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A Luminescent Heterometallic Dirhodium–Silver Chain

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A novel one-dimensional (1D) heterometallic chain, $\{[Rh_2(dfpma)_2(MeCN)_4]_2[Ag(MeCN)_4]\}[PF_6]_5$ (**1**), is afforded from the in situ reaction of $[ClRh(cod)]_2$ with $[Ag(MeCN)_4][PF_6]$ and dfpma (dfpma = bis(difluorophosphine)methylamine). Dichroic crystals, which are obtained from $MeCN/Et_2O$ solutions, crystallize in the monoclinic space group *C*2/*m* with $a = 13.570(5)$ Å, $b = 20.895(9)$ Å, $c = 13.810(6)$ Å, $\beta = 104.904(7)°$, $V = 3784(3)$ Å^3, $Z = 4$. X-ray diffraction studies reveal an asymmetric unit comprising two Rh^I_2 dimers and a square planar Ag^I cation; this subunit propagates to form a 1D heterometallic chain. Compound **1** displays novel spectroscopic properties in the solid state, including temperature-dependent luminescence.

One-dimensional (1D) extended systems have captured the imaginations of chemists interested in the ground-up design of "molecular wires".[1−3] The construction of such materials from discrete molecular fragments provides the opportunity to tune optical, electrical, and magnetic properties of the extended array. Methods for the preparation of 1D metal systems include the covalent linkage of dimers,[4] the construction of chains possessing direct metal−metal interactions,[5−7] or the noncovalent assembly of homometallic and heterometallic complexes of d^8, d^{10}, and s^2 metal centers.[8−12] We now report the combination of these disparate synthetic approaches to produce a $[Rh^I_2\cdots Ag^I\cdots Rh^I_2]_n^{5+}$ 1D chain, formed from the encapsulation of a d^{10} $[Ag(MeCN)_4]^+$ cation by two valence-symmetric Rh^I_2 dications, $[Rh_2(dfpma)_2(MeCN)_4]^{2+}$ (dfpma = $MeN(PF_2)_2$).

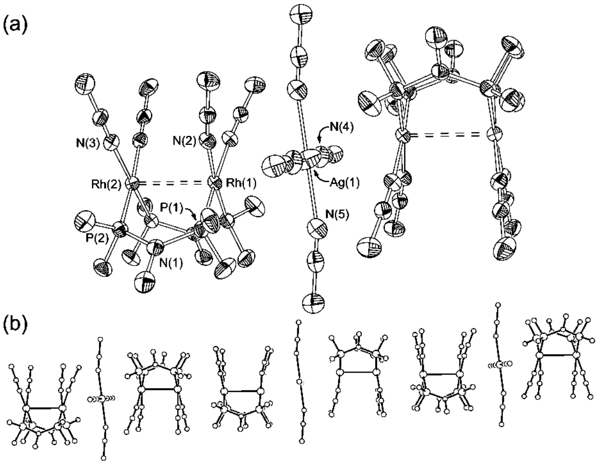

Figure 1. (a) Monomer and (b) chain structures of **1**. The PF_6^- anions have been removed for clarity.

Crystalline $\{[Rh^I_2(dfpma)_2(MeCN)_4]_2[Ag^I(MeCN)_4]\}(PF_6)_5$ (**1**) may be isolated in low yields from the reaction of $Rh^{II}_2(dfpma)_3Cl_4$ with two equiv of $AgPF_6$ in MeCN/THF solution. Conversely, higher yields of **1** are afforded from the reaction of $AgPF_6$ with $[ClRh(cod)]_2$ in MeCN, followed by filtration and treatment with dfpma to give a dark red solution. Slow addition of ether by vapor diffusion at room temperature yields **1** as large red-green iridescent crystals. The dirhodium subunit of the 1D chain, $[Rh^I_2(dfpma)_2(MeCN)_4][PF_6]_2$ (**2**), may be independently prepared by utilizing $TlPF_6$ in place of the silver salt.

