

Synthesis, Characterization, and Studies of Coordination-Polymeres With Isomeric Pyridylcyanoximes: Route to Metal Ribbons With Very Short TI---TI Separations

Daniela Marcano,[†] Nikolay Gerasimchuk,^{*,†} Victor Nemykin,[‡] and Svitlana Silchenko[§]

[†]Department of Chemistry, Temple Hall 431, Missouri State University, Springfield, Missouri 65897, United States

[‡]Department of Chemistry and Biochemistry, University of Minnesota – Duluth, Duluth, Minnesota 55812-2496, United States [§]Absorbtion Systems, Inc., 440 Creamy Way, S. 300, Exton, Pennsylvania 19341, United States

(5) Supporting Information

ABSTRACT: Two isomeric pyridylcyanoximes, H(3PCO) and H(4PCO), containing nitrogen atoms of the heterocycle at 3- and 4-positions, respectively, were synthesized and thoroughly characterized using IR (including ¹⁵N labeling), UV–visible, ¹H, ¹³C one- and two-dimensional NMR spectroscopy, and X-ray analysis. The H(3PCO) exists as a mixture of *syn-* and *anti-*isomers in solutions, contrary to H(4PCO) which is present only as an *anti-*isomer. Both compounds have planar geometry in the solid state and form elegant zigzag chains via H-bonding between the oxime group and the N-atom of the heterocycle. The H(3PCO) and H(4PCO) upon addition of a base form colored conjugated and solvatochromic anions in solutions. The reaction of the hot aqueous solution of Tl₂CO₃ with solid isomeric pyridylcyanoximes leads to TlL, which were characterized by elemental analyses, IR spectroscopy, and X-ray analysis. Both complexes represent three-dimensional coordination polymers of different complexities where cyanoxime anions act as bridging ligands. Thallium(I) atoms in Tl(3PCO) and Tl(4PCO) form infinite, planar "metal



ribbons" with unusually short intermetallic distances: 3.705 Å in Tl(3PCO) and 3.635 Å in Tl(4PCO) respectively, which are close to that in metallic thallium (3.465 Å). The latter compound has the second shortest Tl…Tl thallophillic interaction reported in the literature thus far. Both yellow Tl(3PCO) and orange Tl(4PCO) are insulators at ambient conditions: $R \sim 1 \times 10^{11}$ Ohm.

INTRODUCTION

Coordination polymers with unusual structures and properties have attracted considerable attention due to their interesting topologies and fascinating potential applications in (a) molecular electronics, and (b) as photo- and magnetic materials.¹⁻⁴ The main focus in development and studies of coordination polymers was on transition metals, while less attention was given to main group metals, despite their wellestablished importance in electro- and conventional luminescence, fluorescent sensors, and photovoltaic applications.^{3,5-7} Thus, in the area of molecular electronics search for onedimensional (1D) conductive solids, attention was mainly on mixed valence transition metals homometallic complexes and especially platinum.⁸ Two major types of electric conductors originated from work with the latter metal: MX,9 KCP, and partially oxidized cyano-platinates (POCP)¹⁰ types of 1D solids. The latter compounds contained a certain mix of Pt(II) and Pt(IV) states with direct metal-metal contacts in an identical coordination environment. Further structural derivatives of POCP include dioximates such as BQD,¹¹ PtDMG,¹² and others,¹³ in which there are close --Pt---Pt-- distances in regular columns of 1D solids. It is well established that the two electrons "hopping" between those two oxidation states are responsible for the metallic type room temperature electrical conductivity in both MX and KCP/POCP solids. Poor mechanical properties and solubility in common organic solvents, the loss of metallic conductivity at low temperatures due to the Pierls distortions, and insufficient electronic tunability were main factors that precluded their further development as low density, nonmetal, and nonalloy 1D materials for specific molecular electronics applications.

Among main group metals there are several — Sn, Pb, and Bi — that also exhibit two stable oxidation states that differ by two electrons, but only thallium is the one that readily forms coordination polymers. This metal is especially attractive because its $TI^{1+} \leftrightarrow TI^{3+}$ transition¹⁵ involves the top 6p-6s shells, with those two electrons thought to be coherent and able to form a Cooper pair.¹⁴ In order to provide conditions for the electron "hopping" between metal centers, certain conditions should be met, with one of the most important one being a close mutual spatial location of metal ions in the coordination polymer formed. Metallophilic interactions play an important role in bringing metal centers together.¹⁶

On the other hand, *heterometallic* $TI \cdots M$ (M = Au, Pt, Ag) coordination polymers with short intermetallic separations and metallophilic interactions demonstrated remarkable photo-

Received:January 16, 2012Revised:April 24, 2012Published:April 26, 2012

luminescence.^{17–19} The formation of polymeric *homometallic* and *heterometallic* complexes that form infinite "metallic chains" based on metallophilic interactions was recently reviewed.²⁰

Thallium is a soft, oxophyllic Lewis acid²¹ and in general possesses pronounced halcophylicity readily forming Tl-E bonds (E = S, Se, Te).²² Most of studied Tl complexes contain only oxygen donor atoms around a metal center with only a few examples of other donor atoms.²³ During the last several years, we discovered an interesting group of the oxime-based thallium(I) 1D and two-dimensional (2D) coordination polymers.²⁴ The striking feature of some of those complexes is a formation of a double-stranded zigzag chain with close intermetallic separations which can be utilized in the formation of mixed valence Tl¹⁺/Tl³⁺ species and possibly facilitate 1D electrical conductivity in these otherwise dielectric solids. A successful realization of this project may add thermally stable conducting coordination polymers to the arsenal of tools for microelectronics and molecular electronics. An apparent toxicity of Tl-compounds should not preclude their practicality since similarly toxic arsenides (GaAs, and related), selenides (ZnSe, CdSe), and tellurides (PbTe, CdTe) are widely used today in closed electronic devices with limited access to their components.

We continued investigations in this field, changing the ligand's design in order to keep the favorable double-stranded polymeric motif in place and at the same time bring the metal centers as close to each other as possible. In this work we present a detailed study of two isomeric pyridylcyanoximes shown in Scheme 1 and their two monovalent Tl complexes



with unusually short intermetallic separations. Despite an earlier report on the preparation of these ligands,²⁵ their characterization, crystal structures, and properties were not studied in detail at all. Isomeric H(3PCO) and H(4PCO) pyridylcyanoximes are not able to form chelate complexes contrary to their H(2PCO) analogue^{26,27} but may act as bridging ligands. Moreover, presented here pyridyl cyanoximes provide an important advantage in comparison with other typical building block-ligands for the formation of coordination polymers: these cyanoximes are *ionizable*. Therefore, they alleviate the necessity for the counter-anions in the structures which usually significantly affect the lattice architecture.

In present work we were focused on a search of oximes-based coordination polymers with short intermetallic thallophilic separations. Other types of intermolecular interactions in Tl(I) complexes, such as C…Tl and H…Tl electrostatic contacts, were out of the scope of our investigations but recently were summarized by Morsali.^{23,28} Both reported here Tl(I) pyridylcyanoximes complexes here can be used as building blocks or templates for the synthesis of either *homometallic* Tl¹⁺/Tl³⁺ mixed valence polymers or for the preparation of luminescent *heterometallic* coordination polymers.

EXPERIMENTAL SECTION

Materials and Methods. Starting thallium(I) carbonate, glacial acetic acid, sodium nitrite, and substituted acetonitriles R-CH₂-CN (R = 3-pyridyl, 4-pyridyl groups) were obtained from Aldrich and were used without additional purification. Organic solvents (Spectrum

Chemicals, J.T. Baker) were of HPLC grade and used without additional distillation. Isotopomeric sodium nitrite Na¹⁵NO₂ (~95% enrichment) was purchased from Cambridge Isotope Laboratories. Melting points or decomposition temperatures for synthesized protonated cyanoximes and their Tl(I) salts were determined using the Mel-Temp apparatus (Thomas-Hoover). Thin layer chromatography (TLC) for ligands was carried out on silica-coated glass plates (Merk) with an indicator. An elemental analysis on C, H, N content was performed at the Atlantic Microlab (Norcross, GA).

Solutions Studies. Electrical conductivity of 1 mM solutions of TIL in water (L = studied isomeric pyridyl-cyanoxime anions) was measured at 295 K using the YSI Conductance-Resistance meter model 34. The 1 mM solutions of tetramethylammonium bromide, potassium sulfate, and thallium carbonate (as 1:1 and 1:2 electrolytes, respectively) in DI water were used for the electrode calibration. Measurements of pK_a values for synthesized benz(2-hetroaryl)cyanoximes were carried out using a Sirius Analytical Instruments automated titration station (Sussex, UK) equipped with a temperaturecontrolled bath. Since protonated cyanoximes HL are poorly soluble in water, all measurements were conducted in mixed solvent systems using DMSO as a solubilizing cosolvent. Atenolol and Lidocaine (from Aldrich) were used for calibration of the instrument. Measurements consisted of the three-step multistage titration in water/DMSO mixtures from 20 wt % to 30 wt % with the ionic strength adjusted to 0.15 with KCl. The values were extrapolated to "zero" DMSO content to obtain an aqueous pK_a value using the Yasuda-Shedlovsky procedure. The pH in titration experiments ranged from 3 to 11.

