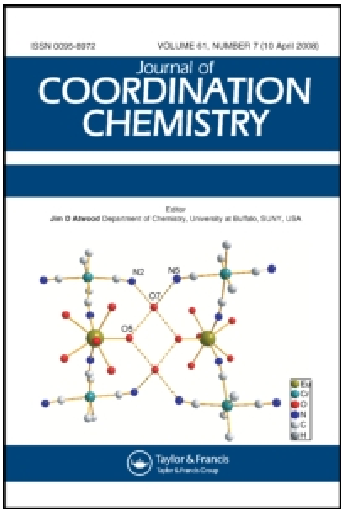

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Xu, Xing-You , Gao, Jian , Wang, Ming-Yan , Wei-Xing, Song, Hai-Bing and Wainwright, Kevin P.(2005) 'Synthesis, crystal structure and antimicrobial properties of a copper(II) complex of an unsymmetrical tripodal ligand', Journal of Coordination Chemistry, 58: 8, 669 — 676

To link to this Article: DOI: 10.1080/00958970500039256

URL: http://dx.doi.org/10.1080/00958970500039256

Journal of Coordination Chemistry
Vol. 58, No. 8, 20 May 2005, 669–676

Synthesis, crystal structure and antimicrobial properties of a copper(II) complex of an unsymmetrical tripodal ligand

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A new copper(II) complex of an unsymmetrical tripodal ligand (NN_2O222) derived from tris(2-aminoethylamine)amine (tren) by substitution of one aminoethyl group by an hydroxyethyl group has been synthesized and characterized by X-ray crystallographic methods as $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$ ($NN_2O222 = $ 2-[bis(2-aminoethyl)amino]ethanol; ImH = imidazole). Crystals of the complex are orthorhombic, space group $Pna2_1$, with $a = 29.983(10)$, $b = 15.568(5)$, $c = 8.127(3)$ Å. Two similar monometallic cations exist in the asymmetric unit and in each case the Cu(II) ion is five-coordinate with tetragonally distorted trigonal bipyramidal geometry. Variable-temperature magnetic measurements show that there is very weak antiferromagnetic interaction between the metal ions. Cyclic voltammetry indicates *quasi*-reversible Cu^{II}/Cu^{I} redox behavior at +44 mV *vs* SCE. An antimicrobial activity study found that the complex is active against *Candida albican*, *Staphylococcus aureus*, *Bacillus pumilus*, *Klebosiella pneumoniae* and *Escherichia coli*, but to no greater extent than $Cu(ClO_4)_2 \cdot 6H_2O$.

Keywords: Tripodal ligand; Copper(II); X-ray structure: Electrochemistry; Antimicrobial behavior

1. Introduction

Cu(II) complexes are of considerable interest because they can provide new materials with useful properties arising, for example, from magnetic exchange [1–3] and electrical conductivity [4]. Others show nonlinear optical [5] and antimicrobial activity [6,7]. In this context Song *et al.* [8] have suggested that fine-tuning of the stereochemical

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500039256

properties of such complexes may be possible by selecting from a family of unsymmetrical tripodal ligands derived from tris(2-aminoethylamine)amine (tren) either by altering the number of methylene groups in the arms of the tripod or by substituting one or more aminoalkyl groups by hydroxyalkyl groups. In this study we report the structure of a Cu(II) complex formed by the ligand NN_2O222, derived from tren by substitution of one aminoethyl group by a hydroxyethyl group. This ligand was first synthesized by Song *et al.* [8], who, on the basis of electronic spectroscopy, proposed that its hydrated Cu(II) complex had square pyramidal geometry in aqueous solution throughout the pH range 3–10, but did not report on the situation in the solid state. By using imidazole (ImH) as a fifth donor we have been able to crystallize the first Cu(II) complex of NN_2O222, $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$, and report that the stereochemistry at the Cu(II) center, in this complex, is closer to trigonal bipyramidal in both of the similar, but crystallographically independent, Cu(II) cations that constitute the asymmetric unit. We also report electrochemical, magnetic and antimicrobial activity of the complex. The interaction of imidazole with Cu(II) is known to be important in determining the activity of many metalloproteins [9,10] and is consequently a feature of interest in its own right.

