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Contribution from the Departments of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502,
2300 RA Leiden, The Netherlands, Lederle Graduate Research Center, University of Massachusetts, Amherst, Massachusetts 01003,
and Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster, FRG

Two Different Copper(II) Coordination Geometries Imposed by Two Closely Related Chelating Imidazole-Thioether (N_2S_2) Ligands. Crystal Structures of (1,6-Bis(4-imidazolyl)-2,5-dithiahexane)chlorocopper(II) Tetrafluoroborate, (1,6-Bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)chloro(tetrafluoroborato)copper(II), and (1,6-Bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)nitrato(thiocyanato-*N*)copper(II)

Elisabeth Bouwman,[1a] Roberta Day,[1b] Willem L. Driessen,*[,1a] Wolfgang Tremel,[1c] Bernt Krebs,[1c] John S. Wood,[1b] and Jan Reedijk[1a]

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The synthesis and spectroscopic properties of copper complexes with the ligands 1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane (abbreviated bidhx) and 1,6-bis(4-imidazolyl)-2,5-dithiahexane (abbreviated bhdhx) are described. The compound [Cu(bhdhx)Cl]BF_4 (A) crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.066$ (3) Å, $b = 8.253$ (2) Å, $c = 11.864$ (3) Å, $\alpha = 104.85$ (2)°, $\beta = 100.46$ (3)°, $\gamma = 114.72$ (2)°, $V = 817.16$ Å^3, and $D_x = 1.79$ g/cm^3 for $Z = 2$. The compound [Cu(bidhx)Cl(BF_4)] (B) crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.975$ (5) Å, $b = 8.347$ (3) Å, $c = 17.156$ (6) Å, $\beta = 116.34$ (2)°, $V = 1793.42$ Å^3, and $D_x = 1.73$ g/cm^3 for $Z = 4$. The compound [Cu(bidhx)(NCS)(NO_3)] (C) crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.641$ (2) Å, $b = 8.040$ (3) Å, $c = 25.480$ (6) Å, $\beta = 92.56$ (2)°, $V = 1973.1$ Å^3, and $D_x = 1.569$ g/cm^3 for $Z = 4$. The structures were solved by heavy-atom techniques and refined by least-squares methods to residual R_w values of 0.039 (A), 0.033 (B), and 0.053 (C). The coordination geometry of the copper ion in compound A is compressed trigonal bipyramidal, with the two imidazole nitrogens along the main axis at 1.94 and 1.96 Å and the chloride anion and the two thioether sulfur atoms at longer distances in the equatorial plane (Cu-Cl = 2.27, Cu-S = 2.53 and 2.49 Å). The copper ion in compound B is in an elongated octahedral geometry, formed by the two imidazole nitrogen atoms (at 1.94 and 1.95 Å), the chloride anion (at 2.30 Å), and one thioether sulfur (at 2.44 Å) in the equatorial plane and one thioether sulfur and a fluorine of the tetrafluoroborate anion in the axial positions at 2.75 and 2.59 Å, respectively. The only difference in composition between compounds A and B is the presence of a methyl group at position 4 of the imidazole moieties of the bidhx ligand. This small difference apparently causes the drastic change in coordination geometry for A and B. The copper ion in compound C is also in an elongated octahedral environment, with the two trans imidazole nitrogens (at 1.97 Å), one thioether sulfur (at 2.37 Å), and one thiocyanate nitrogen (at 1.97 Å) coordinating in the equatorial plane; one thioether sulfur and the nitrate ion are at long semicoordinating distances on the axial positions (Cu-S = 2.75, Cu-O = 2.70 Å). Introducing a stronger coordinating anion, like NCS (compound C), causes only a small change in coordination geometry. The different structures can be understood on the basis of the coordination plasticity of the Cu(II) ion.

Introduction

Currently, the coordinating behavior of imidazole-thioether-containing ligands is being investigated, in particular for mimicking the active site in blue copper proteins. A variety of ligands containing thioether sulfurs and imidazole groups have been synthesized.[2] Coordination compounds of some of these ligands have been reported.[3-6] The ligands 1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane (bidhx) and 1,6-bis(4-imidazolyl)-2,5-dithiahexane (bhdhx) contain the desired 4-substituted imidazole groups, as well as the biologically relevant thioether groups. These ligands are potentially tetradentate N_2S_2 donors. In these cases the thiolate group, required for type I copper protein models, has been substituted by an extra thioether group. A schematic drawing of the ligands bidhx and bhdhx is shown in Figure 1.

A copper bis(thiocyanate) compound of the ligand bidhx could not be obtained;[4,5] instead, a mixed-valence compound Cu_2(bidhx)$(NCS)_3$ and a mixed-anion compound Cu(bidhx)(NCS)(NO_3) crystallized. As a result of these findings and because of the differences in coordination geometries for $CuCl_2$(bidhx) and [CuCl(bidhx)]Cl·$2H_2O$[6], a selection of mixed-anion complexes have been synthesized on purpose. This paper describes the copper chloride/tetrafluoroborate and thiocyanate/nitrate complexes of the ligands bidhx and bhdhx. Single crystals for three of these compounds were obtained. To examine the differences in coordination geometry, which became apparent from their ligand field and EPR spectra, X-ray structure determinations of the three compounds were performed. Striking differences in the coordinating behavior of the ligands in the various compounds have been encountered, which will be discussed in terms of the electronic properties of the Cu(II) ion and the flexibility of the ligands used.

