ELSEVIER

Inorganica Chimica Acta 224 (1994) 171–176

Inorganica Chimica Acta

Note

Crystal structure and magnetic property of a 2D infinite layered copper(II) complex with bridging *trans*-oxamidate and pyrimidine ligands

Zhong Ning Chen[a], Jun Qiu[a], Wen Xia Tang[a,*], Kai Bai Yu[b]

[a]*State Key Laboratory of Coordination Chemistry, Institute of Coordination Chemistry, Nanjing University, Nanjing 210008, China*
[b]*Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu 610041, China*

Received by Editor 27 January 1994; rreceived by Publisher 4 May 1994

Abstract

The complex polymer $[Cu_2(oxen)(pym)_2]_n(ClO_4)_{2n}$, where oxen and pym are *N,N'*-(2-aminoethyl)oxamide dianion and pyrimidine, respectively, was synthesized and characterized by means of X-ray crystallography, magnetic and spectroscopic measurements. It crystallizes in the monoclinic system, space group $P2_1/c$, $Z=4$ with $a=8.143(2)$, $b=8.646(3)$, $c=16.787(5)$ Å and $\beta=97.35(2)°$. The crystal structure of this compound consists of layers of a two-dimensional network arrayed along the *a* axis. Inside the layer, *trans*-oxamidato-bridged copper(II) dimers connected by pyrimidine in an asymmetric fashion spread out along the *bc* plane to form a 2D infinite network. The copper(II) has a square-pyramidal environment with N_3O atoms forming the basal plane and a nitrogen atom from pyrimidine occupying the apical site. The magnetic study of this compound shows a strong antiferromagnetic exchange interaction with $J=-582$ cm^{-1}, due to the efficiency of the oxamidato bridge in undergoing antiferromagnetic coupling between the copper(II) atoms which are separated by about 5.2 Å.

Keywords: Crystal structures; Magnetism; Copper complexes; Oxamidate complexes; Pyrimidine complexes

---

1. Introduction

The magnetic exchange of low-dimensional transition metal complexes has been actively investigated [1–5], particular attention being devoted to 2D and 3D network complex polymers considering that increasing dimensionality is one way to favour bulk magnetic properties [6–10].

Due to their ease of *cis–trans* conformation, N,N'-disubstituted oxamides have played a key role in the design of polymetallic species with magnetic properties [11–17]. The bis-tridentate character of these ligands in *trans*-conformation allows the formation of *trans*-oxamidato-bridged dinuclear copper(II) units which can be linked by bis-monodentate ligands like acetate [18], azide [19] and cyanate [20] to form 1D alternating chains. In order to obtain such complex polymers in a dimensionality larger than 1D, we used bis-monodentate extending bridging ligands like 4,4'-bipyridine, pyrimidine, pyrazine and some potential multidentate ligands like carboxylate as the second ligand to connect the *trans*-oxamidato-bridged copper(II) dimers to synthesize 2D sheet-like or 3D network polymers. We report here the synthesis and crystal structure of a 2D sheet-like complex polymer $[Cu_2(oxen)(pym)_2]_n(ClO_4)_{2n}$ together with description of its magnetic properties.

2. Experimental

2.1. Synthesis

The ligand H_2oxen and its mononuclear compound, Cu(oxen)·$2H_2O$, were obtained according to the literature [21]. The title complex was prepared as follows. To a heated aqueous solution of Cu(oxen)·$2H_2O$ (1 mmol, 40 ml) was added an aqueous solution of copper perchlorate (1 mmol, 5 ml) with stirring. Then an aqueous solution of pyrimidine (1 mmol, 20 ml) was added to the blue solution. After standing at room

---

[*] Corresponding author.

SSDI 0020-1693(94)04011-J

temperature for several days, well shaped black–green prismatic single crystals were obtained by slow evaporation. *Anal.* Calc. for $C_{14}H_{20}N_8O_{10}Cl_2Cu_2$: C, 25.51; H, 3.04; N, 17.01; Cu, 19.30. Found: C, 25.50; H, 3.10; N, 17.10; Cu, 19.29%.

