Copper(I) and Copper(II) Chelates containing Imidazole and Thioether Groups; Synthesis of the Ligand 1,2-Bis(benzimidazol-2′-ylmethylthio)-benzene (bbtb) and the *X*-Ray Crystal Structure at −52 °C of [Cu(bbtb)(H_2O)][ClO_4]$_2$·5EtOH †

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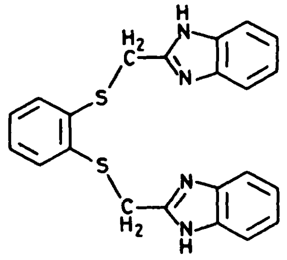
Stable copper(I) and copper(II) complexes of the title ligand (bbtb) have been prepared. The design of the ligand prevents planar four-co-ordination of Cu^{II}. The *X*-ray structure of [Cu(bbtb)(H_2O)][ClO_4]$_2$·5EtOH shows that the co-ordination geometry around the metal ion is trigonal bipyramidal. Two benzimidazole nitrogen atoms occupy axial positions, the equatorial positions being occupied by the two thioether sulphur atoms and an oxygen atom of a co-ordinated water molecule. The structure is compared with recently solved structures of closely related imidazole–thioether chelates. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 18.865(3), b = 12.652(2), c = 17.902(7) Å, β = 101.99(2)°, and Z = 4. The intensities of 5 095 independent reflections were measured on an automatic diffractometer at −52 °C (to prevent decomposition). The structure was solved by direct methods and refined using full-matrix least-squares techniques to a residual R of 0.069 for 2 869 reflections with $I > 2\sigma(I)$. The e.s.r. spectrum of the solid compound [Cu(bbtb)][ClO_4]$_2$·2H_2O is ' exchange narrowed ' and shows only one signal. The ligand-field spectrum is consistent with a trigonal-bipyramidal geometry. The e.s.r. and ligand-field data indicate a co-ordination geometry in solution which is different from the solid state, and in which the unpaired electron is mainly in a $d_{x^2-y^2}$ orbital.

SINCE the discovery of the presence of copper in different proteins, many publications have appeared in the literature dealing with spectroscopic, electrochemical, structural, and functional properties of these systems.[1-8] An interesting class is formed by the blue (type 1) proteins such as azurin, plastocyanin, and stellacyanin. The copper atom at the active site is known to be responsible for electron transport by these enzymes.[9] *X*-Ray structure determinations have shown [10,11] that the copper atom in plastocyanin and azurin is surrounded by two co-ordinating imidazole groups (of histidine), a thioether group (of methionine), and a thiolate function (of cysteine) in a distorted tetrahedral arrangement. The absence of a substantial difference in the shape of the co-ordination polyhedron around copper in the oxidized and reduced forms of the enzymes seems to allow the easy $Cu^{II} \leftrightarrow Cu^{I}$ transition required for the electron-transport process.[7] Another factor determining the redox properties is considered to be stabilization of Cu^{I} by a suitable co-ordination geometry and by ' soft ' donor atoms like sulphur.[12-14] In this respect, the reluctance of thioethers to co-ordinate to Cu^{II} is illustrative. In nearly all cases Cu–S (thioether) co-ordination can only be accomplished by incorporating the thioether donor atom(s) in a multidentate chelating ligand. This concept is widely used in the design of model compounds.[15-18] Recent work has shown [15,19,20] that variations in the relative positions of the thioether sulphurs in the ligand provide a method for controlling the stereochemistry of the complexes.

We now report the synthesis of the new potentially quadridentate ligand 1,2-bis(benzimidazol-2′-ylmethylthio)benzene (bbtb) and the determination of the crystal-structure of [Cu(bbtb)(H_2O)][ClO_4]$_2$·5EtOH by *X*-ray methods. The present benzimidazole thioether ligand is new in the sense that the sulphur atoms are part of the geometrically rigid dithiobenzene group. The results of the present study are compared with those of other recent work on closely related compounds.[18,19]



bbtb

EXPERIMENTAL

Synthesis of the Ligand bbtb.—The four-step reaction sequence used for the preparation of bbtb is shown in the Scheme. The first three steps (i)—(iii) are a modification of the synthesis of *o*-phenylenedithiol (3) which was first described by Hünig and Fleckenstein.[21]

Step (i). This step, involving diazotation of *o*-aminothiophenol with $NaNO_2$ in glacial acetic acid followed by steam distillation of the crude reaction product, was carried out three times in yields up to 69%. *o*-Aminothiophenol (12.5 g, 0.1 mol) was added dropwise to glacial acetic acid (900 cm³) (in a nitrogen atmosphere). After cooling, a solution of $NaNO_2$ (7.0 g, 0.1 mol) in water (50 cm³) was added during 15 min at 20—25 °C. This procedure of adding 0.1 mol of reactant followed by reaction with 0.1 mol of $NaNO_2$ was repeated until 1.0 mol of *o*-aminothiophenol was consumed. After stirring overnight the reaction product was purified by steam distillation. The crystalline solid which formed in the cooled distillate was filtered off and dried *in vacuo* at room temperature (r.t.). More product was obtained by

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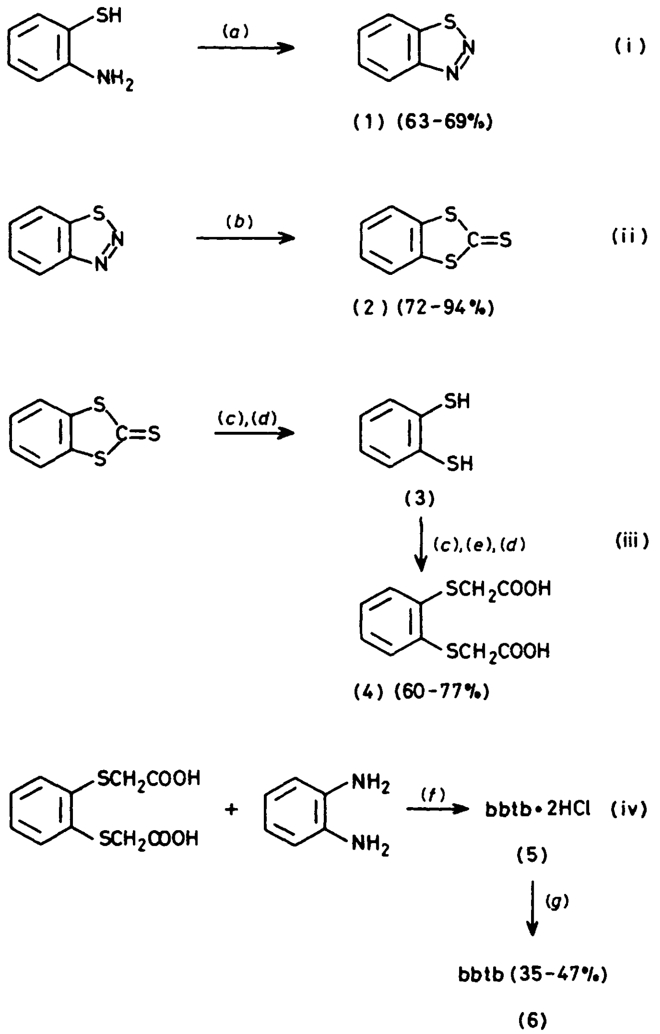
† Aqua[1,2-bis(benzimidazol-2′-ylmethylthio)benzene-$N^{3\prime}N^{3\prime\prime}$-$SS'$]copper(II) perchlorate–ethanol (1/5).



