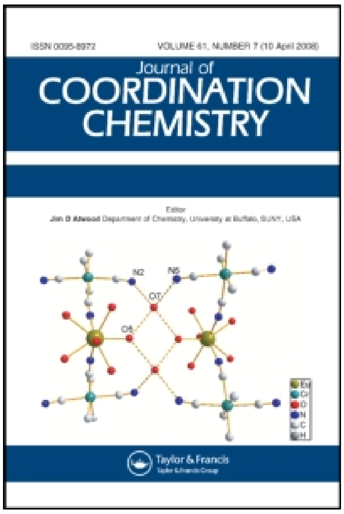

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Zhang, Chen-Xi , Zhang, Yuying and Yang, Yinghua(2006) 'Synthesis, characterization and crystal structure of a novel three-dimensional supramolecular architecture formed by manganese(II) and pyridine-2,5-dicarboxylic acid', Journal of Coordination Chemistry, 59: 4, 389 — 393

To link to this Article: DOI: 10.1080/00958970500252701
URL: http://dx.doi.org/10.1080/00958970500252701

Journal of Coordination Chemistry
Vol. 59, No. 4, March 2006, 389–393

Synthesis, characterization and crystal structure of a novel three-dimensional supramolecular architecture formed by manganese(II) and pyridine-2,5-dicarboxylic acid

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(*Received in final form 27 May 2005*)

A novel three-dimensional supramolecular compound formed by Mn(II) and pyridine-2,5-dicarboxylic acid of formula $[Mn(Pydc)_2(H_2O)_2]$ (Pydc = pyridine-2,5-dicarboxylic acid) has been synthesized and characterized by elemental analyses, IR, electronic spectra, thermogravimetric analysis and X-ray diffraction techniques. The X-ray structure shows that the central Mn(II) ion is coordinated by two water molecules and two chelated Pydc ligands. Water molecules coordinate with Mn(II) ions in the *cis* mode. Intermolecular hydrogen bonds play an important role in stabilization of the lattice and construction of the supramolecular network.

Keywords: Pyridine-2,5-dicarboxylic acid; Mn(II) complex; Crystal structure; Supramolecular networks

1. Introduction

Current interest in supramolecular chemistry and crystal engineering of coordination compounds stems from their fascinating structural diversity and potential applications in many areas such as electrical conductivity, molecular magnetism, molecular sieves and optical materials [1, 2]. Coordination bonding, hydrogen bonding, π–π stacking interactions and electrostatic interactions are all responsible in certain cases for the architectures of supramolecules [3, 4]. Pyridine-2,5-dicarboxylic acid (Pydc), which possesses diverse functional groups, has attracted considerable attention for its ability to link metals to form various architectures [5, 6]. In this paper, we report on the synthesis, characterization and crystal structure of a novel three-dimensional supramolecular complex, $[Mn(Pydc)_2(H_2O)_2]$.

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500252701

2. Experimental

All reagents were of analytical grade and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin–Elmer instrument. IR spectra were recorded on a Shimadzu 408 spectrophotometer in the 4000–600 cm^{-1} region, using KBr pellets. Electronic spectra were recorded on a Shimadzu UV-12101 PC spectrophotometer and TG-DTA studies were carried out on a Dupont thermal analyzer from room temperature to 800°C.

2.1. *Synthesis*

A mixture of Pydc (1.0 mmol, 0.1671 g), $MnCO_3$ (0.5 mmol, 0.0574 g) and water (15 cm^3) was sealed in a 25 cm^3 Teflon-lined stainless steel reactor. The mixture was heated at 150°C for 72 h and then cooled to room temperature to give crystals suitable for X-ray diffraction analysis. Yield: 43%. Anal. Calcd. for $C_{14}H_{12}N_2O_{10}Mn$ (%): C, 39.73; H, 2.86; N, 6.62. Found: C, 39.54; H, 2.96; N, 6.57.

2.2. *X-ray crystallography*

A yellow crystal of dimensions $0.38 \times 0.16 \times 0.08$ mm was mounted on a glass fibre in random orientation. The determination of the unit cell and data collection was performed on a computer-controlled Bruker SMART 1000 diffractometer. Some 1414 independent reflections ($R_{\text{int}} = 0.0183$) in the range $2.68^\circ \le \theta \le 25.01^\circ$ with index ranges $-7 \le h \le 10$, $-13 \le k \le 14$, $-18 \le l \le 18$ were collected at 293(2) K using Mo Kα radiation with a graphite monochromator ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELX-97 [7]. Manganese atom was located from an E-map and other non-hydrogen atoms were determined with successive difference Fourier syntheses. Final refinement used full-matrix least-squares methods (SHELX-97). Crystallographic data and refinement parameters are listed in table 1. Final atomic positional parameters, and selected bond distances and angles are listed in tables 2 and 3, respectively.

