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Synthesis, crystal structure and magnetic properties of a one-dimensional Mn(III) Schiff-base complex bridged by derivative of tetracyano-*p*-quinodimethane

Pei-Pei Yang^a, Zong-Wei Li^a, Xiao-Ling Wang^a, Li-Cun Li^{a,b,*}, Dai-Zheng Liao^a

^a Department of Chemistry, Nankai University, 94 Weijing Road, Tianjin 300071, PR China ^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China

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1. Introduction

Magnetic coordination polymers have attracted intense interest in view of their structure diversity and in the context of moleculebased magnetic materials [1–5]. Their magnetic properties depend on the nature of the interacting metal ions, and can be tuned by the nature of the bridging ligand and by the whole structural arrangement [6,7]. One synthetic strategy widely employed is the use of organic ligand (e.g., salen-type Schiff base) to block several equatorial coordination sites of the paramagnetic cations, leaving two free axial positions to be occupied by bridging ligands that can link adjacent paramagnetic metal centers. An increasing number of manganese(III) coordination polymers based on tetradentate Schiff bases bridged by cyano, azido, oxalato, and nitride have been reported that present a remarkable diversity in bridging topology, and special magnetic properties in recent years [8-15]. Among them, cyanide bridged metal coordination polymers including magnetic materials based on organocyanide ligands such as 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) exhibit interesting electrical, optical and magnetic properties [15-18].

Because of the diverse coordination chemistry of TCNQ [19], a large number of 0-D complexes [20], 1D chains [21-24], and 2-D nets [25-27] have been designed and synthesized. However, few TCNQ-bridged Mn(III) complexes have been reported. Very recently, Miyasaka et al. have reported an alternated 1:1 chain complex of a MnIII salen derivative and the TCNQ monoradical which

E-mail address: ypp@mail.nankai.edu.cn (L.-C. Li).

ABSTRACT

A new one-dimensional manganese(III) Schiff-base complex [Mn(III)(salophen) (MeOTCNO)] · CH₃CN 1 (salophen = N,N'-bis(salicylidene)phenylenediamine) bridged by 7-methoxy-7,7,8,8-tetra-cyano-pquinodimethane (MeOTCNQ), has been synthesized and characterized by X-ray crystallography and magnetic studies. Crystal structure study reveals that complex 1 has a 1D manganese(III) chain bridged by MeOTCNQ ligand which was obtained unexpectedly from tetracyano-p-quinodimethane (TCNQ) reacting with methanol. Noticeably, MeOTCNQ molecules in complex 1 adopt an unusual *cis-syn* coordination mode. The analysis of magnetic data indicates that a weak intrachain antiferromagnetic interaction exists in complex 1.

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displays unambiguous evidence of SCM behavior. From this point of view, we expected to utilize TCNQ as bridging ligand to design a 1D Mn(III) complex based on Schiff bases N,N'-bis(salicylidene)-o-phenylenediamine (salophen). Interestingly, the TCNQ ligand was experienced with nucleophilic addition reaction and MeOTCNO was obtained by chance, which was scarcely observed in previous literature [28]. In this text, we report the crystal structure and magnetic properties of the obtained complex, [Mn(III)(salophen)(MeOTCNQ)] · CH₃CN 1.

2. Experimental

2.1. General

All reagents were purchased commercially and used without further purification. Deionized water was used for the conventional synthesis. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer 240 analyzer. The infrared spectra of the complexes in KBr pellets were obtained on a BIO-RAD FTS 3000 instrument in the range of $4000-400 \text{ cm}^{-1}$ region. The magnetic susceptibility data were recorded using a Quantum Design MPMS-7 SQUID Magnetometer in the temperature range from 2 to 300 K at an applied magnetic field of 1 kG.

2.2. Syntheses of [Mn(III)(salophen)(MeOTCNQ)] · CH₃CN 1

A mixture containing $Mn(ClO_4)_2 \cdot 6H_2O$ (0.0362 g, 0.1 mmol) and salophen (0.0346 g, 0.1 mmol) in 15 mL of CH₃CN stirring for 0.5 h was added a solution of LiTCNQ (0.0213 g, 0.1 mmol) in 5 mL methanol. After stirring for 20 min at room temperature,

Corresponding author. Address: Department of Chemistry, Nankai University, 94 Weijing Road, Tianjin 300071, PR China.

