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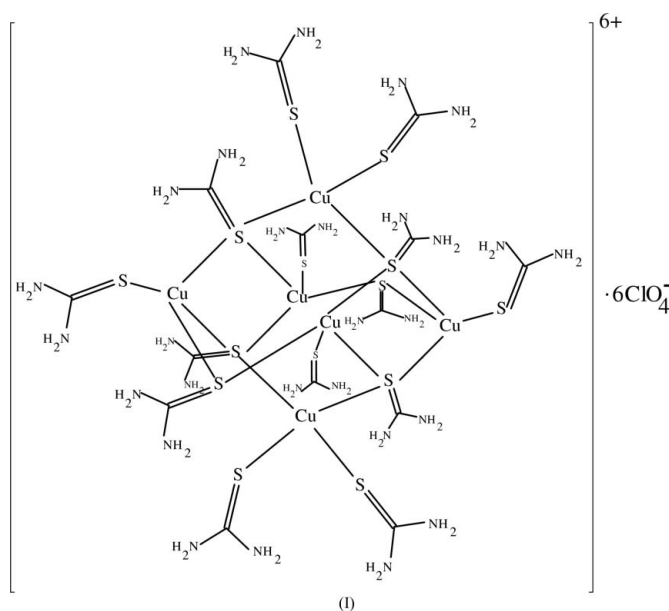
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{Cl}-\text{O}) = 0.011$ Å
 R factor = 0.038
 wR factor = 0.110
Data-to-parameter ratio = 8.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrakis(μ_3 -thiourea)bis(μ_2 -thiourea)octakis(thio-
urea)hexacopper(I) hexakis(perchlorate)

In the title compound, $[\text{Cu}_6(\text{CH}_4\text{N}_2\text{S})_{14}](\text{ClO}_4)_6$, the interesting feature of the structure lies in the closely packed Cu–thiourea core, which is a truncated octahedron of two planes and four points at the edges. The octahedron is truncated parallel to the (101) plane. The Cu–thiourea core has pseudo-centrosymmetry about the centre of the octahedral void. The structure shows inter- and intramolecular N–H...S hydrogen bonds.

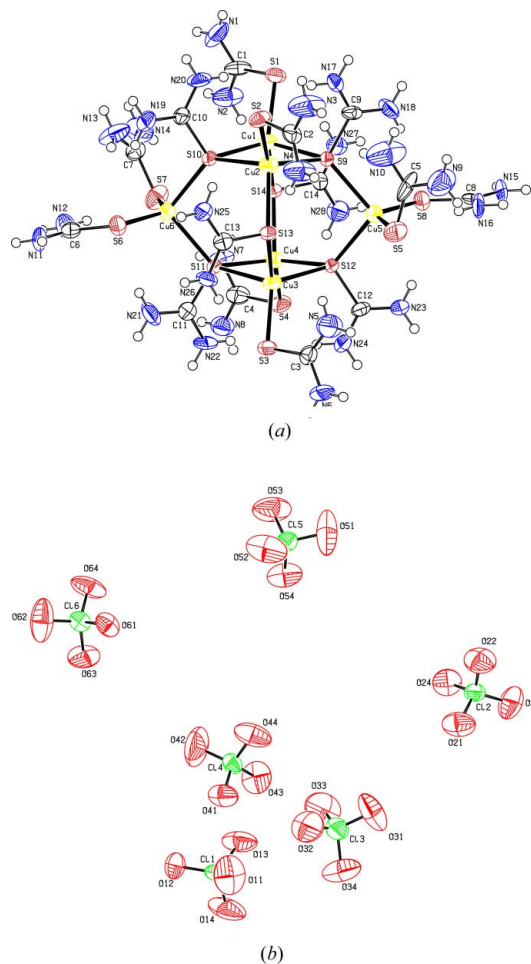
Comment

In organic sulfur compounds, thiourea and its derivatives are of great importance. These compounds have been introduced in almost all branches of chemistry and they are commercialized as dyes, photographic films, elastometry plastics and textiles (Chynoweth, 1955). Thiourea complexes with gold(I) are of interest as medicines for the control of rheumatoid arthritis and in cancer chemotherapy (Parish & Cottrill, 1987).



