

一维链配位聚合物[Mn(acacen){N(CN)₂}]_n的合成、结构和性质的研究

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关键词: 晶体结构 一维链 锰配合物 二氰氨基
分类号: O614.7+11

Synthesis, Structure and Property of One-dimensional Chain Coordination Polymer [Mn(acacen){N(CN)₂}]_n

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The manganese(III) complex [Mn(acacen){N(CN)₂}]_n [H₂acacen=bis(acetylacetone)ethylenediimine] has been synthesized and the structure has been determined. The complex forms a one-dimensional chain structure via the bidentate bridge ligand $\mu_{1,5}$ -[N(CN)₂]⁻ linking [Mn(acacen)] moiety. The magnetic property of the compound (75~300 K) shows the existence of an antiferromagnetic exchange interaction among paramagnetic centers along the chain. CCDC: 244940.

Keywords: crystal structure one-dimensional chain manganese complex dicyanamide

0 Introduction

The first report on coordination compounds with the dicyanamide anion N(CN)₂⁻ (dca) was published by Madelung and Kern in 1922^[1] and its coordinating ability towards 3 d transition metal ions was explored by Köhler and his coworkers in 1960s and 1980s^[2-5]. However, the complexes containing dicyanamide ligand have been the field of intensive research in the last several years^[6-17].

The ligand [N(CN)₂]⁻ is a remarkably versatile

building block for the construction of supramolecular architectures since it may act in a mono-, bi- and tri-dentate coordination mode. Other ligands, such as coordinating amines (Lewis bases), in combination with dicyanamide have been shown to produce novel structure types^[6-8]. Examples of monodentate [N(CN)₂]⁻, where coordination occurs via terminal nitrogen atom have been reported, namely, [Cu(phen)₂{N(CN)₂}] [C(CN)₃]^[9], [Cu(phen)₂{N(CN)₂}]₂ (phen=phenanthroline)^[10], [Ni{N(CN)₂}(4-miez)₄] (4-miez=4-methylimida-

收稿日期:2004-05-12。收修改稿日期:2004-08-26。

江苏省高校自然科学基金(No.03KJB150118)和江苏省有机合成重点实验室开放基金资助项目。

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第一作者:王寿武,男,38岁,讲师;研究方向:化学工程和配位化学。

zole)^[11] and $M\{N(CN)_2\}_2(bpy)m \cdot H_2O$ ($M=Fe, Mn, Co$) ($bpym=2,2'$ -bipyrimidine)^[12]. Many examples of bidentate $[N(CN)_2]^-$ have been reported, such as $[Cu\{N(CN)_2\}_2(phen)]^{[13]}$, $[M\{N(CN)_2\}_2(pyr)_2]$ ($M=Mn, Co$) ($pyr=2$ -pyrrolidone)^[14], $[Cu\{N(CN)_2\}_2(ampym)_2]$ ($ampym=2$ -aminopyrimidine)^[15], $[Ni(tn)_2\{N(CN)_2\}]ClO_4$ (tn =trimethylenediamine)^[16], $[Mn\{N(CN)_2\}_2(py)_2]$ (py =pyridine), $[Mn\{N(CN)_2\}_2(2,2'$ -bipy)] ($2,2'$ -bipy= $2,2'$ -bipyridine) and $[Mn\{N(CN)_2\}_2(4,4'$ -bipy) $\cdot 3/2H_2O]$ ($4,4'$ -bipy= $4,4'$ -bipyridine)^[17], which form one-dimensional chains or two-dimensional sheets. Here we report the structure and properties of dicyanamide complex $[Mn(acacen)\{N(CN)_2\}]_n$ **1** [$H_2acacen$ =bis(acetylacetonate)ethylenediamine].

1 Experimental

1.1 Materials and Physical Measurements

All reagents were of A.R. grade and were used without further purification. $NaN(CN)_2$ was purchased from Aldrich Company. $[Mn(acacen)Cl]$ was prepared as literature described^[18]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyser. IR spectra were obtained on a Nicolet 170SX FT-IR spectrophotometer in the $4000\sim400\text{ cm}^{-1}$ region for KBr pellets. Variable temperature ($75\sim300\text{ K}$) magnetic susceptibility were determined in the solid state using a CAHN-2000 Faraday balance with $[Ni(en)_2]S_2O_3$ as a standard at 6000 G magnetic field.

