Synthesis, Crystal Structure and Magnetic Properties of a Linear Trinuclear Copper(II) Compound with Chloride and 4-Amino-3,5-bis(hydroxymethyl)-1,2,4-triazole as Bridging Ligands†

Petra J. van Koningsbruggen, Jaap W. van Hal, Rudolf A. G. de Graaff, Jaap G. Haasnoot* and Jan Reedijk
Department of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

A new linear trinuclear copper(II) co-ordination compound of the formula $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$, where H_2ahmt = 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole, has been synthesized. The crystal and molecular structure has been solved at 298 K by single-crystal X-ray analysis. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.2233(2)$, $b = 9.2247(2)$, $c = 13.6153(2)$ Å, $\alpha = 113.1441(2)$, $\beta = 105.1577(1)$, $\gamma = 91.2530(2)°$ and $Z = 1$ (trinuclear unit). The least-squares refinement based on 3091 significant reflections converged to $R = 0.0362$ and $R' = 0.0424$. A linear array of three copper(II) ions, with two crystallographically independent copper(II) atoms is the basis for this structure. The copper(II) ions are bridged by two H_2ahmt ligands co-ordinating *via* N^1 and N^2 and an asymmetric chloride bridge [Cu(1)–Cl(1) 2.296(1), Cu(2)–Cl(1) 2.688(1), Cu(1)–Cl(1)–Cu(2) 91.09(4)°]. The Cu(1)···Cu(2) distance is 3.5682(5) Å. The co-ordination geometry around the terminal copper(II) ions is completed by a non-bridging monodentate H_2ahmt ligand co-ordinating *via* N^1, a chloride atom and a hydroxyl group from one of the two bridging H_2ahmt ligands. Magnetic susceptibility measurements (6.5–295 K) are in accord with the trinuclear nature of this compound and could be fitted for an antiferromagnetic interaction ($g = 2.00$ and $J = -16.9$ cm^{-1}) between nearest neighbour copper(II) ions. The X- and Q-band powder EPR spectra are typical for a spin doublet. The presence of two different copper(II) chromophores is evident from the broad asymmetric band in the ligand field spectrum.

Polynuclear copper(II) co-ordination compounds have been investigated frequently, not only because of their interesting magnetic superexchange interactions,[1–7] but also because of their relevance for bioinorganic model systems in copper enzymes.[8] Bridging systems based on the 1,2,4-triazole ring are very interesting, because of their similarity to 1,3-imidazolate bridging found in superoxide dismutase.[9] A particular class of ligands is formed by the 1,2,4-triazoles with chelating oxygen-donating substituents. Recently, some polynuclear nickel(II) co-ordination compounds have been described with the ligand H_2ahmt [4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole, Fig. 1].[10,11] The H_2ahmt ligand is known to occur in three different chemical structures, *i.e.* neutral, mono- and di-anionic; in all different chemical forms it can co-ordinate in several ways to metal ions, namely monodentate, didentate (either dinucleating or chelating), tri- or tetra-dentate. In the cubane-like nickel(II) clusters[10,11] the H_2ahmt ligand is present in these three different chemical forms, and also in several different modes of co-ordination. In the reported nickel(II) dimer $[Ni_8(NCS)_8(ahmt)(Hahmt)_6(H_2ahmt)_4(H_2O)_{12}]$[11] the neutral ligand is present in three different co-ordination modes: mono-, di- and tri-dentate. In the present paper the structure of the first copper(II) complex of H_2ahmt is reported in which the ligand co-ordinates in its neutral form, using three different co-ordination modes. The structure is discussed in relation to the magnetic properties.

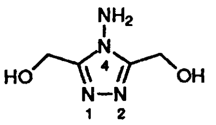

Fig. 1 Atomic labelling of the ligand H_2ahmt

Experimental

Materials and Measurements.—Commercially available solvents, glycolic acid, hydrazine monohydrate and copper(II) chloride dihydrate were used without further purification.

