ELSEVIER

Asymmetric chlorine-bridged zig-zag Cu(II) chains linked together in 2D sheets by strong Watson–Crick type intermolecular double hydrogen bonds of bis(pyrimidin-2-yl)amine ligands: synthesis, structure and antiferromagnetism

Gerard A. van Albada [a], Olivier Roubeau [b], Patrick Gamez [a], Huub Kooijman [c],
Anthony L. Spek [c], Jan Reedijk [a,*]

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

Abstract

A novel polymeric, asymmetric chloro-bridged copper chain with general formula $[\mu\text{-Cl–CuCl(dipm}]_n$ (in which dipm = bis(pyrimidin-2-yl)amine) has been synthesized and characterised by X-ray crystallography and infrared spectroscopy. The chains are organized in 2D sheets by intermolecular double H bonds between pairs of dipm molecules. In addition, EPR and magnetic measurements have been performed, and these have been related to the dinuclear structural details.

The geometry around the copper(II) ion is distorted square pyramidal with the basal plane formed by the two nitrogen atoms of the dipm ligand and two chloride atoms, one of which is bridging. The Cu–N distances are 2.0342(15) and 2.0125(15) Å and Cu–Cl distances are 2.2899(6) and 2.2658(6) Å. The apical position of Cu is occupied by a chloride atom of a neighbouring unit atom at a distance of 2.6520(6) Å, resulting in the polynuclear array in which one chloride anion and the copper ion forms a zig-zag chain. The magnetic interaction between the Cu–Cu atoms is weak antiferromagnetic with a singlet–triplet separation (J) of $-3.2(1)$ cm^{-1}.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Copper; Structure; Magnetism; Chloride bridge

1. Introduction

In the field of supramolecular interactions of coordination compounds not only the direct metal–ligand bonds are of interest, but also hydrogen bonding is of great importance [1–8].

A ligand with interesting hydrogen-bonding properties is the recently developed ligand bis(pyrimidin-2-yl)-amine (abbreviated as dipm) [11–13]. The dipm molecule can both donate and accept hydrogen bonds, and has a more or less linear donor–acceptor array of the ADA type. This type of array is capable of forming so-called Watson–Crick-type hydrogen bonds, as also shown in the literature for the first generation ligand 2-aminopyrimidine [9,10].

So far only two X-ray crystal structure determination of Cu(II) compounds with dipm have been published [11,12], i.e. $[\text{Cu(dipm)(CO}_3\text{)(H}_2\text{O)}](\text{H}_2\text{O})_2$ and $[\text{Cu(dipm)}_2\text{(dicyanamide)(CF}_3\text{SO}_3\text{)}](\text{C}_2\text{H}_6\text{O})_{1/2}$.

In this study the synthesis, the crystal structure, characterization and magnetism of the chloro-bridged

* Corresponding author. Tel.: +33 715274450; fax: 33 715274671.
E-mail address: reedijk@chem.leidenuniv.nl (J. Reedijk).

zig-zag chain compound [μ-Cl–CuCl(dipm)]$_n$ is described, in which such intermolecular hydrogen bonding generates a 2-D network.

2. Experimental

2.1. Materials

The ligand dipm was prepared by the method reported in the literature [13]. The purity was checked by elemental analysis, IR spectroscopy and ^{1}H NMR.

Table 1
Crystal data and details of the structure determination

Compound	$C_8H_7Cl_2CuN_5$
Molecular weight	307.64
Crystal system	monoclinic
Space group	$P2(1)/c$ (no.14)
a (Å)	10.8313(10)
b (Å)	6.6560(10)
c (Å)	14.322(2)
β (°)	96.282(5)
V (Å^3)	1026.3(2)
Z	4
D_{calc} (g cm^{-3})	1.991
$F(000)$	612
μ (mm^{-1})	2.623
Crystal size (mm)	$0.06 \times 0.18 \times 0.25$
Temperature (K)	150
$\theta_{min}\theta_{max}$	1.0; 27.5
Total data collected	32,794
Independent reflections (R_{int})	2351 (0.0549)
Number of refined parameters	148
MULABS trans.range	0.631, 0.0857
Final $R_1(I>2\sigma(I))$, wR_2	0.0219, 0.0592
Goodness-of-fit on F^2	1.123
Minimum and maximum residual density (e Å^{-3})	−0.59; 0.35

All other chemicals were purchased from commercial sources and used as received.

