

A New Thioether-Based (N₂S₂)Copper(II/I) Complex Exhibiting a High Redox Potential

Stéphane Torelli,^[a] Catherine Belle,^{*[a]} Christian Philouze,^[a] Jean-Louis Pierre,^[a] Wassim Rammal,^[a] and Eric Saint-Aman^[b]

Keywords: S ligands / N ligands / Tripodal ligands / Copper / Redox chemistry

From the new ligand bis[2-(*tert*-butylthio)benzyl](2-pyridylmethyl)amine [N₂(StBu)₂], the corresponding complexes [Cu^I{N₂(StBu)₂}]CF₃SO₃ (**1**) and [Cu^{II}{N₂(StBu)₂}] (H₂O)-(CF₃SO₃)]CF₃SO₃ (**2**) were synthesized and characterized by X-ray crystallography. The Cu–S bonds are unusually shortened in **1** and elongated for the axial thioether in **2**.

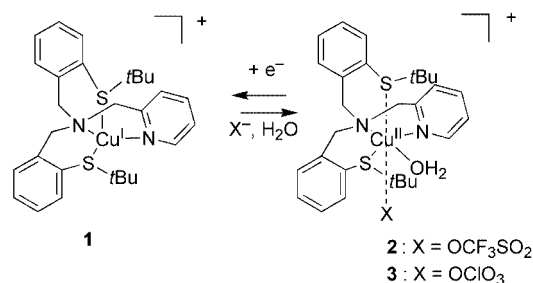
Redox studies show that **1** and **2** interconvert during the electron transfer with a high Cu^{II/I} potential of 0.79 V vs. SCE in CH₂Cl₂.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Blue (type 1) copper proteins involved in electron-transfer processes have, in their active site, a single Cu atom bound to two histidine nitrogen atoms and to one cysteine thiolate group.^[1,2] One additional axial thioether ligand (of methionine) is usually found in the coordination sphere of the copper ion (e.g. plastocyanin^[3] or azurin^[4,5]). The positive Cu^{II/I} redox potential, found in the range of 0.2–0.8 V vs. NHE,^[1] has long held the interest of bioinorganic chemists. Model complexes, described by Kitajima^[6] and more recently by Tolman,^[7] present structural and spectroscopic features close to those of the type 1 site, but significant differences in electrochemical properties are observed. Synthetic copper complexes, for which both Cu^{II} and Cu^I structures are available, could provide information about the structure/redox properties relationships.^[8–10]

We present herein the preparation and characterization, in both the Cu^I and Cu^{II} oxidation states, of a copper complex from a new tripodal N₂S₂ donor ligand (Scheme 1). The Cu^{II/I} redox potential is as high as that found in blue copper proteins. We focused our attention on the role of the thioether ligand; few structurally characterized Cu^{II} and Cu^I complexes involving a long axial Cu–S(thioether) bond have been studied electrochemically.^[11,12]



Scheme 1

Results and Discussion

By adding 1 equiv. of Cu(CF₃SO₃), Cu(CF₃SO₃)₂ or Cu(ClO₄)₂·6H₂O to the ligand N₂(StBu)₂ {bis[2-(*tert*-butylthio)benzyl](2-pyridylmethyl)amine}, the Cu^I (**1**) and Cu^{II} (**2** and **3**) complexes were obtained (Scheme 1).

The X-ray structures of the cationic units are depicted in Figures 1 (for **1** and **2**) and 2 (for **3**). Selected bond lengths and angles are reported in Table 1.

The structure of **1** (Figure 1, A) shows a copper(I) center in a distorted tetrahedral geometry. The Cu–S distances in **1** are similar [Cu–S1 = 2.2421(7) Å and Cu–S2 = 2.2492(7) Å], although shorter than the usual Cu^I–SR₂ bond of 2.33(9) Å.^[10]

The X-ray crystal structure of **2** reveals an elongated octahedral complex for the Cu^{II} redox state (Figure 1, B). Two nitrogen atoms, a thioether group and the water molecule are in the equatorial plane [a deviation of 0.007(3) Å from the mean plane for the copper atom is observed]. Two axial groups complete the octahedron: one StBu [Cu–S = 2.758(1) Å] and one oxygen atom of a CF₃SO₃ anion

^[a] LEDSS, Chimie Biomimétique, UMR CNRS 5616, Université J. Fourier, B. P. 53, 38041 Grenoble Cedex, France
Fax: (internat.) + 33-4/76514836
E-mail: Catherine.Belle@ujf-grenoble.fr

