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Copper(I) complexes of N-centered aliphatic tripodal trithioether ligands – Adjustment of complex geometry by variation of spacer lengths

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ABSTRACT

A series of novel aliphatic tripodal trithioether ligands **4**–**6** differing in the lengths of the alkyl chains between central nitrogen atom and sulfur donor function has been synthesized. The neutral ligands **4–6** react with copper(I) under formation of the mononuclear complexes **7**–**9** featuring exclusive coordination of the metal center by the tertiary amine and the three thioether donor functions of the tripodal ligand. Molecular structures of **7** and **9** show a direct influence of the spacer lengths between central and terminal donor functions on the geometry of the tetracoordinated complex cations. Substitution of one ethylene by a propylene spacer leads to a larger bite angle between the amine and thioether donor functions and effects a tetrahedral distortion for the complex cation in **7**. For the copper(I) compound **9** with a ligand possessing exclusively propylene spacers this effect is increased leading to a tetrahedral geometry of the complex cation.

1. Introduction

Thiols and thioethers are ubiquitious donor functions in the active sites of many naturally occurring metalloenzymes. In the coordination sphere of redox active metal ions such as copper or iron, sulfur-ligands effect a high redox potential, because the reduced metal center is a softer cation and therefore more efficiently coordinated by the soft sulfur donors [1,2]. One of the most prominent examples for this kind of complexes is the intensely blue colored Cu^{II}-site of cupredoxins, which play an essential role in photosynthesis and respiration [2].

Polydentate ligands with tripodal topology are often used for the synthesis of model complexes mimicking the spectroscopic and structural properties of the active sites of metallo proteins [3]. Most of these compounds possess aromatic donor functions like the pyridyl group. Much less effort has been directed towards ligands with aliphatic ligand arms and donor functions. Such aliphatic ligands often differ significantly in their coordination behavior towards metal ions from their aromatic analogs [4].

The most frequently used aliphatic tripodal ligand with sulfur donor functions is the tetradentate tris(2-mercaptoethyl)amine. With a wide range of transition metal ions including iron [5], cobalt [5c], nickel [5b,6], molybdenum [7], tungsten [7], technetium [8], and rhenium [8] it forms mononuclear complexes or polynuclear compounds where the thiolato donor functions bind to two metal centers in a bridging fashion. The ligand tris(3-mercaptopropyl)amine featuring propylene spacers between the central nitrogen atom and the terminal donor groups reacts with tin(IV) to yield a dinuclear complex. In this case the thiolato groups of two ligands do not act as bridging donors but coordinate in a monodentate fashion to two different metal centers [9].

Many thioether derivatives of tris(2-mercaptoethyl)amine with different substituents at the sulfur atom have been described. Due to the limited ability of thioethers to act as bridging donor these ligands react with metal ions preferably to give mononuclear complexes with coordination of additional co-ligands. Complexes with iron [10], cobalt [11,12], nickel [11–13], copper [11,14], zinc [11], silver [15], palladium [16], and platinum [16] have been reported. With ligand tris(2-benzylmercaptoethyl)amine Kaden et al. prepared a copper(I) complex, in which the metal ion is coordinated in a trigonal–pyramidal fashion exclusively by the four donor functions of the tripodal ligand [17].

While all of the ligands mentioned above are symmetric regarding their donor functions as well as the lengths of the spacers between the donor functions, some related asymmetric aliphatic ligands are also known. A direct influence of the lengths of the alkyl chains between central and terminal donor function on the complex geometry was observed for the copper(II) [18] and nickel(II) [19] complexes of the aliphatic tripodal tetraamines **A**–**D** featuring different spacer lengths (Fig. 1). The coordination behavior towards zinc(II) and nickel(II) was investigated for ligands **E** and **F** combining thiol, amine, and alkoxy donor functions and both ethylene and propylene spacers [20]. Ligands exhibiting thiol and thioether donor groups like compound **G** (Fig. 1) coordinate to technetium and rhenium as tridentate ligands *via* their thiolato and amino

