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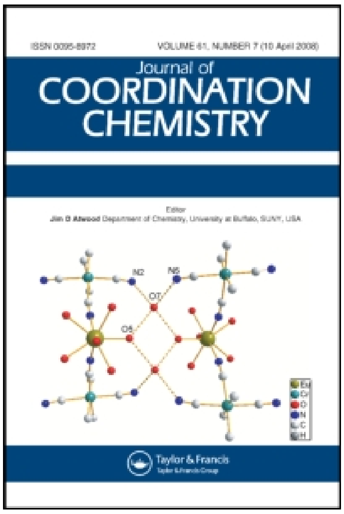

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Synthesis and characterization of a novel Mn complex with 4-(pyridyl-2)-1,2,4-triazole

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SYNTHESIS AND CHARACTERIZATION OF A NOVEL Mn COMPLEX WITH 4-(PYRIDYL-2)-1,2,4-TRIAZOLE

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The molecular structure of a novel manganese complex with 4-(pyridine-2)-1,2,4-triazole has been determined by X-ray analysis. Crystals are triclinic, space group $P\bar{1}$, with $a=10.397(4)$, $b=12.033$, $c=13.920(5)$ Å, $\alpha=115.325(5)$, $\beta=90.449(6)$, $\gamma=109.379(7)^\circ$, $V=1461.8(9)$ Å^3, $Z=2$, $R1=0.0569$, $wR2=0.1113$. The manganese atom lies in a distorted octahedral environment. Two ligand molecules coordinate axially and two *cis*-oriented thiocyanate anions and *cis*-oriented water molecules coordinate to the metal centre. The crystal is stabilized by intramolecular π–π stacking and hydrogen bonding. Magnetic measurements show the complex is a high-spin species in the 77–300 K range.

Keywords: Manganese complex; Crystal structure; 4-(Pyridine-2)-1,2,4-triazole; Magnetic properties

INTRODUCTION

Transition metal complexes of 1,2,4-triazole derivatives are of great interest from both theoretical and practical viewpoints and are the subject of several magnetic studies [1–5]. It is interesting to note that some complexes containing substituted 1,2,4-triazole ligands have spin-crossover properties, which could be used in molecular-based memory devices, displays and optical switches [6,7]. The ligand 4-(pyridyl-2)-1,2,4-triazole (pytrz) is of special interest as it shows diverse coordination modes involving N(1) and N(2) donor atoms. A variety of new types of Cu(II) and Fe(II) complexes with 1,2,4-triazole derivatives has been documented, whereas Mn(II) complexes with 1,2,4-triazole derivatives have been rarely studied. Recently we reported the crystal structure of a series of Cd(II) [8] and Zn(II) complexes with 1,2,4-triazole derivatives [9]. As a continuation of our investigations, we report herein the synthesis and X-ray structure of a new Mn(II) coordination compound with pytrz $[Mn(pytrz)_3(H_2O)_2(NCS)_2]$.

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EXPERIMENTAL

Starting Materials

All chemicals used were of analytical grade. Solvents were purified by conventional methods. The ligand pytrz was synthesized using a literature method [10].

Preparation of [Mn(pytrz)$_3$(H$_2$O)$_2$(NCS)$_2$] (1)

To a solution of pytrz (0.5 mmol) in boiling water (15 cm^3) was added an aqueous solution (3 cm^3) of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol) with stirring. The mixture was filtered into an aqueous solution containing KSCN (1 mmol). A crystal of **1** suitable for X-ray diffraction was obtained by evaporation of the solution. Anal. Calcd. for $C_{15}H_{33}Cl_2CuN_3O_{11}$(%): C, 41.59; H, 3.08; N, 29.42. Found: C, 41.63; H, 3.61; N, 29.55.

Physical Measurements

Elemental analyses (C, H, N) were performed on a PerKin Elmer 240 instrument. IR spectra were recorded on a Nicolet 5DX FTIR spectrophotometer using KBr pellets in the range 4000–400 cm^{-1}. X-ray diffraction data were collected on a BRUKER SMART 1000 CCD detector with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Magnetic susceptibilities of a polycrystalline sample were measured under vacuum on an LDJ9600 vibrating sample magnetometer over the temperature range 77–300 K. The applied filed was 5 kOe.

