Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.093$
$S = 0.985$
3358 reflections
245 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0083 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—N2	1.953 (2)	Cu—O3	2.411 (2)
Cu—N3	1.958 (2)	N4—O1	1.209 (3)
Cu—O4	1.994 (2)	N4—O3	1.248 (3)
Cu—O5	2.018 (2)	N4—O2	1.251 (2)
N2—Cu—N3	94.01 (7)	N2—Cu—O3	85.34 (7)
N2—Cu—O4	164.01 (7)	N3—Cu—O3	104.48 (8)
N3—Cu—O4	99.54 (7)	O4—Cu—O3	99.33 (8)
N2—Cu—O5	100.45 (7)	O5—Cu—O3	86.27 (8)
N3—Cu—O5	162.69 (7)	Cl1—Cu—O3	93.55 (8)
O4—Cu—O5	64.87 (7)	O3—Cu—O2^{i}	160.1 (2)

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The H atoms in the dpyam ligand were located from a difference Fourier map and refined isotropically, whereas those in the propionate group were fixed geometrically and allowed to ride on the attached atoms.

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994). Structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Geometrical calculations: *PARST* (Nardelli, 1983).

The authors acknowledge Khon Kaen University and the National Research Council of Thailand for a research grant and would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1370). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 453–456

Tris(*N*,*N*′-diethylthiourea-*S*)iodocopper(I) and Tris(*N*,*N*′-diethylthiourea-*S*)iodosilver(I)

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Abstract

The structures of the 1:3 mononuclear complexes of copper(I) and silver(I) iodide with diethylthiourea (detu), namely, $[CuI(C_5H_{12}N_2S)_3]$ and $[AgI(C_5H_{12}N_2S)_3]$, are isomorphous. The metal atoms are approximately tetrahedrally coordinated to three S atoms and to one I atom.

Comment

Copper and silver(I) halides or oxyanions form neutral or ionic complexes of various stoichiometries and structural types with thiourea (tu) or substituted thiourea ligands (Pakawatchai *et al.*, 1996). $[Cu(tu)_2Cl]$ and $[Ag(tu)_2Cl]$ are isomorphous and form chain structures containing a trigonally coordinated metal atom, whereas $[Cu(tu)_3Cl]$ has a tetrahedral chain structure (Spofford & Amma, 1968, 1970; Vizzini & Amma, 1966; Okaya & Knobler, 1964). $[Cu(dmtu)_3Cl]$ (dmtu is dimethylthiourea) contains tetrahedrally coordinated Cu^{I} (Girling & Amma, 1971). $[Ag(mtu)_3Cl]$ (mtu is methylthiourea) consists of distorted tetrahedral $[(mtu)_3AgCl]$ units (Lee & Amma, 1972). Copper(I) and silver(I) halides form many MXL_3 complexes, where L is a ligand containing group V donators such as PPh_3, *e.g.* $[XCu(PPh_3)_3]$ (X = F, Cl, Br, I) (Gill *et al.*, 1976; Gulliver *et al.*, 1981; Barron *et al.*, 1987) and $[XAg(PPh_3)_3]$ (X = Cl, Br, I) (Cassel, 1981; Engelhardt *et al.*, 1987; Camalli & Caruso, 1987; Hibbs *et al.*, 1996). For species where L

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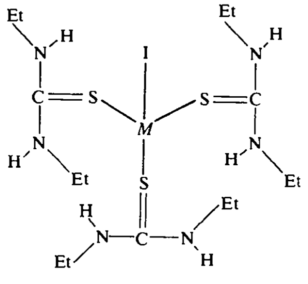
is one of the substituted thiourea ligands dtmu and mtu, the only known examples are [CuCl(dmtu)$_3$] (Girling & Amma, 1971) and [Ag(mtu)$_3$Cl] (Lee & Amma, 1972).



