A Cu^{II} Chain Compound Showing a Ferromagnetic Coupling through Triple N^1,N^2-1,2,4-Triazole Bridges

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[Cu(hyetrz)$_3$](CF$_3$SO$_3$)$_2$·H$_2$O [hyetrz = 4-(2′-hydroxyethyl)-1,2,4-triazole] represents the first structurally characterised ferromagnetically coupled Cu^{II} chain compound containing triple N^1,N^2-1,2,4-triazole bridges. *catena*-[μ-Tris{4-(2′-hydroxyethyl)-1,2,4-triazole-N^1,N^2}copper(II)] bis(trifluoromethanesulfonate) hydrate ($C_{14}H_{23}F_6S_2O_{10}CuN_9$) crystallises in the triclinic space group $P\bar{1}$, a = 13.54(3), b = 14.37(3), c = 15.61(4) Å, α = 95.9(1), β = 104.9(1), γ = 106.5(1)°, V = 2763(11) Å^3, Z = 4 (Cu^{II} units). The Cu^{II} ions are linked by triple N^1,N^2-1,2,4-triazole bridges yielding an alternating chain with Cu1–Cu2 = 3.8842(4) Å and Cu2–Cu3 = 3.9354(4) Å. Analysis of the magnetic data according to a high-temperature series expansion gives a J value of +1.45(3) cm^{-1}. The nature and the magnitude of the ferromagnetic exchange have been discussed on the basis of the structural features.

Introduction

Polynuclear coordination compounds containing derivatives of 1,2,4-triazole have been of increasing interest during the last decade. Several studies have dealt with the search for magneto-structural correlations for transition metal(II) compounds containing N^1,N^2-1,2,4-triazole bridges.[1−14] On the other hand, polynuclear (1,2,4-triazole)iron(II) compounds have been found to yield spin transition materials exhibiting cooperative behaviour.[15−17]

Although a wealth of polynuclear transition metal(II) compounds have been structurally and magnetically characterised, an incomplete picture concerning the interplay of the 1,2,4-triazole derivatives and noncoordinated anions still exists when determining the structural features and the associated magnetic behaviour. Dinuclear Cu^{II} compounds could be obtained by using polyfunctional 1,2,4-triazole derivatives with N-donating substituents, forming five-membered chelate rings. The magnetic properties of these could be fine-tuned by playing upon the coordination geometry of the double N^1,N^2-1,2,4-triazole bridges residing in the equatorial plane of the Cu^{II} ions.[1−7] A correlation between the magnitude of the antiferromagnetic (AF) interaction and the ligand bridge geometry could be established for the first time for this class of compounds.[5,10,11] The geometry of the bridging ligand network appears mainly to be determined by the geometric requirements of the Cu^{II} atom and the spatial disposition of the ligands. Therefore, no direct influence of the incorporated noncoordinated anions in determining the crystal packing and its possible effect on the 1,2,4-triazole bridge geometry could be proposed.

Generally, depending upon the experimental conditions, the reaction of 4-R-substituted 1,2,4-triazole ligands with Cu^{II} salts of potentially noncoordinating anions either yield linear chain Cu^{II} compounds[8,18,19] or linear trinuclear Cu^{II} entities.[20−23] The propagation of the AF exchange is indeed drastically decreased in these triply N^1,N^2-1,2,4-triazole-bridged trinuclear[20] and linear-chain Cu^{II} compounds[8] compared with the dinuclear bis(μ-N^1,N^2-1,2,4-triazole) compounds.[1−7,10] Actually, in these dinuclear systems, the propagation of the AF exchange may proceed very efficiently via the $d_{x^2-y^2}$ orbitals on the Cu^{II} ions which interact with the σ-orbitals of the nitrogen atoms of the bridging ligand, which are all situated in the equatorial plane. The introduction of an additional ligand in the Cu···Cu linkage, as in the case of the linear tri- and polynuclear Cu^{II} systems, brings the equatorial planes of the Jahn−Teller-distorted octahedral Cu^{II} ions in positions canted by about 60° towards one another. Consequently, the AF coupling can only proceed efficiently via a single 1,2,4-triazole ligand, and will be very weak, typically of the order of a few wavenumbers.

Indeed, the AF coupling between nearest-neighbour Cu^{II} ions within the linear trinuclear [Cu$_3${4-(2-pyridyl)-1,2,4-triazole}$_{10}$(H$_2$O)$_2$](ClO$_4$)$_6$·7H$_2$O has been found to be

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-5.41 cm^{-1},[20] whereas the isotropic exchange constant is only $-1.01(2)$ cm^{-1} for the 3-D network built up from linear trinuclear Cu^{II} cations, $[Cu_3\{1,2\text{-bis}(1,2,4\text{-triazol-4-yl})\text{ethane}\}_5(H_2O)_2]^{6+}$.[23] Furthermore, the linear-chain compound $[Cu(hyetrz)_3](ClO_4)_2 \cdot 3H_2O$ [hyetrz = 4-(2′-hydroxyethyl)-1,2,4-triazole] also exhibits a very weak AF coupling of $J = -1.18(2)$ cm^{-1}.[8]

