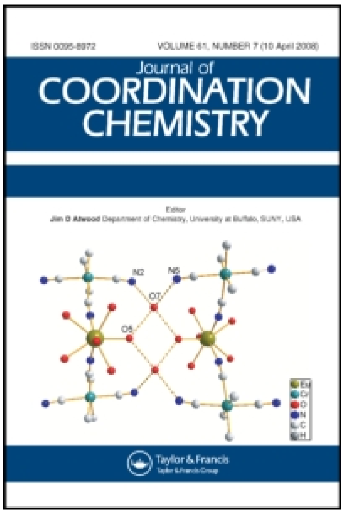

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Preparation, crystal structure and properties of novel Mn(III) complex with 1,3,5-benzenetriacetic acid

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Preparation, crystal structure and properties of novel Mn(III) complex with 1,3,5-benzenetriacetic acid

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The reaction of benzene-1,3,5-triacetic acid (H_3bta) with [Mn(salen)]$ClO_4 \cdot 2H_2O$ yields [Mn(salen)H_2bta]$\cdot 0.5H_2O$ (**1**) [H_2salen = N,N′-bis(salicylideneaminato)ethylene]. Complex **1** was characterized by X-ray crystal structure determination, elemental analysis, FT-IR and ES-MS spectroscopic methods. The X-ray crystallographic study reveals that the complex has a one-dimensional chain structure, and self-organizes to a three-dimensional network by O–H···O hydrogen bonds between the oxygen atom of carboxyl groups without deprotonation and the carbonyl oxygen atom of the bta ligand, and by C–H···O hydrogen bonds between the carbon atom of the salen group and the carboxyl oxygen atom of the bta ligand as well as the salen unit. In addition, **1** was studied by cyclic voltammetry.

Keywords: Manganese(III) complex; Crystal structure; Tricarboxylate ligand; Schiff-base ligand; Cyclic voltammetry

1. Introduction

Coordination chemistry of manganese has attracted considerable interest because of involvement in various biological systems [1–5] and of potential applications in magnetism [6, 7]. It is believed that manganese ion can catalyze important processes in nature occurring in the oxygen-evolving complex (OEC) of photosystem II (PS II), where the manganese coordination sphere is dominated by O and N donors from amino acid side chains. Complexes containing manganese(III)-salen are considered to be simple models for the reactivity of the OEC active site of manganese-containing enzymes [8–12].

Many complexes containing manganese(III) and salen or its derivatives have been reported [13–15], and Mn(II) complexes with benzene-1,3,5-tricarboxylic acid are well studied [16, 17]. However, Mn(III)–salen complexes with flexible multicarboxylate

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ligands are rarely reported. The purpose of our research is to prepare potential models for the active sites of manganese-containing enzymes and at the same time to investigate binding between the $[Mn^{III}(salen)]^+$ species and the multicarboxylate groups. We present here a new chain-like manganese(III) complex, which was synthesized by the reaction of $[Mn(salen)]ClO_4 \cdot 2H_2O$ [H_2salen = N,N′-bis(salicylideneaminato) ethylene] with benzene-1,3,5-triacetic acid (H_3bta).