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the dark brown solution was filtered and allowed to stand for about one week at room temperature to form dark black crystals of [Mn(III)(salophen)(MeOTCNQ)] · CH₃CN. The crystals were collected by suction filtration, washed with a minimum amount of cold methanol, and dried in vacuo. Yield: 65% based on Mn(III). Elemental *Anal.* Calc. for C₃₅H₂₄MnN₇O₃: C, 64.80; H, 3.78; N, 14.62. Found: C, 65.06; H, 3.72; N, 15.18%. IR (KBr): vC–H 3453 cm⁻¹, vC=N 1604 cm⁻¹, vC=N 2181, 2113 cm⁻¹. The IR spectroscopy study on **1** shows significant lower-energy vC=N vibrations at 2181(s) and 2113 cm⁻¹ compared with the monoradical TCNQ form consistently with the vibration bands at 2197 and 2168 cm⁻¹ for Li(TCNQ) [29]. It indicates that TCNQ ligands may be changed in the reaction, which is in agreement with the structure analysis.

2.3. X-ray crystallography

Single-crystal X-ray studies were performed on a Bruker SMART 1000 CCD diffractometer equipped with graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo K α radiation (λ = 0.71070 Å). The structure was solved by direct methods and semi-empirical absorption corrections were applied using the SHELXS-97 program [30]. The final refinement was performed with the SHELXL-97 program [31] by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The hydrogen atoms were generated theoretically onto atoms to which they are attached and refined isotropically with fixed thermal factors. Further details about crystal data and structure refinement are summarized in Table 1. Selected bond lengths and bond angles for the obtained complex are listed in Table 2.

3. Results and discussion

3.1. Structure description

Complex 1 crystallizes in the monoclinic space group $P2_1/n$ and the asymmetrical unit of 1 is depicted in Fig. 1. The repeating unit

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Data collection and process	ing parameters for complex 1
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Complex	C ₃₅ H ₂₄ MnN ₇ O ₃ (1)
Formula weight	645.55
Crystal system	monoclinic
Space group	P12 ₁ /n1
a (Å)	15.381(4)
b (Å)	13.967(3)
c (Å)	15.629(4)
α (°)	90.00
β(°)	116.221(4)
γ (°)	90.00
Volume (Å ³)	3012.0(14)
Ζ	4
D_{calc} (Mg m ⁻³)	1.424
Absorption coefficient (mm ⁻¹)	0.488
F(000)	1328
Crystal size (mm)	$0.16 \times 0.14 \times 0.10$
θ range for data collection (°)	2.06-27.87
Limiting indices	$-20 \le h \le 20$
	$-18 \le k \le 18$
	$-20 \le l \le 20$
Reflections collected/unique [R _{int}]	37331/7182 [0.0581]
Refinement method	full-matrix least-squares on F
Data/restraints/parameters	7182/0/418
Goodness-of-fit on F^2	1.125
Final R indices $[I>2\sigma(I)]$	$R_1 = 0.0530, wR_2 = 0.1088$
R indices (all data)	$R_1 = 0.0629, wR_2 = 0.1139$
Largest peak and hole ($e Å^{-3}$)	0.335 and -0.447
, ,	

Table 2

Selected bond lengths (Å) and angles (°) for complex 1.

