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Oxazolone copper(I) complexes inspired by the methanobactin active site

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ABSTRACT

Two oxazolone-derived potential ligands with enethioether substituents have been synthesized that differ by the terminal thioether moiety (S-Et in L^1, S–C_6H_4(OMe)-2 in L^2). Both L^1 and L^2 behave as bidentate {NS} chelate ligands to form stable complexes with copper(I) triflate that crystallize as dimeric complexes $[L_2Cu_2(OTf)_2]$ (**4** and **5**) featuring a central $\{Cu_2S_2\}$ diamond core with distinctly different Cu–S bonds. L^1 as well as **4** and **5** have been characterized by single crystal X-ray diffraction. NMR spectroscopy including ^{1}H and ^{19}F DOSY experiments reveals that **4** and **5** dissociate into monomeric species [LCu(OTf)] (**4′** and **5′**) in $CDCl_3$ solutions. **4′** and **5′** retain the {NS} binding motif of the oxazolone-derived ligands, but are in slow equilibrium with their {OS} isomers **4″** and **5″** that result from *E*/*Z* isomerization of the exocyclic enethioether double bond.

1. Introduction

Mixed sulfur/nitrogen ligation is often encountered in biological copper sites [1,2]. Prominent examples are the blue copper proteins, the binuclear Cu_A center, or the Cu_Z cluster in nitrous oxide reductase. A new copper binding motif has recently been discovered in methanobactins (mb) [3–5], which are small peptide-derived molecules that appear to be involved in various biological processes in methanotrophic bacteria [6]. Methanobactins bind copper(II) with subnanomolar affinity and reduce it to copper(I) [7,8]. They use two oxazolone rings, each with an appended enethiol group, to host the copper(I) ion in a distorted tetrahedral $\{N_2S_2\}$ coordination environment (Chart 1).

Many copper complexes with thioether-based ligands providing an $\{N_2S_2\}$ donor set have previously been investigated [9,10], mostly with the aim of emulating certain features of the copper binding sites of blue copper proteins. Such complexes exhibit the expected high copper(II/I) redox potentials, as long as ligand flexibility is sufficient for adapting to the stereoelectronic requirements of copper(I). On the other hand, little is known about oxazolone copper chemistry [11], and complexes of chelating oxazolone-derived ligands that bear an appended S-donor are virtually unknown. Here we report two potentially bidentate oxazolone derivatives with an appended enethioether substituent, reminiscent of the chelating {NS} motif of methanobactin, and their copper(I) complexes.

2. Experimental

Oxazolone **3** was prepared as described in the literature [12,13]. All other chemicals were purchased from commercial sources and used as received. Solvents were dried by standard procedures before use. NMR spectra were recorded on either a Bruker Avance III 300 MHz, a Bruker Avance III 400 MHz or a Bruker DRX 500 MHz spectrometer. Chemical shifts were calibrated to the residual proton and carbon signal of the solvent ($CDCl_3$: $\delta_H = 7.27$, $\delta_C = 77.2$ ppm) and to external CH_3NO_2 and $CFCl_3$ for ^{15}N and ^{19}F NMR, respectively. ESI mass spectra were recorded with an Applied Biosystems API 2000 and a BRUKER (HCT ultra). IR spectra from KBr pellets were recorded on a Digilab Excalibur Series FTS 3000 spectrometer. UV/Vis spectra were collected with a Varian Cary 5000. Elemental analyses were performed by the analytical laboratory of the Institute of Inorganic Chemistry at Georg-August-University using an Elementar Vario EL III instrument.

2.1. Synthesis of L^1

L^1 was prepared following the method described in literature [14], starting from 3.00 g (14.49 mmol) of **3**. Yield: 2.23 g (9.57 mmol, 66%). Pale yellow single crystals of the *Z*-isomer suitable for X-ray crystallography were obtained by slow diffusion of

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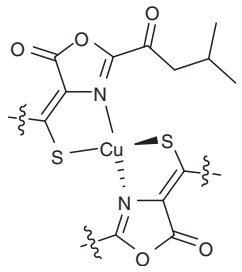


Chart 1. Copper-binding site of methanobactin.

