ELSEVIER

Inorganica Chimica Acta 224 (1994) 11–14

Inorganica Chimica Acta

Preliminary Communication

A new functionalised oligopyridine ligand containing ferrocene as a ball-bearing spacer for metallosupramolecular chemistry

Edwin C. Constable[a,*], Andrew J. Edwards[b], María Dolores Marcos[b], Paul R. Raithby[b], Ramón Martínez-Máñez[c,*], María José L. Tendero[c]

[a] *Institut für Anorganische Chemie der Universität, Spitalstrasse 51, CH-4056 Basel, Switzerland*
[b] *Cambridge Centre for Chemical Crystallography, University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*
[c] *Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain*

Received by Editor 23 April 1994; received by Publisher 16 June 1994

Abstract

A new supramolecular building-block in which a ferrocene moiety has been used as a spacer linking two terpyridyl units has been prepared. The new multidentate ligand 1,1′-bis(2,2′:6′,2″-terpyridin-4′-yl)ferrocene (tft) incorporates two tridentate metal-binding domains. The ligand has been synthesised from ferrocene-1,1′-dicarbaldehyde and 2-acetylpyridine in a two-stage procedure. The reaction of ferrocene-1,1′-dicarbaldehyde with 2-acetylpyridine yields the bis-chalcone 1,1′-[3-oxo-3-(2-pyridyl)prop-2-en-yl]ferrocene which has been structurally characterised: monoclinic, space group $P2_1/c$ (No. 14) with $a = 13.126(3)$, $b = 10.470(2)$, $c = 15.642(3)$ Å, $\beta = 111.62(3)$° and $Z = 4$, R_1 0.052 ($F > 4\sigma(F)$, for 1611 reflections) and R_2 0.125 (all data). The cyclopentadienyl rings of the ferrocene are eclipsed and the two 2,2′:6′,2″-terpyridinyl moieties are in a stacked coplanar conformation. The reaction of this chalcone with *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide and ammonium acetate yielded the new ligand as an orange solid which was structurally characterised: monoclinic, space group $P2_1/c$ (No. 14), $a = 13.268(3)$, $b = 18.147(4)$, $c = 12.458(2)$ Å, $\beta = 90.73(3)$° and $Z = 4$, R_1 0.077 ($F > 4\sigma(F)$, for 2041 reflections) and R_2 0.217 (all data). Once again, the cyclopentadienyl rings of the ferrocene are eclipsed and the two 2,2′:6′,2″-terpyridinyl moieties are in a stacked coplanar conformation.

Keywords: Crystal structures; Ferrocene complexes; Oligopyridine ligand complexes; Metallosupramolecular chemistry

---

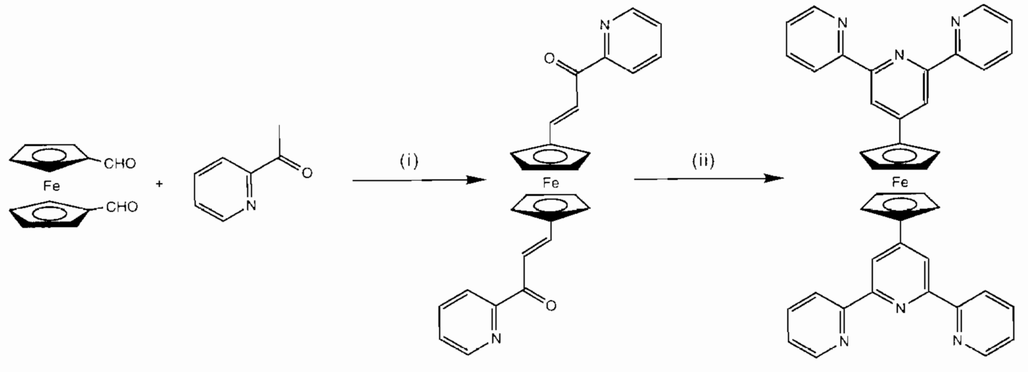
We are currently interested in the application of metallosupramolecular methodology [1,2] to the synthesis of novel molecular architectures. Our basic methodology involves the use of multidentate ligands which can be partitioned into two or more metal-binding domains. Using this approach we and others [2–4] have demonstrated that it is possible to partition oligopyridines into separate domains according to the coordination requirements of specific metal ions, and that the consequence of such partitioning is the formation of (multiple) helicate structures. A natural evolution of this approach was the use of spacer groups to separate the metal-binding domains, and we have utilised this approach for the preparation of double helicates [5]. Recently we and others have described the preparation of a series of rigid rod-like coordination oligomers utilising ligands containing two 2,2′:6′,2″-terpyridine (tpy) metal-binding domains [6,7]. Previously, ferrocenyl groups have been introduced as redox spectators in 2,2′:6′,2″-terpyridines [8] and we now describe a new ligand type containing a ferrocenyl moiety which introduces a degree of flexibility between the metal-binding domains whilst retaining the possibility of electronic communication between metal centres. In the new ligand, 1,1′-bis(2,2′:6′,2″-terpyridin-4′-yl)ferrocene (tft), the central ferrocenediyl unit may be regarded as a molecular ball-bearing [9] about which the pendant tpy groups may rotate with relative ease.

