Inorg. Chem. **2004**, *43*, 2222–2224

Inorganic Chemistry
Communication

Synthesis, Structure, and Magnetism of a Ferric 24-Azametallacrown-8 Complex

Shen Lin,[†,‡] Shi-Xiong Liu,*[,†] Zhong Chen,[§] Bi-Zhou Lin,[||] and Song Gao[⊥]

Department of Chemistry, Fuzhou University, Fuzhou 350002, P. R. China, Department of Chemistry, Fujian Normal University, Fuzhou 350007, P. R. China, Department of Physics, Xiamen University, Xiamen 361005, P. R. China, Institute of Material Physical Chemistry, Huaqiao University, Quanzhou 362011, P. R. China, and Department of Chemistry, Peking University, Beijing 100081, P. R. China

Received October 2, 2003

A new pentadentate *N*-isobutyrylsalicylhydrazidate ligand (H_3ibushz, $C_{11}H_{14}N_2O_3$) and a self-assembly synthesis of the first 24-azametallacrown-8, $[Fe_8(C_{11}H_{11}N_2O_3)_8(CH_3OH)_8]\cdot 0.5CH_2Cl_2\cdot 7.5CH_3OH\cdot 3.5H_2O$, have been reported. Eight Fe(III) ions and eight deprotonated ibushz^{3-} ligands construct a planar 24-membered ring based on the M–N–N–M linkage. The chiralities of the iron atoms on the 24-azametallacrown-8 ring alternate between the Λ and Δ forms. The title octanuclear azametallacrown has no crystallographic centrosymmetry, while all the known metallacrowns and azametallacrowns with an even nuclear number have crystallographic centrosymmetry. The study of ^{1}H NMR spectra suggests that the title compound retains its metallacrown structure in solution at room temperature over a period of at least three months. There exists a strong antiferromagnetic exchange interaction between the iron paramagnetic centers.

Metallacrowns are a new class of metallamacrocycles, which have gained increasing attention over the past decade because of their potentially unique properties.[1−7] These metallacrowns exhibit selective recognition of cations and anions,[1−3] can display intramolecular magnetic exchange interactions,[1,5,6] and can be used as building blocks for two-dimensional or three-dimensional network structures.[8] The ability to control the generation of metallacrowns with different nuclear numbers, desired structures, and properties is still a substantial challenge. Metallacrowns with higher nuclear number are quite rare to date. Only two 30-metallacrown-10 complexes with −[M−N−N]− linkages have been observed.[5]

Metallacrowns are expected to show quite interesting magnetic behavior owing to the incorporation of several transition metal ions in close proximity.[1] The structural features of metallacrown can lead to high magnetic moments per compound through ferromagnetic exchange or coupling to low-spin paramagnetic states.[9] However, only a few examples of metallacrowns with more than six nuclei have been studied magnetically[5] because of the computational difficulties in the calculation of the energy matrix (high dimensions). We now report syntheses, structure, and magnetism of a designed pentadentate ligand *N*-isobutyrylsalicylhydrazidate, **1**, (H_3ibushz, $C_{11}H_{14}N_2O_3$)[10] and octanuclear azametallacrown $[Fe(C_{11}H_{11}N_2O_3)(CH_3OH)]_8\cdot 0.5CH_2Cl_2\cdot 7.5CH_3OH\cdot 3.5H_2O$, **2**.[10] The title ferric metallacrown **2**

---

* To whom correspondence should be addressed. E-mail: shixiongliu@yahoo.com.

[†] Fuzhou University.

[‡] Fujian Normal University.

[§] Xiamen University.

[||] Huaqiao University.

[⊥] Peking University.

(1) Pecoraro, V. L.; Stemmler, A. J.; Gibney, B. R.; Bodwin, J. J.; Wang, H.; Kampf, J. W.; Barwinski, A. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1997; Vol. 45, pp 83−177.

(2) Lah, M. S.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1989**, *111*, 7258.

(3) Lehaire, M.-L.; Scopelliti, R.; Piotrowski, H.; Severin, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1419.

