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Synthesis, crystal structure and magnetic properties of $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$ (tzq = [1,2,3]triazolo-[1,5-*a*]quinoline), a binuclear copper(II) complex with unusual monoatomic formate bridges†

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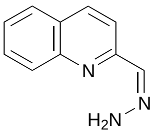
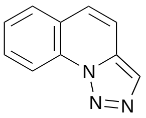
The compound $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$ (tzq = [1,2,3]triazolo[1,5-*a*]quinoline) was obtained under mild conditions by reaction between the hydrazone of quinoline-2-carbaldehyde and copper(II) formate in ethanolic aqueous solution and its crystal and molecular structure have been determined by X-ray diffraction methods: triclinic, space group $P\bar{1}$, $Z = 1$, $a = 8.209(4)$, $b = 12.156(4)$, $c = 12.649(4)$ Å, $\alpha = 63.21(3)$, $\beta = 81.42(3)$, $\gamma = 89.12(3)°$. The compound is built of centrosymmetric neutral dimeric $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]$ entities linked through hydrogen bonds involving water molecules and carboxylate groups. The copper atom is involved in a CuN_2O_2O' chromophore and lies in a tetrahedrally distorted square-pyramidal environment. The four equatorial donors are two *trans* nitrogen atoms from two tzq molecules and two oxygen atoms from two formate groups. One of the oxygens acts as a bridging ligand occupying the apical position of the symmetry-related copper atom in the dimer structure, which is viewed as two edge-sharing distorted square pyramids. This co-ordination behaviour (monoatomic bridging) is very unusual for the HCO_2^- anion. The EPR spectrum is characteristic of a triplet state with non-negligible zero-field splitting. Magnetic susceptibility measurements in the range 1.8–200 K showed weak antiferromagnetic exchange between the copper(II) ions ($2J = -1.05$ cm^{-1}). The observed behaviour is discussed on the basis of the crystal structure and compared with those reported for related μ-oxo carboxylate-bridged $[CuO_2Cu]$ dimers with parallel-planar geometry.

Recently we undertook a study of anhydrous copper(II) formate and characterised some adducts of this compound, with the aim of exploring the chemical and structural factors governing both magnetic and electrical properties in these systems.[1–3] To progress in this subject, we are now developing the study of the interaction between $Cu(HCO_2)_2$ and nitrogen-donor heterocyclic ligands, as several pyridine and quinoline hydrazones. During this investigation we prepared a new copper(II) complex containing one-atom formate bridges.

The occurrence of M−O−M bridges *via* one of the oxygen atoms is not very common in the chemistry of the carboxylate derivatives and in particular for the formate anion. Habitually, the carboxylate group, when acting as a bridging ligand, links adjacent metal centres through both oxygen atoms to form M−O−C−O−M bridges.[4,5] Consequently, only a few examples of systems with μ-oxo carboxylate bridges have been structurally characterised.[6–17] Empirical magnetostructural correlations in these kinds of systems have been of interest in recent years.[11c] As in other one-atom CuX_2Cu dibridged systems,[18–21] the extent of the exchange coupling between the metallic ions has been correlated with relevant topological features of the M−O−M bridges. Notwithstanding, the relative scarcity of well characterised compounds encourages the preparation and characterisation of new μ-oxo carboxylate-bridged systems in order to improve the proposed magnetostructural correlations.





tzq

In the present work we report the synthesis, structure and spectroscopic and magnetic characterisation of a new triazolo-containing copper(II) complex which is, to our knowledge, the first copper(II) formate adduct with monoatomic formate bridges. Its properties are compared with those reported for related systems.

Results and Discussion

We wished to study different copper(II) formate adducts with nitrogen-donor heterocyclic ligands such as several arylhydrazones. With this aim, we used the hydrazone of quinoline-2-carbaldehyde as potential ligand. Notwithstanding, the isolated compound was an unexpected copper(II) formate adduct which contains as N-donor ligand the compound [1,2,3]triazolo-[1,5-*a*]quinoline (hereafter, tzq).