2. Experimental

The ligand 2-[bis(2-aminoethyl)amino]ethanol (NN_2O222) was prepared according to a literature procedure [8]. All other chemicals were obtained from Aldrich and used without purification. Elemental analyses were determined with a Perkin-Elmer 240c instrument. IR spectra were measured (KBr disks) using a Nicolet 5DX FT-IR spectrophotometer. Solution electrical conductivity was measured using a BSD-A digital conductometer (Jiangsu, China) at *ca* 1.0×10^{-3} M in acetonitrile at 289 K. Cyclic voltammograms were obtained on a CHI660 electrochemical analyzer. ES mass spectra measurements were carried out on a LCQ System (Finngann MAT, USA) using methanol as mobile phase. Variable-temperature magnetic susceptibility data were obtained with a CHAN-2000 Faraday-type magnetometer.

2.1. *Synthesis of* $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) in methanol (20 cm^3) was added in portions to 15 cm^3 of a methanol solution containing NN_2O222 (0.147 g, 1 mmol). After stirring for 30 min, an aqueous solution containing imidazole (0.068 g, 1 mmol) was added, and the mixture refluxed for 2 h. The solution was filtered, and the blue product that precipitated from the cooled filtrate was filtered off, washed with methanol and dried in vacuum. Yield 42%; m.p. $>231°C$ (dec.). Anal. Calcd. for $C_9H_{21}Cl_2CuN_5O_{9.5}$(%): C, 22.23; H, 4.32; N, 14.41. Found: C, 22.51; H, 4.36; N, 14.46. IR (cm^{-1}): 3434s $\nu(OH)$; 3231, 3123m $\nu(NH_2)$; 1631, 1545m $\nu(ImH)$; 1089s $\nu(ClO_4)$; m/z(%) 245.1(94), 255.1(100), 323.0(92); Λ_M (CH_3CN): 234 $S\,cm^2\,mol^{-1}$. After collection of the precipitated product, the filtrate was set aside at ambient temperature and blue, single crystals suitable for X-ray structure determination were obtained by slow evaporation over 2 weeks.

2.2. *Crystal structure determination*

A blue, single crystal of dimensions 0.32 × 0.30 × 0.12 mm was mounted on a glass fiber. Crystal data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) over the range $1.36^\circ \leq \theta \leq 25.01^\circ$ with an ω scan mode. Data reduction and cell refinement were performed with Smart-CCD software. An absorption correction using SADABS software was applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXL-97 [11]. All H atoms were placed in calculated positions. Details of data collection and refinement, and crystallographic data, are summarized in table 1.

2.3. *Antimicrobial activity*

As a preliminary screen for antimicrobial activity, the complex $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$ was tested against standard strains of *Candida albicans* CMCC (F) 98 001, *Staphylococcus aureus* CMCC (B) 26 003, *Bacillus pumilus* CMCC (B) 63 202, *Klebosiella pneumoniae* CMCC (B) 46 117 and *Escherichia coli* CMCC (B) 44 102, using the modified agar diffusion method as described in the literature [12]. For comparison, the antimicrobial activity of $Cu(ClO_4)_2 \cdot 6H_2O$ was also tested. Nutrient agar was thawed by heating in a water bath, transferred to plates and frozen at 37°C. Test strains were spread on the agar surface and stainless steel tubes [7.8 mm (od) × 6 mm (id) × 10 mm] placed vertically on the plate; 0.04 cm^3 aliquots of a solution of the copper(II) compound, at various concentrations in DMF, were injected through the tubes. Treated plates were then allowed to incubate at 37°C for 24 h. The diameter of the inhibition zone around the injection point was measured

Table 1. Crystal data and refinement parameters for $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$.

