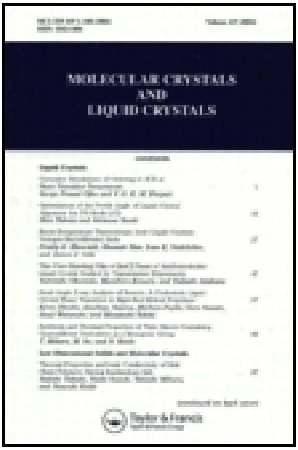
This article was downloaded by: [University of Haifa Library]
On: 09 August 2012, At: 14:47
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Ligand Exchange of Manganese(II) Macrocyclic Pentaamine Complexes: Synthesis, Characterization, and Single-Crystal X-ray Structure Determination

Hai-Yang Tu [a], Ping Liu [a], Cheng-Jin Wang [a], Meng-Xiang Gao [a] & Ai-Dong Zhang [a]

[a] Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, Central China Normal University, Wuhan, China

Version of record first published: 22 Sep 2010

To cite this article: Hai-Yang Tu, Ping Liu, Cheng-Jin Wang, Meng-Xiang Gao & Ai-Dong Zhang (2007): Ligand Exchange of Manganese(II) Macrocyclic Pentaamine Complexes: Synthesis, Characterization, and Single-Crystal X-ray Structure Determination, Molecular Crystals and Liquid Crystals, 469:1, 79-87

To link to this article: http://dx.doi.org/10.1080/15421400701431471

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, 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.

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

Mol. Cryst. Liq. Cryst., Vol. 469, pp. 79–87, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701431471

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

Ligand Exchange of Manganese(II) Macrocyclic Pentaamine Complexes: Synthesis, Characterization, and Single-Crystal X-ray Structure Determination

Hai-Yang Tu
Ping Liu
Cheng-Jin Wang
Meng-Xiang Gao
Ai-Dong Zhang
Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, Central China Normal University, Wuhan, China

[Mn($C_{23}H_{34}ClN_5$)] (manganese(II) {24-chloro-2,21-dimethyl-(4R,9R,14R,19R)-3,10,13,20,26-pentaazatetracyclo[20.3.1.$0^{4,9}$.$0^{14,19}$]hexacosa-1(26),2(3),20(21),22(23), 24-pentaene}, ([Mn(PAHP)]) has been synthesized and characterized by FT-IR spectroscopy, UV-vis, and MS spectra. Single crystals of [Mn(CH_3CH_2OH)Cl($C_{23}H_{34}ClN_5$)]Cl·H_2O and [Mn(H_2O)$_2$($C_{23}H_{34}ClN_5$)]Cl_2·CH_2Cl_2 were obtained by slow evaporation from ethanol-dichloromethane and 1,2-dichloromethane-DMF solution, respectively. X-ray crystallographic study of the complex reveals that the chloride ligand on manganese(II) can be substituted by oxygen-containing ligands, such as methanol.

Keywords: ligand exchange; manganese(II); X-ray crystallography

1. INTRODUCTION

Recently, synthetic metal complexes acting as model compounds of hydrolytic metalloenzymes have attracted much attention [1]. It is well known that manganese plays an important role in many biological systems including photosystem II [2] (water oxidation), catalase [3] (disproportionation of hydrogen peroxide), superoxide dismutase [4] (dismutation of the superoxide radical), and arginase [5]. In addition,

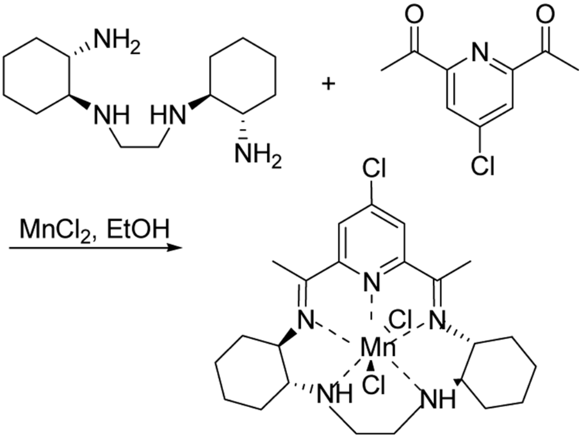
---

Address correspondence to Ai-Dong Zhang, Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, Central China Normal University, Wuhan 430079, China. E-mail: haiytu@mail.ccnu.edu.cn

