

Synthesis and Crystal Structure of Manganese(II) Bipyridine Carboxylato Complexes: $[(\text{bipy})_2\text{Mn}^{\text{II}}(\mu\text{-C}_2\text{H}_5\text{CO}_2)_2\text{Mn}^{\text{II}}(\text{bipy})_2](\text{ClO}_4)_2$ and $[\text{Mn}^{\text{II}}(\text{ClCH}_2\text{CO}_2)(\text{H}_2\text{O})(\text{bipy})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (bipy = 2,2'-bipyridine)

Cungen Zhang^{1), a, b, *} and Christoph Janiak^{a, *}

^a Freiburg, Institut für Anorganische und Analytische Chemie der Universität

^b Shanghai/P.R. China, Chemistry Department, Shanghai Jiaotong University

Received January 26th, 2001.

Dedicated to Professor Erwin Riedel on the Occasion of his 70th Birthday

Abstract. Two manganese(II) bipyridine carboxylate complexes, $[(\text{bipy})_2\text{Mn}^{\text{II}}(\mu\text{-C}_2\text{H}_5\text{CO}_2)_2\text{Mn}^{\text{II}}(\text{bipy})_2](\text{ClO}_4)_2$ (**1**), and $[\text{Mn}^{\text{II}}(\text{ClCH}_2\text{CO}_2)(\text{H}_2\text{O})(\text{bipy})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2**) were prepared. **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.604(3)$, $b = 12.062(3)$, $c = 13.471(3)$ Å, $\alpha = 112.47(2)$, $\beta = 93.86(2)$, $\gamma = 92.87(3)^\circ$, $V = 1211.1(6)$ Å³ and $Z = 1$. In the dimeric, cationic complex with a crystallographic center of symmetry two 2,2'-bipyridine molecules chelate each manganese atom. These two metal fragments are then bridged by two propionate groups in a *syn-anti* conformation. The Mn...Mn distance is 4.653 Å. **2** crystallizes in the mono-

clinic space group $P2_1/c$ with $a = 9.042(1)$, $b = 13.891(1)$, $c = 21.022(3)$ Å, $\beta = 102.00(1)^\circ$, $V = 2569.3(5)$ Å³ and $Z = 4$. **2** is a monomeric cationic complex in which two bipyridine ligands chelate the manganese atom in a *cis* fashion. A chloroacetato and an aqua ligand complete the six-coordination. Only in **2** is the intermolecular packing controlled by weak π -stacking besides C-H... π contacts between the bipyridine ligands.

Keywords: Manganese; 2,2'-Bipyridine ligand; Carboxylato ligands; Crystal structure; Photosystem II

Synthese und Kristallstruktur von Mangan(II)-Bipyridin-Carboxylato-Komplexen: $[(\text{bipy})_2\text{Mn}^{\text{II}}(\mu\text{-C}_2\text{H}_5\text{CO}_2)_2\text{Mn}^{\text{II}}(\text{bipy})_2](\text{ClO}_4)_2$ und $[\text{Mn}^{\text{II}}(\text{ClCH}_2\text{CO}_2)(\text{H}_2\text{O})(\text{bipy})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (bipy = 2,2'-Bipyridin)

Inhaltsübersicht. Es wurden zwei Mangan(II)-Bipyridin-Carboxylato Komplexe $[(\text{bipy})_2\text{Mn}^{\text{II}}(\mu\text{-C}_2\text{H}_5\text{CO}_2)_2\text{Mn}^{\text{II}}(\text{bipy})_2](\text{ClO}_4)_2$ (**1**) und $[\text{Mn}^{\text{II}}(\text{ClCH}_2\text{CO}_2)(\text{H}_2\text{O})(\text{bipy})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2**) dargestellt. **1** kristallisiert in der triklinen Raumgruppe $P\bar{1}$ mit $a = 8.604(3)$, $b = 12.062(3)$, $c = 13.471(3)$ Å, $\alpha = 112.47(2)$, $\beta = 93.86(2)$, $\gamma = 92.87(3)^\circ$, $V = 1211.1(6)$ Å³ und $Z = 1$. In dem dimeren, kationischen Komplex mit einem kristallographischen Inversionszentrum chelatisieren zwei 2,2'-Bipyridinmoleküle jedes Manganatom. Diese beiden Metallfragmente werden dann von zwei Propionatgruppen in *syn-anti*-Konformation verbrückt. Der

