Synthesis, Structure, Spectroscopy, and Magnetism of Unique Propeller-Type Linear Trinuclear Cu^{II} Complexes with In-situ Prepared Formamidine Ligands

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Three new copper(II) linear trinuclear compounds are reported, all of which were synthesized in-situ, with the general formula $[Cu_3(L)_4](CF_3SO_3)_2(Y)_x$, where L is the dehydronated ligand: *N,N′*-bis(pyridine-2-yl)formamidine (abbreviated as Hpdf), *N,N′*-bis(pyrimidine-2-yl)formamidine (abbreviated as Hpmf) and *N,N′*-bis(5-methylpyridine-2-yl)formamidine (abbreviated as Hmpdf), Y = EtOH or H_2O and x = 0.5–1.5. The compounds were characterized by X-ray diffraction, IR, LF, and EPR spectroscopy and by magnetic susceptibility down to 4 K. The structure of the compound $[Cu_3(pmf)_4](CF_3SO_3)_2(H_2O)_{1/2}$ was determined by X-ray crystallography; it was found to crystallise in the triclinic space group $P{-}1$ with $a = 8.529(5)$, $b = 15.760(5)$, $c = 19.639(5)$ Å, $\alpha = 101.793(5)$, $\beta = 101.263(5)$, $\gamma = 102.389(5)°$, $Z = 2$. The structure [Cu–Cu–Cu angle 174.96(11)°] consists of four nearly flat molecules of the ligand, which contribute to the propeller-type structure around the Cu–Cu–Cu axis. A strong antiferromagnetic interaction between the Cu^{II} ions is observed with calculated J values, based on the Hamiltonian $H = -2J(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_2\cdot\mathbf{S}_3) - 2J'\cdot\mathbf{S}_1\cdot\mathbf{S}_3$, of $-174(1)$ cm^{-1}, $-120(1)$ cm^{-1}, and $-167(1)$ cm^{-1} for the compounds studied with L = pdf, pmf, and mpdf, respectively. These values are in agreement with an $S = 1/2$ ground state below temperatures of 120–160 K.

Introduction

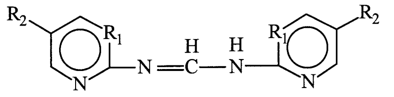
Dinuclear and polynuclear exchange-coupled copper(II) complexes have been extensively studied, although the number of trinuclear compounds investigated magnetically and structurally is still quite limited.[1][2]

Dinuclear systems are well documented not only because of their interesting magnetic interactions,[1] but also because of their relevance for bioinorganic model systems for copper in enzymes.[3] The theory for dinuclear systems is adequate for interpreting the relationship between the isotropic exchange constant and the structural parameters, but linear trinuclear compounds have been discussed to a much lesser extent, mainly due to the fact that the number of such copper(II) compounds is relatively small.

The majority of the known linear trinuclear Cu^{II} compounds of which the structures have been characterised by X-ray crystallography contain an oxygen bridge[4][5] or a mixed (N, Cl, O) bridge[2,6,7] between the Cu^{II} atoms, and only a few contain a nitrogen bridge. In fact a very small number of compounds contain a CuN_{4-6} chromophore around all three copper sites[8] and, of these compounds, two are from external azide bridges.[8b,8d] Of all known trinuclear linear Cu^{II} compounds a limited number of copper(II) complexes have been fully studied magnetically *and* also characterised by X-ray crystallography (see Table 2).

Trinuclear compounds that have a $[Cu{-}N{-}Cu{-}N{-}Cu]_x$ bridge (with an N belonging to a heterocyclic ligand) are rare and, in fact, only two structures have been reported in the literature.[8b,9,10a] Several mixed Mn−Cu−Mn linear trinuclear compounds are also known.[11]

In a preliminary communication[9] we described a novel template synthesis of a new N_4-donor ligand and, as an example, the X-ray structure of such a compound.



N,N′-bis(pyridine-2-yl)formamidine (Hpdf) R_1 = CH, R_2 = H
N,N′-bis(pyrimidine-2-yl)formamidine (Hpmf) R_1 = N, R_2 = H
N,N′-bis(5-methylpyridine-2-yl)formamidine (Hmpdf) R_1 = CH, R_2 = CH_3

In the present study we describe three formamidine compounds synthesized in a similar way, in situ, from 2-aminopyridine, 2-aminopyrimidine, and 2-amino-5-methylpyridine ligands, copper(II) triflate, and triethylorthoformate in alcohol. The study also includes a second X-ray structure of such a compound. To the best of our knowledge this method for the preparation of such formamidine compounds in situ is unique.

