Structural and Magnetic Characterization of a Linear Trinuclear Copper Complex Formed through Ligand Sharing

Yufei Song,[a] Patrick Gamez,[a] Olivier Roubeau,[b] Martin Lutz,[c] Anthony L. Spek,[c] and Jan Reedijk*[a]

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Reaction of bis(2-hydroxybenzyl)-1,3-diamino-2-propanol (H_2bhbdp) with copper perchlorate in methanol leads to the assembly of a trinuclear complex with the general formula $[Cu_3(bhbdp)_2(CH_3OH)_2(ClO_4)_2]$ (**1**). The complex was characterized by X-ray crystallography, Ligand Field, IR and ESR spectroscopy, and magnetic susceptibility. The structure of the complex contains a linear trinuclear array of copper ions [the Cu(1)–Cu(2)–Cu(1a) angle is 180° by symmetry], in octahedral, square planar and octahedral environments, respectively. The external Cu1 and Cu1a centers are coordinated by two amine nitrogens, two phenolate oxygen donors, one methoxide oxygen and one oxygen from a perchlorate, while the central Cu2 is coordinated by four phenolate oxygens through ligand sharing. A strong antiferromagnetic interaction between the adjacent Cu^{II} ions dominates the magnetic properties of **1** leading to an $S = 1/2$ ground state which is fully populated below 150 K.

Introduction

Many multinuclear copper(II) complexes have been reported during the past decades with a great number of simple and intricate bridging ligands.[1−3] This interest arises from the search for models of the active sites of multicopper proteins, like ascorbate oxidase,[4] ceruplasmin[5] or laccase,[6] and from their potential use in catalysis.[7] The trinuclear active site in laccase,[8] the ferromagnetically coupled Cu^{II} triad in the subunit of methane mono-oxygenase[9] and the angled trinuclear Cu^{II} unit as well as the mononuclear type-1 copper(II) centre of ascorbate oxidase from zucchini,[10] have drawn much attention in the study of trinuclear copper systems.[11] In addition, the study of such compounds has allowed a better understanding of the magnetic properties of molecular compounds, because copper(II) ions have the simplest magnetic spin possible i.e. 1/2. Only a limited number of linear trinuclear compounds have been structurally and magnetically characterized until now.[12−14] In particular, there is still no example of Cu−Cu bonding interactions in such closely packed multimetal systems, while many other metal ions do form M−M bonds under the same conditions.[15]

In the present study, a homometallic, linear, trinuclear complex, $[Cu_3(bhbdp)_2(CH_3OH)_2(ClO_4)_2]$ (**1**), was synthesized and characterized, in which, due to the basicity of the coordinated phenols, two octahedral Cu^{II} complexes function as didentate ligands for the square-planar central Cu^{II} ion. Strong anti-ferromagnetic exchange interactions between neighboring Cu^{II} ions are inferred from the temperature dependence of the magnetic susceptibilities of **1**.

Results and Discussion

The trinuclear copper compound of formula $[Cu_3(bhbdp)_2(CH_3OH)_2(ClO_4)_2]$ (**1**) was obtained by reaction of one equivalent of H_2bhbdp with two equivalents of copper(II) perchlorate in methanol. Diethyl ether diffusion into the methanolic solution led to the formation of deep-blue square crystals suitable for X-ray crystallography. A molecular plot representing the complex together with the atom-labeling scheme is shown in Figure 1. The hydrogen-bonding network linking the trinuclear units is presented and depicted in Figure 2.

The asymmetric unit of the coordination compound contains one $[Cu_3(bhbdp)]^{2+}$ cation, one ClO_4^- anion and one coordinated methanol molecule. The $[Cu_3(bhbdp)_2]^{2+}$ cation contains three Cu^{2+} atoms in a linear array. The two terminal Cu^{2+} atoms, Cu(1) and Cu(1a), are coordinated by two amine nitrogens and four oxygen atoms (two phenolate

