Short Communication

Spectroscopic and magnetic properties, and crystal structure of a dimer copper(II) complex via hydrogen bonding with a weak ferromagnetic interaction

José M. Moreno, José Ruiz,
José Manuel Dominguez-Vera
and Enrique Colacio*
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada (Spain)

(Received October 26, 1992; revised February 8, 1993)

Abstract

The preparation, spectroscopic and magnetic properties, and crystal structure of $[Cu(Cl)(HL)(H_2O)]_2 \cdot 6H_2O$ (HL stands for the monodeprotonated form of 4-methyl-amino-1,3-dimethyl-5((2′-carboxyphenyl)azo)uracil) are reported. Crystals are monoclinic, of space group $P2_1/n$, with cell constants $a=7.358(1)$, $b=20.542(4)$ and $c=13.130(3)$ Å, $\beta=93.23(3)°$ and $Z=4$. The structure was solved and refined to $R=0.059$ ($R_w=0.047$). The structure consists of Cl···H–O hydrogen-bonded dinuclear units, which are also coupled via hydrogen bonds to form the tridimensional network. The geometry of each $CuNO_3Cl$ chromophore is almost that corresponding to an ideal square-pyramid. The magnetic results indicate a ferromagnetic ground state. The nature of the magnetic interaction is discussed on the basis of structural data.

Introduction

Many examples of dimer formation through cooperative hydrogen bonding have been reported since Yoneda and Kida [1] first suggested it. Furthermore, some magneto-structural studies have been performed on antiferromagnetic spin-coupled copper(II) complexes via hydrogen bonding [2–9]. Even though some structural factors seem to affect the magnitude of the antiferromagnetic interaction, no general correlation was found.

Relevant to the present paper is the hydrogen bridged trimeric copper(II) complex $[Cu_3(RS\text{-a})_2(RS\text{-ap})_6][CF_3SO_3]_4$ (where *RS*-Hpa and *RS*-Hap represent *R,S*-2-aminopropan-1-ol and *R,S*-1-aminopropan-2-ol, respectively) [8], which, to the best of our knowledge, is the only complex described in the literature showing ferromagnetic behaviour via hydrogen bonding. The structure of this complex consists of layers of unique O–H···O hydrogen-bonded trinuclear units. The weak ferromagnetic behaviour of this compound ($J=0.06$ cm^{-1}) has been explained on the basis of the structural data, which show that the equatorial coordination planes are almost perpendicular, resulting in an unfavourable orientation of the magnetic orbitals of the copper ions.

In the present work we report on the structure and magnetic studies of the hydrogen-bonded dinuclear copper(II) complex $[Cu(Cl)(HL)(H_2O)]_2 \cdot 6H_2O$ (where H_2L is 4-methylamino-1,3-dimethyl-5((2′-carboxyphenyl)azo)uracil) exhibiting a weak, but definite, overall ferromagnetic behaviour.

Experimental

Preparation of the ligand

H_2L was synthesized in two steps. 6-Methylamino-1,3-dimethyluracil was prepared by adding 6-chloro-1,3-dimethyluracil (5 g, 0.03 mol) to a stirred solution of methylamine in water (40 wt.%, 15 ml). After 15 min, a white precipitate was collected, washed with cold water and air-dried (yield 85%). The H_2L ligand was obtained by coupling diazotized anthranilic acid with 6-methylamino-1,3-dimethyluracil, keeping the temperature below 4 °C. The orange-coloured product was collected and then again reprecipitated from dilute NaOH by addition of acetic acid to give an analytical pure sample (yield 45%). *Anal.* Found: C, 52.7; H, 4.8; N, 22.1. Calc. for $C_{14}H_{15}N_5O_4$: C, 53.0; H, 4.7; N, 22.1%. δ_H (300 MHz, DMSO-d$_6$) 3.20 [3H, s, N(4)–CH_3], 3.45 [3H, s, N(1)–CH_3], 3.48 [3H, s, N(3)–CH_3], 7.45 [1H, m,C(12)H], 7.78 [1H, m, C(10)H], 7.87 [1H, m, C(11)H], 8.09 [1H, d, C(13)H], 15.90 [1H, s, COOH]; δ_c (300 MHz, DMSO-d$_6$) 27.86 C(3), 31.71 C(1), 36.35 C(41), 116.31 C(5), 116.61 C(10), 118.21 C(14), 126.23 C(13), 131.56 C(12), 134.76 C(11), 141.92 C(9), 148.11 C(4), 154.16 C(2), 157.68 C(4), 167.43 C(15). IR (KBr, cm^{-1}): 3600–3200 br, ν(O–H) + ν(N–H); 1720, ν(C(2)=O); 1653, ν(C(6)=O); 1467, ν(N=N); 1351, ν(C–O) + δ(OH).