As it is well known, the synthesis of triazole compounds by oxidative cyclisation of hydrazones is usually carried out by means of strong oxidants.[22] In particular, [1,2,3]triazolo[1,5-*a*]-quinoline has been obtained by oxidation of the hydrazone

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† *Non-SI units employed*: G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

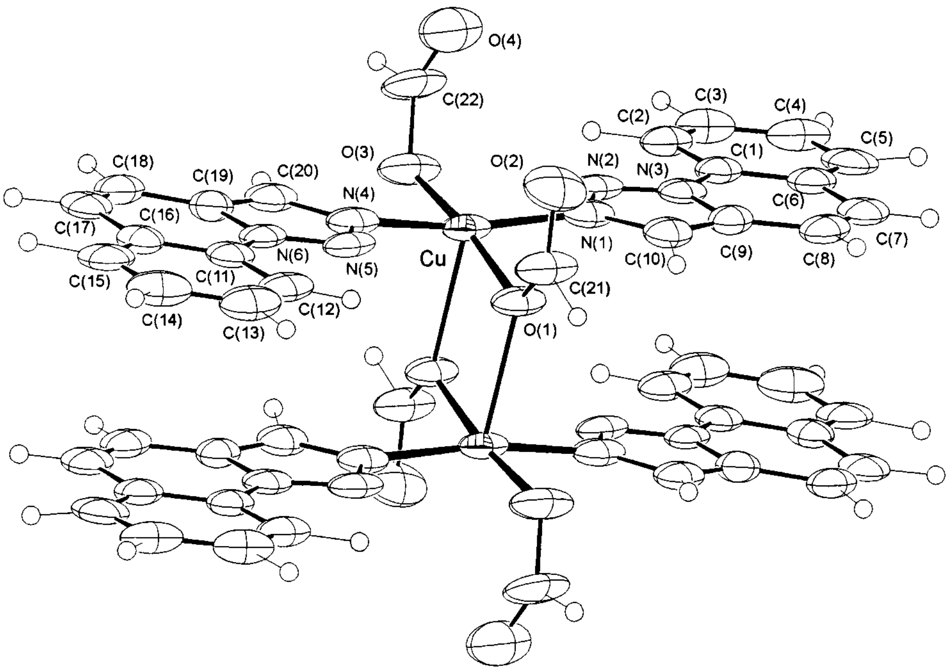

Fig. 1 Perspective view and atomic numbering of the [{Cu(tzq)$_2$(HCO$_2$)}$_2$(μ-HCO$_2$)$_2$] dimeric units

of quinoline-2-carbaldehyde with silver oxide or manganese dioxide.[23] Obviously, in our case the cyclisation was produced under milder conditions than those usually reported. In the literature we have found a reference to a similar observation. Battaglia *et al.*[24] refer to the formation of a triazolopyridine from an acylhydrazone in the presence of copper(II) nitrate, suggesting that the oxidation of the acylhydrazone is induced by molecular oxygen. In our case, some experimental observations lead us to suspect that copper(II) ions may be necessary to promote the oxidative cyclisation. So, when solutions of copper(II) formate and the hydrazone quinoline-2-carbaldehyde were mixed under a nitrogen atmosphere the formation of the triazoloquinoline was likewise observed. In a complementary experiment, a flow of air was passed through a methanolic solution of the aforementioned hydrazone for 24 h and no formation of triazoloquinoline was detected.

Crystal structure

The structure of the new compound [{Cu(tzq)$_2$(HCO$_2$)}$_2$(μ-HCO$_2$)$_2$]·4H$_2$O is built up of centrosymmetric dimeric entities which are linked through hydrogen bonds involving water molecules and formate groups, to give a chain structure running along the [1,1,$\bar{1}$] direction. Fig. 1 shows a perspective view of the dimeric unit with the atomic numbering scheme, and Fig. 2 a perspective view of the crystal packing in the unit cell. Selected bond distances and angles are listed in Table 1.

In the dimeric entity the two metal atoms are connected through the formate groups which act in a monoatomic bridging mode. This co-ordination behaviour is very unusual for the HCO$_2^-$ anions and has been reported for only a few copper(II) formate derivatives: both phases (α and β) of anhydrous copper(II) formate and the [MCu(HCO$_2$)$_4$] (M = Ca or Sr) and [Ca$_2$Cu(HCO$_2$)$_6$] mixed formates.[25,26] However, there is a significant difference between the structural function of the bridging HCO$_2^-$ groups in these systems and that observed in the present compound (see below).

The co-ordination sphere of the copper(II) ions is best described as a distorted square pyramid, thus displaying a 4+1 co-ordination mode (CuN$_2$O$_2$O′ chromophore). The basal co-ordination positions are occupied by two *trans*-oxygen atoms belonging to two formate groups and two nitrogen atoms from two tzq molecules. The five-co-ordination is achieved by linking to an oxygen atom occupying the equatorial site in the co-ordination polyhedron of the centrosymmetrically related copper(II) ion. Therefore, each bridging oxygen simultaneously occupies an equatorial co-ordination site on one copper(II) ion and an apical site on the other Cu^{II}. The topology of the so formed dimers is then viewed as edge-sharing distorted square pyramids. As expected, the axial Cu–O$_{ax}$ bond distance is longer (*ca.* 0.4 Å) than the equatorial Cu–O$_{eq}$ ones. On the other hand, Cu–N, Cu–O$_{ax}$ and Cu–O$_{eq}$ are within the range of values normally found for such bonds.