Experimental Section

Starting Materials. The syntheses of the ligands bidhx and bhdhx have been described in detail elsewhere.[2]

The ^1H NMR spectrum of the ligand bidhx (solvent DMSO-d_6, internal standard HMDS) showed the following signals: 2.19 (s, 6 H, methyl), 2.59 (s, 4 H, ethane), 3.71 ppm (s, 4 H, methylene), 7.68 (s, 2 H, imidazole), 4.87 ppm (broad, N-H). The ^1H NMR spectrum of the ligand bhdhx (solvent DMSO-d_6, internal standard HMDS) showed the following signals: 2.66 (s, 4 H, ethane), 3.68 (s, 4 H, methylene), 6.90 (s, 2 H, imidazole C-4), 7.53 ppm (s, 2 H, imidazole C-2).

The starting materials 1,2-ethanedithiol and 5-methyl-4-imidazolemethanol hydrochloride were commercially available in sufficient purity and were used without further treatment. 4-(Hydroxymethyl)imidazole hydrochloride was prepared following the procedure given by Totter and Darby.[7]

Synthesis of the Complexes. The coordination compounds were prepared by dissolving the hydrated copper(II) chloride (1 mmol) and copper(II) tetrafluoroborate (1 mmol) or copper(II) nitrate (2 mmol) and ammonium thiocyanate (1 mmol) in 10 mL of warm ethanol and adding this solution to a suspension of the ligand (2 mmol) in 25 mL of boiling ethanol. Upon addition of the metal salt, the ligand dissolved almost completely. After filtration of the hot reaction mixture, to remove any impurity, the complex crystallized on cooling. In some cases, however, evaporation of part of the solvent was necessary before crystallization of

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(1) (a) Leiden University. (b) University of Massachusetts. (c) Universität Münster.

(2) Bouwman, E.; Driessen, W. L. *Synth. Commun.* **1988**, *18*, 1581.

(3) van Rijn, J.; Driessen, W. L.; Reedijk, J.; Lehn, J.-M. *Inorg. Chem.* **1984**, *23*, 3584.

(4) Bouwman, E.; Driessen, W. L.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1988**, 1337.

(5) Bouwman, E.; de Gelder, R.; de Graaff, R. A. G.; Driessen, W. L.; Reedijk, J. *Recl.: J. R. Neth. Chem. Soc.* **1988**, *107*, 163.

(6) Bouwman, E.; Burik, A.; ten Hove, J. C.; Driessen, W. L.; Reedijk, J. *Inorg. Chim. Acta* **1988**, *150*, 125.

(7) Totter, J. R.; Darby, W. L. *Org. Synth.* **1944**, *24*, 64.

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Table I. Crystal and Refinement Data for the Compounds [Cu(bhdhx)Cl](BF_4) (A), [Cu(bidhx)Cl(BF_4)] (B), and [Cu(bidhx)(NCS)(NO_3)] (C)

	A	B	C
formula	$CuC_{10}H_{14}BClF_4N_4S_2$	$CuC_{12}H_{18}BClF_4N_4S_2$	$CuC_{13}H_{18}N_6O_3S_3$
fw	440.17	468.23	466.1
a, Å	10.066 (3)	13.975 (5)	9.641 (2)
b, Å	8.253 (2)	8.347 (3)	8.040 (3)
c, Å	11.864 (3)	17.156 (6)	25.480 (6)
α, deg	104.85 (2)	90	90
β, deg	100.46 (3)	116.34 (2)	92.56 (2)
γ, deg	114.72 (2)	90	90
V, Å^3	817.16	1793.42	1973.1
T, K	293	140	296
$F(000)$	443.31	948	956
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Z	2	4	4
D_x, g/cm^3	1.79	1.73	1.569
μ, cm^{-1}	17.89	16.8	14.4
cryst dimens	0.56 × 0.16 × 0.30	0.05 × 0.26 × 0.38	0.08 × 0.18 × 0.27
color	blue-green	green	green
habit	prism	needle	parallellepiped
h values	−16 to 16	0 to 17	0 to 8
k values	−13 to 13	0 to 11	0 to 6
l values	0 to 19	−20 to 20	−23 to 23
scan range θ, deg	2.0–30.0	2.0–27.0	1.0–18.0
transmission factors	0.867–1.088	0.76–1.00	0.97–1.00
intens variation	5.27	0	0
no. of measd reflcns	4973	4382	1345
no. of unique reflcns	4758	3913	1345
no. of reflcns used in refinement	2367[a]	2942[a]	885[b]
R_F[c]	0.0373	0.0362	0.047
R_w[d]	0.0385	0.0325	0.053
max, min $\Delta\rho$ excursions, e/Å^3	0.50, −0.48	0.42, −0.40	0.39, −0.35

[a] $I > 2\sigma(I)$. [b] $I > 1.5\sigma(I)$. [c] $R_F = \sum(||F_o| - |F_c||)/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

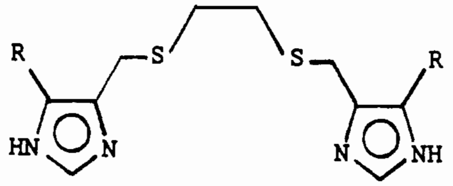

Figure 1. Schematic drawing of the ligands bidhx (R = CH_3) and bhdhx (R = H).

the coordination compound occurred. In the case of [Cu(bidhx)(NCS)(NO_3)] (C) crystals of Cu_2(bidhx)$(NCS)_3$ were obtained as the first crop, and the desired compound C was obtained as the second crop, after 2 mmol of ammonium thiocyanate was added.

