7556

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Copper(I) and Copper(II) Complexes of a New Tetradentate Chelating Ligand Containing Imidazole and Thioether Groups. The X-ray Structure of Trigonal-Bipyramidal [1,6-Bis(*N*-benzylimidazol-2-yl)-2,5-dithiahexane-*N,N,S,S*]-bromocopper(II) Bromide

Paul J. M. W. L. Birker,[1a] Erik F. Godefroi,[1b] Janneke Helder,[1a] and Jan Reedijk*[1a]

Contribution from the Department of Chemistry, Gorlaeus Laboratories, State University Leiden, 2300 RA Leiden, The Netherlands, and the Department of Organic Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands. Received February 16, 1982

Abstract: The synthesis and characterization of the new potentially tetradentate chelating imidazole–thioether ligand 1,6-bis(*N*-benzylimidazol-2-yl)-2,5-dithiahexane, {[$C_3H_2N_2(C_7H_7)$]CH_2SCH_2}$_2$, BBIDH, and some of its Cu^I, Cu^{II}, and Zn^{II} complexes are described. X-ray crystal structure determination showed that the Cu^{II} atom in [Cu(BBIDH)Br]Br·xsolvent is in a trigonal-bipyramidal coordination geometry with two axial imidazole N donor atoms (Cu–N = 1.93 (2) and 1.94 (2) Å) and two thioether S atoms and a Br⁻ ion in the equatorial plane (Cu–S = 2.565 (6) and 2.470 (6) Å, Cu–Br = 2.417 (3) Å). The compound crystallizes in space group $P\bar{1}$ with *a* = 8.397 (2), *b* = 11.415 (2), and *c* = 18.016 (2) Å, α = 103.74 (1), β = 94.49 (2), and γ = 100.48 (2)°, and Z = 2. Intensities of 3982 unique reflections (θ < 22°) were measured on an automatic diffractometer (Mo Kα radiation). The structure was solved by use of direct methods and refined with full-matrix least-squares techniques using the 1793 reflections with $I > 2\sigma(I)$ to a final *R* value of 0.071. From ESR and visible spectra, it was inferred that other solid Cu^{II} compounds also have a trigonal-bipyramidal coordination geometry, with H_2O as the fifth ligand if no halogenide ions are available. The spectra of solutions of the Cu^{II} compounds indicate a change in coordination geometry. In [Cu^I(BBIDH)]⁺, the Cu atom is probably linearly coordinated by two N atoms. The $ZnCl_2$ adduct is a nonelectrolyte. The coordination chemistry of this imidazole–thioether ligand is in this respect not different from its earlier reported benzimidazole-containing analogon, ($C_7H_5N_2CH_2SCH_2$)$_2$, justifying the use of benzimidazole derivatives in model systems for the coordination of Cu in copper proteins.

The geometry of the Cu binding site in the so-called "blue" or type I copper proteins has been known since 1978, when the first X-ray structure of a blue copper protein was solved.[2] In this protein the Cu^{II} atom is coordinated by two histidine imidazole N atoms, a cysteine thiolate S atom, and a methionine thioether S atom in a distorted tetrahedral geometry. The methionine S atom has only a weak interaction with Cu^{II} (Cu–S = 2.9 Å at pH ≃6). The Cu^I atom in the reduced form of the protein is coordinated by the same set of ligand atoms in a geometry that is strongly pH dependent.[3] A crystallographic study of another blue Cu protein, azurin, indicates a similar coordination geometry for Cu^{II}.[4] It has been suggested on the basis of spectral and redox properties that in the Cu proteins stellacyanin and rusticyanin, the two sulfur ligands are two cysteines and two methionines, respectively.[5]

A considerable research effort has been devoted to the syntheses of model compounds exhibiting the typical properties of type I Cu proteins with (i) a low $A_{\parallel}$ (30–60 × 10⁻⁴ cm⁻¹) in their ESR spectra, (ii) a high extinction coefficient (>3000 L mol⁻¹ cm⁻¹) around 600 nm, and (iii) stabilization of both Cu^I and Cu^{II}.[2] So far, no models have been obtained having these three properties simultaneously. In particular, the binding of thiolate groups to Cu^{II} is hard to accomplish in low-molecular-weight compounds, the end product being a, often insoluble, polymeric Cu^I compound and disulfide.[6] The rigid conformation of the protein with only a single cysteine residue near the Cu binding site obviously prevents the formation of disulfide and Cu^I. Nevertheless, it is rather easy to transfer an electron from Cys(S⁻) to Cu^{II} as is evidenced by the low energy of the Cys(S⁻) → Cu^{II} charge-transfer band (near

600 nm, 16 600 cm⁻¹), which is responsible for the intense blue color of these proteins. Stable RS⁻ to Cu bonds in low-molecular-weight compounds have been found in cases where the thiolate S atom forms a bridge between several metal ions[7] so that reduction of RS⁻ is hindered either sterically or by the electron-withdrawing effect of the other metal atoms bonded to RS⁻. One example is known of a well-characterized compound with a RS⁻–Cu^{II} bond most likely stabilized by the steric inaccessibility of the Cu^{II} atom.[6]