Et_2O into a MeCN solution of the product. After 5 days at 60 °C both isomers could be observed in NMR experiments, ratio of *E*/*Z* 1:10. M.p. 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *Z*-isomer: δ 1.48 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, C*H*$_3$), 3.12 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, C*H*$_2$), 7.45–7.51 (m, 2H, C*H*^{meta}), 7.52 (s, 1H, C*H*^{vinyl}), 7.54–7.60 (m, 1H, C*H*^{para}), 8.06–8.08 (m, 2H, C*H*^{ortho}); *E*-isomer: δ 1.47 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, C*H*$_3$), 3.01 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, C*H*$_2$), 7.45–7.51 (m, 2H, C*H*^{meta}), 7.54–7.60 (m, 1H, C*H*^{para}), 7.71 (s, 1H, C*H*^{vinyl}), 8.00–8.03 (m, 2H, C*H*^{ortho}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7 (*C*H$_3$), 29.3 (*C*H$_2$), 125.9 (*C*=CH), 128.0 (*C*^{ortho}), 129.0 (*C*^{meta}), 130.9 (*C*^{ipso}), 132.9 (*C*^{para}), 139.7 (C=*C*H), 161.4 (*C*-Ph), 164.3 (*C*=O) ppm. ^{15}N NMR (40 MHz, $CDCl_3$): δ -145.0 ppm. MS (ESI): *m*/*z* (%) = 272 (18) $[M+K]^+$, 256 (24) $[M+Na]^+$, 234 (100) $[M+H]^+$. IR (KBr): $\tilde{\nu}$ = 3026 (m), 2966 (w), 2858 (w), 1799 (m), 1782 (s), 1638 (s), 1550 (m), 1447 (m), 1327 (m), 1265 (m), 1164 (s), 992 (m), 859 (vs), 840 (s), 804 (m), 692 (s), 608 (w) cm^{-1}. UV/Vis (DCM): λ [nm] (ε_{rel}/L mol^{-1} cm^{-1}) = 243 (0.11), 263 (0.28), 359 (0.71), 376 (0.62). Elemental *Anal.* Calc. for $C_{12}H_{11}NO_2S$ (233.05 g/mol): C, 61.78; H, 4.75; N, 6.00; S, 13.74. Found: C, 61.52; H, 4.74; N, 5.95; S, 13.71%.

2.2. Synthesis of L^2

L^2 was prepared in close analogy to a method described in literature [14], starting from 3.00 g (14.49 mmol) of **3**. To a solution of **3** and 2-methoxybenzenethiol (1.76 mL, 14.49 mmol) in CH_2Cl_2 (120 mL) was added triethylamine (2.01 mL, 14.49 mmol). The reaction was stirred for 1.5 h. The organic layer was washed with aqueous HCl (10%, 120 mL) and water (120 mL) and dried over Na_2SO_4. The solvent was removed and the product was recrystallized from CH_2Cl_2/Et_2O. Yield: 3.75 g (12.06 mmol, 83%). M.p. 155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H, OC*H*$_3$), 6.99 (dd, $^3J_{H,H}$ = 1.6, 7.6 Hz, 1H, C*H*^{5}), 7.05 (dd, $^3J_{H,H}$ = 1.1, 7.9 Hz, 1H, C*H*^{6}), 7.42 (dt, $^3J_{H,H}$ = 1.6, 7.9 Hz, 1H, C*H*^{3}), 7.47–7.62 (m, 4H, C*H*^{4}, C*H*^{meta}, C*H*^{para}), 7.66 (s, 1H, C*H*^{vinyl}), 8.09–8.13 (m, 2H, C*H*^{ortho}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.1 (O*C*H$_3$), 111.6 (*C*^{5}), 119.9 (*C*^{1}), 121.5 (*C*^{6}), 125.7 (*C*=CH), 128.2 (*C*^{ortho}), 128.9 (*C*^{meta}), 130.6 (*C*^{ipso}), 131.3 (*C*^{para}), 133.0 (*C*^{3}), 133.1 (*C*^{4}), 140.0 (C=*C*H), 158.2 (*C*^{2}), 161.6 (*C*-Ph), 164.3 (*C*=O) ppm. MS (ESI): *m*/*z* (%) = 645 (39) $[M_2+Na]^+$, 350 (17) $[M+K]^+$, 334 (98) $[M+Na]^+$, 312 (100) $[M+H]^+$. IR (KBr): $\tilde{\nu}$ = 3055 (w), 3015 (w), 1770 (vs), 1629 (s), 1581 (m), 1477 (m), 1453 (m), 1325 (m), 1294 (m), 1246 (s), 1156 (m), 1070 (m), 1020 (m), 992 (m), 860 (s), 836 (s), 754 (s), 695 (s), 612 (w) cm^{-1}. UV/Vis (DCM): λ [nm] (ε_{rel}/L mol^{-1} cm^{-1}) = 262 (0.20), 281 (0.14), 363 (0.60), 376 (0.65). Elemental *Anal.* Calc. for $C_{17}H_{13}NO_3S$ (311.06 g/mol): C, 65.58; H, 4.21; N, 4.50; S, 10.30. Found: C, 64.38; H, 4.10; N, 4.41; S, 10.39%.

