

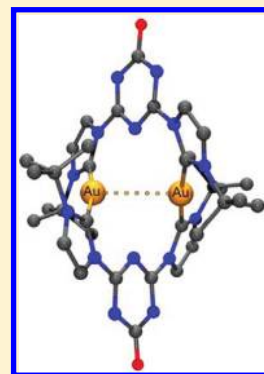
Triazinone-Bridged Neutral Dinuclear Gold(I)-NHC Complex

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S Supporting Information

ABSTRACT: We report the synthesis and characterization of a neutral pincer-type μ^2 - $\eta^2(1\kappa\text{C}_{\text{carbene}}:2\kappa\text{C}'_{\text{carbene}})$ -(C*-N-C*)-ligand-coordinated gold(I)-NHC complex with an emission wavelength of 452 nm. Solid-state structure analysis confirms the dinuclear structure of this complex.



Gold(I)-NHC complexes have recently been shown to be interesting organometallic compounds for catalysis as well as phosphorescent emitters for OLEDs.^{1,2} Mononuclear as well as di- or multinuclear complexes have been reported.² In the mononuclear complexes, the d^{10} -configuration prevents the stabilization of excited states due to the ligand field of the metal, so that the photophysical processes are dominated by intraligand charge transfer (ILCT) and ligand to metal charge transfer (LMCT) processes.³ Thus, it was possible to synthesize blue-phosphorescent Au(I)-carbene complexes⁴ as well as red-emitting Au(I)-thiolate complexes⁵ using different ligands.

Di- and multinuclear Au(I) complexes are known to show aurophilic interactions;^{1,6,7} that is, the intermetallic distance is shorter than the sum of the van der Waals radii.⁸ This effect was first reported by Schmidbaur and describes a bonding type, associated with a bond energy of 5–10 kcal/mol, comparable to that of standard hydrogen bonds.⁹ Since most of these complexes emit from a ³LMCT state, the degree of aurophilic interaction has a crucial influence on the emission properties. It energetically stabilizes the LUMO of the complex, due to empty p_z -orbitals mixing with (destabilized) occupied d_z -orbitals, lowering the energy gap of the frontier orbitals, and leads to a bathochromic shift of the emission wavelength.³ A hypsochromic shift can be observed when increasing the metal–metal distance by elevating the temperature and thus decreasing the metallophilic interaction.¹⁰

Dinuclear Au(I)-NHC complexes have also been reported with a variety of bridging motifs.^{2,11} Recent publications reported chiral dinuclear gold(I) complexes;¹² other examples were used for oxidation chemistry at the gold(I) centers.¹³ However, to the best of our knowledge, all reported complexes have been cationic, since the ligands themselves were neutral. We recently developed an anionic C*-N-C* ligand with a triazinone core as the bridging motif and reported a series of neutral dinuclear Ag(I) complexes.¹⁴ These silver complexes showed similar

metallophilic interactions; therefore we tried to also synthesize the corresponding Au(I) complex. We here report the synthesis and structural and spectroscopic characterization of a dinuclear Au(I) complex, di[4,6-bis(1-*tert*-butylimidazoline-2-ylidene-3-yl)-5*H*-1,3,5-triazin-2-one-5-ide]digold(I) (**2**).

We synthesized **2** by transmetalation of the silver(I) complex **1** with Au(THT)Cl (Scheme 1). Suitable crystals for X-ray diffraction could be obtained by slowly condensing diethyl ether into a solution of **2** in dichloromethane (Figure 1).

As in the analogous Ag(I) complex, the crystal structure of **2** contains *M* and *P* helical structures in the unit cell with the two gold centers located on a C_2 -axis.¹⁴ At 3.28 Å, the gold–gold distance is in the typical range for aurophilic interactions, smaller than the sum of the van der Waals radii.⁸

Figure 2 shows a manifold of hydrogen bonds in the crystal structure. As observed for the silver complexes, also the Au(I) complex **2** shows intermolecular interactions between the triazinone fragment and the NHC backbone (Figure 2: I, II, VI). Additional intermolecular interactions can be found between the triazinone fragment and a hydrogen atom at the *tert*-butyl group (Figure 2: III) as well as intramolecular interactions between the triazinone fragment and two *tert*-butyl groups (Figure 2: IV and V).

■ PHOTOLUMINESCENCE MEASUREMENTS

The absorption and emission spectra of complex **2** are shown in Figures 3 and 4. The absorption maximum was observed at a wavelength of 220 nm independent from the measurement conditions (poly(methyl methacrylate) (PMMA) film (2%) or in the solid state (100% film)) (Figure 3).