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

the manganese(II) complexes exhibit spontaneous magnetization [6]. There has been a growing interest in the study of the macrocyclic polyamine metal complexes because they appear to be efficient catalysts for the hydrolysis of phosphate esters [7]. 3,10,13,20,26-Pentaazatetracyclo [20.3.1.$0^{4,9}$.$0^{14,19}$] hexacosa-1(26),2(3),20(21),22(23),24-pentaene (PAHP) has been used as a ligand in the coordination chemistry of transition metals [8]. In addition, Riley et al. designed and synthesized a manganese(II) complex with a bis(cyclohexylpyridine)-substituted macrocyclic ligand to be a functional mimic of the superoxide dismutase (SOD) enzymes [9].

Recently, we started a systematic study on the interaction of superoxide dismutase mimetics with superoxide using the self-assembly monolayers. One of the goals of this project is to synthesize SOD mimetics for immobilization on self-assembled monolayers. Part of our interest is the synthesis of the derivativable macrocyclic polyamine manganese(II) complexes ([$MnCl_2(C_{23}H_{34}ClN_5)$])(Scheme 1). Interestingly, we found that the methoxy group substituted the chloride ligand when it was crystallized from the methanol–dichloromethane solution (1:1) at 293 K [10]. To determine the structure of [$MnCl_2$ ($C_{23}H_{34}ClN_5$)], herein we describe the synthesis, crystal structure, and characterization of manganese(II) complexes with PAHP crystallized from different solvents. The oxygen on ethanol substitutes a chloride ligand when crystallized from ethanol–dichloromethane solution (1:1); in the mean time, water exchanges two chloride ligands from the manganese(II) complexes.



SCHEME 1 The synthetic route of [M_n(PAHP)]

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

2. EXPERIMENTAL

2.1. General Remarks

Analytical-grade reagents were used without any further purification. N,N'-Bis-{(1R,2R)-[2-(amino)]cyclohexyl}-1,2-diaminoethane has been prepared according to the method described by Riley et al. [11]; 4-chloro-2,6-diacylpyridine was synthesized according to our method [12]. Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets in a Bruker Tensor 27 FT-IR spectrophotometer, and UV-vis spectra were recorded on a Shimadzu UV-3310 spectrophotometer. Mass spectra (MS) were measured on an API2000Lc/MS.

2.2. Synthesis

$[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$ and $[Mn(H_2O)_2(C_{23}H_{34}ClN_5)]Cl_2{\cdot}CH_2Cl_2[MnCl_2(C_{23}H_{34}ClN_5)]$ were synthesized according to the literature procedure in 84% yield [8]. $[Mn(CH_3CH_2O)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$ crystals, appropriate for data collection, were obtained by slow evaporation of an ethanol–dichloromethane solution (1:1) at 293 K. $[Mn(H_2O)_2(C_{23}H_{34}ClN_5)]Cl_2{\cdot}CH_2Cl_2$ crystals, appropriate for data collection, were obtained by slow evaporation of a dichloromethane–DMF solution (20:1) at 293 K.

2.3. Crystal Structure Determination

A suitable crystal was used for data collection. Diffraction data were collected at 293(2) K with a Bruker AXS Smart 4000 CCD diffractormeter using graphite-monochromated (Mo-Ka) radiation ($\lambda = 0.71073$ Å), in Ψ and ω scans mode. The structure was solved by direct methods and refined by a full-matrix least squares on F2 method. Intensity data were corrected for Lorenz and polarization effects, and an empirical absorption correction was performed. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were added geometrically and allowed to ride on their respective parent atoms. The contribution of these hydrogen atoms was included in the structure factor calculations. All calculations were carried out using the HELXL-97 program. All other information regarding the refinement is also recorded in Tables 1 and 2. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 625146 and 625147.