SCHEME Synthesis of the ligand bbtb. (*a*) $NaNO_2$ (H_2O), $MeCO_2H$; (*b*) CS_2 (220 °C), 6 h in autoclave; (*c*) KOH; (*d*) HCl; (*e*) $ClCH_2CO_2^-$; (*f*) HCl (4 mol dm^{-3}), 16 h; (*g*) NH_3 (aq), excess

repeated extraction of the mother-liquor with methylene chloride, washing with a 5% $NaHCO_3$ solution, drying over $MgSO_4$, and evaporating the solvent. The total yield of 1,2,3-benzothiadiazole (1) was 17.7 g (65%).

Step (ii). The product of step (i) was used without further purification for step (ii), being the reaction of compound (1) with CS_2 for 6 h at 220 °C in an autoclave (150 cm^3). This reaction, yielding 1,3-benzodithiole-2-thione (2), was carried out ten times in yields amounting to 94%. An increased reactant concentration compared to the one reported by Hünig and Fleckenstein [21] as well as the absence of 50 atm * N_2 pressure did not affect the product yield. A solution of (1) (15.0 g, 0.11 mmol) in CS_2 (100 cm^3) was kept in an autoclave at 220 °C for 6 h. The reaction mixture was then dissolved in $CHCl_3$, and evaporation of the solvent yielded crude (2) (14.6 g, 72%). Recrystallization from *ca.* 1 : 1 $CHCl_3$–light petroleum (b.p. 40—60 °C) yielded yellow needles, m.p. 163—164 °C.

Step (iii). The recrystallized thione (2) was hydrolyzed in alkaline medium under nitrogen and the resulting compound (3) was not isolated but immediately converted into 1,2-bis(carboxymethylthio)benzene (4) by reaction with monochloroacetic acid. This reaction was carried out three times with yields amounting to 77% for a reaction on 0.05 mol scale. Compound (2) (9.23 g, 0.050 mol) was added to a refluxing solution of KOH (15.1 g, 0.269 mol) in glycol monomethyl ether (170 cm^3) which was flushed with nitrogen, and the reaction mixture was refluxed for 3 h. The solution was acidified with deoxygenated concentrated HCl (21 cm^3) (COS evolution!) [21] and the precipitated dithiol (3) was dissolved by adding a deoxygenated solution of KOH (15.1 g) in water (75 cm^3). Then, a solution of KOH (5.63 g, 0.100 mol) and $ClCH_2COOH$ (9.48 g, 0.100 mol) in water (50 cm^3) was added dropwise during 15 min, the reaction mixture was refluxed for a further hour, again acidified, and cooled. The precipitated product was filtered off, washed twice with ice-cold water to remove the KCl present, and dried *in vacuo* at 80 °C. Yield 9.95 g of a light brown powder, (4) (77%), m.p. 195 °C (decomp.). Infrared spectrum in KBr: 3 460(br) (COOH); 1 710 cm^{-1} (C=O). ^{1}H N.m.r. ([$^2H_6$]-dmso, $SiMe_4$ as reference): δ 12.99 (2 H, br, COOH), 7.27 (4 H, symmetric m, aromatic C–H), and 3.78 (4 H, s, CH_2).

Step (iv). This step involved the conversion of crude compound (4) into the HCl salt of bbtb (5) by means of the well known Phillips condensation [16] in 4 mol dm^{-3} HCl, and subsequent treatment with excess of ammonia to obtain the free ligand (6). This condensation was carried out twice in yields of 35 and 47%, respectively. A mixture of compound (4) (9.88 g, 0.038 mol) and *o*-phenylenediamine (8.27 g, 0.077 mol) in HCl (4 mol dm^{-3}, 210 cm^3) was refluxed for 24 h. Some activated charcoal was added, and after another few minutes of refluxing the solution was filtered whilst hot. The filtrate was cooled in ice and the separated brown crystals were filtered off and treated with excess of ammonia. The, now white, product (6) was dried *in vacuo* at 80 °C (yield 5.37 g, 35%). After recrystallization from ethanol–water (9 : 1 v/v) a white product was obtained, m.p. 181—184 °C (decomp.). Infrared spectrum in KBr: 738 cm^{-1} (benzimidazole groups). For the ^{1}H n.m.r. spectrum, see *Spectroscopic Results*.

Preparation of Copper(II) *Complexes of* bbtb *with* $CuCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(BF_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, *and* $Cu(CF_3SO_3)_2$.—Ligand bbtb (0.5 mmol) was dissolved in refluxing ethanol (15 cm^3) and added to a solution of the copper(II) salt (0.5 mmol) in ethanol (5 cm^3), changing the solution to dark green. After immediate filtration, the solutions were stored in the cold. Crystallization only occurred in the case of the perchlorate compound. These crystals, long thin needles, were stable at −20 °C but dissolved again upon warming to room temperature. The addition of a little triethyl orthoformate for dehydration appeared to improve the crystallization process considerably. The crystals of the perchlorate compound deteriorated when isolated from the mother-liquor, indicating loss of alcohol of crystallization. The remaining solid powder was dried *in vacuo* at 60 °C and stored in a desiccator. Elemental analysis agreed with a composition $Cu(bbtb)(ClO_4)_2{\cdot}2H_2O$ (see *General*).

