The first crystallographically-characterised Cu(II) xanthate

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Metal xanthates are becoming the precursors of choice for the formation of metal sulphide materials [1,2], as their low decomposition temperatures in relation to the more established dithiocarbamates make them compatible with organic polymers for the genesis of hybrid devices [3]. Moreover, they can also be decomposed by UV light, which has recently enabled hierarchical metal sulphide nanostructures to be fabricated at room temperature [4]. While the chemistry of metal xanthates is generally well-developed for much of the Periodic Table [5], there are still systems which have been resistant to development over a number of years. This is particularly so for Cu(II), a situation made more surprising by the important role copper(I) xanthates play as single-source precursors (SSPs) in the fabrication of key metal sulphides such as CuS [6], CuInS2 (CIS) [7,8] and Cu2ZnSnS4 (CZTS) [9–11].

While the literature abounds with the synthesis and structural characterisation of Cu(I) xanthates, either in native form [11–13] or more commonly stabilised by phosphine [14–24], and, occasionally, nitrogen donors [25], reports on the synthesis of Cu(II) xanthates are sketchy. Due to their importance in the colourimetric determination of various metals, several reports have dealt with the spectrochemical analysis of mixtures of Cu(II) xanthates and ROCS2, though the species present in solution were never isolated [26–29]. Where claims for isolated Cu(II) xanthates exist, characterisation has been limited to measurements of their IR, UV spectra and/or magnetic moments [30–35]. To date, the Cambridge Crystallographic Database (CCDC) contains only one entry for such a species [Cu(S2COEt)2(C11H12)]2−1,10-phenanthroline, however the Centre reports "no reply to request for data" [36]. The EPR spectra of Cu(II) xanthates [37], commonly stabilised by incorporation into Ni(II) xanthate matrices [38,39], has been reported, but not the isolation of a pure copper(II) complex. Moreover, one such report [39], along with others [27,32,35], highlights the instability of Cu(II) xanthates with respect to reduction and concomitant formation of the xanthogen, ROC(S)SSC(S)OR.

In this short report, we detail the synthesis and first crystallographic characterisation of a Cu(II) xanthate, stabilised by the bidentate donor TMEDA, namely Cu(S2COEt)2·TMEDA (1).

1. Results and discussion

Cu(S2COEt)2·TMEDA (1) was synthesised from reaction of CuCl2 and two equivalents of K2S2COEt with immediate addition of one equivalent of TMEDA.

\[
\text{CuCl}_2 + 2\text{K}_2\text{S}_2\text{COEt} \xrightarrow{\text{CH}_3\text{OH}, \text{TMEDA}} \text{Cu(S}_2\text{COEt)}_2 \cdot \text{TMEDA}
\]

The product, a green solid, was isolated in 62% yield and is the first authenticated Cu(II) xanthate. 1 has a magnetic moment (1.77 BM) consistent with one unpaired electron on copper and the crystalline material gave satisfactory elemental analysis. 1 is stabilised against reduction to Cu(I) by the TMEDA donor, but is still quite unstable. It is best stored at −20 °C, while at room temperature it decomposes over several days to a red solid, which elemental analysis and EDX measurements suggest is a mixture of Cu(S2COEt)2·TMEDA and ca. 1/4 S8 [found (calc. CuH2N2S2O5Cu): C 28.3(29.7), H 6.6(5.8), N 7.6(7.7) %; EDX, Cu:S 1:4.5]. While this behaviour is consistent with the TGA (which shows evident loss of TMEDA at 50 °C; vide infra, Fig. 2) and anticipated chemical reactivity [reduction to Cu(I)], the nature of this red solid remains unknown.

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In an earlier report, reaction of CuCl2 with K2S2COR (R = substituted aryl group) yielded a green solution but from which only the Cu(I) product Cu2S2COR was isolated, confirming the importance of the TMEDA in stabilising the Cu(II) product against reduction (and oxidation of the xanthate to the xanthogen ROC(S)SSC(S)OR) [35]. The same report did, however, claim the formation of Cu(S2COCH2Me-4)2 as dark brown crystals from the oxidative insertion of Cu(0) into the S–S bond of [4-MeC6H4OC(S)S]2, though only infrared and microanalytical data were presented by way of characterisation [35].

The composition and structure of 1 has been unambiguously confirmed by X-ray crystallography (Fig. 1). The asymmetric unit of 1 consists of one half of the molecule, the remainder generated by a two-fold symmetry operation: 1

\[ x, y, \frac{3}{2} \]

with the geometry at the metal is distorted octahedral, with the shorter and more symmetrical i.e. more iso-bidentate chelation [Ni2.4525(12), 2.4932(12) Å] [41]

\[ r \]

which clearly show localisation of the C–S bonds [S(1) 2.3357(4), S(2) 2.9097(4) Å], which is also apparent in the two C–S bonds, which clearly show localisation of the C–S [S(1) 2.189(4) Å]

\[ r \]

and C=O bonds [S(2) 2.9097(4) Å], which also appears in the two C–S bonds, which clearly show localisation of the C–S [S(1) 2.189(4) Å] and C=O bonds [S(2) 2.9097(4) Å]. Such an asymmetry might, however, be expected as a result of the Jahn–Teller distortion inherent to a \( d^8 \) configuration. The Cu–N bond [Cu–N 2.0876(14) Å] is, however, shorter than in both the related Ni(S2COEt)2 · TMEDA complexes [Fe–N 2.2457(10) Å] [41], though in both these cases the M–S bonds are both shorter and more symmetrical i.e. more iso-bidentate chelation [Ni–S 2.4525(12), 2.4932(12) Å] [40]; Fe–S 2.4832(3), 2.6210(3) Å [41].

