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Exchange interactions in a one-dimensional bromo-bridged copper(II) compound with a ladder-like structure

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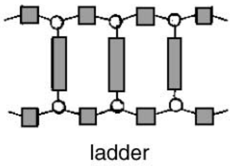
A deep green complex, $[Cu(L)(\mu\text{-}Br)Br]_2$ (L = 1,4-diazacycloheptane) was synthesized and its crystal structure and magnetic properties have been studied. The structure determination reveals that in the binuclear unit each copper(II) occupies a distorted square pyramidal geometry in which each bridging bromine atom is simultaneously ligated in axial and equatorial positions between two adjacent copper(II) centres. The binuclear units are packed along the [101] direction. Each dimer is connected to its two nearest neighbours by two Cu–(μ-Br) ··· H–N–Cu hydrogen bonding interactions resulting in an infinite 1D ladder-like chain. The magnetic data were fitted considering the interdimer interactions using different models to obtain precise results and the susceptibility *vs.* temperature curve for the complex exhibits a maximum at 12 K indicating antiferromagnetic behaviour. Magneto-structural correlations have also been carried out.

Introduction

In the development of magneto-structural correlations in dinuclear coordination complexes the dimeric copper(II) systems have fascinated chemists for several decades.[1–20] The importance of copper(II) lies in its d^9-configuration which involves only one magnetic orbital in exchange processes and on its ability to adopt a wide variety of coordination geometries. The exchange process is observed to be affected by several structural parameters and therefore the establishment of magneto-structural correlations has become a subject of much discussion. The type and magnitude of the magnetic exchange interaction depends on the bridge identity, the metal–metal separation, bridging angles, dihedral angles between the planes containing the metal ions and the metal ion stereochemistries. In the case of dinuclear copper(II) systems the reports currently available in the literature reveal that the best correlations are obtained in dihydroxo-bridged copper(II) where a linear relationship between the singlet–triplet energy gap (J) and Cu–OH–Cu bridging angles, is observed.[1–4] The replacement of OH by OR ligands produces structural distortions yielding complexes with different geometries. On the other hand, the replacement of OH or OR bridging ligands by X (Cl^-, Br^-) with a $[Cu(\mu\text{-}X)_2Cu]_n$[5–20] motif displays a wealth of different structures with a variety of bond distances (Cu–X) and angles (Cu–X–Cu) depending on the coordinated ligands and also on the counter anions. As a consequence, for this type of complex, the superexchange pathway depends on various orbitals, and therefore, each type of structural dimer (or derivative) has to be studied separately in order to draw meaningful magneto-structural correlations. There are more complexes with Cl as bridging ligand than with Br and magneto-structural correlations are more extensive with the chloride bridging ligand. Here we present the synthesis, structure and magnetic properties of a 1D H-bonded ladder-like complex of copper(II) (Scheme 1) constructed *via* dimeric bromo-bridged units, $[Cu(L)(\mu\text{-}Br)Br]_2$ (L = 1,4-diazacycloheptane). Low temperature magnetic data are fitted considering the three different Cu ··· Cu interactions in the one-dimensional ladder-like chain and the best fit parameters lead to the coupling constants $J_1 = -11.76$ cm^{-1}, $J_2 = -3.39$ cm^{-1} and $J_3 = -4.34$ cm^{-1} with identical g factors of 2.06.



Scheme 1

Experimental

Materials

High purity (98%) 1,4-diazacycloheptane (L) was purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyser and copper(II) content was estimated volumetrically.[21] The magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS SQUID magnetometer (applied field 5 T) working in the temperature range 300–4 K. Diamagnetic corrections were estimated from Pascal's Tables.