Preparation of $[Cu(Cl)(HL)(H_2O)]_2 \cdot 6H_2O$

Copper chloride dihydrate (0.17 g, 1 mmol) was added to a stirred suspension of freshly prepared H_2L (0.32 g, 1 mmol) in 50 ml of a methanol–water mixture (4:1) at ambient temperature. Slow evaporation of the

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

resulting deep green solution at 4 °C yielded well developed green crystals suitable for X-ray diffraction study. *Anal.* Found: C, 34.5; H, 4.4; N, 14.4; Cu, 13.2. Calc. for $C_{14}O_8N_5ClH_{21}Cu$: C, 34.6; H, 4.3; N, 14.4; Cu, 13.1%. IR (KBr, cm^{-1}): 3378, ν(N(4)–H); 1717, ν(C(2)=O); 1608, ν(C(6)=O); 1378, ν(N=N); 1588, ν_{as}(COO); 1357, ν_s(COO).

Physical measurements

Microanalyses of C, H and N, IR and EPR spectra and magnetic measurements were performed as already described [10]. Copper was determined thermogravimetrically as CuO, using a Mettler TG-50 thermobalance.

Crystal data

$C_{14}H_{21}N_5O_8ClCu$, monoclinic, $a = 7.358(1)$, $b = 20.542(4)$, $c = 13.130(3)$ Å, $\beta = 93.23(3)°$, $U = 1981.5(7)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.634$ g cm^{-3}, $F(000) = 1028$, μ(Mo Kα) = 1.29 mm^{-1}, crystal dimensions: 0.19 × 0.22 × 0.15 mm.

X-ray data collection and structure determination

Single-crystal data collection was performed at ambient temperature with a Siemens R3m/V diffractometer using graphite monochromatized Mo Kα ($\lambda = 0.71069$ Å) radiation. The unit cell parameters were calculated by least-squares refinement of 25 well-centred reflections in the range $15 < 2\theta < 45$. The data were collected by $\omega/2\theta$ scan mode $(3 \leq 2\theta \leq 60)$. Intensities of four check reflections measured after 60 min showed only statistical variation. A total of 4177 reflections was considered as observed with $F > 4\sigma(F_o)$. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods and subsequent Fourier syntheses of the SHELXTL-PLUS program [11]. In the final refinements, all non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the water molecules were located in difference-Fourier maps and were refined isotropically. The positions of the remaining hydrogen atoms were calculated with isotropic temperature factors ($U = 0.05$), $U = 0.08$ for the nine methyl protons, and were not refined. Neutral atomic scattering and dispersion factors were those included in the program package.

The function minimized was $\Sigma\omega(\Delta F)^2(1/\omega = \sigma^2(F_o))$, resulting in a final $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ value of 0.059 and $R_\omega = [(\Sigma\omega|F_o - F_c|)^2/\Sigma\omega|F_o|^2|^{1/2}$ value of 0.047. Atomic coordinates are given in Table 1.

TABLE 1. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^4)

