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Synthesis of new copper(i) based linear 1-D-coordination polymers with neutral imidazolinium-dithiocarboxylate ligands†

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An imidazolinium-dithiocarboxylate betaine has been applied for the first time as a ligand in a coordination polymer with copper(i) halides. The resulting 1-D-coordination compounds show a linear double chain structure with trigonally coordinated copper(i). The potential of the material as a heterogeneous photocatalyst was explored.

Imidazol(in)ium-dithiocarboxylate betaines (NHC·CS₂) are formal adducts of a corresponding imidazol(in)ium carbene and CS₂. The plane of the negatively charged CS₂ group is almost perpendicular to the positively charged imidazolium ring. Compared to their CO₂ and COS analogues,¹ the CS₂ betaines are known to be stable.^{1,2} After these betaines were described for the first time by Winberg and Coffmann,³ several groups focused their interests towards their chemical behaviour, for example, in (3 + 2) cycloadditions with electron deficient alkynes.⁴ Their application as ligands resulted in several reported metal complexes.⁵ The latter were investigated in a few catalytic reactions.⁶ Moreover, Delaude *et al.* have shown that stereoelectronic parameters of N-heterocyclic carbenes can be determined *via* XRD analysis of their CS₂ adducts due to their outstanding ability to crystallize.⁷

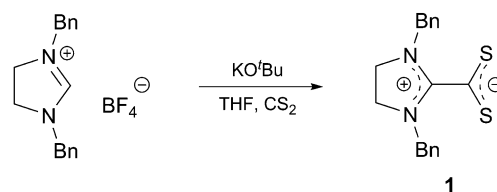
Based on our interest in these betaines, we have recently shown that symmetric imidazolinium-dithiocarboxylates can be successfully applied as organocatalysts for the TMSCN addition to aldehydes⁸ and enantiopure analogues as organocatalysts for an asymmetric Staudinger reaction.⁹ Furthermore, we were able to synthesize a novel class of ionic liquids *via* methylation of the

corresponding betaines. Spectroscopic analysis showed that the resulting red cations have different absorption maxima depending on the solvent and the lipophilicity of the corresponding counter anions.¹⁰ More recently, we reported the application of NHC·CS₂ as colorimetric chemosensors for the detection of Hg²⁺ and Ag⁺.¹¹ As a contribution to a better understanding of the properties of these betaines, we present here their application as neutral ligands for the preparation of copper(i) based 1-D-coordination polymers.

Coordination polymers represent an increasingly important class of new functional materials, and the number of publications has increased exponentially since the mid 1990's.¹² This is due to their high potential in magnetic materials,¹³ catalysis,¹⁴ gas sorption,¹⁵ sensing¹⁶ and optoelectronics.¹⁷ In the present study, the potential of the new material was investigated as a heterogeneous photocatalyst.

Our approach starts with the synthesis¹⁰ (Scheme 1) of the betaine Bz₂ImCS₂ (1) and the determination of its hitherto unknown molecular structure (Fig. 1) for a comparative structural discussion with copper complexes derived thereof.

Molecule 1 shows equal C–S and C–N bond lengths of 1.669(1) and 1.321(1) Å, respectively, and S–C–S as well as N–C–N valence angles of 123.5(1)° and 112.8(1)° (Table 1). The CS₂/CN₂ planes deviate significantly from an orthogonal arrangement exhibiting a dihedral angle of 79.3°. These parameters are comparable to structural data of other crystallised betaines with aromatic and aliphatic N substituents with dihedral angles ranging from 76.5° to 87.9°. ^{4c,4e,7,18}

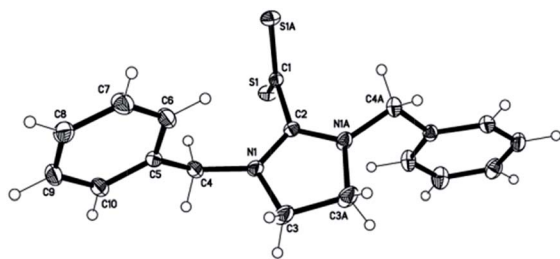


Scheme 1 Synthesis of the betaine Bz₂ImCS₂ (1).

