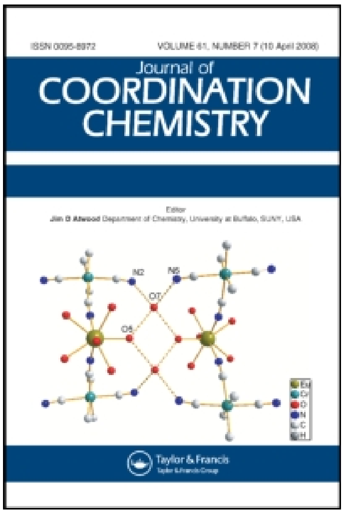

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and luminescent properties of manganese 3,3'-dicarboxy-2,2'-bipyridine induced by hydrolysis of 1,10-phenanthroline-5,6-dione

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To cite this Article Huang, Xianqiang , Dou, Jianmin , Li, Dacheng and Wang, Daqi(2007) 'Synthesis, crystal structure and luminescent properties of manganese 3,3'-dicarboxy-2,2'-bipyridine induced by hydrolysis of 1,10-phenanthroline-5,6-dione', Journal of Coordination Chemistry, 60: 3, 319 — 325

To link to this Article: DOI: 10.1080/00958970600793638

URL: http://dx.doi.org/10.1080/00958970600793638

Journal of Coordination Chemistry
Vol. 60, No. 3, 10 February 2007, 319–325

Synthesis, crystal structure and luminescent properties of manganese 3,3′-dicarboxy-2,2′-bipyridine induced by hydrolysis of 1,10-phenanthroline-5,6-dione

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(*Received 25 October 2005; revised 13 February 2006; in final form 16 February 2006*)

The manganese coordination compound $[Mn(dcb)(H_2O)_4]_n$ has been obtained by hydrothermal synthesis by using $Mn(CH_3COO)_2 \cdot 2H_2O$ and 1,10-phenanthroline-5,6-dione, where dcb = 3,3′-dicarboxy-2,2′-bipyridine. The results of X-ray single-crystal diffraction reveal that the title complex forms a chain-like 1D structure. The complex $[Mn(dcb)(H_2O)_4]_n$ crystallizes in the orthorhombic system, space group $P2(1)2(1)2$, with lattice parameters $a = 13.896(3)$ Å, $b = 6.3507(12)$ Å, $c = 8.3745(15)$ Å, $V = 739.1(2)$ Å^3, $D_c = 1.659$ Mg m^{-3}, $Z = 2$, $F(000) = 378$, GOF = 0.999, $R_1 = 0.0283$, $wR_2 = 0.0719$. The photophysical properties have been investigated with fluorescence excitation and emission spectra.

Keywords: Manganese complex; Chain-like 1D structure; 3,3′-Dicarboxy-2,2′-bipyridine

1. Introduction

Transition metal-organic coordination compounds, which are diverse in structure and property, are currently attracting increasing attention not only because of applications in the areas of catalysis, co-operative magnetic behavior, non-linear optical activity and electrical conductivity, but also owing to their interesting topologies. To design exquisite metal-organic coordination compounds from transition metals and organic ligands with novel architectures and desired functionalities by use of the principles of crystal engineering has been one of the most challenging subjects in coordination chemistry today [1–8].

One efficient route to coordination polymers is to employ a multifunctional ligand to link metal ions in an infinite framework. The heterocyclic ligand 1,10-phenanthroline-5,6-dione has two types of donor atom (nitrogen and oxygen), and shows interesting coordination chemistry. Metal complexes of 1,10-phenanthroline-5,6-dione may exhibit various coordination geometries with 1 : 1, 3 : 2, 2 : 1 and other metal/ligand molar ratios (scheme 1) [9, 10].

Hydrothermal synthesis has exhibited superiority as a powerful method for preparation of new metal-organic coordination compounds [11]. In recent years, the

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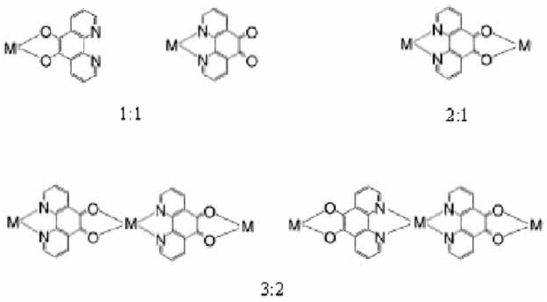
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600793638



