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Magnetic and Spectroscopic Properties of Copper(II) Compounds with Alkyl-Disubstituted Triazoles. X-ray Structure of Bis[μ-4-amino-3,5-bis(aminomethyl)-1,2,4-triazole-N',N^1,N^2,N'']bis[aquabromocopper(II)] Dibromide–2-Water–Methanol

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The crystal and molecular structure of bis[μ-4-amino-3,5-bis(aminomethyl)-1,2,4-triazole-N',N^1,N^2,N'']bis[aquabromocopper(II)] dibromide–2-water–methanol, $[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$ (aamt = $C_4N_6H_{10}$), was determined by single-crystal X-ray diffraction. Crystal data: triclinic, centrosymmetric, space group $P\bar{1}$ with $a = 9.918$ (5) Å, $b = 7.000$ (2) Å, $c = 10.895$ (3) Å, $\alpha = 114.42$ (2)°, $\beta = 94.97$ (3)°, $\gamma = 102.20$ (3)°, $Z = 1$ (dimer), and $V = 660$ (1) Å^3. The refinement of the structure based on 2594 significant reflections attained to $R = 0.031$ and $R_w = 0.034$. The crystallographically independent mononuclear copper units are linked through a symmetry center, giving an approximately planar triazole–diaza-bridged dinuclear cation with a copper–copper distance of 4.069 (7) Å. The axial positions on the copper ions are occupied by a water molecule and a bromide anion. The equatorial coordination around copper consists of ligand nitrogen donor atoms. With aamt a series of isostructural compounds of the general composition $[Cu(aamt)A(H_2O)]_2A_2(H_2O)_x(CH_3OH)_y$ (A = Br^-, ClO_4^-, $CF_3SO_3^-$, BF_4^-, NO_3^-) were synthesized. Intramolecular spin-transfer in the compounds occurs via a superexchange pathway involving the σ-molecular orbitals of the triazole–diaza moiety, leading to an overall antiferromagnetically coupled system with values for the exchange integral in the range $100 \leq -J \leq 112$ cm^{-1}. For all compounds antiferromagnetic behavior was also observed from EPR spectroscopy that clearly shows the "forbidden" $\Delta m_s = 2$ transition and six components in the $\Delta m_s = 1$ region at liquid-nitrogen temperatures.

Introduction

The physical properties of polynuclear compounds containing paramagnetic transition-metal ions have been the subject of intensive studies over the past few decades. Especially in the field of the magnetic properties of these compounds major progress has been made in the understanding of the phenomenon of exchange interactions.[1] Several years of study have provided magnetochemists with a set of rules and a theoretical basis from which a relation between magnetic properties and structural features could be established.[2-12] Empirical data on a variety of compounds, including hydroxo-,[13-17] alkoxo-,[18,19] chloro-,[20-26] bromo-,[27,28] and sulfur-bridged[29] ones, has justified the theoretical approach and in fact led to a correlation of the singlet–triplet energy gap to structural features, in casu the bridging M–X–M angle. For certain values of this bridging angle the coupling between the magnetic ions changes from antiferromagnetic to ferromagnetic. This phenomenon is now commonly referred to as accidental orthogonality.[11] The essential characteristic of accidental orthogonality lies in the fact that for certain values of the structural parameters the antiferromagnetic component of the exchange, being proportional to the overlap integral between the magnetic orbitals, may vanish due to zero overlap. Kahn and co-workers have successfully shown for some dinuclear compounds[30,31] that the state with highest spin multiplicity can also be stabilized on the basis of strict orthogonality between magnetic orbitals. Although most of the success in explaining magnetic properties with this set of symmetry rules comes from data on polynuclear transition-metal compounds, these rules should of course also hold for organic paramagnets. The number of reports on the interaction between paramagnetic transition-metal ions and organic radicals is relatively limited.[32-42] Recently, it has been

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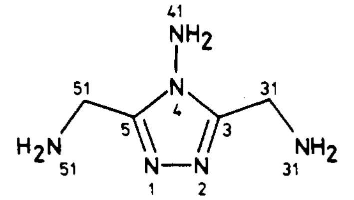

Figure 1. Structural formula and numbering system of 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole.

nicely demonstrated on the interaction between copper(II) ions and an *o*-semiquinone radical that the above-mentioned symmetry rules can also be applied in such a case.[43]

Although the overall magnetic properties of coordination compounds containing polyatomic bridges can easily be rationalized, it seems that the study of these compounds in more detail may give rise to some remarkable results that are also of importance in the field of bioinorganic chemistry.[44-46]

The nature of exchange interaction and its mechanism in small isolated paramagnetic clusters containing only diazine bridges is limited to only a few studies.[44,45,47-53] Since in this case a series of nickel(II) compounds is the only set of comparable compounds for which structural as well as magnetic data were available, an attempt was made to correlate the observed magnetism to structural features with some success.[54] Nevertheless, it seems more logical to use the copper(II) ion with its relatively simple single-ion properties.

