Dimeric Copper(II) Compounds with a Tripodal Imidazole-containing Ligand and bridged by Imidazolate, Benzimidazolate, and Benzotriazolate Ions. Crystal and Molecular Structure of μ-(benzotriazolato-N^1,N^3)-bis{[tris(N^1-methylbenzimidazol-2-ylmethyl)amine-N,N^3,$N^{3'}$,$N^{3''}$]copper(II)} Trinitrate

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A series of dimeric copper(II) co-ordination compounds with general formula $[Cu_2(tmbma)_2(azolate)]X_3$ has been prepared and characterized, where tmbma is the tripodal benzimidazole-containing ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine, azolate is the anion of imidazole, benzimidazole, or benzotriazole, and X = NO_3^-, BF_4^-, or ClO_4^-. Variable-temperature magnetic susceptibility measurements indicate antiferromagnetic interactions with J values of −10 to −18 cm^{-1} (for the benzimidazolate and benzotriazolate compounds) and −28 cm^{-1} (for the imidazolate compounds). *Q*-Band and *X*-band e.s.r. spectra show typical $S = 1$ signals; D values calculated from these spectra range from 0.08 to 0.13 cm^{-1}. The crystal and molecular structure of the title compound has been determined by single-crystal *X*-ray diffraction. The compound crystallizes in the space group $C2/c$, with a = 16.880(2), b = 26.011(1), c = 14.686(1) Å, β = 100.585(7)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined using least-squares techniques to a residual R of 0.050 for 3 327 reflections with $I > 2\sigma(I)$. The structure consists of dimeric cations, having C_2 symmetry, and disordered nitrate anions; the co-ordination geometry around the copper ions can be described as distorted trigonal bipyramidal with three equatorial benzimidazole nitrogen atoms, one axial amine nitrogen atom, and the benzotriazolate ion bridging from an axial position on one copper ion to an axial position on the other copper ion, resulting in a Cu · · · Cu distance of 5.536(2) Å.

X-RAY crystallographic studies [1] of the copper- and zinc-containing enzyme superoxide dismutase have shown that the copper atom is square-planar co-ordinated by four imidazole nitrogen atoms. One of the imidazole groups functions as a bridge between the copper and zinc atom. Temperature-dependent e.s.r. measurements on the modified enzyme, in which Zn^{II} has been substituted by Cu^{II}, show that the two copper(II) ions are antiferromagnetically coupled with a singlet–triplet separation $|2J|$ of *ca.* 52 cm^{-1}.[2] An imidazolate-bridged Fe–Cu site with a large antiferromagnetic coupling ($|J| > 200$ cm^{-1}) has been proposed [3,4] for the 'e.s.r. silent' copper in the widely studied enzyme cytochrome *c* oxidase.[3-13]

Recently, many interesting compounds containing imidazolate-bridged binuclear units were reported as possible models for the enzymes superoxide dismutase and cytochrome *c* oxidase.[14-25] These studies have shown that the magnitude of the antiferromagnetic exchange is strongly dependent upon the geometry of the copper co-ordination, but no magnetic interaction as large as suggested for cytochrome *c* oxidase has been found so far.

In most of the reported binuclear imidazolate-bridged copper(II) compounds the non-bridging ligands are polydentate amine ligands or pyridines; no systems have been reported so far in which the non-bridging ligands are also imidazoles. In this paper a group of stable binuclear compounds is described containing the unit Cu–azolate–Cu; herein azolate stands for the imidazolate (im), benzimidazolate (bzim), or benzotriazolate (bztz) anion. The other ligands around Cu^{II} are provided by the quadridentate imidazole chelate tris(*N*-methylbenzimidazol-2-ylmethyl)amine (abbreviated as tmbma; see Figure 1). The crystal structure of one of the compounds, $[Cu_2(tmbma)_2(bztz)][NO_3]_3$, is reported and the e.s.r. spectra and magnetic susceptibility data are discussed in detail. Some preliminary results were communicated earlier.[26]

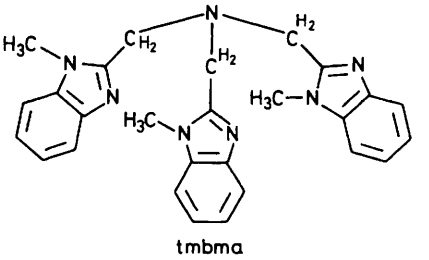

FIGURE 1 Schematic representation of the tripodal ligand tmbma

EXPERIMENTAL

Preparations.—The ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine was prepared from tris(benzimidazol-2-ylmethyl)amine (tbma [27]) using a modification of the methylation procedure first described by Trofimenko.[28] Potassium metal (60 mmol, 2.4 g) was stirred and refluxed in sodium-dried tetrahydrofuran (thf) (100 cm^3) under a stream of dry nitrogen. Then tbma (22 mmol, 9.0 g) suspended in sodium-dried thf (*ca.* 200 cm^3) was slowly added. The mixture was refluxed and stirred for 4 h; the potassium disappeared and a white precipitate was formed. Methyl iodide (150 mmol, 22 g) was slowly added and after a few minutes of stirring the mixture was cooled to room temperature. The white precipitate was filtered off, washed with thf, recrystallized from warm methanol, washed with methanol and diethyl ether, and dried *in vacuo* at 80 °C. Yield: 4.5 g (10 mmol; 50%). M.p. 214—216 °C (Found:

C, 71.5; H, 6.10; N, 21.6. Calc. for $C_{27}H_{27}N_7$: C, 72.1; H, 6.05; N, 21.8%). The ^1H n.m.r. spectrum in [$^2H_1$]trifluoroacetic acid (reference $SiMe_4$) is as expected, with δ 7.80(4) (asymmetric multiplet, aromatic C–H), 4.92(2) (s, CH_2), and 4.14(3) (s, CH_3) (relative intensities in parentheses).

The compound $Cu(BF_4)_2 \cdot 6H_2O$ was prepared from copper(II) carbonate and hydrogen tetrafluoroborate. The other copper salts and imidazole, benzimidazole, and benzotriazole were commercially available and used as received, without further purification.

