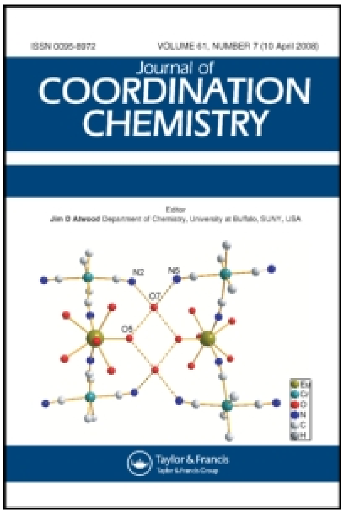


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectra and X-ray crystal structure of a new type of macrocyclic hexanuclear iron(III) cluster

Wei Luo[a]; Bo Li[a]; Feng-ping Xiao[a]; Gong-Zhen Cheng[a]; Zhen-Ping Ji[a]
[a] College of Chemistry and Molecular Science, Wuhan University, Wuhan, Hubei 430072, P.R. China

To cite this Article Luo, Wei , Li, Bo , Xiao, Feng-ping , Cheng, Gong-Zhen and Ji, Zhen-Ping(2007) 'Synthesis, spectra and X-ray crystal structure of a new type of macrocyclic hexanuclear iron(III) cluster', Journal of Coordination Chemistry, 60: 10, 1037 — 1045

To link to this Article: DOI: 10.1080/00958970600990242

URL: http://dx.doi.org/10.1080/00958970600990242

Journal of Coordination Chemistry
Vol. 60, No. 10, July 2007, 1037–1045

Taylor & Francis
Taylor & Francis Group

Synthesis, spectra and X-ray crystal structure of a new type of macrocyclic hexanuclear iron(III) cluster

WEI LUO, BO LI, FENG-PING XIAO, GONG-ZHEN CHENG and ZHEN-PING JI*

College of Chemistry and Molecular Science, Wuhan University,
Wuhan, Hubei 430072, P.R. China

(*Received 10 July 2006; revised 27 August 2006; in final form 1 September 2006*)

A macrocyclic iron(III) 18-azametallacrown-6 compound, $[Fe_6(5\text{-Brashz})_6(H_2O)_6]\cdot 20H_2O$ (5-Brashz = *N*-acetyl-(5-bromosalicylhydrazide)), where the pentadentate ligands bridge the metal ions, was synthesized and characterized. Due to the meridional coordination of the ligand to the metal ion, the ligand is not only bridging the ring metal ions using a hydrazide N–N group, but also enforcing the stereochemistry of the metal ions as a propeller shape with alternating Λ/Δ configuration. The disc-shaped hexanuclear cluster is about 14.5 Å in diameter, 16.8 Å in thickness and has a vacant cavity in the center of the cluster.

Keywords: Azametallacrown; Iron (III); Disc-shaped; Crystal structure; Macrocycle

1. Introduction

Coordination chemistry is an emerging tool for construction of organized supramolecular structure [1]. One of the main strategies for construction of supramolecular structures is self-assembly of the appropriate metal ions and a tailored ligand in an appropriate solvent [2]. Recently, several research groups have been synthesizing and characterizing many new types of inorganic clusters that can serve as inorganic counterparts of the macrocyclic organic host molecules, where the metal center is connected by the bridging ligand. Depending on the intrinsic properties of the metal ions and the ligand used, one, two or three dimensional network structures could be assembled [3].

Metallacrowns are among the first of a new class of molecule known as metallamacrocycles, and have attracted considerable attention in supramolecular chemistry, self-assembly, host-guest chemistry and molecular recognition [4]. Interest in metallacrowns stems not only from their high symmetry and aesthetic molecular frameworks but also from the special magnetic properties associated with them [5].

