

基于 3-甲基-4-对溴苯基-5-(2-吡啶基)-1,2,4-三氮唑的锰配合物的合成和晶体结构

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摘要: 以 3-甲基-4-对溴苯基-5-(2-吡啶基)-1,2,4-三氮唑作为配体(L), 合成了 1 个新的锰配合物[MnL₂(NCS)₂], 对其进行了红外、电喷雾质谱和单晶结构表征, 该配合物属于单斜晶系, 空间群 $P2_1/n$, $a=1.648\ 0(2)\text{ nm}$, $b=0.907\ 07(13)\text{ nm}$, $c=2.191\ 9(3)\text{ nm}$, $\beta=97.454(2)^\circ$, $V=3.248\ 8(8)\text{ nm}^3$, $Z=4$, $R_1=0.043\ 9$ 。单晶结构表明, 锰离子处于 1 个扭曲的八面体配位环境中, 2 个硫氰根离子呈顺式配位, 每个配体 L 通过三氮唑上 1 个氮原子和吡啶上 1 个氮原子参与配位。

关键词: 锰配合物; 晶体结构; 三氮唑

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Synthesis and Crystal Structure of a Manganese Complex with 3-Methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole

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Abstract: A new manganese(II) complex, *cis*-[MnL₂(NCS)₂], (L=3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole), was synthesized and characterized by X-ray crystallography, FTIR and ESI-MS spectra. The complex crystallizes in monoclinic system with space group $P2_1/n$, $a=1.648\ 0(2)$, $b=0.907\ 07(13)$, $c=2.191\ 9(3)\text{ nm}$, $\beta=97.454(2)^\circ$, $V=3.248\ 8(8)\text{ nm}^3$, $Z=4$ with final $R=0.043\ 9$. The manganese atom lies in a distorted octahedral environment with two NCS⁻ ions in the *cis* positions. The ligand L coordinates via one triazole nitrogen and one pyridine nitrogen atom. CCDC: 790351.

Key words: Mn(II) complex; crystal structure; 1,2,4-triazole

0 Introduction

Substituted 1,2,4-triazoles and their complexes have attracted much attention in coordination chemistry because of the interesting structures^[1-2] and specific magnetic properties^[3-6]. Recently, some 4-substituted

3,5-di(2-pyridyl)-1,2,4-triazoles and their metal complexes have been prepared by us and other groups^[7-12]. However, complexes with asymmetrically 3,4,5-trisubstituted 1,2,4-triazole have been little studied so far^[13]. As a continuation of our investigation of the asymmetrical substituted 1,2,4-triazoles^[14-16], we present here

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the synthesis and crystal structure of a new manganese (II) complex with 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole.

1 Experimental

1.1 Materials and measurements

All chemicals used were of analytical grade. Solvents were purified by conventional methods. The ligand L was prepared as reported earlier^[15]. Elemental analyses (C, H, N, S) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectrum was recorded on a Nicolet Avatar 380 FTIR instrument with KBr pellets in the range 4 000~400 cm⁻¹. Electrospray ionization mass spectrum (ESI-MS) was recorded with an LCQ ADVANTAGE MAX mass spectrometer, with MeOH on the mobile phase; the flow rate of the mobile phase was 0.2 cm³·min⁻¹. The spray voltage, the capillary voltage, and the capillary temperature were 4 kV, 40 V, and 260 °C, respectively.

1.2 Synthesis of *cis*-[MnL₂(NCS)₂]

To a solution of KSCN (0.4 mmol) in anhydrous MeOH (3 mL) was added a solution of MnCl₂·4H₂O (0.2 mmol) in MeOH (2 mL). The mixture was stirred for 15 min and filtered. The KCl precipitate was washed with 2 mL of anhydrous MeOH. The methanolic fractions containing Mn(SCN)₂ were collected, and then was

added dropwise to a solution of the L (0.4 mmol) in MeOH (3 mL). A light-yellow microcrystalline product, which formed immediately, was filtered and washed with H₂O, and dried under vacuum to give 0.1 mmol (55%) of the complex. The light-yellow single crystals suitable for X-ray diffraction were obtained by evaporation from an EtOH solution. Elemental analyses calcd. for C₃₀H₂₂Br₂MnN₁₀S₂(%): C 44.96, H 2.77, N 17.48, S 8.00; found (%): C 45.08, H 2.66, N 17.55, S 8.09. IR data (ν , cm⁻¹): 3 085 (m); 2 939 (w); 2 063 (s); 2 043(s); 1 600 (s); 1 536 (m); 1 492 (s); 1 482 (s); 1 341 (m); 1 287 (m); 1 070 (m); 992 (m); 838 (m); 794 (m); 633 (m). ESI-MS: m/z =743.92; 652.92; 499.67; 339.17; 317.25.