The compounds $[Cu_2(tmbma)_2(im)]X_3$ (X = ClO_4, BF_4, or NO_3) were prepared in the following manner: tmbma (2 mmol) was dissolved in hot methanol (*ca.* 50 cm^3) and added to Na(im) (1 mmol) (the sodium salt of imidazole, prepared *in situ* from NaOH in water and imidazole in methanol) in 90% methanol (*ca.* 10 cm^3). This mixture was added to the copper salt (2 mmol) in methanol (*ca.* 10 cm^3). Upon cooling, green solids were obtained, which were filtered off, washed with methanol and diethyl ether, and finally dried *in vacuo* at 60 °C. The other compounds were prepared by an analogous procedure using the sodium salt of benzimidazole, Na(bzim), or of benzotriazole, Na(bztz).

During the preparation of a batch of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$, green single crystals were obtained, which deteriorate and pulverize within seconds. The crystals probably contain loosely held methanol and fall apart when the methanol is lost by the crystals. As a consequence of this rapid decomposition neither spectroscopic data nor elemental analyses were obtained for the crystals themselves.

Physical Measurements.—Infrared spectra of the solid compounds were recorded either on a Perkin-Elmer 297 spectrophotometer in the range 600—4 000 cm^{-1} or on a Perkin-Elmer 580 spectrophotometer in the range 200—4 000 cm^{-1}. Samples were either mulled in Nujol (between KBr pellets) or pelleted in KBr. No indications of decomposition in the KBr pellets were observed. Electronic spectra (4 000—35 000 cm^{-1}) were obtained as solids using a Beckman DK-2 ratio-recording spectrophotometer fitted with a reflectance attachment. Electron spin resonance spectra at *X*-band and *Q*-band frequencies were obtained with Varian E-3, E-9, and E-112 spectrometers at liquid-nitrogen and at room temperatures. The field was calibrated using an AEG proton n.m.r. apparatus. Magnetic susceptibility measurements in the temperature range 4.2—70 K were made either on a model 155 PAR vibrating-sample magnetometer as described in detail by van Ooijen [29] or on a model 150A PAR vibrating-sample magnetometer used with the modifications described by Engelfriet.[30] Copper analyses were carried out using standard ethylenediaminetetra-acetate titrations; [31] all other elemental analyses were performed by the Organisch Chemisch Instituut TNO Utrecht, The Netherlands, or by Dr. Pascher, Bonn, Germany.

X-*Ray Methods.*—A crystal of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ of approximate dimensions 0.50 × 0.17 × 0.13 mm was mounted, together with a thread of filter paper which was first soaked in the mother-liquor, in a thin-walled glass capillary, which was sealed with solid paraffin. Weissenberg photographs taken with Cu-K_α radiation showed systematic absences $h + k = 2n + 1$ for *hkl* and $l = 2n + 1$ for *h0l* and Laue symmetry 2/*m*. This is consistent with *Cc* or *C*2/*c* as possible space groups. The calculated density of 1.394 g cm^{-3} is in reasonable agreement with the experimental value of 1.41(2) g cm^{-3} (measured by flotation in chloroform–hexane) for $Z = 4$. Precise lattice constants were determined by least-squares refinement of the angular settings of 24 reflections with $16 < \theta < 18°$. The resulting unit-cell dimensions were $a = 16.880(2)$, $b = 26.011(1)$, $c = 14.686(1)$ Å, $\beta = 100.585(7)°$, $F(000) = 2\,717$, and $U = 6\,338$ Å^3. Intensity data were collected on a Nonius CAD-4 diffractometer (ω—θ scans) for all reflections with $2 < \theta < 25°$ and with $h > 0$ and $k > 0$ using graphite-monochromated Mo-K_α radiation ($\lambda = 0.713\,71$Å). The scanning rate was adjusted to the required precision of $\sigma(I) < 0.03I$, with a maximum scan time of 120 s per reflection. Each reflection was measured in 96 steps. Sixteen steps at each end of the scan were considered as background. Intensities I and their estimated standard deviations $\sigma(I)$ were calculated from $I = s[P - 2(B_1 + B_2)]$ and $\sigma(I) = s[P + 4(B_1 + B_2)]^{\frac{1}{2}}$, where s is a factor to account for the variable scan speed, P is the scan count, and B_1 and B_2 are the low- and high-angle background counts. Three standard reflections were measured after every 5 400 s of radiation time to check for instrumental instability and crystal decomposition; there was no significant change in their intensities. The intensity of a suitable reflection was measured at different azimuthal positions; this suggested that no absorption correction was necessary (maximum variation 4%; $\mu = 7.7$ cm^{-1}). The intensities of 8 445 reflections were measured, 5 565 of which were symmetry independent and 3 327 were considered as observed, $I > 2\sigma(I)$. The measured intensities were corrected for Lorentz and polarization effects.

Structure Determination of Solvated $[Cu_2(tmbma)_2(bztz)][NO_3]_3$.—A sharpened Patterson synthesis showed many Harker peaks due to the two-fold axis.* This suggested that space group *C*2/*c* was the correct choice. The Patterson map revealed the position of the copper atom at 0.339, 0.384, 0.268. This position was refined together with a scale factor in a least-squares procedure to give a residual R value of 0.43, where $R = |\Sigma||F_o| - |F_c||/\Sigma|F_o|$. A subsequent Fourier synthesis showed the positions of 15 nitrogen and carbon atoms. One more Fourier synthesis after a least-squares refinement gave the positions of all non-hydrogen atoms of the cation, together with some atoms of a nitrate ion (the presence of which was obvious from the elemental analyses of the dried substance, see Table 2), lying on the two-fold axis. Several cycles of Fourier difference syntheses after full-matrix least-squares refinement yielded 18 peaks, which were ascribed to atoms of disordered nitrate molecules. They were included in the refinement as nitrogen or oxygen atoms with occupancies of 25—100%. In their geometry, no separate nitrate ions could be recognized, so that no rigid-body refinement could be carried out. It is, however, possible that some of these disordered atoms are part of methanol molecules, the presence of which is suggested by the rapid decomposition of the crystals when they are isolated from the methanol solution (see Experimental section). In subsequent block-diagonal least-squares refinement cycles, using unit weights, all the atoms of the cation were refined with anisotropic thermal parameters whereas the partially occupied atom positions of nitrate or methanol molecules were refined with isotropic thermal parameters. Since no hydrogen atoms could be located from a Fourier difference map, they were placed at calculated positions (C–H 0.95 Å) [32] and were given isotropic thermal parameters of 4.00 Å^2; they were

* All computer programs were written locally, except ORTEP by C. K. Johnson.

not refined. No hydrogen atoms were included for the methyl groups on the imidazole groups of the ligand. This resulted in a final R value of 0.050 (447 parameters). In the final Fourier difference map, some residual electron density was found (peaks 0.8 e Å^{-3}), probably due to disordered anion or methanol molecules. The parameter shifts of the atoms of the cation were all less than 10% of their standard deviations in a final full-matrix refinement cycle. For the disordered anions the shifts were less than 50% of their standard deviations. Examination of the values of $|F_o|$ and $|F_c|$ suggested that no secondary extinction correction was necessary and none was applied. Scattering factors for neutral atoms were taken for all non-hydrogen atoms from ref. 33 and corrected for the real part of the anomalous dispersion $\Delta f'$; those for copper were also corrected for the imaginary part of the anomalous dispersion $\Delta f''$. The scattering factors for the hydrogen atoms were taken from ref. 34.

