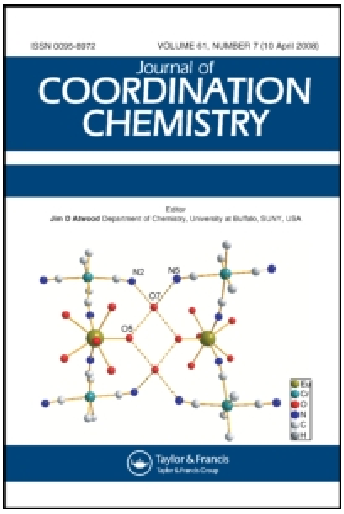

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Influence of carboxamido nitrogen donors on the redox potential of copper(III) complexes

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Influence of carboxamido nitrogen donors on the redox potential of copper(III) complexes

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The synthesis of a new copper(III) complex with aliphatic carboxamido-*N* and thiolato-*S* donors is reported. This complex was thoroughly characterized by ^{1}H NMR, UV–Vis spectroscopy, and cyclic voltammetry, as well as by single crystal X-ray crystallography. The copper(III) state in this complex is more stabilized than in the parent compound with aromatic carboxamido nitrogen donors.

Keywords: Copper(III); Deprotonated amide; Thiolate; High valent metal

1. Introduction

Although the +3 oxidation state of copper has not been detected so far in biological systems, it has been shown to be accessible in a number of synthetic models [1] or to be formed as transient species during catalytic cycles [2]. Stable mononuclear copper(III) complexes have indeed been isolated and thoroughly characterized by several groups. In all these compounds the copper has a square planar environment and is essentially coordinated by two deprotonated amide nitrogens from a peptide [3, 4] or from a synthetic ligand, with donors well known to stabilize high valent metal ions [5]. The coordination sphere of the trivalent copper cation can be completed by various nitrogen [6–10] or oxygen donors [3, 11]. A copper(III) complex with two aromatic carboxamido nitrogens and two alkyl thiolato sulfurs has also been reported. The presence of the thiolato donors appears to strongly stabilize the Cu^{III} state [12]. Replacement of the thiolates by alcoholates leads to a substantial increase of the Cu^{III}/Cu^{II} redox potential [8, 13]. In this article, we report the direct synthesis and spectroscopic characterization

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as well as crystallographic study of a parent bis-thiolato copper(III) complex in which the carboxamido nitrogen donors have been changed from aromatic to aliphatic. This complex shows additional stabilization of the copper(III) state compared to the corresponding aromatic derivative, and this stabilization is reflected in the spectroscopic and crystallographic data.

2. Experimental

2.1. *Materials and physical measurements*

All solvents and chemicals were purchased from SDS, Acros, and Aldrich. CH_3CN and CH_2Cl_2 were dried according to standard procedures and stored under argon. Dried diethyl ether was purchased from Riedel-de-Haën. ^1H NMR spectra were recorded on a Bruker ARX-250 spectrometer, with chemical shifts reported in ppm relative to the residual solvent (CH_3CN, $\delta_H = 1.96$ ppm). IR spectra were obtained neat with a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with a MIRacle single-reflection horizontal ATR unit (zirconium-selenium crystal). HRMS were carried out at ICSN/CNRS, Gif-sur-Yvette, France. Experiments performed under argon were run on a vacuum line. ESI-MS mass spectra were performed on a Thermo Finnigan LCD Advantage spectrometer. UV spectra were recorded on a SAFAS mc^2 spectrometer. Cyclic voltammograms were obtained in deaerated CH_3CN solution at RT using an EGGR-PAR model 173 potentiostat and model interface instruments with a three-electrode system which consists of a NaCl saturated calomel electrode (SCE), a platinum auxiliary electrode, and a glassy carbon working electrode. Tetrabutylammonium hexafluorophosphate (NBu_4PF_6, 0.1 M in CH_3CN) was used as the supporting electrolyte. The potential sweep rate was 50 mV s^{-1}, and under our conditions the potential of the ferrocene/ferrocenium couple was 0.38 V.

2.2. *Synthesis*

Complex **3-Et$_4$N** has been previously prepared by Hanss *et al.* [12]. *N*,*N*′-ethane-1, 2-diylbis[2-mercapto-2methylpropanamide] was synthesized from *S*,*S*′-[1,2-ethanediyl-bis[imino(1,1-dimethyl-2-oxo-2,1-ethanediyl)]]ester [14, 15].

