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SYNTHESIS, CHARACTERIZATION AND MAGNETIC PROPERTIES OF ONE-DIMENSIONAL 4,4′-BIPYRIDINE-BRIDGED MANGANESE(II) COMPLEX: CRYSTAL STRUCTURE OF $[Mn(\mu\text{-}4,4'\text{-bipy})(4,4'\text{-bipy})(NCS)_2(H_2O)_2]_n$

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Abstract—The one-dimensional manganese(II) complex with 4,4′-bipyridine (4,4′-bipy) as bridging ligand, of formula $[Mn(\mu\text{-}4,4'\text{-bipy})(4,4'\text{-bipy})(NCS)_2(H_2O)_2]_n$, has been prepared and characterized by elemental analysis, IR spectra and thermal analysis. Its X-ray crystal structure determination reveals that the local coordination geometry around the Mn^{II} ion is a distorted octahedron. $Mn(NCS)_2(H_2O)_2$ coordination planes are bridged by 4,4′-bipyridines to form an infinite chain structure. A second 4,4′-bipyridine exists in the lattice, linked by hydrogen bonds to coordinated water molecules. The determination of variable-temperature magnetic susceptibilities (74–300 K) shows that the magnetic behaviour obeys the Curie law. There is practically no evidence of any magnetic exchange interaction between the adjacent metal ions.

The propagation of magnetic exchange interaction over large distances is a topic that has attracted considerable interest in recent years. A lot of work has been devoted to the study of exchange interactions between transition-metal ions through extended bridging ligands, such as 4,4′-bipyridine, pyrazine and imidazolate.[1] Many binuclear or chain metal complexes have been prepared which have 4,4′-bipyridine bridging ligands.[2–4] However, until now, all the magnetic investigations show no evidence of any magnetic interaction between 4,4′-bipyridine-bridged metal ions. The reason is not very clear.

For expanding the magnetochemistry studies of 4,4′-bipyridine-bridged complexes to two-dimensional polymer systems, we note that a series of transition-metal complexes with formula $[M(4,4'\text{-bipy})_2(NCS)_2(H_2O)_2]_n$ was reported 10 years ago.[5,6] These complexes are considered as having two-dimensional sheet-like polymer structures as in the crystal structure of $[Fe(\mu\text{-pyrazine})_2(NCS)_2]_n$.[7] The insolubility of the isolated complexes is the reason for the lack of X-ray diffraction studies on single crystals. The structural conclusions were based only on spectroscopic evidence. Now, the use of a slow replacement reaction has allowed us to grow single crystals of $[Mn(4,4'\text{-bipy})_2(NCS)_2(H_2O)_2]_n$ for the first time. The crystal structure determination reveals that the complex has the unexpected one-dimensional polymer structure with one 4,4′-bipyridine existing only as a lattice molecule. Here we report its synthesis, characterization, crystal structure and variable-temperature magnetic properties.

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EXPERIMENTAL

Synthesis

Analytical grade $MnSO_4 \cdot H_2O$, NH_4SCN, pyridine and 4,4′-bipyridine were used without further purification. $Mn(py)_4(NCS)_2$ was prepared according to the literature method.[8] The title complex was prepared as follows: to a stirred solution of $Mn(py)_4(NCS)_2$ (0.5 mmol) in ethanol (15 cm^3) was added 1 mmol 4,4′-bipyridine. The mixture was stirred at room temperature for 1 h and pale yellow microcrystalline powder precipitated out. The solid was collected by filtration, washed with ethanol and ether, and dried *in vacuo*; yield 0.12 g (46%). Found: C, 50.6; H, 4.0; N, 16.6. Calc. for $C_{22}H_{20}N_6O_2S_2Mn$: C, 50.9; H, 3.9; N, 16.2. The pale yellow plate-like crystals suitable for X-ray structure analysis were grown from the filtrate by evaporation for 2 weeks.

Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin–Elmer 240C analyser. IR spectra were obtained with KBr pellets in the 4000–400 cm^{-1} region, using a Nicolet 170 SX FTIR spectrophotometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were measured simultaneously on an LCT-2 instrument with a heating rate of 10°C min^{-1}. Variable-temperature (74–300 K) magnetic susceptibility measurements were carried out with a CAHN-2000 Faraday type magnetometer. The resulting susceptibilities are corrected with Pascal's constant for diamagnetism and the magnetic moments are calculated using the equation $\mu_{eff} = 2.828(\chi T)^{1/2}$.