The general formula of the new compounds is $[Cu_3(L)_4](CF_3SO_3)_2(Y)_x$, where L is the dehydronated ligand: *N,N′*-bis(pyridine-2-yl)formamidine (abbreviated as Hpdf), *N,N′*-bis(pyrimidine-2-yl)formamidine (abbreviated as Hpmf) and *N,N′*-bis(5-methylpyridine-2-yl)formamidine (abbreviated as Hmpdf), Y = EtOH or H_2O and

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$x = 0.5-1.5$. Recently a number of related compounds have been reported with the formula $[M_3(pdf)_4][PF_6]_2$ [where M = Cu^{II}, Co^{II}, Fe^{II}, Cr^{II}], and these were prepared by a different synthetic method[10] involving the initial synthesis of the pdf ligand followed by treatment with PF_6^- as an anion. The structural features of these systems will be compared and discussed.

Synthesis of the Complexes

The compounds are formed in situ by an easy one-step template synthesis of 2-aminopyridine, 2-aminopyrimidine, and 5-methyl-2-aminopyridine for pdf, pmf, and mpdf, respectively, using anhydrous copper(II) triflate in dry ethanol. Upon standing, deep dark green (almost black) crystals of formula $[Cu_3(L)_4](CF_3SO_3)_2(Y)_x$ were formed (Y = EtOH or H_2O, L = dehydronated ligand).

Three Cu^{II} compounds with different formamidine ligands are shown in Table 1 together with some spectral and magnetic features. It must be noted that only a very weak non-coordinating anion like triflate can be used, as stronger binding anions, like perchlorate or nitrate, do not give the same results. Attempts to use this synthetic method to prepare compounds with metals other than Cu^{II} have failed so far. Spectroscopic, magnetic and analytical characterisation showed that all three compounds must have a similar molecular structure. The structure of **1** was reported previously and the structure of **2** is discussed below.

Crystal Structure of Compound 2

X-ray structural analysis of **2** shows a linear arrangement of three Cu^{II} ions surrounded by four ligand molecules in a propeller mode, each of which is tetracoordinated to the three copper atoms. A plot representing this complex, together with the atom labelling scheme, is given in Figure 1 and distances and angles are given in Table 2. The central copper atom Cu2 has a distorted square-planar geometry [with *trans* angles of 168.7(6) and 159.2(6)°] and normal Cu−N distances of about 2.0 Å. The outer copper ions are six-coordinated with, in general, a distorted square-based geometry and a different geometry for each copper. The angles of the basal plane of Cu3 (formed by N117−N217−N317−N423) are 170.7(6)° and 160.9(6)°. The short Cu−N distances Cu3 vary from 2.002(12) to 2.124(14) Å. The axial sites of the geometry are occupied by the nitrogen atoms N223 and N417 with Cu−N distances of 2.31(2) to 2.49(2) Å. The geometry of the copper atoms Cu3 and Cu2 is comparable with those in compound **1**.[9]

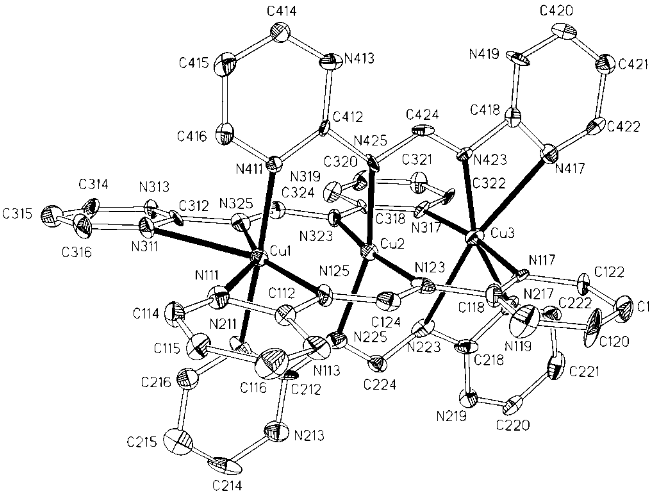

Figure 1. Plot of structure **2** with atom-labelling scheme. H atoms, the non-coordinating triflate anions, and the disordered water molecule are omitted for clarity

