New Complexes with a Sterically Hindered Thiourea: Syntheses and Crystal Structures of $[Co(dchtu)_2Cl_2]$, $[Zn(dchtu)_2(NCS)_2]$ and $[Pb(dchtu)_6](SCN)_2 \cdot 2C_2H_5OH$ (dchtu = N,N'-dicyclohexylthiourea)

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Abstract. New complexes of a sterically hindered thiourea, $[M(dchtu)_2Cl_2]$ (M = Co 1, Ni 2), $[Zn(dchtu)_2(NCS)_2]$ (3) and $[Pb(dchtu)_6](SCN)_2 \cdot 2C_2H_5OH$ (4) (dchtu = N,N'-dicyclohexylthiourea), have been synthesized and characterized. The single crystal structures of 1, 3 and 4 have been determined by single crystal Xray diffraction analyses. Co^{II}, Ni^{II}, and Zn^{II} form 1: 2 compounds with dchtu even if molar excesses of dchtu is used, while Pb^{II} forms 1:6 compound under the same conditions. The dchtu acts as a monodenate S-donor ligand in all the complexes. Co^{II} and Zn^{II} atoms

are tetrahedrally coordinated with two dchtu ligands, and two chloride or isothiocyanate ions, respectively. The Pb^{II} ion in **4** forms an octahedral coordination sphere with six dchtu ligands. The structures of the complexes are stabilized by a system of intermolecular H-bonding.

Keywords: Cobalt; Zinc; Lead; *N*,*N*'-dicyclohexylthiourea; Crystal structures

Introduction

Thioureas are potentially very versatile ligands in coordination chemistry being able to coordinate to metal atoms via either sulfur or nitrogen atoms. Their soft sulfur and hard nitrogen donor atoms provide a multitude of bonding possibilities, therefore exhibiting coordination diversity in metal complexes. In addition, thioureas are able to coordinate to a range of metal atoms either as neutral ligands, as monoanions, or as dianions [1-3]. Furthermore, their physical and chemical properties are modified by the substituents on nitrogen. Now, the chemistry of substituted thiourea derivatives has attracted increasing attention because of their potential use as reagents for the separation or recognition of metal ions [4, 5] and in biological applications [6-8]. There have been many studies on N-alkyl or aryl and N,N'-dialkyl or diaryl substituted thioureas and related ligands coordinated to a series of metals [9-14]. The properties of metal complexes with substituted thiourea derivatives are influenced by the substituents on the nitrogen atoms. For example, the sterically bulky N,N'-disubstituted thiourea-Pd complexes are air- and moisture-stable, and highly active catalysts for palladium-catalyzed Heck reaction of aryl iodides and bromides with olefins [15, 16].

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N,N'-dicyclohexylthiourea (dchtu) is an important symmetrically substituted thiourea derivative. Toshimi et. al. found that the sterically bulky N,N'-dicyclohexylthiourea mixed with copper acetylacetonate is capable of absorbing near IR-rays and provides superior optical materials for shielding sunlight thermic rays [17]. However, the interactions of dchtu with metal atoms still remain unexplored except the only example of a tellurium(II) complex, [Te(dchtu)₂Cl]Cl [18]. To the best of our knowledge there are no examples of transition metal complexes containing dchtu. Now we investigate the reactions of dchtu with Co^{II}, Ni^{II}, Zn^{II}, and Pb^{II} metal ions and obtained the new complexes $[M(dchtu)_2Cl_2]$ (M = Co 1, Ni 2), $[Zn(dchtu)_2(NCS)_2]$ (3) and $[Pb(dchtu)_6](SCN)_2 \cdot 2C_2H_5OH$ (4). The present contribution reports the synthesis and characterization of the new complexes.

Results and Discussion

Synthesis and IR Spectral Studies

The dchtu ligand reacts with Co^{II}, Ni^{II}, and Zn^{II} salts in C₂H₅OH to form exclusively the 1:2 stoichiometric coordination compounds **1**, **2** and **3**, respectively. Using three-fold molar excesses of dchtu in the reactions also give rise to the formation of these 1:2 compounds of dchtu. In contrast, these metal thiourea-type complexes form 1:4 compounds, $[M(tu)_4](NO_3)_2$ (M = Co, Zn) [19, 20], $[Ni(tu)_4]S_2O_3 \cdot H_2O$ [21] (tu = thiourea) under similar conditions. The sterically hindered nature of dchtu is the most likely explanation for the limited degree of substitution in the valence shell of the metal atoms despite the molar excess ligand. However, lead(II) produced a 1:6 compound with dchtu under the



