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### Synthesis of the monosubstituted arylcyanoxime and its Na, Tl(I) and Ag(I) compounds

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# SYNTHESIS OF THE MONOSUBSTITUTED ARYLCYANOXIME AND ITS Na, Tl(I) AND Ag(I) COMPOUNDS

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Nitrosation of 2-chlorophenyl acetonitrile with *t*-butylnitrite under basic conditions (Meyer reaction) resulted in a high-yield preparation of the first substituted arylcyanoxime, 2-chlorophenyl(oximino)acetonitrile, H(2Cl–PhCO) (**HL**). The obtained cyanoxime is readily deprotonated in solution by metal hydroxides or carbonates with the formation of yellow sodium, tetrabutylammonium, thallium(I) and silver(I) derivatives. The crystal structure of the Tl(I) complex was determined. Thallium(I) salt (**TlL**) crystallizes in the monoclinic space group  $P2_1n$  with  $a = 3.8382(7)$ ,  $b = 11.0065(18)$ ,  $c = 20.901(4)$  Å, and  $\beta = 92.447(3)^\circ$ ,  $V = 882.2(3)$  Å<sup>3</sup>,  $Z = 4$ ;  $T = 193$  K (Mo  $K\alpha$  radiation). The structure was solved by direct methods to a final  $R$  of 0.0689 ( $wR2 = 0.1650$ ) for  $I > 2\sigma(I)$ . The crystal structure of the complex is a one-dimensional coordination polymer that consists of centrosymmetric [TlL]<sub>2</sub> dimers in which Tl<sub>2</sub>O<sub>2</sub> rhombohedra are connected to each other at 90.72°. The crystal structure of TlL is an interesting example of the ruffled metal-organic network composed of Tl–O–Tl–O zigzag chains with close (3.838 Å) intermetallic distances comparable to those in metallic thallium (3.42 Å). The cyanoxime anion bridges metal centers and acts as a tridentate ligand where oxygen atoms of the oxime group bond to three different Tl(I) cations with three different bond lengths.

**Keywords:** Cyanoximes; Thallium(I); Silver(I); X-ray analysis

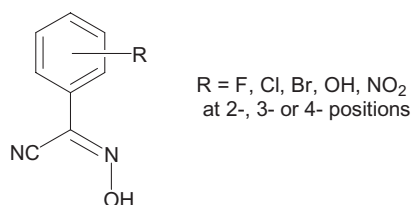
## INTRODUCTION

Monovalent thallium [1–2] and silver [3–5] form numerous polymeric coordination compounds with N,O containing ligands. Silver(I) is used extensively in the design of linear compounds or complexes with low coordination numbers that have applications in crystal engineering [6–8]. Thallium complexes attract attention because of their potential to form mixed valence Tl(I)/Tl(III) compounds with interesting electric conductivity properties [9–13], including high-temperature superconductivity [14–16].

Cyanoximes (compounds with the general formula NC=C=N–OH–R where R is an electron withdrawing group) represent a new class of organic ligands [17,26] that has

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undergone extensive studies during the last several years. This research includes molecules where R groups are CN [18], amide [19,20], thioamide [21,22], carboxylic esters [23], hydrazide [23], ketones [24,25] and heterocycles such as 2-pyridine [26], 2-thiazoline [26,27] 2-selenazoline [28], 2-benzthiazoline [29,30], 2-quinoline [26] and 2-benzimidazoline. A variety of electronic and steric properties of the R groups attached to cyanoxime provide the basis for rational design of ligands for different applications including assembly of the metal-organic framework in coordination polymers. Cyanoximes are of great interest because of their pronounced biological activity, ranging from agricultural pesticide antidote [36] and growth regulation [37] to antimicrobial [38] and cancer antiproliferating [39] properties. Among these ligands, arylcyanoximes had not been sufficiently studied and their metal binding properties were unknown.



SCHEME 1

2-Chlorophenylcyanoxime, H(2Cl-PhCO) (Scheme 1), was first reported in 1968 by Lehmann, Renk and Gadneux [40] who discovered that the oxime and its cyclic derivatives (furazanes and furoxanes) exhibit properties as central nervous system depressants, muscle relaxants and anticonvulsants. The agricultural herbicide antidote properties of 2-chlorophenylcyanoxime and its *O*-cyanoalkyl-esters were found in 1981 by Myatt [41]. A substantial synergistic action of H(2Cl-PhCO) in combination with niclosamide as a powerful molluscicide mixture against crop damage from snails has been recently observed by Wang and Xu [42]. Finally, monosubstituted arylcyanoxime, in the form of *O*-phosphate or thiophosphate esters, showed strong insecticidal activity [43]. In spite of the cited literature data, there were no metal complexes known prior to the investigation reported herein.

