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Research paper

Search for the shortest intermetallic Tl—Tl contacts: Synthesis and characterization of Thallium(I) coordination polymers with several monoand bis-cyanoximes



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ABSTRACT

Five new Tl(I) coordination compounds based on aryl monocyanoximes, such as phenylcyanoxime - HPhCO, 1, 2fluorophenylcyanoxime - H(2F-PhCO, 2, 3-fluorophenylcyanoxime - H(3F-PhCO), 3, of TlL composition, and aryl biscyanoximes, such as 1,3-cyanoxime (benzene) - H2(1,3-BCO, 4 and 1,4-cyanoxime (benzene) - H2(1,4-BCO), 5 of Tl₂L stoichiometry were synthesized and characterized using spectroscopic methods, thermal stability studies, and X-ray analysis. All obtained complexes represent coordination polymers of different complexity, ranging in dimensionality from 1D in Tl(2F-PhCO) to 3D in Tl₂(1,3-BCO). The most interesting feature of all synthesized complexes is the formation of Tl₂O₂ rhombs: non planar and non-centrosymmetric in Tl(PhCO), and planar and centrosymmetric in the other three compounds. These rhombi are interconnected, forming zigzag and ladder-type polymers in which very short thallophilic Tl-Tl distances were observed. Thus, in the structure of Tl₂(1,3-BCO) the closest distance between metal centers was found to be 3.670 Å. This is the second shortest onrecord intermetallic contact in non-organometallic and non-cluster, but Werner type complexes, and is close to that in metallic thallium: 3.456 Å. In all five new coordination polymers the central atom has a stereo-active 6 s^2 lone pair that significantly distorts the shape of the coordination polyhedron of Tl(I). The first time, Tl–O vibrations in Tl₂O₂ rhombs were observed in Raman spectra of the obtained complexes. Thermal analysis studies evidenced stability of all complexes, but Tl(PhCO), to ~200 °C. The Tl₂(1,3-BCO) compound demonstrates properties of the high energy compound, and violently exothermically decomposes at ~ 255 °C with the release of a significant amount of kinetic energy. The final product of anaerobic decomposition of all studied Tl-cyanoximates is metallic thallium sponge.

1. Introduction

In recent years, there has been an upturn in research on a subset of macromolecules known as coordination polymers [1–4]. They can take on a variety of morphologies, being divided according to their dimensionality into 1D, 2D and 3D polymers, with different properties and potential applications. Thus, one-dimensional columnar, zigzag chains, ladder-type, or stacks, are interesting from the standpoint of electrical conductivity [5–8], while two-dimensional sheets of coordination polymers are interesting for catalysis applications [9–11] and magnetic coupling/ordering [12,13]. A specific type of three-dimensional coordination polymers, known as metal–organic frameworks (MOFs), contains large lattices that are mostly empty scaffolds with pores for potential application for gas sorption [14–31]. These structures can accommodate the most important gas, H₂, which is the key

component of 'hydrogen economy' [32-34].

Coordination polymers have attracted a fair deal of attention for their optical and elastic properties, as well as their potential for use in molecular electronics [35], and in certain cases, have even been shown to have antimicrobial properties [36]. A number of coordination polymers that have been synthesized have been shown to exhibit electroluminescence [37], which has garnered attention with regard to the use of the transition metals for coordination polymers with this property, owing to the energy of the triplet state that the metals exhibit [38–42]. Substantial attention with regard to coordination polymers has been given to the transition metals [43–52] with the main group elements largely disregarded recently. Of particular interest in the main group metals is a small cluster of 5p and 6p elements, specifically Tl, Pb, Sb, and Bi, that can exist in two accessible oxidation states which are two electrons apart. Thallium, however, has shown a unique ability among

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its group to form coordination polymers [53,54]. This element is of particular interest with regards to 1D coordination polymers, because of the propensity for 'electron-hopping' between metal centers, as Tl exists in two oxidation states, Tl^{1+} and Tl^{3+} . Such electrical properties may be of use, leading to potential applications in electronics [53]. In this case, very short intermetallic distances would be required for electrical conductivity via electron hopping [55].

In recent years, there has been a discovery of a number of oximebased Tl coordination polymers [53,54], each possessing the 1D motif of Tl atoms with short intermetallic distances, of potential interest in electrical applications. Oximes are ionizable ligands and readily form compounds of TlL composition which excludes the necessity for counter ions commonly present in other types of coordination polymers containing transition metals. Oximes, and their specific subclass - cyanoximes NC-C(=NOH)-R - are known to form 1D and 2D coordination polymers with Ag(I) and Tl(I) [56]. In addition to a series of monocyanoximes [57], bis-cyanoximes are of interest in the formation of coordination polymers as well, and their use has been studied in recent years [58,59]. It should be noted that, though Tl is widely known for its high toxicity, other no less toxic, elements in binary GaAs, selenides, tellurides of Pb and Cd, and halogenides of Hg are already widely used in enclosed electronic devices [53]. Lastly, Tl(I) was found to be a very valuable component of luminescent heterometallic polymeric complexes, with heavy metals such as Pb [60], Au [95] and especially Pt [61-66]. Coordination polymers of Tl(I) with short intermetallic distances represent precursors for these systems especially when metallophilic interactions [67,68] play role in shaping the geometry of complexes formed. Coordination polymers itself represent vigorously developing area of modern inorganic chemistry research due to remarkable range of applications [69].

In this work, we report the synthesis and detailed characterization of four Tl complexes with two mono-cyanoximes such as phenylcyanoxime, NC-C(=NOH)-C₆H₅ (further as H(PhCO)), NC-C(=NOH) -C₆H₄F (later as H(2F-PhCO)), and with two isomeric bis-cyanoximes 1,3-biscyanoxime benzene (later as H₂(1,3-BCO)) and 1,4-bis-cyanoxime benzene (later as H₂(1,4-BCO)) structures, which are shown in Scheme 1. The latter ligands, due to their 120° or 180° angle in mutual orientation of ionizable cyanoxime groups, offer better possibilities for the formation of extended coordination polymers in which close metal-metal separation can be achieved.

2. Experimental part

2.1. General considerations

Precursors for cyanoximes, such as phenyl-acetonitrile C_6H_5 -CH₂CN, 2-fluorophenyl-acetonitrile, and substituted 1,3- and 1,4phenyl-diacetonitriles of $C_6H_4(CH_2CN)_2$ formula were purchased from Sigma-Aldrich. All other chemicals and solvents – *i*-PrOH, NaNO₂, H₂SO₄, and HCl, which were purchased from Fisher Scientific, with sodium metal from Fluka, were of sufficient quality, and used without additional purification. Melting points were determined with the help of pre-calibrated apparatus with urea and naphthalene standards DigiMelt in an open capillary, and reported without correction.