Formula	$C_9H_{21}Cl_2CuN_5O_{9.5}$
M	485.75
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Orthorhombic, $Pna2_1$
Unit cell dimensions	$a = 29.983(10)$ Å
	$b = 15.568(5)$ Å
	$c = 8.127(3)$ Å
V	3794(2) Å^3
Z	4
Calculated density	1.701 g cm^{-3}
Absorption coefficient	1.489 mm^{-1}
$F(000)$	1992
Crystal size	0.32 × 0.30 × 0.12 mm
θ range for data collection	1.36 to 25.01°
Limiting indices	$-35 \leq h \leq 19$, $-17 \leq k \leq 18$, $-9 \leq l \leq 9$
Completeness to $\theta = 25.01$	99.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6537/314/553
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0787$, $wR_2 = 0.1885$
R indices (all data)	$R_1 = 0.1464$, $wR_2 = 0.2312$
Largest diff. peak and hole	0.850 and -0.491 e Å^{-3}

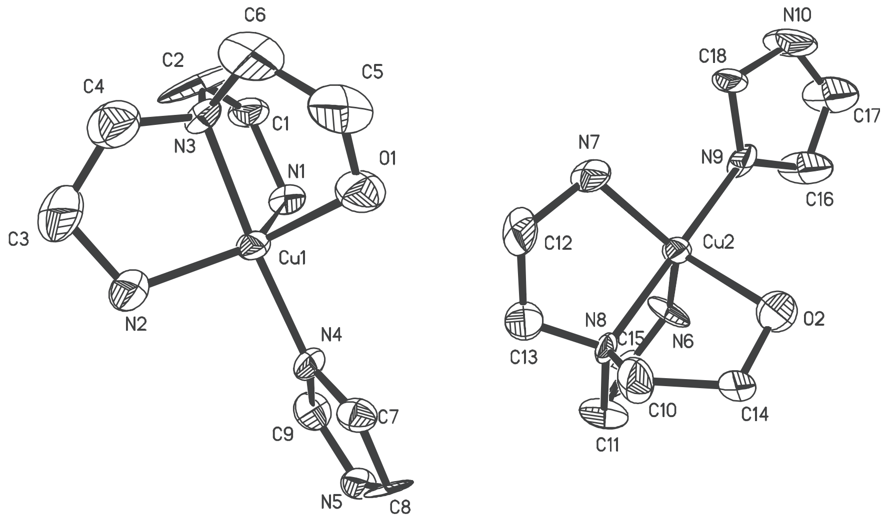

Figure 1. Perspective views of the $[(NN_2O222)Cu(ImH)]^{2+}$ cations showing the atom numbering scheme (ellipsoids at 30% probability). Molecule **a** is on the left and **b** on the right.

and the mean of three replicate determinations is reported. Blank tests showed that DMF alone does not affect the test organisms.

3. Results and discussion

3.1. *Spectroscopic studies*

The composition of the complex was established by elemental analysis, IR, electrical conductivity and ES-MS measurements. IR spectra exhibit absorption bands due to ImH, $-NH_2$ and –OH, which were found to be red-shifted relative to those of the free ligands, indicating coordination though the imidazole nitrogen atom and primary amine nitrogen and hydroxyl oxygen atoms of the multidentate. The strong, unsplit peak at $1088\,cm^{-1}$ shows that the ClO_4^- is uncoordinated. This was confirmed by the molar conductivity of the complex $[\Lambda_M\,(CH_3CN) = 234\,S\,cm^2\,mol^{-1}]$, which is indicative of a 1 : 2 electrolyte. In the ES-MS spectrum, strong peaks at m/z 245.1, 255.1 and 323.0 were observed, corresponding to $[(NN_2O222)Cu^{2+} + OH^- + H_2O]^+$, $[(NN_2O222)Cu^{2+} + CH_3CH_2O^-]^+$ and $[(NN_2O222)Cu(ImH)^{2+} + CH_3CH_2O^-]^+$.

3.2. *Crystal structure*

The crystal structure of the complex consists of $[(NN_2O222)Cu(ImH)]^{2+}$ cations, uncoordinated perchlorate ions and uncoordinated water molecules. In the asymmetric unit there exists two mononuclear cations $[(NN_2O222)Cu(ImH)]^{2+}$ (**a**) and $[(NN_2O222)Cu(ImH)]^{2+}$ (**b**). Perspective views of **a** and **b** are shown in figure 1 and selected bond lengths and angles are given in table 2. In both cations the Cu(II) ion is five-coordinate with an N_4O coordination environment. The geometric parameter τ,

Table 2. Selected bond distances (Å) and bond angles (°) for the complex.