The octahedral geometry of the Cu1 atom is unusual (and is in contrast to compound **1**) in that it has four short Cu−N distances [2.004(13)−2.072(13) Å] and two *cis* elongated Cu−N distances of 2.546(13) and 2.538(12) Å. One angle is normal [N211−Cu1−N411 = 177.5(5)°], but two angles have very large deviations from 180° [N311−Cu1−N125 = 151.5(5), N325−Cu1−N111 = 151.0(5)°]. Such an unusual geometry has been observed previously[12] in a few cases like for the mononuclear species

Table 1. Ligand field and EPR and magnetic data of Cu^{II} compounds with ligands pdf, pmf, and mpdf[a]

Compound	UV-VIS [10^3cm^{-1}]	EPR (solid) room temp.	EPR (solid) 77 K	EPR Frozen sol. in DMF (77 K)	Magnetic Susceptibility Measurements[d]

1[b]
$[Cu_3(pdf)_4](CF_3SO_3)_2(EtOH)_{1.5}$
	17.3
	22.0
	30.3
		$g_{\perp} = 2.11$ (br)
		$g_{//} = 3.6$ (br,w)
			$g_{\perp} = 2.07$
			$g_{//} =$ ca.2.3 (vw)
				$g_{\perp} = 2.07$
				$g_{//} = 2.30$
				$A_{//} = 15.8$ mT
					$J = -174(1)$ cm^{-1}
					$g = 2.16(1)$

2[c] $[Cu_3(pmf)_4](CF_3SO_3)_2(H_2O)_{0.5}$	16.4 21.2 28.7	$g_{\perp} = 2.11$ (br) $g_{//} = 4.1$ (br,w)	$g_{\perp} = 2.07$ $g_{//} =$ ca.2.3 (vw)	$g_{\perp} = 2.07$ $g_{//} =$ca. 2.3 (vw)	$J = -120(1)$ cm^{-1} $g = 2.26(1)$
3 $[Cu_3(mpdf)_4](CF_3SO_3)_2(EtOH)_1$	16.1 20.0 29.6	$g_{\perp} = 2.10$ (br) $g_{//} = 3.7$ (br,w)	$g_{\perp} = 2.07$ $g_{//} =$ ca.2.2 (vw)	$g_{\perp} = 2.07$ $g_{//} =$ ca.2.3 (vw)	$J = -167(1)$ cm^{-1} $g = 2.12(1)$

[a] br = broad, w = weak, vw = very weak. − [b] X-ray crystal structure solved;[9] a related crystal structure was solved for a species with the formula $[Cu_3(pdf)_4](PF_6)_2(CH_3CN)_4(EtOH)_2$.[10a] − [c] X-ray crystal structure solved, this work. − [d] Fitted parameters by Equation (1), see text.

Table 2. Selected bond lengths [Å] and angles [°] for compound **2**

Cu(1)−N(211)	2.005(13)
Cu(1)−N(411)	2.004(12)
Cu(1)−N(125)	2.034(13)
Cu(1)−N(325)	2.072(13)
Cu(1)−N(311)	2.538(12)
Cu(1)−N(111)	2.546(13)
Cu(1)−Cu(2)	2.637(3)
Cu(2)−N(123)	1.971(14)
Cu(2)−N(323)	1.972(13)
Cu(2)−N(425)	2.025(13)
Cu(2)−N(225)	2.069(14)
Cu(2)−Cu(3)	2.652(3)
Cu(3)−N(117)	2.003(12)
Cu(3)−N(423)	2.017(13)
Cu(3)−N(317)	2.030(12)
Cu(3)−N(217)	2.120(15)
Cu(3)−N(223)	2.31(2)
Cu(3)−N(417)	2.49(2)
N(211)−Cu(1)−N(411)	177.5(6)
N(125)−Cu(1)−N(325)	151.1(6)
N(311)−Cu(1)−N(125)	151.5(5)
N(325)−Cu(1)−N(111)	151.0(5)
N(123)−Cu(2)−N(323)	168.7(6)
N(425)−Cu(2)−N(225)	159.2(6)
Cu(1)−Cu(2)−Cu(3)	174.96(11)
N(117)−Cu(3)−N(317)	170.7(6)
N(423)−Cu(3)−N(217)	160.9(6)
N(417)−Cu(3)−N(223)	161.4(5)

Cu(edtb)$^{2+}$. The Cu−Cu distances of 2.637(3) and 2.652(3) Å are slightly shorter than in the comparable pdf compound **1** [which are 2.6618(8) and 2.6676(8) Å],[9] and are close to the shortest known distances for Cu^{II} linear trinuclear compounds (see Table 3). Only in Cu^{I} compounds are shorter distances known in some cases.[13] The linear angle Cu1−Cu2−Cu3 is 174.96(11)° and is close to those for other species[9,10a] of this type.