Analyses. Metal analyses were carried out complexometrically with EDTA as the complexing agent.[8]

Spectroscopic Measurements. Infrared spectra in the 4000–180-cm^{-1} range of the samples pelleted in KBr were recorded on a Perkin-Elmer spectrophotometer, equipped with a PE data station. Solid-state diffuse-reflectance electronic spectra (28 000–5000 cm^{-1}) were recorded on a Perkin-Elmer 330 spectrophotometer, equipped with a PE data station. Electron paramagnetic resonance spectra of the powdered copper(II) compounds were obtained with a Varian spectrometer at X-band frequency at room temperature and 77 K (liquid nitrogen). Nuclear magnetic resonance spectra were obtained on a JNM-PS-100 NMR spectrometer.

Data Collection and Structure Refinement. The data collection for A and C was carried out at room temperature on four-circle Enraf-Nonius CAD4 diffractometers with graphite-monochromatized Mo Kα radiation (λ(Mo Kα) = 0.710 73 Å). Crystal data and additional details of the data collection and refinement for all three structures are presented in Table I. Intensities were corrected for Lorentz and polarization effects. The scanning rate was adjusted to the required precision of $\sigma(I)/I = 0.01$, with a maximum scan time of 120 s/reflection. The instrument and crystal stability were checked every 5400 s of radiation time by measuring three reference reflections: no significant changes in intensities were observed. The position of the heavy metal in A and the positions of the heavy metal and sulfurs in C were calculated from the Patterson map. The other non-hydrogen atoms of A were located by using the program AUTOFOUR.[9] The structure was refined by full-matrix least-squares calculations. As soon as the molecular structure was known, an absorption correction was applied for structure A with a Monte Carlo method, as described by de Graaff.[10] Before correction, measurements at different azimuthal positions of two reflections showed a variation of 20% (A) in the intensities.

The refinement was considered to be complete when the changes in the parameters were smaller than one-third of the standard deviation. Scattering factors were taken from ref 11.

All hydrogen atoms of A were located from difference Fourier maps and were refined, coupled to their parent atoms, to final thermal parameters of 6.16 and 4.13 Å^2. The non-hydrogens of all three structures were refined anisotropically, apart from the methyl carbons of the ligand in compound C. The function minimized was $\sum w(||F_o| - |F_c||)^2$ with $w = 1/\sigma^2(F)$.

X-ray diffraction data for B were collected on an automated SYNTEX-P2_1 four-circle diffractometer, equipped with a Mo Kα source, a graphite monochromator, and a scintillation counter. Unit-cell parameters were obtained at 140 K (with a modified SYNTEX-LT-1 low-temperature device) from the setting angles of 14 machine-centered reflections in the range $12 < 2\theta < 24°$. The data were collected in the $\theta/2\theta$ scan mode. The intensity of one check reflection monitored every 99 scans exhibited only statistical fluctuations in the course of the data collection; the intensity profiles of all reflections indicated stable crystal settings. All calculations were carried out on a Data General Eclipse S/200 computer using the programs of the SHELXTL[12] and XTL[13] program packages. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied (ψ scan). The structure was solved by direct methods (MULTAN,[14] which revealed the positions of the Cu, Cl, S, and F atoms). The remaining atoms were easily found from subsequent Fourier maps. Refinements were carried out with use of anisotropic thermal parameters for all non-hydrogen

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(8) Vogel, A. I. *Quantitative Inorganic Analyses*; Longmans: London, 1961.

(9) Kinneging, A. J.; de Graaff, R. A. G. *J. Appl. Crystallogr.* **1984**, *17*, 364.

(10) de Graaff, R. A. G. *Acta Crystallogr. A* **1973**, *29*, 298.

(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(12) "SHELXTL"; Nicolet XRD Corp.: Madison, WI.

(13) Sparks, R. In *Computational Needs and Resources in Crystalllography*; National Academy of Sciences: Washington, DC, 1973; pp 65–73.

(14) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr. A*, **1971**, *27*, 368.

