

Unprecedented η^3 -M₃ coordination mode in a terpyridine ligand

Javier E. Aguado,^a Maria José Calhorda,^{bc} M. Concepción Gimeno^{*a} and Antonio Laguna^a

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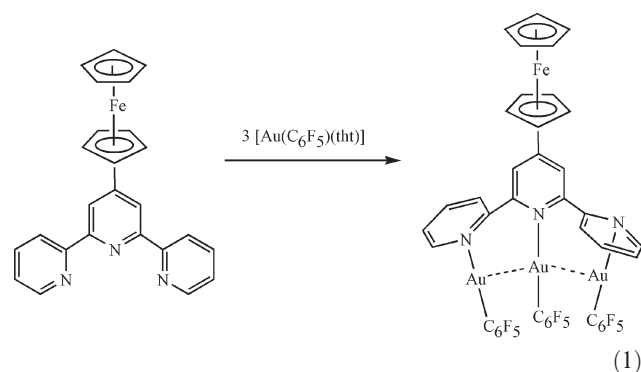
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The gold(I) complex $[\text{Au}_3(\text{C}_6\text{F}_5)_3(\eta^3\text{-Fcterpy})]$ (Fcterpy = 4'-ferrocenyl-2,2':6',2''-terpyridine) represents the first example of a terpyridine ligand bonded to three different metals. The aurophilic interactions present in the molecule may contribute to the overall stability of the system, as was shown by DFT calculations. The positive Mayer indices (0.152 and 0.138), as well as the magnitude of the binding interaction between terpy and the Au(I)L fragments, support this interpretation.

The chemistry of terpyridine ligands has been the subject of numerous studies with several metals induced by the exciting photophysical properties of metal–polypyridyl complexes.¹ In these compounds, the terpyridine acts as a chelating planar tridentate ligand and only in some examples does it act as a bidentate ligand with a non-coordinate residue.² In the past, interesting spiral arrays have been prepared with these ligands that by twisting can accommodate more than one metal center. Thus, some examples have been prepared with silver in which the terpy is bonded to two different metal centers in a supramolecular structure.³ However, the coordination mode in which the three nitrogen atoms are bonded to three different metals is unknown. Only a few complexes with terpyridine and gold have been described and these are gold(III) derivatives, such as $[\text{AuX}(\text{Rterpy})]$ (R = H, SMe, PhOMe),^{4–7} or $[\text{Au}(\text{CN})_2\text{Br}(\eta^2\text{-terpy})]$.⁸ Here we report the first example of a complex in which a substituted terpyridine ligand, 4'-ferrocenyl-2,2':6',2''-terpyridine (Fcterpy),⁹ coordinates to three different gold atoms. The ligand twists the external pyridine rings in opposite directions to accommodate the three metals and these are also bonded through aurophilic interactions that, clearly, contribute to the overall stability of the complex. This compound also represents, to the best of our knowledge, the first example of a gold(I) complex with a terpyridine ligand.

The reaction of the Fcterpy ligand with 3 equivalents of $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ in dichloromethane leads to the synthesis of the compound $[\text{Au}_3(\text{C}_6\text{F}_5)_3(\eta^3\text{-Fcterpy})]$ (Eqn. (1)). The IR spectrum shows the absorptions arising at the pentafluorophenyl rings bonded to gold(I) at 1506(s), 960(s) and 765(m) cm^{-1} . In the ¹⁹F NMR spectrum the three pentafluorophenyl rings are equivalent and consequently only three resonances appear for the *ortho*, *meta* and *para* fluorine. The ¹H NMR shows two multiplets for the α and β protons of the substituted Cp ring, a singlet for the protons of the unsubstituted Cp ring, and five resonances for the five different terpyridine protons. In the mass spectrum (LSIMS+) the molecular peak is not present but the peaks at $m/z = 781$ (40%, $[\text{M} - (\text{AuC}_6\text{F}_5)_2]^+$) and 1145 (8%, $[\text{M} - (\text{AuC}_6\text{F}_5)]^+$) arising at the loss of one or two AuC_6F_5 fragments appear.[†]