Scheme 1. Several coordination modes of 1,10-phenanthroline-5,6-dione ligand.

hydrothermal method has been applied in syntheses of manganese complexes, and a large number of manganese complexes with one-dimensional chain-like, two-dimensional layer-like or three-dimensional net-like open framework structures have been prepared and characterized [12–15]. The title complex has been synthesized by using manganous acetate and 1,10-phenanthroline-5,6-dione by the hydrothermal method. Although 1,10-phenanthroline-5,6-dione was used as the organic reagent in the preparation of the title complex the 2,2′-bipyridine-3,3′-dicarboxylate ligand was unexpectedly found in the final chain-like coordination polymer $[Mn(dcb)(H_2O)_4]_n$, indicating that hydrolysis of 1,10-phenanthroline-5,6-dione to 2,2′-bipyridine-3,3′-dicarboxylate occurred.

2. Experimental

2.1. *Materials and measurements*

The $Mn(CH_3COO)_2 \cdot 2H_2O$ and 1,10-phenanthroline-5,6-dione were commercially available, and used without further purification. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. Elemental analyses were performed with a PE-2400II apparatus. The luminescence (excitation and emission) spectra were determined with a Perkin-Elmer LS-55 spectrophotometer.

2.2. *Synthesis of $[Mn(dcb)(H_2O)_4]_n$*

$Mn(CH_3COO)_2 \cdot 2H_2O$ (0.3 mmol) and 1,10-phenanthroline-5,6-dione (0.3 mmol) were mixed in 12 mL deionized water. After stirring 30 min, the mixture was placed in a 25 mL Teflon-lined reactor and heated at 160 K in an oven for 3 d, then cooling slowly to room temperature and the colorless column crystals of the title complex suitable for X-ray diffraction analysis were obtained. Yield: 74%. $C_{12}H_{14}MnN_2O_8$ (369.19) Anal. Found: C, 39.24; H, 3.87; N, 7.49%. Calcd: C, 39.00; H, 3.79; N, 7.58%. The IR spectrum exhibits a pattern of bands in the range 4000-400 cm^{-1}: 1423 cm^{-1} (ν_{sCOO-}), 1558 cm^{-1} (ν_{asCOO-}).

Table 1. Crystal data and structure refinement for the title complex.

Complex	$[Mn(dcb)(H_2O)_4]_n$
Formula	$C_{12}H_{14}MnN_2O_8$
Relative molecular weight M	369.19
Color	Colorless
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Radiation	Mo-Kα
Crystal system	$P2(1)2(1)2$
Space group	Orthorhombic
Unit dimensions (Å, °)	
a	13.896(3)
b	6.3507(12)
c	8.3745(15)
Volume (Å^3)	739.1(2)
Z	2
Calculated density (Mg m^{-3})	1.659
Absorption coefficient (mm^{-1})	0.938
$F(000)$	378
Crystal size (mm^3)	$0.55 \times 0.49 \times 0.44$
θ range for data collection (°)	2.43–28.36
Reflections/collected/unique	4814/1803 [$R_{(int)} = 0.0424$]
Completeness to $2\theta = 25.01$	98.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1803/0/121
Goodness-of-fit on F^2	0.999
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0283$, w$R_2 = 0.071$
Largest diff. peak and hole (e Å^{-3})	0.228 and −0.516

2.3. *X-ray crystallography*

Diffraction data were collected using a Siemens CCD area-detector and graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least squares using SHELXL-97 [16, 17]. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in table 1.

3. Results and discussion

The title complex crystallizes in the orthorhombic system, space group $P2(1)2(1)2$. Figure 1 shows the coordination geometry and atom labeling in the crystal structure of the title complex, which consists of one Mn ion, one dcb anion and four coordinated water molecules. The Mn(II) ion lies on a crystallographic twofold axis, which bisects one dcb. The central Mn is coordinated with six oxygen atoms, in a distorted octahedral geometry. Two of the six oxygen atoms are from the two coordinated dcb anions with a Mn–O1 bond distances of 2.1769(14) Å, and the other four oxygen atoms are from the four coordinated water molecules with a Mn–O3 bond distances of 2.2009(16) Å and a Mn–O4 bond distances of 2.1990(16) Å. The average bond distance