Synthesis of $[Cu(L)(\mu\text{-}Br)Br]_2$

A methanolic solution (5 cm^3) of L (0.1 g, 1 mmol) was added dropwise to a methanolic solution (15 cm^3) of copper(II)

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Table 1 Crystal data and structure refinement for $[Cu(L)(\mu\text{-}Br)Br]_2$

Formula	$C_{10}H_{24}Cu_2N_4Br_4$
Formula weight	646.68
Space group	$P21/c$ (no. 14)
a/Å	13.8176(16)
b/Å	11.4131(13)
c/Å	13.3206(15)
Crystal system	Monoclinic
β/°	115.157(2)
T/K	295
Z	4
V/Å^3	1901.4(4)
λ(Mo-Kα)/Å	0.71073
$\theta_{\text{min-max}}$/°	1.6–28.3
D_c/g cm^{-3}	2.260
μ(Mo-Kα)/mm^{-1}	10.638
Total data	11954
Unique data (R_{int})	4573, 0.060
Observed data [$I > 2\sigma(I)$]	3234
R	0.0365
wR, S	0.0952, 0.99

bromide (0.223 g, 1 mmol) with constant stirring for 15 min. The resulting deep green solution was filtered and the filtrate was kept in a $CaCl_2$-desiccator. After several days a deep green compound separated out, which was filtered and dried. Single-crystals suitable for X-ray analysis were obtained by diffusing the methanolic solution (5cm^3) with diethyl ether. Yield 75%. Analytical data: Found: C, 18.58; H, 3.69; N, 8.71; Cu, 19.67%. Calc. for $C_{10}H_{24}N_4Br_4Cu_2$: C, 18.52; H, 3.73; N, 8.64; Cu, 19.64%.

Crystallographic data collection and refinement

A suitable single-crystal of the title complex was mounted on a Bruker SMART CCD diffractometer equipped with a graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation source. The unit cell parameters were determined by least squares refinements of all reflections. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction were also employed using the SAINT[22] program. A total 11954 reflections were measured and 3234 were assumed observed the applying the condition $I > 2\sigma(I)$. The structure was solved by Patterson syntheses and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the parent atom. The refinement converged to residual indices $R = 0.0365$; $wR = 0.0952$ with $I > 2\sigma(I)$. Complex neutral atom scattering factors[23] were used throughout. All calculations were carried out using SHELXS-86,[24] SHELXL-97,[25] PLATON-99[26] and ORTEP-3[27] programs. All crystallographic data are summarized in Table 1. Selected bond lengths and angles are given in Table 2 and H-bonding parameters are displayed in Table 3.

CCDC reference number 159343.

See http://www.rsc.org/suppdata/dt/b1/b109571b/ for crystallographic data in CIF or other electronic format.

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu(L)(\mu\text{-}Br)Br]_2$

Br1–Cu1	2.4681(8)	Br1–Cu2	2.7922(8)
Br3–Cu1	2.3883(9)	Br4–Cu2	2.4063(9)
Br2–Cu2	2.4216(8)	Br2–Cu1	2.7756(8)
Cu1–N1	2.009(4)	Cu1–N2	2.014(5)
Cu2–N3	2.009(4)	Cu2–N4	1.998(5)
Cu1–Br1–Cu2	86.32(2)	Cu1–Br2–Cu2	87.59(3)
Br1–Cu1–Br3	96.73(3)	Br1–Cu1–N1	163.34(11)
Br1–Cu1–N2	89.82(11)	Br1–Cu1–Br2	91.93(2)
Br3–Cu1–N1	93.12(13)	Br3–Cu1–N2	162.01(13)
Br3–Cu1–Br2	100.54(3)	N1–Cu1–N2	77.01(17)
Br2–Cu1–N1	99.45(10)	Br2–Cu1–N2	95.95(13)
Br4–Cu2–Br2	96.54(3)	Br4–Cu2–N3	93.31(16)
Br4–Cu2–N4	159.54(14)	Br1–Cu2–Br4	98.63(3)
Br2–Cu2–N3	165.13(14)	Br2–Cu2–N4	90.36(14)
Br1–Cu2–Br2	92.53(2)	N3–Cu2–N4	76.7(2)
Br1–Cu2–N3	96.99(13)	Br1–Cu2–N4	100.30(14)

Table 3 Hydrogen bonds (Å, °) for $[Cu(L)(\mu\text{-}Br)Br]_2$

D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
N–H1 ··· Br2$^{\text{I}}$	0.9105	2.5908	3.397(4)	148.00
N3–H3 ··· Br1$^{\text{II}}$	0.9101	2.6968	3.541(5)	154.70

Symmetry codes: I $1 - x, -y, 1 - z$; II $-x, -y, -z$.