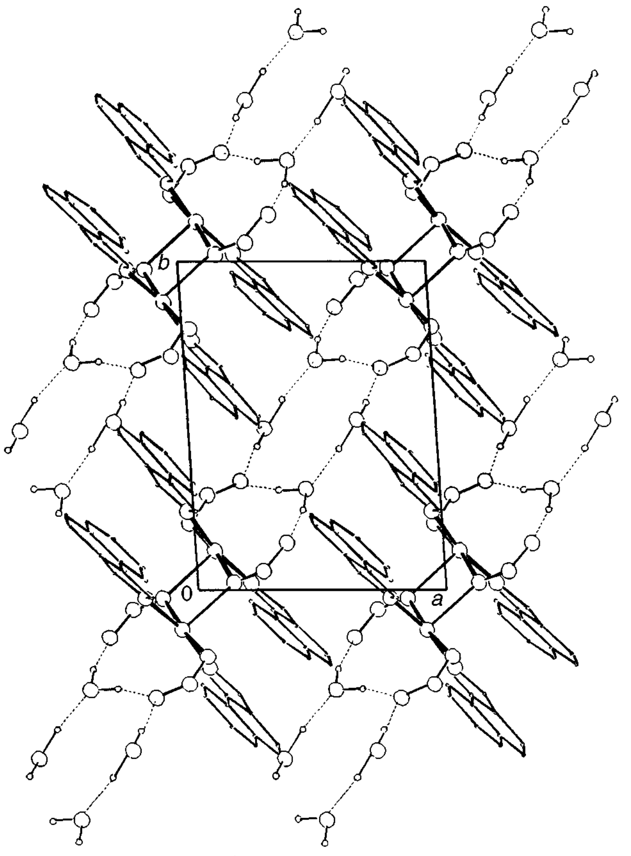

Fig. 2 Perspective view of the crystal packing in the unit cell

The four basal atoms are not coplanar, showing a slight but significant tetrahedral distortion. In fact, the two nitrogen atoms are displaced by 0.165(5) and 0.185(5) Å on one side of the CuN_2O_2 least-squares plane while the two oxygen atoms are 0.116(4) and 0.158(5) Å on the other side, with the copper atom lying nearly on that plane {its very small displacement [0.014(1) Å] is, as usual, towards the apical position}.

The bridging network Cu_2O_2 is strictly planar owing to the inversion centre, with a Cu···Cu separation of 3.339(2) Å. When compared with related systems containing bis(μ-oxo carboxylato) bridges,[6–17] the present compound shows a high value of the bridging angle Cu–O–Cu [$\varphi = 102.2(2)°$] as well as the shortest out-of-plane Cu–O distance [$R_0 = 2.331(4)$ Å]. As a result, the $\varphi : R_0$ ratio (43.9 : 1) is higher than those reported for such systems (see Table 3).

As described above, in the $[Cu_2(HCO_2)_4(tzq)_2]$ units there are two kinds of carboxylate groups. Two formate anions act as monodentate having a structural function 1-*s* whereas the remaining two act in a monoatomic bridging mode, thus exhibiting a 2-*sa* structural function. (In this notation, established by Porai-Koshits,[27] principal number = total co-ordination capacity of carboxylate, subscript = number of metal atoms attached to RCO_2, *a* = *anti* and *s* = *syn*.) To our knowledge, the present compound may by considered singular with the formate groups displaying such a structural function. In other systems where bridging μ-oxo formate ligands are present their structural function (a-4_3-a or *s*-3-*sa*) is different. In both kinds of carboxylate groups the C–O bond distances satisfy the relation $C–O_{coord} > C–O_{uncoord}$, as expected from the polarisation of the charge density towards the metal-bonded oxygen atoms. On the other hand, the large distances between the non-co-ordinating oxygen atoms of the formate ligands and the copper atoms [Cu···O(2) 3.123(6), Cu···O(4) 3.070(5) Å] are indicative that no significant bonding interactions (even semico-ordination)[28] are present.