2.3. Synthesis of $[L^1Cu(SO_3CF_3)]_2$ (**4**)

To a solution of ligand L^1 (58.1 mg, 0.25 mmol, 1.00 eq) in dried and deoxygenated benzene (5 mL) was added $CuSO_3CF_3 \cdot ½\ C_6H_6$ (63.0 mg, 0.25 mmol, 1.00 eq). The reaction was stirred for 3 h. After filtering off the insoluble material, the solvent was removed and the product was dried under reduced pressure to obtain an orange powder (88.2 mg, 0.10 mmol, 40%). Orange crystals for X-ray crystallography were obtained by slow diffusion of Et_2O in a benzene solution of the product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, C*H*$_3$), 3.29 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, C*H*$_2$), 7.66 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, C*H*^{meta}), 7.79 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, C*H*^{para}), 7.85 (s, 1H, C*H*^{vinyl}), 8.42 (d, $^3J_{H,H}$ = 7.4 Hz, 2H, C*H*^{ortho}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7 (*C*H$_3$), 32.2 (*C*H$_2$), 122.3 (*C*^{ipso}), 127.3 (*C*=CH), 129.3 (*C*^{ortho}), 130.1 (*C*^{meta}), 136.2 (*C*^{para}), 141.8 (C=*C*H), 158.6 (*C*=O), 165.8 (*C*-Ph) ppm. ^{15}N NMR (40 MHz, $CDCl_3$): δ −199.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −77.1 ppm. MS (ESI): *m*/*z* (%) = 743 (15) $[L_2Cu_2(SO_3CF_3)]^+$, 529 (100) $[L_2Cu]^+$, 296 (18) $[LCu]^+$. IR (KBr): $\tilde{\nu}$ = 3044 (w), 2982 (w), 2936 (w), 1803 (s), 1621 (s), 1555 (m), 1489 (m), 1450 (m), 1344 (s), 1308 (vs) 1268 (s), 1236 (vs), 1202 (s), 1173 (vs), 1117 (w), 1049 (w), 1021 (vs), 986 (m) 847 (m), 836 (m), 783 (w), 700 (s), 637 (s), 514 (m) cm^{-1}. UV/Vis (DCM): λ [nm] (ε_{rel}/L mol^{-1} cm^{-1}) = 243 (0.10), 263 (0.20), 359 (0.43), 376 (0.37). Elemental *Anal.* Calc. for $C_{26}H_{22}Cu_2F_6N_2O_{10}S_4$ (889.87 g/mol): C, 35.06; H, 2.49; N, 3.15; S, 14.37. Found: C, 35.15; H, 2.67; N, 3.24; S, 14.19%.