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

TABLE 1 Crystal Data and Structural Refinement Parameters of $[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$

Parameter	Value
Empirical formula	$C_{25}H_{42}Cl_3$ Mn N_5 O_2
Formula weight	605.93
Temperature	293(2)
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1) 2(1) 2(1)
Unit cell dimensions	a = 8.6463(6) Å, $\alpha = 90.00^\circ$ b = 18.0769(13) Å, $\beta = 90.00^\circ$ c = 19.0569(13) Å, $\gamma = 90.00^\circ$
Volume	2978.6(4) $Å^3$
Z	4
Density (calculated)	1.351 mg/m^3
Absorption coefficient	0.743 mm^{-1}
F(000)	1276
Crystal size	$0.30 \times 0.20 \times 0.10\,mm^3$
Theta range for data collection	1.55–28.30°
Index ranges	$-11 \le h \le 11$, $-23 \le k \le 23$, $-24 \le l \le 11$
Reflections collected	18286
Independent reflections	7038[R(int) = 0.03111]
Completeness to theta = 28.30°	97.5%
Max. and min. transmission	0.9294 and 0.8079
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	7038/3/346
Goodness of fit on F^2	1.009
Final R indices[$I > 2\sigma(I)$]	R1 = 0.0437, wR2 = 0.0942
R indices (all data)	R1 = 0.0570, wR2 = 0.1004
Extinction coefficient	0.023(16)
Largest diff. peak and hole	0.489 and -0.202e $Å^{-3}$

3. RESULTS AND DISCUSSION

3.1. Spectroscopy

The infrared spectra of $[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$ shows strong sharp bands close to 3474 cm^{-1} and 3405 cm^{-1} for tertial amines on the macrocyclo polyamine. The carbon–hydrogen stretching peaks of hydrogen atoms on pyridine occur at 3076 cm^{-1} and 3029 cm^{-1}. The methyl group vibrations appear at 2932 $cm^{-1}$and 2860 cm^{-1}. The peak of 1643 cm^{-1} is due to C=N stretch vibration. The stretching frequency of pyridine is close to the range of 1578 cm^{-1}, 1475 cm^{-1}, and 1446 cm^{-1}. The UV-vis spectrum of $[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$ shows two absorption at λ max = 297 nm and 223 nm.

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

TABLE 2 Crystal Data and Structural Refinement Parameters of $[Mn(H_2O)_2(C_{23}H_{34}ClN_5)]Cl_2{\cdot}CH_2Cl_2$

Parameter	Value
Empirical formula	$C_{24}\ H_{40}\ C_{l5}\ Mn\ N_5\ O_2$
Formula weight	662.80
Temperature	293(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P_2(1)$
Unit cell dimensions	a = 13.6398(14) Å, $\alpha = 90.00^\circ$ b = 8.0499(8) Å, $\beta = 91.994(2)^\circ$ c = 14.1074(14) Å, $\gamma = 90.00^\circ$
Volume	1548.0(3) $Å^3$
Z	2
Density (calculated)	$1.422\,mg/m^3$
Absorption coefficient	$0.888\,mm^{-1}$
F(000)	690
Crystal size	$0.50 \times 0.10 \times 0.06\,mm^3$
Theta range for data collection	1.44–26.00°
Index ranges	$-16 \le h \le 15,\ -9 \le k \le 9,\ -17 \le l \le 15$
Reflections collected	8508
Independent reflections	5468[R(int) = 0.0378]
Completeness to theta = 26.00°	99.2%
Max. and min. transmission	0.9486 and 0.6651
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5468/7/353
Goodness of fit on F^2	1.062
Final R indices$[I > 2\sigma(I)]$	R1 = 0.0661, wR2 = 0.1470
R indices (all data)	R1 = 0.0894, wR2 = 0.1750
Extinction coefficient	0.031(3)
Largest diff. peak and hole	0.792 and $-0.752e\ Å^{-3}$