The heterometallic chain emerges prominently in the solid-state structure of **1** (Figure 1).[13] The 1D chain, which is surrounded by the PF_6^- anions, propagates perpendicularly

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(1) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1−3.
(2) *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; NATO ASI Series; Kluwer: Dordrecht, 1992.
(3) Mark, J. E.; Allcock, H. R.; West, R., *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, New Jersey, 1992.
(4) D'Alfonso, G. *Chem.*−*Eur. J.* **2000**, *6*, 209−215.
(5) Klüfers, P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 70.
(6) Masciocchi, N.; Moret, M.; Cairati, P.; Ragaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, 471.
(7) Finniss, G. M.; Canadell, E.; Campana, C.; Dunbar, K. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2772.
(8) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.
(9) Balch, A. L. In *Metal*−*Metal Bonds and Clusters in Chemistry*; Fackler, J. P., Jr., Ed.; Plenum: New York, 1990; pp 299−309.
(10) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1.
(11) Williams, J. M.; Schultz, A. J. In *Molecular Metals*; Hatfield, W. E., Ed.; Plenum Press: New York, 1979; p 337−368.
(12) Fackler, J. P. *Prog. Inorg. Chem.* **1976**, *21*, 55.

(13) Crystal data for **1**: $C_{14}H_{24}Ag_{0.50}F_{23}N_8P_{6.50}Rh_2$, fw = 1202.47, monoclinic, space group *C*2/*m*, $a = 13.570(5)$ Å, $b = 20.895(9)$ Å, $c = 13.810(6)$ Å, $\beta = 104.904(7)°$, $V = 3784(3)$ Å^3, $Z = 4$, $D_c = 2.111$ Mg/m^3, $F(000) = 2328$, λ(Mo Kα) = 0.71069 Å, $T = 183$ K, $\mu = 1.537$ mm^{-1}, $2\theta_{max} = 46.58°$, 7662 reflections were collected with 2800 unique ($2.48° \leq \theta \leq 23.29$; $R_{int} = 0.0275$), R1 = 0.0262, wR2 = 0.0664, GOF = 1.011, residuals based on $I \geq 2\sigma(I)$, crystal dimension 0.08 mm × 0.11 mm × 0.13 mm. Data were collected on a Siemens 3-circle platform diffractometer with CCD detector. The structure was solved by the Patterson heavy atom method/standard difference Fourier techniques. Hydrogen atoms were placed in calculated positions.

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to the crystallographic *b* axis, bisecting the unique angle β of the unit cell. A Rh(1)−Rh(2) distance of 3.0498(10) Å within the dimer subunit (Figure 1a) indicates the absence of a formal metal−metal bond between two Rh^I centers, but it is short enough to suggest some degree of $d_{z^2}\sigma^*$ stabilization by the energetically proximate $p_z\sigma$ orbitals.[14−16] An angle of 10.2° between the two canted Rh^I coordination planes is significantly smaller than that observed in open-boat structures of Rh^I_2−pyrazolate complexes.[17] The observation of a valence symmetric Rh^I_2 core is a departure from our previous studies of Group 9 dfpma coordination chemistry. Whereas valence desymmetrized $M_2^{II,0}$ (M = Rh, Ir) cores prevail when three dfpma ligands coordinate the bimetallic center,[18−24] two dfpma ligands are apparently unable to drive the internal disproportionation of the Rh^I_2 core. Accordingly, the asymmetry observed in the PNP backbone of $M_2^{0,II}(dfpma)_3$ complexes[21] is not observed in **1**, which displays symmetric Rh−P (d_{avg} = 2.1586(11) Å) and P−N (d_{avg} = 1.657(3) Å) bond distances. An average Rh−N bond distance of 2.058(3) Å is consistent with the Rh−N distances measured for other Rh^I−acetonitrile complexes containing π-acid ligands.[25] As shown in Figure 1b, two of these $[Rh^I_2(dfpma)_2(MeCN)_4]$ subunits are sandwiched between $[Ag(MeCN)_4]^+$ centers. These adjacent dirhodium subunits are eclipsed (required by symmetry) and rotated by 180°. The Rh(2)···Rh(2)′ contact between dimers is 3.902(2) Å with the metal−metal axes offset by 0.211 Å.