3. Results and discussion

An ORTEP drawing of $[Mn(Pydc)_2(H_2O)_2]$ is shown in figure 1. The central Mn(II) ion lies in a distorted octahedral environment and is coordinated by two Pydc ligands (Mn(1)–N(1), 2.2808(17); Mn(1)–O(1), 2.1982(15) Å) and two oxygen atoms of water molecules (Mn(1)–O(5), 2.1331(15) Å) in a *cis* arrangement. A sketch of the intermolecular hydrogen bonds in the complex is shown in figure 2. Intermolecular hydrogen bonds occur between two oxygen atoms of two different carboxyl groups (O(1AF)–H(1AF)$\cdots$O(3AA), 2.606 Å), uncoordinated carboxylic oxygen atoms and coordinated water molecules (O(5AA)–H(5AA)$\cdots$O(4AD), 2.781 Å). The two types of hydrogen bonds connect the complex molecules into a plane. Coordinated water molecules and carboxylic oxygen atoms in other molecules (O(2AC)–H(2AC)$\cdots$O(5B), 2.629 Å) also generate hydrogen bonds, which give a supramolecular, three-dimensional structure.

Table 1. Crystal data and refinement details for the complex.

Compound	$[Mn(Pydc)_2(H_2O)_2]$
Chemical formula	$C_{14}H_{12}N_2O_{10}Mn$
Formula weight	423.2
Temperature, K	293(2)
Space group	$C2/c$
Unit cell dimensions	$a = 8.607(3)$ Å $b = 12.288(5)$ Å $c = 15.472(7)$ Å $\beta = 100.895(5)^\circ$
Z	4
V, Å^3	1606.8(11)
D_c, Mg m^{-3}	1.749
Absorption coefficient, mm^{-1}	0.884
$F(000)$	860
Scan mode	ω/ϕ
θ range (°)	2.68–25.01
Number of reflections collected	4234
Number of independent reflections	1414
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1414/3/124
Goodness-of-fit on F^2	1.011
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0260$, $wR2 = 0.0735$
R indices (all data)	$R1 = 0.0306$, $wR2 = 0.0757$
Largest diff. peak and hole (e Å^{-3})	0.403 and −0.187

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for the complex.

Atom	x/a	y/b	z/c	U(eq)
Mn(1)	0	1867(1)	2500	30(1)
O(1)	1739(2)	3191(1)	2778(1)	35(1)
O(2)	2392(2)	4625(1)	3644(1)	62(1)
O(3)	−1333(2)	2255(1)	6715(1)	45(1)
O(4)	−1733(2)	738(1)	5922(1)	51(1)
O(5)	1848(2)	684(1)	2693(1)	48(1)
N(1)	211(2)	2269(1)	3957(1)	28(1)
C(1)	1763(2)	3730(2)	3475(1)	33(1)
C(2)	960(2)	3223(1)	4167(1)	27(1)
C(3)	1034(2)	3721(2)	4972(1)	34(1)
C(4)	317(3)	3223(2)	5595(1)	35(1)
C(5)	−430(2)	2234(2)	5392(1)	29(1)
C(6)	−1228(2)	1652(2)	6035(1)	31(1)
C(7)	−455(2)	1781(2)	4568(1)	29(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The IR spectrum of the complex shows characteristic absorptions of a coordinated carboxyl acid. A strong band at 1706 cm^{-1} is assigned to ν(C=O), and that at 1366 cm^{-1} to ν(C–O) vibration. The difference of 340 cm^{-1}, indicating that the carboxyl groups are monodentates, is in accordance with the structure determination [8]. Ring wagging vibrations of pyridine are observed at 691, 754 and 768 cm^{-1}. Two absorption peaks at 3365 and 2958 cm^{-1} are assigned to ν(H–O) of coordinated water molecules. The electronic spectrum of the complex in CH_2Cl_2 solution shows strong absorptions at 228 and 278 nm, assigned to charge transfer transitions of the ligands. The TGA curve indicates that the complex loses two water molecules

Table 3. Selected bond distances (Å) and angles (°) for the complex.

Mn(1)–O(5)	2.1331(15)	O(3)–C(6)	1.304(2)
Mn(1)–O(1)	2.1982(15)	O(4)–C(6)	1.205(2)
Mn(1)–N(1)	2.2808(17)	N(1)–C(7)	1.337(2)
O(1)–C(1)	1.262(2)	N(1)–C(2)	1.347(2)
O(2)–C(1)	1.231(2)		
O(5)#1–Mn(1)–O(5)	94.12(9)	O(1)#1–Mn(1)–N(1)	87.53(5)
O(5)#1–Mn(1)–O(1)	173.69(5)	N(1)–Mn(1)–N(1)#1	154.95(8)
O(5)–Mn(1)–O(1)	90.86(7)	C(1)–O(1)–Mn(1)	122.8(2)
O(1)–Mn(1)–O(1)#1	84.46(8)	C(7)–N(1)–Mn(1)	129.60(12)
O(5)#1–Mn(1)–N(1)	101.78(5)	C(2)–N(1)–Mn(1)	111.89(11)
O(5)–Mn(1)–N(1)	96.68(7)	O(2)–C(1)–O(1)	125.81(17)
O(9)–Cd(1)–N(1)	95.24(6)	O(4)–C(6)–O(3)	124.67(18)
O(1)–Mn(1)–N(1)	73.86(5)	O(3)–C(6)–C(5)	112.08(17)

Symmetry transformation used for #1 is $-x$, y, $-z+1/2$.