Preparation of a Copper(I) *Complex of* bbtb *with* $Cu(ClO_4)$.—The perchlorate, $Cu(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol), was dissolved in CH_3CN (8 cm^3) and stirred with excess of copper powder for 10 min. The colourless solution was filtered into an oxygen-free refluxing solution of bbtb (1.0 mmol) in ethanol (30 cm^3). After stirring in a nitrogen atmosphere for 45 min the reaction mixture was cooled in an ice-bath.

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* Throughout this paper: 1 atm = 101 325 N m^{-2}; 1 G = 10^{-4} T.

Then dry diethyl ether (70 cm^3) was added, causing precipitation of a white solid. This product was rapidly filtered off in a nitrogen stream, dried *in vacuo* at 60 °C, and stored in a desiccator. Elemental analysis agreed with a composition $Cu(bbtb)(ClO_4)\cdot 1.5H_2O$ (see *General*). When dry, this compound appeared to be stable in air; in dimethyl sulphoxide (dmso) solution a rapid change from colourless to green indicated a rapid oxidation of Cu^I to Cu^{II}.

Physical Measurements.—Infrared spectra of the solid compounds were recorded on a Perkin-Elmer 580 spectrophotometer as KBr pellets and Nujol mulls (4 000—250 cm^{-1}). Electronic spectra (35 000—4 000 cm^{-1}) for solutions were obtained on a Beckman DK-2A spectrophotometer and for powders on a similar apparatus fitted with a diffuse-reflectance unit. E.s.r. spectra at X-band frequency were obtained with a Varian E-3 spectrometer at 77 K or r.t. Proton n.m.r. spectra were recorded at 100 MHz on a JEOL-PS 100 spectrometer. Elemental analyses were performed by Dr. Pascher, Bonn, Germany and at the University of Technology, Eindhoven, The Netherlands.

X-*Ray Methods and Structure Determination.*—Because of the previously mentioned instability of the crystals of $[Cu(bbtb)(H_2O)][ClO_4]_2\cdot 5EtOH$ at r.t. all manipulations with this compound were carried out in a cold room (−20 °C). A needle-shaped crystal of approximate dimensions 0.60 × 0.20 × 0.18 mm was picked out of an alcoholic solution of this complex (prepared as described above and containing a few cm^3 of triethyl orthoformate) at −20 °C and immediately sealed in a thin-walled glass capillary tube together with a drop of mother-liquor. Precise lattice constants and the space group ($P2_1/n$) were determined from diffractometer data obtained at −52 °C. Least-squares refinement of the angular settings of 24 reflections with $11 < \theta < 13°$ gave the unit-cell dimensions: a = 18.865(3), b = 12.652(2), c = 17.902(7) Å, β = 101.99(2)°, and U = 4 180 Å^3. The calculated density (D_c) of 1.452 g cm^{-3} is in reasonable agreement with the experimental value (D_m) of 1.40(2) g cm^{-3} (measured by flotation in CCl_4–EtOH) for $Z = 4$. Intensity data were collected on a Nonius CAD-4 diffractometer (ω scans) for all reflections with $2 < \theta < 22°$ and with $h > 0$ using graphite-monochromated Mo-K_α radiation. The scanning rate was adjusted to the required precision of $\sigma(I) < 0.02I$, 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 peak scan count, and B_1 and B_2 are the low- and high-angle background counts respectively. Two standard reflections were measured after every 2 400 s of radiation time to check for instrumental instability and crystal decomposition; during the data collection there was a 10% decrease in intensity for which the data were corrected. The measurement of the intensity of a suitable reflection at different azimuthal positions suggested that no absorption correction was necessary (maximal variation 5%; μ = 8.1 cm^{-1}).

The intensities of 5 400 reflections were measured, 5 095 of which were symmetry independent. 2 869 Reflections with $I > 2\sigma(I)$ were considered as observed. The measured intensities were corrected for Lorentz and polarization effects. The structure was solved in space group $P2_1/n$ using the direct methods program MULTAN 78 and refined with full-matrix least-squares techniques. All non-hydrogen atoms were located in a series of refinements and subsequent Fourier syntheses. In further refinement cycles followed by difference Fourier syntheses all hydrogen atoms could also be found, except the alkyl hydrogens of the five ethanol molecules present in the structure. Disorder in the alkyl groups, as reflected by high thermal parameters for the alcohol C atoms, made it impossible to find proper positions for the hydrogens attached to these carbon atoms. High thermal parameters were also found for the oxygen atoms of one of the two perchlorate anions present. Because of this, the alcohol C atoms and the perchlorate O atoms were refined isotropically in further refinement cycles. All other non-hydrogen atoms were anisotropically refined. The isotropic thermal parameters of all hydrogen atoms were fixed at a value of B = 3.0 Å^2 and only their positions were refined. In all refinement stages unit weights were used.

A final difference Fourier synthesis showed no residual electron densities above 0.4 e Å^{-3} except for some density (0.5—0.6 e Å^{-3}) in the vicinity of one of the chlorine atoms. These peaks, most probably representing some disorder in the positions of the perchlorate anion, were not included in the refinement.

The final values of the residuals are: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.069$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.074$ for the 2 869 observed reflections $[I > 2\sigma(I)]$ used in the refinement.

Atomic scattering factors for neutral atoms were taken from ref. 22 and where appropriate used with correction for the anomalous scattering.

Positional parameters of non-hydrogen and hydrogen atoms are given in Tables 1 and 2 respectively. Observed

