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Metal Chloride Compounds of Chelating Imidazole–Thioether Ligands. Crystal Structures of Dichloro-(1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)copper(II) and {Chloro-(1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)copper(II)} Chloride Dihydrate

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Abstract

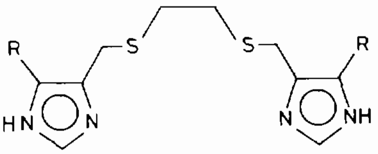
The synthesis and spectroscopic properties of the cobalt, nickel, copper and zinc chlorides of the ligands 1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane (abbreviated bidhx) and 1,6-bis(4(5)-imidazolyl)-2,5-dithiahexane (abbreviated bhdhx) are described. The compound Cu(bidhx)Cl_2 (**A**) crystallizes in the orthorhombic space group *Pbca* with $a = 17.917(2)$, $b = 14.502(4)$, $c = 12.905(2)$ Å, $V = 3353.15$ Å^3, $D_x = 1.651$ g/cm^3 for $Z = 8$. The compound [Cu(bidhx)Cl]Cl·$2H_2O$ (**B**) crystallizes in the triclinic space group *P*-1 with $a = 8.270(5)$, $b = 10.890(5)$, $c = 11.478(5)$ Å, $\alpha = 87.52(4)°$, $\beta = 76.93(5)°$, $\gamma = 71.52(4)°$, $V = 954.5$ Å^3, $D_x = 1.576$ g/cm^3 for $Z = 2$. Both structures were solved by heavy atom techniques and refined by least-squares methods to residual R_w values of 0.037 (**A**) and 0.034 (**B**). The coordination geometry of the copper ion in compound **A** is a compressed octahedron with the two imidazole nitrogens along the main axis at 1.94 and 1.95 Å, and both chloride anions and the two thioether sulfur atoms at relatively large distances in the equatorial plane (Cu–Cl 2.39 and 2.56 Å, Cu–S 2.62 and 2.81 Å). The copper ion in compound **B** is in a distorted trigonal bipyramid, formed by the two imidazole nitrogen atoms in the axial position (1.94 and 1.95 Å), and the two thioether sulfurs and one chloride ion in the equatorial plane (Cu–S 2.53 and 2.46 Å, Cu–Cl 2.29 Å). The nickel and cobalt bidhx chlorides and the copper and nickel bhdhx chlorides are isostructural with compound **A**.

Introduction

The geometry of the copper binding site in Type I copper proteins has been known since 1978 when the first X-ray structure of a blue copper protein was solved [1]. In this protein the copper atom is coordinated by two histidine imidazole nitrogens, a cysteine thiolate sulfur and a methionine thioether sulfur in a distorted tetrahedral geometry. The methionine sulfur is on a very long, weakly coordinating, distance (2.9 Å). A considerable research effort has been devoted to the synthesis of model compounds exhibiting the typical properties of Type I copper proteins. So far, no complete models have been obtained having the characteristics of a blue copper protein. In particular the binding of thiolate groups to copper(II) is hard to accomplish in low-molecular weight compounds. The rigid conformation of the protein with only a single cysteine residue near the copper binding site obviously prevents the formation of disulfide.

Chelating ligands containing both sulfur and nitrogen donor atoms of various nature have been designed and synthesized [2]. The imidazole group has mostly been substituted by other heterocycles, like benzimidazole [3], pyridine [4] and pyrazole [5].

So far not many ligands containing both 4-imidazolyl and sulfur have been reported, due to difficulties in the preparation of these ligands. A new route for the synthesis of imidazole–thioether ligands has been developed and quite a large variety of ligands has been obtained [6].



bidhx (R = CH_3); bhdhx (R = H)

This paper describes the ligand 1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane (bidhx) and the ligand 1,6-bis(4(5)-imidazolyl)-2,5-dithiahexane (bhdhx) and their coordination compounds with some transition metal chlorides. The question arises whether the

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methyl groups in the ligand bidhx have influence in the spectroscopic or electronic behaviour of the coordination compounds. Formation of the compounds could be influenced through sterical hindrance of the methyl groups or of their stacking in the solid state. To investigate the binding in detail and to prove the chelating nature of the ligands some structure determinations have been performed.

Experimental

Starting Materials

The synthesis of the ligands bidhx and bhdhx has been described in detail elsewhere [6].

