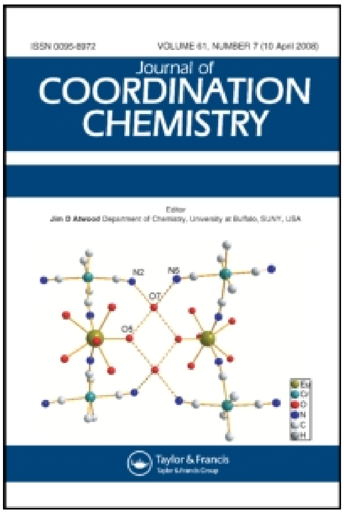

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Multiple secondary interaction arrangement in the crystal structure of <i>cis</i>-dichlorobis(thiourea-S)-zinc(II)

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Multiple secondary interaction arrangement in the crystal structure of dichlorobis(thiourea-S)-zinc(II)

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In our series of investigations into the structural and thermal behaviour of metal thiourea (tu) complexes, the single-crystal X-ray structure of dichlorobis(thiourea-S)-zinc(II) is redetermined at higher accuracy to $R = 0.0315$ proving the space group *Pnma*. Half of the complex molecule is in the asymmetric unit, the Zn and the two Cl atoms lie on the mirror plane. The structure analysis shows tetrahedral coordination of the Zn cation, the coordination sphere of the chloride anions and the extended hydrogen bond network. A chloride ligand is situated in the middle of the sandwich formed by bilayers of the complex molecules. We previously characterized the Cd analogue, allowing a structural comparison between the non-isostructural complexes: Mtu_2Cl_2 (M = Zn, Cd). Also the thermal properties of the complexes and their behaviour in chemical spray pyrolysis (CSP) processes are briefly correlated with the structure and bonding.

Keywords: Zinc-thiourea complex; Zinc coordination; CSP precursor; Structural comparison of thiourea complexes; Complex system of intermolecular interactions

1. Introduction

The single-crystal X-ray structure analysis of the complex molecule of dichlorobis(thiourea-S)-zinc(II) $[ZnCl_2(SC(NH_2)_2)]$ (**1**) is reported as part in the series of structural and thermal studies on metal-thiourea complexes (copper(I) [1–3], tin(II) [4, 5], cadmium(II) [6] and zinc(II) [7–9]).

Thiourea complexes are used as single-source precursors in chemical spray pyrolysis (CSP) processes in order to deposit semiconducting metal sulfide thin films for alternative solar cell fabrication [10–12]. Methods for growing large size single crystals

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of the title compound **1** by slow evaporation [13] and slow cooling techniques have also been worked out [14].

In spite of the fact that there are several references to the structural features of this simple compound, dichlorobis(thiourea-S)-zinc(II) (**1**) [14–18] its structure was published only once in 1958. Kunchur and Truter [19] described the crystal structure in the space group *Pnma*. Their carefully performed structure determination of that time (the intensities were visually estimated and no absorption correction was performed) yielded $R = 14.80\%$, having a very small crystal (0.03 mm diameter) and very few collected reflections (567). No other structural results of complex **1** were published by Cambridge Structural Database [20] until today notwithstanding the revolutionary technical developments and ease of crystallization.

Later, the NLO activity of the compound was recognized. Mary and Dhanuskodi [16] without giving atomic coordinates reported that the space group of the complex might be the non-centrosymmetric $Pna2_1$, based on a cell determination and the preliminary second harmonic generation measurements by Oussaid *et al.* [21]. This problem with the centrosymmetricity of the crystal led to confusion in the literature.

A new group of NLO materials currently attracts considerable interest. There are metal complexes, which crystallize in a centrosymmetric space group but exhibit NLO activity explained by the non-centrosymmetricity of the molecule [22]. Our structure is also an example of this kind of rare compound. Discussion of the space group problem with extended investigation of the non-linear optical activity of dichlorobis(thiourea-S)-zinc(II) $[ZnCl_2(SC(NH_2)_2)]$ (**1**) will be published elsewhere [23].

