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tetrahedro-[Tetrakis{(1-methylimidazoline-2(3*H*)-thionato)copper(I)}]: electrochemical synthesis, thermal analysis, cyclic voltammetry and crystal structure

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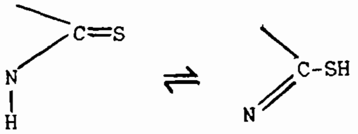
Abstract

The complex, [{Cu(mimt)}$_4$], has been electrochemically synthesised in acetonitrile using a copper anode, a platinum cathode and the parent ligand, 1-methylimidazoline-2(3*H*)-thione (mimtH), with tetrabutylammonium tetrafluoroborate as supporting electrolyte. The colourless diamagnetic complex crystallises in a tetragonal cell, $a = b = 10.1002(6)$, $c = 11.6861(8)$ Å, $V = 1192.2(1)$ Å^3, $Z = 2$(tetramers), space group $P4_2/n$, final conventional $R = 0.043$, from 721 observed reflections with $F > 4\sigma_c(F)$. The tetranuclear complex possesses a crystallographically imposed four-fold inversion axis ($\bar{4}$) and a slightly flattened Cu$_4$ tetrahedron with Cu–Cu distances of 2.671(2) Å, along four of the edges, and 3.132(2) Å along the remaining two opposing edges of the tetrahedron; internal, Cu–Cu–Cu angles, between the shorter Cu–Cu distances, are 71.8(1)°. The deprotonated ligands form μ_2-S, N bridges with three copper(I) atoms on each of the isosceles triangular faces of the Cu$_4$ tetrahedron. The exocyclic thionato-S atom bridges two copper(I) atoms (Cu–S$_{br}$ = 2.307(2) and 2.233(2) Å) and the hetero-N atom bonds to a third metal atom (Cu–N = 1.995(6) Å). Consequently, each copper(I) atom has a S$_2$N-donor set and irregular, trigonal-planar coordination with angles at the metal ranging from 109.3(2)–129.9(1)°. The complex exhibits ligand centred, irreversible redox behaviour in acetonitrile and is stable to aerial oxidation at room temperature. Thermal degradation to the metal occurs in flowing air (275–750 °C) with endothermic decomposition in flowing dinitrogen.

Introduction

The coordination chemistry of heterocyclic thioamides has received substantial attention in recent years [1]. Thione–thiol tautomerism is common among many members of this group of ligands with the thione tautomers dominant in the solid [1]. However in solution, and immediately prior to complexation, the tautomeric equilibrium may be shifted by a number of factors including: the nature of the metal, the presence of base and the nature of the solvent [2].



Copper complexes of heterocyclic thiones typify the rich coordination chemistry which has recently evolved in this field. For example, 1-methylimidazoline-2(3*H*)-thione, mimtH, reacts with mono- and divalent copper salts giving: [Cu(mimtH)$_3$](NO$_3$) [3], [Cu$_2$(mimtH)$_4$Cl$_2$] [4], [Cu$_2$(mimtH)$_5$](SO$_4$)$_2$·3H$_2$O [5], [Cu$_2$(mimtH)$_6$](BF$_4$)$_2$ [6], [{Cu(mimtH)CN}$_n$] [7] and [Cu$_2$(mimtH)$_4$(SCN)$_2$] [8]. The ligand retains the thione tautomeric form in the above complexes, coordinates through the thione-S atom and generates either trigonal [3, 5] or tetrahedral [4, 6–8] environments about the metal. In addition, synthetic routes mostly involve acetone, ethanol or ethanol/acetonitrile mixtures, excess ligand and the appropriate metal salt.

In direct contrast to the above reactions a 1:1 molar ratio of CuCl$_2$·2H$_2$O and mimtH

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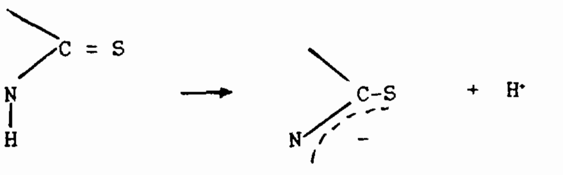
in either methanol [9] or nitromethane [2] produces the chelating N,N′-donating ligand, 1,1′-dimethyl-2,2′-diimidazolylmonosulphide (im-S-im), in $[Cu_2(im\text{-}S\text{-}im)_2Cl_4]$ [9]. The ligand in this complex may be considered to arise from the oxidation and subsequent desulfurisation of mimtH.

