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Copper(I) and Copper(II) Compounds of 1,7-Bis(2-benzimidazolyl)-2,6-dithiaheptane (BBDHp). X-ray Structure of Linearly Coordinated Copper(I) in the Cation [Cu^I(BBDHp)]⁺

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The synthesis of the new ligand 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane (BBDHp, (C₇H₅N₂CH₂SCH₂)₂CH₂) is reported, together with its coordination behavior toward Cu^I and Cu^{II}. Coordination with Cu^{II} salts was studied in organic solvents. No pure solid Cu^{II} compounds could be isolated. Characterization of the Cu^{II} compounds in solution by their visible and ESR spectra suggests that some of the coordination sites of the Cu^{II} ion are occupied by ligand atoms and others by solvent molecules or halogenide ions. A lowest *g* value of 1.93 and a $\Delta m_s = 2$ transition signal in the ESR spectra of frozen solutions, in which the counterions are Br⁻ or Cl⁻, indicate the presence of halogen-bridged Cu^{II} dimers. Stable solid Cu^I compounds with BBDHp have been prepared according to two methods. One is based on the chemical reduction of [Cu^{II}(BBDHp)]²⁺ with Cu powder and the other on the spontaneous reduction of the Cu^{II} compound in solution. Crystalline derivatives of [Cu^I(BBDHp)]⁺ were obtained in the presence of PF₆⁻ and BF₄⁻ ions. The relative amounts of these anions can vary to some extent. A sample analyzing as [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34} crystallizes in the monoclinic space group *I2/c* with *a* = 12.827 (2) Å, *b* = 17.485 (2) Å, *c* = 10.233 (2) Å, β = 103.8 (2)°, *V* = 2228.9 Å³, *d*_{meas} = 1.64 (1) g/cm³, and *d*_{calcd} = 1.66 g/cm³ for *Z* = 4. The structure was solved by direct methods, least-squares refinements, and Fourier methods. The residual *R* value was 0.054 for 1289 independent reflections with *I* > 2σ(*I*), whose intensities were measured on an automatic diffractometer. The Cu^I ion is linearly coordinated by two benzimidazole nitrogen atoms, whereas the thioether sulfur atoms do not have short bonding contacts (Cu-S = 2.9 Å). The Cu^I compounds have been characterized further by their NMR spectra. The design of the ligand apparently prevents bonding of all four potentially coordinating ligand atoms to a single Cu^{II} ion, in a distorted square-planar, trigonal-bipyramidal, or distorted-tetrahedral geometry, so that solid Cu^{II} compounds are not readily formed.

Introduction

Proteins with a type I or "blue" copper center have attracted much attention because they exhibit unusual chemical and physical properties.¹ No other function than electron transport has been established for their role in nature thus far.² This function requires a low transition-state energy for the transition Cu^{II} to Cu^I as well as a specific oxidation-reduction potential, dependent on the position of the enzyme in the electron-transport process.

Structure determination by X-ray crystallography of the two presumably evolutionary related blue copper proteins plastocyanin³ and azurin⁴ showed that the copper atom in these enzymes is coordinated by two imidazole nitrogen atoms, a thioether, and a thiolate sulfur atom. The coordination geometry is highly distorted tetrahedral, both in the oxidized and in the reduced form. Coordination of "soft" ligands, e.g., a thioether sulfur atom, as well as a distorted tetrahedral coordination geometry are supposed to increase the redox potential.⁵ The fact that the environment of the metal atom in the oxidized form differs only slightly from that in the reduced form is likely to lower the transition-state energy.⁶

The ligand 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane (abbreviated as BBDHp; Figure 1) is potentially quadridentate via two benzimidazolenitrogen atoms and two thioether sulfur atoms. Its copper chelates reveal new information about the behavior of copper, surrounded by an N₂S₂-donor system.

Comparison of the results with the results of studies on closely related compounds will emphasize the importance of the coordination geometry imposed by ligand constraints.⁷

Experimental Section

General Data. Solutions of Cu(BF₄)₂ in ethanol were repeatedly filtered before use. All chemicals mentioned in the text were of commercial reagent grade and used without further purification. Copper analyses were carried out with standard EDTA titrations⁸ or with a Perkin-Elmer 460 atomic absorption spectrometer. All other elemental analyses were performed by Dr. Pascher, Bonn, Germany.

Preparation of the Ligand BBDHp. BBDHp was prepared in a two-step synthesis. In the first step (analogous to ref 9), 3,7-dithianonanedioic acid (HOOCCH₂S(CH₂)₃SCH₂COOH) was formed during the slow addition of 0.4 mol (41 mL) of 1,3-dibromopropane to a solution of 0.8 mol (56 mL) of thioglycolic acid in 50% NaOH (250 mL). The solution was refluxed for 1 h. Excess H₂SO₄ (concentrated, p.a.) was added, and after cooling to room temperature the solid product was collected and recrystallized from water. The white needles obtained (yield 50%, melting range 37–39 °C) were identified as 3,7-dithianonanedioic acid by NMR spectroscopy: (vs. (CH₃)₄Si) δ 1.77 (m, 2 H), 2.59 (t, 4 H), 3.16 (s, 4 H), 7.34 (broad, 3.7 H).

The second step was a Phillips acid-catalyzed condensation.¹⁰ 3,7-Dithianonanedioic acid was refluxed during 16 h with 1,2-diaminobenzene (molar ratio 1:2) in 4 N HCl. The green-white precipitate was redissolved in hot water, and immediately after addition of an excess of NH₄OH (concentrated, p.a.) reddish white needles of BBDHp precipitated. These were collected and recrystallized from a 1:1 methanol-water mixture (yield 50%, melting point 230 °C); NMR spectral data: (vs. (CH₃)₄Si) δ 1.71 (m, 1.3 H), 2.80 (t, 3.5 H) 3.86 (s, 5 H), 7.28 (m, 8.1 H), 12.04 (broad, 0.9 H).

Reaction of Cu^{II} with BBDHp in Solution. Cu^{II} compounds of BBDHp can be prepared in solution by adding BBDHp in methanol or dimethylformamide to a solution of CuX₂ (X⁻ = Cl⁻, Br⁻, BF₄⁻, NO₃⁻, or equimolar combinations of these anions) in the same solvent.

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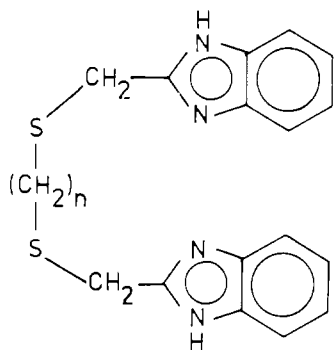


Figure 1. 1,7-Bis(2-benzimidazolyl)-2,6-dithiaheptane (BBDHp) ($n = 3$).

Colorimetric titrations of CuCl_2 and of $\text{Cu}(\text{NO}_3)_2$ in methanol (Job's plot) showed that only 1:1 chelates are formed. No pure solid products however could be obtained; physical measurements therefore were carried out on the solutions containing the appropriate Cu^{II} salt and BBDHp in a 1:1 ratio.

Synthesis of Cu^{I} (BBDHp) Compounds. Cu^{I} compounds of BBDHp can be obtained in two ways. Method 1 involves the chemical reduction of the corresponding Cu^{II} compound with Cu powder. Method 2 is based on the spontaneous reduction of Cu^{II} (BBDHp) in solution. In this case either the solvent or part of the ligand is probably oxidized.

$[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{BF}_4)$ was prepared according to method 1: 347 mg (1 mmol) of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and 368 mg (1 mmol) of BBDHp were dissolved in 20 mL of ethanol. After 30 min of refluxing in the presence of excess Cu powder, the solution was colorless. White needles of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{BF}_4)$ were obtained by allowing the solvent to evaporate under a slow nitrogen stream. The crystals were filtered off and washed with a small amount of methanol and diethyl ether. Anal. Calcd for $\text{CuC}_{19}\text{H}_{20}\text{N}_4\text{S}_2\text{BF}_4$: Cu, 12.2; C, 43.99; H, 3.86; N, 10.80; S, 12.34. Found: Cu, 12.1; C, 44.09; H, 4.01; N, 10.90; S, 12.30. For the NMR spectrum, see Table VI.