2. Experimental

2.1. *Material and synthesis*

Crystal preparation [7]: granulated Zn metal (65.4 mg, 1 mmol) was dissolved in 2.5 mL HCl ($1\,\mathrm{mol\,L^{-1}}$), then 152.3 mg (2 mmol) thiourea was added and dissolved by warming. After several days at room temperature well-grown prism-shaped crystals were obtained. A preparative procedure for **1** is described by Krunks *et al.* [8].

2.2. *Physical measurements*

According to simultaneous TG–DTA measurement, no water of crystallization was present. Microanalysis of $C_2H_8Cl_2N_4S_2Zn$ requires C, 8.33; H, 2.79; N, 19.42. Found: C, 8.10; H, 2.85; N, 19.11%.

2.3. *X-ray crystallography*

A crystal of **1** was mounted on a glass fibre. Cell parameters were determined by least-squares of the setting angles of 25 ($19.05 \leq \theta \leq 20.30°$) reflections. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromator, using ω–2θ scans. Data collection and cell refinement were performed by CAD4 EXPRESS [24] while data reduction by XCAD4 [25]. Backgrounds were measured at 1/2 the total time of the peak scans. The intensities of 3 standard reflections were monitored every 60 min. The intensities of the standard reflections indicated a crystal decay of 1%, thus the data were corrected for decay. The structure was solved by direct methods using SHELXS97 [26] and was refined by anisotropic full-matrix least-squares refinement on F^2 by SHELXL97 [27]. All hydrogen atoms were found on difference Fourier maps, and all hydrogen parameters were refined. Molecular graphics were prepared using PLATON [28] and PXX [29].

3. Results and discussion

The redetermination of the crystal structure of dichlorobis(thiourea-S)-zinc(II) (**1**) with a significantly higher accuracy (table 1) than in the previously published structure [19] is reported here including detailed structural analysis. We report the structure analysis, the description of the extended hydrogen bond network in three dimensions, and the coordination of zinc and chlorine atoms (tables 2 and 3).

Table 1. Crystal data and refinement of dichlorobis(thiourea-S)-zinc(II).

Empirical formula	$C_2H_8Cl_2N_4S_2Zn$
Formula weight	288.51
Crystal system	Orthorhombic
Space group	*Pnma* (No. 62)
a (Å)	13.040(3)
b (Å)	12.767(3)
c (Å)	5.893(1)
$\alpha=\beta=\gamma$ (°)	90
V (Å^3)	981.1(4)
Z	4
ρ (Calcd) (Mg m^{-3})	1.954
Radiation (Å)	0.71073
μ (Mo-Kα) (mm^{-1})	3.419
Type of absorption correction	ψ-scan
$F(000)$	576
Colour, habit	Colourless, platelet
Crystal size (mm^3)	0.10 × 0.30 × 0.45
Temperature (K)	295(2)
θ min–max (°)	3.1, 42.0
(h k l) range	$-24 \leq h \leq 24$; $-24 \leq k \leq 24$; $-11 \leq l \leq 11$
No. of reflections measured	7210
No. of unique reflections	3519
R(int)	0.017
Observed data [$I > 2\sigma$(I)]	1987
No. of parameters	72
R, wR_2^* [$I > 2\sigma$(I)]	0.0315, 0.0757
R, wR_2^* (all data)	0.0672, 0.0836
S	0.95
Max. and av. shift/error	0.00, 0.00
Min. and max. resd. dens. (e Å^{-3})	−0.57, 0.55