The ^{1}H NMR spectrum of the ligand bidhx (solvent DMSO-d_6, internal standard $SiMe_4$) showed the following signals: 2.19 (s, 6H, methyl), 2.59 (s, 4H, ethane), 3.71 (s, 4H, methylene), 7.68 (s, 2H, imidazole), 4.87 (broad, N–H) ppm. The ^{1}H NMR spectrum of the ligand bhdhx (solvent DMSO-d_6, internal standard $SiMe_4$) showed the following signals: 2.66 (s, 4H, ethane), 3.68 (s, 4H, methylene), 6.90 (s, 2H, imidazole C-4), 7.53 (s, 2H, imidazole C-2) ppm.

The starting materials 1,2-ethanedithiol and 4-methyl-5-imidazolemethanol hydrochloride were commercially available of sufficient purity, and were used without further treatment. 4(5)-hydroxymethylimidazole was prepared according to the method of Totter and Darby [7].

Synthesis of the Complexes

The coordination compounds were prepared by dissolving the appropriate hydrated metal chloride (1 mmol) in 5 ml of warm ethanol or methanol and adding this solution to a suspension of the ligand (1 mmol) in 25 ml of boiling ethanol. At the addition of the metal salt, the ligand dissolved almost completely. After filtration of the hot reaction mixture, the complex crystallized on cooling. In some cases evaporation of part of the solvent was necessary before crystallization of the coordination compound occurred. In case of the hydrated bidhx copper complex, some extra water had to be added to the reaction mixture.

Analyses

Metal analyses were carried out complexometrically with EDTA as the complexing agent [8]. Chlorine analyses were carried out potentiometrically with silver nitrate, and $Ag/HgSO_4$ electrodes.

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 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). EPR spectra of frozen solutions of the copper compounds in methanol/DMSO were taken at 77 K.

Data Collection and Structure Refinement

The data collection was carried out at room temperature on a four-circle Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ(Mo Kα) = 0.71073 Å). Crystal data and additional details of the data collection and refinement for both structures are presented in Table I. Reflections with $I > 2\sigma(I)$ were used in the refinement. 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 scantime 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 positions of the heavy metals were calculated from the Patterson maps. The other non-hydrogen atoms were located using the program AUTOFOUR [9]. The structure was refined by full-matrix least-squares calculations. As soon as the molecular structure was known, absorption correction was applied for both structures, 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 38% (A) and 20% (B) 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 compound **B** were located from difference-Fourier maps, and were refined coupled to their parent atoms to a final thermal parameter of 6.87 Å^2 Most of the hydrogen atoms in compound A were also located from difference-Fourier maps, but some were placed on a distance of 0.95 Å to their parent atoms. The thermal parameters of the hydrogen atoms of compound A were refined isotropically, coupled to their parent atoms to final values of 3.3, 5.0, and 6.0 Å^2. The non-hydrogens of both structures were refined anisotropically. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$.

Because of high thermal anisotropy and large standard deviations in the fractional coordinates of compound **A**, extra reflections with $I > \sigma(I)$ were used in the refinement. This resulted in better

TABLE I. Crystal and Refinement Data of the Compounds Cu(bidhx)Cl_2 (**A**) and [Cu(bidhx)Cl]Cl·$2H_2O$ (**B**)

	A	**B**
Formula	$CuC_{12}H_{18}Cl_2N_4S_2$	$CuC_{12}H_{22}Cl_2N_4O_2S_2$
Formula weight	416.87	452.90
a (Å)	17.917(2)	8.270(5)
b (Å)	14.502(4)	10.890(5)
c (Å)	12.905(2)	11.478(5)
α (°)	90	87.52(4)
β (°)	90	76.93(5)
γ (°)	90	71.52(4)
V (Å^3)	3353.15	954.53
F(000)	1709.92	467.51
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	P-1
Z	8	2
D_x (g/cm^3)	1.651	1.576
μ (cm^{-1})	18.641	16.504
Crystal dimensions	0.52 × 0.28 × 0.20	0.40 × 0.22 × 0.32
h values	−18 to 18	−11 to 11
k values	−13 to 13	−15 to 15
l values	0 to 14	0 to 16
Scan range θ	2.0 to 21.0	2.0 to 30.0
No. measured reflections	7536	5804
No. unique reflections	2070	5544
No. used in refinement	1795[a]	3543[b]
R_f [c]	0.1456	0.0275
R_w [d]	0.0371	0.0341
Excursions max,min (e/Å³)	1.04 −0.91	0.33 −0.27

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

standard deviations and less thermal anisotropy, but therefore the final R_f value is rather high.