2.2. Synthesis of ligands and Tl(I) Complexes.

The preparation of compounds reported in this study is outlined in Scheme 2 for both organic ligands and their Tl(I) complexes, with some details for typical syntheses presented below.

2.3. Syntheses of mono- and bis-cyanoximes

H(PhCO). Preparation of this ligand was carried out using benzylcyanide, NC-CH₂-C₆H₅ and commercially-available amylnitrite C₅H₁₁-ONO in isopropanol, according to published procedures [53,71]. Physical parameters such as m.p., TLC R_f value, and ¹H, ¹³C{¹H} NMR spectra, match those reported for this cyanoxime.

H(2F-PhCO) and H(3F-PhCO) [72]. These isomeric monosubstituted arylcyanoximes were prepared in similar fashion and only one prep for the first one will be given in detail. Thus, 0.182 g (7.91 mM) of thinly sliced Na metal was dissolved at 25 °C in *i*-PrOH (100 ml) under a N₂ atmosphere in a 250 ml capacity three-neck flask. Following dissolution of the metal, 10 ml of a 7.90 mM of 2-fluorophenylacetonitrile in isopropanol was added, dropwise, within 2-3 min, to the first solution. The gaseous methylnitrite CH₃-ONO generated in situ was bubbled through the mixture within ~ 20 min, at room temperature under a N2 blanket (Associated content: Electronic Supporting Materials, ESI 2). At this stage, the reaction mixture gained a bright-yellow color. The reaction flask was closed and left in a refrigerator overnight at +4 °C. The solvent was removed under reduced pressure using the rotovap, and the obtained yellow sludge was further dried at room temperature by an oil pump. The foamy solid residue was dissolved in 30 ml of H₂O to form a caustic yellow solution which was dropwise acidified with HCl (1:5 by volume) to $pH \sim 4$, then saturated with solid NaCl to form brine. White powdery cyanoxime H(2F-PhCO) precipitated shortly, and was filtered, washed with cold water dried over P₄O₁₀ in a vacuum desiccator. The yield of the H(2F-PhCO) is 74%, m.p. = 118 °C; $R_f = 0.28$ in the 1:4 ehtylacetate/hexane mobile phase. ¹H NMR in dmso-d₆, ppm: 14.22 for OH (broad singlet 1H); aromatic: 7.68 (m, 1H), 7.57 (m 1H), 7.38(m, 1H), 7.32(m, 1H). According to both ¹H and ¹³C{¹H} NMR spectra this cyanoxime represents single synisomer (ESI 3 and 4). IR spectrum in KBr disk, cm^{-1} : 3257 – ν (OH); 3085,3009 - ν(C-H, arom); 2234 - ν(C≡N); 1493,1462 - ν(C=C); 1056, 972 - v(N-O). UV-visible spectrum (in EtOH): 228 nm ($\varepsilon = 7200$), CN group; 302 nm ($\varepsilon = 8900$), oximino/aryl fragment. High resolution mass-spectrometry for C₈H₅FN₂O calculated: 165.1444 (for M + 1), found 165.0963.

The yield for H(3F-PhCO) was 51%, white powder, m.p. = 115 °C, and $R_f = 0.14$ in 1:4 ethylacetate/hexane mobile phase. The ¹H NMR in dmso-d₆, ppm: 14.11 for OH (singlet, 1H); aromatic region: 7.79 (doublet, 1H); 7.74–7.18 (*meta*-, 3H). UV-spectrum in methanol, π - π



Scheme 1. Chemical formulas of the five reported cyanoximes with their abbreviations.



aryl = phenyl, 2-fluorohenyl, 1,3- and 1,4-disubstituted phenyl groups

Scheme 2. General synthesis of aryl-cyanoximes and their Tl salts.

transitions: 224 nm (ε = 8150; cyano-group), 304 nm (ε = 7770; oximino group). IR spectrum in KBr disk, cm⁻¹: 3254 – ν (OH); 3085,2976 – ν (C–H, arom); 2250,2201 – ν (C \equiv N); 1585,1490 – ν (C=C); 1073, 1009 – ν (N–O). High resolution mass-spectrometry for C₈H₅FN₂O calculated: 165.1444 (for M + 1), found 165.0791. The ¹³C{¹H} spectra showed double set of signals indicating presence of two diastereomers (ESI 5), which was earlier confirmed by the crystal structure of this compound existing as 60:40% mixture of *syn*- and *anti*-isomers respectively [54].

Syntheses of bis-cyanoximes H₂(1,3-BCO) and H₂(1,4-BCO) were analogous, and a general procedure used for the preparation of both compounds, as follows. Thus, 2.00 g (9.3 mM) of aryl-bis-acetonitrile (Scheme 2A) were dissolved in 50 ml of isopropanol. In a separate Erlenmeyer flask with 100 ml of the same solvent thinly sliced metallic sodium, 0.428 g (18.6 mM) was dissolved under a N₂ gas protection to form a clear solution. After mixing both solutions, a flow of colorless, gaseous, CH₃ONO (ESI 2) bubbled for 35 min through the mixture, which immediately changed color from clear to bright yellow. The flask was closed and placed into the refrigerator at +4 °C overnight. The solvent was removed using the rotovap at +40 °C to form a yellow sludge that was further dried using an oil pump at room temperature. A foamy solid residue then was dissolved in distilled water to form a vellow solution, and then dropwise acidified to pH ~ 3 with 25% HCl until a fine, milky-white solid precipitated. The bis-cyanoxime was filtered, washed with cold water, and dried in a vacuum desiccator charged with CaCl₂ and H₂SO₄(c).

The yield for 1,3-BCO was 34%; m.p. = 193 °C (decomposition); $R_f = 0.42$ using 9 : 1 chloroform–methanol mobile phase. Analysis for $C_{10}H_6N_4O_2\cdot0.5H_2O$ calculated (found %): C 53.81 (54.54), H 3.16 (3.16), N 25.10 (24.76). IR spectrum (KBr disk; cm⁻¹, tentative assignments): 1021 ν (N–O), 3293 ν (O–H), 1700 ν (C–N), 1403, 1254, 1232 ν (C–C), 2260 ν (C=N). The NMR ¹H spectrum (complicated, due to presence of two diastereoisomers, δ ppm): 14.07 (minor narrow singlet oxime), 13.96 (main narrow singlet), 8.00 (multiplet, 1H, between two cyanoxime groups), 7.68–7.61 (multiplet, 1H, at *ortho*-positions to cyanoxime groups). The ¹³C{¹H} NMR spectrum, δ ppm (double set of signals due to presence of two isomers) main component: 110.29 (CN) group), 122.45, 127.98, 131.24 (oxime carbon), 130.84, 130.90; minor component: 115.77 (CN group), 126.03, 128.55, 133.09 (oxime carbon), 130.56, 128.65. For 1,3-BCO the UV spectra, λ_{max} , nm (ε , cm⁻¹ × M⁻¹): in methanol 2258 nm (2600), ethanol 2259 nm (6840), *n*-propanol 2260 nm (4160).