(I) M = Cu
(II) M = Ag

The structure determinations of tris(diethylthiourea)-iodocopper(I), (I) (Fig. 1), and tris(diethylthiourea)iodosilver(I), (II) (Fig. 2), confirm the four-coordinate nature of the metal atoms. The structures are isomorphous and consist of discrete [MI(detu)$_3$] molecular units arranged so that the iodide and metal atoms lie on a crystallographic threefold axis which relates the three detu ligands. For (II), one ethyl group (C2 and C3 atoms) of the ligand is disordered. The S—M—S angles in the copper and silver complexes [114.67 (3) and 111.50 (3)°, respectively] are larger than that in [(mtu)$_3$CuCl] [106.4 (1)°], while the Cu—S distance is shorter [2.350 (1) *cf.* 2.360 (1) Å]. This may be due to detu being more sterically demanding than mtu and also to the larger size of iodide compared with chloride, resulting in a weaker ligand–halide interaction and increased S—M—S angle.

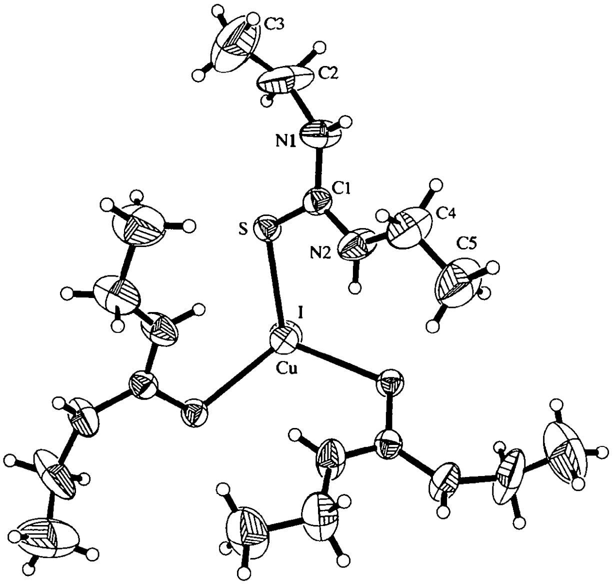


Fig. 1. A 30% displacement ellipsoid plot of (I) with the atom-numbering scheme.

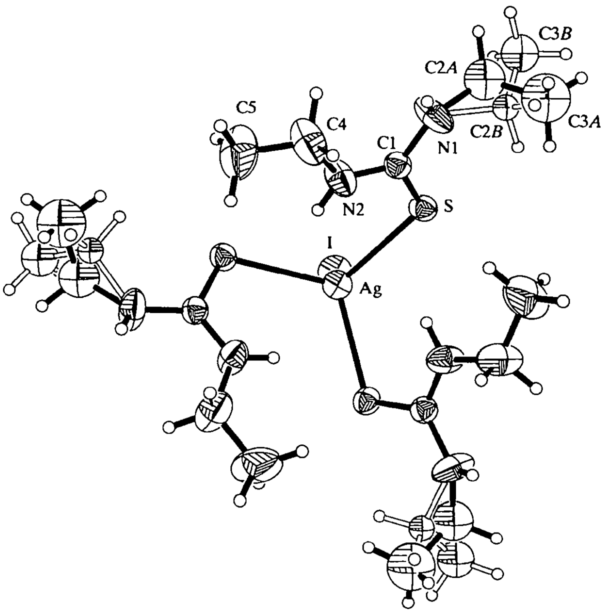


Fig. 2. A 30% displacement ellipsoid plot of (II) with the atom-numbering scheme.

Experimental

The title complexes were obtained by mixing CuI or AgI (2.1 mmol) and *N*,*N*′-diethylthiourea (6.6 mmol) in acetonitrile with warming over a period of 4 h. The solutions were filtered and allowed to cool. Slow evaporation of the filtrates at room temperature yielded crystals suitable for analysis.