Copper complexes involving the thionato mimt anion



with intense charge-transfer absorptions, 600–770 nm, have been reported [10, 11]. The mixed-valence aggregate, $[Cu(II)_2Cu(I)_{10}(mimt)_{12}(MeCN)_4](PPh_4)_2\cdot(MeCN)_2$, is readily prepared from $[Cu(mimtH)_4]ClO_4$, $[Cu_2(MeCO_2)_4(H_2O)_2]$ and mimtH in acetonitrile/methanol (1:1 vol./vol.). The mimt anion in this dark-blue (λ_{max} 625 nm) complex, forms double, triple and quadruple-S,N bridges between the copper atoms [12]. A detailed study of the reactions between $[Cu_2(MeCO_2)_4(H_2O)_2]$ and mimtH, in ethanol, has led to the suggestion that stable mixed-valence aggregates, of general formula $[Cu(II)_2Cu(I)_{10}(mimt)_{12}(solvent)_4]^{2+}$ are readily formed and characterised by an intense absorption in the region 600–700 nm, [2], which is typical of 'blue' copper proteins [13].

The direct electrochemical synthesis of metal complexes from sacrificial metal anodes and alkyl or aryl thiols has been effectively demonstrated with copper and other metals [14]. The resultant thiolates, CuSR, are generally intractable solids. However, in the presence of chelating ligands such as 1,10-phenanthroline, (phen), the complex $[\{Cu(SC_6H_4CH_3\text{-}o)(phen)\}_2]$ has been synthesised and its crystal structure determined [14].

We now report the first electrochemical synthesis and crystal structure of a heterocyclic thionato complex of copper(I).

Experimental

Materials

The ligand, mimtH, as 2-mercapto-1-methylimidazole, tetrabutylammonium tetrafluoroborate and AR grade metallic copper were obtained from Aldrich and were used as supplied.

Electrochemical synthesis and analysis of $[\{Cu(mimt)\}_4]$

The electrochemical synthesis was performed at room temperature in a slim-form 50 ml beaker using a copper anode and a platinum cathode in the form of square plates (*c.* 1 cm^2) with the ligand, mimtH, (0.22 g, 2 mmol) in 25 ml of anhydrous acetonitrile and $[NBu_4][BF_4]$ as supporting electrolyte (1 mM). The reaction mixture was electrolysed for about 5 h using a potential of 10 V and a current of 4 A. The reaction was performed separately with bubbling dinitrogen and atmospheric dioxygen with no significant differences in the results.

The initial product, the dark-blue mixed-valence aggregate, $[Cu(II)_2Cu(I)_{10}(mimt)_{12}(MeCN)_4]^{2+}$, was characterised by its charge-transfer absorption band at 625 nm. The colouration due to this compound rapidly cleared and copper(II) sulfide was gradually deposited at the base of the cell. Colourless, well-formed crystals of $[\{Cu(mimt)\}_4]$ were slowly deposited on the metal electrodes and on the sides of the beaker. These were removed, washed with a small quantity of cold acetonitrile, dried and stored *in vacuo*. The bulk of the dissolved metal (150 mg) was converted into copper(II) sulfide (150 mg, *c.* 80%) with the complex representing a small proportion (45 mg, *c.* 10%) of the yield.

Anal. Calc. for $Cu_4C_{16}H_{20}N_8S_4$, M_r706.81: C, 27.2; H, 2.83; N, 15.86; Cu, 35.96. Found: C, 26.77; H, 3.11; N, 15.11; Cu, 36.0%.

Chemical synthesis of $[\{Cu(mimt)\}_4]$

Equimolar quantities of $[Cu_2(CH_3CO_2)_4(H_2O)_2]$ and mimtH, in distilled water with dropwise addition of aqueous ammonia (2 M) and in ethanol with an equimolar quantity of metallic sodium, produced complexes of empirical formula $[\{Cu(mimt\}]$. The product from the aqueous deprotonation was clearly contaminated with the dodecanuclear mixed-valence aggregate and the product from the sodium de-protonation, although initially colourless, slowly adopted the characteristic dark-blue colouration of the mixed-valence aggregate. Both of the above products had infrared spectra and thermal analysis curves similar to those of the title product but their chemical analyses were generally unsatisfactory due to the presence of unreacted ligand.

Physical methods

Infrared spectra were obtained as CsI discs in the range 4000–200 cm^{-1} on a Perkin-Elmer 684 grating spectrometer. Stanton-Redcroft equipment was used for the thermal analysis curves including: a TG 770 for the thermogravimetric analysis (TG, DTG) with platinum crucibles, column-dried flowing air and sample masses in the region of 6 mg. A DTA 673/4 was used for the differential thermal analysis curves (DTA) with quartz crucibles, flowing dinitrogen and sample masses in the region of 8 mg. Heating rates for both techniques were 20 °C min^{-1}. Quantitative DTA method from ref. 15. Hot-stage microscopy, in static air, was performed with a HSM-5 hot-stage microscope, a Hitachi DK81 video recorder and JVC TM/90 colour monitor.