In this paper we report a convenient one-step synthesis and characterization of 2-chlorophenyl-(oximino)acetonitrile, H(2Cl-PhCO), representative of a family of monosubstituted arylcyanoxime ligands. The crystal and molecular structure of the first metal complex based on 2-chlorophenylcyanoxime, Tl(2Cl-PhCO), is also discussed.

## EXPERIMENTAL

### Materials and Methods

Reagent or analytical grade materials were obtained from commercial suppliers (Aldrich, Malinkrodt) and used without further purification.

For simplicity the following naming scheme is employed throughout for synthesized compounds: H(2Cl-PhCO) as **HL**; Na(2Cl-PhCO), **NaL**; Ag(2Cl-PhCO), **AgL** and Tl(2Cl-PhCO), **TiL**.

**HL** was studied using IR, UV-vis,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and mass spectrometric methods. **NaL**, **AgL** and **TiL** were characterized by elemental analysis and IR spectroscopy, and the crystal structure of **TiL** was determined.

### Spectroscopic Methods and Compound Characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **HL** and **NaL** were recorded on an Avance DRX-500 BRUKER NMR spectrometer at 298 K using standard pulse methods. All solutions were in  $\text{DMSO-}d_6$  (Aldrich;  $\sim 0.01$  M concentration) containing TMS as an internal standard.

IR spectra for solid samples of **HL**, **NaL** and **TiL** were recorded in KBr pellets. Spectra of **AgL** were obtained in nujol mulls since this complex reacts with KBr under pressure yielding AgBr and KL. All IR spectra were recorded in the range 4000 to  $500\text{ cm}^{-1}$  with an FT-IR Nicolet Magna 550 spectrophotometer equipped with Windows OMNIC software.

UV-vis spectra for **HL** and **NaL** or the tetrabutylammonium derivative were obtained using a Varian Bio 100 UV-visible spectrophotometer in 1-cm quartz cuvettes in the range 220–800 nm.

A mass spectrum for **HL** was obtained using Autospec Q and ZAB Finigan spectrometers and a positive FAB technique.

Melting points for the protonated cyanoxime and its thallium(I) and sodium salts were determined in open capillary tubes using a Mel-Temp II apparatus (Thomas Hoover) without correction.

Elemental analyses (C, H, N) were performed at the MicroMass Laboratory of the University of California (Berkeley).

### X-ray Crystallography

X-ray analysis of **TiL**, the first metal complex of a new class of monosubstituted aryl-cyanoximes, was conducted at 193 K on a diffractometer equipped with a BRUKER Smart CCD area detector. A needle type crystal with  $0.4 \times 0.1 \times 0.1$  mm dimensions was selected for structure determination. The  $\theta$  range for data collection was chosen from 1.95 to  $27.10^\circ$ . The limiting indices were  $-4 \leq h \leq 4$ ,  $-14 \leq k \leq 14$ ,  $-22 \leq l \leq 26$ . The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms in the structure of the complex were located on a difference map. Crystal and solution data are presented in Table I. Atomic coordinates for the structure are shown in Table II.

### Synthesis of HL and NaL

Scheme 2 reflects the preparation of **HL**. Sodium metal, 0.152 g (6.6 mmol) was dissolved in  $170\text{ cm}^3$  of absolute 2-propanol under nitrogen flow in an Erlenmeyer flask. In a separate vial were mixed 1.00 g (6.6 mmol) of 2-chlorophenyl-acetonitrile **1** and 0.68 g (6.6 mmol) of *t*-butyl nitrite,  $(\text{CH}_3)_3\text{CONO}$ , in  $5\text{ cm}^3$  of 2-propanol and the mixture was purged with nitrogen. This mixture was added dropwise within 20 minutes at room temperature under a continuous flow of nitrogen to the solution of sodium 2-propoxide. The reaction mixture turned bright yellow and was left at  $4^\circ\text{C}$  overnight. The formed yellow precipitate of practically pure **NaL** was filtered off, washed with

TABLE I Crystallographic data for **TIL**

Empirical formula	C <sub>8</sub> H <sub>4</sub> ClN <sub>2</sub> O <sub>1</sub>
F.wt.	383.95
Crystal system	monoclinic
Space group	P2 <sub>1/n</sub>
<i>a</i> (Å)	3.8382(7)
<i>b</i> (Å)	11.0065(18)
<i>c</i> (Å)	20.901(4)
β(Å)	92.447(3)
Volume (Å <sup>3</sup> )	882.2(3)
<i>Z</i>	4
<i>T</i> (K)	193(2)
λ (Å)	0.71073
<i>D</i> calc. (g cm <sup>-3</sup> )	2.891
μ (mm <sup>-1</sup> )	18.565
<i>F</i> (000)	688
Reflections	
collected (independent)	5699 (1899)
<i>R</i> (all data)	0.0689
<i>wR2</i> (all data)	0.1650