2.2. Synthesis of the compounds

An equimolar amount of dipm (1 mmol) and copper(II) chloride (1 mmol) were each dissolved in an ethanol/water (1:1) mixture (20 ml) and heated till about 40 °C. Then the ligand solution was carefully added to the copper solution and mixed. The green solution was filtered and left to evaporate at room temperature. Green crystals were obtained in a few days (yield 65%); *Anal.* Calc. for $C_8H_7Cl_2N_5Cu$: C, 31.2; H, 2.3; N, 22.7. Found: C, 31.0; H, 2.5; N, 22.8%.

2.3. Physical techniques

C,H,N determinations were performed on a Perkin–Elmer 2400 Series II analyzer.

Ligand-field spectra were obtained on a Perkin–Elmer Lambda900 spectrophotometer using the diffuse-reflectance technique, with MgO as a reference.

FTIR spectra were obtained on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}, res. 4 cm^{-1}).

X-band EPR spectra were recorded on polycrystalline samples at RT and at 77 K with a Jeol RE2X electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard.

Magnetic susceptibility measurement (5–350 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 0.1 T). Data were corrected for magnetisation of the
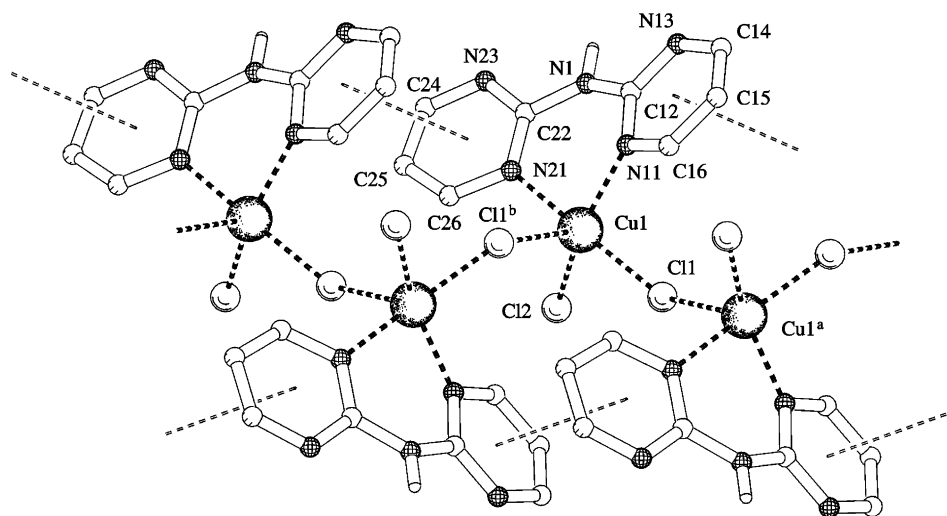

Fig. 1. Perspective plot [16] of the chain in [Cu(dipm)$_2$Cl$_2$]$_n$. Hydrogen atoms bonded to carbon are excluded for clarity. Stacking of pyrimidinyl π-systems is indicated with thin dashed bonds between their geometrical centres. Atoms with suffix "a" and "b" are generated by symmetry operations $(-x,-1/2 + y,1/2-z)$ and $(-x,1/2 + y,1/2-z)$, respectively.