3.2. X-ray Crystallography

$[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$ crystallizes in an orthorhombic space group *P*212121 (see Table 1 for details) with one molecule of water per molecule of complex in the unit cell hydrogen bonded to the bound chloride ligands. A projection view of the molecule with nonhydrogen atoms represented by 50% thermal ellipsoids is shown in Fig. 1, and selected bond lengths and bond angles are listed in Tables 3 and 4. The Mn(II) complex exists in seven-coordinate geometry. The Mn(II) and nitrogen atoms of the macrocycle are coplanar; the coordination sphere is best described as pentagonal bipyramidal. The metal–nitrogen bond distances range from 2.229 to 2.401 Å, with the Mn–N average bond distance being 2.323 Å and the Mn–Cl

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

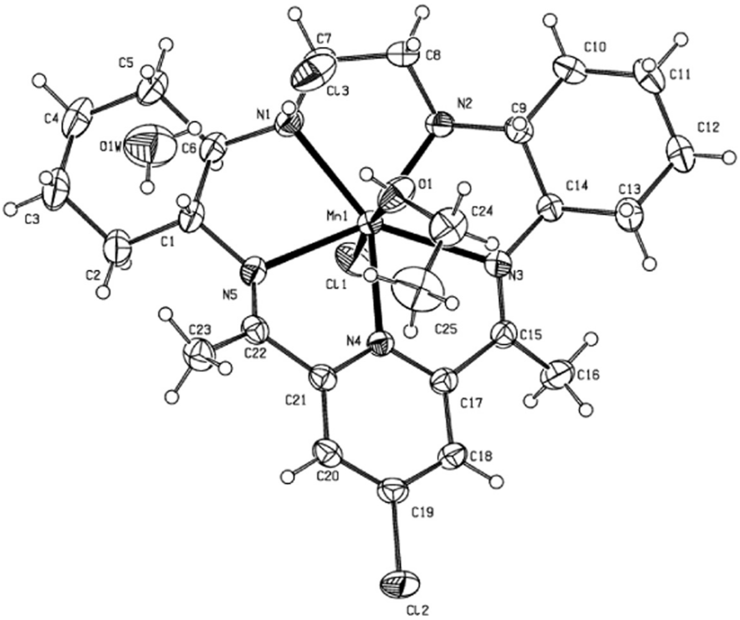


FIGURE 1 Projection view of $[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$ with nonhydrogen atoms represented by 50% thermal ellipsoids.

distance being 2.4971 Å. The Mn–O distance is 2.289 Å, which is shorter than that of Mn–Cl. The Cl–Mn–O angle is approximately 174°, as it appears that the chlorine and oxygen are repelled by the diaxial. The sum of the five N–Mn–N chelate angles adds up to

TABLE 3 Bond Lengths (Å) for $[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl{\cdot}H_2O$

Bond	Length
Mn(1)–N(4)	2.229(2)
Mn(1)–N(2)	2.290(2)
Mn(1)–N(5)	2.343(2)
Mn(1)–Cl(1)	2.4971(8)
N(3)–C(14)	1.476(3)
N(5)–C(1)	1.475(3)
Mn(1)–O(1)	2.289(2)
Mn(1)–N(1)	2.315(2)
Mn(1)–N(3)	2.401(2)
N(3)–C(15)	1.279(3)
N(5)–C(22)	1.263(3)

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

TABLE 4 Bond Angles (deg) for [Mn(CH_3CH_2OH)Cl ($C_{23}H_{34}ClN_5$)]Cl·H_2O

Bond	Angle
N(2)–Mn(1)–N(1)	77.71(8)
N(4)–Mn(1)–N(5)	69.46(8)
N(1)–Mn(1)–N(5)	72.32(8)
N(4)–Mn(1)–N(3)	68.91(7)
N(2)–Mn(1)–N(3)	72.50(8)
O(1)–Mn(1)–Cl(1)	174.37(7)

360.9 (with an average of 72.18), very close to 360 for an ideal planar structure.

