A novel ferrocene–barium sandwich sheet-shaped coordination polymer and its solid-state electrochemistry

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A new 2-D ferrocene-containing sandwich sheet coordination polymer, consisting of a BaO inorganic inner polymer and novel ordered ferrocenyl outer layers, has been achieved and structurally characterized; the solid-state redox properties of the barium complex and the related samarium complex have also been investigated.

In recent years, alkaline earth metal compounds have been increasingly studied owing to their application in different research fields, especially in the search for new precursors for superconductors and complex metal oxides. In this context, their inorganic polymers of different dimensionality have been structurally characterized.[1,2] Among them, barium is an important metal in many of the high-temperature superconductors ($YBa_2Cu_3O_7$, $HgBa_2CuO_4$, $HgBa_2Ca_2Cu_3O_8$).[3]

On the other hand, heteropolynuclear organometallic compounds, especially ferrocene and its derivatives, have been pursued with the objective of generating materials possessing useful electrochemical, magnetic, and optical and non-linear optical properties.[4] These include redox-active materials for modification of electrodes or materials, which can function as multielectron redox systems or biosensors.[5] In general, the molecules containing metallocene units can accommodate a particular transition metal ion at its coordination site and undergo a concurrent redox change.[6] Compared to the well-studied transition metal ferrocenyl-containing compounds, no alkaline-earth metal ferrocenyl compounds have been investigated.

In this communication we use 1,1′-ferrocenedicarboxylic acid as the building block to assemble a mixed-metal coordination polymer, namely, $[BaL(H_2O)]_\infty$ **1** (H_2L = 1,1′-ferrocenedicarboxylic acid). Owing to the inherently flexible coordination geometries and the high coordination numbers of barium, it is particularly attractive for the preparation of new inorganic polymers, as this greater structural ambivalence will lead to the synthesis of interesting structures.[7]

Complex **1**† was obtained by slow diffusion of a methanol solution of H_2L into an aqueous solution of $BaCl_2$ (1 : 1 molar ratio) in the presence of NaOH. Single crystal X-ray structure determination ‡ shows a two-dimensional ferrocenyl-containing sandwich sheet coordination polymer, consisting of a BaO inorganic inner polymer (Fig. 1) and ordered ferrocenyl outer layers. The Ba(II) ion is ligated by two oxygen atoms [O(1), O(3)] from one ferrocenedicarboxylato(−2) ligand, four oxygen atoms [O(1A), O(2B), O(3C), O(2D)] from four other symmetry related ligands and one water molecule. The metal ⋯ metal distances are *ca.* 4.27 and 5.30 Å for Ba(1) ⋯ Ba(1A) and Ba(1) ⋯ Ba(1B), respectively. The ferrocenedicarboxylato moiety exhibits a synclinal staggered conformation (torsion angle *ca.* 43°) and acts as the bridging ligand through carboxylato groups in an unusual μ^3-η^2:η^1-coordination mode. In this case, one oxygen atom is terminally coordinated to the related Ba(II) ions and the second oxygen atom is involved in a monoatomic bridge between the two barium ions. The barium and oxygen atoms compose the two-dimensional inner layers of the slightly wavy sandwich sheets with the ferrocenyl moieties slanting up and down the layers. It seems that the polymeric
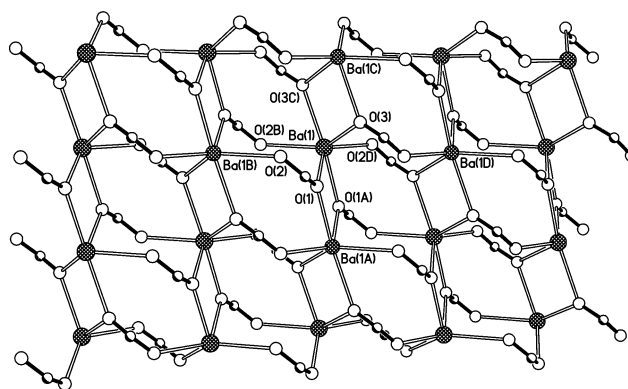

