A double-helix generated from a ferrocenyl-thiosemicarbazato metallo-synthon and its novel hydrogen-bonding cavities

Fang Chen-jie, Duan Chun-ying,* He Cheng and Meng Qing-jin*

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China. E-mail: duancy@nju.edu.cu

Received (in Cambridge, UK) 17th April 2000, Accepted 23rd May 2000

A double helical architecture generated from a readily prepared ferrocenyl-containing bisthiosemicarbazone ligand is described together with its application to the self-assembly of novel supramolecular hydrogen-bonding cavities.

A theme of considerable interest in supramolecular chemistry is the spontaneous and selective formation of organized supramolecular architectures *via* self-assembly.[1] The double-helical structures generated by the complexation of two ligands around metal ions lying on the helical axis retain a unique fascination since life itself is encoded within a double-helical architecture. While the basic features of the design necessary to assemble a double helix are now fairly well established,[2,3] challenges in defining the precise topography or conformation of the helical superstructure remain.

Here, we introduce a ferrocene bridged bisthiosemicarbazone ligand (Fig. 1) to generate a double-helical zinc complex *via* self-assembly. The ferrocene group was chosen as a spacer to separate the two metal binding sites, not only because this spacer is suitable to assemble double-helices,[3] but also because host molecules containing metallocene units can accommodate metal ions at their coordination sites and undergo redox changes.[4]

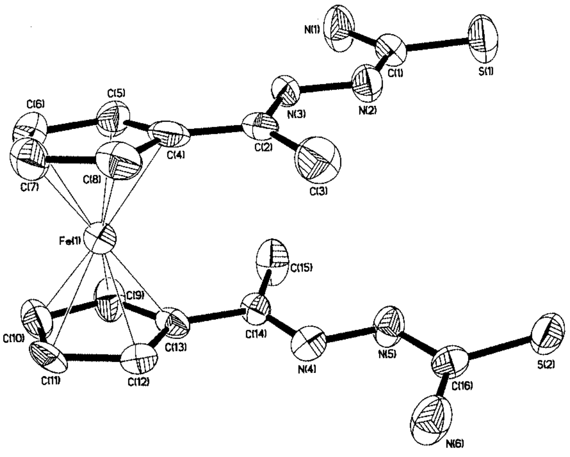

Fig. 1 ORTEP[8] plot of the ligand H_2L, showing the non-hydrogen atoms as 50% probability thermal ellipsoids. Selected bond lengths (Å): S(1)–C(1) 1.686(6), N(1)–C(1) 1.336(8), N(2)–C(1) 1.349(7), N(2)–N(3) 1.386(6), C(2)–C(3) 1.494(8), S(2)–C(16) 1.693(5), N(6)–C(16) 1.322(7), N(5)–C(16) 1.343(7), N(4)–N(5) 1.375(6).

Thiocarbazones and thiosemicarbazones have been used to assemble supramolecular architectures.[5] The hydrogen atoms attached to the amino nitrogen atoms of the thiosemicarbazone moiety have the ability to form donor hydrogen bonds. This kind of non-covalent bond has the potential to assemble smaller, simpler fragments into the desired cavities under favourable conditions, which is important in host–guest chemistry and has applications in chemistry, biology and materials science.[6]

When diacetylferrocene was treated with thiosemicarbazide in ethanol, a red crystalline solid formed readily.‡ Elemental analysis and crystal structure analysis‡ indicated the formation of a bisbidentate ligand $NH_2C(S)N(H)N{=}CMe(C_5H_4)$-$Fe(C_5H_4)CMe{=}NN(H)C(S)NH_2$ H_2L.† The ligand shows a *cis*-configuration with two thiosemicarbazone moieties positioned at the same side with the torsion angle C(2)–C(4)···C(13)–C(14) being −10.8°. Each thiosemicarbazone moiety is coplanar with the Cp ring to which it is attached (the mean deviation from the best plane is 0.09 Å on average). The C–S bond lengths of 1.69 Å agree well with those in related compounds, indicating that the Schiff-base compound H_2L remains as the *thione* tautomer. The two thiosemicarbazone moieties of the ligand adopt a configuration in which the hydrazone nitrogen atoms N(3) and N(6) are *trans* to S(1) and S(2), respectively. Rotation of the H_2NCS fragment by 180° about the C(1)–N(2) and C(16)–N(5) bonds places each pair of the sulfur atoms and the hydrazone nitrogen atoms on the same side, thus enabling H_2L to function as a double anionic N_2S_2 ligand.