The crystal structures of bis(μ_2 -thiourea)hexakis(thiourea)disilver(I) diperchlorate (Udupa & Krebs, 1973), bis[$(\mu_2$ - N,N -dimethylthiourea- S,S -bis(N,N' -dimethylthiourea- S))silver(I)] diperchlorate (Pakawatchai *et al.*, 1996), bis(N,N' -dimethylthiourea- S)gold(I) perchlorate and bis(N,N' -diethylthiourea- S)gold(I) perchlorate (Staples *et al.*, 1997), tetra-thiourea-copper(I) chloride (Lakshmi *et al.*, 2003), and hexakis(thiourea)lead(II) perchlorate (Goldberg & Herstein, 1972) have already been published. The formation of a complex of thiourea with copper perchlorate has already been

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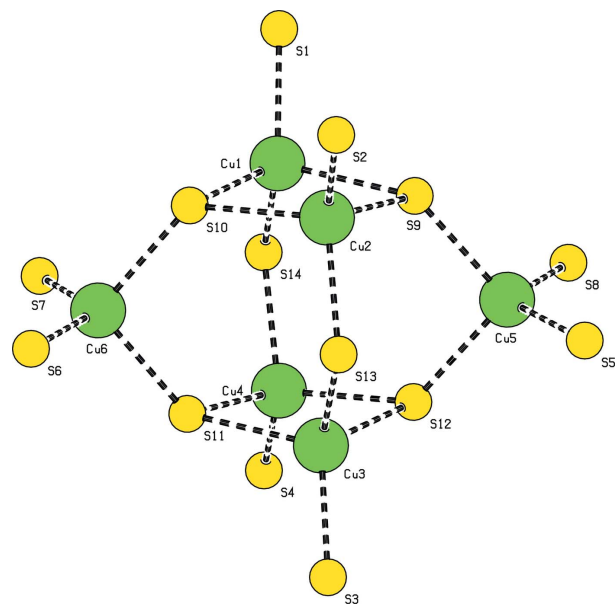
**Figure 1**

(a) The Cu-thiourea cage and (b) the perchlorate groups of (I), showing the atom-numbering schemes and 50% probability displacement ellipsoids.

reported as bis(μ_2 -thiourea)tetrakis(thiourea)dicopper(I) diperchlorate in $P2_1/c$ (Hanic & Durcahska, 1969).

In the present investigation, the title compound, (I), crystallized in the non-centrosymmetric space group Cc with six Cu^{I} cations, 14 thiourea molecules and six perchlorate anions in the asymmetric unit. The high affinity of Cu^{I} for thiourea molecules leads to a truncated octahedron, a cage-like structure. Thiourea molecules coordinate two metal atoms through the S atom in such a manner that the distorted tetrahedral environment of every Cu atom includes four S atoms. This forms a closely packed Cu-thiourea cage, which has a void space inside (Filinchuk *et al.*, 2001). During the structure analysis, it was observed that the unit cell contains large accessible voids in the crystal structure which tend to host disordered solvent water molecules. This affects the diffraction pattern, mostly at low scattering angles; this was corrected with the *SQUEEZE* program (*PLATON*; Spek, 2003). Even though compound (I) crystallizes in a non-centrosymmetric space group, the truncated octahedron has a pseudo-inversion centre.

There are two metal-metal interactions in the structure of (I), with $\text{Cu}\cdots\text{Cu}$ distances of 2.807 (4) and 2.768 (3) Å,

**Figure 2**

The Cu-thiourea cage – a truncated octahedron.