The new ligand was obtained by the Kröhnke methodology [10] as indicated in Scheme 1. The reaction of ferrocene-1,1′-dicarbaldehyde [11] with 2-acetylpyridine (EtOH, NaOH, 0 °C, 30 min) gave the bis-chalcone **1** as a red precipitate (89%). Analytical and spectroscopic data are in agreement with this proposed for-

---

*Corresponding authors.

SSDI 0020-1693(94)04147-N



(i) EtOH, NaOH (aqueous, 2 M), 30 min. (ii) EtOH, *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide, $[NH_4][OAc]$, 2 h, 80 °C.
Scheme 1.

mulation (IR: ν(C=O) 1659 cm^{-1}; FAB-MS: *m/z* = 448). The ^1H NMR spectrum of **1** shows characteristic resonances at δ 4.48 and 4.67 and four pyridyl and two vinyl signals in the range δ 7.36–8.58 (^1H NMR δ 4.48 (t, 4H, C_5H_4), 4.67 (t, 4H, C_5H_4), 7.36 (ddd, 2H, H_5), 7.55 (dt, 2H, H_4), 7.66 (d, 2H, CH), 7.75 (d, 2H, CH), 8.02 (d, 2H, H_3), 8.58 (d, 2H, H_6)). A crystal structural analysis[1] confirmed the structure of **1**, and the molecular structure is depicted in Fig. 1. The cyclopentadienyl rings are eclipsed and the tpy groups are stacked with an intramolecular pyridyl–pyridyl ring distance of 3.893(8) Å.

The reaction of **1** with *N*-[1-oxo-2-(2-pyridyl)-ethyl]pyridinium iodide in ethanol and an excess of ammonium acetate yielded tft in 20% yield as a red solid (MS *m/z* 649). The ^1H NMR spectrum of tft shows two resonances at δ 4.45 and 5.03 ppm and a total of five signals in the aromatic region between δ 7.10 and 8.37 showing that the two terpyridyl domains are equivalent on the NMR time scale (^1H NMR δ 4.45 (t, 4H, C_5H_4), 5.03 (t, 4H, C_5H_4), 7.10 (ddd, 4H, $H_{5,5''}$), 7.63 (dt, 4H, $H_{4,4''}$), 8.03 (s, 4H, $H_{3,5'}$), 8.19 (d, 4H, $H_{3,3''}$), 8.37 (d, 4H, $H_{6,6''}$)).