$[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)$ was prepared by reducing a solution of 170 mg (1 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 368 mg (1 mmol) of BBDHp in a 1:1 ethanol-water mixture (50 mL) with Cu powder, followed by the addition of an equimolar quantity (168 mg) of NaPF_6 to the cold filtrate. Crystallization was performed in the same way as in the case of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{BF}_4)$. White crystals were collected after 24 h and washed with methanol and diethyl ether. Anal. Calcd for $\text{CuC}_{19}\text{H}_{20}\text{N}_4\text{S}_2\text{PF}_6$: Cu, 11.1. Found: Cu, 11.3. The compound was further characterized by its NMR spectrum (Table VI).

$[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$ was prepared according to method 2. To a dark green solution of 347 mg (1 mmol) of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and 367 mg (1 mmol) of BBDHp in a ethanol-water mixture (1:1, v/v) was added 168 mg (1 mmol) of NaPF_6 . Within 48 h white crystals precipitated (room temperature, partial evaporation of the solvent). These were collected and washed with ethanol and diethyl ether. Anal. Calcd for $\text{CuC}_{19}\text{H}_{20}\text{N}_4\text{S}_2(\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$: Cu, 11.4; C, 40.95; H, 3.59; N, 10.06; S, 11.50; P, 3.67; F, 17.5. Found: Cu, 11.4; C, 41.51; H, 3.80; N, 10.16; S, 11.50; P, 3.67; F, 17.5. For the NMR spectrum, see Table VI.

Compounds of Composition $[\text{Cu}(\text{BBDHp})](\text{PF}_6)_x\text{Cl}_y$ ($(x + y) > 1$). Solid compounds of this composition spontaneously crystallized on standing for 2 days from a solution of 1 mmol of CuCl_2 and 11 mmol of BBDHp in ethanol-water (1:1, v/v) after addition of an equimolar amount of NaPF_6 (method 2). The colors of these solid products are green in various degrees of intensity. Apparently they contain variable amounts of Cu^{II} , explaining the nonintegral number of counterions (see Discussion). Anal. Calcd for $\text{CuC}_{19}\text{H}_{20}\text{N}_4\text{S}_2(\text{PF}_6)_{0.97}\text{Cl}_{0.12}$: Cu, 10.6; P, 4.94; Cl, 0.74. Found: Cu, 10.6; P, 4.94; Cl, 0.74. Calcd for $\text{CuC}_{19}\text{H}_{20}\text{N}_4\text{S}_2(\text{PF}_6)_{0.95}\text{Cl}_{0.07}$: Cu, 11.1; P, 5.14; Cl, 0.43. Found: Cu, 10.9; P, 4.77; Cl, 0.38.

Physical Measurements. Electronic spectra in the range 22 000–5000 cm^{-1} in methanol at room temperature were recorded on a Beckman DK-2A spectrophotometer and solid-state spectra on a similar instrument fitted with a reflectance attachment with BaSO_4 as reference material. Infrared spectra from 300 to 4000 cm^{-1} were recorded on a Perkin-Elmer 580 spectrometer. Samples were pelleted in KBr.

ESR spectra at X-band frequencies were obtained with a Varian E-3 spectrometer. Samples were either powdered solids (room tem-

Table I. Crystal and Unit Cell Data of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$

	crystal size	$0.45 \times 0.14 \times 0.10$ mm^3
Weissenberg photographs	Laue symmetry	$2/m$
	systematic absences	$h + k + l = 2n + 1$ for hkl $l = 2n + 1$ for $h0l$ lc or $I2/c^a$
diffractometer measmnts	possible space groups	
	lattice constants (estd std dev)	$a = 12.827(2) \text{ \AA}$, $b = 17.485(2) \text{ \AA}$, $c = 10.233(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 103.8(2)^\circ$, $\gamma = 90^\circ$, $V = 2228.9 \text{ \AA}^3$
unit cell contents	tot no. of reflctn measd	4233
	no. of independent reflctn	2023
	no. of significant reflctn	1289
	no. of molecules/unit cell	4
	mol wt of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$	557.4
	calcd density	1.66 g/cm^3
	obsd density (floatation in $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Br}_2$)	$1.64(1) \text{ g/cm}^3$
	$\mu(\text{Mo K}\alpha)$	12.7 cm^{-1}

^a The structure has been solved in space group $I2/c$ instead of in the standard $C2/c$ space group because in the $I2/c$ setting β is closer to 90° .

perature) or frozen methanolic solutions (77 K). Proton NMR spectra were recorded on a JEOL PS-100 spectrometer in $(\text{CD}_3)_2\text{SO}$.

Conductivity measurements were performed in dimethylformamide with the aid of a Phillips PR 9500 instrument. X-ray powder diagrams were made with a Nonius Guinier-De Wolff camera, using $\text{Cu K}\alpha$ radiation. Magnetic susceptibility at room temperature was measured on a Faraday balance calibrated with $\text{CoHg}(\text{SCN})_4$.

X-ray Methods and Structure Determination. A crystal of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$ was selected for structure determination by X-ray crystallography. Preliminary Weissenberg photographs indicated a space group lc or $I2/c$. Intensity data were collected on a Nonius CAD-4 computer-controlled diffractometer (ω - θ scans) by using graphite-monochromated $\text{Mo K}\alpha$ radiation. Lattice constants were determined by a least-squares refinement of the angular settings of 24 reflections with $12^\circ < \theta < 15^\circ$. Each reflection in the range $2^\circ < \theta < 25^\circ$, $h > 0$ and $k > 0$, was measured in 96 steps. The intensity measurements in 16 steps at each end of a scan was considered as background. The scanning rate was adjusted to the required precision of $\sigma(I)/I < 0.01$ with a maximum scan time of 90 s. The intensity I and its estimated standard deviation $\sigma(I)$ were calculated from $I = s(p - 2(B_1 + B_2))$ and $\sigma(I) = s(P + 4(B_1 + B_2))^{1/2}$, where s is a factor to account for the variable scan speed, P is the peak scan count, B_1 and B_2 are the low- and high-angle background counts. Three standard reflections were measured every 5400 s of radiation time to check for instrumental instability and crystal decomposition. The data were corrected for absorption. Lorentz and polarization corrections were applied in the usual way. Crystal and unit cell data given in Table I.

The position of the Cu atom did not follow unequivocally from a three-dimensional Patterson synthesis. Therefore the direct-methods program MULTAN78¹¹ was used to solve the phase problem. Since Wilson statistics of the data indicated the presence of a symmetry center, the structure was solved in space group $I2/c$. For 166 $|E|$'s greater than 1.2, the set of phases with the highest combined figure of merit was used to calculate an E map. The positions of the Cu and P atoms (on crystallographic twofold axes) as well as the five-membered imidazole ring could be located in this way. The heavy-atom positions were in agreement with the positions of the Harker peaks in the Patterson map.