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Table 1	Selected	bond	distances	/À	and	angles	/°	for	1,	3,	and	4
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	[Co(dchtu) ₂	Cl ₂] (1)			
Co(1)-S(1)	2.2970(11)	Co(1)-Cl(1)	2.2595(9)		
Cl(1)-Co(1)-S(1) $Cl(1)-Co(1)-Cl(1)^{a}$	111.63(4) 118.99(5)	$\begin{array}{c} S(1) - Co(1) - S(1)^a \\ Cl(1) - Co(1) - S(1)^a \end{array}$	114.50(7) 100.40(4)		
	[Zn(dchtu) ₂ (N	[CS) ₂] (3)			
Zn(1) - S(1)	2.3311(12)	Zn(1) - N(3)	1.995(4)		
S(1) - Zn(1) - N(3)	106.91(12)	$S(1) - Zn(1) - S(1)^{a}$	112.57(7)		
$N(3)-Zn(1)-N(3)^{a}$	113.0(2)	$S(1) - Zn(1) - N(3)^{a}$	108.77(13)		
[Pb	(dchtu) ₆](SCN) ₂	2C ₂ H ₅ OH (4)			
Pb(1) - S(1)	2.9636(7)	Pb(1) - S(2)	2.9610(7)		
Pb(1)-S(3)	2.9625(8)				
S(1) - Pb(1) - S(2)	82.66(2)	$S(1) - Pb(1) - S(1)^{a}$	180.0		
S(1) - Pb(1) - S(3)	87.91(2)	$S(1) - Pb(1) - S(2)^{a}$	97.34(2)		
$S(1) - Pb(1) - S(3)^{a}$	92.09(2)	$S(2) - Pb(1) - S(2)^{a}$	180.0		
S(2) - Pb(1) - S(3)	74.10(2)	$S(3) - Pb(1) - S(3)^{a}$	180.0		
$S(2) - Pb(1) - S(3)^{a}$	105.90(2)	$S(3) - Pb(1) - S(1)^{a}$	92.09(2)		

^a Symmetry transformations used to generate equivalent atoms: For 1 and 3: -x+1, y, -z+3/2. For 4: -x+1, -y+1, -z+1.

same conditions, even when less dchtu is used. With thiourea, lead(II) also forms the 1:6 compound $[Pb(tu)_6](ClO_4)_2$ [22]. The effects of sterically hindered substituents on the nitrogen atoms of thiourea decrease with the increase of metal radius.

The IR spectra of the complexes showed characteristic bands due to *N*,*N'*-dicyclohexylthiourea and some important ones are listed in section 2. The presence of a ν (N–H) signal in the region 3072-3125 cm⁻¹ as a weak band in the complexes shows that the ligand is not deprotonated in the complexes. The feature of the broad bands with low intensity is evident that could arise from hydrogen-bonded NH group. A strong ν (C=S) band at 1153 cm⁻¹ in the free ligand shifts to the lower range, 1147-1152 cm⁻¹. This shows that the ligand coordinates to the metal atom via its sulfur donor atom and the magnitude of the coordination shift is similar to that reported in literatures [23–25].

Crystal Structures

The structures of compounds 1, 3, and 4 are depicted in Figures 1-6. Selected bond distances and angles are listed in Tables 1 and 2. As show in Figure 1, the Co^{2+} ion is coordinated by two S atoms from two N,N'-dicyclohexylthiourea ligands and two chlorine atoms. The N,N'-dicyclohexylthiourea ligand coordinates to the Co^{II} atom through its sulfur atom. The Co^{II} atom forms a tetrahedral structure, as evidenced by bond angles around the Co^{II} atom ranging from 100.40(4) to 118.99(5)°. Two Co-S bonds are chemically equivalent and the Co-S distance is 2.2970(11) Å. The distance of Co-Cl bond is 2.2595(9) Å (Table 1). The Co-S bond distances are similar to those observed in the Co^{II} complexes of thiourea [19, 26]. The N,N'-dialkyl substituted thiourea, with the coplanar N₂CS skeletal atoms, can take trans-trans, cis-trans, and cis-cis three possible conformations. N,N'-dimethylthiourea and N,N'diethylthiourea were trans-trans isomers in the solid state