TABLE 1

Positional parameters ($\times 10^4$) of non-hydrogen atoms * of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Cu	3 396(1)	3 848(1)	2 678(1)
N(100)	2 308(3)	4 237(2)	2 535(3)
N(110)	2 911(3)	3 652(2)	1 347(3)
C(110)	1 691(4)	3 959(3)	1 857(4)
N(111)	1 757(3)	3 485(2)	378(3)
C(111)	2 116(4)	3 699(2)	1 181(4)
C(112)	880(4)	3 451(3)	0(5)
C(113)	2 374(4)	3 280(3)	−20(4)
C(114)	3 093(4)	3 387(2)	582(4)
C(115)	2 350(5)	3 016(3)	−845(4)
C(116)	3 082(5)	2 869(3)	−1 046(4)
C(117)	3 811(5)	2 985(3)	−458(4)
C(118)	3 829(4)	3 247(3)	349(4)
N(120)	3 823(3)	4 591(2)	3 034(3)
C(120)	2 465(4)	4 764(3)	2 203(5)
N(121)	3 519(4)	5 422(2)	2 869(4)
C(121)	3 270(4)	4 928(3)	2 708(4)
C(122)	3 052(6)	5 898(3)	2 601(6)
C(123)	4 302(5)	5 394(3)	3 337(5)
C(124)	4 494(4)	4 874(3)	3 442(4)
C(125)	4 844(6)	5 778(4)	3 678(6)
C(126)	5 507(6)	5 623(4)	4 130(6)
C(127)	5 791(5)	5 105(4)	4 248(5)
C(128)	5 246(4)	4 723(3)	3 901(4)
N(130)	3 033(3)	3 580(2)	3 874(3)
C(130)	2 044(4)	4 267(3)	3 451(5)
N(131)	2 125(3)	3 663(2)	4 793(4)
C(131)	2 377(4)	3 823(3)	4 020(4)
C(132)	1 393(5)	3 837(4)	5 137(6)
C(133)	2 661(4)	3 295(3)	5 191(5)
C(134)	3 252(4)	3 239(3)	4 625(4)
C(135)	2 723(5)	3 002(3)	6 006(5)
C(136)	3 366(6)	2 681(3)	6 220(5)
C(137)	3 940(5)	2 635(3)	5 664(5)
C(138)	3 886(4)	2 916(3)	4 863(4)
N(200)	4 403(3)	3 476(2)	2 673(3)
N(201)	5 000	3 770(3)	2 500
C(201)	4 614(3)	2 973(2)	2 605(4)
C(202)	4 212(4)	2 510(3)	2 708(5)
C(203)	4 605(5)	2 069(3)	2 609(5)

* Only the atoms of the cation are listed in this Table.

Final atomic parameters for the non-hydrogen atoms of the cation are given in Table 1. The 18 partially occupied nitrate or methanol atom positions are separately listed in Supplementary Publication No. SUP 23214 (13 pp.),* together with the calculated positional parameters for hydrogen atoms, thermal parameters, and a list of observed and calculated structure factors.

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

RESULTS AND DISCUSSION

General.—All compounds are described by the general formula $[Cu_2(tmbma)_2(azolate)]X_3$; herein azolate stands for a bridging anion imidazolate (im), benzimidazolate (bzim), or benzotriazolate (bztz) and $X = NO_3^-$, BF_4^-, or ClO_4^-; tmbma is the ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine. This ligand was chosen instead of its unmethylated analogue tris(benzimidazol-2-ylmethyl)amine (tbma) [27] since the deprotonation of the bridging heterocyclic ligand had to be carried out in a basic solution. Under such conditions, tbma can lose its imidazole N–H protons as well, allowing the possible formation of polymeric compounds. When $CuCl_2$ or $CuBr_2$ are used in the synthesis, no imidazolate-bridged compounds could be obtained and only $Cu(tmbma)Cl_2$ and $Cu(tmbma)Br_2$ were found.† Apparently, Cl^- or Br^- more readily occupies the fifth co-ordination place of the copper atom than a deprotonated azole. Also, attempts were made to synthesize compounds with 2-methylimidazole as a bridging ligand, in order to study the steric influence of the substituent on the exchange pathway between the copper ions (*cf.* ref. 18). No pure compounds, however, could be isolated.

After isolation and drying, the green compounds appear to be hygroscopic and the exact number of water molecules found in the elemental analyses depends on the particular sample. The samples with the smallest number of water molecules are listed in Table 2, together with their analytical data.

The i.r. spectra of the bridged compounds show only minor differences compared with those of the monomeric $Cu(tmbma)X_2$ compounds. No indications are found for co-ordination of the anions. The i.r. spectrum of some powdered crystals of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ from the batch used for the *X*-ray structure determination was identical to the spectra of earlier obtained powders.

All compounds have in their electronic spectrum an asymmetric absorption around 11 000 cm^{-1}; the high-energy side of the peak is broadened and this suggests a trigonal-bipyramidal co-ordination geometry for the copper atoms.[35-37] The energies of the *d–d* transitions in trigonal-bipyramidal CuN_5 chromophores usually lie in the range 11 000—14 000 cm^{-1}.[38]

Before discussing the e.s.r. and magnetic susceptibility data of these compounds, the structure of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ will be described.

