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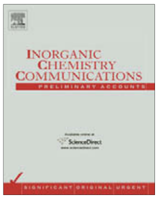

Fe-only hydrogenase active site mimics: $Fe_2(CO)_6(\mu\text{-ADT})$ (ADT = azadithiolate) clusters bearing pendant 2,2′:6′,2″-terpyridine domains and containing alkynylthienylene or alkynylphenylene spacers

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ABSTRACT

We report the syntheses and single crystal structures of two $Fe_2(CO)_6(\mu\text{-ADT})$ (ADT = azadithiolate) clusters bearing pendant tpy (tpy = 2,2′:6′,2″-terpyridine) domains and containing alkynylthienylene or alkynylphenylene spacers between the Fe-only hydrogenase active site mimic and tpy metal-binding unit.

Sources of clean and renewable energy are at the forefront of international research efforts, with hydrogen production being of critical importance. The crystallographic characterization of the active site of Fe-only hydrogenase [1] and the observation that a molecular mimic of the active site in Fe-only hydrogenase can function as an electrocatalyst for proton reduction [2,3], have revitalized interest in the properties of small, sulfur-containing iron carbonyl clusters. It is proposed that the presence of the amine group in the active site facilitates its catalytic role in proton reduction and H_2 evolution [4]. A number of papers have now appeared detailing the syntheses and catalytic properties of Fe-only hydrogenase active site models. Most are based upon an $Fe_2(CO)_6S_2$ core with azadithiolate (ADT) bridge, and the effects of varying the terminal N substituent, or introducing phosphine in place of carbonyl ligands have been investigated [5–16]. Selenium-containing model clusters have also been reported [17]. In order to facilitate light-driven proton reduction, model clusters covalently linked to $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) or $[Ru(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) photosensitizers [14,18–20] or associated with (but not covalently linked to) $[Ru(bpy)_3]^{2+}$ [21,22] have been studied. The photophysical properties of $\{M(tpy)_2\}^{n+}$ units are often poorer than those of $\{M(bpy)_3\}^{n+}$ (bpy = 2,2′-bipyridine) [23]. This problem can be addressed by introducing thienylene or alkynyl spacers to tpy to enhance electronic communication between the latter and the appended functionality [24–33]. We recently described approaches to compounds in which a tpy domain was covalently linked to alkynylthienyl or alkynylbithienyl substituents [34,35]. We now report the synthesis and structural characterization of two $Fe_2(CO)_6(\mu\text{-ADT})$ clusters bearing pendant tpy domains, and containing alkynylthienylene or alkynylphenylene spacers.

The synthesis of **1** (Scheme 1) in a one-pot reaction by reaction of 4-ethynylbenzaldehyde, 2-acetylpyridine and NH_4OH [36] is simpler than the published route [37]. The ^1H NMR spectrum of **1** was assigned by 2D techniques, the signals for H^{C2} and H^{C3} being distinguished by the observation of a NOESY H^{C2}-H^{B3} cross peak. Alkyne **1** or **2** [34] was coupled to **5** [20,22] under Sonogashira conditions [38,39] to give **3** or **4**, respectively [40]. Both compounds are light-sensitive and must be stored in the dark. The electrospray mass spectra of **3** and **4** each showed a parent ion, with the only other intense peak corresponding to loss of six CO ligands. In the IR spectra of the compounds, the pattern of strong absorptions around 2000 cm^{-1} was consistent with the presence of the $Fe_2(CO)_6$ unit.

On going from **1** to **3**, the disappearance of the signal for the alkyne proton (δ 3.19 ppm) and the appearance of a singlet at δ 4.35 ppm for the $N(CH_2)_2$ unit, and signals at δ 7.53 and 6.74 ppm (assigned by NOESY) for the *N*-attached arene ring, confirmed the formation of **3**. The signals for the phenyltpy unit in the ^1H NMR spectrum of **3** were essentially a superimposition of those in **1**. Similarly, the ^1H NMR spectrum of **4** showed the spectroscopic signature of ligand **2** [34] with an additional singlet at δ 4.34 ppm, and signals at δ 7.50 and 6.73 ppm for ring D protons.