The fractional coordinates of the non-hydrogen atoms of **A** and **B** are listed in Table II. Selected bond distances, bond angles and hydrogen bonding distances are given in Table III. See also 'Supplementary Material'.

Results and Discussion

General Considerations

A listing of spectroscopic characteristics (infrared and X-ray powder isomorphism), colour, metal and chlorine analyses of the transition metal compounds with bidhx and bhdhx is given in Table IV. The metal and chlorine determinations already give information about the possible structures of the compounds. Table IV also lists ligand field absorptions and EPR data of the compounds. The compounds have the general formula M(L)Cl_2 (with L = bidhx and bhdhx and M = Co, Ni, Cu, Zn), with two exceptions, namely Zn(bidhx)Cl_2·H_2O and [Cu(bidhx)Cl·$2H_2O$ as a second composition besides Cu(bidhx)Cl_2. The hydrated copper bidhx compound is readily formed when extra water is added to the reaction mixture. The details of the spectral data will be discussed after the descriptions of the crystal structures.

TABLE II. Atomic Coordinates (×10^4) and Equivalent Thermal Parameters (Cu(01), Cl(02), Cl(03), S(04), S(07) × 10^2, others ×10Å^2) of the Non-hydrogen Atoms of Cu(bidhx)Cl_2 (**A**) and Atomic Coordinates (Cu × 10^5, others × 10^4) and Equivalent Thermal Parameters (Cu × 10^3, others × 10^2 Å^2) of the Non-hydrogen Atoms of·[Cu(bidhx)Cl]Cl·$2H_2O$ (**B**)

Atom	x/a	y/b	z/c	B(iso)
A				
Cu(01)	6840(1)	3818(1)	6280(1)	278(3)
Cl(02)	7630(1)	4048(2)	7747(2)	344(8)
Cl(03)	7672(1)	3550(2)	4694(2)	331(8)
S(04)	5733(1)	3520(2)	4992(2)	397(9)
C(05)	4960(5)	3433(7)	5866(7)	43(4)
C(06)	4928(6)	4259(6)	6573(8)	46(4)
S(07)	5619(2)	4203(2)	7570(2)	362(9)
C(10)	5987(6)	2313(6)	4877(8)	41(4)
N(11)	6734(5)	1093(6)	7098(6)	33(3)*
C(12)	6981(5)	1956(7)	7239(8)	26(3)
N(13)	6714(5)	2476(4)	6499(7)	22(3)
C(14)	6308(6)	1930(8)	5851(8)	27(3)*
C(15)	6321(5)	1057(7)	6213(9)	26(4)*
C(16)	5999(6)	224(6)	5777(9)	42(4)
C(20)	5950(6)	5358(6)	7651(8)	34(4)
N(21)	6782(4)	6546(5)	5457(5)	24(3)

(continued)

TABLE II. *(continued)*

Atom	*x/a*	*y/b*	*z/c*	*B*(iso)
C(22)	7025(5)	5660(6)	5318(7)	21(3)
N(23)	6744(5)	5153(4)	6069(5)	22(3)
C(24)	6299(5)	5710(7)	6697(8)	21(3)
C(25)	6340(6)	6578(7)	6331(8)	30(3)
C(26)	5978(6)	7461(6)	6684(8)	38(4)
B				
Cu	87244(4)	8303(3)	84961(3)	2827(10)
Cl(01)	10659(1)	1646(1)	9077(1)	404(2)
Cl(02)	3147(1)	2404(1)	5060(1)	467(2)
S(04)	7307(1)	1721(1)	6772(1)	329(2)
C(05)	6562(3)	364(2)	6591(2)	377(9)
C(06)	5770(3)	−185(3)	7733(2)	392(9)
S(07)	7128(1)	−762(1)	8802(1)	296(2)
C(10)	5349(3)	2899(3)	7633(2)	415(9)
N(11)	4716(3)	3371(2)	10850(2)	340(7)
C(12)	6264(3)	2438(2)	10573(2)	329(8)
N(13)	6679(2)	2132(2)	9413(2)	307(6)
C(14)	5323(3)	2918(2)	8937(2)	310(8)
C(15)	4098(3)	3687(2)	9828(2)	327(8)
C(16)	2385(3)	4669(3)	9798(3)	487(10)
C(20)	8858(3)	−2128(2)	7993(2)	371(9)
N(21)	12912(3)	−1696(2)	6270(2)	334(7)
C(22)	12068(3)	−546(2)	6825(2)	322(8)
N(23)	10538(2)	−550(2)	7500(2)	281(6)
C(24)	10423(3)	−1767(2)	7343(2)	281(7)
C(25)	11888(3)	−2490(2)	6582(2)	327(7)
C(26)	12438(4)	−3841(3)	6098(3)	539(11)
O(30)	120(3)	3901(2)	7167(2)	792(10)
O(40)	3058(3)	4503(2)	3065(2)	545(8)