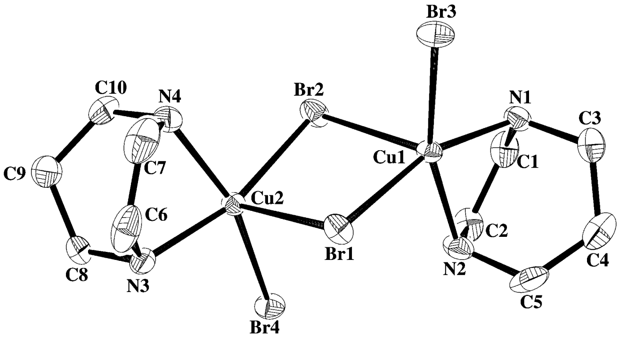


Fig. 1 ZORTEP diagram of $[Cu(L)(\mu\text{-}Br)Br]_2$, with atom labeling scheme and 50% probability ellipsoids for all non-hydrogen atoms.

Results and discussion

Description of the structure

Structural analysis reveals that the complex consists of isolated dimeric $[Cu(\mu\text{-}Br)(L)Br]_2$ units. The ORTEP drawing of the dimeric unit with atom numbering scheme is depicted in Fig. 1. Each copper atom in the dimer is attached to two nitrogen atoms of the cyclic diamine ligand (L), two bridging bromides and one pendant bromide atom. The geometry around each copper atom is distorted square pyramidal with a CuN_2Br_3 chromophore. The two nitrogen atoms (N1, N2) from L and the two bromide atoms (Br1, Br3), one from bridging [Cu1–Br1, 2.4681(8) Å] and another from pendant [Cu1–Br3, 2.3883(9) Å, see Table 2] form the equatorial plane around Cu1 and the axial position is occupied by another bridging bromide atom (Br2) [Cu1–Br2, 2.7756(8) Å]. For Cu2 the equatorial plane is occupied by two nitrogen atoms (N3, N4) from L and two bromide atoms (Br2, Br4) [Cu2–Br2, 2.4216(8) and Cu2–Br4, 2.4063(9) Å]. Another bridging bromide atom (Br1) [Cu2–Br1, 2.7922(8) Å], occupies the apical position. The deviations of Cu1 and Cu2 from the equatorial plane are 0.112 and 0.131 Å, respectively. It is interesting to note that the bridging Br1 atom is in the equatorial position around Cu1 and in the axial position around Cu2 whereas Br2 is ligated in reverse manner. The values of Cu–N bond distances, 1.998(5)–2.014(5) Å, are very close to those observed in previously reported Cu(II) complexes of the same ligand L.[28] The Cu ··· Cu separation in the dimer is 3.606 Å and this is in good agreement with the analogous dimeric Cu(II) systems.[9] Each dinuclear $[Cu_2Br_2]$ unit linked with neighbours by Cu—Br ··· HN–Cu bonds (Table 3) forms a one-dimensional 'ladder-like' structure (Fig. 2). It is important to point out, from a magnetic point of view, the peculiarities in this one-dimensional ladder-like compound are that all Cu ··· Cu distances in the dinuclear unit are equal (3.606 Å), but the distances between the dinuclear entities alternate

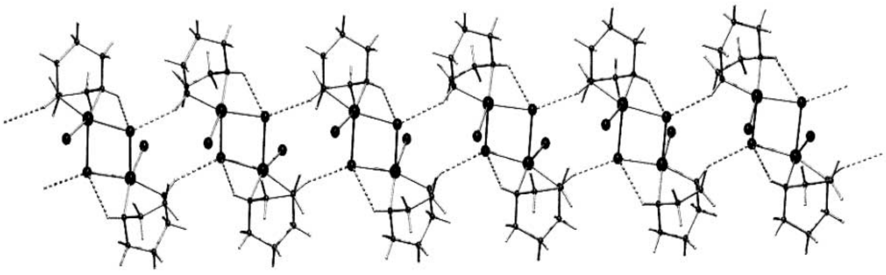


Fig. 2 View of the 1D ladder-like chain built by the dimeric units $[Cu(L)(\mu\text{-}Br)Br]_2$ through H-bonding.

