Speciation of Copper(III)-Betaine Complexes as Starting Point for Electrochemical Copper Deposition from Ionic Liquids

Janine Richter, Maximilian Knies, and Michael Ruck*
The compound $[\text{Cu(bet)}_4]_2[\text{N(CH}_3)_3(\text{CH}_2\text{Cl})][\text{NTf}_2]_5$

Figure S1. Crystal structure of $[\text{Cu(bet)}_4]_2[\text{N(CH}_3)_3(\text{CH}_2\text{Cl})][\text{NTf}_2]_5$ with indicated unit cell in $b$ direction. H atoms are omitted for clarity.
Table S1. Selected interatomic distances $d$ (/ pm) for the complex cations in [Cu(bet)$_4$][N(CH$_3$)$_3$(CH$_2$Cl)][NTf$_2$]$_5$ 2.

| Atom pair | $d$  | Atom pair | $d$  |
|-----------|------|-----------|------|
| Cu1 O1    | 194.6(2) | Cu2 O9    | 195.5(2) |
| Cu1 O3    | 195.4(2) | Cu2 O11   | 194.8(2) |
| Cu1 O5    | 194.6(2) | Cu2 O13   | 195.6(2) |
| Cu1 O7    | 195.4(2) | Cu2 O15   | 195.3(2) |
| O1 C1     | 127.1(4) | O9 C21    | 127.0(4) |
| O2 C1     | 123.5(4) | O10 C21   | 123.6(4) |
| C1 C2     | 152.3(4) | C21 C22   | 153.1(4) |
| C2 N1     | 150.3(4) | C22 N5    | 150.6(4) |
| N1 C3     | 149.6(4) | N5 C23    | 150.2(4) |
| N1 C4     | 149.9(4) | N5 C24    | 150.3(4) |
| N1 C5     | 150.0(4) | N5 C25    | 149.6(4) |
| O3 C6     | 126.8(4) | O11 C26   | 127.4(4) |
| O4 C6     | 123.8(4) | O12 C16   | 123.6(4) |
| C6 C7     | 152.7(4) | C26 C27   | 152.8(4) |
| C7 N2     | 150.7(4) | C27 N6    | 151.0(4) |
| N2 C8     | 150.0(4) | N6 C28    | 150.5(4) |
| N2 C9     | 150.2(4) | N6 C29    | 150.2(4) |
| N2 C10    | 149.9(4) | N6 C30    | 150.0(4) |
| O5 C11    | 126.9(4) | O13 C31   | 127.3(4) |
| O6 C11    | 124.1(4) | O14 C31   | 123.5(4) |
| C11 C12   | 152.6(4) | C31 C32   | 153.6(4) |
| C12 N3    | 150.6(4) | C32 N7    | 150.4(4) |
| N3 C13    | 149.8(4) | N7 C33    | 149.8(4) |
| N3 C14    | 150.1(4) | N7 C34    | 150.1(4) |
| N3 C15    | 150.0(4) | N7 C35    | 149.8(4) |
| O7 C16    | 126.9(4) | O15 C36   | 127.1(4) |
| O8 C16    | 123.8(4) | O16 C36   | 123.7(4) |
| C16 C17   | 152.6(4) | C36 C37   | 152.7(4) |
| C17 N4    | 150.7(4) | C37 N8    | 151.2(4) |
| N4 C18    | 150.2(4) | N8 C38    | 150.2(4) |
| N4 C19    | 149.6(4) | N8 C39    | 149.8(4) |
| N4 C20    | 150.1(4) | N8 C40    | 150.1(4) |
| N13 C49   | 149.8(5) | N13 C50   | 147.7(6) |
| N13 C51   | 149.9(5) | N13 C52   | 149.2(5) |
| C52 Cl1   | 177.6(5) |           |       |
The compound \([\text{Cu}_3(\text{bet})_4\text{Cl}_3][\text{NTf}_2]_3\)

Figure S2. Crystal structure of \([\text{Cu}_3(\text{bet})_4\text{Cl}_3][\text{NTf}_2]_3\) with indicated unit cell in \(c\) direction. H atoms are omitted for clarity.

Table S2. Selected interatomic distances \(d\) (\(\text{pm}\)) for the \([\text{Cu}_3(\text{bet})_4\text{Cl}_3]^{3+}\) cation in \([\text{Cu}_3(\text{bet})_4\text{Cl}_3][\text{NTf}_2]_3\).