The present paper deals with a series of isostructural copper(II) compounds containing 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole (aamt, Figure 1), a tetradentate dinucleating ligand. The coordination compounds, which consist of dinuclear cations of the general composition $[Cu(aamt)A(H_2O)]_2^{2+}$, where A = Br^-, ClO_4^-, $CF_3SO_3^-$, NO_3^-, and BF_4^-, closely resemble the compounds reported earlier with bpt (bptH = 3,5-bis(pyridin-2-yl)-1,2,4-triazole).[44,52] A detailed single-crystal structure determination was undertaken on $[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$ to investigate the subtle structural differences compared to $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$[52] and to rationalize the observed magnetic properties on the basis of them. The magnetic as well as the spectroscopic properties of the series of isostructural compounds will be described.

Experimental Section

Synthesis of the Ligand and Coordination Compounds. The ligand 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole[55] (hereafter abbreviated as aamt) was synthesized by refluxing a mixture of 9 g (0.12 mol) of glycine (Brocacef bv.) and 18 g (0.36 mol) of hydrazine monohydrate (Aldrich) for 60 h. Water was evaporated from the mixture. Water and ethanol were added successively to the residue and evaporated on a water bath under reduced pressure. The residue was left to stand at −20 °C for several hours, after which the ligand solidified as a white hygroscopic product.

Table I. Crystallographic Data for $[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$[a]

chem formula	T = 25 °C
$Cu_2C_9H_{32}N_{12}Br_4O_5$	λ(Mo Kα) = 0.71073 Å
fw = 835.14	ρ_{obsd} = 2.09 (2) g cm^{-3}, ρ_{calcd} = 2.10 g cm^{-3}
space group $P\bar{1}$ (No. 2)	μ = 76.53 cm^{-1}
a = 9.918 (5) Å	transmission coeff = 0.1994–0.6498
b = 7.000 (2) Å	R = 0.031
c = 10.895 (3) Å	R_w = 0.034
α = 114.42 (2)°	
β = 94.97 (3)°	
γ = 102.20 (3)°	
V = 660 (1) Å^3	
Z = 1 (dimer)	

[a] Estimated standard deviations in the least significant digits are given in parentheses.

The coordination compounds were prepared by adding 10 mmol of aamt dissolved in 10 mL of hot methanol to 10 mmol of copper(II) salt dissolved in 20 mL of hot water. The solutions were concentrated and filtered, and the filtrates were left to stand at room temperature. The dark blue crystals or powders that separated from the solutions were filtered, washed with methanol, and dried in air.

All starting materials were commercially available and were used without further purification.

Characterization. IR spectra in the 4000–180-cm^{-1} region were recorded on a Perkin-Elmer 580B spectrophotometer as KBr pellets. Similar structures were determined on the basis of similarities in the band positions and relative intensities of the IR absorptions of the ligand for the different compounds. Since the interpretation of the bonding mode of the anion is not unambiguous due to the possibility of participation in hydrogen bonding, no attempt was made to assign any split components of the anion absorptions.

Electronic spectra in the region 28 000–5000 cm^{-1} were recorded on a Perkin-Elmer 330 spectrophotometer by using the diffuse-reflectance method with MgO as a reference.

Cu, C, N, H, and Br analyses were carried out by the Microanalytical Laboratory of the University College Dublin, Dublin, Ireland. The calculated sample compositions satisfactorily matched the obtained analyses.

Magnetic Measurements. Magnetic susceptibility data were obtained on powdered samples by using an automated Faraday balance[56] in the temperature region 80–300 K. The observed susceptibilities were fitted to the theoretical expression for the susceptibility by means of a nonlinear least-squares SIMPLEX parameter optimalization routine,[57,58] minimizing the residual function defined as $R = [\sum(X_{obs} - X_{calc})^2/\sum(X_{obs})^2]^{1/2}$.

EPR spectra of the powdered compounds were recordered at both room and liquid-nitrogen temperatures on a Varian E-3 spectrometer operating at X-band frequencies (9 GHz).

Collection and Reduction of X-ray Intensity Data. An oblong single crystal of bis[μ-4-amino-3,5-bis(aminomethyl)-1,2,4-triazole-N',N^1,N^2,N'']bis[aquabromocopper(II)] dibromide–2-water–methanol ($[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$, aamt = $C_4H_6H_{10}$) was selected to determine the crystal and molecular structure. The diffraction data were collected on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (graphite-monochromated Mo Kα radiation; λ = 0.71073 Å), applying the ω–2θ scan technique at room temperature. The obtained diffraction data, which showed no systematic decay of intensity due to deterioration of the crystal (checked periodically every 90 min by using selected intensity standards), were corrected for Lorentz and polarization effects. Absorption correction, using the Monte Carlo method,[59] lead to a value for R_{int} of 0.021. Atomic scattering factors for neutral atoms were taken from the literature.[60] Details on crystal data and intensity collection are listed in Table I.