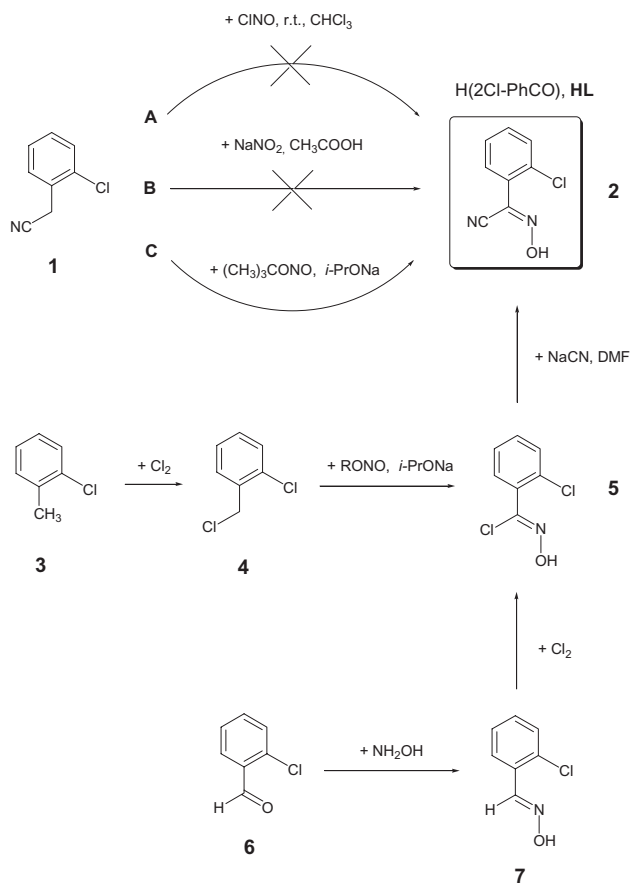
TABLE II Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for **TIL**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Tl (1)	6966 (2)	1176 (1)	-683 (1)	21 (1)
Cl (1)	2261 (14)	2945 (4)	2371 (2)	26 (1)
O (1)	2570 (40)	1004 (11)	217 (6)	22 (3)
N (1)	2310 (40)	2178 (13)	418 (7)	17 (3)
N (2)	-1880 (50)	418 (15)	1488 (9)	27 (4)
C (1)	-30 (50)	3576 (15)	1169 (9)	18 (4)
C (2)	410 (40)	3949 (16)	1788 (9)	17 (4)
C (3)	-270 (50)	5120 (18)	2005 (10)	24 (4)
C (4)	-1630 (60)	5940 (17)	1543 (10)	25 (4)
C (5)	-2140 (50)	5601 (17)	914 (10)	22 (4)
C (6)	-1400 (50)	4410 (16)	718 (9)	17 (4)
C (7)	640 (50)	2318 (16)	948 (9)	16 (4)
C (8)	-700 (50)	1294 (17)	1266 (9)	22 (4)

*U*(eq) is defined as one-third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

Symmetry transformations used to generate equivalent atoms: -*x* + 1, -*y*, -*z*.

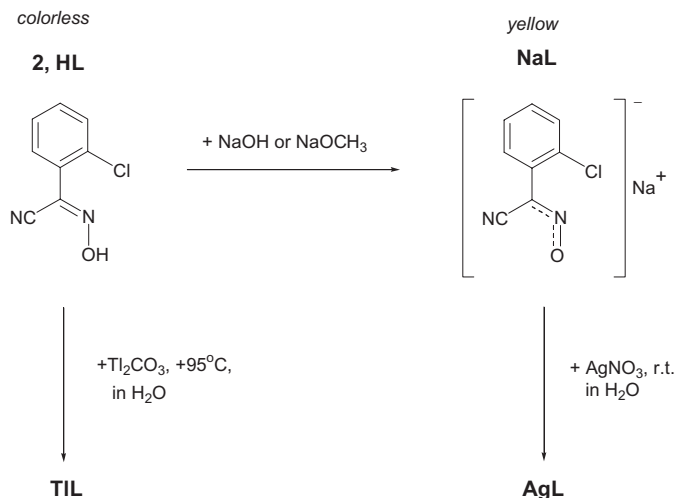
2-proponal, and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. The yield of dry salt is 2.60 g (39%, from 5.95 g expected for the pure oxime). The solvent from the mother liquor was removed completely using a rotary evaporator, leading to a pale yellow solid that was further dried under vacuum at 30°C for 2 h using an oil pump. The solid residue was dissolved in 30 cm<sup>3</sup> of water, acidified to pH ~5 with 1 M HCl, and then saturated with sodium chloride. Three 50-cm<sup>3</sup> portions of diethyl ether were used to extract the desired cyanoxime **HL**. Organic layers were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. The removal of solvent resulted in a white solid, **HL**. The yield: 2.82 g (47%, pure oxime). Thus, the combined yield of the cyanoxime products **HL** and **NaL** was 86%. **HL** has *R*<sub>f</sub> values: 0.27 (EtOAc:hexane = 1:4), 0.52 (C<sub>6</sub>H<sub>6</sub>:MeOH = 9:1), 0.76 (CCl<sub>4</sub>:MeOH = 9:1); m.p. = 112°C. Anal. calcd. for the oxime **HL** (%): C, 53.21; H, 2.79; N, 15.51. Found: C, 53.38; H, 2.77; N, 15.18. Mass spectrometry (pos. FAB): for C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>ClO calculated 180.59, found 181.48 (*M* + 1). <sup>1</sup>H NMR (ppm): 14.15 for