As an approach to the synthesis of analogues of the Cu binding site in Cu proteins, we have earlier synthesized Cu^{II} and Cu^I compounds with the ligands shown in Figure 1a. The philosophy underlying the design of such ligands is the following: (i) the choices of different *n* and Y will impose different steric constraints and therefore most likely different coordination geometries and different redox properties on the metal atoms, (ii) the chelating ligands will force thioether S atoms to bind to Cu^{II}, which they usually are reluctant to do, (iii) the thioether S atoms might stabilize Cu^I, either as a result of the formation of (thioether) S–Cu bonds or—in case they do not form S–Cu bonds—by sterically stabilizing low coordination numbers, (iv) the bulky benzimidazole end groups of the chelating ligands will most likely prevent square-planar coordination around Cu^{II}. The use of bulky benzimidazole end groups has recently been employed by others with the same purpose.[11]

Benzimidazole derivatives can be obtained in high yield from one- or two-step syntheses,[8–11] whereas preparation of chelating imidazole derivatives involves lengthy synthetic procedures (see

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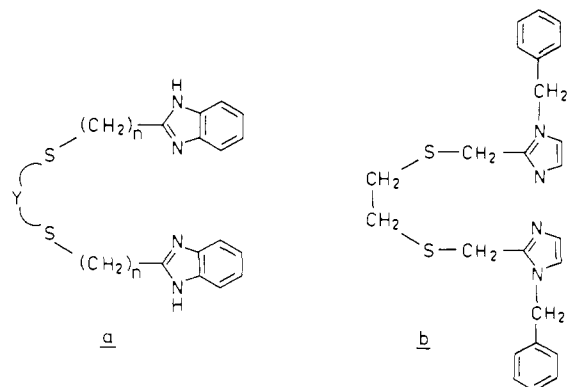(11) Dagdigian, J. V.; Reed, C. A. *Inorg. Chem.* **1979**, *18*, 2623–2626.

Figure 1. Thioether–benzimidazole ligands. (a) BBDH ($n = 1$, Y = $-CH_2CH_2-$);[8] BBDHp ($n = 1$, Y = $-CH_2CH_2CH_2-$);[9] BBDB ($n = 1$, Y = o-C_6H_4).[10] (b) 1,6-bis(N-benzylimidazol-2-yl)-2,5-dithiahexane (BB-IDH).

below). To study the effect of the less voluminous imidazole group, we decided to synthesize the new ligand shown in Figure 1b and its Cu[II] and Cu[I] compounds. The coordination geometry appears to be entirely a consequence of the nature of the donor atoms and the ligand constraints. We therefore conclude from the present study that the expedient use of benzimidazole derivatives in these model studies seems to be justified from a structural point of view.

In the present paper the X-ray structure of one of the Cu[II] compounds with ligand **1b** ([Cu[II](BBIDH)Br]Br·$x$solvent) is described. In addition, the spectroscopic properties of the Cu[II] and Cu[I] compounds of BBIDH are compared with those of the related ligands[8–10] shown in Figure 1a.

Experimental Section

General Information. All reagents and solvents were of commercially available reagent grade quality. The elemental analyses (C, H, N, S) were carried out by Dr Pascher, Bonn, FRG, or by P. van den Bosch and H. Eding, University of Technology, Eindhoven, The Netherlands. Metal analyses were determined by use of standard EDTA titrations. All NMR spectra were run in (CD$_3$)$_2$SO. Spectral parameters are presented in ppm vs. (CH$_3$)$_4$Si.

Preparation of the Ligand 1,6-Bis(N-benzylimidazol-2-yl)-2,5-dithiahexane (BBIDH). This ligand was synthesized in five steps (Figure 2). The first steps were based on earlier literature.[12]

Step 1. 1-Benzylimidazole (75 g, 0.47 mol) was refluxed for 72 h in 600 mL of 37% aqueous formaldehyde. To the solution were then added 3 L of H$_2$O and 120 mL of a 10 N NaOH solution, causing after 15 min the deposition of white solid I. After 4 h, it was filtered off and dried in vacuo: yield 56%; mp 96 °C; ^{1}H NMR δ 4.30 (s, 2 H, CH$_2$), 5.28 (s, 2 H, CH$_2$), 6.86 (s, 1 H, Ar H), 7.15 (s, 1 H, Ar H), 7.34 (m, 5 H, Ar H).

Step 2. A solution of 36 g (0.19 mol) of I in 140 mL of CHCl$_3$ was added dropwise to a solution of 84 mL of SOCl$_2$ in 140 mL of CHCl$_3$ and kept at 15–20 °C. The mixture was then refluxed for 2 h, whereupon solvent and excess SOCl$_2$ were removed. The residue was triturated with 1:1 isopropanol/ether; solid II was then filtered off, rinsed with ether, and dried in vacuo: yield 95%; mp 184 °C; ^{1}H NMR δ 5.35 (s, 2 H, CH$_2$), 5.59 (s, 2 H, CH$_2$), 7.42 (m, 5 H, Ar H), 7.82 (d, 1 H, Ar H), 7.86 (d, 1 H, Ar H).

Step 3. A stirred solution of 16.0 g (0.21 mol) of thiourea and 46.1 g (0.19 mol) of II in 750 mL of dry dimethylformamide was heated to 80 °C for ca. 1 h. Compound III precipitated as a white solid. After the solution was cooled and filtered, washing the solids with dimethylformamide and diethyl ether gave III (97%): mp 193 °C; ^{1}H NMR δ 5.19 (s, 2 H, CH$_2$), 5.55 (s, 2 H, CH$_2$), 7.44 (s, 5 H, ArH), 7.72 (s, 2 H, ArH), 9.7 (br, ~4 H, NH). Anal. (C$_{12}$H$_{16}$N$_4$SCl$_2$) C, H, N.

