Polyhedron 28 (2009) 2087–2091

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Magnetostructural examination of Mn(III) complexes $[Mn(cyclam)X_2]^+$ with strong axial ligands

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ARTICLE INFO

Article history:
Available online 25 February 2009

Keywords:
Magnetic anisotropy
Ligand field
Angular-overlap model (AOM)
Manganese(III)

ABSTRACT

Three novel Mn(III) cyclam complexes, $[Mn(cyclam)(NCBH_3)_2](CF_3SO_3)$, $[Mn(cyclam)(NCBPh_3)_2](CF_3SO_3)$, and $[Mn(cyclam)(NCSe)_2](CF_3SO_3) \cdot H_2O$, have been synthesized. These complexes are in the high-spin state between 4 and 350 K, and show large zero-field splittings. The crystal structure of $[Mn(cyclam)(NCBH_3)_2](CF_3SO_3)$ was determined where the axial elongation of Mn–N bonds is found to be the largest among the homologue complexes. Ligand field in the $[Mn(cyclam)X_2]^+$ complex series was examined by angular-overlap model calculation.

1. Introduction

The magnetism of Mn(III) complexes receives much attention recently because their large magnetic anisotropy serves useful pinning potentials for magnetization reversal in various nanomagnets [1] and their complicated d^4 electron configurations provide a potential for multiple bistabilities including spin-crossover and the Jahn–Teller effects [2–5].

A series of Mn(III) complexes, *trans*-$[Mn(cyclam)X_2]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane, X^- = axial anionic ligand), has been extensively studied, focusing on the electronic structure and magnetic properties, which may take high-spin $(e_g)^1(t_{2g})^3$ or low-spin $(t_{2g})^4$ electron configurations [6–11]. Within the series, only one low-spin species is known with $X^- = CN^-$ [11], and no spin-crossover complexes are reported yet. We are interested in the stronger side of a range of axial ligand field, and obtained three novel complexes with $X^- = NCBH_3^-$ (**1**), $NCBPh_3^-$ (**2**), and $NCSe^-$ (**3**), exploring the spin-crossover boundary on the interaction parameter space. The crystal structure of *trans*-$[Mn(cyclam)(NCBH_3)_2](CF_3SO_3)$ (**1**) was solved and reported in detail. Several known complexes [8,9,11] were also prepared along with novel ones and their magnetic susceptibilities were measured aiming to determine the magnetic anisotropy parameter (uniaxial zero-field splitting parameter D) as a guide scale of axial ligand field. By applying angular-overlap model and extended Hückel molecular orbital calculations, the relation between magnetic anisotropy and electronic structure was discussed for a series of $[Mn(cyclam)X_2]^+$ complexes.

2. Experimental

Commercially available solvents and chemicals were used without further purification. The reaction procedures of **1** and **2** were carried out in ambient atmosphere. The reaction procedure of **3** was performed under an argon atmosphere using standard Schrenk technique. The complex $[Mn(cyclam)(OH_2)_2](CF_3SO_3) \cdot H_2O$ was prepared according to the literature method [8]. Elemental analyses were carried out at the Laboratory for Instrumental Analysis, Graduate School of Engineering, Osaka University. IR spectra were recorded on a JASCO FT/IR-300E.

2.1. Synthesis

2.1.1. $[Mn(cyclam)(NCBH_3)_2](CF_3SO_3)$ (1)

To an aqueous solution (3 mL) of $[Mn(cyclam)(OH_2)_2](CF_3SO_3)_3 \cdot H_2O$ (378 mg, 0.5 mmol) was added an aqueous solution (2 mL) of $NaNCBH_3$ (62.9 mg, 1.0 mmol) at room temperature and the mixture was stirred. Sky-blue solid precipitated immediately was filtered off and dried in air (yield 135 mg, 56%). Infrared spectrum (KBr disk, cm^{-1}): 2184 ($\nu\{C{\equiv}N\}$), 2350 ($\nu\{B–H\}$). *Anal.* Calc. for $C_{13}H_{30}B_2F_3MnN_6O_3S$: C, 32.26; H, 6.25; N, 17.36. Found: C, 31.77; H, 6.18; N, 17.35%. For X-ray crystallographic analysis, an aqueous solution (1.5 mL) of $NaNCBH_3$ (13.1 mg, 0.21 mmol) was carefully layered on an aqueous solution (1 mL) of $[Mn(cyclam)(OH_2)_2](CF_3SO_3)_3 \cdot H_2O$ (76.1 mg, 0.10 mmol) to yield sky-blue single crystals in 2 h.

