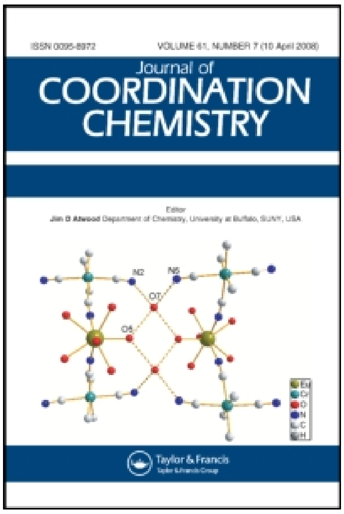

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Crystal Structure of a Polymeric Benzimidazole Complex of Mn(II) Bridged by Succinate

Zhuo Chen[a]; Duan-Jun Xu[a]; Zhen-Yu Li[a]; Jing-Yun Wu[b]; Michael Y. Chiang[b]
[a] Department of Chemistry, Zhejiang University, Hangzhou, China [b] Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, China

To cite this Article Chen, Zhuo , Xu, Duan-Jun , Li, Zhen-Yu , Wu, Jing-Yun and Chiang, Michael Y.(2003) 'Synthesis and Crystal Structure of a Polymeric Benzimidazole Complex of Mn(II) Bridged by Succinate', Journal of Coordination Chemistry, 56: 4, 253 — 259

To link to this Article: DOI: 10.1080/0095897031000068978

URL: http://dx.doi.org/10.1080/0095897031000068978

J. Coord. Chem., 2003, Vol. 56, No. 4, pp. 253–259

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND CRYSTAL STRUCTURE OF A POLYMERIC BENZIMIDAZOLE COMPLEX OF Mn(II) BRIDGED BY SUCCINATE

ZHUO CHEN[a], DUAN-JUN XU[a,*], ZHEN-YU LI[a],
JING-YUN WU[b] and MICHAEL Y. CHIANG[b]

[a]*Department of Chemistry, Zhejiang University, Hangzhou 310027, China;*
[b]*Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, China*

(Received 24 June 2002; In final form 10 October 2002)

The title complex has been prepared and its crystal structure determined by X-ray diffraction methods. The Mn (II) complex is seven coordinate with two benzimidazole (bimid)ligands in axial positions and two succinate and one bimid ligands in the equatorial plane. The succinate bridges Mn (II) atoms to form polymeric chains, linked by intermolecular H-bonding. Free bimid molecules occur in the crystal structure; they link Mn (II) complexes with H-bonds involving N atoms. Aromatic stacking between bimid rings is observed, resulting in a *gauche* confirmation of succinate in the structure. The IR spectrum is assigned based on the crystal structure. The difference of 139 cm^{-1} between symmetric and asymmetric stretching vibrations of carboxyl groups is in line with seven coordination at the Mn (II) atom.

Keywords: Mn (II) polymeric complex; crystal structure; succinate; benzimidazole; aromatic stacking

INTRODUCTION

As model compounds for the active centre of photosystem II [1], multinuclear manganese complexes have attracted much interest. A series of manganese complexes bridged dicarboxylates has been synthesized in our laboratory in past years [2–4]. Their structures show versatile coordination modes of the carboxy1 group [5,6] and suggest the existence of electrostatic interaction between manganese II (Mn (II)) and ligands [7,8], considered as an important factor for oxygen release during photosynthesis [9]. As part of a continuing project, we have prepared a new Mn (II) complex bridged by succinate. X-ray diffraction analysis shows evidence of electrostatic interactions in the polymeric complex.