Single crystals of **3** and **4** suitable for X-ray diffraction [41] were grown by layering a THF solution of **3** with hexane, or a CH_2Cl_2

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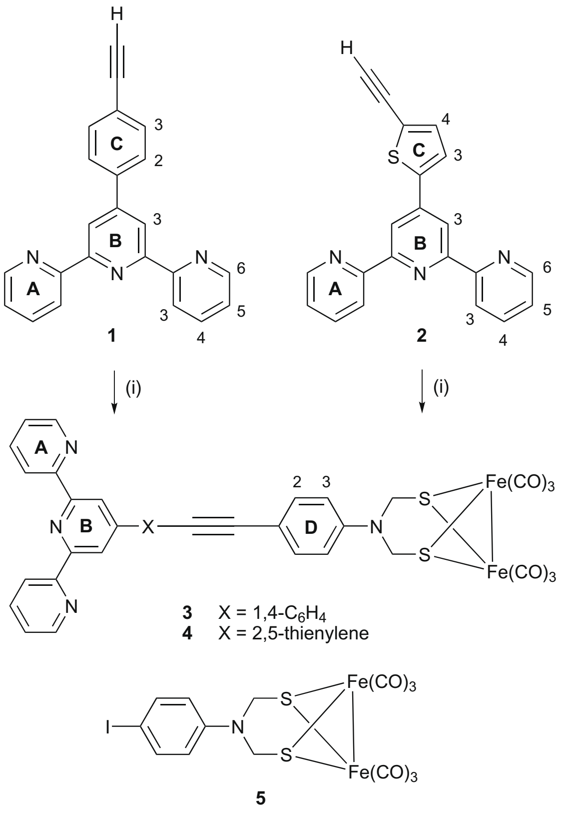
solution of **4** with Et_2O. Figs. 1 and 2 depict the molecular structures. Bond parameters within the $Fe_2(CO)_6(\mu\text{-ADT})$ units in **3** and **4** are similar and are unexceptional. In **3**, the tpy unit is approximately planar (angles between the least squares planes of rings containing atoms N1 and N2, and N2 and N3 are 1.6(1) and 5.0(1)°). The plane of the arene ring containing atom C16 is twisted through 40.0(1)° with respect to the central pyridine ring to which it is attached, and lies 7.2(1)° out of the plane containing the cluster-attached arene ring. In contrast, the tpy, thiophene and arene rings in **4** are closer to being coplanar (angles between the least squares planes of rings containing atoms N1 and N2, N2 and N3, N2 and S1, and S1 and C22 are 3.6(1), 11.7(1), 9.2(1) and 4.4(1)°). These observations indicate that, in the solid state at least, compound **4** exhibits a π-system which extends from the bridging ADT unit to the tpy domain.

The tpy units of adjacent molecules of **4** are π-stacked (distance between rings containing N3 and $N1^i$ = 3.21 Å, symmetry code $i = x, 1 + y, z$). The stacks are arranged so that the lattice contains discrete organic and inorganic cluster domains (Fig. 3). This results in relatively short intermolecular carbonyl O···O contacts of 3.0 Å, similar to those observed in $Fe_2(CO)_9$ [42] and $Fe_3(CO)_{12}$ [43]. In contrast, molecules of **3** are packed so that there is partial interdigitation of organic and iron sulfur cluster domains (Fig. 4a). The dominant feature of the packing is the centrosymmetric, box-like four-molecule embrace shown in Fig. 4b which arises from



Scheme 1. Scheme for the synthesis of **3** and **4**; (i) THF, **5**, NEt_3, $[Pd(PPh_3)_2Cl_2]$, CuI, in the dark. Ring labelling for NMR assignments.

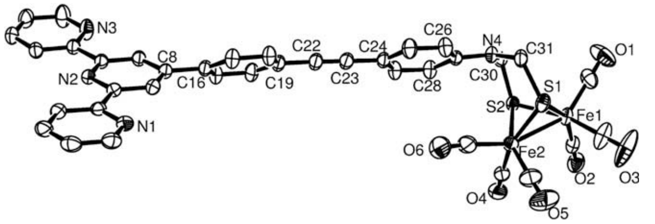


Fig. 1. Molecular structure of **3** (H atoms omitted) with ellipsoids plotted at 40% probability level. Selected bond parameters: Fe1–Fe2 = 2.5029(9), Fe1–S1 = 2.2564(9), Fe1–S2 = 2.2571(8), Fe2–S1 = 2.259(1), Fe2–S2 = 2.2690(9), S1–C31 = 1.853(3), S2–C30 = 1.855(3), N4–C27 = 1.412(3), N4–C30 = 1.423(3), N4–C31 = 1.427(3), C22–C23 = 1.195(4) Å; Fe1–S1–Fe2 = 67.33(3), Fe1–S2–Fe2 = 67.15(3), C27–N4–C30 = 121.3(2), C27–N4–C31 = 121.2(2), C30–N4–C31 = 114.2(2)°.