The maxima of the emission wavelength (Figure 4) have been observed at 452 nm in PMMA (2%) and 464 nm in the

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Scheme 1

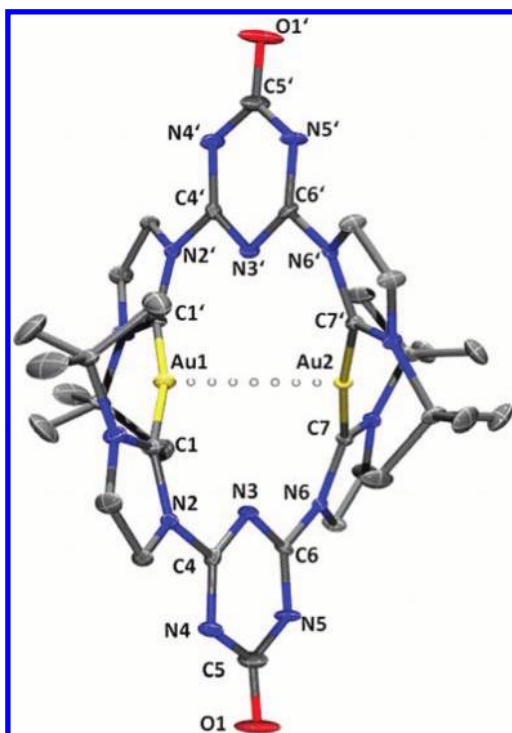
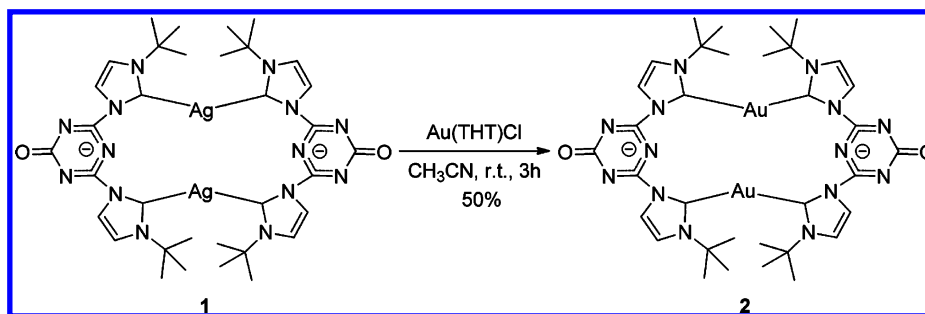


Figure 1. Molecular structure of compound **2** in $C2/c$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected distances (\AA), angles (deg), and torsional angles (deg): Au1...Au2 3.2797(9); Au1–C1 2.046(8); C5–O1 1.228(9); Au2–C7 2.057(6); Au1–N3 2.879(6); Au2–N3 2.982(6); C1–Au1–C1' 169.6(3); C7–Au2–C7' 173.7(3); N4–C4–N2–C1 $-166.2(7)$; N5–C6–N6–C7 $-154.2(7)$.

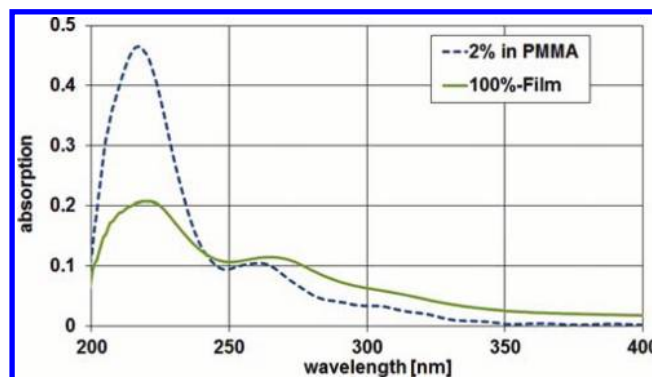


Figure 3. UV-vis absorption spectra of complex **2** in PMMA (2%) and 100% film.

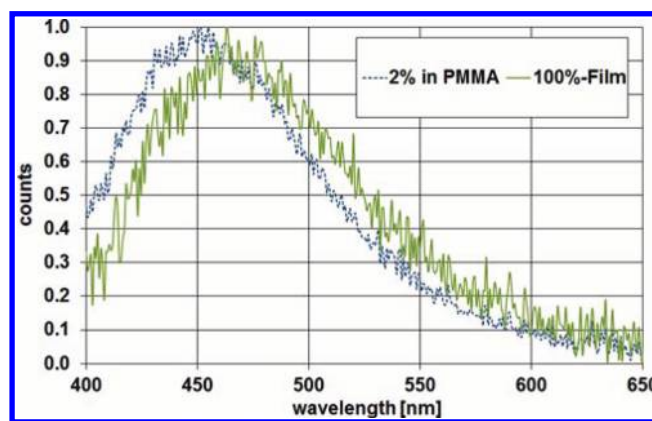


Figure 4. Emission spectra of complex **2** (excitation wavelength, λ_{exc} 300 nm, room temperature). 2% in PMMA: X_{RGB} 0.1826, Y_{RGB} 0.1898 (X and Y are CIE coordinates at room temperature); emission wavelength, λ_{em} 452 nm; quantum yield, radiant exposure under N_2 , ϕ 0.15; average decay lifetime, τ_M 1.64 μs ; 100% film: X_{RGB} 0.1983, Y_{RGB} 0.2413, λ_{em} 464 nm, ϕ 0.06.