Mn...Mn-Abstand beträgt 4,653 Å. **2** kristallisiert in der monoklinen Raumgruppe $P2_1/c$ mit $a = 9,042(1)$, $b = 13,891(1)$, $c = 21,022(3)$ Å, $\beta = 102,00(1)^\circ$, $V = 2569,3(5)$ Å³ und $Z = 4$. **2** ist ein monomeres kationischer Komplex in dem zwei Bipyridinliganden das Manganatom in *cis*-Anordnung chelatisieren. Ein Chloracetato- und ein Aqualligand vervollständigen die sechsfache Koordination. Nur in **2** wird die intermolekulare Packung durch schwache π -Stapelwechselwirkung neben C-H... π -Kontakten kontrolliert.

Introduction

Manganese complexes have drawn great interests in recent years because they can serve as models for the active sites of manganese-containing metal-enzymes such as manganese superoxide dismutase [1], manganese catalase [2], manganese peroxidase [3], manga-

nese ribonucleotide reductase (RR) [4], and photosystem II (PS II) [5]. Structural information on PS II is still limited by the lack of suitable crystals. EXAFS and XANES studies suggest that PS II has two di- μ -oxo manganese dimers connected at one end by two carboxylato ligands [5]. It is reported that carboxylato bridged dimanganese centers that catalyze the decomposition of hydrogen peroxide also appear to be in the active sites of pseudocatalase from *Lactobacillus plan-*

* Dr. C. Zhang, Prof. Dr. Chr. Janiak
Institut für Anorganische und Analytische Chemie
Universität Freiburg
Albertstr. 21
D-79104 Freiburg
E-mail: cungen@uni-freiburg.de, janiak@uni-freiburg.de

¹⁾ Dr. Zhang is on leave from the Chemistry Department of Shanghai Jiaotong University, Shanghai 200240, People's Republic of China.

tarum [6] and catalase from *Thermus thermophilus* [7]. It has been proven by X-ray crystal structure analysis that the active center of RR from *Escherichia coli* also consists of two Mn^{II} atoms which are connected by two carboxylato groups of glutamate residues at a separation of 3.6 Å [8]. Furthermore, it has been revealed by recent biological studies that carboxylato-bridged dimanganese(II) units play key roles also in some non-redox metal-enzymes such as arginase [9], enolase [10], ribonuclease H of HIV 1 reverse transcriptase [11], inorganic pyrophosphatase from *Saccharomyces cerevisiae* [12], DNA polymerase I from *E. coli* [13], and fructose-1,6-bisphosphatase [14]. Recently, two dimanganese(II) carboxylato bridged bipyridine complexes have appeared in which the Mn atoms are bridged by two large carboxylato ligands [15, 16]. In this paper, we report the preparation and crystal structure of a propionato-bridged dinuclear manganese(II) complex [(bipy)₂Mn^{II}(μ-C₂H₅CO₂)₂-Mn^{II}(bipy)₂](ClO₄)₂ **1**, and a monomeric complex [Mn^{II}(ClCH₂CO₂)(H₂O)(bipy)₂]ClO₄ · H₂O **2**.