Atom	x	y	z	U_{eq}[a]
Cu	1506(1)	1144(1)	466(1)	358(2)
C(1)	44(6)	394(2)	−2771(2)	457(18)
Cl(1)	−1910(2)	964(1)	830(1)	521(5)
N(1)	570(4)	1082(2)	−2648(2)	307(12)
C(2)	477(6)	1461(2)	−3516(3)	330(18)
O(2)	−80(4)	1245(1)	−4331(2)	488(12)
C(3)	1103(6)	2481(2)	−4374(2)	438(18)
N(3)	1067(4)	2104(2)	−3419(2)	306(14)
N(4)	2242(5)	2978(2)	−2526(2)	313(15)
C(4)	1621(6)	2384(2)	−2498(3)	251(17)
C(5)	1428(5)	2004(2)	−1594(3)	233(16)
C(6)	1021(6)	1333(2)	−1692(3)	295(17)
O(6)	922(4)	945(1)	−960(2)	388(11)
N(7)	1486(4)	2343(2)	−716(2)	275(13)
N(8)	1368(4)	2076(2)	162(2)	266(13)
C(9)	1198(5)	2548(2)	958(3)	249(16)
C(10)	409(6)	3154(2)	700(3)	330(17)
C(11)	229(6)	3629(2)	1436(3)	439(19)
C(12)	794(6)	3502(3)	2448(3)	422(19)
C(13)	1543(6)	2910(2)	2699(3)	340(18)
C(14)	1742(6)	2411(2)	1984(3)	272(16)
C(15)	2539(6)	1786(2)	2368(3)	310(18)
O(16)	2608(4)	1296(2)	1788(2)	525(13)
O(17)	3106(4)	1758(1)	3279(2)	479(12)
C(41)	3088(6)	3375(2)	−1699(3)	450(19)
O(1W)	2240(5)	232(2)	664(2)	531(15)
O(2W)	5237(5)	8(2)	1899(3)	570(15)
O(3W)	4329(5)	520(2)	3788(2)	576(15)
O(4W)	7577(5)	198(2)	4828(2)	568(15)
H(1WA)	2214(68)	−129(16)	165(27)	1051(202)
H(1WB)	3378(32)	112(21)	1054(27)	659(167)
H(2WA)	4766(72)	155(27)	2559(22)	1291(247)
H(2WB)	6214(52)	317(20)	1739(37)	1181(240)
H(3WA)	3822(54)	944(11)	3561(29)	611(155)
H(3WB)	3492(46)	267(18)	4198(26)	738(174)
H(4WA)	8442(47)	560(15)	4997(31)	670(167)
H(4WB)	6424(42)	372(26)	4492(37)	1247(251)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Description of the structure

The structure consists of Cl···H–O hydrogen-bonded dinuclear units, which are also coupled via hydrogen bonds to form the tridimensional network. A perspective view of the dinuclear unit is shown in Fig. 1, together with the atomic labelling. Selected bond lengths and bond angles are listed in Table 2.

The environment of each copper ion is (4+1). Four short bonds of *c.* 2.0 Å are formed with the O(6), N(8) and O(16) atoms from the monodeprotonated ligand and the O(1w) atom from the coordinated water molecule. The axial position is occupied by the chlorine atom at a longer distance, 2.612(2) Å. The (4+1) coordination mode is compatible with two idealized geometries: square-pyramidal and trigonal bipyramidal. The procedure proposed by Muetterties and Guggenberg [12] locates the coordination polyhedron at *c.* 3% of the $C_{4v} \leftrightarrow D_{3h}$ deformation pathway, the geometry being almost square-pyramidal. In a square-pyramidal