2.2. Physical measurements

Magnetic measurement on a powder sample was carried out with a CAHN-2000 Faraday-type magnetometer in the temperature range 70–300 K. Correction for the diamagnetism of the complex was estimated from Pascal's constant to be -239×10^{-6} emu/mol. The powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer. IR spectra were recorded on a Nicolet FT-IR 170SX spectrophotometer as KBr pellets. Reflectance spectra were run on a Shimadzu UV-240 spectrophotometer.

2.3. Crystal structure determination

The intensity data were collected at room temperature on an R3M/E four circle diffractometer with graphite-monochromated Mo Kα radiation using the θ–2θ scan technique. Details on crystal data, intensity collections and refinements are presented in Table 1. The intensity was corrected for Lorentz–polarization and absorption effects. Structure refinements of the complex were carried out by full-matrix least-square techniques, starting with the position of the heavy atom determined from the experimental Patterson function, and using Fourier and Fourier difference synthesis to locate the lighter atoms. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms from the ΔF map, were refined with a common thermal parameter. The calculations were performed using SHELX 76 programs [22]. Neutral atomic scattering factors were taken from Ref. [23]. Throughout the refinements the function minimized was $\Sigma w(|F_o|-|F_c|)^2$. The atomic coordinates for the non-hydrogen atoms are listed in Table 2. Main bond distances and angles are presented in Table 3.

Table 1
Crystal data and experimental details for the title complex

Formula	$C_{14}H_{20}N_8O_{10}Cl_2Cu_2$
M_r	658.6
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.143(2)
b (Å)	8.646(3)
c (Å)	16.787(5)
β (°)	97.35(2)
V (Å^3)	1172.1(5)
Z	4
D_{calc} (g cm^{-3})	1.87
μ(Mo Kα) (cm^{-1})	21.15
F(000)	664
Crystal dimensions (mm)	0.36×0.46×0.60
T (K)	294
Scan mode	θ–2θ
Scan rate (° min^{-1})	8
Collection range (°)	$2\leqslant2\theta\leqslant52$
Reflections of unique measured	2664
Reflections of unique observed	2125 ($I\geqslant3\sigma(I)$)
Largest shift (e.s.d.)	0.169
R^a	0.0386
$R_w{}^b$	0.0394
Residual extrema (e Å^{-3})	0.853
Goodness of fit	1.625

$^aR=\Sigma|F_o-F_c|/\Sigma|F_o\Sigma|$.

$^bR_w=\Sigma[|F_o-F_c|w^{1/2}]/\Sigma[|F_o|w^{1/2}]$; $w=[\sigma^2(F)+0.0002F^2]^{-1}[1-\exp(-5(\sin\theta/\lambda)^2)]$.

Table 2
Fractional atomic coordinates and isotropic thermal parameters (Å^2) for the title complex

Atom	x	y	z	U
Cu	0.1418(1)	0.0700(1)	0.1459(1)	0.032(1)
Cl	0.6748(1)	0.1465(1)	0.3611(1)	0.045(1)
N(1)	0.1770(3)	0.1015(3)	0.0355(1)	0.035(1)
N(2)	0.3769(4)	0.1577(4)	0.1672(2)	0.044(1)
N(3)	0.0014(3)	−0.1990(3)	0.3341(1)	0.037(1)
N(4)	0.1195(3)	−0.0111(3)	0.2561(1)	0.032(1)
O(1)	−0.0694(3)	−0.0330(3)	0.0941(1)	0.038(1)
O(2)	0.5903(8)	0.2780(5)	0.3279(3)	0.121(2)
O(3)	0.8427(5)	0.1664(8)	0.3872(4)	0.131(3)
O(4)	0.5971(7)	0.1009(9)	0.4274(3)	0.142(3)
O(5)	0.6425(7)	0.0258(5)	0.3053(3)	0.124(2)
C(1)	−0.0701(4)	−0.0385(3)	0.0184(2)	0.032(1)
C(2)	0.3280(5)	0.1789(4)	0.0220(2)	0.048(1)
C(3)	0.4543(5)	0.1413(6)	0.0921(2)	0.056(1)
C(4)	0.0168(4)	−0.1280(4)	0.2652(2)	0.036(1)
C(5)	0.2143(4)	0.0380(4)	0.3224(2)	0.039(1)
C(6)	0.2085(5)	−0.0302(4)	0.3955(2)	0.045(1)
C(7)	0.0981(5)	−0.1478(4)	0.3993(2)	0.043(1)