X-ray Crystallography

A block-like crystal of **1** with dimensions 0.38 × 0.22 × 0.18 mm was selected for lattice parameter determination and collection of intensity data at 293 K using the ω–2θ scan mode. Data were corrected for Lorenz and polarization effects during data reduction. A semi-empirical absorption correction was applied. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL 97 [11,12]. All non-hydrogen atoms were refined anisotropically. Crystallographic data are summarized in Table I. Final selected atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are listed in Table II.

RESULTS AND DISCUSSION

Crystal Structure

An ORTEP drawing of **1** is shown in Fig. 1. Selected bond lengths and angles are listed in Table III. The manganese atom is surrounded by four nitrogen atoms, two from the ligands in axial positions and two from NCS$^-$ anions in the equatorial plane. These, together with two oxygen atoms from water molecules, form a distorted octahedral geometry. The Mn–O(2) distance is 2.260 Å, 0.06 Å longer than Mn–O(1) whereas the Mn–N(14) bond length is 2.157 Å, 0.04 Å longer than Mn–N(13). The Mn, N(1), N(5), N(13) and O(1) atoms are almost co-planar (mean deviation from plane is < 0.11 Å). The ligand coordinates to the manganese atom via the N(1) atom

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TABLE I Crystal data and structure refinement details for the complex

Empirical formula	$C_{23}H_{24}MnN_{14}O_3S_2$
M	663.62
Crystal system	Triclinic
Space group	$P\bar{1}$
a(Å)	10.397(4)
b(Å)	12.033(5)
c(Å)	13.920(5)
α(°)	115.325(5)
β(°)	90.449(6)
γ(°)	109.379(7)
Z	2
D_c (Mg m^{-3})	1.508
F (000)	682
Absorption coefficient (mm^{-1})	0.648
θ range (°)	1.64–26.46
Index range (h, k, l)	(− 12/13, − 9/15, − 17/17)
Reflections collected	8562
Independent reflections	5956 ($R_{\text{int}} = 0.0434$)
Absorption correction	Semi-empirical
Data/restraints/parameters	5956/0/389
Goodness-of-fit on F^2	0.966
Final R, wR indices ($I > 2\sigma(I)$)	0.0569, 0.1113
R, wR indices (all data)	0.1444, 0.1528
Largest diff. peak and hole (e Å^{-3})	0.370, − 0.327

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of the triazole moiety, leaving the N(2) atom of the triazole moiety uncoordinated, comparable to the coordination mode of the related triaryltriazole ligands MBPT in the complex $[Ag(MBPT)(PPh_3)_2]ClO_4$ [13] and of ABPT in mononuclear compounds [14]. Mn–N(1) and Mn–O(1) distances [2.334(4) and 2.260(3) Å, respectively] are longer than those [2.244(5) and 2.194(5) Å] generally observed for octahedral complexes [16]. It is noticeable that the Mn–N bond to one triazole nitrogen is 0.1 Å shorter than that to the other. The pytrz ligand is almost coplanar. The two pytrz ligands involved in coordination make angles of 4.5° and 3.4° between the triazole and pyridyl rings, respectively, whereas the non-coordinating ligand makes an angle of 2.7°. Both NCS^- groups are almost linear [N(13)–C(22)–S(1) = 178.7°; N(14)–C(23)–S(2) = 177.7°].

In the crystal there is a hydrogen bond between O(1A) of a coordinated water molecular and O(3A) of a lattice water molecule [O(1A)···O(3B) = 2.785 Å; O(1A)···O(3A) = 2.886 Å; O(1H)···O(3A) = 2.787 Å; O(1H)···O(3A) = 2.886 Å. Furthermore, O(2A) of a coordinated water molecule is involved in hydrogen bonding with the non-coordinating pytrz group [O(2A)···N(10B) = 2.815 Å].

Neighboring aromatic rings are parallel to each other, separated by 3.35–3.45 Å, indicating the presence of significant π–π stacking interactions.

