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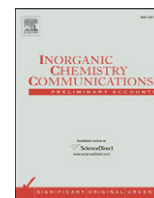
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The first crystallographically-characterised Cu(II) xanthate



Andrew L. Johnson, Michael S. Hill ^{*}, Gabriele Kociok-Köhn, Kieran C. Molloy, Anna L. Sudlow

Centre for Precursor Studies, Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

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ABSTRACT

The copper(II) xanthate $\text{Cu}(\text{S}_2\text{COEt})_2 \cdot \text{TMEDA}$ (**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 Cu_2S .

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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], CuInS_2 (CIS) [7,8] and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) [9–11].

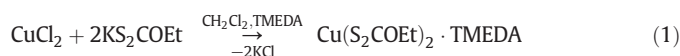
While the literature abounds with the synthesis and structural characterisation of Cu(I) xanthates, either in native form [11–13] or more commonly stabilised by phosphine [14–24], and, occasionally, nitrogen donors [25], reports on the synthesis of Cu(II) xanthates are sketchy. Due to their importance in the colourimetric determination of various metals, several reports have dealt with the spectrochemical analysis of mixtures of Cu(II) salts and ROCS_2^- , 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 [$\text{Cu}(\text{S}_2\text{COC}_6\text{H}_{11})_2 \cdot 1,10\text{-phenanthroline}$], 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 $\text{Cu}(\text{S}_2\text{COEt})_2 \cdot \text{TMEDA}$ (**1**).

1. Results and discussion

$\text{Cu}(\text{S}_2\text{COEt})_2 \cdot \text{TMEDA}$ (**1**) was synthesised from reaction of CuCl_2 and two equivalents of KS_2COEt with immediate addition of one equivalent of 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 $\text{Cu}(\text{S}_2\text{COEt})\text{TMEDA}$ and ca. 1/4 S_8 [found (calc. $\text{C}_9\text{H}_{21}\text{N}_2\text{OS}_4\text{Cu}$): 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.

^{*} Corresponding author.

E-mail address: m.s.hill@bath.ac.uk (M.S. Hill).

In an earlier report, reaction of CuCl_2 with KS_2COR ($R =$ substituted aryl group) yielded a green solution but from which only the Cu(I) product CuS_2COR 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 $\text{Cu(S}_2\text{COC}_6\text{H}_4\text{Me-4)}_2$ as dark brown crystals from the oxidative insertion of Cu(0) into the S-S bond of $[\text{4-MeC}_6\text{H}_4\text{OC(S)S}]_2$, 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 axis passing through the copper and the mid-point of the C-C bond of TMEDA. The geometry at the metal is distorted octahedral, with the ligands disposed in a *cis, cis, cis* arrangement. The bite angle of the xanthate $[\text{S(1)-Cu-S(2)} 68.127(13)^\circ]$ also means that the *trans-S(2)-Cu-S(2')* angle deviates significantly from the ideal $[\text{S(2)-Cu-S(2')} 150.042(19)^\circ]$, while the remaining *trans* angles $[\text{N-Cu-S(1)}, \text{N'-Cu-S(1')} 167.97(4)^\circ]$ are somewhat more regular. The xanthate ligand bonds in a markedly anisobidentate manner $[\text{Cu-S(1)} 2.3357(4), \text{Cu-S(2)} 2.9097(4) \text{ \AA}]$, which is also apparent in the two C-S bonds, which clearly show localisation of the C-S $[\text{S(1)-C(1)} 1.7083(17) \text{ \AA}]$ and C=S bonds $[\text{S(2)-C(1)} 1.6756(17) \text{ \AA}]$. Such an asymmetry might, however, be expected as a result of the Jahn-teller distortion inherent to a d^9 configuration. The Cu-N bond $[\text{Cu-N} 2.0876(14) \text{ \AA}]$ is, however, shorter than in both the related $\text{Ni(S}_2\text{COPr}^i)_2 \cdot \text{TMEDA}$ $[\text{Ni-N} 2.183(4), 2.189(4) \text{ \AA}]$ [40] and $\text{Fe(S}_2\text{COEt)}_2 \cdot \text{TMEDA}$ complexes $[\text{Fe-N} 2.2457(10) \text{ \AA}]$ [41], though in both these cases the M-S bonds are both shorter and more symmetrical i.e. more iso-bidentate chelation $[\text{Ni-S} 2.4525(12), 2.4932(12) \text{ \AA}]$ [40]; $[\text{Fe-S} 2.4832(3), 2.6210(3) \text{ \AA}]$ [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 $\text{TMEDA} + 2 \text{ C}_2\text{H}_4 = 40.8\%$), followed by loss of species such as COS