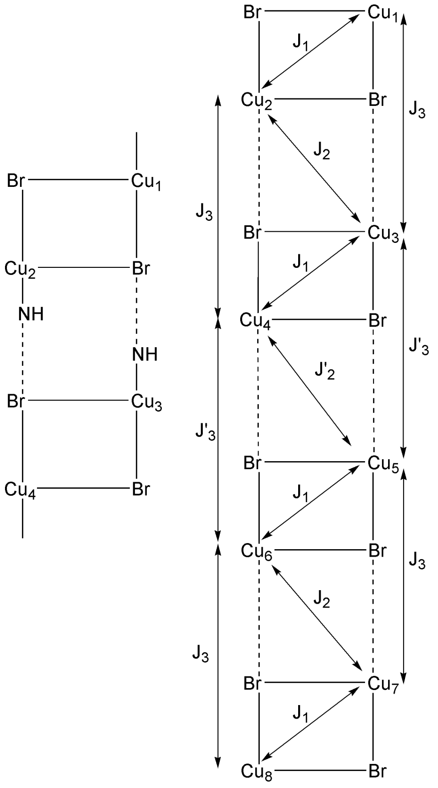


Fig. 3 Magnetic interaction pathways between the different copper(II) centres.

(Fig. 3): Cu1 ··· Cu3 (or Cu2 ··· Cu4) are 7.273 Å and Cu3 ··· Cu5 (or Cu4 ··· Cu6) are 7.312 Å, respectively; Cu2 ··· Cu3 is 6.042 Å and Cu4 ··· Cu5 is 5.956 Å.

Magnetic properties

The magnetic properties of the title complex in the form of χ_M and $\chi_M T$ *vs.* T plots are shown in Fig. 4, being the magnetic susceptibility per twelve copper(II) ions (as explained below). The value of χ_M at room temperature is 0.0155 $cm^3\ mol^{-1}$. The χ_M values increase monotonically until 12 K, attaining a value of 0.18 $cm^3\ mol^{-1}$ and then decrease down to 4 K (0.13 $cm^3\ mol^{-1}$). The presence of a maximum for χ_M at 12 K is clearly indicative of weak global antiferromagnetic behaviour. The value of $\chi_M T$ at room temperature is 4.66 $cm^3\ mol^{-1}$ K which corresponds to twelve spin doublets. The $\chi_M T$ values decrease monotonically until 4 K, attaining a value of 0.52 $cm^3\ mol^{-1}$ K. This feature is characteristic of the presence of weak antiferromagnetic interactions between the Cu(II) ions.

In order to interpret the magnetic properties it is convenient to schematize this tetranuclear entity to see which are the exchange pathways and the possible Hamiltonians to use (Fig. 3). Thus, in the light of previous structural discussions, we have to interpret the magnetic behaviour through a very complicated model with at least five J parameters (J_1, J_2, J_2', J_3 and J_3') (Fig. 3). A Hamiltonian with these five J parameters (along with the g value) would be impossible to solve due to overparameterization and the possible correlation between J values. Taking into account the actual structure we can realize that the alternating Cu ··· Cu distances are very similar and, thus, the corresponding J parameters must be very similar. Consequently, we are going to assume that $J_2 = J_2'$ and $J_3 = J_3'$. As with the Cl analogue,[9] we are going to study the magnetic fit following different steps (from the simplest to the more complicated and, thus, most realistic).