(4) Saalfrank, R. W.; Bernt, I.; Chowdhry, M. M.; Hampel, F.; Vaughan, G. B. M. *Chem. Eur. J.* **2001**, *7*, 2765.

(5) Liu, S.-X.; Lin, S.; Lin, B.-Z.; Lin, C.-C.; Huang, J.-Q. *Angew. Chem., Int. Ed.* **2001**, *40*, 1084.

(6) Gaynor, D.; Starikova, Z. A.; Ostrovsky, S.; Haase, W.; Nolan, K. B. *Chem. Commun.* **2002**, 506.

(7) Alexiou, M.; Dendrinou-Samara, C.; Raptopoulou, C. P.; Terzis, A.; Kessissoglou, D. P. *Inorg. Chem.* **2002**, *41*, 4732.

(8) Moon, M.; Kim, I.; Lah, M. S. *Inorg. Chem.* **2000**, *39*, 2710.

(9) Dendrinou-Samara, C.; Psomas, G.; Iordanidis, L.; Tangoulis, V.; Kessissoglou, D. P. *Chem. Eur. J.* **2001**, *7*, 5041.

(10) Ligand $C_{11}H_{14}N_2O_3$(H_3ibushz): a 4.57 mL (33.4 mmol) portion of 2-methylpropanoyl chloride was added to a solution of 2.94 mL (33.4 mmol) of isobutyric acid and 4.66 mL (33.4 mmol) of triethylamine in 60 mL of chloroform at 0 °C, and then slowly warmed to 25 °C. A white suspension was obtained when 4.238 g (27.9 mmol) of salicylhydrazide was added to the reaction mixture. The resulting suspension was filtered and rinsed with chloroform and diethyl ether (2.14 g. 34.6% yield). Mp: 140−141 °C. Anal. Calcd for $C_{11}H_{14}N_2O_3$ (%): C, 59.44; H, 6.35; N, 12.61. Found: C, 59.38; H, 6.28; N, 12.58. Complex $[Fe_8(C_{11}H_{11}N_2O_3)_8(CH_3OH)_8]\cdot 0.5CH_2Cl_2\cdot 7.5CH_3OH\cdot 3.5H_2O$: a 0.033 g (0.15 mmol) portion of H_3ibushz and 0.035 g (0.15 mmol) of ferric acetate were dissolved in the mixed solvent of 10 mL methanol, 10 mL methylene, and 4 drops of DMF. A black solution was obtained after stirring for 5 min, and then filtered. The black acicular crystals were separated out after the filtrate stood for 5 days. The yield of complex **2** was approximately 58%. Anal. Calcd for $C_{104}H_{158}ClFe_8N_{16}O_{43}$ (%): C, 44.57; H, 5.68; N, 7.80. Found: C, 44.51; H, 5.61; N, 7.72.

10.1021/ic035145w CCC: $27.50

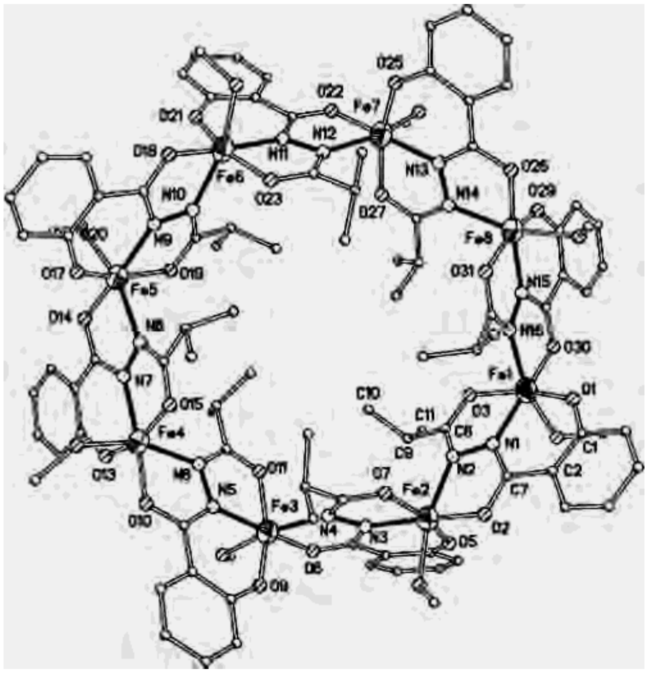

Figure 1. The molecular structure of $[Fe_8(C_{11}H_{11}N_2O_3)_8(CH_3OH)_8]$.