2.4. Synthesis of $[L^2Cu(SO_3CF_3)]_2$ (**5**)

Ligand L^2 (78 mg, 0.25 mmol, 1.00 eq) and $CuSO_3CF_3 \cdot ½\ C_6H_6$ (63.0 mg, 0.25 mmol, 1.00 eq) were dissolved in dried and deoxygenated benzene (5 mL). The reaction mixture was stirred for 3 h. After filtering off the insoluble material, the solvent was removed and the product was dried under reduced pressure to obtain a yellow powder (102 mg, 0.10 mmol, 39%). Yellow crystals for X-ray crystallography were obtained by slow diffusion of Et_2O in a solution of the product in toluene. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.94 (s, 3H, OC*H*$_3$), 6.96–7.11 (m, 2H, C*H*^{5}, C*H*^{6}), 7.41–7.56 (m, 2H, C*H*^{3}, C*H*^{4}), 7.68 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, C*H*^{meta}), 7.79 (t, $^3J_{H,H}$ = 7.4 Hz, C*H*^{para}), 7.88 (s, 1H, C*H*^{vinyl}), 8.46 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, C*H*^{ortho}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.5 (O*C*H$_3$), 112.3 (*C*^{5}), 116.6 (*C*^{1}), 122.0 (*C*^{6}), 122.4 (*C*^{ipso}), 126.9 (*C*=CH), 129.4 (*C*^{ortho}), 130.1 (*C*^{meta}), 132.8 (*C*^{3}), 133.8 (*C*^{4}), 136.2 (*C*^{para}), 142.5 (C=*C*H), 158.4 (*C*^{2}), 159.0 (*C*=O), 165.7 (*C*-Ph) ppm. MS (ESI): *m*/*z* (%) = 899 (5) $[L_2Cu_2(SO_3CF_3)]^+$, 685 (100) $[L_2Cu]^+$, 374 (37) $[LCu]^+$. IR (KBr): $\tilde{\nu}$ = 3062 (w), 2965 (w), 1847 (m), 1811 (m), 1629 (s), 1549 (m), 1479 (m), 1344 (m), 1306 (s), 1263 (m), 1232 (s), 1217 (vs), 1175 (s), 1098 (s), 1023 (vs), 859 (m), 839 (m), 798 (s), 765 (s), 699 (m), 630 (m), 462 (m) cm^{-1}. UV/Vis (DCM): λ [nm] (ε_{rel}/L mol^{-1} cm^{-1}) = 261 (0.31), 281 (0.25), 363 (0.63), 376 (0.67). Elemental *Anal.* Calc. for $C_{36}H_{26}Cu_2F_6N_2O_{12}S_4$ (1045.89 g/mol): C, 41.26; H, 2.50; N, 2.67; S, 12.24. Found: C, 41.81; H, 2.43; N, 2.66; S, 12.10%.

2.5. X-ray crystallography

X-ray data for L^1, **4**, and **5** were collected on a STOE IPDS II diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) by use of ω scans at −140 °C (Table 1). The structures were solved by direct methods and refined on F^2 using all reflections with SHELX-97 [15]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. Face-indexed absorption corrections were performed numerically with the program X-RED [16].

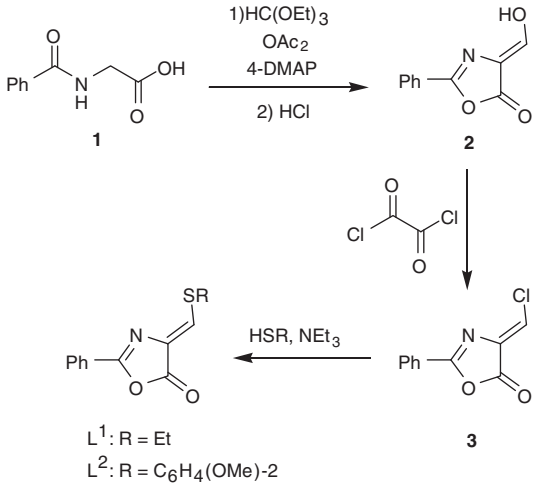
3. Results and discussion

3.1. Synthesis and characterization of ligands

The oxazolone-based ligands L^1 and L^2 (Scheme 1) were synthesized in three steps starting from commercially available hippuric

Table 1
Crystal data and refinement details for L^1, **4**, and **5**.