Mn(1)-O(2)	1.8698(15)	Mn(1)-N(3)	2.3063(19)
Mn(1)-O(1)	1.8713(15)	Mn(1)-N(4)	2.3271(18)
Mn(1)-N(2)	1.9922(17)	N(4) - Mn(1)	2.3272(18)
Mn(1) - N(1)	1.9923(17)		
O(2)-Mn(1)-O(1)	91.61(6)	N(1)-Mn(1)-N(4)	86.30(7)
O(2) - Mn(1) - N(2)	92.88(7)	N(3)-Mn(1)-N(4)	168.79(7)
O(1)-Mn(1)-N(2)	175.49(7)	C(7)-N(1)-Mn(1)	124.66(14)
O(2) - Mn(1) - N(1)	175.09(7)	C(8) - N(1) - Mn(1)	112.66(13)
O(1)-Mn(1)-N(1)	92.88(7)	C(14)-N(2)-C(13)	123.45(18)
N(2)-Mn(1)-N(1)	82.64(7)	C(14)-N(2)-Mn(1)	123.93(14)
O(2) - Mn(1) - N(3)	94.34(7)	C(13)-N(2)-Mn(1)	112.54(13)
O(1) - Mn(1) - N(3)	93.33(7)	C(21)-N(3)-Mn(1)	166.58(17)
N(2)-Mn(1)-N(3)	85.96(7)	C(23)-N(4)-Mn(1)	130.70(16)
N(1)-Mn(1)-N(3)	87.37(7)	C(1)-O(1)-Mn(1)	127.50(13)
O(2) - Mn(1) - N(4)	91.26(7)	C(20)-O(2)-Mn(1)	127.89(14)
O(1)-Mn(1)-N(4)	96.22(6)	N(2)-Mn(1)-N(4)	84.06(7)

consists of the [Mn(III)(salophen)] moiety and the MeOTCNQ ligand in a 1:1 stoichiometry with the Mn atom located on the center of the equatorial plane. The coordination sphere around the Mn ion is an elongated octahedron with the salophen tetradentate ligand surrounding the manganese equatorial plane with bond lengths of Mn(1)-O(1) 1.8713(15), Mn(1)-O(2) 1.8698(15), Mn(1)–N(1) 1.9923(17) and Mn(1)–N(2) 1.9922(17) Å; On the other hand, the two left Mn axial positions are occupied by nitrogen atoms of the MeOTCNQ ligands, which adopt an uncommon cis-syn coordination fashion with Mn(1)-N(3) 2.3063(19) and Mn(1)-N(4A) 2.3272(18) Å. The Mn(1)-N(3)-C(21), Mn(1)-N(4)-C(23) angles in complex **1** are found to be 166.59° and 130.71°, respectively. The axial distortion of the Mn octahedron coordination sphere corresponds to a Jahn-Teller axis typically observed for MnIII salophen analogues (N(3)-Mn(1)-N(4A) 168.79(7)°, symmetry operation, x - 1/2, -y + 1/2, z - 1/2). The two neighboring Mn(III) ions in the 1D chain (shown in Fig. 2) are separated with the shortest distances of Mn1...Mn1A 8.516 Å, indicating that the magnetic interaction of the 1D chain may be very weak.

It is worth to note that the side of TCNQ ligand which is not coordinated with Mn(III) has changed. MeOTCNQ was obtained by the uncoordinated side of TCNQ processing nucleophilic addition with methanol accidentally. The possible mechanism of this addition reaction can be hypothesized as follows. The coordination of TCNQ radical anion with Mn(III) cation makes itself act as an eletrophilic group and the electron cloud of TCNQ migrates to



Fig. 1. The repeating unit of complex 1 (hydrogen atoms and solvent molecule have been omitted for clarity).



Fig. 2. The one-dimensional chain structure in complex 1 (hydrogen atoms and solvent molecule have been omitted for clarity).

Mn(III), rendering the side of TCNQ approaching Mn(III) cation more electrophilic. Therefore, the nucleophilic addition of methanol to TCNQ could be facilitated, affording MeOTCNQ ligand.

3.2. Magnetic properties

The temperature dependence of the magnetic susceptibility for **1** has been investigated at a field of 1000 Oe in the temperature range 2–300 K. The room-temperature μ_{eff} value is around 4.90 μ_{B} per Mn(III) ion, which is in good agreement with the expected value for one isolated spin-only MnIII ion (4.90 μ_{B} for g = 2, S = 2). Upon cooling, the value of μ_{eff} decreases smoothly with a value of 3.65 μ_{B} at 4 K, which indicates an intrachain antiferromagnetic interaction. And then, after a small upturn, it exhibits a relatively abrupt increase on further cooling at about 3.5 K, which can be attributed to the result of spin canting [32–36].