1.2 Preparation

An aqueous solution (15 mL) of $NaN(CN)_2$ (dca) (0.089 g, 1.0 mmol) was added to a methanol solution (20 mL) of $[Mn(acacen)Cl]$ (0.313 g, 1.0 mmol). The result solution was continuously stirred for 30 min and filtered. Well shaped crystals of $[Mn(acacen)\{N(CN)_2\}]$ were obtained from the mother liquor by slow evaporation at room temperature for one week. They were collected by filtration, washed with a small amount of water, and then dried in air. Yield: 83%. Elemental analysis confirmed the organic content (Found(%): C, 48.72; H, 5.18; N, 20.23. Calcd(%). For $C_{14}H_{18}MnN_5O_2$: C, 48.99; H, 5.29; N, 20.41).

1.3 Crystal Structure Determination

A single crystal of the compound **1** with dimen-

sions $0.48\text{ mm} \times 0.21\text{ mm} \times 0.08\text{ mm}$ was selected for data collection at 193.15 K, using a Rigaku Mercury CCD with graphite monochromated $MoK\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$). The structure was solved by direct methods and refined by full-matrix least-squares method using SHELXTL-97^[19]. The positions of all non-H atoms were obtained from successive difference Fourier syntheses. The positions of hydrogen atoms were determined with theoretic calculation. The final R_1 value is 0.061 0 for 194 parameters and 1 779 independent reflections [$I_{obs}>2\sigma(I)$] and wR_2 is 0.152 8. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

CCDC: 244940.

2 Results and Discussion

The selected bond lengths and angles are listed

Table 1 Crystal Data and Structure Refinement for the Complex **1**

empirical formula	$C_{14}H_{18}MnN_5O_2$
temperature	193.15
formula weight	343.27
crystal system	monoclinic
space group	Cc
a/nm	1.234 3(5)
b/nm	1.309 1(5)
c/nm	1.004 0(4)
$\beta/^\circ$	106.330(7)
V/nm^3	1.556 9(11)
Z	4
$D_{calc}/(\text{g}\cdot\text{cm}^{-3})$	1.465
absorption coefficient/ mm^{-1}	0.862
$F(000)$	712
$2\theta_{max}/^\circ$	54.96
index ranges	$-15 \leq h \leq 16$, $-16 \leq k \leq 16$, $-13 \leq l \leq 10$
independent reflections	1779
parameters	194
goodness-of-fit on F^2	1.185
final R_1 and wR_2 [$I>2\sigma(I)$] indices	$R_1=0.061\,0$, $wR_2=0.152\,8$
largest diff. peak and hole/ $(\text{e}\cdot\text{nm}^{-3})$	849 and -496

in Table 2. The crystal structure of the complex **1** reveals one-dimensional chain structure (Fig.1). The Mn(III) atom is coordinated by two nitrogen atoms and two oxygen atoms from acacen ligand [Mn(1)-N(1), 0.193 7(6) nm; Mn(1)-N(2), 0.195 1(7) nm; Mn(1)-O(1), 0.195 3(6) nm; Mn(1)-O(2), 0.193 9(6) nm, which occupy the equatorial positions] and two nitrile nitrogen atoms from two [N(CN)₂]⁻ ligands [Mn(1)-N(3), 0.232 0(9) nm; Mn(1)-N(5A), 0.232 2(8) nm, which occupy the axial positions]. The Mn-N and Mn-O bond lengths [Mn-N=0.193 7(6)~0.195 1(7) nm, Mn-O=0.193 9(7)~0.195 3(6) nm] within the [Mn(acacen)] moiety in **1** are similar to the Mn-N and Mn-O bond

lengths (Mn-N_{aver}=0.196 9(5) nm, Mn-O_{aver}=0.190 1(7) nm) in [Mn(acacen)Cl]^[18] and [Mn-N(1)=0.196 7(5) nm, Mn-N(2)=0.198 0(5) nm, Mn-O(1)=0.191 2(4) nm, Mn-O(2)=0.190 6(4) nm] in [NEt₄]₂[Mn(acacen)][Fe(CN)₆] (NEt₄=tetraethylammonium)^[21]. The Mn-N bond lengths [Mn-N=0.232 0(9)~0.232 2(8) nm] involving dea ligand at the axial positions are similar to the Mn-N bond lengths [Mn-N=0.231 6(4) and 0.231 6(4) nm] involving [Fe(CN)₆]³⁻ in [NEt₄]₂[Mn(acacen)][Fe(CN)₆]. The coordination geometry of the Mn atom can be described as an elongate square bipyramid.