The Structure of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$.—The structure consists of discrete dimeric $[Cu_2(tmbma)_2(bztz)]^{3+}$ cations and NO_3^- ions. The cations have C_2

† Compounds with formula $Cu(tmbma)X_2$ can be prepared analogous to $Cu(tbma)X_2$.[35]

TABLE 2

Analytical data (%) for the azolate-bridged binuclear copper(II) tmbma compounds with calculated values in parentheses

Compound	C	H	N	Cu
$[Cu_2(tmbma)_2(im)][NO_3]_3 \cdot 4H_2O$	50.8(50.7)	4.6(4.8)	19.7(19.7)	9.2(9.4)
$[Cu_2(tmbma)_2(im)][BF_4]_3$	50.6(50.6)	4.5(4.2)	16.1(16.6)	9.3(9.4)
$[Cu_2(tmbma)_2(im)][ClO_4]_3$	48.8(49.2)	4.5(4.1)	16.1(16.1)	9.5(9.1)
$[Cu_2(tmbma)_2(bzim)][NO_3]_3 \cdot 4H_2O$	52.4(52.3)	5.4(4.8)	19.1(19.0)	9.2(9.0)
$[Cu_2(tmbma)_2(bzim)][BF_4]_3 \cdot H_2O$	51.5(51.5)	4.3(4.3)	15.7(15.8)	9.0(9.0)
$[Cu_2(tmbma)_2(bzim)][ClO_4]_3 \cdot 2H_2O$	49.3(49.6)	4.3(4.3)	15.3(15.2)	8.7(8.6)
$[Cu_2(tmbma)_2(bztz)][NO_3]_3 \cdot 2H_2O$	52.3(52.7)	4.5(4.6)	20.1(20.5)	9.3(9.3)
$[Cu_2(tmbma)_2(bztz)][BF_4]_3 \cdot 2H_2O$	49.7(50.0)	4.2(4.3)	16.3(16.5)	9.0(8.8)
$[Cu_2(tmbma)_2(bztz)][ClO_4]_3 \cdot H_2O$	49.3(49.3)	4.1(4.1)	16.2(16.3)	8.7(8.7)

TABLE 3

Interatomic distances (Å) of the cation * in $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ with estimated standard deviations in parentheses

Cu–N(100)	2.073(5)	N(200)–N(201)	1.326(6)
Cu–N(110)	2.041(5)	N(200)–C(201)	1.364(7)
Cu–N(120)	2.094(5)	C(201)–C(202)	1.403(9)
Cu–N(130)	2.083(5)	C(202)–C(203)	1.346(9)
Cu–N(200)	1.959(5)	C(201)–C(201′)	1.394(11)
Cu · · · Cu	5.536(2)	C(203)–C(203′)	1.429(15)

N(110)–C(111)	1.323(7)	N(120)–C(121)	1.307(8)	N(130)–C(131)	1.326(8)
N(110)–C(114)	1.399(8)	N(120)–C(124)	1.392(8)	N(130)–C(134)	1.410(8)
C(111)–C(110)	1.490(9)	C(121)–C(120)	1.487(10)	C(131)–C(130)	1.475(10)
C(111)–N(111)	1.343(8)	C(121)–N(121)	1.358(8)	C(131)–N(131)	1.350(8)
N(111)–C(112)	1.486(8)	N(121)–C(122)	1.481(9)	N(131)–C(132)	1.489(9)
N(111)–C(113)	1.391(8)	N(121)–C(123)	1.376(9)	N(131)–C(133)	1.373(9)
C(113)–C(114)	1.392(9)	C(123)–C(124)	1.392(10)	C(133)–C(134)	1.418(9)
C(113)–C(115)	1.386(9)	C(123)–C(125)	1.385(10)	C(133)–C(135)	1.405(10)
C(115)–C(116)	1.377(10)	C(125)–C(126)	1.366(13)	C(135)–C(136)	1.358(12)
C(116)–C(117)	1.401(10)	C(126)–C(127)	1.392(13)	C(136)–C(137)	1.384(11)
C(117)–C(118)	1.363(9)	C(127)–C(128)	1.385(10)	C(137)–C(138)	1.373(9)
C(114)–C(118)	1.395(9)	C(124)–C(128)	1.381(9)	C(134)–C(138)	1.356(9)
N(100)–C(110)	1.490(8)	N(100)–C(120)	1.493(9)	N(100)–C(130)	1.494(8)

* The atom-numbering scheme is given in Figure 2. The primed and unprimed atoms are related by the symmetry operation $1 - x, y, \frac{1}{2} - z$.

TABLE 4

Interbond angles (°) of the cation in $[Cu_2(tmbma)_2(bztz)][NO_3]_3$, with estimated standard deviations in parentheses *