Crystal structure determination

A suitable single crystal with dimensions $0.2 \times 0.3 \times 0.4$ mm was mounted on a glass fibre and aligned on an Enraf–Nonius CAD-4 diffractometer. Unit cell parameters were determined on the basis of 25 reflections with $9.8 < \theta < 13.4°$. Intensity measurements employed graphite-monochromated Mo-K_α radiation and ω–2θ scan mode in the range $0 < 2\theta < 50°$ at room temperature. During data collection, the intensity of three standard reflections were monitored every 3600 s of X-ray exposure time showed no significant decay. After taking into account Lorentz and polarization effects, an empirical absorption correction with min. 88.18% and max. 99.90% transmission was applied, based on seven PSI scans. The crystal data are listed in Table 1.

The crystal structure was solved using direct methods (MULTAN 86) and difference-Fourier syntheses, and refined by the full-matrix least-squares technique using anisotropic temperature factors. Hydrogen atoms were riding on the related carbon atoms and refined with fixed thermal parameters. Refinement converged at $R = 0.043$ and $R_w = 0.048$ for 2337 observed reflections with $I > 3\sigma(I)$ of 1883 unique ones. A final difference Fourier map exhibited no peaks greater than 0.25 e Å^{-3}. All the computations were performed on a Micro VAXII computer with PDP-plus and ORTEP programs. Complete tables of atomic coordinates and thermal parameters, together with observed and calculated structure factors, have been deposited with the Editor, from whom copies are available on request. Atomic coordinates have

Table 1. Summary of crystal and intensity collection data

Empirical formula	$C_{22}H_{20}N_6O_2S_2Mn$
Formula weight	519.5
Crystal dimensions (mm)	$0.2 \times 0.3 \times 0.4$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.468(3)
b (Å)	9.071(2)
c (Å)	10.178(4)
α (°)	107.77(2)
β (°)	103.67(2)
γ (°)	96.07(2)
V (Å^3)	626.1(8)
Z	1
D_c (g cm^{-3})	1.38
F(000)	267
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
μ (cm^{-1})	6.95
Temperature (K)	298
Scan method	ω–2θ
Scan width (°)	$0.87 + 0.35 \tan \theta$
$2\theta_{max}$ (°)	50.0
$(h,k,l)_{min}$, $(h,k,l)_{max}$	$(-8, -10, 0)$, $(8, 10, 12)$
No. of data collected	2337
No. of unique data	2337
No. of data with $I > 3\sigma(I)$	1883
No. of parameters refined	295
R^a	0.043
$R_w{}^b$	0.048
GOF^c	0.775
Largest shift in final cycle	0.04
Largest difference peak (e Å^{-3})	0.25

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

[c] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{para})]^{1/2}$.

also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

IR spectra and thermal analysis

The procedure for the synthesis of [Mn(4,4′-bipy)$_2$ (NCS)$_2$ (H$_2$O)$_2$]$_n$ has been reported previously by Singh *et al.*[5,6] We have used a modification of this procedure in our study. By the displacement reaction of Mn(py)$_4$(NCS)$_2$ with 4,4′-bipyridine a pale yellow manganese complex has been synthesized. Elemental analysis has confirmed the formula as [Mn(C$_{10}$H$_8$N$_2$)$_2$(NCS)$_2$(H$_2$O)$_2$]$_n$. The IR spectrum of the complex clearly shows the existence of 4,4′-bipyridine, thiocyanate and water molecules. The absorption bands at 2082, 790 and 469 cm^{-1} correspond to ν(C≡N), ν(C—S) and δ(N≡C—S), respectively, consistent with terminally nitrogen-bonded NCS groups.[6] Bands at 3420, 1650 and 872 cm^{-1} are assigned to the vibration absorption of water molecules, indicating that water is coordinated to the manganese ion.[5]

The broad absorption band at 3000–2850 cm^{-1} is perhaps attributable to ν(O—H $\cdots$ X)(X is a highly electronegative nitrogen or sulphur atom), indicating that some kind of hydrogen bond exists in the complex. All the other significant bands, for example 3058 (m), 1596 (vs), 1538 (s), 1406 (s), 1222 (m), 1069 (m), 809 (vs) and 628 (s), are in good agreement with the IR bands of free 4,4′-bipyridine,[9] indicating that some of the 4,4′-bipyridine exists as non-coordinated molecules.[4,10]

The title complex is stable up to approximately 110°C. Its thermal decomposition starts with an endothermic step in the temperature range 110–150°C, which corresponds exactly to the release of two coordinated water molecules (found 6.90; calc. 6.93%). The second endothermic step (200–260°C) clearly shows the loss of one 4,4′-bipyridine molecules (found 28.74; calc. 30.07%). This rather low temperature of 4,4′-bipyridine loss indicates that the complex contain one non-coordinated 4,4′-bipyridine molecule. The third endothermic steps (310–380°C) is followed by one strong exothermic process between 380 and 410°C. The former is in agreement with the normal thermal stability of a bridging 4,4′-bipyridine ligand,[11] and the latter indicates a mixed process of thiocyanate ligand dissociation and Mn^{II} ion being oxidized to MnO$_2$. Both of these steps overlap in the TG curves with a mass loss of 47.13% (calc. 46.26%). Up to 600°C, there is no further change in weight. The final, thermally-stable brown residue is MnO$_2$ (found 17.24; calc. 16.74%).