X-ray powder diffraction photographs were obtained with a Guinier-Hagg parafocussing camera, Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) and Kodirex single-coated X-ray film; line intensities were monitored with a Siemens microdensitometer. Cyclic voltammetry measurements were obtained using a Sycopel Scientific potentiostat and data acquisition system together with a single-compartment three-electrode cell with platinum working and secondary electrodes and a calomel reference electrode. Measurements were taken at room temperature with initial and final ramp amplitudes within the range +2.0 and −2.0 V and variable scan rate; quoted results were obtained at a scan rate of 100 mV s^{-1}. The complex and mimtH were dissolved in dry, dioxygen free acetonitrile at 10^{-3} M concentration with tetrabutyl tetrafluoroborate (1×10^{-1} M) as supporting electrolyte.

Crystal structure analysis

Crystal data

A colourless crystal of [{Cu(mimt)}$_4$], $C_{16}H_{20}N_8S_4Cu_4$, $M_r = 706.81$, of dimensions, 0.12 × 0.16 × 0.48 mm, was used for the data collection. Unit cell dimensions were obtained from the 2θ values (20–25°) of 32 reflections centred on both sides of the direct beam. Tetragonal cell at 295 K with $a = b = 10.1002(6)$, $c = 11.6861(8)$ Å, $V = 1192.2(1)$ Å^3, $Z = 2$(tetramers), space group = $P4_2/n$, $D_c = 1.96$ g cm^{-3}, $F(000) = 704$, $\mu = 38.93$ cm^{-1}, for graphite monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation.

Data collection and processing

A Stoe-Siemens diffractometer was used for the data collection in the ω/θ scanning mode with variable scanning range and time, 2θ range 3–50°, range of indices h, 0 to 12; k, 0 to 12; l, 0 to 13; together with some Friedel opposites, on-line profile fitting [16], three standard reflections with no significant intensity changes, semi-empirical absorption correction, transmission factors 0.24–0.31. Total data 1289, unique data 1051, observed data 721, criterion $F > 4\sigma_c(F)$ with σ_c from counting statistics only, $R_{\text{int}} = 0.019$.

Structure solution and refinement [17]

Direct methods and difference Fourier syntheses were used to locate the non-H atoms which were refined by blocked-cascade least-squares methods to a minimum of $\Sigma w\Delta^2$, ($\Delta = |F_o| - |F_c|$), with anisotropic thermal parameters. Olefinic H atoms were constrained on ring angle external bisectors, C–H = 0.96 Å, methyl H–C–H = 109.5°, two-fold disorder in methyl H atoms with 87:13 (9) (%) occupancy, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Final R ($= \Sigma|\Delta|/\Sigma|F_o|$) = 0.043, R_w($= (\Sigma w\Delta^2/\Sigma wF_o{}^2)^{1/2}$) = 0.037 with $w^{-1} = \sigma^2 F = \sigma_c{}^2(F) + 20 + 22G - 15G^2 - 42H + 24H^2 - 46GH$, where, $G = F_o/F_{\max}$ and $H = \sin\theta/\sin\theta_{\max}$ [18]. $S = 0.088$, 78 parameters. The maximum shift/e.s.d. ratio is 0.004 and the mean is 0.001. The largest peak and the largest hole in the final difference synthesis are 0.45 and −0.44 e Å^{-3}, respectively. Neutral atomic scattering factors from ref. 19. SHELXTL [17] together with local programs were used in the analysis.

Final fractional atomic coordinates are given in Table 1, bond lengths and angles in Table 2, see also 'Supplementary material'.

A perspective drawing of the tetranuclear complex, with the copper atoms and the independent ligand atoms labelled, is given in Fig. 1; unit cell contents, in parallel c projection, are in Fig. 2.

TABLE 1. Atomic coordinates (× 10^4)

Atom	x	y	z
Cu(1)	1048(1)	3044(1)	6861(1)
N(1)	3292(6)	4639(6)	4312(6)
C(1)	2622(12)	5809(9)	3906(9)
S(2)	2352(2)	4874(2)	6509(2)
C(2)	3289(8)	4169(7)	5405(5)
N(3)	4025(6)	3080(5)	5459(5)
C(4)	4537(8)	2870(8)	4371(6)
C(5)	4077(9)	3822(8)	3662(8)

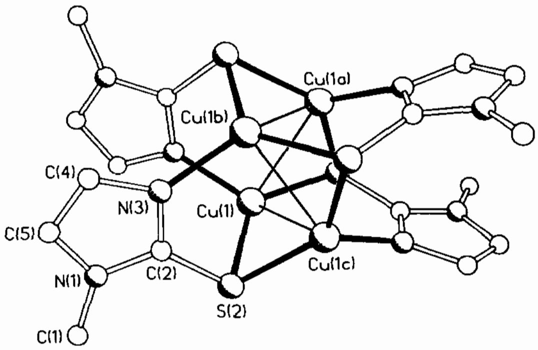


Fig. 1. Perspective diagram of [{Cu(mimt)}$_4$] with the copper atoms and independent ligand atoms labelled.