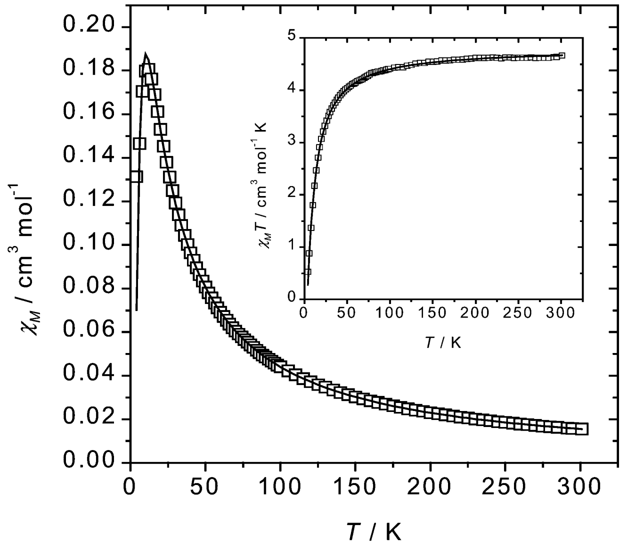


Fig. 4 χ_M *vs.* T and $\chi_M T$ *vs.* T plots for $[Cu(L)(\mu\text{-}Br)Br]_2$. The solid lines correspond to the best fit.

Model A. We can assume, with the aid of the structure (Fig. 1), that the intradimer exchange pathway leads to an exchange interaction that is considerably stronger than those propagated by the interdimer exchange pathways. The use of this model is suggested by the fact that the strong exchange pathway corresponds to a Cu ··· Cu distance (3.606 Å) which is much shorter than the other Cu ··· Cu interdinuclear pathways: from 5.9 to 7.3 Å. With this hypothesis, the magnetic susceptibility can be fitted with the Bleaney–Bowers[29] equation for a couple of $S = ½$ spins. The best fit to our data yielded $J = -11.38\ cm^{-1}$ and $g = 1.91$, which is not acceptable owing to the low g value. Introducing a new J' parameter into the Bleaney–Bowers formula, according to the theory of intermolecular interactions reported by O. Kahn,[30] a reasonably good fit can be obtained with the following parameters: $J = -9.74\ cm^{-1}$; $J' = -15.0\ cm^{-1}$, $g = 2.16$ and $R = 2.5 \times 10^{-4}$. Although the model represented provides a rather precise fit to the experimental data, it is not an acceptable physical picture of the material, since the J' term is greater than the primary interaction parameter (J). The same results have been reported for the Cl analogue.[9]

Model B. The second model that was attempted, following the procedure given by the Cl analogue,[9] was the simplest extended-system model suggested by the structure of the

Table 4 Structural and magnetic parameters for the Cu_2Br_2 core (basal–apical positions, type I) in dinuclear copper(II) complexes bridges by two Br ligands

Compound[a]	Cu–Br_{basal}/Å	Cu–Br_{apical}/Å	Cu–Cu/Å	Φ (Cu–Br–Cu)/°	Φ/R(apical)	τ[b]	J/cm^{-1}	Ref.
$[Cu(meox)_2Br_2]_2$	2.56	2.71	3.63	86.98	32.09	0.26	−7.6	16
$[Cu_2(dien)_2Br_2](ClO_4)_2$	2.42	2.89	3.79	90.64	31.36	0.30	1.4	17
$[Cu(tmso)_2Br_2]_2$	2.45	3.01	3.75	85.97	28.56	0.51	−16.0	6
$[Cu_2(terpy)_2Br_2](PF_6)_2$	2.36	2.82	3.36	88.58	31.41	0.24	−3.7	18
$(3ap)_2[Cu_2Br_6]_2 \cdot H_2O$	2.45	2.79	3.82	93.37	33.46	0.60	−26.9	7
$[Cu(tz)_2Br_2]_2$	2.47	3.12	3.99	90.20	28.91	—	−10.4	19
$[Cu(bp3ca)Br_2]_2 \cdot H_2O$	2.39	3.05	3.79	87.28	28.61	0.1	91.52[c]	14
$[Cu(\alpha\text{-pic})_2Br_2]_2$	2.43	3.87	4.93	100.4	25.94	—	−2.5	20
$[Cu(L)Br_2]_2$	2.42	2.78	3.61	86.31, 87.59	31.27	0.02; 0.1	−11.76	This work

