Synthesis and Characterization of Copper(II) Complexes of a 14-Membered *cis*-N_2S_2 Dibenzo Macrocycle and of Its Bis-acetato and Bis(methylpyridyl) Derivatives

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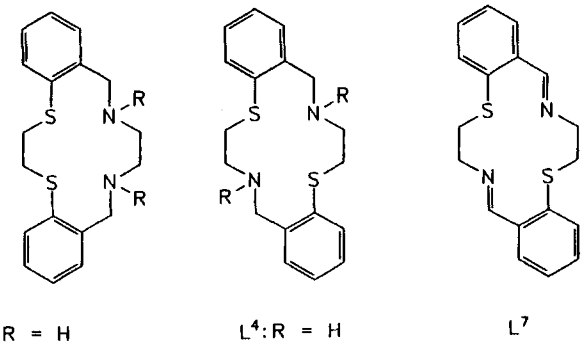
Received April 28, 1995

Key Words: Copper(I) complexes / Copper(II) complexes / N,S-Donor ligands / Macrocyclic ligands

The synthesis and characterization of seven copper coordination compounds with the 14-membered macrocyclic *cis*-N_2S_2 dibenzo ligand 6,7,13,14,15,16,17,18-octahydrodibenzo[*e*,*m*]-[1,4,8,11]dithiadiazacyclotetradecine (L^1) and its *N*,*N'*-bisacetato and -bis(methylpyridyl) functionalized derivatives H_2L^2 and L^3 are described. The structures of five compounds were determined by single-crystal X-ray diffraction. The tetrahedrally distorted square-planar coordination geometry of $[CuL^1](ClO_4)_2$ (**1**) changes upon reduction of copper to a severely distorted tetrahedral geometry in $[CuL^1]Br \cdot MeCN$ (**2**). The Cu−N bond lengths increase from 1.988(3) to 2.029(5) Å; the Cu−S bond lengths decrease from 2.293(1) to 2.255(2) Å. Copper(II) is hexacoordinated in $[CuHL^2]HSO_4 \cdot 2.5\ H_2O$ (**5**) and $[CuHL^2]ClO_4 \cdot H_2O$ (**6**). Both compounds exhibit very similar overall structures in the cationic part. The macrocyclic ring of the ligand is folded along an N···S axis, the octahedral geometry is strongly Jahn-Teller distorted, with O and S donor atoms in the apical positions. Compound **5** contains one very short [2.271(3) Å] and one long [2.701(3) Å] Cu−S (thioether) bond. In $[CuL^3](ClO_4)_2 \cdot 2\ H_2O$ (**7**) one thioether group of the ligand L^3 remains uncoordinated. The coordination polyhedron is rather irregular: Cu−S 2.506(3) and Cu−N 1.960(7)−2.107(8) Å. The compounds were further characterized by electronic and EPR spectroscopy and by cyclic voltammetry. Some relationships to the structural and spectroscopic properties of "blue" copper proteins were found.

Since it became established that the copper binding site in "blue" copper proteins consists of N and S donor atoms there has been intense interest in the copper coordination chemistry involving acyclic and macrocyclic polyamino polythioether ligands. Methods to construct model compounds included the design of ligands consisting of N and S donor atoms. Many N_xS_y donor ligands have been investigated so far[1−5]. Recently, we have started a program to study the ligating properties of the 14-membered *cis*- and *trans*-N_2S_2 macrocycles L^1 and L^4 and of their *N*-functionalized derivatives. Some of our results have been published already[6,7].



L^1:R = H
H_2L^2:R = CH_2COOH
L^3:R = CH_2-pyridyl

L^4:R = H
L^5:R = CH_2COOH
L^6:R = CH_2-pyridyl

L^7

In this work we describe the characterization of $[Cu^IL^1]Br \cdot MeCN$ and of a series of copper(II) complexes with the ligand L^1, and its functionalized derivatives H_2L^2 and L^3. The structural, spectral, EPR, and electrochemical properties of these compounds will be compared with complexes described as possible models of N_2S_2 coordination environments at the active sites of "blue" copper(II) proteins[8].

Results and Discussion

The hexadentate ligands H_2L^2 and L^3 were prepared in moderate yields by one-step reactions from the preformed macrocycle L^1 and α-bromoacetic acid (H_2L^2) or 2-[(*p*-tolylsulfonyl)methyl]pyridine (L^3). According to the IR spectrum H_2L^2 exists in a zwitterionic state: one of the tertiary amine functions is protonated and one of the carboxyl groups deprotonated. The other carboxyl group forms a strong intermolecular hydrogen bond to the carboxylate group of a neighboring ligand molecule as is shown by the high background infrared absorption in the range from 1800 to 600 cm^{-1} with a maximum at 1400 cm^{-1}[9,10]. The preparation of the copper(II) complexes **1** and **3**−**7** was straightforward by using the appropriate inorganic components. All the complexes are stable in air and readily soluble in water. The copper(I) compound $[CuL^1]Br \cdot MeCN$ (**2**) is air-sensitive.

