Dimetallic complexes derived from a novel dinucleating chelating symmetric triazole ligand; crystal structure, magnetic properties and ESR study of bis[μ-3,5-diacetylamino-1,2,4-triazolato-O',N^1,N^2,O'']bis[(nitrato)(aqua)copper(II)] ‡

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Reaction of 3,5-diacetylamino-1,2,4-triazole (Hdaat) with copper(II), nickel(II) and cobalt(II) salts yields dinuclear co-ordination compounds, which were spectroscopically characterized. The crystal and molecular structure of one of the compounds, bis[μ-3,5-diacetylamino-1,2,4-triazolato-O',N^1,N^2,O'']bis[(nitrato)(aqua)copper(II)] **1**, was determined by single-crystal X-ray diffraction. Complex **1** consists of dinuclear units with an inversion center at the midpoint of the Cu–Cu vector. The most remarkable feature of this structure is that the daat ligand forms a six-membered chelate ring [Cu–N3–C3–N1–C2–O1; Cua–N4–C4–N5–C5–O2], in contrast with the five-membered chelate rings always found in comparable triazole derived dimers. This structural feature is studied in the context of the geometry of the bridging system. Variable-temperature ESR spectral and magnetic susceptibility data indicate antiferromagnetic behaviour. The magnetic susceptibility data (4–290 K) are interpreted using the spin Hamiltonian $\hat{H} = -2J(\hat{S}_{Cu1}\cdot\hat{S}_{Cu2})$, and yielded $J = -36$ cm^{-1} and $g = 2.13$. The magnitude of the exchange interaction is compared with previously reported magnetostructural data for related double 1,2,4-triazole-$N1,N2$ bridged dinuclear copper(II) compounds. A correlation between the exchange parameter J and the N–Cu–N angle is described. Variable-temperature magnetic susceptibility measurements (2–300 K) for the Ni(II) and Co(II) analogous compounds confirmed the dimeric nature of these compounds and showed the presence of antiferromagnetic exchange; the corresponding J values are rationalized on the basis of the structural features of the isostructural Cu(II) compound **1**.

Introduction

The mechanism of exchange interaction in small paramagnetic compounds has been the subject of research over the past years.[1–4] Among these compounds, dinuclear copper(II) complexes are probably the best known examples. Studies with dihydroxy-bridged copper(II) dimers have already shown useful correlations between singlet–triplet splitting and structural parameters.[5] A current topic in this field is the interpretation of the magnetic exchange phenomenon in copper(II) compounds containing double diatomic bridges such as the relatively simple diazine fragment, although examples of this type of complex are still quite scarce.[6] Heterocyclic structures with this

NN group, *e.g.* triazole,[7–11] pyrazole,[6,12–18] phthalazine,[19–22] pyridazine[23,24] and thiadiazole derivatives,[25,26] as well as non-closed ring systems such as the acylamidrazones[27] have been used as bridging ligands.

Considerable progress has been made in correlating the magnetic and structural data of dinuclear copper(II) complexes with polyfunctional ligands containing the $N1,N2$ diazine moiety.[11,18] In this class of compounds the approximately planar Cu–(N–N)$_2$–Cu framework is always present. Magnetic exchange occurs *via* the $d_{x^2-y^2}$ orbitals on the Cu(II) ions which overlap with the σ orbitals of the nitrogen atoms of the bridge. Consequently, for an effective propagation of the superexchange, the magnetic orbitals on the copper(II) ions must be directed towards the bridging nitrogen atoms in such a way that an effective electron delocalization can occur *via* these nitrogen atoms. The bridging geometry of the ligand, therefore, influences the efficiency of the exchange pathway.

Slangen *et al.* have investigated a series of copper(II) compounds of polyfunctional 1,2,4-triazole derivatives containing N-donating substituents which form five-membered chelate rings.[10,11] These authors concluded that the isotropic magnetic exchange constant reaches a maximum value when the ligand binds the metal ions in the equatorial plane in the most

symmetric way.[11] Symmetrically substituted triazole ligands such as 3,5-bis(pyridin-2-yl)-1,2,4-triazolato[7,28] (bpt) or 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole[8,9] (aamt) produce compounds with a regular bridging geometry, whereas monosubstituted derivatives such as 3-pyridin-2-yl-1,2,4-triazolato[10,11] (pt) lead to asymmetric 1,2,4-triazole bridges. So, for the bpt and aamt series of compounds, the four Cu–N–N angles are almost identical (from 132.9(8)° to 135.2(2)°). This symmetric bridging allows an optimum overlap of the Cu(II) magnetic orbitals, which is reflected in the corresponding singlet–triplet splittings, with values of $-2J = 194$–236 cm^{-1}. In the case of the pt dimers, the bridging system is asymmetric, the Cu–N2–N1 angles ranging from 123.9(3)° to 126.0(2)° and the Cu2–N1–N2 angles from 138.7(2)° to 140.0(2)°. These differences in geometry result in a less efficient interaction of the magnetic orbitals; therefore, in the pt compounds a decrease in the magnitude of the isotropic exchange constant is observed with $-2J = 96$–102 cm^{-1}.

It has been mentioned that up to now only substituted triazole ligands forming five-membered chelate rings have been used with copper(II). It may be expected that the use of ligands capable of forming six-membered chelate rings may also yield dinuclear copper(II) compounds of this type, although with differences in their structural parameters. We have selected the symmetrically disubstituted 3,5-diacetylamino-1,2,4-triazole (Hdaat) in the belief that the acetylamino group should force the ligand to coordinate to the two metal ions with the formation of a six-membered chelating ring. This paper deals with the first results obtained with this ligand. The preparation of [M(daat)(NO$_3$)(H$_2$O)]$_2$ [M = Cu, Ni and Co] is described. The crystal structure determination of the copper(II) compound has been undertaken to prove the dinucleating properties of the ligand as well as to study the structural relationship between the size of the chelate ring and the geometry of the bridging system and thus with the magnetic behaviour. ESR spectra will be analyzed in relation to the former properties. The spectroscopic and magnetic properties of the Ni(II) and Co(II) analogous compounds are also reported and discussed on the basis of the structural features.