Table 2List of hydrogen bonds in the crystal structures of complexes 1, 3, and 4

D-H	А	d(D····A)	<(DHA)
1			
N(1) - H(1)	Cl(1)	3.486(3)	166(4)
N(2) - H(2)	$Cl(1)^{a}$	3.290(3)	161(3)
3			
N(1)-H(1)	S(2) ^a	3.721(4)	161(4)
4			
N(1) - H(1)	S(3) ^a	3.581(3)	155(3)
N(2) - H(2)	S(4)	3.588(3)	163(3)
N(3) - H(3)	$S(1)^a$	3.746(3)	161(3)
N(4) - H(4)	S(4) ^b	3.494(3)	148(3)
N(5) - H(5)	$S(1)^{a}$	3.602(3)	159(3)
N(6) - H(6)	$N(7)^{c}$	3.004(4)	161(3)

Symmetry transformations used to generate equivalent atoms: For 1: ^a -x+1/2, y-1/2, -z+3/2. For 3: ^a x, y+1, z. For 4: ^a -x+1, -y+1, -z+1; ^b x, y-1, z; ^c x, y, z-1.



Figure 1 Crystal structure of 1 with the labelling scheme (40 % probability ellipsoids). Hydrogen atoms of C-H are omitted for clarity.

[27]. In complex 1, *N*,*N'*-dicyclohexylthiourea exhibits cis-trans conformation (Fig. 1). As evidenced by the crystal structures below, *N*,*N'*-dicyclohexylthiourea in 3 and 4 is also in cis-trans conformation. This difference might be related with the steric hinderance of the cyclohexyl substituents and the H-bonding in the complexes. In 1, the hydrogen bonding interaction is between thioamide (>N-H) groups and Cl⁻ ions. Each of the [Co(dchtu)₂Cl₂] molecules forms four N-H···Cl hydrogen bonds with four neighbor molecules forming a layered hydrogen bonding network perpendicular to the *c*-axis of unit cell (Fig. 2). Since the two ligands are symmetry equivalent, the unique N···Cl distances are 3.486(3) and 3.290(3) Å, and N-H···Cl angles are 166(4) and 161(3)° (Table 2).

The molecular structure of **3** is depicted in Figure 3. The Zn^{2+} ion is also in a tetrahedral coordination, involving two S atoms of two *N*,*N'*-dicyclohexylthiourea ligands and two N atoms of two NCS⁻ anions (Fig. 3). The thiocyanate anion coordinates to the Zn^{2+} ion through its N atom. The



Figure 2 View of the packing of $[Co(dchtu)_2Cl_2]$ molecules showing the hydrogen bond interactions viewed along *c* axis. Hydrogen atoms of C-H are omitted for clarity.



Figure 3 Crystal structure of 3 with the labelling scheme (40% probability ellipsoids). Hydrogen atoms are omitted for clarity.

bond angles at the metal atom vary from 106.91(12) to 113.0(2)° (Table 1). Due to the sterical bulk of the cyclohexyl rings, the S–Zn–S angle (112.57(7)°) is much larger than the corresponding angle observed in Zinc(II) complex with thiourea, [Zn(tu)₂Cl₂] (S–Zn–S: 98.40(3)°) [28]. The Zn–S (2.3311(12) Å) and Zn–N (1.995(4) Å) bond distances are consistent with those observed in literatures for similar zinc(II) thiourea complexes [20, 28, 29]. In **3**, the sulfur atoms of isothiocyanate ions acts as hydrogen bonding acceptors, forming two equivalent N–H…S weak hydrogen bonds with neighbor molecules [N(1)…S(2) = 3.721(4) Å] (Table 2). The [Zn(dchtu)₂(NSC)₂] molecules are arranged in a chain via this hydrogen bonding (Fig. 4). The chains are extended via weak S…S interaction [S…S =



Figure 4 View of the packing of $[Zn(dchtu)_2(NSC)_2]$ molecules showing the hydrogen bond interactions viewed along *c* axis. Hydrogen atoms of C-H are omitted for clarity.



Figure 5 Crystal structure of 4 with the labelling scheme (30%) probability ellipsoids). Hydrogen atoms are omitted for clarity.

3.587 Å] forming a layer along (011) plane of the unit cell (Fig. 4).