The structure of **1** is further distinguished by the coordination geometry about the Ag^I cation. Though transition metal−silver complex adducts are well established,[26−28] in **1** the $[Ag(MeCN)_4]^+$ cation fragment assumes a square-planar geometry as opposed to the tetrahedral geometry that is normally observed for Ag^I coordinated by four acetonitrile ligands.[29−31] The AgN_4 moiety is rigorously planar, as required by crystallographic symmetry, though distinctly different Ag−N bond lengths of 2.290(6) and 2.409(6) Å are observed. The $[Ag(MeCN)_4]^+$ cation is displaced by 0.772 Å above the Rh(1)−Rh(2) vector, and the Ag(1) metal center is located 3.4074(11) Å from Rh(1). Rh(2)−Rh(1)−Ag(1) and Rh(1)−Ag(1)−N(5) bond angles of 166.92(4)° and 84.10(12)°, respectively, are a result of canted AgN_4 planes. This canting directs the occupied d_{z^2} orbital of silver toward the empty p_z orbitals of the offset rhodium dimers.

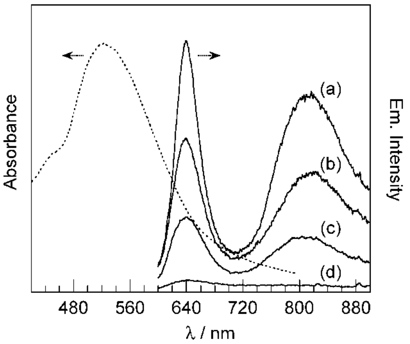

Figure 2. Solid-state absorption and emission spectra of **1**. Emission spectra were acquired at (a) 15, (b) 77, (c) 150, and (d) 298 K with λ_{ex} = 546 nm.

Though emission from d^8−d^{10} mixed-metal complexes is well established,[32,33] in the case of **1**, alignment of the metal-based orbitals along the 1D chain gives rise to curious optical properties. Large hexagonal crystals of **1** are dichroic when viewed with polarized light. The crystal face normal to the metal chain axis is brilliant green, whereas crystal faces viewed from other angles are pale yellow. A strong band at 522 nm and a shoulder at 460 nm dominate the absorption spectrum of **1**.[34] Solids of **1** at room temperature exhibit weak luminescence bands at 641 and 815 nm. Upon cooling, the intensity of these bands increases significantly (see Figure 2). At 15 K, the 641-nm emission decays with a lifetime of 60 ps, whereas the 815-nm emission displays biexponential kinetics (τ_0 = 130 ps, τ_1 = 540 ps). In contrast, a single, intense 547-nm absorption band is observed in the solid-state absorption spectrum of individual rhodium dimer subunits, **2**; a corresponding emission band is centered at λ_{max} = 665 nm (τ = 140 ps). As evidenced by wavelength-dependent lifetimes, each emission band of **1** appears to be derived from a different excited state. This contention is further supported by the excitation spectra of **1** (see Supporting Information), which reveal distinctly different absorption manifolds for each emission band. The spectral properties of the high-energy emission band correspond to an intense band with λ_{max} = 575 nm in the excitation spectrum. The chracteristics of the transition are in accord with the molecular $d_{z^2}\sigma^* \rightarrow p_z\sigma$ excited state of binuclear d^8 complexes.[35] The similarity of the energy maximum and width between the 641-nm and 665-nm emission bands of **1**