[a] e.s.d.s in the least significant digits are given in parentheses. [b] $B_{eq} = (8/3)\pi^2$ trace U. Atoms marked with an asterisk show high thermal anisotropy.

Description of the Structure of Cu(bidhx)Cl$_2$

An ORTEP [12] representation of Cu(bidhx)Cl$_2$, also showing the atomic numbering, is depicted in Fig. 1. The asymmetric unit consists of one molecule of (1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)-dichlorocopper(II). The copper ion is coordinated by two imidazole nitrogens, two thioether sulfur atoms, and two chloride ions in a compressed octahedral geometry, with the two nitrogen atoms along the main axis and the chloride ions and the sulfur atoms on mutual *cis* positions in the equatorial plane. The Cu–N distances are comparable to related compounds with (benz)imidazole groups [3, 13]. The Cu–Cl distances (of 2.39 and 2.56 Å) are relatively long, although not exceptionally, and the equatorial Cu–S distances are so long that the question may arise whether they can still be regarded as coordination bonds [14]. In fact, the distances are comparable with the Cu(II)–S(methionine) distances in plastocyanin and azurin and on the very far end of the range found in thioether-containing copper(II)

TABLE III. Geometry of Cu(bidhx)Cl$_2$ (**A**) and [Cu(bidhx)Cl]Cl·2H$_2$O (**B**)

A

Selected bond lengths (Å) involving non-hydrogen atoms

Cu(01)–Cl(02)	2.388(3)
Cu(01)–Cl(03)	2.562(3)
Cu(01)–S(04)	2.623(3)
Cu(01)–S(07)	2.805(3)
Cu(01)–N(13)	1.980(7)
Cu(01)–N(23)	1.962(6)

Selected bond angles (°)

Cl(02)–Cu(01)–Cl(03)	108.03(8)
Cl(02)–Cu(01)–S(04)	166.8(1)
Cl(02)–Cu(01)–S(07)	87.9(1)
Cl(02)–Cu(01)–N(13)	95.2(3)
Cl(02)–Cu(01)–N(23)	91.4(2)
Cl(03)–Cu(01)–S(04)	84.79(9)
Cl(03)–Cu(01)–S(07)	163.4(1)
Cl(03)–Cu(01)–N(13)	91.8(2)
Cl(03)–Cu(01)–N(23)	95.2(3)
S(04)–Cu(01)–S(07)	79.59(8)
S(04)–Cu(01)–N(13)	80.9(3)
S(04)–Cu(01)–N(23)	90.5(2)
S(07)–Cu(01)–N(13)	91.3(2)
S(07)–Cu(01)–N(23)	79.5(3)
N(13)–Cu(01)–N(23)	168.5(3)

H bond distances (Å)

Cl(02)–N(11)[b]	3.286(8)
N(21)–Cl(03)[b]	3.219(7)
Cl(02)–H(11)[b]	2.397(8)
H(21)–Cl(03)[b]	2.409(7)

B

Selected bond lengths (Å) involving non-hydrogen atoms

Cu–Cl(01)	2.2864(7)
Cu–S(04)	2.5287(7)
Cu–S(07)	2.4621(7)
Cu–N(13)	1.945(2)
Cu–N(23)	1.939(2)

Selected bond angles (°)

Cl(01)–Cu–S(07)	148.07(3)
Cl(01)–Cu–N(13)	93.80(6)
Cl(01)–Cu–N(23)	94.05(6)
S(04)–Cu–S(07)	89.35(2)
S(04)–Cu–N(13)	92.67(6)
S(04)–Cu–N(23)	92.59(6)
S(07)–Cu–N(13)	90.29(6)
S(07)–Cu–N(23)	83.35(6)
N(13)–Cu–N(23)	172.13(8)