All other nonhydrogen atoms belonging to the ligand molecule were found in a series of block-diagonal least-squares refinements and subsequent Fourier syntheses. In further refinement cycles all non-

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Table II. Atomic Positional and Thermal Parameters (\AA^2)^a for $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$ with Their Estimated Standard Deviations in Parentheses

atom ^b	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U_{11}	10^3U_{22}	10^3U_{33}	$(2 \times 10^3) \times U_{12}$	$(2 \times 10^3) \times U_{23}$	$(2 \times 10^3) \times U_{31}$	B_{iso}	occu- pancy
Cu	0	1302 (1)	2500	32 (1)	78 (1)	56 (1)	0	0	38 (1)		1
S	1017 (1)	622 (1)	4158 (2)	54 (1)	77 (1)	46 (1)	-23 (2)	7 (2)	34 (2)		1
N(1)	1450 (4)	1409 (2)	2333 (5)	35 (2)	52 (3)	52 (3)	-4 (5)	-10 (5)	33 (4)		1
C(1)	0	-1071 (8)	2500	82 (8)	63 (8)	100 (11)	0	0	-40 (14)		1
C(2)	1029 (6)	-619 (4)	2162 (9)	57 (4)	56 (5)	75 (5)	-12 (7)	-2 (8)	-2 (8)		1
C(3)	2267 (5)	522 (5)	4210 (8)	43 (4)	73 (5)	60 (5)	6 (8)	6 (8)	9 (7)		1
C(4)	2257 (4)	994 (4)	3002 (7)	34 (3)	51 (4)	58 (4)	-8 (6)	-6 (7)	22 (6)		1
C(5)	1830 (4)	1775 (3)	1312 (6)	40 (3)	40 (3)	53 (4)	-9 (5)	-16 (6)	39 (6)		1
C(6)	1356 (5)	2292 (4)	343 (7)	51 (4)	51 (4)	65 (4)	-4 (6)	-15 (7)	43 (7)		1
C(7)	1942 (7)	2529 (4)	-548 (8)	90 (6)	50 (5)	63 (5)	-31 (9)	9 (7)	37 (9)		1
C(8)	2978 (7)	2266 (5)	-4701 (9)	75 (5)	67 (5)	92 (6)	-41 (9)	-12 (9)	105 (10)		1
C(9)	3460 (6)	1766 (4)	4809 (9)	55 (4)	67 (5)	93 (6)	-15 (8)	-6 (9)	87 (9)		1
C(10)	2870 (5)	1535 (3)	1400 (3)	42 (3)	41 (4)	76 (5)	-10 (6)	-11 (7)	49 (6)		1
N(2)	3118 (4)	1045 (3)	2472 (7)	33 (3)	54 (4)	92 (5)	7 (5)	8 (7)	41 (6)		1
H(1C1)	0	-1340 (40)	1770 (60)							5.0	1
H(1C2)	-1620 (50)	-940 (40)	1820 (70)							5.0	1
H(2C2)	-1150 (50)	-280 (40)	2920 (70)							5.0	1
H(1C3)	2430 (50)	810 (40)	4910 (70)							5.0	1
H(2C3)	2870 (50)	100 (40)	4310 (70)							5.0	1
H(1C6)	620 (50)	2420 (40)	250 (60)							5.0	1
H(1C7)	1670 (50)	2830 (40)	-1110 (70)							5.0	1
H(1C8)	3370 (50)	2490 (40)	-1050 (70)							5.0	1
H(1C9)	4170 (50)	1590 (30)	520 (60)							5.0	1
H(1N2)	3600 (50)	820 (40)	2740 (80)							5.0	1
P	0	4309 (2)	7500	35 (2)	50 (2)	68 (3)	0	0	17 (4)		0.66
F(1)	1205 (4)	4304 (2)	7551 (6)							8.3 (1)	1
F(2)	-300 (7)	4200 (6)	5937 (9)							8.3 (1)	0.63 (1)
F(3)	0	5204 (8)	7500							8.3 (1)	0.58 (1)
F(4)	0	3370 (10)	7500							8.3 (1)	0.42 (1)
F(5)	1301 (9)	5069 (7)	8490 (20)							8.3 (1)	0.44 (1)
F(6)	40 (10)	3680 (10)	6560 (20)							8.3 (1)	0.30 (1)

^a The thermal motion parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*)]$ and $\exp[-B_{\text{iso}}(\sin^2 \theta)/\lambda^2]$. ^b The atomic numbering scheme is given in Figure 2a; the last two symbols in the hydrogen numbering correspond to the parent atom.

hydrogen atoms of the complex cation were refined anisotropically in full-matrix least-squares refinement cycles. Localization of the anions caused some problems. In two successive difference Fourier maps more than six independent peaks were found lying near the P atom, two of which are situated on the twofold axis. The resulting 10 atom positions around the P atom indicate disorder in, and/or superposition of BF_4^- and PF_6^- anions. The highest peak—which was not on a twofold axis—was considered to correspond to a fully occupied F⁻ position. Its positional parameters and isotropic temperature factor were refined. The other peaks were considered to be partially occupied F⁻ atoms. These atoms were given the same temperature factor as the first—fully occupied—F⁻ position and their multiplicities were refined. This resulted in an isotropic B of 8.3 \AA^2 for all F⁻ atoms. The sum of their occupancies amounts to 5.7 F⁻ atoms/ $[\text{Cu}^{\text{I}}(\text{BBDHp})]^+$ ion. The analytical data suggest the presence of 5.32 fluoride atoms. However, no distances corresponding to those in a BF_4^- ion were found, so that any BF_4^- present was considered to be largely disordered. The sum of the multiplicities (5.7) is slightly higher than expected from analyses (5.32). Presumably the highest peak, which is considered to correspond to a fully occupied F⁻ site (i.e., F(1)), represents a partially occupied F⁻ position instead. Figure 3 shows an ORTEP drawing of the disordered PF_6^- ion. The atom labeling as well as the occupancies of the atomic sites are indicated. Difference Fourier syntheses revealed the positions of all hydrogen atoms. Their isotropic thermal parameters were fixed at a value of $B = 5.0 \text{ \AA}^2$, and their positions were refined. In a final difference Fourier map some electron density was found in the vicinity of the P site (peaks 0.42 e/\AA^3 , statistical height 7.83 e/\AA^3). Most likely these peaks also represent parts of the disordered anion molecules, but they have not been included in the refinement. In all refinement stages unit weights were used. The refinement was continued until the parameter shifts were less than 40% of their standard deviations. The final values of the residuals¹² are $R = 0.054$ and R_w and 0.052 for the 1289 observed reflections ($I > 2\sigma(I)$) used in the refinement, and $R = 0.098$ and

Table III. Interatomic Distances (\AA) for $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$ with their Estimated Standard Deviations in Parentheses^{a,b}

Cu-N(1)	1.918 (4)	Cu-S	2.867 (2)
C(1)-C(2)	1.51 (1)	C(5)-C(6)	1.373 (9)
C(2)-S	1.804 (8)	C(6)-C(7)	1.38 (1)
S-C(3)	1.784 (7)	C(7)-C(8)	1.39 (1)
C(3)-C(4)	1.48 (1)	C(8)-C(9)	1.39 (1)
C(4)-N(1)	1.318 (8)	C(9)-C(10)	1.391 (9)
C(4)-N(2)	1.346 (8)	C(10)-C(5)	1.361 (8)
N(1)-C(5)	1.405 (7)	C(10)-N(2)	1.369 (9)
C(1)-H(1C1)	0.88 (6)	C(6)-H(1C6)	0.95 (6)
C(2)-H(1C2)	0.95 (6)	C(7)-H(1C7)	0.79 (7)
C(2)-H(2C2)	1.01 (7)	C(8)-H(1C8)	0.95 (7)
C(3)-H(1C3)	0.86 (7)	C(9)-H(1C9)	0.96 (6)
C(3)-H(2C3)	0.95 (7)	N(1)-H(1N1)	0.73 (7)
P-F(1)	1.534 (5)	P-F(4)	1.65 (2)
P-F(2)	1.565 (9)	P-F(5)	1.65 (1)
P-F(3)	1.57 (1)	P-F(6)	1.45 (2)
F(3)''...N(2)	2.820 (9)	F(3)''...H(1N2)	2.16 (7)
F(5)''...N(2)	3.06 (1)	F(5)''...H(1N2)	2.33 (7)
F(5)'''...N(2)	3.16 (1)	F(5)'''...H(1N2)	2.63 (7)

^a The superscripts correspond to the following symmetry operations: (no superscript) x, y, z ; (') $-x, y, z$; (')' $-x + 1/2, y - 1/2, z + 1$; (')'' $x + 1/2, y - 1/2, z - 1/2$. ^b The atomic numbering scheme is given in Figure 2a; the last two symbols in the hydrogen numbering correspond to the parent atom.