^[b] LEOPR, Laboratoire d'Electrochimie Organique et de Photochimie Redox, UMR CNRS 5630, Université J. Fourier, B. P. 53, 38041 Grenoble, France

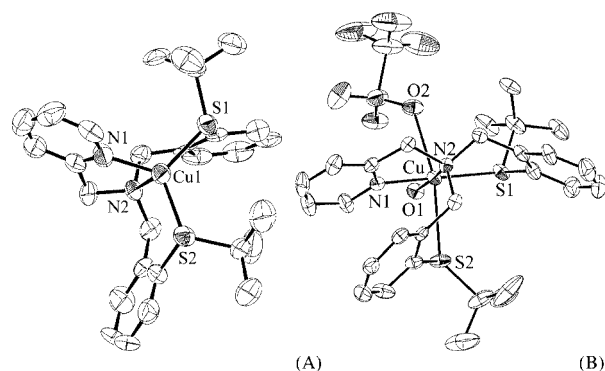


Figure 1. ORTEP view showing 50% displacement ellipsoids with partial atomic labeling for the cation (A) [Cu^I(N₂(S*t*Bu)₂)⁺ of **1** and (B) [Cu^{II}(N₂(S*t*Bu)₂)(H₂O)(CF₃SO₃)⁺ of **2**; hydrogen atoms have been omitted for clarity

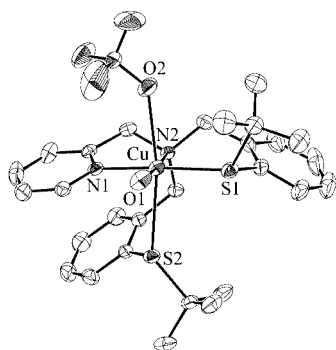


Figure 2. ORTEP view showing 50% displacement ellipsoid with partial atomic labeling for the cation [Cu^{II}(N₂(S*t*Bu)₂)(H₂O)(ClO₄)⁺ of **3**; hydrogen atoms have been omitted

[Cu–O = 2.457(3) Å] at semi-coordinating distances. Interestingly, **2** involves both an equatorial Cu–S(thioether) bond [2.354(1) Å], shorter than usual Cu^{II}–SR₂ bond lengths of 2.42 Å,^[10] and one much longer axial Cu–S(thioether) bond [2.758(1) Å].

Complex **3** was obtained in a similar manner to complex **2** using Cu(ClO₄)₂·6H₂O as the metallic salt. The coordination sphere of the copper center in **3**, as in **2**, is described by an octahedral geometry (see Figure 2) with an oxygen atom of the perchlorate anion coordinated in an axial position. The structural data for the molecular entity **3** is close to that of **2** (see Table 1), except that the axial distances are longer in **3** [Cu–S*t*Bu = 2.822(1) Å and Cu–O = 2.546(3) Å] than in **2**.

Such an octahedral coordination with unequal Cu^{II}–S(thioether) bond lengths is unusual and has only been reported in complexes of non-tripodal ligands.^[13,14]

The Cu–S distances in **2** (or **3**) can be compared to those found for the oxidized azurin,^[4,5] characterized by two axial groups, an S(thioether) atom and a carbonyl oxygen atom of Gly45 in weak interaction with a copper(II) ion (near 3.1 Å). The equatorially bound S(thiolate) ligand (Cys) is 2.12 Å apart from the copper ion.

In CH₂Cl₂, the UV/Vis spectrum of **2** is characterized by a band at 345 nm (ε ≈ 2250 M^{−1}·cm^{−1}) assigned to the S(thioether)→Cu^{II} LMCT band and a copper(II) d–d transition at 721 nm (ε ≈ 130 M^{−1}·cm^{−1}).^[15] In ethanolic solution, the LMCT band appears at 332 nm (ε ≈ 2180 M^{−1}·cm^{−1}) and the d–d band is shifted up to 685 nm (ε ≈ 70 M^{−1}·cm^{−1}). The changes observed in the UV/Vis spectra suggest the displacement of at least one ligand by a solvent molecule in the copper coordination sphere. In a frozen