is the first example of 24-membered metallacrown [24-MN$_{\mathrm{Mn^{III}N(shz)}}$-8], which expands the ring size of known metallacrown clusters from 9-metallacrown-3, 12-metallacrown-4, 15-metallacrown-5, and 18-metallacrown-6 to a 24-membered ring system. This demonstrates that the formation of cyclic metallacrown structure with higher nuclear number is closely related to the number of the donor atoms of the ligand, as well as the rigid nature of the group toward to the center of the metallacrown cavity in the designed ligand. Compared with 18-azametallacrown-6, 24-azametallacrown-8 may result from the steric factor of isobutyryl in the ligand. The introduction of a bulkier group such as a phenyl group at the alkyl site of the ligand resulted in the expansion of the metallacrown ring from octanuclear to the decanuclear metallacrown.[5]

The molecular structure[11] of the title azametallacrown is shown in Figure 1. Eight Fe(III) ions and eight deprotonated *N*-isobutyrylsalicylhydrazidate (ibushz^{3-}) ligands construct a planar 24-membered ring based on Fe−N−N−Fe linkage in the title azametallacrown.

All known metallacrowns and azametallacrowns with even nuclear numbers have a crystallographic inversion center in the center of the cavity at least. However, the title octanuclear azametallacrown has no crystallographic centrosymmetry. The neighboring Fe···Fe interatomic distances are 4.872(2)−4.906(2) Å. The Fe···Fe···Fe interatomic angles in the 24-membered core ring are in the range 129.22(4)−132.59(4)°. These values are quite close to the value of the interior angle in an n-octagon (135°).

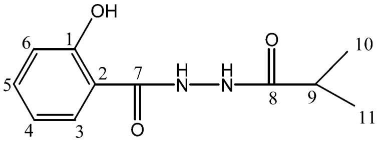

Figure 2. Chemical structure of ligand H$_3$ibushz.

The flexibility around the N−N single bond and the conformational adaptability of the deprotonated pentadentate ligand ibushz^{3-} allow for the formation of the title octanuclear complex and for the propeller configuration of the iron(III) ions. The chiralities of the iron atoms alternate between the Λ and Δ forms.[5,12−16] The four methanol molecules coordinated at the Fe centers with Λ configuration are on one face of the azametallacrown, and the remaining four methanol molecules coordinated at the other Fe centers with Δ configuration are on the other face of the azametallacrown. The two faces of each azametallacrown molecule have opposite chiralities.

The peripheral diameter of the core ring in **2**, measured between the opposite carbon atoms (C29−C77, plus 0.77 Å for the van der Waals radii of carbon), is 20.44 Å. The approximate dimensions of the oval-shaped cavity are about 4.25 Å in internal diameter at the entrance, measured between the opposite carbon atoms in the butyryl groups of the ibushz^{3-} ligands (C34−C82, less 0.77 Å for the van der Waals radii of carbon), about 11.31 Å in diameter, measured between the opposite iron atoms (Fe1−Fe5, Fe2−Fe6, Fe3−Fe7, and Fe4−Fe8, less 1.24 Å for the van der Waals radii of iron) at its widest point.

All iron atoms in **2** (Figure 1) are in a distorted octahedral FeN_2O_4 environment. The equatorial coordination sites of the octahedral iron(III) center are occupied by one phenolate oxygen O(1), one diazine nitrogen N(1), and one carbonyl oxygen O(3) of a trianionic pentadentate ligand ibushz^{3-} and one carbonyl oxygen O(30) of a neighboring ligand ibushz^{3-}, the axial positions occupied by the diazine nitrogen N(16) of the neighboring ligand ibushz^{3-} and oxygen atom O(4) of a coordinated neutral methanol molecule. The bond distances for Fe−N(diazine), Fe−O(phenolate), and Fe−O(carbonyl) are in the ranges 2.045−2.11, 1.901−1.933, and 1.985−2.025 Å, respectively. The Fe(III)−O(CH_3OH) bond distances are from 2.11 to 2.154 Å.