1.3 Crystal structure determination

The well-shaped single crystals of *cis*-[MnL₂(NCS)₂] were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 296(2) K on a Bruker SMART APEX CCD diffractometer using a graphite-monochromated Mo K α (λ =0.071 073 nm) radiation. The structure was solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELXTL software^[17]. All non-hydrogen atoms were anisotropically refined. Crystallographic data are summarized in Table 1.

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Table 1 Crystal data and structure refinement for the complex

Complex	[MnL ₂ (NCS) ₂]	μ / mm ⁻¹	3.034
Empirical formula	C ₃₀ H ₂₂ Br ₂ MnN ₁₀ S ₂	$F(000)$	1 596
Formula weight	801.46	Crystal size / mm	0.30×0.14×0.10
Crystal system	Monoclinic	θ range / (°)	1.46~25.00
Space group	$P2_1/n$	Reflections collected	17 300
a / nm	1.648 0(2)	Independent reflections (R_{int})	5 700 (0.132)
b / nm	0.907 07(13)	Reflections observed ($I>2\sigma(I)$)	3 799
c / nm	2.191 9(3)	Data / restraints / parameters	5700/0/406
β / (°)	97.454(2)	Goodness-of-fit on F^2	0.927
V / nm ³	3.2488(8)	R / wR ($I>2\sigma(I)$)	0.043 9 / 0.094 8
Z	4	R / wR (all data)	0.071 2 / 0.103 9
D_c / (g·cm ⁻³)	1.639	$\Delta\rho_{max}, \Delta\rho_{min}$ / (e·nm ⁻³)	568, -564

2 Results and discussion

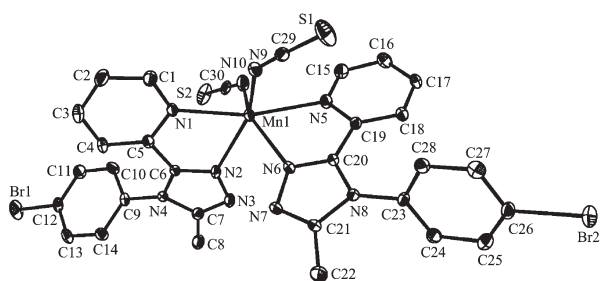
A projection of the structure of *cis*-[MnL₂(NCS)₂] is presented in Fig.1 together with the atomic labeling

system. The complex crystallizes in the monoclinic space group $P2_1/n$. Relevant interatomic distances and angles are given in Table 2.

The manganese atom is surrounded by four

Table 2 Selected bond distances (nm) and bond angles ($^{\circ}$) for the complex

Mn-N1	0.235 2(3)	Mn-N9	0.213 6(3)	N9-C29	0.114 9(5)
Mn-N2	0.228 0(3)	Mn-N10	0.213 0(4)	N10-C30	0.115 7(5)
Mn-N5	0.241 2(3)	Br1-C12	0.190 1(4)		
Mn-N6	0.221 8(3)	Br2-C26	0.189 5(4)		
Mn-N9-C29	143.0(3)	N6-Mn-N5	69.66(11)	S2-C30-N10	178.9(5)
Mn-N10-C30	138.2(4)	N6-Mn-N2	84.81(11)	S1-C29-N9	177.7(4)
N9-Mn-N10	113.51(14)	N1-Mn-N5	165.18(11)		
N9-Mn-N6	88.49(12)	N2-Mn-N1	70.53(11)		

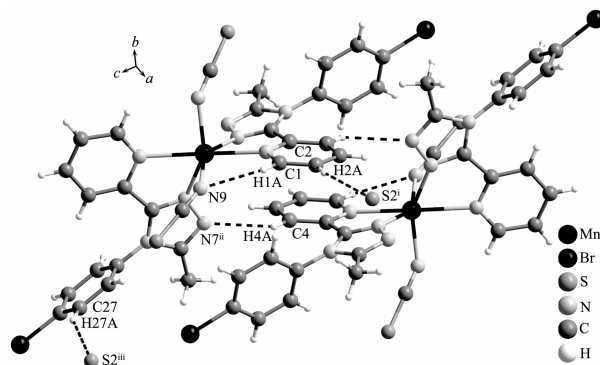


30% probability level for the thermal ellipsoids, hydrogen atoms are omitted for clarity