Table II. Atomic Coordinates and Equivalent Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of Compounds A–C[a]

atom	x/a	y/b	z/c	B(eq)[b,c]	atom	x/a	y/b	z/c	B(eq)[b,c]
				(a) [Cu(bhdhx)Cl](BF_4) (A)					
Cu(01)	0.13358 (6)	0.19089 (6)	0.40196 (4)	3.089 (15)	C(20)	0.3718 (5)	0.6114 (6)	0.4001 (4)	4.06 (13)
Cl(02)	0.2195 (1)	0.0143 (2)	0.4781 (1)	4.58 (3)	N(21)	0.4129 (4)	0.6615 (5)	0.7192 (3)	4.06 (11)**
S(04)	−0.0710 (1)	0.2855 (1)	0.3738 (1)	2.71 (3)	C(22)	0.3084 (5)	0.4790 (6)	0.6595 (4)	3.55 (12)
C(05)	0.0031 (5)	0.4461 (5)	0.2949 (4)	3.35 (12)	N(23)	0.2787 (4)	0.4352 (4)	0.5384 (3)	3.13 (10)
C(06)	0.0845 (4)	0.3951 (6)	0.2072 (4)	3.37 (12)	C(24)	0.3702 (4)	0.6027 (5)	0.5232 (4)	3.24 (12)
S(07)	0.2519 (1)	0.3794 (1)	0.2747 (1)	3.32 (3)	C(25)	0.4539 (5)	0.7422 (6)	0.6349 (4)	4.07 (13)
C(10)	−0.2201 (4)	0.0680 (5)	0.2479 (4)	3.43 (11)	B(3)	0.6704 (6)	0.2146 (7)	0.9425 (5)	4.1 (2)
N(11)	−0.1250 (5)	−0.2886 (5)	0.0913 (3)	5.06 (13)	F(31)	0.8272 (3)	0.3361 (3)	0.9722 (3)	5.00 (8)
C(12)	0.0006 (6)	−0.1697 (6)	0.1878 (4)	4.17 (14)	F(32)	0.6427 (4)	0.0345 (4)	0.9257 (3)	8.76 (14)**
N(13)	−0.0176 (4)	−0.0298 (4)	0.2543 (3)	3.35 (10)	F(33)	0.6252 (4)	0.2816 (4)	1.0354 (3)	8.97 (14)**
C(14)	−0.1613 (5)	−0.0619 (5)	0.1958 (4)	3.23 (11)	F(34)	0.6013 (4)	0.2199 (6)	0.8380 (4)	11.8 (2)
C(15)	−0.2315 (6)	−0.2259 (6)	0.0938 (4)	4.77 (14)					
				(b) [Cu(bidhx)Cl(BF_4)] (B)					
Cu	0.030723	−0.007554	0.292832	1.24 (1)	C(20)	0.191527	−0.158499	0.227523	1.66 (9)
Cl	−0.051896	0.228149	0.297205	1.93 (2)	N(21)	0.059728	0.177231	0.084925	1.58 (8)
S(4)	−0.151436	−0.181520	0.198755	2.08 (2)	C(22)	0.022923	0.182248	0.144325	1.50 (9)
C(5)	−0.082538	−0.370047	0.211621	2.21 (10)	N(23)	0.064022	0.064536	0.200216	1.26 (7)
C(6)	0.013036	−0.351144	0.193226	2.21 (11)	C(24)	0.130023	−0.019838	0.174227	1.26 (7)
S(7)	0.121366	−0.250059	0.282365	1.59 (2)	C(25)	0.127925	0.049733	0.101924	1.50 (9)
C(10)	−0.177233	−0.177658	0.293427	2.13 (10)	C(26)	0.182735	0.008943	0.047424	2.13 (10)
N(11)	0.038124	−0.212433	0.511926	1.74 (8)	B	0.3212 (3)	0.0428 (4)	0.4687 (2)	1.66 (10)
C(12)	0.081529	−0.123240	0.471523	1.58 (8)	F(1)	0.4037 (2)	0.1091 (2)	0.4555 (1)	2.84 (6)
N(13)	0.013023	−0.103032	0.389427	1.42 (7)	F(2)	0.2255 (1)	0.0723 (2)	0.3966 (1)	2.92 (6)
C(14)	−0.079026	−0.183639	0.377525	1.58 (9)	F(3)	0.3179 (2)	0.1130 (2)	0.5404 (1)	2.53 (6)
C(15)	−0.063824	−0.254133	0.453927	1.66 (9)	F(4)	0.3359 (2)	−0.1195 (2)	0.4840 (1)	3.08 (6)
C(16)	−0.133444	−0.355343	0.478137	2.53 (12)					
				(c) [Cu(bidhx)(NCS)(NO_3)] (C)					
Cu	0.7535 (2)	0.0331 (2)	0.37967 (5)	3.76 (4)	C(5)	0.433 (1)	0.171 (2)	0.3819 (4)	5.0 (4)
S(4)	0.5498 (3)	0.0657 (5)	0.4274 (1)	3.97 (9)	C(6)	0.488 (1)	0.322 (2)	0.3525 (4)	4.8 (4)
S(7)	0.6598 (4)	0.3134 (5)	0.3276 (1)	4.9 (1)	C(10)	0.609 (1)	0.228 (2)	0.4716 (4)	4.7 (4)
S(33)	1.1718 (4)	−0.0435 (5)	0.2913 (1)	5.1 (1)	C(12)	0.973 (1)	0.158 (2)	0.4572 (5)	5.3 (4)
O(41)	0.5812 (9)	−0.370 (1)	0.4349 (3)	5.6 (2)	C(14)	0.765 (1)	0.215 (2)	0.4788 (4)	3.8 (3)
O(42)	0.711 (1)	−0.286 (1)	0.4993 (3)	8.0 (3)	C(15)	0.847 (1)	0.265 (2)	0.5196 (5)	5.1 (4)
O(43)	0.7854 (9)	−0.273 (1)	0.4225 (3)	6.9 (3)	C(16)	0.820 (1)	0.352 (2)	0.5698 (6)	6.5 (4)*
N(11)	0.981 (1)	0.234 (1)	0.5053 (4)	6.1 (3)	C(20)	0.636 (1)	0.189 (2)	0.2684 (4)	5.0 (4)
N(13)	0.8414 (9)	0.145 (1)	0.4413 (3)	3.5 (2)	C(22)	0.587 (1)	−0.222 (2)	0.3191 (5)	4.0 (3)
N(21)	0.509 (1)	−0.234 (1)	0.2741 (4)	4.2 (3)	C(24)	0.594 (1)	0.014 (1)	0.2770 (4)	3.4 (3)
N(23)	0.6403 (9)	−0.070 (1)	0.3223 (3)	3.3 (2)	C(25)	0.514 (1)	−0.088 (1)	0.2474 (4)	3.4 (3)
N(31)	0.9304 (9)	−0.004 (1)	0.3459 (3)	4.6 (3)	C(26)	0.440 (1)	−0.062 (2)	0.1928 (5)	4.9 (3)*
N(40)	0.694 (1)	−0.312 (1)	0.4521 (3)	5.4 (3)	C(32)	1.029 (1)	−0.022 (1)	0.3242 (4)	3.5 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] $B(\mathrm{eq}) = (8/3)\pi^2\chi(\tilde{U})$. [c] Starred values were refined isotropically; double-starred values are those of atoms that showed high thermal anisotropy.