*$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

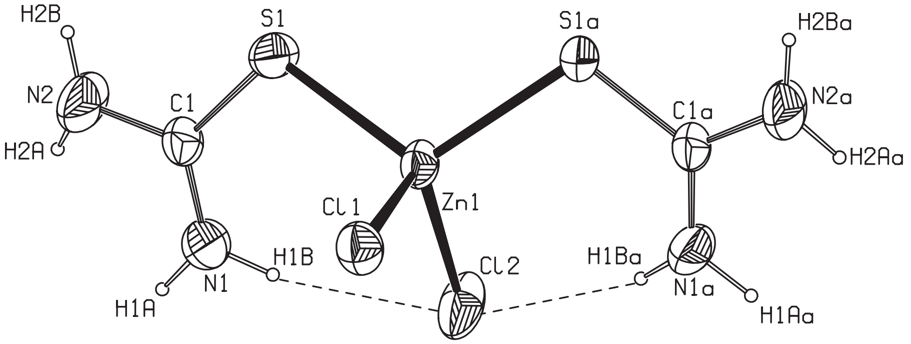

Figure 1. ORTEP diagram of dichlorobis(thiourea-S)-zinc(II). The displacement parameters are at 50% probability. The coordination of Zn^{2+} is highlighted. Atoms with label 'a' are symmetry-generated (x, $-y+0.5$, z). The mirror symmetry is defined by the Zn1, Cl1 and Cl2 atoms.

1 crystallises in the orthorhombic crystal system, space group *Pnma*. 7210 reflections were measured of which 3519 were independent, *R*(int) for the dataset is 0.013. With these data the structure converges to $R = 3.15\%$ (table 1). Several calculations were performed to check the centrosymmetricity of the crystal. *E* statistics [30] on cumulative probability distribution, *N*(*z*), distribution of *E*'s also for all data, and cumulative percentage of mod (E) at 85.46%, all show that *E* statistics strongly indicate that the structure is centrosymmetric. PLATON [28] *N*(*z*) test statistics and normalized *N*(*z*) curves show 57% probability of centrosymmetric arrangement. The Sheldrick [26] mean $|E^2 - 1| =$ 0.963 (expected 0.968 for centrosymmetric and 0.736 for non-centrosymmetric structures). Based on these calculations it can be assured that the structure is centrosymmetric, the correct space group is *Pnma* and not $Pna2_1$.

The ORTEP [28] diagram of the molecular complex is shown in figure 1. Half of the complex can be found in the asymmetric unit. Zn1, Cl1 and Cl2 atoms are in special positions lying on the mirror planes $y = 1/4$ and 3/4. There is an N1–H1B $\cdots$ Cl2 intramolecular hydrogen bond, repeated by the mirror symmetry, stabilizing the complex molecule (table 3). Zn1 and Cl2 are close to the plane determined by the thiourea ligands (0.5864(4) and −0.263(2) Å) while Cl1 is much out of plane (2.885(1) Å).

The Zn^{2+} cation is tetrahedrally coordinated by two chloride anions and two sulfur atoms of the thiourea ligands; one of the sulfurs is symmetry generated atom (x, $-y+0.5$, z) (figure 2a, table 2). Furthermore, there is an additional $Cl2^-$ ligand of a neighbouring complex (x, y, $z-1$), which is in the outer coordination sphere of the Zn^{2+} central ion in the S1–Zn–S1a tetrahedral angle which is more open then the Cl1–Zn–Cl2 angle.

The $Cl1^-$ is coordinated to the core Zn^{2+} and takes part in four N–H $\cdots$ Cl type hydrogen bonds (atoms which are symmetry generated $-x+0.5$, $-y$, $z-0.5$ from one side and $-x+0.5$, $y+0.5$, $z-0.5$ from the other side, respectively) (figure 2a, table 3). The $Cl2^-$ is also coordinated to the Zn^{2+} centre, at a short distance to the S1 (Cl2 $\cdots$ S1 3.393(1) Å) and Zn (Cl2 $\cdots$ Zn1 3.645(1) Å) atoms of the neighbouring complex (figure 2a). If Cl2 is from the asymmetric unit S1a and Zn are generated by the symmetry operation of x, y, $z+1$, while S1b is generated by x, $-y+0.5$, $z+1$.