TABLE 1

Positional parameters (× 10^4) of the non-hydrogen atoms * of $[Cu(bbtb)(H_2O)][ClO_4]_2\cdot 5EtOH$, with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Cu	5 004(1)	788(1)	2 494(1)
S(1)	4 055(2)	−585(3)	2 162(2)
S(2)	5 894(2)	−633(2)	2 833(2)
N(1)	5 290(5)	719(9)	1 508(5)
N(2)	6 004(5)	349(9)	718(6)
N(3)	4 723(5)	729(9)	3 478(5)
N(4)	3 996(6)	471(10)	4 267(6)
C(1)	4 579(6)	−1 761(12)	2 375(6)
C(2)	5 330(7)	−1 782(11)	2 631(6)
C(3)	5 676(8)	−2 752(13)	2 780(8)
C(4)	5 282(9)	−3 681(12)	2 663(8)
C(5)	4 545(8)	−3 649(13)	2 406(9)
C(6)	4 208(8)	−2 711(13)	2 270(8)
C(7)	3 683(7)	−430(13)	3 020(8)
C(8)	4 131(7)	249(10)	3 582(7)
C(9)	4 530(7)	1 123(11)	4 648(7)
C(10)	5 006(7)	1 293(10)	4 150(6)
C(11)	5 614(7)	1 908(12)	4 363(7)
C(12)	5 730(8)	2 364(13)	5 074(8)
C(13)	5 254(9)	2 221(12)	5 563(8)
C(14)	4 659(9)	1 603(13)	5 363(7)
C(15)	6 289(8)	−551(12)	1 988(7)
C(16)	5 852(6)	173(10)	1 409(6)
C(17)	5 504(6)	1 064(11)	347(6)
C(18)	5 040(7)	1 277(10)	839(7)
C(19)	4 450(7)	1 923(13)	621(7)
C(20)	4 350(8)	2 396(12)	−98(7)
C(21)	4 833(8)	2 198(12)	−580(7)
C(22)	5 405(7)	1 534(12)	−374(7)
Cl(1)	2 579(2)	1 740(4)	1 856(2)
Cl(2)	7 448(2)	1 912(3)	2 689(2)
O(1)	5 012(7)	2 343(6)	2 500(7)
O(A)	5 910(7)	3 653(12)	2 012(7)
O(B)	3 989(7)	3 656(10)	2 789(9)

TABLE 1 (*continued*)

Atom	*X/a*	*Y/b*	*Z/c*
O(C)	7 144(7)	−442(13)	132(8)
O(D)	2 962(6)	−89(9)	5 045(6)
O(E)	2 687(6)	1 735(9)	5 758(6)
O(11)	2 466(11)	2 804(19)	1 906(11)
O(21)	3 315(8)	1 517(12)	1 928(8)
O(31)	2 332(10)	1 188(15)	2 426(11)
O(41)	2 260(17)	1 400(26)	1 137(18)
O(12)	7 366(5)	2 921(9)	2 294(6)
O(22)	7 636(6)	1 130(9)	2 201(6)
O(32)	8 020(5)	2 013(9)	3 357(6)
O(42)	6 765(5)	1 638(9)	2 890(6)
C(A1)	5 686(22)	4 104(35)	1 198(23)
C(A2)	5 881(29)	4 825(42)	1 075(28)
C(B1)	3 819(13)	3 811(19)	3 535(13)
C(B2)	4 397(13)	4 416(19)	3 982(13)
C(C1)	7 765(14)	−1 000(20)	713(13)
C(C2)	8 353(14)	−451(20)	879(13)
C(D1)	2 374(9)	−832(14)	4 832(9)
C(D2)	1 762(11)	−338(17)	4 230(11)
C(E1)	2 334(11)	2 614(16)	5 353(11)
C(E2)	2 503(11)	2 693(16)	4 573(11)

* The atomic labels are explained in Figure 1. The oxygen atom of the water molecule is designated by O(1), the oxygen atoms of the alcohol molecules by O(A)—O(E), and the alcohol C atoms by C(A1),C(A2)—C(E1),C(E2). The perchlorate oxygen atoms are designated by O(11)—O(41) [attached to Cl(1)] and O(12)—O(42) [attached to Cl(2)].

TABLE 2

Positional parameters ($\times 10^3$) of hydrogen atoms [a] in $[Cu(bbtb)(H_2O)][ClO_4]_2\cdot 5EtOH$, with estimated standard deviations in parentheses [b]

Atom	*X/a*	*Y/b*	*Z/c*
H(N2)	636(7)	17(11)	64(7)
H(N4)	376(7)	15(11)	448(7)
H(3)	613(7)	−272(11)	298(7)
H(4)	552(7)	−430(11)	274(7)
H(5)	433(7)	−417(11)	230(7)
H(6)	385(7)	−264(13)	216(8)
H(7A)	328(7)	−24(11)	291(7)
H(7B)	358(7)	−104(10)	322(7)
H(11)	592(7)	204(11)	409(7)
H(12)	615(7)	278(10)	524(6)
H(13)	539(7)	253(10)	601(7)
H(14)	438(7)	147(11)	562(7)
H(15A)	627(6)	−123(10)	173(7)
H(15B)	674(7)	−25(10)	217(7)
H(19)	409(7)	210(10)	88(7)
H(20)	393(6)	284(10)	−29(6)
H(21)	473(6)	259(10)	−102(7)
H(22)	565(7)	137(10)	−67(7)
H(O1A)	534(7)	267(11)	233(7)
H(O1B)	469(8)	264(12)	249(8)
H(OA)	616(7)	410(11)	149(7)
H(OB)	365(7)	311(10)	271(7)
H(OC)	729(8)	−54(13)	−15(8)
H(OD)	285(8)	27(12)	522(9)
H(OE)	256(7)	196(11)	610(7)

[a] The H numbering corresponds with the numbering of non-hydrogen atoms; hydrogens attached to the methylene carbons C(7) and C(15) are distinguished by A and B, as are the two hydrogens of the water molecule. The symbols H(OA)—H(OE) represent hydrogens attached to the alcohol-oxygen atoms O(A)—O(E); H(N2) and H(N4) are attached to N(2) and N(4), respectively. The aliphatic hydrogen atoms of the alcohol molecules were not included in the refinement (see text). [b] All isotropic thermal parameters are fixed at a value of $B = 3.0$ Å^2.

and calculated structure factors, thermal parameters of isotropically and anisotropically refined non-hydrogen atoms, and least-squares plane data are available in Supplementary Publication No. SUP 23270 (13 pp.).*

RESULTS AND DISCUSSION

General.—The ligand bbtb was characterized by its melting point, elemental analysis, and by i.r. and ^1H n.m.r. spectral data. Solid $[Cu(bbtb)][ClO_4]_2\cdot 2H_2O$ was characterized by elemental analysis, its i.r. spectrum, and by electronic spectra (e.s.r., ligand field). Alcoholic solutions of the other copper(II)–bbtb complexes were characterized by ligand-field and e.s.r. spectral data only. Finally, the copper(I) compound $[Cu(bbtb)][ClO_4]\cdot 1.5H_2O$ was characterized by elemental analysis and i.r. spectral data. Unfortunately, no reproducible n.m.r. spectrum could be obtained, most probably due to the presence of traces of paramagnetic Cu^{II} in the solution. Elemental analyses of bbtb and its solid copper(II) and copper(I) complexes are given in Table 3. Calculated and experimental values are in reasonable agreement.