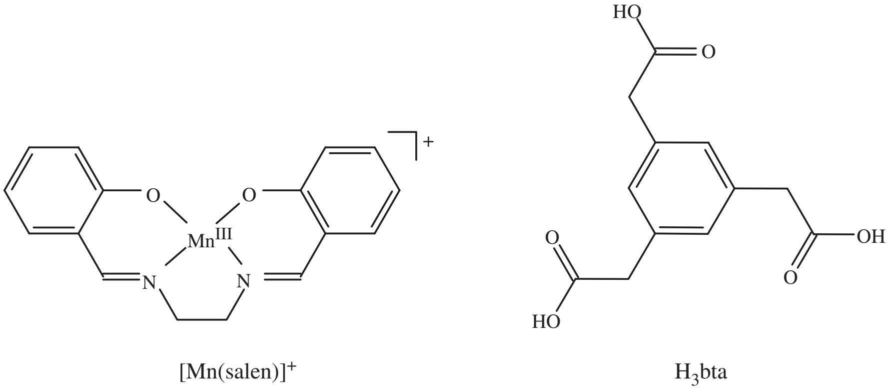
2. Experimental

2.1. *Materials and general methods*

All commercially available chemicals are of reagent grade and used as received without further purification. $[Mn(salen)]ClO_4 \cdot 2H_2O$ and H_3bta (scheme 1) were prepared according to the literature methods [18, 19]. The C, H and N analyses were carried out on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. FT-IR spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr discs. Cyclic voltammograms (CV) were measured on an EG&G M273 potentiostat/galvanostat system using a glassy carbon working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as a reference. The CV measurements were carried out in methanol under dry nitrogen at a scan rate of $50\,mV\,s^{-1}$. Bu_4NClO_4 (0.10 M) was used as a supporting electrolyte. Electrospray mass spectral (ES-MS) measurements were carried out on a LCQ System (Finngan MAT, USA) using a mixing solution of methanol and water (1 : 1) as the mobile phase.

2.2. *Synthesis of [Mn(salen)H_2bta]·0.5H_2O (1)*

To a solution of H_3bta (0.050 g, 0.20 mmol) in methanol (15 mL), 10 mL 2-propanol and $[Mn(salen)]ClO_4 \cdot 2H_2O$ (0.091 g, 0.20 mmol) in water (10 mL) were added. Then, the mixture was stirred for 30 min and filtered. Black crystals were obtained from the filtrate after standing in air at room temperature for about 20 days in 68% yield. Anal. Calcd for $C_{28}H_{26}N_2MnO_{8.5}$(%): C, 57.8; H, 4.5; N, 4.8. Found: C, 57.7; H, 4.8;



Scheme 1. Schematic drawing of $[Mn(salen)]^+$ and H_3bta.

N, 4.9. FT-IR (KBr pellet, cm^{-1}): 3446m(br), 2924w, 1684m, 1626s, 1601s, 1543m, 1469w, 1447s, 1395m, 1327m, 1296s, 1204m, 1151m, 1132m, 906m, 801m, 769m, 758m, 632m, 596m, 470m.

2.3. *X-ray structure determination*

The intensity data for [Mn(salen)H_2bta] · 0.5H_2O were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The structure was solved by direct methods with SIR92 [20], and expanded using Fourier techniques [21]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. The hydrogen atoms except those from water molecules and carboxyl groups were generated geometrically. The hydrogen atoms of the carboxylic acid groups were found in the differential Fourier map and located directly, and their coordinates were refined. All calculations were carried out on an SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [22]. The crystal data are summarized in table 1. Selected bond lengths and angles are listed in table 2. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-233620 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Description of the crystal structure of [Mn(salen)(H_2bta)]·0.5H_2O (1)*

The X-ray crystallographic analysis revealed that the asymmetric unit of **1** contains one [Mn(salen)(H_2bta)] molecule and half a water molecule. As shown in figure 1,

Table 1. Crystallographic data of [Mn(salen)H_2bta]·0.5H_2O (**1**).

Empirical formula	$C_{28}H_{26}N_2MnO_{8.5}$
Formula weight	581.45
Temperature (K)	200
Crystal system, space group	Monoclinic, $P2_1$/n
Unit cell dimensions (Å, °)	$a = 13.3886(5)$ $b = 13.6928(5)$ $c = 14.6443(5)$ $\beta = 106.5160(10)$
Volume (Å^3)	2573.93(16)
Z, Calculated density (gm^{-3})	4, 1.500
Absorption coefficient (mm^{-1})	0.571
$F(000)$	1204
Crystal size (mm)	0.20 × 0.20 × 0.10
θ range for data collection (°)	2.08 to 27.48
Limiting indices	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-19 \leq l \leq 18$
Reflections collected/unique	11152/5879 [R(int) = 0.0389]
Max. and min. transmission	0.945 and 0.830
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.000
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0384$, $wR2 = 0.0568$
R indices (all data)	$R1 = 0.0786$, $wR2 = 0.0602$

