Controlling Carbon Monoxide Binding at Di-iron Units Related to the Iron-only Hydrogenase Sub-site

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Complexes used in this study

Complexes 1, 7 and 8 were synthesised as previously described [1,2]. The complexes 2, 3, 5, 6, 9 and B (X = CH2OH) are new and were synthesised by an extension of the general method used to synthesise 7 and 8. The syntheses of

$[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C(CH}_2\text{S)}_2\text{CH}_2\text{S(C}_6\text{H}_4\text{-p-CN)}\}]$, 2 and $[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C(CH}_2\text{S)}_2(2\text{-pyridine})\}]$, 6 are illustrative and these are described in detail.

$[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C(CH}_2\text{S)}_2\text{CH}_2\text{S(C}_6\text{H}_4\text{-p-CN)}\}]$, 2.

(a) synthesis of ligand, CH3C(CH2S)2CH2S(C6H4)-p-CN, 4-(4-benzonitrilethio)methyl)-4-methyl-1,2-dithiolane

NaH (60 % oil suspension, 0.38 g, 9.4 mmol) was washed with hexane and then dissolved in THF (80 cm$^3$) under a dinitrogen atmosphere. 4-methyl-[1,2] dithiolan-4-yl)methanethiol (0.76 g, 4.6 mmol) was dissolved in THF (5 cm$^3$), added to the solution of NaH and stirred at room temperature. 4-bromo-nitrobenzene (0.93 g, 5.1 mmol) was dissolved in THF (5 cm$^3$), added to the mixture and stirred at 75 °C overnight. Excess of sodium hydride was quenched by ammonium chloride-saturated water and the product was extracted with dichloromethane. The organic phase was dried (MgSO$_4$) and purified by flash chromatography (hexane/chloroform 1:2) to give a red-brown solid (0.30 g, 1.1 mmol, 24 %). Microanalysis: C, H, N, Found (calculated) C$_{12}$H$_{13}$NS$_3$, C, 54.32; H, 5.07; N, 4.96; S, 35.71 (C, 53.90; H, 4.90; N,
δH (400 MHz; solvent CDCl3; standard SiMe4) 1.37 (3H, s, CH3), 2.96 (2H, d, J 11.7 Hz, CH2SS), 3.15 (2H, d, J 11.4 Hz, CH2SS), 3.24 (2H, s, CH2SPh), 7.39 (2H, d, J 8.5 Hz, Ph), 7.54 (2H, d, J 8.5 Hz, Ph); νmax/cm−1 (CN) 2217 (nujol).

(b) [Fe2(CO)5{CH3C(CH2S)2CH2S(C6H4-p-CN)}], 2: [Fe3(CO)12] (0.62 g, 1.2 mmol) was dissolved in toluene (50 cm3). I (0.30 g, 1.1 mmol) was added to the solution. The dark green mixture turned red brown when it was heated at 75 °C for 90 min. The solvent was removed and the compound was purified by flash chromatography under dinitrogen (diethyl ether/hexane 2:1) to give a red-brown powder (0.19 g, 0.37 mmol, 33%).

[Fe2(CO)5{CH3C(CH2S)2CH2SC6H4-p-CN}], 2: Microanalysis: C, H, N Found (calculated), C17H13NO5S3Fe2, 39.52; 2.76; 2.68 (39.33; 2.52; 2.70) νmax/cm−1 (CO) 1933, 1988 and 2051 (CN) 2232 (acetonitrile); δH (400 MHz; solvent CDCl3; standard SiMe4) 0.93 (3H, s, CH3), 1.72 (2H, d, J 14.1 Hz, CH2SFe), 2.30 (2H, d, J 14.2 Hz, CH2SFe), 2.40 (2H, s, CCH2SPh), 7.76 (2H, d, J 8.0 Hz, Ph), 7.90 (2H, d, J 8.3 Hz, Ph).

[Fe2(CO)5{CH3C(CH2S)2CH2SC6H4-p-NO2}], 3: Microanalysis: C, H, N Found (calculated), C16H13NO7S3Fe2, 35.74; 2.50; 2.67 (35.64; 2.43; 2.60). νmax/cm−1 (CO) 1933, 1988 and 2052 (acetonitrile); δH (400 MHz; solvent CDCl3; standard SiMe4) 0.95 (3H, s, CH3), 1.74 (2H, d, J 13.9 Hz, CH2SFe), 2.32 (2H, d, J 13.9 Hz, CH2SFe), 2.44 (2H, s, CCH2SPh), 7.95 (2H, d, J 8.8 Hz, Ph), 8.33 (2H, d, J 8.8 Hz, Ph).