SCHEME 2

OH (singlet, 1H), 7.49 for 6-phenyl (1H; doublet of triplets;  $^1J = 7.3$  Hz,  $^2J = 1.2$  Hz), 7.75 for 3-phenyl (1H; doublet of triplets;  $^1J = 8.0$  Hz,  $^2J = 1.9$  Hz), 7.66 for 4,5-phenyl (2H; complex multiplet).  $^{13}\text{C}$  NMR (ppm): 132.8, 132.2, 131.7, 130.7, 129.3, 128.7, 128.4, 110.4 for CN-group). IR-spectral bands ( $\text{cm}^{-1}$ ): 3350  $\nu(\text{OH})$ , 3090  $\nu_{\text{as}}(\text{C-H})$ , 3070  $\nu_{\text{s}}(\text{C-H})$ , 2239  $\nu(\text{C}\equiv\text{N})$ , 1474  $\nu(\text{C}=\text{C})$ , 1242  $\nu(\text{C}=\text{N})$ , 1080  $\nu(\text{N-O})$ , 770 and 758  $\nu(\text{C-Cl})$ , for *ortho*-substituted Ph-group). UV-vis spectrum of HL in CH<sub>3</sub>OH:  $\lambda_{\text{max}} = 255$  nm ( $\epsilon = 5900$ ), substituted phenyl group; in *t*-C<sub>4</sub>H<sub>9</sub>OH:  $\lambda_{\text{max}} = 256$  nm ( $\epsilon = 6500$ ), substituted phenyl group chromophore. The cyanoxime is soluble in ether, acetone, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub> and ethyl alcohol and insoluble in CCl<sub>4</sub>, hexane and benzene.

NaL can be quantitatively obtained when HL reacts with an equimolar amount of NaOH in water or CH<sub>3</sub>OH or with NaOCH<sub>3</sub> in ether (Scheme 3). Thus, 0.500 g (2.76 mmol) of HL was dissolved in 10 cm<sup>3</sup> of 2-propanol at room temperature and a solution of 0.111 g (2.76 mmol) of powdery NaOH in 5 cm<sup>3</sup> of 2-propanol was added at once to the oxime solution. The color of the reaction mixture immediately turned yellow and precipitate of the same color appeared in the reaction vessel on stirring. The formed precipitate of NaL was filtered, washed with 5 cm<sup>3</sup> of cold 2-propanol and then with 20 cm<sup>3</sup> of diethyl ether and dried under vacuum over P<sub>2</sub>O<sub>5</sub>. The tetra-butylammonium salt has better solubility in the majority of organic solvents and can



SCHEME 3

be obtained quantitatively from the oxime by addition of an equivalent of a fresh solution of  $\text{N}(\text{C}_4\text{H}_9)_4\text{OH}$  (1 M in  $\text{CH}_3\text{OH}$ , Aldrich). Anal. calcd. for sodium salt **NaL** (%): C, 45.41; H, 2.38; N, 13.24. Found: C, 44.72; H, 2.53; N, 12.85. On heating **NaL** decomposes above  $\sim 260^\circ\text{C}$ . IR spectral bands ( $\text{cm}^{-1}$ ): 3090  $\nu(\text{C-H})$  3070,  $\nu(\text{C-H})$ , 2206  $\nu(\text{C}\equiv\text{N})$ , 1483  $\nu(\text{C}=\text{C})$ , 1161  $\nu(\text{N-O})$ , 749 and 728  $\nu(\text{C-Cl})$ , for *ortho*-substituted Ph group). UV-vis spectrum for  $[\text{N}(\text{C}_4\text{H}_9)_4]\text{L}$ , in  $\text{CH}_3\text{OH}$ :  $\sim 220$  nm (shoulder) CN-group, and 289 nm ( $\epsilon = 9300$ ), conjugated nitroso-phenyl fragment; in *t*- $\text{C}_4\text{H}_9\text{OH}$ :  $\sim 230$  nm (shoulder) CN-group, and 307 nm ( $\epsilon = 9600$ ), conjugated nitroso-aryl fragment, and 405 nm ( $\epsilon = 110$ ) nitroso-chromophore. **NaL** is soluble in water, DMF, DMSO and pyridine, sparingly soluble in methanol and insoluble in acetone, ether and aromatic and aliphatic hydrocarbons.