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(14) Mann, K. R.; Gordon, J. G.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553.
(15) Mann, K. R.; Gray, H. B. *Adv. Chem. Ser.* **1979**, *173*, 225.
(16) Rice, S. F.; Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *Coord. Chem. Rev.* **1982**, *43*, 349.
(17) Tejel, C.; Villoro, J. M.; Ciriano, M. A.; López, J. A.; Equizábal, E.; Lahoz, F. J.; Bakhmutov, V. I.; Oro, L. A. *Organometallics* **1996**, *15*, 2967.
(18) Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 4054.
(19) Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 2969.
(20) Kadis, J.; Shin, Y.-g. K.; Dulebohn, J. I.; Ward, D. L.; Nocera, D. G. *Inorg. Chem.* **1996**, *35*, 811.
(21) Heyduk, A. F.; Macintosh, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **1999**, *121*, 5023.
(22) Odom, A. L.; Heyduk, A. F.; Nocera, D. G. *Inorg. Chim. Acta* **2000**, *297*, 330.
(23) Heyduk, A. F.; Nocera, D. G. *Chem. Commun.* **1999**, 1519.
(24) Heyduk, A. F.; Nocera, D. G. *J. Am. Chem. Soc.* **2000**, *122*, 9415.
(25) Prater, M. E.; Pence, L. E.; Clérac, R.; Finniss, G. M.; Campana, C.; Auban-Senzier, P.; Jérome, D.; Canadell, E.; Dunbar, K. R. *J. Am. Chem. Soc.* **1999**, *121*, 8005.
(26) Sykes, A.; Mann, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 8252.
(27) Balch, A. L.; Ghedini, M.; Oram, D. E.; Reedy, P. E. *Inorg. Chem.* **1987**, *26*, 1223.
(28) Ladd, J. A.; Hope, H.; Balch, A. S. *Organometallics* **1984**, *3*, 1838.
(29) Jones, P. G.; Bembeneck, E. *Z. Kristallogr.* **1993**, *208*, 213.
(30) Blaschette, A.; Jones, P. G.; Hamman, T.; Naveke, M.; Schomburg, D.; Cammenga, H. K.; Epple, M.; Steppuhn, I. *Z. Anorg. Allg. Chem.* **1993**, *619*, 912.
(31) Nilsson, K.; Oskarsson, A. *Acta Chem. Scand. Ser. A* **1984**, *38*, 79.
(32) Yip, H. K.; Lin, H. M.; Wang, Y.; Che, C. M. *Inorg. Chem.* **1983**, *32*, 3402.
(33) Striplin, D. R.; Crosby, G. A.; *J. Phys. Chem.* **1995**, *99*, 7977.
(34) Solid-state absorption spectra of **1** and **2** were obtained as mineral oil mulls dispersed on filter paper. Emission data were collected for crystals ground to a powder and cooled in a liquid helium cryostat (λ_{exc} = 546 nm).

and **2**, respectively, suggests an excited-state parentage that is derived from the Rh^{I}_2 unit. The blue-shifted emission of **1** relative to **2** is ascribed to the proximity of the $[Ag(MeCN)_4]^+$ cation. The filled p_z orbital of the Ag^I may destabilize the empty $p_z\sigma$ orbital of the Rh^I dimer, shifting the $d_{z^2}\sigma^* \rightarrow p_z\sigma$ transition to higher energy. Conversely, the 815-nm emission band of **1** corresponds to an intense 701-nm band in the excitation spectrum. A vestige of the transition is observed as a low-energy shoulder in the absorption spectrum of Figure 2.

The $[Rh^{I}_2{\cdots}Ag^{I}{\cdots}Rh^{I}_2]_n^{5+}$ extended chain dissociates in solution, as illustrated by identical solution-phase NMR spectra for **1** and **2**. ^{1}H NMR spectra of the two compounds in CD_3CN display two resonances, assigned to the methyl group of the bridging dfpma ligands (3.07 ppm) and uncoordinated MeCN (1.96 ppm), which exchanges with the CD_3CN solvent. ^{31}P NMR spectra show an apparent triplet resonance at 138 ppm for the phosphines of the dfpma ligands and a low-frequency resonance for the PF_6^- anions. A pair of doublets is observed in the ^{19}F NMR for the dfpma ligands; a single ^{19}F resonance is also observed for the PF_6^- anions.

In conclusion, symmetric Rh^{I}_2 complexes are obtained when two dfpma ligands bridge the binuclear core. These dimers form adducts with Ag^I to give a $[Rh^{I}_2{\cdots}Ag^{I}{\cdots}Rh^{I}_2]^{5+}$ structural unit that repeats to form a linear chain of metal atoms. The perturbation of the d^{10} Ag(I) cation on the electronic properties of the 1D chain is evident upon comparison of the solid-state absorption and emission properties of **1** and **2**. Further studies of the structural and electronic features of this 1D chain incorporating other square planar d^{10} metals should prove intriguing.

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Supporting Information Available: Detailed synthesis for the preparation of **1** and **2** and absorption, emission, and excitation spectra and X-ray crystallographic files in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462.