The first crystallographically-characterised Cu(II) xanthate

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ABSTRACT

The copper(II) xanthate Cu(S\textsubscript{2}CO\textsubscript{Et})\textsubscript{2}·TMEDA (1) (TMEDA = N,N-tetramethylethylenediamine) has been synthesised and is the first structurally-characterised xanthate of copper in the +2 oxidation state. 1 has an octahedral cis, cis, cis-ligand arrangement about the metal, in which xanthate chelation is markedly asymmetric. Both bulk thermal decomposition and film growth by aerosol-assisted chemical vapour deposition (AACVD) using 1 as precursor lead to the formation of CuS.

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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 diithiocarbamates 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 such a species Cu(S\textsubscript{2}CO\textsubscript{Et})\textsubscript{2}·1,10-phenanthroline, however 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) salts and ROC(S)SSC(S)OR. Despite this, 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(S\textsubscript{2}CO\textsubscript{Et})\textsubscript{2}·TMEDA (1).

1. Results and discussion

Cu(S\textsubscript{2}CO\textsubscript{Et})\textsubscript{2}·TMEDA (1) was synthesised from reaction of CuCl\textsubscript{2} and two equivalents of KS\textsubscript{2}CO\textsubscript{Et} with immediate addition of one equivalent of TMEDA.

\[ \text{CuCl}_2 + 2\text{KS}_2\text{CO}_\text{Et} \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} \text{Cu(S}_2\text{CO}_\text{Et})_2 \cdot \text{TMEDA} \]

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(S\textsubscript{2}CO\textsubscript{Et})\textsubscript{2}·TMEDA and ca. 1/4 S\textsubscript{8} [found (calc. Cu\textsubscript{4}H\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: 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; videlic infra, Fig. 2) and anticipated chemical reactivity [reduction to Cu(I)], the nature of this red solid remains unknown.
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)SC(S)OR) [35]. The same report did, however, claim the formation of Cu₅S₄OC₆H₄Me-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

\[ \text{Cu} - \text{S}[\text{1}] - \text{Cu} - \text{S}[\text{2}] - 68.127(13)° \]

which clearly show localisation of the C – S bond of \[ \text{S}[\text{1}] - \text{C}(\text{1}) 1.7083(17) Å \]

and C=S bonds \[ \text{S}[\text{2}] - \text{C}(\text{1}) 1.6756(17) Å \]. Such an asymmetry might, however, be expected as a result of the Jahn-Teller distortion inherent to a \[ d^2 \] configuration. The Cu – N bond [Cu – N 2.0876(14) Å] is, however, shorter than in both the related Ni(S₅COH₄)₂ · TMEDA [Ni – N 2.183(4) Å] [40] and Fe(S₂COEt)₂ · TMEDA complexes [Fe – N \( 2.4257(10) \) 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 Cu₂S, though quantitative EDX indicates


![Fig. 2. TGA of 1.](image2)

![Fig. 3. PXRD of (bottom) the product of the thermal decomposition of 1 at 350 °C (indexed to Cu₂S, PDF 89-2072) and (top) the thin film deposited on glass at 450 °C using 1 as precursor (indexed to Cu₂S, PDF 84-1770).](image3)
a copper-rich Cu$_2$S composition; deposition at 400 °C does not materially alter the appearance of the film, but EDX now corresponds to a Cu$_{2.3}$S stoichiometry. Both films, but particularly that deposited at 450 °C, show a strong (200) preferred orientation (Fig. 3b). The thin film grown at 450 °C is ca. 240 nm thick, corresponding to a growth rate of ca. 4 nm min$^{-1}$.

2. Experimental

2.1. General procedures

All operations were performed under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Dichloromethane was dried using a commercially available solvent purification system (Innovative Technology Inc., MA, USA) and degassed under argon prior to use. Melting points were determined using a Stuart SMP10 Melting Point Apparatus. Elemental analyses were performed externally by London Metropolitan University Elemental Analysis Service, UK. NMR spectra were recorded on a Bruker Avance 400 MHz FT-NMR Spectrometer. Spectra were recorded in CH$_2$Cl$_2$. TGA spectra were recorded using a Perkin Elmer TGA 4000 Thermogravimetric Analyser. Spectra were performed at 400 °C and 450 °C for a duration of 1 h with a nitrogen carrier gas flow rate of 0.3 L/min using ca. 50 mL of a 0.05 M solution of Cu(S$_2$COEt)$_2$·TMEDA in THF. The resulting films were analysed by SEM imaging, EDX measurements and PXRD.

2.2. Crystallography

Experimental details relating to the single-crystal X-ray crystallographic study is given in Table 1. Data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ 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 carrier gas flow rate of 0.3 L/min using ca. 50 mL of a 0.05 M solution of Cu(S$_2$COEt)$_2$·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