Table 1 Crystal data for compounds **1** and **2**

Compound	1	2
Empirical formula	C ₄₆ H ₄₂ Cl ₂ Mn ₂ N ₈ O ₁₂	C ₂₂ H ₂₂ Cl ₂ MnN ₄ O ₈
Formula weight/g mol ⁻¹	1079.66	596.28
Color/shape	yellow/prismatic	yellow/prismatic
Temperature/K	293(2)	289(2)
Crystal system	triclinic	monoclinic
Space group	P $\bar{1}$	P2 ₁ /c
<i>a</i> /Å	8.604(3)	9.042(1)
<i>b</i> /Å	12.062(3)	13.819(1)
<i>c</i> /Å	13.471(3)	21.022(3)
α /°	112.47(2)	90
β /°	107.405(15)	102.00(1)
γ /°	92.87(3)	90
Volume/Å ³	1211.1(6)	2569.3(5)
Z	1	4
D _{calc} /g cm ⁻³	1.480	1.541
μ (Mo-K α)/cm ⁻¹	7.02	7.75
<i>F</i> (000)	554	1220
Crystal size/mm ³	0.39 × 0.23 × 0.22	0.50 × 0.36 × 0.32
2 θ max/°	50.04	51
Reflection collected	6249	5502
Independent reflections	4188 (<i>R</i> _{int} = 0.022)	4779 (<i>R</i> _{int} = 0.0182)
Absorption correction	empirical	empirical
Max. and min. transmission	1.000 and 0.475	0.7931 and 0.7280
Data/restraints/parameters	4177/11/316	4779/6/351
Goodness-of-fit on <i>F</i> ²	1.052	1.052
Final <i>R</i> indices	<i>R</i> 1 = 0.0612,	<i>R</i> 1 = 0.0390,
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> 2 = 0.1554	<i>wR</i> 2 = 0.0818
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0879,	<i>R</i> 1 = 0.0737,
	<i>wR</i> 2 = 0.1872	<i>wR</i> 2 = 0.0891
Maximum, minimum $\Delta\rho/e\text{Å}^{-3}$	0.505 and -0.354	0.286 and -0.258

Table 2 Hydrogen bonding interactions in **2**

D-H...A	D-H	H...A	D...A	D-H...A
O8W-H8A...O2	0.83(1)	1.88(1)	2.697(4)	167(3)
O3-H3A...O2	0.82(1)	1.89(1)	2.675(4)	160(3)
O8W-H8B...O5	0.82(1)	2.10(1)	2.913(4)	170(5)
O3-H3B...O8W_3	0.82(1)	1.90(1)	2.704(4)	168(3)

Symmetry transformation 3 = 1 - *x*, 2 - *y*, -*z*

Experimental

C, H and N analyses were carried out with a Perkin-Elmer CHN-Analyser Model 240.

[Mn(bipy)₂(μ-C₂H₅CO₂)₂Mn(bipy)₂](ClO₄)₂ (**1**)

To an ethanol solution (20 ml) of manganese perchlorate (3.60 g, 10 mmol) was added an ethanolic solution (10 ml) of 2,2'-bipyridine (3.12 g, 20 mmol) with stirring for 10 min. The solution turned yellow. Then, to the mixture was added an ethanolic solution (10 ml) of propionic acid (0.58 g, 10 mmol) and triethylamine (1.00 g, 10 mmol). The mixture was heated to 60 °C and stirred for 2 h. Yellow crystals were obtained by slow evaporation of the solvent. Yield 4.8 g (90%).

Calcd for C₄₆H₄₂Cl₂Mn₂N₈O₁₂ (1079.66): C 51.17, H 3.92, N 10.38. Found C 51.44, H 4.02, N 10.41%. (**Caution:** perchlorate salts may be explosive and only small amount should be applied).

[Mn^{II}(ClCH₂CO₂)(H₂O)(bipy)₂]ClO₄ · H₂O (**2**)

To an aqueous solution (20 ml) of manganese perchlorate (3.60 g, 10 mmol) was added an aqueous solution (10 ml) of 2,2'-bipyridine (3.12 g, 20 mmol) with stirring for 10 min. The solution turned yellow. Then, to the mixture was added an aqueous solution (10 ml) of (mono)chloroacetic acid (0.95 g, 10 mmol) and sodium hydroxide (0.40 g, 10 mmol). The mixture was heated to 60 °C and stirred for 2 h. Yellow crystals were obtained by slow evaporation of the solvent. Yield 5.3 g (90%).