2.1.2. $[Mn(cyclam)(NCBPh_3)_2](CF_3SO_3)$ (2)

A mixture of KCN (130 mg, 2.0 mmol) and BPh_3 (484 mg. 2.0 mmol) in ethanol (2.5 mL) at room temperature was stirred for 1 h to give a clear solution. To an aqueous solution (2 mL) of

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doi:10.1016/j.poly.2009.02.013

$[Mn(cyclam)(OH_2)_2](CF_3SO_3)_3 \cdot H_2O$ (756 mg, 1.0 mmol) was added the ethanolic solution and the mixture was stirred. Immediately yellowish green solid was precipitated and filtered off. The solid was washed by ethanol, and dried in air (yield 357 mg, 38%). Infrared spectrum (KBr disk, cm^{-1}): 2171 ($\nu\{C{\equiv}N\}$). *Anal.* Calc. for $C_{49}H_{54}B_2F_3MnN_6O_3S$: C, 62.57; H, 5.79; N, 8.93. Found: C, 62.30; H, 5.82; N, 8.98%.

2.1.3. $[Mn(cyclam)(NCSe)_2](CF_3SO_3) \cdot H_2O$ (3)

To a solution of KSeCN (143 mg, 0.99 mmol) in acetonitrile (10 mL) was added a solution of $[Mn(cyclam)(OH_2)_2](CF_3SO_3)_3 \cdot H_2O$ (378 mg, 0.50 mmol) in the same solvent (5 mL) at room temperature. The deep purple solution changed to a clear orange solution immediately after stirring. After 20 min, the solution was completely evaporated in vacuo. In half volume of solvent evaporated a dark-orange solid started to precipitate. The solid was washed by ethanol and dried in vacuo (yield 86.7 mg, 28%). Infrared spectrum (KBr disk, cm^{-1}): 2055 ($\nu\{C{\equiv}N\}$). *Anal.* Calc. for $C_{13}H_{26}F_3MnN_6O_4SSe_2$: C, 24.69; H, 4.14; N, 13.29. Found: C, 24.68; H, 3.78; N, 13.23%.

2.2. X-ray structure determination

Single crystal structure determination was performed on the compound **1** at 123 K using a Rigaku RAXIS RAPID imaging-plate area detector with graphite monochromated Mo Kα radiation (λ = 0.071073 nm). The structure was solved by direct methods [12] and expanded using Fourier techniques [13]. The positions of all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included and their positions were refined using a riding model. All calculations were performed using the CRYSTALSTRUCTURE crystallographic software package [14,15]. Detail on the data collections and refinements are summarized in Table 1.

2.3. Magnetic susceptibilities

Magnetic measurements of **1** and **2** were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer equipped with reciprocating sample option (RSO) at magnetic fields of 1.0 and 5.0 T. Magnetic measurement of **3** was carried out on a Quantum Design MPMS-2 SQUID magnetometer at a field of 1.0 T. Polycrystalline samples were mounted in calibrated gelatin capsules held at the center of a polypropylene straw fixed to the end of the sample rod.