The yield for 1,4-BCO was 47%; m.p. = 197 °C (with decomposition); $R_f = 0.26$. Analysis for $C_{10}H_6N_4O_2\cdot H_2O$ calculated (found, %): C 51.73 (52.28), H 3.47 (3.57), N 24.13 (23.36). IR spectrum (KBr disk; cm⁻¹): 3508 ν (O–H), 3324 ν (C–H), 2239 ν (C=N), 1624 (ν (C=N), 1516, 1421, 1409 ν (C=C), 973 ν (N–O), 468 (δ (C=C)). NMR ¹H spectrum (δ ppm): 7.82 (singlet, 2H phenyl group), 13.98 (H, oxime, singlet). The ¹³C{¹H} NMR spectrum (δ ppm): 110.30 (CN-group), 131.90 (oxime carbon), 130.98 (*ipso*-carbon), 126.78 (phenyl group carbon). For 1,4-BCO the UV spectra, λ_{max} , nm (ε , cm⁻¹ × M⁻¹): methanol 2297 nm (3480), ethanol 2300 nm (5370), *n*-propanol 2302 nm (3870).

2.4. Synthesis of Tl(I) cyanoximates

Tl complexes of each cyanoxime were synthesized by adding the solid cyanoxime in small aliquots to a 95 °C aqueous solution of Tl_2CO_3 , as depicted in Scheme 2 (ESI 6 and 7). All Tl-cyanoximates are light stable and non-hygroscopic compounds, soluble in water upon heating and insoluble in common organic solvents such as alcohols, acetone, ether, EtOAc, CH_2Cl_2 and $CHCl_3$, but dissolve in polar donor solvents such as DMF, DMSO, and pyridine. All Tl(I) derivatives of the mono-cyanoximes give a very good elemental analyses data, contrary to the bis-cyanoximates in which carbon content for an unknown reason was off (see below).

The Tl(PhCO) appears as very fine long and thin lemon-yellow needles (ESI 8 and 9).

The Tl(2F-PhCO) represents orange-yellow needles. Elemental analyses calculated (found), %: C – 26.14 (26.02); H – 1.10 (0.95); N – 7.62 (7.59) [71]. The IR spectrum (ATR method, cm⁻¹): ν (C–H) – 3080; ν (C \equiv N) – 2205; ν (C \equiv C) – 1494; ν (CNO) – 1105; ν (N–O) – 995.

The Tl(3F-PhCO) represents bright-yellow needled. Elemental analysis calculated (found), %: C – 26.14 (26.11), H – 1.10 (0.91); C – 7.62

Table 1

Crystal and refinement data for studied in this work Tl-cyanoximates.

2		J			
Parameter	Tl ₂ (1,3-BCO)	Tl ₂ (1,4-BCO)	Tl(PhCO)	Tl(2F-PhCO)	Tl(3F-PhCO)
Formula	$C_{10}H_4N_4O_2Tl_2$	C ₅ H ₂ N ₂ OT1	C ₈ H ₅ N ₂ OT1	C ₈ H ₄ N ₂ OTlF	C ₈ H ₄ N ₂ OTlF
F.W., g/mol	620.91	310.46	349.51	367.5	735.00
Temperature	120(2)	120(2)	120(2)	100(2)	100(2)
Wavelength, λ	0.71073	0.71073	0.71073	1.54178	0.71073
Crystal System	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	C 2/c	P-1	P bca	P 2 ₁ /c	P n a 2 ₁
Unit cell, Å/°	a = 21.672 (4)	a = 3.9696(15)	a = 15.1903(8)	a = 4.1126(4)	a = 14.1040(17)
	b = 7.8698 (13)	b = 6.672(2)	b = 6.8828(3)	b = 6.5823(5)	b = 3.7562(8)
	c = 6.9082(11)	c = 11.149(4)	c = 32.513(3)	c = 30.905(2)	c = 30.905(2)
	$\alpha = 90$	$\alpha = 83.551(5)$	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$
	$\beta = 98.487(2)$	$\beta = 82.254(5)$	$\beta = 90$	$\beta = 93.595(4)$	$\beta = 90$
	$\gamma = 90$	$\gamma = 89.516(5)$	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$
Cell volume, Å ³	1165.3(3)	290.73(17)	3302.1(18)	834.96(12)	1679.1(5)
Z	4	2	8	4	4
D (Calc), Mg/m^3	3.539	3.546	2.812	2.924	2.908
Abs. μ (mm ⁻¹)	27.619	27.675	19.511	37.017	19.210
F(000)	1080	270	2496	656	1312
Cryst. Size, mm	0.10 imes 0.08 imes 0.06	0.1 imes 0.06 imes 0.04	0.5 imes 0.06 imes 0.05	0.62 imes 0.26 imes 0.06	0.080 imes 0.080 imes 0.280
Θ Range	1.90-30.51°	1.86–26.20°	1.85–25.24°	1.90-30.51°	2.89–27.52°
Index Ranges	h: -30 to 30	h: -4 to 4	h: -17 to 17	h: -4 to 4	h: 0 to 17
-	k: −11 to 11	k: -8 to 8	k: -8 to 8	k: 0 to 7	k: 0 to 4
	l: -9 to 9	l: -13 to 13	l: -38 to 38	l: 0 to 34	l: 0 to 40
Reflections total	8280	3208	2894	5056	1261
Independent Refl.	1757	1158	1952	1204	1261
*	[R(int) = 0.0474]	[R(int) = 0.0418]	[R(int) = 0.1013]	[R(int) = 0.0483]	[R(int) = 0.0691]
Completeness, %	99.20%	99.40%	99.80%	91.20%	71.5%
Absorption Method	Semi-empirical	Semi-empirical	Semi-empirical	Numerical	Semi-empirical
T _{max} . and T _{min} .	0.7464/0.3027	0.7453/0.4122	0.2094/0.0645	0.2148/0.0165	0.3090/0.0750
D/R/P**	1757/0/83	1158/0/70	2894/190/217	1204/0/60	1261/334/236
GOF on F^2	1.073	1.035	1.038	1.04	1.59
Final R values $[I > 2\sigma(I)]$	R1 = 0.0388,	R1 = 0.0402,	R1 = 0.0655,	R1 = 0.0740,	R1 = 0.0702,
	wR2 = 0.0813	wR2 = 0.0972	wR2 = 0.1344	wR2 = 0.1949	wR2 = 0.1234
R Indices (all data)	R1 = 0.0480,	R1 = 0.0464,	R1 = 0.1058,	R1 = 0.0740,	R1 = 0.0887,
	wR2 = 0.0862	wR2 = 0.0998	wR2 = 0.1554	wR2 = 0.1949	wR2 = 0.1254
Largest Peak/Hole, e – Å ³	4.628 / -2.785	4.161/-2.118	3.145/-1.864	3.439/-3.288	4.076/-2.977
Volume Taken, Å ³ (%)	830.2 (71.2)	205.8 (70.8)	2200.3 (66.6)	586.2 (70.2)	1162.3 (69.2)
Dimensionality	3D	2D	2D	1D	3D

* – Refinement Method Full-matrix least-sq. on $F^2 **$ – listing of Data, Restraints, and Parameters.

