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Synthesis, crystal structure and magnetic property of an iron(III) coordination polymer with *N*-acyl-salicylhydrazide ligand

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ABSTRACT

A one-dimensional coordination polymer of iron(III) with *N*-dehydroabietoyl-salicylhydrazide (H₃L) ligand, [Fe (HL)Cl(CH₃OH)]_n·nCH₃OH (1), was synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, and infrared spectra analysis. The *N*-dehydroabietoyl-salicylhydrazide ligand in the compound is doubly deprotonated and acts as a tetradentate ligand to Fe(III) ions in tridentate-monodentate/back-to-back fashion, giving rise to a linear chain structure. The 1D chain is further extended to 2D supramolecular network by intermolecular hydrogen bonds. The magnetic study of the compound indicates an antiferromagnetic coupling interaction between Fe(III) ions.

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Metallamacrocycles, an important class of multinuclear clusters, have attracted great research interest for decades because of their intriguing molecular architectures, unique magnetic and catalytic properties, potential use as host systems for various guest molecules' recognition chemistry and as secondary building blocks for the construction of metal-organic frameworks [1-3]. In this context, metallacrowns with [M-N-N]_n cyclic repeating units, known as metalladiazamacrocycles, are an important class of metallamacrocycles and have been intensively studied since the first report of a hexanuclear manganese metalladiazamacrocycle in 1998 [4-6]. This class of metallamacrocycle is typically prepared by using trianionic pentadentate N-acyl-salicylhydrazide or its analogues as ligand and trivalent octahedral metal ion such as Mn(III), Fe(III), Co(III) and Ga (III) as centre ion [7–19]. It has been found that the nature of N-acyl groups of the N-acyl-salicylhydrazide ligand can influence the size and nuclearity of the metallamacrocycle formed. The introduction of a $C\beta$ substituent at the *N*-acyl site of the ligand does not affect the nuclearity of the metallamacrocycle, except for the case that the $C\beta$ position with an extremely bulky residue [20], while the introduction of the C α substituent results in the expansion of the macrocyclic ring to give metallamacrocycle with higher nuclearity. Metalladiazamacrocycles with different nuclearities ranging from 6 to 20 have been obtained by tuning the rigidity and steric volume of the C α substituted moiety [21-27].

For further understanding the coordination chemistry of the *N*-acyl-salicylhydrazide and the influence of the *N*-acyl residue of the ligand on the structures of the complexes formed, we designed and synthesized a new *N*-acyl-salicylhydrazide ligand, *N*-dehydroabietoyl-salicylhydrazide (H₃L) (Scheme 1) [28]. This compound possesses three chiral carbon atoms. More interesting, it bears a rigid and extremely bulky *N*-acyl residue. We hoped that higher nuclear metalladiazamacrocycle would be obtained with such a compound as ligand. However, reaction of H₃L ligand with FeCl₃·6H₂O [29] afforded unexpectedly a one-demensional iron(III) chain [Fe(HL) Cl(CH₃OH)]_n·nCH₃OH (1), but not a metalladiazamacrocycle. To the best of our knowledge, this is the first coordination polymer of trivalent octahedral metal ion bridged only by *N*-acyl-salicylhydrazide ligand. The crystal structure and properties of 1 are discussed in detail as below.

The single-crystal X-ray structural analysis [30] reveals that 1 crystallizes in the triclinic space group *P*1, showing a 1D chain structure with building monomer of [Fe(HL)Cl(CH₃OH)] which comprises one iron ion, one *N*-dehydroabietoyl-salicylhydrazide ligand, one chloride anion and one methanol molecule. As depicted in Fig. 1, the iron(III) ion is six-coordinated in a distorted octahedral geometry with one carbonyl oxygen atom (O2), one phenolic oxygen atom (O1) from a HL^{2−} ligand, one chloride anion (Cl1) and one oxygen atom (O3) of methanol molecule in the equatorial plane. The axial sites are occupied by one hydrazide nitrogen atom (N1) from the same HL^{2−} ligand. The Fe–N and Fe–Cl distances are 2.084 and 2.319 Å, respectively, while the Fe–O distances are in the range 1.874 to 2.134 Å. The *N*-dehydroabietoyl-salicylhydrazide in 1 is doubly

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Scheme 1. Ligand H₃L and basic biding sites in 1.