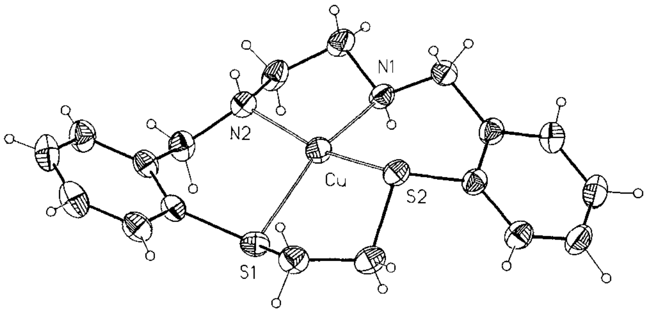
0009−2940/95/1212−1199 $ 10.00+.25/0

Description of the Structures

[CuL^1](ClO$_4$)$_2$ (1)

The structure of the [CuL^1]$^{2+}$ cation in **1** with atomic labeling is given in Figure 1. Table 1 contains selected atom distances and bond angles. The copper(II) ion resides in the macrocyclic cavity and is coordinated by two secondary amine nitrogen atoms [1.987(3), 1.989(3) Å] and two thioether sulfur atoms [2.293(1), 2.293(1) Å]. The square-planar coordination geometry is tetrahedrally distorted, as shown by the N−Cu−S angles of 156.4(1) and 160.2(1)°. The perchlorate ions are semicoordinated in the apical positions at rather long distances [2.691(2) and 2.933(3) Å]. They interact also with the ligand via hydrogen bonds: O(7)···N(1) 2.955(3) and O(3)···N(2) 3.110(4) Å.

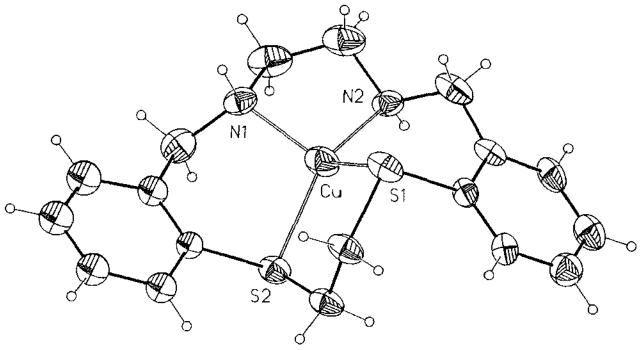
Figure 1. Structure of the [CuL^1]$^{2+}$ ion in]CuL^1](ClO$_4$)$_2$ (**1**)



[CuL^1]Br · MeCN (2)

Figure 2 shows the structure of compound **2**; Table 1 contains the atom distances and bond angles. The tetrahedral geometry in **2** is strongly distorted, with bond angles ranging from 89.7(3) to 133.4(2)°. The distances to equivalent donor atoms vary slightly: Cu−N 2.015(7) and 2.041(6) Å, Cu−S 2.234(2) and 2.277(2) Å. The Br$^-$ ions connect the cations [CuL^1]$^+$ in the lattice via hydrogen bonds, N···Br 3.360(9) and 3.434(8) Å.

Figure 2. Structure of the [CuL^1]$^{1+}$ ion in **2**



[CuHL^2]HSO$_4$ · 2.5 H$_2$O (5) and [CuHL^2]ClO$_4$ · H$_2$O (6)

The hexacoordinated complex ions of both compounds have very similar overall structures but differ significantly in distinct molecular parameters. The structure of the cation and the copper coordination polyhedron of **5** are given in Figures 3 and 4 (left). Selected bond lengths and angles in **5** and **6** are compiled in Table 1. All six donor atoms of the functionalized ligand are coordinated to copper(II). The octahedral coordination geometry is strongly Jahn-Teller-distorted, with O(1) and S(1) in the apical positions. The ligand is folded along the N(2)···S(2) axis of the macrocycle in both cations. So the central ion is not incorporated into the macrocyclic cavity, and all chemically identical donor atoms become *cis*-oriented. Details of the structural differences between **5** and **6** will be discussed in the next section.

Figure 3. Structure of the [CuHL^2]$^+$ ion in **5**

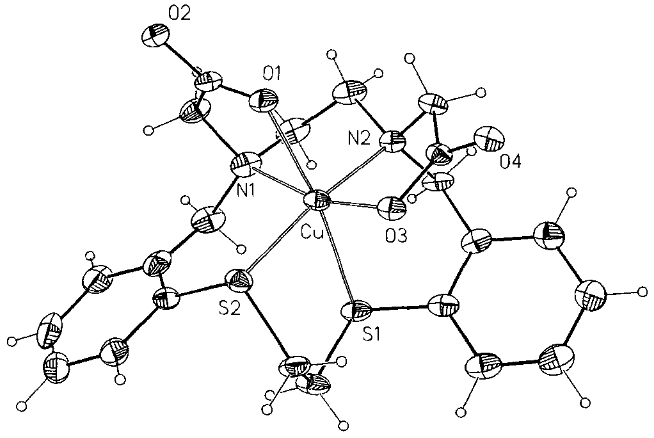
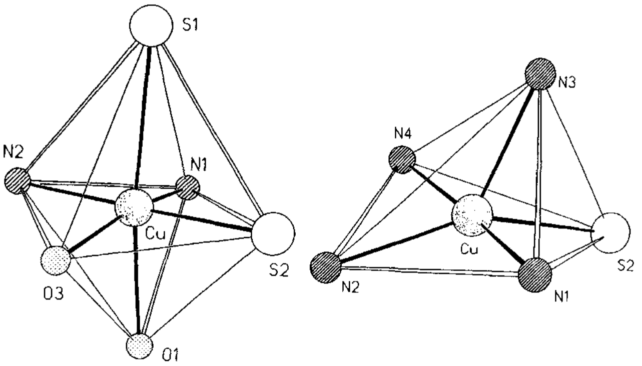


Figure 4. Left: Coordination polyhedron of the metal center in **5**. Right: Coordination polyhedron of the metal center in **7**



[CuL^3](ClO$_4$)$_2$ · 2 H$_2$O (7)

The structure of the [CuL^3]$^{2+}$ ion is given in Figure 5, the coordination polyhedron is shown in Figure 4 (right). Copper(II) is coordinated by five of the six donor atoms of the ligand L^3. One thioether group remains uncoordinated [Cu···S(1) 3.187(3) Å]. The coordination sphere at the copper center can be described as a severely distorted square pyramid derived from an octahedron by removing S(1) from the copper center. The apical N(py) donor N(3) approaches the copper atom closely [2.108(9) Å]. The equatorial bond lengths range from 1.960(7) Å [Cu−N(py)], 2.021(7) and 2.084(7) [Cu−N (amine)] to 2.506(3) Å [Cu−S(2)]. Copper(II) is situated 0.23 Å above the N$_3$S plane.