N(100)–Cu–N(110)	80.4	N(100)–Cu–N(120)	80.3(2)	N(100)–Cu–N(130)	81.8(2)
N(200)–Cu–N(110)	93.9(2)	N(200)–Cu–N(120)	101.4(2)	N(200)–Cu–N(130)	103.2(2)
N(110)–Cu–N(120)	121.9(2)	N(110)–Cu–N(130)	126.6(2)	N(120)–Cu–N(130)	103.8(2)
N(100)–Cu–N(200)	174.1(2)	Cu–N(200)–N(201)	114.0(4)	Cu–N(200)–C(201)	135.4(4)
Cu–N(100)–C(110)	109.1(4)	Cu–N(100)–C(120)	106.0(4)	Cu–N(100)–C(130)	109.8(4)
C(110)–N(100)–C(120)	111.8(5)	C(110)–N(100)–C(130)	109.8(5)	C(120)–N(100)–C(130)	110.3(5)
N(201)–N(200)–C(201)	108.8(5)	N(200)–N(201)–N(200′)	109.5(7)	N(200)–C(201)–C(201′)	106.4(3)
N(200)–C(201)–C(202)	132.6(6)	C(201′)–C(201)–C(202)	120.9(4)	C(201)–C(202)–C(203)	117.5(6)
C(202)–C(203)–C(203′)	121.5(4)				
Cu–N(110)–C(111)	111.6(4)	Cu–N(120)–C(121)	109.8(4)	Cu–N(130)–C(131)	111.1(5)
Cu–N(110)–C(114)	141.6(4)	Cu–N(120)–C(124)	144.3(5)	Cu–N(130)–C(134)	142.6(5)
C(111)–N(110)–C(114)	105.2(5)	C(121)–N(120)–C(124)	105.7(6)	C(131)–N(130)–C(134)	106.2(6)
N(110)–C(111)–N(111)	113.7(6)	N(120)–C(121)–N(121)	113.3(6)	N(130)–C(131)–N(131)	113.0(7)
N(110)–C(111)–C(110)	121.0(6)	N(120)–C(121)–C(120)	121.0(6)	N(130)–C(131)–C(130)	121.6(6)
C(110)–C(111)–N(111)	125.3(6)	C(120)–C(121)–N(121)	125.8(7)	C(130)–C(131)–N(131)	124.9(6)
C(111)–N(111)–C(112)	127.6(6)	C(121)–N(121)–C(122)	127.7(7)	C(131)–N(131)–C(132)	127.0(7)
C(111)–N(111)–C(113)	106.0(5)	C(121)–N(121)–C(123)	106.0(6)	C(131)–N(131)–C(133)	106.7(6)
C(112)–N(111)–C(113)	126.3(6)	C(122)–N(121)–C(123)	126.4(7)	C(132)–N(131)–C(133)	126.3(6)
N(111)–C(113)–C(114)	106.8(6)	N(121)–C(123)–C(124)	106.8(6)	N(131)–C(133)–C(134)	107.5(6)
N(111)–C(113)–C(115)	130.8(6)	N(121)–C(123)–C(125)	130.8(8)	N(131)–C(133)–C(135)	132.9(7)
C(114)–C(113)–C(115)	122.4(7)	C(124)–C(123)–C(125)	122.4(8)	C(134)–C(133)–C(135)	119.6(8)
C(113)–C(115)–C(116)	116.3(7)	C(123)–C(125)–C(126)	116.7(8)	C(133)–C(135)–C(136)	117.5(7)
C(115)–C(116)–C(117)	121.9(7)	C(125)–C(126)–C(127)	122.0(8)	C(135)–C(136)–C(137)	122.2(7)
C(116)–C(117)–C(118)	121.4(7)	C(126)–C(127)–C(128)	121.0(8)	C(136)–C(137)–C(138)	121.1(8)
C(117)–C(118)–C(114)	117.7(6)	C(127)–C(128)–C(124)	117.7(7)	C(137)–C(138)–C(134)	118.4(7)
C(113)–C(114)–C(118)	120.2(6)	C(123)–C(124)–C(128)	120.3(6)	C(133)–C(134)–C(138)	121.2(7)
N(110)–C(114)–C(113)	108.2(6)	N(120)–C(124)–C(123)	108.2(6)	N(130)–C(134)–C(133)	106.5(6)
N(110)–C(114)–C(118)	131.5(6)	N(120)–C(124)–C(128)	131.5(7)	N(130)–C(134)–C(138)	132.2(6)

* The atom-numbering scheme is given in Figure 2: the primed and unprimed atoms are related by the symmetry operation $1 - x, y, \frac{1}{2} - z$.

symmetry. The bond distances of the cation are given in Table 3, while the interbond angles are listed in Table 4. Since the anions are disordered over many positions, they will not be discussed further. The distances and

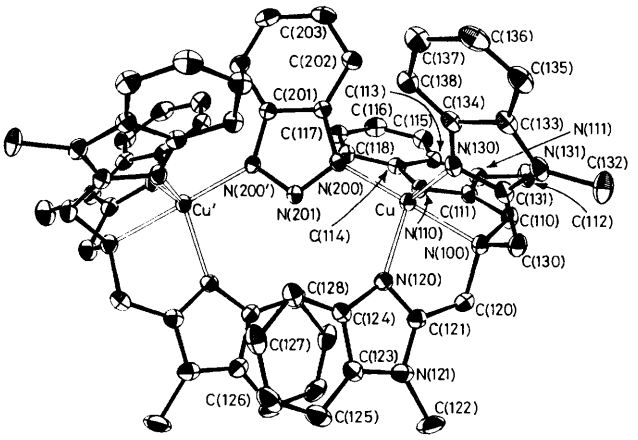

FIGURE 2 ORTEP drawing of the cation in $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ showing the anisotropic vibration ellipsoids (probability 20%). Hydrogen atoms have been omitted for clarity. Bond distances and angles are given in Tables 3 and 4 respectively

angles between the partially occupied atoms, which were included in the refinement, are not included in the Tables.

In Figure 2 a perspective view is shown of the binuclear cation together with the atom-numbering scheme used. Figure 3 gives the detailed co-ordination around each copper(II) ion and part of the bridging benzotriazolate anion.

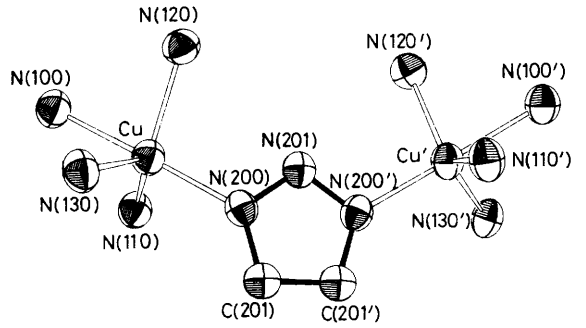

FIGURE 3 Co-ordination geometry of the copper atoms in $[Cu_2(tmbma)_2(bztz)][NO_3]_3$

The co-ordination geometry around each copper atom can be described as distorted trigonal bipyramidal. The copper atom does not exactly 'fit' in the basal plane [N(110), N(120), and N(130)], as can be seen from the N(100)–Cu–N angles of 80.4—81.8°. The copper atom is displaced 0.33 Å in the direction of the bridging benzotriazolate anion. The reason for this probably lies in the conformation of the ligand: if the copper atom lay in the basal plane, the angle Cu–N(110)–C(111) would be smaller than the presently found 111.6° [and so would the corresponding angles around N(120) and N(130)]; this would weaken the bonding of the copper atom by these nitrogen atoms. In other words, the lone pairs of electrons on N(110), N(120), and N(130) are not lying in the basal plane.