Calcd for C₂₂H₂₂Cl₂MnN₄O₈ (596.28): C 44.31, H 3.72, N 9.40. Found C 44.53, H 3.92, N 9.11 (**Caution:** perchlorate salts may be explosive and only small amount should be applied).

Structure Determinations

Data were collected by the ω -scan method with Mo-K α radiation (λ = 0.71073 Å) and the use of a graphite monochro-

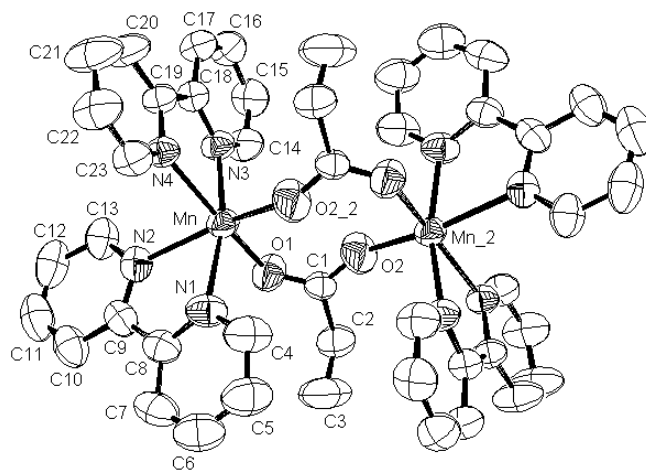


Fig. 1 Molecular structure of the dinuclear complex cation in **1**; hydrogen atoms have been omitted for clarity; selected distances/Å and angles/°

Mn1-O1 2.119(3), Mn1-O2_2 2.107(4), Mn1-N1 2.248(4), Mn1-N2 2.305(4), Mn1-N3 2.258(4), Mn1-N4 2.269(3), O1-Mn1-O2_2 102.3(1), N1-Mn1-N2 71.3(2), N3-Mn1-N4 71.8(1) (symmetry equivalent position _2 = -*x*, 1-*y*, -*z*)

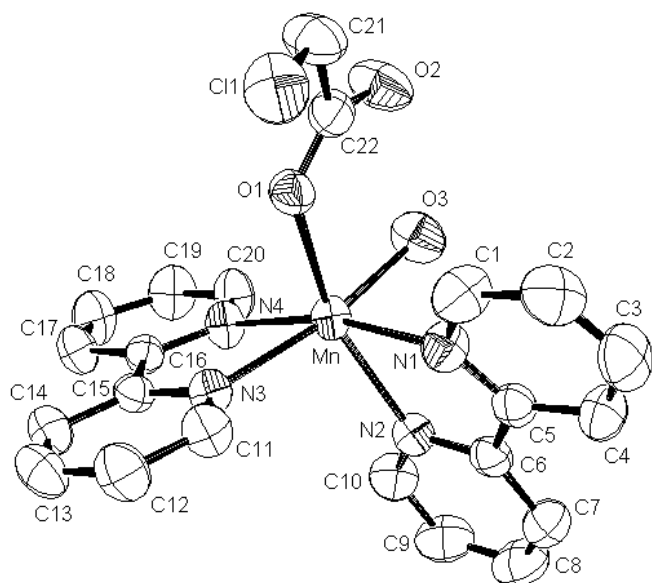


Fig. 2 Molecular structure of the complex cation in **2**; hydrogen atoms have been omitted for clarity; selected distances/Å and angles/°

Mn–O1 2.159(2), Mn–O3 2.171(2), Mn–N1 2.267(2), Mn–N2 2.265(2), Mn–N3 2.218(2), Mn–N4 2.270(2), O1–Mn–O3 88.48(9), O1–Mn–N2 159.97(8), O3–Mn–N3 166.28(9), N1–Mn–N2 72.22(8), N3–Mn–N4 72.78(8).