Thermal decomposition of 1 (Fig. 2) reveals a multi-stage process. Decomposition begins immediately on heating, consistent with the need to keep the compound cold to maintain its integrity. Up to ca. 110 °C the weight loss is consistent with elimination of ligated TMEDA (loss observed 33.1%, theoretical 27.5%) overlapping with the onset of decomposition of the xanthate moiety by a Chugaev mechanism [2]. By ca. 150 °C, these processes are complete (loss observed 43.0%, loss of TMEDA + 2 C2H4 = 40.8%), followed by loss of species such as COS to leave either CuS or Cu2S. The residual weights are somewhat inconclusive: at 300 °C the residual weight (21.1%) is closest to that expected for CuS (22.6%) while at 450 °C it most closely matches Cu2S (obs: 16.4, theo: 18.8%). However, PXRD of the residues at both temperatures (e.g. Fig. 3a) is consistent with Cu2S. These data also suggest some modest volatility for 1.

1 has successfully been used to deposit a thin film by aerosol-assisted chemical vapour deposition (AACVD) at 450 °C. The yellow film consists of grains of ca. 150 nm diameter (Fig. 4a) whose PXRD is best indexed to stoichiometric Cu1.95S, though quantitative EDX indicates

\[ \text{Cu:S} = 2:1 \]

so that the composition of the film is Cu2S with a C2H4 content of ca. 10% of the total weight (loss observed 43.0%, loss of TMEDA + 2 C2H4 = 40.8%). By ca. 150 °C, these processes are complete (loss observed 43.0%, loss of TMEDA + 2 C2H4 = 40.8%), followed by loss of species such as COS to leave either CuS or Cu2S. The residual weights are somewhat inconclusive: at 300 °C the residual weight (21.1%) is closest to that expected for CuS (22.6%) while at 450 °C it most closely matches Cu2S (obs: 16.4, theo: 18.8%). However, PXRD of the residues at both temperatures (e.g. Fig. 3a) is consistent with Cu2S. These data also suggest some modest volatility for 1.

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under an atmosphere of N2. Pyris software was used to record and inter-
corded using a Perkin Elmer TGA 4000 Thermogravimetric Analyser.
The TGA furnace operates at temperatures ranging from 30 to 1000 °C
Spectrometer. Spectra were recorded in CH2Cl2. TGA spectra were re-
by London Metropolitan University Elemental Analysis Service, UK.
Melting Point Apparatus. Elemental analyses were performed externally
powder system (Innovative Technology Inc., MA, USA) and degassed under argon
15 kV. SEM imaging, EDX measurements and PXRD.

2. Experimental

2.1. General procedures

All operations were performed under an atmosphere of dry argon
standard Schlenk line and glovebox techniques. Dichloromethane
was dried using a commercially available solvent purification system
Elemental analyses were performed externally
with a nitrogen carrier

Crystallization data for
CCDC no. 994211

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>1</th>
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<tr>
<td>C12H26CuN2O2S4</td>
<td>C 34.3(34.1), H 6.29(6.21), N 6.54(6.64).</td>
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Immediately causing dissolution of the reagents and formation of a
solution. The solution was left stirring for 30 min by which time the
solution was dark green. The mixture was canulla filtered and the
volume reduced by half. Crystals obtained were obtained on cooling to
−20 °C (0.97 g, 62%, m.p. 66–68 °C). Analysis, found (calc for
C12H26Cu2N2S4O2): C 34.3(34.1), H 6.29(6.21), N 6.54(6.64), µeff 1.77
BM (Evans method).

2.2. Crystallography

Experimental details relating to the single-crystal X-ray crystallo-
graphic study is given in Table 1. Data were collected on a Nonius
Kappa CCD diffractometer at 150(2) K using Mo-Kα radiation
λ = 0.71073 Å; Structure solution followed by full-matrix least-
squares refinement was performed using the WinGX-1.70 suite of
programmes [42].

2.3. Thin film deposition by CVD

All AACVD experiments were performed on an ElectroGas CVD Rig
using an ultrasonic bath to generate an aerosol. Experiments were
performed at 400 °C and 450 °C for a duration of 1 h with a nitrogen car-
rier gas flow rate of 0.3 L/min using ca. 50 mL of a 0.05 M solution of
Cu(S2COEt)2·TMEDA in THF. The resulting films were analysed by
SEM imaging, EDX measurements and PXRD.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.
doi.org/10.1016/j.inoche.2014.09.003. This data include MOL file and
InChIKey of the most important compounds described in this article.

References

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