Another distortion from a regular trigonal-bipyramidal geometry is reflected in the N–Cu–N angles in the basal plane; they deviate from 120° and are far from equal (103.8—126.6°). The reason for this is the steric influence of the benzotriazolate anion; this is illustrated in Figure 4, which shows a projection along the Cu–

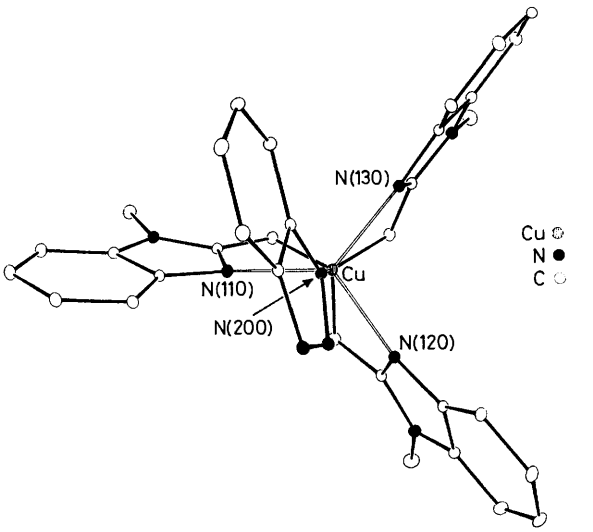

FIGURE 4 Part of the cation in $[Cu_2(tmbma)_2(bztz)][NO_3]_3$, showing the benzotriazolate group, one of the copper atoms, and one of the tmbma ligands. Projection along the Cu–N(100) vector, illustrating the tripod character of the ligand. The N(100) atom is hidden behind Cu

N(100) bond of one half of the cation. The benzimidazole group containing N(110) and the one containing N(130) are bent away from each other and from the phenyl ring of the benzotriazolate group. The N(110)–Cu–N(120) angle cannot be very small either, because of the interaction between the benzimidazole group containing N(120) and the symmetry-related group containing N(120') (see Figure 2). As a consequence, N(120)–Cu–N(130) is relatively small (103.8°).

In spite of these distortions, a trigonal bipyramid is undoubtedly the best description of the geometry around the copper atom in this compound; the structure is certainly not intermediate between square pyramidal and trigonal bipyramidal, as has frequently been found for five-co-ordinate copper(II) complexes.[39,40]

The angles and distances in the benzimidazole parts of the ligand are quite normal.[40-44] The phenyl and imidazole rings are planar, deviations from the least-squares planes through the non-hydrogen atoms of each imidazole or phenyl ring being $\leqslant 0.016$ Å. The dihedral angles between a phenyl ring and its corresponding imidazole ring are not significant: 1.43, 0.75, and 2.20° respectively. The copper atom is lying in the planes of

the imidazole rings; the deviations are 0.389, 0.117, and 0.020 Å for rings I, II, and III respectively.

Only a few structures of compounds containing benzotriazole [45] or the benzotriazolate anion [46-49] have been reported. In these structures the benzotriazolate anion is acting either as a unidentate ligand,[47] a tridentate bridging ligand,[48,49] or as a bidentate bridging ligand, co-ordinating through the nitrogen atoms corresponding to N(200) and N(201) in the present structure.[46] The

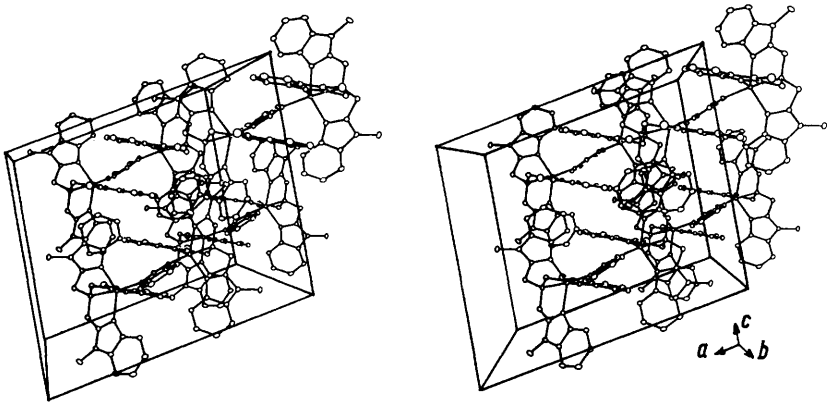

FIGURE 5 Stereodrawing of the unit cell of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$. The disordered anions are not shown

complex $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ is the first crystal structure of a compound in which the benzotriazolate anion is bidentate co-ordinating *via* N(200) and N(200′).

All angles and distances in the bridging benzotriazolate anion are normal [45-49] and the phenyl group and triazole ring are coplanar (dihedral angle = 0.74°). No flattening of the triazole group, as typically found for the corresponding atoms in imidazolate-bridged structures,[14,19] is observed; the angles N(200)–N(201)–N(200′) and C(201)–N(200)–N(201) do not deviate significantly from 108°.

A stereoscopic view of the packing of the $[Cu_2(tmbma)_2(bztz)]^{3+}$ cation is given in Figure 5. Since the anions are disordered, the lattice is probably stabilized by the parallel packing of the benzimidazole groups with N(120). The dihedral angle between this benzimidazole group and the symmetry-related group with N(120′) is 1.3°; for the other two benzimidazole groups the corresponding angles are 59.6 and 87.2° respectively. The spacing between the parallel layers is *ca.* 3.5 Å.

Magnetic Susceptibility and E.S.R. Data.—Variable-temperature (4.2—80 K) magnetic susceptibility data for the present compounds show antiferromagnetic interactions with a maximum in their susceptibility against temperature curves at *ca.* 20—50 K. The magnetism of these complexes is interpreted on the basis of the well known Bleaney–Bowers equation [50] with an additional term to account for paramagnetic impurities, equation (1). Herein PAR stands for a variable fraction

$$\chi_A = (1 - \mathrm{PAR})\frac{N\bar{g}^2\beta^2}{kT}\left[\frac{\exp(2J/kT)}{1 + 3\exp(2J/kT)}\right] + N_\alpha + \mathrm{PAR}\left(\frac{0.405}{T}\right) \quad (1)$$

of paramagnetic (probably monomeric) impurity (with an assumed magnetic moment of 1.80 B.M.* and hence a susceptibility of $0.405/T$ e.m.u. mol^{-1}). The temperature-independent paramagnetism N_α was taken as 60×10^{-6} e.m.u. mol^{-1} for copper.[51] The other symbols have their usual meaning. The parameters PAR, J, and $\bar{g}$ were varied in a least-squares procedure to get a best fit to the experimental data. As a typical example, the susceptibility against temperature data obtained for $[Cu_2(tmbma)_2(im)][ClO_4]_3$ are given in Figure 6 together with a theoretical curve calculated with equation (1) and with $J = 28$ cm^{-1}, $\bar{g} = 2.00$, and PAR = 0.052. The best-fit parameters for a selection of compounds are given in Table 5. The variation in the $\bar{g}$ values is quite large for