Table 1. Selected bond lengths [Å] and angles [°] for **1**, **2** and **3**

1		2		3	
Cu–S1	2.2421(7)	Cu–S1	2.354(1)	Cu–S1	2.359(1)
Cu–S2	2.2492(7)	Cu–S2	2.758(1)	Cu–S2	2.822(1)
Cu–N1	2.023(2)	Cu–N1	2.007(4)	Cu–N1	1.987(4)
Cu–N2	2.123(2)	Cu–N2	2.037(4)	Cu–N2	2.026(3)
		Cu–O1	1.995(3)	Cu–O1	1.958(3)
		Cu–O2	2.457(3)	Cu–O2	2.546(3)
N1–Cu–N2	83.77(8)	N1–Cu–N2	82.7(1)	N1–Cu–N2	83.8(1)
N1–Cu–S1	118.16(7)	N1–Cu–S1	179.1(1)	N1–Cu–S1	176.87(8)
N1–Cu–S2	119.74(7)	N1–Cu–S2	85.9(1)	N1–Cu–S2	82.43(8)
N2–Cu–S1	104.13(6)	N1–Cu–O1	90.4(1)	N1–Cu–O1	91.4(1)
N2–Cu–S2	100.27(9)	N1–Cu–O2	82.6(1)	N1–Cu–O2	87.6(1)
S1–Cu–S2	118.71(2)	N2–Cu–O1	173.1(1)	N2–Cu–O1	174.8(1)
		N2–Cu–O2	90.8(1)	N2–Cu–O2	87.8(1)
		N2–Cu–S1	96.7(1)	N2–Cu–S1	95.6(1)
		N2–Cu–S2	92.9(1)	N2–Cu–S2	91.16(8)
		O1–Cu–O2	88.3(1)	O1–Cu–O2	90.0(1)
		O1–Cu–S1	90.23(9)	O1–Cu–S1	89.3(1)
		O1–Cu–S2	86.62(9)	O1–Cu–S2	90.27(9)
		O2–Cu–S1	98.06(9)	O2–Cu–S1	95.48(9)
		O2–Cu–S2	167.34(9)	O2–Cu–S2	169.99(9)
		S1–Cu–S2	93.55(4)	S1–Cu–S2	94.53(4)

solution of CH_2Cl_2 /toluene (1:1) at 100 K, **2** displays a typical axial EPR spectrum (Figure 3, A), in agreement with the X-ray structure, with $g_{\parallel} = 2.19$, $g_{\perp} = 2.04$, $A_{\parallel} = 181 \times 10^{-4} \text{ cm}^{-1}$. In EtOH/toluene (1:1), two sets of overlapping signals centered at roughly $g_{1\parallel} = 2.17$, $A_{1\parallel} = 176 \times 10^{-4} \text{ cm}^{-1}$ and $g_{2\parallel} = 2.29$, $A_{2\parallel} = 171 \times 10^{-4} \text{ cm}^{-1}$ are observed (Figure 3, B). These features indicate that solvent molecules are involved in the coordination sphere of the metal center, giving rise to the formation of a mixture of complexes.

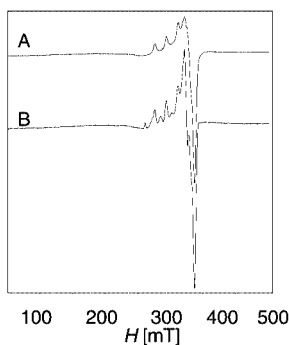


Figure 3. EPR spectrum at 100 K of **2**, at a microwave frequency of 9.419 GHz as a frozen solution, 3 mm in (A) CH_2Cl_2 /toluene (1:1, v/v); (B) EtOH/toluene (1:1, v/v)

Thus, the electrochemical behaviors of **1** and **2** have been examined in coordinating solvents (MeOH or EtOH) and in a noncoordinating solvent (CH_2Cl_2) by CV and RDE experiments. In CH_2Cl_2 + TBAP (0.1 M) solution, the same CV features were found starting either from isolated **1** or from isolated **2**, i.e. compound **2** is the final product of the oxidation of **1** and vice versa (Scheme 1). The CV curve is characterized by a pair of peaks whose potentials depend strongly on the scan rate: their peak-to-peak separation increases from 0.21 V at 5 mVs^{-1} to 1.07 V at 5 Vs^{-1} (Figure 4). At low scan rates, E_{pa} and E_{pc} tend towards constant values of 0.41 V and 0.20 V vs. Fc/Fc^+ . The RDE wave recorded in a CH_2Cl_2 solution of **1** is characterized by $E_{1/2} = 0.54 \text{ V}$ ($N = 600 \text{ rpm}$).