The Mn(III) atoms are bridged through $\mu_{1,5}$ -[N(CN)₂]⁻ ligands through which complex **1** forms one-dimensional chain structure. Each [N(CN)₂]⁻ is coordinated to two metal atoms via two nitrile nitrogen atoms. The amide nitrogen atom are disorder with occupancy factors 0.555 for N(4A) and 0.445 for N(4B). The C≡N bond lengths of nitrile are 0.109 2(12) nm for N(3)-C(13) and 0.109 1(13) nm for N(5)-C(14). Bond angles which occupy the axial positions of the elongate square bipyramid are 164.2 (11)° and 170.6 (10)° for Mn(1)-N(3)-C(13) and Mn(1)-N(5A)-C(14A), respectively. The distance of two manganese atoms separated

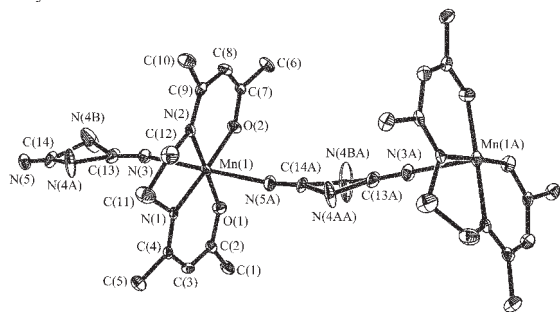


Fig.1 Local coordination of Mn in the complex **1** with 30% thermal ellipsoids

Table 2 Selected Bond Lengths (nm) and Angles (°) for the Complex **1**

Mn(1)-N(1)	0.193 7(6)	Mn(1)-N(2)	0.195 1(7)	Mn(1)-O(1)	0.195 3(6)
Mn(1)-O(2)	0.193 9(6)	Mn(1)-N(3)	0.232 0(9)	Mn(1)-N(5A)	0.232 2(8)
O(1)-C(2)	0.132 8(10)	O(2)-C(7)	0.128 4(10)	N(1)-C(4)	0.133 0(9)
N(1)-C(11)	0.141 4(8)	N(2)-C(9)	0.127 9(10)	N(2)-C(12)	0.147 8(9)
C(1)-C(2)	0.152 1(10)	C(2)-C(3)	0.135 1(12)	C(3)-C(4)	0.138 9(12)
C(4)-C(5)	0.152 6(11)	C(6)-C(7)	0.149 5(11)	C(7)-C(8)	0.140 0(12)
C(8)-C(9)	0.143 5(11)	C(9)-C(10)	0.150 4(10)	C(11)-C(12)	0.151 2(9)
N(3)-C(13)	0.109 2(12)	N(5)-C(14)	0.109 1(13)		
N(1)-Mn(1)-N(2)	85.8(3)	N(1)-Mn(1)-O(1)	92.9(3)	N(2)-Mn(1)-O(1)	178.7(3)
N(1)-Mn(1)-O(2)	177.4(3)	N(2)-Mn(1)-O(2)	92.1(3)	O(1)-Mn(1)-O(2)	89.2(3)
N(1)-Mn(1)-N(3)	87.3(3)	N(2)-Mn(1)-N(3)	91.8(3)	O(1)-Mn(1)-N(3)	88.2(3)
O(2)-Mn(1)-N(3)	91.2(3)	N(1)-Mn(1)-N(5A)	94.9(3)	N(2)-Mn(1)-N(5A)	87.8(3)
O(1)-Mn(1)-N(5A)	92.2(3)	O(2)-Mn(1)-N(5A)	86.6(3)	N(3)-Mn(1)-N(5A)	177.7(4)
Mn(1)-N(3)-C(13)	164.2(11)	Mn(1)-N(5A)-C(14A)	170.6(9)	O(1)-C(2)-C(1)	112.9(7)
O(1)-C(2)-C(3)	126.1(8)	C(1)-C(2)-C(3)	120.9(7)	C(2)-C(3)-C(4)	126.5(8)
N(1)-C(4)-C(3)	123.4(8)	N(1)-C(4)-C(5)	117.9(7)	C(3)-C(4)-C(5)	118.7(7)
O(2)-C(7)-C(6)	116.7(8)	O(2)-C(7)-C(8)	125.3(8)	C(6)-C(7)-C(8)	118.0(7)
C(7)-C(8)-C(9)	125.0(7)	N(2)-C(9)-C(8)	122.4(7)	N(2)-C(9)-C(10)	120.5(7)
C(8)-C(9)-C(10)	117.0(6)	N(1)-C(11)-C(12)	108.1(5)	N(2)-C(12)-C(11)	110.7(5)

