

Metal-Controlled Stereoselectivity in Complex Formation: Assembly of Tetranuclear Copper(I) Complexes with Four Stereogenic Nitrogen Donor Functions in all-(*R*) and all-(*S*) Configurations

Jörg Schneider,^[b,c] Martin Köckerling,^[b] Rodion Kopitzky,^[b] and Gerald Henkel^{*[a]}

Dedicated to Professor Dieter Sellmann

Keywords: Copper / Chirality / N ligands / S ligands / Metal-controlled stereoselectivity

The reaction of *N,N'*-dialkyl-3,7-diazanonane-1,9-dithiolate ($\text{N}_2^{\text{R}}\text{S}_2$) ligands ($\text{R} = \text{Me}, \text{Et}$) with monovalent copper resulted in the formation of the chiral complexes $[\text{Cu}_4(\text{N}_2^{\text{Me}}\text{S}_2)_2]$ (**1**) and $[\text{Cu}_4(\text{N}_2^{\text{Et}}\text{S}_2)_2]$ (**2**) which were characterised by means of X-ray diffraction and spectroscopic techniques. They contain copper atoms in both linear $\{\text{S}-\text{Cu}-\text{S}\}$ fragments, which act as linkers between mononuclear $[\text{Cu}(\text{N}_2^{\text{R}}\text{S}_2)]^-$ subsites, and in $\{\text{CuS}_2\text{N}_2\}$ units within these building blocks, which can be described as incomplete coordination octahedra of unusual design. Due to favourable interplay between the spatial demands of the ligand system and the electronic requirements of the copper atom, the nitrogen donor atoms within the

$[\text{Cu}(\text{N}_2^{\text{R}}\text{S}_2)]^-$ metallo ligands are restricted to identical absolute configurations. The combination of two $[\text{Cu}(\text{N}_2^{\text{R}}\text{S}_2)]^-$ metallo ligands with two further Cu^{I} ions to give the tetranuclear complexes **1** or **2** via $\text{S}-\text{Cu}-\text{S}$ bridges underlies stereochemical control, resulting in optically active systems with (*R,R,R,R*) and (*S,S,S,S*) configurations. Consequently, metallo ligands in their enantiomeric forms cannot combine via $\text{S}-\text{Cu}-\text{S}$ bridges to form optically inactive *meso* complexes with the (*R,R,S,S*) configuration.

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Introduction

For most aerobic organisms the enzyme “cytochrome-c oxidase” is involved in the final step of cell respiration. This enzyme contains the heterodimetallic $\text{Cu}_\text{B}-\text{Fe}_{\text{a}3}$ and the homodimetallic mixed-valence Cu_A centre. The copper atoms of the latter are coordinated by two bridging cysteinyl groups and one terminally bonded histidine residue each. Additional weakly bonded terminal $\text{S}(\text{Met})$ and $\text{O}(\text{Glu})$ donor functions complete the coordination spheres around the copper atoms, which are ca. 2.45 Å apart.^[1] Dinuclear copper complexes containing N/S donor sets have been synthesised as models for specific properties of the Cu_A centre.^[2]

This subject has stimulated our investigations on heteroleptic copper thiolate complexes with ligands containing

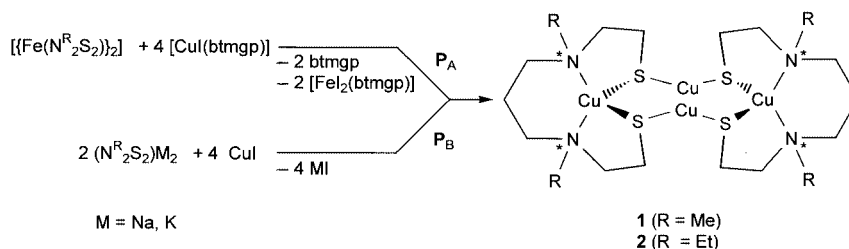
both sulfur and prochiral nitrogen donor functions.^[3] The work described here focuses on the reactions of *N,N'*-dialkyl-3,7-diazanonane-1,9-dithiolate ($\text{N}_2^{\text{R}}\text{S}_2$), which is widely used to stabilise square-planar N_2S_2 ^[4] or trigonal-bipyramidal $\text{N}_2\text{S}_2\text{S}'$ ^[5] ligand fields, with Cu^{I} (a metal known to avoid such coordination situations) resulting in the formation of tetranuclear complexes.

Herein we present the first report of two pathways for the preparation of tetranuclear Cu^{I} thiolate complexes with $\text{N}_2^{\text{R}}\text{S}_2$ ligands that stabilise severely distorted pseudo-tetrahedral N_2S_2 ligand fields. Their metal atom frameworks can be derived from the frequently observed regular metal tetrahedron present, for example in $[\text{Cu}_4(\text{SCH}_2\text{CH}_2\text{S})_3]^{2-}$,^[6] by elongation of one $\text{M}-\text{M}$ edge, leading to a completely planar situation yet unknown in copper thiolate chemistry though other derivatives with two elongated edges^[7] or with more general rhombohedral^[8] or less regular quadrilateral shapes^[9] are known. Both $[\text{Cu}_4(\text{N}_2^{\text{Me}}\text{S}_2)_2]$ (**1**) and $[\text{Cu}_4(\text{N}_2^{\text{Et}}\text{S}_2)_2]$ (**2**), with coordination numbers of 2 and 4 for the metal atoms resulting in CuS_2 and CuN_2S_2 coordination sites, have been synthesised and characterised by means of X-ray structure analysis and spectroscopic techniques.