Upon exhaustive potentiostatic electrolysis at 0.75 V (one exchanged electron), the RDE wave recorded in the resulting solution (Figure 4) matches well with that recorded in an electrolytic solution of **2**, $E_{1/2} = 0.14 \text{ V}$ ($N = 600 \text{ rpm}$). Additionally, the UV/Vis features of both solutions are very close. The starting solution is fully restored upon further exhaustive reduction at -0.2 V . It can be seen that the anodic and cathodic $E_{1/2}$ values determined from RDE experiments performed in solution of **1** or **2** are different.

These results can be analyzed as the simple one-electron transfer depicted in Scheme 1. Simulations of the experimental CV curves allowed the determination of the apparent formal potential and the apparent heterogeneous electron-transfer rate constant of the overall mechanism: $E_{1/2} = 0.30 \pm 0.01 \text{ V}$ and $k^0 = 2.0 \pm 0.9 \times 10^{-4} \text{ cm s}^{-1}$. The low value of k^0 suggests that the overall electrochemical mechanism involves coupled chemical reactions, i.e. the electron

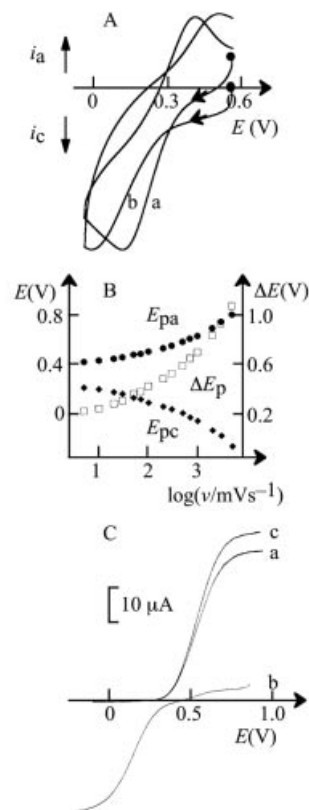


Figure 4. Voltammetric curves of **2** (A) and **1** (C), 1.2 mM, recorded in CH_2Cl_2 + TBAP (0.1 M), WE: glassy carbon ($\phi = 3 \text{ mm}$), E vs. Fc/Fc^+ ; (A) CV at 0.03 (curve a) and 0.3 Vs^{-1} (curve b), normalized current vs. E ; (B) anodic (E_{pa}), cathodic (E_{pc}) peak potential and peak-to-peak (ΔE_{p}) separation vs. scan rate; (C) RDE voltammetry, $N = 600 \text{ rpm}$, initial (curve a), after oxidative electrolysis (0.8 exchanged electron, curve b), after re-reduction (curve c, the increase in the limiting current between curves a and c is due to a partial evaporation of CH_2Cl_2)

transfer implies changes in coordination and geometry during the redox cycle. The overall mechanism can thus be best described by the classic square scheme^[2] in which the electron-transfer steps are followed by coordinate bond formations (or ruptures) accounting for the change in the coordination mode of the copper center according to its redox state, i.e. the electron transfer leads to an unstable intermediate which undergoes a fast rearrangement to yield the stable corresponding complex. Due to their very fast kinetics, the electroactivity of the intermediates could not be seen on the CV curves, the anodic and cathodic processes remaining electrochemically irreversible, even at high scan rate (10 Vs^{-1}). This precluded any precise determination of the kinetic constants by electrochemical simulations.

Intervention of a coupled chemical reaction is further confirmed by examining the electrochemical response of **1** or **2** in coordinating solvents. In an electrolytic EtOH solution of **2**, when scanning towards negative potentials (0.1 Vs^{-1}), the CV curve displays a main cathodic peak at $E_{\text{pc}} = 0.14 \text{ V}$ and a peak of low intensity at $E_{\text{pc}} = -0.15 \text{ V}$. On the reverse scan, only one anodic peak is seen at $E_{\text{pa}} = 0.38 \text{ V}$ (Figure 5). After an exhaustive reduction/re-oxidation cy-

cle, the final CV curve displays the same signals but with different intensities (Figure 5). This results in an ill-behaved RDE wave for **2** characterized by an apparent $E_{1/2} = 0.23$ V ($N = 600$ rpm), while a more resolved RDE wave for **1** is seen at apparent $E_{1/2} = 0.35$ V ($N = 600$ rpm). It can be assumed that in coordinating solvents, solvent molecules are involved in the coordination sphere of the metal center giving rise to the formation of different complexes in equilibrium [as previously observed in UV/Vis and EPR spectra measured in ethanol (see above)].