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Mn1–O2	1.8845(13)	Mn1–O1	1.8828(13)
Mn1–O11	2.1725(14)	Mn1–O15#1	2.3007(14)
Mn1–N2	1.9739(17)	Mn1–N1	1.9927(17)
O2–Mn1–O1	96.02(6)	O2–Mn1–N2	90.65(7)
O1–Mn1–N2	171.38(7)	O2–Mn1–N1	171.48(7)
O1–Mn1–N1	91.81(8)	N2–Mn1–N1	81.24(7)
O2–Mn1–O11	95.08(6)	O1–Mn1–O11	90.22(6)
N2–Mn1–O11	94.63(6)	N1–Mn1–O11	88.23(6)
O2–Mn1–O15#1	89.14(6)	O1–Mn1–O15#1	90.21(5)
N2–Mn1–O15#1	84.43(6)	N1–Mn1–O15#1	87.48(6)
O11–Mn1–O15#1	175.69(6)		

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

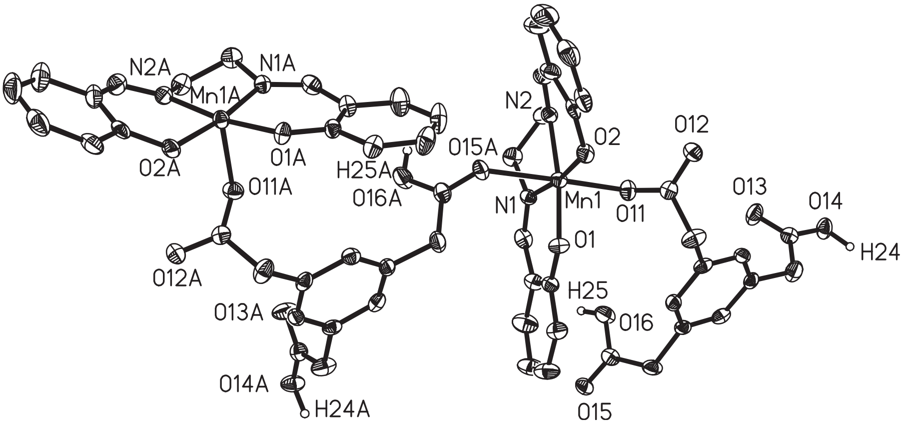


Figure 1. A view of **1** showing the coordination environment around the Mn(III) center (ellipsoids at 50% probability). The solvent molecule and hydrogen atoms (except those of the carboxylic acid) are omitted for clarity.

each manganese atom is six-coordinate with a slightly distorted octahedral coordination geometry from two nitrogen atoms and two oxygen atoms of the salen unit, and two additional oxygen atoms from two different triacid ligands. The resulting four short (two Mn–N and two Mn–O) and two long (Mn–O) bond lengths are due to the Jahn-Teller effect (table 2) [10]. In the equatorial plane, the bond lengths, Mn–N [Mn1–N1 = 1.9927(17) Å, Mn1–N2 = 1.9739(17) Å] and Mn–O [Mn1–O1 = 1.8828(13) Å, Mn1–O2 = 1.8845(13) Å], show typical values for high-spin Mn(III) [13]. The axial Mn1–O15 (protonated carboxyl) bond length [2.3007(14) Å] is longer than that of the Mn1–O11 (deprotonated carboxyl) one [2.1725(14) Å]. In the Mn(III)–salen unit, Mn1 atom and the atoms in the equatorial plane (N1, N2, O2, O1) are coplanar with a mean deviation from the plane of 0.026 Å. The dihedral angles between the equatorial plane and benzene ring planes A and B (labeling shown in figure 2) of the salen unit are 5.2 and 29.4°, respectively. The large dihedral angle between equatorial plane and benzene ring plane B may be explained as the benzene ring plane B of salen acting as an acceptor of C–H$\cdots\pi$ interaction. As exhibited in figure 2, each triacid ligand adopts *cis*, *cis*, *cis* conformation and connects two