On viewing the compound along the Cu−Cu−Cu axis a propeller-type arrangement is visible in which the ligands are almost perpendicular to the axis with angles between the 2 rings of each ligand that vary from 7.21 to 2.10°. These variations are significantly smaller than in compound **1**, in which they vary from 27.73 to 8.19°, as can been seen from Figure 2. Further stabilisation of the lattice is achieved by stacking of pyrimidine rings between different units (ring-ring distances 3.648−3.889 Å), as can be seen in Figure 3.

Hydrogen bonds between the oxygen atoms of the disordered water molecule and the fluorine of the tetrafluoroborate anion are present, with contacts O···F of 2.73 and 3.16 Å.

An X-ray structure of compound **3** could not be obtained due to the very small crystal size, but this compound very closely resembles **1** and **2** both spectroscopically and magnetically, so a very similar structure is anticipated.

Spectroscopy

The ligand field spectra of compounds **1** to **3** all show a broad band with a double maximum at 16.1−17.3 and 20.0−22.0 $\times 10^3$cm^{-1}. In addition, a charge transfer band is observed near $29 \cdot 10^3$ cm^{-1}. The two low-energy absorptions are both assigned to d-d transitions,[14] and it is tempting to assume that the highest energy band originates from the square-planar central Cu atom (even though Cu2 is not perfectly square-planar) and the lowest energy band from the outer six-coordinated Cu atoms.[8c,15]

The IR spectra of the compounds are rather featureless. In the mid-infrared section the characteristic C=N is still observed in the free Hpdf ligand at 1671 cm^{-1} as a strong broad band. In compound **1** a double band occurs at 1604, 1587 cm^{-1}. As the free ligand also has a band at 1602 cm^{-1}, the last band is probably the C=N stretching vibration. This band occurs at 1586 cm^{-1} and 1589 cm^{-1} for **2** and **3**, respectively.

In the far-infrared region a strong and broad vibration is predominant at 364 cm^{-1}, 381 cm^{-1}, and 377 cm^{-1} for compounds **1**, **2**, and **3**, respectively; this band can be assigned to the asymmetric Cu−N vibration.[16] Other weak bands present at lower wavenumbers have not been assigned.

EPR

The EPR spectra of powdered polycrystalline samples of the compounds at room temperature show a very broad absorption (peak to peak separation 36 mT) centered around $g = 2.11$ and a weaker broad absorption which lies around $g = 3.6$ for compounds **1** and **3** and at $g = 4.1$ for compound **2**. These latter absorptions disappear upon cooling to 77 K or lower. The main EPR signal ($g = 2.07$) sharpens upon cooling to 77 K (peak-to-peak separation 9.5 mT) and a very weak $g_{//}$ at ca. $g = 2.3$ becomes visible (no $A_{//}$ resolved) (Figure 4). Such signal sharpening upon cooling is not uncommon with trinuclear compounds.[5f,7c,17] The EPR signals at room temperature at ca. $g = 3.6{-}4.1$ can be assigned to the parallel transitions of the quadruplet state,[18] a state that is almost completely depopulated at 77 K. The narrowing of the other signal seems to be in agreement with this view because only the ground doublet is populated in these conditions. The energy of these signals also varies with the J values (vide infra), a fact that confirms this assignment.

Frozen solution spectra in DMF show (for compounds **2** and **3**) only a broad signal at $g = 2.07$ and a very weak unresolved $g_{//}$ section. Compound **1**, however, shows a well-resolved $g_{//}$ of 2.30 with an $A_{//}$ of 15.8 mT and this is indicative of Cu^{II} in an axial symmetry.[2,14a] This signal is likely to originate from a mononuclear species resulting from dissociation.

Magnetism

The magnetic susceptibility of powdered samples was measured from 4 to 300 K. The magnetic properties of the compounds are summarized in Table 1 and the inverse susceptibility vs. temperature is shown in Figure 5. The inverse susceptibility vs. temperature is almost linear at high temperature, exhibits a broad shoulder and a bend at ca.