[a] Universität Paderborn, Department Chemie, Anorganische und Analytische Chemie, Warburgerstraße 100, 33098 Paderborn, Germany
Fax: (internat.) + 49-(0)5251/60-3423
E-mail: biohenkel@uni-paderborn.de

[b] Gerhard-Mercator-Universität, Fakultät 4, Institut für Chemie, Lotharstr. 1, 47057 Duisburg, Germany

[c] BASF AG Ludwigshafen, Polymer Research, GKD/L – B1, 67056 Ludwigshafen, Germany

Scheme 1. Pathways for the synthesis of the complexes **1** and **2** [btmgp = 1,3-bis(*N,N,N',N'*-tetramethylguanidino)propane]

Results and Discussion

Synthetic Pathways

The *N,N'*-dialkyl-1,3-diazanonane-1,9-dithiolate ($N_2^R S_2$) ligands used here ($R = \text{Me, Et}$) are accessible from the corresponding diaminodithiols, which can be synthesised by reaction of *N,N'*-dialkyl-1,3-diaminopropanes with ethylene sulfide in toluene in sealed glass tubes under strictly anaerobic conditions at high pressure according to the procedure reported by Corbin et al.^[10]

The diamino dithiols, isolated after filtration and removal of the solvent, can be purified by distillation before use. A small excess of ethylene sulfide was used to avoid the survival of unchanged diamines. In these reactions, the small amounts of polyethylene thioethers obtained as side products are less soluble and therefore easily removed by filtration. The use of racemic propylene sulfide instead of ethylene sulfide leads to chiral ligands that are reported elsewhere.^[3,11]

The $[\text{Cu}_4(N_2^R S_2)_2]$ complexes **1** and **2** described here have been prepared by different pathways (P_A and P_B , Scheme 1).

The reaction of the dinuclear compound $[\{\text{Fe}(N_2^{\text{Me}} S_2)\}_2]^{[5a]}$ with the mononuclear complex $[\text{CuI}(\text{btmgp})]^{[12]}$ in a molar ratio of 1:4 in MeCN (pathway P_A) leads by ligand exchange to the tetranuclear complex **1** in fairly good yields. In a more straightforward approach (pathway P_B), **2** is accessible by reaction of CuI with $M_2(N_2^{\text{Et}} S_2)$ ($M = \text{K or Na}$) in almost quantitative yields. The $M_2(N_2^R S_2)$ precursors are obtained by reaction of sodium or potassium methanethiolate with the diaminodithiol and successive removal of the methane thiol formed in this reaction step.

Both complexes **1** and **2** are soluble in THF and other aprotic solvents such as dichloromethane or chloroform, which allows solution studies (NMR, CV, and UV/Vis). Moreover, the complexes contain four nitrogen donor functions that are chiral centres with identical configurations. Within crystals, both enantiomers [all-(*R*) and all-(*S*)] are present.

Crystal Structures

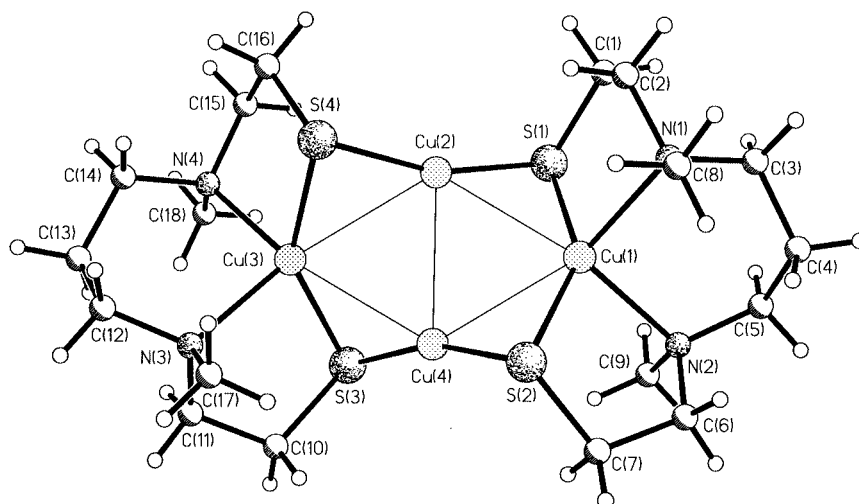
Complex **1** crystallises together with acetonitrile molecules in a 1:1 molar ratio (Table 1). The molecular structure of **1** within these crystals is shown in Figure 1 [all-(*S*) configuration]. Selected interatomic distances and angles

are given in Table 2. The four copper atoms are arranged in a planar rhomboidal fashion with $\text{Cu}\cdots\text{Cu}$ distances of 2.685 Å for the edges (averaged value) and 2.726 and 4.625 Å for the diagonals. The edges of the rhomb are bridged by thiolate-S atoms (average Cu–S distance: 2.217 Å) that reside in opposite pairs above and below the copper plane at an average distance of 1.369 Å.

Table 1. Crystal data for **1** and **2**

Compound	1 ·CH ₃ CN	2
Empirical formula	C ₂₀ H ₄₃ Cu ₄ N ₅ S ₄	C ₂₂ H ₄₈ Cu ₄ N ₄ S ₄
Formula mass	736.043	751.098
Crystal system	monoclinic	tetragonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 4/ <i>c</i> 2
<i>a</i> [Å]	15.832(2)	13.910(2)
<i>b</i> [Å]	15.434(1)	
<i>c</i> [Å]	12.729(1)	15.765(4)
β [°]	104.53(2)	
<i>V</i> [Å ³]	3010.9	3050.3
<i>Z</i>	4	4
<i>D</i> _{calcd.} [g·cm ^{−3}]	1.624	1.635
<i>T</i> [K]	293	150
λ [Å]	0.71073	0.71073
θ range [°]	1.5–25	1.5–27
Index ranges	<i>h</i> 0/+18, <i>k</i> −18/0, <i>l</i> −15/+14	<i>h</i> −17/+17, <i>k</i> −17/0, <i>l</i> −20/0
Refl. total	5189	3587
Refl. unique	5189	1686
<i>R</i> (int)	—	0.024
Observed [<i>I</i> > 2σ(<i>I</i>)]	4203	1586
μ(λ) [mm ^{−1}]	3.083	3.044
Crystal size [mm]	0.84 × 0.53 × 0.19	0.60 × 0.35 × 0.22
Transmission range	0.111–0.041	0.772–0.703
No. of parameters	299	118
<i>S</i> (<i>F</i> ²)	1.118	1.018
<i>R</i> 1 (<i>F</i> , observed)	0.0446	0.0210
<i>wR</i> 2 (<i>F</i> ² , all data)	0.1198	0.0477
Final Δ <i>F</i> [e [−] ·Å ^{−3}]	1.01, −0.39	0.33, −0.32