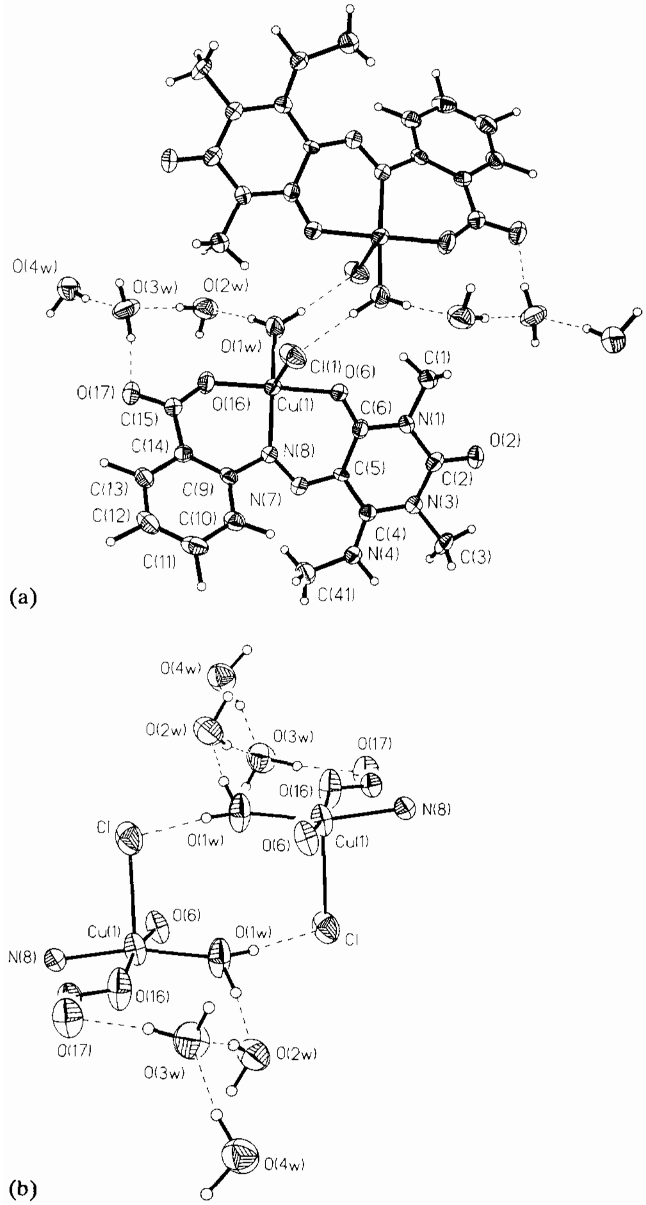

Fig. 1. (a) A perspective view of the dinuclear complex together with the labelling scheme. (b) A simplified view of the $CuClNO_3$ chromophore and hydrogen network along the O(6)–Cu–O(16) angle.

TABLE 2. Selected intramolecular bond lengths (Å) and bond angles (°)

Cu–O(6)	1.941(2)	C(5)–N(7)	1.346(5)
Cu–O(1w)	1.961(3)	N(7)–N(8)	1.284(4)
Cu–O(16)	1.900(3)	N(8)–C(9)	1.435(5)
Cu–N(8)	1.958(3)	C(9)–C(14)	1.411(5)
Cu–Cl(1)	2.611(2)	C(14)–C(15)	1.490(6)
C(6)–O(6)	1.254(5)	C(15)–O(16)	1.264(5)
C(5)–C(6)	1.416(6)	C(15)–O(17)	1.245(4)
O(6)–Cu–O(16)	167.4(1)	N(8)–Cu–Cl(1)	97.8(1)
O(6)–Cu–N(8)	90.2(1)	O(16)–Cu–O(1w)	86.4(1)
O(6)–Cu–O(1w)	88.4(1)	O(16)–Cu–Cl(1)	102.8(1)
O(6)–Cu–Cl(1)	89.1(1)	O(1w)–Cu–Cl(1)	95.8(1)
N(8)–Cu–O(16)	92.3(1)	O(16)–C(15)–O(17)	121.4(4)
N(8)–Cu–O(1w)	166.2(1)		

description, the equatorial atoms are not coplanar but pair-wise distorted, so that O(6) and O(16) are lifted 0.017(7) and 0.018(2) Å, respectively, above the mean basal plane while N(8) and O(1w) are located 0.017(7) and 0.018(5) Å, respectively, below the plane. As usual, the copper(II) ion is lifted by 0.215(9) Å from the mean plane towards the apical Cl(1) atom [13].

It must be pointed out that, unlike the closely related ligand H_2L^1 (H_2L^1 stands for 6-amino-1,3-dimethyl-5(2'-carboxyphenyl)azouracil), which usually coordinates through the nitrogen atoms of the azo and the deprotonated amino group and one of the oxygen atoms of the carboxylate group in a tridentate doubledeprotonated fashion [9, 14], H_2L ligand acts in a monodeprotonated form through the O(6), N(8) and O(16) atoms. A comparison of both coordination modes reveals that, in the $[Cu(Cl)(HL)(H_2O)]_2 \cdot 6H_2O$ complex, the pyrimidine ring of the ligand is twisted by *c.* 180° around the C(5)–N(7) bond to avoid the steric interaction between methyl groups on N(3) and N(4) that would be present if the ligand coordinated through the deprotonated amino group. Thus, the ligand adopts a tridentate coordination mode similar to that showed by the related H_2L^2 ligand (H_2L^2 stands for 1,3-dimethyl-5(2'-carboxyphenyl)azobarbituric acid) [11, 15].