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[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P.O. Box 9502, 2300 RA Leiden, The Netherlands
[b] Centre de Recherche Paul Pascal-CNRS;
115 avenue du Docteur Albert Schweitzer; 33600 Pessac; France
[c] Bijvoet Center for Biomolecular Research, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands
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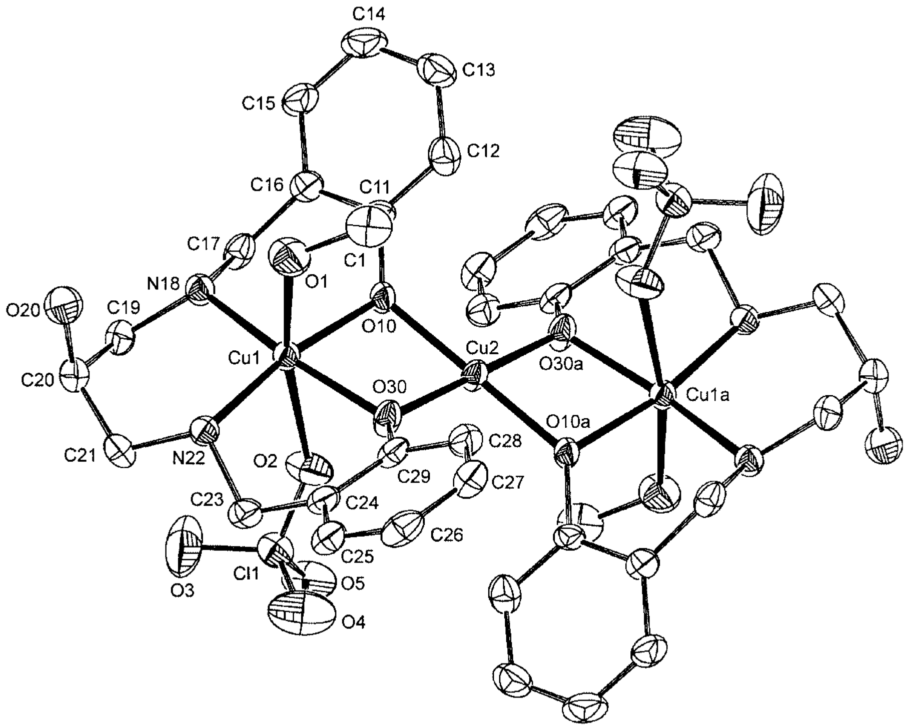

Figure 1. Displacement ellipsoid plot (50% probability level) of the trinuclear copper complex [$Cu_3(bhbdp)_2(CH_3OH)_2(ClO_4)_2$] showing the crystallographic numbering scheme; hdrogen atoms have been omitted for clarity; symmetry operation a: 1 − *x*, 1 − *y*, 1 − *z*; selected bond lengths and angles: Cu1−O30 1.956(3), Cu1−N18 1.996(3), Cu1−N22 2.014(3), Cu1−O10 1.958(3), Cu1−Cu2 2.9869(4), Cu1−O1 2.387(3), Cu1−O2 2.813, Cu2−O10 1.910(2), Cu2 −O30 1.911(3) Å; O10−Cu1−O30 76.59(11), O10−Cu1−N18 91.90(12), O10−Cu1−N22 169.14(11), O30−Cu1−N18 166.22(12), O30−Cu1−N22 92.58(12), N18−Cu1−N22 98.71(13), Cu2−Cu1−O1 100.27(8), Cu2−Cu1−O30 38.87(8), Cu2−Cu1−N22 130.34(9), O1−Cu1−O10 91.92(11), O1−Cu1−O30 92.81(12), O1−Cu1−N18 95.16(13), O1−Cu1−N22 89.40(12)°