Solution and Refinement of the Structure. The structure was solved in space group $P\bar{1}$. The positions of the symmetry-independent heavy atoms (one copper, two bromide anions) were found by using conventional Patterson techniques. Successive cycles of least-squares refinement and Fourier syntheses based on 2594 significant reflections yielded the

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Table II. Atomic Fractional Coordinates (×10^5 for Cu and Br; ×10^4 for C, N, and O) and Isotropic Thermal Parameters (×10^3 Å^2 for Cu and Br; ×10^2 Å^2 for C, N, and O; $B_{iso} = {}^8/_3\pi^2\chi(U)$) of $[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$[a]

atom	*x/a*	*y/b*	*z/c*	B_{iso}
Cu(1)	18152 (4)	12701 (7)	−4640 (5)	2475 (12)
Br(1)	26429 (4)	−27530 (6)	−15402 (5)	4207 (15)*
Br(2)	5288 (1)	1770 (1)	−2896 (1)	381 (3)
Br(2a)	5348 (1)	1873 (1)	−2366 (1)	30 (2)*
N(1)	138 (3)	3 (5)	1437 (3)	230 (6)
N(2)	1357 (2)	855 (4)	1117 (3)	233 (7)
N(4)	1834 (3)	1079 (4)	3159 (3)	223 (7)
N(41)	2511 (3)	1507 (5)	4474 (3)	333 (8)
N(31)	3747 (2)	2758 (4)	806 (3)	259 (7)
N(51)	−2005 (3)	−1788 (5)	2151 (3)	259 (7)
C(3)	2373 (3)	1497 (5)	2160 (3)	226 (8)
C(5)	433 (3)	148 (5)	2653 (3)	217 (8)
C(31)	3828 (3)	2465 (6)	2076 (4)	292 (9)
C(51)	−722 (3)	−642 (6)	3262 (4)	293 (9)
O(1)	1309 (3)	5130 (5)	689 (4)	575 (11)
O(2)	3265 (4)	−3612 (6)	−4764 (4)	770 (14)
H(N311)	3839 (2)	4125 (4)	1060 (3)	43 (3)
H(N312)	4322 (2)	2448 (4)	370 (3)	43 (3)
H(N411)	3027 (3)	2831 (5)	4903 (3)	43 (3)
H(N412)	3339 (3)	627 (5)	4358 (3)	43 (3)
H(N511)	−2138 (3)	−3227 (5)	1973 (3)	43 (3)
H(N512)	−2788 (3)	−1505 (5)	2417 (3)	43 (3)
H(C311)	4283 (3)	3848 (6)	2772 (4)	43 (3)
H(C312)	4354 (3)	1158 (6)	1851 (4)	43 (3)
H(C511)	−924 (3)	556 (6)	4019 (4)	43 (3)
H(C512)	−475 (3)	−1518 (6)	3686 (4)	43 (3)
O(3)	911 (8)	5702 (12)	3231 (8)	61 (2)
C(03)	9 (2)	522 (2)	430 (2)	131 (7)*

[a] Estimated standard deviations in the least significant digits are given in parentheses. B_{iso} values marked with an asterisk show high thermal anisotropy.

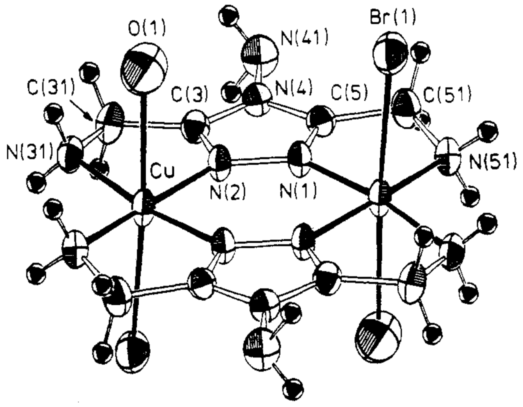

Figure 2. Projection of the structure of the dinuclear cation $[Cu(aamt)Br(H_2O)]_2^{2+}$.

positions of all carbon, oxygen, and nitrogen atoms. The function minimized was $\sum[w(|F_o| - |F_c|)^2]$ with $w = 1/\sigma_{F^2}$ (σ_{F^2}(counting statistics) + $0.021F^2$). The ligand hydrogen atoms were obtained from a final difference Fourier map and were refined with one overall isotropic temperature factor. All non-hydrogen atoms were given individual anisotropic thermal parameters in the refinement. None of the remaining electron densities could be assigned to water or methanol hydrogen atoms due to hydrogen bonding and free rotation effects. The position of the noncoordinating bromide ion is disordered, and subsequently two different positions with different degrees of occupancy had to be used for this ion in the refinement. The methanol molecule, found to be free in the crystal lattice, was refined at half-occupied positions. The final values of the discrepancy indices defined by $R = \sum[(|F_o| - |F_c|)/\sum|F_o|]$ and $R_w = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were $R = 0.031$ and $R_w = 0.034$ with the significant set of reflections. The choice of $P\bar{1}$ was justified by the successful solution of the structure. The atomic positional parameters are listed in Table II and listings of F_o and F_c values and anisotropic thermal parameters for the non-hydrogen atoms are available as supplementary material.[61]

Table III. Selected Distances (Å) and Angles (deg)[a]

