Magnetic Properties

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Cyclic Triradicals Composed of Iminonitroxide–Gold(I) with Intramolecular Ferromagnetic Interactions

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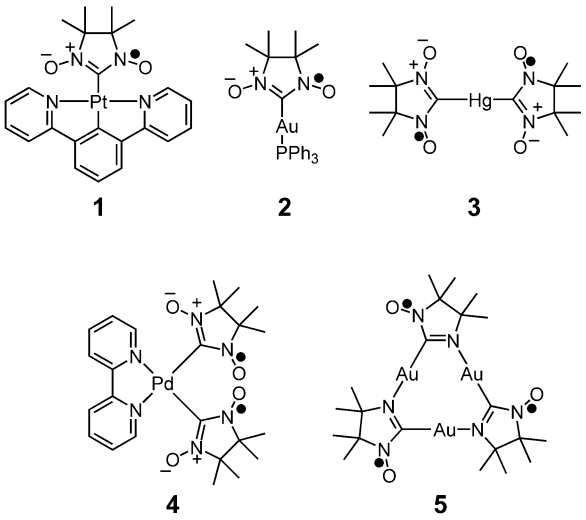
Abstract: *A triangular gold(iminonitroxide-2-ide) trimer complex (**5**) was prepared and investigated to determine its magnetic properties. The results showed that the metalloid triradical is highly stable, even in solution under aerated conditions. The intramolecular exchange interaction of **5** was found to be positive ($J_{intra}/k_B \approx +29$ K), thus showing that **5** is in a quartet ground state. In addition, a silver sandwich complex (**5**-Ag^+-**5**) was prepared and its electronic and magnetic properties were also clarified.*

Recent advances in the development of stable open-shell molecules have led to the synthesis of various fascinating materials such as organic high-spin molecules with large exchange interactions,[1–4] molecule-based magnets,[1,5] radical-based batteries,[2,6] and materials exhibiting unique electronic and spintronic properties.[2,7–10] Nitronyl nitroxide (NN) and iminonitroxide (IN) radicals, shown in Figure 1, are widely utilized as stable spin sources for molecule-based magnets and related materials.[1,5,10–12]

Many studies have reported metal complexes coordinated by oxygen and/or nitrogen atoms in either NN or IN moieties.[1,12] In contrast, only a few studies have investigated metal radical systems coordinated by the carbon atom within the NN-2-ide radical anion(s).[13–17] We have recently reported that these metalloid NN radicals are highly stable and find wide application in various fields such as synthetic and materials science.[14–16] For example, the platinum complex **1** exhibits unique redox properties,[14] and the gold/NN complex **2** can be utilized as an NN source in the cross-coupling reaction with aryl halides in the presence of a palladium(0) catalyst.[16]



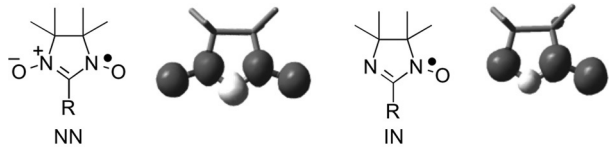


Figure 1. Chemical structures and spin density distributions of nitronyl nitroxide (NN) and iminonitroxide (IN). Positive and negative spin densities are shown as gray and white circles, respectively.

Metal-centered radical systems with two or more spins are also intriguing in terms of their intramolecular exchange interaction, which has been demonstrated by using a stable radical such as NN[13c,15] and a salen-type phenoxyl.[18] The NN-based system can provide clear-cut information on the structure and exchange interaction in metal-centered radical systems. So far, only a few studies have investigated the metal-centered multi-NN-2-ides. Ovcharenko and co-workers reported that the mercury complex **3** shows paramagnetic behavior,[13c] whilst we reported that the exchange interaction of two NNs for the palladium complex **4** was determined to be $J/k_B = -36$ K[15] by temperature dependence of the magnetic susceptibility. Also, other theoretical studies related to [(NN-2-ide)–M–(NN-2-ide)] (M = nonmagnetic metal ion) compounds suggest that the intramolecular exchange interaction between stable radicals is weakly antiferromagnetic.