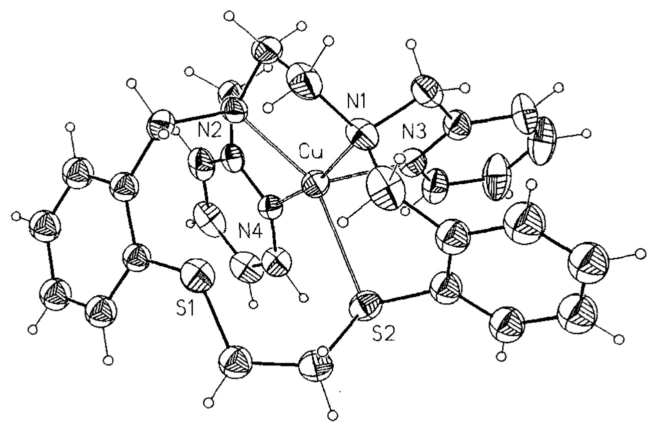


Figure 5. Structure of the $[CuL^3]^{2+}$ ion in **7**. Selected interatomic bond lengths [Å] and angles [deg]: Cu−S(1) 3.187(3), Cu−S(2) 2.506(3), Cu−N(1) 2.021(7), Cu−N(2) 2.084(7), Cu−N(3) 2.107(8), Cu−N(4) 1.960(7); S(2)−Cu−N(2) 151.6(2), S(2)−Cu−N(3) 85.0(2), S(2)−Cu−N(4) 96.6(2), N(1)−Cu−N(2) 88.0(3), N(1)−Cu−N(3) 81.9(3), N(1)−Cu−N(4) 167.2(3), N(2)−Cu−N(3) 123.4(3), N(2)−Cu−N(4) 82.5(3), N(3)−Cu−N(4) 96.2(3), S(2)−Cu−N(1) 95.8(2)

Discussion of the Structures

The coordinating behavior of the 14-membered *cis*-N_2S_2 dibenzo macrocycle towards copper(II) depends strongly on the number and kind of pendant arms present. Compounds **1**, **2**, **5**, **6**, and **7** exhibit different coordination polyhedra and differ significantly in their metal-to-ligand bond lengths. Only in the complex of the unsubstituted ligand L^1 is the central atom situated within the macrocyclic cavity. But the size of the cavity is rather tight, as is shown by the tetrahedral distortion of the coordination sphere. Examples of nearly square-planar copper(II) complexes with 14-membered macrocyclic ligands are $[Cu(cyclam)]^{2+}$ and $[Cu[14]aneS_4)]^{2+}$[11,12]. Here, slightly larger (mean) Cu−N (2.02 Å) and Cu−S (2.303 Å) bond lengths have been observed. In $[CuL^8]^{2+}$, where L^8 is the 15-membered analog of L^1 having a larger ligand cavity, the copper(II) geometry is nearly planar. The Cu−N (2.06 ± 0.01 Å) and Cu−S [2.323(3) and 2.410(3) Å] bond lengths are slightly larger than in **2**[13]. The copper(I) complex of the related unsaturated ligand L^7 shows also an unusual coordination geometry due to the trigonal-planar bond arrangement of the N donor atoms[14].

Compounds **1** and **2** form an interesting pair. Reduction of the metal center leads to an increase of the Cu−N bond lengths by 0.040 Å and to a decrease of the Cu−S bond lengths by 0.038 Å, confirming the preference of copper(I) for sulfur coordination. Parallel to this, the bond angles between the *trans*-oriented bonds at the metal center decrease from **1** to **2** by approximately 23°, and the dihedral angle between the CuN_2 and CuS_2 planes changes from 149 to 119°. Both metal environments deviate then strongly from the usual geometries at the copper(II) and copper(I) centers, determined mainly by the limited size of the ligand cavity and the rigidity of the ligand framework, respectively. The conformational change of the ligand is restricted to the −C−S−C−C−S−C− region.

As already mentioned, compounds **5** and **6** contain copper(II) ions with similar overall structures. In **5** the Cu−S (thioether) bond [2.271(3) Å] is remarkably short, even 0.022(1) Å shorter than in **1**. In comparison, equatorial copper(II) thioether bonds of acyclic and macrocyclic ligands lie usually in the range 2.31−2.48 Å[4,5,15−17]. The metal-to-ligand bond lengths given in Table 1 show that in **5** all bond lengths are significantly shorter than in **6** except Cu−O(1). [The greatest difference (0.15 Å) is observed for the apical Cu−S bond.] Therefore, the ligand field in **5** is stronger than that in **6**. This explains their different colors in the solid state, where **5** forms blue and **6** green crystals. But both **5** and **6** give identical deep blue solutions (vide infra). Therefore, the structural differences are caused by solid-state effects.