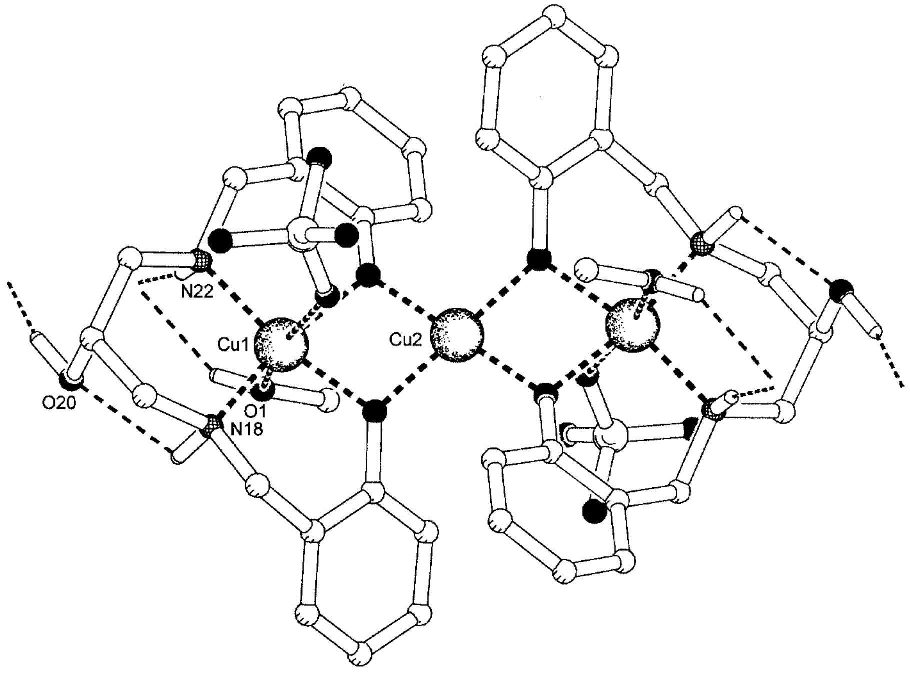

Figure 2. Perspective view exhibiting the hydrogen bonds; intramolecular D−H···A hydrogen bond (D···A, Å): N18−H18N···O20 2.735(5); intermolecular hydrogen bonds (D···A, Å): O1−H1O···O3 2.946(6); O20−H20O···O5 2.869(5); N22−H22N···O3 3.086(5)

oxygens, one methanol oxygen and one oxygen from a ClO_4^-). The central copper(II) atom, Cu(2), is coordinated by four oxygen atoms (from four phenolate oxygens). As Cu(2) occupies an inversion center, the resulting Cu(1)−Cu(2)−Cu(1a) array is linear by symmetry. The two terminal Cu(1) and Cu(1a) atoms are both coordinated by bhbdp^{2-} in a *cis* fashion with respect to the phenolate moieties. Thus, their coordination environment is described as an N_2O_4 donor set. Each phenolate unit further bridges to the central Cu(2) atom of the trinuclear moiety, resulting in a four-coordinate CuO4 chromophore. The central Cu^{2+} ion has a square-planar geometry due to the site symmetry, and the dihedral angle between the two Cu(1)−O(10)−Cu(2) and Cu(1)−O(30)−Cu(2) planes is 18.19(19)°. The terminal Cu(1) ions present a Jahn−Teller-distorted octahedral environment, resulting from the very long axial Cu(1)−O bonds from the semi-coordinated perchlorate O(2) and the methanol O(1). Therefore, the equatorial coordination plane is an N_2O_2 donor set [for Cu(1); N18, N22, O10, O30]. The Cu−O bond lengths of the central Cu(2) atom [1.910(2)−1.911(3) Å] are shorter than those of the equatorial Cu−O bonds of the terminal Cu(1) atoms [1.956(3)−1.958(3) Å], which is attributed to the two different coordination geometries (octahedral and square-planar, respectively). The Cu(2)−Cu(1) distance is 2.9869(4) Å, while the Cu(1)−O−Cu(2) angles of each pair of neighbors are 101.15(12)° and 101.08(12)° respectively for O(30) and O(10). Each Cu_2O_2 pair is almost planar as shown by the Cu(2)−O(30)−O(10)−Cu(1) torsion angle of 165.18(15)°.

Electronic Properties

The ligand-field spectrum of **1** shows three absorption bands centered at approximately 262 nm (38.2×10^3 cm^{-1}), 402 nm (24.8×10^3 cm^{-1}) and 567 nm (17.6×10^3 cm^{-1}). The intensity of the absorption at 402 nm clearly precludes it being a d-d transition, hence this feature is assigned as being due to a phenolate oxygen to Cu^{II} charge-transfer (CT) transition.[14] The absorption at 262 nm is another CT from phenolate oxygen to Cu^{II}. One of these phenolate oxygen to Cu^{II} CT bands is due to the terminal Cu^{II} CT and the other to the central Cu^{II} CT.[14] The transition in the visible region of the electronic spectrum of this complex is a much-less-intense absorption at 567 nm, which is assigned to d-d transitions of both square-planar and octahedral species.[16,17]

Magnetic Susceptibility and ESR

The ESR spectrum of a powered polycrystalline sample of **1** at room temperature shows a broad isotropic copper(II) signal centered around a *g* value of 2.0976. The main EPR signal $g_\perp = 2.0646$ sharpens upon cooling to 77 K and a very weak $g_{//}$ at ca. $g = 2.1945$ becomes visible (no $A_{//}$ resolved). The frozen solution spectrum in a CH_3CN/CH_3OH (1:1) solution shows only a broad signal at $g = 2.0794$. No structural conclusions can be drawn from these spectra.