---

*Corresponding author. Email: wdjizp@126.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600990242

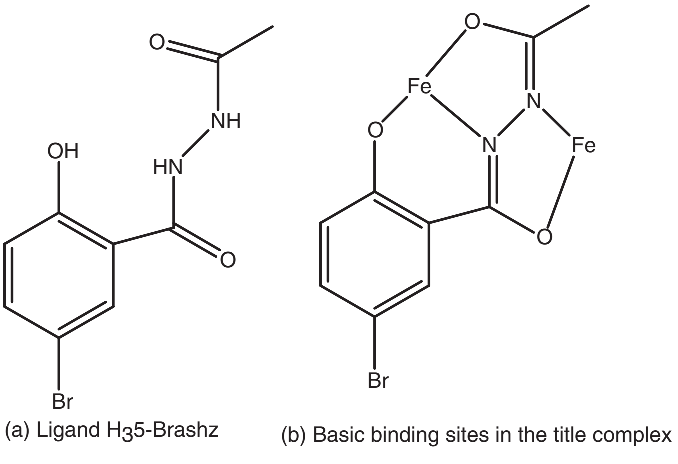
There are two types of metallacrown molecules. The first type has a cyclic structure with interlinked [M–N–O]$_n$ repeat unit, such as 9-metallacrown-3 [4, 6], 12-metallacrown-4 [7–11], 15-metallacrown-5 [10, 12, 13], one or two ions could be coordinated in the center of the ring. The tetradentate, ligands not only serve as a bridging ligand between the metal centers, but also form the five-membered chelate ring using a hydroximate group and the six-membered ring using a iminophenolate group. Chelation gives metallamacrocycles additional stabilization. Another type of metallacrown has a [M–N–N]$_n$ repeat unit, forming 18-azametallacrown-6 [14–18], 24-azametallacrown-8 [19], 30-azametallacrown-10 [20] and 36-azametallacrown-12 [21]. In this type of metallacrown, nitrogen atoms replace all oxygen atoms in the cyclic structure, while there is no metal ion in the center of the ring structure. The pentadentate ligand, bridges the metal ions using a hydrazide N–N group and forms three chelate rings in each metal center.

In this article, we report a new potential pentadentate ligand *N*-acetyl-(5-bromosalicylhydrazide) (**1**) (figure 1a), and a novel iron(III) 18-azametallacrown-6 complex $[Fe(III)_6(5\text{-}Brashz)_6(H_2O)_6]\cdot 20H_2O$ (**2**). The triply deprotonated *N*-acetyl-(5-bromosalicylhydrazide) (5-Brashz^{3-}) ligand bridges the neighboring ions through its hydrazide N–N group as shown in figure 1(b). The existence of intramolecular and intermolecular hydrogen bonds makes the title complex more stable.

2. Experimental

2.1. *Materials and methods*

All analytical grade chemicals and solvents were purchased commercially and used without further purification. Infrared spectra were recorded as KBr pellets in the range 4000–400cm^{-1} on a Perkin-Elmer FTIR 2000 spectrometer. ^{1}HNMR spectra were recorded on a Varian Mercury-VX 300 MHz spectrometer.



(a) Ligand H$_3$5-Brashz (b) Basic binding sites in the title complex

Figure 1. (a) Ligand H$_3$5-Brashz, (b) Basic binding sites in the title complex.

2.2. *Synthesis of N-acetyl-(5-bromosalicylhydrazide)*

The ligand *N*-acetyl-(5-bromosalicylhydrazide) was synthesized by reacting acetic anhydride (2.04 g, 20 mmol) and 5-bromo-salicylhydrazide (3.46 g, 15 mmol) in 50 mL of chloroform at 0°C, then slowly warmed to room temperature and stirred for 1 h. The resulting white precipitate was filtered and rinsed with chloroform and diethyl ether (3.76 g, 92% yield). Calcd for $C_9H_9N_2O_3Br$ (%): C, 39.59, H, 3.33, N, 10.26. Found: C, 39.50, H, 3.50, N, 10.41. ^{1}HNMR (DMSO-d_6): δ 11.936, 10.522, 10.280 (s, 3H, Hs at amides and phenolic OH), 7.597–6.927 (br s, 3H at phenyl), 1.933 (t, 3H at CH_3).

2.3. *Synthesis of [Fe(III)$_6$(5-Brashz)$_6$(H$_2$O)$_6$] • 20H$_2$O*

$H_3$5-Brashz (27.3 mg, 0.1 mmol) was dissolved in 30 mL of DMF, iron nitrate nonahydrate (40.4 mg, 0.1 mmol) in 20 mL DMF was added and stirred. The color of the mixture changed to dark, and it was filtered. After sitting for several days, dark rectangular crystals were obtained from the filtrate. Yield: 70%. Calcd for $C_{54}H_{76}Br_6Fe_6N_{12}O_{44}$ (%): C, 26.87, H, 3.15, N, 6.9, Fe, 13.93. Found: C, 26.91, H, 3.21, N, 7.5, Fe, 14.06.

