

[CoAu₂(CN)₄(NITpPy)₂(H₂O)₂]_n: A New 2-D Interdigitating Complex Containing Dicyanoaurate(I) Anion, a Radical, and Cobalt(II) Ion Incorporating Gold···Gold and Hydrogen Bonding Interactions

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A novel complex, {[CoAu₂(CN)₄(NITpPy)₂(H₂O)₂]_n, **1**, containing the cobalt(II) ion, dicyanoaurate(I) anion, and nitronyl nitroxide radical building blocks, has been prepared and structurally characterized by single-crystal X-ray analysis. The structure of complex **1** illustrates that aurophilicity and hydrogen bonding interactions increase dimensionality, generating a 2-D interdigitating system. The spectroscopic and magnetic properties have been investigated.

The design of multidimensional supramolecular assemblies is an area of intense current interest.¹ This is due not only to their potential applications in electrical conductivity, molecule-based magnets, molecular absorption, ion-exchange, heterogeneous catalysis, etc., but also to their intriguing structural diversity.² In general, the incorporation of moieties capable of transforming hydrogen bonding interactions into supramolecular assemblies is perhaps the

most well-developed method for increasing structural dimensionality.³ Many complexes containing gold(I) centers are known to form weakly bonding interactions with themselves; these “aurophilic” interactions have also the same order-of-magnitude strength as hydrogen bonds (ca. 7–11 kcal/mol).⁴ The supramolecular chemistry of Au(I) is replete with systems that are polymeric by virtue of these Au–Au interactions.⁵

On the other hand, nitronyl nitroxide radicals are useful paramagnetic building blocks⁶ which offer opportunities to design multidimensional and multispin systems.

However, the number of studies dealing with both Au(I) and radicals is still rather limited.⁷ To devote attention to a new example of a three constituent system, in this Com-

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munication we report the synthesis, crystal structure, and spectroscopic and magnetic properties of a novel complex, $\{[\text{CoAu}_2(\text{CN})_4(\text{NITpPy})_2(\text{H}_2\text{O})_2]\}_n$, **1** (NITpPy is 2-(4'-pyridyl)-4, 4, 5, 5-tetramethylimidazole-1-oxyl-3-oxide, and the formula is $\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}_2$), where the presence of $\text{Au}\cdots\text{Au}$ and hydrogen bonding interactions has effectively increased the dimensionality. To our knowledge, this is the first complex containing dicyanoaurate(I) anion, a radical, and a 3d metal.

All reagents used in the synthesis were of analytical grade and were used without further purification. NITpPy was prepared according to the procedure previously reported.⁸ IR spectra were obtained using a Shimadzu IR-408 infrared spectrometer in the $4000\text{--}600\text{ cm}^{-1}$ region. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C analyzer. The luminescent spectra were measured on a Shimadzu RF540 PC spectrophotometer. *Cyanide salts are toxic and should be handled with caution!*

The dark green crystals of **1** were obtained by addition of an aqueous solution of $\text{K}[\text{Au}(\text{CN})_2]$ to a methanolic mixed solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NITpPy.⁹ The crystal is stable to air at room temperature and in a dark environment, but not very stable under heated or lighted conditions.

The X-ray crystal structure of **1** confirms the molecular formula of $\text{CoAu}_2(\text{CN})_4(\text{NITpPy})_2(\text{H}_2\text{O})_2$ and reveals a two-dimensional interdigitating system.¹⁰ The cobalt(II) ion is coordinated to two organic radicals, two dicyanoaurate(I) anions in the equatorial plane, and two water molecules in axial positions (see Figure 1). In the complex, each cobalt assumes a distorted octahedral CoN_4O_2 coordination polyhedron, which is made up of four nitrogen atoms from the cyanide groups and the pyridyl rings in a plane and two oxygen atoms of the H_2O molecules in trans-positions. The crystal comprises two kinds of one-dimensional chains. Each $\text{CoAu}_2(\text{CN})_4(\text{NITpPy})_2(\text{H}_2\text{O})_2$ unit linked by a $\text{Au}\text{--}\text{Au}$ bond forms an infinite zigzag chain with short $\text{Au}\cdots\text{Au}$ distances