TABLE 2. Bond lengths (Å) and angles (°)

Cu(1)-S(2)	2.307(2)	Cu(1)-Cu(1a)	2.671(2)
Cu(1)-S(2a)	2.233(2)	Cu(1)-N(3b)	1.995(6)
N(1)-C(1)	1.442(12)	N(1)-C(2)	1.363(9)
N(1)-C(5)	1.374(11)	S(2)-C(2)	1.751(7)
C(2)-N(3)	1.329(9)	N(3)-C(4)	1.388(9)
C(4)-C(5)	1.352(12)		
S(2)-Cu(1)-Cu(1a)	52.7(1)	S(2)-Cu(1)-Cu(1c)	120.6(1)
Cu(1a)-Cu(1)-Cu(1c)	71.8(1)	S(2)-Cu(1)-S(2a)	129.9(1)
Cu(1a)-Cu(1)-S(2a)	86.9(1)	Cu(1c)-Cu(1)-S(2a)	55.3(1)
S(2)-Cu(1)-N(3b)	109.3(2)	Cu(la)-Cu(1)-N(3b)	133.1(2)
Cu(1c)-Cu(1)-N(3b)	92.4(2)	S(2a)-Cu(1)-N(3b)	120.5(2)
C(1)-N(1)-C(2)	126.3(7)	C(1)-N(1)-C(5)	125.6(7)
C(2)-N(1)-C(5)	108.1(6)	Cu(1)-S(2)-Cu(2)	96.5(2)
Cu(1)-S(2)-Cu(1a)	72.1(1)	C(2)-S(2)-Cu(1a)	106.8(2)
N(1)-C(2)-S(2)	123.4(5)	N(1)-C(2)-N(3)	109.3(6)
S(2)-C(2)-N(3)	127.2(5)	C(2)-N(3)-C(4)	107.0(6)
C(2)-N(3)-Cu(1b)	119.2(5)	C(4)-N(3)-Cu(1b)	132.7(5)
N(3)-C(4)-C(5)	108.9(7)	N(1)-C(5)-C(4)	106.6(8)

Symmetry operators: a: $\frac{1}{2}-y, x, \frac{3}{2}-z$; b: $\frac{1}{2}-x, \frac{1}{2}-y, z$; c: $y, \frac{1}{2}-x, \frac{3}{2}-z$.

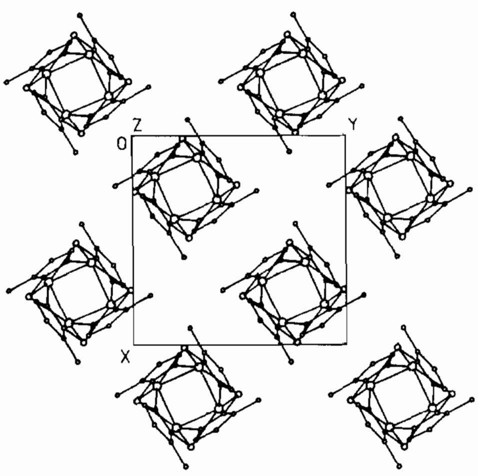


Fig. 2. Unit cell contents in parallel *c* projection.

Results and discussion

Synthesis

An electrochemical cell of the form:

$$Pt(-)/CH_3CN + mimtH/Cu(+)$$

facilitated the one-stage synthesis of $[\{Cu(mimt)\}_4]$ as a result of ligand de-protonation at the cathode:

$$mimtH + e^- \rightarrow mimt^- + \frac{1}{2}H_2$$

followed by metal oxidation and complex formation at the anode:

$$Cu(s) + mimt^- \rightarrow [\{Cu(mimt)\}] + e^-$$

The initial production of $[Cu(II)_2Cu(I)_{10}(mimt)_{12}(MeCN)_4]^{2+}$ is consistent with the reported behaviour of mimtH with copper salts [2], the dark-blue product however cleared from solution relatively quickly. The major by-product of the reaction, copper(II) sulfide, is probably produced by reaction of the complex with unreacted mimtH:

$$[\{Cu(mimt)\}_n] + n(mimtH) \rightarrow nCuS$$
$$+ n(mimt)_2 + \frac{n}{2}H_2(g)$$

The oxidised product, $(mimt)_2$, 1,1′-dimethyl-2,2′-diimidazolyldisulfide, is a well known oxidation product of mimtH [9].