Surprisingly, the magnetic data for the linear trinuclear Cu^{II} compounds $[Cu_3(metrz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$ (metrz = 3-methyl-4-ethyl-1,2,4-triazole)[21] and $[Cu_3(etrz)_9(H_2O)_3](CF_3SO_3)_6$ (etrz = 4-ethyl-1,2,4-triazole),[22] indicate a weak overall ferromagnetic (F) interaction. Unfortunately, the magnetic data could not be satisfactorily interpreted, nor could it be related to the structural features, possibly due to the lack of detailed crystallographic data.

These unprecedented magnetic data might be related to the presence of the trifluoromethanesulfonate anion, which could play an important role in determining the crystal packing of these compounds, thereby indirectly influencing the orientation of the 1,2,4-triazole ligands. In order to check this hypothesis, an extended crystallographic and magnetic study on $[Cu(hyetrz)_3](CF_3SO_3)_2 \cdot H_2O$ has been carried out, which would allow an excellent comparison with the perchlorate derivative on which we reported previously.[8]

Results and Discussion

Description of the X-ray Structure of $[Cu(hyetrz)_3](CF_3SO_3)_2 \cdot H_2O$

A projection of the cationic linear Cu^{II} chain is depicted in Figure 1, and the relevant bond length and bond angle information is given in Table 1.

The coordination polymer consists of a crystallographically independent unit comprising two Cu^{II} ions, Cu1 and Cu3, in special positions and another Cu^{II} ion in a general position (Cu2), along with six symmetry-independent hyetrz ligands. The linear chain running along the *c* axis (see Figure 2) is generated by the inversion involving the crystallographic centres of symmetry located on Cu1 and Cu3. $[Cu(hyetrz)_3](ClO_4)_2 \cdot 3H_2O$[8] crystallises in the monoclinic space group $P2_1/n$, whereas the title compound crystallises in the triclinic space group $P\bar{1}$. However, this does not change the local symmetry around the Cu^{II} ions, since in both compounds the inversion centres are located on the metal ions.

Three hyetrz ligands act as bidentate ligands linking the Cu^{II} ions via the nitrogen atoms N1 and N2. All metal ions are in a distorted (4+2) octahedral environment formed by six N-donating hyetrz ligands. The basal plane is formed by four nitrogen donor atoms with distances between 1.989(3)

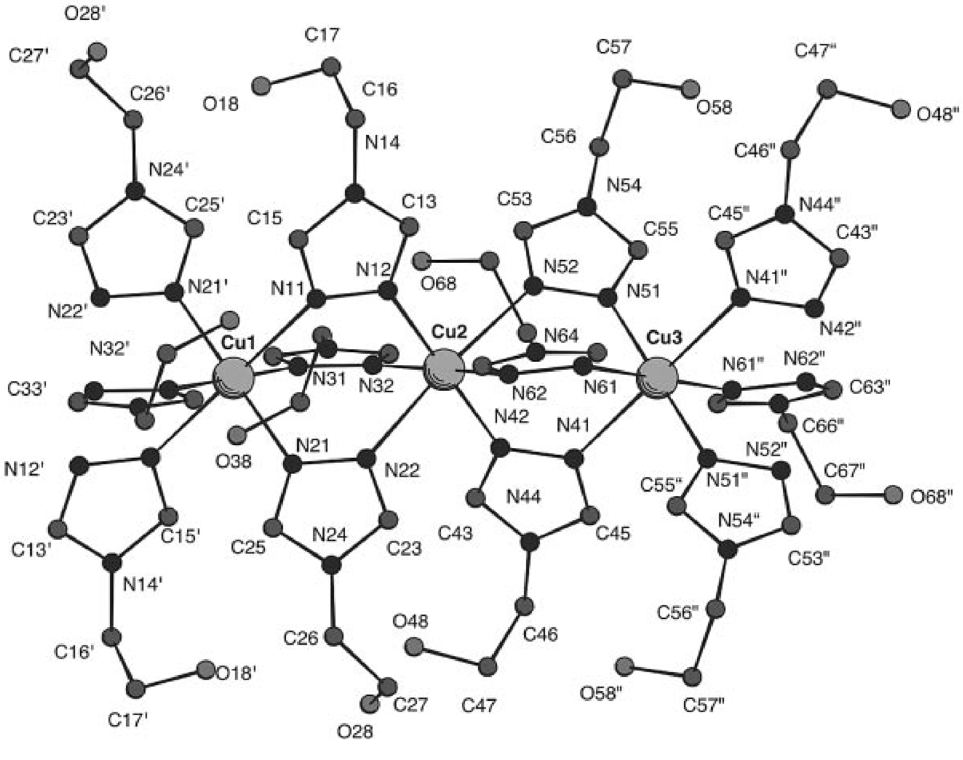

Figure 1. Drawing and atomic labeling system showing the structure of $[Cu(hyetrz)_3](CF_3SO_3)_2 \cdot H_2O$; hydrogen atoms, noncoordinating counter anions, and water molecules have been omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for $[Cu(hyetrz)_3](CF_3SO_3)_2\cdot H_2O$