3. Results and discussion

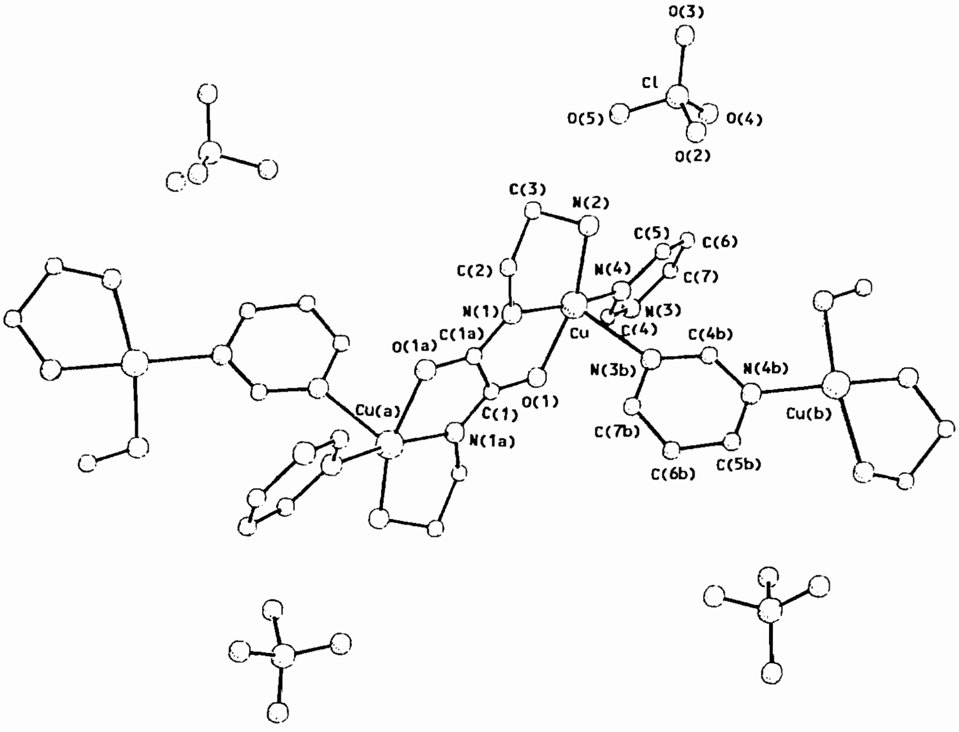
3.1. Description of the structure

The structure of this complex consists of a 2D array of copper(II) ions bridged by bis-tridentate oxen in *trans*-conformation and bis-monodentate pyrimidine in an asymmetric bonding mode. A perspective view of the asymmetric unit along with the atom-labelling scheme and of three symmetry-related units is depicted in Fig. 1. The inversion centre stands at the middle of the C(1)–C(1a) bond. The packing of the 2D sheet parallel to the *bc* plane is shown in Fig. 2.

Copper atoms are in a distorted square-based pyramidal geometry with a CuN_4O chromophore. The equatorial plane is defined by the oxygen (O(1)), amide nitrogen (N(1)) and amine nitrogen (N(2)) atoms of the oxen ligand in *trans*-conformation, and a nitrogen