2.2.1. *N*,*N*′-ethane-1,2-diylbis[2-methyl-2-(methyldithio)propanamide] (1). To a CH_2Cl_2 solution (5 mL) of methyl methane thiosulfonate (167 µL, 1.77 mmol) was added Et_3N (248 µL, 1.77 mmol). After cooling the resulting solution to 0°C, *N*,*N*′-ethane-1,2-diylbis[2-mercapto-2-methylpropanamide] (212 mg, 0.80 mmol) in 10 mL of CH_2Cl_2 was added dropwise with stirring over 30 min. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Volatiles were removed *in vacuo*, and the residue was chromatographed over silica gel (gradient CH_2Cl_2/EtOAc, from 90/10 to 0/100 v : v mixture) to yield **1** as a white powder (227 mg, 80%). HRMS (CI$^+$, CH_4, *m*/*z*): Anal. Calcd (found) for $C_{12}H_{23}N_2O_2S_4$: 355.0642 (355.0655). ^1H NMR (δ, CD_3CN): 7.06 (s, 2H), 3.31 (s, 4H), 2.42 (s, 6H), 1.52 (s, 12H). FT-IR (ATR, cm^{-1}): 1631.

2.2.2. Complex 2-Et$_4$N. To an acetonitrile solution (5 mL) of **1** (211 mg, 0.59 mmol) were added under argon 1 equiv. of $Cu(PF_6)(CH_3CN)_5$ (223 mg, 0.59 mmol) and 2 equiv. of NEt_4OH in MeOH (1.4 M, 847 µL, 1.18 mmol). After stirring the mixture for 2 h at room temperature, the solvent was removed. The crude product was dissolved in acetone (2 mL), filtered over Celite and the solvent evaporated to dryness. After dissolution of the product in a minimum of acetonitrile (1 mL), the complex was precipitated in cold diethyl ether and pure **2-Et$_4$N** was isolated as a dark green powder in quantitative yield (267 mg). Crystals suitable for XRD analysis were obtained by slow diffusion of diethyl ether into the acetonitrile solution. A dark green crystalline material was collected, washed with diethyl ether, and dried *in vacuo*. MS (ESI$^-$, *m*/*z*): 323.4 ([**2**], 100%). ^{1}H NMR (δ, CD_3CN): 3.51 (s, 4H), 3.32 (q, 8H, $^3J_{H-H} = 7.3$ Hz), 1.39 (s, 12H), 1.25 (t, 12H, $^3J_{H-H} = 7.3$ Hz). UV–Vis (acetonitrile): λ_{max} (ε_M) = 408 (7366), 559 (232) nm. FT-IR (ATR, cm^{-1}): 1577.

2.3. *X-ray data collection and structural determination*

Diffraction data are listed in table 1. Structural data for **3-Et$_4$N** and **2-Et$_4$N** were obtained with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å for **3-Et$_4$N** or

Table 1. Crystal data and structure refinement parameters for **3-Et$_4$N** and **2-Et$_4$N**.

Compound	**3-Et$_4$N**	**2-Et$_4$N**
Empirical formula	$C_{11}H_{18}Cu_{0.5}N_{1.5}OS$	$C_{27}H_{54}Cu_{1.5}N_{4.5}O_3S_3$
Molecular weight	251.11	681.24
Color	Green	Green
Crystal system	Orthorhombic	Monoclinic
Space group	*Pccn*	*P2*/*c*
Unit cell dimensions (Å, °)		
a	10.612(1)	22.066(1)
b	11.404(1)	11.312(1)
c	20.473(1)	14.767(1)
α	90	90
β	90	105.05(1)
γ	90	90
V (Å^3)	2477.6(3)	3559.6(4)
Z	8	4
D_{Calcd} (g cm^{-3})	1.346	1.271
Absorption coefficient (mm^{-1})	1.073	1.112
F(000)	1064	1452
Crystal size (mm^3)	0.51 × 0.40 × 0.35	0.70 × 0.05 × 0.30
θ Ranges (°)	1.99 to 25.24	1.91 to 28.40
$h/k/l$	$-12 < h < 12$ $-13 < k < 13$ $-24 < l < 24$	$-29 < h < 29$ $-15 < k < 15$ $-19 < l < 19$
T (K)	293(2)	293(2)
R_{int}	0.078	0.055
Number of reflections collected	46,890	119,316
Number of reflections used $I \geq 2\sigma(I)$	1843	5941
Parameters	141	365
R_1, wR_2 [$I > 2\sigma(I)$]	0.0312, 0.0758	0.0589, 0.1745
Goodness-of-fit on F^2	1.092	1.032
Residual density (e Å^{-3})	−0.276, 0.264	−0.496, 1.524
Refine ls shift/su.max	0.0001	0.006

$\lambda = 0.71069$ Å for **2-Et$_4$N**) on a SMART APEX CCD4K area-detector diffractometer at 293 K. Data integration and global cell refinement were performed with SAINT [16]. Intensity data were corrected for Lorentz and polarization effects and scale variation. A multi-scan absorption correction using SADABS [17] was applied.

