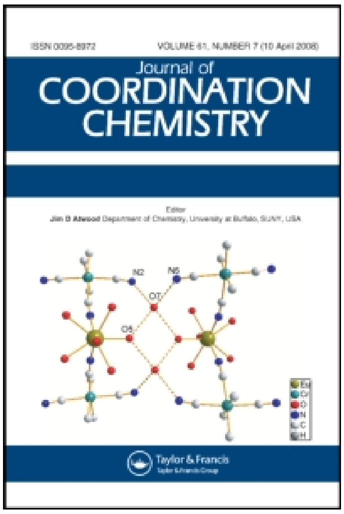
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

SYNTHESIS AND CRYSTAL STRUCTURE OF A SUCCINATOMANGANESE(II) COMPLEX WITH PHENANTHROLINE

Yan Liu[a]; Cungen Zhang[ab]; Duanjun Xu[a]; Yuanzhi Xu[a]; Guanghua Lii[c]
[a] Department of Chemistry, Zhejiang University, Hangzhou, China [b] Department of Applied Chemistry, Jiaotong University, Shanghai, China [c] Chemistry Department, Central University, Taibei, China

To cite this Article Liu, Yan , Zhang, Cungen , Xu, Duanjun , Xu, Yuanzhi and Lii, Guanghua(2001) 'SYNTHESIS AND CRYSTAL STRUCTURE OF A SUCCINATOMANGANESE(II) COMPLEX WITH PHENANTHROLINE', Journal of Coordination Chemistry, 53: 1, 47 — 53

To link to this Article: DOI: 10.1080/00958970108022600

URL: http://dx.doi.org/10.1080/00958970108022600

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 2001, Vol. 53, pp. 47-53
Reprints available directly from the publisher
Photocopying permitted by license only

© 2001 OPA (Overseas Publishers Association) N.V.
Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Downloaded At: 14:24 23 January 2011

SYNTHESIS AND CRYSTAL STRUCTURE OF A SUCCINATOMANGANESE(II) COMPLEX WITH PHENANTHROLINE

YAN LIU[a], CUNGEN ZHANG[a,b], DUANJUN XU[a,*],
YUANZHI XU[a] and GUANGHUA LII[c]

[a]*Department of Chemistry, Zhejiang University, Hangzhou, China;*
[b]*Department of Applied Chemistry, Jiaotong University, Shanghai, China;*
[c]*Chemistry Department, Central University, Taibei, China*

(Received 7 March 2000)

The title complex $[Mn(C_4H_4O_4)(phen)(H_2O)_3]\cdot 2H_2O$ has been prepared and its crystal structure determined by X-ray diffraction methods. The Mn(II) atom has octahedron coordination formed by four oxygen and two nitrogen atoms. The coordination mode of the succinate dianion in the complex is remarkably different from those reported previously. One carboxyl group of the succinate dianion coordinates to the Mn(II) atom as a monodentate and the other carboxyl group is free. The crystal structure consists of the complex and crystalline water molecules. All the oxygen atoms in the structure take part in an H-bonding network and assemble to form a hydrophilic layer, while phenanthroline ligands between neighboring hydrophilic layers to form a hydrophobic layer. Tight stacking interactions of phenanthroline rings are observed in the hydrophobic layer as evidenced by the short distance (3.312 Å) between neighbouring parallel ring planes.

Keywords: Manganese(II); Crystal structure; Succinate; Phenanthroline; Aromatic stacking

INTRODUCTION

Recently, intense efforts have concentrated on elucidating the nature of the biological unit responsible for water oxidation in the photosynthetic apparatus of green plants [1]. The process of water splitting is generally believed to occur at a manganese cluster located in the reaction centre of photosystem II [2]. In order to mimic the manganese cluster, a series of

---

[*] Corresponding author.

bridging complexes of manganese has been synthesized in our laboratory and several crystal structure have been reported [3, 4]. Owing to the possible coordination capability of two carboxyl groups, some dicarboxylic acids, such as oxalic acid, fumaric acid and phthalic acid have been used as the bridging ligand to synthesize multinuclear manganese complexes. In the present work we used succinate acid to try to prepare a binuclear manganese complex, but X-ray analysis of the product revealed that the succinate dianion does not act as a bridging ligand in the complex. We present here the synthesis and crystal structure of the title complex to compare with other complexes bridged by dicarboxylic acids.