Experimental

Materials

The metal salts were reagent grade and used without further purification. The ligand Hdaat was prepared as indicated by van den Bos[29] and recrystallized from boiling water (Found for Hdaat: C, 38.2; H, 4.9; N, 38.2. Calc. for C$_6$H$_9$N$_5$O$_2$: C, 39.3; H, 4.9; N, 38.2%); $\tilde{\nu}_{max}$/cm^{-1} for Hdaat: [ν(C=O)] 1701, 1681s (sp); [ν(C=N) + δ(N–H)] 1638vw (sh), 1605m, 1568s, 1522vw (sh).

Synthesis

[Cu(daat)(NO$_3$)(H$_2$O)]$_2$ 1. Copper(II) nitrate (1.5 mmol) and Hdaat (1.5 mmol) were mixed in a water–methanol (50:50, v/v) solution (40 cm^3). Sea green single crystals (70%) appeared within *ca.* 24 h (Found for **1**: C, 21.4; H, 2.9; Cu, 19.5; N, 25.2. C$_{12}$H$_{20}$Cu$_2$N$_{12}$O$_{12}$ requires C, 22.1; H, 3.1; Cu, 19.5; N, 25.8%); λ_{max}/nm (solid sample) for **1**: 920 (sh) and 695; $\tilde{\nu}_{max}$/cm^{-1} for **1**: [ν(O–H)$_{H_2O}$] 3438ms; [ν(C=O)] 1641s; [ν(C=N) + δ(N–H)] 1603s, 1571s (br); [ν_{asym}(NO$_3$)] 1384s; [ν_{sym}(NO$_3$)] 1034m; [ν(M–O)] 510w.

[Ni(daat)(NO$_3$)(H$_2$O)]$_2$ 2 and [Co(daat)(NO$_3$)(H$_2$O)]$_2$ 3. Nickel(II) or cobalt(II) nitrate (2 mmol) and Hdaat (4.5 mmol) were mixed in hot methanol (70 cm^3). The purple Ni(II) compound (30%) or the pink Co(II) compound (47%) crystallized upon slow evaporation of the solvent at room temperature within a few days (Found for **2**: C, 22.9; H, 3.6; N, 25.1. C$_{12}$H$_{20}$Ni$_2$N$_{12}$O$_{12}$ requires C, 22.5; H, 3.1; N, 26.2%. Found for **3**: C, 22.4; H, 3.9; N, 25.4%. C$_{12}$H$_{20}$Co$_2$N$_{12}$O$_{12}$ requires C,

22.4; H, 3.1; N, 26.2%); λ_{max}/nm (solid sample) for **2**: [$^3A_{2g} \rightarrow {}^3T_{1g}$(F)] 615 and [$^3A_{2g} \rightarrow {}^3T_{1g}$(P)] 360; λ_{max}/nm (solid sample) for **3**: [$^4T_{1g} \rightarrow {}^4T_{1g}$(P)] 535, 515 (multiple structured band); $\tilde{\nu}_{max}$/cm^{-1} for **2**: [ν(O–H)$_{H_2O}$] *ca.* 3400vw; [ν(C=O)] 1658s; [ν(C=N) + δ(N–H)] 1600w (sh), 1565s (br); [ν_{asym}(NO$_3$)] 1385s; [ν_{sym}(NO$_3$)] 1028m; [ν(M–O)] 501mw; $\tilde{\nu}_{max}$/cm^{-1} for **3**: [ν(O–H)$_{H_2O}$] 3419vw; [ν(C=O)] 1658s; [ν(C=N) + δ(N–H)] *ca.* 1600w (sh), 1562s; [ν_{asym}(NO$_3$)] 1384s; [ν_{sym}(NO$_3$)] 1025m; [ν(M–O)] 489mw.

Physical measurements

Electronic spectra using solid samples were registered in the region 800–200 nm on a Shimadzu UV 2101PC spectrophotometer (for **2**,**3**) or in the region 2000–300 nm on a Perkin-Elmer 330 UV-VIS spectrophotometer (for **1**). IR spectra were recorded on a Perkin-Elmer 843 instrument. X-Ray powder diffraction patterns were obtained through a Siemens D500 diffractometer, with a Ni filter, using Cu-Kα radiation.

Magnetic susceptibilities for **1** were measured in the temperature range 4–290 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. Magnetic susceptibility measurements for **2** and **3** (2–300 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants. Magnetic data were fitted to theoretical expressions by means of a Simplex routine,[30] using a computer program written by R. Prins, Leiden University. All parameters (J, g and p) were varied independently during the fitting procedure. This routine minimizes the function $R = |\Sigma|\chi_{obs} - \chi_{calc}|^2/|\Sigma|\chi_{obs}|^2|^{1/2}$.

A Bruker ESP300 spectrometer operating at X- and Q-bands and equipped with standard Oxford low temperature devices was used to record the ESR spectra of compound **1** from 4.2 K to room temperature. The magnetic field was calibrated by a NMR probe and the frequency inside the cavities was determined with a Hewlett-Packard 5352B microwave frequency counter. Single crystals of **1** were glued to a cleaved KCl cubic holder by the 001 face ($c\|X$) with its larger edge parallel to the Z axis of the KCl crystal. The sample holder was glued to an L-shaped plexiglass rod, and rotated with respect to the applied magnetic field using standard Bruker accessories. ESR spectra were recorded rotating the crystal around the X, Y and Z axes, with 5° intervals along 180° in each plane, at room temperature.