Reaction of H_2L with $Zn(MeCO_2)_2{\cdot}2H_2O$ in methanol at reflux gives the binuclear neutral complex Zn_2L_2 **1** *via* self-assembly.† Complex **1** is a stable pale-orange precipitate which is insoluble in most organic solvents. Recrystallization of the compound from DMF by dichloromethane diffusion afforded X-ray quality crystals.‡ The structure of one of the two enantiomers is shown in Fig. 2 and confirms the formation of a double-helix composed of two anionic ligands L^{2-} wrapped around two Zn(II) ions which are separated by 7.74 Å. The complex possesses a crystallographic C_2 axis perpendicular to the helical Zn···Zn axis, with the four coplanar metal atoms forming a slightly distorted rhombus with sides of 5.0 Å and interior angles of 79 and 101°. Each zinc center occupies a four-

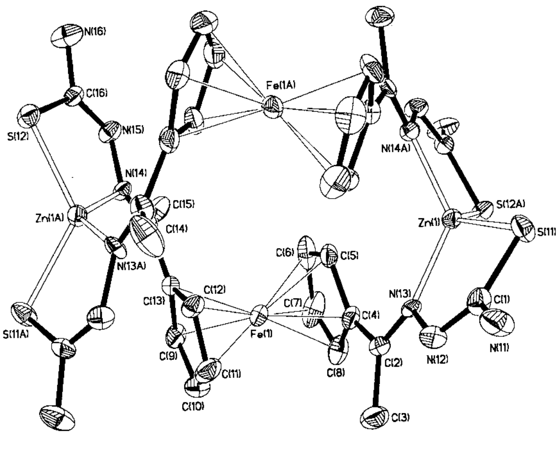

Fig. 2 ORTEP plot of the coordinated zinc(II) complex Zn_2L_2, showing the non–hydrogen atoms as 50% probability thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(13) 2.073(9), Zn(1)–S(11) 2.280(3), S(11)–C(1) 1.730(1), S(12)–C(16) 1.739(1), N(11)–C(1) 1.348(2), N(12)–C(1) 1.289(2), N(12)–N(13) 1.401(1), N(14)–N(15) 1.396(1), N(15)–C(16) 1.305(1), N(16)–C(16) 1.350(2); N(14A)–Zn(1)–N(13) 130.4(3), S(12A)–Zn(1)–S(11) 125.4(8), N(13)–Zn(1)–S(11) 86.6(3), N(14A)–Zn(1)–S(12A) 87.5(2), N(13)–Zn(1)–S(12A) 116.3(3), N(14A)–Zn(1)–S(11) 115.3(3), Symmetry code A: $1-x$, y, $1-z$.

DOI: 10.1039/b003072o

coordinated pseudo-tetrahedral environment bound to atoms S(1) and N(3) from one L^{2-} ligand, and S(2A) and N(4A) from a second ligand (Fig. 2). The dihedral angle between the two coordinated planes is 77°. The Zn–S distances of 2.266(3)–2.274(4) Å and Zn–N distances of 2.059(9)–2.068(9) Å agree well with those in related compounds. The thiosemicarbazone moieties are twisted by *ca*. 50° from the Cp rings to which they are attached with dihedral angles between the two thiosemicarbazone moieties of 73.5°. Coordination to the metal center also forces twisting between the two side chains with a torsion angle C(2)–C(4)···C(13)–C(14) of 128°. No significant deformation of the almost parallel Cp ring is observed. The measured C–S bond distances range from 1.736(11) to 1.748(11) Å and are within the normal range of a C–S single bond,[7] indicating that the thiosemicarbazone moieties L^{2-} adopt the *thiol* tautomeric form in acting as a doubly charged negative ligand. The C–N and N–N bond distances in L^{2-} are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire molecular skeleton.