Fig. 1 The two-dimensional BaO layer of complex **1** with ferrocenyl groups and water molecules omitted for clarity. Selected bond lengths (Å): Ba(1)–O(1) 2.795(4), Ba(1)–O(1A) 2.777(4), Ba(1)–O(2B) 2.746(2), Ba(1)–O(3) 2.769(4). Symmetry codes: A −x, 2 − y, −z; B −x − 1/2, −y + 3/2, −z; C −x − 1, y, −z; D −x − 1/2, y + 1/2, −z.

aggregates featuring sheets of metal ions may have potential as ionic conductors, charge-storage devices, and as biomimetic models.[8]

Polyferrocenes generally undergo reversible one-electron oxidations, with the number of waves being determined by the number of ferrocenyl units. The half-wave potentials of the redox processes and the separation between consecutive waves vary over a wide range depending on the nature of the compounds.[9] The solid-state differential pulse voltammetries[10] of complex **1** and 1,1′-ferrocenedicarboxylic acid (Fig. 2) show
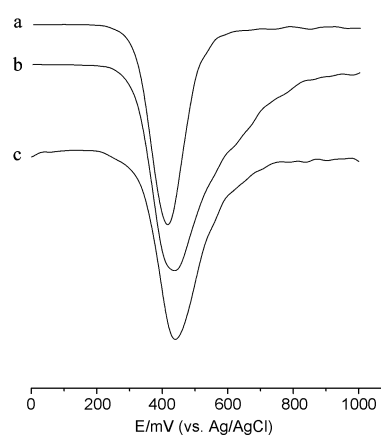

Fig. 2 The solid-state differential pulse voltammograms of complexes **1** (a), **2** (b) and H_2L (c) at a scanning rate of 20 mV s⁻¹ (*vs.* Ag/AgCl).

peaks with half-wave potential ($E_{1/2}$) at 0.42 V for **1**, 0.44 V for H_2L, respectively, corresponding to the redox processes of the ferrocenyl moieties. The half-wave potential of the ferrocenyl moiety seems to be uninfluenced by the Ba(II) ions, which is inconsistent with the previous results of transition metal–ferrocenyl systems.[11] In order to investigate the effect of ions on the half-wave potentials of ferrocenyl moieties extensively, a

lanthanide–ferrocene complex $Sm_2L_3(H_2O)_5$, **2**, was also synthesized. †

Crystal structure analysis shows that complex **2** is a 2-D coordination network constructed from lanthanide-organometallic layers. It should be noted that the Fe(2) ion lies at an inversion centre (0,0,0) and that the water oxygen atom O(3W) lies on a two-fold axis (3/4,y,1/4). Two different types of coordination modes and conformations of ferrocenedicarboxylato ligands are present (Fig. 3): a) each carboxylate
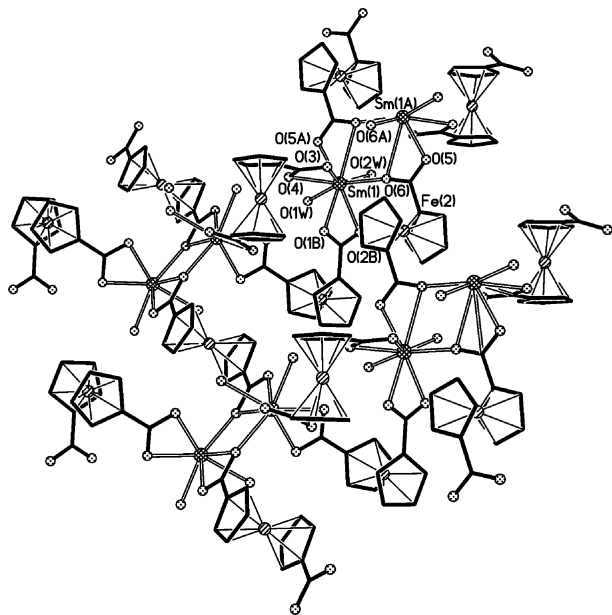

