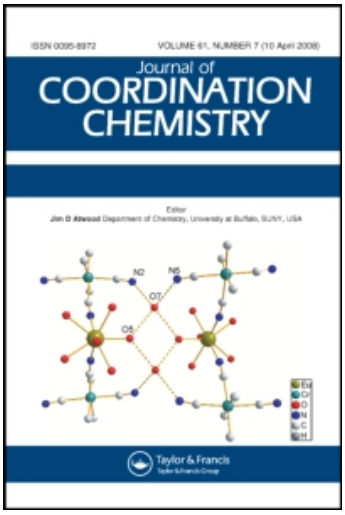

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of a dipeptide-copper(II)- 2-aminomethylbenzimidazole ternary complex

Wen-Long Liu[a]; Yang Zou[a]; Chun-Lin Ni[a]; Zhao-Ping Ni[a]; Yi-Zhi Li[a]; Yuan-Gen Yao[b]; Qing-Jin[a]
[a] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China [b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou 350002, P.R. China

To cite this Article Liu, Wen-Long , Zou, Yang , Ni, Chun-Lin , Ni, Zhao-Ping , Li, Yi-Zhi , Yao, Yuan-Gen and Qing-Jin(2004) 'Synthesis and characterization of a dipeptide-copper(II)- 2-aminomethylbenzimidazole ternary complex', Journal of Coordination Chemistry, 57: 11, 899 — 906
To link to this Article: DOI: 10.1080/00958970410001726362
URL: http://dx.doi.org/10.1080/00958970410001726362

J. Coord. Chem., Vol. 57, No. 11, 20 July 2004, pp. 899–906

SYNTHESIS AND CHARACTERIZATION OF A DIPEPTIDE–COPPER(II)–2-AMINOMETHYLBENZIMIDAZOLE TERNARY COMPLEX

WEN-LONG LIU[a], YANG ZOU[a], CHUN-LIN NI[a], ZHAO-PING NI[a], YI-ZHI LI[a], YUAN-GEN YAO[b] and QING-JIN MENG[a,*]

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China;* [b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou 350002, P.R. China*

(Received 30 September 2003; Revised 13 November 2003; In final form 13 April 2004)

A new ternary complex $[Cu(glygly)(AMBZ)(H_2O)]Cl{\cdot}H_2O$ (**1**) (glygly = glycylglycine anion, AMBZ = 2-aminomethylbenzimidazole) has been prepared and characterized by single-crystal X-ray diffractometry and ESR, electronic and IR spectroscopy. The copper(II) ion has a slightly distorted square-pyramidal coordination, being equatorially coordinated by the bidentate 2-aminomethylbenzimidazole and the bidentate glycylglycine anion and axially by a water molecule. The individual complex molecules are hydrogen bonded to their neighbors, forming a polymeric hydrogen-bonded lattice. Spectroscopic data are in accordance with the crystal structure.

Keywords: Copper(II) complex; Dipeptides; Ternary complex; 2-Aminomethylbenzimidazole

INTRODUCTION

Ternary transition metal complexes are a topic of interest because of their important role in biological systems. The metal ions promote specific protein–nucleic acid interactions through formation of ternary complexes [1,2] and metal–peptide complexes containing heteroaromatic nitrogen bases can mimic substrate-metal ion-enzyme interactions in the active center of enzymes [3,4].

Imidazole and benzimidazole derivatives are important heteroaromatic compounds in biochemistry acting as multidentate ligands rich in coordination chemistry, especially in many copper(II) complexes containing proteins [5,6] and nucleotide systems [7–9]. Some copper ternary complexes coordinated by chelating ligands containing imidazole groups have been described as model compounds for hemocyanin and other copper proteins [10].