With the exception of the four methyl and the eight methylene groups bonded to nitrogen atoms, all other non-H atoms of the complex follow in fairly good approximation the symmetry requirements of three twofold rotation axes, two of which pass through the diagonals of the Cu₄ rhomb and the third being normal to this plane. The overall point symmetry of **1** comes very close to *C*₂ with the twofold axis passing through Cu(2) and Cu(4). Both deprotonated ligand molecules are wrapped around Cu(1) and Cu(3), defining S₂N₂ coordination polyhedra for these two metal atoms, which are neither square-planar nor tetrahedral but

Figure 1. Molecular structure of (S,S,S,S) - $[\text{Cu}_4(\text{N}_2^{\text{Me}}\text{S}_2)_2]$ (**1**)Table 2. Selected atom distances and angles for **1**

Atoms	Distance [Å]	Atoms	Angle [°]
Cu(1)–Cu(2)	2.678(1)	Cu(2)–Cu(1)–Cu(4)	61.1(1)
Cu(1)–Cu(4)	2.687(1)	Cu(1)–Cu(2)–Cu(3)	118.5(1)
Cu(2)–Cu(3)	2.705(1)	Cu(2)–Cu(3)–Cu(4)	61.0(1)
Cu(3)–Cu(4)	2.669(1)	Cu(1)–Cu(4)–Cu(3)	119.4(1)
Cu(2)–Cu(4)	2.726(1)	S(1)–Cu(1)–S(2)	146.7(1)
Cu(1)–S(1)	2.271(2)	S(1)–Cu(1)–N(1)	88.4(1)
Cu(1)–S(2)	2.268(2)	S(1)–Cu(1)–N(2)	112.5(1)
Cu(1)–N(1)	2.214(5)	S(2)–Cu(1)–N(1)	114.2(1)
Cu(1)–N(2)	2.186(4)	S(2)–Cu(1)–N(2)	89.6(1)
Cu(2)–S(1)	2.167(2)	N(1)–Cu(1)–N(2)	96.9(1)
Cu(2)–S(4)	2.157(2)	S(1)–Cu(2)–S(4)	162.7(1)
Cu(3)–S(3)	2.269(2)	S(3)–Cu(3)–S(4)	144.8(1)
Cu(3)–S(4)	2.262(2)	S(3)–Cu(3)–N(3)	89.9(1)
Cu(3)–N(3)	2.186(4)	S(3)–Cu(3)–N(4)	114.7(1)
Cu(3)–N(4)	2.220(4)	S(4)–Cu(3)–N(3)	115.5(1)
Cu(4)–S(2)	2.169(2)	S(4)–Cu(3)–N(4)	88.0(1)
Cu(4)–S(3)	2.173(2)	N(3)–Cu(3)–N(4)	95.5(1)
		S(2)–Cu(4)–S(3)	163.6(1)

can be derived from a (distorted) $\text{S}_2\text{N}_2\text{L}_2$ octahedron (Figure 1) with sulfur and nitrogen atoms at opposite (slightly bent towards L, mean $\text{S}–\text{Cu}–\text{S}$ angle 145.8°) and neighbouring corners (mean $\text{N}–\text{Cu}–\text{N}$ angle 96.2°), respectively, by removal of L. They are central constituents of mononuclear subunits that act as ligands towards Cu(2) and Cu(4), resulting in slightly bent $\text{S}–\text{Cu}–\text{S}$ coordination sites with valence angles of $162.7(1)^\circ$ for Cu(2) and $163.6(1)^\circ$ for Cu(4). As the subunits lack molecular symmetry, the formation of two isomeric forms is possible but only one could be isolated. The other isomer can be obtained by rotating one of the mononuclear subunits of **1** around an axis that passes through Cu(1) and Cu(3). Within the tetranuclear complexes the nitrogen atoms are in identical configurations [all-(*R*) or all-(*S*), respectively]. The average $\text{Cu}–\text{N}$ distance is 2.202 Å , and the valence angles for Cu(1) and Cu(3) range from $88.0(1)^\circ$ [$\text{S}(4)–\text{Cu}(3)–\text{N}(4)$] to $146.7(1)^\circ$ [$\text{S}(1)–\text{Cu}(1)–\text{S}(2)$], showing significant distortions if com-

pared with a regular tetrahedron. Moreover, the angles between the planes defined by the CuS_2 and CuN_2 fragments are calculated to be 73.3 and 71.7° for Cu(1) and Cu(3), respectively, demonstrating significant planarisation tendencies within the coordination polyhedra. The methylene groups connecting the nitrogen atoms in the $\text{N}_2^{\text{Me}}\text{S}_2$ ligand fit into six-membered chelate rings that adopt the chair conformation.

In contrast to the methylated complex **1**, the ethylated variant **2** could be isolated in both isomeric forms (**2a** and **2b**, vide supra). Their structures, in the all-(*R*) configurations, are depicted in Figure 2.