Infrared spectra

De-protonation and S,N-coordination have a marked effect on the IR spectrum of mimtH with all of the major ligand bands, (3100–530 cm^{-1}), showing some degree of perturbation. Weak ν(Cu–S) and ν(Cu–N) bands at 310 and 280 cm^{-1}, respectively, further support S,N-coordination [20].

Description of the structure

The complex occupies a crystallographic four-fold inversion axis ($\bar{4}$) in the tetragonal cell (Fig. 2), consequently the independent species consist of one copper(I) atom and one mimt anion. A further consequence of the imposed crystallographic symmetry is the generation of four equivalent Cu–Cu distances of 2.671(2) Å (1–1a, 1a–1b, 1b–1c, 1–1c, Figs. 1 and 2); the tetrahedron is completed by two further Cu–Cu distances of 3.132(2) Å, (1–1b, 1c–1a). Consequently the Cu_4 tetrahedron is slightly flattened. Each copper(I) atom forms three contacts to neighbouring metal atoms in the tetrahedron, namely, two at 2.671(1) and one at 3.132(2) Å; the four equivalent, internal angles, such as Cu(1a)–Cu(1)–Cu(1c), are 71.8(1)°; Table 2.

The metal atoms in the Cu_4 aggregate are coordinated by four, triply-bridging ligands with each thionato-S atom, S(2), μ_2-*S* bridging two copper(I) atoms, Cu(1) and Cu(1c), and the hetero-N atom coordinating a third metal atom, Cu(1b) (Fig. 1). In effect, each ligand coordinates three metal atoms about each of the isosceles triangular faces of the Cu_4 tetrahedron. Anion coordination is facilitated by the ligand 'bite' (S(2)–N(3) = 2.765(9) Å) and by the fact that the imidazole moiety, as well as the plane defined by N(3)–C(2)–S(2)–Cu(1b), are virtually normal, 95.3 and 92.5°, respectively, to the plane defined by the Cu(1), Cu(1c), S(2) and C(2) atoms (Fig. 1). Each copper(I) atom has an S_2N-donor set, formed from three different ligands (Fig. 1), and irregular, planar, trigonal coordination with angles at the metal ranging from 109.3(2)–129.9(1)° (Table 2).

Selected dimensions from reported tetranuclear aggregates are summarised in Table 3 [21–24]; structural features of tetranuclear thiolate aggregates have also been reviewed [25]. The complexes in Table 3 are reported to contain Cu_4 tetrahedra except for $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$, which is distorted trigonal-pyramidal [24]. Internal (Cu–Cu–Cu) angles and metal separation distances vary significantly from 58.3(5)–96.0(1)° and 2.574(4)–2.791(2) Å, respectively, among the Cu_4 cores. The Cu_4 aggregate in $[\{Cu(mimt)\}_4]$ appears to be comparatively regular with the shorter metal separation distance (2.671(2) Å) close to both the value in the parent metal (2.550 Å) [26] and to the Cu–Cu distance in Coucouvanis's idealised *tetrahedro*-Cu, *octahedro*-S, Cu_4S_6 core (2.64 Å) [21]. Relatively short metal separation distances are not inherently indicative of metal–metal bonding, especially in the presence of bridging ligands. In the current structure the relatively short metal separation distance is probably imposed by the stereochemical requirements of the bridging ligands and only soft metal–metal coupling is likely [27].

The Cu–N distance in $[\{Cu(mimt)\}_4]$ (1.995(6) Å) is significantly longer than the corresponding distance (1.905(5) Å) reported for the imidazole molecule (imzH) in $[Cu_2(imzH)_4Cl]Cl$, which also contains trigonal copper(I) [28]. The difference between the two Cu–N distances is probably more reflective of ligand stereochemistry than fundamental differences in Cu–N, imidazole, bonding.

Asymmetric μ_2-S bridging by the thionato-S atom generates Cu–S_{br} distances of 2.307(2) and 2.233(2) Å and a Cu–S_{br}–Cu angle of 72.1(1)° (Table 2). The mean Cu–S_{br} distance in the current structure is consistent with thione-S [3] and thiolato-S (Table 3) trigonally coordinated copper(I). The mean Cu–S_{br}–Cu angles, with the exception of that of $[\{Cu(S_2CC_6H_4Me-p)\}_4(PPh_3)_2]$, are also similar, among the listed complexes in Table 3. The Cu–S–C angles in the current structure (96.5(2) and 106.8(2)°) are in the range reported for asymmetric, thione-S, μ_2-bridging mimtH in dinuclear copper(I) complexes (96.3(1)–108.2(1)° [4, 6–8]. The S-bridging angles are probably not significant factors in the determination of tetranuclear metal core geometry, (Table 3), but they do reflect the inherent angular flexibility of S-donor ligands, especially in polynuclear assemblies [1, 25].