involving four Cu atoms (Cu1, Cu2, Cu3 and Cu4) to form a cross-sectional plane, with atoms S13 and S14 bisecting the octahedral core into two distorted pyramids (Table 1). Three types of Cu–S–Cu bond angles are observed in the Cu-thiourea cage of (I), namely normal ($= 120^\circ$), compressed ($< 120^\circ$) and expanded ($> 120^\circ$) (Table 1). The compressed Cu–S–Cu bonds are the consequence of the $\text{Cu}\cdots\text{Cu}$ interactions. The cage (truncated octahedron) is formed by four points (atoms) and two parallel planes (Fig. 2). The four points are the centres of the atoms Cu5, Cu6, S13 and S14 and the two planes are the atoms Cu1, S9, Cu2, S10 and Cu3, S11, Cu4, S12. These two planes are parallel to the (101) plane of the unit cell, *i.e.* the octahedral shape is truncated parallel to the *ac* plane. The $\text{Cu}\cdots\text{Cu}$ interactions between these parallel planes through atoms S13 and S14, and the $\text{Cu}\cdots\text{Cu}$ interactions between the atoms in the planes (Cu1, Cu2, Cu3 and Cu4) with the Cu atoms in the edges (Cu5 and Cu6) through atoms S9, S10, S11 and S12, have expanded Cu–S–Cu angles. These expanded Cu–S–Cu angles lead to slightly elongated octahedra along the directions of Cu5 and Cu6. The faces of the truncated octahedra can be described by ten planes constituted by the sets of atoms Cu2/S9/Cu1/S10 (0.089 Å), Cu3/S12/Cu4/S11 (0.0915 Å), Cu2/S10/Cu6/S13 (0.0376 Å), Cu2/S9/Cu5/S13 (0.0863 Å), Cu3/S11/Cu6/S13 (0.0221 Å), Cu3/S12/Cu5/S13 (0.0600 Å), Cu1/S10/Cu6/S14 (0.0545 Å), Cu1/S9/Cu5/S14 (0.0456 Å), Cu4/S11/Cu6/S14 (0.0469 Å) and Cu4/S12/Cu5/S14 (0.0388 Å); the values in parentheses are the r.m.s. deviations of the fitted atoms in the mean plane. The angles between these planes vary from $64.4(2)$ to $89.0(2)^\circ$.

All the thiourea groups in (I) are planar. Of the 14 thiourea molecules, eight are outside the cage (S1–S8) and not involved in bridging between Cu atoms. In the other six thiourea molecules, two (S13 and S14) each bridge two Cu atoms as μ_2 -

bridging ligands and the other four participate in μ_3 -bridging. The tetrahedral geometry of the Cu_4 group is distorted because of the different coordination nature of the thiourea molecules in relation to the Cu atoms.

All the perchlorate groups show nearly tetrahedral symmetry and play a vital role in hydrogen bonding, which stabilizes the crystal structure. The average Cl—O bond distances and O—Cl—O bond angles are 1.407 Å and 109.5°, respectively (Table 1).

The S atoms which are just outside the Cu—thiourea core participate in strong and moderate hydrogen bonding. The $\text{N9—H9B} \cdots \text{S7}^i$ intermolecular bond seems to be a strong bond [3.276 Å and 175°]. Interestingly, there is only one $\text{N—H} \cdots \text{N}$ hydrogen bond ($\text{N2—H2A} \cdots \text{N14}$) found in the three-centred hydrogen-bonding network. The $\text{N—H} \cdots \text{O}$ hydrogen bonds between the thiourea molecules and the perchlorate groups seem to be moderate hydrogen bonds. The excess of acceptor atoms in the structure leads to a large number of three-centred hydrogen bonds (Table 2).

Experimental

$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.0 g, 5.40 mmol) and thiourea (2.25 g, 29.6 mmol) were mixed in water (50 ml) and heated slightly over a water bath to give complete dissolution. Slow evaporation of the solvent yielded a white crystalline powder which was recrystallized from triply distilled water to yield white single crystals of the title complex. **Caution:** Although no problems were encountered in this work, all perchlorate compounds are potentially explosive and should be prepared in small amounts and handled with care.

Crystal data

$[\text{Cu}_6(\text{CH}_4\text{N}_2\text{S})_{14}](\text{ClO}_4)_6$
 $M_r = 2043.65$
 Monoclinic, Cc
 $a = 17.229$ (2) Å
 $b = 15.363$ (3) Å
 $c = 27.639$ (5) Å
 $\beta = 93.30$ (15)°
 $V = 7304$ (2) Å³
 $Z = 4$
 $D_x = 1.859$ Mg m⁻³
 $D_m = 1.845$ Mg m⁻³

D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 11.2$ – 13.6 °
 $\mu = 2.42$ mm⁻¹
 $T = 293$ (2) K
 Block, white
 0.24 × 0.2 × 0.18 mm