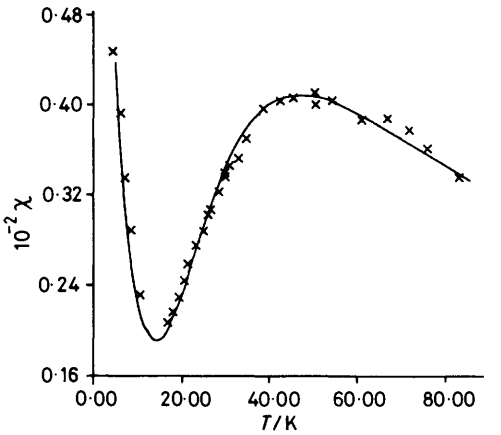

FIGURE 6 The temperature dependence of the magnetic susceptibility (χ/e.m.u. mol^{-1}) of $[Cu_2(tmbma)_2(im)][ClO_4]_3$. The solid line results from a least-squares fit to equation (1)

the various compounds. The $\bar{g}$ values also deviate from those obtained from the triplet e.s.r. spectra (Table 6). The origin for these deviations can be the result of several factors, such as errors in diamagnetic susceptibilities and temperature-independent paramagnetism, variations in the molecular weight due to loss of lattice water molecules, interdimer interactions, and small changes in the co-ordination sphere (bond angles) as a function of

* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2; 1 G = 10^{-4} T; 1 e.m.u. = $4\pi \times 10^{-6}$ m^3.

temperature. The J values, however, are hardly sensitive to these uncertainties because they are mainly determined by the position of the maximum in the susceptibility curve. For the listed examples the J values are supposed to be accurate to ± 1 cm^{-1}. A few samples which gave poorly defined maxima, resulting in less accurate parameters, are not listed in Table 5. Attempts to use the g values from the e.s.r. spectra in the fitting procedure yielded much poorer fits with only slightly larger J values (1—2 cm^{-1}).

TABLE 5

Least-squares fitting parameters for the magnetic data of some of the azolate-bridged binuclear copper compounds

Compound	J/cm^{-1}	$\bar{g}$	PAR *
$[Cu_2(tmbma)_2(im)][NO_3]_3 \cdot 4H_2O$	−28	1.91	0.034
$[Cu_2(tmbma)_2(im)][BF_4]_3$	−28	1.93	0.017
$[Cu_2(tmbma)_2(im)][ClO_4]_3$	−28	2.00	0.052
$[Cu_2(tmbma)_2(bzim)][NO_3]_3 \cdot 4H_2O$	−13	2.02	0.017
$[Cu_2(tmbma)_2(bzim)][BF_4]_3 \cdot H_2O$	−18	2.18	0.038
$[Cu_2(tmbma)_2(bztz)][NO_3]_3 \cdot 2H_2O$	−12	2.01	0.000
$[Cu_2(tmbma)_2(bztz)][ClO_4]_3 \cdot H_2O$	−10	2.03	0.011

* Fraction of monomeric paramagnetic impurity.

As can be seen in Table 5, the antiferromagnetic interactions ($J \approx -28$ cm^{-1}) of the compounds with imidazolate as bridging ligands are significantly larger than the interaction ($J = -10$ to -18 cm^{-1}) in compounds with benzimidazolate or benzotriazolate in the bridge. A possible explanation for this observation is given by Haddad and Hendrickson.[18] They suggested that the overlap of the d_{z^2} copper orbitals (containing the unpaired electrons) with the molecular orbitals of the imidazolate bridge, which most probably are involved in the copper–copper interaction, depends upon the angle α corresponding to Cu–N(200)–N(201): a larger angle would lead to a better overlap. In $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ this angle amounts to 114.0(4)° which is considerably smaller than the corresponding angle in a comparable compound with an imidazolate bridge,[16] 129(1)°, or in compounds with sterically unhindered imidazole ligands (average value for nine ligands: 126°).[52-54] The origin for this smaller angle is most likely the steric interaction of the phenyl ring of the bridging ligand with the tmbma ligand. The crystal structure of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ is the first example of a dimeric copper(II) compound having a benzo-substituted azole as a bridging group. The structure provides further support for the suggestion [18] that the magnitude of the magnetic interaction in imidazolate-bridged copper(II) dimers indeed depends upon the angle α in the bridge.

No explanation is put forward for the difference in J values for compounds with different anions and the same bridging group. The crystal structure of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$ suggests that the anions do not interfere with the bridge between the copper atoms. Only secondary effects, due to differences in crystal packing, may influence the magnitude of α, and therefore J.

The X-band and Q-band e.s.r. powder spectra of the present compounds are typical of $S = 1$ systems.[55-58] An example is depicted in Figure 7. These spectra can be interpreted using the formulae for the $\Delta m = 1$ bands given in ref. 55 and originally derived by Wasserman *et al.*[59] for organic triplets [equations (2)—(7)], where

$$H(X_1) = (2.0023/g_x)[(H_0 - D + E)(H_0 + 2E)]^{\frac{1}{2}} \quad (2)$$

$$H(Y_1) = (2.0023/g_y)[(H_0 - D - E)(H_0 - 2E)]^{\frac{1}{2}} \quad (3)$$

$$H(Z_1) = (2.0023/g_z)[(H_0 - D)^2 - E^2]^{\frac{1}{2}} \quad (4)$$

$$H(X_2) = (2.0023/g_x)\ [(H_0 + D - E)(H_0 - 2E)]^{\frac{1}{2}} \quad (5)$$

$$H(Y_2) = (2.0023/g_y)[(H_0 + D + E)(H_0 + 2E)]^{\frac{1}{2}} \quad (6)$$

$$H(Z_2) = (2.0023/g_z)[(H_0 + D)^2 - E^2]^{\frac{1}{2}} \quad (7)$$

$H(X_1)$ gives the first resonance field in the X direction, $H(X_2)$ gives the second resonance field in the X direction, *etc.*, H_0 is the resonance field for the free electron (at the given microwave frequency), and D and E are the axial