Crystal structure determination and refinement of 1

A sea green, block-shaped crystal ($0.12 \times 0.12 \times 0.24$ mm) showed broad, highly-structured reflection profiles of varying width, indicative of several slightly misaligned individuals. The A-vector method[31] was used to measure each reflection at the ψ angle with minimum anisotropic split. Crystal data and details on data collection and refinement are presented in Table 1. No absorption correction was applied. The structure was solved by automated Patterson methods (DIRDIF-92)[32] and refined on F using full-matrix least-squares techniques (SHELX76).[33] Hydrogen atoms were included in the refinement at calculated positions (N,C–H = 1.08 Å) riding on their carrier atoms. The water hydrogen atoms could not be located. The water molecule is involved in a hydrogen bond with N(2) (d[O$\cdots$N] = 2.91 Å). The hydrogen atom incorporated in this bond is probably disordered over two positions: either bonded to N(2) or O(6). For refinement purposes this hydrogen atom is arbitrarily attached to N(2); the other water hydrogen atom is not included in the refinement.

CCDC reference number 186/1685.

See http://www.rsc.org/suppdata/dt/1999/4269/ for crystallographic files in .cif format.

Results and discussion

X-Ray powder diffraction patterns were recorded for compounds **1**, **2**, and **3**; the three compounds exhibit a similar pattern and so they can be considered isostructural.

Description of the structure of 1

A PLUTON[34] projection of [Cu(daat)(NO₃)(H₂O)]₂ **1** is given in Fig. 1. Selected bond distances and angles involving the copper(II) ions are listed in Table 2. The compound crystallizes in space group $P\bar{1}$, with one dinuclear unit in the unit cell. An inversion centre lies at the midpoint of the Cu–Cu vector. The copper(II) ions are separated by 3.854(6) Å.

The [Cu₂(daat)₂]²⁺ cation is nearly planar. The distance of the copper atoms to the least-squares plane through the ligand is 0.194(2) Å. The metal ions are linked in the equatorial coordination plane by two *N*1,*N*2 bridging 1,2,4-triazolato ligands. The third and fourth basal positions are occupied by two O(acetylamino) atoms from two daat ligands. A nitrate and a water molecule complete the distorted octahedral environ-

ment of Cu(II) in the axial positions. The copper atom is displaced from its equatorial plane [defined by the atoms O2, N4, O1a and N3a] toward the coordinated water molecule by 0.084(2) Å.§

An overview of the structural parameters for dinuclear doubly *N*1,*N*2 1,2,4-triazole bridged copper(II) compounds is given in Tables 3 and 4.¶ In **1**, the Cu–N(triazolato) distances, 1.96(1) and 1.93(1) Å, are in the expected range; the Cu–O(acetylamino) distances, 1.97(1) Å, are shorter than the equivalent Cu–N(triazole substituent) distances reported for related compounds; this reduction in the bond length could be connected with the shorter radii of the donor atom and with the size of the chelating ring (see below). Note that all the other dimers included in Tables 3 and 4 were obtained with nitrogen-substituted 1,2,4-triazole ligands. The study of the coordination chemistry of the 1,2,4-triazole derivatives with chelating oxygen-donor substituents towards Cu(II) has just begun and very few examples can be found in the literature.[35–38] In **1**, the coordination of the oxygen and the nitrogen of daat results in a very favourable six-membered chelate ring [Cu–N3–C3–N1–C2–O1]. This is the most remarkable feature of this structure.

To our knowledge, this is the first dimer reported in which a substituted-triazole ligand chelates copper(II) with the formation of two non-five-membered rings. In order to relate the differently sized chelate ring with the geometry of the bridging system, several parameters corresponding to the doubly *N*1,*N*2 triazole bridged dimers described in the literature have been

Table 1 Crystallographic data for **1**

Formula	C₁₂H₂₀Cu₂N₁₂O₁₂
Molecular weight	651.46
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a, b, c/Å	7.221(8), 8.463(13), 10.585(12)
a, β, γ/°	103.69(11), 98.36(9), 110.57(11)
V/Å³	569.5(1.4)
μ/cm⁻¹	20.33
T/K	298
Total data	3927
Total unique data	2610 (R_{int} = 0.074)
Observed data	1439 [$I > 2.5 \sigma(I)$]
Final R, R_w, S	0.090, 0.119, 2.1

Table 2 Selected bond distances (Å) and angles (°) for [Cu(daat)-(NO₃)(H₂O)]₂[a]

Cu···Cua	3.854(6)	Cu–O2a	1.97(1)
Cu–N4a	1.93(1)	Cu–O6	2.24(2)
Cu–N3	1.96(1)	Cu–O3	2.55(1)
Cu–O1	1.97(1)		
N4a–Cu–N3	102.8(5)	N3–Cu–O3	86.9(5)
N4a–Cu–O1	168.6(4)	O1–Cu–O2a	82.5(4
N4a–Cu–O2a	87.3(4)	O1–Cu–O6	89.9(4)
N4a–Cu–O6	95.7(5)	O1–Cu–O3	85.6(4)
N4a–Cu–O3	89.0(5)	O2a–Cu–O6	92.7(5)
N3–Cu–O1	87.0(4)	O2a–Cu–O3	88.5(4)
N3–Cu–O2a	168.9(4)	O6–Cu–O3	175.2(5)
N3–Cu–O6	91.1(5)		
Cu–N3–N4	128.0(8)	Cua–N4–N3	129.2(8)

[a] Atoms with suffix a are generated by symmetry operation $-x$, $-y$, $2-z$.
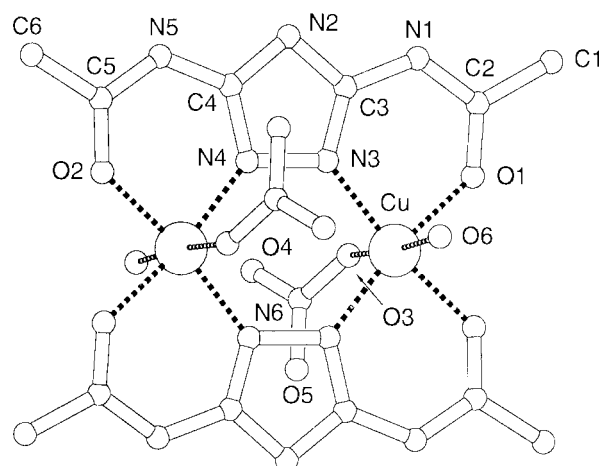

Fig. 1 A PLUTON[34] plot of **1** showing the atom labelling scheme. Additional atoms are generated by the symmetry operation $2-x$, $2-y$, $-z$.