Table 2
Selected bind lengths (Å) and angles (°) for [Cu(dipm)Cl₂]ₙ

Cu1–Cl1	2.2899(6)
Cu1–N11	2.0342(15)
Cu1–Cl1b	2.6520(6)
Cu1–Cl2	2.2658(6)
Cu1–N21	2.0125(15)
Cu1–Cu1a	4.7092(8)
Cl1–Cu1–Cl2	90.06(2)
Cl1–Cu1–N21	177.12(4)
Cl2–Cu1–N11	151.26(4)
Cl1b–Cu1–Cl2	109.90(2)
Cl1b–Cu1–N11	98.21(4)
Cu1–Cl1–Cu1a	144.60(2)
Cl1–Cu1–N11	93.16(5)
Cl1–Cu1–Cl1b	95.54(2)
Cl2–Cu1–N21	88.72(5)
N11–Cu1–N21	86.66(6)
Cl1b–Cu1–N21	87.33(4)

Suffix a denotes $-x, -1/2 + y, 1/2 - z$; suffix b denotes $-x, 1/2 + y, 1/2 - z$.

sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

2.4. Crystallography

Crystals suitable for structure determination were mounted on Lindemann-glass capillaries and transferred into the cold nitrogen stream of a Nonius Kappa CCD diffractometer on rotating anode (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å, $T = 150$ K). Pertinent data for the structure determinations are collected in Table 1. Data were corrected for absorption using an algorithm based on multiple measurements of symmetry-related relfections (PLATON/MULABS [16]). The structure was solved with direct methods using SHELXS-86 [14] and refined on F^2 using SHELXL-

97-2 [15]. The co-ordinates of the amine hydrogen atom were included as parameters in the refinement. The other hydrogen atoms were included on calculated positions riding on their carrier atoms. The displacement parameters of all hydrogen atoms were related to the value of the equivalent isotropic displacement parameters of their carrier atoms. Geometrical calculations and illustration were performed by PLATON [16].

3. Results and discussion

3.1. Crystal structure of [**μ**-Cl–CuCl(dipm)]ₙ

A perspective plot of the title compound showing the numbering scheme is given in Fig. 1 with selected bond distances and angles in Table 2. The copper(II) ion has taken a distorted square pyramidal geometry with the basal plane formed by two pyrimidinyl nitrogen atoms (N11 and N21) of the dipm ligand and two chloride atoms (Cl1 and Cl2). The Cu–N distances are 2.0342(15) and 2.0125(15) Å and the Cu–Cl distances are 2.2899(6) and 2.2658(6) Å. The apical position is occupied by a symmetry-related image of Cl1 at a distance of 2.6520(6) Å from the copper ion. The N–Cu–Cl angles of the base plane are 177.12(4) and 151.26(4)°. The distortion of a square pyramidal coordination sphere can be described by the structural parameter τ, which indicates the relative amount of trigonality ($\tau = 0$ for a pure square pyramid (sp) and $\tau = 1$ for a trigonal bipyramid (tbp) [17]). In this case $\tau = 0.43$, so the geometry can be described as an intermediate between sp and tbp. One of the coordinated chloride anions (Cl1) forms a bridge between two copper ions that are related by a crystallographic twofold screw axis.
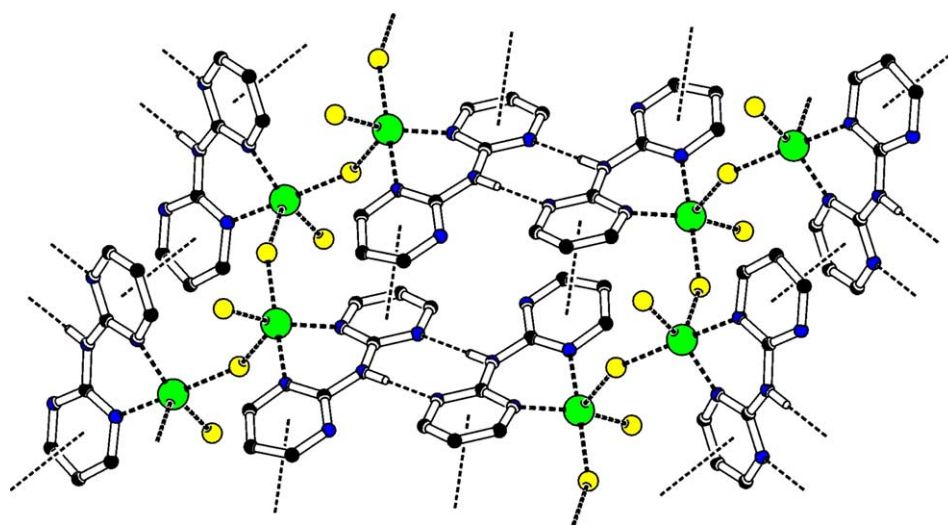