Step 4. A solution of 59.0 g (0.18 mol) of III in 490 mL of 5 N NaOH was refluxed for 70 min under a nitrogen atomosphere. Cooling and scratching caused deposition of IV; it was filtered off, rinsed with small amounts of cold isopropanol and ether, and dried in vacuo: yield 85%; mp 71–74 °C; ^{1}H NMR δ 3.35 (s, 2 H, CH$_2$), 5.50 (s, 2 H, CH$_2$), 6.60 (s, 1 H, Ar H), 6.87 (s, 1 H, Ar H), 7.29 (m, 5 H, Ar H).

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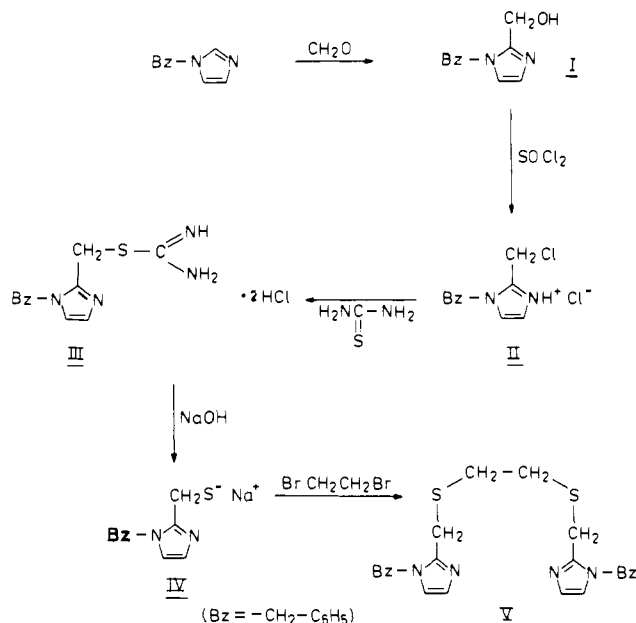

Figure 2. Synthesis of BBIDH.

Step 5. A solution of 1,2-dibromoethane (14.7 g, 0.08 mol) and 35.8 g (0.16 mol) of IV in 850 mL of absolute ethanol was refluxed for 4.5 h under a nitrogen atmosphere. The solvent was then removed in vacuo leaving a residue that was partitioned between 200 mL of toluene and 50 mL of H$_2$O. The separated aqueous fraction was scrubbed twice with 75-mL portions of toluene. Addition of saturated isopropanolic HCl to the combined organic phases furnished the colorless hydrochloride salt of V. This was filtered off, washed with isopropanol and ether, successively, and dried in vacuo; yield 28 g (70%). It was dissolved in 200 mL of warm water that was made alkaline with 5 N NaOH. The free base was then extracted into toluene, which was dried (MgSO$_4$) and evaporated in vacuo. The oily residue gave, on ether trituration, solid brown material. This was dissolved in isopropanol; cautious addition of water produced a crystalline product that was filtered off and dried: yield 44%; mp 80 °C; ^{1}H NMR δ 2.63 (s, 4 H, CH$_2$), 3.81 (s, 4 H, CH$_2$), 5.20 (s, 4 H, CH$_2$), 6.77 (s, 2 H, Ar H), 7.06 (s, 2 H, Ar H), 7.27 (m, 10 H, Ar H). Anal. (C$_{24}$H$_{26}$N$_4$S$_2$) C, H, N, S.

Coordination Compounds with BBIDH. Cu[II](BBIDH)Br$_2$·H$_2$O. A solution of 112 mg (0.5 mmol) of CuBr$_2$ in 10 mL of absolute ethanol containing 1 mL of EOF (triethyl orthoformate) was added to a solution of 217 mg (0.5 mmol) of BBIDH in 25 mL of warm absolute ethanol. Green needle-shaped crystals were obtained after slow cooling of the solution to room temperature. These crystals deteriorated when isolated, most likely due to loss of cocrystallized solvent molecules. The exact number of these could not be determined from the X-ray analysis (see below). The crystals were isolated, washed with ethanol and ether, and dried. The dried compound analysed as Cu(BBIDH)Br$_2$·H$_2$O. Anal. (CuC$_{24}$H$_{28}$N$_4$S$_2$Br$_2$O) Cu, C, H, N.

Cu[II](BBIDH)(ClO$_4$)$_2$·H$_2$O. A solution of 0.37 g (1 mmol) of Cu-(ClO$_4$)$_2$·6H$_2$O in 10 mL of absolute ethanol was added to a solution of 435 mg (1 mmol) of BBIDH in 40 mL of warm absolute ethanol. The blue microcrystalline compound precipitated almost immediately. The solution was cooled to room temperature, filtered off, washed with ethanol, and dried in vacuo. Anal. (CuC$_{24}$H$_{28}$N$_4$S$_2$O$_9$Cl$_2$) Cu, C, H, N.