---

*Corresponding author. E-mail: xudj@mail.hz.zj.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000068978

TABLE I Crystallographic data for $C_{25}H_{22}MnN_5O_4 \cdot C_7H_6H_2$

Crystal size (mm)	0.20 × 0.12 × 0.10
Chemical formula	$C_{32}H28MnN_8O_4$
Formula weight	643.56
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	15.780 (3)
b(Å)	10.338 (2)
c(Å)	19.887 (4)
β(°)	112.79 (3)
V(Å^3)	2991.0 (10)
Z	4
F(000)	1332
Dc(g/cm^3)	1.429
θ range (°)	2.12–24.50
$T(K)$	298
Unique reflections	3909
Reflection with $I > 2\sigma(I)$	1563
R	0.0494
Goodness-of-fit	1.001
$(\Delta\rho)_{\max}$ and $(\Delta\rho)_{\min}$ (e Å^{-3})	0.338, −0.548

EXPERIMENTAL

Synthesis

Some 5 mL of an ethanol solution containing 0.118 g (1 mmol) of benzimidazole (bimid) was mixed with 5 mL of an ethanol solution containing 0.245 g (1 mmol) of Mn (II) diacetate tetrahydrate. After the solution was refluxed for 20 min, an aqueous solution containing 0.118 g (1 mmol) of succinic acid and 0.080 g (2 mmol) of NaOH was added. The mixture was refluxed for 1 h and filtered. The filtrate was kept at room temperature for 1 week to obtain colorless prisms of the title complex.

Physical Measurements

C, N and H contents were analyzed using a Carlo-Erba 1106 instrument. *Anal.* Calc. for $C_{32}H_{28}MnN_8O_4$: C, 59.67; H, 4.39; N, 17.40 Found: C, 59.44; H, 4. 31; N, 17.85. Infrared spectra were recorded using KBr discs with a Nicolet 5DX FTIR spectrophotometer (4000–400 cm^{-1}). The density of single crystals (1.42 g/cm^3) was measured by flotation with a mixture of carbon tetrachloride and cyclohexane.

Diffraction data for a single crystal of the complex were collected on a Rigaku AFC-7S diffractometer. The crystal structure was anisotropically refined using SHELXL-97 [10]. Data collection and structure refinement conditions are summarized in Table I.

RESULTS AND DISCUSSION

Crystal Structure

Final fractional atomic coordinates and equivalent isotropic thermal parameters for nonH atoms are listed in Table II. Selected bond distances and angles are listed in Table III. The molecular structure is illustrated in Fig. 1. In the title complex each Mn (II) atom is coordinated by two succinate dianions and three bimid molecules.

TABLE II Atomic fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameter ($\times 10^3$) of nonH atoms