(7.53). The IR spectrum: ν (C–H) – 3080; ν (C=N) – 2201; ν (C=C) – 1493; ν (CNO) – 1109.

The Tl₂(1,3-BCO) is a dark yellow powder. It is soluble in water at elevated temperatures and insoluble in EtOAc. Anal. Calc. (Found): C: 19.34 (19.98); H: 0.65 (0.7); N: 9.02 (9.17). IR (ATR, cm⁻¹): ν (CN): 2207; ν (C=C): 1441, 1250, 1244; ν (N–O): 1032.

The Tl₂(1,4-BCO) is a bright yellow powder. Anal. Calc. (Found): C: 19.34 (19.50); H: 0.65 (0.60); N: 9.02 (8.77). IR (ATR, cm⁻¹): ν (CN): 2207; ν (C=C): 1396, 1311; ν (N–O): 978.

<u>Safety Note:</u> Although no difficulties or accidents have ever occurred in many years of laboratory work, extreme care should be taken when working with Tl salts because of their high toxicity, water solubility, and the ready absorption through the skin of aqueous Tl_2CO_3 solutions. Wearing of protective gloves is absolutely necessary, while face masks are not, due to very low volatility of ionic thallium(I) compounds.

X-Ray Crystallography. Selected crystals of these complexes were placed into the CryoLoop, or MiTeGen plastic loops and then attached to the copper pin positioned on the goniometer head of the Bruker APEX2 diffractometer, equipped with a SMART CCD area detector. The data sets were measured at temperatures below 150 K. The intensity data for Tl(PhCO), Tl₂(1,3-BCO) and Tl₂(1,4-BCO) were collected in ω scan mode, using the Mo tube (K α radiation; $\lambda = 0.71073$ Å) with a highly oriented graphite monochromator. The intensities were integrated from four series of 364 exposures each, covering 0.5° in ω at 10 to 60 s of exposure time, with the total data set being a sphere.

We should note that two out of five studied crystalline compounds were difficult samples for single crystal analysis. There were poor quality thin, needle habitus crystals of Tl(2F-PhCO) and its isomeric Tl (3F-PhCO) which also turned out to be twinned or multi-domain specimen, yet poor diffractors (ESI 10). We were lucky to reliably determine their crystal and molecular structures, albeit low precision of bonds length to \pm 0.01 Å. These two structures generated several A and B-type alerts that we explained in their checkCIF reports. Very small and poor quality needles of Tl(2F-PhCO) were studied using a more intense Cu tube (K α radiation; $\lambda = 1.54178$ Å). Still, the best selected for studies specimen was the rotational twin crystal. Successful structure solution and refinement was carried using twin law [-1000 - 10101] and BASF 0.241. It was not possible to make a reasonable refinement of atoms in this structure in anisotropic approximation without structure of getting imploded and having nonpositive-definites (NPDs). Therefore, all non-H atoms and Tl centers were chosen to be in isotropic approximation. Similarly, the best selected crystal of Tl(3F-PhCO) complex also turned out to be multicomponent specimen, but was successfully refined as an inversion twin with BASF 0.618 using just two most intense domains. It was not possible to make a reasonable refinement of atoms in this structure in freely in anisotropic approximation without structure of getting imploded and having non-positive-definites (NPDs). In order to avoid the overuse of SIMU, DELU commands we applied ISOR 0.001 restraint and RIGU instruction to keep fully converged structure reasonable. Thallium atoms in the structure appeared with normal thermal parameters. In summary, non-single crystalline specimen used for these studies and approximated as twins contained other smaller domains that contributed into overall electron density count. As such, we observed some 3-4 electrons "ripples" next to Tl atoms, as well as some holes of about the same magnitude of charge. Location of both is the very close proximity to thallium centers and does not have chemical meaning.



Fig. 1. A – Molecular structure and numbering scheme of the asymmetric unit (ASU) in the structure of Tl(PhCO). B – Organization of the one-dimensional coordination polymer in the structure of Tl(PhCO). Two orthogonal views: **B** – normal to [100] plane; **C** – normal [0 1 0] plane showing slightly "slipped" π - π interactions. Arrows indicate asymmetric dimers.

The space group determination in all cases was done with the aid of XPREP software [73]. The absorption correction was performed, using values from face-indexed crystals and numerical values obtained from the set of images recorded with the video-microscope (ESI 11), followed by the SADABS program that was included in the Bruker AXS software package [73-76]. All structures were solved by direct methods, and refined by least squares on weighted F^2 values for all reflections, using the SHELXTL program. The structures reported herein did not have apparent errors, and are well refined. Crystal and refinement data can be found in Table 1, while selected bond lengths and angles are presented in appropriate places in the ESI sections 18,20,27,31. For drawings were using the ORTEP 3v2 [77,78] and Mercury software packages [79]. Thermal ellipsoids in all figures are drawn at their 50% probability level. All four crystal structures have been deposited into the CCDC: 1,969,209 for Tl(PhCO), 1,969,208 for Tl(2F-PhCO), 1,990,393 for Tl(3F-PhCO), 1,969,206 for Tl₂(1,3-BCO) and 19,690,007 for Tl₂(1,4-BCO).

<u>Thermal analysis</u>. The TG analysis was performed on the TA Instrument Q-600, in an alumina crucible, under pure nitrogen flow, in the range between 30 and 1000 °C at 100 \pm 2 ml/min, and a heating rate ranging from 10 °C/min. The crucible was calcined prior to each experiment using the propane torch (ESI 44). Data of the TG analyses were processed using the TA Universal Analysis software package.

Spectroscopy. Diffusion reflectance spectra of all obtained complexes in solid state in the range of 300–850 nm were recorded with the help of CARY Bio 100 equipped with integrating sphere (from Labsphere), while electronic spectra in aqueous solutions were obtained with an HP 8453 spectrophotometer. The IR spectra of Tl(I) cyanoximates were recorded using grinded pure samples of complexes on a Bruker ATR X80 spectrometer, since pressing KBr pellets with thallium complexes leads to the metathesis reaction between Tl(I) and Br⁻ anion. The Raman spectra of these compounds were obtained with the

help of Bruker Vertex S70 spectrophotometer.