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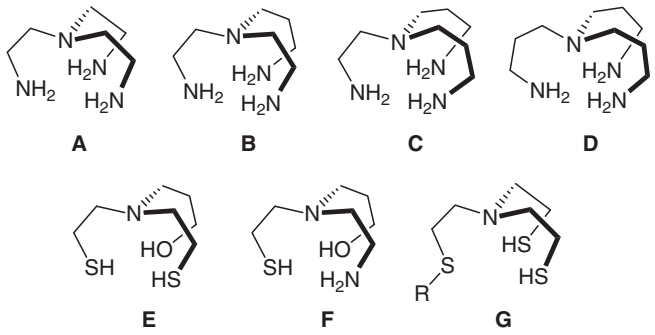


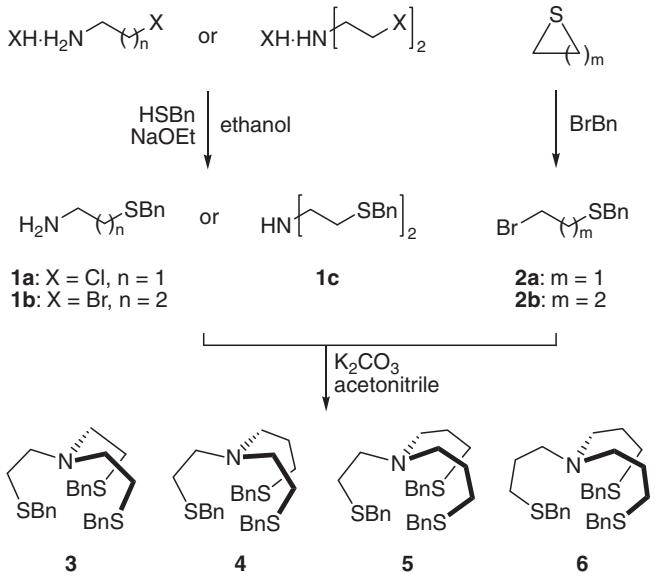
Fig. 1. Aliphatic tripodal ligands with differing spacer lengths (**A**–**D**) [18,19] and asymmetric donor sets (**E**–**G**) [20–22].

donor functions only, yielding complexes with potential use in radiodiagnosis and radiotherapy [21]. Contrary to this situation, all four donor groups of ligand **G** coordinate after deprotonation to the metal center in a mononuclear molybdenum complex [22].

To our knowledge asymmetric tripodal N-centered ligands possessing three thioether donor functions and their metal complexes have not been described yet. Herein we report the synthesis of a series of four aliphatic tripodal ligands (an alternative synthesis of **3** [17] using the carcinogenic tris(2-chloroethyl)amine has previously been reported) possessing a central nitrogen atom in addition to three benzyl thioether donor functions connected to the central nitrogen atom by alkyl chains of differing lengths. The coordination chemistry of these ligands with copper(I) as well as the influence of the lengths of the ligand arms on the geometry of the resulting complexes is also discussed.

2. Results and discussion

The tetradentate ligands **3**–**6** were synthesized as depicted in Scheme 1 starting from 2-chloroethylamine hydrochloride, 3-bromopropylamine hydrobromide or bis(2-chloroethyl)amine hydrochloride, respectively. Substitution of the halides with benzylmercaptane under basic conditions lead to formation of the ω-benzylmercaptoalkylamines **1a**–**c**. 2-Benzylmercaptoethyl-bromide **2a** was prepared *via* a ring opening reaction of thiocyclopropane with benzyl bromide as described previously [23] and compound **2b** was synthesized in an analogous procedure from thiocyclobutane.

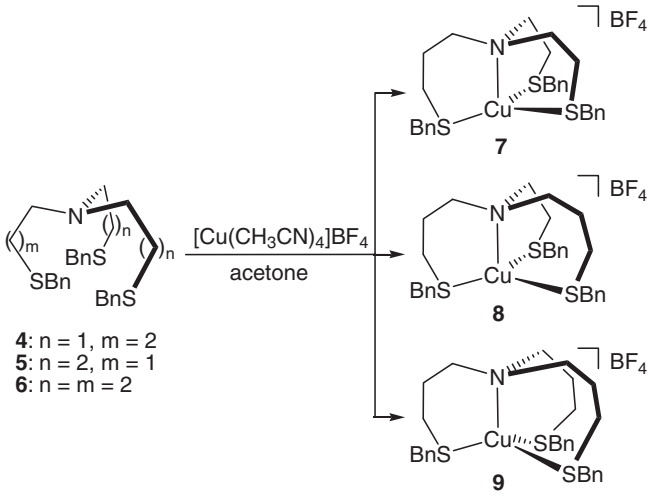


Scheme 1. Synthesis of the symmetric (**3** and **6**) and the asymmetric (**4** and **5**) tripodal ligands.