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)
Mn	6179 (1)	8334 (1)	8598 (1)	43 (1)
0 (1)	5859 (3)	7518 (5)	7403 (3)	50 (1)
0 (2)	7135 (3)	6812 (6)	8250 (3)	60 (2)
0 (3)	4566 (4)	4750 (5)	6010 (3)	66 (2)
0 (4)	5584 (4)	4243 (5)	7091 (3)	71 (2)
N (11)	5424 (4)	6624 (6)	8784 (3)	43 (2)
N (12)	4700 (4)	4712 (6)	8527 (3)	52 (2)
N (21)	7288 (4)	8053 (6)	9695 (3)	50 (2)
N (22)	8369 (4)	6991 (6)	10591 (3)	54 (2)
N (31)	6756 (4)	10114 (7)	8235 (3)	48 (2)
N (32)	6590 (4)	12083 (6)	7742 (3)	52 (2)
N (41)	9679 (5)	4961 (7)	10955 (4)	59 (2)
N (42)	10986 (4)	3871 (7)	11216 (4)	59 (2)
C (1)	6580 (6)	6891 (8)	7588 (4)	50 (2)
C (2)	6828 (5)	6133 (8)	7035 (4)	61 (3)
C (3)	6010 (5)	5739 (8)	6354 (4)	58 (2)
C (4)	5358 (6)	4834 (8)	6514 (5)	48 (2)
C (11)	5318 (5)	5529 (8)	8430 (4)	47 (2)
C (12)	4826 (5)	6511 (8)	9148 (4)	39 (2)
C (13)	4373 (5)	5350 (8)	8986 (4)	47 (2)
C (14)	3731 (6)	4979 (10)	9272 (5)	71 (3)
C (15)	3586 (6)	5856 (11)	9729 (6)	75 (3)
C (16)	4034 (7)	7036 (9)	9898 (5)	72 (3)
C (17)	4677 (6)	7389 (8)	9619 (4)	54 (2)
C (21)	7696 (5)	6955 (8)	9919 (4)	52 (2)
C (22)	8402 (5)	8235 (9)	10820 (4)	48 (2)
C (23)	7724 (5)	8920 (8)	10265 (4)	42 (2)
C (24)	7607 (6)	10213 (9)	10324 (5)	59 (2)
C (25)	8177 (7)	10848 (10)	10936 (6)	74 (3)
C (26)	8851 (7)	10176 (11)	11490 (5)	77 (3)
C (27)	8989 (5)	8895 (11)	11446 (5)	73 (3)
C (31)	6306 (6)	11231 (8)	8111 (4)	53 (2)
C (32)	7388 (5)	10274 (8)	7910 (4)	45 (2)
C (33)	7295 (5)	11495 (9)	7605 (4)	47 (2)
C (34)	7807 (6)	11928 (9)	7227 (4)	64 (3)
C (35)	8446 (6)	11115 (11)	7163 (5)	75 (3)
C (36)	8569 (6)	9888 (11)	7476 (5)	73 (3)
C (37)	8060 (6)	9451 (9)	7859 (5)	68 (3)
C (41)	10573 (7)	4898 (9)	11372 (5)	66 (3)
C (42)	9526 (5)	3896 (8)	10500 (5)	53 (2)
C (43)	10331 (5)	3198 (9)	10663 (4)	50 (2)
C (44)	10379 (6)	2092 (8)	10290 (5)	60 (2)
C (45)	9567 (7)	1726 (9)	9724 (5)	74 (3)
C (46)	8746 (6)	2414 (10)	9552 (5)	75 (3)
C (47)	8727 (5)	3477 (10)	9932 (5)	68 (3)

N11–bimid (the benzimidazole molecule involving the N (11) atom) and N31–bimid ligands occupy axial sites with a normal bond angle of 170.9 (2)°. Another bimid ligand and two succinate dianions coordinate to the Mn (II) in the equatorial plane. Both carboxyl groups are approximately coplanar with the Mn (II) and N (21) atoms, the maximum atomic deviation being 0.216 (5) Å for O (4A).

As shown in Fig. 1, the C1 carboxyl group chelates to the Mn (II) atom with longer Mn–O distances, as expected. The O (2)–Mn–N (21) angle of 81.7° and the O (1)–Mn–O (2) angle of 53.7° imply that the overlap of atomic orbitals between Mn and O (1) bond is less than that between Mn and O(2). However, the Mn–O(1) bond distance