3. Results and discussion

3.1. Preparation of compounds and crystals growth.

X-Ray-suitable crystals of TlL ($L = PhCO^{-}$, 2F-PhCO⁻) and Tl₂L $(L = 1,3-BCO^{2-}, 1,4-BCO^{2-})$ were grown from the mother liquors upon slow cooling in a thermostat within several days. Thus, immediately after the reaction between Tl₂CO₃ with solid HL (or H₂L) to complete CO₂ evolution, the reaction mixture was hot-filtered at 95 °C into long test tubes, already positioned in the large Dewar flask filled with water at that temperature (ESI 6 and 7). These test tubes, with mother liquors, being well insulated from surrounding in 4l of preheated to 95 °C water, were left undisturbed for 5 days. When the system was opened, long needles of Thallium(I) cyanoximates were filtered using gravity filtration and paper filters, and air dried. Crystals of Tl(PhCO), Tl₂(1,3-BCO) and Tl₂(1,4-BCO) suitable for X-ray analysis were harvested right away, while selection of single crystals of Tl (PhCO) and Tl(2F-PhCO) was a challenging task, due to their high propensity for twinning. In fact, the best specimen of the latter complex selected for studies was a pseudo-merohedral twin, containing two components at 24% and 76% contribution.

3.2. Crystal Structures.

Structure of Tl(PhCO). The crystal structures of two TlL complexes (L = 2Cl-PhCO⁻ and 4Br-PhCO⁻) represent uncommon examples of the double-stranded columnar coordination polymers, in which linear arrays of Tl⁺ ions exhibit short intermetallic distances. The distance between π - π interacting haloaryl groups reflects their 'thickness' and affects Tl-Tl separations. Thus, the smallest halogen atom in size, provides the closest inter-thallium distances. In light of that finding, it was very interesting to synthesize the Tl⁺ complex with unsubstituted arylcyanoxime - H(PhCO) - oxime. We postulated that the absence of any halogen atoms at the phenyl group should provide the closest distances between unsubstituted phenyl groups, and will lead to the shortest Tl-Tl separations. This turned out not to be the case: the molecular structure of the Tl(PhCO) is shown in Fig. 1 and exhibits two crystallographically different cyanoxime anions which are differently connected to Tl⁺. Because of the uniqueness of this structure we describe it in detail.

The molecular structure and numbering scheme of a single dimeric unit of Tl(PhCO) is shown in Fig. 1A. This complex crystallizes in the orthorhombic crystal system, and two projections of the unit cell content are presented in Fig. 1B,C, while crystallographic information is shown in Table 1. The values of bond lengths and valence angles in the complex are given in the ESI 18. The crystal structure of Tl(PhCO) represents a highly unusual case of one-dimensional coordination polymers, comprised of a non-centrosymmetric dimer with anions in the trans-anti configuration [79] with two phenylcyanoxime anions PhCOin the structure having different geometries: one is non-planar, while the other one is practically planar. The ligand, that has the shortest Tl2-O1 and Tl1-O1 bonds, is in non-planar configuration similar to that in the structure of the uncomplexed phenylcyanoxime reported recently [80]. The anion is arguably in the nitroso-form judging the shorter O1-N1 bond than N1-C1 in the fragment (ESI 18). In the non-planar anion there are two planar fragments in the structure of the anion: the cyanoxime and phenyl groups joined together at the C1 atom (Fig. 1). The dihedral angle between the two planar fragments C4-C3-C1-N1 and C8-C3-C1-N1 is 14.3°. The second phenylcyanoxime anion is planar, with the value of the dihedral angle between the cyanoxime plane and phenyl group equal at 3.7°. This particular anion has less of the nitrosocharacter: N3–O2 = 1.310 Å and C9–N3 = 1.320 Å (ESI 18). The crystal packing diagram for this complex is also unusual. The structure of Tl₂O₂ rhomb is unconventional too, when compared to those in our



Fig. 2. Intermetallic distances in Tl(PhCO): **A** – the least obstructed view of the 1D zig-zag chain in the structure showing all four closest Tl—Tl distances; **B** – the same arrangement suitably turned to show Tl atoms as wan-der-Waals spheres. H-atoms are omitted for clarity. Symmetry codes for 1: 1 - x, 1 - y, 1 - z; for _1: $\frac{1}{2} + x$, $\frac{1}{2} - y$, 1 - z.

previous studies of Tl-cyanoximes [81–84]. There are two crystallographically different Tl(I) atoms (Figs. 1 and 2). Each has its own unusual zig-zag 1D pattern (ESI 13–16). Examination of the coordination polyhedron reveals an unconventional and, in fact very rare, structure, with regard to the Tl and O atom connectivity. Thallophilic interactions are clearly visible in the structure (Fig. 2B).

The geometry of intermetallic distances in the structure of Tl(PhCO) is shown in Fig. 2, while peculiarities of polymer formation are depicted in ESI 14. Two non-centrosymmetric Tl(PhCO) dimers are joined together by O1 and O2 atoms of the oxime groups, which act as two different bridges (Fig. 2). Thus, O1 atoms form two short contacts between Tl1 and Tl2 centers, while O2 atoms form three slightly longer bonds, with two Tl1 and one Tl2 cations (ESI 14). The distance Tl2 7 -O2 = 3.518 Å is significantly longer than any reasonable chemical bond and represents an electrostatic contact (ESI 16). The resultant Tl₂O₂O' polyhedron is a highly distorted trigonal bipyramid. Some interaction between the Tl atoms and N atoms from the cyano-groups were observed being both within, and between, the polymer chains, which extend structure into puckered sheets. The intra-columnar contact (Tl2-N4) of shortest distance is 3.325 Å, while the shortest inter-columnar Tl-N distance is 3.021 Å [72]. Organization of polymeric columns structure is shown in ESI 12 and 15. Further details of crystal packing in this highly unusual structure of Tl(PhCO) complex are presented in ESI 16. The rarity of the observed crystal structure of this complex is such that there are only a few other structures known that somewhat resemble Tl(PhCO) [87].

Structure of Tl(2F-PhCO). The molecular structure and numbering scheme for this compound are shown in Fig. 3 with the most essential bonds and angles presented in ESI 17. The anion in this complex adopts *trans-anti* (with respect to the oxime group) geometry and is practically



Fig. 3. Fragment of crystal structure of Tl(2F-PhCO): **A** – one cyanoxime and several closest Tl(I) centers, **B** – important bond length in the anion connected to the neighboring Tl(I) atoms, **C** – the same fragment, only metal centers expressed as van-der-Waals spheres emphasizing metallophilic interaction. H-atoms are omitted for clarity. Symmetry codes for positions: #1 is 2 - x; $\frac{1}{2} + y$; $\frac{1}{2} - z$, #1_1 is 1 + x; $\frac{1}{2} - y$; $\frac{1}{2} + z$. #1_2 is 1 - x; $\frac{1}{2} + y$; $\frac{1}{2} - z$, #1_3 is 1 + x; $\frac{1}{2} - y$; 2 + z, and for #1_4 is x; $\frac{1}{2} - y$; $\frac{1}{2} + z$.

planar. Cyanoxime is in the *nitroso* form judging from bond lengths as follows: C7–N1 = 1.408 Å, N1–O1 = 1.335 Å (ESI 18). The crystal structure of this complex represents a truly 1D coordination polymer with the 'building block' as centrosymmetric $[T1(2F-PhCO)]_2$ units containing the planar cyanoxime anion with an inversion center in the middle of a dimer (Fig. 4A). Geometries of the cyanoxime anion in the ASU, as well as intermetallic distances between the closest neighboring Tl atoms, are presented in Fig. 4. There are also short thallophilic interactions in the structure (Fig. 3C).