Cu[II](BBIDH)(NO$_3$)$_2$·H$_2$O. A solution of 217 mg (0.5 mmol) of BBIDH in 25 mL of warm ethanol was mixed with a solution of 121 mg (0.5 mmol) of Cu(NO$_3$)$_2$·3H$_2$O in 10 mL of ethanol. When cooled to room temperature, a blue precipitate was formed, which was filtered off, washed with absolute ethanol, and dried in vacuo. Anal. (CuC$_{24}$H$_{28}$-N$_5$S$_2$O$_4$) Cu.

Zn[II](BBIDH)Cl$_2$. A solution of 68 mg of ZnCl$_2$ dissolved in 10 mL of absolute ethanol and 1 mL of EOF was added to 217 mg (0.5 mmol) of BBIDH in 25 mL of warm absolute ethanol. The white compound precipitated slowly, was filtered off, washed with ethanol and ether, and dried in vacuo: ^{1}H NMR δ 4.34 (s, 4 H, CH$_2$), 5.33 (s, 4 H, CH$_2$), 7.36 (s, 4 H, ArH), 7.47 (s, 10 H, Ar H). One methylene signal is most likely hidden under the solvent peak (2.50 ppm). Anal. (ZnC$_{24}$H$_{26}$N$_4$S$_2$Cl$_2$) Zn.

Cu[I](BBIDH)(ClO$_4$). A solution of 93 mg (0.25 mmol) of Cu(Cl-O$_4$)$_2$·6H$_2$O in 15 mL of acetonitrile was reduced with an excess of Cu powder under a nitrogen atmosphere until the solution was colorless. The

7558 *J. Am. Chem. Soc., Vol. 104, No. 26, 1982*

Birker et al.

Table I. Crystal Data and Data Collection Parameters for [Cu(BBIDH)Br]Br·xsolvent

formula	$CuC_{22}H_{26}N_4S_2Br_2 \cdot x$solvent
a	8.397 (2) Å
b	11.415 (2) Å
c	18.016 (2) Å
α	103.74 (1)°
β	94.49 (2)°
γ	100.48 (2)°
space group	$P\bar{1}$
Z	2
no. of reflcns used for cell constants	24 ($\theta > 10°$)
d_{calcd}	a
d_{obsd} (flotation tetra/toluene)	1.54 (1) g cm^{-3}
λ (Mo Kα^1)	0.709 30
monochromator	graphite
lin abs coeff used	32.3 cm^{-1} b
crystal dimensions	0.45 × 0.10 × 0.03 mm
transmission range	0.72–0.90
diffractometer	Nonius CAD 4
data collection mode	ω–θ
θ range	2–22°
temp	room temperature
criterion for precision	$I > 0.02\sigma(I)$
max scan time per reflcn	90 s
decrease intensity stand refl	14%
standard refl msd	3 reflcns every 5400 s
no. of reflcns msd	7967
no. of unique reflcns	3982
no. of reflcn used ($I > 2\sigma(I)$)	1793
no. of param refined	255
final R	0.071^c
final R_w	0.086^c

a Not known as the number of solvent molecules in the lattice could not be determined (see text). b This value of μ does not account for all cocrystallized solvent molecules. Errors introduced by this approximation are largely compensated by the crystal-size optimization procedure in De Graaff's absorption correction method.[13] c $R = \Sigma ||F_o| - |F_c||/\Sigma F_o$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

excess Cu powder was removed by filtration. The colorless filtrate was mixed under nitrogen with a solution of 217 mg (0.5 mmol) of BBIDH in 5 mL of absolute ethanol and 20 mL of diethyl ether. Slow addition of dioxygen-free diethyl ether resulted in the formation of a white crystalline precipitate. The crystals were filtered off and washed with dioxygen-free diethyl ether. The dry compound is quite stable in air, although after a month the crystals appeared to be slightly greenish: ^{1}H NMR δ 2.90 (s, 4 H, CH$_2$), 4.04 (s, 4 H, CH$_2$), 5.28 (s, 4 H, CH$_2$), 7.20 (s, 2 H, Ar H), 7.44 (m, 12 H, Ar H). Anal. (CuC$_{24}$H$_{26}$N$_4$S$_2$ClO$_4$) Cu, C, H, N, S.

Physical Measurements. Visible spectra were recorded on a Beckman DK-2A spectrophotometer in solution or in the diffuse reflectance mode. ESR spectra were measured on a Varian E3 (X band) and a Varian V4500 (Q band) ESR spectrometer, NMR spectra on a JEOL PS-100 spectrometer. Conductivity measurements were carried out with a Philips PR9500 bridge fitted with a PR9510 cell.

X-ray Data Collection and Solution of the Structure. A crystal of [Cu(BBIDH)Br]Br·xsolvent was selected and transferred, without isolation from the mother liquor, into a thin-walled glass capillary together with some mother liquor. The crystal was separated from the mother liquor, and the capillary was sealed with solid paraffine. The cell dimensions, data collection, and refinement parameters are given in Table I. The data were corrected for absorption by using De Graaff's method.[13] Atomic scattering factors with corrections for anomalous dispersion were taken from the "International Tables for X-ray Crystallography".[14] The structure was solved by use of the direct methods program MULTAN,[15] yielding the positions of Cu, one Br, two S, two N, and two C atoms. All other non-hydrogen atoms of the complex ion and the Br⁻ counterion were located in a series full-matrix least-squares refinements, Fourier and difference Fourier syntheses.[15]

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(14) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(15) All programs used in this analysis were locally written, except MULTAN by P. Main, M. M. Woolfson, and G. Germain, and ORTEP by C. K. Johnson.