deprotonated. It acts as a dianion tetradentate ligand with its phenolic oxygen atom, one hydrazide nitrogen atom (salicylyl side), and one carbonyl oxygen atom (dehydroabietoyl side) binding to one Fe(III) ion in the meridianal mode, and the another carbonyl oxygen atom (salicylyl side) bridging to adjacent Fe(III) ion in a back-to-back mode. The hydrazide nitrogen atom on the dehydroabietoyl side is protonated, and is free from coordination. This tridentate–mono-dentate binding mode of the ligand leads to the formation of the 1D chain structure of 1, as shown in Fig. 2. The neighboring Fe…Fe distance in the chain is 6.264 Å, which is quite larger than those in the Fe(III) metalladiazamacrocycles reported (ca. 4.9 Å) [21,22,31]. The Fe…Fe angle is of 180°, indicating that the 1D chain is perfectly linear. Two end groups around the N–N bond of the HL^{2−} ligand are arranged regularly with all the salicylyl groups on one side and the dehydroabietoyl groups on the other side of the chain.

N-acyl-salicylhydrazide ligands in all complexes of trivalent octahedral metal ions reported so far are triply deprotonated and act as pentadentate ligands to metal ions. The ligand adopts tridentatebidentate/back-to-back fashion to bridge the adjacent metal ions, producing metalladiazamacrocycle with [M-N-N] repeating units. Utilization of ferric chloride as reaction material does not affect the formation of Fe(III) metalladiazamacrocycle [32,33]. In our case, the N-dehydroabietoyl-salicylhydrazide acts as a dianion tetradentate ligand, which is very different from other N-acyl-salicylhydrazides reported. The ligand takes tridentate-monodentate/back-to-back binding mode, leading to the formation of 1D chain coordination polymer, but not metalladiazamacrocycle. Such a result can be ascribed to the steric effect of the N-acyl residue of the N-dehydroabietoyl-salicylhydrazide ligand. The rigid and extremely bulky dehydroabietoyl group will cause very large steric repulsion between N-acyl residues if the ligand takes tridentate-bidentate/back-to-back fashion to form a metalladiazamacrocycle with shorter M···M distance and M···M···M interatomic angle smaller than 180°. Thus, it turns to take tridentatemonodentate fashion, giving rise to a chain structure with longer M···M distance and M···M···M angle of 180°, to release the steric repulsion. Indeed, it can be seen from the references that the M. M distance and the M···M···M interatomic angle increase with the increase of the steric crowding of the N-acyl residues and the expansion of the macrocyclic ring of metalladiazamacrocycle. For example, the average Fe---Fe distances and Fe--Fe interatomic angles are 4.881, 4.889, 4.946 Å and 117.6, 130.9, 140.4° for hexanuclear, octanuclear, and decanuclear iron metalladiazamacrocycles, respectively [21,22,31]. Based on this fact,



Fig. 1. The Fe(III) coordination environment with 50% thermal ellipsoids in the mononuclear unit of 1. All H atoms and guest CH_3OH molecule are omitted for clarity. Symmetry codes: A) x - 1, y, z; B) x + 1, y, z.



Fig. 2. 1D chain of 1 linked by the $O_{carbonyl}$ atom of HL^{2-} ligand. All H atoms and guest CH₃OH molecules are omitted for clarity. Symmetry codes: A) x - 1, y, z; B) x + 1, y, z.

it can be rationally concluded that if the steric crowding of the *N*-acyl residues great enough, the macrocyclic ring will be expanded infinitely, and the M···M distance will increase further and M···M···M angle tend to 180°, which will lead to the broken of the metallmacrocycle and the formation of the coordination chain.

Intermolecular hydrogen bonds are observed in 1. The guest CH₃OH molecule forms hydrogen bonds with the coordinated chloride anion and the coordinated CH₃OH molecule from adjacent 1D chains (O5-H5… Cl1ⁱ, O3-H10C… O5ⁱⁱ, i = x + 1, y - 1, z + 1, ii = x - 1, y, z - 1), which extend 1 into a 2D hydrogen-bonded network as shown in Fig. 3. The O···Cl distance and the O–H···Cl angle are 3.126 Å and 162.0°, while the O···O distance and the O–H···O angle are 2.618 Å and 125.0°, respectively.