Examination of the coordination polyhedron of Tl(2F-PhCO) reveals its essentially trigonal pyramidal structure (Fig. 3A and B). The shortest



Fig. 4. Fragment of the crystal structure of Tl(2F-PhCO) showing two prospective views of isolated 4-unit cells extended along *a*-direction (**A**) and *b*-direction (**B**). The formation of the centrosymmetric dimers Tl_2L_2 is indicated with a blue arrow. Weak F—H interactions are marked with a grey arrow. Hatoms are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Molecular structure and principal atoms numbering scheme for Tl(3F-PhCO) (**A**) and view of the unit cell content along *b*-direction showing lack of center of center of symmetry and stabilizing lattice short C–H—F contacts (**B**).

Tl–O bond length in Tl₂O₂ rhomb is 2.595 Å (Tl1–O1¹) with the second being 2.670 Å (Tl1–O1), and another Tl1—O1 distance in the closest ASU unit being 2.645 Å. The O–Tl–O angles in the Tl₂O₂ rhomb are 77.24° and 101.37° (ESI 19). The [Tl(2F-PhCO)]₂ dimeric units are forming a ladder-type column due to bonding between the Tl1 center and the O1 atom of the similarly aligned neighboring unit (Fig. 4). That 1D extension is also quite well stabilized by 'slipped' π - π stacking interactions between fluoro-phenyl groups (Fig. 5B). In addition, weak, but stabilizing, F—H(phenyl group) interactions between columns are also present (Fig. 4A) at a distance of 2.875 Å. In line with previously determined TlL structures [54,58,88] and other structures presented here, there is a long, non-bonding interaction, most likely of electrostatic nature, between the Tl atoms and the nitrogen atoms of the CN-group. These are intra-columnar Tl1—N2 electrostatic contacts Tl1–N2 at 3.160 Å.

Structure of Tl(3F-PhCO). Structure of this compound is also quite unique and differs entirely from its analogous and isomeric complex Tl (2F-PhCO) described above. First of all there are two crystallographically different metal centers and fluorinated cyanoxime anions (Fig. 5A). This situation is somewhat similar to the structure of Tl (PhCO) discussed above. Secondly, this complex crystallizes in noncentrrosymmetric space group Pna2₁ (Table 1). Then, there is no formation of Tl₂O₂ rhombs, but instead the cyanoxime exhibits rare "sideon" coordination which we previously observed only in one case of Tl(I) pyridine-based cyanoxime [57]. There are two zig-zag chains of Tl1-Tl2—Tl1—Tl2 atoms running parallel a-dimension (Fig. 5B). Both chains are on a top of each other forming an unusual "thallium ladder" with bent at 135.7 and 134.5° (Fig. 6) with very pronounced metallophilic interactions were observed in this structure. Each Tl center has severely distorted octahedral environment with clearly identifiable place for stereoactive $6s^2$ lone pair (ESI 21). Octahedrons of metal atoms both for Tl1 and Tl2 are fused by the face forming infinite chain. Further details of this truly unique structure can be seen in ESI 22. Both cyanoximes are practically planar and are in the nitroso form judging shorter N-O than C-N bonds in that fragment (ESI 20).



Fig. 6. Two different prospective views of partial unit cell content showing geometry of metal atoms in one chain of a "thallium ladder": A – space filling representation indicating very close contacts, and B – angles between atoms.

Structure of Tl₂(1,3-BCO). The 1,3-BCO bis-cyanoxime ligand has a complex ¹H and ¹³C NMR signature which evidences the rather rich stereochemistry of this seemingly simple compound [89]. Restricted rotation around C-C bonds between cyanoxime fragments and the phenyl ring, as well as the presence of syn- and anti- geometrical isomers, are responsible for such conformational richness, explained in ESI 26. In the studied $Tl_2(1,3-BCO)$ complex, ligand's diastereomer 9 is present. The ligand is in the oxime- form (ESI 27), and is not planar, with a small dihedral angle of 11.99° between the cyanoxime fragment and the aromatic ring. One 1,3-biscyanoxime anion, and its closest Tl centers, are presented in Fig. 7A, while the shortest intermetallic distances are shown in Fig. 7C. The bis-cyanoxime acts as bridging ligand (Fig. 8A). Organization of crystal structure and packing into crystal can be viewed in Fig. 8B. There are non-planar and non-centrosymmetric rhombs formed in the structure of Tl₂(1,3-BCO) (ESI 23). As such, it should be especially noticed, the overall structural motif is not the double-stranded "ladder-type" as that for Tl(2F-PhCO)! It is much more complex and can be explained as an interconnected system of both types of planar and non-planar Tl₂O₂ rhombuses (ESI 24 and 25). Thus, the structure of Tl₂(1,3-BCO) also represents an inter-tangled puckered sheets of Tl₂O₂ units with the cyanoxime anions acting as a tridentate bridge between Tl atoms via O atoms (Fig. 8A). Slipped ' π - π stacking' interactions with shortest contact at ~3.95 Å align aromatic rings, which helps in crystal packing (ESI 23). Thus, the structure represents elegant pleated sheets, which, via additional Tl-O contact, are extended into the 3D framework. Details of intermetallic Tl-Tl distances in the structure are shown in Fig. 7C where short thallophilic



Fig. 7. A – Fragment of crystal structure of $Tl_2(1,3-BCO)$ showing one bis-cyanoxime and closest metal centers; **B** – the shortest intermetallic distances in the complex; **C** – a slightly rotated similar view with metal ions expressed as van-der-Waals spheres emphasizing metallophylic interactions.



Fig. 8. A – The ASU in the structure of $Tl_2(1,3-BCO)$ showing atomic numbering scheme and formation of planar centrosymmetric Tl_2O_2 rhomb, **B** – fragment of crystal structure of $Tl_2(1,3-BCO)$ showing details of crystal packing with view along *c*-direction.

interactions were observed as well. The shortest distance was found to be 3.670 A, which amounted to metallophylic interactions. The shortest Tl1—N2 interatomic distance of an intra-columnar nature is 3.541 Å, and the shortest distance between the columns is 3.142 Å. These can be considered only as electrostatic interactions, with no bonding occurring between Tl and the cyano group.