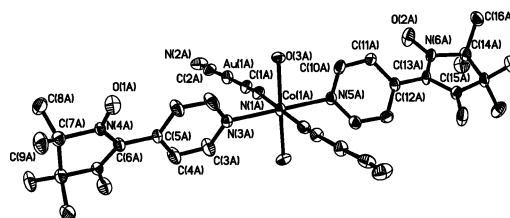


Figure 1. Perspective view of unit of the complex **1** with hydrogens omitted for clarity. Selected bond lengths (\AA) and angles (deg): $\text{Co}(1\text{A})\text{--}\text{N}(3\text{A})$ 2.187(13), $\text{Co}(1\text{A})\text{--}\text{N}(5\text{A})$ 2.142(13), $\text{Co}(1\text{A})\text{--}\text{O}(3\text{A})$ 2.063(9), $\text{Co}(1\text{A})\text{--}\text{N}(1\text{A})$ 2.053(12), $\text{C}(1\text{A})\text{--}\text{Au}(1\text{A})\text{--}\text{C}(2\text{A})$ 178.1(5), $\text{N}(1\text{A})\text{--}\text{C}(1\text{A})\text{--}\text{Au}(1\text{A})$ 178.9(12), $\text{N}(1\text{A})\text{--}\text{Co}(1\text{A})\text{--}\text{N}(3\text{A})$ 90.0(3), $\text{O}(3\text{A})\text{--}\text{Co}(1\text{A})\text{--}\text{N}(3\text{A})$ 90.8(2), $\text{N}(5\text{A})\text{--}\text{Co}(1\text{A})\text{--}\text{N}(3\text{A})$ 180.000(1).

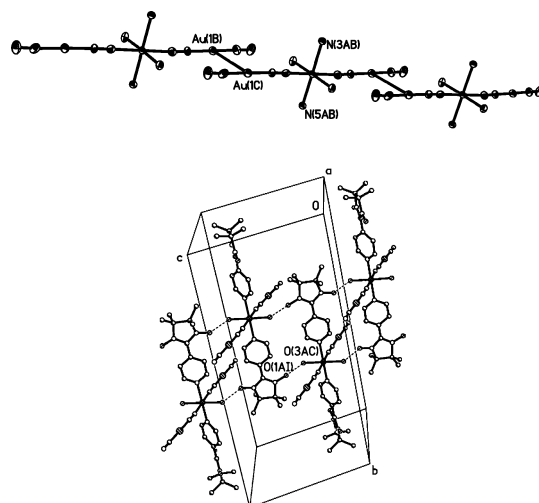


Figure 2. (top) View showing the zigzag chains of **1** via gold-gold interactions (for the sake of clarity, only the N atom of the NITpPy ligand is included); (bottom) view showing the ladder chains of **1** via hydrogen bonding interactions. The $\text{Au}(1\text{B})\text{--}\text{Au}(1\text{C})$ distance is 3.331 \AA , and the $\text{O}(1\text{AI})\text{--}\text{O}(3\text{AC})$ distance is 2.758 \AA .

of 3.331 \AA , less than the sum of the van der Waals radii of Au (3.60 \AA) (see Figure 2 (top)). The shortest interchain contacts between nitroxide groups are equal to $\text{O}(1\text{AD})\text{--}\text{O}(2\text{AH}) = 3.180\text{ \AA}$ (see Supporting Information). All the oxygen atoms of the coordination water molecules and the oxygen atoms of half NO groups between the two adjacent chains are involved in H-bond interactions with $\text{O}(1\text{AI})\cdots\text{O}(3\text{AC})$ distances of 2.758 \AA . By these contacts, $\text{CoAu}_2(\text{CN})_4(\text{NITpPy})_2(\text{H}_2\text{O})_2$ forms another ladder chain along the c -axis (see Figure 2 (bottom)). The two kinds of one-dimensional chains are cross-linked through $\text{CoAu}_2(\text{CN})_4(\text{NITpPy})_2(\text{H}_2\text{O})_2$ units, which further give a two-dimensional system in the ac -plane (Figure 3). The sheets are not planar but accidented. The adjacent accidented sheets are parallel and interdigitated with each other. In this disposition, the NITpPy molecules can interpenetrate into the accidented 2-D array in the ac -plane.