Spectroscopy. All synthesized organic ligands were characterized at 296 K using ¹H, ¹³C NMR, COSY, and HMQC spectroscopy (solutions in DMSO- d_6 and acetone- d_6 ; TMS was an internal standard; Varian INova 400 MHz spectrometer). The UV-visible spectra of protonated ligands HL and their Na+ salts were recorded at room temperature (293 K) on an HP 8354 spectrophotometer in the range 200-1100 nm, using 1 mm and 10 mm quartz cuvettes. Infrared spectra were recorded in the range 500-4000 cm⁻¹ using the FT IR Nicolet Magna 550 spectrophotometer, using KBr matrix for the protonated cyanoximes HL. The IR spectra of TlL, however, were recorded from thick fine pastes in Nujol due to the solid state exchange reactions between KBr and TlL during the pellet preparation. Also, we used starting cyanoximes labeled ¹⁵N (50% diluted for better visibility of splitted IR bands) and their respective Tl(I) complexes for the exact assignment of vibrations with participation of the >C-N-O fragment.

X-ray Crystallography. Yellow thin needles of Tl(3PCO) and orange needles of Tl(4PCO) were obtained after a slow cooling of the filtered reaction mixture during the synthesis (Supporting Information, S1). Suitable single crystals of all obtained compounds - H(3PCO), H(4PCO), Tl(3PCO), and Tl(4PCO) - were mounted either on thin glass fibers, or on plastic loops of the Cryollop/MitiGen devices, and then placed on the goniometer heads. Compounds were studied using a Bruker APEX2 diffractometer equipped with a SMART CCD area detector. The intensity data were collected in ω -scan mode using the Mo tube (K α radiation; $\lambda = 0.71073$ Å) with a highly oriented graphite monochromator. Intensities were integrated from four series of 364 exposures, each covering 0.5° in ω within 60 s of acquisition time, and the total data set being a sphere.²⁹ The space group determination was done with the aid of XPREP software.³⁰ Numerical absorption corrections were applied based on crystal face indexing obtained using actual images recorded by the video-microscope camera for H(4PCO) and two Tl-cyanoximates (S2). The following data processing was performed using the SADABS program that was included in the Bruker AXS software package.³¹ The structures were solved by direct methods and refined by least-squares on weighted F^2 values for all reflections using the SHELXTL program.³⁰ All atoms received assigned anisotropic displacement parameters and were refined without positional constraints. Hydrogen atoms of C-H origin in structures of organic molecules H(3PCO) and H(4PCO) were placed in their idealized geometrical positions and refined isotropically in a riding scheme, while oxime hydrogens O-H were identified on a difference map. Crystal data for all four studied compounds are

Table 1. Crystal Data for Synthesized Isomeric Pyridylcyanoximes and Their Tl(I) Complexes

parameter	H(3PCO)	H(4PCO)	Tl(3PCO)	Tl(4PCO)	
empirical formula	C ₇ H ₅ N ₃ O	C ₇ H ₅ N ₃ O	C ₇ H ₄ N ₃ OT1	C ₇ H ₄ N ₃ OTl	
formula weight	147.14	147.14	350.50	350.50	
wavelength, Å	0.71069	0.71069	0.71073	0.71073	
diffractometer	Rigaku AFC-7R	Bruker APEX2	Bruker APEX2	Bruker APEX2	
temperature, K	296(2)	120(2)	120(2)	173(2)	
crystal system	monoclinic	monoclinic	triclinic	monoclinic	
space group	<i>P</i> 2(1)/ <i>c</i> , #14	P2(1)/c, #14	P1, #2	<i>P</i> 2(1)/ <i>n</i> , #14	
unit cell dimensions, Å, $^\circ$	a = 3.7810(7)	a = 3.728(3)	a = 3.7364(8)	a = 3.8990(4)	
	b = 17.0260(15)	b = 13.938(9)	b = 9.365(2)	b = 12.3800(13)	
	c = 10.941(4)	c = 13.008(9)	c = 12.156(3)	c = 16.7563(17)	
	$\alpha = 90$	$\alpha = 90$	$\alpha = 68.140(2)$	$\alpha = 90$	
	$\beta = 97.510(3)$	$\beta = 90.474(9)$	$\beta = 86.965(3)$	$\beta = 93.536(2)$	
	$\gamma = 90$	$\gamma = 90$	$\gamma = 79.763(3)$	$\gamma = 90$	
volume, Å ³	698.3(3)	675.9(8)	388.43(14)	807.28(14)	
Ζ	4	4	2	4	
density (calc), Mg/m ³	1.400	1.446	2.997	2.884	
absorption coeff, mm^{-1}	0.100	0.104	20.737	19.956	
F(000)	304	304	312	624	
crystal size, mm	$0.80 \times 0.10 \times 0.04$	$0.4 \times 0.21 \times 0.12$	$0.16 \times 0.10 \times 0.05$	$0.50\times0.20\times0.15$	
$ heta$ range for data, $^\circ$	3.04-27.50	2.14-29.57	1.81-26.73	2.05-27.10	
index ranges	$-4 \le h \le 4$	$-4 \le h \le 4$	$-4 \le h \le 4$	$-4 \le h \le 4$	
	$0 \le k \le 22$	$-18 \le k \le 0$	$-11 \le k \le 11$	$-15 \le k \le 14$	
	$-14 \le l \le 14$	$0 \le l \le 16$	$-15 \le l \le 15$	$-21 \le l \le 21$	
reflections collected	3129	13268	4453	5537	
independent reflections	1598 [R(int) = 0.2682]	1880 [R(int) = 0.1292]	1650 [R(int) = 0.0242]	1755 [R(int) = 0.0597]	
completeness to θ ,%	99.8	99.5	99.6	99.7	
absorption correction	empirical	semiempirical	semiempirical	semiempirical	
T_{max} and T_{min} .	0.996 and 0.9241	0.7461 and 0.5084	0.4488 and 0.1382	0.150 and 0.040	
refinement method		full-matrix LS on F ²			
data/restraints/parameters	1598/0/120	1880/0/101	1650/0/125	1755/0/109	
goodness-of-fit on F^2	0.888	1.038	1.092	1.059	
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0809$	$R_1 = 0.0792$	$R_1 = 0.0262$	$R_1 = 0.0596$	
	$wR_2 = 0.1359$	$wR_2 = 0.1757$	$wR_2 = 0.0600$	$wR_2 = 0.1427$	
R indices (all data)	$R_1 = 0.2902$	$R_1 = 0.1373$	$R_1 = 0.0293$	$R_1 = 0.0828$	
	$wR_2 = 0.2045$	$wR_2 = 0.2067$	$wR_2 = 0.0614$	$wR_2 = 0.1555$	
larg diff. peak∕hole, e·Å ^{−3}	0.234 and -0.221	0.243 and -0.340	2.657 /-1.425	3.493/-3.648	

presented in Table 1, while bond lengths and valence angles are summarized in Table 2. Figures for the crystal structures of these complexes were drawn using Mercury 4.1.2 and ORTEP 32 software³² at a 50% thermal ellipsoids probability level. The PLATON checks of crystallographic data and actual CIF files for reported structures can be found in the Supporting Information.

Solid State Electrical Conductivity Measurements. We attempted to measure conductivity of single crystals of Tl(3PCO) and Tl(4PCO) (Supporting Information, S1) at room temperature using the conventional 2-points method. Thus, thin copper wires were attached to a selected single crystalline specimen positioned on glass slides of 25×25 mm dimensions using Ag-based glue and then dried for 24 h. Two samples of different size crystals of Tl(3PCO) and Tl(4PCO) were used for experiments (Supporting Information, S3). All operations were carried out under the microscope (Meiji) and using a set of microtools (Hampton Research). After the glue was dried during 24 h, the copper wires and contact spots, but not the crystals, were carefully covered with polyurethane to prevent their degradation upon exposure to gaseous Cl₂, or Br₂, I₂ vapors. Samples were dried again for 24 h, and then exposed to halogens in a specially designed glass chamber (Supporting Information, S5). After subjection to halogen during variable times, samples' electrical conductivity was measured at 293 K again, using the Keithley 220 Programmed Current Source and the Keithley 182 Sensitive Digital voltmeter (Supporting Information, S4 and S5).

Synthesis of Ligands and Tl(I) Complexes and Crystal Growth. The 4-pyridylcyanoxime, H(4PCO), was obtained according to the published procedure from commercially available from Aldrich 4-pyridylacetonitrile-hydrochloride, NC-CH₂-C₅H₄N·HCl, and HNO₂ (Supporting Information, S6). However, its isomeric 3-pyridylcyanoxime, H(3PCO), was obtained at basic conditions using gaseous methylnitrite according to our recently patented³³ method (Supporting Information, S7). Thus, a sodium isopropoxide solution was prepared using 0.20 g of thinly sliced pieces of metallic sodium and 70 mL of 2-propanol under flow of nitrogen. A solution of 0.5 mL (5 mmol) of 3-pyridyl acetonitrile (NC-CH2-C5H4N) in 5 mL of isopropanol was added to sodium propoxide solution above was stirred under nitrogen for 20 min. A flow of gaseous methyl nitrite, CH₃ONO, was from a cold (~0 °C) mixture of 30% H₂SO₄ and a solution of NaNO₂ (20 g) dissolved in 70 mL of a 1:1 mixture of CH₃OH/H₂O. The color of the reaction mixture immediately changed to yellow, and after 5 min of methylnitrite bubbling through the reaction mixture it was kept at +4 °C overnight with the following solvent removal using the rotary evaporator. A thick bright-yellow yellow solid residue of Na(3PCO) was dissolved in 30 mL of DI water and acidified with 1 M HCl to pH = 5 and then saturated with solid NaCl. An off-white flaky solid H(3PCO) was filtered off, washed with water, and dried in vacuum desiccator over H_2SO_4 (conc). Yield 80%; compound decomposes at 235–237 $^\circ\text{C}.$ The H(3PCO) is soluble in propanol, DMSO, and acetone, slightly soluble in toluene, THF, acetonitrile, and chloroform, and practically insoluble in water,