Table 1. Selected interatomic bond lengths [Å] and angles [deg] of $[CuL^1](ClO_4)_2$ (**1**), $[CuL^1]Br \cdot MeCN$ (**2**), $[CuHL^2]HSO_4 \cdot 2.5\ H_2O$ (**5**), and $[CuHL^2]ClO_4 \cdot H_2O$ (**6**)

Compound	1	2	5	6
Cu − S(1)	2.293(1)	2.277(2)	2.701(3)	2.850(1)
Cu − S(2)	2.293(1)	2.234(2)	2.271(3)	2.285(1)
Cu − N(1)	1.987(3)	2.015(7)	2.053(9)	2.056(2)
Cu − N(2)	1.989(3)	2.041(6)	2.002(8)	2.024(2)
Cu − O(1)	2.691(1)		2.321(7)	2.297(2)
Cu − O(3)			1.975(7)	1.992(2)
Cu − O(5)	2.933(2)			
O(1) − C(20)			1.219(12)	1.233(3)
O(2) − C(20)			1.297(12)	2.273(3)
O(3) − C(22)			1.270(12)	1.253(3)
O(4) − C(22)			1.247(13)	1.264(3)
S(1)−Cu−N(1)	156.4(1)	133.4(2)	96.0(3)	91.6(1)
S(1)−Cu−N(2)	95.3(1)	101.0(2)	90.9(2)	86.7(1)
S(1)−Cu−S(2)	90.8(1)	98.1(1)	85.3(1)	83.4(1)
S(2)−Cu−N(1)	95.0(1)	102.7(2)	97.0(3)	97.8(1)
S(2)−Cu−N(2)	160.2(1)	139.2(2)	172.3(3)	168.0(1)
N(1)−Cu−N(2)	86.8(1)	89.7(3)	90.0(4)	89.2(1)
S(1)−Cu−O(1)			172.2(2)	170.5(1)
S(1)−Cu−O(3)			98.7(2)	104.4(1)
S(2)−Cu−O(1)			89.6(2)	95.6(1)
S(2)−Cu−O(3)			90.0(2)	91.9(1)
O(1)−Cu−N(1)			78.7(3)	79.2(1)
O(1)−Cu−N(2)			94.8(3)	95.4(1)
O(1)−Cu−O(3)			87.2(3)	85.1(1)
O(3)−Cu−N(1)			164.2(3)	162.2(1)
O(3)−Cu−N(2)			84.0(3)	84.1(1)

In both structures the $[CuHL^2]^+$ ions form infinite chains by means of rather short hydrogen bonds between the noncoordinated oxygen atoms of the carboxyl groups. These structural features are also reflected in the IR spectra of **5** and **6**[9,10]. The spectra exhibit a background absorption of medium intensity, ranging approximately from 1800 to 700 cm^{-1}. However, the hydrogen bond pattern of **5** is different from that of **6**. In the latter the hydrogen bonds are across inversion centers with O(2)···O(2′) 2.445(3) and O(4)···O(4″) 2.442(3) Å. (The hydrogen atoms were located in electron density maps and their U_{iso} values included in the refinement.) O(2) and O(4) belong to the axial and to the equatorial coordinating carboxyl group, respectively. In compound **5** the hydrogen bonds O(2)···O(4′) and O(4)···O(2″) [2.473(10) Å] connect equatorial with axial carboxyl groups. The hydrogen atom could not be located. However, considering the C–O bond length (see Table 1), the proton is very probably situated at O(2). Therefore, C(20)–O(1) has the character of a carbonyl group, O(1) is a rather weak donor. In **6**, however, O(2) atoms of neighboring molecules share the proton. So O(1) is more negatively charged, which allows O(1) to approach the copper center more closely[18]. Analog arguments can be used to explain the different Cu–O(3) bond distances as well. In summary, the different hydrogen bond patterns in compounds **5** and **6** are responsible for the slight variations of the metal-to-ligand distances, which cause the different color in the solid state.

The structure of the $[CuL^3]^{2+}$ ion in compound **7** needs some comment as well: S(1) becomes uncoordinated due to the Jahn-Teller effect. The observed distortions from square prismatic coordination are then mainly caused by the sterical restrictions within the ligand: S(2) is drawn away from the metal center, because it is linked to S(1) through the ethylene bridge, thus giving rise to the large Cu–S(2) bond length [250.3(3) pm] and the small *trans*-basal angle N(2)–Cu–S(2) [151.6(2)°]. Other angular distortions are due to the restricted bite of the pendant methylpyridyl arms[7b].

Finally, some remarks are made on the overall conformation of the ligands L^1, H_2L^2, and L^3 in the present compounds. If one applies the nomenclature of Boeyens and Dobson[19], which was developed to describe saturated macrocycles, to the present structures, L^1 exhibits in **1** a [3434] and in **2** a [13343] conformation. H_2L^2 adopts in **5** and **6** a [13343] conformation like in its cobalt(III) complex[7], but different from its nickel(II) complex[7b]. The five-membered chelate rings exhibit torsional angles of 52 to 59° at the CH_2–CH_2 bonds. L^3 adopts in **7** a [13334] conformation with two *gauche* C–C bonds, one *gauche* C–N, and one *gauche* C–S bond.

The torsion angles within the macrocyclic ring for all structurally elucidated complexes of H_2L^2 and L^3 agree closely for the bonds from S(1) over N(2) and N(1) to C(3). The torsion angles for the remaining four bonds, which include both S donor atoms, differ in the complexes of L^2, H_2L^2, and L^3. We suggest that the metal-to-sulfur distances and the nature (bulkiness) of the pendant chains are the determining factors. Molecular mechanics calculations are under way to rationalize the structures of this and related complexes.