The crystal structure of $[\text{Au}_3(\text{C}_6\text{F}_5)_3(\eta^3\text{-Fcterpy})]$ has been confirmed by X-ray diffraction methods and is shown in Fig. 1.†. The pyridine rings are oriented in such a way as to minimize the steric and probably the electronic repulsions among the three pentafluorophenyl rings. The two outer pyridine rings are situated almost perpendicular to the central one and with the nitrogen atom pointing in opposite directions. The Au⋯Au distances are 3.0678(6) and 3.1559(7) Å, which are typical values for aurophilic interactions. The Au–N distances lie in the range 2.068(10)–2.106(8) Å and are of the same order as those found in complexes with a pentafluorophenyl ligand *trans* to a pyridine unit such as $[\text{Au}(\text{C}_6\text{F}_5)(\text{Fcpy})]$ (2.124(15) Å).¹⁰ The cyclopentadienyl rings are practically eclipsed. In the lattice there are several secondary interactions of the type Au⋯H about 2.7 Å and F⋯H about 2.5 Å which lead to a supramolecular structure.

DFT¹¹ calculations (ADF¹² program) were performed in a model of the $[\text{Au}_3(\text{C}_6\text{F}_5)_3(\eta^3\text{-Fcterpy})]$ complex where the C_6F_5

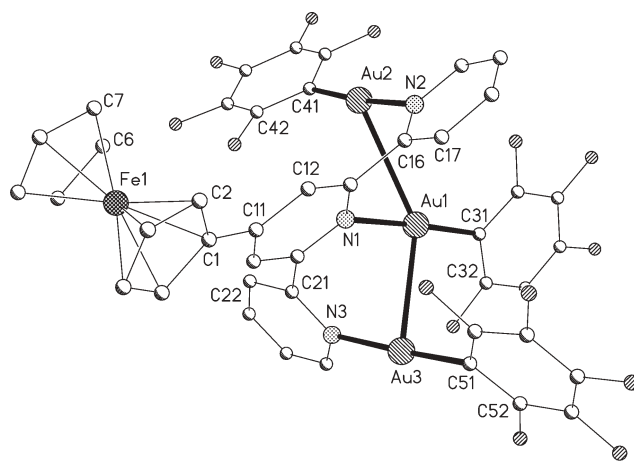


Fig. 1 Molecular structure of $[\text{Au}_3(\text{C}_6\text{F}_5)_3(\eta^3\text{-Fcterpy})]$ in the crystal showing the labelling scheme. Hydrogen atoms are omitted for clarity. Radii are arbitrary.

groups were replaced by CF₃.§ The Au...Au distances, 3.156 and 3.217 Å, are reproduced within ca. 0.05 Å, the three Au–N bonds ranging from 2.030 to 2.166 Å, also very close to experimental values. The calculated Mayer indices¹³ are 0.152 and 0.138, respectively, for the two Au...Au contacts, indicating the existence of the aurophilic interaction.¹⁴ The binding energy between Fcterpy and three Au(CF₃) groups is only 3.8 kcal mol⁻¹ higher than the sum of the binding energies of py and Au(CF₃) (twice) and of ferrocenylypy and Au(CF₃). These three pairs of fragments build an analogue of the complex, without Au...Au interactions and steric constraints. The small difference can be easily overcome by the hydrogen bonding network in the supramolecular structure. Also, three CF₃ model ligands may be less suitable than C₆F₅ to accommodate in the close proximity of the three gold atoms, the real system being probably more stable. This particular bonding mode of terpy allows the complete use of its binding capabilities, keeping gold(I) in its favoured environment with aurophilic interactions.¹⁴

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Javier E. Aguado,^a Maria José Calhorda,^{bc} M. Concepción Gimeno^{*,a} and Antonio Laguna^a

^aDepartamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., E-50009, Zaragoza (Spain)

^bDepartamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, 1749-016, Lisboa, Portugal.