In this work, we report the preparation and magnetic properties of the new metalloid radical **5** with a quartet ground state, that is, a C_3-symmetric cyclic gold(IN-2-ide) trimer with gold(I) atoms linearly coordinated through the imino nitrogen atom (positive spin) on one side and the IN-2-ide carbon atom (negative spin) on the other side.

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The triradical **5** was prepared in a moderate yield by treating **2** with sodium nitrite under acidic conditions. Its structure was characterized by MS, electron-spin resonance (ESR) spectroscopy (see Figure S1 in the Supporting Information), elemental analysis, and X-ray crystal structure analysis.[19] Surprisingly, **5** was very stable and could be purified by conventional column chromatography under aerated conditions.

Single red crystals of **5** suitable for X-ray crystal structure analyses were obtained by recrystallization from a mixed cyclohexane and toluene solution. The triradical **5** has C_3 symmetry with a shallow bowl structure (Figure 2). The bond

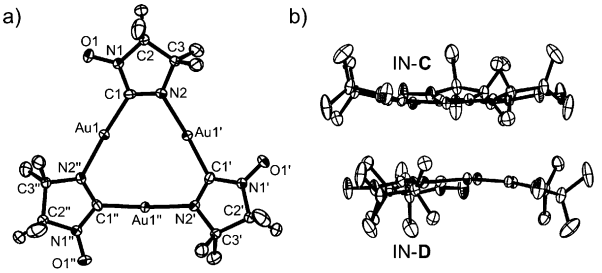

Figure 2. ORTEP views (50% probability) of **5**. a) Top view of **5**. b) Side view of **5**-dimer. Hydrogen atoms and crystal solvents are omitted for clarity. IN-**C** and IN-**D** denote the (x,y,z)–$(x,x-y,1/2-z)$-related nearest IN moieties.

lengths of Au1–C1 [1.981(7) Å] and Au1–N2 [2.054(7) Å] are similar to those of the related trinuclear gold(I) complexes with the associated diamagnetic imidazolates.[20] The bond lengths on the IN moiety fall within the range of typical values: O1–N1: 1.270(6) Å; N1–C1: 1.395(6) Å; and C1–N2: 1.309(8) Å.[4d] Also, **5** formed a dimeric structure with a convex–convex motif (**5**-dimer) and an intermolecular staggered angle of about 30°. In the crystal, two kinds of crystallographically independent cyclohexane molecules (cyclohexane **A** and **B**) were observed as crystal solvents (see Figure S2). Dimers of **5** and the cyclohexane **A** formed a one-dimensional columnar structure by an alternate staking motif, while the cyclohexane **B** was observed between the columnar structures (see Figure S2), thus suggesting that the magnetic interaction between the dimers is very weak.

The magnetic properties of **5** in the polycrystalline sample were elucidated by measuring temperature dependence of $\chi_p T$ (χ_p = the molar paramagnetic susceptibility; the **5**-dimer structure involving six INs is taken as a molecular unit) by means of a SQUID magnetometer in the temperature range between 298 K and 1.9 K under an external magnetic field of 0.1 T (Figure 3). The $\chi_p T$ value at room temperature, 2.461 emu K mol^{-1}, was higher than the theoretical value of magnetically independent six $S = 1/2$ spins ($0.375 \times 6 = 2.25$ emu K mol^{-1} assuming $g = 2.00$). The $\chi_p T$ value gradually increases upon cooling to about 60 K. Thereafter, it rapidly decreased to 0 emu K mol^{-1} below 60 K. This behavior can be explained by the coexistence of an intramolecular ferromagnetic interaction between the IN moieties and a smaller intermolecular (intra-dimer) antiferromagnetic interaction. The observed $\chi_p T$–T curve was analyzed by using the spin

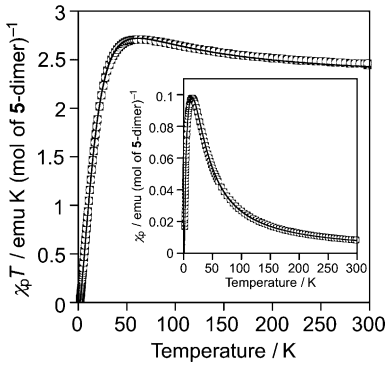

Figure 3. The $\chi_p T$–T plots of **5** for the polycrystalline sample. The solid lines shows the simulation curve based on an equilateral-triangular prism model [$J_{intra}(\mathbf{5})/k_B = +29.3$ K and $J_{inter}(\mathbf{5})/k_B = -12.2$ K].