2.4. *X-ray crystallography*

Crystals of the title complex are very air-sensitive and lose their solvent of crystallization within several seconds. A crystal was therefore mounted in a glass capillary with the mother liquor to prevent the loss of the structural solvents during data collection. The data were recorded on a Siemens Smart CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected at 0°C using the Φ and ω scan technique. The structure was solved by direct methods using SHELXL-97. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were allowed to ride on geometrically ideal positions. The crystallographic data are given in table 1.

3. Results and discussion

3.1. *Structure of the title complex*

The title complex crystallizes in the triclinic system, space group $P\bar{1}$. An ORTEP diagram of it is shown in figure 2. Metrical parameters are found in table 2. The structure exhibits a planar 18-membered ring which forms the iron metallacrown core linked by six Fe (III) ions and six *N*-acetyl-5-bromosalicylhydrazide groups. The deprotonated 5-Brashz^{3-} acts as a trianionic pentadentate ligand, one phenolate oxygen, one carbonyl oxygen and one hydrazide nitrogen in the ligand are bound to one Fe^{3+} cation, and the other carbonyl oxygen plus the other hydrazide nitrogen in the same ligand are chelated to an adjacent Fe^{3+} cation. Therefore, the pentadentate ligand not only bridges the ring metal ions but also forces the stereochemistry of all Fe^{3+} cations into a propeller configuration with alternating Λ/Δ stereochemistry as $\Delta\Lambda\Delta$ or

Table 1. Crystal data and structure refinement for title complex.

Formula	$C_{54}H_{76}Br_6Fe_6N_{12}O_{44}$
Formula weight	2411.83
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	13.120(5)
b	16.889(7)
c	17.016(7)
α	66.368(6)
β	74.418(6)
V (Å^3)	3276(2)
Z	1
Calcd density (mg m^{-3})	1.223
Crystal size (mm)	0.45 × 0.36 × 0.32
θ Range for data collection (°)	2.20–26.00
Data/restraints/parameters	12592/0/554
Goodness-of-fit on F^2	1.409
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1446$, $^a\omega R_2 = 0.3874$

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

ΛΔΛ forms (figure 3) [24]. Three water molecules coordinated at the metal centers with Λ configuration are found on one face of the azametallacrown, and the other three water molecules coordinated to the other metal centers with Δ configuration are found on the other metal face of the azametallacrown. The two faces of the disc-shaped hexanuclear ring have opposite chiralities. Jahn–teller elongation along the z-axis of the iron(III) ion is observed. The average axial bond distance (the average value of Fe–O(11) and Fe–N(2) bond distance: 2.087 Å) is about 0.11 Å longer than average (the average value of Fe–O(9), Fe–O(2), Fe–O(8), Fe–N(3) bond distances: 1.987 Å).The title complex is approximately 14.5 Å in diameter and 16.8 Å in thickness. The approximate dimensions of the oval-shaped cavity is about 4.16 Å in diameter at the entrance (C(18)–C(26), less 0.77 Å for the van der Waals radius of carbon), about 11.6 Å at its largest diameter at the center of the cavity (Fe(1)–Fe(1)a, less 1.28 Å for the van der Waals radius of iron), and approximately 5.6 Å in depth. Even though many non-coordinating water molecules are in the lattice and interact with the cluster using hydrogen bonds, none of them are located on the inside of the cavity.

The crystal packing structure of title complex shows that the disc-shaped hexanuclear clusters are aligned approximately along the crystallographic z-axis, as shown in figure 4. In the crystal packing structure, the hexanuclear metallamacrocycle complex serves as a unit for the gigantic hexagonal packing of the metallamacrocycles.

3.2. *Spectral characterization*

In the IR spectra, the ligand shows stretching bands attributed to C = O, C–N and N–H at 1665, 1635, 1286 and 3216 cm^{-1}, respectively. In the title complex, we see the absence of N–H and C = O stretching vibration bands, but peaks at 1200 and 1654 cm^{-1} due to C–O and C = N. This suggests that the carbonyl oxygen atom and the hydrazide atom coordinate to the metal ion, due to deprotonation of the ligand.