TABLE 3

Elemental analyses of bbtb and two of its copper complexes (calculated values in parentheses)

Compound	Analysis (%)			
	C	H	N	S
$bbtb\cdot 2H_2O$	61.2	5.05	12.8	14.6
	(60.3)	(5.05)	(12.8)	(14.6)
$[Cu(bbtb)][ClO_4]_2\cdot 2H_2O$	37.9	3.00	7.85	
	(37.7)	(3.15)	(8.00)	
$[Cu(bbtb)][ClO_4]\cdot 1.5H_2O$	44.6	3.15	9.25	
	(44.6)	(3.55)	(9.45)	

Spectroscopic Results.—The ^1H n.m.r. spectrum of bbtb (solvent $[^2H_6]$dmso, reference $SiMe_4$) shows two aromatic multiplets at close distance [δ 7.50 (100) and 7.12 (90) p.p.m.; relative intensities given in parentheses] which, because of the absence of lower field signals, probably represent not only the 12 aromatic hydrogens but also the two N–*H* in the benzimidazole groups. A sharp methylene singlet at δ 4.44 (46) p.p.m. represents the four remaining hydrogens present in the ligand molecule. The i.r. spectrum of bbtb shows a strong absorption at 738 cm^{-1} which is assigned to the benzimidazole group. Ligand-field and e.s.r. spectral data of $[Cu(bbtb)][ClO_4]_2\cdot 2H_2O$ are listed in Table 4.

TABLE 4

Ligand-field (cm^{-1}) and *X*-band e.s.r. data (w = weak, s = strong)

Compound	Maxima	g [a]	$g_{\parallel}$ [b]	$g_{\perp}$ [b]	$A_{\parallel}$ [b]/G
$[Cu(bbtb)][ClO_4]_2\cdot 2H_2O$	15 900w, 11 800s [a]	2.10			
$[Cu(bbtb)][ClO_4]_2$	14 500 (120) [c]		2.32	2.06	140

[a] Polycrystalline (r.t.). [b] Frozen ethanol solution (77 K). [c] Ethanol solution; ε (in $dm^3\ mol^{-1}\ cm^{-1}$) in parentheses.

In the solid-state visible reflectance spectrum of $[Cu(bbtb)][ClO_4]_2\cdot 2H_2O$, the low-frequency transition is more intense than the high-frequency band (the two components of the visible absorption have been assigned to $d_{xz},d_{yz}\rightarrow d_{z^2}$ and $d_{xy},d_{x^2-y^2}\rightarrow d_{z^2}$ transitions respectively[23]). This is indicative of trigonal-bipyramidal co-ordination.[23] In ethanol solution, however, only one

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

broad band is observed, suggesting a change in geometry around the copper atom, most probably due to additional solvation of the copper ion.

For a powdered sample of $[Cu(bbtb)][ClO_4]_2{\cdot}2H_2O$ the *X*-band e.s.r. spectrum recorded at r.t. (see Table 4) shows only a single resonance. Presumably, the solid is not magnetically dilute enough to yield an e.s.r. spectrum that allows a firm conclusion about the solid-state geometry. In frozen ethanol solution, however, the e.s.r. spectrum shows two absorptions: $g_{\parallel} = 2.32$ and $g_{\perp} = 2.06$. The hyperfine splitting of the parallel component is well resolved with $A_{\parallel} = 140$ G. These values are consistent with an elongated tetragonal-octahedral, square-planar, or square-based pyramidal stereochemistry but are not likely to arise from copper(II) in a trigonal-bipyramidal environment.[23,24]

In the i.r. spectrum of $[Cu(bbtb)][ClO_4]_2{\cdot}2H_2O$ there is no indication for co-ordination of the anions, since only unsplit asymmetric stretching vibrations (Cl–O) are found near 1 100 cm^{-1}. The same phenomenon applies to the i.r. spectrum of the corresponding copper(I) compound. In both cases the absorption at 1 100 cm^{-1} is broad; this is most likely due to hydrogen bonding with OH groups of water and ethanol molecules (see below).

Crystal Structure.—In crystals of $[Cu(bbtb)(H_2O)][ClO_4]_2{\cdot}5EtOH$ the co-ordination geometry around copper(II) is best described as trigonal bipyramidal with two thioether sulphur atoms, an oxygen atom of a co-ordinated water molecule occupying equatorial positions, and two benzimidazole nitrogen atoms occupying axial sites. The structure of the $[Cu(bbtb)(H_2O)]^{2+}$ cation is shown in Figure 1, together with the atomic numbering scheme used. Interatomic distances and interbond angles are listed in Tables 5 and 6, respectively.

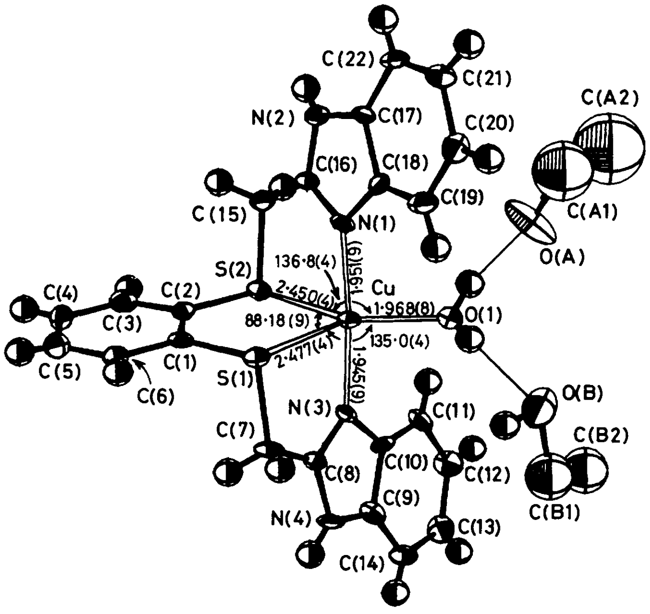

FIGURE 1 ORTEP drawing of the $[Cu(bbtb)(H_2O)]^{2+}$ cation, showing the atomic labelling and the thermal vibration ellipsoids of the atoms (40% probability). The two ethanol molecules which are hydrogen-bonded to the co-ordinated water molecule are labelled (A) and (B)

The N(1)–Cu–N(3) angle of 175.2(3)° is not much different from the ' ideal ' angle of 180°, whereas the S(1)–Cu–S(2) angle of 88.18(9)° is much smaller than the ' ideal ' angle of 120°. The latter is a consequence of the *o*-phenylene bridge between the two sulphur atoms. The Cu–S bond lengths of 2.477(4) and 2.450(4) Å and the