atoms and isotropic parameters for the hydrogen atoms.

The fractional coordinates of the non-hydrogen atoms of A–C are listed in Table II. Selected bond distances, selected bond angles, and hydrogen bonding distances are given in Table III. The estimated standard deviations in the distances and angles were established by using the full correlation matrix. Lists of the atomic coordinates of the hydrogen atoms, of the non-hydrogen anisotropic thermal parameters, of the bond distances and angles, and of the observed and calculated structure factors are available as supplementary material.[15]

Results and Discussion

General Considerations. A listing of spectroscopic characteristics (ligand field and EPR data) and metal analyses of the copper compounds with bidhx and bhdhx is given in Table IV. Together with the metal determinations, already some information about the possible structures of the compounds can be deduced. The presence of the various anions was deduced from the IR spectra. The details of the spectral data will be discussed after the descriptions of the crystal structures.

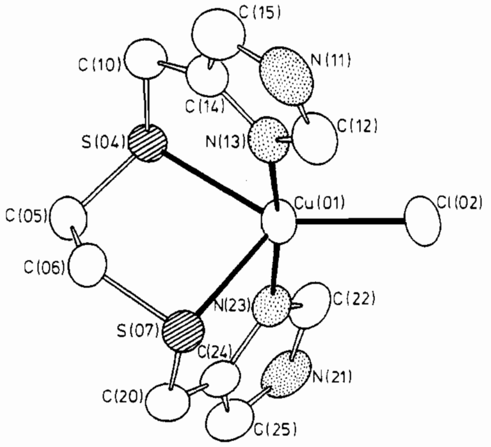

Figure 2. ORTEP projection and atomic labeling of the cation [Cu(bhdhx)Cl]$^+$. For clarity the hydrogen atoms and the BF_4 anion are omitted.

Description of the Structures. The structures of compounds A–C will be described hereafter. Compound A is the copper/chloride/tetrafluoroborate complex of the unmethylated ligand bhdhx, and B is the copper compound with the same anions as in A, but with the methylated ligand bidhx. Compounds B and C are alike but for the anions. Thus, the only difference between A and B is the presence of the methyl groups on the ligands, whereas the differences between B and C are the anions. The crystal and refinement data of all three compounds are given in Table I.

Structure of [Cu(bhdhx)Cl](BF_4) (A). An ORTEP[16] drawing of the cation [Cu(bhdhx)Cl]$^+$, also showing the atomic numbering

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(15) Supplementary material.

(16) Johnson, C. K. "ORTEP"; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table III. Selected Bond Lengths (Å) Involving Non-Hydrogen Atoms, Selected Bond Angles (deg), and H-Bond Distances (Å) for Compounds A–C