Hamiltonian based on an equilateral-triangular prism model (see Figure S3): $H = -2\{J_{intra}(\mathbf{5})(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_1 + S_1' \cdot S_2' + S_2' \cdot S_3' + S_3' \cdot S_1') + J_{inter}(\mathbf{5})(S_1 \cdot S_1' + S_2 \cdot S_2' + S_3 \cdot S_3')\}$, where intramolecular and intermolecular exchange interactions are represented by $J_{intra}(\mathbf{5})$ and $J_{inter}(\mathbf{5})$, respectively.[21] The best-fit parameter values of intermolecular exchange interactions (solid line in Figure 3) are obtained as $J_{intra}(\mathbf{5})/k_B = +29.3$ K and $J_{inter}(\mathbf{5})/k_B = -12.2$ K. The antiferromagnetic interaction of $|J_{inter}(\mathbf{5})|/k_B = 12.2$ K is compatible with the temperature (ca. 15 K) of the maximum in χ_p in the χ_p–T plots (Figure 3; inset).

To ascertain the above assignment of magnetic interactions, we carried out calculations by density-functional theory using *Gaussian 09* program[22] based on the crystal structure (see Table S1). The calculations show that the total energy of the high-spin state of **5** ($S = 3/2$) is lower than that of the low-spin state ($S = 1/2$), and the calculated exchange interaction ($J_{calc\text{-}intra}$) was found to be $J_{calc\text{-}intra}/k_B = +33.3$ K.[23] The spin density maps of the high-spin and low-spin states are shown in Figure S4. The key feature of the ferromagnetic interaction in **5** is induction of positive (up) spin on gold(I), and this spin can be brought about by the spin delocalization from metal d_{xz} orbital to the p orbital (in SOMO) of the imino nitrogen atom having large positive (up) spin, thus producing positive (up) spin on gold(I) (see Figure S5). Then, the usual spin up-down relationship stabilizes the high-spin state. The small spin density thus induced on gold also provides significant effect on the zero-field splitting (ZFS) in the ESR spectrum ($|D/hc| = 0.0414$ cm^{-1}; see Figure S1). The large observed $|D/hc|$ values cannot be explained by the spin–spin dipolar interaction and requires large contribution of the spin–orbit coupling (SOC) induced by the heavy gold atom (see Table S3).[24] In addition, we calculated the intermolecular exchange interaction ($J_{calc\text{-}inter}/k_B = -5.1$ K) between the IN moieties (IN-**C** and IN-**D**, taken from top and bottom **5**s, respectively, in Figure 2b). The calculated results are roughly comparable to the experimental results.

Furthermore, we successfully prepared (**5**-Ag^+-**5**)·X^- (X = PF_6[25] and OTf[26]) by addition of the silver salts. These complexes were also stable under aerated conditions, both in solution and in the solid state. Single orange crystals of (**5**-Ag^+-**5**)·PF_6^- suitable for X-ray crystal structure analyses were obtained by crystallization by mixing a dichloromethane

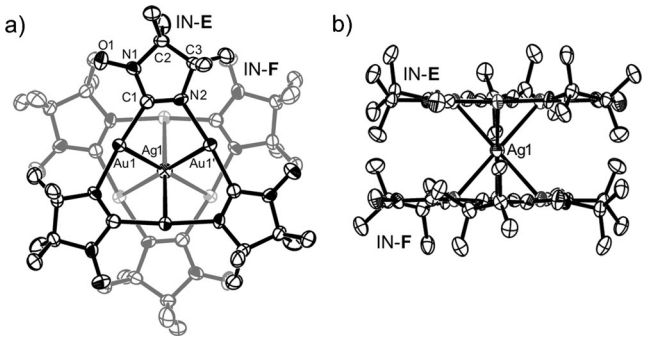

Figure 4. ORTEP views (50% probability) of (**5**-Ag^+-**5**)·PF_6^-. a) Top view; the framework drawn in the light shade belongs to the back-side molecule. b) Side view of (**5**-Ag^+-**5**)·PF_6^-. IN-**E** and IN-**F** denote the S_6-related nearest IN moieties in the silver complex. Hydrogen atoms and counter anions are omitted for clarity.