*Corresponding author. Tel.: +86-25-3597266. Fax: +86-25-3314502. E-mail: mengqj@netra.nju.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00958970410001726362

An understanding of the stereochemical effect of bound ligands on ternary peptide complexes is of great importance and the study of model compounds has led to several structural studies in recent years [11–16]. However, to the best of our knowledge, only one X-ray crystallographic structure of a ternary complex peptide–Cu(II)–benzimidazole or benzimidazole derivative, [Cu(glygly)(benzimidazole)]·$3H_2O$, has been reported [12]. In this work we report the synthesis, spectroscopic characterization and X-ray structure of the ternary peptide complex [Cu(glygly)(AMBZ)(H_2O)]Cl·H_2O (**1**) (glygly = glycylglycine anion, AMBZ = 2-aminomethylbenzimidazole).

EXPERIMENTAL

Reagents and Physical Measurements

The dipeptide, glycylglycine and 2-aminomethylbenzimidazole were purchased from Aldrich and used as received. All other reagents and solvents were analytical grade obtained from commercial sources.

IR spectra using KBr disks were recorded on a Bruker Vector22 spectrophotometer in the 400–4000 cm^{-1} region. UV–Vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Elemental analyses (H, C, N) were carried out using a Perkin Elmer 240C elemental analyzer. ESR spectra were obtained on a Bruker JES-FEIXG spectrometer with X-band frequencies.

Preparation of [Cu(glygly)(AMBZ)(H_2O)]Cl·H_2O (1)

2-Aminomethylbenzimidazole dihydrochloride hydrate (1.98 g, 0.9 mmol) was added, with stirring, to a 10 cm^3 aqueous solution containing glycylglycine (0.16 g, 1.2 mmol). After 10 min, $CuCO_3(OH)$ (0.12 g, 1 mmol) was added and the mixture was stirred for 30 min and then filtered. The resulting green solution was allowed to stand at room temperature. After a few days, blue–green needle-shaped crystals of **1**, suitable for X-ray diffraction, were collected. Yield: 21%. Anal. Calcd. for $C_{12}H_{20}N_5O_5ClCu$(%): C, 34.87; H, 4.88; N, 16.94. Found: C, 34.46; H, 4.95; N, 16.66.

X-ray Crystallography

The diffraction experiments were carried out on a Bruker AXS SMART APEX CCD diffractometer. The program SAMART [17] was used for collecting frames of data, for indexing reflections and for the determination of lattice parameters; absorption corrections were carried out using SADABS [18]. The structure was solved by direct methods and nonhydrogen atoms were anisotropically refined by a full-matrix least-squares method based on F^2 using SHELXTL [19]. All hydrogen atoms were included in the refinement in calculated positions riding on their carrier atoms. The hydrogen thermal displacement parameters were fixed at 1.2 and 1.5 times the equivalent isotropic thermal displacement parameters of their internal and terminal carrier atoms, respectively. A summary of the data collection and structure refinement is presented in Table I. Final coordinates for the nonhydrogen atoms are given in Table II.

TABLE I Crystal data and structure refinement for **1**

Empirical formula	$C_{12}H_{20}N_5O_5ClCu$
Formula weight	413.32
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.533(2)
b (Å)	9.963(2)
c (Å)	10.204(2)
α (°)	104.95(1)
β (°)	100.45(1)
γ (°)	96.71(1)
V (Å^3)	811.9(3)
Z	2
D_{calc} (g cm^{-3})	1.691
μ(Mo Kα) (mm^{-1})	1.544
λ(Mo Kα) (Å)	0.71073
Temp (K)	293(2)
F(000)	426.0
Crystal size (mm^3)	0.4 × 0.30 × 0.30
θ range for data collection	2.12 to 25.0
Index ranges	$-10 \le h \le 9$, $-9 \le k \le 11$, $-12 \le l \le 10$
Reflections collected	2802
Independent reflections	1969
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1969/0/217
R_{int}	0.0587
R_1 [$I > 2\sigma(I)$]	0.0489
wR_2	0.0918
Goodness-of-fit on F^2	1.012
Largest difference: peak and hole (e Å^{-3})	0.57 to −0.49

TABLE II Final coordinates and equivalent isotropic displacement parameters of the nonhydrogen atoms for the complex.