Carbon, H, N and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland. UV/VIS spectra were obtained on a Perkin Elmer 330 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-Band EPR spectra were obtained on a JEOL RE2x spectrometer using an ESR900 continuous-flow cryostat. Q-Band EPR spectroscopy at 22 K was performed on a Varian E-9 spectrometer with a Bruker ER061SR microwave bridge. Mass spectroscopy was carried out on a Kratos MS9/50 spectrometer. Magnetic susceptibilities were measured in the temperature range 6.5–295 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *ca.* 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants. Magnetic data were fitted to theoretical expressions by means of a Simplex routine,[12] with

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: emu = SI × $10^6/4\pi$.

Table 1 Experimental data for the X-ray diffraction study on $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$

Formula	$C_{24}H_{48}Cl_6Cu_3N_{24}O_{12}$
M_r	1268.16
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.2233(2)
b/Å	9.2247(2)
c/Å	13.6153(2)
α/°	113.1441(2)
β/°	105.1557(1)
γ/°	91.2530(2)
Z	1 (trinuclear unit)
U/Å^3	1128.3
D_c/g cm^{-3}	1.86
D_m/g cm^{-3}	1.75
λ (Mo-Kα) (graphite filtered)/Å	0.710 73
Linear absorption/cm^{-1}	18.28
F(000)	645
T/K	298
Scan type	ω–2θ
2θ range/°	4–60
Dataset (h, k, l)	−14 to 14; −13 to 13; 0–19
Unique total data	6562
Unique observed data [$I > 2\sigma(I)$] (n)	3091
No. of parameters refined (p)	316
R^a	0.0362
R'^b	0.0424
S (goodness of fit)^c	1.09
Weighting scheme	$1/[\sigma^2(F) + 0.0025F^2]$

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{\frac{1}{2}}$.

the use of a computer program written by R. Prins. All parameters (J and g) were varied independently during the fitting procedure. This routine minimizes the function $R = (\Sigma|\chi_{obs}-\chi_{calc}|^2/|\Sigma\chi_{obs}|^2|)^{(\frac{1}{2})}$.

Synthesis of 4-*Amino*-3,5-*bis*(*hydroxymethyl*)-1,2,4-*triazole* (H_2ahmt).—Glycolic acid (76 g, 1 mol) was mixed with hydrazine monohydrate (101 g, 2 mol, 100 cm^3) in a large beaker and the mixture was heated in an oil bath at 180 °C until the evaporation of water had ceased. After cooling to room temperature the contents of the beaker solidified and were recrystallized from water, yielding a yellowish compound, which was used without further purification. Yield: 60% (40 g). The melting point of 200 °C is in agreement with literature values.[10,11,13]

Synthesis of $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$.—A boiling solution of $CuCl_2 \cdot 2H_2O$ (2 mmol) in methanol (20 cm^3) was added to a boiling suspension of H_2ahmt (4 mmol) in methanol (50 cm^3) and refluxed further (*ca.* 5 min) until a clear green solution was obtained. The hot solution was filtered and after a few days the green-blue compound crystallized by slowly evaporating the solvent at room temperature. Yield: 60% (Found: C, 22.50; H, 3.80; Cu, 15.45; N, 26.40. Calc. for $C_8H_{16}Cl_2CuN_8O_4$: C, 22.75; H, 3.80; Cu, 15.05; N, 26.50%).