Description of structure

The crystal structure of the title complex is shown in Fig. 1. Selected bond distances and angles are listed in Table 2.

Each repeat unit of the complex consists of Mn(NCS)$_2$(H$_2$O)$_2$, one bridging 4,4′-bipyridine and one non-coordinated 4,4′-bipyridine molecule. The Mn(NCS)$_2$(H$_2$O)$_2$ planar units are bridged by 4,4′-bipyridine in a nearly linear fashion, forming an infinite linear chain in the crystal. Two of these one-dimensional chains pass through the cell in parallel fashion.

The local coordination geometry around the Mn^{II} ion is distorted octahedron. Two coordinated water molecules and thiocyanates with the central Mn^{II} ion are basically co-planar. The average Mn—O bond length is 2.198 Å and the Mn—N bond lengths 2.175 Å. All pyridyl rings of the axially coordinated 4,4′-bipyridine are arranged in one plane and perpendicular to the equatorial planes.

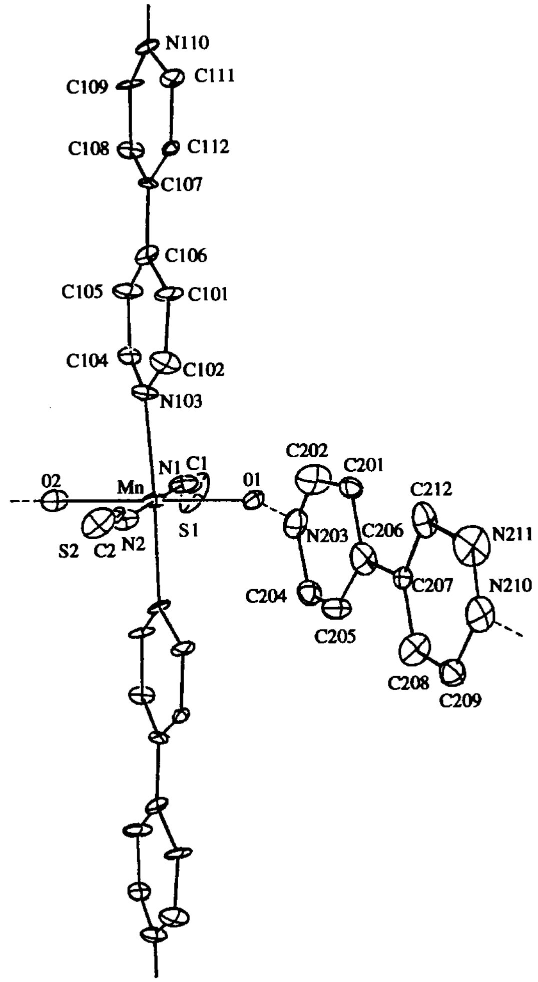

Fig. 1. The molecular structure of the complex [Mn(μ-4,4′-bipy)(4,4′-bipy)(NCS)$_2$(H$_2$O)$_2$]$_n$.

Table 2. Selected bond distances (Å) and angles (°)

Mn—O(1)	2.178(6)	C(101)—C(102)	1.402(9)
Mn—O(2)	2.218(7)	C(102)—N(103)	1.35(1)
Mn—N(1)	2.188(8)	N(103)—C(104)	1.25(2)
Mn—N(2)	2.163(8)	C(104)—C(105)	1.378(8)
Mn—N(103)	2.279(5)	C(105)—C(106)	1.36(1)
Mn—N(110)	2.277(4)	C(106)—C(101)	1.47(2)
N(1)—C(1)	1.14(1)	C(106)—C(107)	1.474(7)
C(1)—S(1)	1.602(9)	C(206)—C(207)	1.50(1)
O(1)—Mn—N(1)	90.3(2)	O(1)—Mn—O(2)	179.3(2)
O(1)—Mn—N(2)	88.8(3)	N(103)—Mn—N(110)	177.5(2)
O(1)—Mn—N(103)	91.2(3)	N(1)—Mn—N(2)	178.8(2)
O(1)—Mn—N(110)	91.1(2)	N(1)—C(1)—S(1)	173.2(6)

The Mn—N bond length (2.278 Å) is equal to the reported one in the related complex [Mn(TTA)$_2$(μ-4,4′-bipy)]$_n$ (2.278 Å).[3] In the coordination octahedron, all the neighbouring bond angles are nearly 90° and opposite bond angles 180°.