Table 3
Main bond distances (Å) and angles (°) for the title complex

Cu–N(1)	1.930(2)	Cu–N(2)	2.047(3)	Cu–N(4)	2.009(2)
Cu–O(1)	2.031(2)	Cu–N(3b)	2.358(3)	Cl–O(2)	1.407(5)
Cl–O(3)	1.391(4)	Cl–O(4)	1.404(6)	Cl–O(5)	1.405(5)
N(1)–C(2)	1.443(5)	N(1)–C(1a)	1.294(4)	N(2)–C(3)	1.486(5)
N(3)–C(4)	1.329(4)	N(3)–C(7)	1.339(4)	N(4)–C(4)	1.333(4)
N(4)–C(5)	1.339(4)	O(1)–C(1)	1.272(3)	C(1)–N(1a)	1.294(4)
C(1)–C(1a)	1.519(6)	C(2)–C(3)	1.497(5)	C(5)–C(6)	1.367(5)
C(6)–C(7)	1.365(5)				
N(1)–Cu–N(2)	82.3(1)	N(1)–Cu–N(4)	167.3(1)		
N(2)–Cu–N(4)	99.3(1)	N(1)–Cu–O(1)	82.7(1)		
N(2)–Cu–O(1)	163.5(1)	N(4)–Cu–O(1)	94.0(1)		
N(1)–Cu–N(3b)	98.8(1)	N(2)–Cu–N(3b)	97.5(1)		
N(4)–Cu–N(3b)	93.5(1)	O(1)–Cu–N(3b)	91.4(1)		
O(2)–Cl–O(3)	115.8(4)	O(2)–Cl–O(4)	107.1(4)		
O(3)–Cl–O(4)	108.0(3)	O(2)–Cl–O(5)	107.2(3)		
O(3)–Cl–O(5)	113.3(4)	O(4)–Cl–O(5)	104.8(4)		
Cu–N(1)–C(2)	116.8(2)	Cu–N(1)–C(1a)	116.3(2)		
C(2)–N(1)–C(1a)	126.6(3)	Cu–N(2)–C(3)	107.7(2)		
C(4)–N(3)–C(7)	116.6(3)	C(4)–N(3)–Cu(a)	128.2(2)		
C(7)–N(3)–Cu(a)	114.4(2)	Cu–N(4)–C(4)	120.2(2)		
Cu–N(4)–C(5)	122.9(2)	C(4)–N(4)–C(5)	116.7(3)		
Cu–O(1)–C(1)	109.8(2)	O(1)–C(1)–N(1a)	129.2(3)		
O(1)–C(1)–C(1a)	118.9(3)	N(1)–C(2)–C(3)	106.8(3)		
N(2)–C(3)–C(2)	108.9(3)	N(3)–C(4)–N(4)	125.4(3)		
N(4)–C(5)–C(6)	121.8(3)	C(5)–C(6)–C(7)	117.5(3)		
N(3)–C(7)–C(6)	122.0(3)				



(a) -x, -y, -z. (b) -x, 1/2+y, 1/2-z.

Fig. 1. A perspective view of the title complex with the atom-labelling scheme.

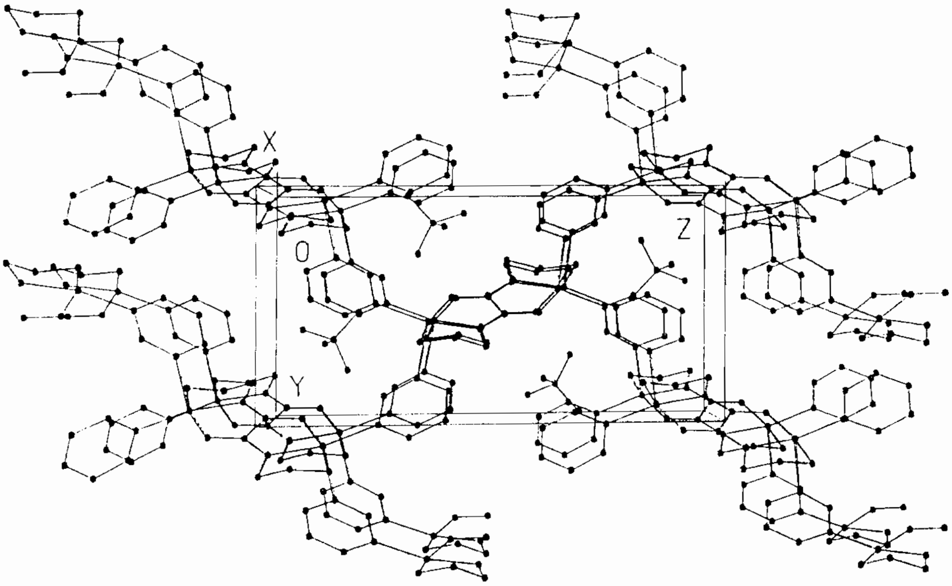


Fig. 2. A view of the crystal packing down the *a* axis for the title complex.