E-mail: mjc@fc.ul.pt

^cInstituto de Tecnologia Química e Biológica (ITQB), Av. da República, EAN, Apt 127, 2781-901, Oeiras, Portugal

Notes and references

† *Preparation*: To a solution of [Au(C₆F₅)(tbt)] (0.135 g, 0.3 mmol) in 20 cm³ of dichloromethane was added Fcterpy (0.041 g, 0.1 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 2 cm³ and addition of hexane gave [Au₃(C₆F₅)₃(η³-Fcterpy)] as a orange solid. Yield 59%. Analytical data: Found, C, 34.25; H, 1.32; N, 3.02. Calc. for C₄₃H₁₉Au₃F₁₅FeN₃: C, 34.21; H, 1.26; N, 2.78%. NMR: ¹H, δ: 4.01 (s, 5H, C₅H₅), 4.32 (m, 2H, C₂H₄), 4.91 (m, 2H, C₅H₄), 8.81 (d, 2H, 6/6'), J(HH) 4.64 Hz), 7.47 (m, 2H, 5/5'), 7.95 (t, 2H, 4/4'), J(HH) 7.69 Hz), 8.39 (m, 2H, 3/3'), 8.42 (s, 2H, 3'/5'). ¹⁹F, -116.6 (m, 6F, o-F), -158.8 (t, 3F, p-F, J(FF) 21.3 Hz), -162.8 (m, 6F, m-F).

‡ *Crystal Data for [Au₃(C₆F₅)₃(η³-Fcterpy)]·CH₂Cl₂*: C₄₄H₂₁Au₃Cl₂F₁₅FeN₃, *M* = 1594.29, monoclinic, space group P2₁/n, *a* = 11.5020(9), *b* = 22.9336(19), *c* = 16.6010(13) Å, β = 102.965(2)°, *V* = 4267.4(6) Å³, *Z* = 4; *D*_c = 2.481 Mg m⁻³, μ(MoKα) = 10.845 mm⁻¹, *F*(000) = 2952, Bruker SMART Apex CCD diffractometer, λ(MoKα) = 0.71073, *T* = 100 K. An orange prism 0.20 × 0.20 × 0.12 mm was used to collect 27998 intensities to 2θ_{max} = 57.4 from which 10107 are independent (*R*_{int} = 0.070). Scan type ω. The structure was solved by direct methods and subjected to anisotropic refinement on *F*² (program SHELXL-97¹⁹). H atoms were included using a riding model. The final *wR*(*F*²) was 0.098 for 10107 reflections and 613 parameters, conventional *R*(*F*) 0.049, *S*(*F*²) 0.826, max Δρ 1.96 eÅ⁻³. CCDC 264992. See <http://www.rsc.org/suppdata/cc/b5/b502515j/> for crystallographic data in CIF or other electronic format.

§ *DFT calculations*: Gradient-corrected geometry optimizations¹⁵ were performed, using the Vosko, Wilk and Nusair local exchange correlation potential,¹⁶ and the Generalized Gradient Approximation (PW91¹⁷). Relativistic effects were treated with the ZORA approximation.¹⁸ Core

orbitals were frozen for Au ([1–4]s, [2–4]p, [3–4]d), Fe ([1–2]s, 2p), and C, N and F (1s). Triple ζ Slater-type orbitals (STO) were used to describe the valence shells of C, N, F (2s and 2p), Fe (3s, 3p, 3d, 4s) and Au (4f, 5d, 6s). A set of two polarisation functions was added to C, N, F (single ζ, 3d, 4f), Fe (single ζ, 4d, 4f), and Au (single ζ, 6p, 5f). Triple ζ STOs with one polarisation function (single ζ, 2p) were used to describe the H (1s) valence shell. Full geometry optimisations were performed without any symmetry constraints.

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