The solution integrity of azametallacrown **2** was investigated in acetonitrile-*d*$_3$, acetone-*d*$_6$, and dimethyl sulfoxide-*d*$_6$ using paramagnetically shifted ^1H NMR spectroscopy. The chemical structure of the ligand H$_3$ibushz and the ^1H NMR spectra of complex **2** in different solvents are shown in Figures 2 and 3, respectively. The chemical shifts and line widths of complex **2** in the three different solvents are quite similar to each other. The assignment of the ^1H NMR spectra was carried out on the basis of the relative intensities, broadening, and substitution of appropriate ligands. Since

---

(11) Crystal data for complex **2**: triclinic, space group $P\bar{1}$, $a = 20.0060(3)$ Å, $b = 20.2800(2)$ Å, $c = 20.6284(1)$ Å, $\alpha = 77.836(1)°$, $\beta = 66.136(1)°$, $\gamma = 66.268(1)°$, $V = 6995.2(1)$ Å^3, $Z = 2$, $D_{\mathrm{calc}} = 1.331$ g cm^{-3}, $F(000) = 2926$, $\mu = 0.904$ mm^{-1}. Siemens Smart CCD 1000 area detector diffractometer, λ(Mo Kα) = 0.71073 Å, 24517 unique reflections ($\theta_{\max} = 25.11°$) were collected, in which 7517 reflections with $I > 2\sigma(I)$ were used for solution (SHELXS-97) and refinement (SHELXL-97). $R = 0.0923$, $R_w = 0.1963$.

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

(13) Kwak B.; Rhee H.; Park S.; Lah M. S. *Inorg. Chem.* **1998**, *37*, 3599.

(14) Kwak, B.; Rhee, H.; Lah, M. S. *Polyhedron* **2000**, *19*, 1985.

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

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

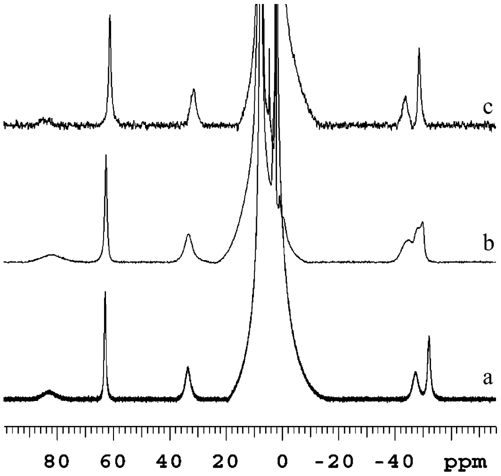

Figure 3. ^{1}H NMR spectra of complex **2** in different solvents: (a) CD_3CN, (b) acetone-d_6, and (c) DMSO-d_6.

the oxygen atom of the methanol coordinates with a paramagnetic ferric ion directly, either the proton in the OH group or protons in the methyl group of the methanol are broadened beyond detection. Because the methyne proton in the C_9 position is close to the paramagnetic ferric ion, the broad peak of 82.7 ppm at low field was readily assigned to the methyne proton. Similarly, the peak at 7.0 ppm was assigned to the peak arising from the methyl protons at the C_{10} and C_{11} positions since the methyl protons are far from the ferric ion. The remaining four peaks at 61.3, 31.4, −43.9, and −48.7 ppm were tentatively assigned to the four unequivalent 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.[12] The large movement of the ^{1}H NMR signals of phenyl protons of the bridging ligand was considered to be the influence of the paramagnetic ferric ions. These results are similar to those reported by Lah.[14] These NMR studies demonstrated that the title metallacrown compound retained its structure in solution at room temperature since its ^{1}H NMR spectra were unchanged for three months. The stability in solution might come from the formation of the three chelating rings around the metal ions.