$R_w = 0.071$ for all 2023 reflections. Inclusion of the weak reflections caused the standard deviations to decrease by about 10%.

Atomic scattering factors for neutral atoms were taken for all nonhydrogen atoms from ref 13 and used with correction for the

(12) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum \sigma^2(F) (|F_o| - |F_c|)^2 / \sum \sigma^2(F) |F_o|^2]^{1/2}$.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol 4.

Table IV. Selected Interbond Angles (Deg) for $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$ with Their Estimated Standard Deviations in Parentheses^{a-c}

N(1)-Cu-N(1)'	168.5	N(1)-Cu-S'	109.7 (2)
N(1)-Cu-S	79.3 (2)	S-Cu-S'	81.79 (8)
C(2)'-C(1)-C(2)	116 (1)	C(3)-C(4)-N(2)	121.9 (6)
C(1)-C(2)-S	110.8 (6)	N(1)-C(4)-N(2)	111.8 (6)
C(2)-S-C(3)	98.7 (4)	C(4)-N(1)-Cu	123.8 (4)
C(2)-S-Cu	73.2 (2)	C(4)-N(1)-C(5)	105.6 (5)
Cu-S-C(3)	87.5 (3)	Cu-N(1)-C(5)	128.9 (6)
S-C(3)-C(4)	113.4 (5)	N(1)-C(5)-C(6)	131.4 (5)
C(3)-C(4)-N(1)	126.3 (6)	N(1)-C(5)-C(10)	108.6 (6)
C(6)-C(5)-C(10)	120.0 (6)	C(9)-C(10)-C(5)	122.4 (7)
C(5)-C(6)-C(7)	117.3 (7)	C(9)-C(10)-N(2)	132.0 (6)
C(6)-C(7)-C(8)	121.9 (8)	C(5)-C(10)-N(2)	105.5 (5)
C(7)-C(8)-C(9)	121.8 (7)	C(10)-N(2)-C(4)	108.5 (5)
C(8)-C(9)-C(10)	116.6 (7)		
C(10)-N(2)-H(1N2)	131 (6)	N(2)-H(1N2)···F(5)'''	131 (7)
H(1N2)-N(2)-C(4)	121 (6)	H(1N2)···F(3)''-P	120 (2)
N(2)-H(1N2)···F(3)''	152 (8)	H(1N2)···F(5)''-P	107 (2)
N(2)-H(1N2)···F(5)'''	180 (10)	H(1N2)···F(5)'''-P	95 (2)

^a The superscripts correspond to the following symmetry operations: (no superscript) x, y, z ; (') $-x, y, -z + 1/2$; (')' $-x + 1/2, y - 1/2, -z$; (')'' $x + 1/2, y - 1/2, z - 1/2$. ^b Additional interbond angles are given in the supplementary material. ^c The atomic numbering scheme is given in Figure 2a; the last two symbols in the hydrogen numbering correspond to the parent atom.

anomalous scattering. The atomic scattering factors for hydrogen atoms were taken from ref 14. Atomic positional and thermal parameters are given in Table II. A table of observed and calculated structure factors is available.¹⁵

Results

Description of the Structure of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$. Interatomic distances and selected interbond angles are listed in Tables III and IV. A full description of the geometry of the PF_6^- ion is given in the supplementary material.¹⁵

ORTEP drawings of the $[\text{Cu}^{\text{I}}(\text{BBDHp})]^+$ ion in two different orientations are given in Figure 2a, b. The cation has C_2 symmetry; Cu and C(1) are situated on a crystallographic twofold axis. The Cu^{I} ion is almost linearly coordinated by two imidazole nitrogen atoms. The Cu-N distance is 1.918 (4) Å. Although in plastocyanin the thioether sulfur atoms at distances 2.90 (to Cu^{II}) and 2.74 Å (to Cu^{I})⁶ are considered to be weakly coordinating, it is unlikely that the two thioether sulfur atoms in $[\text{Cu}^{\text{I}}(\text{BBDHp})]^+$ have significant bonding contacts with the copper ion. In the first place the Cu···S distance is relatively long. Second, the small Cu···S-C(2) and the Cu···S-C(3) angles (73.2 and 87.5°, respectively) suggest that the lone electron pairs on the S atoms do not point toward the Cu^+ ion. Cu-S-C angles in the range 90–106°, being considerably larger than those in the present compound, have been reported for a complex structure in which the thioether sulfur atom is coordinating.¹⁶ The phenyl ring is coplanar with the imidazole ring. Deviations of the carbon and nitrogen atoms from a least-squares plane through these atoms are less than 0.08 Å. The angle between the two benzimidazole planes in one $[\text{Cu}^{\text{I}}(\text{BBDHp})]^+$ ion amounts to 80.5°. The Cu^{I} ion is at a distance 0.49 Å from both planes. The distances F(3)···H(1N2) and F(5)···H(1N2) and the angles F(3)···H(1N2)-N(2) and F(5)···H(1N2)-N(2) (see Tables III and IV) indicate the presence of hydrogen bonds between the cation and the anion.

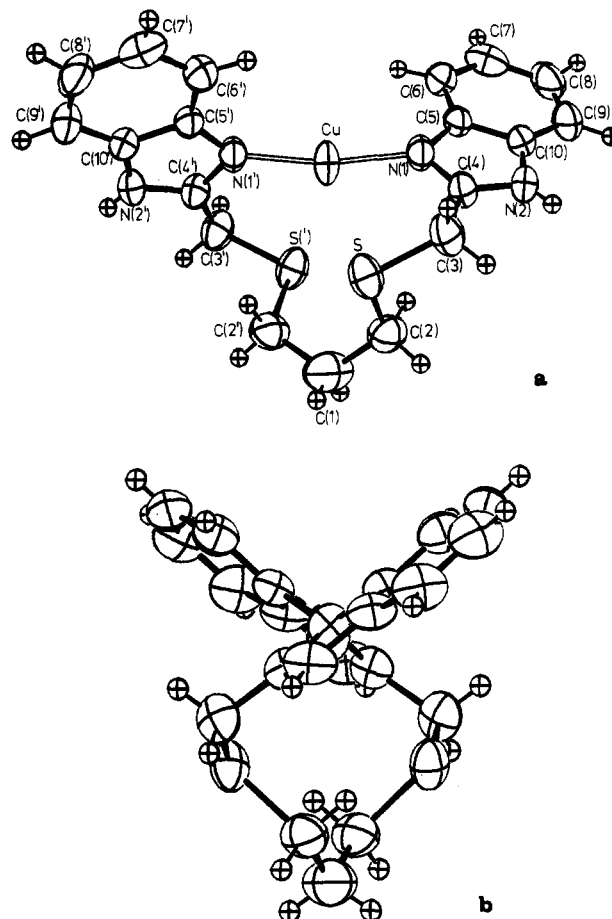


Figure 2. ORTEP drawings of $[\text{Cu}^{\text{I}}(\text{BBDHp})]^+$: a, perspective projection; b, parallel projection of the structure, rotated 90° with respect to part a. Cu and C(1) are situated on a crystallographic twofold axis. An isotropic B of 1.0 Å² has been given to all hydrogen atoms (probability 50%).