H bond distances (Å)

Cl(02)[a]–O(30)[a]	3.129(2)
Cl(02)[a]–O(40)[a]	3.161(2)
Cl(02)[a]–N(21)[d]	3.131(2)
O(30)[a]–Cl(01)[c]	3.213(2)

(continued)

TABLE III. *(continued)*

O(30)[a]–O(40)[b]	2.716(3)
O(40)[a]–N(11)[h]	2.737(3)
Cl(02)[a]–H(32)[a]	2.129(2)
Cl(02)[a]–H(41)[a]	2.366(2)
Cl(02)[a]–H(21)[d]	2.238(2)
H(31)[a]–Cl(01)[c]	2.529(2)
O(30)[a]–H(42)[b]	1.750(3)
O(40)[a]–N(11)[h]	2.737(3)

Symmetry position for A: [b]$1.5 - x$, $0.5 + y$, z. Symmetry positions for B: [a]x, y, z; [b]$-x$, $1 - y$, $1 - z$; [c]$x - 1$, y, z; [d]$2 - x$, $-y$, $1 - z$; [e]x, y, $z - 1$; [f]$1 - x$, $1 - y$, $1 - z$; [g]$x - 2$, $y + 1$, z; [h]$-x$, $1 - y$, $2 - z$.

compounds. The Cu–S–C angles nevertheless indicate that the lone pair orbitals on the sulfur atoms are directed toward the copper ion, as they are close to the expected value of 90–100°. Therefore it is concluded that the sulfur atoms are coordinating, albeit weakly. Apart from being compressed, the coordination octahedron has other distortions apparently originating from the steric constraints imposed by the ligand. The sulfur–copper–nitrogen angles are about 80°. These restricted coordination bond angles are caused by the limited bite of the ligand. This restriction is also observed with other ligands with similar bite [15]. The five-membered ring formed by the copper ion, the thioether sulfur, the two connecting carbons and the imidazole nitrogen imposes a small coordination angle. The bond distances and the angles within the ligand are in the expected range. The imidazole rings are planar with deviations less than 0.01 Å. The unit cell contains eight molecules of Cu(bidhx)Cl_2, one in each octant. Each molecule is bound to two other molecules by four hydrogen bridges between all chloride anions and all available N(1) atoms of the imidazole groups, thus forming infinite chains.

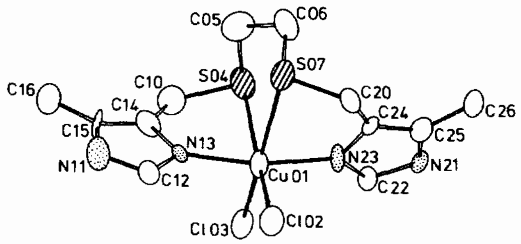

Fig. 1. ORTEP projection and atomic labelling of Cu(bidhx)-Cl_2. For clarity the hydrogen atoms are omitted.

Description of the Structure of [Cu(bidhx)Cl]Cl·$2H_2O$

An ORTEP [12] drawing of the structure, also showing the atomic numbering scheme, is depicted in Fig. 2. The compound chloro(1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane)copper(II) chloride dihydrate forms the asymmetric unit in this triclinic space group (P-1). The copper atom is coordinated by two thioether sulfur atoms on distances of 2.53 and 2.46 Å, two imidazole nitrogens on distances of 1.95 and 1.94 Å and one chloride ion on 2.29 Å in a compressed trigonal bipyramid geometry. The almost linear N(13)–Cu–N(23) moiety defines the main axis. The equatorial positions are occupied by the two sulfur atoms, S(04) and S(07), and the chloride ion, Cl(01). In [Cu(BBIDH)Br]Br·xH_2O (with BBIDH is 1,6-bis(1-benzyl-2-imidazolyl)-2,5-dithiahexane [13] and [Cu(BBDH)Cl]Cl·$2C_2H_5OH$ (with BBDH is 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane) [3] the Cu(II) atom is also trigonal bipyramidal coordinated with two S donor atoms and one halogen