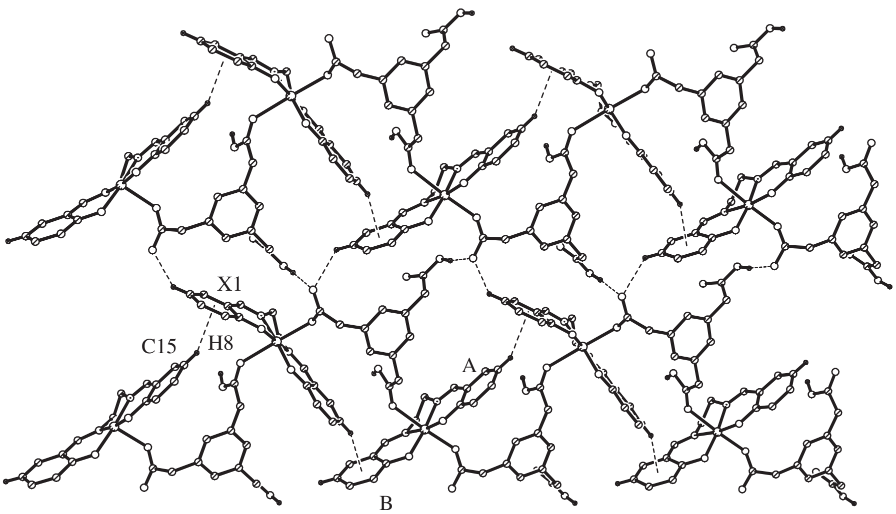


Figure 2. 2D network structure of **1** with hydrogen bonds and C–H···π interaction indicated by dashed lines.

Table 3. Hydrogen bonding data in the complex with distances (Å) and angles (°).

D–H···H	d(D···A)	∠(DHA)
O14–H24···O12#1	2.463(2)	177(2)
O16–H25···O13#2	2.628(2)	171(2)
C1–H1···O13#3	3.323(3)	148
C1–H2···O11#3	3.267(3)	132
C13–H6···O12#4	3.192(3)	130
C14–H7···O2#4	3.497(3)	165
C20–H10···O16#3	3.160(3)	128
C25–H13···O12#5	3.230(3)	136

Symmetry transformations used to generate equivalent atoms: #1 $-1+x$, $-1/2-y$, $-1/2+z$; #2 $1-x$, $1/2+y$, $-1/2-z$; #3 $2-x$, $-y$, $-z$; #4 $1-x$, $1/2+y$, $1/2-z$; #5 x, $-1/2-y$, $1/2+z$.

Mn(III) atoms to give a zigzag one dimensional (1D) chain structure. The salen units also form a zigzag chain by C–H···π interaction between benzene ring planes since the distance between H8 and the centroid (X1) of the benzene group of nearby salen is 2.71 Å, and the C15–H8–X1 angle is 155° [23–25]. The 1D chains are linked together by inter-chain O14–H24···O12($-1+x$, $-1/2-y$, $-1/2+z$) and C25–H13···O12(x, $-1/2-y$, $1/2+z$) hydrogen bonds between the oxygen atom of uncoordinated carboxyl group (without deprotonation) and the oxygen of coordinated carboxyl (deprotonated), and between the carbon atom of benzene of the salen unit and the oxygen atom of coordinated carboxyl (deprotonated) to form an infinite two dimensional (2D) network structure (figure 2). The hydrogen bonding data are summarized in table 3. The 2D networks are further packed together to form a 3D structure, which is stabilized by O–H···O hydrogen bonds between oxygens of carboxyl groups without deprotonation and the carbonyl oxygen atom of the bta ligand, and C–H···O hydrogen bonds between the carbon atom of the salen group and the carboxyl oxygen atom of the bta ligand as well as the salen.