A remarkable property of the Tl₂(1,3-BCO) crystal structure is the presence of a large pore/channel within its lattice. The pore is large, ~ 6.55 Å across, and potentially these pores may be able to hold a variety of gases with smaller kinetic diameters. That variety includes gases such as H₂, SO₂, CO₂, CH₄, and other greenhouse gases [72], and this case represents the first example of porous crystal structures based on cyanoximes. No attempts to measure the surface area inside the channel were made at this stage, but are considered for future work using the BET method.



Fig. 9. A – The GROW fragment in the structure of $Tl_2(1,4-BCO)$ showing the atomic numbering scheme (the inversion center is in the middle of the phenyl ring with respective symmetry codes for #1 position as: -x, -y, -z), and perspective view of several unit cells in the structure of $Tl_2(1,4-BCO)$ showing organization of the crystal lattice: **B** – view along *a*-direction presenting the formation of Tl_2O_2 rhombs, **C** – view along *b*-direction displaying the formation of ladder-type motif and slipped π - π stacking interactions (arrow). H-atoms are omitted for clarity.

Examination of the coordination polyhedron of Tl in the molecule reveals a *T*-shaped arrangement of the surrounding O atoms, with the true structure being of a highly distorted trigonal pyramidal geometry (ESI 28 and 29). The shortest Tl1–O1 bond is 2.561 Å, with the other two metal–oxygen distance also being shorter than the sum of ionic radii of these elements and implying certain degree of covalency in chemical bonding (Fig. 7A).

Structure of Tl₂(1,4-BCO). The bis-cyanoxime ligand in this structure is present as trans-anti-diastereomer 10 (ESI 30 and 32). The atomic numbering scheme for the dianion is shown in Fig. 9A. The ligand is in the oxime form as evident from C1-N1 and N1-O1 bonds being 1.300 Å and 1.393 Å, respectively (ESI 31). The ligand adopts a practically planar structure, with a dihedral angle of 7.77° between the ring and the cyanoxime fragment. Similarly to the Tl(2F-PhCO) and Tl₂(1,3-BCO) complexes described above, there is a formation of distinct centrosymmetric and planar Tl₂O₂ rhombs (Fig. 9B and C). Every C-N-O fragment in the complex has three short Tl1-O1 bonds geometry, which is given in Fig. 10A. The shortest O1-Tl1 distance is 2.559 Å, with the other two being less than 2.7 Å, and all three shorter than the sum of ionic radii of involved elements. The geometry of intermetallic distances in this complex is displayed in Fig. 10B and 10C, with the shortest Tl-Tl metallophylic contact determined to be 3.784 Å. The overall structure motif is columnar (Fig. 9B and C), but with additional Tl1-O contacts, a 'ladder-type' 2D polymer is formed (Fig. 9B). There are two Tl_2O_2 rhombs, slightly different in geometry, and the Tl-Tl-Tl angle is 98.72° in the zig-zag chain of the 'ladder' (ESI 34). Further details of geometry in this arrangement can be viewed in



Fig. 10. Fragment of crystal structure of $Tl_2(1,4-BCO)$: **A** – one cyanoxime and several closest Tl(I) centers showing their bonds and angles, **B** – important bond length in the anion connected to the neighboring Tl(I) atoms, **C** – only closest metal centers expressed as van-der-Waals spheres emphasizing metallophilic interaction.

ESI 24. The π - π stacking is important for the stabilization of this structural motif: the ring-ring separations between the centroids of aromatic fragments in the lattice are 3.970 Å, which are longer than those in other complexes reported here (Fig. 9C). However, it turned out to be sufficient packing in this particular compound. The polymer phenyl rings lie roughly in the same plane and are spaced at a distance of 6.672 Å. The same kind of Tl—N long and electrostatic interactions between Tl atoms and N atoms of the cyano groups, as seen in structures of Tl(PhCO), Tl(2F-PhCO) and Tl₂(1,3-BCO) are also present, as seen in Tl₂(1,4-BCO), but to a lesser extent. The shortest Tl-N interaction, found only within the sheets, is 3.224 Å. The coordination polyhedron of Tl(I) can be best described as a distorted trigonal pyramid (ESI 33).

A plot of intermetallic Tl—Tl distances vs. the size of the halogen atom in Tl(I) cyanoximates is displayed in ESI 35. Lastly, the geometry and motifs of all thallium(I) cyanoximates that contain Tl_2O_2 rhombs, known and studied thus far, are summarized in Table 2.

In summary, based on our findings we can present observed binding modes of cyanoximes in their Tl(I) complexes as it is shown in Scheme 3. Interesting multidentate bridging ability of these new anionic ligands was found and will allow us to move with preparation of heterometallic complexes.

3.3. Spectroscopic properties.

Vibrational spectra. Involvement of the nitrile group of cyanoximes due to conjugation in the overall electronic structure of Tl-complexes was postulated in early works [96,98]. However, only now has it been confirmed by Raman spectroscopy, upon comparison of spectra of uncomplexed, solid cyanoximes with spectra of TlL. Thus, a pronounced low frequency shift in the range 2250–2100 cm⁻¹ was detected for the nitrile group (ESI 37, 39, 41 and 43). Also, for the first time, we were able to identify and assign v^{sym} and v^{asym} Tl–O vibrations in the range of 150–50 cm⁻¹ associated with the Tl₂O₂ rhombs described above (ESI 36, 38, 40 and 42).

3.4. Electronic spectra: absorption and emission.

All synthesized complexes are yellow in color, and demonstrate single absorbance at ~400 nm, due to the $n \rightarrow \pi^*$ transition in the nitroso-chromophore, both in solutions and in solid state [20,30,48,50,97]. When ground powdery samples of TlL and Tl₂L' (L = mono- and L' = bis cyanoximes), are excited at 380 nm, all solid compounds are strongly emissive, with red-shifted for ~30 nm single band for Tl(2F-PhCO) and Tl₂(1,3-BCO), and with the most representative spectrum shown in Fig. 11.

The emission is very bright, and presented some difficulty in obtaining non-truncated spectra, even at the smallest emission/excitation slits, and the lowest integration time of 0.1 s allowed by our fluorimeter. Emission spectra for Tl(PhCO) and Tl₂(1,4-BCO) contain two poorly-resolved bands (ESI 44–47).

3.5. Thermal analysis

Pure organic ligands – cyanoximes – are much less thermally stable than their Tl(I) complexes as we determined studying their TG/DSC properties under pure argon atmosphere. Thus, H(PhCO) melts at 130.2 °C followed by rapid decomposition, while H₂(1,3-BCO) and H₂(1,4-BCO) melt at 135.1° and 149.6 °C respectively. The latter biscyanoximes decompose at 15-19° higher temperatures.