### Synthesis of TIL and AgL

Scheme 3 shows a general approach to the synthesis of complexes of monovalent silver and thallium with cyanoxime-anions. Thus, 0.7158 g (1.5 mmol) of  $\text{Tl}_2\text{CO}_3$  were dissolved in 20  $\text{cm}^3$  of boiling distilled water. Small portions (0.552 g; 3.05 mmol) of the powdery solid cyanoxime were added to hot ( $\sim 95^\circ\text{C}$ ) solution of thallium carbonate within 5 min leading to a bright yellow solution. After all  $\text{CO}_2$  gas had been evolved, the reaction mixture was filtered, and the mother liquor was placed in a large test tube which then was immersed in a Dewar flask containing 5  $\text{cm}^3$  of water at  $95^\circ\text{C}$  for slow cooling. The first portion of long needle crystals of **TIL**, unsuitable for X-ray analysis, was filtered off and the remaining yellow solution was allowed to evaporate at room temperature over three to four weeks. Good quality single crystals of the complex were obtained. The combined yield of **TIL** is practically quantitative; m.p. =  $182^\circ\text{C}$ . Anal. calcd. for  $\text{C}_8\text{H}_4\text{ClN}_2\text{OTl}$  (%): C, 25.02; H, 1.05; N, 7.30. Found: C, 24.84; H, 1.00; N, 7.20. IR spectrum ( $\text{cm}^{-1}$ ): 3073  $\nu(\text{C-H})_{\text{arom}}$ , 3050  $\nu(\text{C-H})_{\text{arom}}$ , 2202  $\nu(\text{C}\equiv\text{N})$ , 1484  $\nu(\text{C}=\text{C})$ , 1098  $\nu(\text{N-O})$ , 749 and 726  $\nu(\text{C-Cl})$ , for *ortho*-substituted Ph group). This thallium(I) complex is soluble in DMF, pyridine and

DMSO, sparingly soluble in cold water, but readily dissolves upon heating. The compound is insoluble in propanol, acetone, benzene and aliphatic hydrocarbons.

The exchange reaction between aqueous solutions of **NaL** and  $\text{AgNO}_3$  (equimolar amounts; at room temperature) leads to a quantitative precipitation of **AgL**. Thus, to 0.500 g (2.47 mmol) of **NaL** dissolved in 25 cm<sup>3</sup> of water at room temperature 0.419 g (2.47 mmol) of  $\text{AgNO}_3$  in 5 cm<sup>3</sup> of water was added at once under intensive stirring. The thick, yellow, silver(I) cyanoximate precipitate was filtered off, washed with 25 cm<sup>3</sup> of water and then with 10 cm<sup>3</sup> of MeOH, and dried in a vacuum desiccator over  $\text{P}_2\text{O}_5$ . Dry **AgL** is a light-sensitive compound. Anal. calcd. for  $\text{C}_8\text{H}_4\text{ClN}_2\text{OAg}$  (%): C, 33.43; H, 1.40; N, 9.75. Found: C, 33.16; H, 1.28; N, 9.66. IR spectrum ( $\text{cm}^{-1}$ ): 2226  $\nu(\text{C}\equiv\text{N})$ , 1478  $\nu(\text{C}=\text{C})$ , 1176  $\nu(\text{N}-\text{O})$ , 748 and 729  $\nu(\text{C}-\text{Cl})$ , for *ortho*-Ph group). The compound decomposes upon heating. **AgL** is soluble in amines such as aqueous ammonia, ethylenediamine, dimethylamine, pyridine, DMF and DMSO, but insoluble in alcohols, acetone,  $\text{CH}_3\text{CN}$ , THF and aromatic and aliphatic hydrocarbons.