The temperature dependence of the product $\chi_m T$ of **1** is shown in Figure 3, together with magnetization vs. field measurements at 1.8 K. Even at 390 K, $\chi_m T$ is much lower than that of three uncoupled Cu^{II} ions (0.593 cm^3·K/mol instead of 1.125 cm^3·K/mol for $g = 2$), thus indicating the presence of strong antiferromagnetic interactions. It decreases upon lowering the temperature to reach a plateau below 150 K at about 0.42 cm^3·K/mol, corresponding to an $S = 1/2$ ground state (0.375 cm^3·K/mol for $g = 2$). Indeed, the magnetization vs. field data at 1.83 K (inset in Figure 3) tend to saturate at a value of 1.06. Below 10 K, a further decrease of $\chi_m T$ sets in, which can only be attributed to intermolecular interactions between $S = 1/2$ trimeric units. Therefore this behavior was modelled using the spin Hamiltonian given in Equation (1).

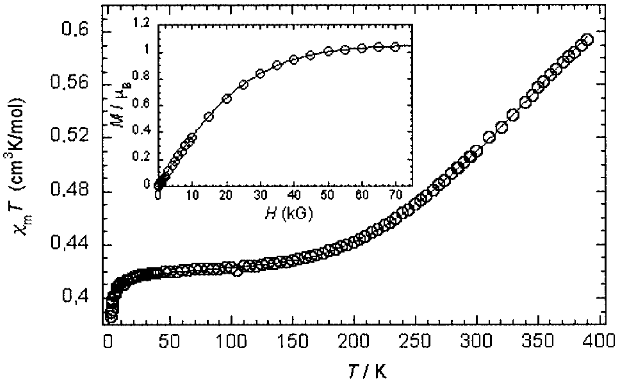

Figure 3. $\chi_m T$ vs. T plot for complex **1**; the solid line is the best fit obtained with a nearest neighbor interaction of $-511(2)$ cm^{-1} (see text); insert: field dependence of magnetization measured at 1.83 K

$$H = g\beta S_z H - J_1(S_1 \cdot S_2 + S_{1a} \cdot S_3) - J_2(S_1 \cdot S_{1a}) - zJ' \langle S_z \rangle S_z \qquad (1)$$

The first term of this hamiltonian corresponds to the Zeeman term, for which a single isotropic *g* tensor has been considered for the two different Cu^{II} ions in **1**. The second and third terms include isotropic nearest neighbor and next-nearest neighbor interactions, respectively, with J_1 representing the exchange parameter between neighboring Cu^{II} ions and J_2 the exchange parameter between terminal Cu^{II} ions. The fourth term takes into account intermolecular interactions in the mean-field approximation,[18] with J' being the intermolecular exchange interaction and z the number of trimeric neighbors, in this case four. In cases like **1**, where the trinuclear array is perfectly linear and the dominant nearest neighbor interaction is antiferromagnetic, J_2 can be neglected, and was thus set to zero. The resulting expression of the molar magnetic susceptibility in the $\beta H/k_B T << 1$ approximation, with an additional term to take into account a Temperature-Independent Paramagnetism (TIP), is given in Equation (2).

$$\chi_M(T) = \frac{N_A g^2 \beta^2 F(T)}{4k_B\left(T - zJ'F(T)\right)} + TIP$$
$$F(T) = \frac{1 + \exp\left(J_1/k_B T\right) + 10\exp\left(3J_1/2k_B T\right)}{1 + \exp\left(J_1/k_B T\right) + 2\exp\left(3J_1/2k_B T\right)} \qquad (2)$$

The best set of parameters obtained (full line in Figure 3) was $J_1 = -511(2)$ cm^{-1}, $g = 2.15(1)$ and $zJ' = -1.9(1)$ cm^{-1} with a TIP value of $61(3) \times 10^{-6}$ cm^3/mol. Thus, the ground state of the trinuclear unit is, in the (S_{total}, $S_1 + S_{1a}$)

format, the doublet (1/2,0), with the excited doublet (1/2,1) and quadruplet (3/2,1) lying 511 and 766 cm^{-1} above it, respectively. It is well-known that in planar dinuclear copper(II) complexes with di-μ-alkoxo bridges, the exchange parameter varies linearly with the Cu−O−Cu angle.[19] Indeed, the value expected for the average Cu−O−Cu angle in **1** — 101.1° — is −495 cm^{-1} and almost perfectly matches the value obtained for J_1 in the present work. In addition, the Cu−Cu separation is large (2.987 Å), indicating that no direct exchange mechanism is likely to contribute to the magnetic coupling. Therefore, the strong antiferromagnetic coupling in **1** is ascribed solely to superexchange mechanisms within the central-terminal copper(II) pairs. The moderately weak intermolecular interactions observed in **1** can be explained by the hydrogen bonding network (see Figure 2) in which the coordinated perchlorate is involved.