[a] meox = 4-Methyloxazole; dien = diethyelenetriamine; tmso = tetramethylene sulfoxide; terpy = 2,2′:6′,2″-terpyridyl; 3ap = 3-aminopyridinium cation; tz = thiazole; bp3ca = 2,2′-bipyridine-3,3′-dicarboxylic acid; α-pic = 2-methylpyridine. [b] τ = Addison parameter for pentacoordinated Cu [$\tau = 0$, square pyramid (*SPY*); $\tau = 1$, trigonal bipyramid (*TBPY*)].[37] [c] This value is extremely high. According to the same authors, "the magnitude of J is suspect, although one can be certain of its ferromagnetic nature". To the best of our knowledge, the shape of the $\chi_M T$ curve indicated in the paper, should correspond to a small J value, ferromagnetic, but not close to 90 cm^{-1}.

compound. This is the alternating-chain model, the equation for which is given in the literature for two kinds of α (being $\alpha = J_1/J_2$).[30,31] With the empirical equation for $0 < \alpha < 0.5$, the best magnetic parameters are $J_1 = -14.60$ cm^{-1}, $\alpha = 0.85$ and $g = 2.12$ which is incoherent with the α value assumed (< 0.5). Using the empirical formula valid for $0.5 < \alpha < 1$, the best fit magnetic parameters are: $J_1 = -10.61$ cm^{-1}, $\alpha = 0.88$ and $g = 2.07$. Obviously, taking into account the structural data, Cu ··· Cu distances and intra and inter pathways between dinuclear units, an α value of 0.88 is difficult to justify because the difference between J_1 and J_2 would be very small.

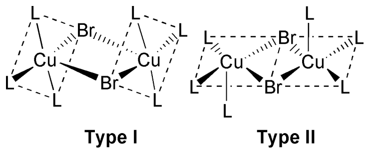
Model C. As pointed out by Chiari *et al.* for the chloro derivative[9] the models that neglect J_1, J_2 and J_3 (*i.e.* exchange interactions between nearest neighbours or next-nearest neighbours in the chain structure depicted in Fig. 3) are not realistic but they did not report the possible fit with this hypothesis for the Cl complex.[9] Thus, a Hamiltonian must be used that simultaneously contains at least J_1, J_2 and J_3, *i.e.*, a Hamiltonian of the form:

$$H = -J_1(S_1S_2 + S_3S_4 + S_5S_6 + S_7S_8 + S_9S_{10} + S_{11}S_{12}) - J_2(S_2S_3 + S_4S_5 + S_6S_7 + S_8S_9 + S_{10}S_{11} + S_{12}S_1) - J_3(S_1S_3 + S_3S_5 + S_5S_7 + S_7S_9 + S_9S_{11} + S_{11}S_1 + S_2S_4 + S_4S_6 + S_6S_8 + S_8S_{10} + S_{10}S_2)$$

This Hamiltonian assumes the J pathways given in Fig. 3. To fit the experimental data we have assumed a ring of twelve atoms with $S = ½$, which should describe the behaviour of an infinite chain. The fit was performed using the CLUMAG program.[32] The fit of the magnetic data assuming identical g factors leads to $J_1 = -11.76$ cm^{-1}; $J_2 = -3.39$ cm^{-1}, $J_3 = -4.34$ cm^{-1}, $g = 2.06$ and $R = 2.2 \times 10^{-5}$ (R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma[(\chi_M T)_{obs}]^2$). These values are realistic because the main pathway is the coupling between Cu1 ··· Cu2 in a dinuclear entity, and the other two interactions are smaller, as expected.

Magneto-structural correlations

Two main types of pyramidal arrangement are found in dinuclear [Cu(μ-Br)$_2$Cu] complexes reported in the literature (Scheme 2),[14,15] showing several distortions: (a) square pyramids sharing one base-to-apex edge but with a parallel basal plane (Type I) and (b) square pyramids sharing a basal edge with coplanar basal planes (Type II). In type I the coordination of the Cu(II) is normally intermediate between square pyramid and trigonal bipyramid.