TABLE IV. Colours, X-ray and IR Type, Metal and Chlorine Content, Ligand Field Absorption Bands ($\times 10^{-3}$ cm^{-1}) and X-band EPR Spectral Data of the Complexes with the Ligands bidhx and bhdhx

Compound	Colour	X-ray type	IR type	Metal exp(calc)	Chlorine exp(calc)	LF and EPR data
bidhx						
$CoCl_2$	purple	A	I	14.2(14.3)	17.1(17.2)	15.8, 6.9 (sh 9.2)
$NiCl_2$	light green	A	I	14.1(14.2)	17.2(17.2)	25.4, 16.1, 9.4 (7.5)
$CuCl_2$	green	A	I	15.2(15.2)	17.3(17.0)	13.7, 8.6; $g_\perp$ 2.20, $g_\parallel$ 2.02
$CuCl_2 \cdot 2H_2O$	dark green	B	II	14.3(14.0)	15.5(15.8)	16.3, 11.5; g_1 2.15, g_2 2.11, g_3 2.03
$ZnCl_2 \cdot H_2O$	white	C	III	15.0(15.0)	16.8(16.9)	
bhdhx						
$CoCl_2$	blue–green		IV	15.5(15.3)	18.6(18.4)	15.9, 7.0 (sh 9.2)
$NiCl_2$	light green	A'	IV'	15.0(15.3)	18.1(18.5)	25.3, 15.8, 9.2
$CuCl_2$	green	A'	IV'	16.2(16.7)	18.4(18.2)	13.5, 8.4; g_1 2.19, g_2 2.17, g_3 2.02
$ZnCl_2$	white		V	16.8(16.7)	18.0(18.2)	

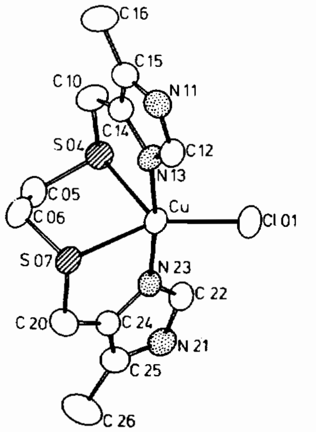

Fig. 2. ORTEP projection and atomic labelling of the cation $[Cu(bidhx)Cl]^+$. For clarity the hydrogen atoms are omitted.

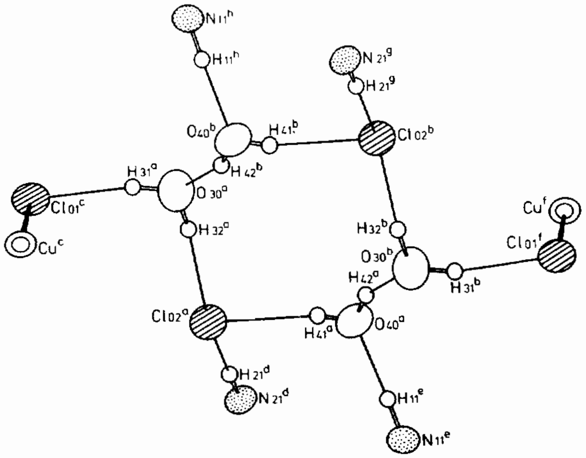

Fig. 3. ORTEP projection of the extended hydrogen bond network formed in the compound $[Cu(bidhx)Cl]Cl \cdot 2H_2O$. Symmetry positions: (a) x, y, z; (b) $-x, 1-y, 1-z$; (c) $x-1, y, z$; (d) $2-x, -y, 1-z$; (e) $x, y, z-1$; (f) $1-x, 1-y, 1-z$; (g) $x-2, y+1, z$; (h) $-x, 1-y, 2-z$.

donor atom on the equatorial plane and also two axial (benz)imidazole nitrogens. The distances between the coordinated atoms and copper atom in these latter compounds are comparable to those in the present compound. The S–Cu–S angles in these structures are close to 90°, which is most probably due to the rigid ethylene bridge between the two S atoms. The structure is stabilized by a complex hydrogen bond system between the N–H groups of the imidazole rings, all available hydrogen atoms of the water molecules and both chloride ions. An ORTEP [12] drawing of the extended hydrogen bonded network is depicted in Fig. 3. Distances between the involved atoms are listed in Table III. The bond distances and angles within the ligand are in the expected range. The imidazole rings are planar with deviations less than 0.01 Å.