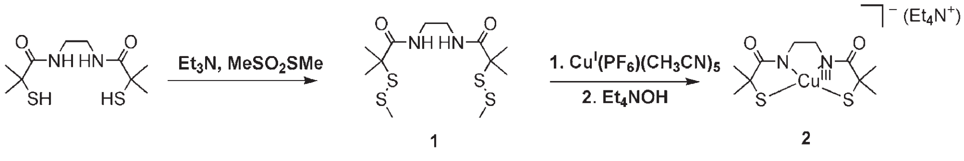
The structures were solved by direct methods using SHELXS-97 [18] and refined by least squares on F^2 using SHELXL-97 [19]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically generated positions and allowed to ride on their parent atom with an isotropic thermal parameter 20% higher than that of the atom of attachment. The drawings of molecules were realized with ORTEP(III) [20].

3. Results and discussion

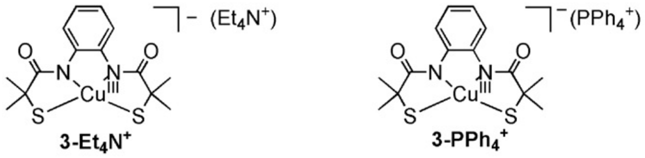
3.1. *Synthesis of complexes*

Complex **2-Et$_4$N** was synthesized in one step by a two-electrons reduction of the disulfide bonds of the bis-disulfide **1** by a copper(I) salt, Cu(CH$_3$CN)$_5$(PF$_6$), in the presence of two equivalents of tetraethylammonium hydroxide in methanol to deprotonate the amides (scheme 1). The solution turned immediately dark orange and the Cu^{III} species **2-Et$_4$N** was isolated by precipitation from acetonitrile into diethyl ether. Its mass spectrum in ESI$^-$ showed a peak at $m/z = 323.4$, 100% corresponding to the anionic part **2**. Complex **2-Et$_4$N** is soluble in most organic solvents, and is stable in the air, in the solid state or in solution.

For comparison we also synthesized the corresponding aromatic complex **3-Et$_4$N** (scheme 2), previously prepared by Hanss *et al.* [12] by a different procedure and crystallized as **3-PPh$_4$** and we solved its crystal structure.



Scheme 1. Synthesis of complex **2**.



Scheme 2. Structures of complexes **3-Et4N$^+$** and **3-PPh$_4$$^+$**.

3.2. *Cyclic voltammetry*

Cyclic voltammogramms of complexes **2-Et$_4$N** and **3-Et$_4$N** [12] recorded in acetonitrile show quasi-reversible Cu^{III}/Cu^{II} reduction waves at $E_{1/2} = -1.32$ and -1.16 V, respectively, *versus* the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple, indicating a 160 mV stabilization of the Cu^{III} state in **2-Et$_4$N** relative to **3-Et$_4$N**. This result is in agreement with the stronger donating character of aliphatic carboxamido nitrogens relative to aromatic ones. This stabilization, added to the effect of the thiolato (replacing the thiolato by alcoholato donors increases the redox potential by 270 mV [8, 13]), makes **2-Et$_4$N** the most stable Cu^{III} complex reported to date, with the lowest Cu^{III}/Cu^{II} reduction potential [8].

3.3. *Spectroscopic studies*

3.3.1. ^{1}H NMR. As expected for copper(III) species, **2-Et$_4$N** and **3-Et$_4$N** are diamagnetic and show C_{2v} symmetry in solution. A comparison of the ^{1}H NMR spectra of **2-Et$_4$N** and **3-Et$_4$N** in CD_3CN reveals that the protons of the methyl groups are more shielded in **2-Et$_4$N** than in **3-Et$_4$N** (1.39 (s, 12H) for **2-Et$_4$N** and 1.51 (s, 12H) for **3-Et$_4$N**).

3.3.2. UV–Vis. Electronic spectra of **2-Et$_4$N** and **3-Et$_4$N** were recorded in acetonitrile (figure 1). The visible region of the spectra of **2-Et$_4$N** and **3-Et$_4$N** exhibits one strong absorption at 408 ($\varepsilon_M = 7366\,M^{-1}\,cm^{-1}$) and 417 nm ($\varepsilon_M = 6130\,M^{-1}\,cm^{-1}$), respectively. Both features are assigned to sulfur-metal charge-transfer bands, on the basis of their locations and intensities [6].