The tripodal ligands **3**–**6** were obtained by reaction of the alkyl bromides **2a** and **2b**, respectively with the ω-benzylmercaptoalkylamines **1a**–**c** under basic conditions in boiling acetonitrile. Compounds **3** and **4** were assembled from **1c** (two ethylene spacers) and one equivalent of the appropriate bromide **2a** (ethylene spacer) or **2b** (propylene spacer). For the synthesis of **5** and **6** one equivalent of the appropriate ω-benzylmercaptoalkylamine **1a** or **1b** was reacted with two equivalents of an alkylbromide of type **2**. All four ligands have been obtained in good yields (87–93%). Compounds **4** and **5** are the first examples for N-centered tripodal ligands featuring three sulfur donor functions linked to the central nitrogen atom by spacers of different lengths (two ethylene and one propylene spacers for **4**, one ethylene and two propylene spacers for **5**).

Ligands **4**–**6** were reacted with copper(I)tetrakisacetonitrile tetrafluoroborate in acetone to yield complexes **7**–**9** in yields of 88–92% (Scheme 2). The colorless complexes are stable towards aerial oxidation most likely due to the steric shielding of the metal centers by the bulky benzyl substituents.

Crystals of **7** and **9** suitable for X-ray diffraction analyses were obtained at ambient temperature by slow diffusion of diethyl ether into a solution of the complexes in acetone. The complex cation in **7** (Fig. 2) contains a Cu^{I} ion tetracoordinated by the four donor functions of one ligand **4**. The coordination geometry in the cation of **7** is best described as trigonal–pyramidal with the tertiary amine donor in the apical position. The metric parameters in this cation are best compared to those of the copper(I) complex cation bearing the symmetrical ligand **3** in $[Cu(\mathbf{3})]PF_6$ reported previously by Kaden et al. [17]. Cation $[Cu(\mathbf{3})]^+$ features three identical ethylene spacers between the amine and thioether donors which leads to three almost equidistant Cu–S bond lengths. Ligand **4** in the cation of **7**, on the other hand, possesses one propylene and two ethylene spacers between the donor groups leading to a significantly shorter Cu–S1 bond lengths (2.2305(7) Å) for the propylene ligand arm in comparison to the ethylene ligand arms (Cu–S2 2.2709(7) Å, Cu–S3 2.2825(7) Å). Possibly due to the presence of one propylene ligand arm, the Cu–N1 bond distance in **7** (2.119(2) Å) is also shorter than the corresponding value in $[Cu(\mathbf{3})]^+$ (2.188(2) Å). The N1–Cu–S bond angles in **7** are also influenced by the unsymmetrical lengths of the ligands arms. The values involving ethylene spacers (N1–Cu–S2 92.06(9)°, N1–Cu–S3 91.63(7)°) are similar to those in $[Cu(\mathbf{3})]^+$ but significantly smaller than the value found for the propylene ligand arm (N1–Cu–S1 105.15(7)°).



Scheme 2. Synthesis of the copper(I) complexes **7**–**9**.

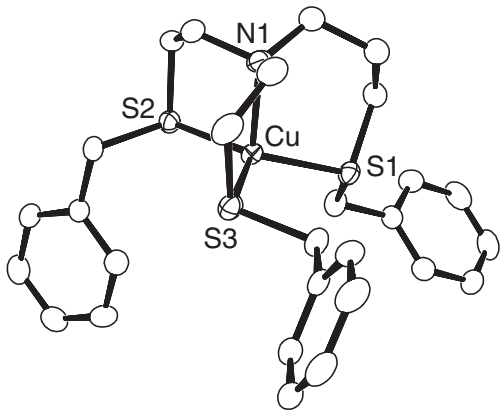


Fig. 2. Molecular structure of the complex cation in **7** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu–N1 2.119(2), Cu–S1 2.2305(7), Cu–S2 2.2709(7), Cu–S3 2.2825(7); N1–Cu–S1 105.15(7), N1–Cu–S2 92.09(6), N1–Cu–S3 91.63(7), S1–Cu–S2 124.02(3), S1–Cu–S3 113.21(3), S2–Cu–S3 119.15(3).