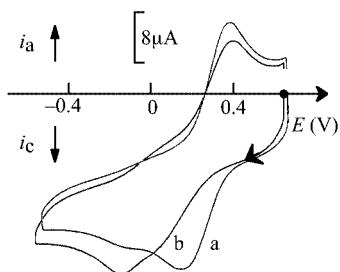


Figure 5. CV curves of **2**, 1.1 mM, recorded in EtOH + TBAP (0.1 M), WE: glassy carbon ($\phi = 3$ mm), E vs. Fc/Fc^+ , $v = 0.1 \text{ V s}^{-1}$; curve (a): initial; curve (b): after an oxidation/reduction cycle

Taking into account $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.49$ V or 0.44 V vs. SCE, in CH_2Cl_2 or EtOH respectively, under our experimental conditions, the **1/2** electrochemical system presents a very high redox potential, similar to that of blue copper proteins (a value of 0.78 V vs. NHE is reported for fungal laccase).^[16] As a consequence, whereas **1** is stable in CH_2Cl_2 or alcohol solution, **2** is partially reduced to the Cu^{I} state even in the presence of air (40% of Cu^{II} is reduced after 1 d in ethanol). High redox potential values have been reported for a few small $\text{Cu}^{\text{II/I}}$ molecular systems^[17] but are rare for related copper systems involving tripodal ligands.^[18,19] Compared to other redox couples involving tripodal N₂S₂ ligands, the **1/2** electrochemical system described herein displays a shift towards higher potentials by 0.2 V .^[10]

Conclusion

The high redox potential of the **1/2** couple could result from a combination of: (i) the lower donating character of the aromatic thioether group compared to an aliphatic thioether group, (ii) the stabilization of the Cu^{I} redox state, as judged from the short $\text{Cu}^{\text{I}}\text{--SR}_2$ bonds, (iii) the long axial $\text{Cu}^{\text{II}}\text{--SR}_2$ bond leading to a weaker interaction, likely to be due to (iv) the geometric constraint afforded by the *t*Bu group. The present study may provide insights into the electron-transfer mechanism of the blue copper proteins. Further studies are in progress to understand the relationship between the subtle changes of the ligand and the deep changes induced in the redox properties of the related complexes.

Experimental Section

General: All chemicals were obtained from commercial sources and used as received. Solvents were purified by standard methods before use. **Caution:** Although no problems were encountered during the preparation of perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.

Spectrometry: Fast-atom bombardment (FAB) mass spectra in the positive mode were recorded with a Nermag R 1010C apparatus equipped with an M scan (Wallis) atom gun (8 kV, 20 mA). ESI mass spectra were obtained with a Bruker Esquire 3000 plus spectrometer with an ion trap. UV/Vis spectra were recorded using a Perkin–Elmer Lambda 2 spectrophotometer equipped with 1.0-cm matched quartz cells and operating in the range 200–900 nm; ϵ values are given in $\text{M}^{-1}\cdot\text{cm}^{-1}$. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer and a Bruker AC 200; chemical shifts (ppm) were referenced to residual solvent peaks. EPR spectra were recorded at 100 K with a Bruker ESP 300 spectrometer operating at 9.4 GHz (X-band), with 3 mM solutions.

Electrochemistry: Electrochemical experiments were carried out using a PAR model 273 potentiostat equipped with a Kipp-Zonen x-y recorder. All experiments were run at room temperature under argon. A standard three-electrode cell was used, with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. All potentials are referred to the regular Fc/Fc^+ redox couple used as internal reference. Vitreous carbon disc electrodes for cyclic voltammetry (CV) (5 mm diameter) and rotating disc electrode (RDE) (3 mm diameter) were polished with 1 μm diamond paste.