The IR spectra of **1** (solid) shows two sharp ν_{CN} bands at 2150 and 2200 cm^{-1} , which can be attributed to the $\text{C}\equiv\text{N}$ stretching vibration. The splitting of $\nu_{\text{C}\equiv\text{N}}$ indicates the presence of two different coordination modes (monodentate and bridging) of the cyanide ligands. It is well-known that the formation of a cyanide bridge shifts ν_{CN} toward higher frequencies.¹¹ The strong band at 2200 cm^{-1} may therefore be attributed to ν_{CN} of the bridging cyanides and that at 2150

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- (9) Synthesis of **1**: A 10 mL methanolic solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36.7 mg, 0.1 mmol) was added to a methanolic solution of NITpPy (47.0 mg, 0.2 mmol). While the mixture was being stirred, a 5 mL aqueous solution of $\text{K}[\text{Au}(\text{CN})_2]$ (57.6 mg, 0.2 mmol) was added to it dropwise. The resulting solution kept at room temperature for three weeks afforded dark green crystals suitable for the X-ray structural analysis. Yield: 48% based on $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{Au}_2\text{CoN}_{10}\text{O}_6$: C, 31.65; H, 3.39; N, 13.19. Found: C, 31.68; H, 3.41; N, 13.21.
- (10) Crystal data: $\text{C}_{28}\text{H}_{36}\text{Au}_2\text{CoN}_{10}\text{O}_6$, $M = 1061.53$, monoclinic, space group $C2/c$, $a = 10.944(5)\text{ \AA}$, $b = 26.094(12)\text{ \AA}$, $c = 12.596(6)\text{ \AA}$, $\alpha = 90^\circ$, $\beta = 111.541(7)^\circ$, $\gamma = 90^\circ$, $V = 3346(3)\text{ \AA}^3$, $Z = 4$, $D_c = 2.107\text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 9.294\text{ mm}^{-1}$, $T = 293(2)\text{ K}$, 7676 data collected, 2911 unique ($R_{\text{int}} = 0.0969$). Final R indices [$I > 2\sigma(I)$], $R_1(F_o) = 0.0624$, $wR_2(F_o^2) = 0.1384$. The data were collected on a Bruker Smart 1000 diffractometer. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program. CCDC reference number 225147 for **1**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-336-033. E-mail: deposit@ccdc.cam.ac.uk. www: http://www.ccdc.cam.ac.uk.)

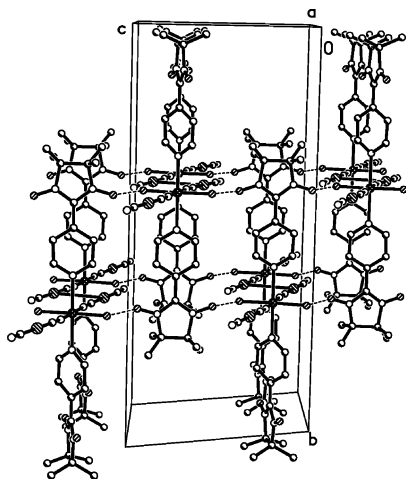


Figure 3. 2-D array in the *ac*-plane of complex **1**.