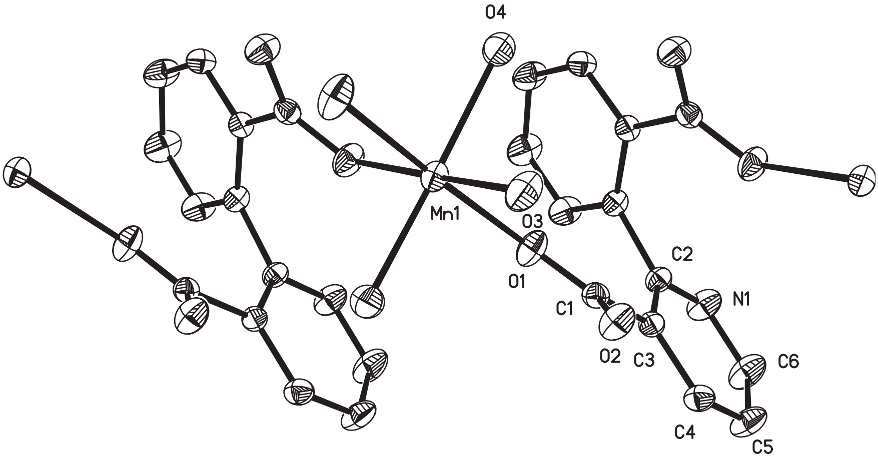


Figure 1. Molecular structure of $[Mn(dcb)(H_2O)_4]_n$.

Table 2. Selected bond distances (Å) and bond angles (°) for the title complex.

Mn(1)–O(1)	2.1768(14)		
Mn(1)–O(4)	2.1990(16)	Mn(1)–O(3)	2.2009(16)
O(1)–Mn(1)–O(1)#1	96.27(7)	O(4)#1–Mn(1)–O(3)#1	88.53(7)
O(1)–Mn(1)–O(4)#1	92.08(6)	O(4)–Mn(1)–O(3)#1	85.87(6)
O(1)–Mn(1)–O(4)	93.12(6)	O(1)–Mn(1)–O(3)	87.82(6)
O(1)#1–Mn(1)–O(4)	92.08(6)	O(1)#1–Mn(1)–O(3)	175.82(6)
O(4)#1–Mn(1)–O(4)	172.20(9)	O(4)#1–Mn(1)–O(3)	85.87(6)
O(1)–Mn(1)–O(3)#1	175.82(6)	O(4)–Mn(1)–O(3)	88.53(7)
O(1)#1–Mn(1)–O(3)#1	87.82(6)	O(3)#1–Mn(1)–O(3)	88.10(9)

Symmetry transformations used to generate equivalent atoms, #1: $-x+2$, $-y$, z.

of Mn–O is 2.1923 Å. The bond angle consisting of Mn and the two carboxylic oxygen atoms is 96.27(7)° (O1–Mn–O1#); the bond angles consisting of Mn with the water oxygen atoms are 88.10(9)° (O3–Mn–O3#) and 88.53(7)° (O3–Mn–O4), respectively. In particular, the bonds of O1–Mn–O3# and O4–Mn–O4# are close to linearity with the bond angles are 175.82(6)° and 172.20(9)°, respectively. Selected bond distances and bond angles for the title complex are listed in table 2.

Figure 2 shows the unit cell of the title complex. The crystal structure of the title complex consists of a 1D polymeric chain built from the connections of Mn(II) ions and dcb anions alternately along the b axis. The dcb anions are bidentate-bridging ligands towards the Mn ions, and the dihedral angle between the two benzene rings on the same side of the chain is 60.3°. In addition, there exists one type of strong intermolecular O–H$\cdots$O and another type of strong intermolecular O–H$\cdots$N hydrogen bonding: the O–H$\cdots$O intermolecular hydrogen bonds between the oxygen atoms of the coordinated water molecules and the uncoordinated oxygen atoms of the bridging carboxylic groups have bond angles of 147.98° (O(3)–H(2)$\cdots$O(2)^{a}), 155.84°, (O(4)–H(3)$\cdots$O(2)^{c}) and 178.85° (O(4)–H(4)$\cdots$O(2)^{d}); the O–H$\cdots$N intermolecular hydrogen bonds between the oxygen atoms of the coordinated water molecules and the pyridyl nitrogen atoms have bond angles of 172.28° (O(3)–H(1)$\cdots$N(1)^{b}).