The temperature dependence of the molar susceptibility χ_{M} and the product $\gamma_{\rm M}T$ for 1, measured at a magnetic field of 1000 Oe in the temperature range of 2-300 K, is shown in Fig. 4. In the high temperature region, the $\chi_{\rm M}T$ value at 300 K is 3.42 cm³ K mol⁻¹, smaller than the expected value of 4.38 cm³ K mol⁻¹ for one spin-only Fe(III) ion with S = 5/2, which is due to the antiferromagnetic interaction between Fe(III) ions in the compound. When the temperature decreases, the $\chi_{\rm M}T$ value decreases gradually from 3.42 cm³ K mol⁻¹ at 300 K to 2.23 cm³ K mol⁻¹ at 60 K, and then abruptly to 0.14 cm³ K mol⁻¹ at 2 K. The $\chi_{\rm M}T$ versus T curve is in agreement with an antiferromagnetic behavior of iron complexes. The best linear fit according to the Curie-Weiss law in the temperature ranging from 70 to 300 K yields C = 4.01 cm³ K mol⁻¹ and a Weiss constant $\theta = -52.95$ K (see the inset of Fig. 4). The negative Weiss constant further suggests the presence of an antiferromagnetic coupling interaction among spin carriers.



Fig. 3. 2D network of 1 formed by intermolecular hydrogen bonds indicated by broken lines.



Fig. 4. Temperature dependence of χ_M and $\chi_M T$ for 1. Inset: temperature dependence of χ_M for 1, representing the best fit of the Curie–Weiss law $\chi_M = C/(T - \theta)$.

In conclusion, an unexpectedly coordination polymer of trivalent octahedral metal ion with *N*-acyl-salicylhydrazide ligand, [Fe(HL)Cl (CH₃OH)]_n·nCH₃OH, was prepared by the reaction of *N*-dehydroabietoyl-salicylhydrazide with FeCl₃·6H₂O. The compound presents a 1D chain structure which is formed by the linkage of the ligand binding in tridentate-monodentate/back-to-back mode. The 1D chain is further extended to 2D supramolecular network by intermolecular O-H···Cl and O-H···O hydrogen bonds. Antiferromagnetic coupling interaction between the Fe(III) ions of the compound is observed.

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Appendix A. Supplementary material

CCDC 806940 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.03.066.

References

- G. Mezei, C.M. Zaleski, V.L. Pecoraro, Structural and functional evolution of metallacrowns, Chem. Rev. 107 (2007) 4933–5003.
- [2] E. Zangrando, M. Casanova, E. Alessio, Trinuclear metallacycles: metallatriangles and much more, Chem. Rev. 108 (2008) 4979–5013.
- [3] Y.F. Han, W.G. Jia, W.B. Yu, G.X. Jin, Stepwise formation of organometallic macrocycles, prisms and boxes from Ir, Rh and Ru-based half-sandwich units, Chem. Soc. Rev. 38 (2009) 3419–3434.
- [4] B. Kwak, H. Rhee, S. Park, M.S. Lah, Synthesis and characterization of [Mn^{III}₆ (*N*-formylsalicylhydrazidate)₆(MeOH)₆]: a new type of macrocyclic hexanuclear manganese cluster, Inorg. Chem. 37 (1998) 3599–3602.
- [5] R.P. John, D. Moon, M.S. Lah, Metalladiazamacrocycles: metallamacrocycles as potential supramolecular host system for small organic guest molecules and supramolecular building blocks for metal organic frameworks, Supramol. Chem. 19 (2007) 295–308.
- [6] M.J. Prakash, M.S. Lah, Metal-organic macrocycles, metal-organic polyhedra and metal-organic frameworks, Chem. Commun. (2009) 3326–3341.
- [7] S. Lin, S.X. Liu, J.Q. Huang, C.C. Lin, Four novel nanometer-sized cobalt azametallacrown complexes, J. Chem. Soc., Dalton Trans. (2002) 1595–1601.
- [8] R.P. John, K. Lee, M.S. Lah, Novel 36-membered dodecanuclear manganese metalladiazamacrocycle, Chem. Commun. (2004) 2660–2661.
- [9] B. Li, D.D. Han, G.Z. Cheng, Z.P. Ji, Synthesis, spectra and crystal structure of a novel 18metallacrown-6 [Mn₆(4-ohashz)₆(CH₃OH)₆]·12CH₃OH, Inorg. Chem. Commun. 8 (2005) 216–218.
- [10] D. Moon, K. Lee, R.P. John, G.H. Kim, B.J. Suh, M.S. Lah, Steric control of a bridging ligand for high-nuclearity metallamacrocycle formation: a highly puckered 60membered icosanuclear metalladiazamacrocycle, Inorg. Chem. 45 (2006) 7991–7993.
- [11] J.M. Dou, M.L. Liu, D.C. Li, D.Q. Wang, Synthesis, characterization, and crystal structure of two manganese metallacrowns: 30-metallacrown-10 and 18-

metallacrown-6 with ligands derived from 3-hydroxy-2-naphthalenecarbohydrazide, Eur. J. Inorg. Chem. 2006 (2006) 4866–4871.