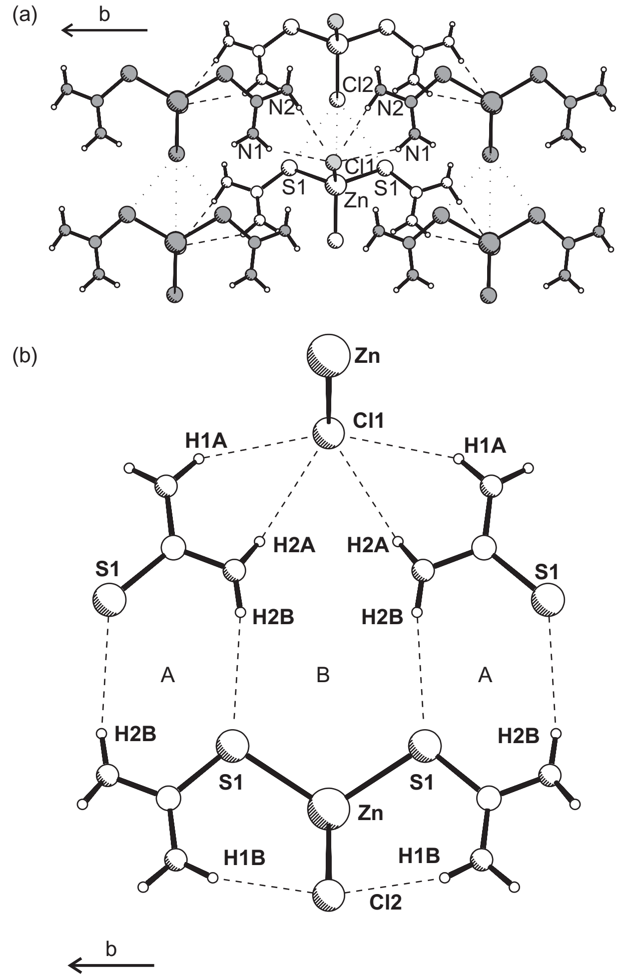

Figure 2. (a) The infinite bilayer sandwich-type structure in the packing diagram of the complex molecule. Dark grey atoms can be found in the upper layer, while open circle atoms represent the atoms in the lower layer. Brick pattern filled $Cl1^-$ atoms are in the upper sheet but they are connected to the complex molecules in the lower sheet. Coordination sphere around $Cl1^-$ and $Cl2^-$ anions can also be observed on the figure. (b) Complex system of the all N–H$\cdots$S type hydrogen bonds in the structure. H1a$\cdots$Cl1 is in the same layer. H1b$\cdots$Cl2 is an intramolecular interaction.

As thiourea is coordinated to Zn^{2+}, elongated C=S double bond and shortened C–N bond lengths can be observed compared to the uncoordinated thiourea molecule. The greater double bond character of the carbon to nitrogen bond on the complex formation is also manifested in the infrared spectra [14].

Two sheets of the complex molecules form a sandwich layer (figure 2a). The infinite bilayer sandwiches are repeated by translation in the crystallographic *a* direction. The $Cl1^-$ ligand of the complex is situated in the middle of the sandwich. The sandwich system is stabilized by secondary interactions. An infinite chain in the crystallographic *b* direction is formed by N–H$\cdots$Cl interactions (table 3) connecting two thioureas in

Table 2. Selected geometric parameters (Å, °) for dichlorobis(thiourea-S)-zinc(II).

Zn1–Cl2	2.2732(6)	S1–C1	1.7126(13)
Zn1–Cl1	2.3105(7)	C1–N1	1.3126(18)
Zn1–S1^{i}	2.3407(5)	C1–N2	1.3185(18)
Zn1–S1	2.3407(5)	Zn1 ··· Cl2^{ii}	3.646(1)
Cl1–Zn1–S1	108.452(15)	Cl2–Zn1–S1	110.496(15)
S1^{i}–Zn1–S1	112.58(2)	Cl1–Zn1–Cl2	106.12(3)
N1–C1–S1	124.11(10)	C1–S1–Zn1	108.42(5)
N1–C1–N2	117.87(13)	N2–C1–S1	118.01(12)

Symmetry codes: (i) x, $1/2-y$, z; (ii) x, y, $z-1$.

Table 3. Hydrogen-bonding geometry (Å, °) for dichlorobis(thiourea-S)-zinc(II).