(N(4)) atom of the pyrimidine ligand bonded axially to another neighboring copper centre through its N(3) atom. The axial site is occupied by the N(3b) atom from another pyrimidine ligand bound equatorially to the next Cu(b) centre by its N(4b) atom. Pyrimidine bridges the copper centres in an antisymmetric fashion with the bond distance of Cu–N(3b) (2.358(3) Å) in the axis being longer than that of Cu(b)–N(4b) (2.009(2) Å) in the equator. The largest deviation from the least-squares plane through N(1)N(2)N(4)O(1) is 0.045 Å at the N(1) site, and the copper centre lies 0.184 Å out of this plane toward the axial N(3b) atom. The bond distance for Cu–N(1) (1.930(2) Å), shorter than that for Cu–O(1) and Cu–N(2) (2.031(2) and 2.047(3) Å, respectively), accords with those found in other oxamidato-bridged copper(II) complexes [19,20,24]. The significant shortening of the Cu–N(1) bond length agrees with the strong basicity of the deprotonated amide nitrogen atom.

The deprotonated oxen ligand adopts the *trans*-conformation forming two five-membered chelate rings on each metal ion. The three atoms (Cu, C(2) and C(1a)) around N(1) lie in a plane with bond angles of 116.8(2), 116.3(2) and 126.6(3)° for Cu–N(1)–C(2), Cu–N(1)–C(1a) and C(2)–N(1)–C(1a), respectively. This fact, together with the bond distances and planarity of the oxamidato bridge, reveals that N(1) and its symmetry-related N(1a) are sp^2-hybridized and that the π-electrons of C(1)–O(1) and C(1a)–O(1a) are delocalized to form a conjugated system. The mean planes of the two pyrimidine ligands (one in the axis and the other in the equator) bound to a copper centre, forming a dihedral angle of 81.5° with each other, have a dihedral angle of 77.6 and 20.9°, respectively, with the mean plane defined by the four bonding atoms in the equator. The copper···copper separations through oxen and pyrimidine bridges are 5.28 and 6.19 Å, respectively.

The oxen and pyrimidine ligands are both planar, with atom-to-mean plane distances no larger than 0.01 Å. From one layer to the next, they are both related by translation, so their mean planes are strictly parallel. They overlap only partially with a distance of 4.03 and 5.16 Å between the mean planes for oxen and pyrimidine ligands, respectively. The shortest interlayer copper···copper distance is 7.72 Å for Cu···Cu(1) where Cu(1) denotes the symmetry operation $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.

3.2. Spectroscopic data

The powder reflectance spectrum of the complex consists of two charge-transfer bands at 26 300 and 27 700 cm^{-1}, and of two broad bands centred at 16 000 and 17 000 cm^{-1} ascribed to d–d transitions with the square-pyramidal surrounding. Compared with the mononuclear compound Cu(oxen)·2H$_2$O in *cis*-conformation with a CuN$_4$ chromophore, the title complex in *trans*-conformation with a CuN$_3$O chromophore exhibits a red shift due to (i) the weaker ligand field associated with an oxygen donor ligand compared with a nitrogen one, and (ii) the lower co-planarity relative to the mononuclear compound Cu(oxen)·2H$_2$O.

The IR spectrum of the complex shows the band of perchlorate at 1074 cm^{-1}. The ν(C=O) stretching frequency of the oxamidato group at 1651 cm^{-1} shifts toward a higher wavenumber compared with that of the mononuclear compound Cu(oxen) (1615 cm^{-1}) owing to the higher bond order of C=O in the polynuclear compound [17]. The ν(NH$_2$) bands are in the normal region between 3100 and 3500 cm^{-1} in the title complex.

3.3. EPR spectra and magnetic properties

The polycrystalline powder room-temperature EPR spectra of the complex consist of a single quasi-symmetric signal centred at $g=2.10$ whose intensities decrease with a decrease in temperature, showing the triplet of the spectra [25]. No half-field transition due to a weak zero-field splitting is observed.