solution of **5** with silver hexafluorophosphate.[27] The complex (**5**-Ag^+-**5**)·PF_6^- has an S_6 symmetrical structure with a rotatory reflection axis through the Ag1 atom (Figure 4). Two units of **5** in (**5**-Ag^+-**5**)·PF_6^- have planar structures, and the stagger angle between them is 60°. The bond lengths around the gold atom within (**5**-Ag^+-**5**), Au1–C1: 1.99(1) Å and Au1′–N2: 2.07(1) Å, are slightly longer than those in **5**-dimer (Figure 2b), probably caused by the coordination of silver to the gold atoms. The Au1–Ag1 bond length [2.8095(5) Å] was smaller than the sum of van der Waals radii of the gold and silver atoms (3.38 Å), thus suggesting Au–Ag interactions.[20,28] The interplanar distance between the **5** units within (**5**-Ag^+-**5**)·PF_6^- was estimated to be 3.96 Å, which is longer than that of **5**-dimer, thus suggesting a smaller magnetic interaction between the **5** units in the silver complex. In addition, a short contact was observed between the oxygen atoms (2.96 Å, in IN-**E** and IN-**G**; see Figure S6b). Moreover each of the three nitroxide oxygen atoms in the **5** moiety of the silver complex makes a three-dimensional network between the silver complexes.

The complex (**5**-Ag^+-**5**)·PF_6^- showed similar magnetic behavior to that of **5**-dimer. The χ_pT–T (χ_p–T) plots (see Figure S7) indicate the presence of ferromagnetic and antiferromagnetic interactions. The trianglar triradical moieties commonly presented ferromagnetic interactions [J_{intra}(**5**) for **5**-dimer, J_{intra}(**5**-Ag^+-**5**) for (**5**-Ag^+-**5**)] for both the silver complex and **5**-dimer. The temperature dependence of the χ_p value of (**5**-Ag^+-**5**) was simulated by an equilateral triangular model [$H = -2\{J_{intra}$(**5**-Ag^+-**5**)(S_1·S_2 + S_2·S_3 + S_3·S_1)}] with the intermolecular interaction zJ_{inter}(**5**-Ag^+-**5**) in the mean-field approximation[29] (see Equations S1–S3) rather than the triangular prism model applied to **5**-dimer. The difference in the magnetic behavior between **5**-dimer and (**5**-Ag^+-**5**) is as follows: **5**-dimer has a moderate antiferromagnetic interaction [J_{inter}(**5**)/$k_B = -12.2$ K] between the triangles in **5**-dimer. In contrast, the silver complex has a much smaller exchange interaction between the triangular moieties in (**5**-Ag^+-**5**) and has a larger antiferromagnetic interaction between the adjacent (**5**-Ag^+-**5**) units, making a three-dimensional-type contact network. The best fit parameters were determined to be J_{intra}(**5**-Ag^+-**5**)/$k_B = +25.0$ K and zJ_{inter}(**5**-Ag^+-**5**) = −9.7 K. The J_{intra}(**5**-Ag^+-**5**)/k_B value is comparable with the J_{intra}(**5**)/k_B value (+29.3 K). The intermolecular interaction J_{inter}(**5**-Ag^+-**5**) is assignable to the oxygen–oxygen contact (2.96 Å) in IN-**E**–IN-**G** (Figure S6b); the magnetic interaction was theoretically estimated to be $J_{calc}/k_B = -4.7$ K using the X-ray-determined geometry. The exchange interaction between the IN-**E** and IN-**F** moieties (Figure 4) within the silver complex were estimated to be much smaller ($J_{calc}/k_B = +0.6$ K; see Table S2),[22,23] and is in accordance with the applied equilateral triangular model.