UV-Vis Spectra

The spectral data are listed in Table 2. The data of **1** are typical of a tetragonal geometry around the metal center with the d-d transition at 570 nm. The cyclic ligand L^1 generates a strong in-plane ligand field. The transition occurs at a rather high energy. In $[Cu(cis\text{-}``N_2S_2")]^{2+}$, where "$N_2S_2$" is an acyclic imidazole thioether ligand, the d-d band is observed at 610 nm[5]. The remaining peaks in the spectrum of **1**, with a higher intensity than the d-d transition, are due to S→Cu and N→Cu charge-transfer transitions. Solvent and solid-state spectra are very similar, indicating identical structures in both states.

Table 2. Electronic spectral data for compounds **1**, $[CuHL^2]PF_6 \cdot MeOH$ (**3**), $[CuHL^2]BF_4 \cdot 1.5\ H_2O$ (**4**), and **5**–**7**

Compound	Solvent/State	λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)
1	MeOH	348 (730), 418 (960), 570 (290)
	solid	353, 436, 582
3	H_2O	626 (200)
4	H_2O	305 sh (3000), 626 (220)
5	H_2O	303 sh (3000), 626 (190)
	solid	310 sh, 623, 943
6	H_2O	305 sh (3000), 626 (190)
	solid	325 sh, 451 sh, 658, 1075
7	MeCN	319 sh (740), 423 sh (90), 670 (110)
	solid	340 sh, 445 sh, 700, 1021

Compounds **3**–**6** give deep blue solutions with the d-d transition at 626 nm and an S→Cu charge-transfer transition at 305 nm. In the solid state the spectra of **5** and **6** are different from each other. Compound **5** forms blue and **6** dark green crystals, caused by a red shift of the d-d and CT transitions from 305 to 325 and from 626 to 658 nm. The difference in the solid state with respect to the copper coordination is indeed corroborated by the structural studies.

In **7** the d-d transition is observed at 670 nm. The ligand L^3 generates a weaker field than L^1 and H_2L^2 do in their complexes. In the solid state-spectrum most peaks are shifted significantly to lower energy. We suggest that the copper coordination in solution and in the solid state may be slightly different.

A comparison of the data in Table 2 with the spectral data of the copper complexes of the related *trans*-N_2S_2 dibenzo ligands H_2L^5 and L^6 shows that the *cis*-N_2S_2 ligands H_2L^2 and L^3 build up slightly stronger crystal fields[7]. In the copper complexes of 14-membered purely aliphatic macrocycles with N_4, *cis*- and *trans*-N_2S_2, or S_4 donor sets the ligand fields are generally stronger than in the complexes of the dibenzo ligands H_2L^2 to L^6[20]. This is attributed to the fact that the aliphatic ligands can incorporate the copper atom into their cavity without significant distortion.

Electrochemistry

Electrochemical measurements were severely hampered by the limited solubility of the complexes under investigation in the appropriate solvents. Reasonable voltammograms could be obtained only from MeCN solutions of compounds **1** and **7**. The reversibility was checked by scanning at various rates and by examining the ratio of cathodic to anodic current. Cyclic voltammetry of **1** shows a quasi-reversible wave at 0.31 V vs SCE corresponding to the Cu^{2+}/Cu^{+} couple. The voltammograms of **7** exhibit an almost reversible process with $E_{1/2} = 0.00$ V vs SCE ($\Delta E p = 0.07$ V) due to the Cu^{2+}/Cu^{+} couple. Addison[21] and Rorabacher[3] proposed empirical relationships for N_xS_{4-x} donor ligands in which various ligand features are assigned quantitative values relative to their influence upon the Cu^{2+}/Cu^{+} potential. Their validity has been confirmed recently by Tran et al. for a series of acyclic polyimidazole-polythioether complexes[5]. But the experimental value for **1** found in our investigation does not agree with both formulas given in the literature. Using these relationships we obtained $E_{1/2}$ values of 0.19[21] and −0.01 V[3] (vs NHE) in contrast to the experimental value of 0.49 V (vs NHE)[22]. This value deviates considerably from the half-wave potential observed for the copper complexes of [14]aneNSSN (−0.01 V)[3] and [14]aneNSNS (0.04 V)[23]. We suggest that this discrepancy is caused by the tetrahedral distortion of the copper environment in **1**, by the rather short Cu−S distances, and by the preorientation of the free ligand. According to Rorabacher[3] and Tran[5] the two fore-mentioned factors destabilize the Cu^{2+} oxidation state. As expected, the $E_{1/2}$ value of compound **7** with N_4S coordination (0.21 V vs NHE[22]) is smaller than the $E_{1/2}$ data of pyridyl-thioether chelates with N_2S_2 coordination[3].