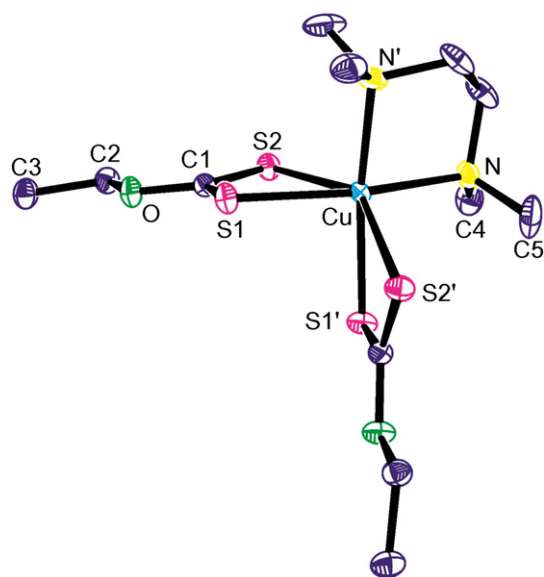


Fig. 1. The structure of **1** showing the labelling scheme used in the text; thermal ellipsoids are at the 50% probability level. Selected metrical data: $\text{Cu-N} 2.0876(14)$, $\text{Cu-S(1)} 2.3357(4)$, $\text{Cu-S(2)} 2.9097(4)$, $\text{S(1)-C(1)} 1.7083(17)$, $\text{S(2)-C(1)} 1.6756(17) \text{ \AA}$; $\text{N-Cu-S(1)} 167.97(4)$, $\text{N-Cu-S(2)} 100.45(4)$, $\text{N-Cu-N'} 85.35(9)$, $\text{N-Cu-S(1')} 93.10(4)$, $\text{S(1)-Cu-S(2)} 68.127(13)$, $\text{S(1)-Cu-S(1')} 90.85(2)$, $\text{S(1')-Cu-S(2)} 90.559(14)$, $\text{S(2)-Cu-S(2')} 150.042(19)$, $\text{N(1')-Cu-S(2)} 101.46(4)^\circ$. Symmetry operation: $1 - x, y, 3/2 - z$.

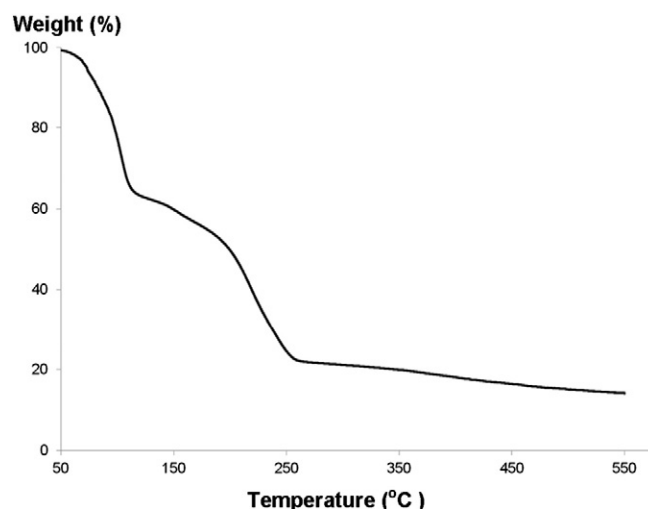


Fig. 2. TGA of **1**.

to leave either CuS or Cu_2S . 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 Cu_2S (obs: 16.4, theo: 18.8%). However, PXRD of the residues at both temperatures (e.g. Fig. 3a) is consistent with Cu_2S . 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 Cu_2S , though quantitative EDX indicates

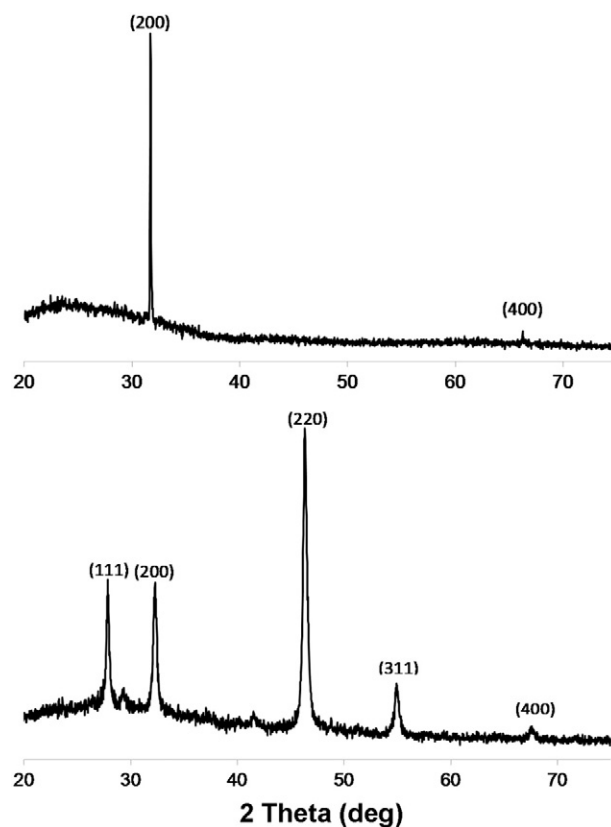


Fig. 3. PXRD of (bottom) the product of the thermal decomposition of **1** at 350°C (indexed to $\text{Cu}_{1.95}\text{S}$, PDF 89-2072) and (top) the thin film deposited on glass at 450°C using **1** as precursor (indexed to Cu_2S , PDF 84-1770).