Compound 4 crystallizes in the monoclinic space group $P\overline{1}$ (no.2) with one formula unit in the unit cell. The Pb²⁺ ion is coordinated by six *N*,*N'*-dicyclohexylthiourea ligands forming a distorted octahedron (Fig. 5). The S–Pb–S bond angles at equatorial positions vary from 74.10(2) to 105.90(2)°. Three Pb–S bond distances are almost equivalent and vary in a narrow range [2.9610(7)–2.9636(7) Å] (Table 1), which is in consistence with those of lead complexes with thiourea [22, 30]. Although the thiocyanate ions have no influence on coordination, they have significant influence on the crystal packing of the [Pb(dchtu)₆]²⁺ cations in **4**. The thiocyanate ion forms three hydrogen bonds with



Figure 6 View of the packing of $[Pb(dchtu)_6](SCN)_2$ molecules showing the hydrogen bond interactions viewed along *a* axis. The cyclohexyl rings are omitted for clarity.

thioamide (>N-H) groups of dchtu ligand via its nitrogen and sulfur atoms [N(6)···N(7) = 3.004(4), N(2)···S(4) = 3.588(3), N(4)···S(4) = 3.494(3) Å] (Table 2). In the crystal structure, each [Pb(dchtu)₆]²⁺ cation is surrounded by six cations, which form a planar hexagon. The central cation interacts with its six neighbors by hydrogen bonding through six thiocyanate ions (Fig. 6). By the connection of thiocyanate ions, the [Pb(dchtu)₆]²⁺ cations form a twodimensional network parallel to the (100) face of unit cell.

The effects of monodenate thione-sulfur coordination are reflected in the thioamide dimensions of the ligand. An average lengthening of the C-S distance and an average shortening of the N-C(=S) one are observed in the complexes. The carbon-sulfur (thione) distance is increased from 1.7013(15) A [31] in the free ligand, to 1.724(3) A, 1.734(4) Å, and 1.716(3)-1.729(3) Å for the coordinated ligands in 1, 3, and 4, respectively. On average, the thioamide carbon-nitrogen distance is correspondingly decreased from 1.338(2) Å [31], in the free ligand to 1.329(4) Å, 1.332(3) Å, and 1.329(4) Å in the coordinated ligand. The carbon-sulfur and carbon-nitrogen bonds lie in intermediate bond lengths between single and double bond, which is attributed to the delocalization of the electrons in the amide bond. This extent of the dimensional changes is consistent with monodenate thione-sulfur coordination of substituted thiourea ligands [10-12].

Experimental Section

Materials and Physical measurements: All chemicals were commercial materials of analytical grade and used without further purification. FT-IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. C, H and N analysis was measured on a MOD 1106 elemental analyzer. *Synthesis of* [Co(dchtu)₂Cl₂] (1): A solution of dchtu (0.197 g, 0.82 mmol) in C₂H₅OH (8 ml) was added to a solution of CoCl₂·6H₂O (0.100 g, 0.42 mmol) in C₂H₅OH (5 ml) followed by stirring for 30 min when a clear blue solution was formed. The slow evaporation of the solution at room temperature formed blue block crystals of 1 in 85 % yield. Anal. Calc. for C₂₆H₄₈N₄S₂Cl₂Co (%): C, 51.14; H, 7.92; N, 9.17. Found: C, 50.98; H, 7.83; N, 9.07. IR data (KBr pellets, cm⁻¹): 3125w (vN-H), 1147s (vC=S), 1524vs (vC-N).

Synthesis of [Ni(dchtu)₂Cl₂] (2): A solution of dchtu (0.197 g, 0.82 mmol) in C₂H₅OH (8 ml) was added to a solution of NiCl₂· 6H₂O (0.100 g, 0.42 mmol) in C₂H₅OH (5 ml) followed by stirring for 30 min when a light yellow solution was formed. The slow evaporation of the solution at room temperature formed yellow precipitate of 2 in 78 % yield. No single crystals of the complex is obtained, even after several attempts. Anal. Calc. for C₂₆H₄₈N₄S₂Cl₂Ni (%): C, 51.16; H, 7.93; N, 9.18. Found: C, 12.22; H, 2.11; N, 9.34. IR data (KBr pellets, cm⁻¹): 3095w (ν N-H), 1149s (ν C=S), 1521vs (ν C-N).

Synthesis of [Zn(dchtu)₂(NCS)₂] (3): A solution of dchtu (0.182 g, 0.76 mmol) in C₂H₅OH (8 ml) was added to Zn(SCN)₂ (0.070 g, 0.38 mmol) suspended in C₂H₅OH (5 ml) and the mixture was stirred for 2 h. The solution formed was filtered. The slow evaporation of the resulted solution at room temperature formed colorless block crystals of **3** in 65 % yield. Anal. Calc. for C₂₈H₄₈N₆S₄Zn (%): C, 50.78; H, 7.30; N, 12.69. Found: C, 50.71; H, 7.21; N, 12.54. IR (KBr pellets, cm⁻¹): 3072w (ν N-H), 1152s (ν C=S), 1526s (ν C-N).