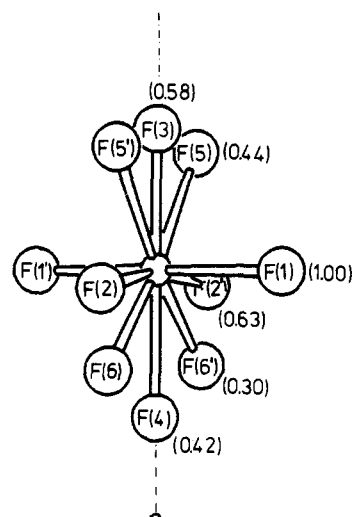


Figure 3. ORTEP drawing of the disordered PF_6^- ion (probability 12%). F(3), P, and F(4) are situated on a crystallographic twofold axis, which is indicated. The occupancies of the various F sites are given in parentheses. 1.00 corresponds to a completely occupied atom site.

In PF_6^- , shown in Figure 3, the disordered fluoride peaks are almost in the same plane. Deviations of F(2), F(5), and F(6) from a plane through F(3) and F(4), perpendicular to P-F(1), are -0.09, -0.02, and +0.13 Å. It seems that the PF_6^- ion may rotate around the P-F(1) axis but that it has some preferential orientations. Presumably not every amine hydrogen atom is connected to the anion via a hydrogen bridge.

(14) Steward, R. F.; Davidson, E. R.; Simpson, W. J. *J. Chem. Phys.* **1965**, *42*, 3175.

(15) Supplementary material.

(16) (a) Braithwaite, A. C.; Rickard, C. E. F.; Waters, T. N. *Inorg. Chim. Acta* **1978**, *26*, 63. (b) Braithwaite, A. C.; Rickard, C. E. F.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1817.

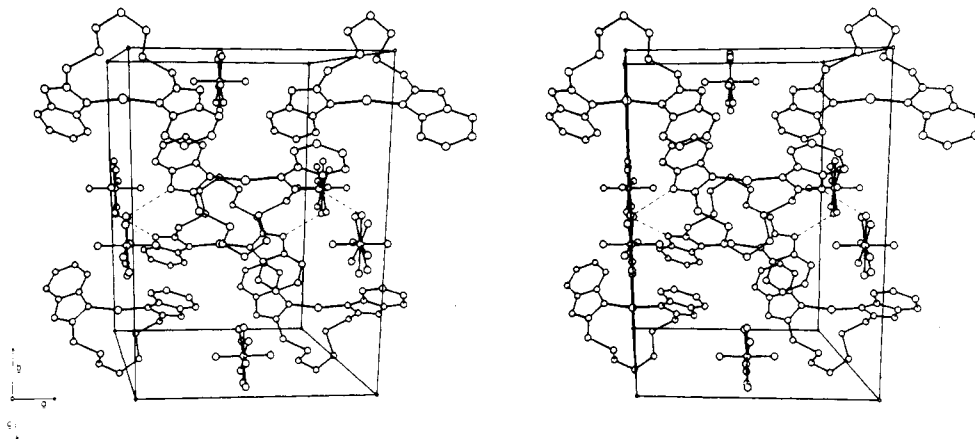


Figure 4. Stereodrawing of the unit cell of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)_{0.66}(\text{BF}_4)_{0.34}$. Only PF_6^- ions are shown, although they cannot account for all anions present. Dashed lines represent hydrogen bonds.

Table V. Visible Spectral Data and Conductivity of Compounds Containing the $\text{Cu}(\text{BBDHp})^{2+}$ Group

anions present in soln	visible spectra ^a				molar conductance ^b $\Lambda, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	$10^3 \nu_1, \text{ cm}^{-1}$	$\epsilon_0, \text{ M}^{-1} \text{ cm}^{-1}$	$10^3 \nu_2, \text{ cm}^{-1}$	$\epsilon_0, \text{ M}^{-1} \text{ cm}^{-1}$	
2 Cl^-	15.4	150	11.8	100	70
$\text{Cl}^- + \text{BF}_4^-$	15.4	150	11.8	100	
$\text{Cl}^- + \text{NO}_3^-$	15.4	130	11.8	90	140 ^c
2 Br^-	15.2	350	11.8	130	150 ^c
$\text{Br}^- + \text{BF}_4^-$	15.2	250	11.8	120	
$\text{Br}^- + \text{NO}_3^-$	15.2	260	11.8	120	
2 BF_4^-	15.6	94	11.8	88	260
2 NO_3^-	15.4	140	11.5	130	250

^a In methanol at room temperature; concentration 2×10^{-3} mol/L. ^b In dimethylformamide at 20.0 °C; concentration 5×10^{-4} mol/L. ^c We observed that under the same experimental conditions the molar conductances of the 1:1 electrolytes $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{BF}_4)$ and $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)$ are $140 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Moreover, the elemental analysis data showed that PF_6^- cannot occupy more than about 0.66 of the anion places. Therefore, the structure has been refined with an occupancy of the P atom of 0.66.

The $[\text{Cu}^{\text{I}}(\text{BBDHp})]^+$ and part of the PF_6^- ions, joined by hydrogen bridges, form chains parallel to the *a* axis. These chains are shown in a stereo plot of the unit cell (Figure 4).

Electronic Spectra and Conductivity. All electronic spectra of $\text{Cu}^{\text{II}}(\text{BBDHp})$ compounds, prepared and measured in situ, show, besides a very intense absorption band in the UV region ($(25\text{--}30) \times 10^3 \text{ cm}^{-1}$), an absorption band at about $15 \times 10^3 \text{ cm}^{-1}$ and a weaker one near $12 \times 10^3 \text{ cm}^{-1}$. Spectral data of $\text{Cu}^{\text{II}}(\text{BBDHp})$ compounds with various anions are summarized in Table V. Compounds in which one or both of the anions is a chloride ion show no significant differences in their electronic spectra, suggesting that a chloride ion is in the coordination sphere. The same holds for bromide as a counterion. This suggestion is supported by the fact that the band maxima of $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{BF}_4)_2$ changes into the spectrum of $[\text{Cu}^{\text{II}}(\text{BBDHp})]\text{Cl}_2$ when KCl in a molar ratio ≥ 1 is added to the solution, as well as by the results of the conductivity measurements, explained below.

The molar conductance Λ in dimethylformamide of $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{BF}_4)$ and $[\text{Cu}^{\text{I}}(\text{BBDHp})](\text{PF}_6)$, which presumably are 1:1 electrolytes, amounts to $140 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (Table V). The molar conductances of some $\text{Cu}^{\text{II}}(\text{BBDHp})$ compounds, prepared by mixing the ligand with stoichiometric amounts of the appropriate (combinations of) Cu^{II} salts, are also given

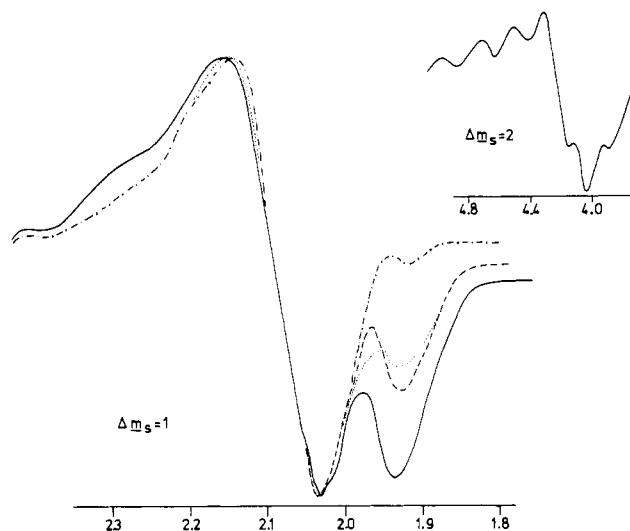


Figure 5. ESR spectra at X-band frequencies of various $\text{Cu}(\text{BBDHp})$ compounds, prepared and measured in situ at 77 K in methanol (see text): —, $[\text{Cu}(\text{BBDHp})\text{Cl}_2]$; ---, $[\text{Cu}^{\text{II}}(\text{BBDHp})\text{Cl}](\text{NO}_3)$; ···, $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{NO}_3)_2 + 2(\text{C}_2\text{H}_5)_4\text{NCl}$; -·-·, $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{NO}_3)_2 + 4(\text{C}_2\text{H}_5)_4\text{NCl}$. Inset: $\Delta m_s = 2$ transition signal in the spectrum of $[\text{Cu}(\text{BBDHp})\text{Cl}_2]$.