§ The mean planes of the N₂O₂ and Cu₂N₄ systems are not rigorously co-planar, the angles between them being 5.3(4)°.

¶ A dinuclear doubly *N*1, *N*2 *pyrazolato* bridged copper(II) compound has also been included for reasons that will be explained later.

Table 3 Selected bond distances (Å) for dinuclear doubly μ-diazine bridged copper(I) compounds[a]

Compound	Cu–N3 [Cua–N3a]	Cu–N4a [Cua–N4]	Cu–O1/N [Cu–O2a/N]	Ref.
[Cu(bpt)(CF₃SO₃)(H₂O)]₂	1.942(3) [1.932(3)]	1.936(3) [1.950(3)]	2.082(3) [2.087(3)]	7
[Cu(aamt)Br(H₂O)]₂Br₂·2H₂O·CH₃OH	1.937(3)	1.950(3)	2.043(2) [2.032(3)]	8
[Cu(aamt)(H₂O)₂]₂[SO₄]₂·4H₂O	1.954(9)	1.96(1)	2.04(1) [2.052(9)]	9
[Cu₂(pt)₂(SO₄)(H₂O)₃]·3H₂O	2.006(4) [1.984(4)]	1.962(4) [1.961(4)]	2.054(4) [2.000(3)][b]	11
[Cu₂(pt)₂(Meim)₂(NO₃)₂(H₂O)₂]·4H₂O	1.981(3)	1.983(3)	2.061(3) [1.981(3)]	10
[Cu₂(pt)₂(4,4′-bpy)(NO₃)₂(H₂O)₂]·4H₂O	1.970(3) [1.978(3)]	1.983(3) [1.988(3)]	2.031(3) [2.066(3)]	10
[Cu₂(pt)₂(Hpz)₂(NO₃)₂(H₂O)₂]	1.980(5)	1.976(4)	2.054(5) [1.983(5)]	10
[Cu(H₂L)Cl]₂·2H₂O[c]	1.967(2)	1.929(2)	2.018(3) [1.917(2)]	6
[Cu(daat)(NO₃)(H₂O)]₂	1.96(1)	1.93(1)	1.97(1) [1.97(1)]	this work

Meim = *N*-methylimidazole; 4,4′-bpy = 4,4′-bipyridine; Hpz = pyrazole; H₃L = 1,1′-(4-methylpyrazole-3,5-diyl)diacetaldehyde dioxime. [a] Values are given in parentheses when they are not crystallographically equivalent to those first cited. [b] Cu–O(sulfate) distance. [c] Data for isomer 1.

Table 4 Magnetic and structural parameters for dinuclear doubly μ-diazine bridged copper(II) compounds (adapted from ref. 11)[a]

Compound	Chelate ring size	Angle/° N3–Cu–O1/N [N4a–Cu–O2a/N]	N3–Cu–N4a [N4–Cua–N3a]	J/cm^{-1}	Angle/° Cu–N3–N4 [Cua–N3a–N4a]	Cua–N4–N3 [Cu–N4a–N3a]	Cu–Cua(Å)	Ref.
[Cu(bpt)(CF₃SO₃)(H₂O)]₂	5	79.1(1) [79.3(1)]	90.2(1) [90.1(1)]	−118	134.9(2) [134.5(2)]	135.2(2) [134.8(2)]	4.085(1)	7
[Cu(aamt)Br(H₂O)]₂Br₂·2H₂O·CH₃OH	5	81.0(1) [80.8(1)]	92.1(1)	−110	134.2(2)	133.7(2)	4.0694(7)	8
[Cu(aamt)(H₂O)₂]₂[SO₄]₂·4H₂O	5	81.5(4) [82.3(4)]	91.9(4)	−97	135.1(8)	132.9(8)	4.088(3)	9
[Cu₂(pt)₂(SO₄)(H₂O)₃]·3H₂O	5	80.1(1) [91.2(1)]^b	94.3(2) [95.0(1)]	−49	139.8(3) [139.8(3)]	124.4(3) [125.3(3)]	4.0265(8)	11
[Cu₂(pt)₂(Meim)₂(NO₃)₂(H₂O)₂]·4H₂O	5	80.4(1) [90.7(1)]^b	95.4(1)	−48	138.7(2)	125.8(2)	4.022(1)	10
[Cu₂(pt)₂(4,4′-bpy)(NO₃)₂(H₂O)₂]·4H₂O	5	80.6(1) [90.7(1)]^b	95.9(1) [95.1(1)]	−51	140.0(2) [138.7(2)]	124.3(2) [126.0(2)]	4.0198(7)	10
[Cu₂(pt)₂(Hpz)₂(NO₃)₂(H₂O)₂]	5	80.5(2) [90.1(2)]^b	96.5(2)	−49	139.6(3)	123.9(3)	3.974(1)	10
[Cu(H₂L)Cl]₂·2H₂O^c	5	78.6(2)	99.8(2)	−159	135.4(4)	124.2(6)	3.832(1)	6
	6	90.9(2)						
[Cu(daat)(NO₃)(H₂O)]₂	6	87.0(4) [87.3(4)]	102.8(5)	−36	128.0(8)	129.2(8)	3.8546(6)	This work