	L^1	**4**	**5**
Empirical formula	$C_{12}H_{11}NO_2S$	$C_{26}H_{22}Cu_2F_6N_2O_{10}S_4$	$C_{36}H_{26}Cu_2F_6N_2O_{12}S_4$
Formula weight	233.28	891.78	1047.91
Crystal size (mm^3)	0.50 × 0.09 × 0.07	0.50 × 0.41 × 0.19	0.32 × 0.30 × 0.27
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a (Å)	15.1194(7)	8.6228(5)	9.5809(4)
b (Å)	4.92240(10)	9.8383(7)	13.5532(5)
c (Å)	15.5644(8)	10.1432(7)	15.0458(7)
α (°)	90	105.164(5)	90
β (°)	105.488(4)	103.241(5)	94.067(3)
γ (°)	90	94.360(5)	90
V ($Å^3$)	1116.30(8)	799.94(9)	1948.81(14)
Z	4	1	2
ρ (g cm^{-3})	1.388	1.851	1.786
F(0 0 0)	488	448	1056
μ (mm^{-1})	0.273	1.684	1.402
T_{min}/T_{max}	0.7651/0.9173	0.4832/0.6135	0.5101/0.7419
θ Range (°)	1.67–26.71	2.15–26.76	2.02–26.74
hkl Range	±19, −6–5, ±19	±10, −12–10, ±12	±12, ±17, ±19
Measured reflections	13070	10572	25693
Unique reflections (R_{int})	2367 (0.0497)	3382 (0.0474)	4119 (0.0501)
Observed reflections ($I > 2\sigma(I)$)	2135	3117	3830
data/restraints/parameters	2367/0/146	3382/0/227	4119/0/281
Goodness-of-fit (F^2)	1.072	1.032	1.047
R_1, wR_2 ($I > 2\sigma(I)$)	0.0335, 0.0887	0.0313, 0.0806	0.0298, 0.0719
R_1, wR_2 (all data)	0.0380, 0.0910	0.0337, 0.0819	0.0325, 0.0732
Residual electron density (e $Å^{-3}$)	−0.267/0.325	−0.725/0.805	−1.009/1.132



Scheme 1. Synthesis of the oxazolone ligands L^1 and L^2 with appended enethioether group.

acid (**1**), in close analogy to procedures reported previously [12–14]. Reaction of key intermediate oxazolone **3** with two different thiols in the presence of triethylamine leads to L^1 and L^2 in 66% or 83% yield, respectively.

L^1 has already been mentioned in a previous report [17], and its constitution is now confirmed by X-ray crystallography; the new compound L^2 has been fully characterized by spectroscopic methods. Pale yellow crystals of L^1 were obtained by slow diffusion of Et_2O into a MeCN solution of the crude product. The molecular structure of L^1 along with selected atoms distances and angles is displayed in Fig. 1.

L^1 shows the expected heterocyclic ring structure and the anticipated disposition of the oxazolone-N and thioether-S atoms (*Z* configuration of the exocyclic double bond), which thus should be well suited for binding copper ions in a {NS}-chelating mode. All metrical parameters of L^1 are in the usual range. In the crystals

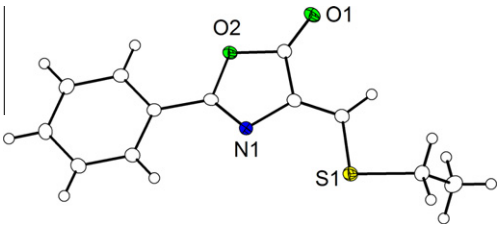


Fig. 1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of L^1. Selected bond lengths [Å] and angles [°]: S1–C10 1.7122(15), S1–C11 1.8107(16), N1–C1 1.2839(19), N1–C3 1.4011(18); C1–N1–C3 105.45(12), C10–S1–C11 100.86(7).

only the *Z*-isomer is found, which seems to be the preferred configuration of L^1. This is supported by NMR experiments: starting from crystalline material of the *Z*-isomer slow isomerization is observed in $CDCl_3$ solution, and after 5 days at 60 °C both isomers could be observed at an equilibrated ratio of *Z*/*E* 10:1.

3.2. Structural and spectroscopic characterization of copper(I) complexes

Copper complexes of the enethioether–oxazolone ligands L^1 and L^2 could be obtained by their reaction with $CuSO_3CF_3 \cdot \frac{1}{2}C_6H_6$ in dried and deoxygenated benzene; the products **4** and **5** were isolated in around 40% yield. Complex formation is evidenced by ESI-MS measurements, which show dominant signals for species $[L_2Cu]^+$ (at m/z = 529 for $[L^1{}_2Cu]^+$ and 685 for $[L^2{}_2Cu]^+$, respectively) as well as additional peaks characteristic for $[LCu]^+$ and $[L_2Cu_2(OTf)]^+$. The IR resonances usually assigned to the C=N stretch show only minor or even negligible shifts upon complexation (1638 cm^{-1} for L^1, 1622 cm^{-1} for **4**; 1629 cm^{-1} for L^2 and **5**).[1] In case of complex **4** orange crystals were obtained by slow diffusion

[1] These IR bands may also comprise components from the conjugated exocyclic C=C bond.