Atom	*x*	*y*	*z*	$U_{(eq)}$ (Å^2)
Cu(1)	0.69160(7)	0.84806(6)	0.74632(6)	0.0299(2)
O(1)	0.6036(4)	0.8031(3)	0.8995(3)	0.0311(11)
O(1W)	0.4765(4)	0.9306(4)	0.6416(3)	0.0537(12)
O(2)	0.7142(3)	0.6430(3)	1.1580(3)	0.0310(11)
O(3)	0.6774(4)	0.8467(4)	1.2916(3)	0.0469(12)
N(1)	1.0033(4)	1.2088(4)	0.8766(4)	0.0326(12)
N(2)	0.8216(4)	1.0268(4)	0.8618(3)	0.0250(12)
N(3)	0.8038(4)	0.8869(4)	0.5985(3)	0.0341(14)
N(4)	0.5852(4)	0.6512(4)	0.6419(3)	0.0291(12)
N(5)	0.4460(4)	0.6407(4)	0.9552(4)	0.0294(12)
C(1)	0.8568(5)	1.1133(5)	0.9974(4)	0.0241(16)
C(2)	0.7968(5)	1.1025(5)	1.1124(4)	0.0301(17)
C(3)	0.8555(6)	1.2073(5)	1.2344(5)	0.0352(17)
C(4)	0.9692(6)	1.3234(5)	1.2428(5)	0.0376(17)
C(5)	1.0299(6)	1.3362(5)	1.1301(5)	0.0364(17)
C(6)	0.9719(5)	1.2309(5)	1.0079(5)	0.0286(17)
C(7)	0.9131(5)	1.0887(5)	0.7951(4)	0.0269(17)
C(8)	0.9080(6)	1.0261(5)	0.6467(5)	0.0346(17)
C(9)	0.4804(5)	0.5939(5)	0.7189(4)	0.0326(17)
C(10)	0.5134(5)	0.6851(5)	0.8648(5)	0.0261(17)
C(11)	0.4679(5)	0.7269(5)	1.0970(4)	0.0315(17)
C(12)	0.6337(5)	0.7411(5)	1.1896(5)	0.0295(17)
O(2W)	0.0807(4)	0.3446(4)	0.5739(3)	0.0555(16)
Cl(1)	0.28610(15)	0.66129(14)	0.39418(13)	0.0466(5)

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

RESULTS AND DISCUSSION

Description of Crystal Structure

The molecular structure of the compound is shown in Fig. 1. Selected bond distances and angles are given in Table III.

The complex [Cu(glygly)(AMBZ)(H_2O)]Cl·H_2O (**1**) exhibits a slightly distorted square-pyramidal geometry around the copper(II) ion, in which the bidentate AMBZ and the bidentate dipeptide anion (glygly) are at the corners of the square. The AMBZ is coordinated to Cu through the NH_2 group and one nitrogen atom N(2) in the imidazole ring [Cu(1)–N(2) = 1.942(4) Å, Cu(1)–N(3) = 2.020(3) Å]. The glycylglycine anion is coordinated to Cu through the terminal NH_2 group and the carbonyl oxygen atom from the same glycine residue [Cu(1)–N(4) = 1.990(4) Å, Cu(1)–O(1) = 1.979(3) Å]. The apical position is occupied by a weakly bonded oxygen atom O(1W) of one water molecule. The axial Cu–O(1W) bond [Cu(1)–O(1W) = 2.298(4) Å] is