Table 2. Selected Geometrical Data for Studied Ligands and Their Tl(I) Compounds

bond length, Å	valence angle, deg		
	H(3PCO)		
C(1)-N(1) = 1.302(6)	N(1)-C(1)-C(2) = 121.0(5)		
C(1)-C(2) = 1.433(8)	N(1)-C(1)-C(3) = 119.5(5)		
C(1)-C(3) = 1.457(7)	C(2)-C(1)-C(3) = 119.5(5)		
C(2)-N(2) = 1.152(6)	N(2) - C(2) - C(1) = 176.6(6)		
C(3)-C(4) = 1.362(7)	N(3)-C(4)-C(3) = 123.9(6)		
C(4)-N(3) = 1.359(6)	N(3)-C(5)-C(6) = 122.7(6)		
C(5)-N(3) = 1.333(7)	C(1)-N(1)-O(1) = 113.5(4)		
N(1)-O(1) = 1.382(5)	N(1)-O(1)-H(1O) = 99(3)		
O(1)-H(1O) = 1.17(7)			
	H(4PCO)		
C(1)-N(1) = 1.287(4)	N(1)-C(1)-C(2) = 121.0(3)		
C(1)-C(2) = 1.430(5)	N(1)-C(1)-C(3) = 118.6(3)		
C(1)-C(3) = 1.455(5)	C(2)-C(1)-C(3) = 120.3(3)		
C(2)-N(2) = 1.133(4)	N(2)-C(2)-C(1) = 178.6(5)		
C(3) - C(4) = 1.385(5)	N(3)-C(5)-C(4) = 122.8(4)		
C(5)-N(3) = 1.335(4)	N(3)-C(6)-C(7) = 123.8(4)		
C(6) - N(3) = 1.324(5)	C(1)-N(1)-O(1) = 112.0(3)		
N(1)-O(1) = 1.362(3)	N(1)-O(1)-H(1O) = 100(2)		
O(1)-H(1O) = 1.00(4)			
	$Tl(3PCO)^a$		
Anion:	Anion:		
C(1)-N(1) = 1.320(9)	N(1)-C(1)-C(2) = 121.0(6)		
C(1)-C(2) = 1.440(10)	N(1)-C(1)-C(3) = 120.1(6)		
C(1)-C(3) = 1.468(10)	C(2)-C(1)-C(3) = 118.9(6)		
C(2)-N(2) = 1.143(10)	N(2)-C(2)-C(1) = 179.8(9)		
C(3)-C(4) = 1.380(10)	N(3)-C(6)-C(5) = 124.2(7)		
C(6)-N(3) = 1.332(10)	N(3)-C(7)-C(3) = 123.2(7)		
C(7)-N(3) = 1.324(10)	O(1)-N(1)-C(1) = 114.6(7)		
N(1)-O(1) = 1.316(8)	C(7)-N(3)-C(6) = 117.6(6)		
Metal center:	Metal center:		
O(1)-Tl(1)#1 = 2.580(6)	N(1)-O(1)-Tl(1)#1 = 118.5(4)		
O(1)-Tl(1) = 2.742(5)	N(1)-O(1)-Tl(1) = 122.6(4)		
Tl(1) - O(1)#1 = 2.580(6)	Tl(1)#1-O(1)-Tl(1) = 118.4(2)		
Tl(1)-Tl(1)#2 = 3.7050(8)	O(1)#1-Tl(1)-O(1) = 61.6(2)		
Tl(1) - Tl(1)#3 = 3.7364(8)	Tl(1)#2-Tl(1)-Tl(1)#3 = 75.801(9)		
Tl(1) - Tl(1)#4 = 3.7364(8)	Tl(1)#2-Tl(1)-Tl(1)#4 = 104.199(9)		
	Tl(1)#3-Tl(1)-Tl(1)#4 = 180.00(3)		
	$T[(4PCO)^b]$		
Anion	Anion		

Anion:	Anion:
C(1)-N(1) = 1.291(18)	N(1)-C(1)-C(2) = 118.3(13)
C(1)-C(2) = 1.46(2)	N(1)-C(1)-C(3) = 123.2(14)
C(1)-C(3) = 1.45(2)	C(2)-C(1)-C(3) = 118.5(12)
C(2)-N(2) = 1.12(2)	N(2)-C(2)-C(1) = 178(2)
C(3)-C(4) = 1.400(19)	N(3)-C(6)-C(7) = 124.0(14)
C(5)-N(3) = 1.37(2)	N(3)-C(5)-C(4) = 121.4(14)
C(6)-N(3) = 1.43(2)	O(1)-N(1)-C(1) = 118.6(14)
N(1)-O(1) = 1.322(17)	C(5)-N(3)-C(6) = 117.6(13)
Metal center:	Metal center:
O(1)-Tl(1)#1 = 2.552(12)	N(1)-O(1)-Tl(1)#1 = 113.7(9)
Tl(1) - O(1)#2 = 2.552(13)	O(1)#2-Tl(1)-N(3) = 83.4(4)
Tl(1)-Tl(1)#3 = 3.6346(11)	O(1)#2-Tl(1)-Tl(1)#3 = 77.6(3)
	N(3)-Tl(1)-Tl(1)#3 = 161.0(3)

^aSymmetry operations to generate equivalent atoms: #1 - x + 1, -y, -z + 1; #2 - x, -y, -z + 1. #3 x - 1, y, z; #4 x + 1, y, z. ^bSymmetry transformations used to generate equivalent atoms: #1 x - 1/2, -y + 1/2, z + 1/2; #2 - x, -y, -z + 2; #3 x + 1/2, -y + 1/2, -z - 1/2.

benzene, carbon tetrachloride, and toluene. Data of the IR spectra (KBr) for isomeric pyridylcyanoximes are summarized in Table 4 and Supporting Information, S8 and S9. The ¹H and ¹³C NMR spectra of the H(3PCO) indicate a mixture of *syn* (32%) and *anti* (68%) geometrical isomers in acetone- d_6 solution appearing as a double set of signals.

Synthesis of Thallium(I) Isomeric Pyridylcyanoximates. A large Dewar flask was filled with 4.5 L of hot water (95°) and kept at this temperature using an immersed resistance heater connected to a thermoregulator. A long, side arm Pyrex filter tube, equipped with a stopper and medium porosity glass filter, was held inside the Dewar flask with hot water. The 0.100 g (0.68 mmol) of solid H(3PCO) or H(4PCO) were added at once into a boiling solution of 0.16 g (0.34

$$2 \text{ HL} + \text{Tl}_2\text{CO}_3 \xrightarrow[95^\circ\text{C}]{H_2\text{O}} 2 \text{ TIL} + \text{H}_2\text{CO}_3 \xrightarrow[H_2\text{O}]{H_2\text{O}} (1)$$

mmol) of Tl₂CO₃ (eq 1). The color of the reaction mixture changed immediately from colorless to bright yellow and immediately after carbon dioxide ceased this slightly turbid solution was hot filtered into the long side arm tube submerged in the Dewar containing 4.5 L of boiling water. The tube was closed with a rubber septum and left inside the Dewar for slow crystallization for several days.³⁴ Fine needles of Tl(3PCO) and Tl(4PCO) suitable for X-ray analysis appeared in the tube (Supporting Information, S1). The Tl(3PCO), as yellow crystalline material, was obtained in combined 95% yield. Compound decomposes above 228 °C. For Tl(3PCO), C7H4N3OTl, calculated (found): C - 23.99 (23.89), H - 1.15 (1.06), N - 11.99 (11.90). The Tl(4PCO), as large orange crystals, isolated at ~90% combined yield. Complex decomposes at 258 °C. For Tl(4PCO), $C_7H_4N_2OTI$, calculated (found): C = 23.99 (23.94), H = 1.15 (1.04), N - 11.99 (11.94). The IR spectra of both TlL are summarized in Table 3.

Both TlL are sparingly soluble in water, insoluble in alcohols, acetone, but very soluble in DMF, DMSO, and pyridine with apparent loss of solid state structures.

Safety note: Although we have not encountered any problems during many years of laboratory work and handling, special care should be taken during work with thallium compounds because of their high toxicity.^{35–37} 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. However, no respiratory tract covers are required since Tl(I) compounds are ionic and not volatile.

RESULTS AND DISCUSSION

Organic Ligands. *NMR Spectra.* According to the ¹³C{¹H} spectrum, H(3PCO) exists in acetone- d_6 as a mixture of two isomers (*syn*- and *anti*-) in solution, since two sets of seven signals were observed (Supporting Information, S10). The ¹H NMR spectrum also revealed two sets of four aromatic proton signals, but only one signal that corresponds to the proton of the oxime group, which is highly deshielded and located at ~13.4 ppm (Supporting Information, S10). COSY and HMQC (Supporting Information, S11) experiments were recorded in order to provide unambiguous assignments of signals of isomers. The ratio between the two geometrical isomers according to ¹H NMR integration was 32:68 = syn/anti. On the basis of published data for other cyanoximes,³⁸ it was assumed that the most abundant isomer is *anti* both in solid state and solutions.