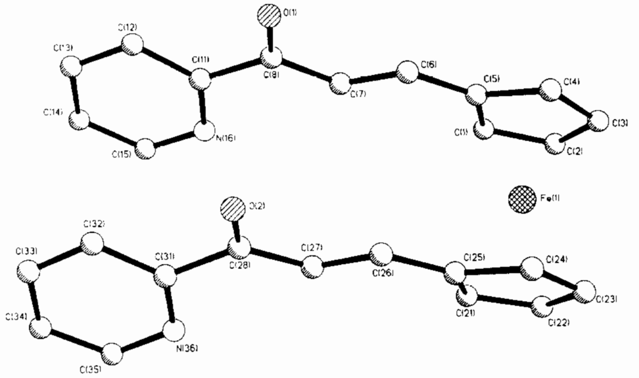


Fig. 1. Molecular structure of **1** with hydrogen atoms omitted for clarity. Bond lengths (Å): C(5)–C(6) 1.456(8), C(6)–C(7) 1.335(7), C(7)–C(8) 1.468(8), C(8)–C(11) 1.498(8), C(8)–O(1), 1.230(6), C(25)–C(26) 1.442(7), C(26)–C(27) 1.337(7), C(27)–C(28) 1.466(8), C(28)–C(31) 1.515(8), C(28)–O(2) 1.213(6), av. Fe–C(Cp ring) 2.048(6), av. C(Cp)–C(Cp) 1.413(8), av. C(tpy)–C(tpy) 1.375(8), av. N–C 1.335(7).

In the solid state tft is indefinitely stable, but dichloromethane solutions become blue after standing in air for several days. Compound **1** and tft are both redox active and exhibit reversible processes in their cyclic voltammograms (CH_2Cl_2; potentials versus internal Fc/Fc^+ reference; $[NBu_4][BF_4]$ as supporting electrolyte) at +0.11 and +0.14 V, respectively (cf. that of 4′-ferrocenyl-2,2′:6′,2″-terpyridine at +0.12 V [8]) and also show irreversible poorly defined reduction processes.

We have determined the solid state structure of the new ligand tft, using orange crystals grown from dichloromethane–ethanol solution. Fig. 2 depicts the solid state molecular structure of tft[2]. Each of the tpy domains

---

[1] Crystal data for **1**: $C_{26}H_{20}N_2O_2Fe$, $M = 448.29$, monoclinic, space group $P2_1/c$ (No. 14) $a = 13.126(3)$, $b = 10.470(2)$, $c = 15.642(3)$ Å, $\beta = 111.62(3)°$, $U = 1998.4(7)$ Å^3, $Z = 4$, $D_c = 1.490$ g cm^{-3}, $F(000) = 928$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, μ(Mo Kα) = 7.82 cm^{-1}. Data collected on a Nicolet P3 diffractometer using a crystal of dimensions 0.25×0.24×0.21 mm by the $2\theta/\omega$ method ($5.00 \leqslant 2\theta \leqslant 45.00°$). Of a total of 2836 reflections, 2623 were unique. Psi absorption correction applied with max. and min. transmission coefficients of 0.635 and 0.485, respectively. The structure was solved by direct methods (SHELXTL PLUS) [12] and refined by full-matrix least-squares analysis on F^2 (SHELX-93) [13] to R_1 0.052 ($F > 4\sigma(F)$, for 1611 reflections) and R_2 0.125 (all data) ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$). Largest peak and hole in the final difference map +0.29, −0.30 e Å^{-3}.

[2] tft: $C_{40}H_{28}N_6Fe$, $M = 648.53$, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.268(3)$, $b = 18.147(4)$, $c = 12.458(2)$ Å, $\beta = 90.73(3)°$, $U = 2999.3(11)$ Å^3, $Z = 4$, $D_c = 1.436$ g cm^{-3}, $F(000) = 1344$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, μ(Mo Kα) = 5.45 cm^{-1}. Data were collected on a Rigaku AFC7 four circle diffractometer coupled to a Mo target rotating anode X-ray source, using a crystal of dimensions 0.23×0.19×0.18 mm by the $2\theta/\omega$ method ($5.00 \leqslant 2\theta \leqslant 45.00°$). Of a total of 4133 reflections, 3917 were unique. The structure was solved by direct methods (SHELXTL PLUS) [12] and refined by full-matrix least-squares analysis on F^2 (SHELX-93) [13] to R_1 0.077 ($F > 4\sigma(F)$, for 2041 reflections) and R_2 0.217 (all data) ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$). Largest peak and hole in the final difference map +1.18, −0.40 e Å^{-3}.