[Mn(H_2O)$_2$($C_{23}H_{34}ClN_5$)]Cl_2·CH_2Cl_2 crystallizes in a monoclinic space group P_21 (see Table 2 for details) with one molecule of dichloromethane per molecule of complex in the unit cell. In Fig. 2, a projection view of the seven-coordinate molecule with nonhydrogen atoms

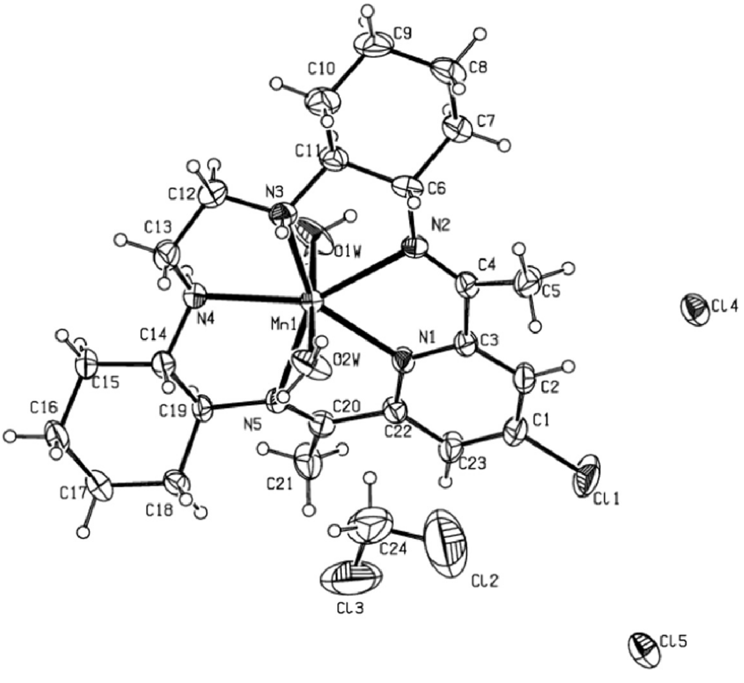


FIGURE 2 Projection view of [Mn(H_2O)$_2$($C_{23}H_{34}ClN_5$)]Cl_2·CH_2Cl_2 with nonhydrogen atoms represented by 50% thermal ellipsoids.

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

TABLE 5 Bond Lengths (Å) for $[Mn(H_2O)_2(C_{23}H_{34}ClN_5)]Cl_2{\cdot}CH_2Cl_2$

Bond	Length
Mn(1)–O(1)W	2.187(6)
Mn(1)–N(1)	2.235(4)
Mn(1)–N(4)	2.289(5)
Mn(1)–N(5)	2.365(4)
N(2)–C(6)	1.474(7)
N(5)–C(19)	1.474(6)
Mn(1)–O(2)W	2.218(6)
Mn(1)–N(3)	2.285(5)
Mn(1)–N(2)	2.359(4)
N(2)–C(4)	1.258(7)
N(5)–C(20)	1.277(7)

represented by 50% thermal ellipsoids is shown, and in Table 5 selected bond lengths are presented. Table 6 presents selected bond angles.

The most remarkable aspect of these two structures is the observation that the molecule of $[MnCl_2(C_{23}H_{34}ClN_5)]$ is present in the unit cell with nonbonded chloride (*i.e.*, the Mn to chlorine distances is 2.464 and 3.115 Å). When we crystallized it from ethanol–dichloromethane, the coordinated chlorine can depart from Mn(II). The Mn–N bond distances range from 2.229 to 2.401 Å and are shorter than observed for corresponding compounds [8]. The oxygen coordinates to the Mn(II) easier than chlorine, so if oxygen exists, (*i.e.*, ethanol), the oxygen should substitute the chlorine, which would release a chloride ion. The same thing occurred when we use DMF, perhaps because there is a trace amount of water in DMF. This substituted ligand possesses a driving force for folding of the ligand so as to adopt a seven-coordinate geometry about the spherically symmetrical Mn(II) ion, which

TABLE 6 Bond Angles (deg) for $[Mn(H_2O)_2(C_{23}H_{34}ClN_5)]Cl_2{\cdot}CH_2Cl_2$

Bond	Angle
O(1)W–Mn(1)–O(2)W	178.4(2)
N(3)–Mn(1)–N(4)	78.6(2)
N(1)–Mn(1)–N(2)	69.76(14)
N(3)–Mn(1)–N(2)	72.06(17)
N(1)–Mn(1)–N(5)	69.13(14)
N(4)–Mn(1)–N(5)	72.10(16)

Downloaded by [University of Haifa Library] at 14:47 09 August 2012

is sufficient to overcome the Columbic attractive force of binding the chloride ion to the positive Mn center.