TABLE 5

Interatomic distances (Å) in $[Cu(bbtb)(H_2O)][ClO_4]_2{\cdot}5EtOH$, with estimated standard deviations in parentheses [a]

Cu–S(1)	2.477(4)	C(18)–C(19)	1.37(2)
Cu–S(2)	2.450(4)	C(19)–C(20)	1.40(2)
Cu–N(1)	1.951(9)	C(20)–C(21)	1.40(2)
Cu–N(3)	1.945(9)	C(21)–C(22)	1.36(2)
Cu–O(1)	1.968(8)	C(17)–C(22)	1.40(2)
S(1)–C(1)	1.78(1)		
S(1)–C(7)	1.83(1)	Cl(1)–O(11)	1.37(2)
S(2)–C(2)	1.79(1)	Cl(1)–O(21)	1.40(1)
S(2)–C(15)	1.82(1)	Cl(1)–O(31)	1.40(2)
N(1)–C(16)	1.31(1)	Cl(1)–O(41)	1.37(3)
N(1)–C(18)	1.39(2)	Cl(2)–O(12)	1.45(1)
N(2)–C(16)	1.34(1)	Cl(2)–O(22)	1.41(1)
N(2)–C(17)	1.37(2)	Cl(2)–O(32)	1.44(1)
N(3)–C(8)	1.32(2)	Cl(2)–O(42)	1.45(1)
N(3)–C(10)	1.40(2)		
N(4)–C(8)	1.33(1)	O(A)–O(A1)	1.54(4)
N(4)–C(9)	1.37(2)	C(A1)–C(A2)	1.02(6)
C(1)–C(2)	1.40(1)	O(B)–C(B1)	1.45(2)
C(2)–C(3)	1.39(2)	C(B1)–C(B2)	1.43(3)
C(3)–C(4)	1.38(2)	O(C)–C(C1)	1.56(3)
C(4)–C(5)	1.37(2)	C(C1)–C(C2)	1.29(3)
C(5)–C(6)	1.34(2)	O(D)–C(D1)	1.44(2)
C(6)–C(1)	1.38(2)	C(D1)–C(D2)	1.54(2)
C(7)–C(8)	1.45(2)	O(E)–C(E1)	1.42(2)
C(9)–C(10)	1.41(2) [b]	C(E1)–C(E2)	1.50(2)
C(10)–C(11)	1.37(2)		
C(11)–C(12)	1.37(2)	N(2)–H(N2)	0.7(1)
C(12)–C(13)	1.39(2)	N(4)–H(N4)	0.8(1)
C(13)–C(14)	1.35(2)		
C(14)–C(9)	1.39(2)	O(1)–H(O1A)	0.9(1)
C(15)–C(16)	1.50(2)	O(1)–H(O1B)	0.7(1)
C(17)–C(18)	1.39(2)		

[a] C–H distances are not listed; they lie in the range 0.7—1.0 Å. [b] The interatomic distances in the five ethanol molecules are rather unrealistic most likely due to a slight disorder in the atomic positions.

TABLE 6

Interbond angles (°) in $[Cu(bbtb)(H_2O)][ClO_4]_2{\cdot}5EtOH$, with estimated standard deviations in parentheses

S(1)–Cu–S(2)	88.18(9)	S(2)–Cu–N(1)	83.5(3)
O(1)–Cu–S(1)	135.0(4)	S(2)–Cu–N(3)	92.8(3)
O(1)–Cu–S(2)	136.8(4)	O(1)–Cu–N(1)	92.7(5)
S(1)–Cu–N(1)	94.2(3)	O(1)–Cu–N(3)	92.1(5)
S(1)–Cu–N(3)	82.6(3)	N(1)–Cu–N(3)	175.2(3)
Cu–N(1)–C(16)	122.0(8)	Cu–S(1)–C(7)	96.2(5)
Cu–N(1)–C(18)	130.6(9)	Cu–S(2)–C(2)	101.4(5)
Cu–N(3)–C(8)	122.9(9)	Cu–S(2)–C(15)	97.4(5)
Cu–N(3)–C(10)	129.0(8)	Cu–O(1)–H(O1A)	119(8)
Cu–S(1)–C(1)	101.2(5)	Cu–O(1)–H(O1B)	122(13)
S(1)–C(1)–C(2)	124(1)	S(2)–C(2)–C(1)	125(1)
S(1)–C(1)–C(6)	117(1)	S(2)–C(2)–C(3)	116(1)
S(1)–C(7)–C(8)	112.1(9)	S(2)–C(15)–C(16)	110.4(9)
N(1)–C(16)–N(2)	112(1)	N(3)–C(8)–N(4)	111(1)
N(1)–C(16)–C(15)	125(1)	N(3)–C(8)–C(7)	124(1)
N(1)–C(18)–C(17)	108(1)	N(3)–C(10)–C(9)	107(1)
N(1)–C(18)–C(19)	131(1)	N(3)–C(10)–C(11)	132(1)
N(2)–C(17)–C(18)	106(1)	N(4)–C(9)–C(10)	106(1)
N(2)–C(17)–C(22)	132(1)	N(4)–C(9)–C(14)	134(1)
N(2)C–(16)–C(15)	123(1)	N(4)–C(8)–C(7)	124(1)

TABLE 6 (*continued*)

C(1)–S(1)–C(7)	101.7(6)	C(2)–S(2)–C(15)	102.0(6)
C(1)–C(2)–C(3)	119(1)	C(4)–C(5)–C(6)	120(2)
C(2)–C(3)–C(4)	120(1)	C(5)–C(6)–C(1)	122(1)
C(3)–C(4)–C(5)	120(2)	C(6)–C(1)–C(2)	119(1)
C(9)–C(10)–C(11)	121(1)	C(12)–C(13)–C(14)	121(1)
C(10)–C(11)–C(12)	117(1)	C(13)–C(14)–C(9)	118(1)
C(11)–C(12)–C(13)	122(1)	C(14)–C(9)–C(10)	120(1)
C(17)–C(18)–C(19)	121(1)	C(20)–C(21)–C(22)	122(1)
C(18)–C(19)–C(20)	118(1)	C(21)–C(22)–C(17)	117(1)
C(19)–C(20)–C(21)	121(1)	C(22)–C(17)–C(18)	121(1)
O(11)–Cl(1)–O(21)	111(1)	O(12)–Cl(2)–O(22)	109.2(6)
O(11)–Cl(1)–O(31)	111(1)	O(12)–Cl(2)–O(32)	108.2(6)
O(11)–Cl(1)–O(41)	109(2)	O(12)–Cl(2)–O(42)	108.7(7)
O(21)–Cl(1)–O(31)	108(1)	O(22)–Cl(2)–O(32)	109.6(7)
O(21)–Cl(1)–O(41)	105(1)	O(22)–Cl(2)–O(42)	109.6(7)
O(31)–Cl(1)–O(41)	112(2)	O(32)–Cl(2)–O(42)	111.5(6)
O(A)–C(A1)–C(A2)	120(5)	O(C)–C(C1)–C(D2)	114(2)
O(B)–C(B1)–C(B2)	107(2)	O(D)–C(D1)–C(D2)	110(1)
O(E)–C(E1)–C(E2)	111(2)		