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

Mn–O(1)	2.386 (5)	Mn–O(2)	2.457 (5)
Mn–O(3A)	2.200 (6)	Mn–O(4A)	2.742 (5)
Mn–N(11)	2.241 (6)	Mn–N(21)	2.224 (6)
Mn–N(31)	2.290 (7)	O(1)–C(1)	1.235 (9)
O(2)–C(1)	1.271 (8)	O(3)–C(4)	1.267 (9)
O(4)–C(4)	1.225 (9)	N(11)–C(11)	1.309 (9)
N(11)–C(12)	1.398 (8)	N(12)–C(11)	1.358 (9)
N(12)–C(13)	1.377 (9)	N(21)–C(21)	1.297 (9)
N(21)–C(23)	1.399 (9)	N(22)–C(21)	1.346 (9)
N(22)–C(22)	1.358 (9)	N(31)–C(31)	1.328 (9)
N(31)–C(32)	1.393 (9)	N(32)–C(31)	1.331 (9)
N(32)–C(33)	1.384 (9)	N(41)–C(41)	1.334 (10)
N(41)–C(42)	1.385 (10)	C(1)–C(2)	1.519 (10)
C(2)–C(3)	1.520 (10)	C(3)–C(4)	1.513 (10)
N(12)···C(1A)	2.844 (8)	N(22)···N(41)	2.838 (9)
N(132)···C(4B)	2.755 (8)	N(42)···O(2C)	2.817 (9)
O(1)–Mn–O(2)	53.8 (2)	O(1)–Mn–O(4A)	80.9 (2)
O(1)–Mn–N(11)	88.0 (2)	O(1)–Mn–N(31)	85.8 (2)
O(2)–Mn–O(3A)	174.9 (2)	O(2)–Mn–N(11)	88.0 (2)
O(2)–Mn–N(21)	81.8 (2)	O(2)–Mn–N(31)	93.6 (2)
O(3A)–Mn–O(4A)	51.2 (2)	O(3A)–Mn–N(11)	94.3 (2)
O(3A)–Mn–N(21)	93.7 (2)	O(3A)–Mn–N(31)	84.4 (2)
04A)–Mn–N(11)	81.5 (2)	O(4A)–Mn–N(31)	91.1 (2)
N(11)–Mn–N(21)	90.1 (2)	N(11)–Mn–N(31)	170.9 (2)
N(21)–Mn–N(31)	99.0 (2)		
N(12)–H(12)–O(1A)	160.6	O(1)–H(22)–N(41)	151.9
N(32)–H(32)–O(4B)	161.2	N(42)–H(42)–O(2C)	171.1

Symmetry code: (A) 1-x, $0.5+y$, $1.5-z$; (B) x, $1+y$, z; (C) $2-x$, $1-y$, $2-z$.

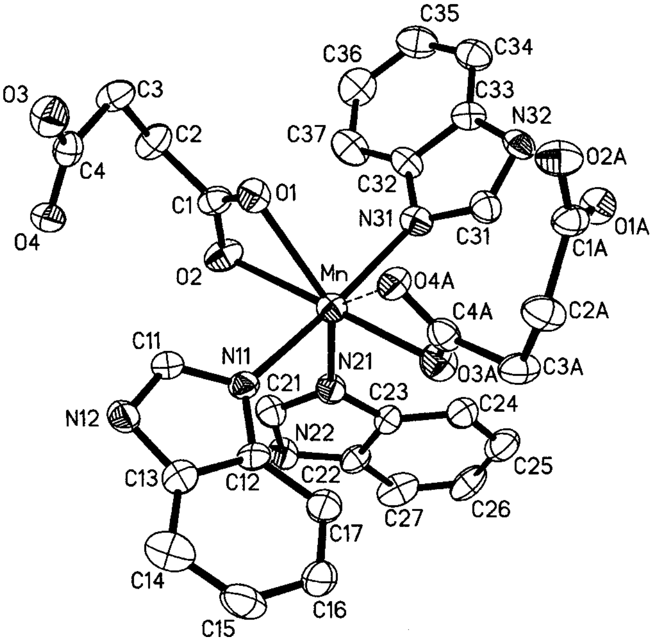

FIGURE 1 The molecular structure of the title complex showing 30% probability displacement ellipsoids. H atoms are omitted for clarity. Dashed lines show the semi-coordination bond. Symmetry code: (A) $1-x$, $0.5+y$, $1.5-z$.