Cu1−Cu2	3.8843(2)	Cu2−N32	2.066(2)
Cu2−Cu3	3.9352(2)	Cu2−N42	1.989(2)
Cu1−N11	2.370(2)	Cu2−N52	2.409(2)
Cu1−N21	2.018(2)	Cu2−N62	2.064(2)
Cu1−N31	2.067(2)	Cu3−N41	2.331(2)
Cu2−N12	1.994(2)	Cu3−N51	2.009(2)
Cu2−N22	2.360(2)	Cu3−N61	2.116(2)
N11−Cu1−N21	89.93(7)	N32−Cu2−N42	90.73(8)
N11−Cu1−N31	86.24(7)	N32−Cu2−N52	98.19(7)
N21−Cu1−N31	91.18(7)	N32−Cu2−N62	175.77(8)
N12−Cu2−N22	91.50(7)	N42−Cu2−N52	87.30(7)
N12−Cu2−N32	88.70(7)	N42−Cu2−N62	92.19(8)
N12−Cu2−N42	179.13(8)	N52−Cu2−N62	85.01(7)
N12−Cu2−N52	92.12(7)	N41−Cu3−N51	88.42(7)
N12−Cu2−N62	88.41(7)	N41−Cu3−N61	86.66(7)
N22−Cu2−N32	86.75(7)	N51−Cu3−N61	89.98(7)
N22−Cu2−N42	89.12(7)		
N22−Cu2−N52	173.93(7)		
N22−Cu2−N62	90.23(7)		
Cu1−N11−N12	123.8(1)	Cu2−N32−C33	127.1(2)
Cu1−N11−C15	125.2(2)	Cu3−N41−N42	126.7(1)
Cu2−N12−N11	122.3(1)	Cu3−N41−C45	125.9(2)
Cu2−N12−C13	129.8(2)	Cu2−N42−N41	124.7(1)
Cu1−N21−N22	120.3(1)	Cu2−N42−C43	127.4(2)
Cu1−N21−C25	131.5(2)	Cu3−N51−N52	125.0(1)
Cu2−N22−N21	128.2(1)	Cu3−N51−C55	126.7(2)
Cu2−N22−C23	124.6(2)	Cu3−N61−N62	125.5(1)
Cu1−N31−N32	129.3(1)	Cu3−N61−C65	127.8(2)
Cu1−N31−C35	124.5(2)	Cu2−N62−N61	128.4(1)
Cu2−N32−N31	125.3(1)	Cu2−N62−C63	122.3(2)

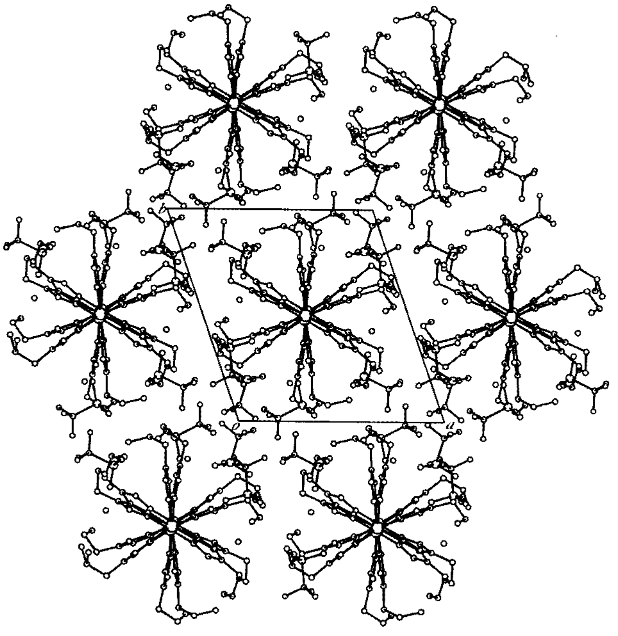

Figure 2. View of the crystal structure of $[Cu(hyetrz)_3](CF_3SO_3)_2\cdot H_2O$ along the *c* axis