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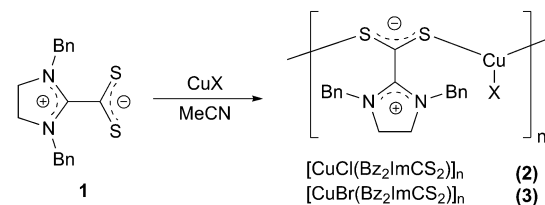
† Electronic supplementary information (ESI) available. Anisotropic displacement ellipsoids are drawn at the 50% probability level. For experimental procedures, characterization data and crystallographic details (CCDC 1008787, 1000389 and 1000390), see DOI: 10.1039/c4ra09033k

Fig. 1 Molecular structure of **1** in the crystalline state.[†]Table 1 Selected bond lengths/Å and angles/° for **1**, **2** and **3**

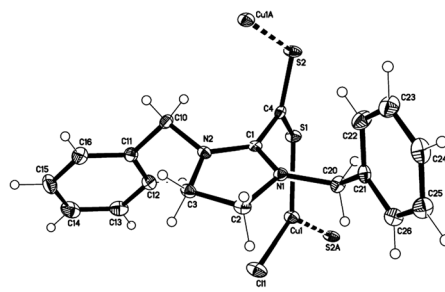
Atoms	Bond length	Atoms	Bond angle
1			
S1–C1	1.669(1)	S1–C1–S1A	130.68(10)
C1–C2	1.493(2)	S1–C1–C2	114.66(5)
C2–N1	1.321(1)	C1–C2–N1	124.01(8)
N1–C3	1.470(2)	N1–C2–N1A	111.97(15)
C3–C3A	1.530(3)	C2–N1–C3	110.98(11)
		N1–C3–C3A	102.92(7)
2			
Cu1–S1	2.244(1)	S1–Cu1–S2A	107.41(3)
Cu1–S2A	2.243(1)	S1–Cu1–Cl1	126.89(3)
Cu1–Cl1	2.194(1)	S2A–Cu1–Cl1	125.66(3)
C4–S1	1.682(3)	C4–S1–Cu1	112.77(10)
C4–S2	1.678(3)	C4–S2–Cu1A	113.52(11)
C1–C4	1.482(4)	S1–C4–S2	124.18(18)
C1–N1	1.317(4)	S1–C4–C1	117.9(2)
C1–N2	1.322(3)	S2–C4–C1	117.9(2)
		C4–C1–N1	123.8(3)
		C4–C1–N2	124.0(3)
		N1–C1–N2	112.2(2)
3			
Cu1–S1	2.244(5)	S1–Cu1–S2A	110.53(2)
Cu1–S2A	2.245(4)	S1–Cu1–Br1	125.39(1)
Cu1–Br1	2.323(3)	S2A–Cu1–Br1	124.02(2)
C4–S1	1.680(2)	C4–S1–Cu1	114.49(5)
C4–S2	1.683(2)	C4–S2–Cu1A	115.11(5)
C1–C4	1.487(2)	S1–C4–S2	123.55(9)
C1–N1	1.319(2)	S1–C4–C1	118.50(11)
C1–N2	1.316(2)	S2–C4–C1	117.95(11)
		C4–C1–N1	123.45(13)
		C4–C1–N2	123.78(13)
		N1–C1–N2	112.78(13)

Reaction of **1** with CuX (X = Cl, Br) in acetonitrile (Scheme 2) leads to deep coloured (red, X = Cl; brown, X = Br) suspensions, from which after filtration and subsequent treatment with diethyl ether results in brown (X = Cl) or orange (X = Br) crystals that separate in the course of a few days. Interestingly, X-ray diffraction studies revealed that compounds **2** and **3** are coordination polymers of composition $[\text{CuX}(\text{Bz}_2\text{ImCS}_2)]_n$, in which single 1D-chains are formed by alternately arranged $\{\text{CuX}\}$ units and betaine ligands (Fig. 2).

Both coordination polymers crystallise isostructurally in the triclinic space group $P\bar{1}$ with Cu(I) atoms adopting trigonal-planar coordination geometries within their S_2X donor sets



Scheme 2 Synthesis of Cu(I) coordination polymers (X = Cl, Br).

Fig. 2 Section of the structure of **2** in the crystalline state.[†]

(mean valence angle 119.99° within **2** and 119.98° within **3**; see Table 1). The Cu–S bonds are equal in length and average to 2.244 Å in both **2** and **3**. Pairs of polymeric chains are linked *via* intermolecular $\text{C}_{\text{benzyl}}\text{H}\cdots\text{S}$ interactions with $\text{H}\cdots\text{S}$ distances of 2.84 (**2**) and 2.79 Å (**3**) and $\text{C-H}\cdots\text{S}$ angles of $141.9(2)^\circ$ (**2**) and $143.5(1)^\circ$ (**3**) to form endless double chains (Fig. 3). Interestingly, the bond lengths within the CS_2 and CN_2 units of the coordinated and free betaine show no significant differences (Table 1). Only the S–C–S bond angles contract from $130.7(1)^\circ$ to $124.1(2)^\circ$ in **2** and to $123.5(1)^\circ$ in **3**. Furthermore, the CS_2/CN_2 planes are now nearly orthogonally arranged with dihedral angles of 87.1° in both coordination polymers.