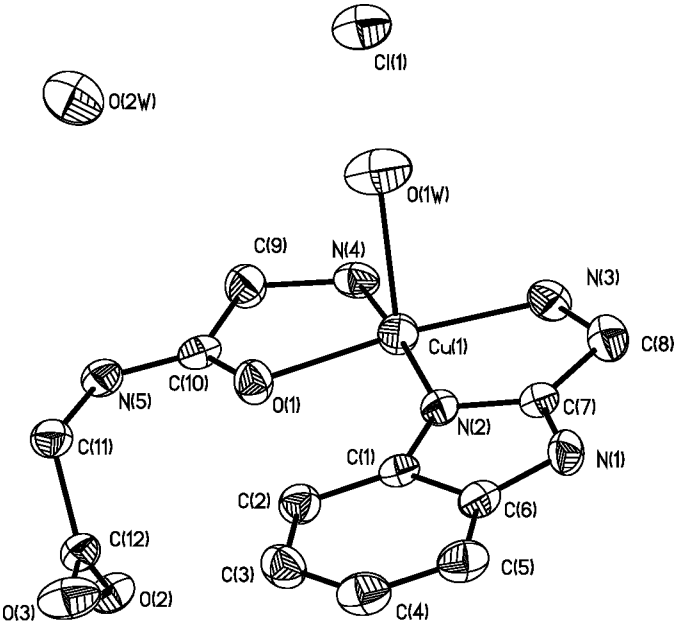

FIGURE 1 The ORTEP view of **1**, with hydrogen atoms omitted for clarity, showing the labeling and the 50% probability thermal ellipsoids.

TABLE III Selected bond lengths (Å) and angles (°) for **1**

Cu(1)–O(1)	1.979(3)	N(2)–Cu(1)–N(3)	84.17(14)	O(1W)–Cu(1)–N(2)	99.12(15)
Cu(1)–O(1W)	2.298(4)	O(1)–Cu(1)–N(2)	94.63(13)	O(1W)–Cu(1)–N(3)	86.62(13)
Cu(1)–N(2)	1.942(4)	N(3)–Cu(1)–N(4)	96.87(14)	O(1W)–Cu(1)–N(4)	89.83(14)
Cu(1)–N(3)	2.020(3)	O(1)–Cu(1)–N(4)	83.36(13)	O(1)–Cu(1)–O(1W)	99.68(13)
Cu(1)–N(4)	1.990(4)	O(1)–Cu(1)–N(3)	173.70(14)	N(2)–Cu(1)–N(4)	171.04(15)

TABLE IV Selected H-bond distances (Å) and angles (°) for **1**

D–H···A	*r(D–H)*	*r(H···A)*	*∠(D–H···A)*	*r(D···A)*	*Symmetry operation*
N(1)–H(1A)···O(2)	0.900	1.957	156.33	2.804	$-x+2, -y+2, -z+2$
N(3)–H(3A)···O(2W)	0.900	2.090	150.56	2.907	$-x+1, -y+1, -z+1$
N(3)–H(3B)···O(3)	0.900	2.240	145.73	3.027	$x, y, z-1$
N(4)–H(4A)···Cl(1)	0.900	2.438	156.05	3.280	
N(4)–H(4B)···Cl(1)	0.900	2.626	141.22	3.375	$-x+1, -y+1, -z+1$
N(5)–H(5A)···O(2)	0.900	1.951	166.77	2.834	$-x+1, -y+1, -z+2$
O(1W)–H(1C)···O(3)	0.850	2.140	124.02	2.709	$-x+1, -y+2, -z+2$
O(1W)–H(1B)···Cl(1)	0.820	2.386	169.51	3.195	
O(2W)–H(2Δ)···O(2)	0.850	2.590	105.00	2.933	$-x+1, -y+1, -z+2$
O(2W)–H(2B)···O(2)	0.850	2.500	113.00	2.933	$-x+1, -y+1, -z+2$
C(2)–H(2)···O(1)	0.930	2.590	128.00	3.247	
C(9)–H(9A)···Cl(1)	0.970	2.790	131.00	3.503	$-x+1, -y+1, -z+1$