3.2. *Properties of complex 1*

The electrochemistry of Mn(III)–salen in solution (MeOH, MeCN, DMSO, DMF) is well-studied [9, 11, 12, 26–28]. The cyclic voltammogram of **1** in MeOH is shown in figure 3, the spectrum and the peaks are similar to those of [Mn(2–OH–SALPN)(OAc)]$_n$ (2-OH-SALPN = dianion of *N*,*N*′-disalicylidene-2-hydroxypropane-diamine) reported previously [29]. The redox of the metal center is quasi-reversible as shown by the peak-to-peak separation, ΔE_p, is 77 ± 4 mV and the $E_{1/2}$ of oxidation process, +0.36 mV *versus* SCE.

The complex was further characterized by electrospray mass spectrometry showing peaks at *m*/*z* 321.0 and 572.8 corresponding to [Mn(salen)]$^+$ and [Mn(salen)(H$_3$bta)]$^+$ species. Both assignments are ensured by good agreement between the observed and calculated isotopic distributions. Figure 4 gives an example for the comparison between the experimental and calculated isotopic distributions for the peak at *m*/*z* = 572.8.

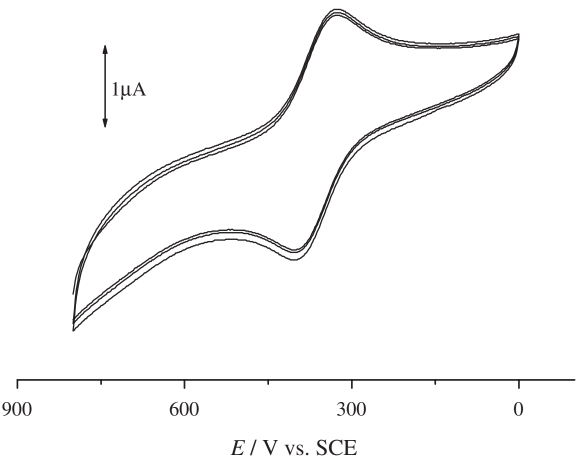


Figure 3. Cyclic voltammogram of **1** in methanol with 0.10 M Bu$_4$NClO$_4$ as supporting electrolyte, and scan rate = 50 mV s^{-1}, measured at a glassy carbon electrode.

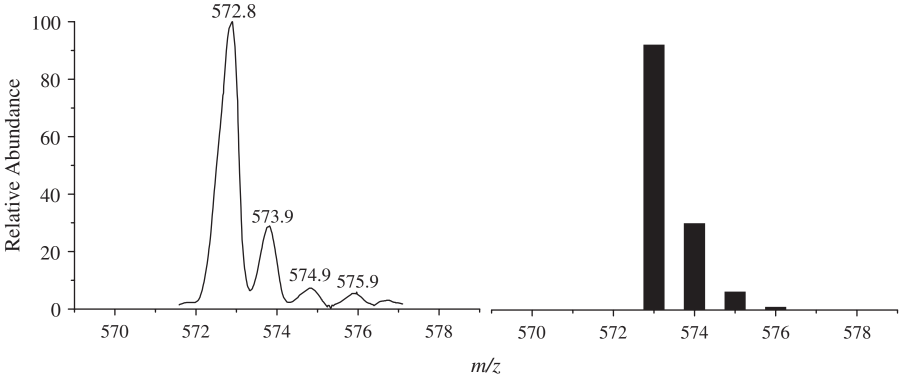


Figure 4. The observed (traces) and calculated (bars) isotopic distributions for the peaks at *m*/*z* 572.8 observed in complex **1**.