[2-(*tert*-Butylthio)benzyl](2-pyridylmethyl)amine: A solution of (2-pyridylmethyl)amine (477 μL , 4.54 mmol) in dry MeOH (10 mL) was added at room temperature to a solution of 2-(*tert*-butylthio)benzaldehyde (1 g, 5 mmol) in dry MeOH (100 mL) under Ar. After 3 h, NaBH_4 (455 mg, 11.5 mmol) was slowly added as a solid and the mixture stirred for an additional 2 h. After acidic treatment (HCl , 4 N), the solvent was removed under reduced pressure. The resulting product was dissolved in H_2O (50 mL) and extracted with CH_2Cl_2 to remove the excess of reduced aldehyde. The aqueous solution was then neutralized with saturated NaHCO_3 and extracted with CH_2Cl_2 ($2 \times 100 \text{ mL}$). The combined organic layers were washed with saturated NaCl, dried with Na_2SO_4 and concentrated under reduced pressure to give a brown oil. Yield: 1.2 g (91%). ^1H NMR (200 MHz, CDCl_3 , TMS): $\delta = 8.51$ (d, $J = 4.8 \text{ Hz}$, 1 H, Py-*H*), 7.51–7.63 (m, 3 H, Py-*H*), 7.07–7.36 (m, 4 H, Ar-*H*), 4.11 (s, 2 H, NCH_2Ar), 3.92 (s, 2 H, NCH_2Py), 3.02 (s, 1 H, NH), 1.25 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (50 MHz, CDCl_3 , TMS): $\delta = 159.3, 148.9, 144.3, 138.5, 136.0, 131.8, 129.4, 128.8, 126.7, 122.0, 121.6, 54.0, 51.6, 46.9, 30.8$ ppm. FAB+ MS: $m/z = 286$ [$\text{M}^+ + \text{H}^+$]. $\text{C}_{17}\text{H}_{21}\text{N}_2\text{S}$ (285): calcd. C 67.80, H 7.58, N 9.44, S 11.86; found C 68.00, H 7.74, N 9.78, S 11.19.

Bis[2-(*tert*-butylthio)benzyl](2-pyridylmethyl)amine [$\text{N}_2(\text{S}t\text{Bu})_2$]: 2-(*tert*-Butylthio)benzaldehyde (847 mg, 4.23 mmol) and glacial acetic acid (878 μL , 15.36 mmol) were added to a solution of [2-(*tert*-butylthio)benzyl](2-pyridylmethyl)amine (1.1 g, 3.84 mmol) in dry MeOH (100 mL) under Ar. After 1 h, NaBH_3CN (1.016 g, 15.36 mmol) was added and the mixture stirred overnight. Then, an acid treatment (HCl , 4 N) was performed and the solvent was removed under reduced pressure. The resulting product was dissolved in H_2O and extracted with CH_2Cl_2 to remove the excess of reduced aldehyde. The aqueous solution was neutralized with saturated NaHCO_3 and extracted with CH_2Cl_2 ($2 \times 100 \text{ mL}$). The combined organic layers were washed with saturated NaCl, dried

Table 2. Crystallographic experimental details for **1–3**

	1 ·0.985CH ₂ Cl ₂	2 ·C ₄ H ₈ O	3
Empirical formula	C ₂₉ H ₃₆ CuF ₃ N ₂ O ₃ S ₃ ·0.985CH ₂ Cl ₂	C ₃₀ H ₃₈ CuF ₆ N ₂ O ₇ S ₄ ·C ₄ H ₈ O	C ₂₈ H ₃₈ Cl ₂ CuN ₂ O ₉ S ₂
Formula mass	760.99	915.54	745.19
Symmetry	triclinic	orthorhombic	monoclinic
Morphology	pale brownish prism	turquoise prism	blue-green platelet
Crystal dimension [mm]	0.18 × 0.15 × 0.10	0.32 × 0.26 × 0.18	0.22 × 0.15 × 0.08
<i>a</i> [Å]	10.271(1)	12.0120(9)	32.86(1)
<i>b</i> [Å]	12.192(1)	16.2009(5)	11.906(4)
<i>c</i> [Å]	14.829(1)	21.616(2)	23.806(5)
<i>α</i> [°]	74.43(1)	90	90
<i>β</i> [°]	86.80(1)	90	129.55(3)
<i>γ</i> [°]	70.97(1)	90	90
<i>V</i> [Å ³]	1690(1)	4206.6(4)	7181(5)
<i>T</i> [K]	100.2	150	293
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	4	8
Diffraction	Enraf–Nonius Kappa CCD	Enraf–Nonius Kappa CCD	Enraf–Nonius CAD-4
Monochromator	graphite	graphite	graphite
Wavelength [Å]	0.7107 (Mo- <i>K</i> _α)	0.7107 (Mo- <i>K</i> _α)	0.7107 (Mo- <i>K</i> _α)
<i>μ</i> [mm ^{−1}]	1.038	0.793	0.922
No. of reflections (measured)	11234	32320	6910
No. of reflections (unique)	4349	7043	6729
No. of reflections	3704 (<i>I</i> > 1σ)	4763 (<i>I</i> > 2σ)	4030 (<i>I</i> > 2σ)
<i>R</i> _{int}	0.039	0.067	0.034
<i>R</i>	0.038	0.056	0.055
<i>R</i> (<i>w</i>)	0.059	0.057	0.065