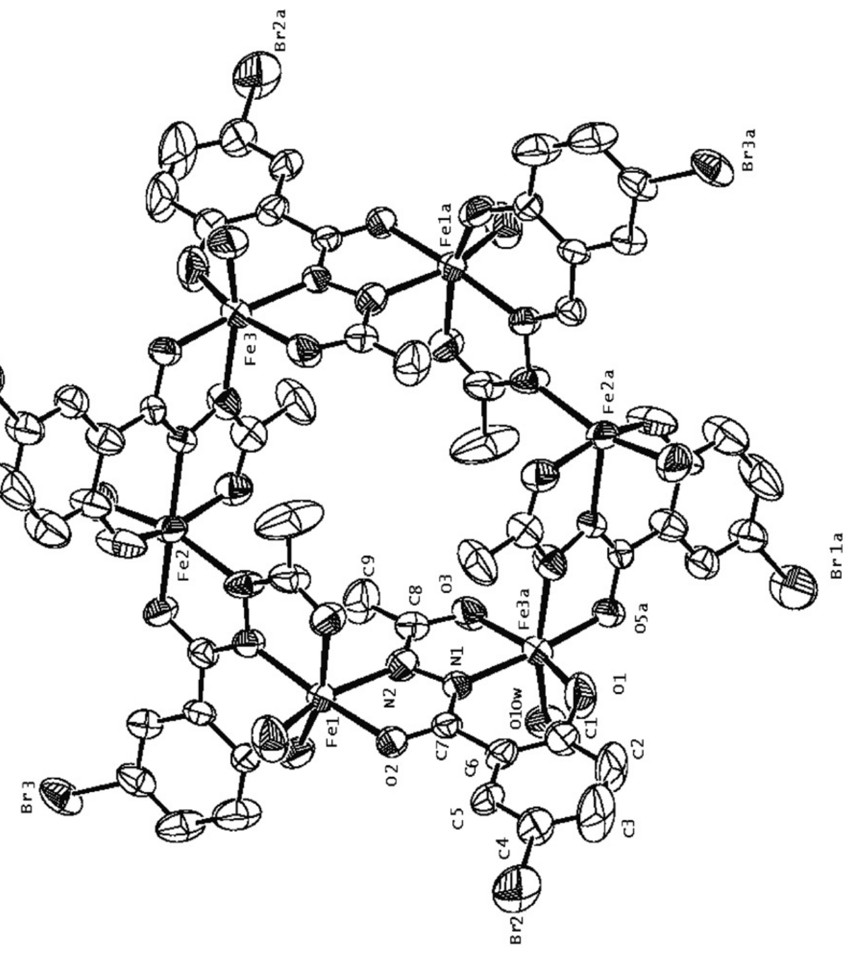
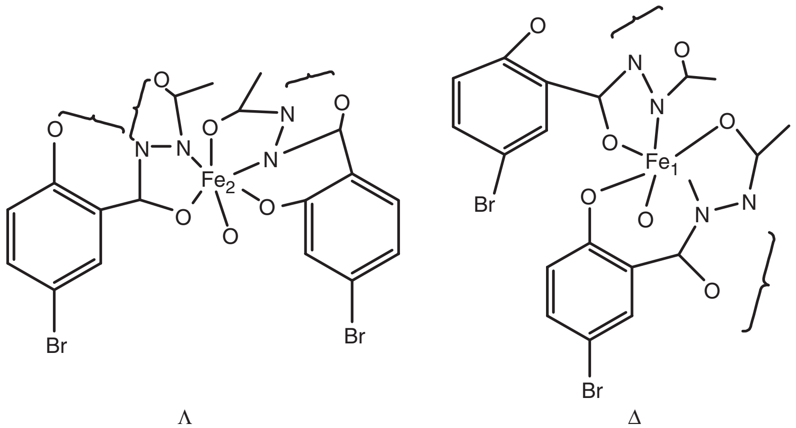


Figure 2. ORTEP diagram of the title complex.

Table 2. Selected bond lengths (Å) and angles (°) in compound **2**.