^{a} Values are given in parentheses when they are not crystallographically equivalent to those first cited. ^{b} These angles do not belong to a chelate ring. ^{c} Data for isomer 1.
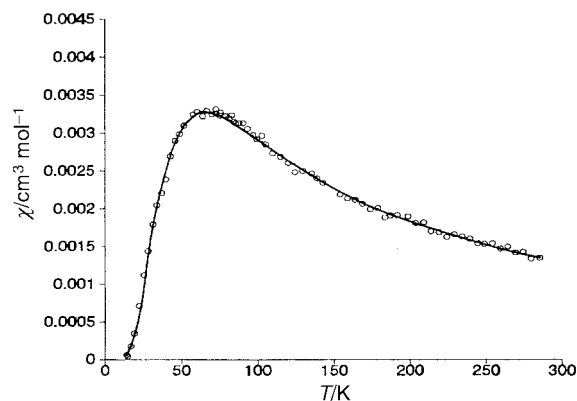
Fig. 2 Plot of magnetic susceptibility *versus* temperature for **1**. The solid line represents the calculated curve ($J = -36$ cm^{-1}, $g = 2.13$ and $p = 0.05\%$).

compiled (see Table 4). These data show that, as expected, six-membered chelate rings have larger bite angles than five-membered ones; so, in the daat compound, the bite angles N3–Cu–O1 of 87.0(4) Å and N4a–Cu–O2a of 87.3(4) Å are about 6–8° larger than those observed in the five-membered chelate rings of bpt,[7] aamt[8,9] or pt,[11,10] the triazole derivatives used up to now. This structural correlation can be illustrated by comparison with the data, also included in Table 4, of the doubly pyrazolato bridged compound [Cu₂(H₂L)₂Cl₂]·2H₂O.[6] The ligand is symmetrically substituted but one oxime moiety coordinates *via* the nitrogen atom, resulting in a five-membered chelate ring, whereas the other oxime group coordinates *via* the oxygen atom, resulting in a six-membered chelate ring. The bite angle in the former case is 78.6(2)° and in the latter is 90.9(2)°; these values lie in the range of those observed for the five-membered triazole systems and for the six-membered daat compound, respectively (Table 4).

The six-membered chelate forming coordination mode of **1** is connected with significant changes in the geometry of the approximately planar Cu–(N–N)₂–Cu framework:‖ the N3–Cu–N4a angle of 102.8(5)° is almost 13° larger than for the bpt compound.[7] This trend is also observed in the case of the pyrazole dimer, with an intermediate value for this angle, as expected for having simultaneously one five- and one six-membered ring. Table 4 suggests that an increase in the N3–Cu–O1 bite angle is accompanied by an increase in the N3–Cu–N4a bridging angle. This possible correlation should be logically restricted to substituted ligands in which the rigidity of the chelate ring is not decisive.

On the other hand, in **1**, the *N*1,*N*2 1,2,4-triazole bridging mode is symmetrical with Cu–N3–N4 and Cua–N4–N3 angles of 128.0(8)° and 129.2(8)°, respectively. These values are about 6° smaller than those observed for the bpt compound.[7]

Magnetic properties

Variable-temperature magnetic susceptibility measurements for [Cu(daat)(NO₃)(H₂O)]₂ **1** have been performed on a powdered sample in the temperature range 4–290 K. The results are displayed in Fig. 2. The shape of the susceptibility plot is typical of an antiferromagnetic coupled dinuclear species with the maximum susceptibility occurring between 65 and 70 K. A least-squares fit on the modified Bleaney–Bowers eqn. [(1)]

$$\chi_m = (1 - p)(2N\beta^2 g^2/kT)[3 + \exp(-2J/kT)]^{-1} + \chi_p p \quad (1)$$

for $S = 1/2$ dimers[39] yielded $J = -36$ cm^{-1}, $g = 2.13$ and $p =$

‖ The maximum deviation from the plane defined by Cu, Cua, N3, N4, N3a, N4a is 0.02(2) Å, and it corresponds to the N3a atom. The Cu–(N–N)₂–Cu plane and the triazolato ring planes form a dihedral angle of 3.2°.

0.05%, where $2J$ is the singlet–triplet energy gap related to the intradimer interaction defined by the spin Hamiltonian eqn. (2), p denotes the fraction of paramagnetic impurity present in the sample and N, g, β, k and T have their usual meanings.

$$\hat{H} = -2J(\hat{S}_{Cu1} \cdot \hat{S}_{Cu2}) \qquad (2)$$

Table 4 lists J values and structural parameters (N–Cu–N/Cu–N–N angles and Cu–Cua distances) for the dinuclear compounds referred to in the previous part of this article. As indicated in the Introduction, attempts at correlating the magnetic and structural properties of copper(II) dimeric compounds containing double NN diatomic bridges have begun. Slangen *et al.* provided the first conclusions from a set of doubly bridged copper(II) $N1,N2$ triazole compounds.[10,11] These authors reported the J value and the structural parameters of the bridge for different pt compounds, where pt is an asymmetric substituted triazole ligand, and compared these values with those previously published for bpt and aamt, two symmetrically substituted triazole derivatives (as mentioned earlier). The parameters considered were the angles of the Cu–(N–N)$_2$–Cu framework. Slangen *et al.*[10,11] observed that the more symmetric was the bridge, which means more similarity among the four Cu–N–N angles, the larger was the singlet–triplet splitting. This fact led them to establish that there is a relation between the Cu–N–N angles and the magnitude of the isotropic exchange constant. In Table 4 we have added to the data studied by Slangen *et al.*[11] those corresponding to the daat dimer. Table 4 shows that compound **1**, in spite of its symmetrical bridging system, presents the lowest $-J$ value and that the N–Cu–N angle is the parameter which seems to be directly related with the J value: a decrease in the isotropic exchange constant occurs when the N–Cu–N angle increases towards values far from the ideal 90°. Table 4 also indicates that data on previously reported compounds have already demonstrated this tendency but, at that stage (with only those data), it was difficult to establish whether *the degree of symmetry* in the bridge (Cu–N–N/Cu–N′–N′ angles) or the *N–Cu–N angle* was the structural feature which could be correlated with J. As there is an obvious connection between all the parameters of the bridging system, imposed by the geometry of the planar or nearly planar Cu–(N–N)$_2$–Cu framework, more compounds are required to confirm this correlation. On the other hand, with the data available, it cannot be stated yet if the former relationship is linear in the N–Cu–N angle, such as observed for planar bis(hydroxo)-bridged copper(II) compounds:[5,13] the straight line fit ($-J$ *vs.* θ) for the 8 data of Table 4 {excluding [Cu(H$_2$L)Cl$_2$]·2H$_2$O} gives a low correlation coefficient of 0.833; if data of compound **1** are not included, the correlation coefficient improves: 0.956. A possible explanation might be that also the type of substituent on the triazole ring could influence the magnetic exchange.[18]