Table II. Positional Parameters^a for Non-Hydrogen Atoms^b in [Cu(BBIDH)Br]Br·xsolvent

atom	$10^4x/a$	$10^4y/b$	$10^4z/c$
Cu	8971 (4)	1686 (3)	549 (2)
Br(1)	11516 (4)	1288 (3)	1052 (2)
Br(2)	4292 (4)	5709 (3)	1571 (2)
S(1)	7906 (7)	3618 (5)	1154 (4)
S(2)	6481 (6)	1036 (5)	−397 (3)

atom	$10^3x/a$	$10^3y/b$	$10^3z/c$
N(1)	613 (2)	96 (2)	216 (1)
N(2)	775 (2)	104 (2)	129 (1)
N(3)	989 (2)	237 (2)	−24 (1)
N(4)	997 (2)	280 (2)	−137 (1)
C(1)	659 (3)	−17 (2)	198 (2)
C(2)	762 (3)	−11 (2)	143 (2)
C(3)	684 (3)	166 (2)	172 (1)
C(4)	671 (3)	297 (2)	180 (1)
C(5)	644 (3)	352 (2)	36 (1)
C(6)	541 (3)	223 (2)	−4 (1)
C(7)	731 (2)	156 (2)	−117 (1)
C(8)	905 (3)	225 (2)	−92 (1)
C(9)	1146 (3)	308 (2)	−23 (1)
C(10)	1149 (3)	332 (2)	−95 (2)
C(11)	506 (3)	130 (3)	274 (2)
C(21)	947 (3)	302 (2)	−211 (1)
C(12)	600 (3)	200 (3)	352 (2)
C(13)	706 (4)	140 (3)	385 (2)
C(14)	796 (5)	191 (3)	458 (2)
C(15)	788 (4)	311 (3)	495 (2)
C(16)	676 (5)	370 (4)	466 (2)
C(17)	585 (5)	316 (3)	393 (2)
C(22)	878 (3)	186 (2)	273 (1)
C(23)	952 (3)	84 (2)	285 (2)
C(24)	890 (3)	−17 (3)	347 (2)
C(25)	754 (3)	−21 (2)	399 (2)
C(26)	684 (4)	82 (2)	384 (2)
C(27)	744 (3)	187 (2)	324 (1)

	$10^3x/a$	$10^3y/b$	$10^3z/c$	occupancy^c
O(31)	329 (7)	408 (6)	277 (3)	0.53 (6)
O(32)	287 (6)	472 (4)	308 (2)	0.76 (6)
O(33)	87 (5)	341 (4)	328 (2)	0.70 (5)
O(34)	132 (4)	407 (3)	281 (2)	0.92 (5)
O(41)	675 (3)	761 (3)	304 (2)	1.03 (5)
O(42)	722 (3)	692 (3)	374 (2)	1.01 (5)

a Estimated standard deviations in parentheses. b The atomic numbering is as in Figure 3. c Atoms on fully occupied general positions have an occupancy of 1.0

The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$. Other, statistical, weighting schemes proved to be less satisfactory. The space group $P\bar{1}$ proved to be the correct choice. Full-matrix least-squares refinement of all positional and isotropic thermal parameters of all non-hydrogen atoms resulted in high temperature factors and unrealistic interatomic distances in the benzene rings. These interatomic distances were therefore constrained in a Waser constraints procedure[16] and refined with isotropic temperature factors. Hydrogen atoms were placed at their calculated positions (C–H = 1.0 Å) and were given fixed isotropic temperature factors ($B_{iso} = 6.0$ Å^2). All other atoms of the complex ion and the Br⁻ counterion were refined with anisotropic temperature factors. After complete refinement of this model, several peaks of significant height were found in a difference Fourier map. Attempts to recognize separate partially occupied sites of ethanol molecules failed, even with constrained molecular geometries, as several isotropic temperature factors rose to unacceptably high values. Nevertheless, the presence of solvent molecules seemed likely, as the isolated crystals rapidly deteriorated. As possibly the best compromise, the six highest peaks were considered to be oxygen atoms (of ethanol or water molecules). Their positions and occupancies were refined with isotropic temperature factors fixed at $B = 6.0$ Å^2. Eleven very low but yet significant peaks, some of which were less than 1.2 Å^2 away from the Br⁻ counterion, were not included in the refinement. The atomic positional parameters for non-hydrogen atoms and the occupancy parameters are listed in Table II. Tables of thermal parameters and positions of H atoms are available.[17] The final residuals

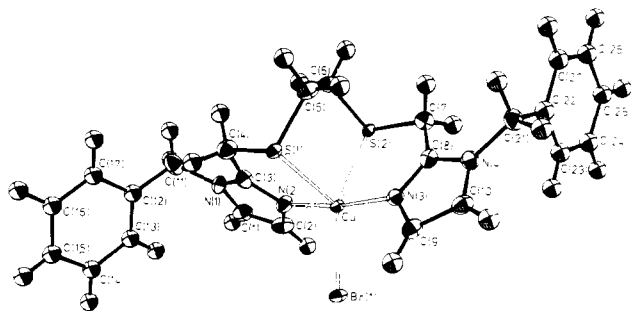(16) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091–1094.

