperature (Figure 2), indicating small exchange interaction among the two NO radicals in **1**. Therefore, the Dirac-van-Vleck exchange Hamiltonian $H = J\,\vec{S}_1\vec{S}_2$ has been included in the analysis of $\chi(T)$. Agreement between calculated and measured magnetic moment was obtained for a small but positive coupling constant J, i.e. for antiparallel alignment of the two NO spins $S_1 = 1/2$ and $S_2 = 1/2$ within **1**. To further corroborate this indication EPR measurements were performed on **1** in different solvents (Figure 3). The observed five-line pattern indeed manifests a slight antiparallel spin coupling in the biradical system **1**[15]. EPR measurements of polycrystals of **1** yield a single line (not shown) because of spin-spin relaxation effects in the solid[16].

Figure 2. Temperature dependence of the effective magnetic moment of **1**; TIP = $95 \cdot 10^{-6}$ cm^3 mol^{-1}; $\chi = -560 \cdot 10^{-6}$ cm^3 mol^{-1}

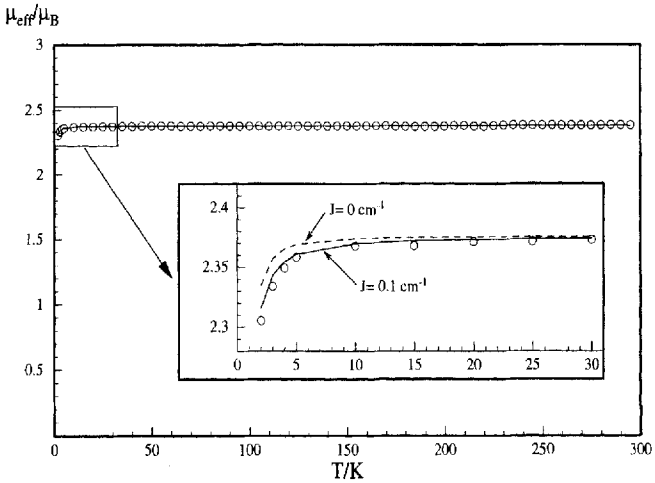
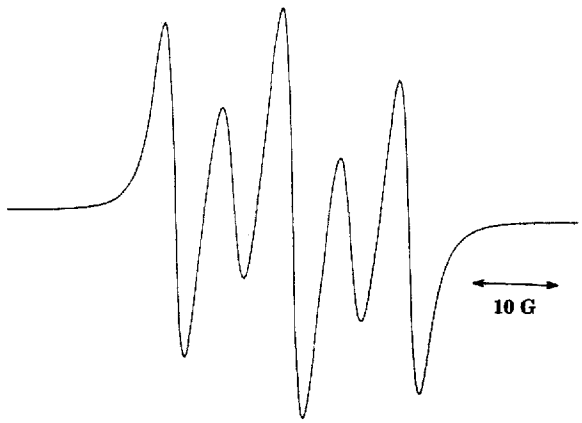


Figure 3. EPR spectrum of **1** in methanol (20 °C); practically the same spectrum was observed in acetone



Generous support by the *Fonds der Chemischen Industrie* is gratefully acknowleged. We thank Prof. *L. B. Volodarsky*, Novosibirsk, for discussions and the referees for valuable comments.

Experimental

2,5-Dihydro-4,5,5-trimethyl-2,2-di-2-pyridylimidazole-1-oxyl (**L**) was prepared as published[2]. – EPR spectra (X band) in solution: Varian E-Line Spectrometer with a Varian E-101 microwave bridge. – EPR spectra (X band) of solid **1**: Bruker ER 200 spectrometer. – Magnetic measurements: SQUID magnetometer (MPMS, quantum design). – IR: Nicolet 520 FT-IR.

Bis(2,5-dihydro-4,5,5-trimethyl-2,2-di-2-pyridylimidazole-1-oxyl)-disilver Bis(hexafluoroantimonate) (**1**): A solution of 2,5-dihydro-4,5,5-trimethyl-2,2-di-2-pyridylimidazole-1-oxyl (35.5 mg, 0.126 mmol) in methanol (2 ml) was dropped into a solution of $AgSbF_6$ (43.4 mg, 0.126 mmol) in methanol (3 ml). After 3 d brown-red crystals were separated and dried in vacuo (53 mg, 67%). Single crystals for the X-ray structural determination were obtained by layering a solution of 2,5-dihydro-4,5,5-trimethyl-2,2-di-2-pyridylimidazole-1-oxyl (22 mg) in methanol (1.5 ml) with a solution of $AgSbF_6$ (20 mg) in methanol (2.5 ml). – IR (KBr): $\tilde{\nu}$ = 1632 cm^{-1} m (C=N), 1597 m (py), 1590 m (py), 1469 s, 1434 s, 770 s, 658 vs, 290 vs (in polyethylene). – $C_{32}H_{34}Ag_2F_{12}N_8O_2Sb_2$ (1249.9): calcd. C 30.75, H 2.74, N 8.97; found C 30.86, H 2.81, N 8.82.

Crystal Structure Determination[17]: $C_{32}H_{34}Ag_2F_{12}N_8O_2Sb_2$ (1249.9); crystal size 0.2 × 0.2 × 0.2 mm^3; Syntex-Nicolet diffractometer; temperature 20 °C, monoclinic; $P2_1/n$; a = 11.307(4), b = 13.242(7), c = 13.847(5) Å; β = 98.29(3)°, V = 2051.6(15) Å^3; Z = 4; $d_{calcd.}$ = 2.34 g · cm^{-3}; 2Θ range 4.28–45.10; μ(Mo-K_α) = 2.40 mm^{-1}; semi-empirical absorption correction (0.429–0.501); collected data $-12 \leq h \leq 0$, $0 \leq k \leq 14$, $-14 \leq l \leq 14$; 2855 total reflections; 2696 independent reflections ($R_{int.}$ = 0.066); 1977 observed reflections [$F > 4\sigma(F)$]; 265 parameters; structure solution by Patterson; program SHELXTLPLUS 4.11/V; refinement by full-matrix least squares; $R1$ = 0.0427; $wR2$ = 0.0925 [F)] > 4σ(F]; max./min. residual electron density 0.83/−0.61 eÅ^{-3}.

[☆] Dedicated to Professor *Marianne Baudler* on the occasion of her 75th birthday.

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[17] Further details of the crystal structure determination are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-59179, the names of the authors, and the journal citation.

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