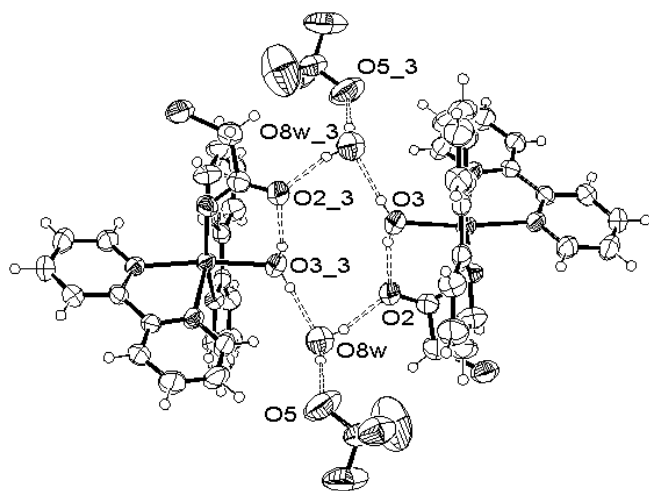


Fig. 3 Hydrogen bonding scheme in **2** (symmetry equivalent position 3 = 1 – x, 2 – y, –z).

mator on a Siemens Smart CCD (for **1**) and a Bruker P4 (for **2**) four-circle diffractometer. The structures were solved by direct methods (SHELXS-97) [17]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [18]. All non-hydrogen positions were found and refined with anisotropic temperature factors. The hydrogen atoms were placed at calculated positions using appropriate riding models and an isotropic temperature factor of $B_{\text{eq}}(\text{H}) = 1.2 B_{\text{eq}}(\text{C})$. The H atoms on the water molecule of **2** were found from a difference Fourier synthesis and refined isotropically with free temperature factors. Crystal data are

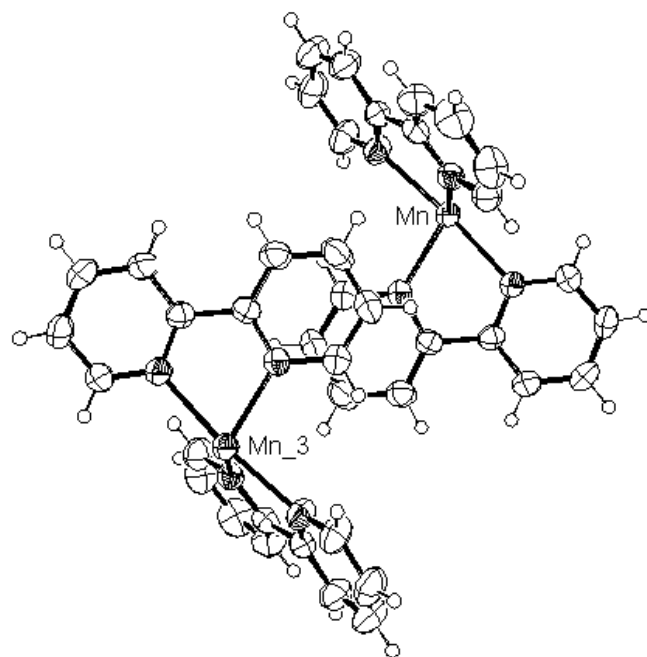


Fig. 4 Intermolecular weak p-stacking and C–H... π contacts between the bipyridine ligands in **2**; only the Mn(bipy)₂ fragment is shown for clarity (symmetry equivalent position 3 = –x, 1 – y, –z).

listed in Table 1. Graphics were obtained with ORTEP 3 for Windows [19]. Hydrogen bonding computations for the crystal structure discussion were carried out with PLATON for Windows [20]. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. CCDC-158891 for **1**, CCDC-158892 for **2**).