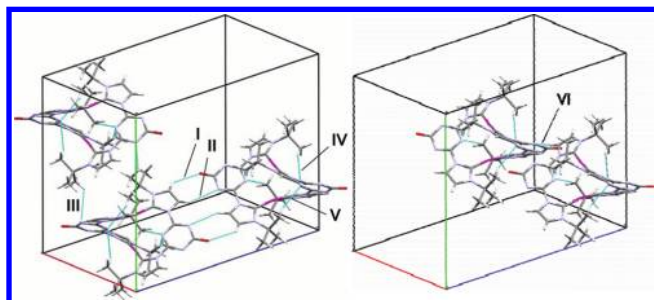


Figure 2. Part of the unit cell of **2** showing intra- and intermolecular hydrogen bonds along the b - and c -axes (left) as well as the a -axis. Distances (in \AA): I 2.493, II 2.712, III 2.949, IV 2.902, V 2.882, VI 2.438.

solid state (100% film). The slightly bathochromic shift could be caused by a small increase of the intramolecular auriphilic interaction as a result of geometrical changes in the complex due to packing effects. Compared to previously reported intermolecular Au...Au interactions caused by aggregation of the metal centers with possible additional emission bands at higher wavelengths,¹⁰ this shift is not significant. Compared to the analogous silver complex, the emission wavelength maximum (417 nm)¹⁴ is significantly shifted toward higher wavelengths.

CONCLUSION

We were able to synthesize and characterize the first example of a novel neutral dinuclear Au(I) complex with an anionic C*-N-C* NHC ligand. Each of the two gold centers is coordinated by both bidentate ligands, which are helically twisted around the metal–metal axis. The complex shows a strong photoluminescent emission in the blue region of the spectrum at 460 nm and no significant shift of the emission maximum due to aggregation.

EXPERIMENTAL SECTION

General Experimental Methods. All chemicals used were obtained from commercial suppliers and used without further purification. The silver(I)-NHC complex¹⁴ and Au(THT)Cl¹⁵ were synthesized according to published procedures. The NMR spectra were recorded with a Bruker AC 300 P spectrometer and referenced internally to the references of the solvent. ¹H NMR spectra were recorded at 300.13 MHz; ¹³C NMR spectra at 75.475 MHz. Elemental analyses were measured by the analytical laboratory of the department using a Eurovektor Hekatech EA-3000 elemental analyzer.

Synthesis of Di[4,6-bis(1-tert-butylimidazoline-2-ylidene-3-yl)-5H-1,3,5-triazin-2-on-5-ide]digold(II), 2. A 100 mg amount of silver(I)-NHC complex **1** and 71.8 mg of Au(THT)Cl are stirred in 10 mL of acetonitrile at room temperature for 3 h under exclusion of light, whereupon the formed suspension is filtered through Celite and concentrated in vacuo. The raw product is precipitated by addition of about 20 mL of diethyl ether, filtrated, washed twice with 10 mL of diethyl ether, then dried in vacuo to give the product as a white solid. Crystals suitable for X-ray diffraction were obtained by slowly condensing diethyl ether into a solution of **2** in dichloromethane. Yield: 60 mg (50%). ¹H NMR (CDCl₃): δ 8.05 (s, 4H, N-CH=CH), 7.12 (s, 4H, N-CH=CH), 1.49 (s, 36H, CH₃) ppm. ¹³C NMR (CDCl₃): δ 181.94 (s, C_{carbene}), 169.03 (C_{ipso}), 162.77 (C_{ipso}), 118.72 (CH), 117.82 (CH), 59.10 (C_{ipso}), 30.64 (CH₃) ppm. ESI/MS (*m/z*): 1075.3 [M - H]⁺. Anal. Calcd for C₃₄H₄₄Au₂N₁₄O₂·CH₂Cl₂: C, 36.25; H, 4.00; N, 16.91. Found: C, 36.00; H, 3.87; N, 16.95.

Structure Determination. Preliminary examination and data collection were carried out on a NONIUS κ-CCD device with an Oxford Cryosystems cooling system at the window of a sealed fine-focus X-ray tube with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The reflections were integrated. Raw data were corrected for Lorentz and polarization effects and, arising from the scaling procedure, for latent decay. An absorption correction was applied using SADABS.¹⁶ After merging, the independent reflections were all used to refine the structure. The structures were solved by a combination of direct methods^{17,18} and difference Fourier synthesis.¹⁹ All non-hydrogen atom positions were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and then refined using the SHELXL-97 riding model. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The residual electron density in the crystal structure could not be localized to specific atom positions, and therefore PLATON-SQUEEZE^{20,21} was used. Details of the structure determinations are given in the Supporting Information. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.²² All calculations were performed with the programs COLLECT,²³ DIRAX,²⁴ EVALCCD,²⁵ SIR92,¹⁷ SADABS,¹⁶ the SHELXL-97 package^{19,26,27} and ORTEP-III.²⁸ Graphics were generated and processed with the programs PLATON,^{20,21} ORTEP-III,²⁸ MERCURY,²⁹ and POV-RAY.³⁰

ASSOCIATED CONTENT

Supporting Information

The crystallographic information files of complex **2** as well as the crystallographic details of the measurements are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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