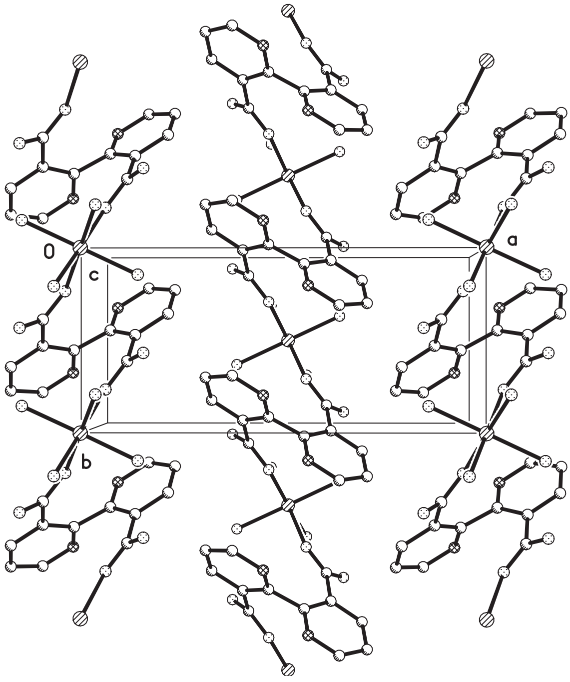


Figure 2. The unit cell of $[Mn(dcb)(H_2O)_4]_n$.

Table 3. Hydrogen bonds (Å) for the title complex.

$D–H\cdots A$	d(D–H)	$d(H\cdots A)$	$d(D\cdots A)$	∠(DHA)
$O(3)–H(1)\cdots N(1)^b$	0.992	1.779	2.765	172.28
$O(3)–H(2)\cdots O(2)^a$	0.824	2.011	2.745	147.98
$O(4)–H(3)\cdots O(2)^c$	0.737	2.211	2.899	155.84
$O(4)–H(4)\cdots O(2)^d$	0.807	1.908	2.716	178.85

For symmetry transformations used to generate equivalent atoms: (a) $-x+2$, $-y$, z; (b) $-x+2$, $-y+1$, $z-1$; (c) $x+1/2$, $-y+1/2$, $-z$; (d) $-x+2$, $-y+1$, z.

The interchain hydrogen bonds are a novel alternate fashion, and consolidate the stacked arrangement leading to a 3D supramolecular architecture. The detailed data of hydrogen bonding for the title complex are shown in table 3.

The title complex exhibits an intense blue photoluminescence upon radiation with UV light in the solid state at room temperature. Under the emission wavelength of 440 nm, the excitation band of the title complex (solid state sample) possesses two main peaks at 238 and 320 nm, respectively. The emission spectrum under the excitation wavelength of 238 nm shows a broad band ranging from 370 to 550 nm, and the maximum emission wavelength is at 447 nm. We further measured the emission spectrum of the free malic acid, which shows one emission at 390 nm, indicating that the dbc ligand has no emission in the visible region but when it is bound to a Mn center, blue luminescence is observed, as shown in figure 3. The lower energy band would be

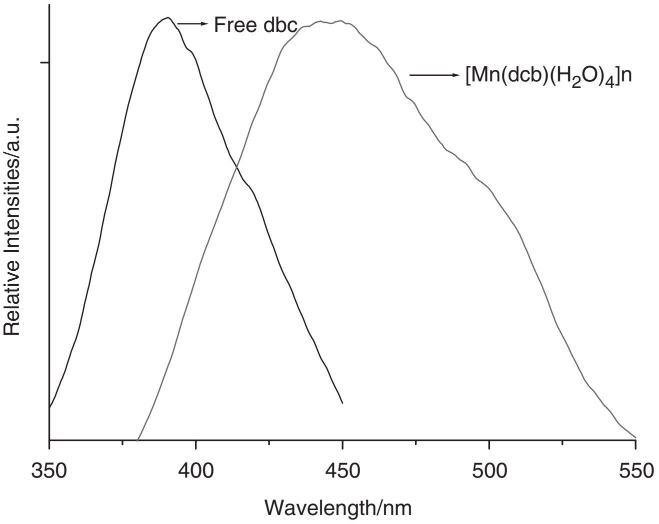


Figure 3. Luminescent emission spectra of [Mn(dcb)(H$_2$O)$_4$]$_n$.

assigned to the ligand-to-metal charge transfer (LMCT), and the observed luminescence of the complex is attributed to the coordinated dbc ligand [18].

Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (No: CCDC-284167). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank the National Natural Science Foundation of China (No. 20371025) for financial support.

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