Cu(1)–N(2)	1.935(4)	Cu(2)–N(9)	1.951(3)
Cu(1)–N(4)	1.947(2)	Cu(2)–N(8)	2.006(3)
Cu(1)–N(3)	2.017(3)	Cu(2)–N(7)	2.016(3)
Cu(1)–O(1)	2.097(5)	Cu(2)–N(6)	2.070(5)
Cu(1)–N(1)	2.175(4)	Cu(2)–O(2)	2.123(5)
N(2)–Cu(1)–N(4)	96.36(13)	N(9)–Cu(2)–N(8)	176.31(18)
N(2)–Cu(1)–N(3)	87.20(15)	N(9)–Cu(2)–N(7)	95.98(14)
N(4)–Cu(1)–N(3)	175.99(18)	N(8)–Cu(2)–N(7)	85.76(14)
N(2)–Cu(1)–O(1)	130.9(3)	N(9)–Cu(2)–N(6)	95.11(13)
N(4)–Cu(1)–O(1)	94.9(2)	N(8)–Cu(2)–N(6)	81.30(18)
N(3)–Cu(1)–O(1)	81.3(2)	N(7)–Cu(2)–N(6)	130.4(3)
N(2)–Cu(1)–N(1)	121.6(3)	N(9)–Cu(2)–O(2)	97.84(15)
N(4)–Cu(1)–N(1)	95.6(2)	N(8)–Cu(2)–O(2)	84.06(19)
N(3)–Cu(1)–N(1)	84.11(18)	N(7)–Cu(2)–O(2)	119.9(3)
O(1)–Cu(1)–N(1)	104.53(15)	N(6)–Cu(2)–O(2)	106.14(19)

which provides an indication of the degree of trigonality of the structure (equaling unity for D_{3h} symmetry and zero for C_{4v}), has been calculated according to the method of Addison *et al.* [13] as 0.75 and 0.77 for Cu(1) and Cu(2), respectively. This indicates that the geometrical disposition of the donor atoms around Cu(1) and Cu(2) is better described as distorted trigonal bipyramidal, with the tertiary amine and the imidazole occupying the axial sites, in both cases, rather than distorted square pyramidal. The angles subtended at Cu(II) by the axial ligands are 176.0(2) and 176.3(2)° in **a** and **b**, respectively. Interestingly, the manner of the distortion towards square planar geometry differs for each cation. In the case of cation **a**, it occurs in the direction of N(1), with the Cu(1)–N(1) distance elongated to 2.175(4) Å, compared to Cu(1)–N(2) at 1.935(4) Å, and the N(2)–Cu(1)–O(1) angle is the largest of the three equatorial angles at 130.9(3)°. In the case of cation **b**, the smaller tetragonal distortion (larger τ value) is towards the oxygen donor, as suggested by Song *et al.* [8] on the grounds that, for Cu(II), –OH is likely to be a poorer ligand than $-NH_2$. The Cu(2)–O(2) separation is 2.123(5) Å, compared to 2.097(5) Å in cation **a**, and the N(6)–Cu(2)–N(7) angle is the largest of the equatorial angles at 130.4(3)°. Cu(1) and Cu(2) lie above their respective trigonal planes (towards imidazole), by 0.2021 and 0.2240 Å. The distance between Cu(1) and Cu(2) is 7.145 Å, suggesting almost no interaction between them.

3.3. *Antimicrobial activity*

In a preliminary screen, $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ were investigated for antimicrobial activity. Values for the diameter of the inhibition zones for the growth of various microorganisms, created in response to treatment with the compounds, dissolved in DMF at varying concentrations, are listed in table 3. These data show that, to differing extents, the compounds tested exhibited antibacterial activity against all the bacterial organisms examined. The compounds became more active as their concentration increased, and for $[(NN_2O222)Cu(ImH)]\ (ClO_4)_2 \cdot 0.5H_2O$ the highest antimicrobial activity was against *E. coli*. $Cu(ClO_4)_2 \cdot 6H_2O$ exhibited somewhat higher antimicrobial activity, consistent with a report on a related complex [12].

Table 3. Diameter of the bacterial growth inhibition zones.

