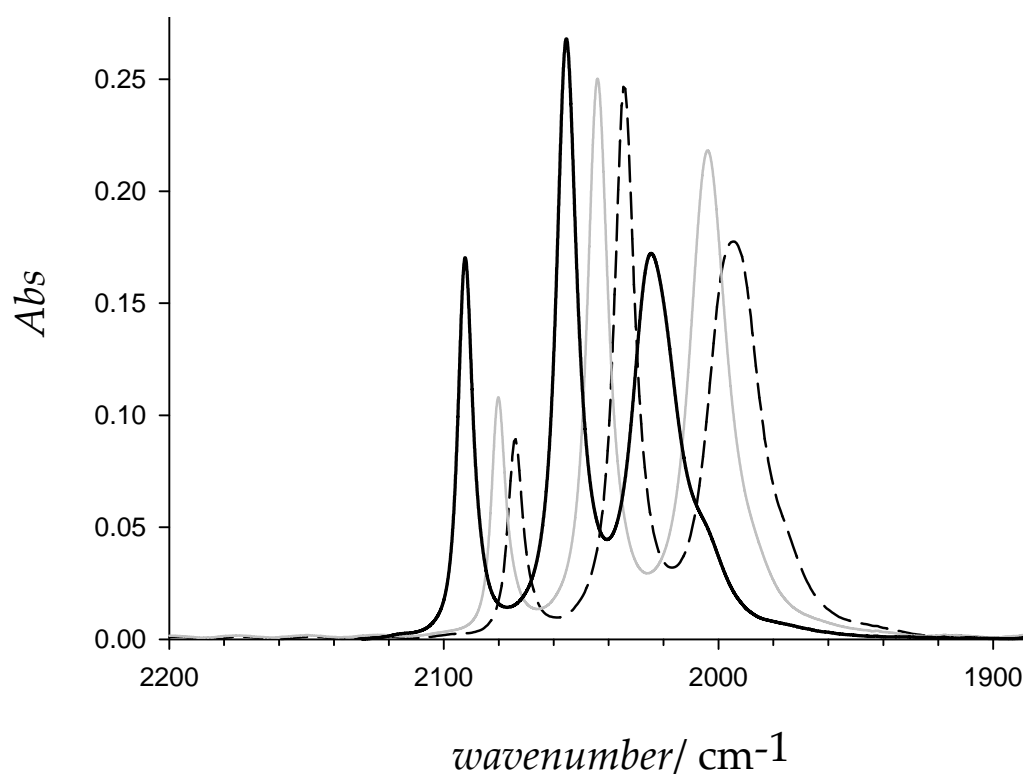


Influence of an electron-deficient bridging *o*-carborane on the electronic properties of an [FeFe] hydrogenase active site model

Lennart Schwartz,^a Lars Eriksson,^b Reiner Lomoth,^a Francesc Teixidor,^c Clara Viñas,^c and Sascha Ott^a

CO Region of the IR spectra of complexes 1-3



IR spectrum of 3 mM solutions of complex **1** (black solid line), $[\text{Fe}_2(\mu\text{-bdt})(\text{CO})_6]$ (**2**, gray line) and $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$ (**3**, dashed line) in CH_3CN (bdt = benzene-1,2-dithiolate, pdt = propane-1,3-dithiolate).

Wavenumber/ $E_{p,c}$ correlation

Figure 3 was constructed from the following values:

Complex	wavenumber maxima	$E_{p,c}$	ref
Fe ₂ cdt(CO) ₆ (1)	2092, 2055, 2024	-0.92	this work
Fe ₂ bdt(CO) ₆ (2)	2080, 2044, 2004	-1.31	¹⁾
Fe ₂ pdt(CO) ₆	2074, 2034, 1995	-1.67	²⁾
Fe ₂ (SCH ₂ N(PhBr)CH ₂ S)(CO) ₆	2077, 2038, 2000	-1.53	²⁾
Fe ₂ (SCH ₂ N(CH ₂ PhBr)CH ₂ S)(CO) ₆	2074, 2036, 1997	-1.56	³⁾

cdt = carborane dithiolate; bdt = benzenedithiolate; pdt = propyldithiolate.