In conclusion, we have designed and synthesized a unique triangular metalloid triradical **5**, which was found to be stable under aerated conditions in both solution and the solid state. In the crystals obtained from cyclohexane, **5** forms a dimer. The temperature dependence of the magnetic susceptibility of **5** clearly indicates a quartet ground state with $J_{intra}/k_B = +29.3$ K. We also prepared the silver complex (**5**-Ag^+-**5**)·PF_6^- with $J_{intra}/k_B = +25.0$ K. These compounds are the first ferromagnetic metalloid triradicals having the unique bonding N(IN)–Au–C(IN). The application of this ferromagnetic structure and its extension to the intercalation of functional molecules are currently in progress.

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[1] a) O. Kahn, *Molecular Magnetism,* Wiley-VCH, Weinheim, **1993**; b) *Molecular Magnetism* (Eds.: K. Itoh, M. Kinoshita), Kodansha & Gordon and Breach, Tokyo, **2000**; c) *Magnetism: Molecules to Materials II* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**; d) *π-Electron Magnetism From Molecules to Magnetic Materials* (Ed.: J. Veciana), Springer, Berlin, **2001**; e) D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets,* Oxford University Press, New York, **2006**.

[2] Y. Morita, S. Suzuki, K. Sato, T. Takui, *Nat. Chem.* **2011**, *3*, 197–204.

[3] a) W. T. Borden, in *Diradicals* (Ed.: W. T. Borden), Wiley, New York, **1982**, pp. 1–72; b) P. G. Wenthold, J. Hu, R. R. Squires, W. C. Lineberger, *J. Am. Chem. Soc.* **1996**, *118*, 475–476; c) S. Suzuki, K. Okada, in *Organic Redox Systems* (Ed.: T. Nishinaga), Wiley, Hoboken, **2016**, pp. 269–285.

[4] For example, see:a) N. C. Yang, A. J. Castro, *J. Am. Chem. Soc.* **1960**, *82*, 6208; b) K. Mukai, K. Ishizu, M, Nakahara, Y. Deguchi, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3363–3364; c) A. Rajca, K. Shiraishi, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2007**,

129, 7232 – 7233; d) S. Suzuki, T. Furui, M. Kuratsu, M. Kozaki, D. Shiomi, K. Sato, T. Takui, K. Okada, *J. Am. Chem. Soc.* **2010**, *132*, 15908 – 15910; e) P. J. Boratyński, M. Pink, S. Rajca, A. Rajca, *Angew. Chem. Int. Ed.* **2010**, *49*, 5459 – 5462; *Angew. Chem.* **2010**, *122*, 5591 – 5594; f) A. Rajca, A. Olanktwanit, S. Rajca, *J. Am. Chem. Soc.* **2011**, *133*, 4750 – 4753; g) S. Suzuki, in *Chemical Science of π-Electron Systems* (Eds.: T. Akasaka, O. Atsuhiro, S. Fukuzumi, H. Kandori, Y. Aso), Springer, Tokyo, **2015**, pp. 323 – 335.

[5] a) Y. Masuda, M. Kuratsu, S. Suzuki, M. Kozaki, D. Shiomi, K. Sato, T. Takui, Y. Hosokoshi, X.-Z. Lan, Y. Miyazaki, A. Inaba, K. Okada, *J. Am. Chem. Soc.* **2009**, *131*, 4670 – 4673; b) M. Kuratsu, S. Suzuki, M. Kozaki, D. Shiomi, K. Sato, T. Takui, T. Kanzawa, Y. Hosokoshi, X.-Z. Lan, Y. Miyazaki, A. Inaba, K. Okada, *Chem. Asian J.* **2012**, *7*, 1604 – 1609.

[6] a) H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737 – 738; b) Y. Morita, S. Nishida, T. Murata, M. Moriguchi, A. Ueda, M. Satoh, K. Arifuku, K. Sato, T. Takui, *Nat. Mater.* **2011**, *10*, 947 – 951.