D–H ··· A	D–H	H ··· A	D ··· A	∠(D–H ··· A)
N1–H1A ··· Cl1^{i}	0.84(3)	2.71(3)	3.4951(16)	157(2)
N1–H1B ··· Cl2	0.94(3)	2.28(3)	3.2043(16)	166(2)
N2–H2A ··· Cl1^{i}	0.92(3)	2.65(3)	3.5137(19)	158(2)
N2–H2B ··· S1^{ii}	0.88(4)	2.88(4)	3.647(2)	147(3)

Symmetry codes: (i) $1/2-x$, $-y$, $1/2+z$; (ii) $1-x$, $-y$, $-z$.

the same sheet by a Cl1^{-} bridge coming from a third complex in the other sheet of the sandwich. There are three short contacts of the Cl2^{-} ion to the neighbouring complex in its own layer. N–H ··· S type hydrogen bonds join the bilayer sandwiches connecting them in the diagonal of the *ac* crystallographic direction (figure 2b, table 3). The N–H ··· S hydrogen bond is repeated by the mirror symmetry defined by Cl1–Zn–Cl2 atoms forming a chain (–A–B–A–B–A–) of two connecting and periodically repeating different loops in the crystallographic *b* direction. The graph set analysis [31] of the hydrogen bond pattern indicates that 'A' is homodromic $R_2^2(8)$, while 'B' is antidromic $R_4^3(10)$.

There are 13 different tetrahedrally coordinated dihalogeno metal thiourea complexes including clathrates in the Cambridge Structural Database [20] (ASULAB [32] ($P-1$), CLSTUZ [19] (*Pnma*), COTUCL11 [33] (*Cc*), CTURCD02 [34] ($Pmn2_1$), FOBBAZ [35] ($I2/a$), HGITUR [36] (*Pnma*), LOXSAS [37] ($P-1$), PEKSUT [34] (*Pnam*), SURTEB01 [35] ($I2/a$), SURTEC01 [35] ($I2/a$), ZZZAWD01 [34] ($P2_1/c$), OBUMAA [38] ($P-1$) and DAJBAS [39] ($P-1$), listing the structure with the lowest *R* value if more structure determinations are published). They contain divalent Zn, Co, Cd, Fe, Te and Hg central atoms, and chloride, bromide or iodide as ligands in addition to the two thiourea ligands. In accordance with the Valance Shell Electron Pair Repulsion theory [40] with the increasing size of the van der Waals radius of the central cation the M–Cl distance increases, the Cl–M–Cl angle decreases in the complex, while the S=C bond is getting longer, C–N bond shorter and N–C–N angle larger in the thiourea molecule.

The structure and thermal properties of the title compound **1** may now be compared with those of the cadmium complex **2** [6]. Both complexes have the same composition and both contain tetrahedrally (2 × tu, 2 × Cl) coordinated divalent group 12 metal ion, without being isostructural, though. Unit cell volume of **1** in the space group *Pnma* is approximately double (1.98) the unit cell volume of **2** in the space group $Pmn2_1$. While being typical for Zn^{2+}, the coordination number of 4 is quite seldom encountered with the larger Cd^{2+} ion. Both **1** and **2** have been successfully used for CSP depositions of CdS [6] and ZnS [8] thin films, whereupon the strong M–S bonds are retained but most of the chlorine is expelled as HCl. In an oxidizing environment, the M–S bonds must compete with M–O bonds trying to replace them, *i.e.* oxidation may take place. In this respect, Cd^{2+} behaves like a type-*b* cation preferring M–S bonding over the M–O attractions while Zn^{2+} has been classified as a type-*a* cation lying close to the borderline [41]. This difference in affinities may certainly influence the impurity levels in the ZnS and CdS thin films prepared by spray pyrolysis from **1** and **2**, respectively. In general, thermal decompositions of **1** and **2** are extremely complex involving several gaseous products and solid intermediates and giving rise to elemental and phase impurities [6–9].

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 293388. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 044-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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