Unlike the expected two-dimensional sheet-like structure in [Fe(μ-pyrazine)$_2$(NCS)$_2$]$_n$,[7] the title complex has a one-dimensional chain structure with half of the 4,4′-bipyridines as bridging ligands and the other half as non-coordinated molecules in the crystal lattice. The coordinated water molecules are hydrogen-bonded to the nitrogen atoms of the non-coordinated 4,4′-bipyridine. The distances O(1)—N(203) and H(W12)—N(203) are 2.726 and 1.744 Å, respectively, and the angle O(1)—H(W12)—N(203) is 167.9(5)°. The N(210) is hydrogen-bonded to the O(2)′ atom of a neighbouring one-dimensional chain. O(2)′—N(210), H(W22)′—N(210) and O(2)′—H(W22)′—N(210) are 2.758 Å, 1.889 Å and 173.7°, respectively. Similarly, the O(2) is hydrogen-bonded to the N(210)′ atom of another non-coordinated 4,4′-bipyridine. Thus, [Mn(μ-4,4′-bipy)(NCS)$_2$(H$_2$O)$_2$]$_n$ one-dimensional chains are linked by non-coordinated 4,4′-bipyridine relying on hydrogen bonds, forming a network system.

The crystal structure description is exactly in agreement with the result of IR spectra and thermal analysis.

Magnetic properties

The magnetic susceptibility of the title complex as a function of temperature is plotted in Fig. 2. The solid lines are least-squares fits to the data. the magnetic susceptibility obeys the Curie law: $\chi_m = C/T-\theta$ ($C = 4.03$ and $\theta = 0$ K). The magnetic moment is constant in the temperature range 75–300 K with a value of 5.64 B.M. [*cf* the spin-only value (5.92 B.M.) of the manganese(II) ion ($S = 5/2$)]. Thus, there is practically no magnetic interaction between the Mn$^{\mathrm{II}}$ ions through the 4,4′-bipyridine bridges.

Up to now, all the magnetic investigations of 4,4′-bipyridine-bridged complexes show practically no evidence of magnetic interaction. For the reported complexes [Cu$_2$(tren)$_2$(4,4′-bipy)](BPH$_4$)$_4$,[12] [Cu$_2$(dien)$_2$(4,4′-bipy)(ClO$_4$)$_2$](ClO$_4$)$_2$,[2] [Cu$_2$(TTA)$_4$(4,4′-bipy)],[13] [Mn(TTA)$_2$(4,4′-bipy)]$_n$,[3] [Ni(salal)$_2$(4,4′-bipy)]$_n$[14] and [Cu(acac)$_2$(4,4′-bipy)]$_n$,[14] the largest magnetic exchange coupling constant is under -0.9 cm^{-1}.[2] Haddad *et al.*[12] considered that 4,4′-bipyridine is too long to propagate magnetic interactions. Here we give another explanation. The carbon–carbon bond length between pyridyl rings of 4,4′-bipyridine [for example C(106)—C(107), C(206)—C(207)], compared with the usual sp^2–sp^2 C—C single bond length of

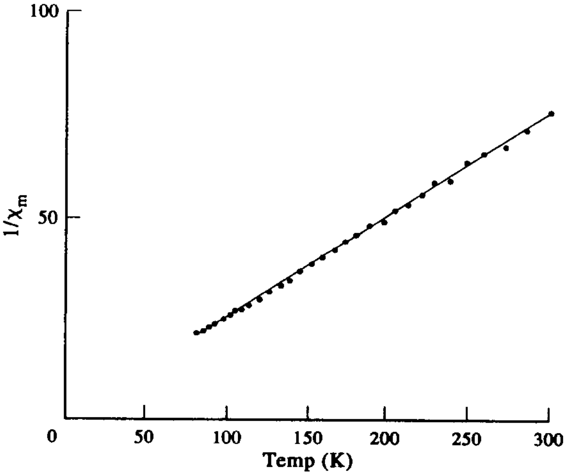

Fig. 2. The temperature dependence of the inverse molar magnetic susceptibility. The straight line is a least-squares fit to the data.

1.50 Å and C=C double bond length of 1.35 Å, is practically of single bond character. The very weak conjugation effect leads to the fact that the two pyridyl rings of 4,4′-bipyridine often display larger dihedral angles.[15,16] Because the π-type electron transfer pathway is hindered at this C—C single bond, it is concluded that 4,4′-bipyridine is not a significant bridge for propagating an exchange interaction between paramagnetic metal ions.

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