Similar to **1**, both isomers are assembled from identical dissymmetric mononuclear subunits with significantly distorted defect-octahedral CuN_2S_2 coordination sites that act as ligands towards additional copper ions. The structure of **2a** (Figure 2, bottom) is closely related to that of **1**. The molecule occupies a twofold rotation axis that passes through Cu(2) and Cu(2a) and is crystallographically imposed. For the other isomeric form (**2b**; Figure 2, top) a twofold rotation axis of crystallographic origin passes through the centre of the Cu_4 rhomb normal to the metal plane. Crystals of **2** contain both isomers in a disordered fashion. The superposition of two conformationally different molecules with twofold rotation axes that are normal to each other results in the crystallographic site symmetry 22_2 . This overall symmetry is reduced towards **2** for the individual complex molecules. The existence of potentially possible conformers with at least one mononuclear subunit possessing twofold symmetry can be excluded from geometric considerations: for all these cases, the valence angle at the central carbon atom of the propylene chain [C(4)] must adopt a value of ca. 132° , which is much too large to be physically meaningful. For both **2a** and **2b**, the $\text{Cu}\cdots\text{Cu}$ distances are $2.647(1) \text{ Å}$ for the edges of the Cu_4 rhomb and $2.675(1)$ and $4.570(1) \text{ Å}$ for the short and long diagonals, respectively. These values compare nicely with those of **1**, as do the $\text{Cu}–\text{S}$ and $\text{Cu}–\text{N}$ distances and the overall metal coord-

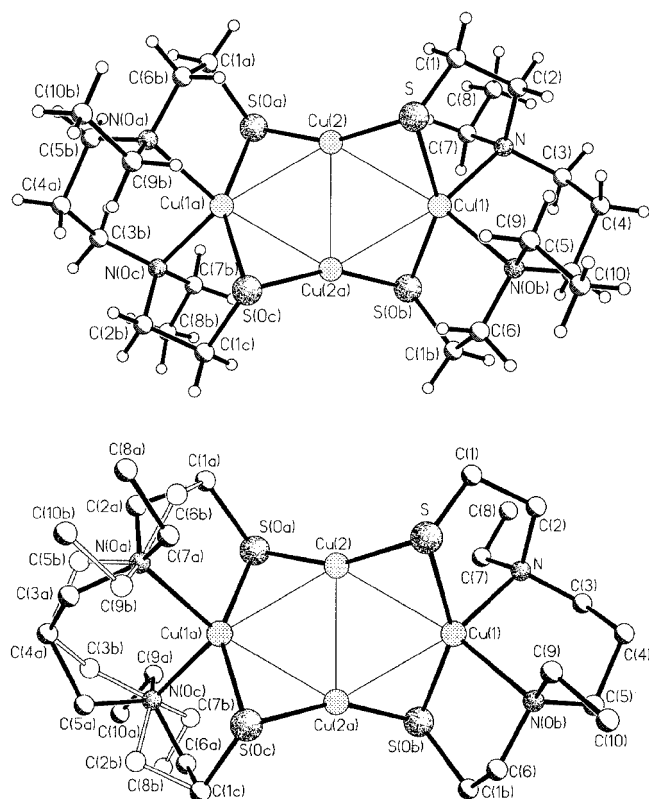


Figure 2. Top: structure of (R,R,R,R) - $[\text{Cu}_4(\text{N}_2^{\text{Et}}\text{S}_2)_2]$ (**2b**); bottom: structure of (R,R,R,R) -**2a** with superimposed structure of **2b** (without H atoms; alternative atomic positions shown as open circles)

dination. Selected interatomic distances and angles for both conformers of **2** are given in Table 3.

Table 3. Selected atom distances and angles for **2** (symmetry codes: ' : $y - 1/2, x + 1/2, -z + 2$; '' : $-x + 1, -y + 2, z$)

Atoms	Distance [Å]	Atoms	Angle [°]
Cu(1)–Cu(2)	2.647(1)	Cu(2)–Cu(1)–Cu(2)'	60.7(1)
Cu(2)–Cu(2)'	2.675(1)	Cu(1)–Cu(2)–Cu(1)''	119.3(1)
Cu(1)–S	2.273(1)	Cu(1)–Cu(2)–Cu(2)'	59.7(1)
Cu(1)–N	2.196(2)	S–Cu(1)–S'	149.1(1)
Cu(2)–S	2.172(1)	S–Cu(1)–N	88.8(1)
		S–Cu(1)–N'	111.7(1)
		N–Cu(1)–N'	97.9(1)
		S–Cu(2)–S''	157.8(1)

Spectroscopic Properties

Infrared and Raman Spectra

In the region above 1350 cm^{-1} , the IR spectra of **1** and **2** show strong $\nu_{\text{as}}/\nu_{\text{s}}$ and $\delta_{\text{as}}/\delta_{\text{s}}$ bands of the CH_2 and CH_3 groups. The bands between ca. 1300 cm^{-1} and 1200 cm^{-1} should be attributed to wagging modes of the CH_2 groups, the high intensities being consistent with their great number. A complicated pattern in the range of 1150 to ca. 1000 cm^{-1} with only small differences in frequencies between **1**

and **2** is probably a superposition of $\nu_{\text{C-N}}$ bands, frequencies originating from C–C vibrations and bands associated with the rocking mode of the CH_3 groups (969 cm^{-1}). The bands between 800 and 1000 cm^{-1} can be traced back to C–C stretching and CH_3 rocking vibrations. In the expected region for the $\nu_{\text{C-S}}$ vibration, four bands are observed. The infrared and Raman spectra of **2** are compared in Figures 3 and 4.