Data collection

Nonius MACH3 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.568$, $T_{\max} = 0.647$
 7120 measured reflections
 6610 independent reflections
 5203 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 25.0$ °
 $h = 0 \rightarrow 20$
 $k = -1 \rightarrow 18$
 $l = -32 \rightarrow 32$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.110$
 $S = 1.03$
 6610 reflections
 829 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 13.3767P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.86$ e Å⁻³
 Absolute structure: Flack (1983), with 228 Friedel pairs
 Flack parameter: 0.015 (17)

Table 1 Selected geometric parameters (Å, °).

Cu1—S9	2.455 (2)	Cu3—S3	2.271 (3)
Cu1—Cu2	2.807 (4)	Cu3—Cu4	2.768 (3)
Cu2—S9—Cu5	119.08 (13)	Cu4—S11—Cu3	71.02 (14)
Cu2—S9—Cu1	71.69 (14)	Cu6—S11—Cu3	129.45 (11)
Cu5—S9—Cu1	132.65 (11)	Cu3—S12—Cu5	117.68 (13)
Cu1—S10—Cu6	117.02 (13)	Cu3—S12—Cu4	71.04 (14)
Cu1—S10—Cu2	72.07 (15)	Cu5—S12—Cu4	130.08 (11)
Cu6—S10—Cu2	128.04 (11)	Cu2—S13—Cu3	120.77 (14)
Cu4—S11—Cu6	120.88 (13)	Cu1—S14—Cu4	119.27 (13)

Table 2 Hydrogen-bond geometry (Å, °).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1—H1A \cdots O43 ⁱ	0.86	2.43	3.080 (17)	133
N1—H1A \cdots O33 ⁱⁱ	0.86	2.59	3.289 (19)	139
N2—H2A \cdots O43 ⁱ	0.86	2.32	2.997 (14)	136
N2—H2A \cdots N14	0.86	2.55	3.125 (15)	125
N2—H2B \cdots S14	0.86	2.74	3.556 (10)	158
N3—H3A \cdots O42	0.86	2.57	3.30 (2)	143
N4—H4A \cdots O41	0.86	2.21	3.068 (13)	177
N4—H4B \cdots S13	0.86	2.67	3.500 (10)	163
N5—H5B \cdots S13	0.86	2.92	3.725 (11)	157
N6—H6A \cdots O31	0.86	2.47	3.153 (15)	137
N6—H6A \cdots O52	0.86	2.55	3.140 (17)	127
N6—H6B \cdots S8 ⁱⁱⁱ	0.86	3.00	3.528 (10)	121
N7—H7A \cdots O54 ^{iv}	0.86	2.45	3.121 (14)	135
N7—H7B \cdots S14	0.86	2.79	3.624 (9)	164
N8—H8A \cdots O51 ^{iv}	0.86	2.16	3.009 (15)	171
N8—H8B \cdots O12 ^v	0.86	2.60	3.430 (13)	162
N9—H9B \cdots S7 ^{vi}	0.86	2.42	3.276 (12)	175
N10—H10B \cdots S9	0.86	2.66	3.422 (12)	149
N11—H11A \cdots O23 ⁱⁱ	0.86	2.25	3.000 (16)	146
N12—H12A \cdots O24 ⁱⁱ	0.86	2.49	3.270 (16)	152
N12—H12A \cdots O41 ⁱⁱ	0.86	2.59	3.177 (14)	126
N12—H12B \cdots S7	0.86	2.72	3.571 (12)	171
N13—H13A \cdots O31 ⁱⁱ	0.86	2.11	2.954 (13)	166
N13—H13B \cdots O53 ⁱⁱ	0.86	2.40	2.947 (15)	122
N14—H14A \cdots O33 ⁱⁱ	0.86	2.22	3.016 (16)	153
N14—H14B \cdots O61	0.86	2.53	3.341 (14)	157
N15—H15A \cdots O62 ^{vi}	0.86	2.26	3.078 (16)	160
N16—H16A \cdots O61 ^{vi}	0.86	2.31	3.098 (12)	152
N16—H16A \cdots O54 ^{vii}	0.86	2.60	3.124 (12)	120
N16—H16B \cdots S5	0.86	2.58	3.439 (10)	173
N17—H17A \cdots O21 ^{vii}	0.86	2.23	2.994 (14)	147
N17—H17B \cdots S2	0.86	2.73	3.507 (10)	151
N18—H18A \cdots O21 ^{vii}	0.86	2.23	2.991 (14)	147
N18—H18B \cdots S8	0.86	2.64	3.483 (10)	166
N19—H19A \cdots O63 ^{viii}	0.86	2.50	3.230 (14)	144
N19—H19B \cdots S6	0.86	2.72	3.565 (10)	167
N20—H20A \cdots O63 ^{viii}	0.86	2.25	3.033 (13)	152
N20—H20B \cdots S1	0.86	2.71	3.485 (10)	150
N21—H21A \cdots O64 ⁱⁱⁱ	0.86	2.48	3.236 (13)	147
N21—H21A \cdots O43 ⁱⁱ	0.86	2.58	3.067 (13)	117
N21—H21B \cdots S6	0.86	2.66	3.507 (11)	168
N22—H22A \cdots O64 ⁱⁱⁱ	0.86	2.27	3.075 (13)	155
N22—H22B \cdots O13 ^v	0.86	2.50	3.070 (15)	124
N23—H23A \cdots O32	0.86	2.61	3.134 (15)	121
N23—H23B \cdots S8	0.86	2.89	3.623 (9)	144
N24—H24A \cdots O22 ^v	0.86	2.30	3.096 (14)	154
N24—H24B \cdots O13 ^v	0.86	2.45	3.035 (13)	126
N25—H25A \cdots O12	0.86	2.19	2.981 (13)	154
N25—H25B \cdots S2	0.86	2.73	3.570 (10)	166
N26—H26A \cdots O12	0.86	2.29	3.061 (13)	149
N26—H26B \cdots S3	0.86	2.68	3.519 (9)	166
N27—H27A \cdots S3 ^{vii}	0.86	2.97	3.497 (9)	121
N27—H27B \cdots S1	0.86	2.68	3.532 (10)	170
N28—H28A \cdots S2 ^v	0.86	2.98	3.415 (9)	114
N28—H28B \cdots S4	0.86	2.75	3.594 (11)	167