Cu–Cu′	4.0694 (7)	N(2)–C(3)	1.303 (4)
Cu–Br(1)	2.8971 (6)	N(4)–N(41)	1.410 (4)
Cu–N(2)	1.937 (3)	N(4)–C(3)	1.361 (4)
Cu–N(31)	2.043 (2)	N(4)–C(5)	1.358 (4)
Cu–O(1)	2.647 (3)	N(31)–C(31)	1.478 (4)
Cu–N(1)′	1.950 (3)	N(51)–C(51)	1.492 (4)
Cu–N(51)′	2.032 (3)	C(3)–C(31)	1.487 (4)
N(1)–N(2)	1.371 (3)	C(5)–C(51)	1.492 (4)
N(1)–C(5)	1.289 (4)	O(3)–C(03)	1.58 (3)

N(2)–Cu–N(31)	81.0 (1)	Cu–N(31)–C(31)	113.5 (2)
N(2)–Cu–N(1)′	92.1 (1)	Cu′–N(1)–N(2)	133.7 (2)
N(2)–Cu–N(51)′	171.3 (1)	Cu′–N(1)–C(5)	118.1 (2)
N(31)–Cu–N(1)	171.8 (1)	Cu′–N(51)–C(51)	113.6 (2)
N(31)–Cu–N(51)	105.7 (1)	N(2)–N(1)–C(5)	108.2 (2)
N(1)′–Cu–N(51)	80.8 (1)	N(1)–N(2)–C(3)	107.7 (3)
N(2)–Cu–O(1)	87.9 (1)	N(41)–N(4)–C(3)	129.8 (2)
N(31)–Cu–O(1)	86.0 (1)	N(41)–N(4)–C(5)	124.3 (3)
N(1)′–Cu–O(1)	89.4 (1)	C(3)–N(4)–C(5)	105.9 (3)
N(51)′–Cu–O(1)	87.1 (1)	N(2)–C(3)–N(4)	108.8 (2)
N(2)–Cu–Br(1)	91.00 (8)	N(2)–C(3)–C(31)	118.9 (3)
N(31)–Cu–Br(1)	88.18 (8)	N(4)–C(3)–C(31)	132.2 (3)
N(1)′–Cu–Br(1)	96.32 (9)	N(1)–C(5)–N(4)	109.3 (3)
N(51)′–Cu–Br(1)	94.64 (8)	N(1)–C(5)–C(51)	119.1 (3)
O(1)–Cu–Br(1)	174.22 (7)	N(4)–C(5)–C(51)	131.6 (3)
Cu–N(2)–N(1)	134.2 (2)	N(31)–C(31)–C(3)	107.7 (3)
Cu–N(2)–C(3)	118.0 (2)	N(51)–C(51e)–C(5)	107.1 (3)

[a] Primed atoms are generated by −*x*, −*y*, −*z*; estimated standard deviations in the least significant digits are given in parentheses.

Results and Discussion

Description of the Structure. A projection of the dinuclear cation is shown in Figure 2, together with the atomic labeling system used. Relevant bond lengths and angles are listed in Table III. The structure of $[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$ consists of dinuclear $[Cu(aamt)Br(H_2O)]_2^{2+}$ cations, bromide ions, and noncoordinating water and methanol molecules. Both metal ions, which are projected on each other through the crystallographic center of symmetry at the middle of the copper–copper vector, are separated by a distance of 4.069 (7) Å within the dinuclear cation. The equatorial coordination around each copper can be described as distorted square planar. The two symmetry-dependent copper ions are shifted 0.15 Å out of the least-squares plane through the equatorial dinitrogen donor atoms, in the direction of the axially coordinated bromide anion. The Cu(1)–O(1) and Cu(1)–Br(1) distances are 2.647 (3) and 2.8971 (6) Å, respectively. Both axial ligands tend to bend from the center of symmetry toward the exo side of the molecule, leading to an O(1)–Cu(1)–Br(1) angle of 174.22 (7)°, which is of the same order of magnitude as found earlier for related compounds.[51,52,62] The equatorial coordination around the copper consists of four strongly coordinating ligand nitrogen atoms at distances ranging from 1.937 (3) to 2.043 (2) Å. As could have been expected considering the more flexible character of an aminomethyl group compared to e.g. a pyridine group,[52] the outermost angle N(31)–Cu(1)–N(51) of 105.7 (1)° is significantly smaller than the values of 111.1 (1) and 111.3 (1)° found for the related $[Cu(bpt)(CF_3SO_3)(H_2O)]$ (bpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazolate anion). The innermost angle as well as the bite angle of the ligand of this compound being 92.1 (1) and 80.8 (1)°, respectively, are 1–2° larger than those found for structures containing heterocyclic triazole substituents but are still in the range expected for this type of ligand. The packing of the molecule is governed by hydrogen bonding. As the position of the noncoordinating Br(2) is disordered, its electron density is located on two positions, named Br(2) and Br(2a), with Br(2) having the highest degree of occupancy. The free bromide Br(2) and the related Br(2a) as well as the free methanol molecule are all involved in intermolecular hydrogen bonding. All intermolecular hydrogen bonds are given in Table IV. Although some hydrogen atoms could not be found

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[61] Supplementary material.

[62] Prins, R.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J.; Gehring, S.; Haase, W. To be published.