Fe(1)–O(9)	1.878(10)	Br(1)–C(14)	1.885(14)
Fe(1)–O(2)	2.004(7)	Br(2)–C(4)	1.880(12)
Fe(1)–O(8)	2.023(9)	Br(3)–C(24)	1.896(13)
Fe(1)–N(3)	2.043(9)	C(1)–O(1)	1.289(13)
Fe(1)–O(11)	2.069(9)	C(1)–C(2)	1.420(18)
Fe(1)–N(2)	2.105(10)	C(1)–C(6)	1.387(15)
N(1)–N(2)	1.392(12)	C(2)–C(3)	1.41(2)
N(3)–C(19)	1.309(13)	C(16)–N(5)	1.318(14)
N(3)–N(6)	1.398(13)	C(17)–O(6)	1.315(14)
N(4)–N(5)	1.391(12)	C(11)–O(4)	1.304(15)
N(6)–N(3)	1.398(13)	C(8)–O(3)	1.231(15)
O(9)–Fe(1)–O(2)	100.0(4)	C(1)–C(6)–C(5)	119.5(10)
O(9)–Fe(1)–O(8)	160.1(4)	O(2)–C(7)–N(1)	120.7(10)
O(2)–Fe(1)–O(8)	99.3(3)	O(2)–C(7)–C(6)	119.5(9)
O(9)–Fe(1)–N(3)	86.7(4)	N(1)–C(7)–C(6)	119.9(10)
O(2)–Fe(1)–N(3)	172.1(4)	O(3)–C(8)–N(2)	124.1(11)
O(8)–Fe(1)–N(3)	74.5(3)	O(3)–C(8)–C(9)	118.6(11)
O(9)–Fe(1)–O(11)	97.2(5)	N(2)–C(8)–C(9)	116.9(13)
O(2)–Fe(1)–O(11)	83.4(3)	C(11)–C(10)–C(15)	120.0(11)
O(8)–Fe(1)–O(11)	89.8(4)	O(5)–C(16)–N(5)	122.7(9)
N(3)–Fe(1)–O(11)	91.6(4)	O(5)–C(16)–C(10)	118.5(10)
O(9)–Fe(1)–N(2)	92.6(5)	N(5)–C(16)–C(10)	118.7(10)
O(2)–Fe(1)–N(2)	75.4(3)	N(4)–C(17)–O(6)	121.0(11)
O(8)–Fe(1)–N(2)	87.6(4)	N(4)–C(17)–C(18)	118.6(11)
N(3)–Fe(1)–N(2)	108.8(4)	C(3)–C(2)–C(1)	120.5(4)
O(11)–Fe(1)–N(2)	157.9(4)	C(4)–C(3)–Br(1)	119.5(3)
O(1)–C(1)–C(6)	124.1(10)	C(3)–C(4)–C(5)	120.2(5)
O(1)–C(1)–C(2)	117.1(11)	O(6)–C(17)–C(18)	118.0(4)
C(6)–C(1)–C(2)	118.9(11)	O(7)–C(19)–N(3)	120.4(9)
C(3)–C(2)–C(1)	121.1(14)	O(7)–C(19)–C(20)	117.3(10)
N(1)–C(7)–C(1)	119.2(4)	N(3)–C(19)–C(20)	122.3(10)
C(3)–C(4)–Br(2)	117.4(10)	O(9)–C(21)–C(20)	120.3(11)



Λ Δ

Figure 3. The propeller configurations for the Fe (III) ring ions.

The solution integrity of the metallacrown in acetone-d$_6$ was investigated by using paramagnetically shifted ^{1}HNMR resonances from protons on the ligand (figure 5). Since the oxygen atom of the water molecules coordinates with a paramagnetic iron ion directly, either the proton in the OH group or protons in the methyl group of the

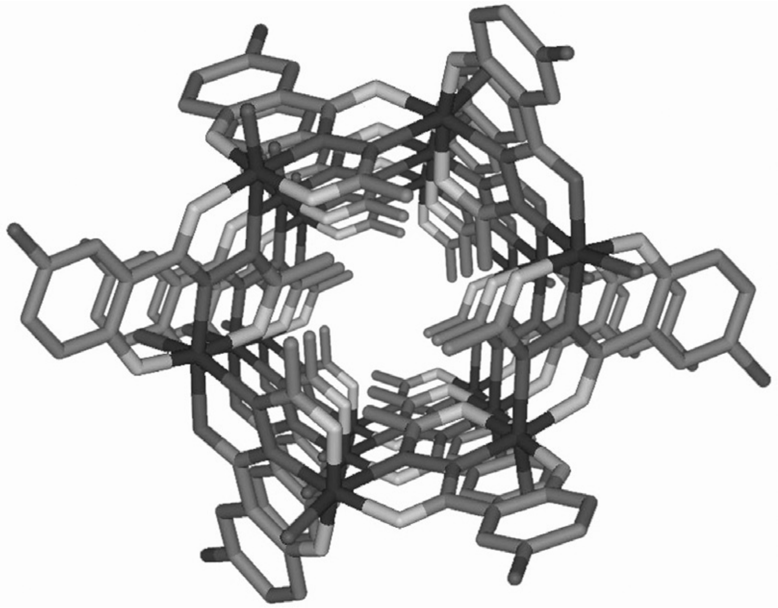


Figure 4. The packing structure of the title complex along the *x*-axis. Noncoordinating hydrogen groups in the lattice are omitted. H atoms are omitted for clarity.