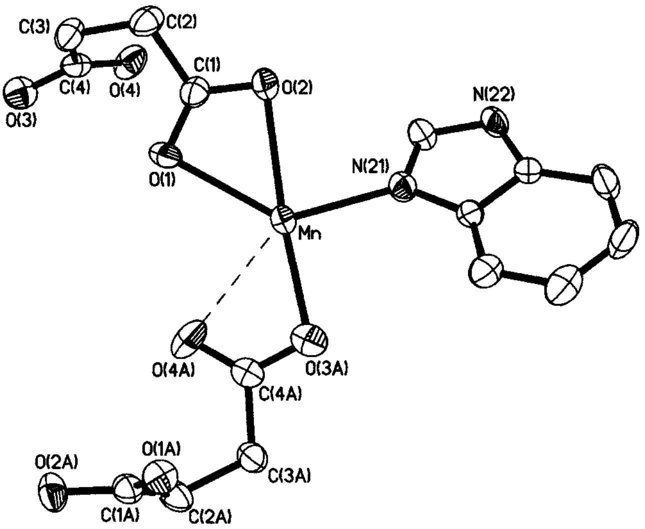

FIGURE 2 Coordination geometry in the equatorial plane around the Mn (II) atom. Dashed line shows the semi-coordination bond. Symmetry code: (A) $1-x$, $0.5+y$, $1.5-z$.

of 2.386 (5) Å is significantly shorter than the Mn–O (2) bond distance of 2.457 (5) Å. This is considered as evidence for the existence of electrostatic interaction between Mn (II) and the ligand.

The position of the O (4A) atom is notable. O (4A) is located in such a position that the C(1) and C(4A) carboxyl groups are approximately axially symmetric about the Mn–N (21) axis as shown in Fig. 2. O (4A) atom may thus take part in coordination to Mn (II). As the Mn–O (4A) distance of 2.752 Å is rather longer than the Mn–O (1) distance of 2.385 Å, it is better to describe the chemical interaction between O (4A) and Mn (II) atoms as involving semicoordination. The small deviation of 0.261Å of O (4A) from the equatorial coordination plane supports this conclusion. Therefore the geometry of the title complex can be described as $(5+2)$ coordinate rather than six coordinate with a distorted octahedron environment. The five coordination in the equatorial plane clearly suggests electrostatic interaction in the complex.

In most similar complexes, the carbon skeleton of succinate displays a *trans*-configuration and all carbon atoms possess good planarity [11,12]. In the complex the C(1)–C(2)–C(3)–C(4) torsion angle of 62.7° shows a *gauche* conformation of the succinate dianion. In addition, aromatic stacking (see Fig. 3) is observed between bimid molecules. This stacking is usual arrangement for aromatic rings [13,14], and we consider that the *gauche* conformation of the succinate results from it.

With chelation of both terminal carboxyl groups, succinate bridges Mn (II) atoms to form polymeric chains along the *b* axis. The chains link by intermolecular H-bonding between coordinated bimid and succinate to construct a three dimensional supramolecular structure. Free bimid molecules occur in the crystal structure, and these also link to the complex chains with H-bonds. H-bonding parameters are given in Table III.

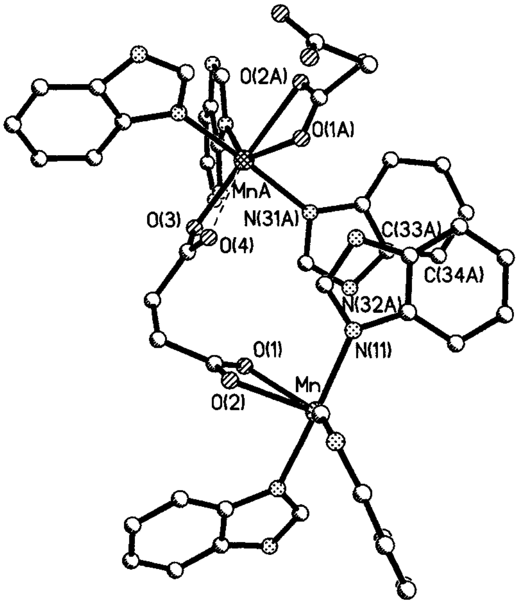

FIGURE 3 Aromatic stacking viewed along the normal to the N11–bimid mean plane. The dihedral angle between N11–bimid and N31A–bimid mean planes is 7.1°.