Table IV. Interatomic Distances (Å) and Angles (deg) for Hydrogen-Bonding Interactions with Esd's in Parentheses[a]

N(51)···Br(1)^6	3.500 (3)	N(51)–H(N511)···Br(1)^6	176.52 (6)	H(N511)···Br(1)^6	2.581 (3)
N(51)···Br(2)^1	3.424 (3)	N(51)–H(N512)···Br(2)^1	165.07 (6)	H(N512)···Br(2)^1	2.562 (3)
N(51)···Br(2a)^1	3.334 (3)	N(51)–H(N512)···Br(2a)^1	159.51 (7)	H(N512)···Br(2a)^1	2.491 (3)
N(41)···Br(2)^2	3.534 (3)	N(41)–H(N412)···Br(2)^2	151.30 (7)	H(N412)···Br(2)^2	2.518 (3)
N(31)···Br(2)^3	3.411 (3)	N(31)–H(N311)···Br(2)^3	151.99 (6)	H(N311)···Br(2)^3	2.628 (3)
N(31)···Br(2a)^3	3.293 (3)	N(31)–H(N311)···Br(2a)^3	162.07 (7)	H(N311)···Br(2a)^3	2.465 (3)
N(41)···O(2)^4	3.065 (5)	N(41)–H(N411)···O(2)^4	145.2 (1)	H(N411)···O(2)^4	2.319 (5)
O(1)···O(3)	2.705 (9)				
O(1)···O(1)^5	2.816 (6)				
O(2)···O(3)^3	2.868 (8)				

[a] Atoms marked with a number are generated by symmetry operations: (1) $-x, -y, -z$; (2) $1 - x, -y, -z$; (3) $1 - x, 1 - y, -z$; (4) $x, 1 + y, 1 + z$; (5) $-x, 1 - y, -z$; (6) $-x, -1 - y, -z$.

in the refinement, several short contacts are indicative of hydrogen bonding and are also given in Table IV.

Electronic and Magnetic Properties. The electronic spectra of all five compounds show broad asymmetric absorptions with their maxima located near 16.4×10^3 cm^{-1} with a weak shoulder on the low-energy side at 12.2×10^3 cm^{-1}. Furthermore, a charge-transfer band is observed at about 30.5×10^3 cm^{-1}. The features observed in these spectra are in agreement with an axially distorted octahedral coordination geometry around copper(II).[63,64] Following the literature on the subject, the broad absorption can be assigned to the $^2E_g \leftarrow {}^2B_{1g}$ transition, with the low-energy shoulder originating from the $^2A_{1g} \leftarrow {}^2B_{1g}$ transition. A shoulder on the low-energy side of the charge-transfer band, often found for dinuclear copper(II) species,[52,64,65] could not be observed.

The EPR spectra recorded on polycrystalline samples can be interpreted as triplet-state spectra originating from exchange-coupled pairs of copper(II) ions.[66–69] The polycrystalline EPR spectra of the compound $[Cu(aamt)(ClO_4)(H_2O)]_2(ClO_4)_2$ at both room temperature and 77 K are shown in Figure 3. From these spectra the $\Delta m_s = \pm 1$ and the selection-rule forbidden $\Delta m_s = \pm 2$ transitions with hyperfine components are easily recognized. Furthermore, it can be seen that the $\Delta m_s = \pm 1$ transition is nicely split into six components, commonly designated as the Hz_1, Hy_1, Hx_1, Hx_2, Hz_2, and Hy_2 field transitions, corresponding to former observations made on systems having two unpaired electrons. This splitting of the $\Delta m_s = \pm 1$ is known to originate from axial and rhombic zero-field-splitting effects.[69] At liquid-nitrogen temperatures some of the compounds, viz. $[Cu(aamt)(ClO_4)(H_2O)]_2(ClO_4)_2$, $[Cu(aamt)(NO_3)(H_2O)]_2(NO_3)_2$, and $[Cu(aamt)(BF_4)(H_2O)]_2(BF_4)_2(H_2O)_2$, become magnetically diluted, resulting in the presence of isolated triplet states, as recognized from the copper-hyperfine lines on both the Hz absorptions. It is now well established that within these kind of compounds the orientation of the **g** tensor and the zero-field-splitting tensor is not coaxial. In fact single-crystal EPR studies on $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ revealed that for these planar triazole-bridged species the *y* component of both tensors have a mutual angle of 51 (9)°.[44] The similarity of the spectra of copper compounds with bpt as well as with aamt indicates that the situation with regard to the magnitude of the principal components of the tensors and their mutual angles for the aamt compounds is essentially the same. This means that for the compounds reported here the **D** tensor not merely originates from dipole–dipole interactions. The present case appears to be the intermediate situation between the limits of strong dipolar versus strong anisotropic exchange contributions to the zero-field-splitting tensor. The exchange contributions therefore originate from an isotropic exchange mechanism involving the ground-state magnetic $d_{x^2-y^2}$ orbital of one ion and the excited d_{xy} orbital of the other ion. To obtain information with regard to the magnitude of the zero-field splitting, a set of equations proposed by Wasserman et al.[68] was used to calculate the axial (**D**) and rhombic (**E**) zero-field-splitting parameters. It should nevertheless be stressed that the information from this procedure is in fact only a rough indication for the values of these parameters, since the equations only hold for the situation where the **g** and **D** tensors are coaxial. The data on the absolute values of the **g** and **D** tensors that were obtained from minimization of the sum of squares between observed and calculated EPR transitions are listed in Table V.