Symmetry code: A: $x+1/2, -y+1/2, z-1/2$.

by bridging ligand $[\text{N}(\text{CN})_2]^-$ is 0.900 2 nm. **1** and $[\text{NEt}_4]_2[\text{Mn}(\text{acacen})][\text{Fe}(\text{CN})_6]$ have similar one-dimensional chain structure and the difference of two complexes is the bridge group which $\mu_{1,5}-[\text{N}(\text{CN})_2]^-$ in former and $[\text{Fe}(\text{CN})_6]^{3-}$ in latter^[21] link $[\text{Mn}(\text{acacen})]$ moiety.

2.2 IR and Magnetic Measurement

The IR spectrum of **1** shows bands: 3 588w, 3 052 w, 2 963w, 2 917w, 2 855w, 2 288s, 2 222m, 2 164vs, 1 586s, 1 505s, 1 431m, 1 393s, 1 281s, 1 231m, 1 111w, 1 019w, 945m, 799m, 772w, 687m, 652w, 486s and 455w cm^{-1} . The characteristic bands of the dicyanamide ligand are due to the $\nu_s + \nu_{as}(\text{C-N})$ and $\nu(\text{C}\equiv\text{N})$. 2 288 cm^{-1} band is a $\nu_s + \nu_{as}(\text{C-N})$ vibration. 2 222 and 2 164 cm^{-1} bands are due to the presence of $\text{C}\equiv\text{N}$ stretching vibrations. The strong 1 585 and 1 505 cm^{-1} bands are associated with the stretching vibrations of the unsaturated $\text{C}=\text{N}$, $\text{C}=\text{C}$, and $\text{C}=\text{O}$ linkages in the acacen ligand.

The magnetic moment of **1** is 3.83~4.24 B.M. for one Mn(III) in the temperature range 75~300 K. The value is lower than the spin-only value (4.90 B.M.) for one $S=2$ high spin and large than the spin-only value (3.87 B.M.) for one $S=3/2$ lower spin. Variable temperature magnetic susceptibility studies in the temperature range 75~300 K showed that **1** obeys the Curie-Weiss law, $\chi_m = C/(T-\theta)$, with value of $\theta = -23.927$ K, $C = 2.411 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ (Fig.2). This value of θ of **1** is larger than these values of θ of $\mu_{1,5}-[\text{N}(\text{CN})_2]^-$ bridging compounds, such as -5.15 K for $[\text{Ni}(\text{tn})_2][\text{N}(\text{CN})_2]\text{ClO}_4$ ^[16], -1.90 K for $\text{Mn}[\text{N}(\text{CN})_2]_2(\text{py})_2$, -3.5 K for $\text{Mn}[\text{N}(\text{CN})_2]_2(2,2'-\text{bipy})$, -4.7 K for $\text{Mn}[\text{N}(\text{CN})_2]_2(4,4'-$

$\text{bipy})$ ^[17], -0.76 K for $\text{Mn}[\text{N}(\text{CN})_2]_2(\text{bpym}) \cdot \text{H}_2\text{O}$, -7.6 K for $\text{Fe}[\text{N}(\text{CN})_2]_2(\text{bpym}) \cdot \text{H}_2\text{O}$ and -5.4 K for $\text{Co}[\text{N}(\text{CN})_2]_2(\text{bpym}) \cdot \text{H}_2\text{O}$ ^[12], indicating antiferromagnetic coupling, and antiferromagnetic coupling is typical for bridging dicyanamide compounds.

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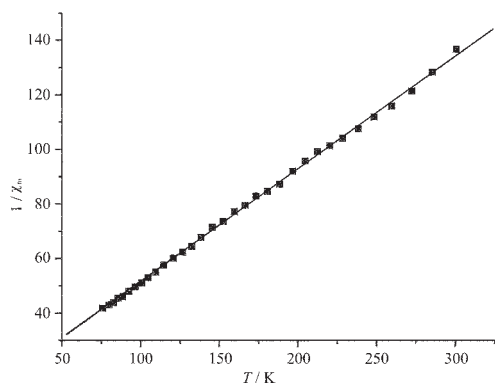


Fig.2 Plot of $1/\chi_m$ versus T for the complex **1**