Fig. 2. Perspective plot [16] of the two-dimensional network of zig-zag chains, linked by hydrogen bonds. Stacking of pyrimidinyl π-systems is indicated with thin dashed bonds between their geometrical centres. Hydrogen atoms bonded to carbon are excluded for clarity.
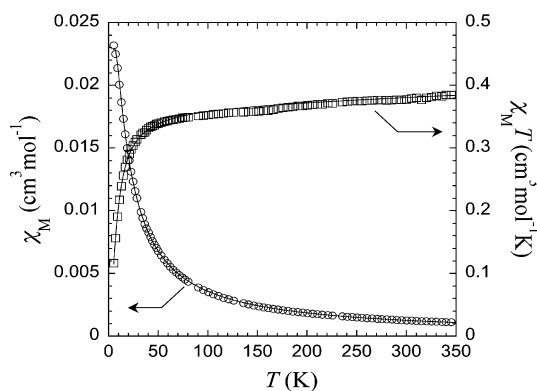
Fig. 3. Plots of temperature dependence of the molar magnetic susceptibility χ_M ($\bigcirc$) and the $\chi_M T$ product ($\square$) for the title compound. The solid lines represent the calculated curves for the parameters $J = -3.2(1)$ cm^{-1} and $g = 1.98(1)$ (see text).

The chlorine anion occupies a position in the basal coordination plane of the first copper ion and the apical coordination position of the second copper ion. The resulting zig-zag chain of Cu1 and Cl1 is the backbone of a polynuclear array running parallel to the crystallographic b-axis. The array is stabilized by stacking of the pyrimidine ring containing N11 on a symmetry-related image of the ring containing N21 (see Fig. 1). The distance between the geometric centres of the rings is 3.6780(12) Å, the acute angle between the planes through the ring systems is 19.80(9)°.

A neighbouring pair of symmetry-related polynuclear chains is linked through hydrogen bonds which are donated by the amine nitrogen N1 to the pyrimidinyl nitrogen N13. The N$\cdots$N distance of this hydrogen bond is 2.964(2) Å, the N–H$\cdots$N angle is 175(2)°. A crystallographic inversion centre doubles this hydrogen bond into a so-called Watson–Crick pair of hydrogen bonds. The resulting two-dimensional network runs parallel to the lattice planes (1 0 −2) and is displayed in Fig. 2.

3.2. Magnetic properties

The EPR spectrum measured as a polycrystalline powder at RT shows a very broad isotropic signal, which sharpens up at 77 K with a $g = 2.15$. No (hyper) fine structure is resolved.

The magnetic behaviour of the title compound, measured as a powdered sample from 5 to 350 K, is shown in Fig. 3 as the temperature dependence of its molar magnetic susceptibility χ_M and its product with temperature, $\chi_M T$. The $\chi_M T$ product at room temperature, 0.377 cm^{3}mol^{-1}K, is in agreement with uncoupled $S = 1/2$ (0.378 cm^{3}mol^{-1}K). A steady decrease is observed down to 0.353 cm^{3}mol^{-1}K at 75 K, after that a sharp decrease down to 0.118 cm^{3}mol^{-1}K at 5 K, which can only arise from antiferromagnetic interactions between nearest neighbours along the chain. In view of the regular uniform Cu^{ax}–Cl–Cu^{eq} bridge within the chain in the title compound, the expression of the susceptibility for a

Table 3
Cu(II) polymeric compounds with a single Cl bridge and a Cu(N/O)$_2$Cl$_2$(Cl) chromophore