4. CONCLUSIONS

[$MnCl_2(C_{23}H_{34}ClN_5)$] was synthesized by reacting *N*,*N′*-bis-{(1*R*,2*R*)-[2-(amino)]cyclohexyl}-1,2-diaminoethane with 4-chloro-2,6-diacetylpyridine in the presence of $MnCl_2$. X-ray determination of the $[Mn(CH_3CH_2OH)Cl(C_{23}H_{34}ClN_5)]Cl \cdot H_2O$ and $[Mn(H_2O)_2(C_{23}H_{34}ClN_5)]Cl_2 \cdot CH_2Cl_2$ revealed that ethanol and water substitute the ligand of chloride in the manganese(II) complex.

ACKNOWLEDGMENTS

The authors are grateful to the Central China Normal University, the National Natural Science Foundation of China (Grant No. 20241001), and Hubei Natural Science Foundation of China (Grant No. 2006ABA180) for financial support.

REFERENCES

[1] Williams, N. H., Takasaki, B., Wall, M., & Chin, J. (1999). *Acc. Chem. Res.*, *32*, 485.

[2] (a) Fufezan, C., Zhang, C., Krieger-Liszkay, A., & Rutherford, A. W. (2005). *Biochemistry*, *44*, 12780; (b) Mikata, Y., Wakamatsu, M., So, H., Abe, Y., Mikuriya, M., Fukui, K., & Yano, S. (2005). *Inorg. Chem.*, *44*, 7268.

[3] Mizobata, J., Kagawa, M., Murakoshi, N., Kusaka, E., Kameo, K., Kawara, Y., & Nagai, J. (2000). *Eur. J. Biochem.*, *267*, 4264.

[4] Gultneh, Y., Tesema, Y. T., Yisgedu, T. B., Butcher, R. J., Wang, G., & Ye, G. T. (2006). *Inorg. Chem.*, *45*, 3023.

[5] Kanyo, Z. F., Scolnik, L. R., Ashe, D. E., & Christianson, D. W. (1996). *Nature*, *383*, 554.

[6] Das, A., Rosair, G. M., Fallah, M. S. E., Ribas, J., & Mitra, S. (2006). *Inorg. Chem.*, *45*, 3301.

[7] Li, S.-A., Yang, D.-X., Li, D.-F., Huang, J., & Tang, W.-X. (2002). *New J. Chem.*, *26*, 1831.

[8] Krämer, R. (2000). *Angew. Chem. Int. Ed.*, *39*, 4469.

[9] (a) Salvemini, D., Wang, Z.-Q., Zweier, J. L., Samouilov, A., Macarthur, H., Misko, T. P., Currie, M. G., Cuzzocrea, S., Sikorski, J. A., & Riley, D. P. (1999). *Science*, *286*, 304; (b) Aston, K., Rath, N., Naik, A., Slomczynska, U., Schall, O. F., & Riley, D. P. (2001). *Inorg. Chem.*, *40*, 1779.

[10] Tu, H., Wang, C., Meng, X., & Zhang, A. (2006). *Acta Cryst.*, *E62*, m500.

[11] Riley, D. P., Neumann, W. L., Henke, S. L., Lennon, P., Aston, K. W., Salvemini, D., Sikorski, J. A., Fobian, Y. M., Grapperhaus, M. L., & Kusturin, C. L. (2001). US Patent 6214817.

[12] Jing, C., Tu, H., Pan, K., & Zhang, A. (2006). *Huaxue Shiji*, *28*, 53.