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研究简报

四(1-乙基咪唑)二异硫氰酸锰的晶体结构和热性能

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Crystal and Thermal Behavior of Tetrakis(1-ethylimidazole-kN^3)diisothiocyanatomanganese(Ⅱ)

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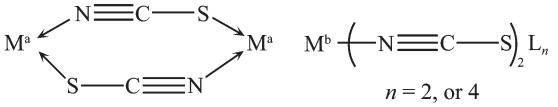
Abstract: A complex $[Mn(NCS)_2(Eim)_4]$ (where Eim=1-ethylimidazole) has been synthesized and structurally characterized by X-ray diffraction single-crystal structure analysis. The compound crystallizes in the Orthorhombic space group *Pbca* with the cell parameters: a=1.618 9(3) nm, b=1.787 4(4) nm, c=1.999 4(4) nm, and V=5.786(2) nm^3, Z=8. In the structure, each Mn atom is coordinated by four Eim ligands and a pair of monodentate isothiocyanic groups, affording a compressed octahedral MnN_6 core. The NCS^- anions are trans and four N atoms from the Eim ligands define the equatorial plane. The C–H$\cdots\pi$ supramolecular interactions between C-H and imidazole rings of Eim link the molecules into independent chains running along the c-axis. The thermal gravity (TG) data indicates that thermal decomposition of the title complex takes place in two steps, the residue is Fe. CCDC: 646113.

Key words: manganese(Ⅱ) complexes; thiocyanato complexes; TG-DTG; crystal structure

0 Introduction

In past decades, complexes containing thiocyanate group and alkylimidazole have received extensive attention. A review of the literature [1~12] showed that, in general, class a metals containing Cd(Ⅱ) and Cu(Ⅱ)) are bridged by a pair of SCN^- groups through both ends, resulting in a chain-like structure comprising (-N-C-S-M^a)$_2$ eight-membered rings, whereas class b metals containing Co(Ⅱ), Ni(Ⅱ) and Zn(Ⅱ) exhibit preferential bonding through the nitrogen end of the pseudohalide ion. The classic coordination modes exhibited by the thiocyanate group towards M^{2+} ion are shown below (Scheme 1).

However, the literature available for studies on



Scheme 1 Classic coordination modes of class a and b metals

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mangangese(Ⅱ) complexes containing thiocyanate groups and alkylimidazole is scarce. In this paper, we report here the synthetic, structural and thermal work on Mn(Ⅱ)-Eim-SCN complex.

1 Experimental

1.1 Physical measurements

Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Electronic spectra were taken on a UV-Vis-NIR spectrophotometer. TG and DTG curves were recorded on a NETZSCH-Geratebau GmbH thermoanalyser in flow of N_2, in the temperature range from 20 ℃ to 700 ℃, with a heating rate of 10 ℃·min^{-1}.

1.2 Synthesis

The title complex was prepared by the reaction of 1-ethylimidazole (1.92 g, 20 mmol) with $MnCl_2·4H_2O$ (0.98 g, 5 mmol) and potassium thiocyanate (0.98 g, 10 mmol) by means of hydrothermal synthesis in a stainless-steel reactor with a Teflon liner at 383 K for 24 h. Single crystals suitable for X-ray measurements were obtained by recrystallization from ethyl acetate at room temperature. The C, H and N content was determined by elemental analysis (Anal. Cald. (%) for $C_{22}H_{32}MnN_{10}S_2$, C, 47.56; H, 5.81; N, 25.21. Found (%): C, 47.50; H, 5.69; N, 24.99).

1.3 Structural determination

The crystal with approximate dimensions of 0.30 mm × 0.20 mm × 0.15 mm was selected for the structure analysis. The data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo $K\alpha$ (λ=0.071 073 nm) radiation at the temperature of 293(2) K, using an ω-2θ scan mode (2.32°<θ<25.98°). A total of 5 659 reflections were collected. Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction using NRCVAX[13] program.

The structure was solved by direct methods using SHELXS-97[14]. All the non-hydrogen atoms were refined on F^2 anistropically by full-matrix least squares method using SHELXL-97 [14]. All hydrogen atoms were placed in calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached. The contributions of these hydrogen atoms were included in structure-factor calculations. The final cycle of full-matrix least-squares refinement based on 5 538 independant reflections (R_{int}=0.012 9) gave R_1=0.075 2, wR_2=0.100 3. While the final least-square cycle gave R_1=0.034 1, wR_2=0.052 5 for 4 963 observed reflections with $I>2\sigma(I)$. The weighting scheme is $w=1/[\sigma^2(F_o^2)+(0.034\,1P)^2]$, where $P=(F_o^2+2F_c^2)/3$. The maximum shift $(\Delta/\sigma)_{max}$ equals 0.000. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography[15]. Crystal and refinement data for the title complex are listed in Table 1.