An isomer shift (IS) of 0.38 mm s^{-1} and quadrupole splitting parameter (QS) of 1.23 mm s^{-1} shown in the solid-state Mössbauer spectrum of title compound are characteristic of high-spin Fe(III) ions.[17,18]

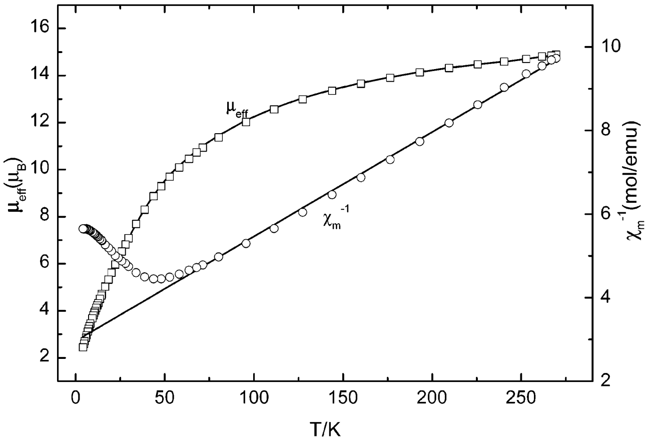

Figure 4. The effective magnetic moment (μ_{eff}) and the inverse susceptibility ($\chi_m{}^{-1}$) data as a function of temperature (T) for complex **2**, where open dots (○) depict observed results, and solid lines (—) attached to $\chi_m{}^{-1}$ and μ_{eff} depict fitting curves based on the Curie−Weiss law and on a simplified exchange fit, respectively.

There are eight six-coordinate iron(III) ions that are paramagnetic in title compound **2**. The paramagnetic centers were likely to interact since there was a bond pathway to facilitate superexchange between the ions. As shown in Figure 4, with decreasing temperature, the molar effective magnetic moment (μ_{eff}) values first decrease slightly till reaching 10.27 μ_B at 60 K, and then decrease rapidly after 60 K till reaching 2.44 μ_B at 4.2 K. The μ_{eff} value at 270 K is 14.89 μ_B, which is smaller than the sum value expected for eight spin-only paramagnetic systems with $S = 2.5$ ($\mu_{\text{eff}} = 16.73\ \mu_B$). This behavior is characteristic of antiferromagnetic exchange coupling between the Fe(III) spin $^5/_2$ centers, a feature common to most polynuclear iron complexes. Except for the very low temperature data, the temperature dependence of the magnetic susceptibility is typical of a Heisenberg chain of antiferromagnetically coupled $S_i = {}^5/_2$ ions.[18] This is further suggested by a negative Weiss constant $\theta = -118.3$ K, derived from the Curie−Weiss law fit in the temperature ranging from 63 to 272 K. The magnetic superexchange interaction would propagate between the neighboring centers (J_1) and between the near-neighboring centers (J_2). J_3 is neglected because of the distances between the opposite centers being beyond 11.633(2) Å. When the eight Fe(III) centers are simplified to be arranged in the symmetry of D_{8h}, a least-squares fit for the data with $T > 63$ K obtains the parameters $J_1/k = -5.65(4)$ K and $J_2/k = -3.11(6)$ K and the agreement factor $F = \sum[(\chi_{\text{obs}} - \chi_{\text{cal}})^2/\chi_{\text{obs}}] = 3.33 \times 10^{-3}$. The negative values of J demonstrate an antiferromagnetic coupling between the paramagnetic centers.

Acknowledgment. We are grateful for financial support from the National Natural Science Foundation of China (20171012), Natural Science Foundation of Fujian Province, China (E0110010, 2002J001), and the foundation for University Key Teacher by the Ministry of Education.

Supporting Information Available: Experimental details describing IR, UV, NMR, solid-state Mössbauer spectra, and variable-temperature magnetic susceptibility data. Bond distances and angles. Crystallographic data in CIF format (with CCDC number 217067). This material is available free of charge via the Internet at http://pubs.acs.org.

IC035145W

---

(17) Chen, K.-D.; Fan, Y.-N.; Hu, Z.; Yan, Q.-J. *J. Solid State Chem.* **1996**, *121*, 240.

(18) Taft, K. L.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823.