The water molecules [O(5) and O(6)] are involved in moderate hydrogen bonds as indicated by the values of the intermolecular O···O and O···H distances and the corresponding O–H···O angles listed in Table 2. The O(5) molecule is bonded, acting as H-donor, to two non-co-ordinated oxygen atoms [O(2) and O(4)] of two formate groups, and also acts as H-acceptor towards an O(6) water molecule. The O(6) molecule, acts as a H-donor towards the O(5) molecule and the oxygen atom O(4). So, the $[Cu_2(HCO_2)_2(tzq)_2]$ units form infinite chains –[Cu(O,O)Cu]–[OCO···O(5)···O(6)···OCO]$_2$–[Cu-(O,O)Cu]– (the axis of which runs parallel to the $[1,1,\bar{1}]$ direction) as a result of the hydrogen-bond interactions with the water molecules, affording an interdimer Cu···Cu distance of 11.22(3) Å.

The tzq molecules are nearly planar within experimental error, with the maximum distance of any ring atom to its least-squares plane being 0.03 Å in each tzq molecule. They are slightly twisted with regard to the basal CuN_2O_2 plane [angles of 13.4(1) and 12.3(1)°]. On the other hand, the internal bonding parameters are comparable to those reported for related heterocyclic systems.[24,29–31] With regard to the co-ordinating ability of tzq, its behaviour as a ligand is consistent with expectations. Both non-bridgehead nitrogen atoms N(1) and N(2) would appear to be available sites for co-ordination. Preliminary studies[32] on the site of quaternisation of these types of compounds indicate that N(1) is the alkylation position. Hence, the behaviour of tzq as a monodentate ligand through the N(1) atoms is in accordance with previous experimental data as well as theoretical considerations.

Table 1 Selected bond lengths (Å) and angles (°) for the $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$ complex

Copper co-ordination sphere			
Cu–O(1)	1.950(4)	Cu–N(4)	2.015(6)
Cu–O(3)	1.915(5)	Cu–O(1$^{\rm I}$)	2.331(4)
Cu–N(1)	2.023(5)		
N(4)–Cu–O(1$^{\rm I}$)	90.6(2)	O(3)–Cu–N(1)	92.3(2)
N(1)–Cu–O(1$^{\rm I}$)	99.9(2)	O(1)–Cu–O(1$^{\rm I}$)	77.8(2)
N(1)–Cu–N(4)	169.2(2)	O(1)–Cu–N(4)	89.8(2)
O(3)–Cu–O(1$^{\rm I}$)	94.7(2)	O(1)–Cu–N(1)	89.9(2)
O(3)–Cu–N(4)	89.3(2)	O(1)–Cu–O(3)	172.5(2)
Formate ions			
O(1)–C(21)	1.267(9)	O(3)–C(22)	1.268(7)
O(2)–C(21)	1.223(7)	O(4)–C(22)	1.207(1)
O(1)–C(21)–O(2)	127.1(7)	O(3)–C(22)–O(4)	127.7(8)

Symmetry operator: I $-x, -y, -z$.

Table 2 Hydrogen bonds in the $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$ crystal

X–H···Y/Å	X–H/Å	X···Y/Å	H···Y/Å	X–H···Y/°
O(5)–H(501)···O(2)	1.04	2.82(1)	1.79	167
O(5)–H(502)···O(4)	0.99	2.81(1)	1.89	154
O(6)–H(601)···O(5)	1.16	2.83(1)	1.72	158
O(6)–H(602)···O(4$^{\rm I}$)	1.07	2.96(1)	1.89	174

Symmetry operator: I $-x+1, -y+1, -z-1$.

Electron spin resonance spectroscopy

The room-temperature polycrystalline powder EPR spectra at Q-band (Fig. 3) and X-band have been recorded and also the X-band spectrum at 4.2 K (Fig. 4). In all cases the spectrum shows the typical features of a triplet state with non-negligible zero-field splitting. In the X-band spectra the resonance corresponding to $\Delta M_S = \pm 2$ is clearly visible, together with four wide

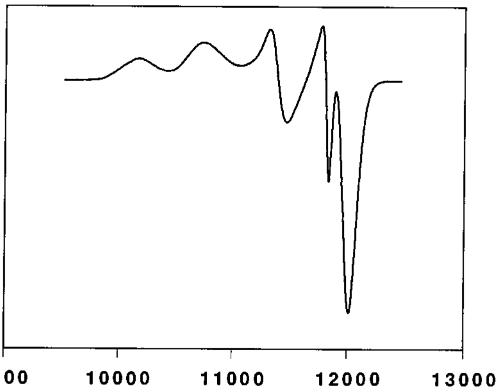

Fig. 3 The EPR powder spectrum (Q-band) of $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$ at room temperature