Figure 3. Ortep drawing of the [Cu(BBIDH)Br]$^+$ ion showing the anisotropic vibration ellipsoids of the anisotropically refined atoms (probability 5%). Isotropically refined benzene carbon atoms have been drawn with fixed isotropic temperature factors ($B = 6.0$ Å^2).

based on the 1793 reflections with $I > 2\sigma(I)$ used in the refinement are $R = \sum ||F_o| - |F_c||/\sum F_o = 0.071$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.086$. A table of atomic thermal parameters and a listing of observed and calculated structure factors are available.[17]

Results and Discussion

Description of the Structure. The structure consists of discrete [Cu(BBIDH)Br]$^+$ cations, a bromide counterion, and disordered solvent molecules. The complex ion (see Figure 3) has no crystallographic symmetry. Bond lengths and angles are given in Table III. The coordination geometry around Cu^{II} is distorted trigonal bypyramidal, with two thioether S atoms and a Br$^-$ ligand in the equatorial plane and two imidazole N atoms in axial positions. The [Cu(BBIDH)Br]$^+$ ion does not possess groups that are suitable for interionic hydrogen-bond interactions. The stability of the crystal lattice is most likely maintained by the parallel packing of the benzene rings of adjacent [Cu(BBIDH)Br]$^+$ ions (see Figure 4). The disordered solvent molecules serve to fill holes in the crystal lattice. The partially occupied solvent atom sites included in the refinement are within hydrogen-bond distance from Br$^-$ ions or close to each other. Interatomic distances involving these disordered atoms are not separately listed. The closest contact of the Br$^-$ counterion to a non-hydrogen atom of the complex ion is Br(2)–C(7″) = 3.81 (2) Å (″ = 1 – x, 1 – y, 1 – z). The shortest distance from Cu to an atom outside the complex ion is Cu–Br(1′) = 3.831 (4) Å (′ = 2 – x, –y, –z). The Br(1) atom can be considered as a very asymmetric pseudobridging group between two Cu atoms in different complex ions that are related by an inversion center. This long Cu···Br(1′) distance is at best a very weak bonding interaction, in view of known Cu$_2$Br$_2$ and Cu$_2$Cl$_2$ groups in well-characterized Cu(II) dimers.[18] The two Br(1) atoms in this pseudobridged unit are 4.469 (6) Å apart. The Cu–Cu distance is 4.589 (4) Å.

Comparison with Related Structures. There is a growing family of Cu compounds with imidazole–thioether ligands.[8-11,18a,19] The most closely related structures are those with the ligands shown in Figure 1a. In [Cu(BBDH)Cl]Cl·2C$_2$H$_5$OH,[8] the Cu^{II} atom is also trigonal-bipyramidal coordinated by two thioether S atoms and a halogenide in the equatorial plane and by two axial imidazole N atoms. In [Cu(BBDB)(H$_2$O)](ClO$_4$)$_2$·5C$_2$H$_5$OH,[10] an analogous copper coordination was found with a H$_2$O in the equatorial plane instead of the halogen ion. In all these compounds, the S–Cu–S angles are close to 90°. This distortion from ideal trigonal symmetry is imposed by the rigid bridging groups (Y in Figure 1a) between the S atoms. The dimensions of the coordination polyhedron around copper in the present [Cu^{II}(BBIDH)Br]$^+$ ion are similar to those in [Cu^{II}(BBDH)Cl]$^+$.[8] The key geometrical

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(17) Supplementary Material. See paragraph at end of paper for ordering information.

(18) (a) Cohen, B.; Ou, C. C.; Lalancette, R. A.; Borowski, W.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1979**, *18*, 217–220. (b) Estes, E. D.; Estes, W. E.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 1–5. (c) Marsh, W. E.; Bowman, T. L.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chim. Acta* **1982**, *59*, 19–24.

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Table III. Interatomic Distances (Å) and Interbond Angles (Deg) in [Cu(BBIDH)Br]Br·$x$solvent^a