and 2.116(3) Å, whereas two hyetrz ligands are coordinated in the axial positions at significantly longer distances [2.328(3)−2.409(3) Å]. This distribution of Cu−N distances is the signature for a static Jahn−Teller distortion, as has comparably been found for $[Cu(hyetrz)_3](ClO_4)_2\cdot 3H_2O$[8] and $[Cu(4\text{-amino-1,2,4-triazole})_3](ClO_4)_2\cdot 0.5H_2O$.[18] The range of Cu−N distances is, however, slightly larger for $[Cu(hyetrz)_3](CF_3SO_3)_2\cdot H_2O$. All Cu^{II} ions are not significantly displaced from their equatorial coordination plane [δ(Cu2) ≈ 0.02 Å]. The least-squares planes through the equatorial planes of the Cu^{II} octahedra make angles of 55.51(7)° for Cu1 and Cu2, 50.40(6)° for Cu2 and Cu3, which is slightly different from what has been found for $[Cu(hyetrz)_3](ClO_4)_2\cdot 3H_2O$. In that case, the least-squares planes through the equatorial planes of the octahedrally coordinated Cu^{II} ions make angles of 46(1)° for Cu1 and Cu2, 53(3)° for Cu2 and Cu3.[8] The important distortions from O_h symmetry around the Cu^{II} ions imply that the three hyetrz ligands linking neighbouring Cu^{II} ions do not conserve a perfect trigonal symmetry, as has been observed for the perchlorate derivative. The deviation from threefold symmetry is, however, significantly more pronounced for the present compound. All 1,2,4-triazole rings are fairly planar; the deviation from the least-squares plane through the ring atoms is smaller than 0.01(1) Å. The least-squares planes through the hyetrz ligands linking Cu1 and Cu2 are 52.4(1)° for hyetrz-1 and hyetrz-2, 59.3(1)° for hyetrz-2 and hyetrz-3, and 74.1(1)° for hyetrz-1 and hyetrz-3. This very much resembles the bridging mode between Cu1 and Cu2 in the perchlorate derivative with angles between the least-squares planes of 54(2)° for hyetrz-1 and hyetrz-2, 69(2)° for hyetrz-2 and hyetrz-3, and 64.6(4)° for hyetrz-1 and hyetrz-3. It is important to notice that there are significant differences in the bridging mode between Cu2 and Cu3 for both Cu^{II} hyetrz linear-chain compounds. In fact, for $[Cu(hyetrz)_3](CF_3SO_3)_2\cdot H_2O$ the threefold symmetry of the triple hyetrz linkage between Cu2 and Cu3 shows severe distortions, yielding angles of 77.1(1)° between hyetrz-4 and hyetrz-5, 61.4(1)° between hyetrz-5 and hyetrz-6, and 46.3(1)° between hyetrz-6 and hyetrz-4. On the other hand for $[Cu(hyetrz)_3](ClO_4)_2\cdot 3H_2O$,[8] the threefold symmetry of the triple hyetrz linkage between Cu2 and Cu3 shows comparable distortions as does Cu1 and Cu2 with angles of 50(3)° between hyetrz-4 and hyetrz-5, 71(1)° between hyetrz-5 and hyetrz-6, and 66(3)° between hyetrz-6 and hyetrz-4.

These differences in the hyetrz bridging geometry for $[Cu(hyetrz)_3](CF_3SO_3)_2\cdot H_2O$ is also reflected by the Cu−Cu distances, which are significantly different for the two pairs of the Cu^{II} ions, i.e., Cu1−Cu2 = 3.8843(2) Å, whereas Cu2−Cu3 = 3.9352(2) Å. This indeed is in contrast to $[Cu(hyetrz)_3](ClO_4)_2\cdot 3H_2O$, where the analogy between the two linkages leads to quasi equal Cu−Cu separations with Cu1−Cu2 = 3.8530(8) Å and Cu2−Cu3 = 3.8293(2) Å.[8]

Careful inspection of the triple N^1,N^2-1,2,4-triazole geometry between Cu1 and Cu2 reveals similar features as found in $[Cu(hyetrz)_3](ClO_4)_2\cdot 3H_2O$ for both Cu−Cu linkages; hyetrz-1 links Cu1 and Cu2 with a long distance [Cu1−N11 = 2.370(2) Å] and a rather small angle [Cu1−N11−N12 = 123.8(1)°] involving Cu1, whereas the distance (Cu2−N12 = 1.994(2) Å] and angle [Cu2−N12−N11 = 122.3(1)°] involving Cu2 may be considered as normal. Maintaining these Cu^{II} ions under these geometric dispositions, apparently requires an extremely large Cu1−N11−N12−Cu2 torsion angle of −28.98(9)°. Also, hyetrz-2 shows considerable asymmetry in the bridging mode with respect to the Cu−N bond lengths. As for hyetrz-1, the short distance [Cu1−N21 = 2.018(2) Å] corresponds to a normal Cu1−N21−N22 angle of 120.3(1)°. However, for hyetrz-2 the long Cu2−N22 distance of 2.360(2) Å is now accompanied by a much larger Cu2−N22−N21 angle of 128.2(1)°. In this case, a torsion angle of −16.31(9)° is required. In contrast, hyetrz-3 links Cu1 and Cu2 with approximately identical Cu1−N31 = 2.067(2) Å and Cu2−N32 = 2.066(2) Å distances. However, the N^1,N^2-1,2,4-triazole bridging mode shows a rather high degree of asymmetry with respect to the Cu−N−N bond angles, which are Cu1−N31−N32 = 129.3(1)° and Cu2−N32−N31 = 125.3(1)°. The torsion angle Cu1−N31−N32−Cu2 is only −3.27(9)°.