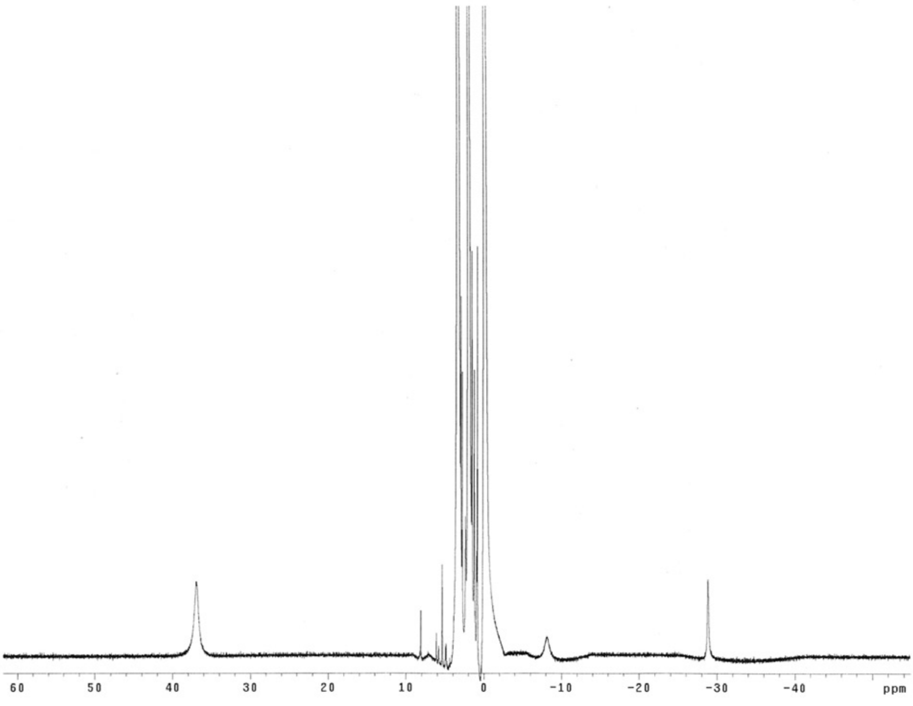


Figure 5. ^{1}HNMR spectrum of the title complex in acetone-d_6.

methanol are broadened beyond detection. Because the methyl proton next to carbonyl is close to the paramagnetic manganese ion, the broad peak of 37 ppm at low field was readily assigned to the methyl proton. The peaks around −8, −29 and +8.2 ppm were tentatively assigned to the phenyl protons of the bridging ligands. Similar upfield peaks of the manganese metallacrown were observed and assigned to the phenyl protons of the salicylhydroximate(shi^{3-}) ligand using deuterium exchange experiments [22]. The large shift of the ^{1}HNMR signals of the phenyl protons of the bridging ligand was considered to be the influence of the paramagnetic manganese [23]. The ^{1}HNMR study demonstrated that the title metallacrown compound retained its structure in solution at room temperature since its ^{1}HNMR spectra was unchanged for a few months. The stability of the metallacrown might come from the formation of the three chelating rings around the metal ions.

4. Conclusion

This new type of hexanuclear iron cluster has a vacant cavity in the center of the cluster. The variation of the diameters of the holes implies that the metallacrown has some degree of flexibility. Five donor atoms (from three chelating rings) and an additional donor atom (from a solvent molecule) coordinate each metal center in the metallacrown, which makes the metallacrown more stable in solution. In addition to the stability and flexibility of the metallacrown, the presence of the replaceable solvent site suggests that the hexanuclear iron metallacrown could be used as a building block for molecular frameworks. Due to the opposite chiralities of the two faces, the disc-shaped macrocyclic cluster might have interesting chiral recognition properties.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC reference numbers 613083 for the title complex. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgement

We are grateful to the National Natural Science Foundation of China for the financial support (Grant No. 20171035).