EPR Spectra

Room-temperature solution EPR spectra of compounds **1** and **3**−**6** show the expected four hyperfine lines, due to the interaction of the unpaired electron with the nuclear spin of the copper nucleus (^{63,65}Cu: I = 3/2). Like the UV/Vis spectra the EPR data in Table 3 confirm that the solutions of compounds **3**−**6** contain identical $[Cu(HL^2)]^+$ species. The room-temperature spectrum of **1** is different herefrom, because no axial coordination is possible by the ligand L^1. More informative are the spectra of frozen solutions at 77 K: From the signals of compound **1** a rather large $g_{\|}$ (2.316) and an anusual small hyperfine coupling constant $A_{\|}$ ($98 \cdot 10^{-4}$ cm^{-1}) were calculated, indicating that the coordination sphere at the copper center is strongly distorted from planarity. For comparison, in copper(II) complexes of 14-membered $N_{4-x}S_x$ aliphatic macrocyclic ligands the following parameters have been measured: [14]aneS_4: $g_{\|}$ = 2.085, $A_{\|}$ = $165 \cdot 10^{-4}$ cm^{-1}[24]; [14]aneNSSN: $g_{\|}$ = 2.145, $A_{\|}$ = $170 \cdot 10^{-4}$ cm^{-1}[25], and [24]aneN_4: $g_{\|}$ = 2.186, $A_{\|}$ = $205 \cdot 10^{-4}$ cm^{-1}[26]. These values demonstrate the rather undistorted square planar coordination of copper(II) in the respective complexes. The EPR parameters of compounds **3** and **7** are indicative for a less distorted coordination in the equatorial plane. In compound **7**, with $A_{\|}$ smaller than **6**, at least one apical donor with a short distance to the metal center should be present. This was confirmed by the structural study.

With the exception of $A_{\|}$ in compound **1** the values observed for $A_{\|}$ in this study are much larger than those reported for the "blue" copper proteins, e.g. for plastocyanin $A_{\|}$ = 66 cm^{-1}[27]. This is valid for most compounds synthesized in modelling studies so far. It is suggested to be caused by the absence of thiolate groups and of the typical distorted tetrahedral geometry around the copper site in these proteins[5].

Conclusions

The structural parameters of the compounds **1**, **2**, **5**, **6**, and **7** confirm their spectroscopic and electrochemical behavior. The tetrahedral distortion, which is connected in the "blue" copper proteins with short Cu−S (thiolate) (2.07 Å) and long Cu−S (thioether) (2.90 Å) distances cannot be modelled by means of these ligands. But compared to earlier examples[28] more pronounced short [2.269(3) Å] and long [2.700(5) Å] Cu−S distances were observed together in a single compound. Like in the "blue" copper proteins one sulfur donor is in the apical position and one in the equatorial position. But in nature the equatorial S donor atom belongs to a thiolate group with a Cu−S distance of only 2.07 Å[8]. In the UV-Vis study the d-d transitions were observed for **4**−**6** with a slightly increased intensity in the spectral range, where the "blue" copper proteins absorb. But high ε values can probably only be observed, if copper is coordinated at least by one thiolate group[29].

Table 3. EPR Parameters for compounds **1** and **3**−**7**

a) Isotropic Parameters (from solutions at 298 K)

compound	solvent	g_{iso}	$A_{iso} \cdot 10^4$, cm^{-1}
1	MeOH	2.072	78
3	MeOH	2.104	75
4	H_2O	2.103	71
5	H_2O	2.111	71
6	H_2O	2.103	71

b) Anisotropic Parameters (from frozen MeOH solutions)

compound	$g_{\|}$	$g_{\perp}$	$A_{\|} \cdot 10^4$, cm^{-1}
1	2.318	2.027	98
3	2.343	2.041	195
7	2.410	2.062	141

N. E. is indebted to the *Fonds der Chemischen Industrie* for a Studienabschlußstipendium. We thank *M. Laege* for collecting the X-ray data sets at low temperature and the *Deutsche Forschungsgemeinschaft* for the financial support.

Experimental

IR: Perkin-Elmer 683, KBr disks. − ^1H and ^{13}C NMR: Bruker AC 200, 200 and 75.47 MHz, respectively. − MS: Varian CH5, 70 eV. − UV/Vis: Measured in the solid state ($BaSO_4$ as standard) and in solution by using a Shimadzu UV-3100 spectrometer. − EPR: Bruker ESP 300 X-band spectrometer. Elemental analyses: Organisch-Chemisches Institut der Universität Münster, Germany. − Electrochemical measurements: Wenking POS 73 potentiostat. − Cyclic voltammetry: Carried out at room temp. in MeCN or DMSO solutions by using 0.1 M $[nBu_4N][ClO_4]$ as supporting electrolyte. Platinum electrodes were used as the working and as the auxiliary electrode in conjunction with a SCE reference electrode. $E_{1/2}$ values, determined as $(E_a + E_c)/2$, were calibrated relative to an external ferrocene standard ($E_{1/2}$ = 0.390 V).

Synthesis of the Ligands: The ligand L^1 was prepared by a modification of the original procedure[30] as described in ref.[7]. H_2L^2 was prepared from L^1 and α-bromoacetic acid[7].

Ligand L^3: A solution of L^1 (1.0 g, 3 mmol), 2-[(*p*-tolylsulfonyl)-methyl]pyridine (1.6 g, 6 mmol), and triethylamine (0.8 g, 8 mmol) in acetone (40 ml) was stirred for 2 d at room temp. The solvent was then removed and the yellow-brown oily residue dissolved in ethanol. After a few days colorless crystals of L^3 formed. Yield: 0.90 g (59%), m.p. 94°C. − IR: $\tilde{v}$ = 3050 cm^{-1} m, 2975 s, 2905 s, 2810 s, 1585 s, 1250 s, 1195 vs, 765 m, 750 vs. – ^{1}H NMR (200 MHz, CDCl$_3$, 25°C, TMS): δ = 2.79 (s, 4H, CH$_2$S), 3.22 (s, 4H, NCH$_2$CH$_2$), 3.67 (s, 4H, CH$_2$-phenyl), 3.75 (s, 4H, (CH$_2$-pyridyl), 7.05–7.40 (m, 12H, CH-phenyl/pyridyl), 7.54 [td, 2H, pyridyl H, ^3J(HH) = 7.7, ^4J(HH) = 1.8 Hz], 8.46 [ddd, 2H, pyridyl H, ^3J(HH) = 4.9, ^4J(HH) = 1.7, ^5J(HH) = 0.9 Hz]. – ^{13}C NMR (50 MHz, CDCl$_3$, 25°C, TMS): δ = 34.90 (SCH$_2$), 51.87 (NCH$_2$), 56.88 (CH$_2$-phenyl), 60.72 (CH$_2$-pyridyl), 121.63, 122.96, 126.74, 127.44, 131.01, 132.43, 135.00, 136.07, 141.23, 148.64, 159.84 (aromatic). – MS, *m/z* (%): 512 (15) [M$^+$]. – $C_{30}H_{32}N_4S_2$ (512.7): calcd. C 70.27, H 6.28, N 10.93; found C 70.33, H 6.28, N 11.04.