To the best of our knowledge, **2** and **3** are the first imidazolinium dithiocarboxylate copper complexes known so far. Coordination polymers with other dithiocarboxylates and copper are also not known. In this context, it should be mentioned that several mono-¹⁹ and polynuclear^{19b,20} copper dithiocarboxylate complexes as well as other dithiocarboxylate compounds with metals, such as gold,²¹ manganese,²² cadmium²³ and mercury²⁴ have been described.

The one-dimensional chain within crystals of **2** and **3** consisting of alternating Cu(I) and sp^2 hybridized negatively charged CS_2 units define an infinite 1-dimensional $\text{d}-\pi$ system. Taking into account that copper containing 1-D-coordination polymers have shown potential as catalysts²⁵ and have been applied as a photoactive material for dye-sensitized solar cells,²⁶ it was decided to investigate the potential of the new material as a heterogeneous photocatalyst in case of a thiol–ene reaction. This reaction is of exceptional importance because of its wide spectrum of applications in synthetic sulphur chemistry.²⁷ In a preliminary study, the addition of thiophenol to styrene was explored with white light (Scheme 3). This reaction has been, for example, catalysed with the photocatalyst $\text{Ru}(\text{bpz})_3^{2+}$ under homogenous conditions.²⁸ However, the application of reusable



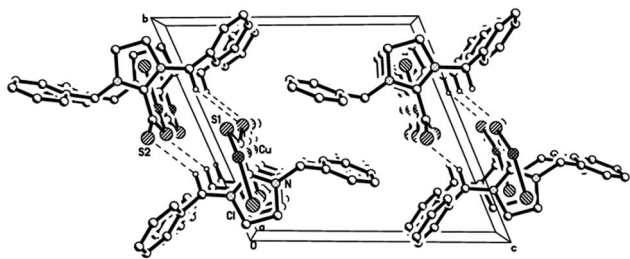
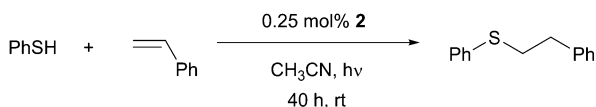


Fig. 3 Crystal packing of **2** and **3** viewed along with intermolecular $C_{\text{benzyl}}-H \cdots S$ contacts shown as dotted lines. H-atoms not involved in bonding are omitted.



Scheme 3 Catalysed thiol-ene reaction of thiophenol with styrene.

heterogeneous systems based on low-cost and better biocompatible metals would be beneficial.

The existence of **2** and **3** is restricted to the crystalline state. Any attempts to dissolve the compounds are expected to result in depolymerisation reactions. ES-MS and NMR analysis (see ESI Fig. S1–S4[†]) of solutions obtained from reactions of **2** and **3** with dimethylsulfoxide or methanol confirm the formation of the mononuclear complexes $[Cu(Bn_2ImCS_2)_2]^+[CuX_2]^-$ ($X = Cl, Br$). This observation supports our assumption that a breakup of the 1-D-coordination polymer takes place upon solvent attack. The stability of **2** and **3** towards acetonitrile allowed for probing the crystals as heterogeneous catalyst. In the case of **2**, the formation of the photoproduct in 60% yield after 40 h was observed. A control reaction in the absence of light gave a yield of 23%, while under light conditions in the absence of crystalline **2** a yield of 34% was found. When the reaction was carried out with a solution obtained from **2** and dichloromethane, no catalytic activity was found, again suggesting that the electronic properties of the intact copper coordination polymer in the solid state are essential for the catalytic activity. Compound **3** showed no activity. A difference in the catalytic activity of different halide ligands on transition metal complexes is rare but not unknown, and cannot always be predicted.²⁹ Although the catalytic activity of compound **2** is moderate, this is the first example of a coordination polymer containing copper suited to be a heterogeneous photo-redox catalyst.

Conclusions

In conclusion, an imidazolium-dithiocarboxylate has been applied for the first time as a ligand towards copper(i) halides. The resulting 1-D-coordination polymers **2** and **3** show a linear structure with $\{CuX\}$ units attached to negatively charged CS_2 donor groups of the betaine resulting in an infinite d- π system. The potential of the material as a heterogeneous photocatalyst was shown in a radical thiol-ene reaction for the first time. Presently, we investigate the catalytic activity of our material with

other thiols and try to optimize the reaction conditions also by using other imidazolium-dithiocarboxylates. Besides investigations directed towards regioselective photoredox reactions, the use as dyes in TiO_2 based photovoltaic cells is explored as well.

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