3.3.3. Infrared. FT-IR spectra of **2-Et$_4$N** and **3-Et$_4$N** display a strong stretching mode at 1577 and 1592 cm^{-1}, respectively, indicative of deprotonated amide donors.

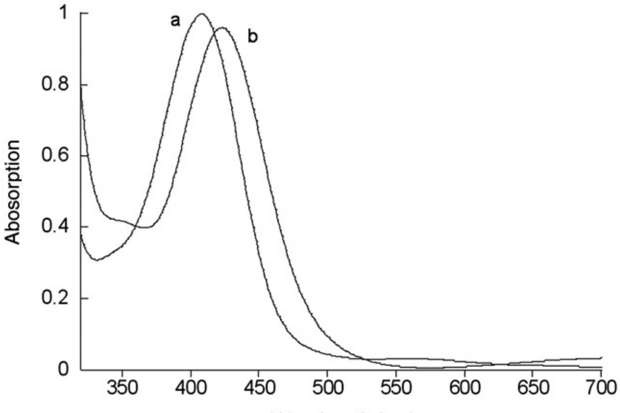


Figure 1. Electronic spectra of **2-Et$_4$N** (a) and **3-Et$_4$N** (b) (0.13 mM in acetonitrile).

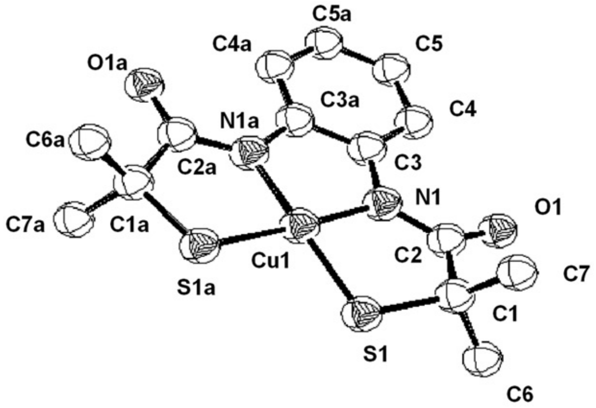


Figure 2. ORTEP diagram of **3**. Displacement ellipsoids are drawn at the 50% probability level. The H atoms are omitted for clarity.

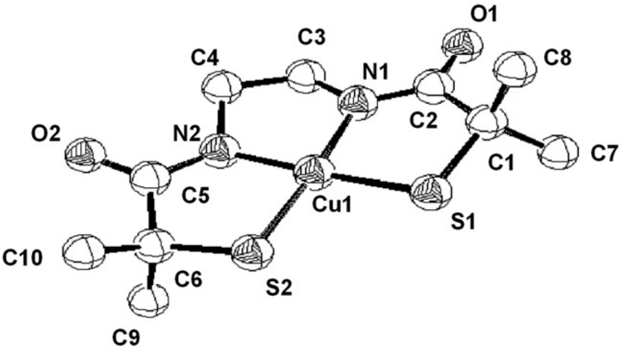


Figure 3. ORTEP diagram of **2**. Displacement ellipsoids are drawn at the 50% probability level. The H atoms are omitted for clarity. This view shows only one complex (Cu in 4g).

3.4. *Crystallographic studies*

Complexes **2-Et$_4$N** and **3-Et$_4$N** were crystallized from acetonitrile solutions layered with diethyl ether. Crystallographic data and collection parameters are given in table 1. ORTEP diagrams of **3-Et$_4$N** and **2-Et$_4$N** are depicted in figures 2 and 3. Table 2 lists the most relevant bond distances and angles.

The molecular structure of **3-Et$_4$N** (space group *Pccn*) consists of one discrete copper complex and one Et$_4$N cation. The copper lies on a two-fold axis parallel to **c** (4c position) which passes through the ligand. The nitrogen of Et$_4$N is located on a twofold axis parallel to **c** (4d position). The copper is coordinated to two carboximado-*N* and two thiolato-*S* donors in a square-planar coordination with a slight tetrahedral distortion (Td twist = 3.6(1)° [21]. Atomic deviations from the best plane through N1, S1, N1a, and S1a (P1) are within ±0.05 Å. The dihedral angle between P1 and the phenyl plane through C3, C4, C5, C3a, C4a, and C5a is 1(1)°. The 3-D structure of **3-Et$_4$N** is mainly generated by ionic interactions between Et$_4$N$^+$ and the anionic **3**. Propagation of these interactions produces chains of Et$_4$N$^+$ ($x = 1/4$, $y = 3/4$, z) and **3** ($x = 3/4$, $y = 3/4$, z) running parallel to the **c** axis, the phenyl planes being approximately perpendicular to the [1 1 0] direction.

