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Tris(allylthiourea-κS)chlorozinc(II) chloride

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.037
wR factor = 0.093
Data-to-parameter ratio = 29.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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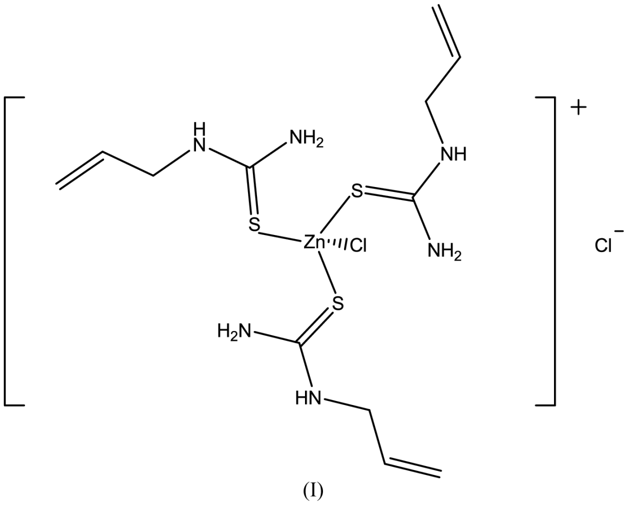
The title complex, $[ZnCl(C_4H_8N_2S)_3]Cl$, comprises $[ZnCl(ATU)_3]^+$ cations (ATU is allylthiourea) and Cl^- anions, both of which lie on threefold axes. The three S atoms of the allylthiourea molecules and one Cl atom coordinate the Zn atom in a tetrahedral arrangement. The crystal packing is mainly determined by weak N—H···Cl hydrogen bonds.

Comment

N-Allylthiourea (abbreviated as ATU) is a chemically interesting ligand that has attracted recent attention as its transition-metal complexes exhibit interesting properties and applications, *e.g.* copper complexes used in copper electroplating (Olijnyk *et al.*, 2003), rhenium(III) complexes for radiotherapeutic purposes (Gambino *et al.*, 2002), and cadmium or mercury compounds for non-linear optical applications (Yuan *et al.*, 1993).



(I)

The title compound, $[ZnCl(ATU)_3]Cl$, (I), is a non-linear optical material investigated in our group with the guidance of the theoretical double radical model (Xu *et al.*, 1987) as part of a continuing intensive study of ATU complexes of group IIB elements for non-linear optics. As a new member of this series (Yuan *et al.*, 1993), (I) has a similar structure to related species but belongs to a different space group.

The crystal structure of (I) comprises $[ZnCl(ATU)_3]^+$ (Fig. 1) and Cl^- ions, each disposed about a common threefold axis. In the cation, the Zn atom is four-coordinate, being surrounded by three ATU molecules, acting as monodentate ligands through the S atoms, and one Cl atom. The Zn—Cl1 and Zn—S distances [2.3092 (13) and 2.3283 (8) Å, respectively; Table 1] are both longer than the sum of single-bond covalent radii (2.24 and 2.29 Å, respectively; Pauling, 1960), and shorter than the sum of the Shannon (1976) ionic radii, *i.e.* 2.41 and 2.44 Å, respectively, which indicates that the two bonds have intermediate covalent and ionic character. The values are comparable to the average values reported in other complexes in which Zn is four-coordinated by S and Cl atoms (*e.g.* Kunchur & Truter, 1958; Lopez-Garzon *et al.*, 1993). The S═C and average C—N distances [1.713 (3) and 1.326 (4) Å, respectively] agree well with the values found in other metal–allylthiourea complexes (*e.g.* Chiesi *et al.*, 1971; Ferrari *et al.*, 1972; Filinchuk *et al.*, 1996), which appear to be, respectively, longer and shorter than the values reported in free allylthiourea of 1.656 (10) and 1.366 (12) Å, respectively (Dragonette & Karle, 1965), the large uncertainties notwithstanding. These variations reflect the coordination of the S atom to the central element.

The bond angles around the Zn atom range from 108.58 (3) to 110.34 (3)°, similar to those in $Zn[S{=}C(NH_2)_2]_2Cl_2$ (Kunchur & Truter, 1958), indicating little deviation from the ideal tetrahedral value of 109.5°. The distorted tetrahedral geometry is an important factor leading to their high non-linear optical effect.

Atom Cl2 functions as a hydrogen-bond acceptor in the structure, forming six N—H···Cl bonds with three adjacent molecules, where the nine S atoms lie in the same plane (Table 2). Each molecule provides –NH_2 and –NH– groups from one ATU ligand as two donors. There are also three intramolecular hydrogen bonds of the type –N—H···Cl1.