Cu–S(1)	2.565 (6)	N(1)–C(1)	1.38 (3)	N(4)–C(8)	1.34 (2)
Cu–S(2)	2.470 (6)	N(1)–C(3)	1.36 (3)	N(4)–C(10)	1.38 (3)
Cu–Br(1)	2.417 (3)	N(1)–C(11)	1.45 (3)	N(4)–C(21)	1.46 (3)
Cu–N(2)	1.94 (2)	N(2)–C(3)	1.31 (3)	C(7)–C(8)	1.51 (3)
Cu–N(3)	1.93 (2)	N(2)–C(2)	1.38 (3)	C(11)–C(12)	1.52 (3)
S(1)–C(4)	1.80 (2)	C(1)–C(2)	1.37 (3)	C(21)–C(22)	1.50 (3)
S(1)–C(5)	1.79 (2)	C(3)–C(4)	1.49 (3)	O(31)–Br(2)	3.23 (7)
S(2)–C(6)	1.79 (2)	N(3)–C(8)	1.33 (2)	O(32)–Br(2)	3.41 (7)
S(2)–C(7)	1.78 (2)	N(3)–C(9)	1.41 (2)	O(41)–Br(2)	3.27 (7)
C(5)–C(6)	1.53 (3)	C(9)–C(10)	1.39 (3)		
S(1)–Cu–S(2)	87.9 (2)	S(1)–C(4)–C(3)	111 (2)		
S(1)–Cu–N(2)	81.8 (6)	S(2)–C(7)–C(8)	111 (2)		
S(1)–Cu–N(3)	93.8 (5)	S(1)–C(5)–C(6)	116 (1)		
S(2)–Cu–N(2)	89.8 (6)	S(2)–C(6)–C(5)	118 (2)		
S(2)–Cu–N(3)	83.1 (6)	N(1)–C(3)–C(4)	124 (2)		
S(1)–Cu–Br(1)	122.5 (2)	N(2)–C(3)–C(4)	127 (2)		
S(2)–Cu–Br(1)	149.6 (2)	N(3)–C(8)–C(7)	125 (2)		
N(2)–Cu–N(3)	171.8 (8)	N(4)–C(8)–C(7)	125 (2)		
N(2)–Cu–Br(1)	93.6 (5)	C(3)–N(1)–C(11)	127 (2)		
N(3)–Cu–Br(1)	94.7 (5)	C(1)–N(1)–C(11)	125 (2)		
Cu–S(1)–C(4)	97.0 (8)	N(1)–C(11)–C(12)	113 (2)		
Cu–S(1)–C(5)	97.1 (7)	C(8)–N(4)–C(21)	128 (2)		
Cu–S(2)–C(6)	100.7 (8)	C(10)–N(4)–C(21)	124 (2)		
Cu–S(2)–C(7)	98.6 (7)	N(4)–C(21)–C(22)	114 (2)		
C(4)–S(1)–C(5)	104 (1)	C(11)–C(12)–C(13)	117 (3)		
C(6)–S(2)–C(7)	100 (1)	C(11)–C(12)–C(17)	125 (3)		
Cu–N(2)–C(2)	128 (2)	C(12)–C(13)–C(14)	123 (3)		
Cu–N(2)–C(3)	123 (2)	C(13)–C(14)–C(15)	118 (4)		
C(2)–N(2)–C(3)	109 (2)	C(14)–C(15)–C(16)	120 (3)		
Cu–N(3)–C(8)	123 (2)	C(15)–C(16)–C(17)	120 (4)		
Cu–N(3)–C(9)	130 (2)	C(12)–C(17)–C(16)	120 (4)		
C(8)–N(3)–C(9)	108 (2)	C(13)–C(12)–C(17)	118 (3)		
N(1)–C(3)–N(2)	109 (2)	C(21)–C(22)–C(23)	122 (2)		
N(1)–C(1)–C(2)	106 (2)	C(21)–C(22)–C(27)	117 (2)		
C(1)–N(1)–C(3)	109 (2)	C(22)–C(23)–C(24)	119 (3)		
C(1)–C(2)–N(2)	108 (2)	C(23)–C(24)–C(25)	122 (3)		
N(3)–C(8)–N(4)	111 (2)	C(24)–C(25)–C(26)	116 (2)		
C(8)–N(4)–C(10)	107 (2)	C(25)–C(26)–C(27)	124 (3)		
N(4)–C(10)–C(9)	108 (2)	C(22)–C(27)–C(26)	118 (3)		
N(3)–C(9)–C(10)	106 (2)	C(23)–C(22)–C(27)	121 (2)		

^{a} Atomic numbering is shown in Figure 3. Bond lengths in the benzene rings were constrained in a Waser constraints procedure. Bond lengths and angles in the benzene rings are therefore not separately listed. Structural parameters involving the hydrogen atoms (which were placed at calculated positions) are not listed either. Estimated standard deviations are given in parentheses.

Table IV. Geometries around Cu^{II} in Thioether Benzimidazole Chelates

compound^a	Cu–N, Å	Cu–S, Å	N–Cu–N, deg	S–Cu–S, deg
[Cu(BBIDH)Br]$^+$	1.94 (2)	2.565 (6)	71.8 (8)	87.9 (2)
	1.93 (2)	2.470 (6)		
[Cu(BBDH)Cl]$^+$	1.961 (6)	2.561 (2)	65.9 (2)	90.39 (6)
	1.968 (6)	2.434 (2)		

^{a} For abbreviations, see Figure 1.

parameters for both compounds are compared in Table IV. The reader is referred to ref 8 for an extensive comparison with other published Cu–N and Cu–S distances. The Cu–Br(1) distance of 2.417 (3) Å is within the range of 2.34–2.79 Å found for monomeric and dimeric five-coordinate Cu compounds with a terminal bromo ligand.[20]

ESR, NMR, and Ligand-Field Spectra and Conductivities. The relevant spectral parameters of the Cu^{II}BBIDH compounds are listed in Table V. The rhombic set of g values recorded for the

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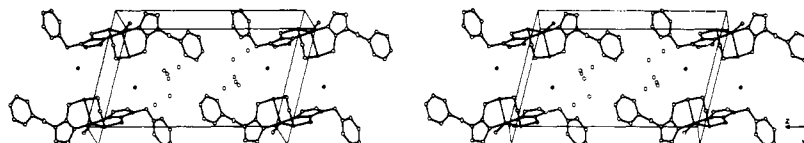
Figure 4. Stereodrawing of the unit cell of [Cu(BBIDH)Br]Br·$x$solvent. Br⁻ counterions are represented by black dots. Unconnected open circles are the partially occupied solvent molecule sites.