There was found to be a very distinct difference between the thermal properties of the Thallium(I) mono-cyanoximates and bis-cyanoximates. The former complexes melt with quickly followed decomposition, while the latter complexes exhibit strongly exothermic and violent decomposition. The least thermally-stable compound was determined to be Tl(PhCO), which melts with decomposition at 157 °C, while Tl(2F-PhCO) melts at 204 °C, and then quickly begins decomposing at 226 °C. Thallium bis-cyanoximates Tl₂(1,3-BCO) and Tl₂(1,4-BCO) are more thermally-stable, and undergo rapid decomposition at 262 °C and 283 °C respectively. The most interesting finding is that Tl₂(1,3-BCO) violently decomposes at once (ESI 48 and 49) with a considerable magnitude of the exo-effect, demonstrating the properties of a heat-activated, high energy compound [98]. In this context it should be noted that other heavy metals salts containing also toxic lead (II) and mercury(I,II) are widely used in specific applications for highenergy compounds [70,100–102], and discovery similar properties for thallium(I) Werner-type complex was, actually, a surprise. Also, release of kinetic energy upon decomposition of Tl₂(1,3-BCO) leads to dislocation of the crucible from the thermal analyzer balance pan. Thus, the enthalpy of rapid decomposition of a sample of this complex within several seconds - is 175 \pm 15 kJ/mol. Further details of the thermal behavior of that complex are presented in ESI 50-53 explaining this rare phenomenon. Interestingly, similar behavior was not observed for the analogous Tl₂(1,4-BCO) complex, and silver(I) cyanoximates of AgL composition [99,103], despite a great chemical similarity between monovalent Ag and Tl. However, we recently found several other Cu(II) cyanoximes-based compounds which exhibit properties of high energy compounds. [99] The final product of complexes' thermal decomposition in an inert atmosphere (N₂) is metallic thallium, which appears as fine shiny sponge (Fig. 12; ESI 54).

4. Conclusions.

In summary of the conducted investigation, we report:

Table 2

Specific details of geometry around metal centers in studied Tl-arylcyanoximates and in some other complexes with different types of ligands. The shortest distance is indicated in bold italic type font.

Complex	Tl—O arrangement	Tl—Tl distances, Å	Reference
Thallium(0)			
Metallic thallium	hexagonal close packed	3.456, <i>a</i> , hexagonal	[86]
		3.438, a, hexagonal	[87]
		3.362, I-centered cube	[87]
Thallium(I)			
Tl(PhCO)	Non-centrosymmetric, non-	4.042 (inner dimer)	This work
	planar Tl ₂ O ₂ rhombs forming	4.194, 4.033,	
	2D polymer	3.770	
Tl(2Cl-PhCO)	Centrosymmetric Tl ₂ O ₂	4. 184 (inner dimer)	[85]
	rhombs forming 1D columns	4.440, 3.838	
Tl(4Br-PhCO)	centrosymmetric Tl ₂ O ₂	4. 097 (inner dimer)	[50]
	rhombs forming 1D columns	4.435, 4.058	
Tl(2F-PhCO)	centrosymmetric Tl ₂ O ₂	4.114 (inner dimer)	this work
	rhombs forming 2D polymer	4.113, 4.301, 3.950	
		3.748	
Tl(3F-PhCO)	metal ladder, no of Tl ₂ O ₂	3.802, 3.846 (intra strand)	this work
	double-stranded	3.756 (inter strand)	
Tl ₂ (1,3-BCO)	presence of both	4.214 (intra dimer)	this work
	centrosymmetric and non-	4.160, 4.282	
	centrosymmetric, non-planar Tl ₂ O ₂ rhombs	3.670	
	forming complex 3D network		
Tl ₂ (1,4-BCO)	centrosymmetric Tl ₂ O ₂	4.330 (intra dimer)	this work
	rhombs forming 2D polymer	3.970, 3.967	
		3.784	
Tl ⁺ (thalla-dicarbollide) ⁻ *	metallophilic Tl—Tl	3.67	[88]
Tl(C ₅ (CH ₂ -Ph) ₅)**	metallophilic Tl—Tl	3.63	[89]
Tl(C ₅ H ₅)**	metallophilic Tl—Tl	3.99	[90]
[Tl(C ₅ (1,3- <i>t</i> -Bu ₂)] ₂ **	metallophilic Tl—Tl dimer	3.76	[91]
$[Tl_6{SiMe_2}(N-t-Bu)_6]^{***}$	metallophilic Tl—Tl	3.152	[92]
	two edge sharing cubes	3.180	
Thallium(II)			
Tl ₂ {Si(<i>t</i> -Bu ₃) ₂ }***	linear, with direct Tl-Tl bond	2.97	[93]
Tl ₂ {Si(SiMe ₃) ₃ } ₂ ***	linear, with direct Tl-Tl bond	2.914	[94]

* - thallium anionic ligand: dicarbollide, [3,1,2-TlC2Me2B9H9]⁻; ** - cyclopentadiene (Cp) based compounds; *** - organosilyl derivatives.





 μ^1 -N-, μ^3 -oxo-bridging and

N-O "side-on" coordination

 μ^{1} -N-, and μ^{3} -oxo-bridging







TI₁

 μ^2 -N, μ (NO) + μ^2 -oxo-bridging

 μ^2 -N, μ (NO) + μ^3 -oxo-bridging

 TI_2

Scheme 3. Observed bridging binding modes in studied coordination polymers of Tl(I).

- Preparation of five new Tl(I) coordination polymers based on two groups of anionic ligands: mono- and bis-cyanoximes.
- Determination of five crystal structures of new compounds with a new interesting finding: the unexpected formation of unusual non-



Fig. 11. Reflectance and emission spectra of solid sample of Tl_2(1,3-BCO); T = $+\,25~^\circ\text{C}.$

planar and non-centrosymmetric Tl_2O_2 dimers in the structure of Tl (PhCO), and side-on coordination of the *nitroso*-groups in Tl(3F-PhCO).

- The finding of a spacious, ~6.5 Å wide channel in the structure of Tl₂(1,3-BCO) complex which allows its further exploration for potential gas sorption purposes.
- Tabulation of all known Tl(I) structures with cyanoximes that contain Tl₂O₂ rhombs.
- Spectroscopic characterization of all obtained compounds, and detection of low-frequency Tl–O vibrations, the first time.
- One compound Tl₂(1,3-BCO) demonstrated properties of a high



Fig. 12. A – thermal analysis traces in usable temperature range for a sample of high-energy $Tl_2(1,3-BCO)$; B – actual microscope photograph of the alumina crucible after thermal decomposition reaction, showing metallic thallium sponge.

energy compound.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119597.

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