CCDC: 646113.

Table 1 Crystal and structure refinement data for the title complex

Empirical formula	$C_{22}H_{32}MnN_{10}S_2$	Crystal size / mm	0.30 × 0.20 × 0.15
Formula weight	555.64	θ range for data collection / (°)	1.98~25.96
Temperature / K	293(2)	Limiting indices	$0 \leqslant h \leqslant 19, 0 \leqslant k \leqslant 22, 0 \leqslant l \leqslant 24$
Crystal system	Orthorhombic	Reflections collected	5 659
Space group	*Pbca*	Independent reflections (R_{int})	5 538, (0.012 9)
a / nm	1.618 9(3)	Reflections ($I>2\sigma(I)$)	4 963
b / nm	1.787 4(4)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.999 4(4)	Data / restraints / parameters	5 538 / 0 / 317
V / nm^3	5.786(2)	Goodness-of-fit on F^2	0.988
Z	8	R indices (all data)	R_1=0.0752, wR_2=0.100 3
D_c / (Mg·m^{-3})	1.276	Final R indices [$I>2\sigma(I)$]	R_1=0.034 1, wR_2=0.052 5
μ / mm^{-1}	0.63	Largest diff. peak and hole / (e·nm^{-3})	559 and −466
F(000)	2 328		

2 Result and discussion

Fig.1 s hows the structure of the title complex, showing displacement ellipsoids at 50% probability level and the atom-numbering scheme, and Fig.2 shows the 1D packing arrangement linked by C–H···π interactions along the *c* axis. Selected bond lengths and bond angles are presented in Table 2. Intermolecular interactions are presented in Table 3.

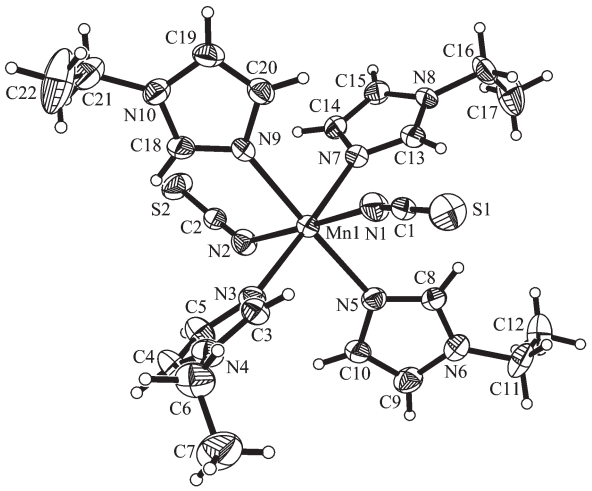

Fig.1　Structure of the title complex, showing displacement ellipsoids at 50% probability level and the atom-numbering scheme

The molecular structure of the title complex is shown in Fig.1. The Mn atom displays a compressed

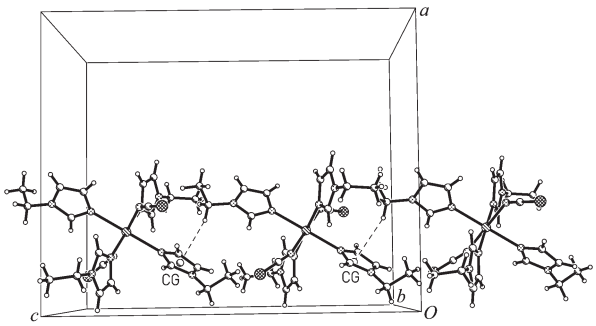

Fig.2　1D packing arrangement linked by C–H···π (symmetry code: *x*, 1/2−*y*, 1/2+*z*) interactions along the *c* axis

octahedral coordination geometry, with six N atoms from two thiocyanate anions and four Eim ligands. The equatorial plane of the complex is formed by four Mn-N (Eim) bonds, and the axial positions are occupied by two N-bonded NCS groups. The bond lengths of Mn-N3, N5, N7, N9 are 0.225 8(5), 0.226 1(5), 0.225 9(5) and 0.224 6(5) nm, respectively, which are comparable to the Mn-N (Him) [Him is 1H-imidazole] distances reported previously, e.g. 0.224 6(3) nm in $[(Him)_6(im)_2Mn_3]_n$[16] [im is protonated 1H-imidazole], 0.221 3(3) nm in $[Mn(Him)_4(H_2O)_2Cl_2]$[17], but longer than those protonated Mn-N (im) bond, e.g. 0.208 4(4) nm in $[(Him)_6(im)_2Mn_3]_n$[16]. The Mn-N(NCS) bond lengths of 0.223 2(5) and 0.225 0(5) nm are also comparable to the Mn-N (NCS) distances