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References

[1] N.A. Law, M.T. Caudle, V.L. Pecoraro. *Adv. Inorg. Chem.*, **46**, 305 (1999).
[2] V.K. Yachandra, K. Sauer, M.P. Klein. *Chem. Rev.*, **96**, 2927 (1996).
[3] C. Tommos, G.T. Babcock. *Acc. Chem. Rev.*, **31**, 18 (1998).
[4] G. Christou. *Acc. Chem. Res.*, **22**, 328 (1989).
[5] M.L. Ludwig, K.A. Pattridge, W.C. Stallings. *Manganese in Metabolism and Enzyme Function*, p. 405, Academic Press, New York (1986).
[6] Z.J. Zhong, X.Z. You, T.C.W. Mak. *Polyhedron*, **13**, 2157 (1994).
[7] N. Matsumoto, Y. Sunatsuki, H. Miyasaka, Y. Hashimoto, D. Luneau, J.-P. Tuchagues. *Angew. Chem. Int. Ed.*, **38**, 171 (1999).
[8] L.E. Andreasson. *Biochim. Biophys. Acta*, **973**, 465 (1989).
[9] V.L. Pecoraro, W.M. Butter. *Acta Crystallogr.*, **C42**, 1151 (1986).
[10] H.L. Shyu, H.H. Wei, Y. Wang. *Inorg. Chem. Acta*, **290**, 8 (1999).
[11] A. Panja, N. Shaikh, M. Ali, P. Vojtíšek, P. Banerjee. *Polyhedron*, **22**, 1191 (2003).
[12] C. Chen, D. Huang, X. Zhang, F. Chen, H. Zhu, Q. Liu, C. Zhang, D. Liao, L. Li, L. Sun. *Inorg. Chem.*, **42**, 3540 (2003).
[13] K. Oyaizu, T. Nakagawa, E. Tsuchida. *Inorg. Chem. Acta*, **350**, 184 (2000).
[14] J.-P. Costes, F. Dahan, B. Donnadieu, M.-J.R. Douton, M.-I.F. Garcia, A. Bousseksou, J.-P. Tuchagues. *Inorg. Chem.*, **43**, 2736 (2004).
[15] S. Sailaja, K. Rajender Reddy, M.V. Rajasekharan, C. Hureau, E. Rivière, J. Cano, J.-J. Girerd. *Inorg. Chem.*, **42**, 180 (2003).
[16] M.J. Plater, M.R. St. J. Foreman, E. Coronado, C.J. Gómez-García, A.M.Z. Slawin. *J. Chem. Soc., Dalton Trans.*, 4209 (1999).
[17] M.J. Plater, M.R. St. J. Foreman, R.A. Howie, J.M.S. Skakle, E. Coronado, C.J. Gómez-García, T. Gelbrich, M.B. Hursthouse. *Inorg. Chem. Acta*, **319**, 159 (2001).
[18] H. Li, Z.J. Zhong, C.Y. Duan, X.Z. You, T.C.W. Mark, B. Wu. *J. Coord. Chem.*, **41**, 183 (1997).
[19] H.-F. Zhu, Z.-H. Zhang, W.-Y. Sun, T.-a. Okamura, N. Ueyama. *Cryst. Growth Des.*, **5**, 177 (2005).
[20] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori. SIR92: *J. Appl. Cryst.*, **27**, 435 (1994).
[21] DIRDIF94: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits. The DIRDIF94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1994).
[22] teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX (1999).
[23] Z. Dominguez, H. Dang, M.J. Strouse, M.A. Garcia-Garibay. *J. Am. Chem. Soc.*, **124**, 7719 (2002).
[24] H. Suezawa, T. Yoshida, M. Hirota, H. Takahashi, Y. Umezawa, K. Honda, S. Tsuboyama, M. Nishio. *J. Chem. Soc., Perkin Trans.*, **2**, 2053 (2001).
[25] H. Takahashi, S. Tsuboyama, Y. Umezawa, K. Honda, M. Nishio. *Tetrahedron*, **56**, 6185 (2000).
[26] L. Gaillon, N. Sajot, F. Bedioui, J. Devynck. *J. Electroanal. Chem.*, **345**, 157 (1993).
[27] A. Doménech, P. Formentín, H. García, M.J. Sabater. *J. Phys. Chem.*, **B106**, 574 (2002).
[28] Q. Shi, R. Cao, X. Li, J. Luo, M. Hong, Z. Chen. *New J. Chem.*, **26**, 1397 (2002).
[29] J.A. Bonadies, M.J. Maroney, V.L. Pecoraro. *Inorg. Chem.*, **28**, 2044 (1989).