Table 3. Linear Cu^{II} trinuclear compounds for which the X-ray structure and magnetism has been published[d,e]

Compound[a]	Bridging atom(s) between adjacent copper atoms[b]	Cu−Cu distance(s)	Cu−Cu−Cu angle	*2J* value [cm^{-1}]	Reference (s = structure, m = magnetism)
$[Cu_3(H_2ahmt)_6Cl_4]Cl_2$	$(Cu-N-N-Cu)_2$ $Cu-Cl-Cu$	3.568(2)	180.0	−16.9	[2] (s,m)
$[Cu_3(attn)_2(H_2O)Cl_2]Cl_4(H_2O)_4$	$(Cu-N-N-Cu)_2$ $Cu-Cl-Cu$	3.5426(1)	180.0	−75.1	[7d] (s,m)
$Cu_3Cl_8(adeH)_2$	$Cu-N-C-N-Cu$ $(Cu-Cl-Cu)_2$	3.479(2)	180.0	−16.1	[7a] (s) [7b] (m)
$[Cu_3(L2)_2(N_3)_2](NO_3)_2 \cdot 2\,H_2O \cdot 2\,CH_3OH$	$Cu-O-N-Cu$ $Cu-N_{azide}-Cu$[c]	3.4008(5)	180.0	−266	[5d] (s,m)
$Cu_3(L1)_2(CH_3COO)_4$	$Cu-O-C-O-Cu$ $Cu-O-Cu$	3.319(1)	180.0	−9.7	[5f] (s,m)
$Cu_3(deae)_2(benzoato)_4(EtOH)_2$	$Cu-O-C-O-Cu$ $Cu-O-Cu$	3.211(6)	180.0	28.7	[4c] (s) [5a] (m)
$Cu_3(dbae)_2(benzoato)_4(EtOH)_2$	$Cu-O-C-O-Cu$ $Cu-O-Cu$	3.188(1)	180.0	30.1	[5a] (s,m)
$[Cu_3(\textit{racemo}\text{-amat})_2](ClO_4)_2$	$(Cu-O-Cu)_2$	2.940(1)	176.9(1)	−212	[5e] (s,m)
$[Cu_3(LH)_4]Cl_2$	$Cu-O-C-N-Cu$ $Cu-N-C-N-Cu$ $Cu-N-Cu$	2.812(4) 2.782(3)	175.85(10)	−41	[5c] (s,m)
$[Cu_3(pdf)_4](CF_3SO_3)_2(EtOH)_{1.5}$	$(Cu-N-Cu)_2$	2.6618(8) 2.6676(8)	175.19(2)	−174(1)	[9] (s) this work (m)
$[Cu_3(pmf)_4](CF_3SO_3)_2(H_2O)_{0.5}$	$(Cu-N-Cu)_2$	2.636(3) 2.652(3)	174.93(11)	−120(1)	this work (s,m)

[a] L1 = *N*-Methyl-*N'*-(4-methoxysalicylidene)-1,3-propanediamine; amat = 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-diol; LH = 2-tolylsulfonylamido-7-hydroxy-1,8-naphthyridine; L2 = 3-[{2-(2-pyridinyl)ethyl}imino]-2-butanone oximato; adeH = adenine; H_2ahmt = 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole; attn = 1,9-bis(3-amino-4*H*-triazol-5-yl)-3,7-dithianonane; dbae = 2-dibutylaminoethanol; deae = 2-diethylaminoethanol; Hpdf = *N,N'*-bis(pyridine-2-yl)formamidine; Hpmf = *N,N'*-bis(pyrimidine-2-yl)formamidine. − [b] When nothing is mentioned the N, O, and C atoms belong to an organic molecule. − [c] Another structure with bridging azide ions has been published recently, although only limited magnetic observations were given. The structure has the formula $[Cu_3(\mu\text{-}N_3)_4(L)_2]$ (in which L = hydridotris(3,5-dimethylpyrazolyl)borate, Cu−Cu distances of 3.082(3), 3.03(3) Å and reported to have a weak antiferromagnetic coupling. − [d] Structures with a copper distances > 5.5 Å and/or Cu−Cu−Cu angles < 170° are excluded, see for instance ref.[17] and ref.[22] − [e] After submitting the manuscript three more compounds were published for which the X-ray structure and the magnetic properties were measured; compound $[Cu_3(pytrz)_{10}(H_2O)_2](ClO_4)_6 \cdot 7\,H_2O$ (pytrz = 4-(2-pyridyl)-1,2,4-triazole), Cu−Cu distance 3.8540(7) Å and $J = -5.41$ cm^{-1}[26] and the compounds: $[Cu_3(L)_2(Me_2en)_2(H_2O)_2] \cdot 7\,H_2O$,$[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (H_3L = 3,5-pyrazoledicarboxylic acid, Me_2en = *N,N*-dimethylethylenediamine) with Cu−Cu distances of 4.3992(13) and 4.4532(12) Å, respectively, and *J* values of −15 cm^{-1} and −19 cm^{-1}, respectively.[27]