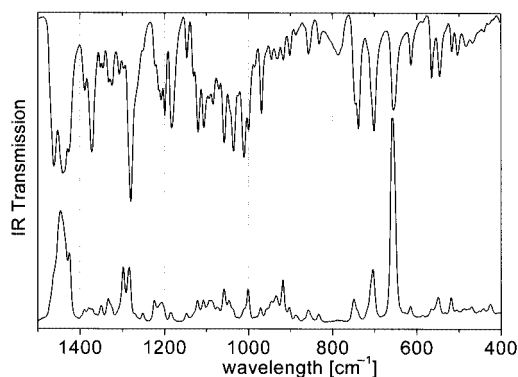


Figure 3. Infrared (top) and Raman (bottom) spectra of **2** (MIR region)

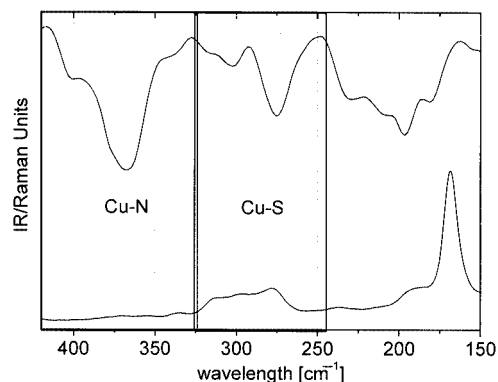


Figure 4. Infrared (top) and Raman (bottom) spectra of **2** (FIR region)

The strong Raman line at 656 cm^{-1} is assigned to the fully symmetric stretch of the C–S groups. This line can be correlated with a weak band in the infrared spectrum which is shifted by 3 cm^{-1} .

As expected for these compounds, in the region down to 400 cm^{-1} , several deformation modes of the heterocyclic five- (CuSC_2N) and six-membered (CuNC_3N) chelate rings are observed.

Based on the infrared and Raman spectra of **2**, the $\nu_{\text{Cu-N}}$ and $\nu_{\text{Cu-S}}$ frequencies can be allocated as illustrated in Figure 4. The $\nu_{\text{Cu-N}}$ frequencies occur in the range from 325 to 420 cm^{-1} (central frequency at 368 cm^{-1}), whereas the $\nu_{\text{Cu-S}}$ frequencies are assigned to bands in the range 250 – 325 cm^{-1} (main frequencies at 276 and 303 cm^{-1}), especially in the Raman spectra. This assignment agrees with the observed relative intensities of the $\nu_{\text{Cu-S}}$ and the

$\nu_{\text{Cu-N}}$ bands, which can be correlated with the higher polarizability of sulfur compared with nitrogen.

NMR Spectra

As a representative example, complex **2** was investigated by NMR spectroscopy. Because different conformers were detected in the crystalline state, a mixture of chemically different states should also be present in solution. Accordingly, the ^1H NMR spectrum is very complicated, and so no attempts to allocate signals have been made. Nevertheless, two predominant forms can be identified by different resonances of their methyl groups in accordance with the crystal structure. At room temperature, two overlapping triplets with significant differences in their intensities and coupling constants are resolved ($\Delta^3J \approx 0.2$ Hz), whereas at higher temperatures (333 K) these differences vanish.

Consistent with this assumption, two sets (each of six signals) of carbon atoms are observed in the ^{13}C NMR spectrum for **2**. The signals at $\delta = 8.43$ and 8.54 ppm can be assigned to the methyl groups (positive signal in DEPT-135) of the conformers.

Electrochemistry

Cyclic voltammetry measurements of complex **2**, dissolved in THF, show only irreversible oxidation and reduction events at +610 and –90 mV (vs. GKE), respectively.^[13]

Discussion

As the $\text{Cu}_4\text{N}_4\text{S}_4$ cores of the conformers **2a** and **2b** are identical, we shall use **2** here instead of **2a** or **2b**. Both tetranuclear complexes **1** and **2** contain identical mononuclear subunits with the copper atom in a distorted N_2S_2 environment which can be derived from an $\text{N}_2\text{S}_2\text{L}_2$ octahedron by removal of L (vide supra). This spatial arrangement is controlled by the steric requirements of the alkylene spacers connecting the donor functions, which do not allow for a more regular tetrahedral situation. The deviation from tetrahedral symmetry is best reflected by the S–Cu–S valence angle, which is as large as 149.1° in **2** and of comparable size in **1**. Similar analogies between **1** and **2** with respect to other structural features of their $\text{Cu}_4\text{N}_4\text{S}_4$ cores also exist. For clarity, numerical values of **1** are omitted in the following discussion. The vector which passes through the copper atoms of both subunits bisects the S–Cu–S and N–Cu–N triangles. Both CuN_2S_2 polyhedra within each tetranuclear molecule are rotated against each other by ca. 90° around this Cu–Cu vector in such a way that the CuS_2 fragment of one subunit and the CuN_2 fragment of the other are coplanar. As both CuN_2S_2 polyhedra face each other via their S_2 edges, the sulfur atoms form a distorted tetrahedron with opposite edges being 4.382, 4.262 and 4.858 Å in lengths, respectively. The edges that belong to individual CuN_2S_2 polyhedra are bridged by Cu(1). From geometrical considerations, the arrangement of the sulfur

atoms should allow for the incorporation of a total of four additional copper atoms into places defined by the centres of the edges of the S_4 tetrahedron that connect the CuN_2S_2 units. For the complexes described here, only one half of these positions are occupied by copper [Cu(2) and Cu(4) in **1**, Cu(2) in **2**] in such a way that planar metal arrangements are formed. This half is associated with the shorter S...S edges of the S_4 tetrahedron, resulting in distorted linear S–Cu–S units. It is noteworthy that these additional copper atoms are shifted from the centres of the S...S edges towards the centroid of the S_4 tetrahedron and approach each other at 2.675 Å, a distance that is only marginally longer than that observed between Cu(2) and Cu(1) (2.647 Å), indicating some degree of attractive Cu...Cu interactions.