According to the ¹³C{¹H} NMR spectra, the H(4PCO) compound in acetone- d_6 has only one set of five signals indicating that the only one geometrical isomer is present in solution. Since the crystal structure of this compound shows its

Table 3. Tl(I) Coordination Polymers with Closest Intermetallic Separations

Building block Geometry (A), symmetry, and structural features		Rets.	Bui
symmetric core structure with TITI mirror plane 2.443 2.656 T dihedral angle 111.32° oxygen atom from pentafluorophenol	3.594	[49]	Tl ₂ t non
centrosymmetric dimers with side-on NO coordination $N \xrightarrow{2.899}_{2.898} \xrightarrow{2.552}_{0} \xrightarrow{0}_{0}$ adder-type structure; N-atoms also involved into lattice buildup	3.635	this work	Two rho diff
dihedral angle between TIO ₂ and TIN ₂ planes is 110.91° O 2.998 2.793 O N 2.752 N	3.652	[56]	TI4
symmetric core structure with TITI mirror plane 2.577 2.658 TI dihedral angle 111.98°	3.669	[57]	Two rho diff
	Geometry (A), symmetry, and structural features symmetric core structure with TITI mirror plane $2.443 \qquad 12.656 \qquad 12.657 \qquad 12.656 \qquad 12$	Geometry (A), symmetry, and structural features distance, Å symmetric core structure distance, Å 3.594 3.594 3.594 3.594 3.594 3.635 3.635 3.635 3.635 1.652 1.6	Geometry (A), symmetry, and structural featuresShortest 1111 distance, ÅKets. distance, Åsymmetric core structure with T1T1 mirror plane 3.594 [49] 2.443 2.656 dihedral angle 111.32° oxygen atom from pentafluorophenol 3.635 this workcentrosymmetric dimers with side-on NO coordination 3.635 this work N 2.899 N 2.652 2.652 N 3.635 this workadder-type structure; N-atoms also involved into lattice buildup 3.652 [56]dihedral angle between TIO2 and TIN2 planes is 110.91° 3.652 [56] O 2.998 2.030 2.577 2.658 3.669 [57]symmetric core structure with T1T1 mirror plane 3.669 [57]dihedral angle 111.98° 2.659 2.658 3.669 [57]

Table 4. Data of the IR Spectroscopic Studies and X-ray Analysis for Isomeric Pyridylcyanoximes and Their Tl(I) Complexes

	vibrational and geometrical parameters of the C-N-O group				
	bands with participation of the C–N–O fragment (15 N label), cm ⁻¹				
compound	ν (C=N)	ν(N- 0)	δ(C- N-O)	bond length (Å)	C–N– O angle (°)
H(3PCO)	1512 (1505)	1081 (1071)	764 (755)	C-N = 1.302	113.5
				N-O = 1.382	
Tl(3PCO)	1376 (1365)	1291 (1285)	850 (844)	C - N = 1.320	114.6
				N-O = 1.316	
H(4PCO)	1503 (1497)	1086 (<i>1080</i>)	769 (758)	C-N = 1.287	112.0
	1025 (<i>1017</i>)			N-O = 1.362	
Tl(4PCO)	1405 (1399)	1301 (1296)	832 (828)	C-N = 1.291	118.6
				N-O = 1.322	

anti configuration, the same was assumed for its structure in solution. The ¹H NMR spectra also show one set of three multiplets; two of those corresponding to two aromatic proton peaks and the third one corresponding to the proton of an even more deshielded oxime group at 14.4 ppm (Supporting Information, S12).

Acidity Studies. Molecules of isomeric pyridyl-cyanoximes possess both basic and acidic sites (Scheme 1). Values of pK_a



for H(3PCO) are 3.25 ± 0.01 (amine) and 6.72 ± 0.01 (oxime), while for H(4PCO) these are 4.00 ± 0.03 and 6.31 ± 0.02 , respectively (Supporting Information, S13). The presence of the CN group in H(3PCO) and H(4PCO) causes a rather dramatic increase from 4 to 6 orders of magnitude in acidity of studied ligands, as opposed to traditional monoximes and dioximes. Moreover, an electron-withdrawing effect of the cyanoxime fragment in general significantly lowers the basicity of the pyridine group and brings it almost to the level of chloropyridines (Supporting Information, S13), which are known to be poor ligands. Nevertheless, H(3PCO) and H(4PCO) are much better ligands than cyano-pyridines and are able to form a variety of transition metal complexes.³⁹

UV-Visible Spectra of Anionic Cyanoximes. Pure organic isomeric pyridylcyanoximes are colorless substances, as the vast majority of other cyanoximes are, including substituted arylcyanoximes. However, the deprotonation of H(3PCO) and H(4PCO) with a base leads to the formation of colored anions (Figure 1, and Supporting Information, S14). The $\pi \rightarrow \pi^*$ transition in the anion underwent a bathochromic shift and a significant increase in intensity due to the charge delocalization compared to the protonated oxime (Figure 1A; Supporting Information, S14, S16), while the $n \rightarrow \pi^*$ transition in the anion exhibited a pronounced solvatochromic effect (Figure 1B). The wavelength difference between visible spectra of yellow anions in alcohols and pink-red anions in aprotic DMF and DMSO is \sim 70–80 nm, which corresponds to \sim 9 kJ/ mol energy associated with the formation of H-bonds of medium strength in H-bonded solvates in EtOH or PrOH (Supporting Information, S15). Spectra of 3PCO⁻ and 4PCO⁻ anions in aprotic solvents consist of two lines, as opposed to a



Figure 1. Electronic spectra of protonated 3-pyridylcyanoxime H(3PCO) and its anion as Na-salt in *n*-propanol at 10^{-5} M concentrations in 1 mm cell (A), and solvatochromism of 3PCO⁻ anion (as NBu₄⁺ salt) in several solvents at 5 mM concentrations in 1 cm cuvette (B).

single line in H-bonded solvents (Supporting Information, S17 and S18), which is similar to a negative solvatochromism of NC-C(NO)-C(O)NH₂⁻ anion⁴⁰ and substituted heteroaryland aryl-cyanoximes.⁴¹

Crystal Structures of Isomeric Pyridylcyanoxime Ligands. Crystals of both compounds turned out to be weak diffractors and exhibited a tremendous propensity for forming a multidomain specimen upon even a very slow crystallization. Eventually, after many trials suitable, thin single crystals were found and structures of both compounds were reliably determined despite these difficulties and high R(int) values in diffraction experiments. Crystal and refinement data for both compounds are presented in Table 1, while selected bond distances and angles for both structures are shown in Table 2.

3-Pvridvlcvanoxime, H(3PCO). This compound in the solid state adopts a practically planar trans-anti configuration (Figure 2A). We were unable to find crystals of respective syn-isomer among specimen selected for crystallographic studies. Perhaps due to its different solubility than the trans-anti isomes it was not present in the mixture at the time of crystals selection. Bond lengths and angles in the heterocyclic 3-pyridyl ring are normal. The term trans- indicates that the oxime group is on the opposite side of the N3 atom via the C3-C1 bond. The cyano group is linear $\angle N2-C2-C1 = 176.67^{\circ}$, but is slightly off the plane of the molecule with a torsion angle of $\angle N1 O1-C1-C3 = 3.99^\circ$. Bond lengths in the cyano group is N2-C2 = 1.153 Å, and in the oxime group are N1-O1 = 1.382 Å and C1-N1 = 1.302 Å (Table 2). The packing diagram (Supporting Information, S19A) shows the formation of the planar chains formed due to the intermolecular hydrogen bonds between the H1O and N3 atom of the aromatic pyridine ring, where N3 is the donor atom, with angles of \angle N3-H1O-O1 = 169.99° and distances of N3–H1O = 1.497 Å and H1O–O1 = 1.166 Å.

4-Pyridylcyanoxime, H(4PCO). The cyanoxime also adopts planar anti configuration (Figure 2B) evidenced by torsion angles in the molecule less than 1°. Bond lengths and angles in the heterocyclic 4-pyridyl ring are normal. Bond distances for the cyano group and the oxime group are N2-C2 = 1.133 Å, O1-N1 = 1.362 Å, C1-N1 = 1.287 Å, respectively. Values of the angles O1-N1-C1 and N2-C2-C1 are 111.95° and 178.60° (Table 2), being normal for cyanoximes.⁴² The packing diagram for H(4PCO) indicates the formation of a layered structure with slipped $\pi - \pi$ interactions with a separation of 4pyridyl π systems distances close to 3.4 Å (Supporting Information, S19B). Also, there are hydrogen bonds between the oxime group and the nitrogen atoms of the heterocyclic ring which connect individual molecules into chains running parallel to the "c" direction. H-bond parameters: ∠N3-H1O- $O1 = 173.99^{\circ}$ and distances of N3(donor)-H1O = 1.600 Å and H1O-O1 = 1.004 Å.

Metal Complexes. Properties in Solution. Solutions conductivity of synthesized isomeric Tl-cyanoximates was



Figure 2. Molecular structures and numbering schemes for H(3PCO) (A) and H(4PCO) (B) showing top and side views. An ORTEP drawing at 50% thermal ellipsoids probability level.

Crystal Growth & Design

measured against some common soluble K^+ salts due to similarities of some of chemical properties of monovalent thallium and potassium. Values of solutions' conductivity indicate the formation of 1:1 electrolytes upon compounds' dissolution. The UV–visible spectra of Tl(3PCO) and Tl(4PCO) in solutions are identical to those of alkali metal salts and, therefore, indicate the loss of solid state polymeric structures.

Crystal Structures of Isomeric Tl(I)-pyridylcyanoximates. Prior to description of crystal structures of the obtained TlL, it is important to mention some reference distances⁴³ between the metal ion and N, O donor atoms of the ligands: the sum of ionic radii for Tl–O = 2.85 Å and Tl–N = 2.96 Å. Also, Tl(I) has 6s² *inert electron pair* that despite its supposedly spherical nature shows pronounced spatial directionality.⁴⁴ Thus, it can be often visualized in crystal structures in an open cleft nearby Tl(I) centers.²¹ Therefore, in numerous monovalent thallium complexes 6s² electron pair acts as a lone pair and as such it is frequently called a *stereochemically active* pair.^{17a,22} An additional explanation for that phenomenon was recently also summarized by Morsali⁴⁵ as well.