## RESULTS AND DISCUSSION

Three different routes exist for the preparation of ligand **2** (Scheme 2). Chlorination of 2-chlorotoluene (**3**) or 2-chlorobenzaldehyde (**6**) leads in two steps to the same chloroal-doxime **5**, which can be converted at elevated temperatures into cyanoxime (**2**). We found 2-chlorophenyl-acetonitrile (**1**), which is commercially available, to be the best starting compound for the preparation of cyanoxime **2**. Similarly, other compounds shown in Scheme 1 can be obtained from their respective acetonitriles, and this work is in progress. There are several ways to introduce an oxime group into acetonitrile **1** using the Meyer reaction [31] (Scheme 2). However, our attempts to use nitrosations **A** and **B** in acidic conditions with nitrosyl chloride or nitrous acid failed, and only route **C** resulted in high yield of cyanoxime **2** (Scheme 2). The heterogeneous reaction between the solid protonated cyanoxime and the hot solution of  $\text{Tl}_2\text{CO}_3$  shown in Scheme 3 is the best and easiest way of obtaining the crystalline samples of Tl(I) complexes. Previously, we employed this method in thallium(I) chemistry [20,30,32].

Single crystals suitable for X-ray analysis were obtained only for the thallium(I) complex. Crystallographic data for this complex are presented in Table I. All attempts to grow crystals of **AgL** were unsuccessful. One of the problems encountered during the work with the latter complex is its significant light sensitivity.

Atomic coordinates and isotropic displacement parameters for **TlL** are listed in Table II. The crystal structure of **TlL** represents an interesting coordination polymer composed of **TlL** centrosymmetric dimers (Figs. 1 and 2). Dimeric units form  $\text{Tl}_2\text{O}_2$  rhombic arrangements and are connected to ruffled polymeric sheets via oxygen atoms of the nitroso-group, which exhibits a bridging function upon coordination to the metal center. The crystal structure is organized in two adjacent zigzag chains that form sheets by means of van der Waals forces between 2-chlorophenyl groups (Fig. 3). Inside each sheet there are  $\pi$ - $\pi$  stacking interactions between aryl groups with distance of 3.83 Å.

There are two slightly different rhombic units in the structure ( $\text{Tl}_2\text{O}_2$ ) that are marked as **A** and **B** on Fig. 3. The dihedral angle between these planar individual rhombuses is 90.72°. The geometry of **A** is: distance  $\text{Tl1}_3 - \text{Tl1} = 4.184 \text{ \AA}$ , angles  $\text{Tl1}_3 - \text{O1} - \text{Tl1} = 107.72^\circ$  and  $\text{O1} - \text{Tl1}_3 - \text{O1} = 72.28^\circ$ . The geometry of **B** is:  $\text{Tl1}_3 - \text{Tl1} = 4.440 \text{ \AA}$ ,



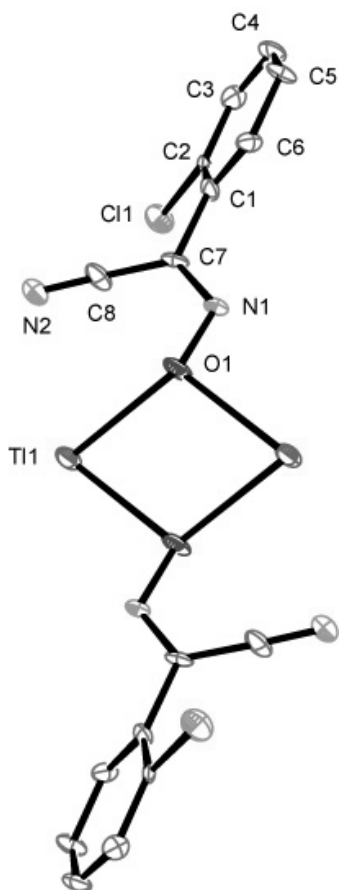


FIGURE 1 An ORTEP drawing at 50% probability level of the structure of a dimeric **Tl** unit with the numbering scheme. Hydrogen atoms are omitted for clarity.

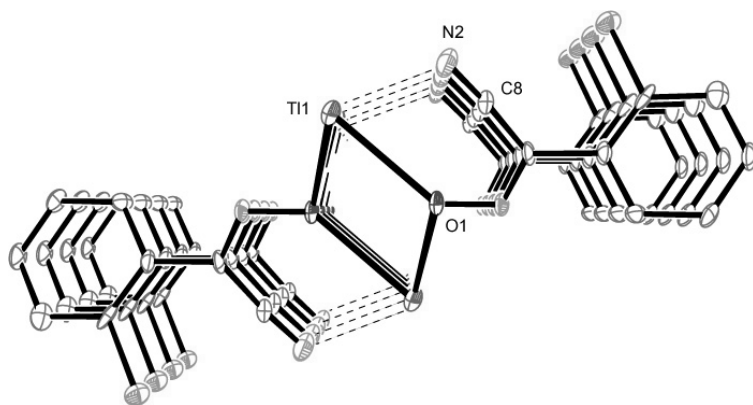


FIGURE 2 Crystal structure of the complex: perspective view along the Tl—Tl direction.