References

[1] (a) C. Janiak. *Angew. Chem. Int. Ed. Engl.*, **36**, 1431 (1997); (b) M.J. Zaworotko. *Angew. Chem., Int. Ed. Engl.*, **37**, 1211 (1998).

[2] (a) M. Asakawa, P.R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M.T, Gandolfi, O. Kocian, L. Prodi, F.M. Raymo, J.F. Stoddart, M. Venturi. *J. Am. Chem. Soc.*, **119**, 302 (1997); (b) Y.M. Jeon, J. Kim, D. Whang, K. Kim. *J. Am. Chem. Soc.*, **118**, 9790 (1996); (c) M. Berger, F.P. Schemidtchen. *J. Am. Chem. Soc.*, **118**, 8947 (1996); (d) C.F. van Nostrum, R.J.M. Nolte. *J. Chem. Soc., Chem. Commun.*, 2385 (1996).

[3] J.J. Bodwin, A.D. Cutland, R.G. Malkani, V.L. Pecoraro. *Coord. Chem. Rev.*, **216**, 489 (2001).

[4] M.S. Lah, M.L. Kirk, W. Hatfield, V.L. Pecoraro. *J. Chem. Soc., Chem. Commun.*, 1606 (1989).

[5] M.S. Lah, V.L. Pecoraro. *J. Am. Chem. Soc.*, **111**, 7258 (1989).

[6] V.L. Pecoraro. *Inorg. Chim. Acta*, **32**, 6008 (1989).

[7] G. Psomas, C. Dendrinou-Samara, M. Alexiou, A. Tsohos, C.P. Raptopoulou, A. Terzis, D.P. Kessissoglou. *Inorg. Chem.*, **37**, 6556 (1998).

[8] M.S. Lah, V.L. Pecoraro. *Inorg. Chem.*, **30**, 878 (1991).

[9] A.J. Stemmler, J. Kampf, V.L. Pecoraro. *Inorg. Chem.*, **34**, 2271 (1995).

[10] B.R. Gibney, D.P. Kessissoglou, J.W. Kampf, V.L. Pecoraro. *Inorg. Chem.*, **33**, 4840 (1994).

[11] M.S. Lah, B.R. Gibney, D.L. Tierney, J.E. Penner-Hahn, V.L. Pecoraro. *J. Am. Chem. Soc.*, **115**, 5857 (1993).

[12] D.P. Kessissoglou, J. Kampf, V.L. Pecoraro. *Polyhedron*, **13**, 137 (1994).

[13] A.D. Cutland, R.G. Malkani, J.W. Kampf, V.L. Pecoraro. *Angew. Chem., Int. Ed. Engl.*, **39**, 2689 (2000).

[14] B. Kwak, H. Rhee, S. Park, M.S. Lah. *Inorg. Chem.*, **37**, 3599 (1998).

[15] S. Lin, S.-X. Liu, B.-Z. Lin. *Inorg. Chim. Acta.*, **69**, 328 (2002).

[16] S. Lin, S.-X. Liu, J.-Q. Huang, C.-C. Lin. *J. Chem. Soc., Dalton*, 1595 (2002).

[17] B. Li, D.-D. Han, G.-Z. Cheng, Z.-P. Ji. *Inorg. Chem. Commun.*, **8**, 216 (2005).

[18] B. Kwak, R. Hakjune, M.S. Lah. *Polyhedron*, **19**, 1985 (2000).

[19] C. Dendrinou-Samara, M.C. Zaleski, A. Evagorou, J.W. Kampf, V.L. Pecoraro, D.P. Kessissoglou. *Chem. Commun.*, 2668 (2003).

[20] S.-X. Liu, S. Lin, B.-Z. Lin, C.-C. Lin, J.-Q. Huang. *Angew. Chem., Int. Ed. Engl.*, **40**, 216 (2001).

[21] R.P. John, K. Lee, M.S. Lah. *Chem. Commun.*, 2660 (2004).

[22] B.R. Gibney, H. Wang, J.W. Kampf, V.L. Pecoraro. *Inorg. Chem.*, **35**, 6184 (1996).

[23] S. Lin, S.-X. Liu, Z. Chen, B.-Z. Lin, S. Gao. *Inorg. Chem.*, **43**, 2222 (2002).

[24] The Λ/Δ stereochemistry was defined using a skew line convention for the six-coordinated complexes based on the octahedron as described in *Inorg. Chem.*, **1**, 9 (1970).