Results and Discussion

The crystal structure of **1** consists of a dinuclear dicationic complex of formula $[\text{Mn}(\text{bipy})_2(\mu\text{-C}_2\text{H}_5\text{CO}_2)_2\text{Mn}(\text{bipy})_2]^{2+}$ with two perchlorate counter anions, as shown in Fig. 1. The two manganese fragments in the dinuclear or dimeric complex are related by a crystallographic inversion center. The two metal atoms are bridged by two propionate groups. Compound **1** represents just the third structurally characterized dinuclear, dicarboxylate-bridged Mn(bipy)₂ complex [15, 21]. Each manganese atom has a six-coordination with the two bipyridine molecules coordinating to the metal atom in the *cis*-manner having an average bite angle of 71.5°. *Cis*-arrangement and bite angle are as seen e.g. in $[\text{Mn}(\text{N}_3)_2(5,5'\text{-diaminobipy})_2]$ [22] and in $[\text{Mn}(\text{NCS})_2(\text{bipy})_2]$ [23]. As in these complexes, the Mn–N(bipy) bonds in **1** *trans* to the oxygen atom of the carboxylate group also show some lengthening. The propionate ligands bridge the two manganese atoms in a *syn-anti* fashion which is comparable to $[\text{Mn}(\text{bipy})_2(\mu\text{-C}_6\text{H}_5\text{CO}_2)_2\text{Mn}(\text{bipy})_2]^{2+}$ [15] and the unpublished compound, $[\text{Mn}(\text{bipy})_2(\mu\text{-CH}_3\text{CO}_2)_2\text{Mn}(\text{bipy})_2]^{2+}$ [16]. The non-

bonding interatomic Mn···Mn separation within the dimeric cation in **1** is 4.653 Å, a little bit longer than that found in $[\text{Mn}(\text{bipy})_2(\mu\text{-C}_6\text{H}_5\text{CO}_2)_2\text{Mn}(\text{bipy})_2]^{2+}$ (4.51 Å) and $[\text{Mn}(\text{bipy})_2(\mu\text{-CH}_3\text{CO}_2)_2\text{Mn}(\text{bipy})_2]^{2+}$ (4.583 Å). This agrees with reports that *syn-anti* carboxylato bridges yield an expanded dimetallic center relative to the *syn-syn* carboxylato bridging mode [16]. No π -stacking or significant C–H··· π contacts between the bipyridine ligands are evident in the crystal packing of **1**, contrary to what is often found for aromatic nitrogen containing ligands [24].

Compound **2** contains mononuclear cationic manganese complexes. The two bipyridine ligands chelate the manganese atom again in a *cis* fashion. A water molecule and a chloroacetato group complete the six-fold coordination geometry of the metal atom (Fig. 2). The Mn–N bond *trans* to the aqua ligand is somewhat shortened. The coordination is significantly distorted from a pseudo-octahedral ligand arrangement. Hydrogen bonding interactions between aqua ligands, water molecules, chloroacetato groups, and the free perchlorate anions combine two complex molecules as shown in Fig. 3 and Table 2 [25]. The intermolecular packing is further controlled by weak π -stacking and C–H··· π contacts between the bipyridine ligands as illustrated in Fig. 4 [24, 26].

Acknowledgements. C. Z. thanks the Alexander von Humboldt Foundation for the award of a postdoctoral fellowship. We appreciate the continuous support of the Fonds der Chemischen Industrie and the DFG through grant Ja466/10-1.