EXPERIMENTAL

Synthesis

Solid $MnCO_3$ (1.15 g, 10 mmol) was added to an aqueous solution (25 cm^3) containing succinic acid (1.18 g, 10 mmol) with stirring and heating until no more CO_2 was released. An ethanol solution (10 cm^3) containing 1,10-phenanthroline (1.98 g, 10 mmol) was slowly added to the above solution with continuous stirring and refluxing for 30 min. After the solution changed colour to yellow, the reaction mixture was cooled to room temperature and filtered. Yellow single crystals were obtained from the solution by slow evaporization of the solvent.

C, N and H were analyzed using a Carlo-Erba 1160 instrument. *Anal.* Calc. for $C_{16}H_{22}N_2O_9Mn$(%): C, 43.54; N, 6.35; H, 5.03; Found: C, 43.42; N, 6.30; H, 4.99.

Downloaded At: 14:24 23 January 2011

Crystal Structure Determination

A prismatic crystal of the title complex with approximate dimensions 0.23 × 0.20 × 0.40 mm was mounted on a glass fibre. X-ray diffraction intensity data were collected on a Rigaku AFC7R diffractometer up to a 2θ value of 50.0° with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan technique. A total of 4224 independent reflections was collected, of which 3534 reflections were considered as observed [$I > 3\sigma(I)$] and used for the structure determination. Usual Lp and empirical adsorption corrections were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares

Downloaded At: 14:24 23 January 2011

procedures using the SHELX program package [5]. H atoms were located in a difference Fourier map and fixed during structure refinement. Anisotropic refinement including all the non-H atoms converged to agreement factors $R = 0.046$ and $R_w = 0.054$ where $w = 1/[\sigma^2(F) + 0.004458\ F^2]$. Atomic scattering factors were taken from International Tables for X-ray Crystallography [6]. Final fractional atomic coordinates and equivalent isotropic thermal parameters for all the non-H atoms are listed in Table I.

Crystal Data

$C_{16}H_{22}N_2O_9Mn$, $Mr = 441.3$, triclinic, $P\bar{1}$, $a = 7.5871(4)$, $b = 9.3240(6)$, $c = 13.9178(9)$ Å, $\alpha = 85.648(5)$, $\beta = 74.547(5)$, $\gamma = 77.134(5)°$, $V = 925.01(10)$ Å^3, $Z = 2$, $F(000) = 458.00$, $D_c = 1.58\ \mathrm{g \cdot cm^{-3}}$, $\mu(\mathrm{Mo}K\alpha) = 0.77\ \mathrm{mm^{-1}}$, $S = 1.1755$, $(\Delta\rho)_{\max} = 0.74$, $(\Delta\rho)_{\min} = -0.34\ \mathrm{e \cdot Å^{-3}}$.