In our previous work with Tl(I) coordination polymers we found the formation of a double-stranded, "ladder-type" coordination-polymers as a dominant motif in crystal structures with cyanoximes. It was first observed in 1993,^{24c} reported at several occasions,⁴⁶ and then recently summarized.²¹ Also, a similar polymeric staircase structure consisting of Tl₂O₂ skewed rhombs in thallium(I) orthonitrophenolate was later reported by Harrowfield.⁴⁷ Other main group heavy metal cations, such as Ge(II), Pb(II), and Bi(III), also were found to form M₂O₂ rhombs in a variety of complexes⁴⁸ extending this peculiar structural motif well beyond Tl(I) compounds. In all cases the metal ion has a stereoactive lone pair.

TI(3PCO). The molecular structure and numbering scheme for Tl(3PCO) is shown in Figure 3. Selected bond lengths and valence angles are presented in Table 2. The 3PCO⁻ anion in this complex acts as a complex unsymmetric tetradentate bridge between four thallium atoms: three are connected to one oxygen atom of the CNO group, and one Tl is bound to the N3 atom of the heterocycle (Figure 3A). The unit cell content in the structure of Tl(3PCO) is shown in Supporting Information, S20. Organization of Tl(3PCO) crystal structure can be best described as 1D columns connected with each other by means of weak extra coordination to the Tl centers N-atoms of the pyridine group and van der Waals forces as well (Figure 4). In turn, these columns are formed by centrosymmetric [Tl-(3PCO)]₂ dimers stacked into double-stranded, ladder-type Tl₂O₂ sheets (Figure 5A). Two adjacent and slightly different $[Tl_2O_2]$ rhombs (labeled as 1 and 2) are bent with an 87.0° angle between them and represent a building block of such an interesting ladder-type 1D polymeric motif, and rhombs geometry is shown in Figure 5B. There are three intermetallic distances in that building block: $Tl1...Tl1_2$ (in 2) = 4.571 Å, Tl1...Tl1 = 3.736, $Tl1...Tl1_2$ (in 1) = 3.705 Å with the latter two being very short. Thus, a planar "metal ribbon" is formed as seen in the space filling representation showing partial overlap between Tl atoms (Supporting Information, S21A). There are also three short covalent bonds (less than the sum of van der Waals and even ionic radii) between the oxygen atom of the ligand Tl1–O1 2= 2.580 Å, and the oxygen atom of the oxime group of the neighboring pyridylcyanoxime group Tl1-O1 =2.742 Å, and finally another, longer contact Tl1 2-O1 = 2.839Å. (Figures 3 and 5). The nitrogen atom of the neighboring



Figure 3. Numbering scheme for $3PCO^{-}$ anion and its closest cationic surrounding (A), and one Tl(I) cation and its closest cyanoximes environment with respected distances (B) in the crystal structure of Tl(3PCO). The shortest intermetallic separation here is 3.705 Å. Symmetry operations for #1: x, y, z; for #2: -x, -y, -z. H-atoms in B are omitted for clarity.



Figure 4. Organization of crystal structure of Tl(3PCO): perspective view. Shown formation of columns connected with each other by means of van der Waals forces. H-atoms are not shown for clarity.

molecule at a distance Tl1-N3 = 2.916 Å provides an additional, weaker contact that stabilizes the lattice and is responsible for joining individual 1D columns (Figure 4) into a 3D polymer. Thus, the coordination number of Tl(I) in this complex is four and can be best described as distorted trigonal pyramid (Figure 6). The lone $6s^2$ pair of Tl(I) is stereochemically active and occupies the space in an open cleft between N3 and O1 2 atoms (Figure 6). The shortest $Tl\cdots$ H distance is





Figure 5. Three orthogonal projections of the double-stranded (ladder) polymeric motif in 1D columns on the structure of TI(3PCO) (A), and its "building block" – two adjacent different Tl_2O_2 rhombs (B).



Figure 6. Coordination polyhedron of metal ion in the structure of Tl(3PCO): two orthogonal views. The $6s^2$ lone pair of Tl(I) occupies an open cleft behind the O1–O1_2–N3 plane seen on the right picture.

3.493 Å between the metal and 4H-hydrogen atom of the neighboring column of the polymeric complex.

TI(4PCO). Molecular structure and the numbering scheme for Tl(4PCO) are shown in Figure 7, while the unit cell content is presented in Supporting Information, S22. The 4PCO⁻ anion in the complex also acts as an unsymmetric tetradentate bridge between four thallium atoms: two metal ions bound only to the oxygen atom of the CNO-fragment, one metal ion has "sideon" coordination to the N-O group in the CNO-fragment, and one Tl ion is bound to the N3 atom of the heterocycle (Figure 7A). The organization of the crystal structure is shown in Figure 8. The structure of Tl(4PCO) represents a 3D coordination polymer that is best described as pleated sheets which are formed by 1D columns connected into the 3D network by the nitrogen atom of the 4-pyridyl group (Figures 8 and 9). The heterocyclic groups stabilize the lattice due to slipped $\pi - \pi$ stacking, with the shortest distance being ca. 3.61 Å. The cyanoxime ligand is clearly in the *oxime* form as judged



Figure 7. Numbering scheme for $4PCO^{-}$ anion and its closest cationic surrounding (A), and one Tl(I) cation and its closest cyanoximes environment (B) in the crystal structure of Tl(4PCO). The shortest intermetallic separation is 3.635 Å. Symmetry operations #1: x, y, z; #2: -x + 1/2, y + 1/2, -z + 1/2; #4: x + 1/2, -y + 1/2, z + 1/2. H-atoms in B are omitted for clarity.

from the shorter C1-N1 distance than the N1-O1 bond (Table 2). Similar to the previous structure, there are three short covalent (less than the sum of ionic radii) distances between the oxygen atom of the parent anion Tl1 4-O1 =2.552 Å, the nitrogen atom of the neighboring pyridyl group Tl1 1-N3 = 2.813 Å, and the oxygen atom of the oxime group of neighboring molecule Tl1 4-O1 = 2.839 Å (Figure 7). Also, there are two more and slightly longer contacts between the N-O group and Tl center, positioned in a "side-on" fashion with a formation of a three-membered chelate ring: Tl1_2-N1 and Tl 2-O1 distances are 2.899 Å and 2.898 Å, respectively, and $\langle N1-Tl1_2-O1 = 26.4^{\circ}$ (Figures 7 and 10). Thus, the coordination number of Tl(I) is five, and the coordination polyhedron represents a distorted trigonal pyramid capped with a "side-on" coordinated oxime group from a neighboring molecule. A sterochemically active lone pair occupies space in an open cleft opposite O1 2-N1 2-O1 4-N3 plane (Figure 10). The shortest Tl···H distance similar to Tl(3PCO) complex was found to be also 3.493 Å and is between the 3H-atom of the ligand and the neighboring polymeric column.

It should be noted especially that there are two very short Tl…Tl distances in the structure (Supporting Information, S21B). The closest Tl…Tl interlayer contact inside the unit's 1D column is 3.635 Å, while the intralayer separation is 3.899 Å (Figure 7A). Indeed, they are very close to that in the metallic thallium, hexagonal α -phase³⁵ with Tl–Tl = 3.465 Å. In fact, this is the second shortest distance reported in the literature for



Figure 8. Organization of crystal structure of Tl(4PCO): perspective view of the unit cell content along the a-axis.



Figure 9. Two orthogonal views of a double-stranded motif in the column of Tl(4PCO) with more distant 4-pyridine groups (2.813 Å) shown bonded to the metal center as dashed lines (Å), and the "building block" – two adjacent Tl₂O₂ rhombs (B).

intermetallic separations: the first one is 3.594 Å in the case of heterometallic Tl···Au pentafluorophenole based complex.⁴⁹ In that the polymeric compound thallium(I) also forms a nonplanar symmetric Tl₂O₂ rhomb as a building block. Results of the CCDC database search for several complexes with the shortest intermetallic distances in Tl(I) polymers are summarized in Table 3. Observed structural arrangement of Tl-atoms in both structures represent a planar "metal ribbon" displayed in S21B. These ribbons provide a good incentive for the future attempt of preparation of homometallic mixed valence Tl(I)/Tl(III) complexes for studies of their electrical conductivity, or for the preparation of heterometallic Tl····M (M = Au, Pt, Ag) compounds that may exhibit photoluminescence or vaporochromism. Found short intermetallic separations in Tl(I)-cyanoximates are due to the "metallophilic" interactions that lately were increasingly often found in coinage metal and platinum complexes.¹⁷ The latter are known for their 1D electrical conductivity.^{8–13,55}

IR Spectra of ¹⁵N Labeled Ligands and Their TI(I) Complexes. Since crystal structures of thallium complexes were determined, it was interesting to find how binding modes of cyanoximes in these coordination polymeric complexes are reflected in their IR spectra. For that purpose we synthesized both ligands and their TI(I) cyanoximates labeled with ~50% ¹⁵N on the oxime group. This degree of enrichment allows observation of the split bands with participation of the C–N– O fragment in the IR spectra of complexes as opposed to the



Figure 10. Coordination polyhedron of metal ion in the structure of Tl(4PCO): two orthogonal views. The stereochemically active $6s^2$ lone pair of Tl(1) occupies an open cleft behind the N3–O1 2–N1 2 plane seen on the left picture.

Scheme 2



shift only that is often difficult to measure reliably. This approach proved to be fruitful in our earlier studies of $Ag(I)^{50}$ and other metallocyanoximates.⁴¹ Vibrational bands associated with the C-N-O fragment, together with its geometrical features, are summarized in Table 4, while actual spectra are shown in Supporting Information, S8 and S9. Uncomplexed starting cyanoximes H(3PCO) and H(4PCO) demonstrate a low intensity $\nu(C=N)$ band at ~1500 cm⁻¹ and an intense band of $\nu(N-O)$ at ~1090 cm⁻¹, sometimes split into two and assigned as ${}^{as}\nu(N-O)$ and ${}^{s}\nu(N-O)$.⁵¹ The high intensity of the latter is due to the considerable dipole moment change $d\mu/d\mu$ dx during vibrations in this polar group. The deprotonation of cyanoximes leads to the significant redistribution of the electron density in the C-N-O fragment, leading to its "leveling" (Scheme 2). This is also reflected in changes in bond lengths in the group from HL to L⁻ where the C-N bond lengthened with a concomitant decrease of the N-O bond.