The temperature dependence of the magnetic moment per copper atom of $[Cu_2(oxen)(pym)_2]_n(ClO_4)_{2n}$ in the form μ_{eff} versus T is shown in Fig. 3. The μ_{eff} for each copper atom at 300 K is only 0.92 BM, lower than the moment value for a paramagnetic system with $S=1/2$. This fact together with the smooth decrease of μ_{eff} with T in the range 300–70 K is indicative that an antiferromagnetic exchange at temperatures higher than 300 K is operative between the copper atoms. As one looks at the structure of the complex, two different exchange pathways are possible, one through the oxen and the other through the pyrimidine bridging ligand. It is now well established that $C_2X_2Y_2^{2-}$ (X, Y = O, N, S) ligands are very efficient in propagating magnetic interaction between two copper centres relatively far from each other when both the sets of oxygen and nitrogen donors occupy equatorial coordination sites in the metal environments with $|J|>300$ cm^{-1} ($H=-JS_1S_2$) [13]. On the other hand, bridging ligands like pyrazine and pyrimidine are known to be unable to transmit efficiently magnetic coupling as shown in $[Cu_2(dien)_2(pyz)](ClO)_4)_4$ [26] and $[Cu_2(dien)_2(pym)](ClO_4)_4$ [27] with $|J|<5$ cm^{-1}, so the magnetic exchange transmitted by the pyrimidine bridge in this complex is expected to be very small relative to the strong exchange by the oxen ligand and is negligible. Therefore, although the crystal structure suggests a sheet-like 2D network, it should be possible to interpret the data with a simple modified Bleaney–Bowers equation, since the magnetic system for this compound behaves as a sheet-like 2D network of weakly interacting dimers.

$$=\frac{2Ng^2\beta^2}{KT}\left[3+\exp\left(-\frac{J}{KT}\right)\right]^{-1}(1-\rho)+\frac{Ng^2\beta^2}{2KT}\rho+2N_\alpha \quad (1)$$

Since the molar susceptibility at low temperature is close to Pascal's constant used for diamagnetic correction, the susceptibility was only measured up to 70 K. Fitting the experimental data to Eq. (1) yields a best fit with the parameters $J=-582$ cm^{-1}, $\rho=1.1\%$ and $R=2.1\times10^{-4}$ by putting $g=2.10$ which is the average value measured from EPR spectra on a powder sample.

Alternatively, we fitted the data by the empirical expression proposed by Hatfield for alternating chains [28] or by a modification of the Bleaney–Bowers expression (2), taking into account the intermolecular interactions J' between z neighbours by means of a zJ' term in a molecular field approach.

$$\chi_M=\frac{2Ng^2\beta^2}{K(T-zJ')}(1-\rho)\left[3+\exp\left(-\frac{J}{KT}\right)\right]^{-1}+\frac{Ng^2\beta^2}{2KT}\rho+2N_\alpha \quad (2)$$

We found the intramolecular J value for this compound close to the value obtained from expression (1), without significant improvement of the fits. This result strongly supports our first hypothesis: the magnetic behaviour of the sheet-like polymer can be interpreted essentially within the binuclear (pym)Cu(oxen)Cu(pym) unit.

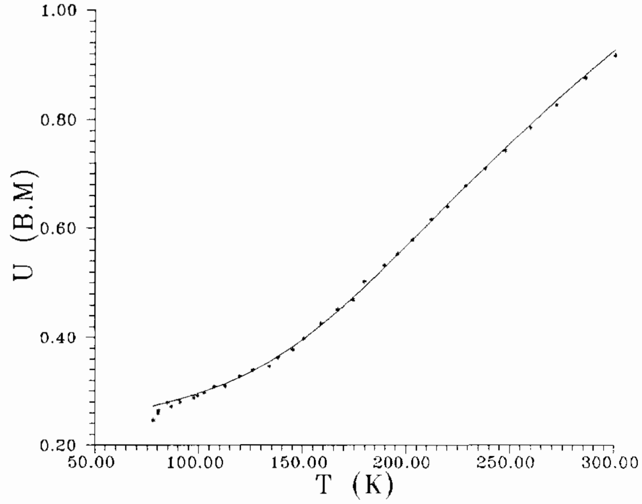


Fig. 3. Experimental (∗) and calculated (–) temperature dependence of μ_{eff} for the title complex.