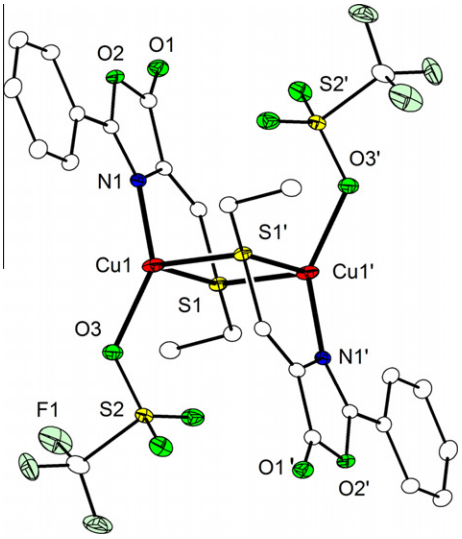


Fig. 2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1–N1 1.9681(16), Cu1–O3 1.9914(16), Cu1–S1′ 2.3720(6), Cu1–S1 2.5967(6), S1–Cu1′ 2.3720(6), Cu1···Cu1′ 3.2663(5); N1–Cu1–O3 140.47(7), N1–Cu1–S1′ 107.06(5), O3–Cu1–S1′ 111.97(5), N1–Cu1–S1 82.15(5), O3–Cu1–S1 98.22(5), S1–Cu1′–S1′ 97.937(19), Cu1–S1′–Cu1′ 82.063(18). Symmetry operation used to generate equivalent atoms: (′) $1-x$, $1-y$, $1-z$.

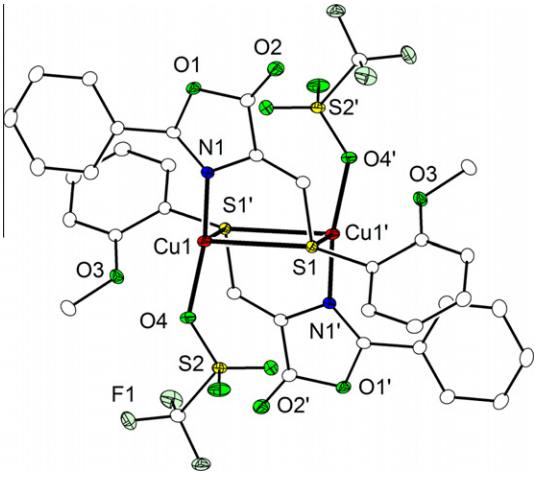


Fig. 3. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1–N1 1.9558(16), Cu1–O4 1.9738(14), Cu1–S1′ 2.3561(6), Cu1–S1 2.8398(5), Cu1···O3 3.0634(14), Cu1···Cu1′ 3.3874(4); N1–Cu1–O4 135.96(7), N1–Cu1–S1′ 111.55(5), O4–Cu1–S1′ 112.48(5), N1–Cu1–S1 79.91(5), O4–Cu1–S1 93.80(4), S1–Cu1′–S1′ 99.205(16), Cu1–S1′–Cu1′ 80.795(16). Symmetry operation used to generate equivalent atoms: (′) $1-x$, $1-y$, $1-z$.

of Et_2O into a benzene solution of the product. Complex **5** forms yellow crystals by slow diffusion of Et_2O into a toluene solution of the product. Molecular structures of **4** and **5** are shown in Figs. 2 and 3, respectively; selected atoms distances and angles are collected in Table 1.