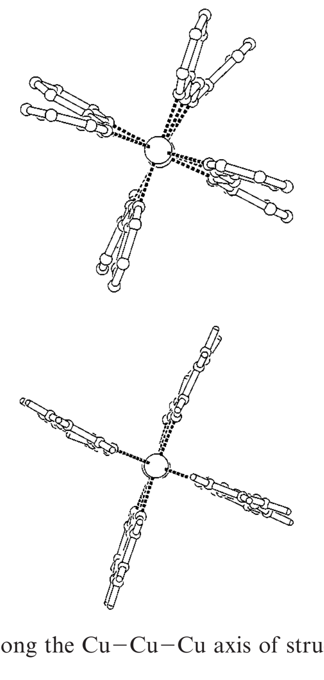

Figure 2. View along the Cu−Cu−Cu axis of structure **1**[9] and **2**

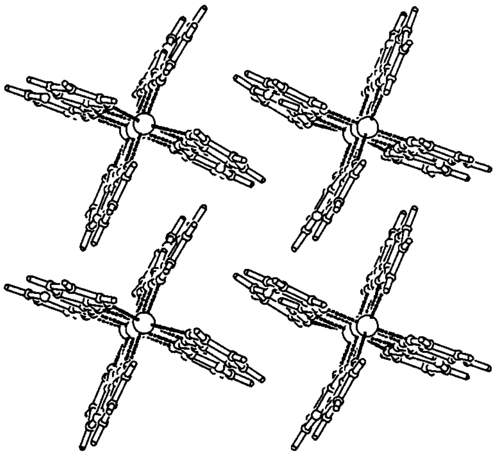

Figure 3: Packing of structure **2**, showing the stacking of the molecules. Uncoordinated triflate and water molecules are ommitted for clarity

120−160 K and is again linear at low temperatures; this behaviour is characteristic of linear trinuclear compounds

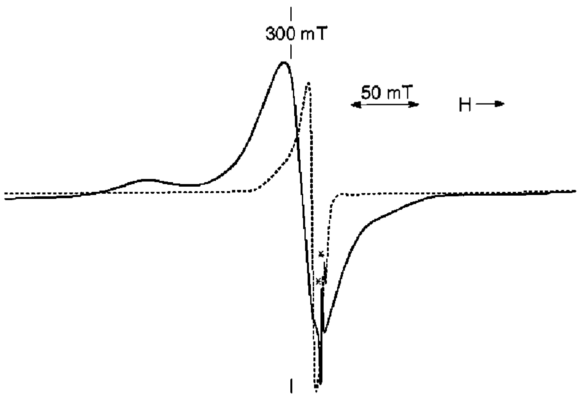

Figure 4. EPR signal of (**2**) as a powdered solid at room temperature (straight line) and at 77 K (dotted line) ("*" denotes dpph); for an explanation see text

with a strong antiferromagnetic exchange interaction between neighbouring paramagnetic metal ions.[5f,7b,19]

The effective magnetic moment μ_B per Cu at room temperature is 1.35, 1.50, 1.35 for compounds **1**, **2**, and **3**, respectively, and decreases gradually until it becomes almost constant with a value of ca. 1.05−1.10 μ_B, which is appropriate for a system with a spin = 1/2 ground state; such values have also been found for other linear Cu trinuclear compounds.[4f,5c,5f,8a,8c]

The magnetic data were fitted to the theoretical expression for the magnetic susceptibility of linear trinuclear $S = 1/2$ systems, which was based on the Hamiltonian:[5f,7b,7c,20]

$$H = -2J(\mathrm{S1{\cdot}S2} + \mathrm{S2{\cdot}S3}) - 2J'{\cdot}\mathrm{S1{\cdot}S3}$$

in which J is the interaction between adjacent nuclei (J_{12}) and J' the interaction between terminal nuclei (J_{13}). In a trinuclear linear Cu compound the magnetic interaction (J_{12}) between neighbouring copper ions is the dominant pathway of the interaction, and the interaction between the terminal copper ions (J_{13}) can be neglected (i.e. J_{13} is almost zero).[2,5f,7b,10a] Only if the linearity is far from 180°, or in triangular cases, can the value for J_{13} not be neglected.[21]

The magnetic susceptibility is then defined by Equation (1):

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

(N, g, μ_B, k, and T have their usual meanings, the exchange parameter is denoted as J. The g tensor was assumed to be equal for all individual metal ions).