Rather reasonable correlations between geometrical features of HL, TlL, and IR spectra were established (Supporting Information, S23). It is notable that coordination of both anions to Tl(I) centers significantly increased the rigidity of the C-N-O fragment that is reflected in the high energy shift of its δ (C–N–O) bending vibration (Table 4). Thus, the angle at the nitrogen atom in TlL is approaching 120° suggested for its sp² hybridization state in anionic cyanoximes and direct involvement in the aforementioned redistribution of electron density in conjugated planar anions (Table 4; Supporting Information, S23). It is important to note that observed frequencies in the IR spectra of TlL are different from those in spectra of silver(I) cyanoximates,^{50,51} which is in a good agreement with (a) different binding modes of the ligands in both coordination-polymeric complexes, (b) different electronic structure of anions in TlL (in the oxime form) compared to AgL (in the nitroso form).

Preliminary Data for Solid State Single Crystal Electrical Conductivity Studies. Solid crystalline samples of yellow Tl(3PCO) and orange Tl(4PCO) complexes are insulators at room temperature, and their resistivity is in the range of $(1-2) \times 10^{11}$ Ohm. We were interested to know whether very close intermetallic separations in "metallic ribbons" in structures of Tl(3PCO) and Tl(4PCO) could be an important factor in the electrical conductivity of these

complexes after Tl(I) centers could be partially oxidized to Tl(III). We attempted a heterogeneous oxidation of our samples with gaseous of halogens. These are the most common oxidizers used for such reactions, for example, in well studied partial oxidation of kappa-phases of tetrathio- and tetraselenofulvalenes. Thus, we investigated the effect of Cl₂, and I₂ and Br₂ vapors on electrical conductivity of monocrystalline samples of isomeric Tl(3PCO) and Tl(4PCO) complexes (Supporting Information, S3–S5). After treatment with Br₂ and I₂ vapors at saturating conditions at room temperature within many hours a small decrease in Tl(4PCO) samples' resistivity to $1.6 \pm 0.2 \times$ 10^{10} and 2.2 \pm 0.3 \times 10^{10} Ohm, respectively, was detected. Also, these samples clearly demonstrated an ohmic behavior as evidenced from expected voltage changes upon variations in ×10 or ×100 times in the current load. The above values appeared to be low, but it should be kept in mind that the sample sizes of single crystals of the studied complexes were very small: only ~0.2-0.4 mm across. A small increase in the conductivity of Tl(4PCO) we attribute to possible reaction between bromine or iodine and the cyanoxime anions. This may lead to the formation of either halogenated compounds, or intercalated with halogens systems with perhaps a narrower band gap, where some charge motion across $\pi - \pi$ stacked halogenated pyridyl-groups could be probable. It is known that bromine and iodine atoms can form very close interhalogen contacts in some organic crystals,⁵² and even in Tl-complexes^{24a,53} or form polyatomic anions which might be the cause of their better electrical conductivity. Studied samples did become slightly darker after prolonged exposure to Cl₂ (S5), but not sufficient for consideration of the formation of mixed valence Tl^{1+/3+} complexes that should exhibit low energy CT-band and gain an intense color.⁵⁴ Thus, it appears that the effect of dry halogens on the conductivity of Tl-cyanoximates seems to be unrelated to metal centers. Since the size of crystalline samples used for electrical conductivity studies was very small (in the range 2-4 mg; Supporting Information, S3 and S4) it proved to be rather difficult to detach them after exposure to halogens from the glass slide and electrodes. Therefore, no attempts to investigate possible halogenation of the cyanoxime anion in Tl(3PCO) and Tl(4PCO) were made at this point.

Our first experiments with dry halogens showed their inability to oxidize Tl(I) at the studied ambient experimental

Crystal Growth & Design

conditions perhaps due to (a) kinetic reasons such as a limited access of oxidizer to TI(I) centers because of the tight binding of protective organic ligands in formed coordination polymers (Supporting Information, S24, S25); (b) absence of traces of moisture that frequently provides conditions for transport of electrons. Although heterogeneous reaction of solid samples of our Tl-cyanoximates with dry halogens were unsuccessful, we plan different routes to originate mixed valence species: (1) use the electrochemical oxidation of thallium(I) in solutions, and (2) prepare these complexes from the mixture of respective monovalent TlL and trivalent TlL₃ compounds.

CONCLUSIONS

Two isomeric pyridylcyanoxime ligands with heterocyclic nitrogen atoms at 3- and 4- positons were synthesized using developed high yield procedures, and then characterized using UV–visible and ¹H, ¹³C NMR spectroscopic methods and X-ray analysis.

Crystal structures of both isometic pyridylcyanoximes showed their planar geometry and *anti*-configuration of the oxime group contrary to some *syn*-arylcyanoximes studied in the past.

Monovalent thallium complexes Tl(3PCO) and Tl(4PCO) were obtained in high yield and characterized by solutions electrical conductivity, UV–visible and IR-spectroscopy, and X-ray analysis. These compounds are coordination polymers in which cyanoxime anions act as bridging ligands using the oxygen atom of the C-NO group and nitrogen atom of the heterocycle. Both complexes form a double-stranded, "ladder-type" motif. We found very short intermetallic distances in these complexes Tl···Tl = 3.705 Å and 3.635 Å in Tl(3PCO) and Tl(4PCO), respectively, which is close to 3.465 Å in metallic thallium. The intermetallic separation in the latter is the second shortest found in the literature. Thus, metal cations form planar metal ribbons which can be considered as suitable precursors for mixed metal (Tl···Au, Tl···Pt, or Tl···Ag) or mixed valence Tl¹⁺/Tl³⁺ complexes.

We plan in the nearest future: (a) to generate of mixed valence polymeric compounds in polar aprotic solvents using electrochemical methods; (b) to prepare separately TlL and TlL₃ complexes with isomeric pyridylcyanoximes and then cocrystallize them. Solid state electrical conductivity studies of such systems will follow. Also, we plan to synthesize *heterometallic* coordination polymers using TlL and [Au-(CN)₃]⁻, PtR₂(CN)₂ which may exhibit metallophilic interactions and possibly show photoluminescence.

ASSOCIATED CONTENT

S Supporting Information

Actual photographs of crystal samples of Tl-cyanoximates (S1); face indexing of single crystals of synthesized compounds (S2); hardware setup for solid state electrical conductivity measurements crystal samples and hardware for conductivity measurements (S3–S5); synthesis of H(4PCO) (S6); experimental setup for the nitrosation reaction using gaseous methylnitrite (S7); FTIR spectra of ¹⁵N labeled and unlabeled H(3PCO) (S8); FTIR spectra of labeled and nonlabeled with ¹⁵N H(4PCO) and Tl(4PCO) (S9); 1D and 2D NMR spectra of H(3PCO) and H(4PCO) (S10–S12); pK values for studied ligands and related compounds (S13); UV–visible spectra of anionic 4PCO⁻ in different solvents (S14); tabulated electronic spectra of isomeric anionic cyanoximes in different solvents (S15); resonance forms and charge delocalization in isomeric pyridyl-cyanoxime anions (S16); full line shape analysis for both anions (S17 and 18); crystal packing diagrams for both ligands (S19); unit cell content in the structure of Tl(3PCO) (S20); "metal ribbons" in Tl(3PCO) and Tl(4PCO) coordination polymers shown in space filling representation (S21); unit cell content in the structure of Tl(4PCO) (S22); correlations between bond length and valence angles in studied compounds and their IR spectra (S23); space-filling views of lattices of Tl(3PCO) (S24); and Tl(4PCO) showing shielding of metal centers by cyanoxime ligands (S25). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: (417) 836-5165; e-mail: NNGerasimchuk@ MissouriState.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Help from Dr. Kartik Ghosh and Dr. Ram Gupta (Department of Physics, Materials Science and Astronomy of MSU) with electrophysical measurements is greatly appreciated. N.G. is very grateful to Ms. Alex Corbett for technical help during the manuscript preparation, and to Dr. Charles L. Barnes for the initial structure determination of Tl(4PCO).

REFERENCES

(1) Suh, M. P.; Cheon, Y. E.; Lee, E. Y. Coord. Chem. Rev. 2008, 252, 1007–1026.

(2) Yaghi, O. M.; Okeeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.

(3) Ockwig, N. W.; Delgado-Friedrichs, O.; Okeeffe, M.; Yaghi, O. M. Acc. Chem. Res. 2005, 38, 176.

(4) Cheetham, C. N.; Rao, C. N. R.; Feller, R. K. Chem. Commun. 2006, 46, 4780–4795.

(5) Dutta, S. K.; Perkovic, M. W. Inorg. Chem. 2002, 41, 6938.

(6) Strasser, A. A.; Vogler, A. J. Photo-chem. Photobiol. 2004, A, 165, 115.

(7) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. J. Am. Chem. Soc. **2009**, 131, 6050.