Experimental

$ZnCl_2$ and ATU (molar ratio 1:3) were dissolved in deionized water and diethyl ether, respectively. They were then mixed together with stirring for 30 min. After standing for 24 h, the solution divided into two layers, and a pale-yellow oily solid appeared in the ether layer. The oily solid was separated and dissolved in a small volume of ethanol. Small colourless single crystals of $[ZnCl(ATU)_3]Cl$ were obtained by the slow evaporation of this solution. The powder second harmonic generation (SHG) test has indicated that the SHG efficiency of the $[ZnCl(ATU)_3]Cl$ crystal is comparable to that of urea.

Crystal data

$[ZnCl(C_4H_8N_2S)_3]Cl$
$M_r = 484.82$
Trigonal, $R3$
$a = 11.0498$ (4) Å
$c = 16.0416$ (11) Å
$V = 1696.24$ (15) Å^3
$Z = 3$
$D_x = 1.424$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 46 reflections
$\theta = 5.0$–$12.5°$
$\mu = 1.61$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.45 × 0.40 × 0.31 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1996)
$T_{min} = 0.522$, $T_{max} = 0.607$
2412 measured reflections
2190 independent reflections
1849 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$
$\theta_{max} = 30.0°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -22 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: 0.2%

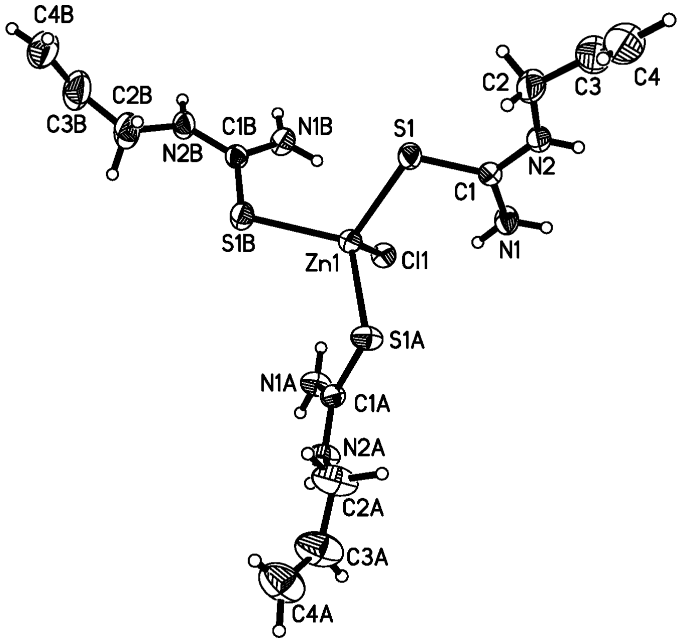


Figure 1
Molecular structure of the cation in $Zn[Cl(ATU)_3]Cl$; the cation has threefold symmetry. Displacement ellipsoids are shown at the 30% level. H atoms have been omitted. [Symmetry codes: (A) $1 - x + y$, $2 - x$, z; (B) $2 - y$, $1 + x - y$; z.]

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.093$
$S = 1.01$
2190 reflections
74 parameters
H-atom paramteres constrained
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.0198P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0156 (10)
Absolute structure: Flack (1983), 1082 Friedel pairs
Flack parameter = 0.002 (15)

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl1	2.3092 (13)	N1—C1	1.325 (4)
Zn1—S1	2.3283 (9)	C1—N2	1.327 (4)
S1—C1	1.713 (3)	N2—C2	1.458 (5)
Cl1—Zn1—S1	108.58 (3)	N1—C1—N2	117.3 (3)
S1—Zn1—S1^{i}	110.34 (3)	N1—C1—S1	122.8 (3)
C1—S1—Zn1	106.65 (11)	N2—C1—S1	119.9 (2)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl2^{ii}	0.86	2.53	3.308 (3)	151
N1—H1*B*···Cl1	0.86	2.54	3.338 (3)	154
N2—H2*A*···Cl2^{ii}	0.86	2.46	3.255 (3)	154

Symmetry code: (ii) $x - \frac{1}{3}, y - \frac{2}{3}, \frac{1}{3} + z$.

H atoms were placed geometrically (C—H = 0.93–0.97 Å and N—H = 0.86 Å) and refined using the riding-model approximation, with $U_{iso} = 1.2U_{eq}$(C,N).

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Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Bruker, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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