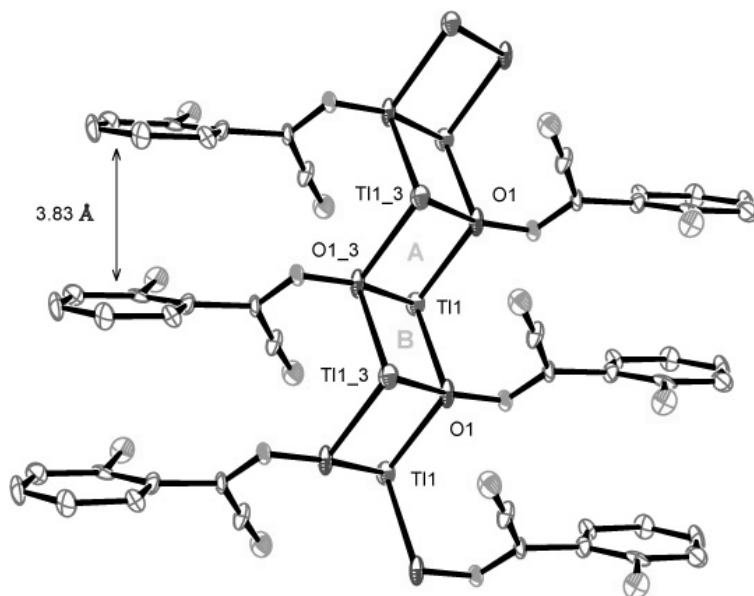


FIGURE 3 Organization of polymeric motif in the structure of **TIL**. Two different  $\text{Ti}_2\text{O}_2$  rhombic subunits are indicated as **A** and **B**. An ORTEP representation with 50% probability of thermal ellipsoids.

TABLE III Selected bond length (Å) and valence angles in the structure of **TIL**

Bond length (Å)		Valence angle (°)	
Ti(1)–O(1)	2.587 (13)	O(1)–Ti(1)–O(1)#1	72.3 (5)
Ti(1)–O(1)#1	2.594 (13)	N(1)–O(1)–Ti(1)	102.3 (10)
Cl(1)–C(2)	1.770 (18)	N(1)–O(1)–Ti(1)#1	140.0 (10)
O(1)–N(1)	1.364 (18)	Ti(1)–O(1)–Ti(1)#1	107.7 (5)
N(1)–C(7)	1.31 (2)	C(7)–N(1)–O(1)	114.6 (15)
N(2)–C(8)	1.17 (3)	C(2)–C(1)–C(7)*	124.1 (17)
C(1)–C(2)*	1.36 (3)	C(6)–C(1)–C(7)*	117.7 (16)
C(1)–C(6)*	1.40 (3)	C(1)–C(2)–Cl(1)	119.8 (14)
C(1)–C(7)	1.49 (2)	N(1)–C(7)–C(8)	120.2 (16)
C(7)–C(8)	1.42 (3)	N(1)–C(7)–C(1)	118.0 (16)
		C(8)–C(7)–C(1)	121.6 (16)
		N(2)–C(8)–C(7)	175 (2)

\*Geometry of phenyl group is normal and not shown.

angles  $\text{Ti1}_3\text{–O1–Ti1} = 110.69^\circ$  and  $\text{O1–Ti1}_3\text{–O1} = 69.31^\circ$ . The closest intermetallic distance  $\text{Ti1–Ti1}$  in the complex is  $3.383 \text{ \AA}$ , which is comparable to that in metallic thallium ( $3.456 \text{ \AA}$ ). There are two  $\text{Ti1–O1}$  bonds in a dimer (Fig. 1, Table III) where the shortest,  $2.587 \text{ \AA}$ , is significantly less than the sum of the ionic radii [33] of monovalent thallium and oxygen ( $2.79 \text{ \AA}$ ). There are also close non-bonding contacts between thallium(I) centers and cyano-group N2 atoms in the structure (Fig. 2). Apparently, the nitrogen atom of the cyano-group acts as a bridge since it is located between two closest thallium atoms (Figs. 2 and 3). On the other hand, each thallium atom in the structure has two contacts  $\text{Ti1–N2}$  and  $\text{Ti1}_3\text{–N2}$  of different length ( $3.072$  and  $3.119 \text{ \AA}$ ) from two adjacent cyanoxime anions to the same  $\text{Ti}$  atom in the polymeric structure (Fig. 3). These distances are only slightly shorter than the sum of