References

- [1] W. C. Stallings, K. A. Patridge, R. K. Strong, M. L. Ludwig, *J. Biol. Chem.* **1985**, 260, 16424.
- [2] J. E. Halm, C. J. Bender, *J. Am. Chem. Soc.* **1988**, 110, 7554.
- [3] H. Wariishi, L. Akileswaran, M. H. Gold, *Biochem.* **1988**, 27, 5365.
- [4] V. L. Pecoraro, *Manganese Redox Enzymes*; Verlag Chemie: New York, 1992.
- [5] J. Limburg, J. S. Vrettos, L. M. Liable-Sands, A. L. Rheingold, R. H. Crabtree, G. W. Brudvig, *Science* **1999**, 283, 1524. C. W. Hoganson, G. T. Babcock, *Science* **1997**, 277, 1953. V. K. Yachandra, V. J. DeRose, M. J. Latimer, I. Mukerji, K. Sauer, M. P. Klein, *Science*, **1993**, 260, 675.
- [6] G. S. Waldo, J. E. Penner-Hahn, *Biochem.* **1995**, 34, 1507.
- [7] S. V. Khangulov, V. V. Barynin, N. V. Voevodskaya, A. I. Grebenko, *Biochim. Biophys. Acta* **1990**, 1020, 305.
- [8] M. Atta, P. Nordlund, A. Aberg, H. Eklund, M. Fontecave, *J. Biol. Chem.* **1992**, 267, 20682.
- [9] R. S. Reczkowski, D. E. Ash, *J. Am. Chem. Soc.* **1992**, 114, 10992.
- [10] R. R. Poyner, G. H. Reed, *Biochem.* **1992**, 31, 7166.
- [11] J. F. Davies, Z. Hostomska, Z. Hostomsky, S. R. Jordan, D. A. Matthews, *Science* **1991**, 252, 88.
- [12] B. S. Cooperman, A. A. Baykov, R. Lahti, *Trends Biochem. Sci.* **1992**, 17, 262.
- [13] L. S. Beese, J. M. Friedman, T. A. Steitz, *Biochem.* **1993**, 32, 14095.
- [14] Y. Zhang, J. Y. Liang, S. Huang, H. Ke, W. N. Lipscomb, *Biochem.* **1993**, 32, 1844.
- [15] B. Albela, M. Corbella, J. Ribas, I. Castro, J. Sletten, H. Stoeckli-Evans, *Inorg. Chem.* **1998**, 37, 788.
- [16] R. L. Rardin, W. B. Tolman, S. J. Lippard, *New J. Chem.* **1991**, 15, 417 and reference to G. Christou unpublished work cited therein.
- [17] G. M. Sheldrick, *SHELXS-97, Programs for the Solution of Crystal Structures*, University of Göttingen, Germany, 1997.
- [18] Sheldrick, G. M. *SHELXL-97, Programs for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
- [19] M. N. Burnett, C. K. Johnson, *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-6895, 1996. L. J. Farrugia, *ORTEP 3 for Windows*, Version 1.0.1 β , University of Glasgow, 1997. L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, 30, 565.
- [20] A. L. Spek, *Acta Crystallogr.* **1990**, A46, C34. PLATON Version 29-11-98. Windows implementation: L. J. Farrugia, University of Glasgow, 1998.
- [21] P.-R. Wie, Q. Li, W.-P. Leung, T. C. W. Mak, *Polyhedron* **1997**, 16, 897.
- [22] C. Janiak, S. Deblon, H.-P. Wu, M. J. Kolm, P. Klüfers, H. Piotrowski, P. Mayer, *Eur. J. Inorg. Chem.* **1999**, 1507.
- [23] M. V. Veidis, B. Dockum, F. F. Charron, Jr., W. M. Reiff, T. F. Brennan, *Inorg. Chim. Acta* **1981**, 53, L197.
- [24] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885. C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski, T. G. Scharmann, *J. Chem. Soc., Dalton Trans.* **1999**, 3121. H.-P. Wu, C. Janiak, L. Uehlin, P. Klüfers, P. Mayer, *Chem. Commun.* **1998**, 2637.
- [25] For related examples of hydrogen-bonded networks see ref. [22] and C. Janiak, S. Temizdemir, T. G. Scharmann, A. Schmalstieg, J. Demtschuk, *Z. Anorg. Allg. Chem.* **2000**, 626, 2053. C. Janiak, T. G. Scharmann, W. Günther, F. Girgsdies, H. Hemling, D. Lentz, *Chem. Eur. J.* **1995**, 1, 637. C. Janiak, T. G. Scharmann, H. Hemling, D. Lentz, J. Pickardt, *Chem. Ber.* **1995**, 128, 235.
- [26] C. Janiak, S. Temizdemir, S. Dechert, *Inorg. Chem. Commun.* **2000**, 3, 271. C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M. J. Kolm, T. G. Scharmann, O. M. Zipffel, *Eur. J. Inorg. Chem.* **2000**, 1229.