The data corresponding to [Cu(H$_2$L)Cl$_2$]·2H$_2$O have been included in Table 4 to complete the comparison. Its J value does not fit with the ratio, as expected, because the N–N pyrazole bridges propagate the exchange more efficiently than the triazole ones.[6,18,21] So, the above correlation only applies for the $N1,N2$-triazole systems, although similar relations between structural parameters and magnetic data should be expected for copper(II) compounds containing other diatomic ligand bridges.[13] In this sense, we consider of interest a recent study by Hanot *et al.* on a series of doubly pyrazolate-bridged compounds.[18] They observed that, in the pyrazolato-bridged systems, the absolute J value decreases with the asymmetry of the Cu–(N–N)$_2$–Cu framework, and that $|J|$ decreases as the Cu–N–N angle increases in the symmetric case. The trend exhibited by the triazole-bridged systems is different (Table 4). Besides, in the pyrazolate group, the relation between the N–Cu–N angle and J is not clear.

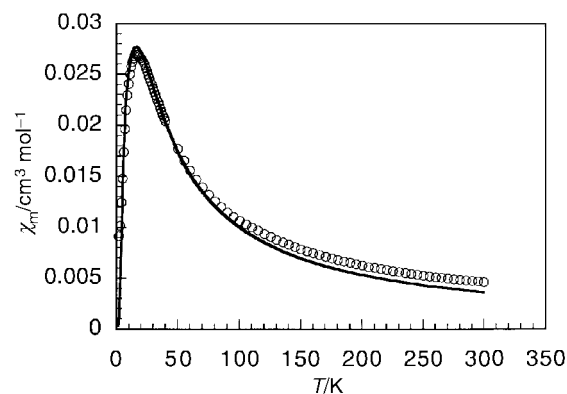The magnetic behaviour of [Ni(daat)(H$_2$O)(NO$_3$)]$_2$ **2** is

Fig. 3 Plot of magnetic susceptibility *versus* temperature for **2**. The solid line represents the calculated curve ($J = -5.51$ cm^{-1}, $g = 2.12$).
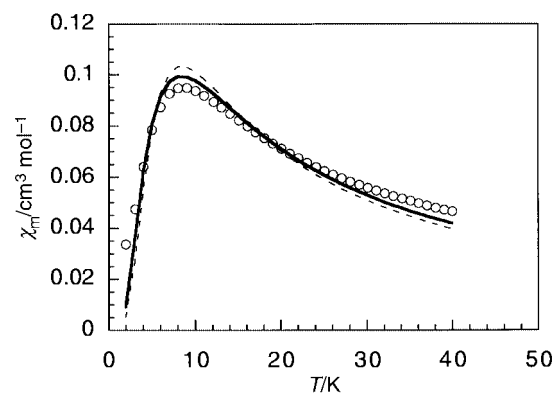

Fig. 4 Plot of magnetic susceptibility *versus* temperature for **3**. The solid line represents the curve calculated using the Ising model ($J = -7.5$ cm^{-1}, $g = 7.84$); the dashed line represents the curve calculated using the Heisenberg model ($J = -4.7$ cm^{-1}, $g = 3.1$).

shown in Fig. 3 in the form of a χ *versus* T plot, χ being the magnetic susceptibility per dinuclear nickel(II) compound and T the temperature. The behaviour of a dinuclear nickel(II) compound is found with a maximum in the χ *versus* T curve at about 17 K. The magnetic data have been interpreted using expression (3) for the molar magnetic susceptibility for $S = 1$

$$\chi = (2Ng^2\beta^2/kT) ((5 + e^{4x})/(5 + 3e^{4x} + e^{6x})) \qquad (3)$$

dimers[40] in which $x = -J/kT$ and $2J$ is the energy gap defined by the phenomenological spin Hamiltonian with quantum spin operators $\hat{S}_{Ni1}$ and $\hat{S}_{Ni2}$ (eqn. (4)):

$$\hat{H} = -2J(\hat{S}_{Ni1} \cdot \hat{S}_{Ni2}) \qquad (4)$$

In eqn. (3), N, g, β, k and T have their usual meanings. A good fit for the χ *versus* T data has been obtained for the parameters $g = 2.12(2)$ and $J = -5.51(5)$ cm^{-1}. Inclusion of additional parameters such as zero-field splitting (d) for Ni(II) and/or intercluster exchange (zJ') did not improve the fit to the experimental data.