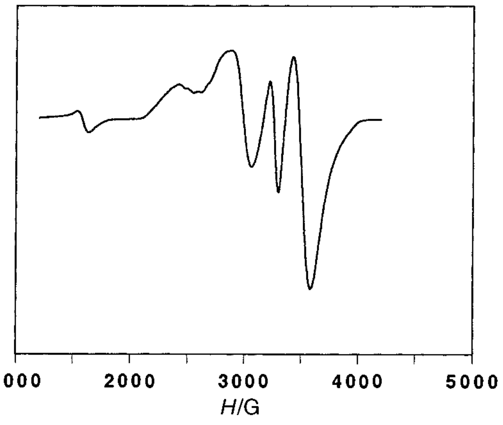

Fig. 4 The EPR powder spectrum (X-band) of $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$ at 4.2 K

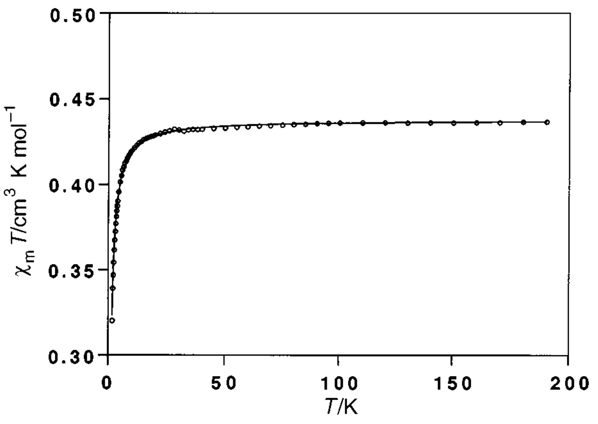

Fig. 5 Magnetic behaviour of $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$

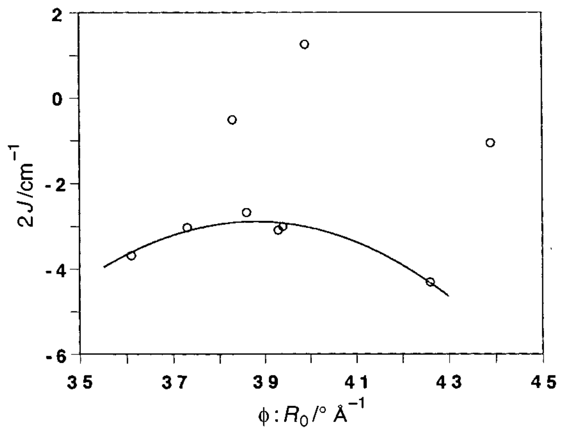

Fig. 6 Variation of $2J$ *vs.* $\varphi : R_O$

features corresponding to the $\Delta M_S = \pm 1$ region. On the contrary, the 'half field' signal is not observed in the Q-band spectrum while five features are resolved in the principal region. Moreover, in the low-temperature X-band spectrum seven copper hyperfine lines are roughly observed in the 2400 G region with an average separation of 80 G. The number of lines and the hyperfine separation (one half that expected for a monomeric copper compound) fully confirm the dimeric nature of the complex. The resonance field of the four fine features in the X-band spectra can be generated[33] with $g_z = 2.34$, $g_x = g_y = 2.07$, $|D| = 500$ G and E approximately zero (D and E are the zero-field splitting parameters). With this set of values only four of the five lines observed in the Q-band spectrum are explained. Notwithstanding, the fifth one situated at 11 800 G is appreciably less intense than the other four and may be due to a perpendicular component ($g = 2.05$) from a monomeric impurity, which is not observed in the X-band spectrum owing to the width of the lines. The g values are consistent with the structural findings corresponding to a CuN_2O_2O' chromophore with the copper(II) ions involved in a nearly square-pyramidal coordination and subsequently with a basically $d_{x^2-y^2}$ fundamental state. The found D value must by the sum of the dipolar and exchange contributions. Taking the crystallographic Cu · · · Cu distance of 3.34 Å, a dipolar contribution of 800 G is expected[34] which is considerably different from the observed D. The only explanation for this fact is that the exchange contribution must be important, despite the low value of the isotropic coupling constant (see below), which is not unusual. Several complexes with small J and large D(exchange) and *vice versa* have been reported.[35] In addition to this, the existence of non-collinear g and D tensors must lead to erroneous assignments of the transitions in the powder spectra and single-crystal measurements would be necessary. Unfortunately, the size of the available crystals is not suitable for EPR experiments and the question remains unanswered.