Cu–N bond lengths of 1.951(9) and 1.945(9) Å are in good agreement with analogous interatomic distances in other published compounds.[18,20,25–29] The Cu–O(1)(water) bond length of 1.968(8) Å is close to the Cu–N distances. The angles O(1)–Cu–S(1) of 135.0(4) and O(1)–Cu–S(2) of 136.8(4)° are nearly equal and indicate the presence of a pseudo-two-fold axis along the Cu–O(1) bond. The dihedral angle between the two least-squares planes through the benzimidazole groups was calculated to be 76.5(2)°. A stereodrawing of the unit cell showing the packing of the molecules is presented in Figure 2. Intermolecular hydrogen-bonding distances are given in Table 7.

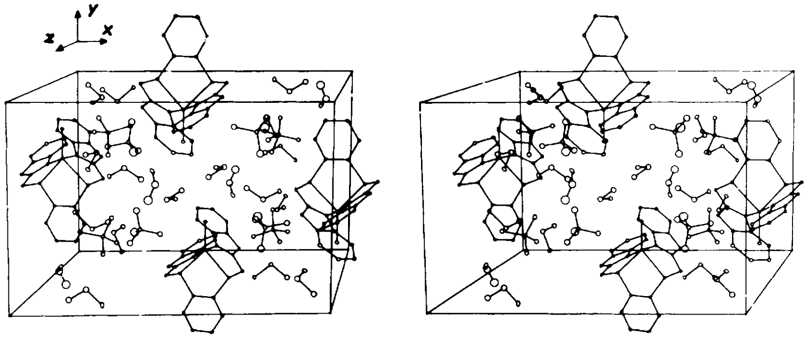

FIGURE 2 Stereodrawing of the unit-cell contents of [Cu(bbtb)(H$_2$O)][ClO$_4$]$_2$·5EtOH

TABLE 7

Intermolecular hydrogen-bonding distances (Å) in [Cu(bbtb)(H$_2$O)][ClO$_4$]$_2$·5EtOH, with estimated standard deviations in parentheses [*]

O(1)–O(A)	2.64(2)	H(O1A)–O(A)	1.8(1)
O(1)–O(B)	2.68(2)	H(O1B)–O(B)	2.0(1)
N(2)–O(C)	2.77(1)	H(N2)–O(C)	2.1(1)
N(4)–O(D)	2.71(1)	N(N4)–O(D)	2.0(1)
O(D)–O(E)	2.74(1)	H(OD)–O(E)	2.1(1)
O(B)–O(11)	3.17(3)	O(OB)–O(11)	2.4(1)
O(B)–O(21)	3.24(2)	O(OB)–O(21)	2.5(1)
O(A)–O(12)	2.84(2)	H(OA)–O(12)	2.9(1)
O(1)–O(21)	3.32(2)	O(O1B)–O(21)	2.9(2)
O(1)–O(42)	3.35(2)	O(O1A)–O(42)	3.0(1)
O(C)–O(41′)	2.99(3)	H(OC)–O(41′)	2.4(1)
O(E)–O(12″)	2.97(1)	H(OE)–O(12″)	2.3(1)

[*] Primes indicate the symmetry operation $1 - x, -y, -z$, double primes $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

The co-ordinated water molecule has an internal bond angle H(O1A)–O(1)–H(O1B) of 115(13)°. It is hydrogen bonded to two ethanol molecules *via* relatively strong hydrogen bonds, O(1)–O(A) 2.64(2) and O(1)–O(B) 2.68(2) Å. Hydrogen bonding also occurs between the two benzimidazole N–H groups and two other alcohol molecules [N(2)–O(C) 2.77(1) and N(4)–O(D) 2.71(1) Å]. Moreover, one of the perchlorate anions is hydrogen bonded by two of its oxygen atoms to one alcohol molecule, as indicated by the distances O(11)–O(B) 3.17(3) and O(21)–O(B) 3.24(2) Å. Three perchlorate anions are hydrogen bonded by only one of their oxygen atoms to different alcohol molecules [O(A)–O(12) 2.84(2), O(C)–O(41′) 2.99(3), and O(E)–O(12″) 2.97(1) Å]. The distance O(D)–O(E) 2.74(1) Å indicates additional hydrogen bonding between two alcohol molecules. Finally, very weak hydrogen bonds exist between one oxygen atom of each of two perchlorate anions and the co-ordinated water molecule, as shown by the distances O(1)–O(21) 3.32(2) and O(1)–O(42) 3.35(2) Å. Since nearly all hydrogen bonds in the lattice involve alcohol molecules, it is not surprising that loss of alcohol of crystallization leads to complete deterioration of the crystals.

Comparison with Related Structures.—Table 8 shows relevant interatomic distances and interbond angles in closely related copper chelates having a general structural formula as depicted in Figure 3. The crystal structures of these compounds have been solved recently.[18,19,30]

The structures of (7)—(9) have in common that the co-ordination geometry around Cu^{II} is trigonal bipyramidal, with two (benz)imidazole nitrogen atoms as axial and two thioether sulphur atoms, as well as a third donor X (see Figure 3), at equatorial positions. The present chelate (8) shows that if weakly co-ordinating anions like perchlorate are present the co-ordination sphere of the metal ion can also be completed by a neutral solvent molecule (in this case, H$_2$O). The presence of an *o*-phenylene bridge instead of an ethylene bridge does not seem to have a strong influence on the S–Cu–S angle and on the Cu–S distances (see Table 8). There is a significant difference, however, between the N–Cu–N angles. This angle is larger in (8) than in (7) by almost 10°, and is even larger than in the copper(I) compound (10). A compari-