The exocyclic thioketonic C–S distance in the mimt anion (1.751(7) Å) shows significant lengthening relative to the corresponding distance in the parent, mimtH, ligand (mean 1.685(2) Å [29]. The value is also close to the corresponding thiolate $C–S^-$ distance (mean 1.749(14) Å) reported for phenyl thiolate in $[Cu(PhS)_3]^{2-}$ [21]. These observations suggest that the charge on the mimt anion is predominantly centred on the exocyclic thionate-S atom.

Previously reported tetranuclear complexes of heterocyclic thiones involved exclusive use of the parent ligands and the generation of planar, centrosymmetric, Cu_4 rhomboid cores [30–32]. In contrast, mono-thiolate (PhS^-, MeS^-) and dithiolate (S_2-*o*-xyl^{2-}) ligands generate Cu_4S_6 cores with *tetrahedro*-Cu, *octahedro*-S geometry [21–23]. By virtue of the generation of a $Cu_4S_4N_4$ core in $[\{Cu(mimt)\}_4]$ the mimt anion exhibits the characteristics of both aryl/alkyl thiolate and heterocyclic thionate ligands and produces a novel structural form. A similar structure, with a Cu_4S_8 core, and a μ_2-S,S coordinating dithiolate anion is, in principle, also possible. However, in $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$ the inclusion of the two phosphine ligands causes two of the copper(I) atoms to adopt tetrahedral, rather than trigonal geometry, and the production of a $Cu_4S_8P_2$ core [24]. With this exception Cu_4S_8 cores appear to be elusive entities [21].

Thermal analysis

The complex decomposes to the metal, in flowing air, in the temperature range 275–850 °C (Fig. 3(a)). The agreement between theoretical (64.0%) and experimental (64.0%) mass losses is within experimental error (+/−2.0%) and is consistent with the empirical formulation of the complex. The major mass loss (51.0%; 275–470 °C) consists

TABLE 3. Selected dimensions among tetranuclear copper(I) aggregates with S-donor ligands

	$(Ph_4P)_2[Cu_4(SPh)_6]$	$(NMe_4)_2[Cu_4(SMe)_6]$	$(PPh_4)_2[Cu_4(S_2\text{-}o\text{-xyl})_3]$	$[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2\}]$	$[\{Cu(mimt)\}_4]$
Coordination core	Cu_4S_6	Cu_4S_6	Cu_4S_6	$Cu_4S_8P_2$	$Cu_4S_4N_4$
Cu–Cu–Cu (°)					
Range	58.3(5)–61.6(5)		59.1(1)–60.7(1)	76.9(1)–96.0(1)	71.8(1)
Mean $(\sigma_n)^a$			60.0(0.5)	84.4(10.2)	78.1(1)
Cu–Cu(Å)					
Range	2.692(5)–2.772(5)	2.673(2)–2.791(2)	2.699(2)–2.739(2)	2.574(4)–2.766(2)	2.671(2)–3.132(2)
Mean (σ_n)	2.760(20)	2.721(41)	2.726(16)	2.664(78)	2.885(302)
Cu–S(Å)					
Range	2.242(10)–2.338(10)	2.247(2)–2.315(3)	2.244(3)–2.300(3)	2.227(4)–2404(4)	2.307(2)–2.233(2)
Mean (σ_n)	2.290(30)	2.278(2)	2.272(2)	2.307(80)	2.270(52)
Cu–S–Cu (°)					
Range	72.5(4)–75.1(4)	74.3(12)		73.3(1)–95.5(2)	72.1(1)
Mean (σ_n)	73.8(10)	74.3(12)		84.4(15.7)	72.1(1)
S–Cu–S (°)					
Range	101.2(7)–138.1(7)	111.1(1)–128.2(1)	112.7(1)–129.8(1)	90.3(2)–136.6(2)	129.9(1)
Mean (σ_n)	120(10.0)	119.9(5.8)	119.9(5.6)	115.0(12.5)	129.9(0.1)
Reference	21	22	23	24	this work