First, according to the structure of complex **1**, we fitted the experimental susceptibility by using the expression for antiferromagnetic one-dimensional S = 2 chain given by Hiller et al. [37]. The expression for the magnetic susceptibility is given by Eq. (1), where A = 2.0, B = 71.938, C = 10.482, D = 955.56. The J parameter is based on the Heisenberg–Hamiltonian $\hat{H} = -2J\sum_{i\neq j} \hat{S}_i \hat{S}_j$.

$$\chi_{\rm m} = \frac{Ng^2\beta^2}{kT} \frac{A+Bx^2}{1+Cx+Dx^3}$$

$$\chi = |J|/kT$$
(1)

The simulative model provides a good result from 300 to 9 K. The best fit of the magnetic data leads to $J = -0.2 \text{ cm}^{-1}$, g = 2.01 and the agreement factor $R = 1.35 \times 10^{-3}$ (R is defined as $\sum (\chi_m^{\text{calcd}} - \chi_m^{\text{obsd}})^2 / (\chi_m^{\text{obsd}})^2$). This fit is indicated in Fig. 3 as a solid line, which show the magnetic coupling between Mn(III) ions is very weak.

As well known, the Mn(III) ion usually has an important zerofield splitting [38]. The decrease of $\chi_M T$ product in the low temperature region may be due to the zero-field splitting of the ground state of the Mn(III) ion and/or very weak Mn(III)–Mn(III) magnetic interactions. Thus we analyzed the same set of data by the following equations including both single ion zero-field splitting (*D*) and weak magnetic coupling between Mn(III) ions with the use of molecular field approximation [39]:



Fig. 3. Temperature dependence of $\chi_M T$ for 1 at 1000 Oe fitted by using the expression for antiferromagnetic one-dimensional chain; the solid lines represent the best fit of the data.



Fig. 4. Temperature dependence of $\chi_M T$ for **1** at 1000 Oe fitted by using the equations including both single ion zero-field splitting (*D*) and intermolecular effects with the use of molecular field approximation; the solid lines represent the best fit of the data.

$$\begin{split} \chi_{\rm ZFC} &= \frac{\chi_{\parallel} + 2\chi_{\perp}}{3} \\ \chi_{\parallel} &= \frac{2Ng_{\parallel}^2\beta^2}{kT} \frac{\exp(-D/kT) + 4\exp(-4D/kT)}{1 + 2\exp(-D/kT) + 2\exp(-4D/kT)} \\ \chi_{\perp} &= \frac{Ng_{\perp}^2\beta^2}{kT} \frac{(6/x)(1 - \exp(-x) + (4/3x)(\exp(-x) - \exp(-4x))}{1 + 2\exp(-x) + 2\exp(-4x)} \\ x &= D/kT \end{split}$$

$$\chi = \frac{\chi_{\rm ZFC}}{1 - 2zJ\chi_{\rm ZFC}/N\beta^2 g^2}$$

The best agreement between calculated and experimental values of the susceptibility above 9 K was found with zJ = -0.47 cm⁻¹, g = 1.99, D = -7.87 cm⁻¹, the agreement factor $R = 1.8 \times 10^{-4}$ (R is defined as $\sum (\chi_m^{calcd} - \chi_m^{obsd})^2 / (\chi_m^{obsd})^2$). The D value is in good accord with the reported literature [40]. This fit is indicated in Fig. 4 as a solid line.

4. Conclusions

In summary, a new 1D manganese(III) chain bridged by MeO-TCNQ ligand based on salophen Schiff base was prepared and characterized crystallographically and magnetically. Here, MeO-TCNQ ligand was gained from TCNQ processing nucleophilic addition with methanol. The analysis of magnetic data shows that the magnetic coupling between Mn(III) ions in complex **1** is very weak. Considering the zero-field splitting of MnIII ion, we get the best agreement with zJ = -0.24 cm⁻¹, g = 1.99, D = -7.87 cm⁻¹.

Supplementary data

CCDC 690670 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.

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