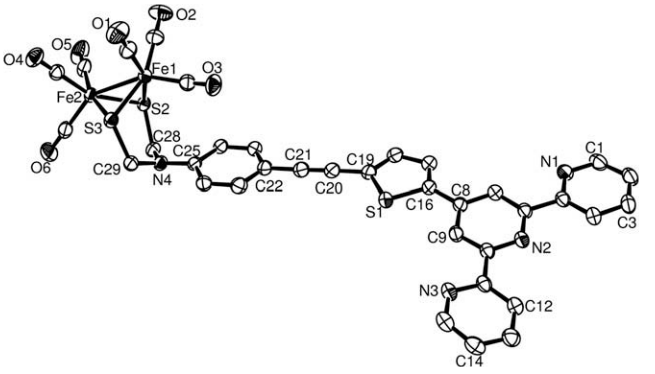


Fig. 2. Molecular structure of **4** (H atoms omitted); ellipsoids plotted at 40% probability level. Selected bond parameters: Fe1–Fe2 = 2.5193(6), Fe1–S3 = 2.2423(7), Fe1–S2 = 2.2665(7), Fe2–S2 = 2.2505(7), Fe2–S3 = 2.2532(8), S2–C28 = 1.849(2), S3–C29 = 1.861(3), N4–C25 = 1.397(2), N4–C29 = 1.427(3), N4–C28 = 1.429(3), C20–C21 1.190(3) Å; Fe2–S2–Fe1 = 67.80(2), Fe1–S3–Fe2 = 68.17(2), C25–N4–C29 = 121.8(2), C25–N4–C28 = 120.4(2), C29–N4–C28 = 113.7(2), C16–S1–C19 = 91.7(1)°.

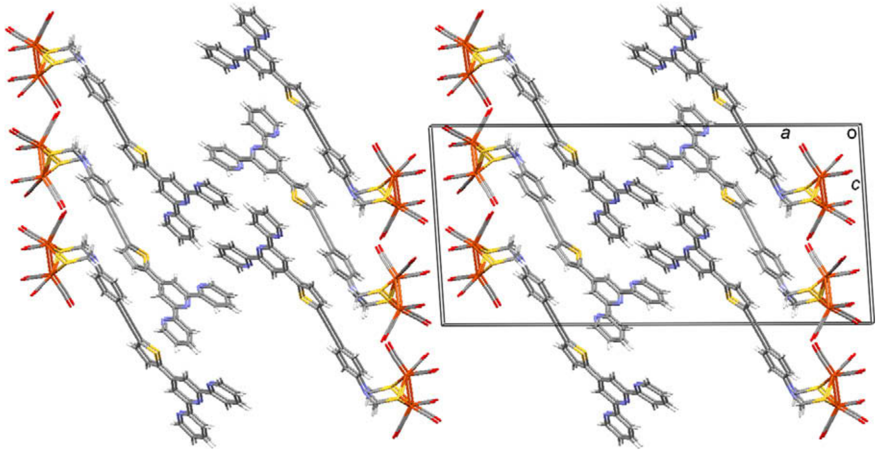


Fig. 3. Packing of molecules of **4**, showing layered organic and iron sulfur cluster domains.