X-Ray Crystallography.—A blue-green block-shaped crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was selected for X-ray structure analysis and mounted on an Enraf–Nonius CAD-4 four-circle diffractometer and measured at room-temperature using graphite-monochromated Mo-Kα radiation. Crystal data and data collection parameters are presented in Table 1. The unit-cell parameters were determined from 25 reflections in the range $10 < \theta < 12°$. The 3091 reflections (of 6562 measured), for which $I > 2\sigma(I)$, were corrected for Lorentz and polarization effects, and for absorption applying the program DIFABS.[14] Copper and chlorine atoms were located by direct methods.[15] The structure was solved by automatic Fourier techniques, using the computer program AUTOFOUR.[16] Full-matrix least-squares refinement on F of non-hydrogen atoms yielded their positional and anisotropic thermal parameters. The hydrogen atoms were located from a Fourier difference map, and were positionally refined with the parent atoms with one overall isotropic thermal parameter for each group of hydrogen atoms; *i.e.* aliphatic hydrogen atoms, amino hydrogen atoms and hydroxy hydrogen atoms. The model converged to $R = 0.0326$ and $R' = 0.0424$. The final Fourier difference map showed no residual density other than a peak of 0.65 e Å^{-3} near C(29) indicating some positional disorder. Scattering factors for neutral atoms were taken from the literature.[17] All calculations were carried out on a VAX/IBM 3083 with the program SHELXS 86 and locally written or modified programs. Final fractional coordinates for non-hydrogen atoms are given in Table 2. Bond distances and angles are given in Table 3. The preparation of the illustrations was done with ORTEP.[18]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Structure of $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$.—An ORTEP[18] projection of the structure of the linear trinuclear copper(II) cation and the atom numbering are shown in Fig. 2. The central copper(II) ion Cu(1) lies on the crystallographic inversion centre and shows distorted octahedral co-ordination with 2 N-donor atoms of the triazole ligands [Cu(1)–N(11) 2.023(3) Å] and two chloride atoms in the equatorial plane [Cu(1)–Cl(1) 2.296(1) Å]. Two ligand N(triazole) atoms act as axial ligands at slightly longer distances [Cu(1)–N(21) 2.554(3) Å]. The distances from the bridging chlorides to the terminal metal ions are quite long [Cu(2)–Cl(1) 2.688(1) Å]. The Cu(1)–Cl(1)–Cu(2) angle of this very asymmetric chloride bridge is 91.09(4)°. Atom Cu(1) is linked to the terminal Cu(2) atoms *via* this chloride atom and also *via* two N^1,N^2-bridging 1,2,4-triazole ligands. It should be noted that the two triazole ligands co-ordinate differently. Triazole 1 bridges the copper(II) ions in a rather symmetric manner. The Cu–N(triazole) distances [2.023(3) and 2.079(2) Å, respectively], are in the normal range for N^1,N^2-bridging 1,2,4-triazole ligands.[3–7,19,20] The second H_2ahmt ligand connects the two metal ions in a very unusual asymmetric manner with a large N(21)(triazole) distance to Cu(1) [2.554(3) Å] and a very short N(22)(triazole) [1.966(3) Å] distance to Cu(2). Furthermore, the ligand binds to Cu(2) in a chelating co-ordination mode. The Cu(2)–O(28) distance is very long [2.663(3) Å] and the bite angle N(22)–Cu(2)–O(28) of 70.0(1)° is significantly smaller than the angles that have been found in the nickel(II) cubane cluster with this ligand.[10,11] In that case the ligand acts as a chelating, dianionic, tetradentate ligand, with N–Ni–O bite angles between 77.0(5) and 79.2(5)°.

The co-ordination geometry around Cu(2) is completed by a monodentate ligand co-ordinating *via* N^1 at a short distance [2.059(4) Å] and a co-ordinating chloride atom at 2.254(1) Å. The equatorial planes of the co-ordination octahedra around Cu(1) and Cu(2) make an angle of 139.8(1)°. The Cu(1) ··· Cu(2) distance is 3.5682(5) Å, which is somewhat shorter than has been found in a triple 1,2,4-triazole-bridged copper(II) compound [*i.e.* 3.719(7) Å].[11,19] The lattice chloride atoms are involved in a complex inter- and intra-molecular hydrogen-bond network.

Some linear trinuclear co-ordination compounds of this type, *i.e.* containing two 1,2,4-triazole ligands bridging *via* N^1,N^2 and a halogen anion, have been reported previously[20–22] although not with chloride. Two cobalt(II) compounds[21,22] and a copper(II) compound[20] containing fluoride have been structurally characterized. The cobalt(II) compounds contain 1,2,4-