Magnetic Properties

The temperature-dependent variation of the magnetic susceptibility in the form of χ_m and χ_m^{-1} T is show n in Fig. 2 for **1**. The data show that the complex is paramagnetic in the 77–300 K range. For the high-spin complex a magnetic moment of 5.62 BM/Mn^{2+} is observed, as expected. The μ_{eff} value is in the normal range observed for high-spin manganese(II) complexes ($\mu_{\text{eff}} = 5.6$–6.1 BM) of O_h symmetry, Over the whole temperature range (77–300 K), the magnetic behaviour of **1** can be interpreted

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TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for the complex

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Mn(1)	2174(1)	3824(1)	2609(1)	37(1)
N(1)	1594(4)	2240(3)	3241(3)	39(1)
N(2)	1616(4)	2381(3)	4290(3)	46(1)
N(3)	859(3)	260(3)	3160(3)	33(1)
N(4)	294(4)	1551(3)	3502(3)	42(1)
N(5)	2689(4)	5474(3)	2157(3)	38(1)
N(6)	2638(4)	5299(4)	1110(3)	48(1)
N(7)	3315(3)	7428(3)	2222(3)	34(1)
N(8)	3873(4)	9459(3)	3695(3)	43(1)
N(9)	1697(4)	− 2773(4)	6300(3)	54(1)
N(10)	1775(4)	− 2666(4)	5353(3)	47(1)
N(11)	2412(3)	− 670(3)	6693(3)	37(1)
N(12)	3025(4)	1334(4)	6659(3)	51(1)
N(13)	425(4)	2555(4)	1358(3)	57(1)
N(14)	3785(5)	3229(4)	1830(3)	54(1)
C(1)	1150(4)	977(4)	2601(3)	39(1)
C(2)	1180(5)	1201(4)	4214(4)	45(1)
C(3)	406(4)	− 1145(4)	2757(3)	32(1)
C(4)	135(5)	− 1959(4)	1668(4)	51(1)
C(5)	− 255(5)	− 3289(5)	1333(4)	60(1)
C(6)	− 358(5)	− 3751(4)	2081(4)	54(1)
C(7)	− 86(5)	− 2851(5)	3146(4)	52(1)
C(8)	3097(4)	6740(4)	2795(3)	36(1)
C(9)	3004(5)	6473(4)	1175(3)	46(1)
C(10)	3752(4)	8825(4)	2637(3)	33(1)
C(11)	4004(5)	9401(5)	1968(4)	48(1)
C(12)	4418(5)	10756(5)	2432(5)	63(2)
C(13)	4569(5)	11453(5)	3519(5)	62(2)
C(14)	4291(5)	10789(5)	4122(4)	53(1)
C(15)	2093(5)	− 1571(5)	7074(4)	51(1)
C(16)	2210(5)	− 1417(5)	5605(4)	46(1)
C(17)	2847(4)	742(4)	7268(4)	37(1)
C(18)	3044(5)	1368(5)	8381(4)	53(1)
C(19)	3435(6)	2722(5)	8882(4)	66(2)
C(20)	3634(5)	3383(5)	8280(5)	62(2)
C(21)	3432(5)	2665(5)	7178(5)	62(2)
C(22)	− 543(5)	1682(4)	800(3)	42(1)
C(23)	4833(6)	3184(4)	1608(4)	44(1)
S(1)	− 1926(2)	439(2)	32(1)	76(1)
S(2)	6321(2)	3102(2)	1329(1)	72(1)
O(1)	3880(3)	5265(3)	4051(2)	50(1)
O(2)	891(3)	4709(3)	3706(2)	57(1)
O(3)	3422(3)	4913(3)	5889(2)	62(1)

by the Curie–Weiss law with Curie value and Weiss constant of 3.45(3) emu K mol^{-1} and − 5.2(2) K, respectively.