in Table V. Comparison with the molar conductances of the 1:1 electrolytes shows that $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{NO}_3)_2$ and $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{BF}_4)_2$ are 1:2 electrolytes, whereas $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{NO}_3)\text{Cl}$ and $[\text{Cu}^{\text{II}}(\text{BBDHp})]\text{Br}_2$ are 1:1 electrolytes. The molar conductance of a solution containing CuCl_2 and BBDHp in a 1:1 ratio is reproducibly smaller. This may be the result of the formation of dimeric species (see also the section on ESR spectra below). From the results it is tentatively concluded that at least one chloride or bromide ion—if present—is tightly bonded and that the compounds should preferably be formulated de.g., as $[\text{Cu}^{\text{II}}(\text{BBDHp})\text{Br}]\text{Br}$ and $[\text{Cu}^{\text{II}}(\text{BBDHp})\text{Cl}](\text{NO}_3)$. Furthermore, since all electronic spectra roughly have the same shape, solvent molecules are assumed to coordinate when no halogen ions are available.

ESR Spectra. ESR spectra at X-band frequencies of $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{NO}_3)_2$ and $[\text{Cu}^{\text{II}}(\text{BBDHp})](\text{BF}_4)_2$ measured in frozen methanol immediately after preparation indicate the presence of more than one species. Although a colorimetric titration showed that 1:1 chelates are formed, apparently different surroundings of the copper ion may occur in solution, whose ligand field spectra however are not resolved.

The ESR spectra of $[\text{Cu}(\text{BBDHp})\text{Cl}_2]$ and $[\text{Cu}^{\text{II}}(\text{BBDHp})\text{Cl}](\text{NO}_3)$, obtained under the conditions mentioned above, are shown in Figure 5. In both spectra a $\Delta m_s = 2$ signal

Table VI. NMR Spectral Data of BBDHp and Some of Its Cu^I Coordination Compounds

compd ^a	δ vs. (CH ₃) ₄ Si ^b				
	H ₂ (C1)	H ₄ (C2)	H ₄ (C3)	H ₈ (ar) ^c	
BBDHp	1.71 (m, 1.1 H)	2.80 (t, 2.8 H)	3.86 (s, 4.0 H)	7.16, 7.40 sy (m, 8.1 H)	12.04 (b, 0.7 H)
[Cu ^I (BBDHp)](BF ₄)	1.99 (b, 2.0 H)	2.70 (b, 3.8 H)	4.26 (b, 4.0 H)	7.24, 7.54 as (b, 8.5 H)	13.09 (b, 1.3 H)
[Cu ^I (BBDHp)](PF ₆)	2.03 (b, 2.2 H)	2.77 (b, 3.9 H)	4.33 (b, 4.0 H)	7.34, 7.61 as (b, 8.8 H)	13.30 (b, 1.5 H)
[Cu ^I (BBDHp)](PF ₆) _{0.66} (BF ₄) _{0.34}	1.99 (b, 2.1 H)	2.73 (b, 4.0 H)	4.30 (b, 4.0 H)	7.28, 7.56 as (b, 9.0 H)	13.09 (b, 0.8 H)

^a For nomenclature of the protons, see Description of the Structure of [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34}; ar = aromatic protons. ^b Key: s = singlet; t = triplet; m = multiplet; b = broad. ^c The aromatic proton signal was split into two major peaks, whose positions are indicated. Key: sy = peaks are symmetric; as = peaks are asymmetric with respect to each other. Since we observed that this asymmetry increases when part of the copper ions is oxidized by air, this phenomenon might be due to trace amounts of Cu^{II}.

with a seven-line pattern—typical of Cu^{II} dimers¹⁷—is observed. The $\Delta m_s = 2$ signal of [Cu(BBDHp)Cl₂] is shown in the inset.

ESR spectra of frozen methanolic solutions of [Cu^{II}(BBDHp)](NO₃)₂ and N(C₂H₅)₄Cl in molar ratios 1:2 and 1:4 are also shown in Figure 5. The spectra resemble the spectra of [Cu(BBDHp)Cl₂] and of [Cu^{II}(BBDHp)Cl](NO₃). The intensity of the peak at $g_{\text{eff}} = 1.93$ varies in comparison with the intensity of the peak at $g_{\text{eff}} = 2.04$ as a function of the amount of chloride ions added. The peak at $g_{\text{eff}} = 1.93$, which must result from a spin triplet dimeric Cu^{II} species, decreases in intensity paralleling the disappearance of the half-field signal.

Spectra of [Cu^{II}(BBDHp)Br]Br and [Cu^{II}(BBDHp)Br](NO₃) (in methanol at 77 K) resemble the spectrum of [Cu^{II}(BBDHp)](NO₃)₂ + 4N(C₂H₅)₄Cl. A small shoulder at $g_{\text{eff}} = 1.93$ and an extremely weak $\Delta m_s = 2$ transition signal are observed.

In general, the ESR spectra of the Cu^{II}(BBDHp) compounds are difficult to interpret because more than one species presumably is present. In halogenide-containing solutions both monomeric and dimeric species occur. Moreover, the number of monomeric species in these solutions is larger than one, as deduced from the copper hyperfine splittings in the g_{\perp} region. Also the number of superhyperfine lines on g_{\perp} (see Figure 5) is larger than expected, and the lines have different intensities. For a single species one would expect five lines (two N atoms coordinating). The observation of five moderately strong lines, apart from three to five weaker lines, agrees with at least two different Cu^{II} species coordinated by BBDHp. These additional lines are not expected to originate from dimeric species because the value of the splitting is normal for N-donor ligands bound to Cu^{II}, i.e., around 15 G.¹⁸ It is clear anyway that one of the frozen-solution species is a dimeric species, as evidenced by the line at $g_{\text{eff}} = 1.93$ and the $\Delta m_s = 2$ transition. Apparently the concentration and the number of chloride ions determine the concentration of the dimeric species. The concentration is maximal for a Cu:Cl ratio of 1:2; addition of more Cl⁻ results in a decreasing dimer signal, presumably due to the formation of more monomeric species such as [Cu(BBDHp)Cl₂]. Because Cl-bridged dimeric Cu^{II} compounds have been frequently found in the literature,^{16b,19} dimeric Cl-bridged [(BBDHp)CuCl₂Cu(BBDHp)]²⁺ might well occur in solution. With the ligand 3,4-bis((2-aminoethyl)thio)toluene (also an N₂S₂ donor set) such a Cl-bridged species has even been reported in solid state.^{16b}

Pure and Partially Oxidized Cu^I Compounds. No pure Cu^{II}(BBDHp) compounds could be obtained in solid state.

Addition of an excess of diethyl ether to solutions of Cu^{II}(BBDHp) with various anions resulted in the precipitation of green powders, which all showed broad absorption bands in their infrared spectra, indicating a high degree of impurity. These powders could not be recrystallized from any common solvent. Slow addition of diethyl ether by vapor diffusion did not yield pure products either.

In a solution of [Cu^{II}(BBDHp)Cl₂] and NaPF₆, however, light green crystals of composition [Cu(BBDHp)](PF₆)_xCl_y ($x + y > 1$) grew within 1 day. The intensity of the green color varies somewhat (see Experimental Section), but totally colorless crystals of [Cu^I(BBDHp)](PF₆) could only be obtained by reduction of Cu^{II} with an excess of Cu powder and successive crystallization in an inert atmosphere. Only [Cu^{II}(BBDHp)](BF₄)₂ spontaneously yielded colorless crystals of [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34} without the aid of Cu powder after addition of PF₆⁻.