As usual, the tridentate behaviour of the ligand results in the formation of two six-membered rings having in common the Cu–N(8) bond. Bond lengths and angles in the ligand do not significantly differ from those found in the copper(II) complexes obtained by us with the ligands H_2L^1 and H_2L^2 [9, 10, 14, 15]. The pyrimidine and phenyl rings are almost planar with deviations from the least-square plane less than 0.07 Å. The pyrimidine and phenyl rings are not coplanar but twisted by an angle of 36° to each other.

The mononuclear entities are held together, mainly, by $Cl \cdots H{-}O(1w)^I$ hydrogen bonds ($I = -x, -y, -z$) of 3.145(3) Å. Besides the fairly strong $Cl \cdots H{-}O(1w)^I$ hydrogen bonding, other $Cl \cdots H{-}N$, $Cl \cdots H{-}O$ and $O \cdots H{-}O$ hydrogen bonds are present in the structure. Relevant intra- and inter-molecular hydrogen bond distances and angles are listed in Table 3.

Spectroscopic and magnetic properties

The polycrystalline X-band EPR spectrum of the complex at 90 K appears axial ($g_{\parallel} = 2.25$ and $g_{\perp} = 2.08$), as expected for a copper(II) ion with either $d_{x^2-y^2}$ or d_{xy} ground state. The signals are devoid of any hyperfine structure and no half-field signal transition is observed. The EPR spectrum of the complex, in DMSO solution

TABLE 3. Intra- and inter-molecular hydrogen-bond lengths (Å) and angles (°)

	Distance	Cl(O)···H–O(N)
Cl···O(1w)^{I}	3.145(3)	174(3)
Cl···N(4)^{II}	3.150(4)	^{a}
Cl···O(2w)^{III}	3.249(4)	161(4)
O(1w)···O(2w)	2.702(5)	169(4)
O(2w)···O(3w)	2.810(5)	168(5)
O(3w)···O(4w)	2.765(5)	168(5)
O(3w)···O(17)	2.767(5)	172(4)
O(3w)···O(4w)^{IV}	2.780(5)	166(3)
O(4w)···O(2)^{V}	2.934(5)	166(4)

I = $-x$, $-y$, $-z$; II = $-1+x$, $1-y$, $-z$; III = $1-x$, y, z; IV = x, $1+y$, z; V = $-x$, $1-y$, $-z$.

[a] The hydrogen atom was not found in the difference Fourier map.

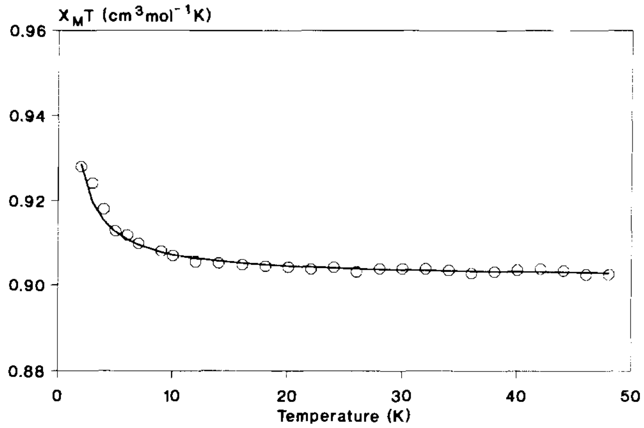

Fig. 2. Plot of the $\chi_M T$ product vs. temperature. The solid line was generated from the best-fit magnetic parameters.

at 90 K, exhibits an intense and quasi isotropic resonance at $g = 2.06$ and a half-field signal at 4.02 indicating the existence of a populated triplet. Moreover, in the region 2700–3000 G, four poorly resolved copper hyperfine lines can be observed with an average spacing of 91×10^{-4} cm^{-1}, which would correspond to the hyperfine components of a pair of $\Delta M = 1$ zero-field splitting transition. The other three lines of this seven-line pattern are obscured by the intense quasi isotropic signal. There should be another seven-line pattern resulting from the zero-field splitting at a much higher field position. However, none of its components were located in the spectrum.