Fe2(CO)5{CH3C(CH2S)2CH2SC6H4-p-NH2}], 5: Microanalysis: C, H, N Found (calculated), C16H15NO5S3Fe2, 37.76; 2.99; 2.66 (37.74; 2.97; 2.75). νmax/cm−1 (CO) 1928, 1983 and 2048 (acetonitrile); δH (400 MHz; solvent CDCl3; standard SiMe4) 0.83 (3H, s, CH3), 1.66 (2H, d, J 13.7 Hz, CH2SPh), 2.25 (4H, d, J 13.4 Hz, 2×CH2SFe), 3.95 (2H, s, NH2), 7.95 (2H, d, J 8.8 Hz, Ph), 8.33 (2H, d, J 8.8 Hz, Ph).
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Note: complex 4 was generated in situ by treatment of 5 with 1.2 equivalents of HBF₄·Me₂O in MeCN under CO at 1 atmosphere.

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[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C(\text{CH}_2\text{S})_2(2-pyridine)}\}] \quad (A, \ X = 2\text{-pyridine}), \ 6: \text{To a solution of Fe}_3(\text{CO})_{12} \ (0.216, \ 0.4\text{mmol}) \text{in dry toluene (5ml) was added 2-methyl-2-(pyridin-2-yl) propane-1,3-dithiol (0.079g, 0.4mmol) in dry toluene (10ml) under N}_2. \text{The reaction was heated at 110 °C for 4 hours with stirring. After removing the solvent, the reaction residues were purified using flash chromatography (eluting system: ethyl acetate and } n\text{-hexane at a ratio of 1:4). A greenish brown band was collected. Removal of the solvents under vacuum yielded a black-green solid. The crude product was redissolved in CH}_3\text{CN (10ml) and insoluble materials were filtered off under N}_2. \text{Both slow evaporation and storing at low temperature (-20 °C) of the filtrate gave single crystals suitable for X-ray diffraction structural determination. Microanalysis: C, H, N Found (calculated), C_{14}H_{11}NO_5S_2Fe_2, 37.40; 2.50; 3.15 (37.44; 2.47; 3.12). FTIR (CH}_3\text{CN}) \nu_{\text{CO}}: 2048.6, 1978.2, 1914.1\text{cm}^{-1}; \text{MS (ES+): (M+1)/}z = 450.8, (M-CO+1)/z = 422.3. \text{Protonation of 6 in dichloromethane using excess HBF}_4\cdot\text{Et}_2\text{O under CO atmosphere produces the moisture-sensitive hexacarbonyl complex C (X = 2-pyridinium) 5. Storing this solution in dichloromethane at low temperature produces single crystals suitable for structure analysis. The infrared spectrum has the characteristic IR pattern of a diiron hexacarbonyl complex.}
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[\text{Fe}_2(\text{CO})_5\{\text{CH}_3\text{C(\text{CH}_2\text{S})_2(\text{CH}_2\text{NH}_2)}\}] \quad (A, \ X = \text{CH}_2\text{NH}_2), \ 9: \text{Microanalyses: C, H, N Found (calculated), C}_{10}H_{11}NO_5S_2Fe_2, 29.63; 2.72; 3.61 (29.95; 2.76; 3.49). FTIR (acetonitrile) \nu_{\text{CO}}: 2043.9, 1972.1, 1906.5\text{ cm}^{-1}. \text{MS (ESI, -): (m+1)/}z = 402. \text{ }^1\text{H NMR (CDCl}_3): 0.704 \text{ (s, 3H), 1.692 \text{ (d, 2H, J=13.4Hz), 2.173 \text{ (broad, 2H), 2.335 \text{ (d, 2H, J=13.6Hz), 2.663 \text{ (broad, 2H).}}}
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[Fe₂(CO)₆{CH₃C(CH₂S)₂CH₂OH}] (B, X = CH₂OH): Microanalyses: C, H, N

Found (calculated), C₁₁H₁₀O₇S₂Fe₂, 30.68; 2.47; <0.1 (30.72; 2.34; 0.00). FTIR (CH₃CN) νCO: 2074.1, 2033.7, 1998 cm⁻¹