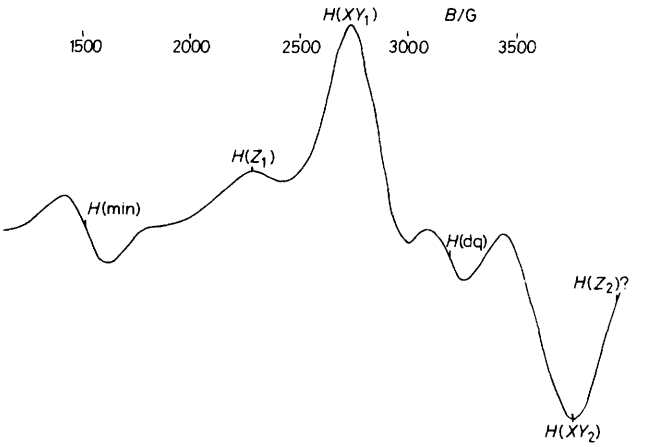

FIGURE 7 X-Band powder e.s.r. spectrum of $[Cu_2(tmbma)_2(im)][NO_3]_3 \cdot 4H_2O$. The weak signal at *ca.* 3 200 G is most likely due to a monomeric impurity

and rhombic zero-field splitting parameters respectively (expressed in Gauss). In addition to these $\Delta m_s = 1$ lines, two formally forbidden $\Delta m_s = 2$ transitions may be observed in the $S = 1$ systems with resonance fields [55] given by equations (8) and (9) where H(min) gives the

$$H(\text{min}) = (2.0023/g_{\text{min.}})[H_0^2/4 - D^2/3 - E^2]^{\frac{1}{2}} \quad (8)$$

$$H(\text{dq}) = (2.0023/g_{\text{av.}})[H_0^2 - D^2/3 - E^2]^{\frac{1}{2}} \quad (9)$$

resonance field for a formally forbidden transition between states with $m_s = -1$ and $+1$ respectively and H(dq) is a seldomly observed double-quantum transition (two photons are absorbed). In Figure 7 H(dq) might be hidden under the signal of the monomeric impurity at *ca.* 3 200 G. The parameters $g_{\text{min.}}$ and $g_{\text{av.}}$ are related to g_x, g_y, and g_z by the expressions (10)—(13).[55]

$$g_{\text{min.}} = (g_\perp^2 \sin^2 a + g_z^2 \cos^2 a)^{\frac{1}{2}} \quad (10)$$

$$g_\perp = (g_x g_y)^{\frac{1}{2}} \quad (11)$$

$$\cos^2 a = [9 - 4(D2.0023\beta/h\nu)^2]/[27 - 36(D2.0023\beta/h\nu)^2] \quad (12)$$

$$g_{\text{av.}} = (\tfrac{2}{3} g_\perp^2 + \tfrac{1}{3} g_z^2)^{\frac{1}{2}} \quad (13)$$

In most of the present compounds, $H(X_1)$ cannot be observed separately from $H(Y_1)$, and $H(X_2)$ not from $H(Y_2)$, indicating that the rhombic zero-field splitting E is either very small or equal to zero and that g_x and g_y are equal. The spectra of $[Cu_2(tmbma)_2(bztz)][ClO_4]_3$ and $[Cu_2(tmbma)(bztz)][NO_3]_3$, however, can only be interpreted assuming a rather large rhombic zero-field splitting, E. Rough values for $g_{\|}$, $g_{\perp}$, D, and E which reasonably fit with the observed spectra (X-band and Q-band) of the bridged compounds are given in Table 6.

TABLE 6

E.s.r. parameters derived from X-band and Q-band powder spectra for the azolate-bridged copper dimers

Compound	$\lvert D \rvert$ cm^{-1}	$\lvert E \rvert$ cm^{-1}	$g_{\|}$	$g_{\perp}$
$[Cu_2(tmbma)_2(im)][NO_3]_3 \cdot 4H_2O$	0.12	0.00	2.16	2.14
$[Cu_2(tmbma)_2(im)][BF_4]_3$	0.09	0.00	2.16	2.16
$[Cu_2(tmbma)_2(im)][ClO_4]_3$	0.09	0.00	2.16	2.14
$[Cu_2(tmbma)_2(bzim)][NO_3]_3 \cdot 4H_2O$	0.08	0.00	2.17	2.16
$[Cu_2(tmbma)_2(bzim)][BF_4]_3 \cdot H_2O$	0.13	0.00	1.90 *	2.11
$[Cu_2(tmbma)_2(bzim)][ClO_4]_3 \cdot 2H_2O$	0.10	0.00	2.19	2.14
$[Cu_2(tmbma)_2(bztz)][NO_3]_3 \cdot 2H_2O$	0.10	0.025	2.16	2.16
$[Cu_2(tmbma)_2(bztz)][BF_4]_3 \cdot 2H_2O$	0.13	0.00	1.89 *	2.10
$[Cu_2(tmbma)_2(bztz)][ClO_4]_3 \cdot H_2O$	0.09	0.025	2.21	2.15

* Not very accurate, due to overlap of $H(XY_2)$ and $H(Z_2)$.

The D values for these compounds are in the range normally found for copper(II) dimers.[56-58] Only a few of the present compounds show spectra with $g_{\|} < g_{\perp}$ (as expected for trigonal-bipyramidal geometries with a d_{z^2} ground state). Since the magnitude of the magnetic interactions does not show large unexpected differences, all these compounds are supposed to have roughly the same geometry as the one found for $[Cu_2(tmbma)_2(bztz)][NO_3]_3$. Further, one must bear in mind that this method of determining g values is not very accurate.

Attempts to synthesize compounds in which imidazolate bridges between Cu^{II} and Zn^{II}, in order to determine more accurate values for $g_{\|}$, and $g_{\perp}$, have failed so far; they yielded complexes which were not isomorphous with the present ones (i.r. and X-ray powder diagrams). The differences between g values determined from magnetic susceptibility measurements and from e.s.r. spectra, which are significant in a few cases, are not further discussed. Origins for the large uncertainties were given above.

E.s.r. spectra of the compounds in solution (dimethyl sulphoxide or methanol) indicate that decomposition occurs, since normal $S = \frac{1}{2}$ spectra were obtained. Probably dimeric units exist in solution only in a pH-dependent equilibrium with the monomers;[14] this was not investigated further.

Concluding Remarks.—The compounds described in this paper are the first examples of imidazolate-bridged copper(II) dimers, which are stabilized by a ligand containing the (biologically relevant) imidazole groups, *i.e.* tmbma. The dimeric nature of the compounds is indicated by magnetic susceptibility measurements and by e.s.r. spectra and is proved by the X-ray crystal-structure determination of $[Cu_2(tmbma)_2(bztz)][NO_3]_3$.

The results of this work, especially the small magnetic interactions J, add proof to the suggestions [12,13] that an imidazolate-bridged Fe^{III}–Cu^{II} centre is not likely to be the origin of the anomalous magnetic behaviour of cytochrome *c* oxidase.

Finally, it should be remarked that the crystal structure described in this paper supports the suggested trigonal-bipyramidal geometry for some of the tbma compounds described earlier.[35]

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