(8) (a) Miller, J. S. Ann. N. Y. Acad. Sci. 1978, 313, 25-60.
(b) Krogman, K. Angew. Chem., Int. Ed. 1969, 8, 35-42. (c) Williams, J. M.; Schultz, A. J.; Underhill, A. E.; Carneiro, K. Extended Linear Chain Compounds; Miller, J. S., Ed.; Springer: New York, 1982; Vol. 1, pp 73-118; (d) O'Neill, J. H.; Underhill, A. E. Solid State Commun. 1979, 29, 557-560. (e) Marks, T. J.; Kalina, D. W. Extended Linear Chain Compounds; Miller, J. S., Ed.; Springer: New York, 1982; Vol. 1, pp 197-331; (f) Underhill, A. E.; Watkins, D. M.; Williams, J. M.; Carneiro, K. Extended Linear Chain Compounds; Miller, J. S., Ed.; Springer: New York, 1982; Vol. 1, pp 1197-331; (f) Underhill, A. E.; Watkins, D. M.; Williams, J. M.; Carneiro, K. Extended Linear Chain Compounds; Miller, J. S., Ed.; Springer: New York, 1982; Vol. 1, pp 119-156; (g) Stevens, G. C. Platinum Met. Rev. 1979, 23 (1), 23-28.

(9) (a) Kimura, N.; Ishimaru, S.; Ikeda, R.; Yamashita, M. J. Chem. Soc. Faraday Trans. **1998**, 94, 3659–3663. (b) Gel'fman, M. I.; Salischeva, O. V.; Pugachev, V. M. Russ. J. Inorg. Chem. **2001**, 46 (1), 98–100. (c) Fedotova, T. N.; Minacheva, L. Kh.; Kuznetsova, G. N. Russ. J. Inorg. Chem. **2003**, 48 (8), 1282–1287. (d) Scott, B.; Bracewell, B. L.; Johnson, S. R.; Swanson, B. I. Chem. Mater. **1996**, 8 (2), 321– 323.

(10) (a) O'Neil, J. H.; Underhill, A. E.; Toombs, G. A. Solid State Commun. 1979, 19, 13–18. (b) Nagasawa, H. J. Phys. Soc. Jpn. 1978, 45 (2), 701–702. (c) Kobayashi, H.; Kobayashi, A. Mol. Cryst. Liq. Cryst. 1982, 81 (1–4), 197–204. (d) Nagasawa, H. Phys. Status Solidi, B: Basic Res. 1982, 109 (2), 749–759. (e) Nagasawa, H. Kotai Butsuri 1981, 16 (7), 397–401. (f) Kobayashi, H.; Kobayashi, A.; Asaumi, K.; Minomura, S. Solid State Commun. 1980, 35 (3), 293–296. (11) (a) Megnamisi-Belombe, M. J. Solid State Chem. **1979**, 27 (3), 389–396. (b) Brill, J. W.; Megnamisi-Belombe, M.; Novotny, M. J. Chem. Phys. **1978**, 68 (2), 585–592.

(12) (a) Takeda, K.; Shirotani, I.; Yakushi, K. *Chem. Mater.* **2000**, *12* (4), 912–916. (b) Yamamoto, K.; Kamata, T.; Yoshida, Y.; Yase, K.; Fukaya, T.; Mizukami, F.; Ohta, T. *Chem. Mater.* **1998**, *10* (5), 1343–1349. (c) Kamata, T.; Kodzasa, T.; Ushijima, H.; Yamamoto, K.; Ohta, T.; Roth, S. *Chem. Mater.* **2000**, *12* (4), 940–945.

(13) (a) Underhill, A. E.; Watkins, D. M. Solid State Commun. 1980, 36, 477–480. (b) Endres, H. Acta Crystallogr., Sect. C 1985, 41, 1047.
(c) Brianso, J. L.; de Matheus, M. Afinidad. 1982, 39, 271. (d) Endres, H.; Liebich-Brudy, G. Z. Naturforsch., B. Chem. Sci. 1986, 41, 137.
(e) Ferraris, G.; Viterbo, D. Acta Crystallogr., Sect. B. 1969, 25, 2066.
(f) Kanakubo, M.; Yamamoto, K.; Honda, K.; Ushijima, H.; Kamata, T.; Mizukami, F.; Ohta, T. Anal. Sci. 1999, 15, 107.

(14) (a) Bardeen, J.; Cooper, L. N.; Schriefer, J. R. *Phys. Rev.* 1957, 108, 1175. (b) Ma, G.; Kritikos, M.; Maliarik, M.; Glaser, J. *Inorg. Chem.* 2004, 43 (14), 4328–4340. (c) Fernandez, E. J.; Jones, P. G.; Laguna, A.; Lopez-de-Luziriaga, J. M.; Monde, M.; Perez, J.; Olmos, E. M. *Inorg. Chem.* 2002, 41 (5), 1056–1063. (d) Fernandez, E. J.; Lopez-de-Luziriaga, J. M.; Monge, M.; Montiel, M.; Olmos, E.; Perez, J.; Lagina, A.; Mendiazabal, A.; Mohamed, A.; Fackler, J. P. *Inorg. Chem.* 2004, 43 (12), 3573–3581.

(15) (a) Khoshtariya, D. E.; Dolidze, T. D.; Zusman, L. D.; Lindberg, G.; Glaser, D. Inorg. Chem. 2002, 41 (7), 1728–1738. (b) Zusman, L. D.; Beratan, D. N. J. Phys. Chem. 1997, 101 (22), 4136–4141.
(c) Fernandez-Valverde, S. M.; Gilles, D. J. Chem. Soc. Faraday Trans. 1986, 82 (9), 2825–2831. (d) Bourgault, D.; Martin, C.; Michel, C.; Hervieu, M.; Raveau, B. Physica C: Superconductivity 1989, 158 (3), 511–518. (e) Tsirlina, G. A.; Petrii, O. A. J. Electroanal. Chem. 1996, 401 (1–2), 33–43. (f) Karppinen, M; Yamauchi, H. J. Supercond. 1998, 11 (1), 39–42.

(16) (a) Pyykko, P.; Desclaux, J. P. Acc. Chem. Res. 1979, 12, 276.
(b) Schmidbaur, H. Gold Bull. 2000, 33 (1), 3-10. (c) Kim, M.; Taylor, T. J.; Gabbai, F. P. J. Am. Chem. Soc. 2008, 130, 6332-6333.
(d) Filatov, A. S.; Hietsoi, O.; Sevrygina, Y.; Gerasimchuk, N. N.; Petrukhina, M. A. Inorg. Chem. 2010, 49 (4), 1626-1633. (e) Lin, T. P.; Wade, C. R.; Perez, L. M.; Gabbai, F. P. Angew. Chem., Int. Ed. 2010, 49, 6357-6360.

(17) Tl···Pt: (a) Chen, W.; Liu, F.; Matsumoto, K.; Kishi, S.; Kato, M. *Inorg. Chem.* **2006**, *45* (14), 5552–5560. (b) Fornies, J.; Garsia, A.; Lalinde, E.; Moreno, T. *Inorg. Chem.* **2008**, *47* (9), 3651–3660. (c) Falvello, L. R.; Fornies, J; Garde, R.; Garsia, A.; Lalinde, E.; Moreno, M. T.; Steiner, A; Tomas, M.; Uson, I. *Inorg. Chem.* **2006**, *45* (6), 2543–2552. (d) Fornies, J.; Fuertes, S.; Martin, A.; Sicilia, V.; Gil, B.; Lalinde, E. *Dalton Trans.* **2009**, 2224–2234. Diez, A.; Fornies, J.; Gomez, J.; Lalinde, E.; Martin, A.; Moreno, T. M.; Sanchez, S. *Dalton Trans.* **2007**, 3653–3660.

(18) Tl…Au: (a) Wang, S.; Fackler, J. P.; King, C.; Wang, J. C. J. Am. Chem. Soc. **1988**, 110 (10), 3308–3310. (b) Fernandez, E. J.; Lopez-de-Luzuriaga, J. M.; Monde, M.; Olmos, E. M.; Perez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P. J. Am. Chem. Soc. **2003**, 125 (8), 2022–2023. (c) Fernandez, E. J.; Laguna, A.; Lopez-de-Luziriaga, J. M.; Montiel, M.; Olmos, E. M.; Perez, J. Organometallics **2005**, 24 (7), 1631–1637. Fernandez, E. J.; Laguna, A.; Lopez-de-Luziriaga, J. M.; Monde, M.; Montiel, M.; Olmos, E. M. Inorg. Chem. **2007**, 46 (8), 2953–2955. (d) Arka, M.; Aroz, T.; Gimeno, C. M.; Kulsar, M.; Laguna, A.; Lasanta, T.; Lippolis, V.; Lopez-de-Luziriaga, J. M.; Monde, M.; Olmos, E. M. Eur. J. Inorg. Chem. **2011**, 2288–2297.

(19) Tl…Ag/Cu: (a) Burini, A.; Bravi, R.; Fackler, J. P.; Galassi, R.; Grant, T. A.; Omary, M. A.; Pietroni, B. R.; Staples, R. J. *Inorg. Chem.* 2000, 39 (15), 3158–3165. (b) Holzner, C.; König, K.-H.; Goesmann, H. *Monatsh. Chem.* 1994, 125, 1339–1352.

(20) Doerrer, L. H. Comm. Inorg. Chem. 2008, 29, 93-127.

(21) Gerasimchuk, N. Polymers 2011, 3, 2-37.

(22) Cotton, A. F.; Wilkinson, G.; Murillo, C. A.; Bohman, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons, New York, 1999.

(23) Akhbari, K.; Morsali, A. *Coord. Chem. Rev.* **2010**, *17–18*, 1977–2006.

(24) (a) Robertson, D.; Cannon, J.; Gerasimshuk, N. Inorg. Chem.
2005, 44 (23), 8326-8342. (b) Robertson, D.; Barnes, C.; Gerasimchuk, N. J. Coord. Chem. 2004, 57 (14), 1205-1216.
(c) Gerasimchuk, N. N.; Domasevitch, K. V.; Kapshuk, A. A.; Tchernega., A. N. Russ. J. Inorg. Chem. 1993, 38 (11), 1718-1722.
(d) Gerasimchuk, N. N.; Tchernega, A. N.; Kapshuk., A. A. Russ. J. Inorg. Chem. 1993, 38 (9), 1530-1534.