(a) [Cu(bhdhx)Cl](BF_4) (A)[a]			
Cu(01)–Cl(02)	2.266 (1)	Cu(01)–N(13)	1.944 (3)
Cu(01)–S(04)	2.488 (1)	Cu(01)–N(23)	1.956 (3)
Cu(01)–S(07)	2.534 (1)		
Cl(02)–Cu(01)–S(04)	146.00 (5)	S(04)–Cu(01)–N(13)	82.0 (1)
Cl(02)–Cu(01)–S(07)	125.31 (5)	S(04)–Cu(01)–N(23)	92.03 (9)
Cl(02)–Cu(01)–N(13)	92.9 (1)	S(07)–Cu(01)–N(13)	91.7 (1)
Cl(02)–Cu(01)–N(23)	95.3 (1)	S(07)–Cu(01)–N(23)	82.3 (1)
S(04)–Cu(01)–S(07)	88.55 (4)	N(13)–Cu(01)–N(23)	171.7 (1)
N(21)–F(32)′	2.991 (5)	H(21)–F(32)′	2.314 (4)
N(21)–F(33)″	2.950 (5)	H(21)–F(33)″	2.191 (5)
N(11)–F(33)‴	3.173 (5)	H(11)–F(33)‴	2.633 (5)
N(11)–F(31)‴	2.843 (4)	H(11)–F(31)‴	1.950 (4)
(b) [Cu(bidhx)Cl(BF_4)] (B)[b]			
Cu–Cl	2.299 (1)	Cu–N(13)	1.952 (3)
Cu–S(4)	2.747 (1)	Cu–N(23)	1.939 (3)
Cu–S(7)	2.436 (1)	Cu–F(2)	2.592 (2)
Cl–Cu–S(4)	97.1 (1)	Cl–Cu–S(7)	176.7 (1)
Cl–Cu–N(13)	93.8 (1)	Cl–Cu–N(23)	93.9 (1)
Cl–Cu–F(2)	98.5 (1)	S(4)–Cu–S(7)	83.9 (1)
S(4)–Cu–N(23)	100.3 (1)	S(4)–Cu–N(13)	81.3 (1)
S(4)–Cu–F(2)	163.0 (1)	S(7)–Cu–N(13)	89.4 (1)
S(7)–Cu–N(23)	82.8 (1)	S(7)–Cu–F(2)	80.9 (1)
N(13)–Cu–N(23)	171.8 (1)	N(13)–Cu–F(2)	90.7 (1)
N(23)–Cu–F(2)	85.5 (1)		
N(11)–Cl′	3.197 (4)	H(21)–F(4)″	2.30 (4)
H(11)–Cl′	2.56 (4)	N(21)–F(1)‴	2.927 (3)
N(21)–F(4)″	2.817 (4)	H(21)–F(1)‴	2.35 (3)
(c) [Cu(bidhx)(NCS)(NO_3)] (C)[c]			
Cu–S4	2.370 (4)	Cu–N13	1.968 (9)
Cu–S7	2.746 (4)	Cu–N23	1.969 (8)
Cu–O43	2.70 (1)	Cu–N31	1.968 (9)
S4–Cu–S7	84.0 (1)	S7–Cu–N31	100.8 (3)
S4–Cu–O43	88.6 (2)	O43–Cu–N13	93.2 (4)
S4–Cu–N13	83.0 (3)	O43–Cu–N23	88.0 (3)
S4–Cu–N23	89.0 (3)	O43–Cu–N31	87.2 (4)
S4–Cu–N31	174.6 (3)	N13–Cu–N23	171.9 (4)
S7–Cu–O43	166.1 (2)	N13–Cu–N31	93.9 (4)
S7–Cu–N13	97.6 (3)	N23–Cu–N31	94.2 (3)
S7–Cu–N23	80.1 (3)		
N(11)–O(43)′	2.861 (3)	H(11)–O(43)′	1.910 (8)
N(11)–O(42)′	3.011 (15)	H(11)–O(42)′	2.249 (9)

[a] Symmetry positions: (′) $x, y + 1, z$; (″) $1 - x, 1 - y, 2 - z$; (‴) $x - 1, y - 1, z - 1$. [b] Symmetry positions: (′) $-x, -y, 1 - z$; (″) $0.5 - x, 0.5 + y, 0.5 - z$; (‴) $-0.5 + x, 0.5 - y, -0.5 + z$. [c] Symmetry position: (′) $2 - x, -y, 1 - z$.

Table IV. Metal Contents and Spectroscopic Data (Ligand Field and EPR) for the Mixed-Anion Compounds with the Ligands bidhx and bhdhx

compd	metal % fnd (calc)	EPR[a]	EPR[a]
[Cu(bhdhx)Cl](BF_4)	14.2 (14.4)	16.5, 11.1	$g_\perp = 2.12$, $g_\parallel = 2.02$
[Cu(bidhx)Cl(BF_4)]	13.6 (13.6)	16.3, 11.8	$g_1 = 2.19$, $g_2 = 2.10$, $g_3 = 2.02$
[Cu(bidhx)(NCS)(NO_3)]	13.5 (13.6)	16.5, 11.4 (sh)	$g_1 = 2.16$, $g_2 = 2.03$
[Cu(bhdhx)(NCS)(NO_3)]	14.6 (14.5)	16.2, 11.1 (sh)	$g_1 = 2.14$, $g_2 = 2.07$, $g_3 = 2.03$

[a] At room temperature.