Compound (I)

Crystal data

[CuI($C_5H_{12}N_2S$)$_3$]
M_r = 587.14
Trigonal
$P31c$
a = 12.686 (1) Å
c = 9.314 (2) Å
V = 1298.1 (3) Å^3
Z = 2
D_x = 1.502 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 39 reflections
θ = 6.13–12.46°
μ = 2.283 mm^{-1}
T = 293 (2) K
Cube
0.62 × 0.44 × 0.32 mm
Colourless

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scans (Siemens, 1994)
$T_{\min}$ = 0.404, $T_{\max}$ = 0.685
3282 measured reflections
1422 independent reflections
1163 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 30°
$h = -17 \rightarrow 1$
$k = -1 \rightarrow 17$
$l = -1 \rightarrow 13$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.081$
$S = 0.994$
1422 reflections
80 parameters
H atoms: riding model
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.034 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.02 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cu	1/3	2/3	0.38141 (9)	0.0548 (2)
I	1/3	2/3	0.09628 (2)	0.0738 (2)
S	0.18385 (8)	0.46675 (8)	0.44064 (13)	0.0519 (2)
N1	−0.0001 (5)	0.3622 (4)	0.6268 (6)	0.0791 (13)
N2	0.1187 (4)	0.5636 (4)	0.6474 (5)	0.0774 (12)
C1	0.0959 (4)	0.4648 (4)	0.5817 (4)	0.0521 (8)
C2	−0.0467 (11)	0.2446 (6)	0.5562 (12)	0.138 (4)
C3	−0.0416 (18)	0.1581 (12)	0.6280 (17)	0.198 (7)
C4	0.0492 (8)	0.5748 (6)	0.7665 (9)	0.110 (2)
C5	0.0772 (13)	0.6923 (9)	0.7987 (14)	0.143 (4)

Compound (II)

Crystal data

$[AgI(C_5H_{12}N_2S)_3]$
$M_r = 631.45$
Trigonal
$P31c$
$a = 12.792$ (1) Å
$c = 9.3350$ (10) Å
$V = 1323.09$ (14) Å^3
$Z = 2$
$D_x = 1.585$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 5.55–12.41°$
$\mu = 2.177$ mm^{-1}
$T = 293$ (2) K
Cube
0.40 × 0.34 × 0.30 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scans (Siemens, 1994)
$T_{\min} = 0.433$, $T_{\max} = 0.520$
3329 measured reflections
1452 independent reflections
990 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{\max} = 30°$
$h = -17 \rightarrow 1$
$k = -1 \rightarrow 18$
$l = -1 \rightarrow 13$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.070$
$S = 0.901$
1452 reflections
88 parameters
H atoms: riding model
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0036 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (3)

Table 2. *Selected geometric parameters (Å, °)*

Parameter	(I) (*M* = Cu)	(II) (*M* = Ag)
M—S	2.350 (1)	2.593 (1)
M—I	2.656 (1)	2.774 (1)
S—C1	1.716 (4)	1.711 (4)
C1—N1	1.330 (6)	1.335 (6)
C1—N2	1.291 (6)	1.306 (6)
S—*M*—S^i	114.67 (3)	111.50 (3)
S—*M*—I	103.58 (4)	107.35 (3)
M—S—C1	111.3 (1)	110.9 (2)

Symmetry code: (i) $-x + y, 1 - x, z$ for (I); $1 - x + y, 1 - x, z$ for (II).

The title structures were solved by direct methods and refined by full-matrix least-squares techniques. In (II), atoms C2 and C3 showed disorder with implausible N—C and C—C lengths. The disordered ethyl group was modelled with alternative sites for C2 and C3. The occupancies of C2 and C3 were initially refined and then fixed at 0.80 for C2*A* and C3*A*, and at 0.20 for C2*B* and C3*B*. The disordered atoms were refined anisotropically with N—C and C—C distances restrained. In (I), the U^{ij} values for C2 and C3 suggest a similar but less marked disorder and the introduction of alternative sites for the atoms was not considered necessary. All H atoms in (I) and (II) were fixed geometrically and allowed to ride on those atoms to which they are attached.