$$^a\sigma_n = \sqrt{\frac{\Sigma x^2 - \frac{(\Sigma x^2)}{n}}{n}}$$

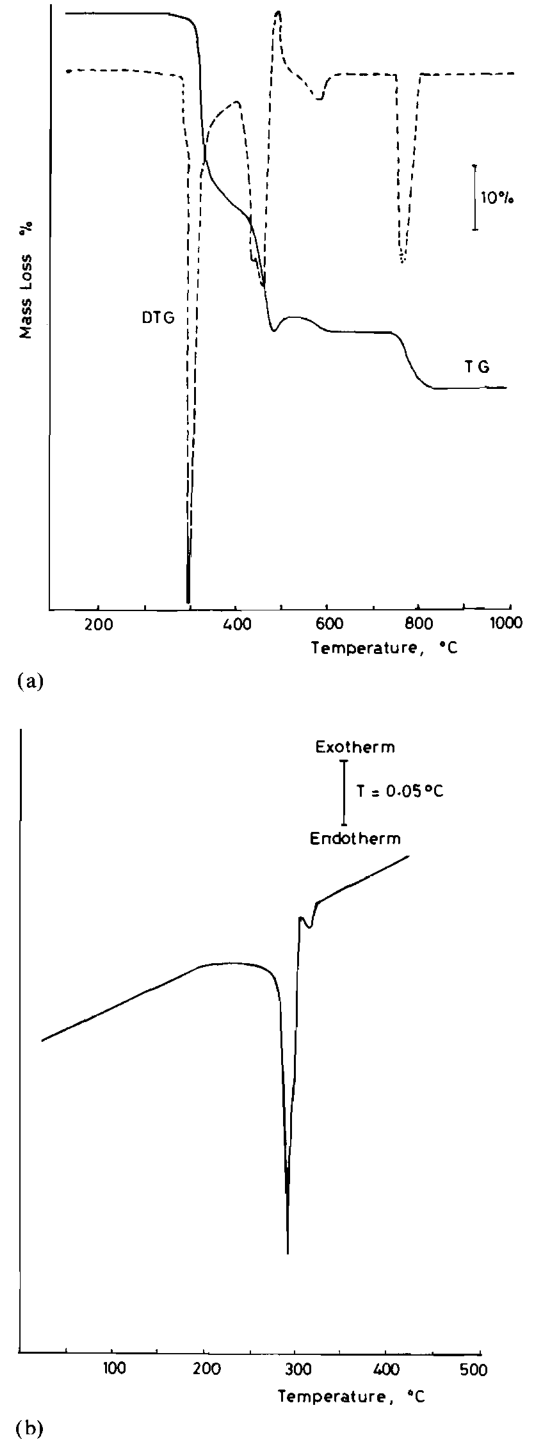


Fig. 3. Thermal analysis curves of [{Cu(mimt)}$_4$]: (a) TG, DTG in flowing air, (b) DTA in flowing dinitrogen. Heating rates 20 °C min^{-1}.

of two contiguous TG and DTG curves and is consistent with the production of copper(I) sulfide (theor. mass loss 46.0%), together with some residual elemental sulfur. The initial mass loss (30%; 275–360 °C) is consistent with the production of copper(I) thiocyanate ($M_r = 121.0$, theor. mass loss 31.0%) which, presumably, results from the decomposition of the bulk of the ligand which lies outside the coordinated N–C–S moiety. Ligand de-sulfurisation, with concomitant production of copper sulfides, is a common feature of the thermal behaviour of copper(I) complexes of mimtH [3, 5–8].

The small mass increase (3.0%; 470–490 °C), which follows the production of copper(I) sulfide, is due to the superficial oxidation of the sulfide. The extent of this oxidation is variable and is greatest for large sample masses (8 mg <) and fast heating rates (20 °C <) [7]. For other complexes in this series the usual behaviour at this stage of the decomposition normally involves smooth oxidation of the sulfide residues to copper(II) oxide [3, 5–8]. Production of the metal, in the current instance (theor. mass loss 11.0%; 560–770 °C), suggests that the residues, prior to the final oxidation stage, are primarily composed of copper(I) oxide and copper(I) sulfide. Such mixtures are known to produce the metal on heating [33]

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

The stoichiometry of the above reaction (theor. mass loss 10.0%) appears to be critical, however, because there were several instances in the current study where the total mass losses were significantly less than the theoretical value (64.0 ± 2.0%).

A DTA study, in flowing dinitrogen, produced largely non-reproducible curves, mostly due to excessive base-line drift (Fig. 3(b)). The most prominent and constant feature of the curves consists of a substantial endotherm ($\Delta T_i = 150$, $\Delta T_p = 220$ and $\Delta T_f = 250$ °C) with a small shoulder ($\Delta T_p = 300$ °C). The magnitude of the endotherm ($\Delta H_r = 100 \pm 10$ kJ mol^{-1}) is consistent with decomposition, as well as melting, of the complex.