Table 2. Selected bond distances (Å) and angles (°) for **3-Et$_4$N** and **2-Et$_4$N**.

3-Et$_4$N		**2-Et$_4$N**			
Cu1–N1	1.861(1)	Cu1–N1	1.849(3)	Cu2–N3	1.846(3)
		Cu1–N2	1.843(3)		
Cu1–S1	2.145(6)	Cu1–S1	2.158(1)	Cu2–S3	2.152(1)
		Cu1–S2	2.146(1)		
S1–Cu1–S1^{a}	92.10(4)	S1–Cu1–S2	94.46(5)	S3–Cu2–S3^{b}	95.23(6)
N1–Cu1–N1^{a}	86.95(1)	N1–Cu1–N2	87.07(1)	S3–Cu2–N3	89.05(1)
		S2–Cu1–N2	88.93(1)	N3–Cu2–N3^{b}	86.8(2)
S1–Cu1–N1	90.53(6)	S1–Cu1–N1	89.47(1)		
S1a–Cu1–N1	176.37(6)	S1–Cu1–N2	175.90(1)	S3–Cu2–N3^{b}	174.86(1)

Symmetry code: a: $-x+3/2$, $-y+3/2$, z; b: $-x$, y, $-z+1/2$.

The asymmetric unit of **2-Et$_4$N** (space group *P2/c*) consists of two crystallographically independent but chemically equivalent complexes: one Cu, labeled Cu1, is in general 4g position and the other Cu, noted Cu2, lies on a two-fold helicoïdal axis parallel to **b** (2e position). The N atoms of two Et$_4$N$^+$ are located in 4g and 2f positions. The Cu atoms have a square planar N$_2$S$_2$ arrangement similar to that of **3-Et$_4$N**. The donor environment is slightly tetrahedrally distorted (Td twist = 2.7(2)° for Cu1 and 8.9(2)° for Cu2). The Cu1 and Cu2 atoms deviate respectively by −0.032(1) and 0 Å (as a result of crystallographic symmetry) from the best plane through N1, N2, S1, and S2.

For **3-Et$_4$N** and **3-PPh$_4$** [12], bond lengths are similar but space groups and crystal systems are different. Indeed, **3-Et$_4$N** crystallizes in an orthorhombic system with space group *Pccn* whereas **3-PPh$_4$** as well as **2-Et$_4$N** crystallize in a monoclinic system with space group *P2$_1$/n* and *P2/c*, respectively. These dissimilarities between **3-Et$_4$N** and **3-PPh$_4$** are likely related to two cations with different steric constraints. Bond distances and angles in all complexes are in the range of those reported for square-planar carboxamido copper(III) complexes [3, 8, 12], but a significant difference in the Cu–N and Cu–S bond lengths is nevertheless observed between **2-Et$_4$N** and **3-Et$_4$N** (or **3-PPh$_4$**) (table 2). The Cu–N distances are shorter in **2-Et$_4$N** than **3-Et$_4$N**, while Cu–S distances are longer. Obviously, the greater the electron density on carboxamido, as in **2-Et$_4$N** compared to **3-Et$_4$N**, the shorter is the Cu–N bond. Associated elongation of the Cu–S bond in **2-Et$_4$N** relative to **3-Et$_4$N** results from a *trans* effect between the carboxamido nitrogen and the thiolato group. Because the lone pair on the amide nitrogen is delocalized over the aromatic ring of **3-Et$_4$N**, the N1–C3 bond is shorter in **3-Et$_4$N** (1.42 Å) than in **2-Et$_4$N** (1.444 Å). Furthermore, the C3–C3a (1.425 Å) bond in **3-Et$_4$N** is significantly longer than any of the other bonds in the aromatic ring (1.381–1.388 Å), suggesting a slight participation in the structure of a Cu^{I} quinone-imine species resulting from two-electron oxidation of the ligand by Cu^{III}. Similar oxidation has been previously observed in a Fe(NO) complex derived from the same ligand [22] and more generally from complexes derived from *o*-phenylene diamide ligands [23].

4. Conclusion

We report a new copper(III) complex with a N$_2$S$_2$ coordination with the most stabilized copper(III) center reported so far. Our results completes previous studies on copper(III) complexes and highlight the fact that with ligands occurring in natural systems, such as thiolato and deprotonated amides which can be found in the Cys–X–Cys sequence present in a number of (metallo)proteins, stable copper(III) derivatives may be obtained.

Supplementary material

CCDC 703711 and 703712 contain supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgments

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