Table 2 Fractional atomic coordinates for the non-hydrogen atoms in the compound $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)*	0	0	0
Cu(2)	0.326 00(10)	0.236 47(11)	0.157 52(7)
Cl(1)	0.184 76(10)	−0.038 09(11)	0.121 25(7)
Cl(2)	0.534 06(10)	0.162 92(11)	0.153 71(7)
Cl(3)	0.033 81(10)	0.270 62(22)	0.575 77(15)
N(11)	0.132 8(3)	0.040 7(4)	−0.076 5(3)
N(12)	0.252 7(3)	0.148 5(4)	−0.015 6(3)
C(13)	0.303 9(4)	0.173 1(4)	−0.087 4(4)
N(14)	0.224 0(4)	0.080 7(4)	−0.192 1(3)
C(15)	0.119 5(4)	−0.001 0(5)	−0.183 1(4)
N(16)	0.248 7(4)	0.078 1(5)	−0.289 9(3)
C(17)	0.427 3(4)	0.284 5(5)	−0.060 8(4)
O(18)	0.535 9(3)	0.206 0(4)	−0.094 2(3)
C(19)	0.011 7(5)	−0.121 0(5)	−0.281 1(4)
O(20)	−0.062 4(4)	−0.046 5(4)	−0.348 3(3)
N(21)	0.036 9(4)	0.299 5(4)	0.119 6(3)
N(22)	0.173 7(3)	0.362 8(4)	0.155 8(3)
C(23)	0.183 5(4)	0.516 9(4)	0.186 9(4)
N(24)	0.056 6(4)	0.556 6(4)	0.170 8(3)
C(25)	−0.032 1(4)	0.420 6(5)	0.130 8(4)
N(26)	0.017 9(4)	0.709 0(4)	0.189 4(4)
C(27)	0.312 6(4)	0.628 0(5)	0.235 1(4)
O(28)	0.420 3(3)	0.538 2(3)	0.213 1(3)
C(29)	−0.181 1(5)	0.415 4(5)	0.110 3(4)
O(30)	−0.240 2(4)	0.440 9(4)	0.015 0(4)
N(31)	0.357 9(4)	0.304 7(4)	0.326 2(3)
N(32)	0.315 3(4)	0.446 4(4)	0.386 8(3)
C(33)	0.315 1(4)	0.444 8(5)	0.481 5(4)
N(34)	0.355 0(4)	0.307 5(4)	0.486 3(3)
C(35)	0.380 5(5)	0.222 5(5)	0.387 7(4)
N(36)	0.368 2(4)	0.267 1(4)	0.578 3(3)
C(37)	0.271 9(5)	0.569 2(5)	0.573 2(4)
O(38)	0.251 4(3)	0.707 8(3)	0.553 1(3)
C(39)	0.432 8(5)	0.065 7(5)	0.363 7(4)
O(40)	0.557 9(3)	0.083 5(4)	0.448 1(3)

* Atom Cu(1) lies on a special position.

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$ with e.s.d.s in parentheses*

Cu(1) ··· Cu(2)	3.5682(5)	Cu(2) ··· Cu(2′)	7.1364(5)
Cu(1)–Cl(1)	2.296(1)	Cu(1)–N(11)	2.023(3)
Cu(1)–N(21)	2.554(3)		
Cu(2)–Cl(1)	2.688(1)	Cu(2)–Cl(2)	2.254(1)
Cu(2)–N(12)	2.079(4)	Cu(2)–N(22)	1.966(3)
Cu(2)–N(31)	2.059(4)	Cu(2)–O(28)	2.663(3)
Cl(1)–Cu(1)–N(11)	86.9(1)	N(11)–Cu(1)–Cl(1′)	93.1(1)
Cl(1)–Cu(1)–N(21)	92.11(8)	N(11)–Cu(1)–N(11′)	180.0(0)
Cl(1)–Cu(1)–Cl(1′)	180.00(0)	N(11)–Cu(1)–N(21)	92.0(1)
Cl(1)–Cu(1)–N(11′)	93.1(1)	N(21)–Cu(1)–Cl(1′)	87.89(8)
Cl(1)–Cu(1)–N(21′)	87.89(8)	N(21)–Cu(1)–N(11′)	92.0(1)
N(11)–Cu(1)–N(21)	88.0(1)	N(21)–Cu(1)–N(21′)	180.0(0)
Cl(1)–Cu(2)–Cl(2)	101.03(4)	Cl(2)–Cu(2)–N(31)	96.5(1)
Cl(1)–Cu(2)–N(21)	82.4(1)	N(12)–Cu(2)–N(22)	84.7(1)
Cl(1)–Cu(2)–N(22)	98.1(1)	N(21)–Cu(2)–O(28)	101.9(1)
Cl(1)–Cu(2)–O(28)	166.76(7)	N(21)–Cu(2)–N(31)	167.9(1)
Cl(1)–Cu(2)–N(31)	88.4(1)	N(22)–Cu(2)–O(28)	70.0(1)
Cl(2)–Cu(2)–N(12)	92.9(1)	N(22)–Cu(2)–N(31)	88.9(1)
Cl(2)–Cu(2)–N(22)	160.2(1)	O(28)–Cu(2)–N(31)	85.5(1)
Cl(2)–Cu(2)–O(28)	91.34(7)		
Cu(1)–Cl(1)–Cu(2)	91.09(4)	Cu(2)–N(12)–C(13)	130.5(3)
Cu(1)–N(11)–N(12)	121.2(3)	Cu(2)–N(22)–N(21)	124.3(3)
Cu(1)–N(11)–C(15)	130.6(3)	Cu(2)–N(22)–C(23)	126.5(3)
Cu(1)–N(21)–N(22)	111.6(2)	Cu(2)–O(28)–C(27)	106.7(2)
Cu(1)–N(21)–C(25)	138.4(3)	Cu(2)–N(31)–N(32)	118.7(3)
Cu(2)–N(12)–N(11)	122.0(3)	Cu(2)–N(31)–C(35)	131.3(3)