The difference observed in the two unequal bridging modes is confirmed by the torsion angles for the ligands linking Cu2 and Cu3: −13.5(1), −11.3(1), and −20.3(1)° for hyetrz-4, hyetrz-5, and hyetrz-6, respectively. This is in sharp contrast to $[Cu(hyetrz)_3](ClO_4)_2·3H_2O$, where the torsion angles for the hyetrz ligands, having short Cu−N distances, are about −11°. The triflate derivative has corresponding ligands with torsion angles of up to −20°.

The large deviation from threefold symmetry for the present linear Cu^{II} chain is also confirmed by the fact that Cu2 is displaced by 0.238(1) Å from the Cu1−Cu3 axis, as well as by the zig-zag character of the linear chain. The latter is illustrated by the angle of 173.003(6)° between the vectors through the pairs of Cu^{II} ions (Cu1,Cu2) and (Cu2,Cu3), which is slightly smaller than the 175.18(2)° found for the perchlorate analogue. Clearly, in order to establish the linkage of Cu^{II} ions in Jahn−Teller-distorted octahedra, by triple μ-N^1,N^2-1,2,4-triazole bridges, the geometrical disposition of the ligands becomes such that important deviations from the ideal threefold axis running through the Cu^{II} ions are required. This may be illustrated by Figure 2 showing a view of the linear-chain structure along the *c* axis.

The third coordination sphere is occupied by the noncoordinated water molecules and triflate anions, which are situated between the linear chains. It is important to notice the orientation of the triflate anions, which appear to direct themselves towards the hydroxyethyl substituents of the hyetrz ligands. The relatively short O···O contacts listed in Table 2 provide evidence for a pronounced hydrogen bonding network between the triflate anions, the hydroxyethyl groups and the lattice water molecules as observed in the trinuclear Fe^{II} spin crossover compound $[Fe_3(hyetrz)_6(H_2O)_6](CF_3SO_3)_6$.[24] Unfortunately, an extended analysis of the hydrogen bonding interactions could not be carried out, since the hydrogen atoms concerned could not be located and because of the positional disorder in the triflate anions. As observed for $[Cu(hyetrz)_3](ClO_4)_2·3H_2O$, the terminal hydroxy groups of the ligands are highly agitated. The hyetrz-3 oxygen atom is shared between two split locations O38 and O39 with occupancy of 1/2 on each site. There appears to be a short O28···O48 contact of 2.690(5) Å. This would imply the occurrence of a hydrogen bond between hydroxy groups from hyetrz ligands, originating from neighbouring (i.e., intrachain) triple μ-triazole links. Also in the present compound, there is no indication for hydrogen bonding interactions taking place between hydroxyethyl groups of hyetrz ligands originating from different linear Cu^{II} chains (i.e., interchain).

Table 2. Interatomic distances (up to 3 Å) for the hydrogen bonding interactions in $[Cu(hyetrz)_3](CF_3SO_3)_2·H_2O$ (labeled atoms are generated by symmetry operations: a: 1 − *x*, −*y*, −*z*; b: 1 − *x*, 1−*y*, −*z*)

O18···O87a	2.961(5)
O38···O96b	2.821(8)
O58···O106	2.791(4)
O39···O120	2.825(9)
O48···O120	2.883(5)
O58···O110	2.874(5)
O28···O48	2.690(5)
O110···O95	2.857(6)

Even if the substitution of the perchlorate anion by the triflate anion does not change the local Cu^{II} symmetry, the respective position of the cationic chains is affected by the cell difference between the two compounds. An illustration of this change is the triangle drawn normally to the axes of three adjacent chains. In the perchlorate compound it is equilateral with the length of one side being 13.6±0.2 Å, whereas in the triflate compound it is distorted at 13.0, 14.1, and 16.3 Å.

Spectroscopic Properties

The UV/Vis spectrum of $[Cu(hyetrz)_3](CF_3SO_3)_2·H_2O$ shows a broad asymmetric band with a maximum situated at $15.4·10^3$ cm^{-1}, which is in agreement with the presence of CuN_6 chromophores, as well as with the tetragonal distortion of the Cu^{II} octahedra.[25]

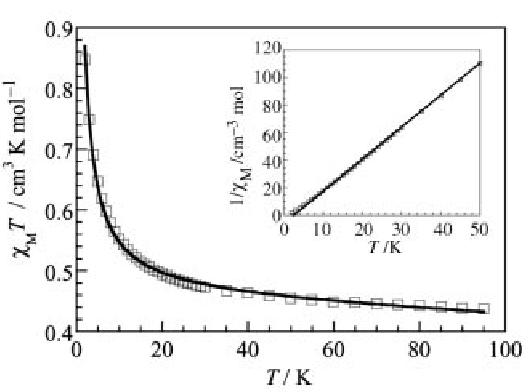

Figure 3. Observed (white squares) and calculated [line; $J = +1.45(3)$ cm^{-1}, $g = 2.20(1)$] $\chi_M T$ vs. T curves for $[Cu(hyetrz)_3](CF_3SO_3)_2·H_2O$; the $1/\chi_M$ vs. T curve is displayed in the insert

Magnetic Measurements

The magnetic behaviour of $[Cu(hyetrz)_3](CF_3SO_3)_2{\cdot}H_2O$ is shown in Figure 3 in the form of a $\chi_M T$ vs. T plot, χ_M being the molar magnetic susceptibility and T the temperature.