[7] a) S. K. Pal, M. E. Itkis, F. S. Tham, R. W. Reed, R. T. Oakley, R. C. Haddon, *Science* **2005**, *309*, 281 – 284; b) A. Iwasaki, L. Hu, R. Suizu, K. Nomura, H, Yoshikawa, K. Awaga, Y. Noda, K. Kanai, Y. Ouchi, K. Seki, H. Ito, *Angew. Chem. Int. Ed.* **2009**, *48*, 4022 – 4024; *Angew. Chem.* **2009**, *121*, 4082 – 4084.

[8] a) S. Nishida, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui, K. Nakasuji, *Angew. Chem. Int. Ed.* **2005**, *44*, 7277 – 7280; *Angew. Chem.* **2005**, *117*, 7443 – 7446; b) Y. Morita, S. Suzuki, K. Fukui, S. Nakazawa, H. Kitagawa, H. Kishida, H. Okamoto, A. Naito, A. Sekine, Y. Ohashi, M. Shiro, K. Sasaki, D. Shiomi, K. Sato, T. Takui, K. Nakasuji, *Nat. Mater.* **2008**, *7*, 48 – 51.

[9] a) M. M. Matsushita, H. Kawakami, Y. Kawada, T. Sugawara, *Chem. Lett.* **2007**, *36*, 110 – 111; b) M. M. Matsushita, H. Kawakami, T. Sugawara, M. Ogata, *Phys. Rev. B* **2008**, *77*, 195308; c) T. Sugawara, H. Komatsu, K. Suzuki, *Chem. Soc. Rev.* **2011**, *40*, 3105 – 3118.

[10] a) Y. Kawanaka, A. Shimizu, T. Shinada, R. Tanaka, Y. Teki, *Angew. Chem. Int. Ed.* **2013**, *52*, 6643 – 6647; *Angew. Chem.* **2013**, *125*, 6775 – 6779; b) A. Ito, A. Shimizu, N. Kishida, Y. Kawanaka, D. Kosumi, H. Hashimoto, Y. Teki, *Angew. Chem. Int. Ed.* **2014**, *53*, 6715 – 6719; *Angew. Chem.* **2014**, *126*, 6833 – 6837; c) A. Shimizu, A. Ito, Y. Teki, *Chem. Commun.* **2016**, *52*, 2889 – 2892.

[11] a) E. F. Ullman, J. H. Osiecki, D. G. B. Boocock, R. Dracy, *J. Am. Chem. Soc.* **1972**, *94*, 7049 – 7059; b) M. J. A. El-Haj, *J. Org. Chem.* **1972**, *37*, 2519 – 2520; c) B. M. Dooley, S. E. Bowles, T. Storr, N. L. Frank, *Org. Lett.* **2007**, *9*, 4781 – 4783.

[12] a) S. L. Veber, M. V. Fedin, A. I. Potapov, K. Y. Maryunina, G. V. Remanenko, R. Z. Sagdeev, V. I. Ovcharenko, D. Goldfarb, E. G. Bagryanskaya, *J. Am. Chem. Soc.* **2008**, *130*, 2444 – 2445; b) M. Fedin, V. Ovcharenko, R. Sagdeev, E. Reijerse, W. Lubitz, E. Bagryanskaya, *Angew. Chem. Int. Ed.* **2008**, *47*, 6897 – 6899; *Angew. Chem.* **2008**, *120*, 7003 – 7005; c) V. I. Ovcharenko, S. V. Fokin, E. Y. Fursova, O. V. Kuznetsova, E. V. Tretyakov, G. V. Remanenko, A. S. Bogomyakov, *Inorg. Chem.* **2011**, *50*, 4307 – 4312.

[13] a) R. K. Leute, E. F. Ulman, U.S. Patent 3,697,535, **1969**; b) R. Weiss, N. Kraut, F. Hampel, *J. Organomet. Chem.* **2001**, *617*, 473 – 482; c) S. V. Fokin, G. V. Romanenko, M. Baumgarten, V. I. Ovcharenko, *J. Struct. Chem.* **2003**, *44*, 864 – 869.

[14] X. Zhang, S. Suzuki, M. Kozaki, K. Okada, *J. Am. Chem. Soc.* **2012**, *134*, 17866 – 17868.