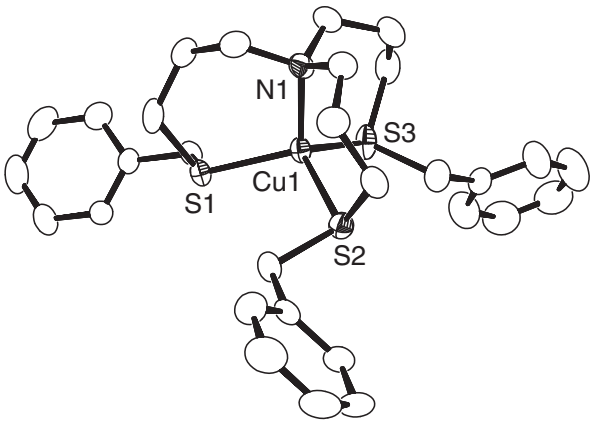


Fig. 3. Molecular structure of one of the four complex cations of **9** in the asymmetric unit (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–N1 2.086(4), Cu1–S1 2.2742(11), Cu1–S2 2.2907(12), Cu1–S3 2.2733(12); N1–Cu1–S1 108.64(10), N1–Cu1–S2 108.34(10), N1–Cu1–S3 107.63(11), S1–Cu1–S2 108.61(4), S1–Cu1–S3 116.62(4), S2–Cu1–S3 106.74(4).

Compound **9** crystallizes in the cubic space group $P2_13$. The asymmetric unit contains two formula units which reside on general positions. Each asymmetric unit contains two additional 1/3 formula units which reside on a threefold rotation axis. Thus the asymmetric unit contains 2 and 2/3 formula units. The metric parameters of complex cations on general and on special positions differ only marginally and slight differences are probably caused by packing effects.

One complex cation of **9** which resides on a general position is depicted in Fig. 3. The coordination environment around the copper atom bearing the symmetrical ligand **6** is now best described as tetrahedral with all three N1–Cu–S angles being of similar magnitude (range 108.64(10)–107.63(11)°) and significantly larger than 90°. The Cu–S bond distances are almost equally long falling in the narrow range of 2.2733(12)–2.2907(12) Å. A similar situation has been observed for complex cation $[Cu(\mathbf{3})]^+$ bearing the symmetrically (ethylene bridged) ligand **3**.

3. Conclusions

The geometry of the tetracoordinated copper(I) complexes bearing the tripodal trithioether ligands **3**–**6** has been shown to be strongly dependent on the length of the alkyl chains between the central nitrogen atom and the terminal thioether donor functions. A similar situation has been observed previously for copper(II) complexes bearing tripodal tetramines derived from tris(2-aminoethyl)amine [18] where the variation of the lengths of the spacers between the central and terminal nitrogen atoms allowed for a change of the coordination geometry from trigonal–bipyramidal to tetragonal–pyramidal. A related change of the coordination environment of copper(I) complexes with S_3N ligands from trigonal–pyramidal to tetrahedral has been demonstrated for complexes **7**–**9**.

4. Experimental

4.1. Materials and methods

All manipulations were carried out under argon using Schlenk or glovebox techniques. 2-Benzylmercaptoethylbromide (**2a**) was synthesized following a published procedure [23]. Solvents were dried by standard methods and freshly distilled prior to use. Elemental analyses were performed with a Vario EL III Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, University of Münster.