At 300 K, the $\chi_M T$ value is 0.409 $cm^3{\cdot}mol^{-1}{\cdot}K$, which is approximately the value expected for a single uncoupled Cu^{II} ion. The value of $\chi_M T$ progressively increases upon cooling, after which the $\chi_M T$ value starts to increase rather abruptly below 40 K reaching a value of 0.847 $cm^3{\cdot}mol^{-1}{\cdot}K$ at 2 K. This behaviour is characteristic for compounds with an overall F interaction between the metal(II) ions. The occurrence of an F interaction is also illustrated by the $1/\chi_M$ vs. T plot displayed in the insert of Figure 3. A qualitative analysis of the magnitude of the F interaction has been made based on the Curie−Weiss law, $1/\chi_M = (T - \theta)/C$, yielding a Curie constant C of 0.41(1) $cm^3{\cdot}K{\cdot}mol^{-1}$ and a Curie−Weiss temperature θ of 3.9(2) K. The magnetic data have been interpreted using the expression for the molar magnetic susceptibility of an $S = 1/2$ linear chain with a high-temperature series expansion proposed by Baker [Equation (1)],[26] in which $x = J/2kT$ and J is the isotropic exchange parameter defined by the phenomenological spin Hamiltonian [Equation (2)].

$$\chi_M = \left(\frac{Ng^2\mu_B{}^2}{4kT}\right)\cdot \left(\frac{1+5.79799x+16.902653x^2+29.376885x^3+29.832959x^4+14.036918x^5}{1+2.79799x+7.008678x^2+8.6538644x^3+4.5743114x^4}\right)^{2/3} \tag{1}$$

$$\mathbf{H} = -J[\Sigma_{i<j}\,\mathbf{S}_i{\cdot}\mathbf{S}_j] - g\mu_B H\,\Sigma_i\mathbf{S}_i \tag{2}$$

In Equation (1), N, g, μ_B, k, and T have their usual meanings. The g factor must be considered as an average value of the local Zeeman factors and intercluster exchange interactions were supposed to be negligible. The assumption of negligible magnetic exchange between second neighbour Cu^{II} ions is justified in view of the study of the triply N^1,N^2-1,2,4-triazole-bridged $Fe^{II}-Fe^{II}-Fe^{II}$ [24,27] and $Co^{II}-Co^{III}-Co^{II}$ [28] trinuclear clusters, where the central metal ion is diamagnetic, and no magnetic interactions could be detected between the paramagnetic terminal metal ions. A good fit in the temperature range 2−100 K has been obtained for the parameters $g = 2.20(1)$ and $J = +1.45(3)$ cm^{-1} (see Figure 3).

The magnetisation as a function of the applied magnetic field has been recorded at 2 K (see Figure 4). Upon applying a magnetic field, the magnetisation increases progressively, reaching a value of 1.007 $N\mu_B$ at 50 kOe. The value corresponds to the theoretical value of ca. 1 $N\mu_B$ expected for an $S = 1/2$ ion, as may be calculated from Equation (3).

$$M_{sat} = Ng\mu_B S \tag{3}$$

The X-band powder EPR spectrum recorded for $[Cu(hyetrz)_3](CF_3SO_3)_2{\cdot}H_2O$ at 298 K only shows a rather broad (about 2000 Gauss) isotropic signal at $g = 2.09$, which may be the signature for exchange broadening. Furthermore, no indication for Cu···Cu exchange splittings is observed.[25]

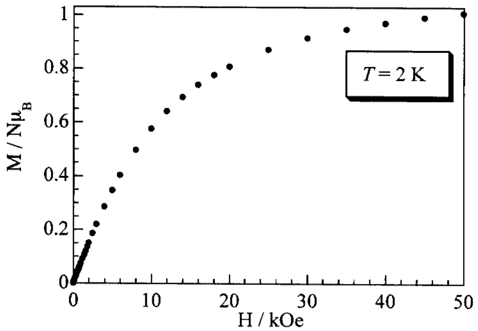

Figure 4. Magnetisation as a function of the applied magnetic field recorded at 2 K for $[Cu(hyetrz)_3](CF_3SO_3)_2{\cdot}H_2O$