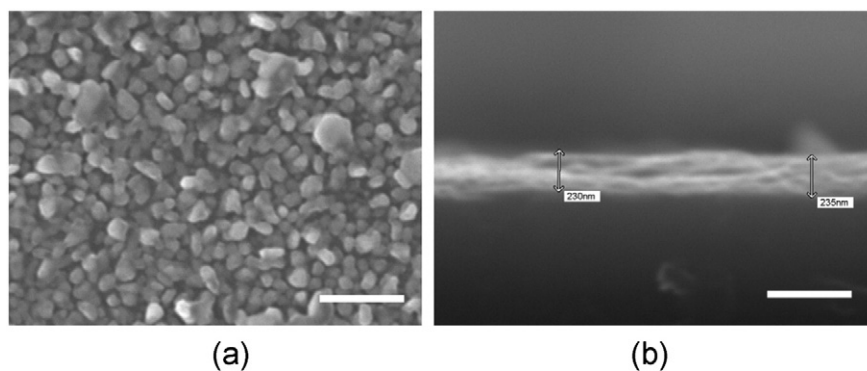


Fig. 4. SEM of the Cu_2S film deposited on glass by AACVD at $450\text{ }^\circ\text{C}$ using **1** as precursor.

a copper-rich $\text{Cu}_{2.3}\text{S}$ composition; deposition at $400\text{ }^\circ\text{C}$ does not materially alter the appearance of the film, but EDX now corresponds to a $\text{Cu}_{2.02}\text{S}$ stoichiometry. Both films, but particularly that deposited at $450\text{ }^\circ\text{C}$, show a strong (200) preferred orientation (Fig. 3b). The thin film grown at $450\text{ }^\circ\text{C}$ 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 utilising 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_2Cl_2 . TGA spectra were recorded using a Perkin Elmer TGA 4000 Thermogravimetric Analyser. The TGA furnace operates at temperatures ranging from 30 to $1000\text{ }^\circ\text{C}$ under an atmosphere of N_2 . Pyris software was used to record and interpret the data. SEM images and EDX measurements were taken on a JEOL JSM 6480LV Scanning Electron Microscope using an accelerating voltage of 15 kV.

Synthesis of $\text{Cu}(\text{S}_2\text{COEt})_2 \cdot \text{TMEDA}$ (**1**): CuCl_2 (0.50 g, 3.7 mmol) and KS_2COEt (1.19 g, 7.4 mmol) were stirred in CH_2Cl_2 (20 mL) to form a brown/yellow suspension. TMEDA (0.43 g, 3.7 mmol) was added

immediately causing dissolution of the reagents and formation of a green solution. The solution was left stirring for 30 min by which time the solution was dark green. The mixture was cannula filtered and the volume reduced by half. Crystals obtained were obtained on cooling to $-20\text{ }^\circ\text{C}$ (0.97 g, 62%, m.p. $66\text{--}68\text{ }^\circ\text{C}$). Analysis, found (calc for $\text{C}_{12}\text{H}_{26}\text{CuN}_2\text{O}_2\text{S}_4$): C 34.3(34.1), H 6.29(6.21), N 6.54(6.64). μ_{eff} 1.77 BM (Evans method).

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 $150(2)\text{ K}$ using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). 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 $400\text{ }^\circ\text{C}$ and $450\text{ }^\circ\text{C}$ 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 $\text{Cu}(\text{S}_2\text{COEt})_2 \cdot \text{TMEDA}$ 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.

Table 1
Crystallographic data for **1**.

	1
Chemical formula	$\text{C}_{12}\text{H}_{26}\text{CuN}_2\text{O}_2\text{S}_4$
Formula mass	422.13
Crystal system	Monoclinic
$a/\text{\AA}$	21.1341(3)
$b/\text{\AA}$	8.0275(1)
$c/\text{\AA}$	14.9706(2)
$\beta/^\circ$	133.318(1)
Unit cell volume/ \AA^3	1847.86(5)
Space group	$\text{C2}/c$
Absorption coefficient, μ/mm^{-1}	1.638
No. of reflections measured	13265
No. of independent reflections	2113
R_{int}	0.0519
Final R_1 values ($I > 2\sigma(I)$)	0.0270
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0660
Final R_1 values (all data)	0.0304
Final $wR(F^2)$ values (all data)	0.0679
Goodness of fit on F^2	1.119
CCDC no.	994211

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