Magnetic properties

The present compound does not show a maximum in susceptibility in the studied temperature range. Notwithstanding, a plot of $\chi_m T$ *vs.* the temperature (Fig. 5) exhibits a significant decrease at $T < 8$ K, corresponding to a variation of μ_{eff} between 1.82 (at 8 K) and 1.60 μ_B (at 1.8 K) per copper atom, indicating weak antiferromagnetic interactions between the copper(II) ions.

Taking into account the crystal structure of the present compound and in light of the very large interdimer Cu · · · Cu distance, the only non-negligible interactions between the paramagnetic centres must be the intradimer ones. To support this assumption, we considered the limit function proposed by Coffman and Buetter[36] for long-range antiferromagnetic exchange, which has the form $-2J = 1.35 \times 10^7 \exp(-1.8R)$. For a Cu · · · Cu interdimer exchange pathway distance of *ca.* 17.5 Å the absolute J value would be expected to be less than 10^{-6}–10^{-7} cm^{-1}. So, the studied compound might be considered, from the magnetic point of view, as an assembly of non-interacting dimers. The magnetic behaviour of $[Cu_2(HCO_2)_4(tzq)_2]\cdot 4H_2O$ may be described by means of a dimer exchange equation. Since the exchange coupling constant is expected to be small (possibly $|J| \approx g\mu_B H \approx 1$ cm^{-1}) the application of the Bleaney–Bowers[37] expression would be inappropriate. Therefore, the data were fitted using expression (1)

$$\chi = [Ng\mu_B \sinh(g\mu_B H/kT)]\{H[\exp(-2J/kT) + 2\cosh(g\mu_B H/kT) + 1]\}^{-1} + N\alpha \quad (1)$$

derived from the exchange Hamiltonian $\hat{H} = 2J(\hat{S}_1\cdot\hat{S}_2) + g\mu_B H(\hat{S}_1 + \hat{S}_2)$ for a pair of exchange-coupled $S = \frac{1}{2}$ ions, which takes account of the external field.[38] The solid line in Fig. 5 represents the least-squares fit and with the g value fixed at 2.16 (obtained from the Curie constant) a $2J$ value of -1.05 cm^{-1} was obtained, with the agreement factor $R = 4.74 \times 10^{-5}$ {R is defined as $\Sigma[(\chi_m)_{obs} - (\chi_m)_{calc}]^2/\Sigma[(\chi_m)_{obs}]^2$}.

This behaviour may be understood in terms of the nature of the orbitals involved in the exchange interactions together with the structure of the bridging network. As discussed above, in the present compound the unpaired electron of the copper(II) ion is essentially described by a magnetic orbital built from the $d_{x^2-y^2}$ metallic orbital with little contribution from the d_{z^2} orbital, and localised basically in the basal planes, which are nearly normal to the direction of the exchange propagation. Hence, as is usual for axial-equatorial (parallel-planar) copper(II) dimers, the observed weak coupling must be attributed to the small z^2-type character acquired by the magnetic orbitals.

If the obtained $2J$ value is compared with those reported for related systems, some considerations may be drawn. In general, for dibridged $[CuX_2Cu]$ dimers with parallel-planar geometry, the existence of straightforward correlations between the singlet–triplet splitting ($2J$) and several structural parameters, such as the Cu–X–Cu (φ) and L–Cu–X (α) angles and the out-of-plane Cu–X distance (where L is the ligand in *trans* position with respect to the bridging X atom) has been investigated. Thus, for di-μ-halogeno bridged copper(II) dimers, Hatfield and co-workers[19] have pointed out that a smooth correlation exists between the singlet–triplet energy gap and the $\varphi : R_O$ ratio: $2J$ increases with increasing $\varphi : R_O$ until it reaches a maximum value after which further increase in $\varphi : R_O$ leads to a reduction of $2J$. On the other hand, the influence of the distortion in the metal atom environment on the exchange parameters for these systems (parallel-planar dimers) has been pointed out, and several attempts to correlate the magnitude of $2J$ with the distortion of the copper(II) polyhedron have been carried out. In particular, for dibridged μ-halogeno copper(II) dimers the existence of a rough correlation between $2J$ and the α angle has

Table 3 Relevant structural and magnetic data for $[(LCu)(\mu\text{-}RCO_2)_2(CuL)]$ systems containing μ-oxo carboxylate-bridged Cu_2O_2 units