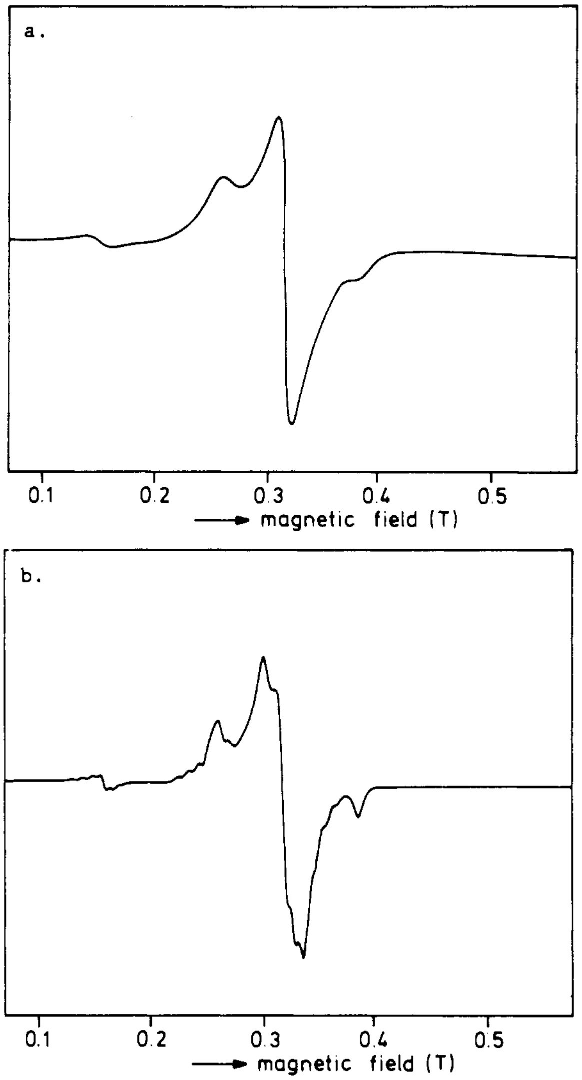

Figure 3. X-Band EPR spectra of $[Cu(aamt)(ClO_4)(H_2O)]_2(ClO_4)_2$ at (a) room temperature (frequency 9.528 GHz) and (b) 77 K (frequency 9.195 GHz).

To obtain information about the magnitude of the exchange-coupling constant between the two copper centers in the dimers,

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Table V. EPR Data for the Copper(II)-aamt Compounds[a]

compd	g_x	g_y	g_z	D, cm^{-1}	E, cm^{-1}
$[Cu(aamt)(ClO_4)(H_2O)]_2(ClO_4)_2$	2.07 (6)	2.02 (6)	2.26 (7)	0.058 (8)	0.016 (4)
$[Cu(aamt)(NO_3)(H_2O)]_2(NO_3)_2$	2.05 (7)	2.03 (7)	2.16 (8)	0.059 (9)	0.013 (5)
$[Cu(aamt)(BF_4)(H_2O)]_2(BF_4)_2(H_2O)_2$	2.05 (9)	2.04 (9)	2.25 (11)	0.06 (1)	0.014 (6)
$[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$	2.07 (6)	2.02 (6)	2.26 (7)	0.058 (8)	0.016 (4)
$[Cu(aamt)(CF_3SO_3)(H_2O)]_2(CF_3SO_3)_2CH_3OH$	2.06 (9)	2.04 (9)	2.26 (11)	0.06 (1)	0.012 (6)

[a] Esd's are given in parentheses.

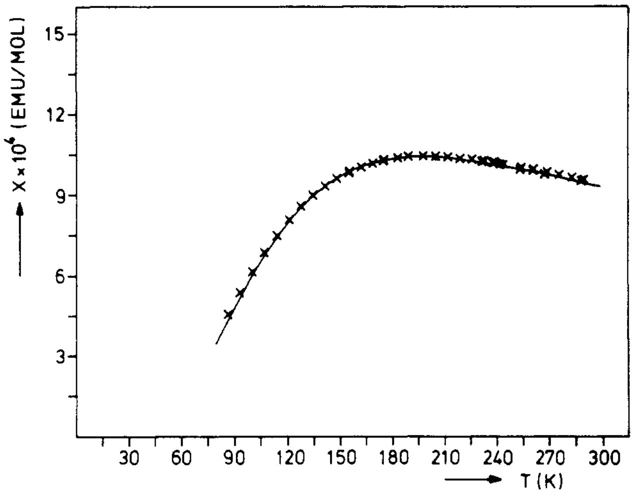

Figure 4. Plot of the magnetic susceptibility vs temperature for $[Cu(aamt)(ClO_4)(H_2O)]_2(ClO_4)_2$. The solid line indicates the calculated susceptibility with parameters $g = 2.12$, $J = -110.7$ (2) cm^{-1}, $p = 0$, and $\chi_{dia} = -79$ (3) × 10^{-6} emu/mol.