While both the dichloromethane molecules and water molecules lie outside the cavity of the helix, X-ray diffraction analysis of the complex reveals that helices of each enantiomer interact with each other through hydrogen bonds forming an infinite tube as shown in Fig. 3. The imino nitrogen atoms of the thiosemicarbazone moieties act as H-bond acceptors while the amino nitrogen atoms act as donors, these pair up with the corresponding imino and amino nitrogen atoms of a parallel helix forming hydrogen bonds. The N···N separations are 3.18(1) and 3.16(1) Å for N(11)···N(15B) ($1-x$, $1+y$, $1-z$) and N(16)···N(12C) ($1-x$, $-1+y$, $1-z$), respectively, while N–H···N angles are 156(1) and 171° for N(11)–H(11B)···N(15B) and N(16)–H(16A)···N(12C), respectively. The one-dimensional tube contains alternate cavities and walls (the double-helix molecules) reminiscent of a train. Each 'coach' includes two hydrogen bonded dimeric water molecules with an O···O separation of *ca*. 2.93 Å. The O···O vector occupies a C_2 axis perpendicular to the helical Zn···Zn axis. No obvious hydrogen bonds are seen between the guest molecules and the host.

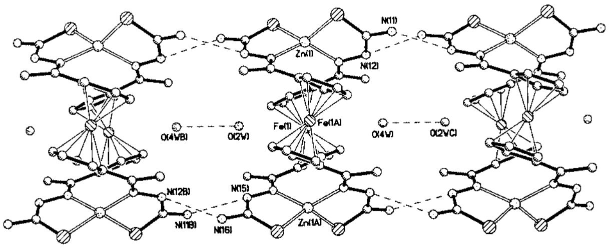

Fig. 3 View of the hydrogen-bonding one-dimensional tube with included water molecules. Symmetry code B: $1-x$, $1+y$, $1-z$; C: $1-x$, $-1+y$, $1-z$.

The ferrocene-bridged double-helical complex derived here from an inexpensive and readily prepared bisthiosemicarbazone ligand and its novel hydrogen-bonding supramolecular 'train-like' system with each 'coach' of the train including two water molecules is interesting in that it provides an unusual example in metallo-supramolecular chemistry. This self-assembled nano-structure showing host–guest interactions shows potential for broadening the scope for further work in self-assembly. The development of new ligand systems containing the functional ferrocene group and application to assemble supramolecular cavities are in progress.

This work is supported by the National Natural Science Foundation of China.

Notes and references

† *Preparations*: H_2L: five drops of glacial acetic acid were added to a mixture of thiosemicarbazide (0.36 g, 4 mmol) and diacetylferrocene (0.54 g, 2 mmol) in ethanol solution (15 mL). A red solid formed after refluxing for 4 h which was isolated, washed with ethanol and dried under vacuum. $C_{16}H_{20}FeN_6S_2\cdot CH_3CH_2OH$: Calc. C, 46.8; H, 5.7; N, 18.2. Found: C, 46.3; H, 5.5; N, 17.9%.

Zn_2L_2: thiosemicarbazone (0.42 g, 1 mmol) and zinc acetate (0.22 g, 1 mmol) were mixed in 25 mL methanol. After refluxing for 4 h, a pale-orange solid formed which was isolated, washed with methanol and dried under vacuum. $C_{32}H_{36}Fe_2N_{12}S_4Zn_2\cdot H_2O\cdot CH_3OH$: Calc: C, 39.4; H, 4.2; N, 16.7. Found: C, 40.0; H, 4.4; N, 16.3%.