TABLE I Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
Mn	0.08539(5)	0.41654(4)	0.31807(3)	0.0206(1)
O(1)	−0.1572(3)	0.5844(2)	0.3817(1)	0.0287(6)
O(2)	−0.3851(3)	0.5258(2)	0.3307(2)	0.0336(7)
O(3)	−0.7898(3)	0.9413(2)	0.6101(2)	0.0337(7)
O(4)	−0.7314(3)	1.0065(2)	0.4505(2)	0.0362(7)
O(5)	−0.1073(3)	0.2906(2)	0.2818(1)	0.0274(6)
O(6)	0.1115(3)	0.2893(2)	0.4502(2)	0.0348(7)
O(7)	0.2391(3)	0.5697(2)	0.3495(2)	0.0365(8)
O(8)	1.1238(3)	−0.1276(3)	0.3219(2)	0.0409(8)
O(9)	1.0802(5)	0.0392(4)	0.1400(2)	0.0612(11)
N(1)	0.3322(3)	0.2724(3)	0.2138(2)	0.0257(7)
N(2)	0.1129(3)	0.5232(3)	0.1621(2)	0.0248(7)
C(1)	−0.3190(3)	0.6143(3)	0.3670(2)	0.0214(7)
C(2)	−0.4381(4)	0.7667(3)	0.3923(2)	0.0257(8)
C(3)	−0.5790(4)	0.7673(3)	0.4948(2)	0.0281(8)
C(4)	−0.7097(4)	0.9168(3)	0.5198(2)	0.0236(8)
C(5)	0.4465(4)	0.1531(3)	0.2390(2)	0.0338(9)
C(6)	0.5851(5)	0.0620(4)	0.1687(3)	0.0405(11)
C(7)	0.6031(5)	0.0947(4)	0.0685(3)	0.0394(10)
C(8)	0.4881(4)	0.2195(3)	0.0394(2)	0.0311(9)
C(9)	0.3531(4)	0.3076(3)	0.1149(2)	0.0238(8)
C(10)	0.0197(4)	0.6525(3)	0.1371(2)	0.0345(10)
C(11)	0.0411(5)	0.7060(4)	0.0400(3)	0.0380(11)
C(12)	0.1622(5)	0.6224(4)	−0.0357(2)	0.0381(11)
C(13)	0.2694(4)	0.4845(3)	−0.0140(2)	0.0301(9)
C(14)	0.2405(4)	0.4416(3)	0.0880(2)	0.0238(8)
C(15)	0.5070(5)	0.2641(4)	−0.0631(2)	0.0380(11)
C(16)	0.4027(5)	0.3920(4)	−0.0877(2)	0.0370(11)

Downloaded At: 14:24 23 January 2011

RESULTS AND DISCUSSION

The molecular structure of the title complex is illustrated in Figure 1 with the atom numbering scheme. Selected bond distances and angles, together with the atomic separations involved in H-bonds, are listed in Table II. The Mn(II) atom in the complex exhibits slightly distorted octahedral coordination geometry. One phenanthroline ligand chelates and three water molecules coordinate to an Mn(II) atom with normal bond distances and angles. A carboxyl of the succinate dianion coordinates to the Mn(II) atom as a monodentate, another O atom [O(2)] of the same carboxyl group H-bonding to a coordinated water molecule of the neighbouring complex as shown in Table II.

Several structures of succinato metal complexes have been reported. The succinate dianion usually bridges neighboring metal ions to form a multinuclear complex with a variety of bridging modes of carboxyl groups. For example, the succinate dianion can bridge two ions as a bis-monodentate to form a binuclear complex [7], both carboxyl groups of a succinate dianion can *u*-bridge four metal ions to form a tetranuclear complex [8], and succinate can bridge manganese atoms to form an infinite complex chain [9], *etc.* However, the coordination mode of the succinate dianion in the present complex is remarkably different from those previously reported. The succinate dianion does not act as a bridging ligand, only one carboxyl group coordinating to the Mn(II) atom as a monodentate and the

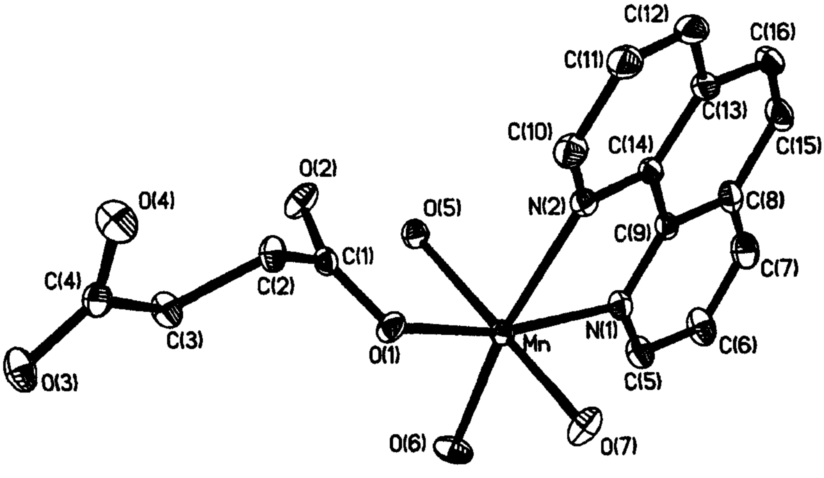


FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

TABLE II Selected bond distances (Å), angles (°) and atomic separations involved in H-bonds (Å)