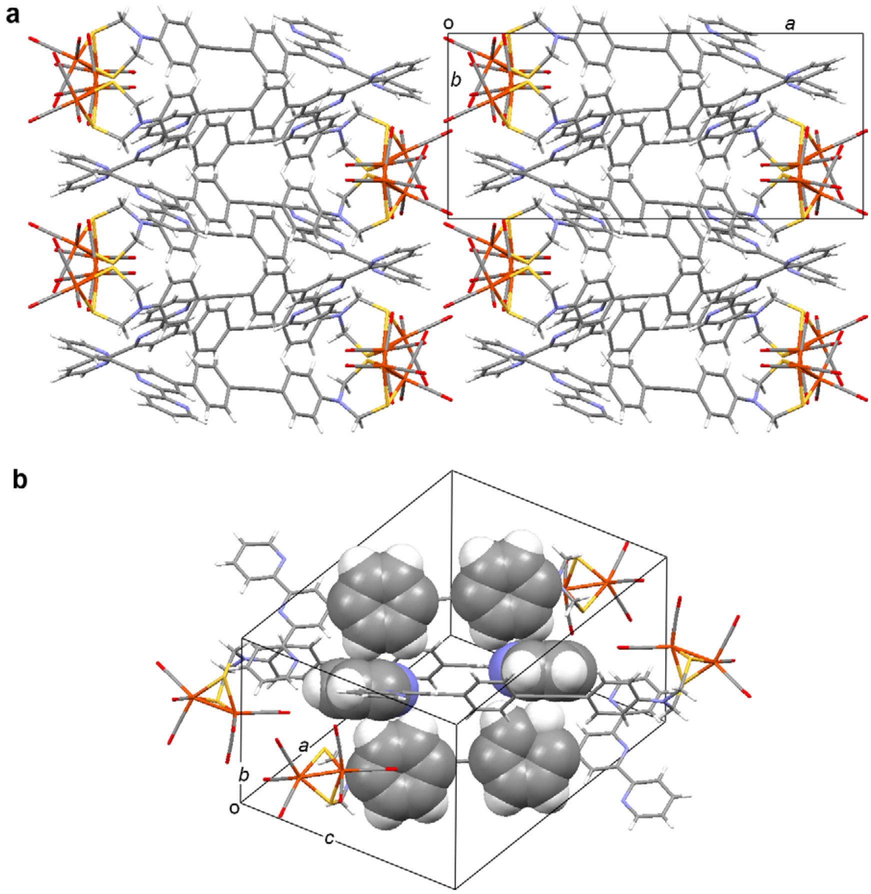


Fig. 4. (a) Packing of molecules of **3**; and (b) the four-molecule embrace in **3**.

edge-to-face $\mathrm{CH}\cdots\pi$ interactions between the arene and pyridine rings. The C28–H28A bond points towards the centroid of the pyridine ring containing $\mathrm{N1}^{i}$ ($\mathrm{C28{-}H28A}\cdots$centroid = 2.83 Å, symmetry code $i = 1 - x$, $^{1}/_{2} + y$, $^{3}/_{2} - z$), while C21–H21A is directed towards the centroid of the ring containing $\mathrm{N1}^{ii}$ ($\mathrm{C21{-}H21A}\cdots$centroid = 2.71 Å, symmetry code $ii = x$, $^{1}/_{2} - y$, $-^{1}/_{2} + z$).

In conclusion, we have prepared and characterized two $\mathrm{Fe_2(CO)_6(\mu\text{-}ADT)}$ clusters bearing pendant tpy domains coupled through alkynylthienylene or alkynylphenylene spacers. The aim of their incorporation is to enhance electronic communication between the iron sulfur cluster and tpy metal-binding unit. Future studies will focus on the synthesis of heteroleptic ruthenium(II) complexes containing **3** or **4**.

Acknowledgements

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Appendix A. Supplementary material

CCDC 724617 and 724618 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.06.003.

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[36] **1**: 4-Ethynylbenzaldehyde (0.490 g, 3.77 mmol) was added to a stirring mixture of 2-acetylpyridine (0.88 cm^3, 0.95 g, 7.85 mmol), NH_4OH (20 cm^3, 25% aq. solution) in EtOH (30 cm^3). KOH pellets (0.48 g, 8.6 mmol) were added slowly to the stirring mixture. A yellow precipitate formed as the solution was stirred for 15 h at room temperature. **1** was collected by filtration, washed with EtOH and isolated as a light yellow solid (0.50 g, 40%). The melting point (188–191 °C) agreed with that published [37]. ^1H NMR (500 MHz, $CDCl_3$) δ/ppm 8.73 (s overlapping d, 4H, H^{B3+A6}), 8.68 (d, J = 7.9 Hz, 2H, H^{A3}), 7.90 (d, J = 8.2 Hz overlapping m, 4H, H^{C2+A4}), 7.66 (d, J = 8.3 Hz, 2H, H^{C3}), 7.36 (m, 2H, H^{A5}), 3.19 (s, 1H, $H^{C\equiv CH}$).