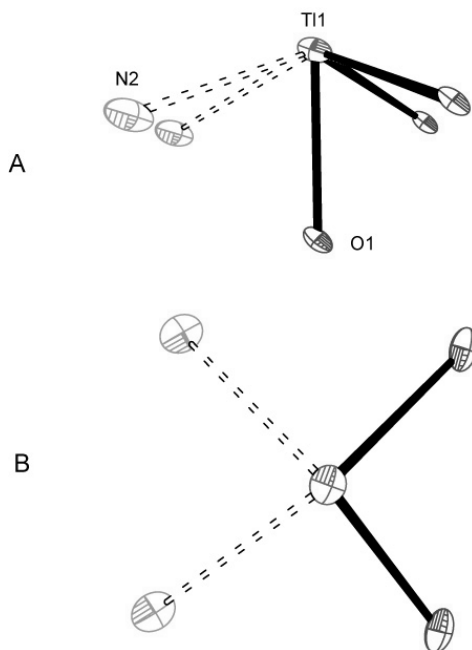


FIGURE 4 Structure of coordination polyhedron of Tl(I) atom in complex: *A*, side view, *B*, top view.

Shannon's ionic radii [33] of Tl(I) and nitrogen, 3.18 Å. The origin of such interactions is electrostatic attraction and not coordination, owing to unsuitable orientation of the cyano-group. Thus, corresponding to Tl1—N2 is the contact angle C8—N2—Tl1 of 89.9°, and the value of C8—N2—Tl1<sub>3</sub> is 120.0° for the Tl1<sub>3</sub>—N2 contact. These angles are substantially less than the expected ~180° angle for the most common linear binding of the cyano-group to the metal center. The latter is commonly observed, for example, in numerous metal complexes containing coordinated acetonitrile or linearly bridged cyano-groups. In such structures the non-bonding electron pair of the nitrogen atom of the CN group is oriented at a 180° angle to a triple bond. The Tl1—N2—Tl1<sub>3</sub> angle in **TIL** is 76.6°. Therefore, as mentioned above, Tl1—N2 contacts are not coordination bonds, but rather electrostatic interactions that help in packing the molecules of the complex into a crystal. Similar interactions have been observed in the structure of Tl[Ag(CN)<sub>2</sub>] [44].

The cyanoxime anion is non-planar in **TIL**. There are two almost planar fragments in the structure of the ligand, the aryl group and the cyanoxime fragment. 2-Chlorophenyl attached to C7 forms one plane with a torsion angle C7—C1—C6—C2 = 176° while in the cyanoxime fragment, the value of the torsion angle C8—C7—N1—O1 is 0.4°. The angle between these two planes is 48.2°. The anion is in the *oxime*-form since the bond length N1—C7 is shorter than the O1—N1 bond (Table III). The ligand adopts a *trans-anti* configuration in the structure.

The thallium(I) center has five contacts to the cyanoxime in the structure. There are three short bonds to the bridging oxygen atoms O1 of the oxime-group and two contacts to the bridging N2 atoms of the cyano-group (Figs. 3 and 4) discussed earlier. This situation is typical for crystal structures of large main group metal cations such as Tl(I), Sn(II), Pb(II) and Bi(III). In the structure of **TIL**, we consider the metal center to

be three-coordinate with a stereoactive  $6s^2$  lone pair directed in the open cleft away from the  $Tl_2O_2$  rhombuses (Figs. 1 and 4). Therefore, the geometry of coordination polyhedron can be described as a distorted trigonal pyramid. The shortest Tl—Tl distance in the structure is 3.838 Å, which is only slightly greater than the shortest distance in metallic thallium (3.456 Å, *a*, hexagonal) [34].

## CONCLUSION

High-yield preparation for substituted arylocyanoximes was developed using 2-chlorophenylcyanoxime. The obtained compound readily forms alkali metal derivatives as well as complexes with Ag(I) and Tl(I). The synthesized compounds were characterized using spectroscopic and structural methods. The crystal structure of the Tl(I) complex presents an interesting coordination polymer with a well-organized  $Tl_2O_2$  rhombic network that might be useful for the design of the mixed-valence compounds exhibiting electric conductivity.

## Notes

Special care should be taken during work with thallium compounds because of their high toxicity; 600 mg represents a lethal dose [34]. Thallium compounds are heavy, and the density of all conventional Tl(I) salts is typically  $\sim 3 \text{ g/cm}^3$  or greater, often leading to misjudgment of the amount of a compound by volume. Another peculiarity of this element is the ability of its solutions to permeate through the skin, which is attributed to the strong similarities between cations of thallium(I) and potassium. Both Tl(I) carbonate and cyanoximates are water-soluble compounds, and that emphasizes the *absolute necessity* for wearing protective gloves at all times when working with these compounds. Complete information about thallium antidote can be found in ref. [35].

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