| Atom pair | \(d\) (\(\text{pm}\)) | Atom pair | \(d\) (\(\text{pm}\)) |
|-----------|----------------|-----------|----------------|
| Cu1 Cl1   | 246.4(1)      | Cu2 Cl1   | 243.3(1)      |
| Cu1 Cl2   | 231.3(1)      | Cu2 O2    | 195.7(2)      |
| Cu1 O1    | 197.0(2)      | Cu2 O3    | 196.0(2)      |
| Cu3 Cl2   | 226.5(1)      | Cu3 O4    | 193.7(2)      |
| N1 C1     | 150.1(3)      | N2 C6     | 149.5(3)      |
| N1 C2     | 150.2(3)      | N2 C7     | 150.1(3)      |
| N1 C3     | 149.8(3)      | N2 C8     | 149.6(3)      |
| N1 C4     | 150.9(3)      | N2 C9     | 150.9(3)      |
| C4 C5     | 152.0(3)      | C9 C10    | 152.2(3)      |
| C5 O1     | 124.7(2)      | C10 O3    | 125.0(3)      |
| C5 O2     | 124.9(3)      | C10 O4    | 125.4(3)      |
The compound \([\text{Cu}_2(\text{bet})_4]\text{[Cu}_6\text{Cl}_{10}]\)

**Figure S3.** Crystal structure of \([\text{Cu}_2(\text{bet})_4]\text{[Cu}_6\text{Cl}_{10}]\) 4 with indicated unit cell in \(b\) direction. H atoms are omitted for clarity.

**Table S3.** Selected interatomic distances \(d\) (/ pm) for \([\text{Cu}_2(\text{bet})_4]\text{[Cu}_6\text{Cl}_{10}]\) 4.

| Atom pair | \(d\) (pm) | Atom pair | \(d\) (pm) |
|-----------|----------|-----------|----------|
| Cu1 Cu1   | 269.1(1) | C7A N2    | 155.1(15) |
| Cu1 O1    | 195.1(4) | C7B N2    | 145.3(19) |
| Cu1 O2A   | 190.1(8) | N2 C8     | 155.1(13) |
| Cu1 O2B   | 209.0(9) | N2 C9     | 136.3(9)  |
| Cu1 O3    | 194.8(5) | N2 C10    | 143.8(10) |
| Cu1 O4A   | 213.5(10)| Cu1 Cl1   | 244.2(2)  |
| Cu1 O4B   | 184.7(8) | Cu2 Cl1   | 221.9(2)  |
| O1 C1     | 122.8(7) | Cu2 Cl2   | 222.4(2)  |
| O2A C1    | 135.3(11)| Cu2 Cl5A  | 226.8(2)  |
| O2B C1    | 122.2(10)| Cu2 Cl5B  | 250.3(18) |
| C1 C2     | 151.4(8) | Cu2 Cl5C  | 267.3(18) |
| C2 N1     | 150.9(7) | Cu3 Cl2   | 226.1(2)  |
| N1 C3     | 148.7(7) | Cu3 Cl3   | 226.5(2)  |
| N1 C4     | 149.2(8) | Cu3 Cl4   | 235.4(2)  |
| N1 C5     | 148.0(7) | Cu4 Cl3   | 224.4(2)  |
| O3 C6     | 120.8(9) | Cu4 Cl4   | 229.7(2)  |
| O4A C6    | 127.8(12)| Cu4 Cl5A  | 225.4(2)  |
| O4B C6    | 132.7(10)| Cu4 Cl5B  | 205.8(18) |
| C6 C7A    | 151(2)   | Cu4 Cl5C  | 194(3)    |
| C6 C7B    | 159(2)   |           |           |
Decomposition of [Hbet][NTf₂]

Figure S4. Evidence for the decomposition of [Hbet][NTf₂]: the gas evolving during the reaction of equimolar amounts of [Hbet][NTf₂] and [Hbet]Cl was conducted through (a) an aqueous potassium iodide solution and, subsequently, overlaid with n-hexane. Violet colouring of the upper phase indicated the oxidation of iodide to iodine by chlorine. (b) Conduction through an aqueous calcium hydroxide solution. White precipitation upon heating indicates the formation of carbon dioxide.

The dissolution of CuO + [Hbet][NTf₂] and CuO + [Hbet]₂[NTf₂]Cl in different solvents

Table S4. Observations upon the dissolution of CuO + [Hbet][NTf₂] and CuO + [Hbet]₂[NTf₂]Cl in different solvents

| Solvent     | CuO + [Hbet][NTf₂]                      | CuO + [Hbet]₂[NTf₂]Cl                     |
|-------------|----------------------------------------|------------------------------------------|
| Water       | Blue solution                          | Yellow solution, light brown solid       |
| Methanol    | Blue solution                          | Yellow solution                          |
| Ethanol     | Blue solution                          | Green solution, green-blue precipitation |
| 1-Propanol  | Low dissolution, yellow solution       | Slightly light green solution, green-blue precipitation |
| n-Butanol   | Negligible dissolution                 | Yellow solution, green-blue precipitation |
| Ethylene glycol | Blue solution                 | Orange solution                          |
| Ethyl acetate| Negligible dissolution                | Yellow solution, green-blue precipitation |
| Acetone     | Blue solution                          | Green-brown solution, green-blue precipitation |
| Acetonitrile| Blue solution                          | Green-brown solution, green-blue precipitation |
| Sulfolane   | Green solution                         | Green solution                           |
Figure S5. Experimental diffractograms of the precipitations obtained from the sample CuO + [Hbet]_2[NTf_2]Cl in different solvents in the range 5° ≤ 2θ ≤ 90°.