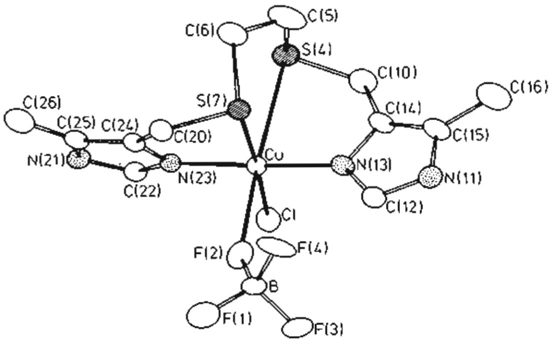

Figure 3. ORTEP projection and atomic labeling of the compound [Cu(bidhx)Cl(BF_4)]. For clarity the hydrogen atoms are omitted.

scheme, is depicted in Figure 2. The compound (1,6-bis(4-imidazolyl)-2,5-dithiahexane)chlorocopper(II) tetrafluoroborate forms the asymmetric unit in this triclinic space group ($P\bar{1}$). The copper(II) ion is in a compressed trigonal-bipyramidal geometry, with both imidazole nitrogens in the axial positions (Cu–N = 1.95 Å) and both thioether sulfurs and the chloride ion in the equatorial plane (Cu–S = 2.50, Cu–Cl = 2.27 Å). The BF_4 anion is not coordinated but is hydrogen bonded to the imidazole N(1) hydrogens. The trigonal bipyramid is a geometry often encountered with this type of ligand. Compounds with the more bulky ligands bbdh (1,6-bis(2-benzimidazolyl)-2,5-dithiahexane)[17] and bbidh (1,6-bis(1-benzyl-2-imidazolyl)-2,5-dithiahexane)[18] with copper chloride and copper bromide show a similar coordination geometry, with comparable coordinating distances (Cu–N = 1.96, Cu–S = 2.5 Å). However, in these latter compounds, the bulky phenyl groups on the ligands may prevent the other halogen ion from coordinating. With the ligand bhdhx a copper chloride has been prepared with both chloride anions coordinating in an octahedral geometry.[6]

The imidazole rings are planar, with deviations from the least-squares plane less than 0.01 Å. The bond distances and angles are within the expected range. The highest peak in the final difference Fourier map was 0.50 e/Å^3 and was found near the tetrafluoroborate group, which is slightly disordered.

Structure of [Cu(bidhx)Cl(BF_4)] (B). An ORTEP[16] projection of the compound [Cu(bidhx)Cl(BF_4)], also showing the atomic numbering, is depicted in Figure 3. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the cell. The asymmetric unit consists of one molecule of (1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)chloro(tetrafluoroborato)copper(II). Although bidhx differs only slightly from the ligand bhdhx, the coordination geometry of the copper(II) ion has changed dramatically. The copper(II) ion is in an elongated octahedral geometry, with the two imidazole nitrogens, one thioether sulfur atom, and the chloride ion in the equatorial plane. The other thioether sulfur is at a very long distance (2.75 Å) in an axial position. The BF_4 anion resides at the sixth position of the copper coordination sphere at a distance of 2.59 Å, which is remarkably short for a coordinating tetrafluoroborate. The imidazole rings are planar with deviations less than 0.01 Å. Bond lengths and angles of the ligand are within the expected range.

As can be seen from these data and Figure 3, the ligand bidhx is coordinated asymmetrically, with one thioether sulfur at a short distance and the other sulfur atom at a rather long coordinating distance. This asymmetrical binding is also encountered in compound C, described hereafter.

Most striking is the difference in coordination geometry of B compared with A (vide supra). Although only two extra methyl groups are present on the outside of the ligand in compound B, the coordinating geometry of the copper ion changes from trigonal bipyramidal to elongated octahedral. The only explanation for this phenomenon seems to be the packing/stacking of the molecules.

Structure of [Cu(bidhx)(NCS)(NO_3)] (C). An ORTEP[16] representation of the structure of [Cu(bidhx)(NCS)(NO_3)] is shown in Figure 4. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the cell. The copper(II) ion is surrounded by the ligand bidhx, one thiocyanate, and one nitrate in an elongated octahedral geometry. The imidazole rings are planar, with deviations from the least-squares planes being less

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(17) Birker, P. J. M. W. L.; Helder, J.; Henkel, G.; Krebs, B.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 307.

(18) Birker, P. J. M. W. L.; Godefroi, E. F.; Helder, J.; Reedijk, J. *J. Am. Chem. Soc.* **1982**, *104*, 7556.

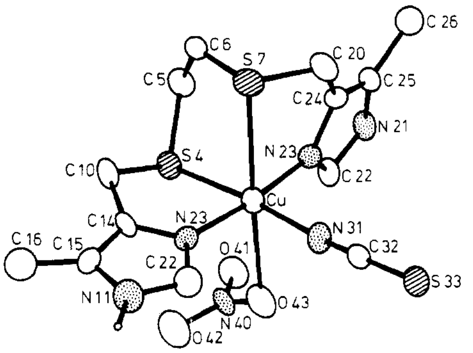

Figure 4. ORTEP projection and atomic labeling of the compound [Cu(bidhx)(NCS)(NO_3)]. For clarity the hydrogen atoms are omitted.

than 0.015 (12) Å. The bond distances and angles in the ligand are within the expected range.

The ligand binds asymmetricaly, with one thioether sulfur at a long distance (2.75 Å) in an axial position. The other thioether sulfur coordinates at a much shorter distance, with the two imidazole nitrogens and the thiocyanate nitrogen in the equatorial plane. The other axial position is occupied by the nitrate oxygen, again at a rather long coordinating distance of 2.70 Å. The coordinating oxygen is also hydrogen bonded to an imidazole N(11) nitrogen of a neighboring molecule related through a center of symmetry. The N(11)–O(43) distance is 2.86 (1) Å. This structure is comparable with the above described structure of B, with the most striking difference being the relatively long coordinating distance of the nitrate anion, which is in fact known to be a stronger coordinating ligand than tetrafluoroborate.