Concluding Remarks

X-ray structures of polymeric chain compounds containing triple N^1,N^2-1,2,4-triazole bridges have long been hard to establish and only a few examples forming Cu^{II} structures are known.[8,18,19] Structural information on these compounds are of great interest since the fascinating X-ray structure of the corresponding Fe^{II} spin transition materials has not yet been solved.[16] $[Cu(hyetrz)_3](CF_3SO_3)_2{\cdot}H_2O$ represents the first example of a linear Cu^{II} chain of this family exhibiting an overall F interaction. This F coupling of $J = +1.45(3)$ cm^{-1} is rather weak, but certainly significant. The isotropic exchange J results from the competition between ferromagnetic and antiferromagnetic contributions [Equation (4)].[29]

$$J = J_{AF} + J_F \tag{4}$$

Generally, it may be expected that for Cu^{II} ions linked by polyatomic bridging ligands such as μ-N^1,N^2-1,2,4-triazoles, the F contribution is very small, and only the AF part significantly contributes to the overall magnetic interaction.[26] This for instance is the case for $[Cu(hyetrz)_3](ClO_4)_2{\cdot}3H_2O$, where a weak AF coupling [$J = -1.18(2)$ cm^{-1}] has been found.[8] The reasons for these differences in magnetic behaviour are likely to originate from significant differences in structural parameters.

Actually, the present complex has a linear-chain structure, which deviates somewhat more from threefold symmetry as compared with $[Cu(hyetrz)_3](ClO_4)_2{\cdot}3H_2O$. This mainly originates from the larger distortions observed in the Cu2−Cu3 linkage, leading to a more pronounced zigzag character of the linear chain, and importantly, to larger Cu−N−N−Cu torsion angles, which reach values of up to −20°. In both chains, the AF contribution of the exchange only proceeds via one N^1,N^2-1,2,4-triazole bridge out of the three bridging ligands. These are the ligands linking the Cu^{II} ions with short Cu−N distances, i.e., hyetrz-3 and hyetrz-6. In both compounds, these ligands are indeed differently oriented with respect to the Cu^{II} ions, and thus with respect to the magnetic orbital situated on the Cu^{II} ions; these subtle variations in the structural parameters may change the magnetic properties. All of these factors may contribute to a reduction of the magnitude of the J_{AF} component, and for particular values of the structural parameters the J_F component may start to dominate. As a consequence the overall magnetic interaction may switch from AF to F. Apparently, the two linear-chain compounds represent two borderline cases, where either AF or F coupling is taking over. At this stage, it is rather hazardous to draw conclusions concerning the influence of a change in a structural parameter on the magnetic orbital overlap, and thus on the magnitude of the J_{AF} component. For this purpose, theoretical calculations would probably be worthwhile.

It is remarkable that in all the antiferromagnetically coupled triple N^1,N^2-1,2,4-triazole-bridged Cu^{II} compounds, the Cu−N−N−Cu torsion angles, involving the ligands responsible for the exchange coupling, are very low, i.e., 7.9(7)° and 4.9(8)° for $[Cu_3\{1,2\text{-bis}(1,2,4\text{-triazol-4-yl})\text{ethane}\}_5(H_2O)_2]^{6+}$,[23] or close to −11° for $[Cu(hyetrz)_3](ClO_4)_2{\cdot}3H_2O$,[8] whereas these are rather large for the present ferromagnetically coupled triflate chain.

An overall weak F coupling has also been found for the linear trinuclear Cu^{II} compounds $[Cu_3(metrz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$,[21] and $[Cu_3(etrz)_9(H_2O)_3](CF_3SO_3)_6$.[22] The magnetic data could not, however, be related to the structural parameters. Only an X-ray crystallographic study of a low quality at 298 K has been reported for $[Cu_3(metrz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$, revealing rather short Cu···Cu separations of 3.719(7) Å, which could be related to the dynamic Jahn−Teller effect involving the central Cu^{II} ion leading to a perfectly symmetric octahedron with six relatively short Cu−N distances of 2.14(5) Å. It may be expected that upon decreasing temperature the dynamic Jahn−Teller distortion freezes into a static Jahn−Teller distortion. Since the F coupling occurs at these low temperatures, the non-detailed room-temperature structure could not provide any information on how the structural features may be related to the magnetic interaction observed for this compound.

An interesting structural feature in the ferromagnetically coupled Cu^{II} systems mentioned above, as well as in $[Cu(hyetrz)_3](CF_3SO_3)_2{\cdot}H_2O$ is the presence of the noncoordinated trifluoromethanesulfonate anion. It may be thought that this type of bulky anion determines, in some way, the crystal packing and in turn indirectly the geometry of the triple N^1,N^2-1,2,4-triazole bridge network. This may proceed in such a way that accidental orthogonality may occur, i.e., for certain values of the structural parameters the competition of J_{AF} and J_F results in taking over the F component, yielding an overall F interaction in triple 1,2,4-triazole-bridged Cu^{II} compounds.