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[40] **3**:**1** (48 mg, 0.144 mmol), **5** (75 mg, 0.127 mmol), $[Pd(PPh_3)_2Cl_2]$ (18 mg, 0.025 mmol), NEt_3 (4.3 cm^3) and CuI (14 mg, 0.074 mmol) were added to THF (15 cm^3) under argon in the dark. The reaction mixture was stirred in the dark at room temperature for 20 h. Solvent was then removed *in vacuo*. The product was purified by column chromatography in the dark (Al_2O_3, CH_2Cl_2) and **3** was collected as the second, red fraction (12 mg, 12%). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 8.76 (s, 2H, H^{B3}), 8.74 (d, J = 4.8 Hz, 2H, H^{A6}), 8.69 (dd, J = 8.0, 0.6 Hz, 2H, H^{A3}), 7.91 (d, J = 8.1 Hz overlapping m, 4H, H^{C2+A4}), 7.66 (d, J = 8.0 Hz, 2H, H^{C3}), 7.53 (d, J = 8.7 Hz, 2H, H^{D2}), 7.37 (dd, J = 7.4, 4.8 Hz, 2H, H^{A5}), 6.74 (d, J = 8.7 Hz, 2H, H^{D3}), 4.35 (s,4H,H_2^{CH}). ESI MS *m/z* 795.0 $[M + H]^+$ (calc. 795.0), 627.0 $[M - 6CO + H]^+$ (calc. 627.0); IR (solid, ν_{CO}/cm^{-1}) 2069, 2021, 1998. **4**:**1** (55 mg, 0.162 mmol), **5** (36 mg, 0.061 mmol), $[Pd(PPh_3)_2Cl_2]$ (9.0 mg, 0.013 mmol), NEt_3 (10 cm^3) and CuI (14 mg, 0.074 mmol) were added to THF (15 cm^3) under argon in the dark. The mixture was stirred in the dark at room temperature for 16 h. After solvent removal, column chromatography in the dark (Al_2O_3, hexane:ethyl acetate 7:3) yielded **4** as the second, red fraction (50 mg, 24%). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.74 (d, J = 4.7 Hz, 2H, H^{A6}), 8.67 (s, 2H, H^{B3}), 8.64 (d, J = 7.9 Hz, 2H, H^{A3}), 7.88 (td, J = 7.7, 1.5 Hz, 2H, H^{A4}), 7.67 (d, J = 3.8 Hz, 1H, H^{C3}), 7.50 (d, J = 8.7 Hz, 2H, H^{D2}), 7.36 (m, 2H, H^{A5}), 7.30 (d, J = 3.8 Hz, 1H, H^{C4}), 6.73 (d, J = 8.7 Hz, 2H, H^{D3}), 4.34 (s, 4H, H^{CH2}). ESI MS *m/z* 800.9 $[M + H]^+$ (calc. 800.9), 631.9 $[M - 6CO]^+$ (calc. 631.9); IR (solid, ν_{CO}/cm^{-1}) 2073, 2028, 2001.

[41] **3**: $C_{37}H_{22}Fe_2N_4O_6S_2$, M = 794.43, orange plate, monoclinic, space group $P2_1/c$, a = 23.298(5), b = 10.238(2), c = 15.598(3) Å, β = 100.82(3)°, U = 3654.5(13) $Å^3$, Z = 4, D_c = 1.444 Mg m^{-3}, $\mu(\text{Mo-K}_\alpha)$ = 0.958 mm^{-1}, T = 223(2) K, 88,925 reflections collected, merging r = 0.0944. Refinement of 460 parameters using 8383 independent reflections against F^2 converged at final $R1$ = 0.0493 ($R1$ all data = 0.0544), $wR2$ = 0.1078 ($wR2$ all data = 0.1102), gof = 1.237. **4**: $C_{35}H_{20}Fe_2N_4O_6S_3$, M = 800.46, red needle, monoclinic, space group $P2_1/c$, a = 33.425(7), b = 6.468(1), c = 15.499(3) Å, β = 93.50(3)°, U = 3344.6(12) $Å^3$, Z = 4, D_c = 1.590 Mg m^{-3}, $\mu(\text{Mo-K}_\alpha)$ = 1.108 mm^{-1}, T = 223(2) K, 56,648 reflections collected, merging r = 0.1693. Refinement of 452 parameters using 7687 independent reflections against F^2 converged at final $R1$ = 0.0461 ($R1$ all data = 0.0497), $wR2$ = 0.1097 ($wR2$ all data = 0.1134), gof = 1.054.

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