Table 2　Selected bond lengths (nm) and bond angles (°) for the title complex

Mn(1)-N(1)	0.223 2(5)	Mn(1)-N(7)	0.225 9(5)	N(1)-C(1)	0.113 9(7)
Mn(1)-N(9)	0.224 6(5)	Mn(1)-N(5)	0.226 1(5)	N(2)-C(2)	0.115 6(6)
Mn(1)-N(2)	0.225 0(5)	S(1)-C(1)	0.163 2(7)		
Mn(1)-N(3)	0.225 8(5)	S(2)-C(2)	0.162 4(6)		
N(1)-Mn(1)-N(9)	89.55(18)	N(9)-Mn(1)-N(7)	88.67(16)	N(7)-Mn(1)-N(5)	90.39(17)
N(1)-Mn(1)-N(2)	178.40(19)	N(2)-Mn(1)-N(7)	89.82(18)	C(1)-N(1)-Mn(1)	164.3(5)
N(9)-Mn(1)-N(2)	88.84(18)	N(3)-Mn(1)-N(7)	177.48(18)	C(2)-N(2)-Mn(1)	143.5(5)
N(1)-Mn(1)-N(3)	91.52(19)	N(1)-Mn(1)-N(5)	88.48(18)	N(1)-C(1)-S(1)	179.4(6)
N(9)-Mn(1)-N(3)	89.51(16)	N(9)-Mn(1)-N(5)	177.82(17)	N(2)-C(2)-S(2)	178.5(6)
N(2)-Mn(1)-N(3)	88.39(18)	N(2)-Mn(1)-N(5)	93.12(17)		
N(1)-Mn(1)-N(7)	90.22(18)	N(3)-Mn(1)-N(5)	91.48(17)		

Table 3　Intermolecular interactions of the title compound

D-H-A	Symm	H···A / nm	D···A / nm	D-H-A / (°)
C(6)-H(6B)-Cg(1)	*x*, 1/2−*y*, 1/2+*z*	0.279	0.371 2	159
C(19)-H(19A)-S(2)	*x*−1/2, +*y*, −*z*+1/2+1	0.299	0.385 6	155

Cg(1): N7-N8/C13-C15.

reported previously, e.g. 0.220 1 (4) nm in $[Mn(Py)_4(NCS)_2]$ [Py is pyrazole][18].

The values of the bond angles around manganese are close to those expected for a regular octahedral geometry (Table 2), the largest angular deviation being observed for N2-Mn1-N5 93.12(17)°. The four imidazole rings are planar as expected. The thiocyanate ligands are almost linear [179.4(6)° and 178.5(6)° for N1-C1-S1 and N2-C2-S2, respectively], whereas a significant bending is displayed at the Mn-N-C-S linkage [164.3(5)° and 143.5(5)° for C1-N1-Mn 1 and C2-N2-Mn1, respectively].

In the crystal, There exist C–H $\cdots\pi$ supramolecular interactions between C-H and imidazole rings of Eim (Table 3) which link the molecules into independent chains running along the *c*-axis (Fig.2). There exist secondary weak C–H $\cdots$ S intermolecular interactions between the neighboring chains which link the one-dimensional chains into a two-dimensional lamellar structure alone the *ac* plan.

The solution electronic spectrum of the title complex in C_2H_5OH exhibits an intense band at 208 nm, which is assigned to the $n \rightarrow \pi^*$ transition of the Eim ligands. There are not other transition peaks in electronic spectrum being assigned to LMCT and $d \rightarrow d$ transition.

For the title complex, there are two steps of weight loss in the course of thermal decomposition (Fig.3). On the base of weight changes, the four heat-absorption peaks which take place at 91.6, 173.8, 275.4 and 361.0 ℃ correspond to the loss of four Eim ligands, respectively (found 69.27% calc. 69.20%). Then, about 18.97% weigh loss in the TG curve between 361 to 700 ℃ is attributed to the loss of two SCN groups (found 18.97% calc. 20.91%). The residue is Mn (found 11.83% calc. 9.89%).

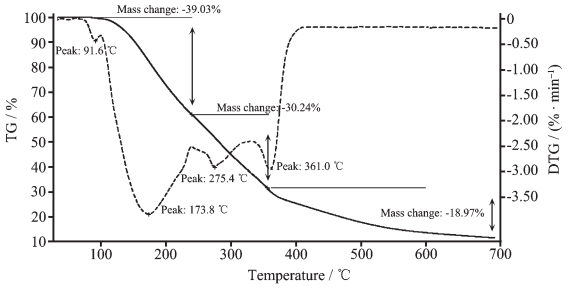

Fig.3 TG/DTG curve of the title compound

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