(25) (a) Lukaszczyk, A.; Martin, H.; Diel, P.; Fory, W.; Gatzi, C.; Kristinson, H.; Muller, B.; Muntwyler, R.; Pachlatko, J. P. Oxime derivatives and their use in the protection of cultivated plants (Ciba-Geigy A. G., Switzerland), European Patent 12158 A2, 1980; (b) Gerasimchuk, N.; Maher, T.; Durham, P.; Domasevitch, K. V.; Wilking, J.; Mokhir, A. *Inorg. Chem.* **2007**, *46* (18), 7268–7284.

(26) Gerasimchuk, N. N.; Nagy, L.; Schmidt, H. G.; Roesky., H. Russ. J. Inorg. Chem. **1992**, 37 (4), 818–823.

(27) (a) Gerasimchuk, N. N.; Zhmurko, O. A.; Tyukhtenko, S. I. *Russ. J. Inorg. Chem.* **1993**, 38 (2), 282–287. (b) Gerasimchuk, N. N.; Domasevitch, K. V. *Russ. J. Inorg. Chem.* **1992**, 37 (10), 1163–1167 (and references therein).

(28) Mohammadi, M.; Akhbari, K.; Mazloomifar, A.; Ramazani, A.; Morsali, A.; Bruno, G.; Rudbari, H. A. J. Inorg. Organomet. Polym. Mater. **2012**, 22 (1), 288–294.

(29) SAINT: Data Integration Program; Bruker AXS: Madison, WI, 1998.

(30) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Sheldrick, G. M. SADABS Area-detector Absorption Correction, 2.03; University of Göttingen, Göttingen, Germany, 1999.

(31) Software Package for Crystal Structure Solution, APEX 2; Bruker AXS: Madison, WI, 2009.

(32) (a) Farrugia, L. J. Appl. Crystallogr. 1997, 30, 565. (b) Burnett, M. N.; Johnson, C. K. ORTEP III: Report ORNL-6895; Oak Ridge National Laboratory: Oak Ridge, TN, 1996.

(33) Charlier, H.; Gerasimchuk, N. Cyanoxime Inhibitors of Carbonyl Reductase and methods of Using Said Inhibitors in Treatments Involving Antracyclines. Patent USA, #7,727,967 B2, 2010.

(34) Robertson, D.; Barnes, C.; Gerasimchuk, N. J. Coord. Chem. 2004, 57 (14), 1205–1216.

(35) Emsley, J. *The Elements*, 2nd ed; Clarendon:Oxford, U.K., 1991; p 192.

(36) Glaser, J. In Advances in Inorganic Chemistry; Sykes, A. J., Ed.; Academic Press: San Diego, 1995; Vol. 43, p 1.

(37) Heydlauf, H. Eur. J. Pharmacol. 1969, 6, 340.

(38) Ilkun, O. T.; Archibald, S.; Barnes, C. L.; Gerasimchuk, N.; Biagioni, R.; Silchenko, S.; Gerasimchuk, O. A.; Nemykin, V. Dalton Trans. 2008, 37, 5715–5729.

(39) Markano, D. M. S. Thesis: Pyridylcyanoximes and their metal complexes. Missouri State University; Springfield, MO, 2007.

(40) Gerasimchuk, N.; Esaulenko, A. N.; Dalley, K. N.; Moore, C. Dalton Trans. **2010**, 39, 749–764.

(41) Goeden, L.; Gerasimchuk, N.; Durham, P.; Barnes, C.; Cannon, J. F. Inorg. Chim. Acta **2008**, 361, 1983–2001.

(42) Mokhir, A.; Domasevich, K.; Dalley, K.; Kou, X.; Gerasimchuk, N.; Gerasimchuk, O. *Inorg. Chim. Acta* **1999**, *284*, 85–98.

(43) (a) *CRC, Handbook of Chemistry and Physics,* 63rd ed.; CRC Press: Boca Raton, FL, 1982–1983; p F-179; (b) atomic sizes and interatomic distances from a comprehensive source of information about properties of elements are available online at http:// webelements.com.

(44) (a) Rayner-Canham, G. *Descriptive Inorganic Chemistry*, 2nd ed.; W. H. Freeman and Co.: New York, 2001; p 241. (b) Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ , 1998; p 244.

(45) (a) Ahkbari, K.; Morsali, A. J. Mol. Struct. **2008**, 878 (1–3), 65– 70. (b) Ahkbari, K.; Morsali, A. Inorg. Chim. Acta **2009**, 362 (6), 1692–1700. (46) (a) Gerasimchuk, N.; Domasevich, K. V. An excursion into coordination chemistry of thallium: design of new types of mixed valence coordination polymers as potential electric conductors. In *Proceedings of 36th International Coordination Chemistry Conference* (*ICCC-36*); July 18–24, 2004, Merida, Mexico; p 236; (b) Gerasimchuk, N. N.; Domasevitch, K. V., Barnes, C.; Dalley, N. K. Design of oxime-based metal-organic networks for one-dimensional coordination polymers. In *Proceedings of the 37th International Coordination Chemistry Conference (ICCC-37)*; August 13–18, 2006, Cape Town, South Africa; Oral Abstracts Book, p 194.

(47) (a) Harrowfield, J. M.; Sharma, R. P.; Shand, T. M.; Skelton, B. W.; White, A. H. Aust. J. Chem. 1998, 51 (8), 707-722.
(b) Harrowfield, J. M.; Sharma, R. P.; Skelton, B. W.; White, A. H. Aust. J. Chem. 1998, 51 (8), 735-745.

(48) Lead: Mohammadnezhad, G.; Amini, M. M.; Langer, V. Acta Crystallogr. 2010, C66, m44–m47. Germanium: Scrick, A. C.; Rheingold, A. L.; Weinert, C,S. Dalton Trans. 2011, 40, 6629–6631. Bismuth: (a) Lopatin, S. I. Russ. J. Gen. Chem. 2001, 71 (9), 1347–1350. (b) Stavila, V.; Davidovich, R. L.; Gulea, A.; Whitmire, K.H. Coord. Chem. Rev. 2006, 250 (21–22), 2782–2810. (c) Bachman, R. E.; Whitmire, K. H.; Thurstou, J. H.; Gulea; Stavila, O.; Stavila, V. Inorg. Chim. Acta 2003, 346, 249–255.

(49) Childress, M. V.; Milar, D.; Alam, T. M.; Kreisel, K. A.; Yap, G. P. A.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L.; Doerer, L. H. *Inorg. Chem.* **2006**, *45*, 3864.

(50) Glower, G.; Gerasimchuk, N.; Biagioni, R.; Domasevitch, K. V. Inorg. Chem. **2009**, 48 (6), 2371–2382.

(51) (a) Köhler, H.; Zeifert, B. Z. Anorg. Allg. Chem. 1970, 379 (1), 1–8. (b) Domasevitch, K. V. Russ. J. Gen. Chem. 1997, 67 (12), 1825–1831. (c) Arulsami, N.; Bohle, S. J. Org. Chem. 2000, 65 (4), 1139–1143. (d) Bohle, S. D.; Conclin, B. J.; Hung, C. H. Inorg. Chem. 1995, 34 (10), 2569–2581. (e) Lampeka, R. D.; Zubenko, A. I.; Skopenko, V. V. Theor. Exp. Chem. 1984, 20 (5), 519–525.

(52) (a) Wilett, R. D.; Galeriu, C.; Landee, C. P.; Turnbull, M. M.; Twamley, B. Inorg. Chem. 2004, 43 (13), 3804–3811 (and references therein). (b) Akkernlan, F.; Buschmann, J.; Lentz, D.; Luger, P.; Rödel, E. J. Chem. Cryst. 2003, 33 (12), 969–975. (c) Jones, P. G.; Kus, P. Z. Naturforsch. 2010, 65b (4), 433. (d) Jones, P. G.; Kus, P. Z. Naturforsch. 2007, 62b, 725–731. (e) Zerbe, E.-M.; Freytag, M.; Jones, P.; Blaschette, A. Z. Naturforsch. 2007, 62b, 1157–1166.

(53) Ahkbari, K.; Morsali, A. Inorg. Chem. Commun. 2007, 10 (10), 1189-1193.

(54) (a) Allen, G. C.; Hush, N. S. Prog. Inorg. Chem. 1967, 8, 357– 390. (b) Hush, N. S. Prog. Inorg. Chem. 1989, 30, 1–73. (c) Brill, J. W.; Megnamisi-Belombe, M.; Novotny, M. J. Chem. Phys. 1978, 68 (2), 585–592. (d) Matsumoto, K.; Ochiai, M. Coord. Chem. Rev. 2002, 231, 229–238. (e) Matsumoto, K.; Sakai, K. Adv. Inorg. Chem. 1999, 49, 375–427. (f) Iwatsuki, S.; Mizushima, C.; Morimoto, N.; Muranaka, S.; Ishihara, K.; Matsumoto, K. Inorg. Chem. 2005, 44 (22), 8097– 8104.

(55) Givaja, G.; Amo-Ochoa, P.; Gomez-Garsia, C.; Zamora, F. Chem. Soc. Rev. 2012, 41, 115–147.

(56) Domasevitch, K. V.; Skopenko, V. V.; Mokhir, A. A. Zh. Neorg. Khimii (Russ. J. Inorg. Chem.) **1995**, 40, 781.

(57) Fernandez, E. J.; Laguna, A.; Lopez-Luiziraga, J. M.; Monde, M.; Montiel, M.; Olmes, M. E.; Perez, J. Organometallics. 2004, 23, 774.