[CuL^1](ClO$_4$)$_2$ (**1**): Solutions of L^1 (0.1 g, 0.3 mmol) in methanol (10 ml) and of Cu(ClO$_4$)$_2$ · 6 H$_2$O (0.11 g, 0.3 mmol) in methanol (10 ml) were combined and refluxed for 1 h to yield dark green plate-like crystals of **1** after cooling. Yield: 0.16 g (90%). – IR: ṽ = 3200 cm^{-1} m (NH), 1100 vs (ClO$_4$), 750 m (CH), 620 (ClO$_4$). – Suitable crystals for X-ray analysis were obtained by diffusion of diethyl ether into a solution of the compound in acetone. – $C_{18}H_{22}Cl_2CuN_2O_8S_2$ (592.9): calcd. C 36.46, H 3.74, N 4.72; found C 36.46, H 3.66, N 4.80.

[CuL^1]Br · MeCN (**2**): L^1 (0.1 g, 0.3 mmol) and CuBr (0.043 g, 0.3 mmol) were suspended in MeCN (30 ml) under N$_2$. The resulting green suspension was refluxed for 30 min. From the filtrate colorless, air-sensitive crystals of **2** formed. Yield: 0.085 g (55%). – IR: ṽ = 3155 cm^{-1} vs (νNH), 1468 vs, 1460 vs, 1065 s, 750 vs. – $C_{20}H_{25}BrCuN_3S_2$ (515.0): calcd. C 46.64, H 4.89, N 8.16; found C 46.43, H 4.73, N 7.93.

[CuHL^2]PF$_6$ · MeOH (**3**): To a solution of H$_2$L^2 (0.1 g, 0.21 mmol) and CuCl$_2$ (0.03 g, 0.21 mmol) in methanol was added NaPF$_6$ (0.07 g, 0.42 mmol). The solution was refluxed for 1 h. From the filtrate a dark blue, microcrystalline powder formed within 24 h. Yield: 0.13 g (87%). – IR: ṽ = 1695 cm^{-1} m (CO), 1630 m, br (CO), 840 vs (PF$_6$), 760 s (CH), 555 s (PF$_6$). – $C_{23}H_{29}CuF_6N_2O_5PS_2$ (686.1): calcd. C 40.26, H 4.26, N 4.08; found C 40.57, H 4.42, N 4.15.

[CuHL^2]BF$_4$ · 1.5 H$_2$O (**4**): A solution of H$_2$L^2 (0.1 g, 0.21 mmol) and Cu(BF$_4$)$_2$ · 6 H$_2$O (0.073 g, 0.21 mmol) in ethanol (30 ml) was refluxed for 1 h and filtered. Upon cooling blue, rhomb-like crystals formed after 24 h. Yield: 0.12 g (91%). – IR: ṽ = 1695 cm^{-1} s (CO), 1640 s (CO), 1080 vs (BF$_4$), 765 s (CH). – $C_{22}H_{28}BCuF_4N_2O_{5.5}S_2$ (623.0): calcd. C 42.42, H 4.53, N 4.50; found C 42.52, H 4.61, N 4.39.

[CuHL^2]HSO$_4$ · 2.5 H$_2$O (**5**) *and [CuHL^2]ClO$_4$ · H$_2$O* (**6**) were prepared by the same procedure as above using CuSO$_4$ · 5 H$_2$O (0.053 g, 0.21 mmol) and Cu(ClO$_4$)$_2$ · 6 H$_2$O (0.078 g, 0.21 mmol) as starting materials. Yield: 0.11 g of **5** (81%), blue rhomb-like crystals. – IR: ṽ = 1710 cm^{-1} s, br (CO), 1625 s, br (CO), 1120 vs, br (SO$_4$), 760 vs (CH), 620 s (SO$_4$). – $C_{22}H_{31}CuN_2O_{10.5}S_3$ (651.2): calcd. C 40.54, H 4.80, N 4.30; found C 40.28, H 4.67, N 4.29. – Yield: 0.11 g of **6** (86%), green prismatic crystals. – IR: ṽ = 1710 cm^{-1} m (CO), 1615 s (CO), 1090 vs (ClO$_4$), 760 s (CH), 625 s (ClO$_4$). – $C_{22}H_{27}ClCuN_2O_9S_2$ (626.6): calcd. C 42.17, H 4.34, N 4.47; found C 42.47, H 4.37, N 4.43.