magnetic susceptibility measurements were carried out as a function of the temperature. The magnetic susceptibility in the region 80–300 K, as well as the theoretical curve of $[Cu(aamt)(ClO_4)(H_2O)]_2(ClO_4)_2$, is shown in Figure 4. When only the nearest neighbor interactions are considered, the derivation of the theoretical expression for the susceptibility of an interacting set of copper(II) ions is fairly straightforward, for it only requires the solution of the eigenstates of an effective spin Hamiltonian that can be expressed as $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2)$. The obtained eigenstates are a spin-singlet and a spin-triplet separated by an energy of $2J$. The theoretical expression for the temperature dependence of the susceptibility of the exchange-coupled pair per mole of copper ions then becomes

$$\chi = \frac{Ng^2\beta^2}{kT}(3 + e^{-2J/kT})^{-1}(1 - p) + \chi_{TIP} + p\frac{Ng^2\beta^2}{4kT} + \chi_{dia}$$

where, apart from the exchange part, corrections are added for temperature-independent paramagnetism (TIP), paramagnetic impurity (p) present in the sample, and underlying closed-shell paramagnetism. In this formula, which is a modified form of the Bleaney–Bowers equation,[70] N, β, and k are fundamental constants and g, J, and p are adjustable parameters. For the temperature-independent paramagnetism 60 × 10^{-6} emu/mol has been used. Refinement of the parameters results in an unacceptable large range for the value of g, when compared to the findings from EPR spectroscopy. Therefore an alternative procedure was used. Average values for g were calculated from EPR spectra, and these values were kept constant in the refinement of the magnetic susceptibility data. The value for the susceptibility due to diamagnetism, initially calculated from Pascal constants,[71] was now treated as an adjustable parameter. Paramagnetic impurities are of little influence in the high-temperature region; the parameter p was kept constant at a value of $p = 0$. Since the magnetic data of all compounds show a maximum around 200 K, it can be concluded that in all cases the nature of the interaction was antiferromagnetic, leading to a spin-singlet electronic ground state and an excited spin-triplet state. The values for the parameters obtained from the refinement are listed in Table VI. Since there is no reason to assume significantly different J values for this series of isostructural compounds, it seems appropriate to report an average J value for the compounds with aamt, being $J = -109$ (6) cm^{-1}. It must be stated that the parameter J is merely a phenomenological constant that in itself does not contain any information regarding the origin of the mechanism of the exchange process. Nevertheless, several authors[1-14] have clearly shown that an antiferromagnetic spin-transfer mechanism originates from the occurrence of overlap density between the magnetic orbitals. This phenomenom can be the result either of a direct exchange or of a so-called superexchange pathway, in which spins are coupled through a (ligand) bridging system. Considering the relatively large copper–copper distance encountered in this study, it must be assumed that the observed interaction is the result of the existence of a superexchange pathway through the bridging triazole–diaza moiety. It has been well accepted now that such a pathway is mainly governed by σ-overlap density between the metal and ligand molecular orbitals.[11,72] From the tendency of the chromophore encountered in this study to more closely resemble the ideal situation required for maximum overlap density compared to the situation reported in the study of dinuclear copper compounds with the 3,5-bis(pyridin-2-yl)-1,2,4-triazolate anion (bpt),[52] larger values for $|J|$ are expected to be found. The range of J values reported earlier is fairly large and overlaps the range of J values reported in this paper. A reexamination of the previously reported data following the procedure outlined above results in a somewhat smaller value for $|J|$. The exchange coupling constant for the compounds with bpt was found to be $J = -97$ (10) cm^{-1}. Consequently, it can be assumed that the geometrical differences between the in-plane coordination around the copper ions in the compounds with bpt and in the compounds with aamt are significant enough to result in a noticeable effect on the low-lying electronic levels as determined from temperature-dependent magnetic susceptibility measurements.

Table VI. Magnetic Data for the Copper(II)-aamt Compounds[a]

compd	g_{av}	$-J$, cm^{-1}	χ_{dia}, 10^{-6} emu/mol
$[Cu(aamt)(ClO_4)(H_2O)]_2(ClO_4)_2$	2.12	110.7 (2)	79 (3)
$[Cu(aamt)(NO_3)(H_2O)]_2(NO_3)_2$	2.08	112 (1)	18 (11)
$[Cu(aamt)(BF_4)(H_2O)]_2(BF_4)_2(H_2O)_2$	2.12	112.0 (5)	98 (6)
$[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2CH_3OH$	2.12	110 (1)	294 (12)
$[Cu(aamt)(CF_3SO_3)(H_2O)]_2$-$(CF_3SO_3)_2CH_3OH$	2.12	99.9 (4)	250 (5)

[a] Esd's are given in parentheses.

Concluding Remarks

The present study has shown that the dinucleating ligand 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole is very suitable for studying exchange-coupled pairs of copper(II) ions.

The compounds discussed in this paper show a strong antiferromagnetic interaction between the copper(II) ions, which must be the result of a very effective superexchange pathway, mainly

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determined by σ-overlap density between metal and ligand molecular orbitals.