4.2. Synthesis of 3-benzylmercaptopropylbromide (*2b*)

A sample of benzylbromide (25.0 g, 338 mmol) was added to thietane (40.1 mL, 338 mmol) and the reaction mixture was heated to 50 °C for 16 h. Compound **2b** was isolated from the raw product by distillation (94 °C, 0.05 mbar). Yield: 72.54 g (296 mmol, 89%) of a colorless liquid. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 7.34 (m, 5H, Ar-H), 3.74 (s, 2H, SCH_2Ph), 3.50 (t, 2H, $BrCH_2$), 2.56 (t, 2H, SCH_2), 2.08 (quint, 2H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 138.0 (Ar-C_{ipso}), 128.6, 128.4, 126.6 (Ar-C), 36.1 (SCH_2Ph), 32.1 ($BrCH_2$), 31.8 (SCH_2), 29.3 ($CH_2CH_2CH_2$).

4.3. General method for the synthesis of ω-benzylmercaptoalkylamines *1a–c*

Benzylthiol (23.7 mL, 200 mmol) and the appropriate amount of ω-chloroalkylamine hydrochloride were added subsequently to 200 mL of a 2 M solution of sodium ethoxide in ethanol. The mixture was heated under reflux for 4 h. Subsequently, the solvent was removed *in vacuo*. The residue was dissolved in 30 mL of water and extracted twice with dichloromethane (50 mL each). The combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The compounds were purified by distillation.

4.3.1. Synthesis of 2-benzylmercaptoethylamine (*1a*)

Compound **1a** was synthesized from 2-chloroethylamine hydrochloride (23.2 g, 200 mmol). Yield: 32.06 g (199 mmol, 96%) of a colorless liquid (bp 94 °C at 0.03 mbar). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 7.25 (m, 5H, Ar-H), 3.65 (s, 2H, SCH_2Ph), 2.76 (t, 2H, SCH_2), 2.43 (t, 2H, NCH_2), 1.34 (NH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 138.0 (Ar-C_{ipso}), 129.7, 128.9, 127.4 (Ar-C), 43.7 (SCH_2Ph), 36.4 (SCH_2), 36.1 (NCH_2). MALDI-MS (TOF, positive ions, *m/z*): 168 $[M+H]^+$. *Anal.* Calc. for $C_9H_{11}BrS$ (167.27): C, 64.62; H, 7.83; N, 8.37. Found: C, 64.66; H, 7.92; N, 13.78%.

4.3.2. Synthesis of 3-benzylmercaptopropylamine (*1b*)

Compound **1b** was synthesized from 3-chloropropylamine hydrochloride (26.00 g, 200 mmol) as described for **1a**. Yield: 24.62 g (135.8 mmol, 68%) of a colorless liquid (bp 98 °C at 0.07 mbar). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 7.28 (m, 5H, Ar-H),

3.66 (s, 2H, SCH_2Ph), 2.70 (t, 2H, SCH_2), 2.45 (t, 2H, NCH_2), 1.64 (quint, 2H, $CH_2CH_2CH_2$), 1.13 (NH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 138.0 (Ar-C_{ipso}), 129.7, 128.9, 127.4 (Ar-C), 43.7 (SCH_2Ph), 36.4 (SCH_2), 36.1 (NCH_2), 29.5 $CH_2CH_2CH_2$.

*4.3.3. Synthesis of N,N-bis(2-benzylmercaptoethyl)amine (**1c**)*

The product was synthesized from *N,N*-bis(2-chloropropyl)amine hydrochloride (17.85 g, 100 mmol). Yield: 26.95 g, (84.9 mmol, 85%) of a colorless oil (bp 180 °C at 0.07 mbar). ^1H NMR (200.1 MHz, $CDCl_3$): δ 7.28 (m, 10H, Ar-H) 3.66 (s, 4H, SCH_2Ph), 2.70 (t, 4H, SCH_2), 2.45 (t, 4H, NCH_2), 1.13 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 138.0 (Ar-C_{ipso}), 129.7, 128.9, 127.4 (Ar-C), 43.7 (SCH_2Ph), 36.4 (SCH_2), 36.1 (NCH_2) ppm. MALDI-MS (TOF, positive ions, *m/z*): 318 $[M+H]^+$. *Anal.* Calc. for $C_{18}H_{23}NS_2$ (317.52): C, 68.09; H, 7.30; N, 4.41. Found: C, 67.01; H, 7.32; N 4.46%.