Fig. 4 displays the magnetic behaviour of [Co(daat)(H$_2$O)(NO$_3$)]$_2$ **3** in the form of a χ *versus* T plot. The behaviour of a dinuclear cobalt(II) compound is found with a maximum in the χ *versus* T curve at about 9 K. The interpretation of the data for the Co(II) complex is more complicated since the orbital moment is only partly quenched.[41,42] The combined action of the spin–orbit coupling and the low-symmetry ligand field results in a splitting of the $^4T_{1g}$ level into six Kramer doublets. The magnetic properties at low temperatures will be determined by the ground state doublet, since at temperatures lower than about 40 K this doublet will be the only populated level in the single-ion approximation. Therefore, for Co(II) compounds the magnetic properties can be described in terms of an effect-

ive spin $S' = 1/2$, with anisotropic g values. Since we have no information on the anisotropy of the g tensor, the magnetic data have been fitted to the predictions of Heisenberg (taking into account an isotropic g tensor; expression (5))[43] and Ising

$$\chi = (Ng^2\beta^2/kT)\,(1/(3 + e^{-2x})) \qquad (5)$$

(taking into account a strong uniaxial anisotropy of the g tensor, which is characterized by $g_\parallel \gg g_\perp$; expression (6))[44] for dimers with $S = 1/2$.

$$\chi = (Ng^2\beta^2/kT)\,(1/(6 + 6e^{-x})) \qquad (6)$$

Here $x = -J/kT$ and $2J$ is the energy gap defined by the phenomenological spin Hamiltonian mentioned above (eqn. (4)) with quantum spin operators $\hat{S}_{Co1}$ and $\hat{S}_{Co2}$. Fitting to the temperature range 2–40 K yielded $g = 3.1(1)$ and $J = -4.7(2)$ cm^{-1} for the Heisenberg model, whereas the Ising model yielded a better agreement with $g = 7.84(5)$ and $J = -7.5(1)$ cm^{-1}.

When the superexchange interactions are propagated through ligands which coordinate in the equatorial coordination sphere, it would not be unexpected to find similarity in the magneto-structural correlations for Cu(II) and Ni(II) related systems. This has already been reported by Nanda *et al.* for phenoxy-bridged dinuclear nickel(II) compounds.[3a] These authors explain that even though the magnetic orbitals for the nickel(II) are $d_{x^2-y^2}$ and d_{z^2}, the involvement of the symmetric d_{z^2} orbitals in exchange coupling will be minimal in centrosymmetric complexes. More recently, van Koningsbruggen *et al.* have analyzed the magnetic and structural data for two doubly $N1,N2$ 1,2,4-triazole bridged dinuclear nickel(II) compounds, one of them with symmetrical bridging and the other one with asymmetrical bridging systems;[45] they encountered a bridge-angle dependence of J for these two Ni(II) compounds identical to that previously described for the analogous copper(II) compounds. Although structural data for the [Ni(daat)-(H$_2$O)(NO$_3$)]$_2$ **2** compound are not available, we may assume that the corresponding bridging parameters, at least as far as angles in the equatorial Ni(II) coordination environment are concerned, should not differ much from those of the iso-structural Cu(II) compound (this has already been observed in other Ni(II)–Cu(II) dimeric couples).[10,11,45] Taking into account these limitations, we have tried to rationalize the magnetic behaviour of **2** by comparison with the compounds of ref. 45 and 46. The Ni(II) daat compound doesn't show satisfactorily the same trend observed for the Cu(II) compounds, *i.e.* decreasing isotropic exchange constants upon increasing N–Ni–N angles. Therefore more information is needed before proper conclusions can be reached.

With regard to the Co(II) compound **3**, and assuming a $S' = 1/2$ formalism, a situation comparable to that of the Ni(II) and Cu(II) systems should be found; however, the literature data available on this type of doubly $N1,N2$ 1,2,4-triazole bridged dinuclear cobalt(II) compound are even more scarce than for the Ni(II) case, in part due to the lack of crystal structures,[46,47] and also do not allow further conclusions.

Spectroscopic characterization

ESR spectroscopy of 1. The X-band ESR powder spectrum of **1** recorded at room temperature displays a signal with an unusual resolution. Two features are remarkable in the $\Delta m_s = 1$ region: (i) a strong bump centred at about 2913 G, and (ii) a derivative crossing the baseline suggesting an axial g tensor with $g_\parallel = 2.31$ and $g_\perp = 2.11$ as principal values. The $g_\perp$ value, however, is higher than the value expected for an elongated Cu(II) octahedron and therefore this tentative assignment may be considered doubtful. A weak signal can also be observed as a shoulder on the high field side of the spectrum (around
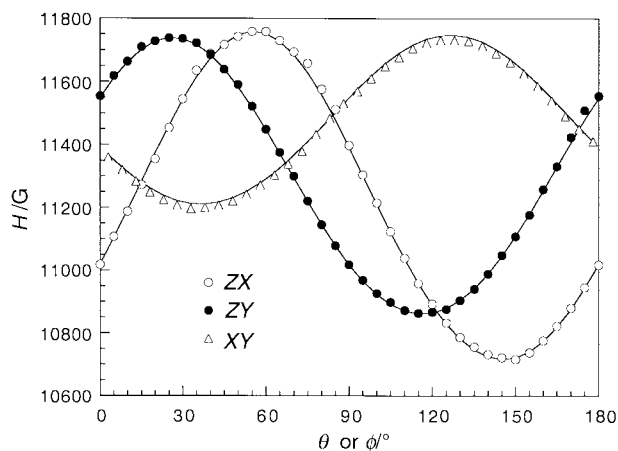
Fig. 5 Angular variation of the resonance field measured at room temperature and 34.1 GHz in three orthogonal planes of a single crystal of **1**. The solid lines are obtained with a least-squares fit of the data to a g^2 tensor.

3650 G). This signal is split into two components at $g = 1.87$ and $g = 1.81$ below 50 K. The $g < 2$ values suggest the existence of zero-field splitting effects in the triplet state. Finally, a $\Delta m_s = 2$ transition is observed at lower fields (1580 G), in good agreement with the dimeric nature of the complex. The intensity of this band is *ca.* 0.005 times lower than that of the $\Delta m_s = 1$ transition. As expected, the spectrum vanishes below 20 K due to the antiferromagnetic interaction in the dimer which leads to a diamagnetic $S = 0$ ground state.