4. Supplementary material

Lists of observed and calculated structure factors, complete bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atoms parameters are available from the authors on request.

References

[1] G. De Munno, M. Julve, M. Verdaguer and G. Bruno, *Inorg. Chem., 32* (1991) 2215.
[2] H. Oshio and V. Nagashima, *Inorg. Chem., 31* (1991) 3295.
[3] B. Chrari, J.H. Helms, O. Piovesana, T. Tarantelli and P.F. Zanazzi, *Inorg. Chem., 25* (1986) 870.
[4] C. Benelli, D. Gatteschi, D.W. Carneigie, Jr. and R.L. Carlin, *J. Am. Chem. Soc., 107* (1985) 2560.
[5] E. Coronado, M. Drillon, A. Fuertes, D. Beltran, A. Mosset and J. Galy, *J. Am. Chem. Soc., 108* (1986) 900.

[6] M. Julve, M. Verdaguer, G. De Munno, J.A. Real and G. Bruno, *Inorg. Chem., 32* (1993) 795.

[7] J.A. Real, G. De Munno, M.C. Munoz and M. Julve, *Inorg. Chem., 30* (1991) 2701.

[8] H. Tamaki, J.Z. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, *J. Am. Chem. Soc., 114* (1992) 6974.

[9] V. Gadet, T. Mallah, I. Castro and M. Verdaguer, *J. Am. Chem. Soc., 114* (1992) 9213.

[10] J.S. Haynes, S.J. Rettig, J.R. Sams, R. C. Thompson and J. Trotter, *Can. J. Chem., 65* (1987) 420.

[11] A. Bencini, M. Di Varia, A.C. Fabretti, D. Gatteschi and Z. Zanchini, *Inorg. Chem., 23* (1984) 1620.

[12] J. Ribas, A. Garcia, R. Costa, M. Monfort, S. Alvarez, C. Zanchini, X. Solans and M.V. Domenech, *Inorg. Chem., 30* (1991) 841.

[13] O. Kahn, *Angew. Chem., Int. Ed. Engl., 24* (1985) 834.

[14] V.G. Albano, C. Castellari, A.C. Fabretti and A. Giusti, *Inorg. Chim. Acta, 191* (1992) 213.

[15] Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem., 25* (1986) 439.

[16] F. Lloret, Y. Journaux and M. Julve, *Inorg. Chem., 29* (1990) 3967.

[17] H. Ojima and K. Nonoyama, *Coord. Chem. Rev., 92* (1988) 85.

[18] A. Bencini, C. Benelli, A.C. Fabretti, G. Franchini and D. Gatteschi, *Inorg. Chem., 25* (1986) 1063.

[19] F. Lloret, M. Julve, J.A. Real, J. Faus, R. Ruiz, M. Mollar, I. Castro and C. Bois, *Inorg. Chem., 31* (1992) 2956.

[20] F. Lloret, M. Julve, J. Faus, R. Ruiz, I. Castro, M. Mollar and M. Philoche-Lerisalles, *Inorg. Chem., 31* (1992) 784.

[21] H. Ojima and K. Yamada, *Nippon Kagaku Zasshi, 89* (1968) 490.

[22] G.M. Sheldrick, *SHELX 76*, a program for crystal structure determination. University of Cambridge, UK, 1976.

[23] *International Tables for X-Ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974.

[24] H. Okawa, N. Matsumoto, M. Koikama, K. Takede and S. Kida, *J. Chem. Soc., Dalton Trans.,* (1990) 1383.

[25] M. Julve, G. De Munno, G. Bruno and M. Verdaguer, *Inorg. Chem., 27* (1988) 3160.

[26] M. Julve, M. Verdaguer, J. Faus, F. Tinti, J. Morntal, A. Monge and E. Gutierrz-Puebla, *Inorg. Chem., 26* (1987) 3520.

[27] Z.N. Chen and W.X. Tang, unpublished work.

[28] W.E. Hatfield, *J. Appl. Phys., 52* (1981) 1985.