*4.4. General procedure for the synthesis of ligands **3**–**6***

A sample of the ω-benzylmercaptoalkylamine was dissolved in 150 mL of acetonitrile and the appropriate amount of ω-benzylmercaptoalkylbromide and potassium carbonate (40 g, 240 mmol for coupling to the primary amines **1a** and **1b**, 20 g, 120 mmol for coupling to the secondary amine **1c**) were added. The reaction mixture was heated under reflux for 16 h and after removal of the solvent *in vacuo* the ligands were purified by column chromatography (aluminum oxide, THF/*n*-hexane 1:1).

*4.4.1. Synthesis of N,N,N-tris(2-benzylmercaptoethyl)amine (**3**)*

The published procedure for the preparation of **3** [17] was altered to avoid the highly toxic and carcinogenic starting material *N,N,N*-tris(2-chloroethyl)amine ("N-Lost"). Ligand **3** was synthesized from *N,N*-bis(2-benzylmercaptoethyl)amine **1c** (4.92 g, 15.5 mmol) and 2-benzylmercaptoethylbromide **2a** (3.58 g, 15.5 mmol). Yield: 6.92 g (14.8 mmol, 95%) of a colorless oil. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.10 (m, 15H, Ar-H), 3.72 (s, 6H, SCH_2Ph), 2.55 (t, 6H, NCH_2), 2.34 (t, 6H, SCH_2). $^{13}C\{H\}$ NMR ($CDCl_3$, 50.3 MHz): δ 139.0 (Ar-C_{ipso}), 129.9, 128.8, 127.5 (Ar-C), 51.1 (NCH_2), 39.2 (SCH_2Ph), 38.7 (SCH_2). MALDI-MS (TOF, positive ions, *m/z*): 468 $[M+H]^+$. *Anal.* Calc. for $C_{27}H_{33}NS_3$ (467.76): C, 69.33; H, 7.11; N, 2.99. Found: C, 69.20; H, 7.33; N 3.22%.

*4.4.2. Synthesis of N,N-bis(2-benzylmercaptoethyl)-N-(3-benzylmercaptopropyl)amine (**4**)*

Ligand **4** was synthesized from *N,N*-bis(2-benzylmercaptoethyl)amine **1c** (6.00 g, 18.9 mmol) and 3-benzylmercaptopropylbromide 2b (4.63 g, 18.9 mmol). Yield: 8.09 g (16.8 mmol, 89%) of a colorless oil. ^1H NMR (300.1 MHz, $CHCl_3$): δ 7.10 (m, 15H, Ar-C), 3.72 (s, 6H, SCH_2Ph), 2.55–2.34 (m, 12H, NCH_2 and SCH_2), 1.74 (quint, 2H, $CH_2CH_2CH_2$). $^{13}C\{H\}$ NMR (50.3 MHz, $CDCl_3$): δ 139.0 (Ar-C_{ipso}), 129.9, 126.6 (Ar-C), 55.5 (NCH_2CH_2S), 51.1 ($NCH_2CH_2CH_2S$), 38.7 (SCH_2Ph), 33.2 (SCH_2), 30.4 ($CH_2CH_2CH_2$). MALDI-MS (TOF, positive ions, *m/z*): 482 $[M+H]^+$. *Anal.* Calc. for $C_{28}H_{35}NS_3$ (481.79): C, 69.80; H, 7.32; N, 2.91. Found: C, 69.92; H, 7.22; N 2.78%.

*4.4.3. Synthesis of N-(2-benzylmercaptoethyl)-N,N-bis-(3-benzylmercaptopropyl)amine (**5**)*

