

# X-Ray crystallographic analysis of D,L-[Fe<sub>2</sub>{SCH<sub>2</sub>CH(CH<sub>2</sub>OH)S}(CO)<sub>6</sub>] reveals a hydrogen-bonded cyclic hexamer with ordered optical centres

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A novel organometallic cyclic hexamer with ordered optical centres is described.

Bridging thiolate complexes of the general type [Fe<sub>2</sub>(SR)<sub>2</sub>(CO)<sub>6</sub>] are receiving renewed attention as precursors to cyano-complexes<sup>1–5</sup> that have structural similarities to the di-iron sub-site of all-iron hydrogenases.<sup>6,7</sup> The dithiolate complex D,L-[Fe<sub>2</sub>{SCH<sub>2</sub>CH(CH<sub>2</sub>OH)S}(CO)<sub>6</sub>] **A** was synthesised by reaction of D,L-2,3-dimercapto-1-propanol and Fe<sub>3</sub>(CO)<sub>12</sub><sup>†</sup> and was of interest because the hydroxy group on the ligand backbone can be derivatised.<sup>8</sup> We determined the X-ray crystallographic structure of **A** from well-formed crystals grown in MeCN and were surprised to find the following.

Firstly, **A** forms a supramolecular centrosymmetric structure in which hydrogen-bonding links six molecules as a cyclic hexamer of graph set R<sub>6</sub><sup>h</sup>(12), Fig. 1. Secondly, the optically active

only other example of which we are aware is comprised of bis-(pentafluorophenyl)methanol units<sup>10</sup> where the six molecules are related by  $\bar{3}$  symmetry. The conformation in this R<sub>6</sub><sup>h</sup>(12) system is a very shallow chair with O atoms  $\pm 0.181$  Å from the mean plane and O...O...O...O torsion angles of  $\pm 26.1^\circ$ . Hydrogen-bonding is marginally weaker in this hexamer than in the **A** hexamer, O...O distances being 2.702(4) Å at 293° as compared with an average of 2.668(3) Å for the latter.

In crystals of **A**, there are three independent molecules.<sup>11</sup> They have very similar dimensions and conformations, differing principally in the orientation of the C–O bond in the thiolate ligand (two are *trans* to the C–S bond, one is *trans* to the C–C bridging bond). Fig. 2 shows a view of one monomeric unit. The

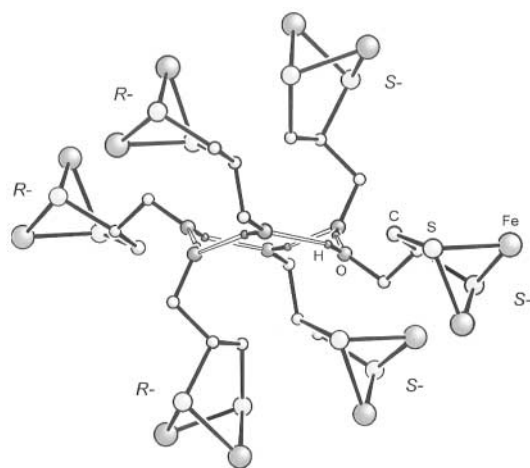


Fig. 1 View of the hexameric structure of **A**. The three carbonyl ligands on each iron atom and the Fe–Fe metal bonds are omitted for clarity.

centres are ordered in an enantiomerically pure RRRSSS arrangement.

The hydrogen bonding in the hexameric structure is strong, as indicated by the three unique O...O distances of 2.661(3), 2.671(3) and 2.671(3) Å with corresponding O...H distances of 1.97(4), 1.99(3) and 1.93(3) Å, and O–H...O angles 159(4), 168(4) and 171(4)° respectively. The prototypical hydrogen-bonded R<sub>6</sub><sup>h</sup>(12) motif is the unstable cyclic water hexamer which has been detected by infrared spectroscopy in liquid helium droplets.<sup>9</sup> Theoretical calculations indicate that the water hexamer adopts a chair conformation, as is also seen in the X-ray crystal structure of the **A** hexamer, Fig. 1. Thus the O atoms are displaced by  $\pm 0.275(3)$ ,  $\pm 0.309(3)$  and  $\pm 0.393(3)$  Å from the mean plane of the hexamer's six oxygen atoms and O...O...O...O torsion angles are  $\pm 49.1(2)$ ,  $\pm 39.9(1)$  and  $\pm 54.4(2)^\circ$ .

Discrete OH...O bonded cyclic hexamers appear rare. The

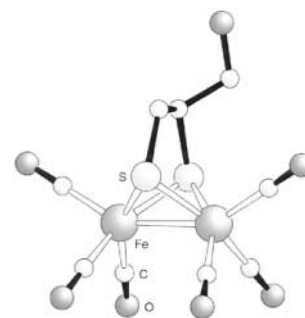


Fig. 2 View of the monomeric di-iron hexacarbonyl unit.

average bond distances and angles for the {Fe<sub>2</sub>S<sub>2</sub>} units are unexceptional, being very similar to those of related structures. For example, the mean Fe–Fe and Fe–S distances, 2.499(3) and 2.2387(8) Å, are close to those in the complex [{Fe(CO)<sub>3</sub>}<sub>2</sub>-(μ-SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S)] which are 2.5125(9) and 2.251(3) Å respectively.<sup>4</sup> The S–C–S bridging unit in each molecule of **A** is essentially planar.