- [12] L.F. Jin, F.P. Xiao, G.Z. Cheng, Z.P. Ji, Synthesis, crystal structure and bioactivity of a novel 18-metallacrown-6 [Mn₆(H₂O)₆(anshz)₆]·10DMF, J. Organomet. Chem. 691 (2006) 2909–2914.
- [13] L.F. Jin, F.P. Xiao, G.Z. Cheng, Z.P. Ji, Synthesis, crystal structure and bioactivity of a novel 18-metallacrown-6 [Mn₆(H₂O)₆(abshz)₆]·36H₂O, Inorg. Chem. Commun. 9 (2006) 758–760.
- [14] M. Park, R.P. John, D. Moon, K. Lee, G.H. Kim, M.S. Lah, Two octanuclear gallium metallamacrocycles of topologically different connectivities, Dalton Trans. (2007) 5412–5418.
- [15] F.P. Xiao, L.F. Jin, W. Luo, G.Z. Cheng, Z.P. Ji, Synthesis, characterization and bioactivity of a novel 18-metallacrown-6: [Mn(pcshz)(CH₃OH)]₆·4CH₃OH·4H₂O, Inorg. Chim. Acta 360 (2007) 3341–3346.
- [16] K. Lee, R.P. John, M. Park, D. Moon, H.C. Ri, G.H. Kim, M.S. Lah, Steric control of the nuclearity of metallamacrocycles: formation of a hexanuclear gallium metalladiazamacrocycle and a hexadecanuclear manganese metalladiazamacrocycle, Dalton Trans. (2008) 131–136.
- [17] Z.J. Chen, 24-Membered octanuclear manganese metalladiazamacrocycle, Inorg. Chem. Commun. 12 (2009) 636–638.
- [18] T.P. Shu, Z.J. Chen, H.M. Feng, J.L. Wen, K.W. Lei, Novel 18-membered hexanuclear metallamacrocycle: synthesis, crystal structure, and magnetic properties, Inorg. Chem. Commun. 12 (2009) 672–674.
- [19] Y.T. Chen, J.M. Dou, D.C. Li, S.N. Wang, A mixed-type of azametallacrown containing [Mn₆(pnhz)₆(DMF)₄(H₂O)₂] and [Mn₆(pnhz)₆(DMF)₂(H₂O)₄] constructed by a flexible pentadentate ligand, Inorg. Chem. Commun. 13 (2010) 167–170.
- [20] W.L. Liu, K.J. Lee, M. Park, R.P. John, D. Moon, Y. Zou, X.F. Liu, H.C. Ri, G.H. Kim, M.S. Lah, Novel 48-membered hexadecanuclear and 60-membered icosanuclear manganese metallamacrocycles, Inorg. Chem. 47 (2008) 8807–8812.
- [21] S.X. Liu, S. Lin, B.Z. Lin, C.C. Lin, J.Q. Huang, [30]metallacrown-10 compounds: [Mn (C₁₄H₉N₂O₃)(CH₃OH)]₁₀·5CH₂Cl₂·16CH₃OH·H₂O and [Fe(C₁₄H₉N₂O₃)(CH₃OH)] 10·3CH₂Cl₂·12.5CH₃OH·5H₂O, Angew. Chem. Int. Ed. 40 (2001) 1084–1087.
- [22] S. Lin, S.X. Liu, Z. Chen, B.Z. Lin, S. Gao, Synthesis, structure, and magnetism of a ferric 24-azametallacrown-8 complex, Inorg. Chem. 43 (2004) 2222–2224.
- [23] R.P. John, K. Lee, B.J. Kim, B.J. Suh, H. Rhee, M.S. Lah, Modulation of the ring size and nuclearity of metallamacrocycles via the steric effect of ligands: preparation and characterization of 18-membered hexanuclear, 24-membered octanuclear, and 30-membered decanuclear manganese metalladiazamacrocycles with α- and β-Branched N-Acylsalicylhydrazides, Inorg. Chem. 44 (2005) 7109–7121.
- [24] R.P. John, J. Park, D. Moon, K. Lee, M.S. Lah, Encapsulation of a guest molecule in a strained form: an extended 36-membered dodecanuclear manganese metallamacrocycle that accommodates a cyclooctane in the S₄ symmetry conformation, Chem. Commun. (2006) 3699–3701.
- [25] R.P. John, M. Park, D. Moon, K. Lee, S. Hong, Y. Zou, C.S. Hong, M.S. Lah, A chiral pentadecanuclear metallamacrocycle with a sextuple twisted Möbius topology, J. Am. Chem. Soc. 129 (2007) 14142–14143.