So that the amount of Cu^{II} in [Cu^I(BBDHp)](PF₆) and in [Cu^I(BBDHp)](PF₆)_{0.97}Cl_{0.12} could be defined, the molar magnetic susceptibility (χ_M) was measured and corrected for diamagnetism. The magnetic susceptibility (χ_{dia}) was calculated according to ref 20. χ_{dia} amounts to 0.30×10^{-6} cm³/mol for these compounds. $\chi_M - \chi_{\text{dia}}$ is 0 for [Cu^I(BBDHp)](PF₆) and 0.12×10^{-3} cm³/mol for [Cu(BBDHp)](PF₆)_{0.97}Cl_{0.12} resulting in an effective magnetic moment μ for the latter of 0.54 μ_B . From these values the ratio Cu^{II}:(Cu^I + Cu^{II}) is estimated to be about 0.1.²¹

The colorless crystals are ESR silent. A solid-state ESR spectrum of [Cu(BBDHp)](PF₆)_{0.97}Cl_{0.12} (light green) has been recorded at room temperature. Two g values are present ($g_{\parallel} = 2.19$ and $g_{\perp} = 2.07$). The hyperfine splitting of the parallel component is well resolved ($A_{\parallel} = 130$ G), presumably because the Cu^{II} centers are magnetically diluted in Cu^I. The above spectrum is not similar to any of the Cu^{II}(BBDHp) ESR spectra in methanol at 77 K. Yet it is possible that a minor component in solution has the same coordination geometry as Cu^{II} in the solid product. The compounds [Cu(BBDHp)](PF₆)_xCl_y ($x + y > 1$) show in their electronic spectra a major absorption band at 15 400 cm⁻¹ with a shoulder at 11 800 cm⁻¹. These values are nearly identical with those observed for [Cu(BBDHp)Cl₂] in solution. These spectral data of the light green compounds are consistent with an elongated tetragonal-octahedral or square-coplanar stereochemistry but have never been observed for Cu^{II} in a trigonal-bipyramidal environment.²²

Powder diagrams of [Cu^I(BBDHp)](PF₆), [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34}, and the partially oxidized products [Cu(BBDHp)](PF₆)_{0.97}Cl_{0.12} and [Cu(BBDHp)](PF₆)_{0.95}Cl_{0.07} show that the compounds are X-ray isomorphous. The structure of [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34} (see

(17) Reedijk, J.; Knetsch, D.; Nieuwenhuys, B. *Inorg. Chim. Acta* **1971**, *5*, 568.

(18) E.g.: Rubinson, K. A. *J. Am. Chem. Soc.* **1979**, *101*, 6105 and references cited therein.

(19) (a) Roundhill, S. G. N.; Roundhill, D. M.; Bloomquist, D. R.; Landee, C.; Willett, R. D.; Dooley, D. M. Gray, H. B. *Inorg. Chem.* **1979**, *18*, 831. (b) Beckingsale, P. G.; Morcom, A. T.; Rickard, C. E. F.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1977**, 2135.

(20) Figgis, B. N.; Lewis, J. *Techn. Inorg. Chem.* **1967**, *6*, 142.

(21) $\mu = [(3k/N)\chi T]^{1/2}$; if all copper present is Cu^{II}, then $\mu = 1.73 \mu_B$ and $\chi = 1.28 \times 10^{-3}$ cm³/mol. Cu^{II}:(Cu^I + Cu^{II}) = $\chi_{\text{meas}}/1.28 \times 10^{-3}$.

(22) Hathaway, B. J.; Billing, D. E. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143 and references cited therein.

section on the description of the structure) consists of monomeric [Cu^I(BBDHp)]⁺ and PF₆⁻ ions, held together by hydrogen bridges. No BF₄⁻ ions are observed, presumably because they are completely disordered. It may therefore be assumed that the X-ray isomorphous compounds also exhibit disorder. The spectral data of the Cu^{II} compounds show that the coordination geometry of the mixed Cu^I/Cu^{II} compounds cannot be the same—at least not at the Cu^{II} ion sites—as the linear coordination of Cu^I, which was found in the present X-ray structure. It seems therefore likely that in this case disorder is not only present in the anions, but also in the cations.

Weissenberg photographs of a crystal of [Cu^I(BBDHp)](BF₄) indicated that this structure is not isomorphous with [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34}. The structure of this crystal was not investigated further.

Table VI summarizes the NMR spectral data of some Cu^I(BBDHp) chelates, as well as the data for the free ligand. Sugiura²³ observed a large shift (0.6 ppm) of the signal of the aliphatic proton located next to the coordinating thiol sulfur atoms, whereas the other signals remained in the same place. However, we found that H(C1), H(C2), and H(C3) were shifted only 0.3, 0.2, and 0.4 ppm, respectively, with respect to the corresponding signal in the free ligand. The shifts of the aliphatic proton signals in the complex compounds are likely to arise from the influence of the copper atom rather than from coordination of the thioether sulfur atoms. The NMR spectral data thus agree with the conclusion that at best weak bonds exist between the thioether sulfur atoms and the copper ion.

Discussion

Reluctance of Cu^{II}(BBDHp) Compounds to Crystallize. Cu^{II}(BBDHp) compounds could not be obtained pure in the solid state. The ESR spectra of Cu^{II}(BBDHp) in frozen methanolic solution suggest that Cu^{II} ions are present, coordinated by BBDHp, halogen ions, and/or solvent molecules in more than one geometry.

It appears from studies on space-filling models that the geometric requirements of the ligand prevent bonding of all four potentially coordinating atoms to one Cu^{II} ion at the same time. Presumably in some complex molecules only one nitrogen and two thioether sulfur atoms have bonding contacts with the Cu^{II} ion whereas the other coordination sites are filled by solvent molecules or (in some cases bridging) halogen ions. In other molecules other ligand atoms could be coordinating, and the various geometries might interconvert rapidly. This could be the reason for the reluctance of Cu^{II}(BBDHp) chelates to crystallize.

The impossibility of BBDHp to be folded in such a conformation that a single stable Cu^{II} chelate is formed explains the failure of the attempts to obtain solid Cu^{II}(BBDHp) products and accounts also for the fact that the Cu^{II} ion is relatively easily reduced in the presence of BBDHp. Some molecules will have a stereochemistry which favors Cu^I when two benzimidazole nitrogen atoms are bonded and two thioether sulfur atoms are at relatively large distances. The presence of thioether sulfur atoms nevertheless also might lower the redox potential sufficiently so that Cu powder and even solvent and or ligand molecules are able to reduce the Cu^{II}(BBDHp) ions. Apparently crystals in which the copper ion is nearly linearly coordinated by the imidazole nitrogen atoms and in which the ligand molecules are connected via hydrogen bridges to PF₆⁻ ions are quite stable. Crystallization then causes the equilibrium to shift toward Cu^I, with a preferred coordination number of 2.

Comparison of the Structure of [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34} with Related Structures. (i) A number of structures in which a Cu^I ion is linearly coordinated by two nitrogen atoms have been reported.²⁴⁻²⁷ The Cu^I-N distances are in the range 1.86–1.94 Å (which is short in comparison to Cu^I-N distances in structures with a higher coordination number²⁷) and the N-Cu-N angles vary from 171–179°. The fact that the N-Cu-N angle in the present structure is slightly smaller (168.5°) might be due to weak Cu-S interactions. Interestingly in all structures in which Cu^I is linearly coordinated by nitrogen atoms always a weakly interacting atom is present at a rather long distance (N at distances 2.92²⁴ and 2.77^{25a} Å, Cu at distances 2.45,²⁶ 2.66,²⁷ and 3.04²³ Å).