* Primed atoms are generated by $-x$, $-y$, $-z$.

triazoles which link the metal ions in a rather symmetrical fashion and short Co–F distances [1.992(1)–2.058(2) Å] leading to Co ··· Co distances of *ca.* 3.40 Å. In the copper(II) fluoride compound, the fluorine bridge is asymmetric with Cu–F distances of 2.20(1) and 1.91(1) Å and Cu–F–Cu 81.2(5)°, and a Cu ··· Cu distance of 3.362(3) Å has been found.[20] The somewhat larger metal–metal distance observed in the present copper(II) chloride compound is mainly due to the larger size of chloride compared to fluoride.

The only copper(II) 1,2,4-triazole (Htrz) compound containing μ-chloride ions is $[\{Cu(Htrz)Cl_2\}_\infty]$.[23–25] In this infinite chain all metal ions are linked *via* a symmetric didentate N^1,N^2-1,2,4-triazole bridge and two asymmetrical μ-chlorides (Cu–Cl 2.34 Å, Cu′–Cl 2.77 Å, Cu–Cl–Cu′ 83.2°), with a Cu ··· Cu′ distance of 3.40 Å.

Spectroscopic Measurements.—The presence of two different geometries around copper(II) is reflected in the UV/VIS spectrum, which shows a very broad asymmetric band centred around 12 900 cm^{-1}, and which is in agreement with the presence of CuN_4Cl_2 and CuN_3OCl_2 chromophores.[26]

The X-band powder EPR spectrum recorded at 298–60 K shows an asymmetrical signal around $g = 2.17$. At low temperatures the spectrum becomes more resolved and shows signals at $g = 2.07$ and 2.28 (see Fig. 3). Similar EPR spectra have been reported for the linear trinuclear $[Cu_3(Hade)_2Cl_8]\cdot 4H_2O$ (ade = adenine), and are typical for a spin doublet ground state.[27] The Q-band EPR spectrum recorded at 22 K yielded $g_\perp = 2.07$ of and $g_\parallel = 2.28$, which is typical for copper(II) ions in an axial symmetry.[26]

Magnetic Properties.—The linear trinuclear nature of this copper(II) cluster is confirmed by the magnetic susceptibility data (6.5–295 K). The inverse susceptibility *vs.* temperature curve (Fig. 4) exhibits a change in the slope, characteristic for linear trinuclear compounds with antiferromagnetic exchange interaction between nearest neighbours.[28–30] At 295 K the value of χT per copper(II) ion is 0.330 cm^3 mol^{-1} K, which is about the value expected for a single uncoupled copper(II) ion. The value of χT decreases upon cooling, reaching a value of 0.135 cm^3 mol^{-1} K at 6.5 K. This behaviour is characteristic for compounds having an overall antiferromagnetic interaction between the metal ions. The magnetic data were fitted to the theoretical expression for the magnetic susceptibility of linear trinuclear $S = \frac{1}{2}$ systems,[31] which was based on the phenomenological spin Hamiltonian with quantum spin operators $\hat{S}_1$ and $\hat{S}_2$: $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2)$. The magnetic susceptibility is then defined by equation (1), where N, g, β, k and T have their usual

