Unprecedented η^3-M_3 coordination mode in a terpyridine ligand

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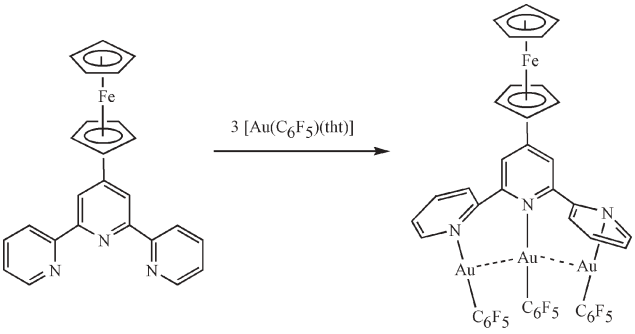
The gold(I) complex [$Au_3(C_6F_5)_3(\eta^3$-Fcterpy)] (Fcterpy = 4′-ferrocenyl-2,2′:6′,2″-terpyridine) represents the first example of a terpyridine ligand bonded to three different metals. The aurophilic interactions present in the molecule may contribute to the overall stability of the system, as 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 [AuX(Rterpy)] (R = H, SMe, PhOMe),[4–7] or [$Au(CN)_2Br(\eta^2$-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 [$Au(C_6F_5)$(tht)] in dichloromethane leads to the synthesis of the compound [$Au_3(C_6F_5)_3(\eta^3$-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 ^{19}F NMR spectrum the three pentaflorophenyl rings are equivalent and consequently only three resonances appear for the *ortho*, *meta* and *para* fluorine. The ^{1}H 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%, [M − $(AuC_6F_5)_2]^+$) and 1145 (8%, [M − $(AuC_6F_5)]^+$) arising at the loss of one or two AuC_6F_5 fragments appear.†



(1)

The crystal structure of [$Au_3(C_6F_5)_3(\eta^3$-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 [$Au(C_6F_5)$(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.

DFT[11] calculations (ADF[12] program) were performed in a model of the [$Au_3(C_6F_5)_3(\eta^3$-Fcterpy)] complex where the C_6F_5

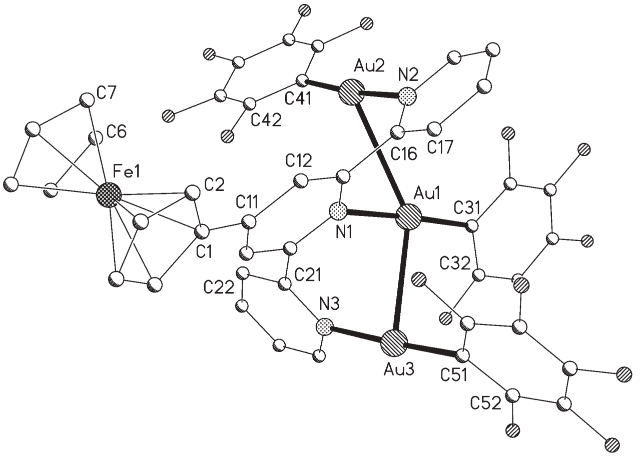


Fig. 1 Molecular structure of [$Au_3(C_6F_5)_3(\eta^3$-Fcterpy)] in the crystal showing the labelling scheme. Hydrogen atoms are omitted for clarity. Radii are arbitrary.

groups were replaced by CF_3.§ 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 indices[13] 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 $Au(CF_3)$ groups is only 3.8 kcal mol^{-1} higher than the sum of the binding energies of py and $Au(CF_3)$ (twice) and of ferrocenylpy and $Au(CF_3)$. 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 CF_3 model ligands may be less suitable than C_6F_5 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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Notes and references