0.32 Å longer than the Cu–O bond lengths in the basal plane. The metal lies 0.10 Å out of the least-squares basal plane, towards O(1W). The two chelating rings are almost coplanar; the dihedral angle between the best mean planes Cu(1)O(1)C(10)C(9)N(4) and Cu(1)N(3)C(8)C(7)N(2) is 3.7°. Usually the peptide is coordinated to a metal through a deprotonated amide nitrogen in ternary Cu(II) peptide complexes [11–16]. Here the carbonyl oxygen atom O(1) is preferred to the peptide nitrogen N(5) as a metal binding site at pHs where the amide proton is not dissociated, as in the dipeptide complex $[Cu(tach)(glygly)]^+$ [20].

Closer inspection of the structure reveals that the crystal packing is dominated by a network of intermolecular hydrogen contacts involving the water molecules, carboxylate oxygen atoms and Cl^- ions. Neighboring complex molecules are hydrogen bonded to each other through the carboxylate oxygen atoms from the glycylglycine anion to the amino nitrogen atom from AMBZ and to the amino nitrogen atom from the glycylglycine anion [N(5)–H(5A)···O*(2) = 2.83 Å, N(3)–H(3B)···O*(3) = 3.03 Å], forming an infinite chain along the *c*-axis (Fig. 2). Two Cl^- anions are hydrogen bonded to two opposite complex molecules through the N(4)–H(4A)···Cl(1), N(4)–H(4B)···Cl*(1), O(1W)–H(1B)···Cl*(1), C(9)–H(9A)···Cl(1) interactions. Hydrogen-bonding interactions involving the water molecule O(2W) and the carboxylate oxygen O(2) [N(1)–H(1A)···O*(2) = 2.80 Å, N(3)–H(3A)···O(2W) = 2.91 Å, O(2W)–H2A···O*(2) = 2.93 Å, (O2W)–H(2B)···O2 = 2.93 Å] involve different chains producing a three-dimensional network structure (Fig. 3).

IR Spectra

In the IR spectrum, an absorption at 3425 cm^{-1} corresponds to the presence of water. The peak at 3242 cm^{-1} is attributed to ν_s(NH) and $\nu_{as}(NH_2)$. The typical strong band at 1617 cm^{-1} is related to ν(C=O) of the glycylglycine moiety. The ν_{as}(COO) is assigned to the strong band at 1578 cm^{-1} whereas ν_s(COO) is attributed to the 1383 cm^{-1} peak. The peaks of ν(C=O) and ν_{as}(COO) overlap with the ν(ring) and the [δ(NH) + ν_s(C=N)] peaks of the AMBZ moiety. Two peaks at 1475 and 1383 cm^{-1} are due to the δ_{as} and δ_s of the methyl group. ν_s(C–N) and [δ(NH) (NH in-plane bending) + ν(C=N)] appear at 1019 and 1131 cm^{-1}, respectively. The strong peak at 776 cm^{-1} is attributed to the ν(C–H) of the phenyl ring. Other bands, possibly related to the compound, could be