$$\chi_m = (Ng^2\beta^2/4kT)[1 + \exp(-2J/kT) + 10\exp(J/kT)]/ \\ [3 + 3\exp(-2J/kT) + 6\exp(J/kT)] \quad (1)$$

meanings. The exchange parameter is denoted as J. The g-tensor was assumed to be equal for all individual metal ions and intercluster exchange interactions were supposed to be negligible. The assumption of negligible magnetic exchange between the terminal metal ions is justified in view of the study on the 1,2,4-triazole bridged $Fe^{II}{}_3$[32] and Co^{II}–Co^{III}–Co^{II}[33] clusters, where the central metal ion is diamagnetic, and no magnetic

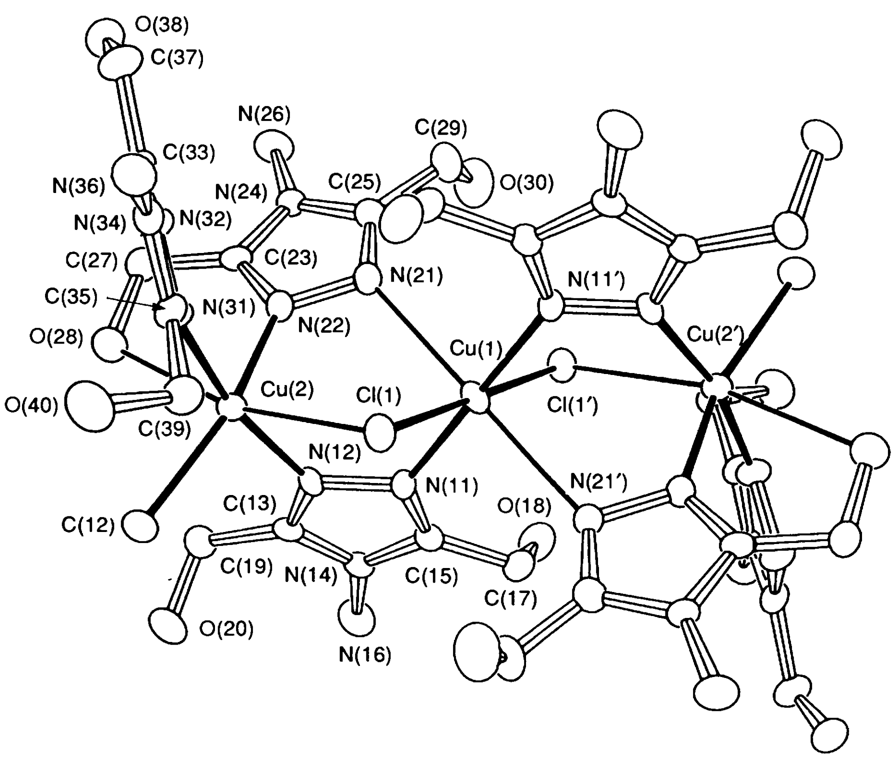

Fig. 2 An ORTEP[18] drawing and atomic labelling system showing the structure of $[Cu_3(H_2ahmt)_6Cl_4]^{2+}$

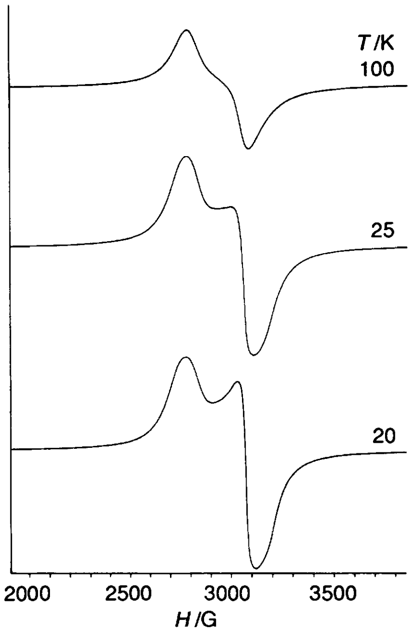

Fig. 3 X-Band powder EPR spectra of $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$ at 100, 25 and 20 K

interactions could be detected between the paramagnetic terminal metal ions. A good fit has been obtained for the parameters $J = -16.9$ cm^{-1} and $g = 2.00$. Fig. 4 depicts the calculated and observed curves.