As has already been pointed out, the distorted “tetrahedral” CuN_2S_2 coordination sites are characterised by extremely wide S–Cu(1)–S valence angles of 149.1° . This situation can therefore alternatively be regarded as a first-order distorted linear S–Cu–S coordination with additional secondary bonds to nitrogen atoms. In this picture, four of the six edges of the S_4 tetrahedron are occupied by copper atoms, two of which are displaced towards the centroid whereas the remaining ones are shifted in the opposite direction to avoid Cu...Cu interactions that are too short to be stable.

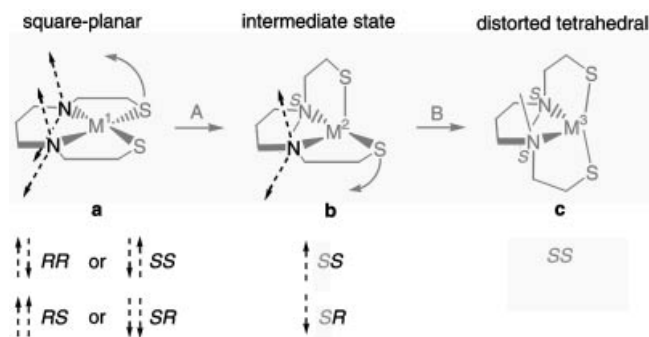
The complex $[\text{Cu}_4\{\text{SC}_6\text{H}_2(i\text{Pr})_3\}_4]$ has recently been identified by Schröter-Schmidt and Strähle as containing a polycyclic Cu_4S_4 framework similar to that of **1** and **2**.^[8b] In this case, however, the S_4 tetrahedron is drastically flattened if compared with those in **1** and **2**, and the short diagonal of the Cu_4 rhomb (3.383 Å) is much longer than the edges (2.700 Å). Though secondary Cu–N bonds are lacking in this example, two of the copper atoms are also displaced away from the centroid of the S_4 polyhedron (Cu...Cu 4.207 Å), whereas the others are shifted towards each other at a distance of 3.383 Å. Comparable geometrical features have also been found by Becker et al. and by Block et al. in the tetranuclear thiolate complexes $[\text{Cu}_4\{\text{SSi}(\text{OrBu})_3\}_4]$ ^[8c] and $[\text{Cu}_4\{\text{SC}_6\text{H}_3(2,6\text{-SiMe}_3)_2\}_4]$,^[8a] respectively.

Coordination principles in tetranuclear thiolate complexes with planar copper frameworks that are different from those observed in **1** and **2** have been found in $[\text{Cu}_4\{\text{SC}_6\text{H}_2(2,4,6\text{-}i\text{Pr})_3\}_4(\text{bipy})_2]$ ^[14] and $[\text{Cu}_4(\text{S}t\text{Bu})_4(\text{PPh}_3)_2]$,^[15] respectively. In both cases, two mononuclear $[\text{Cu}(\text{SR})_2\text{L}]$ subunits with tetrahedral CuN_2S_2 or trigonal-planar CuPS_2 coordination sites act as ligands towards “naked” Cu^{I} ions, forming linear S–Cu–S units within cyclic Cu_4S_4 frames. Due to the non-linearity of the S–Cu–S fragments within the CuN_2S_2 and CuPS_2 coordination sites, these frames contain sulfur atoms in planar arrangements. Both frames differ in the magnitude of their Cu–S–Cu angles. For $[\text{Cu}_4\{\text{SC}_6\text{H}_2(2,4,6\text{-}i\text{Pr})_3\}_4(\text{bipy})_2]$,^[14] both acute and obtuse angles are present, whereas only acute angles are observed in $[\text{Cu}_4(\text{S}t\text{Bu})_4(\text{PPh}_3)_2]$.^[15]

Of more general importance is the new finding that ligands derived from 3,7-dialkyl-3,7-diazanonane-1,9-dithiol-

ate stabilise complexes of coordination number 4 with a nonplanar ligand field. In principle, the spatial arrangement of the ligand donor functions fits perfectly well into a square-planar coordination geometry. This coordination mode has frequently been observed for Ni^{II} and, to a lesser extent, also for Cu^{II} and Pd^{II} .^[4] In all these cases, the absolute configurations of the two nitrogen donor atoms are mirror images, resulting in optically inactive *meso* complexes. In contrast, the mononuclear subunits of **1** and **2** should be optically active as the stereogenic nitrogen atoms are in the same absolute configuration. The observed nonplanar arrangement of the N_2S_2 donor set can be derived from a planar case by rotation of the CuS_2 fragment around the bisector of the $\text{S}-\text{Cu}-\text{S}$ angle. This rotation is accompanied by a drastic widening of the $\text{S}-\text{Cu}-\text{S}$ valence angle induced by the restricted $\text{S}\cdots\text{N}$ bite distance.

To analyse the stereochemical consequences of this rotation with respect to the individual absolute configurations of the nitrogen atoms within the monomeric subunits, we will discuss a hypothetical stepwise mechanism (Scheme 2) starting from the square-planar arrangement.