Compound[a]	In-plane co-ordination	R_O/Å	φ/°	α/°	φ : R_O/° $Å^{-1}$	α : $2R_O$/° $Å^{-1}$	$2J$/cm^{-1}	Ref.
1 $[\{CuL^1(MeCO_2)\}_2]$	*cis*-N_2O_2	2.665(4)	96.3(5)	188.7	36.1	35.4	−3.68	11(*c*)
2 $[\{CuL^2(MeCO_2)\}_2]$	*cis*-N_2O_2	2.577(2)	96.1(1)	192.7	37.3	37.4	−3.02	11(*c*)
3 $[\{CuL^3(MeCO_2)\}_2]$	*cis*-N_2O_2	2.512(5)	96.9(2)	186.6	38.6	37.1	−2.66	9, 11(*b*)
4 $\{[\{CuL^4(MeCO_2)\}_2]\cdot 2H_2O\}_\infty$	*cis*-N_2O_2	2.498(8)	98.1(3)	188.7	39.3	37.7	−3.08 (−4.52)[b]	11(*b*)
5 $[\{CuL^5(MeCO_2)\}_\infty]\cdot 2MeOH$	*cis*-N_2O_2	2.495(6)	98.3(5)	184.2	39.4	36.9	−3.00 (−15.76)[b]	11(*a*)
6 $[\{CuL^6(MeCO_2\}_2]\cdot H_2O\cdot EtOH$	NO_3	2.446(2)	95.7(1)	190.4	39.9[c]	37.0[c]	+1.26	8
		2.651(1)	102.6(1)	186.5				
7 $[\{Cu(PhCONHCH_2CO_2)(H_2O)\}_2]\cdot 2H_2O$	O_4	2.37(1)	101.0(5)	183.6	42.6	38.7	−4.30	6, 7
8 $[\{CuL^7(MeCO_2)\}_2]$	*cis*-N_2O_2	2.490(1)	95.34(5)	188.9	38.3	37.9	−0.50	13
9 $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$	*trans*-N_2O_2	2.331(4)	102.2(2)	187.5	43.9	40.2	−1.05	This work

[a] HL^1 = *N*-(5-Bromosalicylidene)-*N*-methylpropane-1,3-diamine, HL^2 = *N*-methyl-*N*′-(5-nitrosalicylidene)propane-1,3-diamine, HL^3 = *N*-methyl-*N*′-salicylidenepropane-1,3-diamine, HL^4 = *N*-(5-methoxysalicylidene)-*N*-methylpropane-1,3-diamine, HL^5 = *N*,*N*′-[bis(2-*o*-hydroxybenzylideneamino)ethyl]ethane-1,2-diamine, HL^6 = *N*-(2-hydroxy-1,1-dimethylethyl)salicyleneamine, HL^7 = 7-amino-4-methyl-5-azahept-3-en-2-onate. [b] Magnetic behaviour described as alternting chain. [c] Mean value.

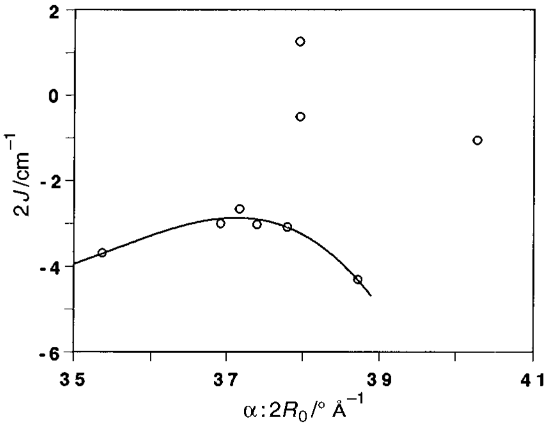

Fig. 7 Variation of $2J$ *vs.* α : $2R_O$

been proposed, only for severe distortions (α < 160°) significant effects on the $2J$ values being observed.[20,21]

With regard to parallel-planar di-μ-oxo-bridged dimers, the great diversity of bridging groups as well as of metal environments has hampered the analysis of possible magnetostructural correlations in such systems. Notwithstanding, for μ-oxo carboxylate-bridged systems Chiari *et al.*[11c] suggested that $2J$ correlates with the φ : R_O ratio in a similar manner to that reported for parallel-planar μ-halogeno-bridged dimers. In Table 3 are gathered the most relevant data for the structural and magnetically characterised μ-oxo carboxylate-bridged systems. In addition, Figs. 6 and 7 show the variation of $2J$ *vs.* φ : R_O and α : $2R_O$, respectively, with the solid lines corresponding to the apparent correlations outlined in the literature. In both cases the compounds **6**, **8** and **9** (see Table 3) deviate clearly from the suggested correlations. For **6**, which is the only one displaying ferromagnetic behaviour, the lack of a symmetry centre in the Cu_2O_2 core besides the low angle has been invoked to explain its behaviour.[8,11c] In **8** the most relevant structural feature (in relation to the Cu_2O_2 core) is, again, the low value of φ (the lowest amongst those in Table 3). Finally, regarding to the present compound, the possible interaction through the nearly parallel triazolo ligands,[39] as well as the different electron-withdrawing ability of formate compared with the corresponding acetate group, might be invoked.