(ii) Recently the crystal structures of one Cu^I and several Cu^{II} chelates containing two or more benzimidazole groups have been determined. They show a variety of coordination geometries.²⁵ The potentially hexadentate ligand *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine (EDTB) contains four benzimidazole groups. In the compound [Cu₂(EDTB)](ClO₄)₂, both Cu^I ions are linearly coordinated by two benzimidazole nitrogen atoms.^{25a} As in [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34}, the crystal structure is stabilized by hydrogen bridges between the protonated benzimidazole nitrogen atom and the anion, in such a way that infinite cation-anion chains are formed. [Cu₂(EDTB)](ClO₄)₂ is very stable toward oxidation by air.²⁸ The [Cu₂(EDTB)]²⁺ compound cannot however be prepared by chemical reduction of Cu^{II}(EDTB) since apparently the reduction has too high a transition-state energy. As appears from the crystal structure of [Cu^{II}(EDTB)](BF₄)(BF₃OC₂H₅)·H₂O, the coordination geometry around Cu^{II} is biccapped square pyramidal.^{25c} Four benzimidazole and two amine nitrogen atoms are involved.

In crystals of [Cu^{II}(BBDH)Cl]Cl·2C₂H₅OH (in which BBDH stands for 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane; Figure 1, *n* = 2) the coordination geometry of the Cu^{II} ion is trigonal bipyramidal. Two benzimidazole nitrogen atoms are in the axial and two thioether sulfur atoms as well as a Cl⁻ ion are in the equatorial positions.⁷ [Cu^{II}(BBDH)]²⁺ also is easily reduced by Cu powder, but no crystals suitable for X-ray diffraction studies have been obtained thus far. The design of the BBDH ligand (Figure 1, *n* = 2) apparently forces the imidazole nitrogen as well as the thioether sulfur atoms to coordinate in such a way that the Cu^{II} compound is stabilized. On the contrary the BBDHp ligand (Figure 1, *n* = 3) is designed so that not all four potentially coordinating atoms can bind to the metal ion at the same time. Linear coordination of only two imidazole nitrogen atoms favor the Cu^I oxidation state.

The copper compounds of these benzimidazole containing ligands tend to crystallize in such a way that the benzimidazole planes are as parallel as possible. This results in glide planes and 2₁ axes. Crystallization in space group *C2/c* (which can be transformed to *I2/c*) used in the structure determination of [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34} is frequently observed.^{25b}

In reported crystals of chelates containing benzimidazole always a certain amount of disorder is present. Often counterions which are hydrogen bonded to the ligand molecules are present in more than one orientation.

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Concluding Remarks

From the results presented in this paper it is concluded that both Cu^I and Cu^{II} coordination compounds of the ligand BBDHp (Figure 1, $n = 3$) exist. Cu^{II}(BBDHp) compounds, however, are not stable and were not obtained in the solid state. The design of the BBDHp ligand implies that not all four potentially coordinating atoms may bind to one copper ion at the same time. This causes in solution a rapid interconversion of various coordination geometries in which only two or three ligand atoms are involved. Linear coordination by the imidazole nitrogen atoms stabilizes Cu^I. Crystals of Cu^I(BBDHp) with large counterions, which provide the possibility of hydrogen bridge formation (PF₆⁻, BF₄⁻), are easily obtained.

Comparison of Cu^I and Cu^{II} chelates of the closely related ligand BBDH (Figure 1, $n = 2$) reveals that stabilization of a particular oxidation state of copper is strongly influenced by ligand constraints. Although the distance between the copper ion and the "soft" (Cu^I stabilizing) thioether sulfur atoms in [Cu^{II}(BBDH)Cl]Cl·2C₂H₅OH is shorter than in [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34} nevertheless in the former the Cu^{II}, in the latter the Cu^I oxidation state is preferred. This is due to the fact that in the solid Cu^{II}(BBDH) compound the coordinating thioether sulfur atoms and a chloride ion complete

trigonal-bipyramidal stereochemistry, whereas in the solid Cu^I(BBDHp) compound linear coordination by two imidazole nitrogen atoms occurs and coordination of the thioether sulfur atoms is prevented. In copper-containing electron-transporting enzymes a small change in the coordination geometry of the copper ion, brought about by changes in the tertiary structure of the protein, may cause destabilization of a particular oxidation state. The low molecular weight ligands BBDH and BBDHp resemble this property of biological macromolecules.

Studies on related systems are under investigation.

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Registry No. BBDHp, 57698-68-7; [Cu^I(BBDHp)](PF₆)_{0.66}(BF₄)_{0.34}, 81372-13-6; [Cu^I(BBDHp)](BF₄), 81372-14-7; [Cu^I(BBDHp)](PF₆), 81372-15-8; 3,7-dithianonanedioic acid, 5065-18-9; 1,2-diaminobenzene, 95-54-5; Cu, 7440-50-8.

Supplementary Material Available: Listing of observed and calculated structure factors and a table with additional interbond angles for the PF₆⁻ anion (7 pages). Ordering information is given on any current masthead page.

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Bis(pentamethylcyclopentadienyl)carboxylato and -dithiocarbamato Derivatives of Neodymium(III) and Ytterbium(III). Crystal Structure of Bis(pentamethylcyclopentadienyl)(diethyldithiocarbamato)ytterbium(III)

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The pentamethylcyclopentadienyl derivatives (Me₅C₅)₂Yb(O₂CR), where R is Me₃C or CF₃, (Me₅C₅)₂Yb(S₂CNEt₂), and (Me₅C₅)₂Nd(S₂CNEt₂) have been prepared by metathetical exchange reactions on the anionic species, [(Me₅C₅)₂MCl₂]⁻. The crystal structure of (Me₅C₅)₂Yb(S₂CNEt₂) has been determined by single-crystal X-ray diffraction methods. The crystals are monoclinic, C₂/c, with cell dimensions $a = 12.268$ (4) Å, $b = 15.536$ (6) Å, $c = 14.269$ (5) Å, $\beta = 105.23$ (3)°, and $V = 2624$ Å³. For $Z = 4$ the calculated density is 1.50 g/cm³. The structure was refined to a conventional R factor of 0.039 with 2179 data where $F^2 > 3\sigma(F^2)$. The Yb(III) atom is bonded to two sulfur atoms and to two pentamethylcyclopentadienyl groups. The Yb atom lies on a crystallographic twofold axis. The dithiocarbamate ligand is disordered in the structure. The Yb-S distance is 2.70 (1) Å, and the average of five Yb-C distances is 2.63 (3) Å.

Introduction

In attempting to develop the chemistry of reactive organometallic lanthanide systems, we have had an interest in preparing neutral, base-free pentamethylcyclopentadienyl derivatives of the di- and trivalent metals. The strong Lewis acid nature of these metals has led to isolation of trivalent species such as (C₅Me₅)₂YbCl₂Na(OEt₂)₂ and (C₅Me₅)₂YbCl(THF),^{1,2} as well as the divalent species Yb(C₅Me₅)₂(THF) and Eu(C₅Me₅)₂(THF).³ The neutral base-free systems are of interest since these coordinatively unsaturated species are expected to exhibit a rich chemistry and, perhaps, to lead to compounds of unusual structural types.

Isolation of (C₅Me₅)₂YbCl₂Na(OEt₂)₂ and (C₅Me₅)₂YbCl(THF) suggests that a chelating ligand that can donate four electrons to the metal could yield neutral, base-free trivalent compounds. Such compounds might then be useful

for preparation of the base-free ytterbium(II) metallocenes if reduction in a noncoordinating solvent can be effected. Since carboxylate (RCO₂⁻) ligands have been effectively utilized as leaving groups in transition-metal chemistry, they seemed to be ideally suited for this task. Another chelating ligand, diethyldithiocarbamate (Et₂NCS₂⁻), is electronically similar but contains the softer sulfur atoms as donors. Because little is known about the properties of sulfur-based ligands in molecular lanthanide systems, we have conducted a low-temperature magnetic susceptibility study as well as an X-ray crystal structure determination of (C₅Me₅)₂Yb(S₂CNEt₂).

Results and Discussion

Preparation of the carboxylate and dithiocarbamate derivatives of ytterbium is straightforward. The analogous neo-

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