Ligand **5** was synthesized from 2-benzylmercaptoethylamine **1a** (5.02 g, 30.0 mmol) and 3-benzylmercaptopropylbromide **2b** (14.71 g, 60.0 mmol). Yield: 13.89 g (28.0 mmol, 93%) of a colorless oil. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.10 (m, 15H, Ar-C), 3.72 (s, 6H, SCH_2Ph), 2.55–2.34 (m, 12H, NCH_2 and SCH_2), 1.74 (quint, 4H, $CH_2CH_2CH_2$). $^{13}C\{H\}$ NMR (50.3 MHz, $CDCl_3$): δ 139.0 (Ar-C_{ipso}), 129.9, 126.6 (Ar-C), 55.5 (NCH_2CH_2S), 51.1 ($NCH_2CH_2CH_2S$), 38.7 (SCH_2Ph), 33.2 (SCH_2), 30.4 ($CH_2CH_2CH_2$). MALDI-MS (TOF, positive ions, *m/z*): 496 $[M+H]^+$. *Anal.* Calc. for $C_{29}H_{37}NS_3$ (495.81): C, 70.25; H, 7.52; N, 2.83. Found: C, 70.11; H, 7.68; N, 2.64%.

*4.4.4. Synthesis of N,N,N-tris-(3-benzylmercaptopropyl)amine (**6**)*

Ligand **6** was synthesized from 3-benzylmercaptopropylamine **1b** (5.44 g, 30.0 mmol) and 3-benzylmercaptopropylbromide **2b** (14.71 g, 60.0 mmol). Yield: 13.32 g (26.1 mmol, 87%) of a colorless oil. ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.10 (m, 15H, Ar-C), 3.72 (s, 6H, SCH_2Ph), 2.55–2.34 (m, 12H, NCH_2 and SCH_2), 1.74 (quint, 6H, $CH_2CH_2CH_2$). $^{13}C\{H\}$ NMR (50.3 Hz, $CDCl_3$): δ 139.0 (Ar-C_{ipso}), 129.9, 126.6 (Ar-C), 51.1 (NCH_2), 38.7 (SCH_2Ph), 33.2 (SCH_2), 30.4 ($CH_2CH_2CH_2$). MALDI-MS (TOF, positive ions, *m/z*): 510 $[M+H]^+$. *Anal.* Calc. for $C_{30}H_{39}NS_3$ (509.84): C, 70.67; H, 7.71; N, 2.75. Found: C, 70.52; H, 7.62; N 2.68%.

*4.5. General procedure for the synthesis of the copper(I) complexes **7**–**9***

Copper(I)tetrakisacetonitrile tetrafluoroborate (79 mg, 0.25 mmol) was dissolved in 15 mL of acetone. To this solution was added a solution of one of the tripidal ligands **4**–**6** (0.25 mmol) in 10 mL of acetone. The reaction mixture was stirred for 30 min at ambient temperature. Subsequently, diethyl ether (50 mL) was added dropwise and the precipitated colorless solid was collected by filtration and dried in vacuo.

*4.5.1. Synthesis of [Cu(**4**)](BF$_4$) (**7**)*

The complex was prepared from ligand **4** (120 mg, 0.25 mmol). Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of the complex in acetone. Yield: 147 mg (0.23 mmol, 92%) of a colorless solid. ^1H NMR (300.1 MHz, [D_6]acetone): δ 7.48–7.32 (m, 15H, Ar-H), 4.16–4.08 (m, 6H, SCH_2Ph), 3.14–2.80 (m, 12H, NCH_2 and SCH_2), 2.06(quint, 2H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_6]acetone: δ 136.8 (Ar-C_{ipso}), 129.5, 126.8 (Ar-C) 59.7 ($NCH_2CH_2CH_2SCH_2Ph$), 52.4 ($NCH_2CH_2SCH_2Ph$), 38.8 (NCH_2CH_2S), 38.2 ($NCH_2CH_2CH_2S$), 33.5 (NCH_2CH_2S), 33.4 ($NCH_2CH_2CH_2S$), 24.3 ($NCH_2CH_2CH_2S$). MALDI-MS (TOF, positive ions, *m/z*): 632 $[M+H]^+$. *Anal.* Calc. for $C_{28}H_{35}NBCuF_4S_3$ (632.15): C, 53.20; H, 5.58; N, 2.22. Found: C, 53.72; H, 5.26; N, 2.48%.