Table 1
Crystal data and structure refinement for **1**.

trans-$[Mn(cyclam)(NCBH_3)_2](CF_3SO_3)$	
Formula	$C_{13}H_{30}B_2F_3MnN_6O_3S$
Formula weight	484.03
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.6989(5)
b (Å)	13.3506(8)
c (Å)	19.3131(10)
α (°)	90.0
β (°)	90.0
γ (°)	90.0
V (Å^3)	2242.9(2)
Z	4
D_{calc} (g cm^{-3})	1.433
Crystal color, habit	blue, prism
Crystal dimensions (mm)	0.15 × 0.10 × 0.10
$F(000)$	1008.00
μ (Mo Kα)	7.315 cm^{-1}
R_1 [$I > 1.50\sigma(I)$]	0.0717
wR_2 [$I > 1.50\sigma(I)$]	0.0823
Goodness of fit	1.070
Flack parameter [16]	0.49

3. Results and discussion

3.1. Molecular structure of $[Mn(cyclam)(NCBH_3)_2](CF_3SO_3)$ (1)

Crystal structure was determined for the complex **1** which crystallizes in the non-centrosymmetric space group $P2_12_12_1$. The molecular structure is depicted in Fig. 1. The counter anion $CF_3SO_3^-$ links neighboring complex cations via weak hydrogen bonds O···H–N forming a chain structure along c-axis (Fig. 2).

The coordination environment around Mn(III) is elongated-octahedron type. The equatorial Mn–N distances fall in a range of 0.2004–0.2034 nm. The axial Mn–N distances are significantly longer than them, being 0.2209 and 0.2215 nm. These values are the longest among axial Mn–N distances in the hitherto-reported $[Mn(cyclam)X_2]^+$ complexes [6–11]. The Mn–N and N≡C bonds in $Mn \cdots NCBH_3$ axial coordination are non-collinear with the Mn–N–C angle of 169.4–173.7°, which gives rise to a small deviation from tetragonal symmetry, while the axial Mn–N bond is almost normal to the equatorial N_4 plane with the tilt angle of 1.06° (Table 2).

3.2. Magnetic properties

Isofield magnetizations of **1** and **2** were measured from 2 to 350 K, and the ones of **3** were from 4 to 350 K. All the compounds showed effective magnetic moments μ_{eff} of 4.9–5.2μ_B at room temperature, which agree well with the spin-only value of 4.9μ_B (S = 2) expected for a high-spin d^4 electron configuration of Mn(III) (Fig. 3). The μ_{eff} drops observed at low temperature should be attributable to the zero-field splitting accompanying with tetragonal coordination environment, rather than to antiferromagnetic intermolecular interactions. The uniaxial zero-field splitting

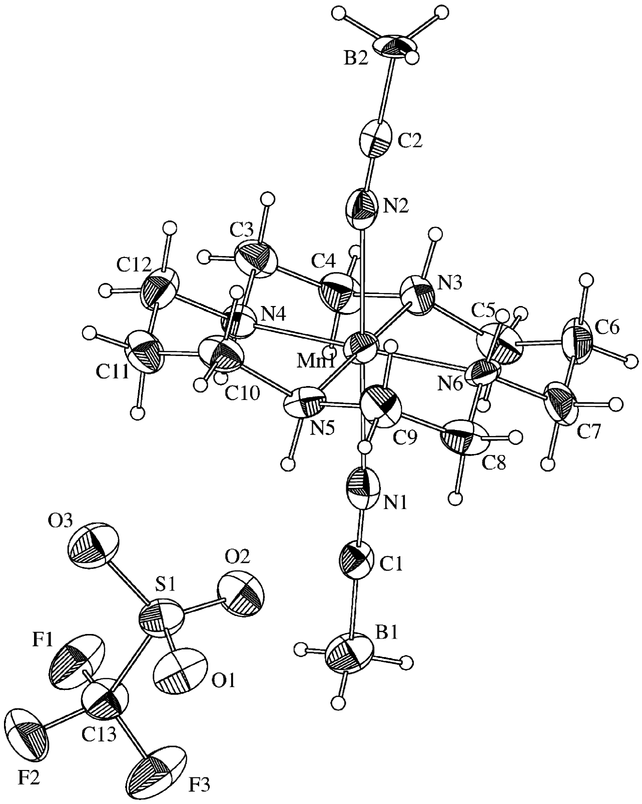

Fig. 1. Molecular structure of *trans*-$[Mn(cyclam)(NCBH_3)_2](CF_3SO_3)$ (**1**). All H atoms are shown as open circles, and thermal ellipsoids for heavier atoms are drawn at the 50% probability level.