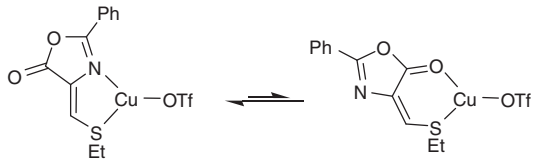
In contrast to expectation, the molecular structures of **4** and **5** in the solid state consist of two dimerized $[LCu(O_3SCF_3)]$ units instead of the anticipated species $[L_2Cu](O_3SCF_3)$, even if an excess of the ligand is used. Within the dimeric compounds, which feature crystallographically imposed inversion symmetry, the copper atoms are bridged by two sulfur atoms of the respective thioether side arms of the ligands. Cu1···Cu1′ separations in the resulting distorted $\{Cu_2S_2\}$ diamond cores are 3.27 Å (**4**) and 3.39 Å (**5**). Due to the inversion symmetry the $\{Cu_2S_2\}$ units are flat and the sum of the S–Cu–S and Cu–S–Cu angles is 360°. All copper atoms can be described as having strongly distorted tetrahedral coordination geometries in which two sulfur atoms and one nitrogen atom from the oxazolone ligands and one oxygen atom from the triflate counter ion coordinate the respective metal center. The two Cu–S distances are quite different, however, so that the coordination geometry around the copper atom may also be described as trigonal pyramidal with an additional weak Cu–S interaction. The difference between the two Cu-S bonds is particularly pronounced in complex **5** (2.37 versus 2.84 Å), which thus is reminiscent of the rather rare seesaw type arrangement of donor atoms. Although the additional oxygen-donor from the anisole group of the L^2 ligand in **5** is too far away from the metal center to be considered as a copper-oxygen interaction ($d_{Cu\cdots O}$ = 3.06 Å) it seems to prevent the formation of a more regular tetrahedral geometry.

Interestingly complexes **4** and **5** are only the second and third structurally characterized examples in which a thioether group (R–S–R′) acts as a bridging ligand in a $\{Cu_2S_2\}$ diamond core in the solid state. More common for RS-based ligands are compounds with carbothioyl (e.g. thiourea), thiolato- or thiocyanato-bridged copper atoms. The Cu–S bond lengths and Cu···Cu distances in **4** and **5** are comparable to those reported for the only other compound with a $\{Cu_2(\mu\text{-R–S–R}')_2\}$ core, namely *catena*-(bis(μ_3-1,3,5,7-tetramethyl-2,4,6,8-tetrathia-adamantane)-bis(μ_3-chloro)-bis(μ-chloro)-tetracopper) [18]. In the latter complex the Cu–S bonds show only slight differences (2.37 versus 2.40 Å) and the Cu···Cu′ distance is somewhat longer (3.47 Å), which probably originates from the otherwise different bonding situation.

The triflate counter ion acts as a co-ligand in **4** and **5**. The Cu–O bond distance of about 2 Å agrees with those reported for related copper(I) compounds containing triflate ions such as, e.g. $[(Ph_3P)_2Cu(NCMe)(O_3SCF_3)]$ (2.18 Å) [19] or η^2-*cyclo*-octene (2.05 Å) or bis(pyrazolyl)methane-based CO-complexes of copper(I) (~2.1 Å) [20]. The Cu–O distances, however, seem to depend on the type of other coordinating ligands. For example, in a series of copper(I) triflate complexes with 4,7-phenanthroline Cu–O distances ranging from 2.3 Å to 2.6 Å have been observed [21].

Solutions of **4** and **5** in $CDCl_3$ remain yellow even under aerobic conditions for several hours and only gradually turn green due to formation of Cu^{II} species, showing that the oxazolone-based {NS} ligands impart significantly stability to Cu^{I}. However, according to NMR experiments the speciation of the CU^{I} complexes in solution turned out to be more complicated than expected. All NMR experiments were carried out under anaerobic conditions. Dissolving crystals of **4** in $CDCl_3$ gives a clean ^1H NMR spectrum of a species **4′**, where differences in chemical shifts compared to the free ligand L^1 are most pronounced for the vinylic proton (7.52 ppm in the free ligand versus 7.85 ppm in **4′**) and the *ortho* protons of the phenyl group (8.08 ppm in the free ligand versus 8.42 ppm in **4′**). ^1H DOSY experiments gave diffusion coefficients (1.58×10^{-10} m^2 s^{-1} for the free ligand, 1.38×10^{-10} m^2 s^{-1} for **4′**) that are at variance with a dimeric structure **4** but in agreement with a monomeric $[L^1Cu(OTf)]$ composition with tightly bound OTf group (^{19}F DOSY: 2.09×10^{-10} m^2 s^{-1} for the free OTf^- anion, 1.38×10^{-10} m^2 s^{-1} for **4′**).[2] Furthermore, within several days at 60 °C a new set of signals appears. The new compound **4″** shows significant changes for the resonances of the vinylic proton (singlet at 8.66 ppm) and the phenyl *ortho* protons (doublet at 8.23 ppm), but an only slightly different diffusion coefficient (1.29×10^{-10} m^2 s^{-1}). Equilibrium is reached after ten days with a ratio **4′**:**4″** of around