Mn-O(1)	2.163(2)	Mn-O(5)	2.240(2)
Mn-O(6)	2.141(2)	Mn-O(7)	2.167(3)
Mn-N(1)	2.269(2)	Mn-N(2)	2.296(2)
O(1)-C(1)	1.265(3)	O(2)-C(1)	1.253(4)
O(3)-C(4)	1.256(3)	O(4)-C(4)	1.248(3)
N(1)-C(5)	1.336(4)	N(1)-C(9)	1.366(3)
N(2)-C(10)	1.327(4)	N(2)-C(14)	1.356(3)
C(1)-C(2)	1.515(3)	C(2)-C(3)	1.537(4)
C(3)-C(4)	1.524(3)		
O(1)-Mn-O(5)	88.3(1)	O(1)-Mn-O(6)	99.4(1)
O(1)-Mn-O(7)	83.8(1)	O(1)-Mn-N(1)	165.0(1)
O(1)-Mn-N(2)	91.9(1)	O(5)-Mn-O(6)	94.2(1)
O(5)-Mn-O(7)	170.8(1)	O(5)-Mn-N(1)	89.8(1)
O(5)-Mn-N(2)	87.6(1)	O(6)-Mn-O(7)	91.9(1)
O(6)-Mn-N(1)	95.6(1)	O(6)-Mn-N(2)	168.6(1)
O(7)-Mn-N(1)	96.5(1)	O(7)-Mn-N(2)	87.8(1)
N(1)-Mn-N(2)	73.2(1)	Mn-O(1)-C(1)	130.5(2)
Mn-N(1)-C(5)	126.7(2)	Mn-N(1)-C(9)	114.8(2)
Mn-N(2)-C(10)	127.8(2)	Mn-N(2)-C(14)	114.5(2)
C(1)-C(2)-C(3)	111.4(2)	C(2)-C(3)-C(4)	112.8(2)
O(1)-O(6)[b]	2.831(3)	O(2)-O(7)[c]	2.732(3)
O(3)-O(5)[d]	2.679(3)	O(3)-O(8)[b]	2.710(3)
O(4)-O(6)[e]	2.641(3)	O(4)-O(8)[f]	2.823(3)
O(5)-O(9)[c]	3.023(3)	O(7)-O(8)[e]	2.791(3)
O(8)-O(9)	2.926(3)		

Symmetry codes: [b] $-x, 1-y, 1-z$.
[c] $-1+x, y, z$.
[d] $-1-x, 1-y, 1-z$.
[e] $-1+x, 1+y, z$.
[f] $-2+x, 1+y, z$.

other carboxyl group free from coordination. All the uncoordinated O atoms of the succinate dianion link to water molecules through H-bonds as indicated in Table II.

The carbon skeleton of the succinate possesses good planarity, the torsion angle C(1)-C(2)-C(3)-C(4) being 176.3°. The carboxyl groups are not coplanar with the carbon skeleton of the succinate, the dihedral angle between the succinate plane and coordination plane defined by N(1), N(2), O(1) and O(6) atoms is 24.0°.

The crystal structure consists of complex and crystalline water molecules. An extensive H-bonding network exists in the crystal structure as verified by the atomic separations listed in Table II. It is convenient for structural description to look on the title complex molecule as a detergent molecule, *i.e.*, to look on the complex as being constituted of a hydrophobic part (the phenanthroline ligand) and a hydrophilic part (succinate anion and water molecules). All the oxygen atoms in the structure take part in the H-bonding network and assemble to form the hydrophilic layer, and phenanthroline

Downloaded At: 14:24 23 January 2011

ligands lie between neighboring hydrophilic layers to form the hydrophobic layer. The phenanthroline ligands located between the hydrophilic layer are something like the detergent micelles distributed in an aqueous solution.