Compounds Containing bidhx

The stoichiometry of the compounds has been established from the metal and halogen determinations. The cobalt, nickel and copper compounds are mutually IR and X-ray powder isomorphous. The ligand field spectrum of the nickel compound is typical for six-coordinated octahedral nickel ions ($Dq = 940$ cm^{-1} and $B = 885$ cm^{-1}).

The observed EPR spectrum of the copper compound **A** agrees with a compressed geometry with a $d(z^2)$ ground state. No hyperfine splitting is observed and the peaks are very sharp, apparently due to exchange narrowing processes [16]. The structure and spectroscopic data are very much comparable to those of the compound $Cu(bidhp)Cl_2$ (where bidhp is 1,7-bis(5-methyl-4-imidazolyl)-2,6-dithiaheptane) [14, 17]. In spite of the more extended bridge between the two thioether sulfur atoms in bidhp (propylene instead of ethylene), the bond angle S–Cu–S has hardly changed, and has not influenced the coordination sphere of the copper ion. The ligand field spectrum of compound $[Cu(bidhx)Cl]Cl \cdot 2H_2O$ (**B**) agrees with a trigonal bipyramidal coordination environment of the copper ion. The powder EPR spectrum is rhombic (see Table IV).

EPR of a frozen solution of compound **A** in methanol/DMSO (77 K) yielded spectra clearly indicating the presence of two species with different g and A values: when dissolved in methanol both the distorted octahedron and the trigonal bipyramid are probably present. However, the spectra were not easily reproduced, most probably due to variable solvent exchange effects [3]. Therefore these spectra are not discussed.

Although the cobalt compound is isomorphous with the nickel and copper compounds, the direct environment of the cobalt ion is more probably tetrahedral according to its ligand field spectrum. A likely explanation for this phenomenon could be that the sulfur atoms, which are at a large distance from the central metal ion in the copper compound (*vide infra*), are at an even longer distance in this cobalt complex, thus enforcing a more tetrahedral geometry in terms of ligand field effects, as is also observed for the cobalt bidhp compounds [18], and in related benzimidazole compounds [19]. The zinc compound contains one extra water molecule. Attempts to prepare cobalt and copper dopes in the zinc compound have been undertaken. However, these dopes were different from the parent zinc compound (X-ray and IR). Therefore, no conclusions about the geometry of the $ZnCl_2$ compound can be drawn.

Compounds Containing bhdhx

As is depicted in Table IV, the copper and nickel bhdhx chlorides are isomorphous (X-ray powder, only slight differences in the IR spectra) with the cobalt, nickel and copper bidhx chlorides. Although the methyl group on the imidazoles is lacking, the complexes crystallize in the same crystal symmetry. Co(bhdhx)Cl_2 is a dark blue–green amorphous powder with ligand field parameters indicating that the cobalt ion is in a tetrahedral environment, analogous to the cobalt bidhx compound (see above). The ligand field spectrum of the nickel bhdhx compound again indicates an octahedral geometry (Dq = 920 cm^{-1}, B = 900 cm^{-1}). The ligand field spectrum of the copper compound is also basically in agreement with an octahedral geometry. The EPR spectrum of the copper compound clearly indicates an inversed axial, *cis*-distorted symmetry [16]. The cobalt and zinc compounds are amorphous, and they do not show an X-ray diffraction pattern.

Concluding Remarks

The present study has made clear that the ligands bidhx and bhdhx are good complexing agents. In most compounds the ligands act as tetradentates and coordinate through two imidazole nitrogens and two thioether sulfur atoms. Six and five coordination is observed, although for the cobalt and zinc compounds the sulfur coordination is not well established. The ligand bidhx is the first N_2S_2 donor ligand which yields two different coordination numbers for the copper ion. For other N_2S_2 donor ligands either five coordination [3, 13] or six coordination [14] was observed. This five coordination is most probably due to the steric constraint of these ligands, whereas in the case of compound **B** the extended hydrogen bond network in the solid state (Fig. 3) might play a decisive role in establishing the five coordination.

Although the ligands bidhx and bhdhx are very similar, the complex-forming behaviour is rather different: the chloride compounds of the ligand bidhx are readily formed, where the ligand bhdhx often yields oils or amorphous products. Also, products with varying stoichiometries were obtained with bhdhx in some cases.

Supplementary Material

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 from the authors on request.

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