[2] For spherical particles of a given mass density and solvent viscosity the diffusion coefficient *D* is proportional to the inverse cubic root of the mass of the particle. Data for **4′** and **4″** give effective radii of 3.9 ± 0.1 and 4.2 ± 0.1 Å, which is much smaller than the value of ~5.8 Å estimated for **4**.



4' 4''

Scheme 2. Slow equilibrium between monomeric species **4**′ and **4**″ in $CDCl_3$ solution.

1:0.25. Cooling the solution to 243 K leads to broadening of the signals for **4**″ (at 223 K also the signals of **4**′ become broader due to increased viscosity), but no change of the signal ratio is observed, presumably because of slow interconversion between **4**′ and **4**″. ^{15}N chemical shifts (−145 ppm in the free ligand, −199 ppm in **4**′) and three-bond coupling constants ($^3J_{HCO}$ = 3.5 Hz, $^3J_{HN}$ = 4.5 Hz in the free ligand and in **4**′, $^3J_{HCO}$ = 11 Hz for **4**″) finally revealed that **4**′ and **4**″ are isomers of the exocyclic C=C double bond such that the copper center in **4**″ is no longer coordinated by the nitrogen but rather the carbonyl oxygen atom (Scheme 2).

ESI mass spectrometry does not provide any further information, since characteristic peaks for $[L^1Cu]^+$, $[L^1{}_2Cu]^+$ and $[L^1{}_2Cu_2(OTf)]^+$ (which are observed for freshly prepared solutions of the crystalline material) are still the major signals detected, even after prolonged aging. A cyclic voltammetry experiment of a solution of **4** in CH_2Cl_2 shows only irreversible processes, both in anodic and cathodic scans. Furthermore, the electrochemical response is not stable over time, which is possibly due to the gradual formation of several species in solution.

Similar phenomena are observed in the NMR spectra of **5** (resonance for the vinylic proton at 7.88 ppm in $[L^2Cu(OTf)]$ (**5**′), 8.56 ppm in the isomer **5**″), though in this case **5**″ forms in only small amounts (<5%). All attempts to grow crystals from the aged solutions gave the parent compounds **4** and **5**, respectively. Interestingly, as evidenced by ^1H NMR spectroscopy, the original reaction mixtures obtained by mixing L^1 (or L^2) and $CuOTf{\cdot}\frac{1}{2}C_6H_6$ also contain several species prior to crystallization, but some of these species feature resonances that are still different from **4**′ and **4**″ (or **5**′ and **5**″).

4. Conclusions

Two oxazolone-derived ligands with appended thioether donors have been synthesized, emulating the oxazolone-based {NS} binding motif found in methanobactins. In contrast to expectation, however, these ligands do not form mononuclear tetrahedral complexes $[L_2Cu^I]^+$, but (at least in the crystalline material) dimeric species $[L_2Cu^I{}_2(OTf)_2]$ with bridging thioether–S and a central $\{Cu_2S_2\}$ diamond core. This rare structural motif features two distinctly different Cu–S interactions, and hence the coordination geometry of the metal ions deviates strongly from an ideal tetrahedron. In $CDCl_3$ solutions the monomeric complexes $[LCu^I(OTf)]$ with *Z* configuration of the exocyclic double bond and {NS} binding motif are in slow equilibrium with the *E* isomer featuring an {OS} binding motif. Synthetic efforts to link two oxazolone-based subunits into a chelating ligand scaffold that enforces the tetrahedral $\{N_2S_2\}$ coordination environment found in methanobactins are underway.

Acknowledgment

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Appendix A. Supplementary material

CCDC 813638, 813639 and 813640 contain the supplementary crystallographic data for compounds L^1, **4** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.070.

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