		Diameter of inhibition zone (mm)				
Compound	Concentration (mg/mL)	*Candida albicans*	*Staphylococcus aureus*	*Bacillus pumilus*	*Klebosiella pneumoniae*	*Escherichia coli*
$[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$	15.0	22.9	22.4	21.6	22.0	25.5
	7.5	18.3	20.0	20.2	19.1	23.8
	3.8	15.2	16.6	18.8	17.6	21.1
	1.9	14.4	13.1	14.9	16.1	19.5
$Cu(ClO_4)_2 \cdot 6H_2O$	15.0	24.1	29.3	26.4	23.2	25.3
	7.5	20.8	27.1	25.6	22.8	23.4
	3.8	17.3	25.3	23.1	20.6	20.1
	1.9	16.4	20.5	20.1	18.9	19.8

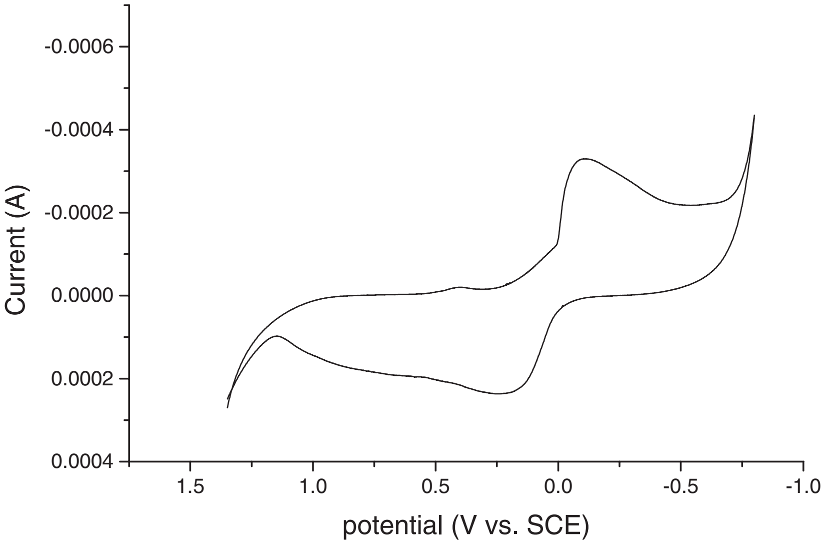

Figure 2. Cyclic voltammogram of $[(NN_2O222)Cu(ImH)]^{2+}$ at a scan rate of 1 mV s^{-1}.

3.4. *Redox behavior*

Cyclic voltammetry measurements for $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$ were carried out in aqueous sodium dihydrogen phosphate and disodium hydrogen phosphate buffer solution, at pH 6.8, using a three-electrode cell equipped with a glassy carbon working electrode, a saturated calomel reference electrode and a platinum wire counter electrode. The working electrode was polished successively with fine emery paper and aluminum oxide powder on chamois leather before use. It was then activated in 0.01 M H_2SO_4 solution and sonicated in water for 20 s. Cyclic voltammograms were recorded in the potential range 1.4 to -0.8 V at a scan rate of 1 m V s^{-1}. Figure 2 shows that $[(NN_2O222)Cu(ImH)]^{2+}$ undergoes a single-electron transfer process, assigned to the Cu(II)/Cu(I) couple. Cyclic voltammetric data for the redox couple are summarized in table 4. The peak separation ($\Delta E = 305$ mV) and the I_{pa}/I_{pc} value (0.88) indicate *quasi*-reversible electrode behavior.

Table 4. Cyclic voltammetric data for $[(NN_2O222)Cu(ImH)]^{2+}$.

Redox couple	E_{pa} (V)	E_{pc} (V)	ΔE (mV)	$E_{1/2}$ (mV)	I_{pa}/I_{pc}
Cu^{II}/Cu^{I}	0.197	−0.108	305	44.5	0.88