Derivatives of 1,2,4-triazole are very useful for obtaining diazine-type bridged polynuclear transition metal(II) compounds having relatively short metal−metal distances. All possibilities are provided for fine-tuning the magnetic properties of the corresponding polynuclear Cu^{II} compounds by playing on the nature of the bridging units (number and geometry). Now these possibilities can also be extended towards F interactions for the chain compounds.

Experimental Section

Starting Materials: Commercially available solvents, hydrazine monohydrate, triethyl orthoformate, 2-hydroxyethylamine, and copper(II) trifluoromethanesulfonate were used without further purification.

Synthesis of 4-(2′-hydroxyethyl)-1,2,4-triazole (hyetrz): The ligand hyetrz has been prepared as already described.[8]

Synthesis of $[Cu(hyetrz)_3](CF_3SO_3)_2{\cdot}H_2O$: $Cu(CF_3SO_3)_2$ (0.21 g, 0.6 mmol), dissolved in water (10 mL), was added to hyetrz (0.2 g, 1.8 mmol), dissolved in water (10 mL). The reaction mixture was filtered. After a couple of weeks, blue prism-shaped single crystals were collected after slow evaporation of the solvent at room temperature. Crystals were washed with water and air-dried. Yield: 175 mg, 40%. IR (KBr): $\nu_{as}(SO_3^-)$ = 1269 cm^{-1}.

Physical Measurements: IR spectra were carried out with a Perkin−Elmer Paragon 1000 FT-IR spectrophotometer. UV/Vis spectra were recorded with a CARY 5E spectrophotometer using the diffuse reflectance technique, with polytetrafluoroethylene as a reference. X-band powder EPR spectra were obtained with a Bruker ER083CS electron spin resonance spectrometer. Magnetic susceptibilities were carried out in the temperature range 300−2 K with a quantum design MPMS-5S SQUID magnetometer. Magnetic data were corrected for diamagnetic contributions, which were estimated from the Pascal constants and were fitted to theoretical expressions by means of a Simplex routine. All parameters (J, g) were varied independently during the fitting procedure. This routine minimises the function $R = (\chi_{obs} - \chi_{calc})^2/[(\chi_{obs})^2]^{1/2}$.

Crystallographic Data Collection and Structure Determination: A blue, hexagonal crystal of approximate dimensions 0.60 × 0.50 × 0.35 mm was analysed at room temperature with an ENRAF-NONIUS CAD4 diffractometer using the monochromated Mo-K_α X-ray radiation (λ = 0.7073 Å). Accurate unit-cell parameters were obtained by least-squares refinement from 20 centred reflections in the range 15° ≤ θ ≤ 16°. Crystal data and details of data collection and refinement are given in Table 3. The intensities of three standard reflections, each monitored over 2 h, revealed no significant decay over the course of data collection. A semiempiric correction of absorption, based on ψ scans of three axial reflections, was applied.[31] The structure was solved by direct methods with the program SIR92.[32] Structure refinement based on F^2 was carried out by extended block-diagonal matrix methods, each block constituted by a chemical entity as Cu, hyetrz, CF_3SO_3, H_2O. Locations of hydrogen atoms which can be predicted were generated geometrically (C−H = 1.0 Å) and included in the refinement with an isotropic fixed thermal parameter. All non-hydrogen atoms were refined with anisotropic thermal parameters. The high values of thermal parameters of the oxygen atoms of the triflate and the hydroxy groups suggest disordered positions of these entities. One oxygen atom belonging to a hydroxy group was located on two different disordered sites with an occupancy factor of 1/2. Final reliability factors converged to $R(F) = 0.038$ and $wR(F^2) = 0.120$. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography.[33] A final difference Fourier map showed residual density less than ±0.24 e·Å^{-3}. Final positional parameters are listed in the supplementary material deposited at the CCDC. Illustrations and calculations were carried out using programs written or modified locally. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-185233. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data for $[Cu(hyetrz)_3](CF_3SO_3)_2 \cdot H_2O$

Empirical formula	$C_{14}H_{23}CuF_6N_9O_{10}S_2$
Formula mass	719.1
T [K]	298
Colour	blue
Dimensions [mm]	0.60 × 0.50 × 0.35
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	13.54(3)
b [Å]	14.37(3)
c [Å]	15.61(4)
α [°]	95.9(1)
β [°]	104.9(1)
γ [°]	106.5(1)
V [Å^3]	2763(11)
Z	4
$\rho_{calcd.}$ [g·cm^{-3}]	1.729
λ [Å] (Mo-K_α)	0.71073
μ [mm^{-3}]	1.031
Measured reflections	18256
Observed reflections	10448
R(int.)	0.010
S	1.09
R[a]	0.038
wR[a]	0.120

[a] $R = |F_o| - |F_c|/|F_o|$ for observed reflections, $wR = [w(F_o^2 - F_c^2)^2/wF_o^2]^{1/2}$, $w = 1/(\sigma^2(F_o^2) + 0.025F^2)$, $F = (2F_o + F_c)/3$.

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