A good fit has been obtained for the parameters $J = -174(1)\ \mathrm{cm^{-1}}$, $-120(1)\ \mathrm{cm^{-1}}$, and $-167(1)\ \mathrm{cm^{-1}}$, for compounds **1**, **2**, and **3**, respectively.

From these values, and also from Figure 5, it can be seen that compounds **1** and **3** have almost the same behaviour and probably also a very similar structure, which is not surprising as the methyl group will fall at the outer ends of the trinuclear structure and the Cu1−Cu2−Cu3 chromophore can remain the same. Compound **2** has a quite different ligand and, therefore, some other differences (e.g. geometry) in the structure (see Figure 2) and J value are also observed.

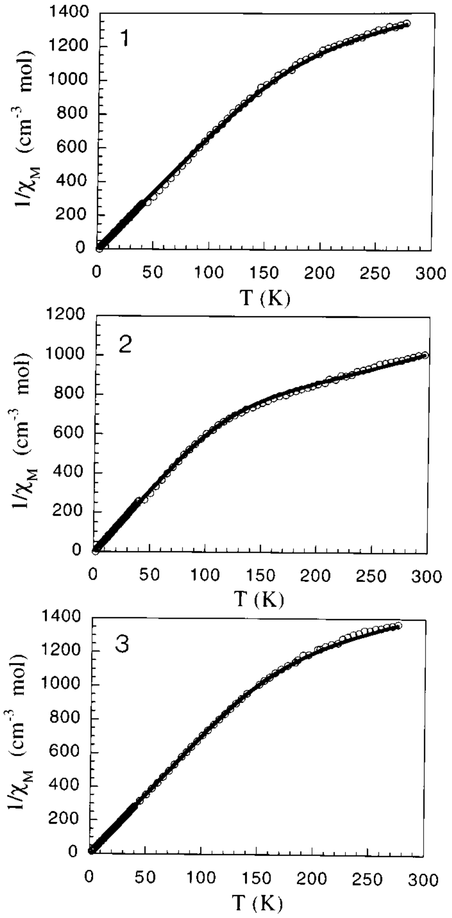

Figure 5. Inverse molar susceptibility ($1/\chi$) (O) as a function of the temperature of compounds **1**, **2**, and **3**. The full curves represent the theoretical curves (see text and Table 1)

Concluding Remarks

In Table 3, a number of the copper(II) compounds is listed with decreasing Cu−Cu distances, studied both magnetically *and* by use of X-ray crystallography. A number of relevant crystallographic and magnetic parameters are also listed. By comparing these magnetic values it can be concluded that the metal-metal distance is one of the important factors, except when the bridging unit is azido,[5d] oxamido,[17] or thiooxamido.[22] The (relatively) strong antiferromagnetism ($J = -98.7$ and $-483\ \mathrm{cm^{-1}}$) for these last two ligands has been attributed to the superexchange by the orbitals of oxygen and/or sulfur, although the Cu−Cu distances are large (about 5−5.5 Å), but it must also be noted that the Cu−Cu−Cu angle deviates markedly from linearity (154−165°)[17,22,23] in these cases. The strong antiferromagnetic coupling ($J = -212\ \mathrm{cm^{-1}}$, Cu−Cu distance 2.940 Å) in the compound [Cu$_3$(*racemo*-amat)$_2$](ClO$_4$)$_2$ (in which amat = 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-

diol) has been attributed to the same superexchange of the p orbitals of the oxygen.[5e]

Two Cu^{II} compounds have been described with a smaller Cu−Cu separation than that reported in this paper. The compounds $[Cu_3(bipyam)_4X_2]\cdot H_2O$ [in which bipyam = bis(2-pyridyl)amide and X = Cl or Br] have a Cu−Cu separation of 2.471 and 2.468 Å and a strong antiferromagnetism has been suggested of < -500 cm^{-1},[8a,8c] although their magnetism has not been reported. The only linear trinuclear compounds (of which the X-ray structure has been measured) that exist with short Cu−Cu distances between 2.466−2.348 Å involve Cu^{I}, and there are several examples.[13] Only two compounds, which are related to each other, have a ferromagnetic coupling.[5a] In order to understand more about magnetism further research will be needed on strictly linear trinuclear Cu^{II} compounds.

Experimental Section

General: C, 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 Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. − X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. − FTIR spectra were obtained on a Perkin−Elmer Paragon 1000 FTIR spectrophotometer by using KBr pellets or films between KBr disks.