The Q-band powder spectra are also unusual. The only change observed when cooling the sample from 300 to 100 K is a slight narrowing of the absorption lines. The complexity of the spectra could be apparently attributed to the sum of both axial and rhombic signals. This fact led us to consider the possible existence of impurities in the samples; the hypothesis was, however, disregarded after performing different measurements with samples obtained by powdering single crystals from several preparations. Attempts to fit the spectra taking into account a triplet state with zero-field splitting (D and E) contributions were undertaken (the compound is a dimer and the half-field signal is observed at room temperature), but they were unsuccessful. On the other hand, it is well known that complicated ESR spectra may arise for a two-metal system when the g tensor is misaligned with respect to the zero-field splitting D tensor (in other words, when the coordinates systems in which the g and D tensors are diagonalized do not coincide). In these cases, the extrema of the derivative ESR spectrum may appear along directions which do not correspond to axes of either system.[48] From this point of view, the bump centred at about 10620 G ($g = 2.30$) and the derivative signal at 11715 G ($g = 2.08$) could be considered as the parallel and perpendicular components of an axial g tensor, respectively; these $g_\parallel$ and $g_\perp$ values would be reasonable for such a Cu(II) system. The additional signals at 11350 and 12150 G could be attributed to extreme values of the D tensor, probably strongly misaligned with respect to the g tensor, since the off-axis extreme effects increase in intensity with the size of the D tensor components and the g–D misalignment.

Preliminary single crystal measurements carried out at room temperature (Fig. 5) have allowed us to determine the principal values of the g tensor, being $g_1 = 2.305$, $g_2 = 2.075$, and $g_3 = 2.071$. These values, within experimental deviations, are in good agreement with the assumption of an axial g tensor, as derived from the powder spectra. The g values are also in accordance with a $d_{x^2-y^2}$ ground state for a copper(II) ion in an elongated octahedral geometry.[49] But the most striking feature of the single crystal measurements is the observation of two signals for orientations with high field absorption

($H > 11300$ G), which corroborate the presence of a relatively small zero-field splitting term. The fine structure, however, is not well resolved for all orientations. Only one Lorentzian signal is detected for the higher g values ($2.15 < g < 2.30$). This fact indicates, apart from the strong g–D misalignment, the presence of interdimeric exchange interactions which can cause a collapse of the fine structure in different orientations. The strength of these interactions should be necessarily weak, lower than 0.1 cm^{-1}, and of the same order of magnitude as the zero-field splitting term, otherwise a total collapse of the fine splitting would be produced. Single crystal measurements at low temperatures, on both X- and Q-bands, are in progress in order to confirm this hypothesis from the determination of the D tensor, the angular variation of the linewidth and, finally, the J' interdimeric parameter.

Data available in the literature from single crystal ESR studies allow a comparison among the anisotropic exchange propagation capabilities of various ligand systems.[13] To our knowledge, only data for one triazole bridged compound have been reported so far;[50] this compound, highly asymmetric, contains a single triazole bridge. Compound **1** described here is highly symmetric and contains a double triazole bridge. One aim of our current research is to provide data which contribute to a better understanding of the anisotropic exchange interaction in this group of bridging ligands.

Diffuse reflectance spectra

The electronic spectrum of compound **1** shows an asymmetric band with the maximum located at 694 nm and a weak shoulder on the low-energy side at 920 nm. These features are in agreement with an axially distorted octahedral coordination geometry around copper(II) (it is a CuN_2O_4 chromophore).[49,51] Furthermore, a clearly distinguishable peak is observed at 28.2×10^3 cm^{-1}, which could be attributed either to a charge-transfer band or to the high-energy absorption for copper(II) dimers frequently present in this region of the spectra.[7,51,52] The spectra of compounds **2** and **3** have also been recorded; the observed maxima (see Experimental section) are in agreement with an octahedral MN_2O_4 chromophore.[53]

Infrared spectra

The IR spectrum of the ligand Hdaat, to our knowledge not described so far, has been obtained together with those of its Cu, Ni and Co compounds (see Experimental section). Compounds **1**, **2** and **3** present similar spectra as expected from their isostructural character. Note the lower frequency value of the ν(C=O) band of the copper complex (1641 cm^{-1}) compared to that of the Ni and Co compounds (1658 cm^{-1}); this fact could be explained considering that Cu(II) forms stronger bonds than Ni(II) or Co(II).

Conclusions

For the first time, the ligand Hdaat, a symmetrically substituted triazole, has been studied with regard to its ligand properties. The synthesis, crystal structure, ESR spectra and magnetic properties of the dinuclear copper(II) complex [Cu(daat)-(NO$_3$)(H$_2$O)]$_2$ **1** have been described. This compound represents the first case reported in which a substituted 1,2,4-triazole ligand forms four *six-membered* chelate rings with the metal ions [Cu–N3–C3–N1–C2–O1; Cua–N4–C4–N5–C5–O2] while related dinuclear bis(μ-diazine)copper(II) compounds described in the literature contain either all *five-membered* chelate rings (*e.g.* the *triazole* derivatives: bpt, aamt and pt) or simultaneously both *five-* and *six-membered* chelate rings (*e.g.* the *pyrazole* H$_2$L-containing dinuclear compound). The relevance of the size of the chelate ring is due to its relation with the geometry of the bridging system and so with the magnitude of the magnetic interaction. The structure of the present compound seems to indicate that the increase in the size of the chelating ring and the concomitant increase in the bite angle go accompanied by an increase in the N–Cu–N angle of the bridging system. More examples of dinuclear compounds with different six-membered chelate rings are required to confirm this possible conclusion. On the other hand, this dinuclear structure, symmetrically bridged, results in a magnetic interaction parameter $-J$ of 36 cm^{-1}, which is significantly lower than those exhibited by the symmetrically triazole-bridged compounds ($-J = 118$–97 cm^{-1}) reported so far. A comparison of the structural bridge parameters of **1** with those available in the literature for doubly triazole (symmetrically or asymmetrically) bridged systems points to the large N–Cu–N angle of **1** as the key, supporting a correlation in these triazole dicopper(II) complexes: a larger N–Cu–N angle gives a lower magnetic exchange ($2J$ value).

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