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Supplementary Material Available: Table SII, listing anisotropic thermal parameters (1 page); Table SI, listing observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Metallomacrocycles: Synthesis, X-ray Structure, Electrochemistry, and ESR Spectroscopy of Mononuclear and Heterodinuclear Complexes

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A number of novel heterodinucleating ligands have been synthesized by Ba^{2+}-templated (1:1) macrocyclization of the dialdehydes **7**, **8**, and **20** with the diamines **9** and **21**. The ligands have both a cavity suitable for complexation of transition-metal cations and a cavity for complexation of alkali- or alkaline-earth-metal cations. The resulting barium complexes could be converted into the heterodinuclear complexes **1–3**, **10–13**, **23–25**, and **28** upon reaction with nickel, copper, or zinc acetate. The mono-transition-metal complexes **14–17**, **26**, **27**, and **29** could be obtained by removing the barium salt from the polyether cavity. Their ^1H NMR, IR, and mass spectra are discussed, and four heterodinuclear complexes have been analyzed by X-ray crystallography. The nickel/barium complex **3**·MeOH ($C_{35}H_{44}BaCl_2N_2NiO_{19}$) crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 15.096$ (4) Å, $b = 20.278$ (4) Å, $c = 13.818$ (4) Å, $\beta = 93.61$ (1)°, and $Z = 4$. The nickel/barium complex **10**·H_2O crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 9.096$ (3) Å, $b = 11.491$ (7) Å, $c = 17.119$ (5) Å, $\alpha = 92.38$ (2)°, $\beta = 102.27$ (1)°, $\gamma = 98.63$ (2)°, and $Z = 2$. The nickel/sodium complex **14**·sodium picrate crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 14.697$ (5) Å, $b = 14.574$ (7) Å, $c = 14.782$ (3) Å, $\beta = 96.08$ (1)°, and $Z = 4$. The zinc/barium complex **25**·3DMF crystallizes in the monoclinic system, space group $C2/c$, with $a = 24.301$ (5) Å, $b = 26.232$ (4) Å, $c = 22.468$ (7) Å, $\beta = 119.06$ (2)°, and $Z = 8$. In the complexes **3**·MeOH, **10**·H_2O, and **14**·sodium picrate the coordination of the nickel cation is square planar. The zinc cation in **25**·3DMF has a square-pyramidal coordination with a DMF molecule at the axial position. The distance between the two metal ions in the complexes **3**·MeOH, **10**·H_2O, **14**·sodium picrate, and **25**·3DMF is 3.63–3.70 Å. The electrochemical properties of the complexed transition-metal cations in the heterodinuclear complexes and mono-transition-metal cation complexes have been investigated by polarography and cyclic voltammetry. The half-wave potential is dependent on the nature of the transition-metal cation and the mode of coordination. Complexation of alkali-metal (Li^+, Na^+, and K^+) or alkaline-earth-metal (Ba^{2+}) cations in the polyether cavity resulted in anodic shifts of the half-wave potential up to 213 mV; the bivalent Ba^{2+} induced the largest shifts. The shifts of the half-wave potential are also dependent on the ring size and rigidity of the polyether cavity. Cyclic voltammetry of the nickel/barium complex **10** and the copper/barium complex **12** revealed a chemically reversible but electrochemically irreversible reduction at scan rates of 0.5–6 and 1–6 V/s, respectively. A relatively slow adsorption process was observed for the nickel complex **15**, and the reduction was chemically reversible but electrochemically irreversible at scan rates of 50 mV/s to 2 V/s. The zinc/barium complex **25** undergoes an irreversible two-electron reduction at $E_{1/2} = -1.466$ V, whereas the nickel and copper complexes **10–17**, **23**, **24**, **28**, and **29** undergo a one-electron reduction. The ESR spectra of a number of copper containing and heterodinuclear complexes are in line with the redox properties.

Introduction

The area of dinucleating ligands able to form homo- and heterodinuclear complexes is of great interest because of a variety of reasons.[1] First, they may serve as models for metalloproteins like superoxide dismutase, oxidases, and peptidases.[2] The dinuclear copper-containing complexes attract a great deal of attention because of the two copper centers in the active site of copper proteins like hemocyanin, which transport O_2, and the monooxygenases tyrosinase and dopamine β-hydroxylase, which incorporate oxygen (from O_2) into organic substrates.[3] Very recently Karlin and co-workers[4] have reported that symmetrical dicopper complexes are able to bind molecular oxygen reversibly at low temperature. Second, such dinuclear complexes may bind and activate small molecules. Floriani and co-workers have shown this beautifully for CO_2 and CO_2-like molecules.[5] They prepared acyclic $[L^{2-}Co^{I}]^{-}M^{+}$ (M = Na, K, Cs) complexes in which the Co^{I} center acts as a Lewis base and the M^+ center as a Lewis acid. Third, dinuclear complexes can be applied as bifunctional catalysts as was shown by McKenzie and Robson[6] for a dipalladium complex in the hydration of acetonitrile. They observed a pathway involving concerted action of the two metal centers. Both Collman et al.[7] and Leznoff et al.[8] have reported the electrocatalytic re-

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