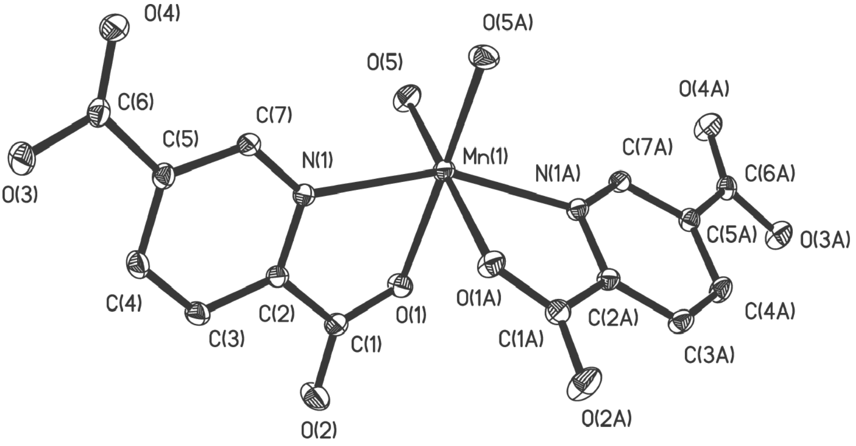

Figure 1. Structure of the complex with the atom labelling scheme (22% probability ellipsoids are shown).

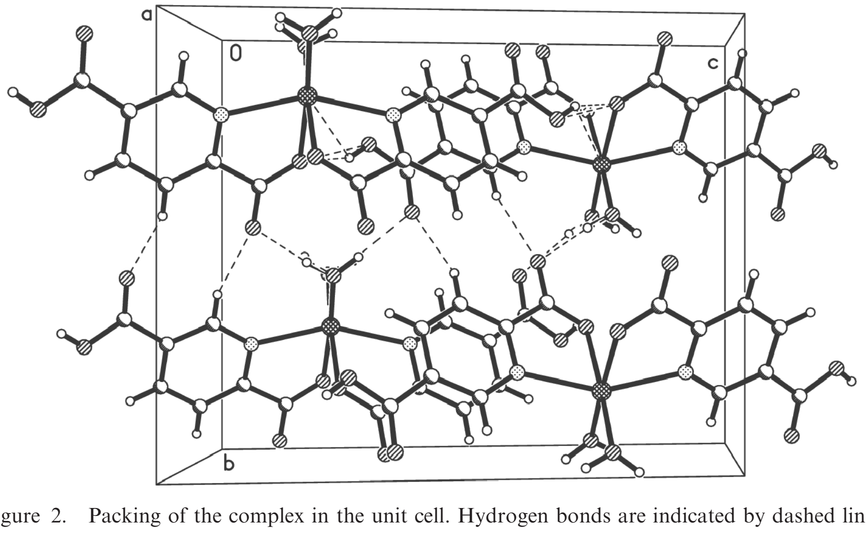

Figure 2. Packing of the complex in the unit cell. Hydrogen bonds are indicated by dashed lines.

at 160°C (calc.: 8.51%; found: 8.71%). Both Pydc groups are lost in three steps at 304 (28.56%), 396 (32.64%) and 465°C (10.72%).

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 225815. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Nankai University Foundation (No. 043182511).

References

[1] O. Kahn. *Molecular Magnetism*, VCH Publishers, New York (1993).

[2] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).

[3] C.M.R. Juan, B. Lee. *Coord. Chem. Rev.*, **183**, 81 (1999).

[4] P. King, R. Clerac, C.E. Anson, C. Coulon, A.K. Powell. *Inorg. Chem.*, **42**, 3492 (2003).

[5] X. Zhang, D. Huang, C. Chen, Q. Liu, D. Liao, L. Li. *Inorg. Chem. Commun.*, **8**, 22 (2005).

[6] Y. Liang, R. Cao, W. Sun, M. Hong, W. Zhang. *Angew. Chem. Int. Ed.*, **18**, 39 (2000).

[7] G.M. Sheldrick. *SHELXS-97, Program for the Refinement of Crystal Structures from Diffraction Data*, University of Göttingen, Germany (1997).

[8] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **33**, 227 (1980).