Fig.1 Projection of the structure of complex with the atomic labeling system

nitrogen atoms from two L ligands and two nitrogen atoms from two NCS^- ions to form a distorted octahedral geometry. Each L ligand coordinates to manganese atom through N atom of the pyridyl ring and N atom of the triazole, which is similar to the coordination modes in the related complexes^[9,18-21]. It is worthwhile to note that two NCS^- groups are in a *cis* arrangement and almost linear (N9-C29-S1 , $177.7(4)^{\circ}$ and N10-C30-S2 , $178.9(5)^{\circ}$). However, the Mn-N-C(S) linkages are bent (Mn-N9-C29 , $143.0(3)^{\circ}$ and Mn-N10-C30 , $138.2(4)^{\circ}$), which are smaller than those found in an analogous *cis*- NCS^- Mn(II) complex (Mn-N6-C21 , $163.5(3)^{\circ}$ and Mn-N7-C20 , $170.9(3)^{\circ}$)^[19]. The Mn-N9 and Mn-N10 bond lengths (0.213 6(3), 0.213 0(4) nm) are shorter than the Mn-N1 and Mn-N5 distances (0.235 2 (3), 0.241 2(3) nm). These results are similar to those found in two homologous Mn(II) complexes, *trans*- $[\text{MnL}_2(\text{NCS})_2]$ ^[18] [$\text{L}^1 = 4-(p\text{-methylphenyl})\text{-3,5-bis(pyridin-2-yl)-1,2,4-triazole}$] and *cis*- $[\text{MnL}_2(\text{H}_2\text{O})_2(\text{NCS})_2]$ ^[19] [$\text{L}^2 = 4-(p\text{-methoxyphenyl})\text{-3,5-bis(pyridin-2-yl)-1,2,4-triazole}$]. The ligand L in complex is non-planar. The triazole ring with N2 atom makes dihedral angles of $15.8(3)^{\circ}$ and

$72.3(3)^{\circ}$ with the N1-containing pyridyl ring and Br1-containing phenyl ring, respectively. While the triazole ring with N6 atom makes dihedral angles of $6.3(3)^{\circ}$ and $71.7(3)^{\circ}$ with the N5-containing pyridyl ring and Br2-containing phenyl ring, respectively. The crystal structure is further stabilized by weak intermolecular $\text{C-H}\cdots\text{N}$ and $\text{C-H}\cdots\text{S}$ hydrogen bonds (Fig.2 and Table 3).



Symmetry codes: ⁱ 1-x, -y, -1-z; ⁱⁱ 1-x, 1-y, -1-z; ⁱⁱⁱ 1/2+x, 1/2-y, 1/2+z

Fig.2 Hydrogen bonding interactions in the complex

In the IR spectrum of the complex, there are two bands at 2 063(s) and 2 043(s) cm^{-1} , attributable to the $\text{C}\equiv\text{N}$ stretching vibrations of two thiocyanate groups, which shows that two NCS^- ions are in a *cis* arrangement^[19]. This feature is in agreement with the results of X-ray analysis. A band at 1 600(s) cm^{-1} can be assigned to the coordinated pyridine ring. In addition, the diagnostic symmetrical stretching frequency of Ar-Br is at 1 070(m) cm^{-1} .

The structure of *cis*- $[\text{MnL}_2(\text{NCS})_2]$ in solution was also studied by electrospray ionization mass spectrometry (ESI-MS)^[22-23]. The base peak at m/z 743.92 is $[\text{MnL}_2(\text{NCS})]^+$ ion and the peak at m/z 499.67 is $[\text{MnL}_3]^{2+}$.

The peaks at m/z 652.92, 339.17 and 317.25 are $[\text{NaL}_2]^+$, $[\text{NaL-H}]^+$ and $[\text{L}]^+$, respectively.

3 Conclusions

A new manganese(II) complex with 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole has been synthesized and characterized by elemental analyses, IR, ESI-MS spectra and X-ray crystal structure analysis. The manganese atom is in a distorted octahedral environment and coordinated by two *cis*-oriented thiocyanate anions. Each ligand coordinates via one triazole nitrogen atom and one pyridine nitrogen atom.

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