Scheme 2

Focusing our attention only in type I (such as in the title complex), the number of possible parameters which influence the magnetic coupling is high and, thus, the possibility to correlate structural data with magnetism is limited. As can be seen from Table 4 almost all complexes are antiferromagnetically coupled, and J is small (from -27 cm^{-1} to -2.5 cm^{-1}). Only two complexes are ferromagnetic. In our complex, distances and angles are in the range reported for all other complexes and thus $J = -11.7$ cm^{-1} is normal.

The τ distortion (Table 4) may be the most important parameter: if τ was 0 (ideal square pyramid, with the magnetic orbital in $d_{x^2-y^2}$) the overlap between the two Cu(II) ions would be nil and, thus, the coupling would be zero or slightly ferromagnetic. For $\tau = 1$, the *TBPY* geometry would give magnetic orbitals centred on d_{z^2}, thus the overlap would also be zero. The overlap is only possible (to give antiferromegnetic coupling) when the geometry of the Cu(II) ions is a mixture of *SPY* and *TBPY*, such as in all the cases reported in Table 4. Thus, the ferromagnetic coupling in two complexes (Table 4) is difficult to interpret.

The other parameters have drawn the attention of several workers.[33] It has been suggested that the most reliable parameter is the ratio φ/R, R being the longer distance of Cu to the bridging halide.[33b] In our case, $\varphi = 86.31$ and 87.59°, very close to 90°; $\varphi/R = 31.55$ and 30.90° Å^{-1}, very similar to values reported for the chloro derivative (32.98° Å^{-1}), which is expected to lead to weakly antiferromagnetic interaction (Table 4).[14] Even if less theoretically studied,[34,35] the δ distortion (torsion angle between Cu1–Br1–Cu2–Br2 which enhances the non-planarity) creates a greater ferromagnetic contribution. In the present case, the δ dihedral angle is 10.3°, being 0° in all other complexes in Table 4. As a summary, weak interactions have been observed for unsymmetrical bridged complexes (Type I)[14] with a very few examples of ferromagnetism among them.[12] Recently, it has been suggested that a completely satisfactory explanation for the J (intradimer) value is not presently available and, for example, that J depends on both φ and R and not just their ratio.[14] More examples are needed to explain satisfactorily the magnetic behaviour.

Finally, regarding this intradimer [Cu$_2$Br$_2$] exchange pathway, it is clear in the literature that chloro and bromo complexes show similar magnetic behaviour, with the bromo complexes being more antiferromagnetic,[14,36] as expected for the greater delocalization that gives the bromide bridge and, thus, greater overlap. In the bromo complex, $J = -11.76$ cm^{-1}, while for the chloro complex J *ca.* -5 cm^{-1} (not fully calculated).[9]

The last point concerns the very weak antiferromagnetic interaction between the dimers in the ladder-like one-dimensional complex (Fig. 3). This weak interaction is logical, depending on the hydrogen bonding distance between Cu–Br ··· HN–Cu. These interactions are always weak and antiferromagnetic.