The observed singlet–triplet gap energies in μ-oxo carboxylate-bridged copper(II) dimers span a very cramped range (from −4.30 to +1.26 cm^{-1}) and only little variations are observed with the different structural parameters; for instance, for related parallel-planar di-μ-halogeno-bridged copper(II) dimers the $2J$ values are spread over a much wider range (from *ca.* −83 to *ca.* +7 cm^{-1}). Consequently, subtle changes in the metal atom environment, either structural variations or chemical modifications (*i.e.* the different nature of the ligands), might produce critical shifts (between the observed range of experimental values) in the singlet–triplet gap energy. Hence, further data for μ-oxo carboxylate-bridged copper(II) dimers are necessary in order to be more specific about the magnetostructural correlation in such systems, which is presently an open question.

Table 4 Crystal data for the complex

Formula	$C_{44}H_{40}Cu_2N_{12}O_{12}$
Symmetry, space group	Triclinic, *P*1
a/Å	8.209(4)
b/Å	12.156(4)
c/Å	12.649(4)
α/°	63.21(3)
β/°	81.42(3)
γ/°	89.12(3)
U/$Å^3$, Z	1112.2(8), 1
D_c/g cm^{-3}, M	1.58, 1115.96
$F(000)$, μ/cm^{-1}	542, 10.4
Maximum final shift/error	0.002
Final Δ*F* peak/e $Å^{-3}$	0.32
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.042
$R' = [\Sigma w(\Delta F^2)/\Sigma w F_o^2]^{\frac{1}{2}}$	0.046

Experimental

Preparation of $[\{Cu(tzq)_2(HCO_2)\}_2(\mu\text{-}HCO_2)_2]\cdot 4H_2O$

The hydrazone of quinoline-2-carbaldehyde was synthesized as described by Boyer *et al.*[23] A solution of this hydrazone (1 mmol) in ethanol (50 cm^3) was added with stirring to an aqueous solution of copper(II) formate tetrahydrate (1 mmol in 25 cm^3). Immediately, a dark red solution was formed, which became brown in a few hours. Thus, a brown powder appeared in 72 h. After filtration, the resulting blue greenish solution was allowed to stand at room temperature and blue prismatic crystals formed after 2 weeks. Crystals were filtered off, washed with ethanol–water (1 : 1) and stored in a desiccator over silica gel (Found: C, 50.4; H, 4.0; Cu, 12.2; N, 15.3. $C_{22}H_{20}CuN_6O_6$ requires C, 49.9; H, 4.2; Cu, 12.0; N, 15.9%).

Physical measurements

Polycrystalline powder EPR spectra were recorded at room temperature on a Bruker ESP-300 spectrometer. Magnetic susceptibility was measured by means of a commercial SQUID magnetometer, Quantum Design model MPMS7, down to 1.8 K.

X-Ray crystallography

Diffraction measurements of the selected blue prismatic crystal, with approximate size 0.15 × 0.20 × 0.25 mm, were carried out at room temperature using an Enraf-Nonius CAD-4 single-crystal diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The unit-cell dimensions were determined from the angular settings of 25 reflections with $8 < \theta < 12°$. The intensity data for 4938 reflections were measured in the limits $1 < \theta < 26°$ using the ω–2θ scan technique, variable speed, width $(0.80 + 0.35 \tan \theta)°$ in ω, and maximum scan time of 60 s per reflection in the hkl ranges 0–10, −14 to 14, −15 to 15. Two reflections were measured every hour as intensity controls without significant decay. Some doubly measured reflections were averaged, $R_{\mathrm{int}} = 0.004$, resulting in 4357 independent reflections of which 2254 were considered observed with $I > 2\sigma(I)$.

The structure was solved by direct methods using the program SIR 92.[40] All non-hydrogen atoms were anisotropically refined by least squares on F using the X-RAY 76 system[41] with a unit weighting scheme. The hydrogen atoms, kept fixed in the refinement with a common isotropic thermal parameter, were located by difference synthesis. Geometrical calculations were made with PARST.[42] Atomic scattering factors and anomalous dispersion corrections were taken from ref. 43. All calculations were performed on a VAX6410 computer. Other relevant parameters of the crystal structure determination are listed in Table 4.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and its reference number 186/476.

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