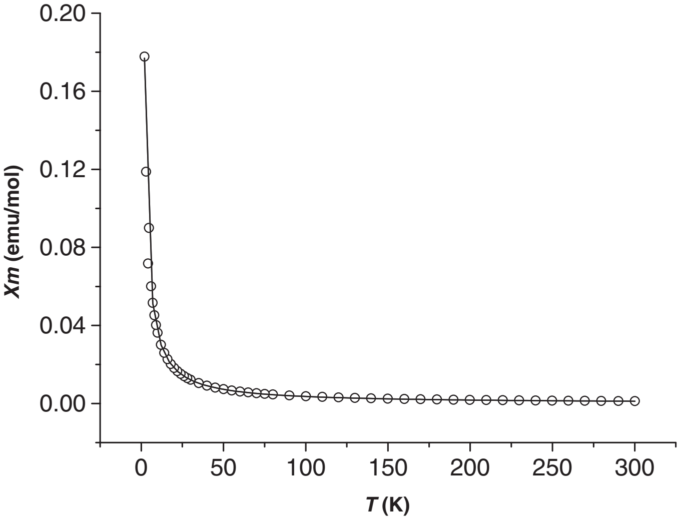

Figure 3. Temperature dependence of the magnetic susceptibility of $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$.

3.5. *Magnetic properties*

Molar magnetic susceptibilities for $[(NN_2O222)Cu(ImH)](ClO_4)_2 \cdot 0.5H_2O$ were measured in the temperature range 2–300 K. The temperature variation is shown in figure 3. The data best fit (fitting constant $F = 9.1 \times 10^{-6}$, correlation coefficient $R = 0.993$) the Curie–Weiss formula, $\chi_m = C/(T - \theta)$, with $C = 0.36479\,\text{emu mol}^{-1}$ and $\theta = -0.0642\,\text{K}$. This indicates only weak antiferromagnetic exchange between the Cu(II) centers.

Supplementary data

Crystallographic data for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 249266. 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 or http:\\www.ccdc.cam.ac.uk).

Acknowledgements

This project was supported by the National Natural Science Foundation of China (No. 50372028).

References

[1] R. Maurya, P. Sharma, D. Sutradhar, *Synth. React. Inorg. Met. Org. Chem.*, **33**, 669 (2003).

[2] T.S. Kassem, M.A. El-Sayed, H.M. Refaat, A. El-Dissouky, *Synth. React. Inorg. Met. Org. Chem.*, **32**, 1769 (2002).

[3] Y.T. Li, C.W. Yan, C.Y. Zhu, H.S. Guan, *Synth. React. Inorg. Met. Org. Chem.*, **34**, 1165 (2004).

[4] Y. Aydogdu, F. Yakuphanoglu, A. Aydogdu, E. Tas, A. Cukurovali, *Mater. Lett.*, **57**, 3755 (2003).

[5] H.Y. Bie, J.H. Yu, J.Q. Xu, J. Lu, Y. Li, X.B. Cui, X. Zhang, Y.H. Sun, L.Y. Pan, *J. Mol. Struct.*, **660**, 107 (2003).

[6] K. Nomiya, A. Yoshizawa, N.C. Kasuga, H. Yokoyama, S. Hirakawa, *Inorg. Chim. Acta*, **357**, 1168 (2004).

[7] A. Valent, M. Melnik, D. Hudecová, B. Dudová, R. Kivekäs, M.R. Sundberg, *Inorg. Chim. Acta*, **340**, 15 (2002).

[8] B. Song, J. Reuber, C. Ochs, F.E. Hahn, T. Lügger, C. Orvig, *Inorg. Chem.*, **40**, 1527 (2001).

[9] J.L. Pierre, P. Chautemps, S. Refaif, C. Beguin, A.E. Marzouki, G. Serratrice, E. Saint-Aman, P. Rey, *J. Am. Chem. Soc.*, **117**, 1965 (1995).

[10] P.K. Coughlin, S.J. Lippard, A.E. Martin, J.E. Bulkowski, *J. Am. Chem. Soc.*, **102**, 7616 (1980).

[11] G.M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).

[12] N. Raman, A. Kulandaisamy, K. Jeyasubramanian, *Synth. React. Inorg. Met. Org. Chem.*, **32**, 1583 (2002).

[13] A.W. Addison, T.N. Rao, J. Reedijk, J. Rijn, G.C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1349 (1984).

[14] X.Y. Xu, T. Zheng, W.X. Ma, A. Khaled, M.X. Zhang, Q.L. Liu, S.R. Grguric, V.M. Dinovic, G.N. Kaluderovic, T.J. Sabo, *J. Coord. Chem.*, **55**, 711 (2002).