¹⁾ $E_{1/2} = -1.27$ V according to: J.-F. Capon, F. Gloaguen, P. Schollhammer and J. Talarmin, *J. Electroanal. Chem.*, 2006, **595**, 47-52. $E_{p,c}$ was calculated by $E_{p,c} = E_{1/2} - 0.04$ V (half of the practical peak to peak separation). In addition, the compound was remade and measured.

²⁾ From: S. Ott, M. Borgström, M. Kritikos, R. Lomoth, J. Bergquist, B. Åkermark, L. Hammarström and L. Sun, *Inorg. Chem.*, 2004, **43**, 4683-4692.

³⁾ From: S. Ott, M. Kritikos, B. Åkermark, L. Sun and R. Lomoth, *Angew. Chem. Int. Ed.*, 2004, **43**, 1006-1009.

Experimental Section

General procedure

1,2-Dithiol-1,2-o-carborane was prepared according to the literature procedure (H. D. Smith, C. O. Obenland and S. Papetti, *Inorg. Chem.*, 1966, **5**, 1013-1015). Solvents were of reagent grade and used without further purification. $\text{Fe}_3(\text{CO})_{12}$ (was purchased from Aldrich and used as received. Flash chromatography was performed on Merck silica gel SI-60Å (35-70).

NMR-Spectroscopy

^1H NMR spectra were recorded on a JEOL Eclipse+ 400 MHz spectrometer together with the JEOL Delta NMR Processing Software version 4.3. in deuterated chloroform. Residual protic solvent peaks CHCl_3 ($\delta_{\text{H}} = 7.26$ ppm) were used as internal references. ^{13}C NMR and ^{11}B NMR spectra were recorded on the same instrument operating at a frequency of 100.6 MHz using the central signal of CDCl_3 ($\delta = 77.0$ ppm) as reference signal, and at 128.3 MHz, using a $\text{BF}_3\text{Et}_2\text{O}$ as external standard, respectively.

IR-Spectroscopy

IR absorption spectra were recorded between 1000 and 5000 cm^{-1} at a resolution of 1 cm^{-1} on a Bruker FT-IR spectrometer (IFS 66v/S) with the sample as solution in a liquid-sample-cell (Bruker A140) between CaF_2 windows and a pathlength of 125 μm . The solutions were prepared in CH_3CN (Sigma-Aldrich, spectroscopic grade).

Electrochemistry

Cyclic voltammetry were carried out using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). The working electrode was a glassy carbon disc (diameter 3 mm, freshly polished) for voltammetry. A glassy carbon rod was used as counter electrode. The reference electrode was a non-aqueous Ag^+/Ag electrode (CH Instruments, 0.010 M AgNO_3 in acetonitrile) with a potential of -0.08 V *vs.* the ferrocenium/ferrocene (Fc^+/Fc) couple in acetonitrile as an external standard. All potentials reported herein are quoted *vs.* the Fc^+/Fc couple by adding -0.08 V to the potentials measured *vs.* the Ag^+/Ag electrode. All solutions were prepared from dry acetonitrile (Sigma-Aldrich, spectroscopic grade, dried with MS 3 Å) with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) as supporting electrolyte that has been dried in vacuum at 383 K.

Synthesis

$\text{Fe}_3(\text{CO})_{12}$ (484 mg, 0.96 mmol) and 1,2-dithiol-1,2-*o*-carborane (200 mg, 0.96 mmol) were dissolved in 20 ml of degassed toluene. The reaction mixture was refluxed for 40 min under argon atmosphere. The solvent was then removed by rotary evaporation and the product was purified by column chromatography (using hexane as eluent) affording the title compound as a red solid (102 mg, 23% yield).