[15] S. Suzuki, H. Yokoi, M. Kozaki, Y. Kanzaki, D. Shiomi, K. Sato, T. Takui, K. Okada, *Eur. J. Inorg. Chem.* **2014**, 4740 – 4744.

[16] R. Tanimoto, S. Suzuki, M. Kozaki, K. Okada, *Chem. Lett.* **2014**, *43*, 678 – 680.

[17] a) D. G. B. Boocock, R. Darcy, E. F. Ullman, *J. Am. Chem. Soc.* **1968**, *90*, 5945 – 5946; b) O. N. Chupakhin, I. A. Utepova, M. V. Varaksin, E. V. Tretyakov, G. V. Romanenko, D. V. Stass, V. I. Ovcharenko, *J. Org. Chem.* **2009**, *74*, 2870 – 2872.

[18] a) T. J. Dunn, M. I. Webb, K. Hazin, P. Verma, E. C. Wasinger, Y. Shimazaki, T. Storr, *Dalton Trans.* **2013**, *42*, 3950 – 3956; b) M. Kawai, T. Yamaguchi, S. Masaoka, F. Tani, T. Kohzuma, L. Chiang, T. Storr, K. Mieda, T. Ogura, R. K. Szilagyi, Y. Shimazaki, *Inorg. Chem.* **2014**, *53*, 10195 – 10202; c) R. M. Clarke, K. Hazin, J. R. Thompson, D. Savard, K. E. Prosser, T. Storr, *Inorg. Chem.* **2016**, *55*, 762 – 774.

[19] CCDC 1473134 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[20] a) A. Burini, R. Bravi, J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, B. R. Pietroni, R. J. Staples, *Inorg. Chem.* **2000**, *39*, 3158 – 3165; b) T. Osuga, T. Murase, K. Ono, Y. Yamauchi, M. Fujita, *J. Am. Chem. Soc.* **2010**, *132*, 15553 – 15555; c) T. Osuga, T. Murase, M. Fujita, *Angew. Chem. Int. Ed.* **2012**, *51*, 12199 – 12201; *Angew. Chem.* **2012**, *124*, 12365 – 12367; d) T. Osuga, T. Murase, M. Hoshino, M. Fujita, *Angew. Chem. Int. Ed.* **2014**, *53*, 11186 – 11189; *Angew. Chem.* **2014**, *126*, 11368 – 11371.

[21] In the equilateral-triangular prism model, the spin Hamiltonian with six $S = 1/2$ spins was numerically diagonalized to give eigenenergies, from which the temperature dependence of $\chi_p T$ was calculated.

[22] *Gaussian 09*, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[23] K. Yamaguchi, T. Kawakami, Y. Takano, Y. Kitagawa, Y. Yamashita, H. Fujita, *Int. J. Quantum Chem.* **2002**, *90*, 370 – 385.

[24] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa, T. Takui, *Phys. Chem. Chem. Phys.* **2014**, *16*, 9171 – 9181.

[25] Because of the low solubility of (**5**-Ag^+-**5**)·PF_6^-, (**5**-Ag^+-**5**)·OTf^- was used for measuring the UV-vis spectrum (see Figure S8). The X-ray crystal structure analyses showed these two complexes to be isomorphic. We could not analyze fully the crystal structure of (**5**-Ag^+-**5**)·OTf^- because of the disorder structure of the OTf ion.

[26] The complex (**5**-Ag^+-**5**)·OTf^- was prepared by the similar procedure using AgOTf. See the Supporting Information for detail.

[27] CCDC 1473133 [(**5**-Ag^+-**5**)·PF_6^-] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[28] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441 – 451; b) D. M. P. Mingos, *J. Chem. Soc. Dalton Trans.* **1996**, 561 – 566.

[29] a) B. E. Myers, L. Berger, S. A. Friedberg, *J. Appl. Phys.* **1969**, *40*, 1149 – 1151; b) B. Chiari, A. Cinti, L. David, F. Ferraro, D. Gatteschi, O. Piovesana, P. F. Zanazzi, *Inorg. Chem.* **1996**, *35*, 7413 – 7418.

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