Programs used for data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994); for structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); for structure refinement: *SHELXL*93 (Sheldrick, 1993); for geometrical calculations: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1356). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 456–458

Magnesium Sulfate Tetraurea Monohydrate

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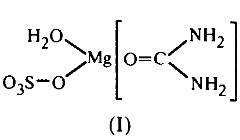
Abstract

In the title adduct, $MgSO_4.4CH_4N_2O.H_2O$ {aqua(sulfato-*O*)tetrakis(urea-*O*)magnesium, $[Mg(SO_4)(CH_4N_2O)_4(H_2O)]$}, the Mg atoms have octahedral coordination, formed by one water and four urea molecules, and one sulfate O atom. The neutral $MgSO_4(urea)_4.H_2O$ clusters are dimerized into centrosymmetric units through two O—H···O hydrogen bonds held together in a network where urea molecules act as both hydrogen-bond donors and acceptors.

Comment

The industrial methods for preparation of the widely used defoliant $Mg(ClO_3)_2$ use mainly $NaClO_3$ and $MgCl_2$ as starting materials (Martinov, 1957; Harvey, 1986). Our investigations (Todorov *et al.*, 1998) on the structure and applicability of $Mg(ClO_3)_2.6CH_4N_2O$, a new defoliating agent with improved purity and biological activity synthesized from $MgSO_4$, $NaClO_3$ and urea, prompted us to investigate the ternary system $MgSO_4$–urea–H_2O. Sulaimankoulov (1971) studied its solubility diagram which revealed only compound $MgSO_4.CH_4N_2O.3H_2O$. Recently, we have recognized a new adduct, $MgSO_4.4CH_4N_2O.H_2O$, (I), and this paper reports its crystal structure.



(I)

The structure of the title compound consists of Mg atoms bonded to four urea O atoms, one water molecule and an SO_4 tetrahedron (Fig. 1). The Mg—O distances are within the typical range 2.064 (2)–2.098 (2) Å, while O—Mg—O angles lie between 84.30 (7) and 94.85 (7)°. The values for C—O—Mg angles are in the relatively narrow range 136.19 (15)–149.89 (15)°. The torsion angles N1—C—O—Mg, used to describe the deviation from the urea in-plane coordination (Macíček *et al.*, 1995), are 1.4 (4), 15.4 (3), −20.5 (4) and 12.3 (4)°, for *U*3 (where *U*3 is urea molecule 3), *U*1, *U*2 and *U*4, respectively. They show a larger, but not significant, deviation around the latter three molecules.

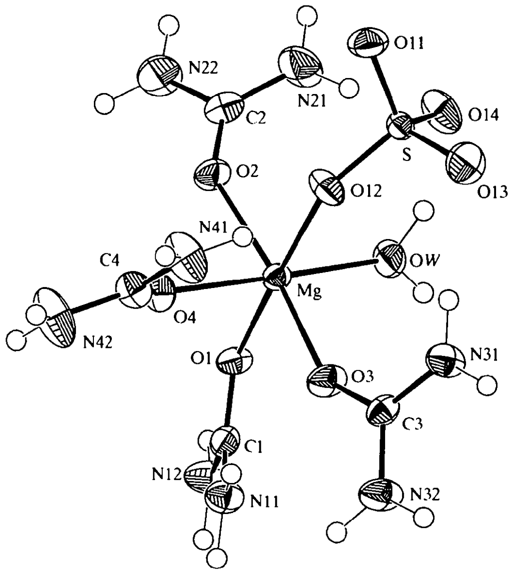


Fig. 1. A view of the title cluster with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms are arbitrarily small.

The SO_4 group has ordinary tetrahedral geometry. The longest S—O distance of 1.482 (2) Å is at the coordinated O atom and the bonds to the terminal O atoms are shorter by more than 7σ. The Mg—O12—S angle of 139.30 (10)° indicates that atom O12 does not coordinate to the Mg atom through either an ion–dipole interaction or through an sp^3 orbital.

The neutral $MgSO_4.4CH_4N_2O.H_2O$ clusters are held together by an extensive network of hydrogen

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