*4.5.2. Synthesis of [Cu(**5**)](BF$_4$) (**8**)*

The complex was prepared from ligand **5** (124 mg, 0.25 mmol). Yield: 140 mg (0.22 mmol, 88%) of a colorless solid. ^1H NMR (300.1 MHz, [D_6]acetone): δ 7.51–7.32 (m, 15H, Ar-H), 4.13–4.00 (m, 6H, SCH_2Ph), 3.09–2.82 (m, 12H, NCH_2 and SCH_2), 2.04 (quint, 4H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_6]: δ 136.2 (Ar-C_{ipso}), 130.1, 126.4 (Ar-C), 59.5 ($NCH_2CH_2CH_2SCH_2Ph$), 54.7 ($NCH_2CH_2SCH_2Ph$), 40.4 (NCH_2CH_2S), 39.4 ($NCH_2CH_2CH_2S$), 33.3 (NCH_2CH_2S), 32.4 ($NCH_2CH_2CH_2S$), 23.7 ($NCH_2CH_2CH_2S$). MALDI-MS (TOF, positive ions, *m/z*): 646 $[M+H]^+$. *Anal.* Calc. for $C_{29}H_{37}NCuBF_4S_3$ (646.17): C, 53.90; H, 5.77; N 2.17. Found: C, 53.98; H, 5.22; N, 2.28%.

*4.5.3. Synthesis of [Cu(**6**)](BF$_4$) (**9**)*

The complex was prepared from ligand **6** (127 mg, 0.25 mmol). Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of the complex in acetone. Yield: 148 mg (0.22 mmol, 88%) of a colorless solid. ^1H NMR (300.1 MHz, [D_6]acetone): δ 7.51–7.32 (m, 15H, Ar-H), 4.13–4.00 (m, 6H, SCH_2Ph), 3.09–2.82 (m, 12H, NCH_2 and SCH_2), 2.04 (quint, 6H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_6]acetone): δ 136.8 (Ar-C_{ipso}), 129.5, 128.2 (Ar-C), 61.0 (SCH_2Ph), 39.6 (NCH_2), 33.0 (SCH_2), 23.1 ($CH_2CH_2CH_2$). MALDI-MS (TOF, positive ions, *m/z*): 660 $[M+H]^+$. *Anal.* Calc. for $C_{30}H_{39}NCuBF_4S_3$ (660.20): C, 54.88; H, 5.95; N, 2.12. Found: C, 54.92; H, 5.42; N, 2.18%.

4.6. X-ray diffraction studies

X-ray diffraction data were collected at $T = 153(2)$ K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART [24] program package. Structures were solved with the SHELXS-97 [25] package using the heavy-atom method and were refined with SHELXL-97 [26] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

4.6.1. Crystal data for [Cu(**4**)]BF_4 (**7**)

$C_{28}H_{35}NBCuF_4S_3$, $M = 632.15$, colorless prism, monoclinic, space group $P2_1/c$, $a = 11.078(2)$, $b = 16.161(2)$, $c = 16.622(2)$ Å, $\beta = 107.557(3)^\circ$, $V = 2837.2(7)$ Å^3, $Z = 4$, $\rho_{calc} = 1.480$ g cm^{-3}, $\mu = 1.037$ mm^{-1}, 27290 measured intensities, 6517 unique intensities ($R_{int} = 0.0502$), 5325 observed intensities [$I \geqslant 2\sigma(I)$], 379 parameters, $R = 0.0459$, wR(all) = 0.1072, GOF = 1.032, largest peak/hole 0.781/−0.292 (e Å^{-3}).

4.6.2. Crystal Data for [Cu(**6**)]BF_4 (**9**)

$C_{30}H_{39}NBCuF_4S_3$, $M = 660.20$, colorless prism, cubic, space group $P2_13$, $a = 29.5335(10$ Å, $V = 25759.9(15)$ Å^3, $Z = 32$, $\rho_{calc} = 1.362$ g cm^{-3}, $\mu = 0.916$ mm^{-1}, 212,388 measured intensities, 15,177 unique intensities ($R_{int} = 0.0977$), 12721 observed intensities [$I \geqslant 2\sigma(I)$], 961 parameters, $R = 0.0393$, wR(all) = 0.1083, GOF = 1.057, largest peak/hole 1.724/−0.298 (e− Å^{-3}). The asymmetric unit contains two formula units on general positions in addition to $2 \times 1/3$ formula units where the copper and boron atoms reside on special positions on a threefold axis.

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