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (vi) $x, -y + 1, z - \frac{1}{2}$; (vii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (viii) $x + \frac{1}{2}, y - \frac{1}{2}, z$.

All H atoms were placed in geometrically calculated positions, with N–H = 0.86 Å, and included in the refinement using the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The highest peak is located 1.00 Å from atom Cl1.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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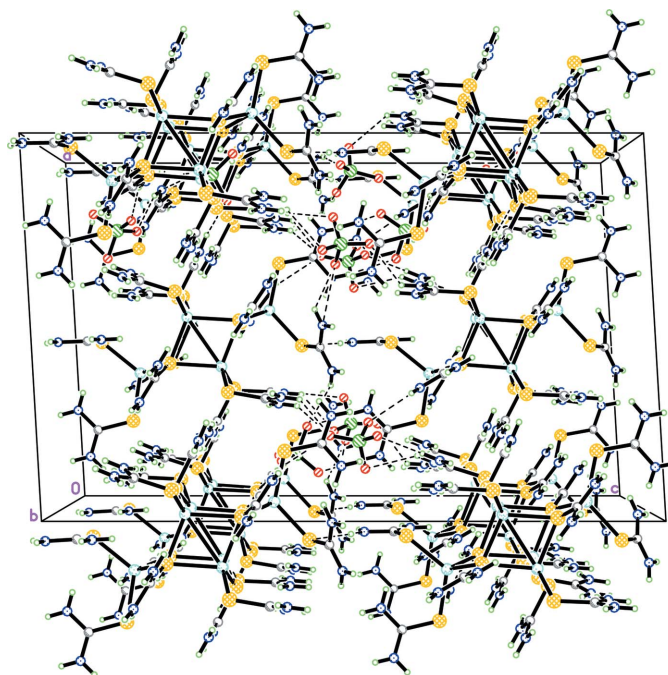


Figure 3

A packing diagram of the molecule, viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

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