In the mixed-valence compound Cu_2(bidhx)$(NCS)_3$ the ligand is bound asymmetrically[4] with coordinating distances similar to those found for B and C.

Spectroscopic Results. The metal contents and LF and EPR data of the four mixed-anion compounds with the general formula Cu(L)Cl(BF_4) and Cu(L)(NCS)(NO_3) (with L = bidhx, bhdhx) are given in Table IV. The characteristic IR vibrations of the anions NCS^- (2100 cm^{-1}), NO_3^- (1300 cm^{-1}), and BF_4^- (1050 cm^{-1}) were easy to recognize in the IR spectra. The metal contents together with the IR spectra readily indicated the correct stoichiometry of the obtained compounds. The ligand field spectrum of [Cu(bhdhx)Cl](BF_4) (A) already suggested a trigonal-bipyramidal geometry of the copper ion, confirmed by the axial EPR spectrum of this compound with its "reversed" *g* values.[19] The molecular structure of this compound was therefore not surprising. On the other hand, the geometry of the compound [Cu(bidhx)Cl(BF_4)] (B) could not be deduced from its spectroscopic data alone. The solid-state ligand field spectrum can be interpreted as being trigonal bipyramidal, but the EPR spectrum was rhombic. Finally, the crystal structure proved the presence of an elongated octahedral geometry.

The ligand field spectrum of the [Cu(bidhx)(NCS)(NO_3)] (C) compound indicates elongated octahedral geometry. The geometry of the copper(II) ion is best compared with the copper(II) ion in the mixed-valence compound Cu_2(bidhx)$(NCS)_3$.[4]

The ligand field spectrum of the related compound [Cu(bhdhx)(NCS)(NO_3)] (no crystal structure) also agrees with an elongated octahedral symmetry. The coordination geometry of this compound may possibly be the same as for compound C. However, the chloride/tetrafluoroborate compounds (A and B) illustrate that one has to be careful in assigning structures of copper(II) compounds from ligand field spectra only.

Concluding Remarks. The ligand bidhx is the first N_2S_2 ligand that shows the flexibility of two coordinating modes: it coordinates asymmetrically with one thioether sulfur at a much longer distance than the other one, or it coordinates symmetrically.

Striking is the large structural difference of the two chloride/tetrafluoroborate compounds although the ligands are almost identical. The observed difference in coordination geometry (trigonal bipyramidal versus elongated octahedral) is most probably only due to the packing of the molecules. It is unlikely that the difference in coordination geometry is due to steric hindrance, because with the dichloride copper(II) compounds of both ligands isomorphism was encountered.[6] Another remarkable feature is the relatively strong coordinating BF_4 anion in compound B. This BF_4 anion is coordinated at an even shorter distance than the NO_3 anion in C. Until the early 1970s, perchlorate and tetrafluoroborate were considered to be noncoordinating anions.[20,21] However, in the last decade several crystal structures with coordinated BF_4 anions were published;[22,23] even bridging bidentate BF_4 anions were encountered.[24,25]

In summary, three different coordination geometries are encountered for the copper ion with the ligand bidhx. An octahedral compound, Cu(bidhx)Cl_2, with two chlorides coordinating and a trigonal-bipyramidal compound, [Cu(bidhx)Cl]Cl·$2H_2O$, with only one chloride coordinating, have been reported previously.[6] On replacement of the noncoordinating chloride by BF_4, a similar geometry would be expected, but instead another geometry, namely elongated octahedral with the BF_4 anion coordinating at a relatively short distance, resulted.

The three structures, described in this paper, give a further demonstration of the flexibility of the copper ion.[19,26] Other examples of different geometries with thioether–imidazole ligands around the copper ion are the compounds $Cu(L)_3(BF_4)_2$, in which L = 1-methyl-2-(2-(methylthio)ethyl)imidazole, described by Glass et al.[27] In these compounds two different surroundings of the copper(II) ion, viz. trigonal bipyramidal and square pyramidal, were found with the same ligand, the same anions, and the same stoichiometry.

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Registry No. A, 117559-21-4; B, 117559-22-5; C, 117605-18-2.

Supplementary Material Available: Tables of bond distances, bond angles, hydrogen coordinates, and anisotropic temperature factors (12 pages); tables of structure factors (33 pages). Ordering information is given on any current masthead page.

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(19) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

(20) Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1173.

(21) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *5*, 331.

(22) Kindberg, B. L.; Griffith, E. H.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1977**, 461.

(23) Gaughan, A. P.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657.

(24) Nakai, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1637.

(25) Foley, J.; Kennefick, D.; Phelan, D.; Tyagi, S.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2333.

(26) Hathaway, B. J. *Struct. Bonding (Berlin)* **1984**, *57*, 55.

(27) Glass, R. S.; Sabahi, M.; Hojjatie, M.; Wilson, G. S. *Inorg. Chem.* **1987**, *26*, 2194.