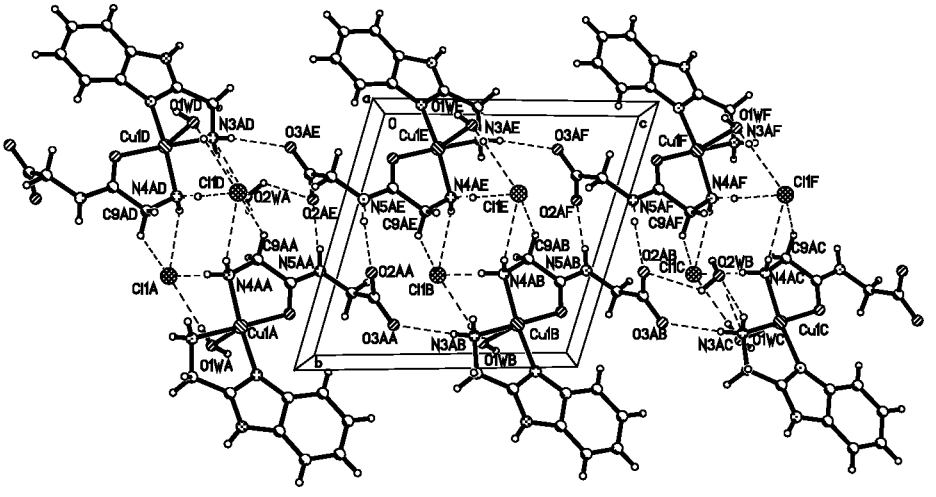

FIGURE 2 Hydrogen-bond network structure in **1**, showing an infinite chain along the *c*-axis.

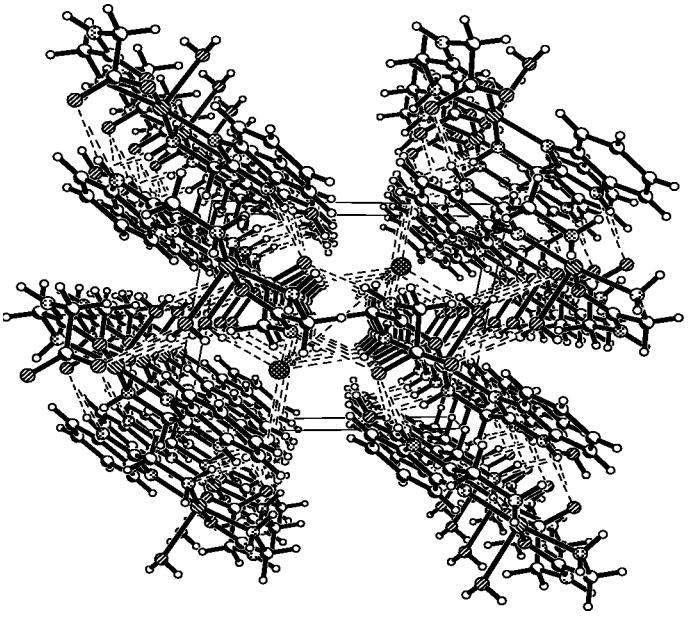

FIGURE 3 A view of the packing of **1** along the *b*-axis, showing a three-dimensional network structure.

tentatively assigned: 1545 cm^{-1} [ν Phe ring, ν(C–H)]; 1457 cm^{-1} [ν Phe ring, ν(C=C)]. These features are in agreement with the crystal structure.

Electronic Spectra

The d–d transition spectrum of the complex in MeOH presents a broad band centered at about 647 nm, suggestive of square-pyramidal geometry about Cu(II) [21]. The π–π*

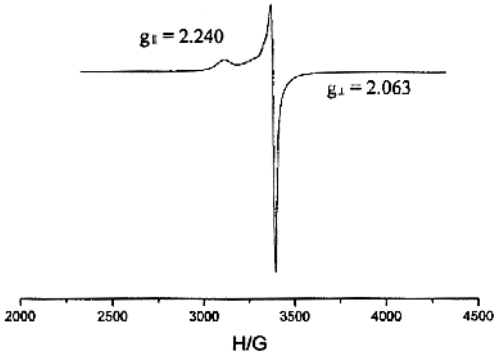

FIGURE 4 X-band ESR spectrum of **1** polycrystalline powder at 298 K.

intraligand transition bands involving the imidazole moiety and the benzene ring of the AMBZ ligand appear at 239 nm and 270 nm, respectively. The blue-shifted band at 275 nm associated with the imidazole shows clear evidence of C=N coordination to the copper center.