Figure S6. IR spectra of the precipitations obtained from the sample CuO + [Hbet]_2[NTf_2]Cl in different solvents compared to [Hbet][NTf_2] in the range 500 cm⁻¹ ≤ ν ≤ 4000 cm⁻¹. The position of ν_as COO (1770 cm⁻¹) is highlighted in green and the intensive bands originating from [NTf_2]⁻ are marked in orange.
Experimental infrared spectroscopy. IR spectroscopy was performed on a Bruker Vertex 70 FTIR spectrometer with attenuated total reflection (ATR) accessory in a radiation range from 500 cm\(^{-1}\) to 4000 cm\(^{-1}\) with 32 scans per measurement and a resolution of 2 cm\(^{-1}\). Data analysis was performed with the programme OPUS. Before the measurement, the sample was washed with the respective solvent and directly put on the ATR window.

Polishing of the steel electrodes

![Polished electrodes](image)

Figure S7. SEM images of the surface of the steel electrodes (a) before and (b) after the surface polishing process. The polishing leads to a significantly smoother surface and the removal of larger imperfections.

Copper deposition

![Experimental diffractogram](image)

Figure S8. Experimental diffractogram of the precipitation obtained from the sample CuO + aq. [Hbet][NTf\(_2\)] + [Hbet]Cl (D) in the range 5° ≤ 2\(θ\) ≤ 90° compared to the reflection pattern of copper calculated from single crystal data.
Figure S9. SEM image and EDX maps of a section of the steel electrode immersed into the solution CuO + [Hbet]Cl in aqueous [Hbet][NTf₂] for 30 minutes after rinsing with acetone.

Figure S10. SEM image and EDX maps of a section of the steel electrode immersed into the solution CuO + [Hbet][NTf₂] + [Hbet]Cl for 30 minutes at −0.5 V after rinsing with acetone.

Figure S11. SEM image of an isle section of the steel electrode immersed into the solution CuO + [Hbet][NTf₂] + [Hbet]Cl for 30 minutes at −0.5 V after rinsing with acetone with the EDX measuring points indicated. Overview of the results of EDX measurements at these points. The high amount of Fe originates from the steel electrode. A low amount of Cu is present in chloride-rich organic material.

| EDX composition / at. % | Element | Pos. 1 | Pos. 2 | Pos. 3 | Pos. 4 | Average |
|-------------------------|---------|--------|--------|--------|--------|---------|
|                         | C       | 36 %   | 28 %   | 38 %   | 24 %   | 32 %    |
|                         | N       | -      | 5 %    | -      | 4 %    | -       |
|                         | O       | 17 %   | 11 %   | 16 %   | 9 %    | 13 %    |
|                         | Cl      | 23 %   | 26 %   | 24 %   | 30 %   | 26 %    |
|                         | Fe      | 21 %   | 19 %   | 20 %   | 31 %   | 23 %    |
|                         | Cu      | 2 %    | 11 %   | 3 %    | 1 %    | 4 %     |
Figure S12. SEM image of a section between the isles of the steel electrode immersed into the solution CuO + [Hbet][NTf₂] + [Hbet]Cl for 30 minutes at −0.5 V after rinsing with acetone with the EDX measuring points indicated. Overview of the results of EDX measurements at these points. The high amount of Fe originates from the steel electrode. Cu is present besides organic material.

| Element | Pos. 1 | Pos. 2 | Pos. 3 | Average |
|---------|--------|--------|--------|---------|
| C       | 15 %   | 11 %   | 12 %   | 13 %    |
| O       | 18 %   | 27 %   | 26 %   | 24 %    |
| F       | 2 %    | -      | -      | -       |
| Fe      | 62 %   | 52 %   | 53 %   | 55 %    |
| Cu      | 3 %    | 10 %   | 9 %    | 7 %     |

Figure S13. SEM images and EDX maps of a section of the steel electrode immersed into the solution CuO + [Hbet][NTf₂] in sulfolane for 30 minutes at −3.0 V after rinsing with acetone.
Figure S14. SEM images and EDX maps of a section of the steel electrode immersed into the solution CuO + [Hbet][NTf₂] + [Hbet]Cl in sulfolane for 30 minutes at –3.0 V after rinsing with acetone.

Figure S15. SEM image and EDX maps of a section of the steel electrode immersed into the solution CuO + [Hbet][NTf₂] + [Hbet]Cl in acetonitrile for 30 minutes at –3.0 V after rinsing with acetone.