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References

1 P. J. Hay, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1975, **97**, 4884.
2 D. J. Hodgson, *Prog. Inorg. Chem.*, 1975, **19**, 173.
3 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.
4 M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259.
5 W. E. Marsh, K. C. Patel, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1983, **22**, 511.
6 C. P. Landee and R. E. Greeney, *Inorg. Chem.*, 1986, **25**, 3771.
7 J. T. Blanchette and R. D. Willet, *Inorg. Chem.*, 1988, **27**, 843.
8 B. Scott and R. Willet, *Inorg. Chim. Acta*, 1988, **141**, 193.
9 B. Chiari, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem.*, 1990, **29**, 1172.
10 M. T. Garland, J. Y. Saillard and E. J. Spodine, *Crystallogr. Spectrosc. Res.*, 1992, **22**, 467.
11 G. D. Fallon, B. Moubaraki, K. S. Murray, A. M. van der Bergen and B. O. West, *Polyhedron*, 1993, **12**, 1989.
12 M. A. Romero, J. M. Salas, M. Quirós, M. P. Sánchez, J. Romero and D. Martín, *Inorg. Chem.*, 1994, **33**, 5477.
13 S. S. Tandon, L. K. Thompson and J. N. Bridson, *Inorg. Chem.*, 1994, **33**, 490.
14 S. Menon, M. V. Rajasekharan and J. P. Tuchagues, *Inorg. Chem.*, 1997, **36**, 4341.
15 G. Pon, R. D. Willet, B. A. Prince, W. T. Robinson and M. M. Turnbull, *Inorg. Chim. Acta*, 1997, **255**, 325.
16 W. E. Marsh, T. L. Bowman, W. E. Hatfield and D. J. Hodgson, *Inorg. Chim. Acta*, 1982, **59**, 19 and references therein.
17 D. K. Towle, S. K. Hoffmann, W. E. Hatfield, P. Singh, P. Chaudhuri and K. Wieghardt, *Inorg. Chem.*, 1985, **24**, 4393 and references therein.
18 T. Rojo, M. I. Arriortua, J. L. Mesa, R. Cortés, G. Villeneuve and D. Beltran, *Inorg. Chim. Acta*, 1987, **134**, 59 and references therein.
19 M. James, H. Kawaguchi and K. Tatsumi, *Polyhedron*, 1998, **17**, 1843.
20 P. Singh, D. Y. Jeter, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 1657.
21 A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longman, New York, 4th edn., 1978.
22 Bruker, SMART and SAINT, Bruker AXS Inc., Madison, WI, USA, 1998.
23 A. J. Wilson, *International Tables for Crystallography*, Kluwer, Dordrecht, 1992, vol. C, Tables 4.2.6.8 and 6.1.1.4.
24 G. M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1985.
25 G. M. Sheldrick, SHELXL-97, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1997.
26 A. L. Spek, PLATON, Molecular Geometry Program, University of Utrecht, The Netherlands, 1999.
27 ORTEP-3 for windows: L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
28 P. S. Mukherjee, T. K. Maji, G. Mostafa, T. Mallah and N. Ray Chaudhuri, *Inorg. Chem.*, 2000, **39**, 5147.
29 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.
30 O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993, p. 132.
31 (*a*) W. E. Hatfield, *J. Appl. Phys.*, 1981, **52**, 1985; (*b*) J. W. Hall, W. E. Marsh, R. R. Weller and W. E. Hatfield, *Inorg. Chem.*, 1981, **20**, 1033.
32 The series of calculations were made using the computer program CLUMAG, which uses the irreducible tensor operator (ITO) formalism: D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.*, 1993, **123**, 231.
33 (*a*) W. E. Hatfield, in *Magnetostructural Correlations in Exchange Coupled Systems*, R. D. Willet, D. Gatteschi and O. Kahn, eds., Reidel, Dordrecht, The Netherlands, 1985, p. 555; (*b*) R. D. Willet, in *Magnetostructural Correlations in Exchange Coupled Systems*, R. D. Willet, D. Gatteschi and O. Kahn, eds., Reidel, Dordrecht, The Netherlands, 1985, p. 389.
34 O. Castell, J. Miralles and R. Caballol, *Chem. Phys.*, 1994, **179**, 377 and references therein.
35 (*a*) B. C. Gerstein, R. M. Gehring and R. D. Willet, *J. Appl. Phys.*, 1971, **43**, 1932; (*b*) S. A. Roberts, D. R. Bloomquist, R. D. Willet and H. W. Dodgen, *J. Am. Chem. Soc.*, 1981, **103**, 2103; (*c*) H. A. Groenendijk, H. W. Blote, A. J. Van Duynevelt, R. M. Gaura, C. P. Landee and R. D. Willet, *Physica B (Amsterdam)*, 1981, **106**, 47.
36 (*a*) G. O'Bannon and R. D. Willet, *Inorg. Chim. Acta*, 1981, **53**, L131; (*b*) R. D. Willet, *Inorg. Chem.*, 1986, **25**, 1918; (*c*) B. Scott, U. Geiser, R. D. Willet, B. Patyal, C. P. Landee, R. E. Greeney, T. Manfredini, G. C. Pellacani and A. B. Corradi, *Inorg. Chem.*, 1988, **27**, 2454.
37 A. W. Addison, T. N. Rao, J. Reedjik, J. van Rijn and C. G. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.