‡ *Crystal data*: for H_2L: $C_{16}H_{22}FeN_6OS_2$, M = 434.37, monoclinic, space group: $C2/c$, a = 29.0219(14), b = 8.797(2), c = 18.447(2) Å, β = 125.94(1)°, U = 3812.7(11) Å^3, Z = 8, D_c = 1.513 Mg m^{-3}, μ = 1.029 mm^{-1}, $F(000)$ = 1808, T = 293(2) K. 3350 independent reflections measured, 2297 observed [$F > 4\sigma(F)$]. Refinement on all data and 323 parameters converged at $R1$ = 0.0647, $wR2$ = 0.1512, respectively.

For **1**$\cdot 2CH_2Cl_2\cdot 2H_2O$: $C_{34}H_{44}Cl_4Fe_2N_{12}O_2S_4Zn_2$, monoclinic, space group $C2$, a = 30.076(6), b = 9.6742(18), c = 21.693(5) Å, U = 4675.4(17) Å^3, Z = 4, D_c = 1.655 Mg m^{-3}, $F(000)$ = 2368, μ = 2.075 mm^{-1}. 4849 independent reflections measured, 4240 observed [$F > 4\sigma(F)$]. Refinement on all data and 553 parameters converged at $R1$ = 0.070, $wR2$ = 0.177, respectively.

Intensities were collected on a Siemens P4 four circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using the ω–2θ scan mode. Data were corrected for Lorentz-polarization effects during data reduction using XSCANS,[9] and a semi-empirical absorption correction from ψ-scans was applied. The structures were solved by direct methods and refined on F^2 *via* full-matrix least-squares methods using SHELXTL version 5.0.[10]

CCDC 182/1653. See http://www.rsc.org/suppdata/cc/b0/b003072o/ for crystallographic files in .cif format.

1 J. M. Rivera, T. Martin and J. Rebek, Jr, *Science*, 1998, **279**, 1021; M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469; L. J. Prins, J. Huskens, F. D. Jong, P. Timmerman and D. N. Reinhoudt, *Nature*, 1999, **398**, 498; P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154.

2 J.-M. Lehn, *Supramolecular Chemistry—Concept and Perspectives*, VCH, Weinheim, 1995; *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Pergamon, Oxford, 1996, vol. 9, pp. 213–252; C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; A. Bilyk, M. M. Harding, P. Turner and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1994, 2783.

3 M. J. Hannon, S. Bunce, A. J. Clarke and N. W. Alcock, *Angew. Chem., Int. Ed.*, 1999, **38**, 1277; N. Yoshida, H. Oshio and T. Ito, *Chem. Commun.*, 1998, 63; M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin and W. Errington, *Chem. Commun.*, 1997, 1807; M. J. Hannon, C. L. Painting and N. W. Alcock, *Chem. Commun.*, 1999, 2023.

4 P. D. Beer, P. A. Gale and G. Z. Chen, *J. Chem. Soc., Dalton Trans.*, 1999, 1897; M. Buda, J.-C. Moutet, E. Saint-Aman, A. De Cian, J. Fischer and R. Ziessel, *Inorg. Chem.*, 1998, **37**, 4146.

5 C. Y. Duan, B. M. Wu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1996, 3485; C. Y. Duan, Z. H. Liu, X. Z. You, F. Xue and T. C. W. Mak, *Chem. Commun.*, 1997, 381; C. He, C. Y. Duan, C. J. Fang, Y. J. Liu and Q. J. Meng, *J. Chem. Soc., Dalton Trans*, 2000, 1207.

6 J. De Mendoza, *Chem. Eur. J.*, 1998, **4**, 1373; J. Rebek Jr., *Acc. Chem, Res.*, 1999, **32**, 278; L. R. MacGillivray and J. L. Atwood, *Angew. Chem. Int. Ed.*, 1999, **38**, 1018.

7 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, G. G. Watson and R. Taylor, in *Structure Correlation*, ed. H. B. Buigi and J. D. Dunitz, VCH, Weinheim, 1994, vol. 2, Appendix A., pp. 751–778.

8 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, TN, USA, 1965.

9 XSCANS, Version 2.1, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

10 Siemens, SHELXTL, Version 5.0, Siemens Industrial Automation, Inc. Analytical Instrumentation, Madison, WI, 1995.