Discussion

The crystal structure of the present compound shows that also in copper(II) compounds the neutral 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole ligand is able to co-ordinate in various ways. The co-ordination behaviour of the H_2ahmt ligand is quite different from that of the related 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole (aamt).[6,7] With the latter only a doubly didentate bridging co-ordination mode of the neutral ligand has been found. The origin of this difference lies in the fact that the oxygen substituents are more electronegative than the nitrogen substituents and are more readily available for hydrogen bonding and less for co-ordination.

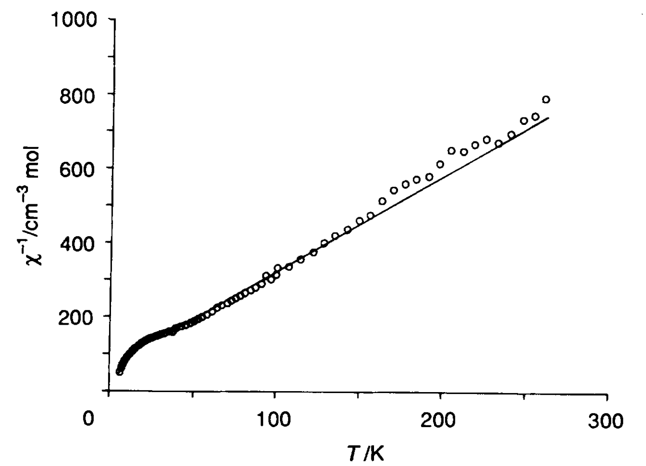

Fig. 4 Observed (o) and calculated (—; $J = -16.9$ cm^{-1}, $g = 2.00$) χ^{-1} *vs.* T curves for $[Cu_3(H_2ahmt)_6Cl_4]Cl_2$

The present results show that chloride ions can be incorporated in a linear array of copper(II) ions linked by double N^1,N^2-1,2,4-triazole bridges. Two asymmetrical bridging chlorides in combination with a single N^1,N^2-triazole bridge have already been described.[23-25]

It is extremely difficult to understand the mechanism of the interaction between paramagnetic centres in polymetallic compounds, where the metal ions are linked by at least two non-similar ligands. Then the observed magnetic interaction must be resolved into contributions arising from each Cu–ligand–Cu linkage. In general, several physical and structural parameters are important in determining the magnetic properties.[1,2] The main parameters are: the distance between the paramagnetic centres, the M–X–M (X = bridging ligand donor atom) angle, the extent of planarity of the bridging network, as well as the nature of the bridging ligand (*i.e.* in particular the electron density on the bridging group and the intrinsic properties of the anions).[1,34] In the present compound the Cu(1)–Cl(1)–Cu(2) angle is only 91.09(4)° and the chloride ion is rather electronegative; nevertheless an antiferromagnetic coupling between the copper(II) ions has been found. When the orientation of the magnetic orbitals on both copper(II) ions is examined, it is seen that those on Cu(1) and Cu(2) can only have a significantly large overlap *via* triazole 1. This implies that the pathway for antiferromagnetic superexchange proceeds mainly *via* the σ orbitals of the triazole ligand which links the metal ions in a rather symmetric fashion.

Although a series of linear trinuclear nickel(II) compounds containing μ-N^1,N^2-1,2,4-triazole ligands as well as bridging anions have been reported,[22,29,35–38] the literature dealing with the related copper(II) compounds is rather limited. Only two linear trinuclear copper(II) compounds containing μ-N^1,N^2-1,2,4-triazoles have so far been structurally characterized.[11,19,20] A detailed comparison with the magnetic data of these copper(II) compounds is not possible, since no accurate data are available as yet for all compounds. It would be worthwhile to extend the research on this class of copper(II) compounds, since here each metal centre has only one unpaired electron and the magnetic orbital model for describing the magnetic exchange interactions can be applied easily.[39,40]

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