Scheme 2. Metal-controlled stereochemistry ($\text{M}^1 = \text{Ni}^{\text{II}}$; $\text{M}^2 = \text{Mn}^{\text{II}}$, Fe^{II} ; $\text{M}^3 = \text{Cu}^{\text{I}}$); the possible positions for the alkyl substituents are indicated by dashed arrows

In this situation (Scheme 2, **a**), each nitrogen atom can, principally, adopt both (*R*) or (*S*) conformations independently. In step A, we shift one of the sulfur atoms into a position such that the $\text{Cu}-\text{S}$ bond is normal to the remaining CuN_2S plane. Such arrangements have been observed in the dinuclear complexes $[\{\text{Fe}(\text{N}_2^{\text{Me}}\text{S}_2)\}_2]^{\text{[5]}}$ and $[\{\text{Mn}(\text{N}_2^{\text{Et}}\text{S}_2)\}_2]^{\text{[5]}}$. This procedure has stereochemical consequences with respect to the absolute configuration of the nitrogen atom directly connected with the shifted sulfur atom. If we look from the midpoint of the $\text{N}\cdots\text{N}$ edge to the copper atom and we shift the sulfur atom of the left-hand side upwards, the nitrogen atom on the same side has to adopt the (*S*) configuration. The absolute configuration of the other nitrogen atom is not restricted by this procedure. Thus, both diastereomeric forms, namely those with (*S,S*) and (*R,S*) configurations, should be possible (Scheme 2, **b**). In fact, the complex $[\{\text{Fe}(\text{N}_2^{\text{Me}}\text{S}_2)\}_2]^{\text{[5]}}$ is an example of a system which adopts the (*R,S*) configuration, whereas in $[\{\text{Mn}(\text{N}_2^{\text{Et}}\text{S}_2)\}_2]^{\text{[5]}}$ the (*S,S*) configuration is observed. In the next step (B), the second sulfur atom is shifted into the opposite direction such that both $\text{Cu}-\text{S}$ bonds are more or less par-

allel (Scheme 2, **c**). Both nitrogen atoms are now restricted to adopt the (*S,S*) configuration. This situation holds for both **1** and **2**. In the complex $[\text{MoO}_2(\text{N}_2^{\text{Me}}\text{S}_2)]$, a related situation has been observed.^[16] The same process based on opposite shifts finally leads to the (*R,R*) configuration.

As a consequence of the spatial restrictions induced by the alkylene spacers of the polyfunctional ligands, a tetrahedral coordination geometry which requires $\text{S}-\text{Cu}-\text{S}$ valence angles in the order of 109° cannot be achieved, and the rotation process is expected to converge against a limiting angle that is smaller than 90° , in accordance with our observations.

In both complexes **1** and **2** all of the four N atoms of the diamino dithiolate ligands are stereogenic centres with identical absolute configurations. The crystals are racemic mixtures of the two enantiomers [all-(*R*) and all-(*S*)], whereas diastereomers (*R,R,S,S*) have not been observed. The combination of monomeric subunits that are mirror images to tetranuclear complexes (in their *meso* forms) via bridging Cu ions is not possible due to steric requirements of the thiolate-S functions, which cannot form additional $\text{S}-\text{Cu}$ bonds with suitable geometries. As an important consequence of this spatial control, tetranuclear complexes of the type described above must be optically active, and the assembly of any optically inactive form (with *meso* configuration) is therefore strictly forbidden.

Racemic mixtures of the type described here may play an important role as auxiliaries if it is possible to activate or deactivate one enantiomer selectively by a further chiral component.^[17]

Conclusions

Here we have gained control of the stereochemistry of nitrogen donor functions in N_2S_2 ligands by adjusting the spatial demands with metal-specific coordination properties. For Cu^{I} , the coordination of N_2S_2 ligands can only be achieved if both nitrogen atoms adopt the same absolute configuration [(*R,R*) or (*S,S*)]. These mononuclear chiral CuN_2S_2 units have been found to act pairwise as bifunctional sulfur donor ligands towards monovalent copper ions, forming stable tetranuclear complexes with planar metal frames. The observation that this step is absolutely stereoselective, allowing only combinations of units with identical configurations, should be of more general importance. The stereochemical control can be traced back to an interplay between the coordination properties of the sulfur donor functions of the metallo ligand and the bonding requirements of the bridging copper ions. Consequently, the combination of units with opposite configurations, leading to optically inactive *meso* complexes (*R,R,S,S*), is strictly forbidden. These novel complexes might find applications in chemical and catalytic processes.

Experimental Section

General Remarks: All manipulations were performed under pure dinitrogen using Schlenk techniques or a glove box using abs. sol-

vents. *N,N'*-Diethyl-3,7-diazanonane-1,9-dithiole is readily accessible by procedures described in the literature.^[10] The complexes used as starting materials, $[\{\text{Fe}(\text{N}_2\text{S}_2\text{Me})\}_2]$ and $[\text{CuI}(\text{btmgp})]$, were synthesised by reaction of $[\text{Fe}\{\text{N}[\text{Si}(\text{Me})_3]_2\}_2]$ with stoichiometric amounts of *N,N'*-diethyl-3,7-diazanonane-1,9-dithiole and addition of btmgp to CuI, respectively.

Physical Measurements: All measurements were performed under strictly anaerobic conditions. IR spectra were obtained using a Bio-Rad FTS-7 (1) and a Bruker IFS 66v (2) spectrometer. ^1H NMR spectra for 2 were obtained with a Bruker Avance DRX 500 spectrometer and solvent signals were used as an internal standard [calibrated on $\delta = 7.240$ (^1H), 77.00 (^{13}C)].