Fig. 3 The two-dimensional layer of complex **2** showing the various conformations and coordination modes of the ligands. Selected bond lengths (Å): Sm(1)–O(1B) 2.450(4), Sm(1)–O(2B) 2.489(5), Sm(1)–O(3) 2.463(4), Sm(1)–O(4) 2.517(4), Sm(1)–O(5A) 2.401(5), Sm(1)–O(6) 2.378(4), Sm(1)–O(1W) 2.451(4), Sm(1)–O(2W) 2.479(4). Symmetry codes: A $-x$, $1 - y$, $-z$; B $-x + 1/2$, y, $-z + 1/2$.

group of synclinal eclipsed ligands (torsion angle 62.7°) adopts a bidentate chelating mode, chelating one samarium atom; b) each carboxylate group of antiperiplanar ligands adopts a less common tridentate μ-η^2:η^1-coordinating mode. The local coordination geometry around the Sm(III) ion is nine-coordinate. Two synclinal eclipsed ligands chelate to one samarium atom through the carboxylate oxygen atoms, occupying four coordination sites of the Sm(III) ion. The remaining five coordination sites of the Sm(III) ion are taken by three carboxylate oxygen atoms from the two antiperiplanar ligands and two water oxygen atoms. The nearest Sm · · · Sm distance is *ca.* 4.26 Å. The macrocyclic unit constituting the basic building block of the structure is [Sm_6(*syn*-L)$_2$(*anti*-L)$_2$]. Each Sm_6 building unit is linked together through Sm–O bonding, creating a two-dimensional brickwall-structure with two kinds of cycles (Fig. 3). The solid-state differential pulse voltammetry of **2** also shows one peak with the half-wave potential ($E_{1/2}$) at 0.43 V, consistent with the result for the Ba(II) complex.

In summary, we have demonstrated the formation of two 2-D mixed-metal coordination polymers led by the reaction of ferrocenyl-based bridging ligands with alkaline-earth and lanthanide metal ions. The solid-state electrochemical studies show that the alkaline-earth and lanthanide metal ions all contribute small effects to the redox potentials of ferrocenyl-based bridging ligands, which differ from those of transition metal ions. The conformational flexibility of the ligand may have led to the various novel topological structures observed.[12] This approach of incorporating functional groups into the metal–organic frameworks presents opportunities for the design of functional solids.