FIR-FTIR spectra were obtained on a Bruker 113v infrared spectrophotometer as polyethylene mulls (600−100 cm^{-1}, mirror velocity 0.099 cm/sec, resolution 2 cm^{-1}, Mylar 3.5 Å beam splitter). Magnetic susceptibility measurements (4−300 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Synthesis of the Compounds: 2-aminopyridine, 2-amino-5-methylpyridine, and 2-aminopyrimidine were obtained from Acros Organics; Anhydrous copper(II) triflate was obtained from Strem Chemicals. The solvents were commercially available and used without further purification. Ethanol was dried with magnesium sulfate.

General Synthesis: 1.2 mmol of dry $Cu(CF_3SO_3)_2$ and 1.2 mmol of the ligand were each dissolved in ca. 10 mL of dry ethanol. The solutions were carefully heated to about 40 °C on a lamp-heating device. To each solution ca. 5 mL of triethylorthoformate was added. The copper solution was added carefully to the amino compound solution and filtered to remove any un-dissolved material. After a few days a blackish (green) crystalline material was obtained, which was filtered off and air-dried. Yields varied from 55 to 65%.

Compound **1** $\{[Cu_3(pdf)_4](CF_3SO_3)_2(EtOH)_{1.5}\}$ could also be synthesized directly from the copper(II) triflate salt and the ligand Hpdf (which is known from a synthesis reported in the literature[24]) in dry ethanol, with triethylorthoformate used to remove any water from the ethanol.

Elemental Analysis: Compound **1:** $[Cu_3(pdf)_4](CF_3SO_3)_2(EtOH)_{1.5}$, $(C_{49}H_{45}Cu_3F_6N_{16}O_{7.5}S_2)$; calcd. C 43.70, H 3.37, N 16.64, Cu 14.16; found C 43.21, H 3.19, N 16.56, Cu 13.64; Compound **2:** $[Cu_3(pmf)_4](CF_3SO_3)_2(H_2O)0.5$, $(C_{38}H_{29}Cu_3F_6N_{24}O_{6.5}S_2)$; calcd. C 35.26, H 2.26, N 25.97, Cu 14.73; found C 35.71, H 2.46, N 25.62, Cu 13.95; Compound **3:** $[Cu_3(mpdf)_4](CF_3SO_3)_2(EtOH)_1$, $(C_{56}H_{58}Cu_3F_6N_{16}O_7S_2)$; calcd. C 46.84, H 4.07, N 15.61, Cu 13.28; found: C 46.19, H 3.95, N 15.64, Cu 13.27.

X-ray Crystallographic Studies: Crystal data for $[Cu_3(pmf)_4](CF_3SO_3)_2(H_2O)_{0.5}$: $C_{38}H_{28}Cu_3F_6N_{24}O_{6.5}S_2$, M = 1293.6, triclinic, space group $P-1$ (no. 2), a = 8.529(5), b = 15.760(5), c = 19.639(5) Å, α = 101.793(5), β = 101.263(5), γ = 102.389(5)°, V = 2444(2) Å^3, Z = 2, D_c = 1.759 g cm^{-3}, T = 193(2) K, μ = 1.477 mm^{-1}, F(000) = 1300, 6141 reflections measured, 5939 independent (R_{int} = 0.0423), (range $2.53 < \theta < 24.00°$), refined data/parameters: 5939, 686; largest difference peak and hole 1.658 and −0.803 e·Å^{-3}.

A blackish (green) crystal with dimensions of 0.14 × 0.10 × 0.03 mm was selected, mounted onto the glass fibre using the oil drop method[25a] and measured with a Rigaku AFC-7S diffractometer, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), $\omega - 2\theta$ scans. Data reduction was performed using the TEXSAN[25b] package. The intensity data were corrected for Lorentz and polarization effects and for absorption and extinction. All non-H atoms were refined anisotropically. The disordered water atoms O1 and O2 with a population parameter of 0.25 were refined isotropically. The H atoms, except those of the disordered water, were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The structure was solved using direct methods SHELXS-97.[25c] The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1197P)^2 + 3.4200P]$, where $P = (F_o^2 + 2F_c^2)/3$ was adopted. The refinement method was full-matrix least-squares on F^2 using the SHELXL97[25d] package converged to $R1\ [I > 2\sigma(I)] = 0.109$, $wR2 = 0.255$ (all data), $S = 1.034$.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116049. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336−033, E-mail: deposit@ccdc.cam.ac.uk].

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