with Na₂SO₄ and concentrated under reduced pressure. Addition of pentane afforded the product as a pale beige powder. Yield: 1.2 g (68%), m.p. 95 °C. ¹H NMR (200 MHz, CDCl₃, TMS): δ = 8.53 (d, *J* = 4.8 Hz, 1 H, Py-*H*), 7.50–7.60 (m, 3 H, Py-*H*), 7.07–7.36 (m, 8 H, Ar-*H*), 4.15 (s, 4 H, NCH₂Ar), 3.92 (s, 2 H, NCH₂Py), 1.25 (s, 18 H, *t*Bu) ppm. ¹³C NMR (50 MHz, CDCl₃, TMS): δ = 160.6, 148.9, 145.0, 139.0, 136.5, 132.7, 129.1, 129.6, 126.6, 122.9, 121.9, 60.7, 57.0, 47.3, 31.3 ppm. FAB+ MS: *m/z* = 465 [*M*⁺ + H⁺]. C₂₈H₃₆N₂S₂ (464): calcd. C 71.86, H 7.88, N 5.92, S 13.68; found C 72.37, H 7.81, N 6.03, S 13.80.

[Cu^I{N₂(*Sr*Bu)₂}(CF₃SO₃) (1): Copper(I) trifluoromethanesulfonate (0.230 g, 0.43 mmol, toluene complex) was added to a solution of N₂(*Sr*Bu)₂ (0.2 g, 0.43 mmol) in CH₂Cl₂ (20 mL). The solution was stirred for 10 min and diethyl ether added (10 mL). After 24 h, **1** was obtained as a polycrystalline pale powder. Yield: 65% (0.188 g). Crystals of **1** suitable for X-ray crystallography were obtained by layering hexane onto a CH₂Cl₂ solution of **1**. ESI MS: *m/z* = 527 [N₂(*Sr*Bu)₂ + 1 Cu⁺]. ¹H NMR (300 MHz, CD₃CN, TMS): δ = 8.68 (d, *J* = 4.7 Hz, 1 H, Py-*H*), 7.79 (t, *J* = 7.0 Hz, 1 H, Py-*H*), 7.81–7.37 (m, 5 H, Ar-*H* + Py-*H*), 7.27 (d, 1 H, Ar-*H*), 3.89 (s, 4 H, NCH₂Ar), 3.78 (s, 2 H, NCH₂Py), 1.17 (s, 18 H, *t*Bu) ppm.

[Cu^{II}{N₂(*Sr*Bu)₂}(H₂O)(CF₃SO₃)](CF₃SO₃) (2): Copper(II) trifluoromethanesulfonate (0.155 g, 0.43 mmol) was added to a solution of N₂(*Sr*Bu)₂ (0.2 g, 0.43 mmol) in EtOH (20 mL). The solution was stirred for 10 min and diethyl ether added (10 mL). After 24 h at −20 °C, **2** was obtained as a polycrystalline blue powder. Yield: 70% (0.250 g). Crystals of **2** suitable for X-ray crystallography were obtained vapor diffusion of diethyl ether into an ethanol solution

of **2**. FAB MS (NBA matrix): *m/z* = 678 [N₂(*Sr*Bu)₂ + 1 Cu²⁺ − H₂O + 1 CF₃SO₃ + 1 H⁺]. C₃₀H₃₈CuF₆N₂O₇S₄ (844): calcd. C 42.67, H 4.54, Cu 7.53, F 13.5, N 3.32, S 15.19; found C 42.31, H 4.56, Cu 7.31, N 3.31, S 15.85.