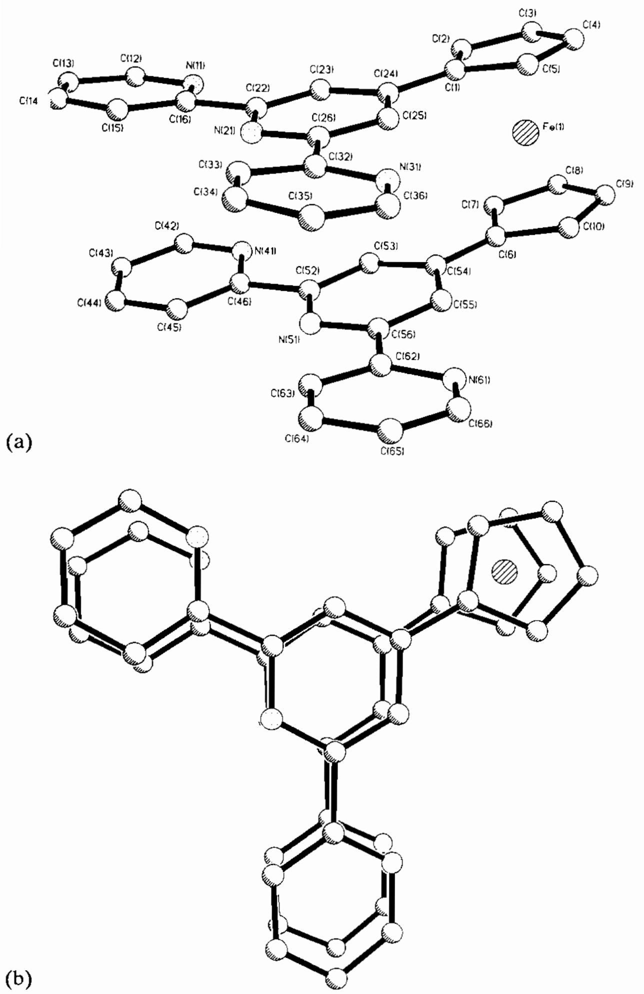


Fig. 2. (a) Crystal structure of tft with hydrogen atoms omitted for clarity. Bond lengths (Å): C(1)–C(24) 1.464(11), C(6)–C(54) 1.461(11), av. Fe–C(Cp ring) 2.042(9), av. C(Cp)–C(Cp) 1.416(11), av. C(tpy)–C(tpy) 1.376(13) Å, av. N–C 1.337(10). The second view (b) emphasises the stacking of the tpy domains.

adopts a *trans–trans* conformation about the interannular C–C bonds as reported for other tpy ligands. The terpyridine units are approximately coplanar (torsion angles of 2.7(8)–10.5(8)° between directly bonded rings) and are also near-coplanar with the attached cyclopentadienyl rings (torsion angles ≈6 °). The two tpy domains are eclipsed and stacked with an average stacking distance of 3.653(10) Å. The two cyclopentadienyl rings of the ferrocene are also in an eclipsed conformation. An intermolecular terpyridyl–terpyridyl distance of 3.570(11) Å is found in the solid state.

Preliminary studies of the coordination properties of tft with first-row transition metal ions have been made. For example, the trinuclear complex $[Ni(tft)_2][PF_6]_2$ in which each tft acts as a tridentate ligand has been isolated (FAB-MS: *m/z* 1646 $\{[(tpy)Fc(tpy)Ni(tpy)Fc(tpy)][PF_6]_2\}$, 1500 $\{[(tpy)Fc(tpy)Ni(tpy)Fc(tpy)][PF_6]\}$, 1356 $\{[(tpy)Fc(tpy)Ni(tpy)Fc(tpy)]\}$, 706 $\{[(tpy)Fc(tpy)Ni]\}$.

Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters for **1** and tft have been deposited with the Cambridge Crystallographic Data Center.

Acknowledgements

We thank the University of Basel (E.C.C.) and SERC for support (A.J.E.). R.M.-M. thanks the CICYT (PB91-0807-CO2) and the Ministerio de Educación y Ciencia for support.

References

[1] E.C. Constable, *Chem. Ind.*, (1994) 56.
[2] E.C. Constable, *Prog. Inorg. Chem.*, *42* (1994) 67.
[3] E.C. Constable, A.J. Edwards, P.R. Raithby and J.V. Walker, *Angew. Chem.*, *32* (1993) 1465, and refs. therein; E.C. Constable, M.A.M. Daniels, M.G.B. Drew, D.A. Tocher, J.V. Walker and P.D. Wood, *J. Chem. Soc., Dalton Trans.* (1993) 1947, and refs. therein; E.C. Constable, *Tetrahedron, 48* (1992) 10013, and refs. therein.
[4] K.T. Potts, M. Keshavarz-K, F.S. Tham, H.D. Abruña and C. Arana, *Inorg. Chem.*, *32* (1993) 4422, 4436, 4450; K.T. Potts, M. Keshavarz-K, F.S. Tham, C. Arana and H.D. Abruña, *Inorg. Chem.*, *32* (1993) 5477.
[5] E.C. Constable, M.J. Hannon and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1993) 1883; *Angew. Chem.*, *31* (1992) 230.
[6] E.C. Constable, M.J. Hannon, A.M.W. Cargill Thompson, D.A. Tocher and J.V. Walker, *Supramol. Chem.*, *2* (1993) 243; E.C. Constable, A.M.W. Cargill Thompson and D.A. Tocher, *Supramol. Chem.*, *3* (1993) 9; G.R. Newkome, F. Cardullo, E.C. Constable, C.N. Moorefield and A.M.W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, (1993) 925; F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E.C. Constable and A.M.W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, (1993) 942; E.C. Constable, A.M.W. Cargill Thompson and D.A. Tocher, *Makromol. Symp.*, *9* (1994) 219; E.C. Constable, A.M.W. Cargill Thompson and S. Greulich, *J. Chem. Soc., Chem. Commun.*, (1993) 1444, and refs. therein.
[7] M. Beley, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, *32* (1993) 4539; M. Beley, S. Chodorowski, J.-P. Collin and J.-P. Sauvage, *Tetrahedron Lett.*, (1993) 2933; F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E.C. Constable and A.M.W. Cargill Thompson, *J. Am. Chem. Soc.*, in press; refs. therein.
[8] E.C. Constable, A.J. Edwards, R. Martínez-Máñez, P.R. Raithby and A.M.W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, (1994) 645; B. Farlow, T.A. Nile, J.L. Walsh and A.T. McPhail, *Polyhedron, 12* (1993) 2891; E.C. Constable, R. Martínez-Máñez, A.M.W. Cargill Thompson and J.V. Walker, *J. Chem. Soc., Dalton Trans.*, (1994) 1585.

[9] J.C. Medina, I. Gay, Z. Chen, L. Echegoyen and G.W. Gokel, *J. Am. Chem. Soc., 113* (1991) 365; J.C. Medina, C. Li, C.G. Bott, J.L. Atwood and G.W. Gokel, *J. Am. Chem. Soc., 113* (1991) 366; E.C. Constable, *Angew. Chem., Int. Ed. Engl., 30* (1991) 407.

[10] F. Kröhnke, *Synthesis,* (1976) 1.

[11] G.G.A. Balavoine, G. Doisneau and T. Fillebeen-Khan, *J. Organomet. Chem., 412* (1991) 381.

[12] *SHELXTL PLUS,* Program Version 4.0, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.

[13] G.M. Sheldrick, *SHELX 93,* University of Göttingen, Germany, 1993.