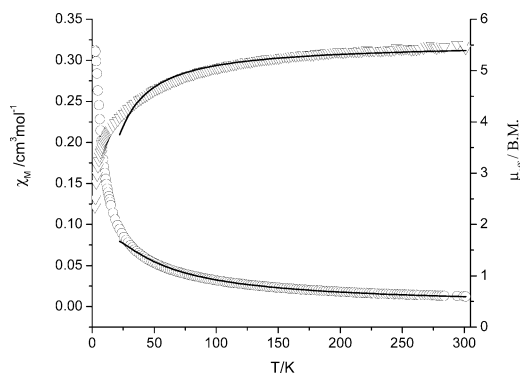


Figure 4. Plots of χ_M and μ_{eff} vs T for complex **1**, the solid line showing the best fit to the values.

cm^{-1} to the terminal ones. The diagnostic ν_{NO} vibration was found at 1360 and 1378 cm^{-1} .

Complex **1** is luminescent and exhibits spectra that are very similar to that of the NITpPy ligand alone at room temperature. Because the investigations on luminescence behavior of this kind of complex are very limited, further work is needed in this area for a explanation of luminescence of the present complex.

The magnetic susceptibility for complex **1** was measured on an MPMS SQUID susceptometer over the temperature range 2–300 K with an applied field of 10000 G. The plots of χ_M and μ_{eff} versus T are shown in Figure 4. A μ_{eff} value of 5.43 μ_B was observed at room temperature; this value is

higher than the expected spin-only value of 4.58 μ_B for one $S_{\text{Co}} = 3/2$ and two $S_{\text{rad}} = 1/2$ spins, indicating that an important orbital contribution of cobalt(II) ($^3T_{1g}$) ion is involved. Upon cooling, the μ_{eff} value decreases regularly, approaching a minimum around 2 K with $\mu_{\text{eff}} = 2.34 \mu_B$.

Neglecting magnetic interaction between neighboring NO groups of NITpPy radicals through space, the decrease of the effective magnetic moment versus the temperature presumably originates from the following factors: (i) the orbital degeneracy of the cobalt(II) center, and (ii) magnetic interaction between cobalt(II) ion and nitroxide radical through the pyridine ring. A quantitative treatment of the susceptibility, including the orbital degeneracy of the cobalt(II) center, cannot be carried out due to the lack of a theoretical model for this kind of system. As a preliminary treatment, we used the spin Hamiltonian $\hat{H} = -2J(\hat{S}_{\text{Co}}\hat{S}_{\text{rad}1} + \hat{S}_{\text{Co}}\hat{S}_{\text{rad}2})$ and deduced the resulting magnetic susceptibility expression given by eq 1:

$$\chi_M = \{[Ng^2\beta^2/4k(T - \theta)](A/B)\} + N\alpha \quad (1)$$

$$A = 10 + \exp(-5J/kT) + 10 \exp(-2J/kT) + 35 \exp(3J/kT)$$

$$B = 2 + \exp(-5J/kT) + 2 \exp(-2J/kT) + 2 \exp(3J/kT)$$

$$N\alpha = 120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$$

where J corresponds to the coupling between the cobalt(II) ion and the radical and $N\alpha$ is the temperature-independent paramagnetism. The least-squares analysis of magnetic susceptibility data in the temperature range from 300 to 20 K leads to $J = -6.04 \text{ cm}^{-1}$, $g = 2.25$, $\theta = 0.97 \text{ K}$, and $R = 3.37 \times 10^{-3}$ (the agreement factor defined as $R = \sum(\chi_{\text{obs}} - \chi_{\text{cal}})^2 / \sum(\chi_{\text{obs}})^2$); the fitting for the magnetic susceptibility data below 20 K was unsuccessful, which may be attributed to the spin-orbit coupling effect in cobalt(II) centers.

In conclusion, when the dicyanoaurate anion and radical are used as building blocks, the interplay between covalent and aurophilic bonding interactions has been shown to be an appropriate approach to prepare Au-radical-M compounds exhibiting interesting structures and physical properties. This is the first example of a complex containing gold(I), a radical, and cobalt.

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Supporting Information Available: Figure of projection showing the zigzag chains of **1** via gold-gold interactions. Magnetic susceptibility data. Crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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