Notes and references

† Syntheses of [BaL(H$_2$O)]$_\infty$ **1** and [Sm$_2$L$_3$(H$_2$O)$_5$]$_\infty$ **2**: A solution of 1,1′-H$_2$L (0.055 g, 0.20 mmol) and NaOH (0.016 g, 0.40 mmol) in methanol (7 mL) was layered onto a solution of BaCl$_2$ (0.042 g, 0.20 mmol) or SmCl$_3$ (0.034 g, 0.13 mmol) in water (3 mL). The solutions were left for 15 days at room temperature in darkness to afford X-ray quality orange block crystals in good yields.
   Calc. for C$_{12}$H$_{10}$BaFeO$_5$ **1**: C, 33.7; H, 2.4. Found: C, 33.5; H, 2.3%. IR (KBr, cm^{-1}): 3424s, 1638w, 1525vs, 1483vs, 1395s, 1354m, 1189w, 795m.
   Calc. for C$_{36}$H$_{34}$Sm$_2$Fe$_3$O$_{17}$ **2**: C, 35.8; H, 2.8. Found: C, 36.0; H, 3.1%. IR (KBr, cm^{-1}): 3406m, 1655w, 1560vs, 1480s, 1390s, 1358m, 1346m, 1187w, 1036m, 817m.
‡ Crystal data for **1**: C$_{12}$H$_{10}$BaFeO$_5$, M_r = 427.39, monoclinic, space group $C2/m$, a = 7.752(1), b = 9.978(1), c = 15.082(2) Å, β = 95.279(2)°, V = 1161.5(3) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 4.631 mm^{-1}, 3522 reflections measured, 1438 independent reflections (R_{int} = 0.063), R_1 = 0.034, wR_2 = 0.081 for 1309 observed reflections [$I > 2\sigma(I)$]. All carbon and oxygen atoms in the ferrocene group are refined as disordered with the s.o.f. (site occupancy factor) fixed at 0.5, except for the atoms C(3), C(4), C(9) and C(10), which occupied special positions. Although the space group is not uniquely determined by the systematic absences, which are possibly space groups $C2$ and Cm, the refinements of the structure using both $C2$ and Cm space groups reveal similar disorder of the ferrocene moieties to those in the $C2/m$ space group and it is believed that $C2/m$ might be the most possible space group for such a crystal.
   Crystal data for **2**: C$_{36}$H$_{34}$Sm$_2$Fe$_3$O$_{17}$, M_r = 1209.88, monoclinic, space group $P2/n$, a = 11.268(1), b = 10.292(1), c = 17.206(2) Å, β = 91.574(2)°, V = 1994.6(3) Å^3, T = 293 K, Z = 2, μ(Mo-Kα) = 4.037 mm^{-1}, 12109 reflections measured, 4642 independent reflections (R_{int} = 0.0762), R_1 = 0.048, wR_2 = 0.130 for 3634 observed reflections [$I > 2\sigma(I)$]. Intensities of complexes **1** and **2** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using SMART and SAINT[13] programs. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods and SHELXTL version 5.1.[14] CCDC reference numbers 197598 and 197599. See http://www.rsc.org/suppdata/dt/b2/b211201a/ for crystallographic data in CIF or other electronic format.

 1 (*a*) K. M. Fromm, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2799; (*b*) K. F. Tesh, D. J. Burkey and T. P. Hanusa, *J. Am. Chem. Soc.*, 1994, **116**, 2409; (*c*) S. C. Goel, M. A. Matchett, M. Y. Chiang and W. E. Buhro, *J. Am. Chem. Soc.*, 1991, **113**, 1844; (*d*) K. M. Fromm, *Chem. Commun.*, 1999, 1659.
 2 (*a*) T. Hascall, K. Ruhlandt-Senge and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 356; (*b*) J. K. Brask, T. Chivers and M. Parvez, *Angew. Chem., Int. Ed.*, 2000, **39**, 958; (*c*) B. Borup, J. A. Samuels, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1994, **33**, 994.
 3 (*a*) R. J. Cava, *Science*, 1990, **247**, 656; (*b*) S. N. Putlin, E. V. Antipov, O. Chmaissem and M. Marezio, *Nature*, 1993, **362**, 226; (*c*) A. Schilling, M. Cantoni, J. D. Guo and H. R. Ott, *Nature*, 1993, **363**, 56.
 4 (*a*) H. Plenio, C. Aberle, Y. Al Shihadeh, J. M. Lloris, R. Martinez-Manez, T. Pardo and J. Soto, *Chem. Eur. J.*, 2001, **7**, 2848; (*b*) P. Jutzi, N. Lenze, B. Neumann and H. G. Stammler, *Angew. Chem., Int. Ed.*, 2001, **40**, 1424; (*c*) N. J. Long, *Metallocenes: An Introduction to Sandwich Complexes*, Blackwell Science Inc., Cambridge, MA, 1998.
 5 (*a*) F. Barrière, N. Camire, W. E. Geiger, U. T. Mueller-Westerhoff and R. Sanders, *J. Am. Chem. Soc.*, 2002, **124**, 7262; (*b*) K. D. Demadis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*, 2001, **101**, 2655; (*c*) J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248.
 6 (*a*) P. D. Beer, *Adv. Inorg. Chem.*, 1992, **39**, 79; (*b*) F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1999, **121**, 4538; (*c*) C. J. Fang, C. Y. Duan, H. Mo, C. He, Q. J. Meng, Y. J. Liu, Y. H. Mei and Z. M. Wang, *Organometallics*, 2001, **20**, 2525.
 7 (*a*) K. G. Caulton, M. H. Chisholm, S. R. Drake, K. Folting and J. C. Huffman, *Inorg. Chem.*, 1993, **32**, 816; (*b*) K. G. Caulton,