Compound[a]	Cu geometry[a] (τ)	Chromophore	Cu–μ-Cl–Cu angle	Cu–Cu distance	Cu–μ-Cl distance	Magnetism J[b]	References[a]
Cu(dmso)Cl$_2$	Dist.sq.pyr. (0.44)	CuO$_2$Cl$_2$(Cl)	144.6(1)	4.757(2)	2.702(2)	−6.1 [−9.6]	[20] (s) [21] (m)* [22] (m)
Cu(ImH)Cl$_2$	Dist.sq.pyr. (0.12)	CuN$_2$Cl$_2$(Cl)	117.0	4.37	2.751(6)	−2.1 [−5.36]	[22] (m) [23] (s) [24] (m)*
Cu(dipm)Cl$_2$	Dist.sq.pyr (0.43)	CuN$_2$Cl$_2$(Cl)	144.60(2)	4.7092(8)	2.6520(6)	−3.2(1)	This work
Cu(bpy)Cl$_2$	Dist.sq.pyr. (0.21)	CuN$_2$Cl$_2$(Cl)	107.5(1)	4.01	2.674(3)	−2.3	[25] (s + m)
Cu(caf)(H$_2$O)Cl$_2$	Dist.sq.pyr. (0.29)	CuNOCl$_2$ (Cl)	128.1	4.597(2)	2.788(2)	+0.48	[22] (m) [26] (s)
Cu(maep)Cl$_2$	Dist.sq.pyr. (0.17)	CuN$_2$Cl$_2$(Cl)	113.58(5)	4.263(2)	2.785(2)	+1.58	[22] (m) [27] (s)
Cu$_2$ (dpp)Cl$_4$	Dist.sq.pyr. (0.26)	CuN$_2$Cl$_2$(Cl)	98.46(4)	3.688	2.5600(13)	+6.0(1)	[28] (s + m)

[a] Abbreviations: dist. sq.pyr = distorted square pyramidal, s = structure, m = magnetism; dmso = dimethylsulfoxide, ImH = imidazole, bpy = 2,2′-bipyridine, caf = caffeine, maep = 2-(2-methylaminoethyl)pyridine, dpp = 2,3-bis(2-pyridyl)pyrazine.
[b] J given in brackets are results of magnetic measurements done by the reference with an asterisk.
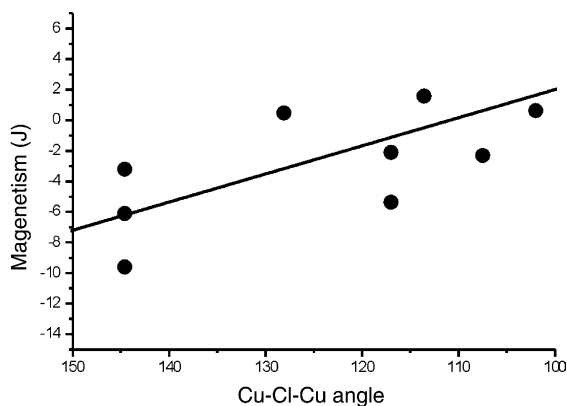
Fig. 4. Plot of magnetic interaction (*J*) versus the Cu–µ-Cl–Cu angle. The straight line is the averaged linear plot between the points.

uniform Heisenberg chain [18,19] has been used to reproduce the experimental data. A fixed TIP value of 6×10^{-5} cm^3 mol^{-1}, usually observed in Cu(II) compounds was added, while the interaction parameter *J* and the Landé factor *g* were left free, resulting in the best fit parameters $J = -3.2(1)$ cm^{-1} and $g = 1.98(1)$. In a square-pyramidal Cu(II) centre, the spin density will be mostly in the $d_{x^2-y^2}$ orbital, and therefore exchange coupling pathways involving axial ligands (and therefore the d_{z^2} orbital), such as the chloride ion here, is expected to be small, which is in good agreement with the small *J* value obtained.