Synthesis of [Pb(dchtu)₆](SCN)₂ · 2C₂H₅OH (4): A solution of dchtu (0.223 g, 0.93 mmol) in C₂H₅OH (10 ml) was added to Pb(SCN)₂ (0.100 g, 0.31 mmol) suspended in C₂H₅OH (5 ml) and the mixture was stirred for 2 h. The clear colorless solution formed was filtered. The slow evaporation of the solution at room temperature formed light yellow block crystals of 4 in 45 % yield (based on dchtu). Reaction of dchtu and Pb(SCN)₂ in C₂H₅OH in a 4:1 mole ratio also produce 4 but with a higher yield (70 %). Anal. Calc. for C₈₄H₁₅₆N₁₄S₈O₂Pb (%): C, 54.30; H, 8.46; N, 10.55. Found: C, 54.22; H, 8.36; N, 10.41. IR (KBr pellets, cm⁻¹): 3105w (ν N-H), 1151s (ν C=S), 1523s (ν C-N).

Crystal Structure Determination

Data were collected on a Rigaku Mercury CCD diffractometer at 193(2) K using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) with a ω -scaning mode in the range 6.14 $\leq 2\theta \leq 50.68$ for 1, $6.22 \le 2\theta \le 50.68$ for 3, and $6.24 \le 2\theta \le 50.70$ for 4. The crystals of size $0.30 \times 0.20 \times 0.12 \text{ mm}^3$, $0.26 \times 0.20 \times 0.18 \text{ mm}^3$, and $0.50 \times 0.23 \times 0.23$ mm³ were used for data collection for 1, 3 and 4, respectively. An absorption correction was applied for all data with multi-scan. The structures were solved with direct methods using SHELXS-97 [32] and structure refinements were done against F² with SHELXL-97 [33]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters using a riding model. The atom of C(12) in 4 is disordered and the occupancies of disordered C/C' are assigned as 65 % and 35 %. Technical details of data acquisition and selected refinement results are summarized in Table 3. Crystallographic data for the structural analyses have been de-

	1	3	4	
Formula	C ₂₆ H ₄₈ N ₄ S ₂ Cl ₂ Co	$C_{28}H_{48}N_6S_4Zn$	$C_{84}H_{156}N_{14}S_8O_2Pb$	
Formula weight	610.63	662.33	1857.90	
Crystal system	monoclinic	monoclinic	triclinic	
Space group	C2/c (no.15)	C2/c (no.15)	<i>P</i> 1 (no.2)	
a / Å	11.405(2)	24.046(4)	12.4692(11)	
b / Å	14.592(3)	8.9058(14)	14.9151(9)	
c / Å	19.419(4)	19.038(4)	14.9843(11)	
$\alpha / ^{\circ}$	90.00	90.00	60.813(3)	
β/°	91.130(5)	125.748(4)	87.599(6)	
y/°	90.00	90.00	79.837(5)	
$V/Å^3$	3231.2(11)	3308.9(11)	2391.6(3)	
Ζ	4	4	1	
T / K	193(2)	193(2)	153(2)	
$D_{calc} / g \cdot cm^{-3}$	1.255	1.330	1.290	
F(000)	1300	1408	984	
μ/mm^{-1}	0.846	1.022	1.989	
Scane range / °	$6.14 \le 2\theta \le 50.68$	$6.22 \le 2\theta \le 50.68$	$6.24 \le 2\theta \le 50.70$	
Index range	$-13 \le h \le 12$	$-27 \le h \le 28$	$-15 \le h \le 15$	
-	$-17 \le k \le 17$	$-9 \le k \le 10$	$-17 \le k \le 17$	
	$-21 \le l \le 23$	$-22 \le l \le 22$	$-18 \le l \le 16$	
Collected reflections	15813	15953	23378	
Independent reflections	$2951 [R_{int} = 0.0539]$	$3038 [R_{int} = 0.0458]$	$8675 [R_{int} = 0.0233]$	
Reflections with $(I > 2\sigma(I))$	2535	2605	8631	
Parameters	168	186	519	
$R1 \ (I > 2\sigma(I))$	0.0591	0.0624	0.0263	
$wR2 \ (I > 2\sigma(I))$	0.0722	0.1405	0.0682	
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min}$ /e Å ⁻³	-0.360/0.385	-0.504/0.646	-0.910 / 1.089	
Goodness-of-fit	1.138	1.149	1.064	

 Table 3
 Crystal data and structure refinement details for complexes 1, 3, and 4

posited with the Cambridge Crystallographic Data Centre, CCDC Nos. 635441-635443. These data can be obtained free of charge via www.ccdc.cam.ac.uk.

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