ESR Spectra

The X-band ESR spectrum of a polycrystalline powder of the ternary complex recorded at room temperature shows no hyperfine splitting with the values: $g_{\|} = 2.240$, and $g_{\perp} = 2.063$ (Fig. 4). These spectra are consistent with a square-pyramidal stereochemistry. The values of $g_{\|} > g_{\perp} > g_e$ imply that the 3d unpaired electron of the copper(II) ion should occupy the $d_{x^2-y^2}$ orbital. These results are in agreement with the symmetry of the copper derived from the X-ray structure determination.

Acknowledgments

This work was supported financially by the National Natural Science Foundation of China (Nos. 2017022 and 29831010), the Science and Technology Department of Jiangsu Province and the Center of Materials Analysis of Nanjing University.

Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC No. 218112 for compound **1**. Copies of this information can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

References

[1] G.L. Eichhorm, In: H. Sigel (Ed.), *Metal Ions in Biological Systems*, Vol. 10 (Marcel Dekker, New York, 1980), pp. 1–21.

[2] C. Helene and J.C. Maurizot, *CRC Crit. Rev. Biochem.* **10**, 213 (1981).
[3] H. Sigel, B.E. Fischer and B. Prijs, *J. Am. Chem. Soc.* **99**, 4489 (1977).
[4] H. Sigel and D.B. McCormick, *Acc. Chem. Res.* **3**, 201 (1970).
[5] J.M. Brown, L. Powers, B. Kincaid, J.A. Larrabee and T.G. Spiro, *J. Am. Chem. Soc.* **102**, 4210 (1980).
[6] A. Larrabee and T.G. Spiro, *J. Am. Chem. Soc.* **102**, 4217 (1980).
[7] I.S. de la Cueva, A.G. Sicilia, J.M. González, E. Bugella, A. Castiñeiras and J. Niclós-Gutiérrez, *Reactive Funct. Polym.* **36**, 211 (1998).
[8] N. Shahima Begum and H. Manohar, *J. Chem. Soc., Dalton Trans.* 2277 (1992).
[9] N. Shahima Begum, M. Damodara Poorjary and H. Manohar, *J. Chem. Soc., Dalton Trans.* 1507 (1989).
[10] P.J.M.W.L. Birker, H.M.J. Hendriks and J. Reedijk, *Inorg. Chim. Acta* **55**, L17 (1981).
[11] A. García-Raso, A. Terrón, J.J. Fiol, E. Molins and C. Miravitlles, *Polyhedron* **14**, 2537 (1995).
[12] A. García-Raso, A. Terrón, J.J. Fiol, B. Adrover, E. Molins and C. Miravitlles, *Polyhedron* **15**, 1829 (1996).
[13] A. García-Raso, A. Terrón, J.J. Fiol, B. Adrover, E. Molins and I. Mata, *J. Chem. Soc., Dalton Trans.* 1031 (1998).
[14] A. García-Raso, J.J. Fiol, B. Adrover, A. Caubet, E. Espinosa, I. Mata and E. Molins, *Polyhedron* **21**, 1197 (2002).
[15] A. García-Raso, J.J. Fiol, B. Adrover, V. Morono, I. Mata, E. Espinosa and E. Molins, *J. Inorg. Biochem.* **95**, 77 (2003).
[16] T. Yajima , M. Okajimaa, A. Odani and O. Yamauchi, *Inorg. Chim. Acta* **339**, 445 (2002).
[17] *SMART and SAINT: Software Reference Manuals, Version 6.22* (Bruker AXS Inc., Madision, WI, 2000).
[18] G.M. Sheldrick, *SADABS: Software for Empirical Absorption Correction* (University of Göttingen, Germany, 1996).
[19] *SHELXTL: Reference Manuals, Version 6.10* (Bruker AXS Inc., Madision, WI, 2000).
[20] X.S. Tan, Y. Fujii, T. Sato, Y. Nakano and M. Yashiro, *J. Chem. Soc., Chem. Commun.* 881 (1999).
[21] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn (Elsevier, New York, 1986).