Table V.   ESR and Ligand Field Spectral Parameters and Conductivities of BBIDH Compounds

	ligand-field maxima		X band ESR					molar conductance,^{g} ohm^{-1} cm^2 mol^{-1}
	ν_1, 10^3 cm^{-1}	ν_2, 10^3 cm^{-1}	g_1	g_2	g_3	A_{Cu}, G	A_N, G	
Cu(BBIDH)Br$_2$·H$_2$O	16.0 (w)	11.2 (S)^a		2.12 (br)			c, e	52
	15.7 (300)	11.8 (140)^b	2.02	2.11	2.24	115 (g_3)	15 (g_2)^{d,f}	
Cu(BBIDH)(ClO$_4$)$_2$·H$_2$O	16.1 (w)	11.5 (S)^a	2.02	2.09	2.19		c	144
		14.7 (80)^b	2.00	2.11	2.25	115 (g_3)	15 (g_2)^d	
Cu(BBIDH)(NO$_3$)$_2$·H$_2$O	16.1 (w)	11.4 (S)^a	2.02	2.08	2.20		c	134
		14.9 (245)^b	2.12 ($g_\parallel$), 2.25 ($g_\perp$)			115 ($g_\parallel$)	15 ($g_\perp$)^d	
Zn(BBIDH)Cl$_2$								h

^{a} Solid reflectance spectra, diluted in MgCO$_3$. ^{b} In (CH$_3$)$_2$SO/ethanol solution. Extinction coefficients in parentheses. ^{c} Powder spectra at 77 K. ^{d} Frozen (CH$_3$)$_2$SO/ethanol solution at 77 K. ^{e} At Q band frequency the spectrum showed three g values at 2.03, 2.12, and 2.20. ^{f} There is an additional minor peak at $g = 1.94$, which is indicative for a dimeric species. ^{g} 0.001 M in DMF at 25 °C. ^{h} Nonelectrolyte.

solid powders are consistent with the severe distortions from the ideal axially symmetric trigonal-bipyramidal (D_{3h}) symmetry. The true symmetry of the complex ion cannot be higher than approximately C_2. The low values found for g_1 obey Hathaway's criterion for trigonal-bipyramidal coordination with a d$_{z^2}$ ground state (lowest $g < 2.03$).[21] Trigonal-bipyramidal coordination can be achieved with a halogenide as the fifth ligand as in [Cu(BBIDH)Br]Br·$x$solvent (see above) or with a H$_2$O ligand at the fifth coordination site as in ref 10. The ESR spectra in frozen solution, however, are compatible with a more distorted geometry, e.g., elongated octahedral or distorted square-pyramidal coordination. The molar conductivities show that the bromide compound behaves as a 1:1 electrolyte in solution. The different geometry of the compound in solution is therefore not a result of the binding of additional Br⁻ but must arise either from a rearrangement of the five ligand donor atoms or from the binding of solvent molecules. The ligand-field spectra of the solid compounds are as expected for trigonal-bipyramidal Cu^{II} compounds. The d-orbital energies in such a symmetry are d$_{z^2}$ > d$_{yz}$, d$_{yz}$ > d$_{xy}$, d$_{x^2-y^2}$, or d$_{z^2}$ > d$_{xy}$, d$_{x^2-y^2}$ > d$_{xz}$, d$_{yz}$.[21] The first sequence is more likely in the BBIDH compounds where the equatorial ligands (S, S, Br) are much weaker than the axial imidazole nitrogen ligands. In this case, the visible spectrum has two bands with the more intense band at lower frequency (cf., Table V). The spectra of the Cu^{II}BBIDH compounds have a different shape in solution, again indicating that a different coordination geometry exists in solution. Unfortunately, it is not possible to deduce the exact coordination geometry in solution from the available spectroscopic information.

The Zn^{II} compound is a nonelectrolyte and is possibly a four- or six-coordinated structure with strong Zn–Cl bonds. The Zn^{II}- and Cu^{I}BBIDH compounds are diamagnetic and allow the measurement of well-resolved NMR spectra (see Experimental Section). The structure of the Cu^I compound is likely to be analogous to that of the Cu^I compound of BBDHp (Figure 1),[9]

i.e., a linear coordination of Cu^I by two imidazole N atoms and long Cu–S distances (2.867 (2) Å in Cu(BBDHp)$^+$).[9]

Conclusions

Tetradentate ligands with a N (imidazole)–S (thioether)–S (thioether)–N (imidazole) sequence of donor atoms that are capable of forming three five-membered chelate rings around Cu^{II} appear to lead consistently to trigonal-bipyramidal coordination of the copper(II) ion. A water molecule or a halogenide ion can be bonded to Cu^{II} as the fifth ligand. ESR and ligand-field spectra of solid powders are as expected for the observed coordination geometry. The spectra of these compounds in solution indicate a different coordination geometry. These ligands stabilize the Cu^I oxidation state.

The coordination geometries and spectral properties of Cu compounds with ligands containing imidazoles as the N donor groups appear to be the same as those of benzimidazole derivatives, indicating that the use of benzimidazole groups in model studies is a relevant approach.

The reactivity of these compounds toward additional (e.g., thiolate) ligands is being investigated.

Supplementary Material Available: Tables of hydrogen positions and thermal parameters and a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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