[Cu^{II}{N₂(*Sr*Bu)₂}(H₂O)(ClO₄)](ClO₄) (3): Copper(II) perchlorate hexahydrate (0.271 g, 0.715 mmol) was added to a solution of N₂(*Sr*Bu)₂ (0.3 g, 0.65 mmol) in EtOH (20 mL). The solution was stirred for 10 min and diethyl ether/THF added (10 mL). After 24 h at −20 °C, **3** was obtained as a polycrystalline green-blue powder. Yield: 45% (0.218 g). Crystals of **3** suitable for X-ray crystallography were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of **3**. FAB MS (NBA matrix): *m/z* = 628 [N₂(*Sr*Bu)₂ + 1 Cu²⁺ − H₂O + 1 ClO₄ + 1 H⁺]. UV/Vis (CH₂Cl₂): λ (ε) = 357 (4146), 706 nm (392 M^{−1}·cm^{−1}); (EtOH): λ = 338 (3954), 655 nm (149 M^{−1}·cm^{−1}). EPR (9.6 GHz, 100 K, 3 mm, CH₂Cl₂/toluene, 1:1): *g*_{||} = 2.22, *g*_⊥ = 2.06, *A*_{||} = 175 × 10^{−4} cm^{−1}; (EtOH/toluene, 1:1) main features at: *g*_{||} = 2.22, *g*_⊥ = 2.02, *A*_{||} = 170 × 10^{−4} cm^{−1}.

X-ray Crystallographic Studies: Crystal data and crystallographic experimental data for complexes **1–3** are listed in Table 2. In both structures, collected reflections were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods and refined using the TEXSAN software package.^[20] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameters. CCDC-203164 (**1**), -203165 (**2**) and -203166 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-0333; E-mail: deposit@ccdc.cam.ac.uk].

- [1] R. H. Holm, P. Kennepohl, E. I. Solomon, *Chem. Rev.* **1996**, 96, 2239–2314.
- [2] M. C. Feiters, in *Metal ions in biological systems, Probing of proteins by metal ions and their low-molecular-weight complexes* (Eds.: A. Sigel, H. Sigel), New York, **2001**, vol. 38, pp. 522–534.
- [3] J. M. Guss, H. C. Freeman, *J. Mol. Biol.* **1983**, 169, 521–563.
- [4] G. E. Norris, B. F. Anderson, E. N. Baker, *J. Am. Chem. Soc.* **1986**, 108, 2782–2785.
- [5] E. N. Baker, *J. Mol. Biol.* **1988**, 203, 1071–1095.
- [6] N. Kitajima, K. Fujisawa, Y. Moro-oka, *J. Am. Chem. Soc.* **1990**, 112, 3210–3212.
- [7] P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **2000**, 122, 6331–6332.
- [8] A. W. Addison, N. T. Rao, E. Sinn, *Inorg. Chem.* **1984**, 23, 1957–1967.
- [9] K. K. Nanda, A. W. Addison, R. J. Butcher, M. R. McDevitt, T. N. Rao, E. Sinn, *Inorg. Chem.* **1997**, 36, 134–135.
- [10] E. A. Ambundo, M. V. Deydier, A. J. Grall, N. Agüera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. A. Ochrymowycz, D. B. Rorabacher, *Inorg. Chem.* **1999**, 38, 4233–4242.
- [11] K. D. Karlin, P. L. Dahlstrom, J. Zubieta, *Transition Met. Chem.* **1981**, 6, 314–315.
- [12] K. D. Karlin, J. K. Yandell, *Inorg. Chem.* **1984**, 23, 1184–1188.
- [13] E. Bouwman, R. Day, W. L. Driessen, W. Tremel, B. Krebs, J. S. Wood, J. Reedijk, *Inorg. Chem.* **1988**, 27, 4614–4618.
- [14] H. Wu, C. R. Lucas, *Inorg. Chem.* **1993**, 32, 526–531.
- [15] E. I. Solomon, K. W. Penfield, D. E. Wilcox, *Struct. Bonding* **1983**, 53, 1–57.
- [16] V. T. Taniguchi, B. G. Malmström, F. C. Anson, H. B. Gray, *Proc. Natl. Acad. Sci. U. S. A.* **1982**, 79, 3387–3389.
- [17] S. Flanagan, J. Dong, K. Haller, S. Wang, W. R. Scheidt, R. A. Scott, T. R. Webb, D. M. Stanbury, L. J. Wilson, *J. Am. Chem. Soc.* **1997**, 119, 8857–8868.
- [18] K. D. Karlin, S. E. Sherman, *Inorg. Chim. Acta* **1982**, 65, L39–L40.
- [19] T. N. Sorrell, D. L. Jameson, *Inorg. Chem.* **1982**, 21, 1014–1019.
- [20] TEXSAN, *Single Crystal Structure Analysis Software*, Version 1.7, Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, **1995**.

Received February 6, 2003