TABLE 8

Some relevant interatomic distances (Å) and interbond angles (°) in closely related copper chelates[a] (with estimated standard deviations in parentheses)

Compound	Cu–S(1)[b]	Cu–S(2)[d]	Cu–N(1)[b]	Cu–N(3)[b]	Cu–X	S–Cu–S	N–Cu–N	X–Cu–S(1)[b]	X–Cu–S(2)[b]	α/°[c]
(7) $[Cu^{II}(bbte)Cl]Cl\cdot 2EtOH$[d]	2.561(2)	2.434(2)	1.961(6)	1.968(6)	2.241(2)	90.39(6)	165.9(2)	127.29(8)	142.18(8)	
(8) $[Cu^{II}(bbtb)(H_2O)][ClO_4]_2\cdot 5EtOH$[e]	2.477(4)	2.450(4)	1.951(9)	1.945(9)	1.968(8)	88.18(9)	175.2(3)	135.0(4)	136.8(4)	76.5(2)
(9) $[Cu^{II}(bbite)Br]Br\cdot xEtOH$[f]	2.570	2.471	1.903	1.903	2.415	88.0	171.2	122.5	149.5	
(10) $[Cu^{I}(bbtp)][PF_6]_{0.66}[BF_4]_{0.34}$[g]	2.867(2)	2.867(2)	1.918(4)	1.918(4)		81.79(8)	168.5			80.5

Plastocyanin (pH *ca.* 6): Cu^{II}–N(His37) 2.04; Cu^{I}–N(His37) 2.07; Cu^{II}–S(Cys84) 2.13; Cu^{I}–S(Cys84) 2.11; Cu^{II}–N(His87) 2.10; Cu^{I}–N(His87) 2.82; Cu^{II}–S(Met92) 2.90; Cu^{I}–S(Met92) 2.68 Å.[3]

[a] For definition of R, X, and Y see Figure 3. [b] The numbering is in accordance with Figure 1. The ' long ' Cu–S bond is always opposite the ' larger ' X–Cu–S angle. [c] Angle between least-squares benzimidazole planes. [d] $Y = -(CH_2)_2-$, $X = Cl^-$, R = H; ref. 18. [e] $Y = o\text{-}C_6H_4<$, $X = H_2O$, R = H, this work. [f] $Y = -(CH_2)_2-$, $X = Br^-$, $R = CH_2Ph$; ref. 30. [g] $Y = -(CH_2)_3-$, X = absent, R = H; ref. 19.

TABLE 9

Some relevant distances (Å) and angles (°) in structurally related compounds containing a co-ordinated water molecule, with estimated standard deviations in parentheses

Compound	Cu–O	Cu–N(eq) (× 2)	Cu–N(ax) (× 2)	N(ax)–Cu–N(ax)	Ref.
$[Cu^{II}(bipy)_2(H_2O)]S_2O_6$	2.158(13)	2.013(7), 2.013(7)	1.977(7), 1.977(7)	174.6(5)	33
$[Cu^{II}(bipy)_2(H_2O)]S_6O_6$	2.050(5)	2.025(5), 2.125(6)	1.974(5), 1.980(5)	179.1(2)	32
$[Cu^{II}(phen)_2(H_2O)][NO_3]_2$	2.18(1)	2.03(1), 2.03(1)	1.99(1), 1.99(1)	171.0(4)	34
$[Cu^{II}(phen)_2(H_2O)][BF_4]_2$	2.238(8)	2.041(7), 2.041(7)	1.985(6), 1.985(6)	172.8(4)	35

bipy = 2,2′-Bipyridyl, phen = 1,10-phenanthroline, eq = equatorial, ax = axial.

son between the X–Cu–S angles in (7)—(9) shows a remarkable asymmetry in the trigonal plane for both (7) and (9). A likely explanation is the concurrence of asymmetric long-range hydrogen bonding. In contrast, the two X–Cu–S angles are almost equal in (8), so that of all three compounds (7)—(9) compound (8) has the most symmetric equatorial plane. In (10) the nature of the bridge between the sulphur atoms prevents co-ordination of all four potential donor atoms at the same time, making possible an almost linear co-ordination of the two benzimidazole nitrogen atoms. Consequently, the Cu^{I} oxidation state is favoured and copper(II) compounds of bbtp are spontaneously reduced to Cu^{I} when this ligand reacts with a solution of a copper(II) salt.[19]

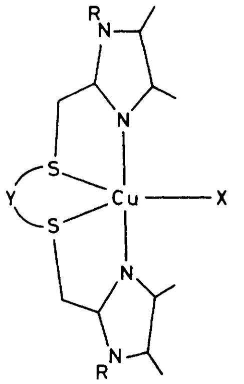

FIGURE 3 The general structure of the trigonal-bipyramidal $[Cu^{II}(N_2S_2)X]$ compounds. For definitions of R, X, and Y see Table 8

Although stable copper(I) analogues of (7) and (8) exist, no crystals suitable for *X*-ray diffraction have been obtained, so far. For comparison some relevant distances from the crystal structure of plastocyanin[31] are also presented in Table 8 (for the oxidized as well as the reduced form). In the literature only a few examples of trigonal-bipyramidal copper(II) compounds have been reported that contain a co-ordinated water molecule.[32-35] Four examples of these have the general formula $[Cu(L\text{-}L)_2(H_2O)][anion]_2$, where L–L = 2,2′-bipyridyl[32,33] or 1,10-phenanthroline.[34,35] All these compounds show a distortion towards a square-pyramidal geometry, although the distortions as deduced from the N(eq)–Cu–OH_2 and N(ax)–Cu–N(ax) angles are relatively small. This is further illustrated in Table 9, where some data for the present compound are compared with those for the other four compounds. The most striking difference is the length of the Cu–OH_2 bond which is only 1.968(8) Å in our compound, but which varies from 2.050 to 2.238 Å in the other compounds.

Conclusions.—The ligand bbtb is in a series of closely related chelating agents containing (benz)imidazole and thioether functions, all having different steric constraints. In the solid state its copper(II) chelate appears to possess trigonal-bipyramidal geometry, with two azole nitrogens at axial and two thioether atoms at equatorial positions. Remarkable in the present chelate is the co-ordinated water molecule occupying the third equatorial position in the trigonal plane. Electronic spectra indicate a different co-ordination geometry in alcoholic solution, either due to additional solvation or to geometrical changes induced by the solvent. Further studies on related compounds having different steric constraints are in progress.

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