[CuL^3](ClO$_4$)$_2$ · 2 H$_2$O (**7**): Solutions of L^3 (0.1 g, 0.2 mmol) in ethanol (20 ml) and of Cu(ClO$_4$)$_2$ · 6 H$_2$O (0.072 g, 0.2 mmol) in ethanol (10 ml) were combined and refluxed for 1 h. From the filtrate green prismatic crystals of X-ray quality formed within 24 h. Yield: 0.13 g (80%). – IR: ṽ = 1610 cm^{-1} m, 1465 m, 1090 vs (ClO$_4$), 760 s (CH). – $C_{30}H_{36}Cl_2CuN_4O_{10}S_2$ (811.2): calcd. C 44.42, H 4.47, N 6.91; found C 44.66, H 4.30, N 6.89.

All other chemicals were obtained from commercial sources and used without further purifications. Solvents were dried according to standard procedures.

Many of the compounds described here contain perchlorate anions. Although no accidents have occurred, the use of perchlo-

Table 4. Crystal structure determination: Crystal data and experimental data

compound	**1**	**2**	**5**	**6**	**7**
crystal system	triclinic	monoclinic	rhombohedral	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$R\bar{3}$	$P\bar{1}$	$P2_1/c$
a, Å	8.920(2)	12.085(2)	27.432(4)	9.214(2)	14.807(3)
b, Å	10.988(2)	15.085(3)	–	11.973(2)	12.816(3)
c, Å	13.040(3)	12.229(2)	17.546(4)	12.900(3)	18.659(4)
α, deg	90.27(3)	–	–	76.55(3)	–
β, deg	105.50(3)	100.40(3)	–	70.06(3)	91.05(3)
γ, deg	110.08(4)	–	–	73.31(3)	–
V, Å^3	1150(1)	2193(1)	11435(4)	1267(1)	3540(1)
Z	2	4	18	2	4
d_{calc}, g·cm^{-3}	1.712	1.559	1.678	1.642	1.522
μ, mm^{-1}	1.412	3.02	1.161	1.188	0.946
crystal size, mm^3	0.5x0.35x0.15	0.2x0.15x0.1	0.43x0.23x0.12	0.5x0.5x0.3	0.35x0.35x0.08
T, K	293	293	77	293	293
absorption correction	ψ-scan	–	ψ-scan	ψ-scan	ψ-scan
max, min. transmission	0.84, 0.71	–	0.82, 0.75	0.75, 0.63	0.94, 0.81
diffractometer	CAD 4	CAD4	Siemens P3/V	CAD 4	CAD 4
scan method	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ
2θ range, °	4-50	4-50	4-54	4-54	4.5-51
data measured	4000	3325	5796	5214	5035
independent data	3738	2851	5456	4892	4751
data with $I \geq 2.0\sigma(I)$)	3334	1660	2658	4466	2979
no. of parameters	386	204	298	450	397
R	0.038	0.047	0.11	0.032	0.068
wR	0.048	0.049	0.35	0.037	0.069
res.el.dens., e/Å^3	0.53	0.46	1.49	0.75	0.70

rate is hazardous because of the possibility of explosion, especially when the compounds are anhydrous.

X-Ray Structure Determinations[31]: Table 4 contains the crystal data and the experimental details of the structural work. Investigation of the oscillation and Weissenberg photographs of crystals of compounds **1**, **2** and **4**–**7** mounted on glass fibers allowed the determination of Laue symmetries and approximate cell parameters. Intensity data were collected for **1**, **2**, **6**, and **7**[32] at 298 K with a Nonius CAD4 diffractometer and for **5** at 77 K with a Siemens P3/V diffractometer (both equipped with a graphite monochromator) by using the ω-2Θ scan method and Mo-K_α radiation, $\lambda = 0.71069$ Å. All computations were carried out by using the SHELXTL structure solution package, with the exception of compound **5**, where the programm SHELXL-93 was applied[33]. Least-squares refinement using 25 reflections yielded the cell dimensions given in Table 4. An empirical absorption correction based on azimuthal scans of several reflections was applied to the intensities measured.

The structures of **1**, **5**, and **7** were solved by means of the Patterson method, the structures of **2** and **6** by direct methods. Refinements with the exception of structure **5** were carried out by means of the full-matrix least-squares method minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was $w^{-1} = \sigma^2(F_o) + g \cdot F_o^2$ with $g = 3 \cdot 10^{-4}$ for **1** and **6**, $4 \cdot 10^{-4}$ for **2** and **7**. In general, all nonhydrogen atoms were refined anisotropically. Hydrogen atoms at carbon and oxygen atoms could be located in difference electron density maps and successfully refined for compounds **1** and **6**. They are included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters ($U = 0.08$ Å^2) for compounds **2**, **5**, and **7**. The structure of **5** was refined by using restraints for the sulfate ions. It shows disorder with respect to the positions of the HSO_4^- ion and the water of crystallization. The 18 HSO_4^- ions per unit cell occupy a sixfold (special) site (s.o.f. = 1) and an eighteenfold (general) site (s.o.f. = 0.67). Some unresolved electron density in this region is attributed to disordered water molecules.

For compound **7** the carbon atoms within the aromatic rings were refined isotropically by restraining the rings to regular hexagons (C–C 1.395 Å), because of the small number of reflections. Criteria for a satisfactory complete analysis were the ratios of the root-mean-square shift to the standard deviation and the absence of significant features in the final difference maps.

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[32] For compound **4** a poor intensity data set could be measured and the structure refined to *R* equals 0.14. According to the crystal data and the refined parameters there is not doubt that **4**, the BF_4^- salt of $[CuHL^2]$+, and **5**, the HSO_4^- salt of $[CuHL^2]^+$, are isostructural.

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