- [26] X.F. Liu, W.L. Liu, K. Lee, M. Park, H.C. Ri, G.H. Kim, M.S. Lah, A dodecanuclear metallamacrocycle having a multidentate bridging ligand in two different binding modes, Dalton Trans. (2008) 6579–6583.
- [27] W. Luo, X.T. Wang, X.G. Meng, G.Z. Cheng, Z.P. Ji, Metal coordination architectures of N-acyl-salicylhydrazides: the effect of metal ions and steric repulsion of ligands to their structures of polynuclear metal complexes, Polyhedron 28 (2009) 300–306.
- [28] Synthesis of H₃L: A sample of dehydroabieticacyl chloride (4.8 g, 15 mmol) was added dropwise to 100 mL of chloroform at 0 °C containing 1 mL (7 mmol) of triethylamine. After stirring for 30 min, the solution was slowly warmed to room temperature. Then, salicylhydrazide (3.4 g, 22 mmol) was added and the resulting solution was further stirred for 24 h. A yellow precipitate of H₃L was isolated by filtration and recrystallized from ethanol and H₂O solutions (71%, Yield). Anal. Calc. for C₂₇H₃₄N₂O₃ (%): C, 74.62; H, 7.89; N, 6.45. Found: C, 74.91; H, 8.04; N, 6.27. IR data (KBr pellets, cm⁻¹): 3278(m), 2957(s), 2930(s), 1637(s), 1590(s), 1520(s), 1495(m), 1384(m), 1360(m), 1250(m), 1210(m), 826(m), 754(m).
- [29] Synthesis of 1: a methanol solution (8 mL) of FeCl₃· 6H₂O (0.0270 g, 0.1 mmol) was slowly added to a methanol solution (5 mL) of H₃L (0.0435 g, 0.1 mmol). The resulting solution was further stirred at ambient temperature for 3 h and then filtered. The filtrate was allowed to evaporate at room temperature, giving dark brown block crystals of 1 suitable for single-crystal X-ray diffraction after two weeks (55% Yield based on Fe). Anal. Calc. for C₂₉H₄₀CIFeN₂O₅ (%): C, 59.25; H, 6.86; N, 4.76. Found: C, 58.98; H, 6.97; N, 4.57. IR data (KBr pellets, cm⁻¹): 3383(m), 2950(m), 1598(m), 1554(m), 1485(s), 1433 (s), 1408(m), 1245(m), 1108(m), 757(m).
- [30] The single-crystal X-ray crystallography diffraction study on 1 was performed at 187(2) K using a Bruker CCD Area Detector with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using the SHELXS-97 program package and refined against F^2 by full-matrix least-squares methods with SHELXL-97. Crystal data for 1: $M_r = 586.92$, triclinic, space group P1, a = 6.2641(8) Å, b = 7.7728(9) Å, c = 15.6593(18) Å, $\alpha = 82.270(2)^\circ$, $\beta = 88.132(2)^\circ$, $\gamma = 73.884(2)^\circ$, V = 725.82(15) Å³, Z = 1, $D_c = 1.345$ g cm⁻³, $\mu = 0.651$ mm⁻¹, 4487 measured data, 3746 unique, $R_{int} = 0.0172$. $R_1 = 0.0309$ for observations of $l \ge 2\sigma(l)$, $w_R = 0.0872$ for all data, GOF = 1.039.
- [31] S. Lin, S.X. Liu, B.Z. Lin, Synthesis, crystal structure and magnetic properties of a novel iron(III) 18-azametallacrown-6 compound, Inorg. Chim. Acta 328 (2002) 69–73.
- [32] L.F. Jin, H. Yu, S.X. Wu, F.P. Xiao, Iron(III) coordination induced novel 18metallacrown-6 complex: esterification and isolation of the ligand, Dalton Trans. (2009) 197–201.
- [33] T.P. Shu, J.L. Wen, H.M. Feng, K.W. Lei, H.Z. Liang, Synthesis, structural characterization and magnetic properties of a novel metallacrown [Fe₆ (amshz)₆(C₃H₇NO)₆] ⋅ CH₃OH, Solid State Sci. 11 (2009) 2180–2183.