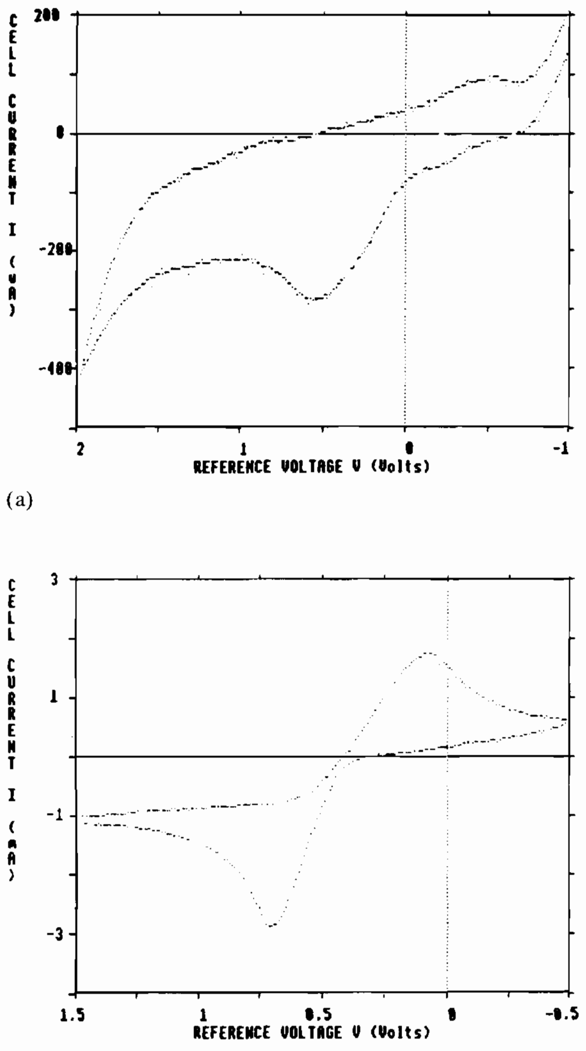
Hot-stage microscopy, in static air, confirmed the occurrence of simultaneous melting and decomposition of the complex (*c.* 280 °C) and the production of copper(I and II) sulfides (*c.* 280–400 °C). The solid residues were also identified by X-ray powder diffraction.

Electrochemistry

Cyclic voltammetry (CV) of the parent ligand, mimtH (Fig. 4(a)), shows pseudo-reversible behaviour in acetonitrile with approximately equal areas for the cathodic (E_{red} + 0.10 V)

$$\text{mimtH} + e^- \rightarrow \text{mimt}^- + \frac{1}{2} H_2$$

and anodic (E_{ox} + 0.74 V)



(a)

(b)

Fig. 4. Cyclic voltammetry curves: (a) mimtH, (b) $[\{Cu(mimt)\}_4]$ in acetonitrile, scan rate $100\ mV\ s^{-1}$.

$$2\ mimt^- \rightarrow (mimt)_2 + 2e^-$$

peaks of the cycle.

The complex exhibits irreversible redox behaviour, in acetonitrile (Fig. 4(b)), with the CV profile consisting of a single broad anodic peak ($E_{ox}+0.50$ V) and a slight discontinuity ($E_{red}-0.5$ V) on the cathodic peak of the cycle. The broad anodic peak is indicative of ligand centred oxidation of the complex with the ligand probably converted to 1,1′-dimethyl-2,2′-diimidazoyldisulfide, $(mimt)_2$. The relatively featureless profile of the cathodic peak suggests that the oxidation product is not redox stable and that it probably decomposes at the working electrode with the discontinuity attributed to the reduction of vestigial, complexed, copper(I).

In effect, the presence of the redox sensitive mimt anion clearly compromises the production of a redox-stable, metal-centred, Cu(II)/Cu(I) couple, in $[\{Cu(mimt)\}_4]$. The observed peak potential ($E_{ox}+0.5$ V) for the complex is, however, consistent with the known ability of unsaturated heterocyclic molecules such as imidazole to stabilise copper(I) [34].

Conclusions

Stimulated by the successful electrochemical synthesis of $[\{Cu(mimt)\}_4]$ we have also electrochemically synthesised nickel, $[Ni(mimt)_2]$ and silver, $[Ag(mimt)]$ complexes from the parent metal and mimtH, as well as the copper(I) complex of thiazole-2-thionate, $[Cu(tzt)]$. Electrochemical synthesis of heterocyclic thionato metal complexes is clearly of general applicability given the wide range of heterocyclic thiones available and their known propensity to coordinate to most metals [1]; many novel thionato complexes are clearly possible by such means.

Supplementary material

Anisotropic thermal parameters for the non-H atoms, H atom coordinates with isotropic thermal parameters, least-squares mean planes with dihedral angles and structure factor tables are available from the authors on request.

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