M. H. Chisholm, S. R. Drake, K. Folting, J. C. Huffman and W. E. Streib, *Inorg. Chem.*, 1993, **32**, 1970; (*c*) H. Bock, T. Hauck, C. Nather, N. Rosch, M. Staufer and O. D. Haberlen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1353; (*d*) D. Guo, B. G. Zhang, C. Y. Duan, K. L. Pang and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2002, 3783.

8 (*a*) P. G. Bruce, *Solid State Electrochemistry*, Cambridge University Press, Cambridge, 1993; (*b*) T. Nakamura, T. Akutagawa, K. Honda, A. E. Underhill, A. T. Coomber and R. H. Friend, *Nature*, 1998, **394**, 159.

9 (*a*) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086; (*b*) T. R. Weaver, T. J. Mayer, S. A. Adeylmi, G. M. Brown, R. P. Eckberg, E. Hatfield, E. C. Johnson, R. W. Murray and D. Unterker, *J. Am. Chem. Soc.*, 1975, **97**, 3039.

10 The solid-state voltammograms were measured by using a carbon-paste working electrode; a well-ground mixture of each bulk sample and carbon paste (graphite and mineral oil) was set in the channel of a glass tube and connected to a copper wire. A platinum-wire counter electrode and an Ag/AgCl reference electrode were used. Measurements were performed by using a three-electrode system in 0.1 mol dm^{-3} NaClO$_4$ aqueous solutions at a scan rate of 20 mV s^{-1}, in the range 0–1.0 V. The ferrocene in the solid state was also used as external standard with $E_{1/2} = 0.25$ V *vs.* Ag/AgCl electrode.

11 (*a*) R. Horikoshi, T. Mochida and H. Moriyama, *Inorg. Chem.*, 2002, **41**, 3017; (*b*) C. Y. Duan, Y. P. Tian, Z. H. Liu, X. Z. You and T. C. W. Mak, *J. Organomet. Chem.*, 1998, **570**, 155; (*c*) P. Stepnicka, I. Cisarova, J. Podlaha, J. Ludvik and M. Nejezchleba, *J. Organomet. Chem.*, 1999, **582**, 319; (*d*) A. Ion, M. Buda, J. C. Moutet, E. Saint-Aman, G. Royal, I. Gautier-Luneau, M. Bonin and R. Ziessel, *Eur. J. Inorg. Chem.*, 2002, 1357; (*e*) Y. M. Xu, P. Saweczko and H. B. Kraatz, *J. Organomet. Chem.*, 2001, **637**, 335; (*f*) S. S. Sun, J. A. Anspach and A. J. Lees, *Inorg. Chem.*, 2002, **41**, 1862.

12 (*a*) D. Guo, H. Mo, C. Y. Duan, F. Lu and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2002, 2593; (*b*) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, D. M. Proserpio and F. Grepioni, *Chem. Commun.*, 2002, 1080.

13 SMART and SAINT, Area Detector Control and Integration Software, Siemens Analytical X-ray Systems, Inc., Madison, WI, 1996.

14 G. M. Sheldrick, SHELXTL, V5.1, Software Reference Manual, Bruker AXS, Inc., Madison, WI, 1997.