In summary, the ligand bis(2-hydroxybenzyl)-1,3-diamino-2-propanol allows the formation of a stable, linear, homometallic, trinuclear complex $[Cu_3(bdbhp)_2(CH_3OH)_2(ClO_4)_2]$. A strong antiferromagnetic coupling between adjacent copper(II) ions in the triad dominates the magnetic properties of this complex. Further studies of its catalytic activity for the polymerization of 2,6-dimethylphenol (DMP) and oxygen binding chemistry at room temp. and low temperature are under investigation. By developing additional model systems of copper proteins, a better insight may be obtained into the magnetic properties of multicopper proteins and the relationship between structure and activity.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial sources and used as received. The ligand bis(2-hydroxlybenzyl)-1,3-diamino-2-propanol was prepared from salicylaldehyde and 1,3-diamino-2-propanol by reductive amination in methanol with $NaBH_4$. C,H,N analyses were carried out by the Microanalysis Department of Leiden University. Infrared spectra were recorded on a Perkin−Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR as a sample support. X-Band EPR spectra were recorded on a JEOL ESR spectrometer equipped with an Esprit 330 data system, at room temperature and at 77 K, with dpph as an internal reference (g = 2.0036). The ligand-field spectra of the solid compounds were recorded in the 300−2000 nm range on a Perkin−Elmer Lambda 900 UV/Vis/NIR spectrometer in the diffuse reflectance mode with MgO as reference. Field cooled measurements (300 to 1.8 to 390 K) of the magnetization of smoothly powdered microcrystalline **1** (m = 23.71 mg) were performed with a Quantum Design MPMS-7XL squid magnetometer in a 1kG applied field. Corrections for diamagnetic contributions of the sample (5.26 × 10^{-4} cm^3/mol) to the magnetic susceptibility were calculated using Pascal's constants.

Preparation of the Compound: A solution of the ligand (12.1 mg, 0.01 mmol) in methanol (2 mL) was added to copper(II) perchlorate (29.8 mg, 0.02 mmol) in methanol (2 mL). Diffusion of diethyl ether into the solution led to the formation of brown crystals after one day. Yield 36% (1.9 mg). $C_{36}H_{48}Cl_2Cu_3N_4O_{16}$ (1054.3): calcd. C 40.97, H 4.55, H 5.31; found C 40.58, H 4.32, N 5.55. IR (solid): $\tilde{\nu}$ = 3536, 3268, 3232, 1600, 1486, 1456, 1247, 1041, 759, 625 cm^{-1}. UV/Vis/NIR (solid): λ_{max} = 24875 cm^{-1}. EPR (solid, room temp.): g = 2.0976.

Crystal structure determination: $C_{36}H_{48}Cl_2Cu_3N_4O_{16}$, mol. wt. = 1054.30, brown needle, 0.24 × 0.06 × 0.06 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 11.4981(2), b = 13.7442(2), c = 16.0767(3) Å, β = 123.5141(8)°, V = 2118.26(7) Å^3, Z = 2, D_x = 1.653 g/cm^3, μ = 1.694 mm^{-1}. 21805 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.59 Å^{-1}; 3641 reflections were unique (R_{int} = 0.086). An absorption correction based on multiple measured reflections was applied (0.68−0.91 transmission). The structure was solved by direct methods (SHELXS-97[20]) and refined with SHELXL-97[21] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. C−H hydrogen atoms were refined as rigid groups; O−H and N−H hydrogen atoms were located in the difference Fourier map and kept fixed in that position. 278 refined parameters, no restraints. R values [$I > 2\sigma(I)$]: $R1$= 0.0398, $wR2$ = 0.0998. R values [all refl.]: $R1$= 0.0696, $wR2$ = 0.1142. GoF = 1.091. Residual electron density between −0.76 and 1.13 e/Å^3. Molecular illustration, structure checking and calculations were performed with the PLATON package.[22]

CCDC-210106 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk)

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[1] [1a] L. Gutierrez, G. Alzuet, J. A. Real, J. Cano, J. Borras, A. Castineiras, *Inorg. Chem.* **2000**, *39*, 3608. [1b] G. A. van Albada, M. E. Quiroz-Castro, I. Mutikainen, U. Turpeinen, J. Reedijk, *Inorg. Chim. Acta* **2000**, *298*, 221. [1c] I. Riggio, G. A. van Albada, D. D. Ellis, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta* **2001**, *313*, 120.