Moreover, a tight stack of phenanthroline rings is observed in the hydrophobic layer. The overlap stack fashion of the neighboring phenanthroline rings related by a crystallographic inversion centre located at $1-x$, $1-y$, $-z$ is illustrated in Figure 2, viewed normal to the phenanthroline ring plane. Mean plane equations and atomic deviations from the mean planes are presented in Table III. The equations in Table III indicate that the phenanthroline rings are parallel to each other and the distance between neighbouring parallel planes is 3.312 Å, about 0.3 Å

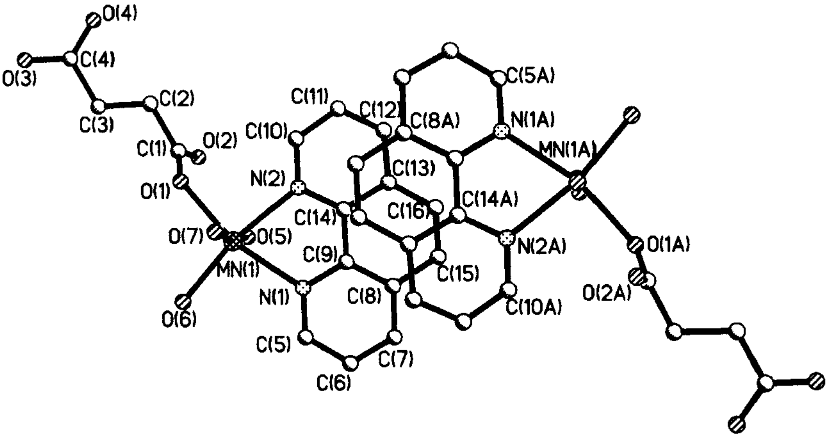


FIGURE 2 The overlap stack of the phenanthroline rings viewed normal to the ring plane; the molecule with suffix A is related to the original one by an inversion centre located on $1-x$, $1-y$, $-z$.

TABLE III Mean plane equations and atomic deviations (Å) from the mean plane, where X, Y and Z are the coordinates in the orthogonal unit cell in Å

(1)	Equations of the mean planes
	Mean plane **1** defined by N(1), N(2), C(5) to C(16) atoms: $0.6549X+0.6600Y+0.2844Z=4.7937$
	Mean plane **2** defined by N(1A), N(2A), C(5A) to C(16A) atoms: $0.6549X+0.6600Y+0.2844Z=8.1061$
(2)	Atomic deviation from the mean plane **2**
	N(1) 3.354; N(2) 3.408; C(5) 3.260; C(6) 3.205; C(7) 3.277; C(8) 3.357; C(9) 3.385; C(10) 3.299; C(11) 3.204; C(12) 3.239; C(13) 3.323; C(14) 3.381; C(15) 3.355; C(16) 3.327.

Downloaded At: 14:24 23 January 2011

shorter than the van der Waals thickness of the phenyl ring [10]. The tight stack of aromatic rings in the crystal structure is also evidenced by very short intermolecular distances of 3.298(3) Å (C(8)–C(12A)) and 3.406(3) Å (C(16)–C(14A)).

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (No. 29973036).

Downloaded At: 14:24 23 January 2011

References

[1] S. Bruckner, L. Menabue and M. Saladini, *Inorg. Chim. Acta* **24**, 185 (1993).
[2] J. B. Vincent and G. Christou, *Adv. Inorg. Chem.* **28**, 197 (1989).
[3] Y. Yin, W. Chen, D. Xu, W. Niu and Y. Xu, *J. Coord. Chem.* **47**, 99 (1999).
[4] D. Cheng, Y. Liu, D. Xu and Y. Xu, *J. Coord. Chem.* **48**, 495 (1999).
[5] G. M. Sheldrick, *SHELX93, Program for Crystal Structure Refinement* (University of Göttingen, Germany, 1993).
[6] *International Tables for X-ray Crystallography* (Kynoch Press: Birmingham, England; Present distributor: Kluwer Academic Publishers, Dordrecht, 1974), Vol. IV, p. 72.
[7] W. N. Seik, *Acta Crystallogr.* **C54**, 745 (1998).
[8] V. G. Kumar Das, *Acta Crystallogr.* **C49**, 754 (1993).
[9] M. P. Gupta, R. D. Sahu, Raja Ram and P. R. Maulik, *Z. Krist.* **163**, 155 (1983).
[10] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (John Wiley & Sons, New York, 1972), p. 155.