Infrared Spectra

Stretching is observed at 1432 cm^{-1} (ν_s (COO)) and 1529 cm^{-1} (ν_{as} (COO)) for the C(1) carboxyl group, and at 1432 cm^{-1} (ν_s (COO)) and 1571 cm^{-1} (ν_{as} (COO)) for the C(4) carboxyl group. The $\Delta\nu$ (ν_{as} (COO)$-\nu_s$ (COO)) value (97 cm^{-1}) for the C1 carboxyl group is in agreement with those found in other complexes with a chelating carboxyl group [15]. The $\Delta\nu$ value (139 cm^{-1}) for the C(4) carboxyl group is slightly smaller than that found for the chelating coordination mode and is close to (140–160 cm^{-1}), that reported for complexes with a bridging carboxyl group [16–18]. In carboxyl complexes with monodentate coordination mode, the $\Delta\nu$ value is often found in the range of 210–250 cm^{-1} [19,20]. In the present complex, great difference in $\Delta\nu$ values is consistent with the strucural study.

Acknowledgments

The project was supported by the National Natural Science Foundation of China (29973036).

Supplementary Material

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

References

[1] J.B. Vincer and G. Christou, *Ave. Inorg. Chem.* **28**, 197 (1989).
[2] D. Xu, A. Xie, Y. Xu, K. Nishikawa and N. Yasuoka, *J. Coord. Chem.* **43**, 115 (1998).

[3] D. Cheng, Y. Liu, D. Xu and Y. Xu, *J. Coord. Chem.* **48**, 495 (1999).
[4] Y. Liu and D. Xu, *J. Coord. Chem.* **56**, 1 (2003).
[5] P. Charpin, G. Chevrier, M. Lance, D. Vigner and F. Tinti, *Acta Crystallogr.* **C43**, 216 (1987).
[6] Y. Liu, C. Zhang, D. Xu, Y. Xu and G. Lii, *J. Coord. Chem.* **53**, 47 (2001).
[7] J. Nie, L. Liu, Y. Luo and D. Xu, *J. Coord. Chem.* **53**, 365 (2001).
[8] M. Hu, D. Xu and D. Cheng, *J. Coord. Chem.* **55**, 11 (2002).
[9] J. Nie, PhD dissertation, Zhejiang University, China (2002).
[10] G.M. Sheldrick, *SHELXL-97. Program for Crystal Structure Refinement* (University of Göttingen, Germany, 1997).
[11] E.A.H. Griffith, N.G. Charler and E.L. Amma, *Acta Crystallogr.* **B38**, 262 (1982).
[12] Y. Liu, D. Xu, J. Nie, J. Wu and M.Y. Chiang, *J. Coord. Chem.* **56**, 3 (2003).
[13] Z. Li, D. Xu, W. Shi, D. Chen, J. Wu and M.Y. Chiang, *Chin. J. Chem.* **20**, 309 (2002).
[14] Z. Li, D. Xu, J. Nie, Z. Wu, J. Wu and M.Y. Chiang, *J. Coord. Chem.* **55**, 12 (2002).
[15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (John Wiley and Sons, New York, 1978) p. 235.
[16] Y. Yin, W. Chen, D. Xu, W. Niu and Y. Xu, *J. Coord. Chem.* **47**, 99 (1999).
[17] Y. Liu, D. Xu and J. Liu, *J. Coord. Chem.* **47**, 99 (2001).
[18] D. Xu, A. Xie, Y. Xu, K. Nishikawa and N. Yasuoka, *J. Coord. Chem.* **43**, 237 (1998).
[19] D. Cheng, C. Feng, M. Hu, Y. Zheng, D. Xu and Y. Xu, *J. Coord. Chem.* **52**, 245 (2001).
[20] M. Hu, D. Cheng, J. Liu and D. Xu, *J. Coord. Chem.* **53**, 7 (2001).