[2] V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, A. E. Tsohos, E. G. Bakalbassis, A. Terzis, S. P. Perlepes, *Inorg. Chem.* **1997**, *36*, 5270.

[3] X. S. Tan, Y. Fujii, R. Nukada, M. Mikuriya, Y. Nakano, *J. Chem. Soc., Dalton Trans.* **1999**, 2415.

[4] A. Messerschmidt, A. Rossi, R. Ladenstein, R. Huber, M. Bolognesi, G. Gatti, A. Marchesini, R. Petruzzelli, A. Finazzi-Agro, *J. Mol. Biol.* **1989**, *206*, 513.

[5] P. Kyritsis, A. Messerschmidt, R. Huber, G. A. Salmon, A. G. Sykes, *J. Chem. Soc., Dalton Trans.* **1993**, 731.

[6] R. Huber, *Angew. Chem. Int. Ed. Engl.* **1989**, *101*, 849.

[7] [7a] J. Reedijk, E. Bouwman, *Bioinorganic Catalysis.* Marcel

Dekker, Inc, **1999**. [7b] P. Gamez, P. G. Aubel, W. L. Driessen, J. Reedijk, *Chem. Soc. Rev.* **2001**, *30*, 376.

[8] D. J. Spira-Solomon, M. Allendorf, E. I. Solomon, *J. Am. Chem. Soc.* **1986**, *108*, 5316.

[9] H. H. T. Nguyen, A. K. Shiemke, S. J. Jacobs, B. J. Hales, M. E. Linstrom, S. I. Chan, *J. Biol. Chem.* **1994**, *269*, 14995.

[10] A. Messerschmidt, in *Bioinorganic Chemistry of Copper* (Eds.: K. D. Karlin, Z. Tyeklar), Chapman & Hall, New York, **1993**, p. 471.

[11] L. Gutierrez, G. Alzuet, J. A. Real, J. Cano, J. Borras, A. Castineiras, *Eur. J. Inorg. Chem.* **2002**, 2094.

[12] [12a] G. A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Eur. J. Inorg. Chem.* **1998**, 547. [12b] G. A. van Albada, P. J. van Koningsbruggen, I. Mutikainen, U. Turpeinen, J. Reedijk, *Eur. J. Inorg. Chem.* **1999**, 2269.

[13] [13a] F. Akagi, Y. Nakao, K. Matsumoto, S. Takamizawa, W. Mori, S. Suzuki, *Chem. Lett.* **1997**, *2*, 181. [13b] L. Cronin, P. H. Walton, *Inorg. Chim. Acta* **1998**, 241.

[14] [14a] M. H. W. Lam, Y. Y. Tang, K. M. Fung, X. Z. You, W. T. Wong, *Chem. Commun.* **1997**, *21*, 957. [14b] T. C. Higgs, K. Spartalian, C. J. O'Connor, B. F. Matzanke, C. J. Carrano, *Inorg. Chem.* **1998**, *37*, 2263.

[15] J. F. Berry, F. A. Cotton, P. Lei, C. A. Murillo, *Inorg. Chem.* **2003**, *42*, 377.

[16] B. J. Hathaway, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gill and J. A. McCleverty), Pergamon Press Oxford, **1987**, Vol.5.

[17] L. P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons, P. Thornton, *J. Chem. Soc., Dalton Trans.* **1990**, 3835.

[18] O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., **1991**.

[19] L. Merz, W. Haase, *J. Chem. Soc., Dalton Trans.* **1980**, 875.

[20] G. M. Sheldrick (1997). SHELXS-97. *Program for crystal structure solution.* University of Göttingen, Germany.

[21] G. M. Sheldrick (1997). SHELXL-97. *Program for crystal structure refinement.* University of Göttingen, Germany.

[22] A. L. Spek (2003). PLATON. A multipurpose crystallographic tool. Utrecht University, The Netherlands.

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