IR Data

In the IR there are several broad, medium-intensity bands at 3854, 3802, 3751, 3736 and 3630 cm^{-1}, mainly attributed to H–O–H stretching vibrations, suggesting the existence of hydrogen-bonding interactions [15]. The very strong bands at 2100 cm^{-1} are assigned to C≡N stretching of two *cis*-oriented thiocyanate groups. These results are in agreement with the X-ray analysis. A band at 1607 cm^{-1}(s) and two bands at 1591 and

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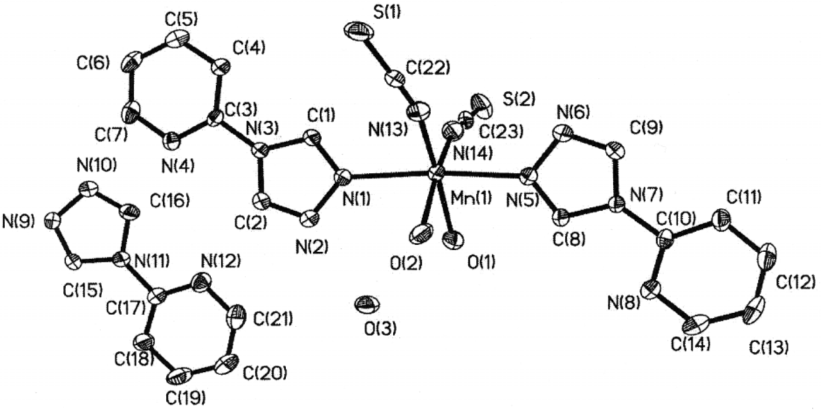

FIGURE 1 ORTEP diagram and atom labelling system for $[Mn(pytrz)_3(H_2O)_2](ClO_4)_2 \cdot 4H_2O$. Hydrogen atoms are omitted for clarity.

TABLE III Selected bond lengths (Å) and angles (°) for the complex

Mn(1)–N(13)	2.122(4)	Mn(1)–O(2)	2.197(3)
Mn(1)–N(5)	2.235(3)	Mn(1)–O(1)	2.260(3)
N(13)–Mn(1)–N(14)	101.11(16)	N(13)–Mn(1)–O(2)	91.19(15)
N(14)–Mn(1)–O(2)	167.68(14)	N(13)–Mn(1)–N(5)	94.54(14)
N(14)–Mn(1)–N(5)	90.94(14)	O(2)–Mn(1)–N(5)	88.79(12)
N(13)–Mn(1)–O(1)	173.81(14)	N(14)–Mn(1)–O(1)	85.08(14)
O(2)–Mn(1)–O(1)	82.62(12)	N(5)–Mn(1)–O(1)	85.29(12)
N(13)–Mn(1)–N(1)	87.90(14)	N(14)–Mn(1)–N(1)	93.55(13)
O(2)–Mn(1)–N(1)	86.11(12)	N(5)–Mn(1)–N(1)	174.39(13)

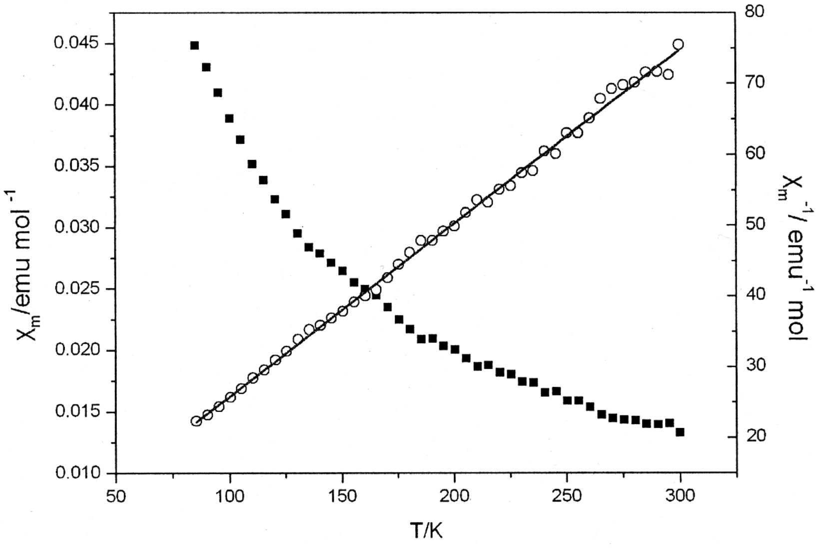

FIGURE 2 Magnetic behaviour of the complex: χ_m(■) and χ_m^{-1} (o) vs. T plot for 1.

1573 cm^{-1}(w) can be assigned to uncoordinated pyridine ring vibrations. The triazole out-of-plane ring absorption is observed at about 629 cm^{-1} [16].

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Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 225196. Copies can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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