The magnetic susceptibility of a powdered sample of the complex was investigated in the temperature range 250–2 K. The thermal variation of the product $\chi_M T$ is represented in Fig. 2 from 48 to 2 K. From 250 to *c.* 40 K, $\chi_M T$ remains practically constant and equal to 0.903 cm^3 mol^{-1} K, which is the value expected for an isolated copper(II) ion with a g value of 2.18. On further lowering the temperature, $\chi_M T$ increases, yielding a value of *c.* 0.93 cm^3 mol^{-1} K at 2 K, which is indicative of the weak, but definite, ferromagnetic behaviour.

The best fit of the experimental data to the Bleaney–Bowers equation [16] was found with $2J/k = 0.13$ K and $g = 2.19$ with $R = 6 \times 10^{-5}$. The presence of a weak ferromagnetic coupling can be explained on the basis of the structure of the complex. In an almost idealized square-pyramidal geometry (see above), the magnetic orbital, occupied by the unpaired electron of the Cu(II), is of the d_{xy} type. From the structural data, a pathway for the observed spin coupling could be CuCl(1)···HO(1w)^{I}Cu^{I} (I = $-x$, $-y$, $-z$), which involves an axial position where the spin density is very weak. As consequence, a very poor overlap of the magnetic orbitals centred on the Cu(II) ions is expected [17]. This fact would cause a reduction of the antiferromagnetic contribution (J_{AF}) so that the ferromagnetic contribution (J_F) becomes predominant. The existence of additional hydrogen bonds, which involve more extended pathways, would contribute to a much less extent to the interaction.

Acknowledgements

The authors are grateful to DGCYT for the project of investigation PB88-0482 and to the Junta of Andalucía for financial support. J.M.M. and J.M.D-V. are grateful to thc Ministry of Education and Science for a grant.

References

1 H. Yoneda and S. Kida, *J. Am. Chem. Soc., 82* (1960) 2139.
2 J. A. Bertrand, P. G. Eller, E. Fujita, M. O. Lively and D. G. VanDerveer, *Inorg. Chem., 18* (1979) 2419.
3 J. A. Bertrand, E. Fujita and D. G. VanDerveer, *Inorg. Chem., 19* (1980) 2022.
4 L. Walz, H. Paulus and W. Haase, *J. Chem. Soc. Dalton Trans.,* (1985) 913; (1985) 1243.
5 H. Muhonen, *Inorg. Chem., 25* (1986) 4692.
6 F. Nepveu, S. Gehring and L. Walz, *Chem. Phys. Lett., 128* (1986) 300.
7 E. Hilms, H. Elias, H. Paulus and L. Walz, *J. Chem. Soc., Dalton Trans.,* (1986) 2169.
8 G. Nieuwpoort, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Dalton Trans.,* (1983) 531.
9 E. Colacio, J. P. Costes, R. Kivekäs, J. P. Laurent, J. Ruiz and M. Sundberg, *Inorg. Chem., 30* (1991) 1475.
10 E. Colacio, J. M. Dominguez-Vera, J. P. Costes, R. Kivekäs, J. P. Laurent, J. Ruiz and M. Sundberg, *Inorg. Chem., 31* (1992) 774.
11 *SHELXTL-PLUS program,* X-ray Instrument Group, Nicolet Instrument Corp., Madison, WI, 1990.
12 E. L. Muetterties and L. J. Guggenberg, *J. Am. Chem. Soc., 96* (1974) 1748.
13 B. J. Hathaway, *Struct. Bonding (Berlin), 57* (1984) 55.

14 E. Colacio, J. P. Costes, R. Kivekäs, J. P. Laurent and J. Ruiz, *Inorg. Chem., 29* (1990) 4240.

15 E. Colacio, J. Ruiz, J. M. Moreno, R. Kivekäs, M. Sundberg, J. M. Dominguez-Vera and J. P. Laurent, *J. Chem. Soc., Dalton Trans.,* (1993) 157.

16 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A, 214* (1952) 451.

17 O. Kahn, in R. D. Willett, D. Gatteschi and O. Kahn (eds.), *Magneto-Structural Correlations in Exchange Coupled Systems,* Reidel, Dordrecht, 1985.