X-ray Crystallographic Studies: Single crystals of 1·MeCN were obtained as yellow blocks by slow cooling of a solution of 1 in MeCN. Suitable yellow crystals of 2 were obtained by slow diffusion of diethyl ether into a MeCN solution of the complex. Crystals were sealed in a glass capillary (1) under an inert gas or mounted on top of a glass capillary with silicon grease (2). Diffraction data were collected at room temperature (1) with a Siemens-Stoe-AED-2 or at 150 K (2) with a Siemens P4RA four-circle diffractometer utilizing monochromated Mo- K_α radiation. The data were corrected for absorption (ψ -scan method), as well as for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS-86).^[18] Refinements were done by full-matrix least-squares methods on F^2 with anisotropic thermal displacement parameters for all non-hydrogen atoms using the SHELXL-97 program suite.^[19] Hydrogen atoms were fixed on idealised positions and refined with a common isotropic temperature factor. Crystals of 2 are composed of individual complex molecules 2a and 2b which occupy the same crystallographic position in a statistical manner. A summary of relevant crystal data is given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-203954 (1) and -203955 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of Compounds

$[\text{Cu}_4(\text{N}_2\text{S}_2\text{Me})_2]$ (1) (Pathway A): A solution of $[\text{CuI}(\text{btmgp})]$ (0.175 g, 0.38 mmol) in MeCN was added dropwise, at room temperature, to a suspension of $[\{\text{Fe}(\text{N}_2\text{S}_2\text{Me})\}_2]$ (0.105 g, 0.19 mmol) in MeCN (15 mL). The mixture was refluxed for 30 min and then filtered. On slow cooling of the filtrate, 1 was obtained as light yellow crystals. Yield: 0.168 g; 60%, based on Cu^I. IR (KBr): $\tilde{\nu} = 2957\text{--}2920$ s, $2841\text{--}2799$ vs, 2247 m (ν_{CN}), 1458 vs, 1381 m, 1362 m, 1314 m, 1294 s, 1260 m, 1229 s, 1200 vs, 1152 m, 1088 m, 1053 s, 1044 vs, 1032 vs, 993 vs, 959 m, 936 m, 910 m, 893 m, 870 m, 760 vs, 723 vs, 652 m, 600 w, 550 w, 525 w, 467 m, 426 m, 368 m cm^{-1} .

$[\text{Cu}_4(\text{N}_2\text{S}_2\text{Et})_2]$ (2) (Pathway B): *N,N'*-Diethyl-3,7-diazanonane-1,9-dithiole (0.501 g, 2 mmol) was dissolved in tetrahydrofuran (15 mL) and treated with a slurry of potassium methanethiolate (0.345 g, 4 mmol) in tetrahydrofuran (10 mL). The yellow slurry was stirred at 40°C for 30 min and the solvent removed in vacuo. The resultant colourless residue was suspended in tetrahydrofuran (20 mL) and again stirred for 30 min at the same temperature. After removal of the solvent under reduced pressure the obtained colourless residue was treated with a solution of copper(I) iodide (0.762 g, 4 mmol) in acetonitrile (25 mL) and the resulting mixture refluxed for 20 min. The solvent was then removed in vacuo and the residue

resuspended in tetrahydrofuran (70 mL). After stirring for 16 h, the mixture was filtered and 2 obtained as yellow crystals by slow diffusion of diethyl ether into the clear yellowish filtrate. Yield: 0.413 g; 55%, based on Cu^I. $\text{C}_{31}\text{H}_{59}\text{CuN}_6\text{S}$ (751.06): calcd. C 35.18, H 6.44, N 7.46, S 17.09; found C 35.31, H 6.45, N 7.48, S 16.92. IR (KBr): $\tilde{\nu} = 2957$ vs, 2922 vs, 2824 vs, 1441 s, 1373 m, 1324 m, 1281 vs, 1199 m, 1183 m, 1120 m, 1085 m, 1036 m, 1011 s, 969 m, 917 w, 902 w, 857 w, 787 m, 739 m, 701 m, 656 m, 614 w, 565 m, 503 w, 483 w cm^{-1} . FIR (polyethylene pellet): $\tilde{\nu} = 565$ vs, 546 s, 517 m, 503 s, 484 m, 471 m, 451 vw, 438 w, 401 m, 368 vs, 303 w, 276 m, 229 m, 197 s, 181 m, 145 w, 120 m, 110 m, 89 m, 66 m cm^{-1} . Raman (capillary): $\tilde{\nu} = 2922$ vs, 2873 m, 2851 m, 2730 w, 1446 w, 1333 vw, 1298 w, 1206 w, 1121 vw, 1093 vw, 1059 w, 1002 w, 934 vw, 918 w, 858 vw, 832 vw, 749 vw, 704 w, 658 m, 615 vw, 550 vw, 519 vw, 471 vw, 425 vw, 278 m, 237 w, 169 m, 120 m, 84 w cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 1.08$ (t, $^3J = 7.08$ Hz, CH_3), 1.10 (t, $^3J = 7.26$ Hz, CH_3 , 2b), 1.67 ("quint", $^3J = 5.09$ Hz, $\text{CH}_2\text{--CH}_2\text{CH}_2\text{--}$), 2.06 ("quint", $^3J = 6.9$ Hz), 2.33 (m), 2.50 (m), 2.64 (m), 2.69 (m), 2.77 (m), 2.93 (t, $^3J = 7.08$ Hz, H) ppm. ^{13}C NMR (125.75 MHz, CDCl_3 , 298 K): $\delta = 8.43$ (CH_3 , 2a), 8.54 (CH_3 , 2b), 21.89 (C, 2b), 27.66 (C, 2a), 27.85 (C, 2b), 29.18 (C, 2a), 46.82 (C, 2a), 50.28 (C, 2b), 53.09 (C, 2a), 53.99 (C, 2b), 56.13 (C, 2a), 56.87 (C, 2b) ppm. DEPT-135, $^1\text{H}^{13}\text{C}$ -COSY, $^1\text{H}^1\text{H}$ -COSY were used for allocation of the signals.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. J. S. thanks the Stiftung Stipendienfonds des Verbandes der Chemischen Industrie for granting a Kekulé fellowship.

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Received October 12, 2002