† *Preparation:* To a solution of $[Au(C_6F_5)(tht)]$ (0.135 g, 0.3 mmol) in 20 cm^3 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 cm^3 and addition of hexane gave $[Au_3(C_6F_5)_3(\eta^3\text{-Fcterpy})]$ as a orange solid. Yield 59%. Analytical data: Found, C, 34.25; H, 1.32; N, 3.02. Calc. for $C_{43}H_{19}Au_3F_{15}FeN_3$: C, 34.21; H, 1.26; N, 2.78%. NMR: ^1H, δ: 4.01 (s, 5H, C_5H_5), 4.32 (m, 2H, C_5H_4), 4.91 (m, 2H, C_5H_4), 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′). ^{19}F, −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* $[Au_3(C_6F_5)_3(\eta^3\text{-Fcterpy})]\cdot CH_2Cl_2$: $C_{44}H_{21}Au_3Cl_2F_{15}FeN_3$, $M = 1594.29$, monoclinic, space group $P2_1/n$, $a = 11.5020(9)$, $b = 22.9336(19)$, $c = 16.6010(13)$ Å, $\beta = 102.965(2)°$, $V = 4267.4(6)$ Å^3, $Z = 4$; $D_c = 2.481$ Mg m^{-3}, μ(MoKα) = 10.845 mm^{-1}, F(000) = 2952, Bruker SMART Apex CCD difractometer, λ(Mo–Kα) = 0.71073, $T = 100$ K. An orange prism 0.20 × 0.20 × 0.12 mm was used to collect 27998 intensities to $2\theta_{max} = 57.4$ 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-97[19]). 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 $\Delta\rho$ 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 optimizations[15] were performed, using the Vosko, Wilk and Nusair local exchange correlation potential,[16] and the Generalized Gradient Approximation (PW91[17]). 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.

1 E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 69.
2 See for example: (*a*) G. B. Deacon, J. M. Patrick, B. W. Skelton, N. C. Thomas and A. H. White, *Aust. J. Chem.*, 1984, **37**, 929; (*b*) N. C. Thomas and J. Fischer, *J. Coord. Chem.*, 1990, **21**, 119; (*c*) E. C. Constable, M. J. Hannon, A. M. W. Cargill Thompson, D. A. Tocher and J. V. Walker, *Supramol. Chem.*, 1993, **3**, 243; (*d*) R. Chotalia, E. C. Constable, M. J. Hannon and D. A. Tocher, *J. Chem. Soc. Dalton Trans.*, 1995, 3571.
3 See for example: (*a*) K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruña and C. R. Arana, *Inorg. Chem.*, 1993, **32**, 4422; (*b*) E. C. Constable, A. J. Edwards, M. J. Hannon and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1994, 1991; (*c*) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.*, 1998, 2659; (*d*) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuburger and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 2000, 945; (*e*) M. H. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs and N. W. Alcok, *Chem. Eur. J.*, 2002, **8**, 2225–2238; (*f*) Y. Cui and C. He, *J. Am. Chem. Soc.*, 2003, **125**, 16202.
4 L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1983, **105**, 4293.
5 H. Q. Liu, T. C. Cheung, S. M. Peng and C. M. Che, *J. Chem. Soc., Chem. Commun.*, 1995, 1787.
6 B. Pitteri, G. Marangoni, F. Visentin, T. Bobbo, V. Bertolasi and P. Gilli, *J. Chem. Soc., Dalton Trans.*, 1999, 677.
7 U. Sampath, W. C. Putnam, T. A. Osiek, S. Touami, J. Xie, D. Cohen, A. Cagnolini, P. Droege, D. Klug, C. L. Bernes, A. Modak, J. K. Bashkin and S. S. Jurisson, *J. Chem. Soc., Dalton Trans.*, 1999, 677.
8 V. Ferreti, P. Gilli, V. Bertolasi, G. Marangoni, P. Pitteri and G. Ghessa, *Acta Crystallogr. Sect. C*, 1992, **48**, 814.
9 E. C. Constable, A. J. Edwards, R. Matínez-Máñez, P. R. Raithby and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 645.
10 E. M. Barranco, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna and M. D. Villacampa, *J. Organomet. Chem.*, 1999, **592**, 258.
11 R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press: New York, 1989.
12 (*a*) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders and T. Ziegler, ‘Chemistry with ADF’, *J. Comput. Chem.*, 2001, **22**, 931–967; (*b*) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391; (*c*) ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
13 (*a*) I. Mayer, *Chem. Phys. Lett.*, 1983, **97**, 270; (*b*) I. Mayer, *Int. J. Quantum Chem.*, 1984, **26**, 151; (*c*) MAYER version 1.2.3, A. J. Bridgeman and C. J. Empson, The University of Hull, (2004). Freely available from http://www.hull.ac.uk/php/chsajb/mayer/.
14 (*a*) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (*b*) P. Pyykkö, N. Runerberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451.
15 (*a*) L. Fan and T. Ziegler, *J. Chem. Phys.*, 1991, **95**, 7401; (*b*) L. Versluis and T. Ziegler, *J. Chem. Phys.*, 1988, **88**, 322.
16 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
17 (*a*) A. D. Becke, *J. Chem. Phys.*, 1988, **88**, 1053; (*b*) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev.*, 1992, **B46**, 6671.
18 E. van Lenthe, A. Ehlers and E. J. Baerends, *J. Chem. Phys.*, 1999, **110**, 8943.
19 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.