Three adjacent molecules in the cyclic hexamer are of the same chirality (and form the asymmetric unit); thus the chiral ordering of the molecules in the centrosymmetric structure is RRRSSS. As far as we are aware, this represents the first example of this type of chiral ordering in an achiral cyclic hexamer; neither RRRSSS nor RSRSRS cyclic structures have hitherto been reported. The segregation of enantiomeric centres in the racemate hexamer might be viewed as primitive self-resolution at the molecular rather than crystal lattice level, the latter demanding regular packing of *R* and *S* enantiomers as a racemic conglomerate.<sup>14</sup>

## Notes and references

<sup>†</sup> Preparation of [Fe<sub>2</sub>{SCH<sub>2</sub>CH(CH<sub>2</sub>OH)S}(CO)<sub>6</sub>]: A mixture of 1.98 g (3.9 mmol) Fe<sub>3</sub>CO<sub>12</sub>, 0.39 mL (3.7 mmol) 2,3-dimercapto-1-propanol (95%) and 100 mL toluene was stirred at 100 °C for 1 h. The red solution was filtered through silica gel (70–230 mesh) leaving a black insoluble material. A yellow fraction was extracted first and the dark orange solution was finally collected by elution with more toluene. Solvent was removed under vacuum and replaced by 10 mL MeCN.

MeCN was evaporated down, leaving an orange powder; Yield: 50%. This powder was dissolved in 5 mL MeCN and this was removed slowly under vacuum, giving dark orange prism crystals.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  2.01 (1H, dd,  $^2J$  13.0,  $^3J$  5.4 Hz, CHHCH), 2.72 (1H, dd,  $^2J$  13.0,  $^3J$  7.5 Hz, CHHCH), 2.83 (1H, m,  $\text{CH}_2\text{CHCH}_2$ ), 3.44 (1H, dd,  $^2J$  11.6,  $^3J$  6.6 Hz, CHHOH), 3.52 (1H, dd,  $^2J$  11.6,  $^3J$  6.3 Hz, CHHOH).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.95 (1H, OH). FTIR (in  $\text{CH}_3\text{CN}$ ):  $\nu(\text{CO})$  1992 (s,br), 2032 (ms), 2074 (s) and  $\nu(\text{OH})$  3483 (m,br)  $\text{cm}^{-1}$ . EIMS:  $m/z$  234  $\{\text{M} - 6\text{CO}\}^+$ , 176  $\{[\text{Fe}_2\text{S}_2]\}^+$ . Mössbauer spectrum: (solid, 77 K, referenced to 25  $\mu\text{m}$  Fe-foil at 295 K): doublet; isomer shift +0.007  $\text{mm s}^{-1}$ ; quadrupole splitting 0.85  $\text{mm s}^{-1}$ .

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- 11 Crystal structure analysis of A:  $\text{C}_9\text{H}_6\text{Fe}_2\text{O}_7\text{S}_2$ ,  $M = 402.0$ . Triclinic, space group  $F\bar{1}$  (equiv. to no. 2; this cell is the preferred, most orthogonal cell),  $a = 18.834(2)$ ,  $b = 26.405(3)$ ,  $c = 18.300(2)$  Å,  $\alpha = 97.249(9)$ ,  $\beta = 102.212(8)$ ,  $\gamma = 94.503(9)^\circ$ ,  $V = 8772(2)$  Å<sup>3</sup>.  $Z = 24$  (monomer units),  $D_c = 1.83$  g cm<sup>-3</sup>,  $F(000) = 4800$ ,  $T = 293(1)$  K,  $\mu(\text{Mo-K}\alpha) = 2.3$  mm<sup>-1</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å. Dark orange prism crystal,  $0.55 \times 0.48 \times 0.36$  mm, mounted on glass fibre and coated with epoxy resin. Photographic examination; measurements of cell dimensions and diffraction intensities (12750 unique reflections,  $\theta_{\text{max}} = 30^\circ$ ) on a Nonius CAD4 diffractometer. Corrections for absorption and to remove negative intensities. Solution by direct methods, SHELXS;<sup>12</sup> refinement by full-matrix least-squares methods, SHELXL.<sup>13</sup> All hydrogen atoms included in idealised positions, then refined freely. All other atoms refined anisotropically. Final  $R_1$  and  $wR_2$  values 0.054 and 0.079 for all data; for 8642 'observed' data,  $R_1 = 0.031$ . CCDC reference number 169367. See <http://www.rsc.org/suppdata/dt/b1/b107595k/> for crystallographic data in CIF or other electronic format.
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