^1H NMR (400 MHz, CDCl_3): δ = 4.3-1.5 (broad, *BH*) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 205.1, 82.7 ppm; ^{11}B NMR (128 MHz, CDCl_3): δ = 1.69 (d, 2B, $^1J(\text{B-H})$ = 149 Hz), -4.29 (d, 4B, $^1J(\text{B-H})$ = 141 Hz), -9.22 (d, 2B, $^1J(\text{B-H})$ = 161 Hz), -12.78 (d, 2B, $^1J(\text{B-H})$ = 155 Hz).

Anal. calculated for $\text{C}_8\text{O}_6\text{H}_{10}\text{S}_2\text{B}_{10}\text{Fe}_2$ * 5% toluene: C, 20.47; H, 2.15. Found: C, 20.50; H, 2.16 %.

Crystallographic details:

Single crystal X-ray diffraction patterns were recorded with a Stoe IPDS diffractometer on a rotating anode Mo-radiation source ($\lambda = 0.71073 \text{ \AA}$) with ϕ -scans of 1° width. Total rotation range was 200° . The sample-detector distance was 60 mm and with the diameter of the image plate being 180 mm this gave $\max 2\theta \approx 56^\circ$.

Indexing, cell refinements and integration of reflection intensities were performed with the STOE IPDS software [1]. Numerical absorption correction was performed with the program X-RED [2] using multiple measurements of symmetry equivalent reflections and verifying the crystal shape with program X-shape [3]. The structure was solved by direct methods using SHELXS97 [4] giving electron density maps where most of the non-hydrogen atoms could be resolved. The rest of the non-hydrogen atoms were located from difference electron density maps and the structure model was refined with full matrix least square calculations on F^2 using the program SHELXL97-2 [5]. All non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen's, which were placed at geometrically calculated positions and let to ride on the atoms they were bonded to, were given isotropic displacement parameters calculated as $\xi \cdot U_{\text{eq}}$ for the non-hydrogen atoms with $\xi = 1.2$ for borane hydrogen's.

Selected crystal data are given in table 1

Table 1. Selected crystal data for **1** and **2**

code	Ls127
Empirical formula	$\text{C}_8 \text{H}_{10} \text{B}_{10} \text{Fe}_2 \text{O}_6 \text{S}_2$
Temperature, K	293(2)
Fw	486.08
Crystal system	Monoclinic
Space group	$P 2_1/c$
a, \AA	11.496(8)
b, \AA	13.232(6)
c, \AA	13.727(5)
α , $^\circ$	90
β , $^\circ$	110.860(17)
γ , $^\circ$	90
V, \AA^3	1951.2(18)
Z	4
ρ_{calc} , g cm^{-3}	1.655
μ (MoK α), (mm^{-1})	1.723
N(meas), N(uniq), R(int)	26970, 3945, 0.0992
N(obs), N(par), S (GoF)	3511, 253, 1.03
R1, wR2 both with ($I > 2\sigma(I)$)	0.0331, 0.0886
R1, wR2 (all data)	0.0370, 0.0919
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ (e/\AA^3)	-0.417 – 0.559

References

- 1) STOE IPDS diffractometer control software, version 2.87. Stoe & Cie GmbH Darmstadt, Germany
- 2) X-RED, absorption correction program, version 1.09, Stoe & Cie GmbH Darmstadt, Germany
- 3) X-SHAPE, Crystal Optimisation for Numerical Absorption Correction, version 1.2, Stoe & Cie GmbH Darmstadt, Germany
- 4) Sheldrick, G.M. (1990). *Acta Cryst.* A46, 467-473
- 5) Sheldrick, G.M. (1997). Computer program for the refinement of crystal structures, Göttingen, Germany
- 6) DIAMOND - Visual Crystal Structure Information System, CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn, Germany