4. Conclusions

In this study a novel Cu(II) zig-zag polymeric compound with a single asymmetric chloro bridge is synthesized and the magnetic interaction between the Cu ions is measured. Due to the fact that the coordination of the Cu(II) has a intermediate geometry between sp and tbp, with a ground state predominantly $d_{x^2-y^2}$, and the chloro bridge is of the apical type, which lead to poor coupling between copper centres. In Table 3 a number of other µ-chloro bridged compounds with a similar type of chromophore are presented and compared. The magnetism in all cases is low and varies from $J = +6.0$ to -9.6. In all cases the Cu–Cu distance is large (>3.7 Å), however the only distinct variation appears to be the Cu-µ-Cl–Cu bridge which varies from 98.46° to 144.6°. When plotting this angle to the magnetic interaction *J*, a weak trend is observed between these two parameters (Fig. 4). Due to the fact that the deviations are large (see also examples in Table 3 of some compounds with different measured *J* values) and also that other factors can play a role, no direct correlation conclusion can be taken from it. More compounds of a similar nature are needed to study this correlation in detail.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-233989. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

References

[1] A.M. Beatty, Cryst. Eng. Commun. 3 (2001) 243 (article no. 51), and references cited therein.
[2] M.R. Sundberg, Rev. Inorg. Chem. 20 (2000) 195.
[3] M. Tadokoro, K. Nakasuji, Coord. Chem. Rev. 198 (2000) 205.
[4] Y. Sugiyama, K. Adachi, S. Kawata, H. Kumagai, K. Inoue, M. Katada, S. Kitagawa, Cryst. Eng. Commun. 2 (2000) 174 (article no. 32).
[5] M.M. Bishop, L.F. Lindoy, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (2002) 377.
[6] S.R. Marshall, C.D. Incarvito, W.W. Shum, A.L. Rheingold, J.S. Miller, Chem. Commun. (2002) 3006.
[7] A. Mohamadou, G.A. van Albada, H. Kooijman, B. Wieczorek, A.L. Spek, J. Reedijk, New J. Chem. 27 (2003) 983.
[8] Y.S. Xie, Q.L. Liu, H. Jiang, J. Ni, Eur. J. Inorg. Chem. (2003) 4010.
[9] G.A. van Albada, M.E. Quiroz-Castro, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chim. Acta 298 (2000) 74.
[10] G.A. van Albada, W.J.J. Smeets, A.L. Spek, J. Reedijk, J. Chem. Cryst. 30 (2000) 11.
[11] G.A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Acta Cryst. C 58 (2002) m179.
[12] H. Kooijman, A.L. Spek, G.A. van Albada, P. Gamez, J. Reedijk, Acta Cryst. C 60 (2004) m51.
[13] W. Yao, K. Kavallieratos, S. de Gala, R.H. Crabtree, Inorg. Chim. Acta 311 (2000) 45.
[14] G.M. Sheldrick, SHELXS86 Program for crystal structure determination, University of Göttingen, Germany, 1986.
[15] G.M. Sheldrick, SHELXL-97-2 Program for crystal structure refinement, University of Göttingen, Germany, 1997.
[16] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
[17] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc. Dalton Trans. (1984) 1349.
[18] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.
[19] J.W. Hall, W.E. Marsh, R.R. Weller, W.E. Hatfield, Inorg. Chem. 20 (1981) 1033.

[20] R.D. Willett, K. Chang, Inorg. Chim. Acta 4 (1970) 447.
[21] N.T. Watkins, D.Y. Jeter, W.E. Hatfield, Trans. Faraday. Soc. 67 (1971) 2431.
[22] W.E. Estes, W.E. Hatfield, J. Chem. Soc., Dalton Trans. (1980) 2121.
[23] B.K.S. Lundberg, Acta. Chem. Scand. 26 (1971) 3977.
[24] J.A.C. van Ooijen, J. Reedijk, J. Chem. Soc., Dalton Trans. (1978) 1170.
[25] M. Hernández-Molina, J. González-Platas, C. Ruiz-Pérez, F. Lloret, M. Julve, Inorg. Chim. Acta 284 (1999) 258.
[26] G. Bandoli, M. Cingi Biagini, D.A. Clemente, G. Rizzardi, Inorg. Chim. Acta 20 (1976) 71.
[27] R.A. Bream, E.D. Estes, D.J. Hodgson, Inorg. Chem. 14 (1975) 1672.
[28] H. Grove, J. Sletten, M. Julve, F. Lloret, J. Chem. Soc., Dalton Trans. (2001) 2487.